1-1-2005

Effect of temperature and pH on biological oxidation of antifreeze coolant using a packed column aerator

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EFFECT OF TEMPERATURE AND pH ON BIOLOGICAL OXIDATION OF ANTIFREEZE COOLANT USING A PACKED COLUMN AERATOR

by

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A Project Report

presented to Ryerson University

in partial fulfillment of the requirements

for the degree of Master of Engineering

in

Chemical Engineering

Toronto, Ontario, Canada, 2005

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Acknowledgements

I would like to express my sincere appreciation to Dr. Huu Dung Doan, my advisor, for his professional support, and understanding. His academic guidance is invaluable. My deep gratitude also goes to Dr. J. Wu, and Dr. Ginette Turcotte providing me their scientific insight during the course of my study.

My thanks also go to the faculty members and staff of the Department of Chemical Engineering for their contribution to my career development during my program in the University.

I also want to thank to the management and staff of my employer organization, Wollin Canada Inc., who supported me throughout the study period especially during the experimental work of this project.

I deeply thank Mrs. Jennifer Rasksen, Noha Oraha, Wasif Rizvi and Mr. Imran Asghar for their friendship and emotional encouragement.

I am especially indebted to my parents, and my brothers, for their love and understanding of my neglect of them during the busy time.

Abstract

Abstract

Simulated wastewater containing 0.75 % (v/v) antifreeze was treated biologically using a 0.18-m diameter packed column aerator with a 0.4-m high packed bed of 20-mm polypropylene spheres. Effects of liquid temperature and pH on the biological oxygen demand (BOD_5) removal were investigated. All experiments were performed under an air flux of 0.0080 $kg \cdot m^{-2} \cdot s^{-1}$ and a liquid flux of 14.8 $kg \cdot m^{-2} \cdot s^{-1}$. An increasing trend of the BOD_5 removal with temperature was observed when liquid temperature was increased from 16 to 32 °C by 4-degrees increments. When the wastewater pH was increased from 4 to 10 (by one-pH unit increments), the BOD_5 removal was increased by 18%. The averaged BOD_5 removal in the order of 90% (from the initial value of about 900 mg/L down to 80 mg/L) was obtained after 96 hours of treatment. The stripping effect was accounted for about 75 mg/L of the overall BOD_5 change, i.e. about 9% of the overall BOD_5 removal. In addition, the BOD_5 removal due to the biomass in the packed column was also monitored. A decrease of about 15% in the BOD_5 removal was observed without packing in the packed column aerator.

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Nomenclature

B_1	DO of seed control before incubation (mg/l)
B_2	DO of seed control after incubation (mg/l)
BOD_5	Biological oxygen demand
C	Dissolved oxygen concentration (g/m^3)
DO_1	Dissolved oxygen of diluted sample immediately after preparation (mg/l)
DO_2	Dissolved oxygen of diluted sample after 5 days of incubation at 20 ^{0}C (mg/l)
EG	Ethylene glycol
f	Ratio of seed in diluted sample to seed in seed control
k	Rate constant (hr^{-1})
L	Concentration (mg/l)
L_e	BOD remaining at time t (mg/l)
L_o	Ultimate BOD (mg/l)
M	Mass transfer rate of oxygen per unit time (g/s)
P	Decimal volumetric fraction of sample used
PEG	Polyethylene glycol
PG	Propylene glycol
y	BOD_5 exerted at any time (mg/l)

CHAPTER # 1

1.0-INTRODUCTION

Large quantities of de-icing agents are used in automobile engine coolants and at many airports to de-ice air planes before taking off during winter. The removal of ice and snow and prevention of their accumulation on aircraft surfaces is a mandatory requirement, this has been effectively achieved with the use of propylene glycol (PG) and ethylene glycol (EG) based aircraft de-icer fluids (ADFs). Glycol-based de-icing fluids are the only ones certified by the United States Federal Aviation Administration to ensure passenger safety [1]. EG based fluids are the most common deicing / anti-icing fluids used in North America [2]. The highest reported releases of ethylene glycol to the environment are to land from aircraft de-icing/anti-icing operations, with subsequent release to the aquatic environment. Ethylene glycol is also released to the environment in manufacturing and processing waste streams and as the result of disposal of industrial and consumer products containing this compound. Natural levels of ethylene glycol are considered to be insignificant relative to amounts released from anthropogenic sources.

Melted snow and runoff water, containing EG, may cause sever disturbance in sewage treatment, or may leave a toxic and harmful effect on aquatic life in rivers or lakes. Waste of automobile coolants is also creating the same problem since it mainly contains EG.

Ethylene glycol belongs to the simplest group of organic chemicals of the chemical family of glycols, which are characterized by two hydroxyl (OH) groups at adjacent positions in a hydrocarbon chain. The octanol/water partition is very low, and hence, bioaccumulation is not significant [3]. Under most environmental condition glycols are not volatile because of their low vapour pressure.

Upon release to the environment, the compound is expected to partition to and be transported in surface water and groundwater. Because of its high solubility in water and lack of adsorption or partitioning into soils, ethylene glycol will have a high mobility in soil and potential to leach into groundwater. Ethylene glycol is rapidly degraded in all environmental media and it does not persist or bioaccumulate.

Biodegradation is the most important transformation process in surface waters and soil. The biological degradation of the organic matters could be aerobic and anaerobic. For aerobic oxidation of wastewater, the removal of the Biological Oxygen Demand (BOD) is enhanced by aeration of the wastewater. Biodegradability is known as the removal of organic compounds by using microorganisms in the biological waste treatment process. There are several techniques used for the determination of biodegradability such as the biological oxygen demand and the petrochemical method [4].

Temperature and pH are the most important factors for water and wastewater treatment. They have direct influence on biological treatment systems. They also affect the biological growth and the reaction rate and are the key parameters for the biodegradation of any substance in the wastewater.

The objective of this thesis project is to determine the rate of biological degradation of Ethylene Glycol at different temperatures and pH at constant liquid and air flux, to achieve the highest removal rate of the BOD. An automotive coolant wastewater was treated using a packed column. While air is blown from the bottom, the packed column provides a good oxygen transfer from air to the wastewater and hence acts as an excellent aerator.

CHAPTER # 2

2.0 – Ethylene glycol: SUMMARY OF CRITICAL INFORMATION

2.1 Identity

Ethylene glycol belongs to the simplest group of organic chemicals of the chemical family of glycols, which are characterized by two hydroxyl (OH) groups at adjacent positions in a hydrocarbon chain.

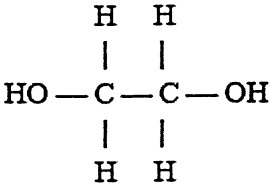

Figure 1.1 Chemical structure of ethylene glycol.

2.2 Physical/Chemical properties

Ethylene glycol also known as monoethylene glycol and 1,2-ethanediol, a clear, colourless, odourless, relatively non-volatile, viscous liquid [5]. It has a sweet taste and imparts a warming sensation to the tongue when swallowed [6]. Ethylene glycol has a relatively low vapour pressure (7–12 Pa at 20°C) [3, 7] and a low Henry's law constant of 5.8×10^{-6} Pa·m^3/mol [7, 8]. It is completely miscible in water [9, 10]. It is very hygroscopic and will absorb up to 200% of

its weight in water at 100% relative humidity [10]. The octanol/water partition coefficient of ethylene glycol is very low (i.e., log Kow = –1.36) [3].

2.3 Production and uses

Total worldwide capacity for ethylene glycol is over 10 million tonnes per year, with major increases expected in the future [11]. Worldwide demand for ethylene glycol stems from the production of fibre and PET. In lesser quantities, ethylene glycol may also be used in asphalt emulsion paints; as a coolant and heat transfer fluid; in low-pressure laminates; in brake fluids; in glycol diacetate production; in low freezing dynamite; as a solvent mixture for cellulose esters and ether; and in cellophane, cosmetics (up to 5%), lacquers, alkyd resins, printing inks, wood stains, leather dyeing, textile processing, humectants, ballpoint pen inks, detergents, solvents, polyurethane foam, medicinals, adhesives and other products [12, 13].

Available data indicate that projected annual production capacity for the ethylene glycols (mono-,di-, and triethylene glycols) in Canada increased to 907,000 tonnes in 1999 from 524,000 tonnes in 1992. In 1996, approximately 810,000 tonnes of ethylene glycols (mono-, di-, and tri-) were exported from Canada. Import volumes in 1996 were estimated at 31,300 tonnes [11].

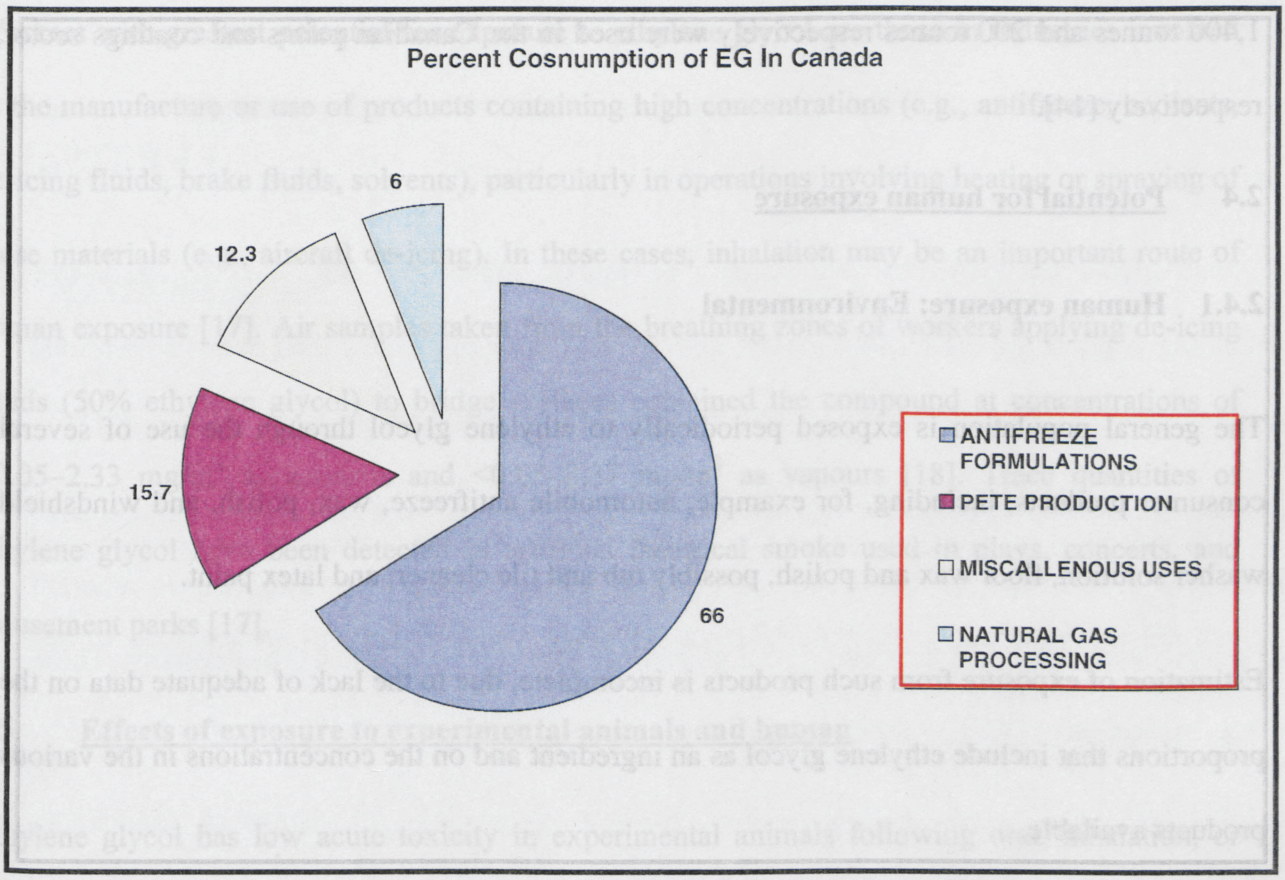

Figure 2.2: Percent consumption of EG in Canada. [11]

In Canada, the majority of ethylene glycol is used in antifreeze formulations (primarily for automotive vehicle engines, but also for aircraft de-icing), at 66% (105,000 tonnes) of domestic consumption [11]. An estimated 7,700 kilotonnes of ethylene glycol were used in 1996 for aircraft de-icing/anti-icing [14]. The amount used for the production of the polyester PETE in 1996 was relatively small, at 25,000 tonnes (15.7% of domestic consumption). Six per cent or 9,500 tonnes were used in natural gas processing to assist in the removal of water and to prevent ice formation. The remaining 19,500 kilotonnes were used in the production of solvents, including use as a component in latex paint formulations to guard against paint freezing and as antifreeze liquid injected into hoses used to pump liquid explosives [11]. In 1995 and 1996,

1,400 tonnes and 200 tonnes respectively were used in the Canadian paints and coatings sector, respectively [14].

2.4 Potential for human exposure

2.4.1 Human exposure: Environmental

The general population is exposed periodically to ethylene glycol through the use of several consumer products, including, for example, automobile antifreeze, wax, polish, and windshield washer solution, floor wax and polish, possibly tub and tile cleaner, and latex paint.

Estimation of exposure from such products is incomplete, due to the lack of adequate data on the proportions that include ethylene glycol as an ingredient and on the concentrations in the various products available.

Although automobile coolant (i.e., antifreeze) and winter windshield washer fluid are expected to contain the highest concentrations of ethylene glycol, human exposure to these products is expected to be infrequent and of short duration for a small number of individuals and negligible for the majority of the general population [15].

2.4.2 Human exposure: Occupational

Based on the US National Occupational Exposure Survey conducted by the National Institute of Occupational Safety and Health [16], an estimated 1.5 million workers are potentially exposed to ethylene glycol each year. Contact with the skin and eyes is the most likely route of worker exposure to ethylene glycol.

Workers with greatest potential for exposure to ethylene glycol are those in industries involved in the manufacture or use of products containing high concentrations (e.g., antifreeze, coolants, de-icing fluids, brake fluids, solvents), particularly in operations involving heating or spraying of these materials (e.g., aircraft de-icing). In these cases, inhalation may be an important route of human exposure [17]. Air samples taken from the breathing zones of workers applying de-icing fluids (50% ethylene glycol) to bridge surfaces contained the compound at concentrations of <0.05–2.33 mg/m^3 as aerosols and <0.05–3.37 mg/m^3 as vapours [18]. Trace quantities of ethylene glycol have been detected in artificial theatrical smoke used in plays, concerts, and amusement parks [17].

2.5 Effects of exposure to experimental animals and human

Ethylene glycol has low acute toxicity in experimental animals following oral, inhalation, or dermal exposure. In both humans and animals, ethylene glycol has induced only minimal dermal irritation. Nasal and/or throat irritation were reported in a small number of subjects inhaling ethylene glycol, while higher concentrations produced severe irritation. In the limited number of identified *in vitro* and *in vivo* studies, ethylene glycol has not been genotoxic.

Available data from acute poisoning cases (humans) and repeated-dose toxicity studies (experimental animals) indicate that the kidney is a critical organ for the toxicity of ethylene glycol in both humans and experimental animals. Consistently, metabolic acidosis and degenerative non-neoplastic changes in the kidney (including dilation, degeneration, and deposition of calcium oxalate in the tubules) have been observed at lowest doses in a range of species.

Terrestrial organisms are much less likely to be exposed to ethylene glycol and generally show low sensitivity to the compound. Concentrations above 100,000 mg/litre were needed to produce toxic effects on yeasts and fungi from soil.

Ethylene glycol has generally low toxicity to aquatic organisms. But Tests using de-icer containing ethylene glycol showed greater toxicity to aquatic organisms than observed with the pure compound, indicating other toxic components of the formulations.

Laboratory tests exposing aquatic organisms to stream water receiving runoff from airports have demonstrated toxic effects and death. Field studies in the vicinity of an airport have reported toxic signs consistent with ethylene glycol poisoning, fish kills, and reduced biodiversity. These effects cannot definitively be ascribed to ethylene glycol [15].

CHAPTER # 3

3.0 – Literature review

3.1 Treatment of wastewater containing ethylene glycol

Several processes can be used to decompose EG. In different studies it has been established that EG can be degraded up to 99%. The role of the biodegradation in the ultimate fate of EG has been examined in numerous studies, using a variety of microbes as well as methods of measuring biodegradability as explain in detail below. Various studies have also examined aerobic and anaerobic treatment, UV treatment with Fenton's reagent, photo Fenton system, fluidized bed treatment, methylene blue and riboflavin treatment, and enzymatic processes for the degradation of EG.

The result of many studies confirmed that EG underwent extensive primary and ultimate biodegradation and was considered readily biodegradable.

The removal of EG has also been extensively tested using methods that stimulate environmental conditions. Method used includes semi continuous activated sludge (SCAS), river die away (RDA) assay and tests that used soil or groundwater. The results of simulation test show that EG are extensively biodegradable in SCAS and RDA assays, as well as in soil or groundwater.

Means & Anderson [19] measured the biodegradation of ethylene glycol under aerobic conditions in five different tests using various aqueous media. Degradation was monitored using oxygen uptake, dissolved organic carbon removal, or carbon dioxide production. Ethylene glycol was readily degraded in all tests with a lag period of up to 3 days. Degradation to 10% or less of the starting concentration was reported in all tests after between 1 and 21 days.

Price *et al.*, [20] assessed the biodegradation of ethylene glycol in both fresh and salt water over a 20-day incubation period. Concentrations of up to 10 mg ethylene glycol/litre were used. In fresh water, 34% degradation was observed after 5 days, rising to 86% by day 10 and 100% by day 20. Degradation was less in salt water with degradation 20% after 5 days and 77% after 20 days.

Assuming that the BOD removal follows a first order kinetics, half lives (for 50% BOD removal) generally ranged from 3 to 8 days for both primary and ultimate biodegradation [21].

Boatman *et al.*, [22] used acclimated sewage sludge as inoculum and a concentration of ethylene glycol equivalent to 20 mg carbon/litre. Significant degradation, as measured by carbon dioxide production, did not occur until day 14 of the test (an estimated lag period of 8–10 days was reported). By day 21, 71% of the ethylene glycol was degraded.

The fate effect and potential environment risk of EG in the environment were examined by Charles *et al.*, [23] EG undergoes rapid biodegradation in aerobic and anaerobic environments (100% removal of EG with 24 to 28 days in air EG is decomposed by a photo chemical reaction that produces hydroxyl radicals with a half life of 2 days.

Dwyer *et al.*, [24] assessed the degradation of ethylene glycol in methanogenic enrichments of bacteria obtained from municipal sewage sludge. The bacterial inoculum was dominated by two morphological types of bacteria, *Methanobacterium* sp. and *Desulfovibrio* sp. A concentration of 36 mmol ethylene glycol/litre (2.2 g/litre) was incubated at 37 °C, and, based on analysis of the compound, 100% of the glycol was metabolized within 12 days. Products of degradation included ethanol, acetate, and methane.

Following a spill of ethylene glycol in New Jersey, USA, in which 15,000 litres of coolant containing ethylene glycol as antifreeze at 275 g/litre were spilled, concentrations of the glycol in soil and groundwater were measured at 4.9 and 2.1 g/litre, respectively. A remediation procedure was initiated involving the pumping of nitrogen, phosphate, and oxygen-saturated water into the contaminated ground; after 26 days, 85–93% of the glycol had been degraded by naturally occurring microorganisms. After 9 months, the concentration of ethylene glycol was below the detection limit of 50 mg/litre [25].

The bioremediation of EG and PG using the aerobic biological fluidized bed (BFB) technology was evaluated by Wen *et al.*, [26] under steady-state conditions, they found that BFB reactors were capable of achieving a good total organic carbon (TOC) removal (greater than 96%) in the bed after 1.7 hours with a TOC loading as high as 0.88 g/l-day. They concluded that the observed BFB process efficiency and stability are attributed to the high immobilized biomass inventories attained in the reactors by using porous particles for cell immobilization and retentions.

Schoenberg *et al.*, [27] determined the degradation rate constants for Both PG-based and EG-based Type I de-icing fluids and showed that both were almost completely degradable anaerobically. Aerobic degradation of glycol based fluid type 1 aircraft de-icing fluids (ADF)

was characterized using suspended growth fill and draw reactors. First order degradation rate constant of 3.5/d for the PG based type-1, ADFs and 5.2/d for the EG based type ADFs were obtained through continuous-culture means under mesophilic conditions (35 °C).

3.2 Packed column in wastewater treatment

The use of fixed bed reactors has been shown to be effective in the treatment of biodegradable organic matter [28, 29, 30].

The removal of the BOD in a counter-current packed-bed bioreactor was shown to be effective by Doan & Wu, [31]. A dilute concentration in the order of 200 ppm propylene glycol methyl ether (PGME) was selected as a model pollutant from an electro-coating process, where it was demonstrated that the BOD could be reduced to 70% after four days of treatment compared with 10% removal from a stagnant tank. When compared to natural draft operation as in trickling filter, 40% of the BOD removal was obtained. It was also noted that the effect of airflow rate didn't have a significant effect on the removal of the BOD.

Degradation of EG using a packed column aerator was investigated by Khan & Doan [32]. Under a constant liquid flowrate of 5.5 $kg{\cdot}m^{-2}s^{-1}$ the BOD removal increased when the air flux was increased from 0.0069 to 0.014 $kg{\cdot}m^{-2}s^{-1}$. However, further increases of the air flowrate beyond 0.014 $kg{\cdot}m^{-2}s^{-1}$ did not affect the BOD removal rate significantly. On the other hand with a constant air flowrate when the liquid flux was increased from 5.5 to 11, 16.5, and 55 $kg{\cdot}m^{-2}s^{-1}$, the percent BOD removal appeared to decrease slightly. It was also found that the increase in amount of seeding has no significant effect on BOD removal. The averaged BOD removal of about 90% was obtained after 72 hours of treatment.

3.3 Effect of Temperature on ethylene glycol degradation

The rate of biodegradation depends on numerous factors, including ambient temperature, type and number of microorganisms present, acclimation and the concentration of ethylene glycol in the water body.

Among these factors temperature is particularly important, and it has a profound effect on the degradation of ethylene glycol, as reported by Evans & David [33], who studied the aerobic degradation of ethylene glycol from river water samples at temperatures of 4, 8 and 20 °C. At 20 °C, ethylene glycol was completely degraded in 3 days, but at lower temperatures bacterial activity was reduced. In all river waters tested, and at 8 °C, degradation was complete within 14 days. Degradation at 4 °C was substantially slower, with degradation of less than 20% after 14 days for river water samples with limited suspended matter and a starting ethylene glycol concentration of 10 mg/l.

Similarly, following the protocol for conducting biological oxygen demand tests [34] using acclimated soil bacteria and the ethylene glycol concentration of 50 mg/l, biodegradation rate constants were determined to be 0.033, 0.06 and 0.167 per day at temperatures of 4, 10 and 20 °C, respectively [35]. Corresponding biodegradation half-lives are 21, 12 and 4 days, respectively, assuming a first-order rate of reaction.

Examination of the effect of temperature on the growth of bacterial cultures on a medium containing ethylene glycol as the only carbon source revealed that at temperatures of 4, 8 and 14 °C, the growth was 6.9, 7.4 and 9.2%, respectively, of that observed in bacteria incubated at 25 °C [36]. Rate constants for biodegradation of 100 mg ethylene glycol/L by non-acclimatized activated sludge at 20 °C were 0.026–0.035 per hour [37].

Mcgahey & Bouwer [38] monitored the utilization of ethylene glycol as substrate by microorganisms naturally occurring in soil and groundwater over time; while substrate concentration, soil type, temperature and nutrient level were varied. Their aim was to establish rates of biodegradation of ethylene glycol in simulated subsurface environments. . Batch studies at 100 and 1000-ppm ethylene glycol demonstrated that increasing substrate concentration decreased the rate of its biotransformation as the first-order kinetic rate constant decreased from 1.01 to 0.95 $days^{-1}$. Further increase in initial concentration to 10,000-ppm resulted in minimal substrate disappearance from solution which was likely due to oxygen limitation. Studies with two different soils under identical environmental conditions and substrate concentrations indicated soil type had a clear effect on biodegradation rate. Lowering the temperature from 25 to 10 °C for a given soil retarded the degradation rate by a factor of 2.44, but at each temperature greater than 99% removal was achieved in less than 7 days. Groundwater served as a satisfactory bacterial inoculum and generated a rate constant only slightly lower (0.76 $days^{-1}$) than that found for the soils. It is important to note that ethylene glycol concentration and temperature play important roles in governing the overall degradation rate; in the above study, the temperature of the groundwater was considerably higher than that which would be found under natural conditions in Canada.

Klecka *et al.*, [39] showed that reducing temperature in the sandy silt inoculum from 25 °C to 10 °C resulted in a decrease in the rate constant from 2.09 to 1.19/day and an increase in the half-life from 6 to 14 h; however, nearly complete degradation was observed at both temperatures within the incubation period. Biodegradation rates of ethylene glycol-based aircraft de-icing fluids were examined in soil microoraganism at 8 °C. Initial concentrations of 390–4900 mg ethylene glycol/kg soil were degraded at around 20 mg/kg per day.

Bielefeldt *et al.*, [40] researched on glycol based fluids which are used to de-ice aircraft for safe operation around the world. PG removal was investigated using a 15-cm deep saturated sand column. For all flow rates and loading conditions (8 to 25 °C temperature and concentration was 39 to 52 mg/kg) tested, biodegradation greater than 99% was achieved. The results indicate a favourable potential to degrade PG in either engineered biofilters or the natural subsurface.

Nedwell [41] investigated the effect of environmental temperature on the affinity of microorganisms for substrates and experimentally proved that affinity decreases consistently as temperature drops below the optimum temperature for growth. At temperatures below their optimum for growth microorganisms will become increasingly unable to sequester substrates from their environment because of lowered affinity, exacerbating the near-starvation conditions in many natural environments.

3.4 Effect of pH on ethylene glycol degradation

Stewart *et al.*, [42] studied the biodegradability of ethylene glycol, acrylic acid, acrolein and allyl alcohol using a methanogenic acetate enrichment culture. EG was found to be degraded to less than 5 mg/l with spikes up to 10,000 mg/l in the influent. Ethylene glycol and acrylic acid were found to be suitable for anaerobic treatment whereas allyl alcohol and acrolein were not suitable at the selected concentrations using a methanogenic culture.

Methylene blue and riboflavin were evaluated by Dietrick *et al.* [43] to determine the photosensitizer's ability to degrade ethylene glycol. Degradation rates of ethylene glycol in riboflavin solutions exposed to sunlight ranged from 0.22 ± 0.11 to 1.52 ±0.50 mg/l-h. Significant degradation rate were noted in system using 6 and 10 mg/l riboflavin at pH values of 4, 7, and 10. Methylene blue used as a photodynamic sterilization and as a photsensitizer. No

significant degradation was found in the system using methylene blue as the photosensitizing agent. These results indicate that losses of ethylene glycol significant at the 95% confidence level can occur at or near neutral pH and require relatively low concentrations of riboflavin. Although the results do not indicate a fast removal of ethylene glycol, a useful mechanism of ethylene glycol removal was proposed, providing insight into the potential for ethylene glycol degradation with other chemical removal processes, particularly advanced oxidation methods. In their study the authors concluded that the ethylene glycol loss in the riboflavin system was not dependent on pH. Unlike methylene blue, which is confined to higher pH values for optimal reactivity, riboflavin activity sustain over with a wide range of pH values. In the case of ethylene glycol degradation in this system, an optimal pH was not apparent; indicating that neither riboflavin activity nor ethylene glycol reactivity was pH dependent.

Dietrick *et al.*, [44] showed that the photo Fenton system has the potential to be used as a method to reduce the COD of airport wastewater by degrading ethylene glycol. They investigated the degradation of EG in photo Fenton system. Ethylene glycol loss rate constant of $1.0 \pm 0.40\ h^{-1}$ were achieved in the systems containing ethylene glycol at concentrations of 1000 mg/l. A high TOC loss was also noted in UV/ H_2O_2 systems. The system was found to be sensitive to pH. The optimal pH range was found to be pH 2.8±3. Since this is an optimal pH range for degradation of several different compounds, it is most likely the optimal pH for OH^- production as opposed to an optimal pH for degradation of a specific substrate. The optimal pH of 3.0 found for ethylene glycol degradation does not represent the optimum for $[Fe(OH)(H_2O)_5]^+_2$ speciation. The photo Fenton reaction is inhibited by other iron species at the optimal pH for $[Fe(OH)(H_2O)_5]^+_2$ that may result in a more complex iron species optimization scheme for the process.

In another study, by Dietrick *et al.*, [45] photo Fenton reagents effectively reduced the concentration of ethylene glycol. Oxidation of EG in aqueous solutions was found to occur with the addition of Fenton's reagent. Further conversion was observed upon UV irradiation. The pH range studied was 2.5 to 9 with initial H_2O_2 concentrations ranging from 100 to 1000 mg/l. The application of the method to airport storm water could potentially reduce the chemical oxygen demand by the conversions of EG to oxalic and formic acid. EG removal was enhanced by exposure to UV light after treatment with Fenton's reagent.

The enzymatic degradation of EG was also investigated by using lipase [46]. At pH of 3, 5, and 7.2 the weight loss ($mmol/m^2$) for lipase was 1.2, 1.5, and 2.4 and for the buffer it was 1.1, 1.1, and 2.2, respectively. These result showed the dependence on the pH of weight loss of lipase degraded at 37°C for 12 hr. The lipase showed the greatest activity at pH of 5.

The influence of temperature and pH on the acidification of a synthetic gelatin based wastewater was investigated using an upflow anaerobic reactor. Gelatin degradation efficiency and rate, degree of acidification, and formation rate of volatile fatty acids and alcohols all slightly increased with temperature. Temperature affected the acidogenesis of gelatin according to the Arrhenius equation. The study was divided into two phases. In phase I, the operational pH level was kept at 5.5, seven runs were conducted to examine the influence of temperature at 20, 25, 30, 37, 45, and 55 ^{0}C; In phase II, the temperature was kept at 37 ^{0}C, seven runs at pH ranging from 4.0 to 7.0 were undertaken. The pH of the mixed-liquor was controlled by titration using a solution of 4N NaOH or 4N HCl. The reactor was operated at each temperature or pH level for 36–43 days to ensure reaching steady state before changing the temperature or pH level to the next level. Compared with temperature, pH had a more significant effect on the acidogenesis. Gelatine degradation efficiency substantially increased with pH, from 60.0% at pH 4.0 to 97.5%

at pH 7.0. The degree of acidification increased from 32.0% at pH 4.0 to 71.6% at pH 6.5, but dropped to 66.8% when pH increased to 7.0. Lowering operational temperature generally leads to a decrease in the maximum specific growth and substrate utilization rate [47].

The study done by Safferman *et. al.* [48] demonstrated the feasibility of treating storm water contaminated with airport de-icing fluid (ethylene glycol) in a batch-loaded aerobic fluidized bed reactor. The treatment of the contaminated storm water in batches eliminated the operational problems common to a continuously loaded aerobic fluidized bed reactor. Most significantly, excess biofilm growth and the accompanying maintenance and operational problems were controlled through endogenous respiration. Ethylene glycol and chemical oxygen demand removal rates of 710 and 2,200 $g/m^3/day$, respectively, were achieved in the batch-loaded reactor. An additional benefit of the batch-loaded process is the low quantity of sloughed biofilm, which results in a low level of effluent solids (16 mg/L total suspended solids). As a result, secondary clarification and associated sludge treatment might not be required. In addition, they measured the removal rates for batch-loaded and continuously loaded fluidized bed reactors. These values were compared with each other and with more conventional wastewater treatment processes.

CHAPTER # 4

4.0 – EXPERIMENTAL

4.1 Experimental Apparatus

The experimental apparatus used in the present study is presented in figure 4.1. The apparatus was operated in batch recirculation mode with a counter-current flow of wastewater entering the top of the packed column and air entering the bottom of the column. A 1/3 hp Bur cam Pump (Burke Group, Inc. Quebec, Canada) was used to pump the wastewater from the bottom of the holding tank to the top of packed column.

The packed column was constructed from clear PVC pipe with an internal diameter of 18.0 cm and a total height of 60 cm. The bed depth was 44 cm and filled with hollow polypropylene spheres with a diameter of 1.3 cm. Filtered compressed air from a laboratory bench was used. A rotameter (Dwyer® Instrumentation Inc., Michigan City, IN) having a range of 0 to 1000 scfh was used to measure the air flow. Another rotameter (Fabco Plastics, Maple, On) with a range of 0 to 10 l/min was also used for liquid flow measurement. A by-pass line leading back to the holding tank from the outlet of the pump was used to provide for mixing in the tank as well as to regulate the liquid flow rate.

A copper-cooling coil with an internal diameter of 0.95 cm, 300 cm in length, with a diameter of 15.24 cm, was placed in the storage wastewater tank to maintain the wastewater at a certain temperature. An automatic immersed 150 W heater (Ebo-Jager, Darmstadt, Germany) with a measuring range of 18 to 34 °C was also placed in the tank to regulate the temperature of the

tank. A Go!Temp® probe (Vernier software and technology Beaverton, OR) was placed at the centre of the holding tank to collect data for liquid temperature and record in a computer via USB interface.

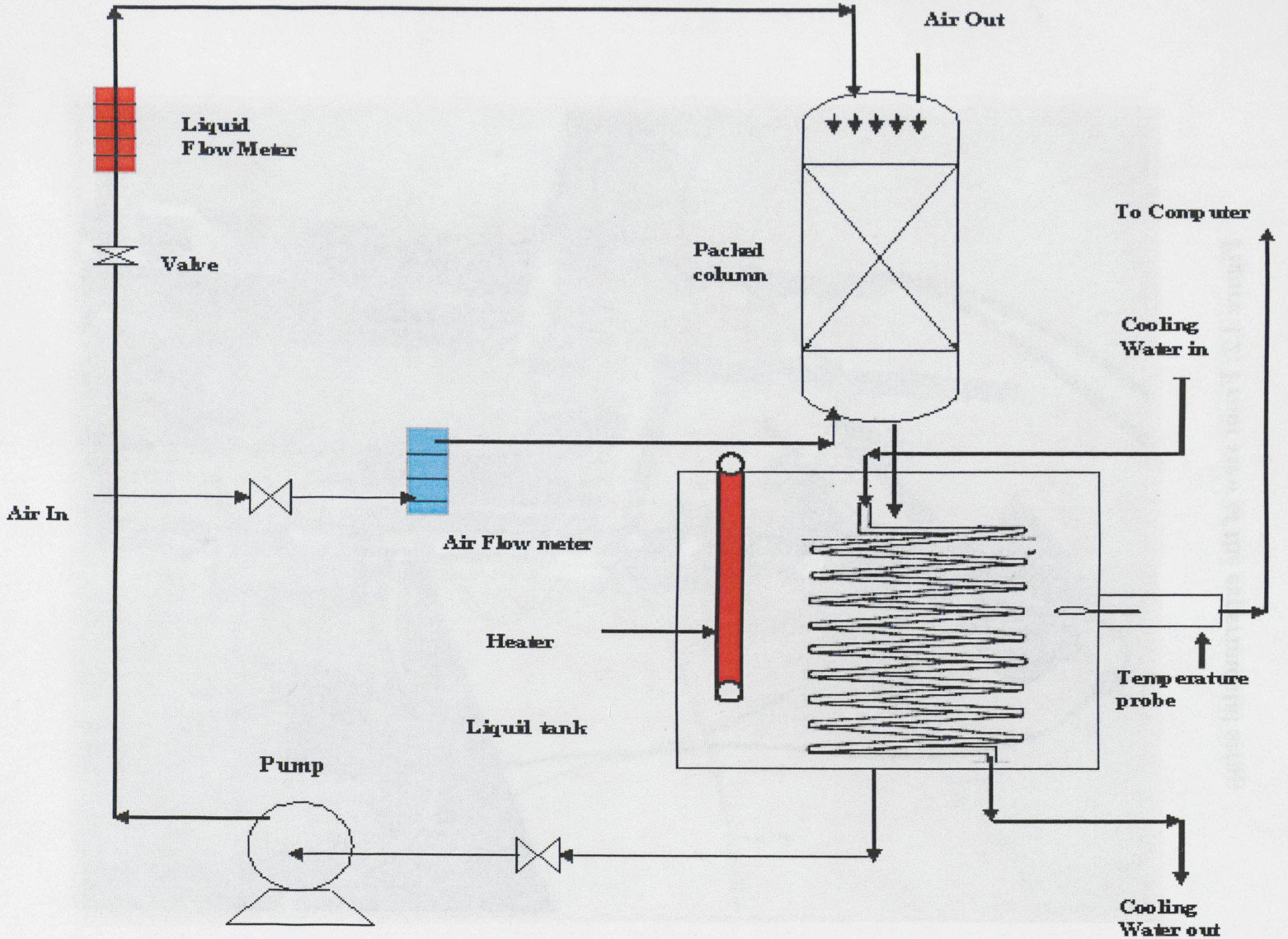

Figure 4.1: Schematic diagram of the experimental setup used in this study

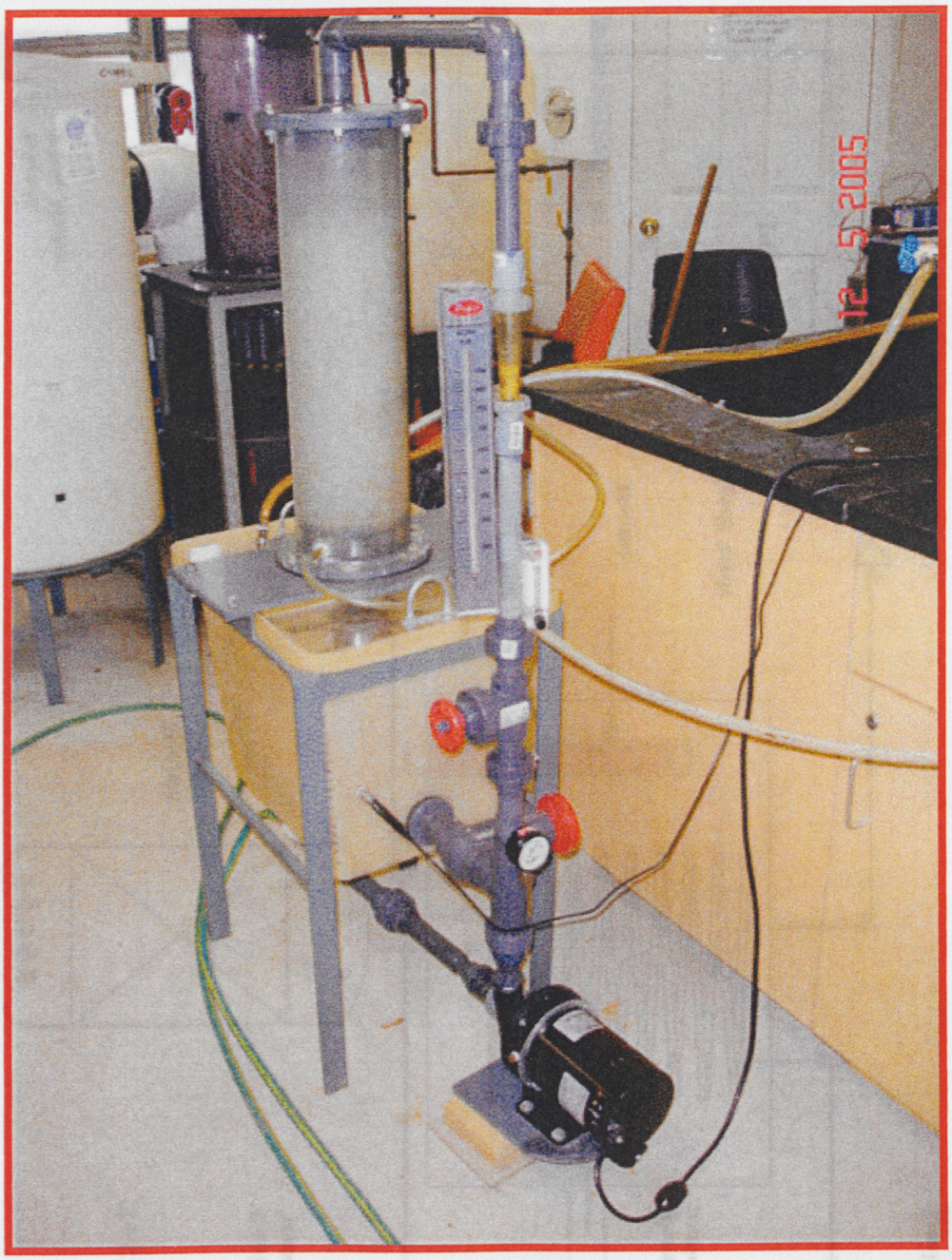

Figure 4.2: Front view of the experimental setup

Figure 4.3: Back view of the experimental setup

4.2 Experimental Design

The objective of this project was to study the effect of temperature and pH on the removal of biological oxygen demand (BOD) of the wastewater. In order to evaluate the effects of temperature and pH, the experiments were done at constant air and liquid flux rate at various temperature and pH levels.

The first phase of research project was done by treating simulated wastewater at different temperatures. The following table summarizes the factors used for the first phase.

- **Table 4.1 Experimental design to study the effect of temperature on wastewater**

RUN	TEMPERATURE	LIQUID FLUX	AIR FLUX	*SEEDING
	^{o}C	kg $m^{-2}s^{-1}$	kg $m^{-2}s^{-1}$	at 0 hr
1	16	14.8	0.0080	4 capsules
2	20	14.8	0.0080	4 capsules
3	24	14.8	0.0080	4 capsules
4	28	14.8	0.0080	4 capsules
5	32	14.8	0.0080	4 capsules

*Note: 1 capsule contains 0.110g biomass on dry basis.

The second phase of research project was done by treating simulated wastewater at different pH values. The following table summarizes the factors used for the second phase.

Table 4.2 Experimental design to study the effect of pH on wastewater

RUN	pH	LIQUID FLUX	AIR FLUX	*SEEDING
		kg $m^{-2}s^{-1}$	kg $m^{-2}s^{-1}$	at 0 hr
6	4	14.8	0.0080	4 capsules
7	5	14.8	0.0080	4 capsules
8	6	14.8	0.0080	4 capsules
9	7	14.8	0.0080	4 capsules
10	8	14.8	0.0080	4 capsules
11	9	14.8	0.0080	4 capsules
12	10	14.8	0.0080	4 capsules

*Note: 1 capsule contains 0.110g biomass on dry basis.

The effect of seeding on the biological oxygen demand of simulated wastewater has been checked by the following run.

Table 4.3 Experimental design to study the effect of seeding on wastewater

RUN	SITUATION	TEMPERATURE	LIQUID FLUX	AIR FLUX
		^{o}C	kg $m^{-2}s^{-1}$	kg $m^{-2}s^{-1}$
13	Without seeding	20	14.8	0.0080

One separate run has been conducted to study the effect of packing on the biological oxygen demand of simulated wastewater.

Table 4.4 Experimental design to study the effect of packing on wastewater

RUN	SITUATION	TEMPERATURE	LIQUID FLUX	AIR FLUX
		^{o}C	kg $m^{-2}s^{-1}$	kg $m^{-2}s^{-1}$
14	Without packed column	20	14.8	0.0080

4.3 Laboratory equipment used

The following is a list of instrumentation used in the present study.

Table 4.5 List of instrumentation used

Instrument	Manufacturer	Model	Precision
Dissolved oxygen meter	YSI Inc. (Yellow springs, Ohio, USA):	52 CE	see appendix for sample calculations
Incubator	VWR Int.: (VWR Int., Mississauga, Canada)	2005	± 1.0 ^{o}C
pH meter	Precise Int.: (Leici Instruments Factory, Shanghai, China)	PHS-3C	± 0.01
Balance	Scientech Inc., Boulder Colorado,USA)	SP-150	± 0.0001 g high range ± 0.001 g low range

4.4 Experimental Procedure

4.4.1 Activities prior to experimental runs

Prior to any experimental run the apparatus was cleaned with deionized water. Deionized water was flushed through the system for 24 hours. Once completed the system was drained and allowed to dry.

All glassware was cleaned before any run and before samples were taken. Glassware was cleaned by using a mild detergent, followed by three rinses with tap water, and a final rinse with deionized water.

Seed solution used for BOD measurements was prepared a day before a run. One Polyseed® (InterLab Inc., The Woodlands, Texas) capsule was added to a clean, dry 500 mL Erlenmeyer flask containing a magnetic stir bar. 500 mL of deionized water was added to the flask. The seed solution was then mechanically stirred and aerated for at least 5 hours. The aerated seed solution was then stoppered and placed in an incubator at 20 °C. The seed solution was used for the duration of a run.

The dilution water used for BOD measurements was aerated deionized water. Approximately 3 L of deionized water was added to a clean, dry 4 L Erlenmeyer flask. Filtered, compressed air was bubbled into the water for at least 30 minutes using Tygon tubing. Prior to inserting the tubing into the water, it was cleaned with a mild detergent and tap water, and then rinsed with deionized water. During the aeration period the dilution water was placed in a cold-water bath to reduce the temperature to 20±1 °C.

Before any experimental work was started a check was performed to ascertain the quality of the deionized water. After experimentation commenced, periodic checks were performed.

4.4.2 Preparation of simulated wastewater

The simulated wastewater used for the biological treatment was made by adding 300 ml of antifreeze coolant (Motomaster, Toronto, Canada), and 4 Polyseed ® (InterLab Inc., The Woodlands, Texas) capsules containing freeze dried microorganisms to the holding tank. The volume of simulated wastewater used for all experimental runs was 40 litres.

A range of pH from 4 to 10 for different runs of for phase II of the project was desired. This was done by adding solutions of 1 N solution of NaOH (J.T. Baker Inc., Phillipsburg, NJ) to increase the pH of the simulated wastewater and 1 N HCl (Merck KGaA, Darmstadt, Germany) to decrease the pH of the simulated wastewater to the desired level. Solutions of NaOH and HCl were prepared as indicated in the CRC Handbook of Chemistry and Physics. During the 96 hours of treatment Buffer solutions (VWR Int., Mississauga, Canada) of pH 4 and 7 had been added to wastewater accordingly to adjust the pH to the desired level.

Samples were collected in clean, dry 100 mL beakers. Prior to obtaining the sample the beaker was rinsed with the wastewater. Analysis was performed immediately upon obtaining the sample.

4.4.3 Analysis of wastewater samples

Analysis of the wastewater samples was performed in accordance with the Standard Methods [49]:

- Standard Method 5210B, for 5-Day Biochemical Oxygen Demand

- Standard Method 4500-H+, for pH measurements

Biochemical Oxygen Demand, BOD in short, is defined as the amount of dissolved oxygen, which is needed by microorganisms for the oxidation and conversion of organic substances in sample of water under defined conditions over specific period [50].

For BOD determination dissolved oxygen measurements were performed on diluted wastewater samples. An 80 ml sample was collected from the holding tank. 300 ml BOD bottles were used in which aliquots of the sample were added. To each of the aliquots, 10 ml of seed solution was added. The BOD bottle was then filled with dilution water and a dissolved oxygen probe was used to measure the dissolved oxygen. The measurements were taken once any visible air bubbles had disappeared in the bottle. Upon completion of the measurement the BOD bottle was topped up with dilution water and stoppered. A tin foil "cap" was than placed over the stopper. The bottle with the sample was then incubated at 20 °C for a period of 5 days.

One seed control solution containing of 10 ml of the seed solution with the balance distilled water and a blank bottle of distilled water were also prepared. These bottles were also incubated at 20 °C for a period of 5 days. Prior to any dissolved oxygen measurement, the probe was calibrated according to the manufacturer's instructions.

After 5 days, the dissolved oxygen value was measured again and the BOD_5 value of the water samples was calculated from the following equation.

$$BOD_5, mg/l = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P} \tag{4.1}$$

where:

D_1 = Dissolved oxygen of diluted sample immediately after preparation, mg/l

D_2 = Dissolved oxygen of diluted sample after 5 days of incubation at 20 °C, mg/l

P = decimal volumetric fraction of sample used

B_1 = Dissolved oxygen of seed control before incubation, mg/l

B_2 = Dissolved oxygen of seed control after incubation, mg/l

f = ratio of seed in diluted sample to seed in seed control

The pH measurements were performed using a pH meter. A two point calibration was performed using buffer solutions of pH 4 and pH 7, prior to each set of measurements to insure that the readings were accurate.

CHAPTER # 5

5.0 –Result and discussion

5.1 Effect of temperature on BOD removal

The effect of temperature on biological oxidation of the simulated wastewater containing antifreeze coolant was investigated.

The experiments (see Table 4.1) with temperatures of 16, 20, 24, 28 and 32 °C while keeping the air and liquid flux rate constant were carried out. It was found that the percentage of BOD_5 removal increased when the temperature was increased as shown in Figure 5.1

It was observed that there was a swift BOD_5 removal at the initial stage of the treatment but it gradually became moderate towards the end of the treatment time. For all runs, it was found that approximately 50% BOD_5 was removed during the first 48 hours. During this same time interval for run 4 and 5 at 28 °C and 32 °C respectively, more than 65% of BOD_5 was removed. However for all runs at 16, 20, 24, 28 and 32 °C the percentage of BOD_5 removal at 96 hours was 90.7, 91.7, 92.9, and 93.8. 95.6, respectively, showing a marginal increase of about 1% in BOD_5 removal.

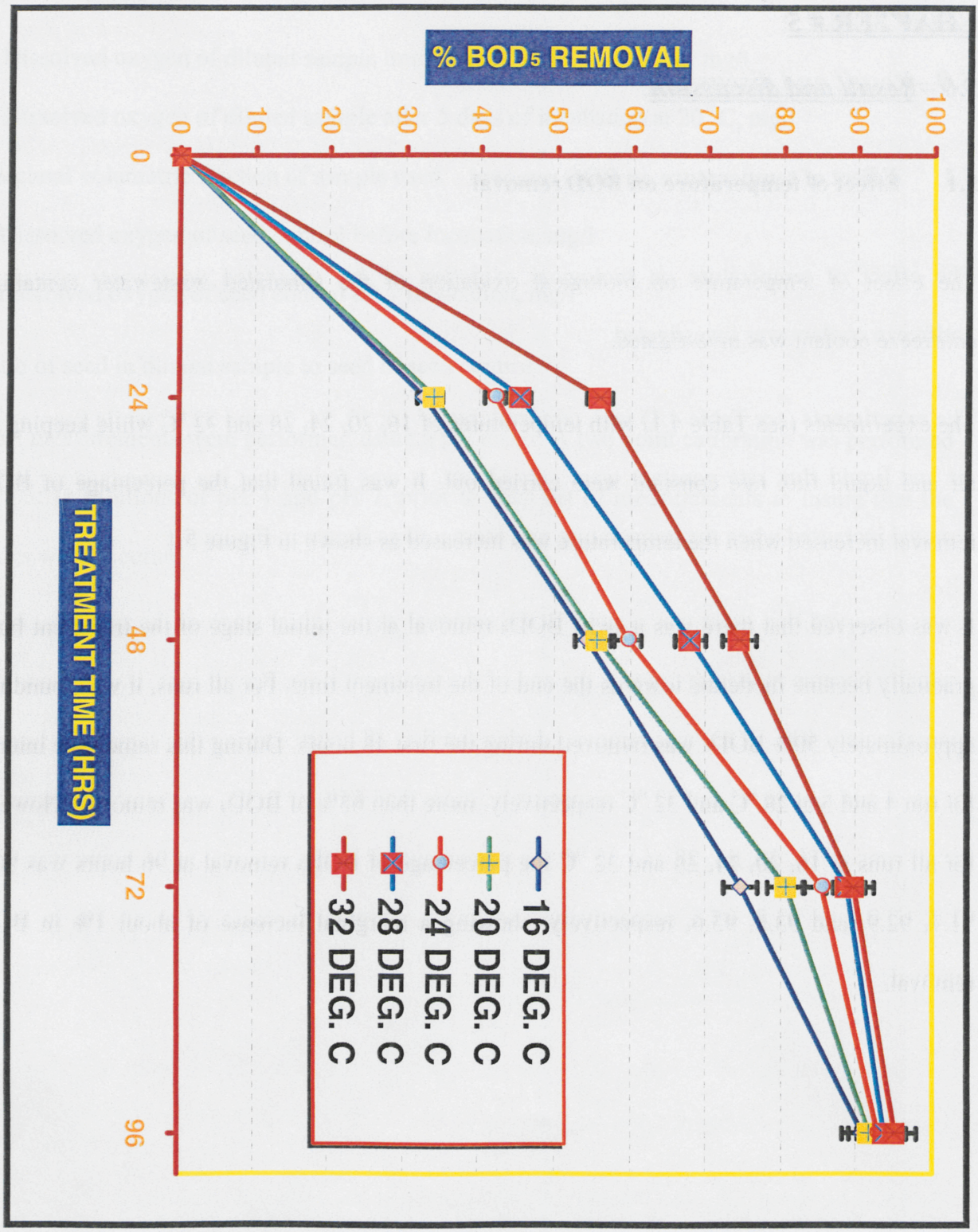

Figure 5.1: % BOD_5 removal at different temperatures vs. treatment time at a fixed liquid and air flux of 14.8 $kg \cdot m^{-2} \cdot s^{-1}$ and 0.0080 $kg \cdot m^{-2} \cdot s^{-1}$ respectively.

It was expected that increase in temperature caused decreases in the quantity of oxygen present in the simulated water. Consequently, if there was not enough dissolved oxygen in the system the microorganisms would not be able to oxidize the organic matter, which in turn hindered the BOD_5 removal. The trend in Figure 5.1 shows that increases in temperature did not hinder the BOD_5 removal, especially for long treatment times i.e., 96 hours. This indicates that the aeration provided a sufficient amount of oxygen in the simulated wastewater for the oxidation of organic matter by the microorganisms. On the other hand increases in temperature may have a strong effect on reaction kinetics of the system, i.e., reaction rate constants.

It was expected that a higher temperature would result in a higher BOD removal since temperature would have a profound effect on the microorganisms activities, not only in governing the rate of reaction, but also giving rise to a significant alteration in the microbial community structure. In terms of the removal efficiency higher temperatures give rise to higher rates of BOD_5 removal up to 35-40 ^{o}C [51]. Phaup & Gannon [52] reported that the rate of metabolism and growth of microorganisms was reduced at lower temperature, which was illustrated by the location and pattern of the slime growth in polluted water. For example, the slime growths in Altamaha river (Georgia USA) in the summer (30 ^{o}C) was limited to150 to 250 m below the effluent source whereas in the winter (10 ^{o}C) it extended for 24-64 kms. Also, the affinity of microorganisms for substrates decreased consistently as the temperature dropped below the optimum point for growth. Higher temperatures resulted in increased biological activity that in turn enhanced the rate of substrate removal [41]. Researchers [33, 35, 36, and 38] have used different methods to study the effects of temperature on EG degradation and found that increases in temperature had a profound effect on the organics degradation resulting in higher degradation rates at higher temperatures.

From the experimental data on the BOD_5 the removal with the treatment time, the values of the rate constant (k) were found from the slopes of the line of the logarithmic oxygen utilization (BOD_5) versus time (t). Assuming a first order kinetics for the BOD removal plots of the logarithmic oxygen utilization versus time (t) can be found in Appendix C, and D, for each of the five runs. Detailed model is given in section 5.5.

Table 5.1: Comparison of rate constant (k) for run 1-5 carried out at different temperatures for the biological oxidation of EG during 96 hours of biological treatment.

RUN	TEMPERATURE	RATE CONSTANT(k)
	^oC	hr^{-1}
1	16	0.0239
2	20	0.0258
3	24	0.0279
4	28	0.0297
5	32	0.0313

As shown in Table 5.1 the rate constants increase with increases in wastewater temperature. The values obtained are in agreement with the hypothesis that increases in temperature, increases the microbial activity which in turn increase the reaction rate. It is also observed that for all the runs the reaction rate constant increase steadily i.e. an increment of 4 ^oC in temperature gives a steady increase of 0.002 per hour in the reaction rate.

5.2 Effect of pH on BOD_5 removal

The effect of the pH on the BOD_5 removal for wastewater containing EG was also investigated. The runs were performed (as detailed in Table 4.2) while keeping the temperature, air and liquid flux constant at 20 °C, 0.0080 kg $m^{-2}s^{-1}$, 14.8 $kg^{-2}s^{-1}$ respectively. The data obtained are plotted in Figure 5.2.

The BOD_5 removal was less with pH in the acidic region (4, 5, and 6) for a short treatment time.

One reason could be the addition of HCl to the simulated wastewater, which was necessary to lower the pH of simulated wastewater at the start of the experiment. The pH value for simulated wastewater was 9 and it was reduced down to acidic region by the addition of 1 N HCl as discussed in section 4.4.2. Approximately 150- 350 ml of HCl was added to lower the pH of the wastewater at 0 hr to bring it to down to the desired pH value for that run. Although the acid used was at a low concentration (1 N), the presence of a good amount of chlorine ions in the simulated wastewater could affect the microbial growth or reduce their microbial activity or microbial affinity for the antifreeze coolant.

It can also be observed that BOD_5 removal values are very low (11.6, 12.5, and 14.0 respectively for pH 4, 5, and 6 respectively after 24 hrs, which might be due to the initial delay (incubating) period of the microbial activity because of the presence of Cl ions added in the form of HCl to adjust the pH of the simulated wastewater.

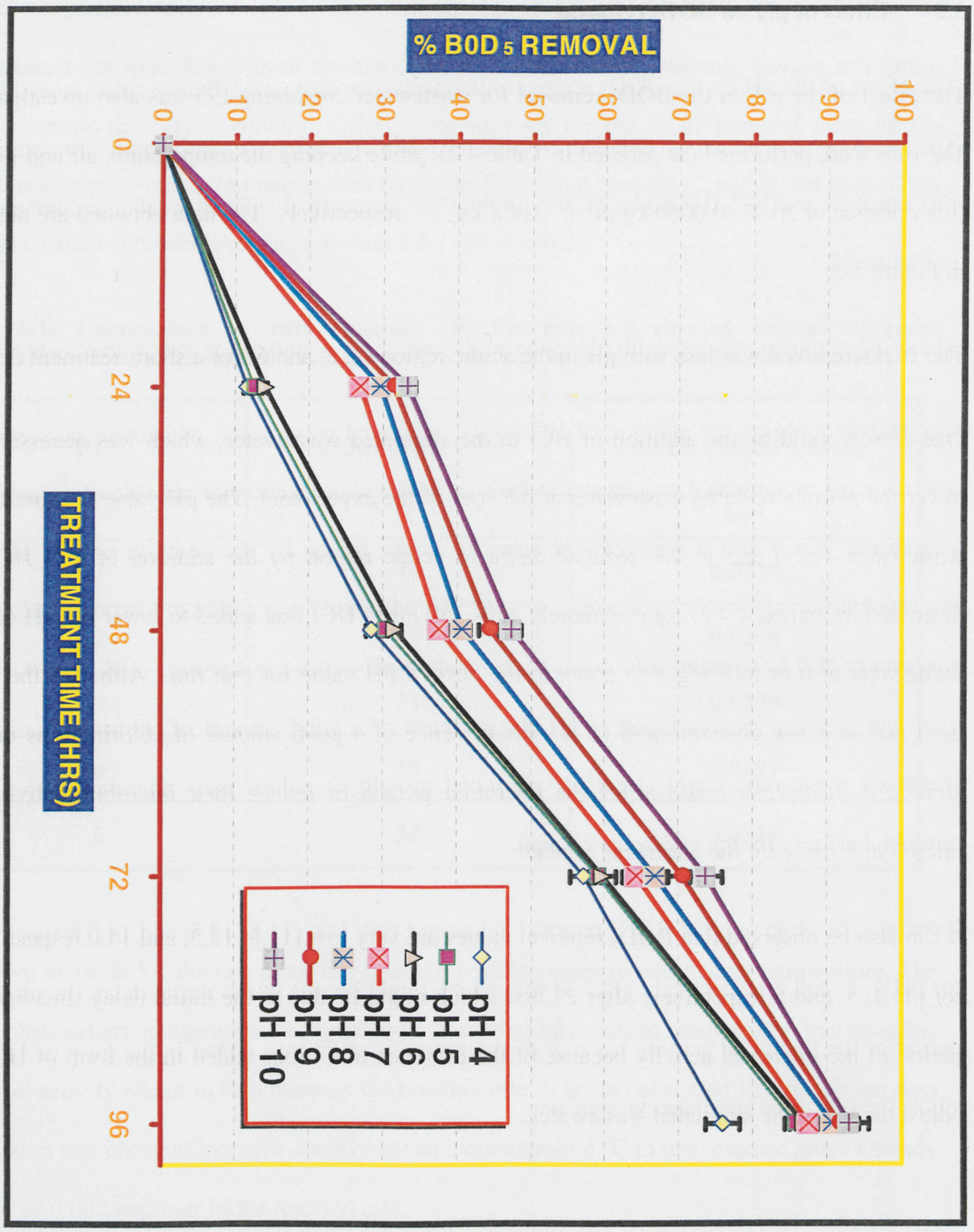

Figure 5.2: % BOD_5 removal at different pH vs. treatment time at a fixed liquid and air flux of 14.8 $kg \cdot m^{-2} \cdot s^{-1}$ and 0.0080 $kg \cdot m^{-2} \cdot s^{-1}$ respectively.

It is a well known fact that application of chlorine to wastewater results in reduction of Biochemical oxygen demand of wastewater. Whether chlorine is employed for the prevention of sulphide production in long sewer outfalls, or for the disinfection of sewage effluents, introduction of chlorine effects a reduction of BOD concurrent with the accomplishment of these purposes [53]. Therefore, presence of chlorine ions might hinder the percent reduction of BOD_5 in the acidic region.

On the other hand, it was observed that runs carried out by keeping the pH of the simulated wastewater constant at 8, 9 and 10 (i.e. basic region) resulted in higher percent of BOD_5 removal. It is evident that the run carried at lowest pH of 4 gives the lowest values of BOD_5 removal at different treatment time and the run carried out at high pH of 10 gives the highest BOD_5 removal. After 96 hours of treatment the percent removal increased to 90.7, 91.6, and 92.9 at pH 8, 9, and 10 as compared to 75.9, 85.7, and 86.8 at pH 4, 5, and 6 respectively. This could be attributed to the nature and type of microorganisms present in the simulated wastewater, which were more active at basic conditions resulting in rapid degradation of EG glycol in basic region than acidic region.

The rate constant (k) was found by taking the slope of the line of the logarithmic oxygen utilization (BOD_5) versus time (t). A plot of the logarithmic oxygen utilization versus time (t) can be found in Appendix C, and D, for run 6-12.

Table 5.2: Comparison of rate constant (k) for run 6-12 carried out at different pH at constant temperature of 20^0C for the biological oxidation of EG during 96 hours of biological treatment.

RUN	pH	RATE CONSTANT (k)
		hr^{-1}
6	4	0.0150
7	5	0.0159
8	6	0.0168
9	7	0.0182
10	8	0.0200
11	9	0.0219
12	10	0.0242

From Table 5.1, it can be seen that increases in the pH of the simulated wastewater resulted in enhancing the rate of reaction as the rate constants increase with increases in wastewater pH. The lowest reaction rate value i.e., .0150 per hour is obtained on the low pH of 4, and highest reaction rate value of 0.0242 per hour is obtained with the pH of 10 showing a fast reaction at pH in the basic region.

5.3 Effect of stripping on the BOD_5 removal

The effect of stripping on the BOD_5 removal of wastewater was evaluated by running the experiments with and without seeding. The wastewater sample was made up from distilled water and antifreeze coolant (0.75% v/v). There were no microorganisms in the wastewater sample

initially. Seed material (InterLab Inc., The Woodlands, Texas) was added to provide microorganisms to the wastewater sample when the experiment was started. A comparison of the BOD_5 removal with and without the addition of microorganisms was made. The air flux rate of 0.0080 $kg \cdot m^{-2} \cdot s^{-1}$ and a liquid flux of 14.8 $kg \cdot m^{-2} \cdot s^{-1}$ were maintained throughout the run.

In the absence of the seed material, i.e. no biological oxidation, the percentage BOD_5 removal was 8% after 96 hours of treatment. On the other hand, the percentage BOD_5 removal with an addition of four capsules of Polyseed (0.11 g of biomass per capsule on a dry basis) at the beginning of the treatment process i.e., 0 hour, was 91% after 96 hours of treatment. The addition of the seed material improved the BOD_5 removal by 83 %. This also indicated that air stripping, in the absence of microorganisms, could remove 8% of the BOD_5 in the wastewater after 96 hours of treatment.

The experimental values for the percentage of BOD_5 removal affected by the addition of seeding as plotted in Figure 5.3.

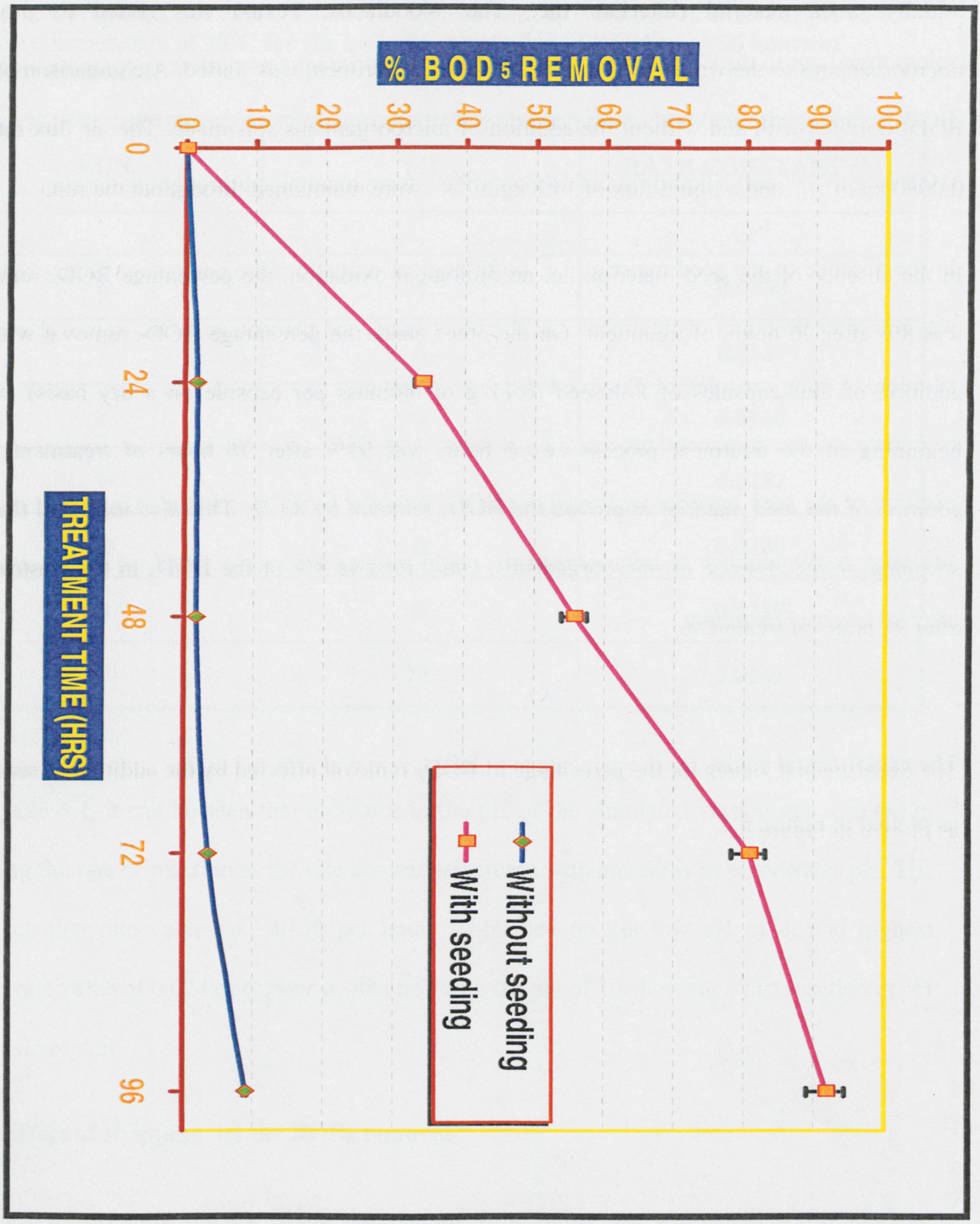

Figure 5.3: Comparison of Percent BOD_5 removal with and without seeding vs. treatment time at a fixed liquid and air flux of 14.8 $kg \cdot m^{-2} \cdot s^{-1}$ and 0.0080 $kg \cdot m^{-2} \cdot s^{-1}$ respectively.

A theoretical assumption can be made that the percentage of BOD_5 removal will increase by the addition of seeding. This assumption is based on the fact that seeding is done to ensure that enough microorganisms are present in the wastewater in order to completely oxidize the organic material. It is expected that without seeding the BOD_5 removal will be low. Without seeding the amount of microorganisms in the wastewater might not be sufficient for the oxidation of organic matter, which will results in a low percentage of BOD_5 removal. It is expected that with seeding the percentage of BOD_5 removal will be high. Since the amount of microorganisms present in the wastewater will be sufficient for the oxidation of the organic matter.

A summary of the reaction rate constants obtained with and without seeding is presented in Table 5.3, which shows an increase in the rate of reaction when the wastewater is seeded with microorganisms.

Table 5.3: Comparison of rate constant (k) for situations of with and without seeding for the biological oxidation of EG during 96 hours of biological treatment

RUN	SITUATION	TEMPERATURE	RATE CONSTANT(k)
		^{o}C	hr^{-1}
2	With Seeding	20	0.0258
13	Without Seeding	20	0.0009

The values for reaction rate constant obtained indicates that for the case of no seeding provided to the simulated wastewater reaction rate was low i.e., 0.000921. This can be attributed due to the absence of microorganisms to oxidise EG and the reaction rate was solely because of air

stripping. Under similar operating conditions reaction rate increased to 0.025789 when seeding was provided at the start of the treatment process to the simulated wastewater.

5.4 Effect of the packed bed on BOD_5 removal

To investigate the effect of the packed bed on reduction of BOD_5, an experiment was performed in which no packing was employed and the results obtained were compared with the experiments in which packing was employed. This was done so as to examine the oxidation of the biological matter, EG, from the suspended microbes in the holding tank.

Fig 5.4 shows the comparison of the normalized BOD_5 versus the treatment time for runs carried out with and without column packing.

As presented in Figure 5.4, the presence of packing appears to provide some increase in the oxidation of EG. After 96 hours of treatment a removal of 76% BOD was obtained in a situation when packing was not employed. On the other hand, 91% BOD removal increased after 96 hours of treatment when packing was employed. This shows an increase of 15% showing the effectiveness of an aerated packed column in biological oxidation to treat wastewater containing antifreeze coolant.

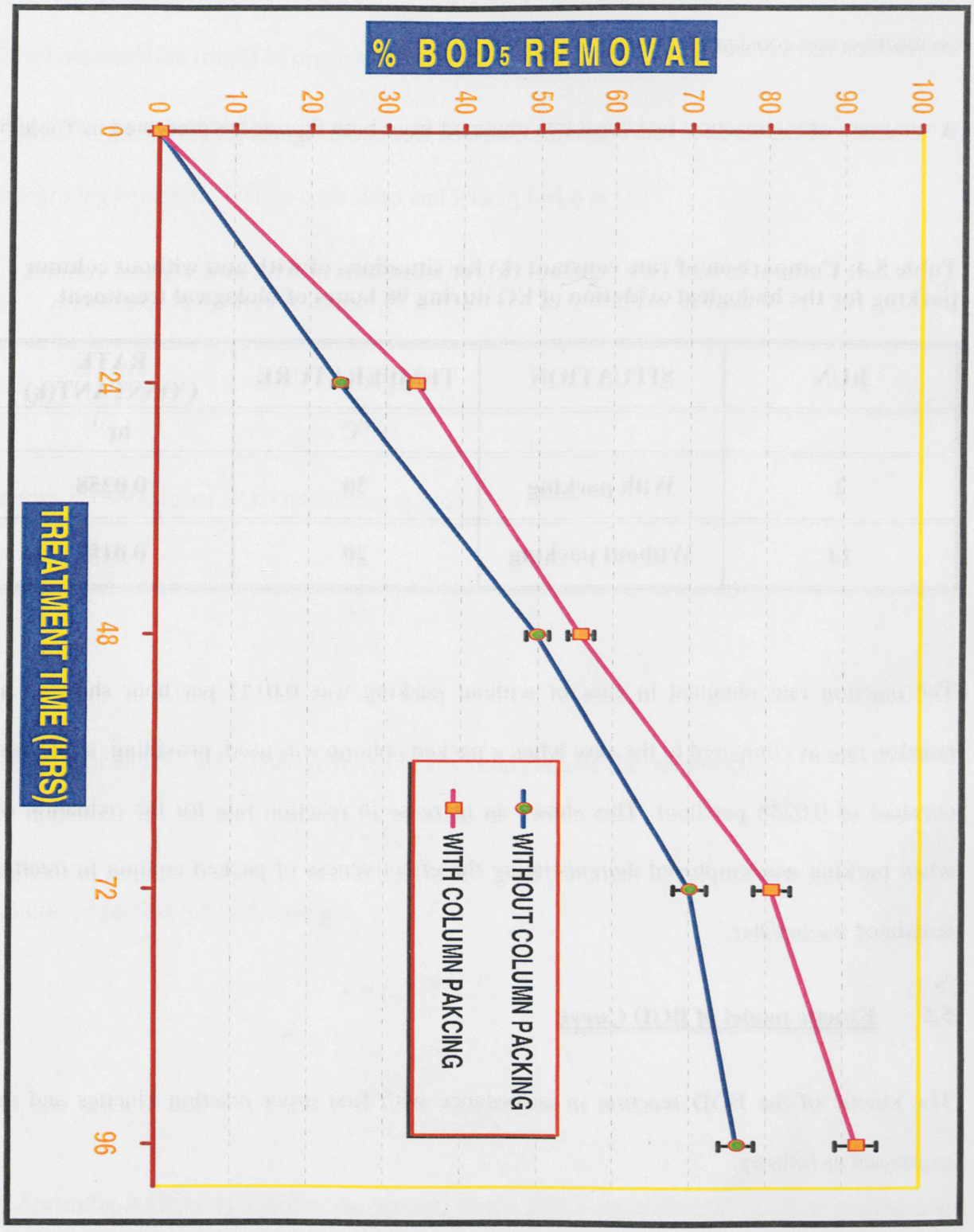

Figure 5.4: Comparison of % BOD_5 removal with column packing and without column packing vs. treatment time at a fixed liquid and air flux of 14.8 $kg \cdot m^{-2} \cdot s^{-1}$ and 0.0080 $kg \cdot m^{-2} \cdot s^{-1}$ respectively.

The reaction rate constant for the case of packing material represents the effect of packed column on reaction rate constant.

A summary of the reaction rate constants obtained from both figures are presented in Table 5.4

Table 5.4: Comparison of rate constant (k) for situations of with and without column packing for the biological oxidation of EG during 96 hours of biological treatment.

RUN	SITUATION	TEMPERATURE	RATE CONSTANT(k)
		^{o}C	hr^{-1}
2	With packing	20	0.0258
14	Without packing	20	0.0157

The reaction rate obtained in case of without packing was 0.0157 per hour showing a low reaction rate as compared to the case when a packed column was used, providing a reaction rate constant of 0.0258 per hour. This shows an increase in reaction rate for the oxidation of EG when packing was employed demonstrating the effectiveness of packed column in treating the simulated wastewater.

5.5 Kinetic model of BOD Curve

The kinetic of the BOD reaction in accordance with first order reaction kinetics and can be expressed as follows:

$$\frac{dL}{dt} = -kL \qquad (5.1)$$

where

L is the concentration (mg/l) of organic matter at time (t)

k is the reaction rate constant

By integrating equation (5.1) on both sides and letting L=Lo at t=0

$$\int_{L_o}^{L} \frac{dL}{L} = -k \int_{o}^{t} dt \tag{5.2}$$

$$\ln \frac{L}{L_0} = -kt \tag{5.3}$$

Therefore, the amount of BOD remaining at time t;

$$\frac{L}{L_0} = e^{-kt} \tag{5.4}$$

$$L = L_0 e^{-kt} \tag{5.5}$$

The amount of BOD that had been exerted at any time t equals (i.e. removed):

$$y = L_0 - L \tag{5.6}$$

Substituting equation 5.5 in 5.6 we get

$$y = L_0 - L_0 e^{-kt} \tag{5.7}$$

$$y = L_0 (1 - e^{-kt}) \tag{5.8}$$

From Appendix-A (Run-5) a plot of the amount of the BOD_5 remaining versus time produces an exponential decay. The amount of BOD_5 removal versus time also shows an exponential curve as shown in Figure 5.5

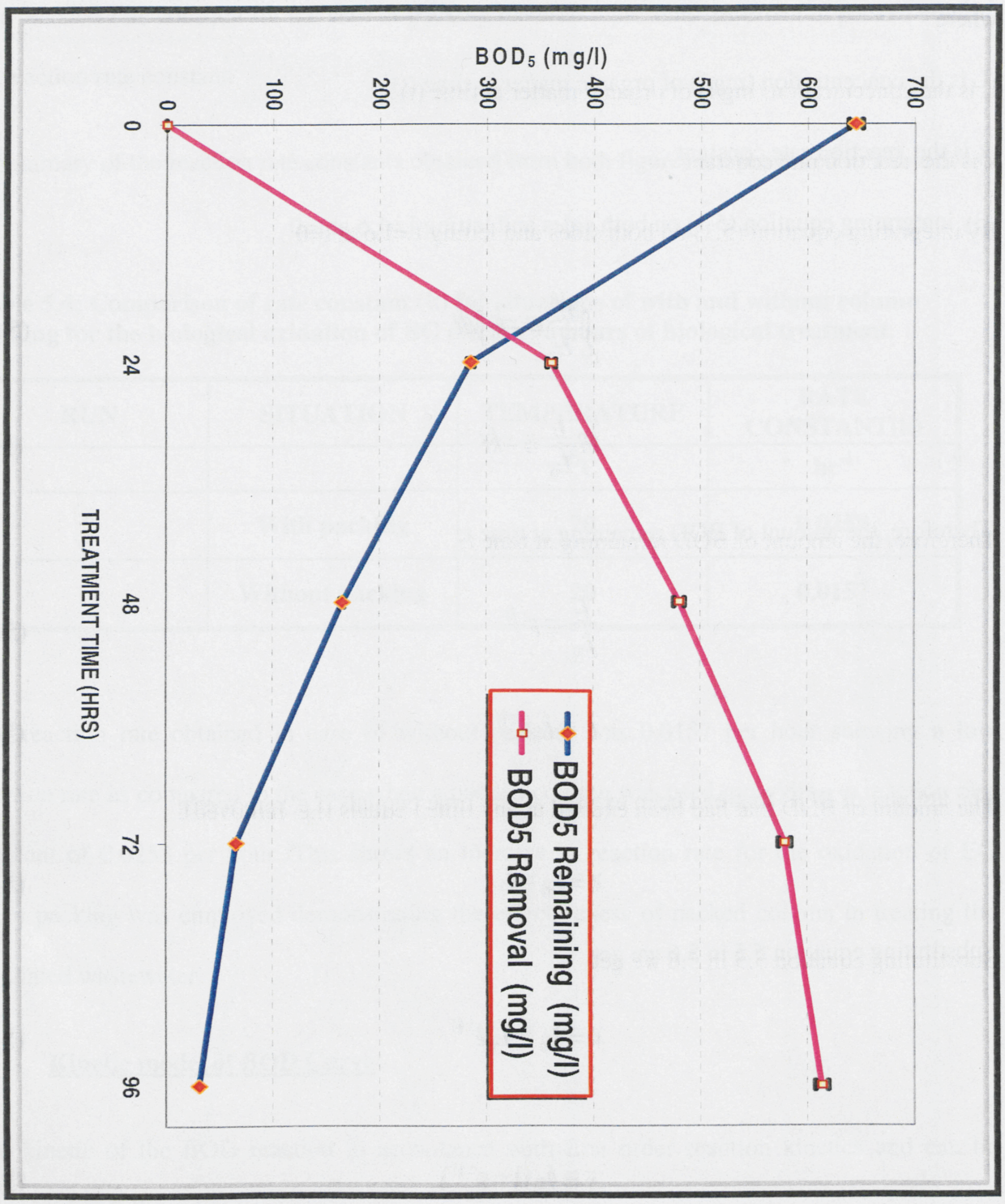

Figure 5.5: Changes in the concentration of BOD_5 removal and the BOD_5 remaining

From Table 5.1 runs 1-5 for temperature (16-32) at operational conditions, found that, temperature has direct effect on BOD removal. Therefore, k values are averaged and the averaged k is 0.02772. The first order kinetics for the BOD removal of antifreeze can be written as below.

$$y = L_0(1 - e^{(-0.02772)t}) \tag{5.9}$$

Also from Table 5.2 runs 6-12 for pH 4-10 at operational conditions, found that, pH has direct effect on BOD removal. Therefore, k values are averaged and the averaged k is 0.0188. The first order kinetics for the BOD removal of antifreeze can be written as below.

$$y = L_0(1 - e^{(-0.0188)t}) \tag{5.10}$$

5.6 The temperature dependence of the rate constant K - Arrhenius relationship

The temperature dependence of the rate and equilibrium constants can also be estimated using the van't Hoff- Arrhenius relationship.

$$K = A\exp^{(-\frac{E}{RT})} \tag{5.11}$$

where

A = constant,

K = rate coefficient, (Hr)

E = activation energy, (joules per mole)

R = universal gas constant, (J K^{-1} mol^{-1})

T = temperature, (^{0}Kelvin).

To calculate the k value by Arrhenius relationship described in equation 5.11, a graph is plotted between the natural logarithm of the reaction rate (ln k) vs. temperature (1/T).

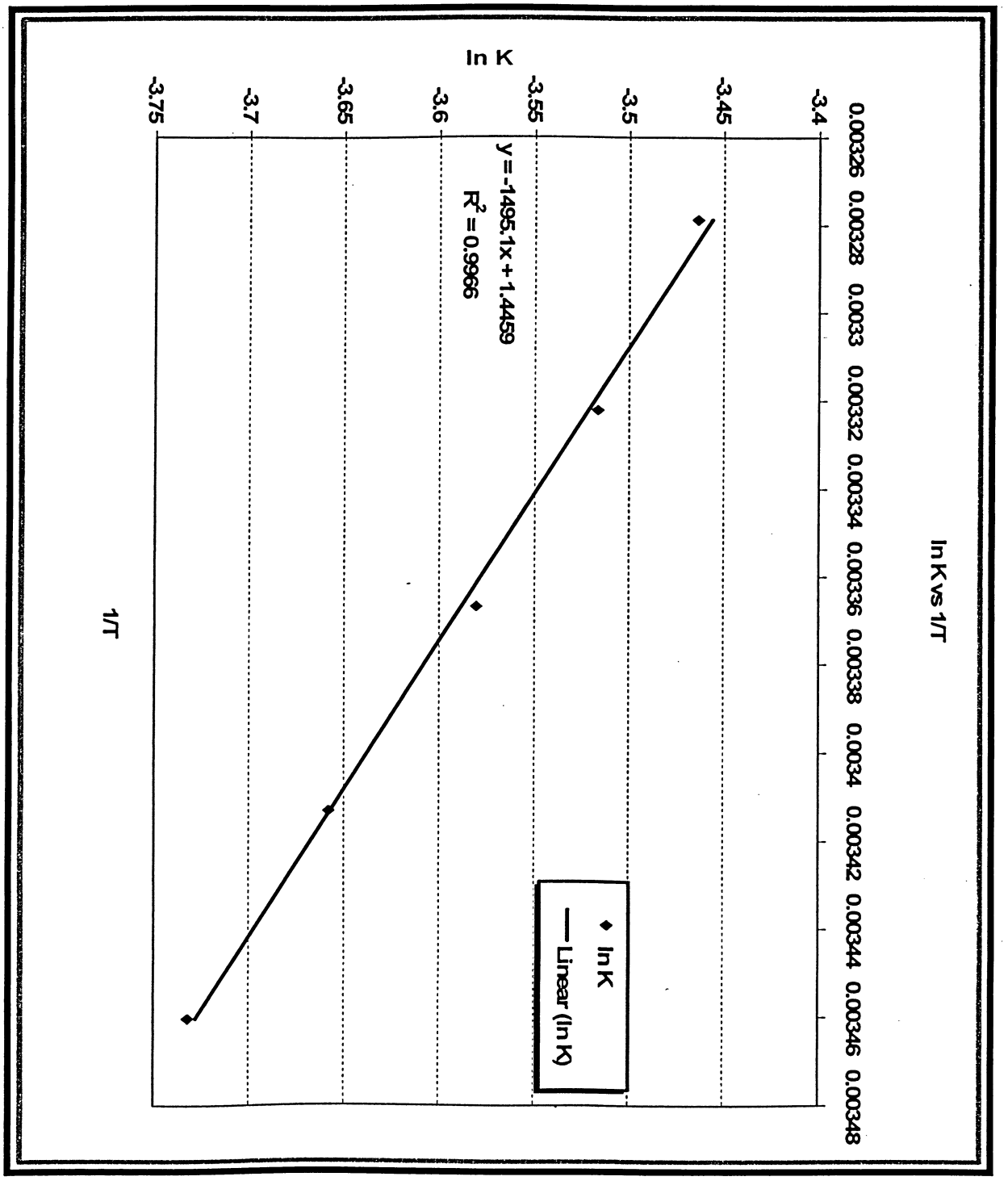

Figure 5.6: The relationship between temperature and the reaction rate constant.

From graph the values of A (y intercept) and E/R (slope) were obtained and by putting these values in equation 5.11, we get the values of reaction rate constant k. A comparison of values obtained by Arrhenius equation and by experiments (From Table5.1) is given in Table 5.5.

Table 5.5: Comparison of rate constant (k) obtained experimentally and by Arrhenius equation

TEMPERATURE	REACTION RATE	
	By Experiments	By Arrhenius equation
	k	K
^0C	Hr^{-1}	Hr^{-1}
16	0.0239	0.0241
20	0.0258	0.0258
24	0.0279	0.0277
28	0.0297	0.0296
32	0.0313	0.0316

The values obtained are in agreement with the values obtained experimentally.

Conclusion

- For the biological treatment of the simulated wastewater containing 0.75 % (v/v) antifreeze with a air flux of 0.0080 $kg \cdot m^{-2} \cdot s^{-1}$ and a liquid flux of 14.8 $kg \cdot m^{-2} \cdot s^{-1}$, an increasing trend of the BOD_5 removal with temperature was observed when liquid temperature was increased from 16 to 32 ^{o}C by 4-degrees increments.

- When the wastewater pH was increased from 4 to 10 (by one-pH unit increments), the BOD_5 removal was increased by 18%. Though less BOD removal occurred in the acidic region (i.e. pH 4, 5, 6) than in basic region. (i.e. pH 8,9,10) of treatment.

- Biological oxidation of organic matter (EG) present in antifreeze coolant was shown to be effective by using a forced air packed-bed reactor. After 96 hours of treatment 91% reduction in BOD resulted with packed column as compared to 76 % reduction in BOD_5 without packed column.

- The experimental values showed that the BOD_5 removal increased when the simulated wastewater was seeded. The addition of the seed material improved the BOD_5 removal by 82 %.

Recommendations

- Under the present arrangement a real wastewater sample form an airport facility could be used to examine the performance of the apparatus towards treating this wastewater.

- Real low temperature values (i.e. on which de-icing of the aircrafts being done), should be chosen in the experimental design and their effect should be studied. This will lead to more valuable data on EG degradation in wastewater on low temperature and demonstrate the effectiveness of the present set up in treating the wastewater at the airports.

- Further investigation should be done on the effect of temperature on EG removal while keeping the pH constant at optimum value of 10.

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APPENDEX-A: Summary of experimental data

RUN: 1 @ constant temperature of 16 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_{1o}	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
HR	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
0	8.15	2.40	8.10	7.70	1605	1623.00	0.00	0.00	3.21
	8.22	2.35	8.10	7.70	1641				
24	8.90	4.90	8.50	8.10	1080	1095.00	528.00	32.53	3.04
	8.80	4.70	8.50	8.10	1110				
48	9.00	6.30	8.10	7.90	750	742.50	880.50	54.25	2.87
	8.90	6.25	8.10	7.90	735				
72	8.60	6.95	8.10	7.90	435	411.00	1212.00	74.68	2.61
	8.40	6.91	8.10	7.90	387				
96	8.90	8.00	8.10	7.70	150	150.00	1473.00	90.76	2.18
	8.90	8.00	8.10	7.70	150				

RUN: 2 **@ constant temperature of 20 ^{0}C**

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	Mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	8.10	2.80	8.10	7.90	1530	1555.50	0.00	0.00	3.19
	8.10	2.63	8.10	7.90	1581				
24	8.70	5.10	8.10	7.90	1020	1027.50	528.00	33.94	3.01
	8.70	5.05	8.10	7.90	1035				
48	8.40	5.30	8.50	7.70	690	690.00	865.50	55.64	2.84
	8.40	5.30	8.50	7.70	690				
72	8.60	7.30	8.80	8.50	300	300.00	1255.50	80.71	2.48
	8.60	7.30	8.80	8.50	300				
96	8.90	8.40	8.40	8.33	129	129.00	1426.50	91.71	2.11
	8.90	8.40	8.40	8.33	129				

RUN: 3 @ constant temperature of 24 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	Mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	8.80	5.60	8.80	8.70	930	930.00	0.00	0.00	2.97
	8.80	5.60	8.80	8.70	930				
24	8.80	6.70	8.80	8.50	540	540.00	390.00	41.94	2.73
	8.80	6.70	8.80	8.50	540				
48	8.80	6.75	8.80	8.00	375	375.00	555.00	59.68	2.57
	8.80	6.75	8.80	8.00	375				
72	8.20	7.50	7.70	7.45	135	135.00	795.00	85.48	2.13
	8.20	7.50	7.70	7.45	135				
96	8.30	7.75	8.40	8.00	45	66.00	864.00	92.90	1.82
	8.40	7.71	8.40	8.00	87				

RUN: 4 @ constant temperature of 28 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	Mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	8.30	5.60	7.40	7.35	795	795.00	0.00	0.00	2.90
	8.30	5.60	7.40	7.35	795				
24	8.00	6.30	8.30	8.05	435	435.00	360.00	45.28	2.64
	8.00	6.30	8.30	8.05	435				
48	7.90	7.00	7.80	7.75	255	255.00	540.00	67.92	2.41
	7.90	7.00	7.80	7.75	255				
72	8.10	7.70	8.10	8.00	90	90.00	705.00	88.68	1.95
	8.10	7.70	8.10	8.00	90				
96	8.00	7.62	8.40	8.18	49	49.20	745.80	93.81	1.69
	8.00	7.62	8.40	8.18	49				

RUN: 5 @ constant temperature of 32 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	7.90	5.70	7.40	7.35	645	645	0.00	0.00	2.81
	7.90	5.70	7.40	7.35	645				
24	8.00	6.70	8.30	8.05	315	285.0	360.00	55.81	2.45
	8.00	6.90	8.30	8.05	255				
48	8.30	7.60	8.30	8.15	165	165.0	480.00	74.42	2.22
	8.30	7.60	8.30	8.15	165				
72	8.50	8.00	8.50	8.25	75	66.0	579.00	89.77	1.82
	8.50	8.06	8.50	8.25	57				
96	8.20	7.63	8.70	8.23	31	31.20	613.80	95.16	1.49
	8.20	7.63	8.70	8.23	31				

RUN: 6 **@ constant pH 4**

constant temperature of 20 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	8.10	5.20	8.00	7.90	840	840.00	0.00	0.00	2.92
	8.00	5.10	8.00	7.90	840				
24	7.60	4.75	8.50	8.10	735	742.50	97.50	11.61	2.87
	7.70	4.80	8.50	8.10	750				
48	8.00	5.70	8.40	8.10	600	600.00	240.00	28.57	2.78
	8.20	5.90	8.40	8.10	600				
72	8.00	6.60	8.10	8.00	390	360.00	480.00	57.14	2.56
	8.00	6.80	8.10	8.00	330				
96	8.00	7.50	7.00	6.90	120	200.00	640.00	76.19	2.30
	8.00	7.40	7.00	6.90	150				

RUN: 7 **@ constant pH 5**

constant temperature of 20 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	7.80	4.90	8.00	7.90	840	840.00	0.00	0.00	2.92
	7.80	4.90	8.00	7.90	840				
24	8.00	5.10	8.50	8.10	750	735.00	105.00	12.50	2.87
	8.00	5.20	8.50	8.10	720				
48	8.10	5.90	8.40	8.10	570	585.00	255.00	30.36	2.77
	8.10	5.80	8.40	8.10	600				
72	7.20	5.90	8.10	8.00	360	345.00	495.00	58.93	2.54
	7.20	6.00	8.10	8.00	330				
96	8.00	7.50	8.20	8.10	120	120.00	720.00	85.71	2.08
	8.00	7.50	8.20	8.10	120				

RUN: 8 **@ constant pH 6**

constant temperature of 20 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	8.20	5.00	8.50	8.10	840	855.00	0.00	0.00	2.93
	8.30	5.00	8.50	8.10	870				
24	8.50	5.80	8.50	8.20	720	735.00	120.00	14.04	2.87
	8.50	5.70	8.50	8.20	750				
48	8.10	5.90	8.40	8.10	570	585.00	270.00	31.58	2.77
	8.10	5.80	8.40	8.10	600				
72	7.20	5.90	8.10	8.00	360	345.00	510.00	59.65	2.54
	7.20	6.00	8.10	8.00	330				
96	7.20	6.80	8.20	8.10	90	112.50	742.50	86.84	2.05
	7.10	6.55	8.20	8.10	135				

RUN: 9 **@ constant pH 7**

constant temperature of 20 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	7.20	4.00	8.50	8.10	840	840.00	0.00	0.00	2.92
	7.20	4.00	8.50	8.10	840				
24	8.50	6.00	8.50	8.20	660	615.00	225.00	26.79	2.79
	8.40	6.20	8.50	8.20	570				
48	8.40	6.50	8.40	8.20	510	525.00	315.00	37.50	2.72
	8.40	6.40	8.40	8.20	540				
72	8.10	6.90	8.40	8.10	270	300.00	540.00	64.29	2.48
	8.20	6.80	8.40	8.10	330				
96	7.20	6.60	8.20	7.80	60	105.00	735.00	87.50	2.02
	7.10	6.20	8.20	7.80	150				

RUN: 10 @ constant pH 8

constant temperature of 20 ^{0}C

constant air flow rate of 0.0080 $kg \cdot m^{-2} \cdot s^{-1}$

constant liquid flow rate of 14.8 $kg \cdot m^{-2} \cdot s^{-1}$

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	8.00	4.90	8.50	8.10	810	810.00	0.00	0.00	2.91
	8.00	4.90	8.50	8.10	810				
24	8.70	6.40	8.60	8.20	570	570.00	240.00	29.63	2.76
	8.70	6.40	8.60	8.20	570				
48	8.60	6.10	8.60	7.70	480	480.00	330.00	40.74	2.68
	8.60	6.10	8.60	7.70	480				
72	8.80	7.10	8.80	8.00	270	270.00	540.00	66.67	2.43
	8.80	7.10	8.80	8.00	270				
96	8.30	7.70	8.40	8.00	60	75.00	735.00	90.74	1.88
	8.40	7.70	8.40	8.00	90				

RUN: 11 @ constant pH 9

constant temperature of 20 ^{0}C

constant air flow rate of 0.0080 $kg \cdot m^{-2} \cdot s^{-1}$

constant liquid flow rate of 14.8 $kg \cdot m^{-2} \cdot s^{-1}$

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	8.00	4.90	8.50	8.10	810	810.00	0.00	0.00	2.91
	8.00	4.90	8.50	8.10	810				
24	7.60	5.20	7.80	7.30	570	555.00	255.00	31.48	2.74
	7.60	5.30	7.80	7.30	540				
48	7.70	6.00	7.90	7.70	450	450.00	360.00	44.44	2.65
	7.70	6.00	7.90	7.70	450				
72	8.10	7.20	8.00	7.90	240	240.00	570.00	70.37	2.38
	8.10	7.20	8.00	7.90	240				
96	8.10	7.80	8.20	8.00	30	67.50	742.50	91.67	1.83
	8.20	7.65	8.20	8.00	105				

RUN: 12 @ constant pH 10

constant temperature of 20 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	7.80	4.60	8.50	8.10	840	855	0.00	0.00	2.93
	7.80	4.50	8.50	8.10	870				
24	7.90	5.80	8.30	8.00	540	570.0	285.00	33.33	2.76
	8.00	5.80	8.20	8.00	600				
48	7.90	6.20	8.20	8.00	450	450.0	405.00	47.37	2.65
	7.90	6.20	8.20	8.00	450				
72	8.50	7.30	8.50	8.00	210	225.0	630.00	73.68	2.35
	8.50	7.20	8.50	8.00	240				
96	8.20	7.50	8.60	8.00	30	60.00	795.00	92.98	1.78
	8.20	7.30	8.60	8.00	90				

RUN: 13 without seeding

@ constant temperature 20 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

Time	DO1	DO2	B1	B2	BOD5	BOD5,ave	ΔBOD5	%BOD5	log
HR	Mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	
0	8.10	5.20	8.00	7.90	840	840.00	0.00	0.00	2.92
	8.00	5.10	8.00	7.90	840				
24	7.60	4.50	8.50	8.10	810	825.00	15.00	1.79	2.92
	7.70	4.50	8.50	8.10	840				
48	8.00	5.00	8.40	8.10	810	825.00	15.00	1.79	2.92
	8.10	5.00	8.40	8.10	840				
72	8.00	5.10	8.20	8.00	810	810.00	30.00	3.57	2.91
	8.00	5.10	8.20	8.00	810				
96	7.80	5.10	7.00	6.90	780	765.00	75.00	8.93	2.88
	7.80	5.20	7.00	6.90	750				

RUN: 14 **without packed column**

@ constant temperature of 20 ^{0}C

constant air flow rate of 0.0080 kg·m^{-2}·s^{-1}

constant liquid flow rate of 14.8 kg·m^{-2}·s^{-1}

4 Capsules at 0-hour

Time	DO_1	DO_2	B_1	B_2	BOD_5	$BOD_{5,ave}$	ΔBOD_5	$\%BOD_5$	log
Hour	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
0	8.20	5.40	7.00	6.60	720	750.00	0.00	0.00	2.88
	8.20	5.20	7.00	6.60	780				
24	8.50	6.30	8.50	8.20	570	570.00	180.00	24.00	2.76
	8.40	6.20	8.50	8.20	570				
48	8.40	6.90	8.40	8.20	390	375.00	375.00	50.00	2.57
	8.30	6.90	8.40	8.20	360				
72	8.10	7.00	7.10	6.70	210	225.00	525.00	70.00	2.35
	8.20	7.00	7.10	6.70	240				
96	7.20	6.50	7.70	7.40	120	180.00	570.00	76.00	2.26
	7.10	6.40	7.70	7.40	120				

APPENDEX-B:

Sample calculation for BOD_5

$$BOD_5, mg/l = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

where:

D_1 = Dissolved oxygen of diluted sample immediately after preparation, mg/l

D_2 = Dissolved oxygen of diluted sample after 5 days of incubation at 20° C, mg/l

P = decimal volumetric fraction of sample used

B_1 = Dissolved oxygen of seed control before incubation, mg/l

B_2 = Dissolved oxygen of seed control after incubation, mg/l

f = ratio of seed in diluted sample to seed in seed control

At 0 hour of treatment, the BOD_5 values for Run 12 (pH 10) of the two trials can be calculated by above equation.

$$BOD_{5,1} = \frac{[(7.80 - 4.60) - (8.50 - 8.10)\frac{10}{10}]}{\frac{1}{300}} = 840$$

$$BOD_{5,2} = \frac{[(7.80 - 4.50) - (8.50 - 8.10)\frac{10}{10}]}{\frac{1}{300}} = 870$$

Therefore the average BOD_5 can then be calculated as:

$$BOD_{5,avg} = \frac{[(BOD_{5,1}) + (BOD_{5,2})]}{2}$$

$$BOD_{5,avg} = \frac{[(840) + (870)]}{2} = 855$$

At 24 hour of treatment, the BOD_5 values for two trials for the same run can be calculated as:

$$BOD_{5,1} = \frac{[(7.90 - 5.80) - (8.30 - 8.00)\frac{10}{10}]}{\frac{1}{300}} = 540$$

$$BOD_{5,2} = \frac{[(8.0 - 5.80) - (8.20 - 8.00)\frac{10}{10}]}{\frac{1}{300}} = 600$$

Therefore the average BOD_5 can then be calculated as:

$$BOD_{5,avg} = \frac{[(540) + (600)]}{2} = 570$$

At 48 hour of treatment, the BOD_5 values for two trials for the same run can be calculated as:

$$BOD_{5,1} = \frac{[(7.9 - 6.20) - (8.20 - 8.00)\frac{10}{10}]}{\frac{1}{300}} = 450$$

$$BOD_{5,2} = \frac{[(7.9-6.20)-(8.20-8.00)\frac{10}{10}]}{\frac{1}{300}} = 450$$

Therefore the average BOD_5 can then be calculated as:

$$BOD_{5,avg} = \frac{[(450)+(450)]}{2} = 450$$

At 72 hour of treatment, the BOD_5 values for two trials for the same run can be calculated as:

$$BOD_{5,1} = \frac{[(8.50-7.30)-(8.50-8.00)\frac{10}{10}]}{\frac{1}{300}} = 210$$

$$BOD_{5,2} = \frac{[(8.50-7.20)-(8.50-8.00)\frac{10}{10}]}{\frac{1}{300}} = 240$$

Therefore the average BOD_5 can then be calculated as:

$$BOD_{5,avg} = \frac{[(210)+(240)]}{2} = 225$$

At 96 hour of treatment, the BOD_5 values for two trials for the same run can be calculated as:

$$BOD_{5,1} = \frac{[(8.20-7.50)-(8.60-8.00)\frac{10}{10}]}{\frac{1}{300}} = 30$$

$$BOD_{5,2} = \frac{[(8.20 - 7.30) - (8.60 - 8.00)\frac{10}{10}]}{\frac{1}{300}} = 90$$

Therefore the average BOD_5 can then be calculated as:

$$BOD_{5,avg} = \frac{[(30) + (90)]}{2} = 60$$

APPENDIX-C:

Sample calculation for rate constan

Calculating rate constant using Log- Differential Method

We know that

$$\log (L) = \log (L_o e^{-kt})$$

$$\log (L) = -kt (\log e) + \log (L_o)$$

$$\text{slope} = - k \log e$$

$$k = -\text{slope}/\log e$$

$$k = -\text{slope}/0.4343$$

Using Excel, a linear regression equation can be found.

The slope of the equation is equivalent to the rate constant k.

Therefore from Fig. D.1, rate constant FOR Run 1, can be found by the equation

$$y = -0.0104x + 3.2809$$

$$k = \frac{-0.0104}{0.4343}$$

$$k = -0.0239 / hr$$

APPENDIX-D

Graphs of log (BOD_5) vs. Treatment time

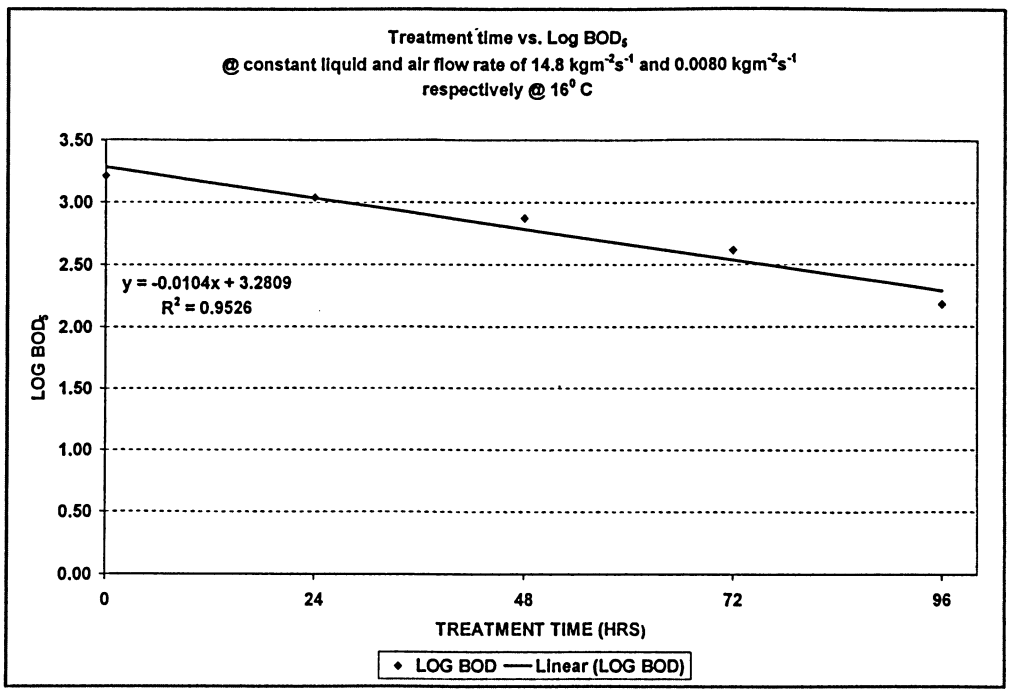

Figure D.1- Rate constant for RUN-1

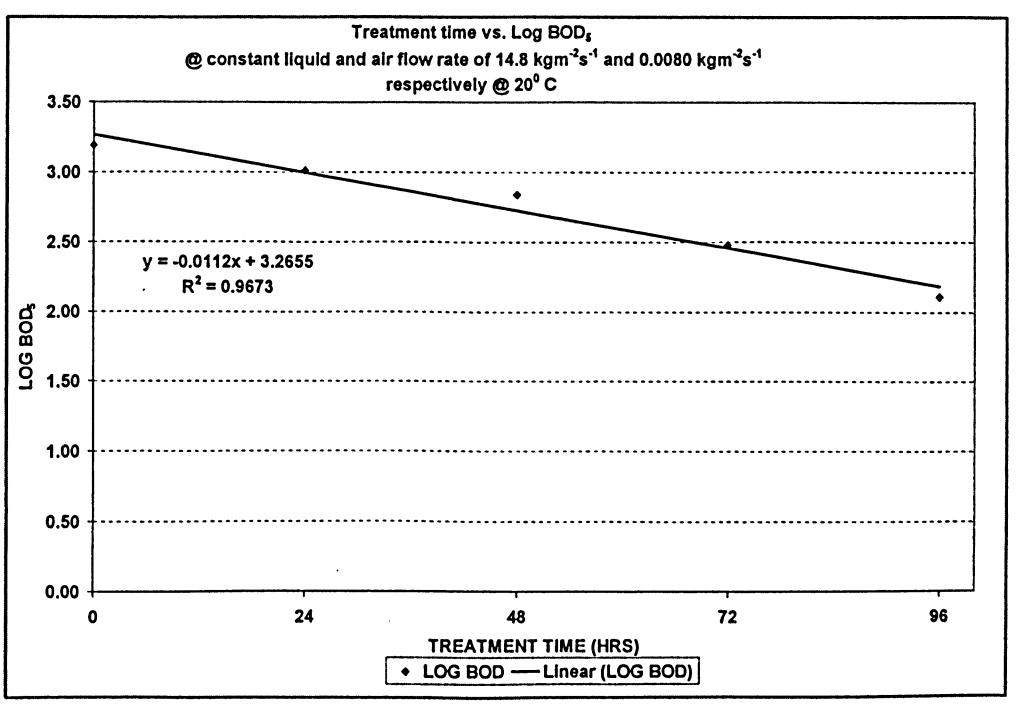

Figure D.2- Rate constant for RUN-2

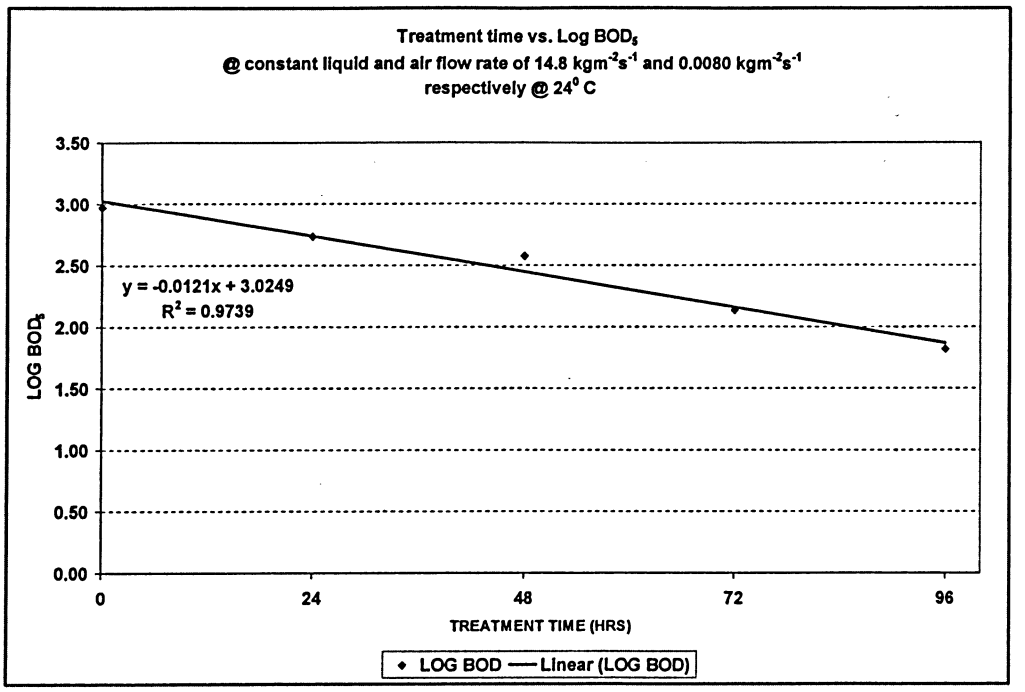

Figure D.3- Rate constant for RUN-3

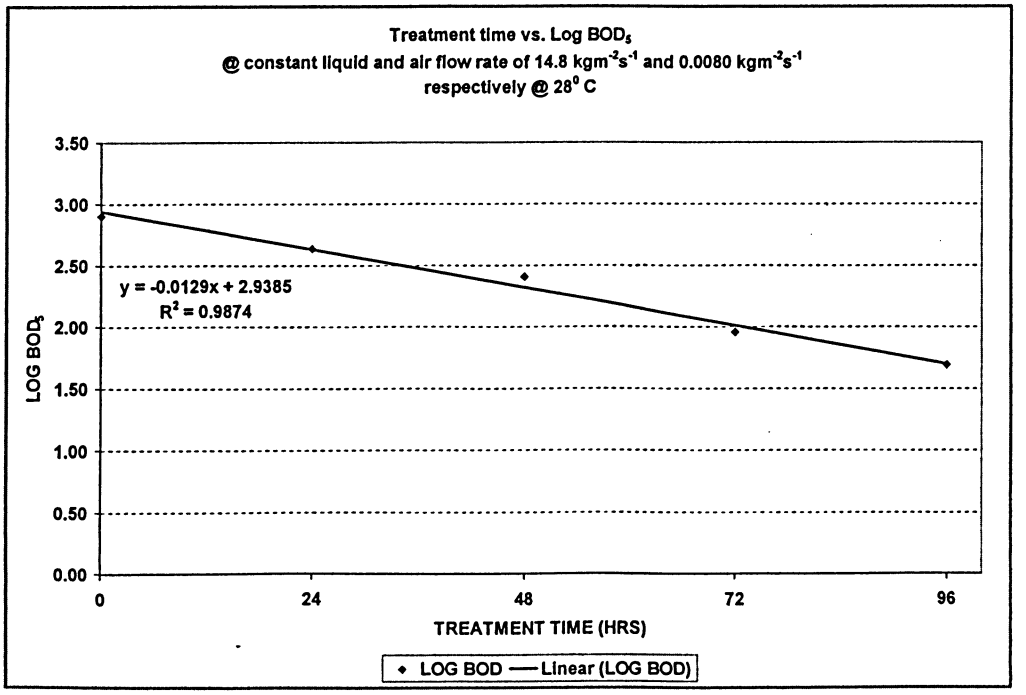

Figure D.4- Rate constant for RUN-4

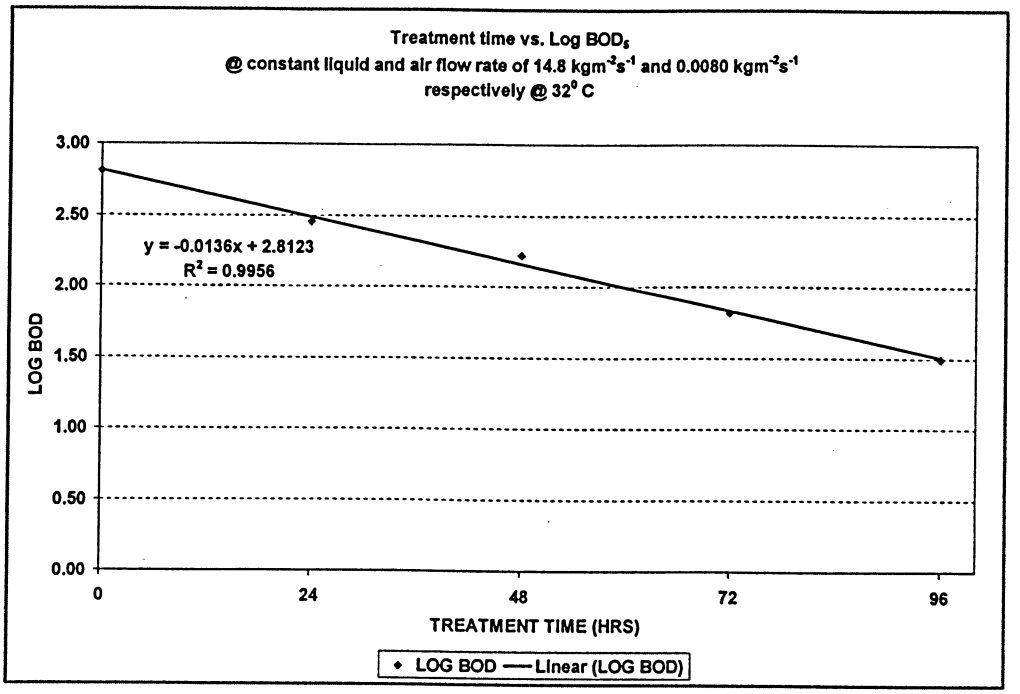

Figure D.5- Rate constant for RUN-5

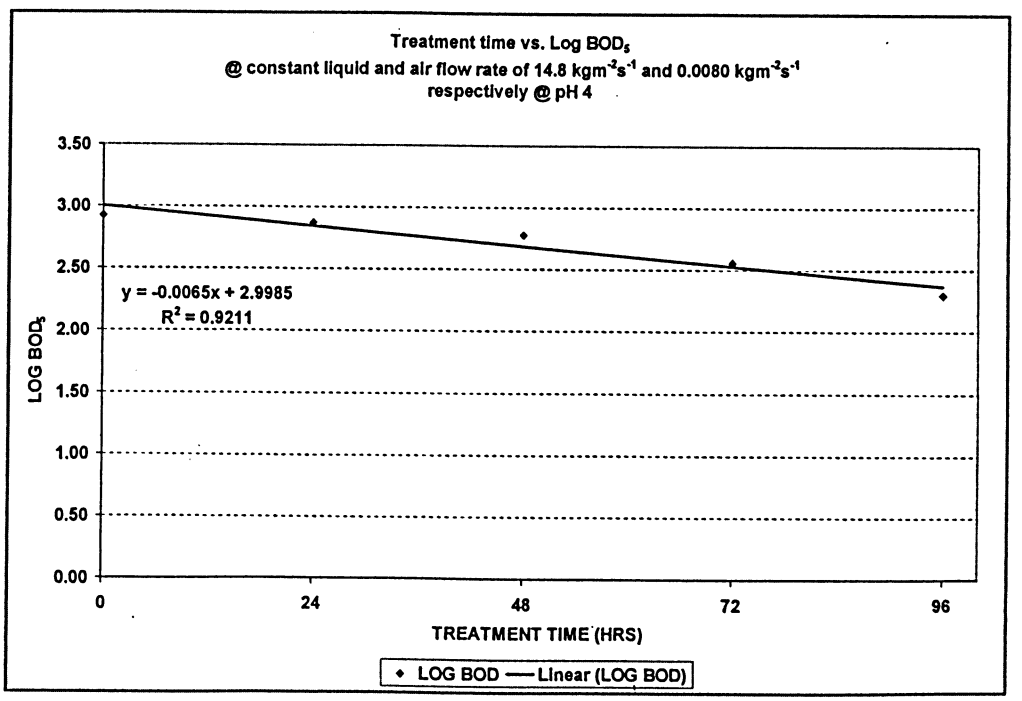

Figure D.6- Rate constant for RUN-6

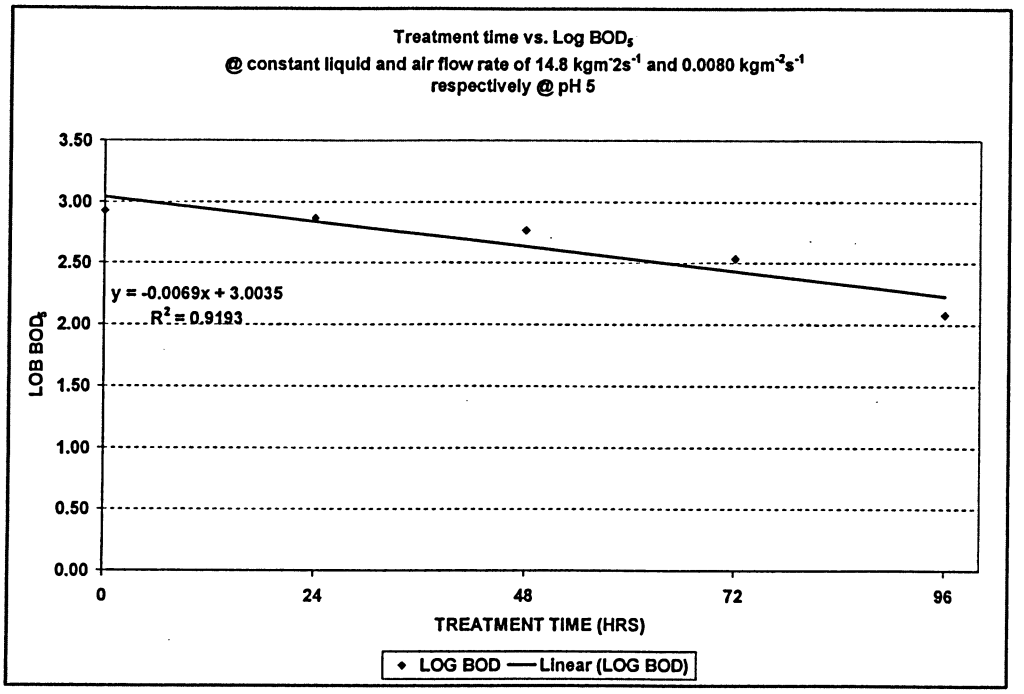

Figure D.7- Rate constant for RUN-7

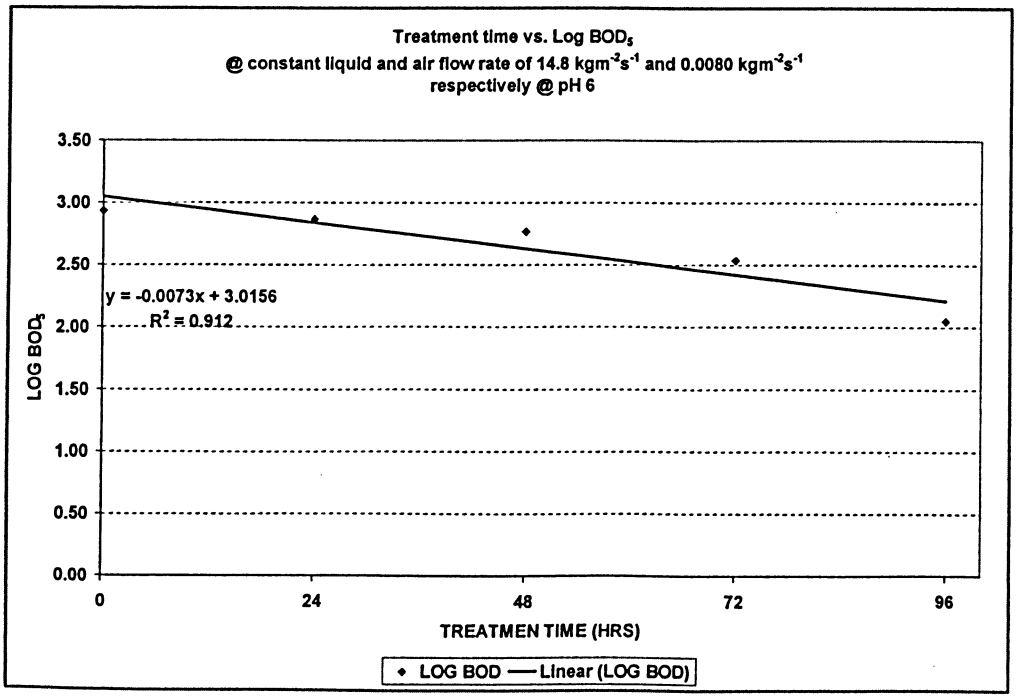

Figure D.8- Rate constant for RUN-8

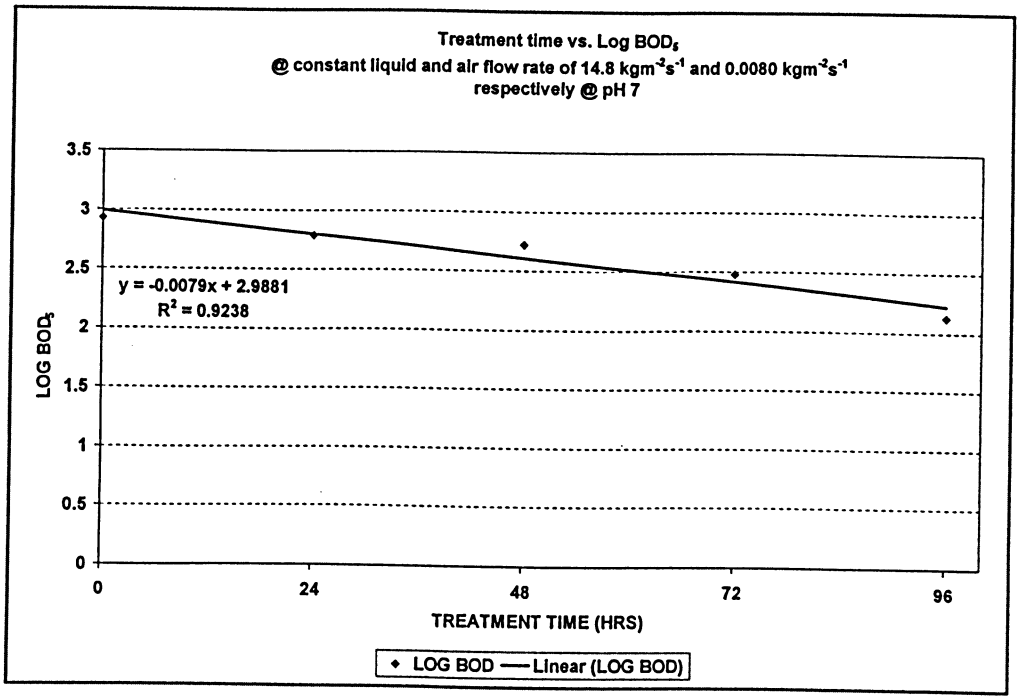

Figure D.9- Rate constant for RUN-9

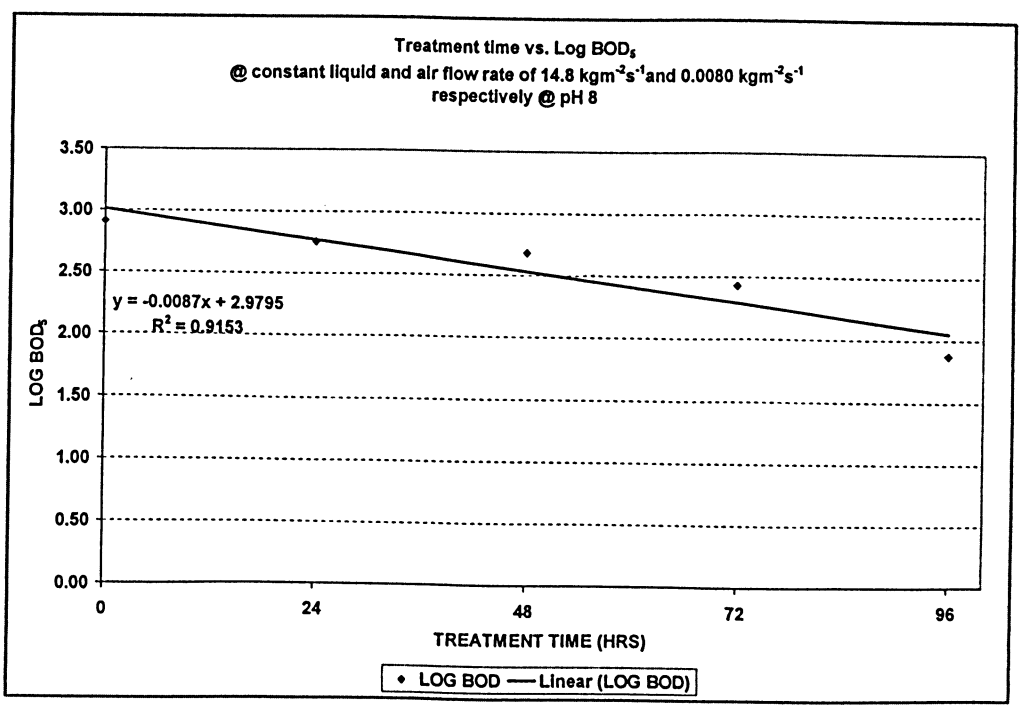

Figure D.10- Rate constant for RUN-10

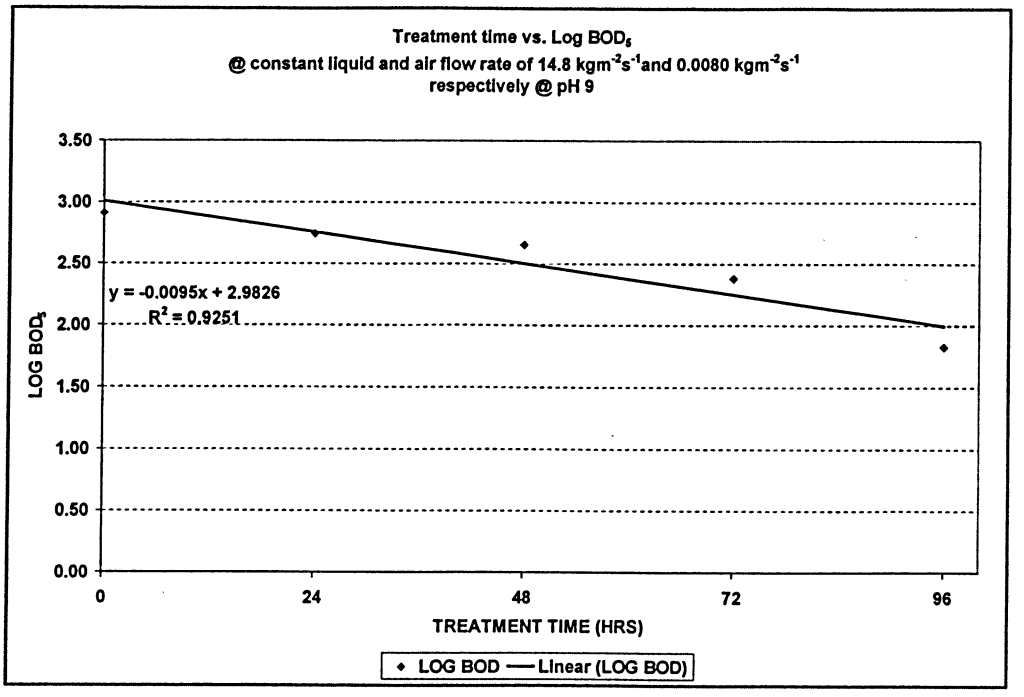

Figure D.11- Rate constant for RUN-11

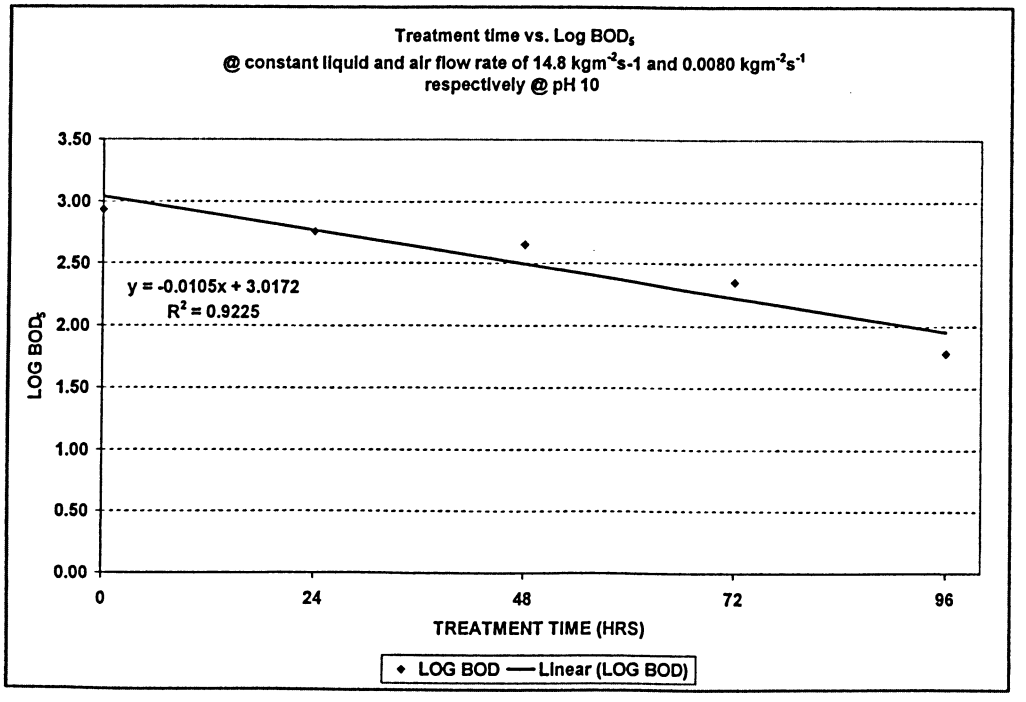

Figure D.12- Rate constant for RUN-12

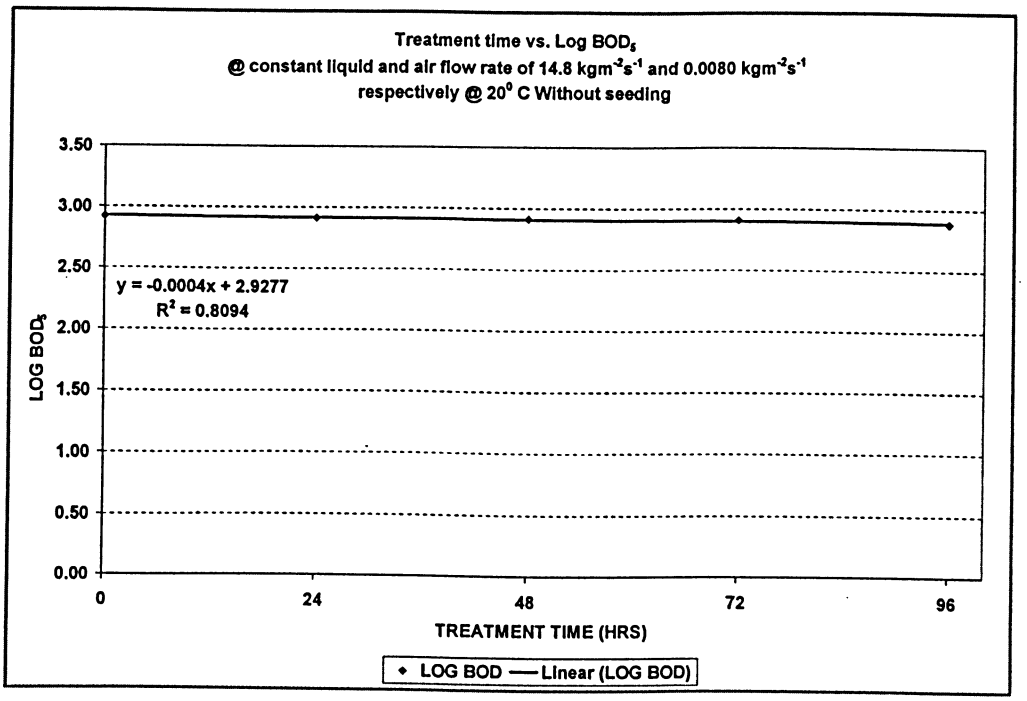

Figure D.13- Rate constant for RUN-13

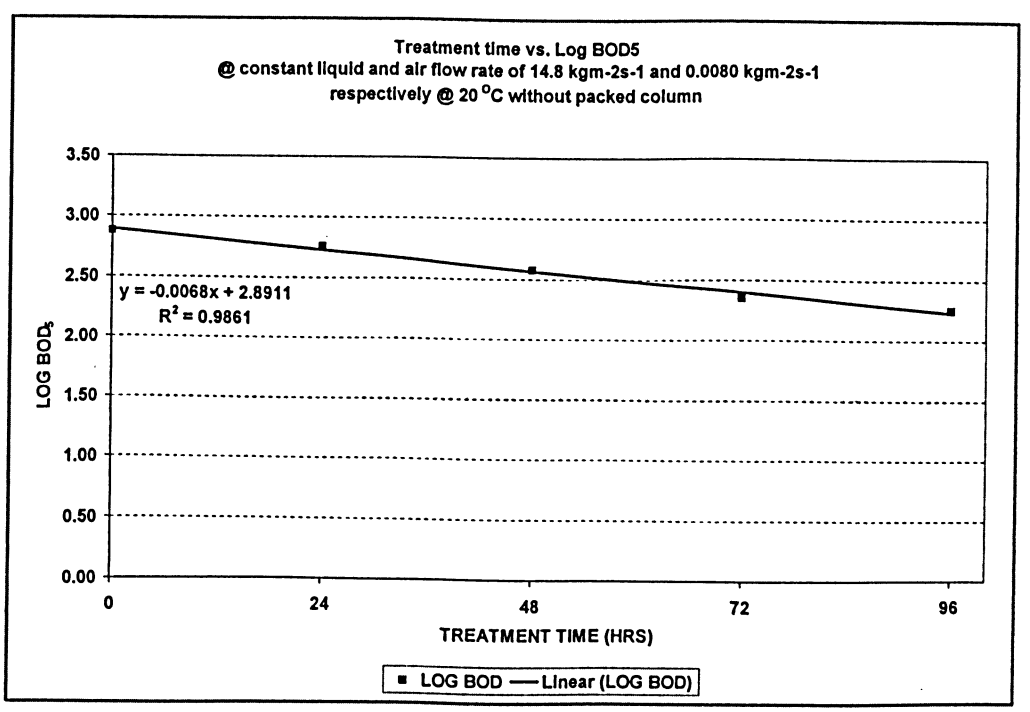

Figure D.14 Rate constant for RUN-14

APPENDEX-E:

E-1 Error analysis

In performing experiments, errors play a factor in obtaining good results. The errors in experimental data are those factors that are always vague to some extent and carry some amount of uncertainty. A reasonable definition of experimental uncertainty/error may have a great deal depending on the circumstances of the experiment.

Uncontrollable errors associated with the standardized BOD_5 test, temperature, air, and liquid flow rate fluctuations with the experimental apparatus are factors that contributed to the discrepancies among the experiments. For the present project the measurement of dissolved oxygen was very crucial in determining the biological oxygen demand. The dissolved oxygen meter (YSI Incorporated Ohio, USA, Model 52-C) must be turn on 10 minutes to stabilize before taking the measurement, otherwise there would be discrepancies among the DO readings. The membrane of the dissolved oxygen probe should be perfectly flat, smooth and without leaks.

The kline and Mc clintok method is used for estimating uncertainty in experimental results [55].

The 5- day BOD for a seeded wastewater sample is given by the following expression:

$$BOD_5, mg/l = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P} \qquad \text{(E.1)}$$

The uncertainty associated in measuring the volumes of seed and sample, and the uncertainty in the volume of the BOD bottle were assumed to be negligible in comparison to the errors associated with the DO; D_1, D_2, B_1 and B_2.

E-2 Calculation associated with uncertainty in dissolved oxygen measurements.

The error associated with dissolved oxygen measurements were calculated from the manufacture's instructions. Examples calculations is based on the initial DO measurements for Run.3

Instrument accuracy ±0.1 % plus 1 last significant figure

± 0.001x 8.64 +0.01 = 0 .0186

Probe background*: background factor @ 20 °C x (1-a/b)c

±.01 x (1-8.64/9.08) x 8.3 = 0.069

Probe non linearity ±0.3% of reading

±0.003 x 8.3 = 0.0249

Temperature compensation ±0.2% of DO reading per °C of temperature difference between sample and calibration temp

±(22.5-20.6) x 0.002 x 8.3 =0 .035

*a is the calibration value (dissolved oxygen reading):

b is the solubility of oxygen in fresh water at 760 mm Hg and at the measurement temperature

c is the measured dissolved oxygen value.

The resulting errors were combined to determine the probable error in the dissolved oxygen measurement by a root mean square calculation

RMS error= $\sqrt{0.0186^2 + 0.069^2 + 0.0249^2 + 0.035^2} = \pm 0.0837$ mg/l