NOTE TO USERS

BIOLOGICAL TREATMENT OF WASTEWATER CONTAINING AUTOMOTIVE ANTIFREEZE SOLUTION USING A PACKED COLUMN

by

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Abstract

Simulated wastewater samples containing antifreeze were treated biologically using a packed column as an aerator. The objective of this project is to determine the rate of biological degradation of ethylene glycol at different air flow rates, liquid flow rates, and varied seeding rates at different time intervals, to achieve the highest removal rate of the BOD. The biological oxygen demand (BOD) of the wastewater was measured. Under a liquid flowrate of 5.5 $kg{\cdot}m^{-2}s^{-1}$ the BOD removal increased when the air flowrate was increased from 0.0069 to 0.0414 $kg{\cdot}m^{-2}s^{-1}$. However, further increases of the air flowrate beyond 0.0138 $kg{\cdot}m^{-2}s^{-1}$ did not affect the BOD removal rate significantly. On the other hand, with a constant air flowrate when the liquid flowrate was increased from 5.5 to 11, 16.5, and 27.5 $kg{\cdot}m^{-2}s^{-1}$, 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 the wastewater treatment.

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Nomenclature

a	Area where diffusion occurs (m^2)
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)
C_i	Concentration of dissolved oxygen at the interface (g/m^3)
C_l	Concentration of oxygen (g/m^3)
D_c	Diffusion coefficient of oxygen in the water (m^2/s)
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)
DEG	Diethylene glycol
EG	Ethylene glycol
f	Ratio of seed in diluted sample to seed in seed control
H_c	Henry's constant
k	Rate constant (hr^{-1})
k_c	Liquid phase mass transfer coefficient (m/s)
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
P_b	Partial pressure of oxygen in bulk gas (atm)
p_l	Equilibrium pressure of oxygen dissolved in the liquid (atm)
PEG	Polyethylene glycol
PG	Propylene glycol
TOC	Total organic carbon
X_1	Independent variable
X_2	Independent variable
y	BOD_5 exerted at any time (mg/l)

1. INTRODUCTION

A large quantity of de-icing agents is used in automobile engine coolants and at many airports to de-ice air planes before taking off during winter. De-icing agents usually contain ethylene glycol (EG), polyethylene glycol (PEG), diethylene glycol (DEG) and propylene glycol (PG). EG based fluids are the most common deicing / anti-icing fluids used in North America [1], EG is commonly used in the production of antifreezes, asphalts, emulsion paints, heat transfer agents, brake fluids, polyester fibers and films, solvent and deicing fluids for planes [2].

EG belongs to a group of organic compounds named aliphatic alcohols that are characterized by the presence of two hydroxyl functional groups. The octanol-water coefficient of EG is very low, and hence, bioaccumulation is not expected to be significant [3]. Under most environmental conditions glycols are not volatile because of their low vapor pressure.

In Canada, about 60% of EG, which consumed in 1991, was used in the production of aircraft deicing fluids/antifreeze fluids and all weather automobile cooling system fluids. An additional 11% was used for the production of polyethylene terephthalate which is often generically referred to as PET, or simply polyester. Minor uses include the processing of oil and gas and the production of solvent, explosives, cellulose film, and glycol esters. Canada's production of EG has increased from 97,000 tons in 1976 to 513,200 tons in 1993. Industry expansion increased total EG production capacity to 850,000 tons, in 1995 [4]. Production capacity was expected to remain constant at 850,000 tons in 1998. Global demand for EG is expected to increase by more than 5% annually [5].

Chemical product information (*CPI) product profiles (1996)* indicated that antifreezes for aircraft deicing and automobile cooling system contributed to about 70% of the EG used in Canada. Disposal of spent antifreeze is a major source of glycol compounds to the environment [6]. Melted snow and runoff water, containing EG, mix with municipal sewage water and end up in river and lakes. Many investigations have proved that wastewater containing EG may cause a severe disturbance in the sewage treatment, or may leave a toxic effect on the aquatic life in rivers or lakes. Waste of automobile coolants also creates the same problem since it mainly contains EG. EG in wastewater can be degraded by a biological oxidation process. The biological degradation of organic matters could be aerobic or anaerobic. In aerobic oxidation of wastewater, the removal of the biological oxygen demand (BOD) is enhanced by aeration of the wastewater. Biodegradability is known as the extent of the removal of organic compounds by using microorganisms in a biological waste treatment process. There are several techniques used for the determination of biodegradability such as the biological oxygen demand and the petrochemical method [7].

The objective of this project is to determine the rate of biological degradation of ethylene glycol at different air flow rates, liquid flow rates, and varied seeding rates at different time intervals, 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.

2. A REVIEW OF DIFFERENT BIOLOGICAL TREATMENT PROCESSES

2.1 Stages of Wastewater Treatment

A number of physical (sedimentation, filtration, equalization, etc.), chemical (precipitation, neutralization, coagulation, softening, etc.), and biochemical (activated sludge, aerobic and anaerobic digestion, rotating biological contactor, packed bed, etc.), processes are used in environmental engineering field. Wastewater treatment plants are usually classified as primary, secondary or tertiary (advanced) treatment processes, depending on the purification level to which the plants provide treatment [8].

2.1.1 Primary Treatment

In primary treatment, a physical operation (usually sedimentation) is used to remove the floating and settable materials in wastewater [9]. This process is the first step to treat wastewater. Untreated wastewater initially enters a primary treatment process. In the primary treatment, a bar screening is usually used to remove large objects and insoluble particle that can damage the treatment plant. Wastewater then enters into large settling basins. Due to gravity, sedimentation occurs during which the solids will settle to the bottom to form sludge, while oil and grease remain on the top and are removed by a skimmer. Primary treatment only removes one fifth of BOD and hardly any dissolved mineral. This is the least effective method of treatment [10].

2.1.2 Secondary Treatment

Secondary treatment involves removing the remaining organic molecules that are left over from the primary treatment process. Biological process is commonly used to remove organic matters. The effluent is brought in contact with oxygen and aerobic microorganisms to help break down organic matter. The combination of primary and secondary treatment can remove up to 90% of BOD. The two main methods used for the secondary treatment are a suspended growth process (also known as an activated sludge process), and a fixed film process (also known as a trickling filter) [10].

2.1.3 Tertiary Treatment

Primary and secondary treatment processes removed the majority of BOD and solids in the wastewater. The tertiary treatment process removes any remaining nitrates, phosphates, and heavy metals that are left over from the primary and secondary treatment processes. These inorganic compounds can cause eutrophication of the surface water receiving the effluent, which causes algae to grow. Unlike primary treatment process, tertiary treatments are usually chemical processes [10].

2.2 Trickling Filter

Trickling filter or percolating biological filter has been used to provide the biological wastewater treatment of municipal and industrial wastewaters for nearly a hundred years. Trickling filter is a popular alternative to an activated-sludge process. Trickling filter is a non-submerged fixed-film biological reactor using rock or plastic packing over which wastewater is distributed continuously. A trickling filter is filled with packing material on which the

biofilm grows. The size of a trickling filter depends on the BOD load per unit reactor volume [11].

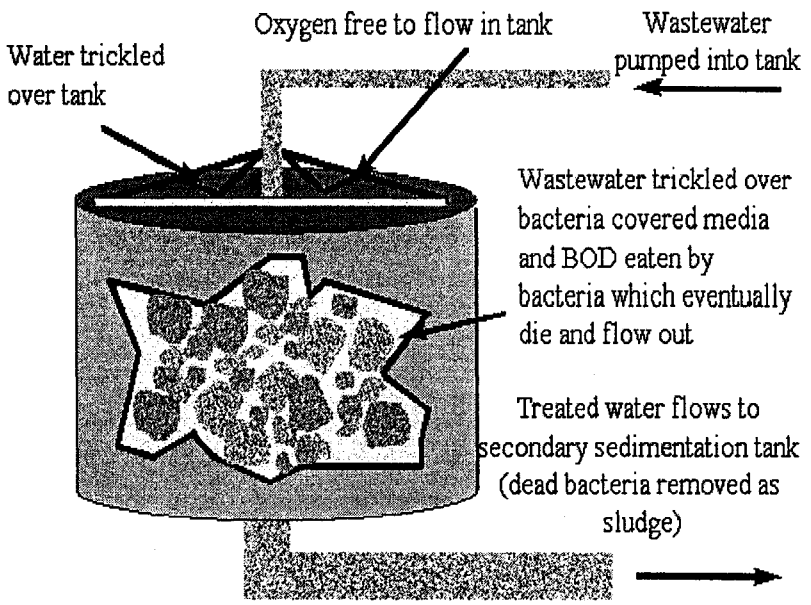

Figure 2.1: Schematic diagram for a trickling filter [12]

The biological treatment in a trickling filter is a fixed film biological process that removes BOD and suspended solids in the wastewater. Wastewater containing organic contaminants is in contact with microorganisms that are fixed or attached to the surface of filter media. The depth of the packing ranges from 0.9 to 2.5 m (3 to 8 ft), and is 1.8m (6ft) on an average. Rock filter beds are usually circular, and wastewater is distributed over the top of the bed by a rotary distributor. Many conventional trickling filter using rock as packing material have been

converted to plastic packing to increase treatment capacity. Virtually all new trickling filter are now filled with plastic packing [13].

Two or more trickling filters may be connected in series, and sewage can be re-circulated in order to increase treatment efficiencies. In predicting the performance of trickling filter, the organic and hydraulic loading, and the degree of treatment required are among the important factors that must be considered [14]. This technology is however less effective in treating wastewater with a high concentration of soluble organic compounds [15].

2.3 Rotating Biological Contactors

Rotating biological contactors (RBC) were first installed in West Germany in 1960, and later introduced into the United States of America. An RBC consist of a series of closely spaced circular disks of polystyrene or polyvinyl chloride that are submerged in wastewater and rotated through it. The disks are attached to a horizontal shaft and are provided at standard radius of approximately 3.5m. RBC plants have found widespread application in small and medium size wastewater treatment plants in particular. The RBC plants are compact, causing little impact on landscape. In addition, they produce sludge with a good settling ability and digestibility characteristics [16].

In an RBC, wastewater comes into contact with a biological medium in order to facilitate the removal of contaminants. The biological growth, which attached to the disks, assimilates the organic materials in the wastewater.

Aeration is provided by the rotating action that exposes the disks to the air after contacting the wastewater. Excess biomass is sheared off in the tank where the rotating action of the disks keeps the solids in suspension. Eventually the flow of the wastewater carries the solids out of the system and into a clarifier where they are separated. By arranging several sets of disks in series, it is possible to achieve a high degree of organic removal and nitrification [17].

Where a single RBC is not sufficient to achieve the desired level of treatment, a series (train) of RBCs is normally used. The performance of an RBC depends on the temperature and concentration of the pollutants, and the rate at which the treatment is expected to proceed. Studies have shown that, in terms of BOD removal, there is a critical hydraulic retention time of 3 hours and that any further increase in the retention results in little or no improvement in performances. Both hydraulic and organic loading rate criteria are used in sizing units for secondary treatment [18].

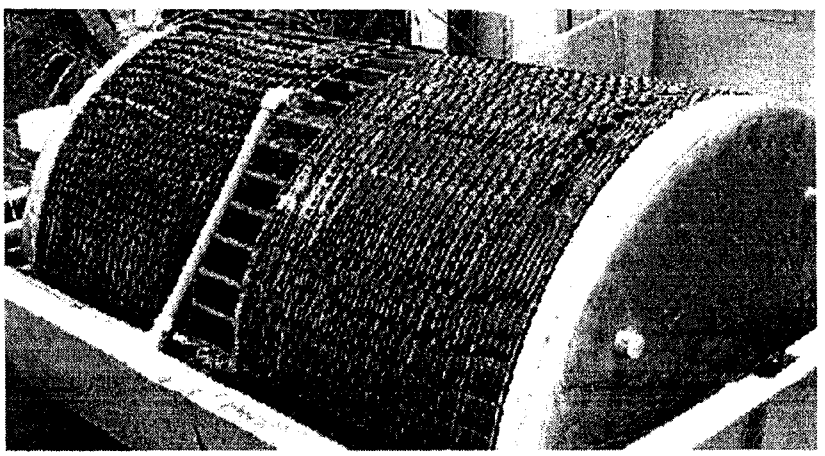

Figure 2.2: Picture of a rotating biological contactor [19]

Advantages of RBC

1) Operation is simple and operation costs are relatively low.
2) RBC units are covered to prevent algae growth, excessive heat loss in cold conditions, and UV exposure.
3) Short contact periods are required because of the large active surface.
4) Short retention time.
5) Low power requirements.
6) Low sludge production and excellent process control [11]

Disadvantages of RBC

1) Shaft bearing and mechanical drive require frequent maintenance.
2) Requirement for covering RBC units in cold climates to protects against freezing.
3) Structural failure of the shaft, media support systems.
4) Less than anticipated treatment performance.
5) Excessive development of nuisance organisms.
6) Development of excessive or uneven biomass growth.
7) Inadequate performance of air-driven systems to rotate the shaft [11]

The key advantage in using RBCs rather than trickling filter is that RBCs are easier to operate under varying load conditions as keeping the solids medium wet is easier. On the other hand, it is difficult to control the growth of biomass using RBCs [20].

2.4 Activated Sludge Processes

The activated sludge process is commonly used for the biological treatment of municipal and industrial wastewaters. The antecedents of the activated sludge process date back to the early 1880s by Dr. Angus Smith.

The activated sludge process consists of the following three components:

1) A reactor in which the microorganisms responsible for the treatment of wastewater are kept in suspension and aerated
2) Liquid solids separation, usually in sedimentation tank
3) A recycle system for returning solids removed from the liquid-solids separation unit back to the reactor [11]

Activated sludge process is the most widely used biological treatment process, in part because the recirculation of the biomass allows microorganisms to adapt to the changes in wastewater composition in a relatively short acclimation period [21].

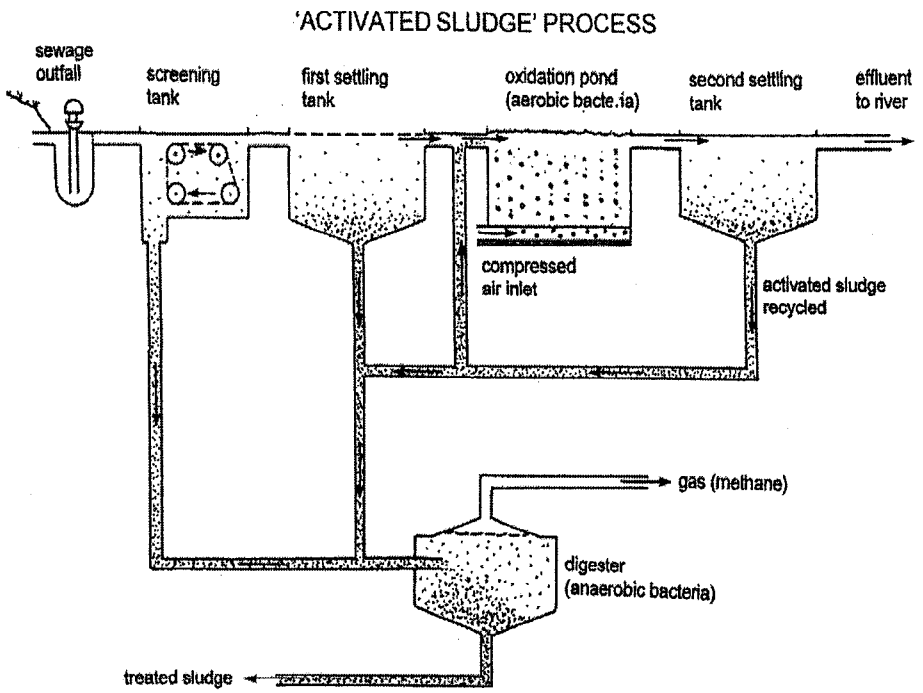

Figure 2.3: Schematic diagram of an activated sludge system [22]

The wastewater from the primary treatment process enters an aeration tank, or a bioreactor, where it is then mixed with microorganisms and oxygen. Oxygen is provided by using either aerators or diffusers. The microorganisms then grow into brownish lumps known as flocs, which are mostly aerobic microorganisms that feed on each other, and the nutrients in the wastewater. As nutrients are consumed, new cells are produced to form sludge in the effluents. As a result, settling occurs and the effluent water then either undergoes tertiary treatment, or is discharged. The sludge and water are then separated by a clarifier. A part of the sludge is then recycled back into a tank to act as a seed for the continuous process [23].

The main advantages of the activated sludge process are:

1) The plant occupies a smaller area compared with trickling filters.

2) The process produces no offensive smell.

3) Sludge has a greater fertilizer value.

4) The process is capable of treating dissolved, suspended and colloidal matter [24].

2.5 Lagoon

Lagoons are relatively shallow earthen basins varying in depth from 2 to 5 ft, provided with mechanical aerators on floats or fixed platforms. The mechanical aerators are used to provide oxygen for the biological treatment of wastewater, and to keep the biological solids in suspension. Suspended growth aerated lagoons are operated on either a flow through basis or with solids recycle [11].

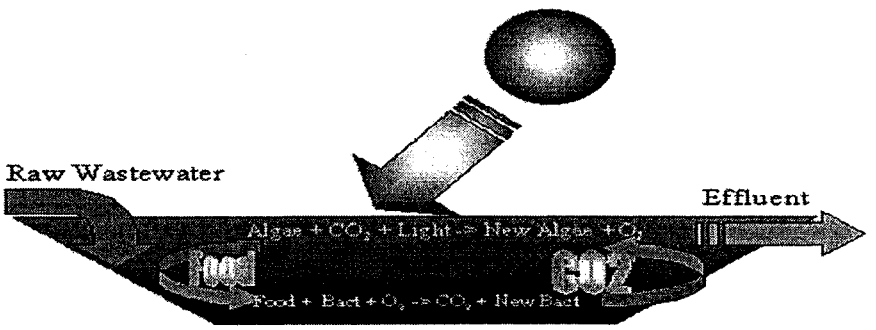

Figure 2.4: Schematic diagram of an aerobic lagoon [25]

Lagoons are fitted with a liner to prevent seepage, and aerators to supply air at all depth. The classification of lagoon depends on the oxygen availability to the lagoon.

Aerobic lagoons are two to five feet in depth and are kept aerobic by mechanical mixing while facultative lagoons are three to nine feet in depth and have no forced aeration, which results in an upper, middle and lower zone of liquid. The upper zone operates aerobically; the lower zone operates anaerobically, while the middle zone contains facultative bacteria [26].

The principle types of suspended growth lagoons process, classified based on the manner in which the solids are handled, are as follows:

1) Facultative partially mixed
2) Aerobic flow through with partial mixing
3) Aerobic with solids recycle and nominal complete mixing

Differences in the manner in which the solids are handled affects the treatment efficiency, power requirements, hydraulic and solids retention time, sludge disposal, and environmental considerations [27].

2.6 Packed Column in Wastewater Treatment

Packed columns, also called packed towers that are widely used in chemical industry, also find a new application in water and wastewater treatment. A packed column consists principally of a cylindrical tower, packing material contained in the tower, a centrifugal blower, and a water pump. It is used for continuous contact of liquid and gas in both counter current and

co-current flow. A packed column reactor is filled with some type of packing material, such as rock, slag, steel, ceramic, or now more commonly, plastic. With respect to liquid flow, a packed bed can be operated in either the downflow or upflow mode [11]. The extremely large surface area provided by packing in a column, combined with forced air flowing counter-current to the flow of the wastewater provides high liquid-gas transfer compared with other conventional aeration methods.

The quantity of air pumped in relation to the amount of water flowing through the column is known as air-to water ratio [28]. In general, aeration is used for transferring oxygen to water for the biological degradation of pollutants. The driving force for mass transfer is the difference of oxygen concentration between the gas and liquid phases. Equilibrium concentration of a solute in air is directly proportional to the concentration of the solute in water at a specific temperature.

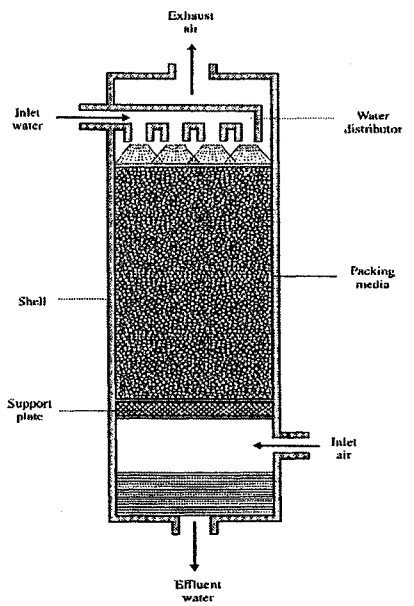

Figure 2.5: Schematic diagram of a typical packed column [17]

3. LITERATURE REVIEW

3.1 Treatment of Wastewater Containing Ethylene Glycol (EG)

Several processes can be used to decompose EG. In different studies, it has been established that EG can be degraded up to 99% [29]. 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 explained 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 results of many studies confirmed that EG underwent extensive primary and ultimate biodegradation and was considered readily biodegradable. Nearly complete biodegradation of EG occurred in hours under aerobic conditions [30]. In another study by Boatman, *et al.*,[31] the biodegradation of EG is as extensive and rapid as primary aerobic biodegradation. Degradation rates ranged from 70% production of the theoretical CO_2 in 2 days and up to 91% in 21 days [31]. 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 [30].

The removal of EG has also been extensively tested using methods that simulate environmental conditions. Methods used include semi-continuous activated sludge (SCAS), river die-away (RDA) assays and tests that used soil or groundwater. The results of simulation tests show that EG is extensively biodegradable in SCAS and RDA assays, as well as in soil or

groundwater. In water from several rivers, EG was completely degraded in 3 days at 20 ^{0}C, in 5 to 14 days at 8 ^{0}C, and in 11 to 14 days at 4 ^{0}C [32].

The fate, effect, and potential environmental risks of EG in the environment were examined by Charles *et.al.*, EG undergoes rapid biodegradation in aerobic and anaerobic environments (~100% removal of EG within 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 [33].

In various soils and at different temperatures EG at concentration of 100–1000 mg/kg, was aerobically degraded with primary degradation half-lives of 6 to 17 hours. However at a concentration of 10,000 mg/kg EG a substantial inhibition of degradation was observed [34].

Glycol biodegradation was observed in soil gathered near airport runways. The concentration of EG in soil is ranging from 392–5278 mg/kg. EG was extensively degraded at the rates of 20 and 93 mg EG/kg soil per day at temperatures of 8 ^{0}C and 20 ^{0}C respectively [35].

Anaerobic biodegradation appears to be extensive for EG when active anaerobic microbial consortia are used. Removal of approximately 75–100% EG over one to several weeks was obtained in various test systems used to measure the anaerobic biodegradation of EG [36], [37].

Charles developed generalized degradation half-lives that one may anticipate in various environmental compartments. The author also estimated the half-life of EG to be 2–12 days in surface water, 4-24 days in groundwater, and 2–12 days in soil, based on unacclimated

microorganism populations. The author further estimated aerobic biodegradation half-lives to be 8–48 days, and wastewater treatment plant efficiencies to be 88–100% [38].

EG was found to be degraded to less than 5 mg/l with spikes up to 10,000 mg/l in the influent. Higher concentrations of EG led to pH inhibition even with an addition of $CaCO_3$ at 6000 mg/l of wastewater to moderate the pH [39].

EG and Propylene glycol (PG) are also treated in a 15-cm deep sand bed column. The biodegradation of greater than 99% was achieved for all flow rates and loading conditions (8 to 25^0 C temperature and concentration was 39 to 52 mg/kg) tested [40].

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 rates were noted in systems 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 photosensitizer. No significant degradation was found in the system using methylene blue as the photosensitizing agent [41].

The enzymatic degradation of EG estimated by weight loss was enhanced significantly by the presence of a lipase and increased by the incorporation of glycol. The weight loss also increased with increases in the adipic acid (6A) content and n, the number of repeat unit in adipic acid, which could be correlated to the increase of the water absorption and the increase in the concentration of aliphatic ester linkages in the main chain of the enzyme [42].

The bioremediation of EG and PG using the aerobic biological fluidized bed (BFB) technology was evaluated by Wen *et. al.* [43] Under steady-state conditions, they found that BFB reactors were capable of achieving a good total organic carbon (TOC) removal (> 96%) in the bed after 1.7 hours with a TOC loading as high as 0.88 g/l- day [43].

Aerobic degradation of glycol based Type 1 aircraft de-icing fluids (ADFs) was characterized using suspended growth fill and draw reactors. Both type of ADFs tested showed near complete anaerobic degradation. 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 ^{0}C) [44].

Degradation of EG in photo Fenton systems was investigated by Dietrick *et. al.* [45]. EG loss rate constant of 1.0 ± 0.40 h/d was achieved in photo Fenton systems containing of 1000 mg EG/l. EG was converted to formic acid resulting in a loss of calculated chemical oxygen demand. The optimal pH was 3.0, significant decreases in the degradation rate were observed at pH below 2.8 and above 3.2. A high TOC loss was also noted in UV/ H_2O_2 systems [45].

In another study of degradation of EG using Fenton's reagent and UV by Dietrick *et. al,* oxidation of EG in aqueous solution was found to occur with the addition of Fenton's reagent [46]. Further conversion was observed upon UV irradiation. The pH range studied was 2.5 to 9.0 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 acids. They also found that smaller H_2O_2 doses were

associated with increases in the ratio EG removed per unit H_2O_2. EG removal was enhanced by exposure to UV light after treatment with Fenton's reagent [46].

3.2 Biochemical Oxygen Demand (BOD)

The most widely used parameter of organic pollution applied to both wastewater and surface water is the 5-day biochemical oxygen demand, (BOD_5) [47]. The more organic matter there is (e.g. in the sewage), the greater the number of microbes. The more microbes there are, the greater the need for oxygen to support them, consequently the higher BOD. It is the most important parameter for the design and operation of industrial treatment plants. BOD is a reliable gauge of the organic pollution in water. One of the main reasons for treating sewage or wastewater prior to its return to a water resource is to lower its BOD, which in return reduces its need of oxygen and thereby lessens its demand from the streams or rivers into which it is released [48]. In order to get meaningful results, the sample must be diluted with distilled water so as to reduce the concentration of the pollutants in the concentrated solution. For samples containing large population of microorganism, seeding is not necessary. If required, the dilution water is "seeded" with a bacterial culture that has been present in the wastewater.

The Biochemical Oxygen Demand (BOD) is also an useful indication of the water quality because of the following factors:

a) BOD is used to determine the approximate quantity of oxygen that will be required to biologically stabilize the organic matter present in wastewater.

b) BOD can be used to measure the efficiency of unit operations in wastewater treatment processes.

c) BOD is used to estimate the size of wastewater treatment facilities [49].

The BOD depends upon the temperature, the concentration of organic matter, the nature of the organic matter, the concentration of bacteria and the type of the bacteria. Assuming the rate of oxidation of organic matter at any instant is proportional to the amount of oxidizable matter present, it can be represented by a first-order reaction [50].

BOD is exerted by the following three classes of materials:

a) Carbonaceous organic materials usable as a source of food by aerobic organisms.

b) Oxidizable nitrogen derived from nitrite, ammonia and organic nitrogen compounds that serve as a food source for specific bacteria (Nitrosomomas and Nitrobacter).

c) Chemical reducing compounds such as Fe^{2+}, and S^{2-} which are oxidized by dissolved oxygen.

Organic matter present in a sample is primarily metabolized by bacteria in early stages. Some of the organic matter is oxidized, and the remainder is transformed into new bacteria cells. As the supply of these organic matter, or "food" for the microorganisms becomes scare, some types of bacteria including protozoa will predate on the living and dead bacteria present. The different mixtures of organic components and amount of seed can shift the duration and the maximum population of the individual microbial groups. However, it is generally true that

oxygen uptake in the initial stages is higher than in the latter stages because of not only the higher concentration of the organic matter but also the higher degradability of the organic matter is initially than after it has been transformed into microbial cells [51].

The BOD of a water sample is determined by measuring the change in dissolved oxygen in water over a specific time with an oxygen probe or by an iodo-metric titration. The BOD test has been standardized by requiring the test to be run in the dark at 20°C for 5 days. The 5-day BOD, or BOD_5, is the oxygen used by microorganisms in the water sample over 5 days of incubation. The BOD test is normally carried out in a standard BOD bottle. Details about the test can be found in *Standard Methods for the Examination of Water and Wastewater* [9].

3.3 Oxygen Transfer to Wastewater In Packed bed

Packed beds are widely used in for continuous gas-liquid contact operations in chemical industry. Over the past fifty years a number of mass transfer theories have been proposed to explain the mechanism of gas transfer across gas-liquid interfaces. The simplest and most commonly used is the two-film theory proposed by Lewis and Whitman in 1924 [52]. The penetration model proposed by Higbie in 1935 [53], and the surface-renewal model proposed by Danckwerts in 1951 [54], were more theoretical and take into account more of the physical phenomena involved. The two film theories remain popular because, in more than 95% of the situations encountered, the result obtained were essentially the same as those obtained with the more complex theories. The liquid is distributed over the packed bed and the gas is introduced at the bottom of the tower. The liquid trickles down the packed bed exposing a large surface area to contact rising gas.

The rate of the mass transfer of a gas-phase controlled system is expected to increase with the increase of the gas flow rate. This is due to the fact that, as the gas flow rate is increased, the thickness of the gas film at the gas-liquid interface decreases, which results in the lowering of the resistance to mass transfer. Also, due to the counter flow of gas and liquid, high gas flow rate increases the retention time of liquid in the packing [11].

Although for the gas-phase controlled system the resistance to mass transfer in the liquid film is negligible, the overall mass transfer rate could still vary with liquid flow rate. This is due to the fact that higher liquid flow rate will result in a better liquid distribution over the packing, which increases the effective area of the packing that is available for the mass transfer. Therefore, the overall mass transfer rate is expected to increase with liquid flow rate [55].

For effective BOD removal, oxygen, wastewater, and microoganisms must be brought into contact. Under steady state conditions, the rate of mass transfer of a gas through gas film must be equal to the rate transfer through liquid film. Using Fick's first law of Diffusion, the rate of the molecular diffusion of a gas in liquid can be defined. The mass rate (M) of oxygen per unit time is proportional to the oxygen concentration gradient normal to the area where diffusion occurs (dC/dy), which is expressed by the following equation: [11]

$$M = -D_c a \frac{dC}{dy} \qquad (1)$$

Where, a is the area where diffusion occurs, C is the dissolved oxygen concentration, y is the linear dimension normal to the area considered, and D_c is the diffusion coefficient of oxygen in the water. This equation describes the diffusion of gas into a liquid at the liquid film [54].

The concentration profile of oxygen in the gas-liquid contacting device can be depicted as in the following sketch:

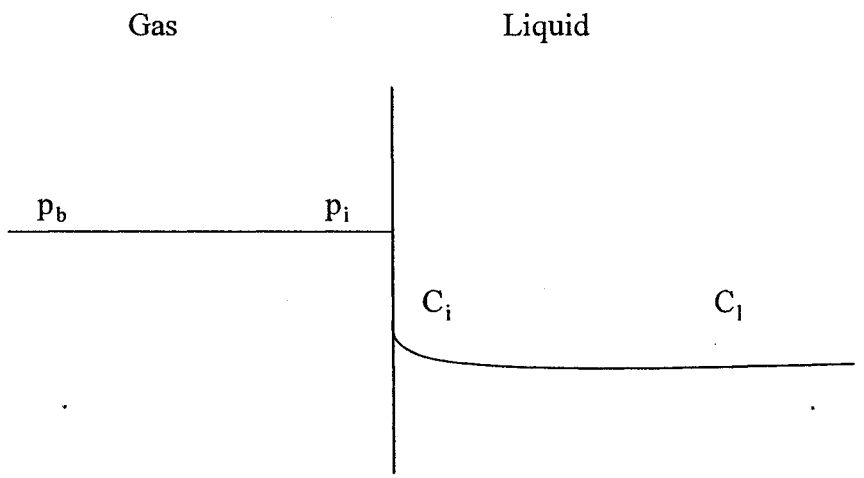

Figure 3.1: Profile of O_2 concentration in a gas-liquid contacting device

The rate transfer for any transfer process, is the product of a transfer driving force and a transfer coefficient. For dissolved oxygen, the driving force is the difference between the oxygen in the gas phase and the liquid phase. For gas phase, the rate of mass transfer is expressed in terms of partial pressure and so equation (1) can be rearranged to describe the mass transfer of oxygen in the gas phase by the equation:

$$M = k_g a(p_b - p_i) \qquad (2)$$

Where, M is the mass rate of oxygen, a is the interfacial area , p_b is the partial pressure of oxygen in bulk gas in bulk gas, p_i is the equilibrium pressure of oxygen dissolved in the liquid at the gas-liquid interface, and k_g is the gas mass transfer coefficient. This equation gives the oxygen transfer rate in the gas phase [54].

The partial pressure gradient is the driving force in the gas phase, while the concentration gradient is the driving force in the liquid phase. The mass transfer rate of oxygen in the liquid phase can also be expressed below [54]:

$$M = k_c a(C_i - C_l) \quad (3)$$

Where, k_c is the liquid phase mass transfer coefficient, C_i is the concentration of dissolved oxygen at the interface, and C_l is the concentration of dissolved oxygen in the bulk liquid.

The interfacial concentration (C_i) is the concentration of the dissolved oxygen in the liquid phase at the gas-liquid interface. At the interface, p_i and C_i are in equilibrium, according to Henry law as below:

$$C_i = p_i H_c \quad (4)$$

Where Hc is the Henry Law constant for oxygen.

The mass transfer rate is usually expressed in terms of the bulk concentration (p_b and C_l), since these concentration can be measured easily as compared to the interfacial concentration (p_i and C_i). Therefore, in order to find M, the interfacial concentration (p_i and C_i) are eliminated. This is done by rearranging equation (2) to solve for p_i:

$$p_i = p_b - \frac{M}{k_g a} \quad (5)$$

By multiplying H_c to equation (5):

$$p_i H_c + \frac{M}{k_g a} H_c = p_b H_c$$

or

$$\left(\frac{H_c}{k_g a}\right) M = p_b H_c - p_i H_c \qquad (6)$$

By rearranging equation (3) the following expression for C_i is obtained:

$$C_i = C_l + \frac{M}{k_c a} \qquad (7)$$

or

$$\left(\frac{1}{k_c a}\right) M = C_i - C_l \qquad (8)$$

By adding equation (6) and (8):

$$M = \frac{p_b H_c - C_l}{(H_c / k_g a) + (1/k_c a)} \qquad (9)$$

A fictitious liquid phase concentration (C^*) is defined as the concentration of oxygen that is in equilibrium with the oxygen in the bulk gas. C^* can be readily obtained from Henry Law with the known partial pressure of oxygen in the bulk gas. Henry Law for oxygen can be rewritten as:

$$C^* = p_b H_c \qquad (10)$$

Substitution of equation (10) in equation (9):

$$M = \frac{C^* - C_l}{(H_c / k_g a) + (1/k_c a)} \qquad (11)$$

An overall mass transfer coefficient (k_l a) for the liquid phase is defined by the following equation:

$$\frac{1}{k_l a} = \frac{H_c}{k_g a} + \frac{1}{k_c a} \qquad (12)$$

Therefore equation (11) can be rewritten as:

$$M = k_l a(C^* - C_l) \qquad (13)$$

I. METHODOLOGY

I.1 Process Description

A 18-cm diameter cylinder filled with plastic spheres of 2 mm diameter was used as an aerator as shown in Figures 4.1, 4.2, and 4.3. The height of packing bed was 40 cm. Simulated wastewater containing EG was placed in a liquid tank. Wastewater was pumped from the liquid tank to the top of the column, liquid flowrate was measured using a rotameter (Dwyer Instrumentation Inc.). Air entered the bottom of the packed tower counter-current to the liquid stream. The air flow was also measured by a rotameter. The wastewater leaving the packed tower went back to the liquid tank where it was recirculated back to the packed column. A copper cooling coil was put in the wastewater tank to maintain the wastewater at 20°C.

4.2 Experimental Procedure

The objective of this project was to study the effect of seeding the wastewater, and air and liquid flowrate on the removal of biological oxygen demand (BOD) of the wastewater. Seeding was done to add microorganisms to the simulated wastewater that did not have microorganisms originally. In order to evaluate the effects of seeding using Polyseed ®, and liquid and air flow rate on the BOD removal, pH of wastewater was 6.9 to 7.3, a series of runs set at different flow rates of air and liquid with different amounts of seeding were carried out. Followings are different levels of the parameters of interest:

- Levels of air flowrate 0.0069, 0.0138, 0.0207, 0.0276, 0.0345, and 0.0414 kg $m^{-2}s^{-1}$.
- Levels of liquid flowrate: 5.5, 11, 16.5, and 27.5 kg $m^{-2}s^{-1}$.
- Seeding: various amounts and frequencies can be found in Table 4.1

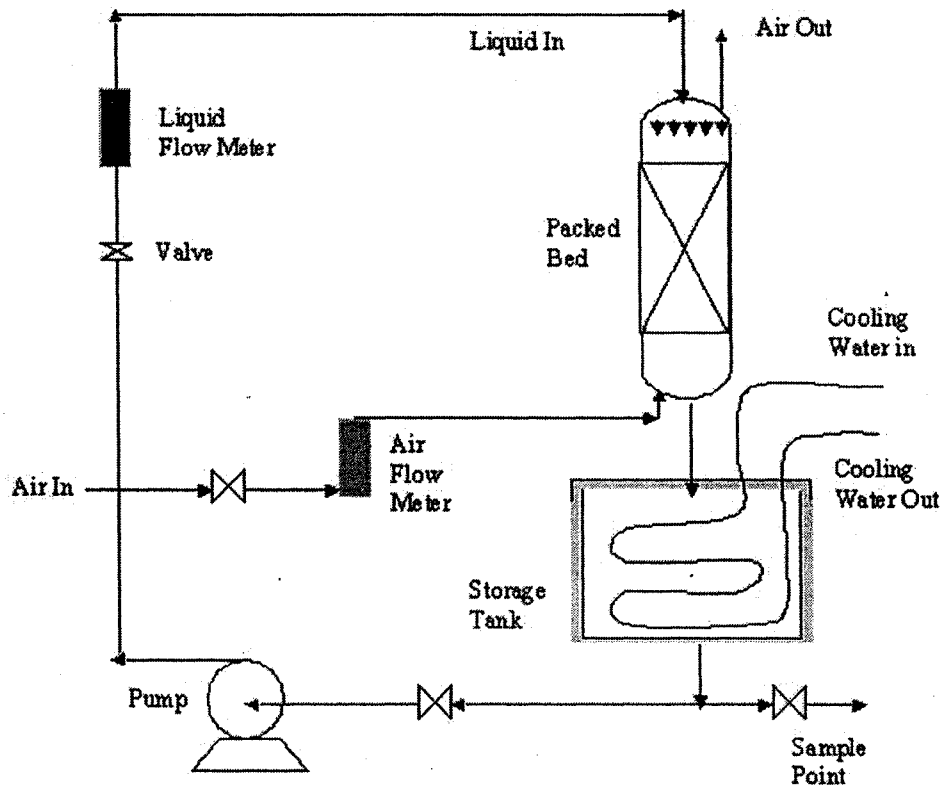

Figure 4.1: Schematic diagram of the experimental setup used in the present study

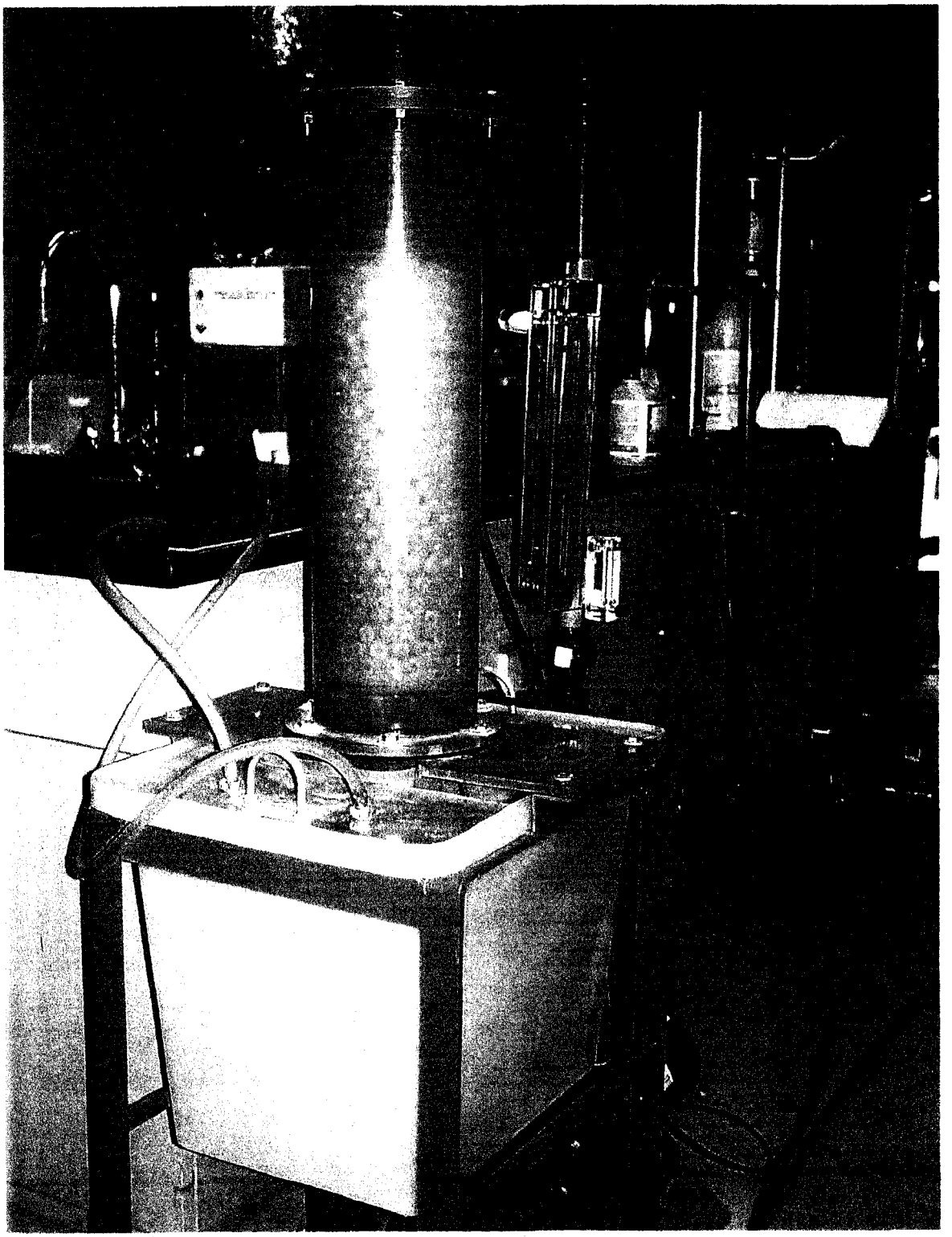

Figure 4.2: Front view of the experimental setup

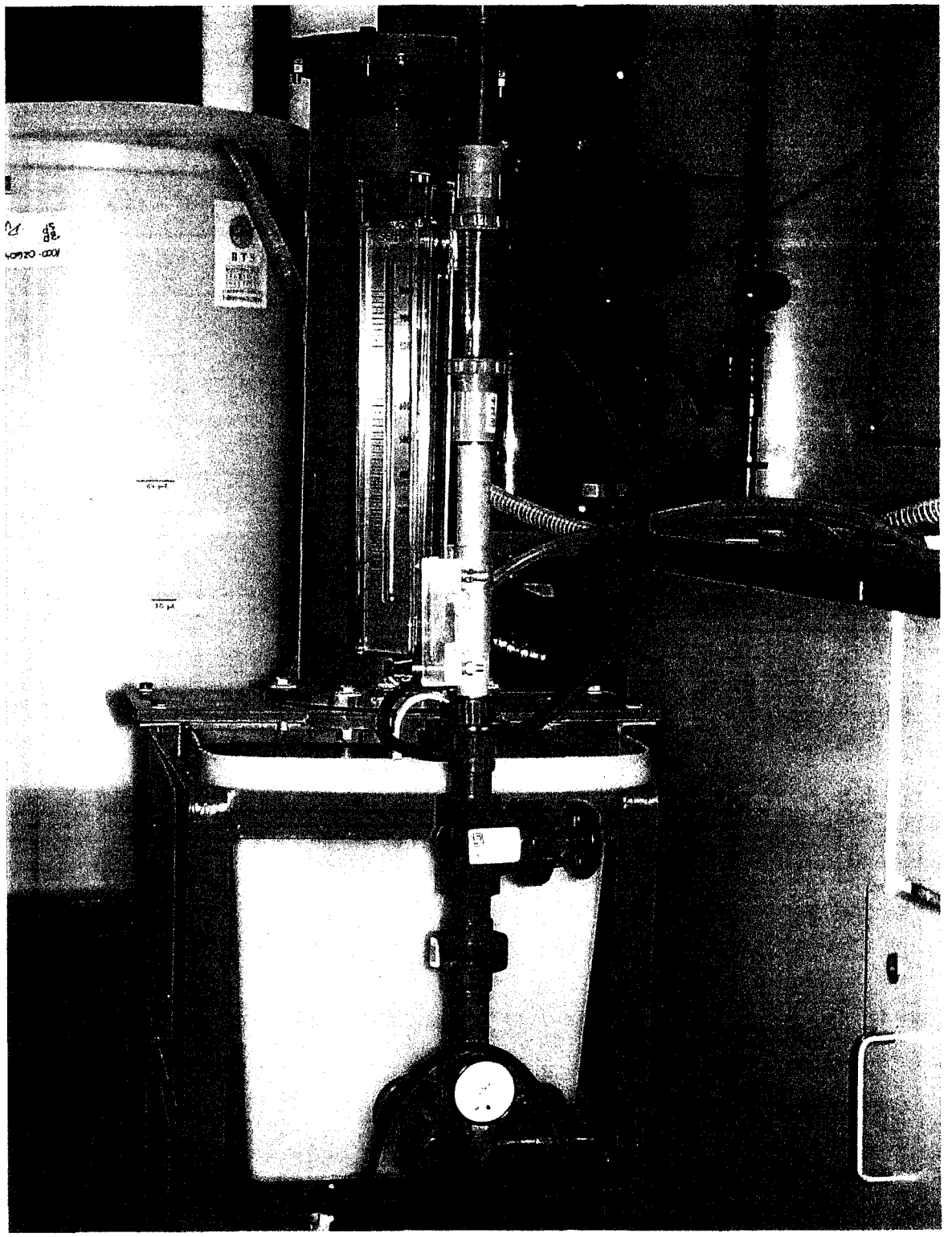

Figure 4.3: Back view of the experimental setup

Table 4.1: Experiments with varied air flow rates at a fixed liquid flow rate of 5.5 kg $m^{-2}s^{-1}$

Run	Air Flow Rate (kg $m^{-2}s^{-1}$)	Amount of Seeding Put in Wastewater*
1	0.0069	2 capsules at 0 hour
2	0.0069	6 capsules at 0 hour
3	0.0069	Without seeding
4	0.0069	2 capsules at 0, 24, and 48 hours
5	0.0138	2 capsules at 0, 24, and 48 hours
6	0.0207	2 capsules at 0, 24, and 48 hours
7	0.0276	2 capsules at 0, 24, and 48 hours
8	0.0345	2 capsules at 0, 24, and 48 hours
9	0.0414	2 capsules at 0, 24, and 48 hours

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

Table 4.2: Experiments with varied liquid flow rates at an airflow rate of 0.0069 kg $m^{-2}s^{-1}$

Run	Liquid Flow Rate (kg $m^{-2}s^{-1}$)	Amount of Seeding Put in Wastewater
10	5.5	2 capsules at 0, 24, and 48 hours
11	11	2 capsules at 0, 24, and 48 hours
12	16.5	2 capsules at 0, 24, and 48 hours
13	27.5	2 capsules at 0, 24, and 48 hours

A total of four samples were taken for each run. For every sample taken, the amount of dissolved oxygen was initially measured using a DO meter (Model 52C, YSI Incorporated Yellow springs, Ohio, USA) and the sample was incubated for five days at 20^0 C. After five days, the amount of dissolved oxygen in the samples was measured again. The BOD_5 of the wastewater was then calculated.

4.3 Biological Oxygen Demand Analysis

Biological oxygen demand (BOD) is the quantity of oxygen required for the biological oxidation of waterborne substances under test conditions. Materials, which may contribute to the BOD, include carbonaceous organic materials usable as a food source by aerobic

organisms, oxidizable nitrogen derived from nitrites, ammonia and organic nitrogen compounds which serve as foods for specific bacteria [55].

BOD_5 can be calculated using the following equation:

$$BOD_5 = \frac{[(D_1 - D_2) - (B_1 - B_2)]f}{p}$$

Where,

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

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

P = Decimal volumetric fraction of sample used

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

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

f = Ratio of the seed in the sample to seed in control(%seed in D_1 / % of seed in B_1)

One Polyseed® capsule is diluted with 300 ml distilled water. This solution is used as a seed control. The dissolved oxygen of a seed control was also measured. The seed control acts as a blank for quality control, and so the initial and final dissolved oxygen levels should be similar. Similar values indicate that the values determined for the wastewater sample are correct. That is, if the initial and final dissolved oxygen values for the seed control are similar, the dissolved oxygen values for the sample are acceptable. Detailed calculation is shown in Appendix B.

The test procedure of BOD for wastewater had a number of steps. At first the sample had to be aerated for at least fifteen to twenty minutes, which allowed the initial dissolved oxygen of the BOD sample to be at saturation. After aeration, the sample was put into a standard 300 ml

BOD bottle. The dissolved oxygen in the sample was then measured, using a calibrated dissolved oxygen meter.

The solubility of oxygen in water varies with water temperature. The dissolved oxygen meter must be calibrated at the temperature of the wastewater sample. The sample bottle was put on top of a stir plate, with a stir bar inside the bottle. The oxygen level in the liquid at the membrane surface was continuously depleted. Therefore, in order to read the dissolved oxygen measurement accurately the water must be in a continuous motion [9].

After the dissolved oxygen of the sample bottle was taken, the wastewater bottle was incubated at 20^0C. The sample bottle must not have any air bubbles present. Some dilution water was added to the bottle and the cap was placed carefully to prevent air bubbles to be entrapped in the bottle. The glass collar around the cap should also be covered with water. An over cap such as parafilm paper or aluminium foil can be placed over the bottle stopper to prevent the evaporation of the water seal. These procedures insure that no air present in the BOD bottle.

After five days, the sample bottle was taken out of the incubator. The dissolved oxygen of the water sample in the bottle was then immediately measured. The BOD_5 of the wastewater was then calculated from initial and final dissolved oxygen values [2].

5. RESULTS AND DISCUSSION:

5.1 Effect of Air Flow Rate on BOD Removal

It can be expected that the percentage of BOD removal will be increased as the air flow rate increases. This is due to the fact that there must be enough dissolved oxygen in the wastewater for the complete oxidation of organic matter. If there is not enough dissolved oxygen, the moicrooganisms will not be able to oxidize the organic matter, which in turn hinders the BOD removal. An air flow in contact with the wastewater allows the mass transfer of oxygen from the air into the wastewater. Aeration helps to maintain a sufficient amount of oxygen in the wastewater for the complete oxidation of organic matter. It was expected that at a low air flow rate of 0.0069 kg $m^{-2}s^{-1}$, the percentage of BOD removal would be low. At a low air flow rate, the mass transfer of oxygen from the air into the wastewater was low. A low level of oxygen in the wastewater will cause the microoganisms to oxidize a small amount of organics. On the other hand, at a higher air flow rate of 0.0414 kg $m^{-2}s^{-1}$, the percentage of BOD removal would be high. Since the mass transfer of oxygen from the air into the wastewater would be high. A level of oxygen in the wastewater would thus be sufficient for the microorganisms to oxidize a large amount of the organic matters.

It was found that the percentage of BOD removal generally increased when the air flow rate increased as shown in Figure-5.1. It was expected that a higher air flow rate would result in a higher BOD removal. However, the percentage of BOD removal after 72 hours of treatment at the air flow rate of 0.0414 kg $m^{-2}s^{-1}$ was not that much higher than the BOD removal at 0.0069, 0.0138, 0.0207, 0.0276, and 0.0345 kg $m^{-2}s^{-1}$. For all treatment time (24, 48, 72 hours)

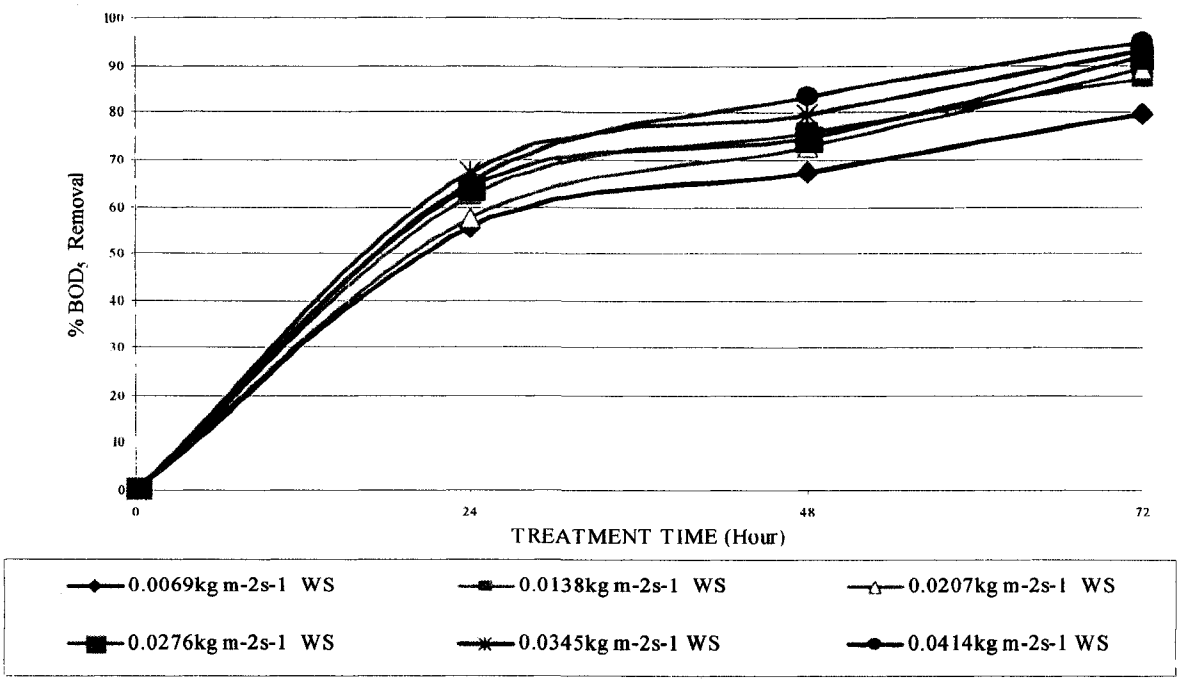

Figure 5.1: %BOD_5 Removal of at varied air flow rates vs. treatment time at a fixed liquid flow rate of 5.5 kg $m^{-2}s^{-1}$

the BOD removal did not change significantly when the air flow rate was increased beyond 0.0138 kg $m^{-2}s^{-1}$ as can be seen in Figure-5.2.

From Appendix A, for seeding at 0, 24, and 48 hours and, at 0.0069 kg $m^{-2}s^{-1}$ air flow rate (Run 4), the percentage of BOD removal after 72 hours of treatment was 80%. When the air flow rate was increased to 0.0345 kg $m^{-2}s^{-1}$ (Run 8), the percentage of BOD removal only increased to 93.2%. When the air flow rate was further increased to 0.0414 kg $m^{-2}s^{-1}$ (Run 9), the percentage of BOD removal only increased to 94.7%. When evaluating Appendix A, it is observed that for all the other runs at different amounts of seeding, the percentage of the BOD removal at the air flow rate of 0.0414 kg $m^{-2}s^{-1}$ is generally not that much higher than the percentage of the BOD removal at the air flow rates 0.0138 and 0.0069 kg $m^{-2}s^{-1}$.

The oxygen transfer rate from air to water in the packed column aerator decreased when the dissolved oxygen concentration in the liquid increased. Once the dissolved oxygen concentration in the wastewater was close to saturation, the oxygen transfer rate from air to liquid became very small regardless of the air flow rate. Since the saturated dissolved oxygen concentration in the wastewater is rather small (at 20 °C is 9.09 mg/l), the oxygen transfer from air to liquid was not significantly improved when the air flow rate was increased to 0.0414 kg $m^{-2}s^{-1}$. As a result, the percentage of BOD removal at 0.0414 kg $m^{-2}s^{-1}$ was not that much significantly higher than the percentage of BOD removal at 0.0138 and 0.0069kg $m^{-2}s^{-1}$. Therefore, to save energy and cost, the air flow rate should be set at 0.0138 kg $m^{-2}s^{-1}$ for this experimental set-up to get an acceptable BOD removal.

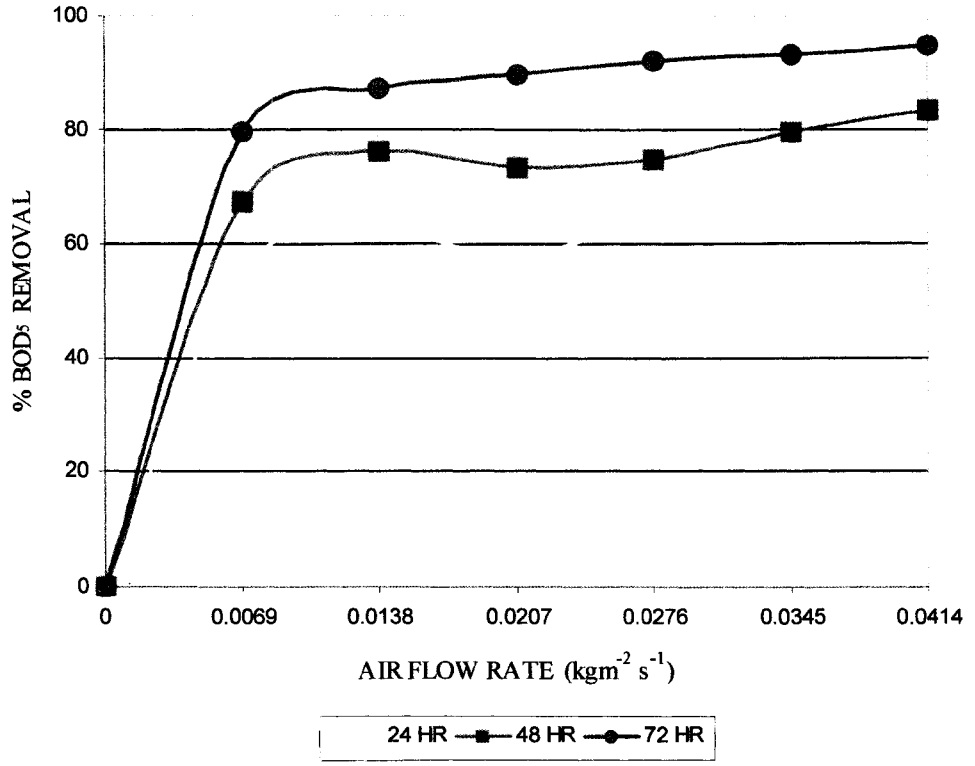

Figure 5.2: % BOD_5 removal vs. air flow rate at liquid flow rate of 5.5 kg $m^{-2}s^{-1}$

5.2 - Effect of Liquid Flow Rate on BOD Removal

The effect of the liquid flow rate on the BOD removal of wastewater containing EG was also investigated. The experiments with liquid flow rates of 5.5, 11, 16.5, and 27.5 kg $m^{-2}s^{-1}$, while keeping the air flowrate constant at 0.0069 kg $m^{-2}s^{-1}$ were carried out. The data obtained are plotted Figure-5.3. The BOD removal was reduced by 30% with liquid rate for a short treatment time (24 or 48 hours), this removal may be due to a lower concentration of dissolved oxygen (DO) in water, which was necessary for the oxidation of organic material under an aerobic treatment. Aeration rate must be adequate to provide a sufficient DO concentration to

fulfil the BOD requirements of the waste. Therefore, keeping the air flowrate constant and increasing liquid flowrate resulted in the decrease of BOD removal. On the other hand, increasing the air flowrate and keeping the liquid flowrate constant resulted in a higher percent of BOD removal. However at longer treatment time, i.e., 72 hrs, the effect of liquid rate on the BOD removal became moderate with a decrease of 10% in the BOD removal, when liquid rate was increased from at 5.5 to 27.5 kg $m^{-2}s^{-1}$ as can be seen in Figure 5.4.

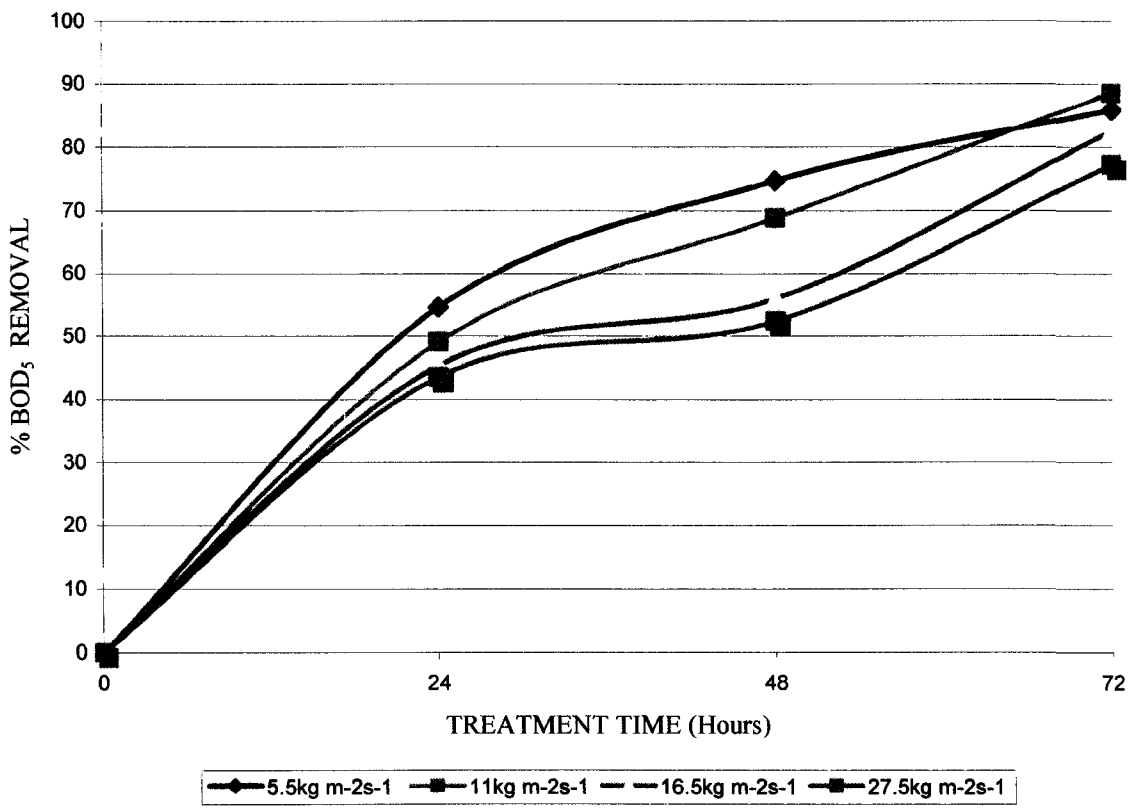

Figure 5.3: % BOD_5 removal at varied liquid flow rates vs. treatment time at a fixed air flow rate of 0.0069 kg $m^{-2}s^{-}$

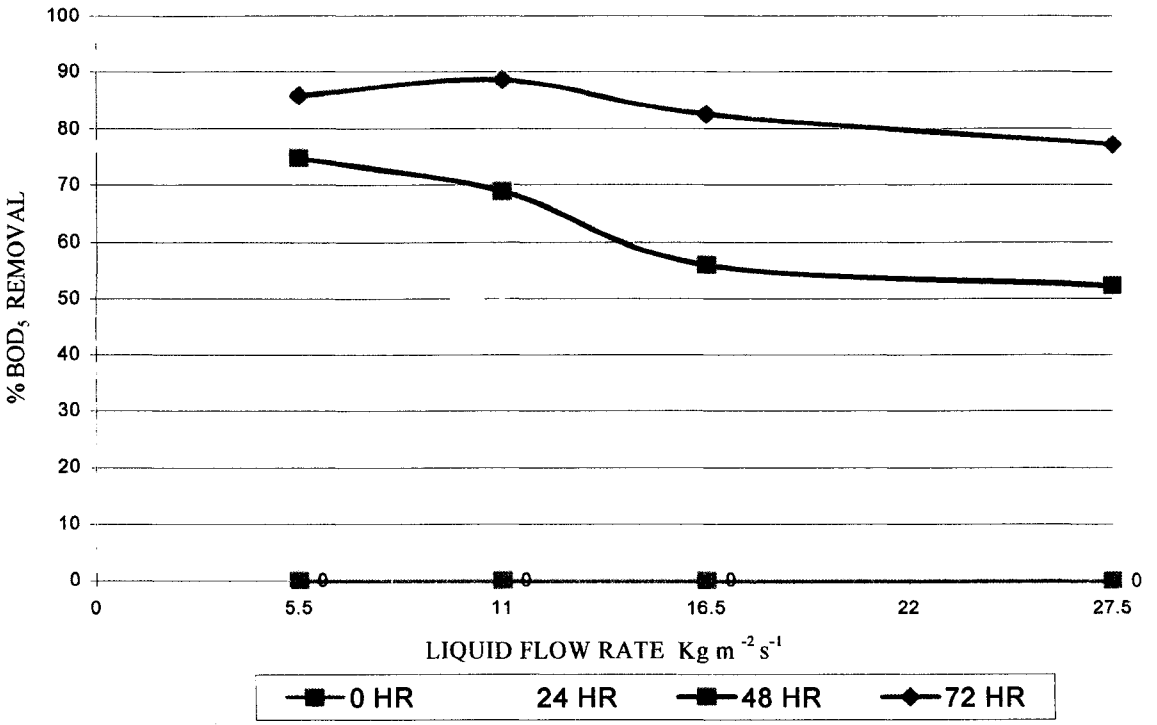

Figure 5.4: %BOD_5 removal at varied liquid flow rates with a fixed air flow rate of 0.0069 kg m^{-2} s^{-1}

5.3 Effect of Seeding on BOD Removal

The effect of seeding on the BOD removal of wastewater was evaluated by running the experiments with different amounts of seeding. The experimental values for the percentage of BOD removal affected by the different amounts of seeding are plotted in Figure-5.5.

A theoretical assumption can be made that the percentage of BOD removal will increase as the amount of seeding increases. 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 for low amount of seeding, the percentage of

BOD removal will be low. At a low amount seeding, the amount of microorganisms in the wastewater might not be sufficient for the oxidation of organic matter, which will result in a low percentage of BOD removal. It is expected that for a high amount of seeding, the percentage of BOD removal will be high. Since the number of microorganisms present in the wastewater will be sufficient for the oxidation of the organic matter.

It was expected that the percentage of BOD removal would be increased when the amount of seeding increases. However, from the evaluation Figure-5.5, it was found that the percentage of BOD removal did not always increase when the amount of seeding increased. The BOD_5 removed for initial seeded wastewater sample was about 3 times higher than that of the unseeded sample as shown in Figure-5.5. Nevertheless additional seeding at 24 and 48 hours of treatment did not increased the BOD removal significantly. This might be due to the fact that with the initial seeding the amount of microorganisms in the wastewater was sufficient to oxidize the organic matter, hence additional seeding did not significantly increase the percentage of BOD removal.

It was also found that when the amount of the initial seeding was increased to 6 polyseed capsules, the percentage of the BOD removal was not that much different than the BOD removal with a lower amount of initial seeding (2 capsules). When the amount of seeding was increased, more microoganisms were present in the wastewater sample to oxidize the organic matter. However, when the amount of microorganisms in the wastewater was already sufficient to oxidize the organic matter, an additional input of seeding did not significantly increase the biological oxidation of organic matters in the waste since the organic concentration because a rate limiting factor. Therefore, by adding more seeding material into

the wastewater, the percentage of BOD removals were not significantly higher than when there was no additional seeding since the latter already has a high amount of microorganisms. In Figure:5.3, seeding at 0 hours in both runs are not showing similar value, it may be due to the uncertainty/error in experiment. Detail information can be seen in Appendix E.

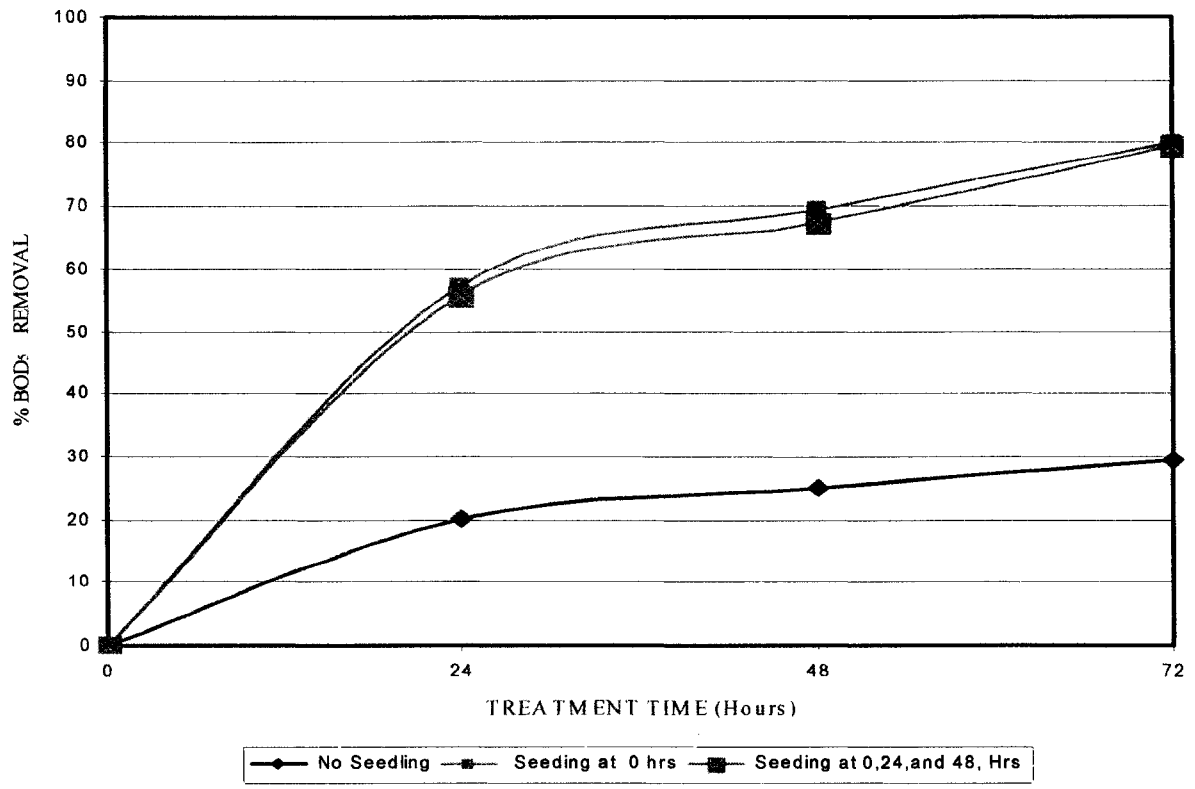

Figure 5.5: % BOD removal at varied amount of seeding vs. treatment time with fixed air flow rate 0.0069 kg $m^{-2}s^{-1}$ and liquid flow rate 5.5 kg $m^{-2}s^{-}$

5.4- Kinetic Model of BOD Curve

The kinetic of the BOD reaction is in accordance with first order reaction kinetics and can be expressed as follows: [10].

$$\frac{dL}{dt} = -kL \qquad (14)$$

Where,

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

k is the reaction rate constant

By integrating equation (1) on both sides and letting L = Lo at t=0

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

$$\ln\frac{L}{L_0} = kt$$

Therefore, the amount of BOD remaining at time t:

$$\frac{L}{L_o} = e^{-kt}$$

$$L = L_o e^{-kt} \qquad (15)$$

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

$$y = L_o - L \qquad (16)$$

Substituting equation (2) in (3) we get [49]

$$y = L_o(1 - e^{-kt}) \qquad (17)$$

From Appendix-A (Run-8), 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 a exponential curve as shown in Figure 5.6.

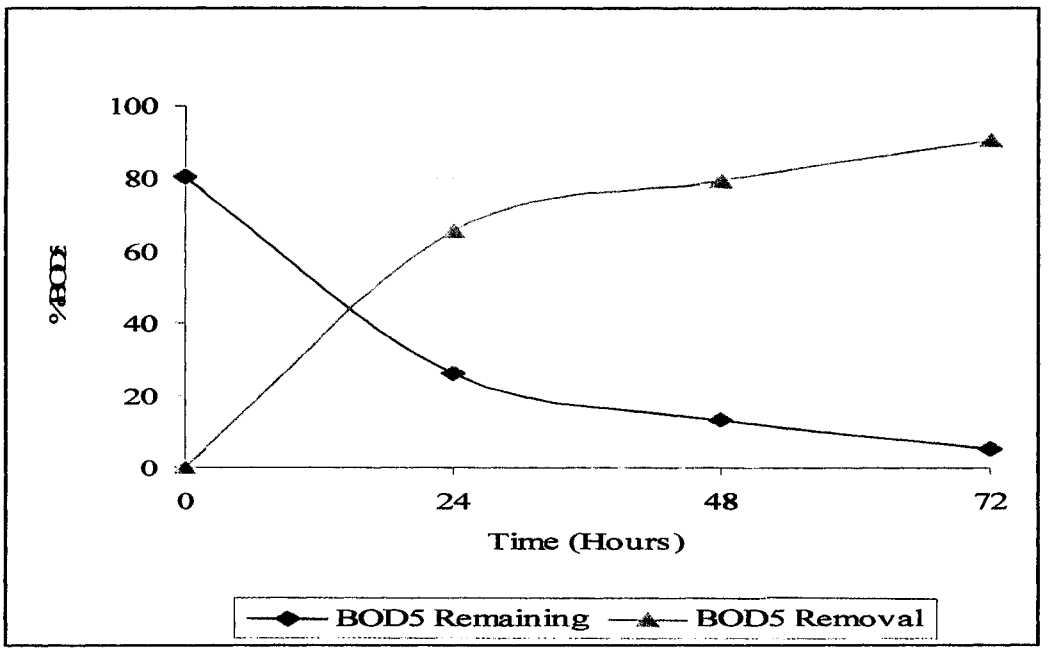

Figure 5.6: Changes in the concentration of BOD_5 remaining and BOD_5 removal

From Table-5.1, runs 4 to 10 at liquid flow rate 5.5 kg $m^{-2}s^{-1}$, and gas flow rate 0.0069, 0.0138, 0.0207, 0.0276, 0.0365, and 0.0414 kg $m^{-2}s^{-1}$, found that, gas flow rate has effect of the BOD removal. Therefore, k values are averaged and the averaged k is 0.03 h^{-1} at average temperature "T" 22^0 C (295 ^{0}K).

The first order kinetics for the BOD removal of antifreeze can be written as below

$$y = L_o(1 - e^{-0.03t}) \qquad (18)$$

5.5- Effect of Temperature and Other Parameters on Rate Constant

The rate constant (k) was found by taking the slope of the line of the logarithmic oxygen utilization (y) versus time (t). A plot of the logarithmic oxygen utilization versus time (t) can be found in Appendix C, and D, for each of the eleven runs.

Table 5.1: Rate constant (k) for the BOD removal at different operational conditions

S/No:	Run	Rate Constant k (hr^{-1})	Temperature (^{o}C)
1	4	0.0216	20
2	5	0.0244	18
3	6	0.0306	22
4	7	0.0338	22
5	8	0.0363	23
6	9	0.0389	24
7	10	0.0269	22
8	11	0.0294	21
9	12	0.0227	20
10	13	0.0193	19

When evaluating Table 5.1, it was observed, that rate constants vary considerably at each S/No: The rate constants of S/No: 3 to 8 are higher than for S/No: 1, 2, 9, and 10.

This can be explained by the fact that a different runs EG may be not properly mixed in tank, or in other words, the EG used for the runs were collected from a tank that is not mixed. If the EG is not properly mixed, the EG in the water are not equally distributed. Therefore, it is possible that the concentration of the EG in the water used for S/No: 1, 2, 9, and 10, will not have the same concentration of EG in the water used for S/No: 3 to 8, since the sample was collected at different times. This can be the one cause, that's why the rate constant for S/No: 3 to 8 are significantly higher than most of the rate constant for S/No: 1, 2, 9, and 10. Therefore the rate constant depends on the concentration of EG used in water.

In other hand, some rate constant in S/No: 1, 2, 9, and 10 are different, the rate constant of S/No: 1 and 9 are slightly higher than the others S/No. It may be the result of an increase in temperature. The temperature of EG wastewater for all the runs was maintained at 20^0C, however the temperatures of the wastewater for some of the runs were lower or higher than 20^0C. For example, the temperature for S/No: 6 was 24^0C, which caused its rate constant to be higher than the others rate constants for S/No: 3 to 8. Similarly, it can be seen in Table 5.1 that some of the rate constant are higher than others; therefore, temperature affects the rate constant.

6. CONCLUSION AND RECOMENDATIONS

6.1 Conclusion

The experimental values showed that the percentage of BOD removal did not increase significantly when the air flow rate was increased beyond 0.0138 kg $m^{-2}s^{-1}$ It was also found that the BOD removal at a high air flow rate of 0.0414 kg $m^{-2}s^{-1}$ was not significantly higher than the low air flow rates of 0.0069 and 0.0138 kg $m^{-2}s^{-1}$. Therefore, the flow of 0.0138 kg $m^{-2}s^{-1}$ was sufficient for a packed bed column aerator.

It was found that the percentage of BOD removal decreased when liquid flowrate was increased, for 24 hours treatment. However, the decrease in the BOD removal was subdued with longer treatment time, i.e., 72 hours.

The experimental values showed that the percentage of BOD removal did not always increase when the amount of seeding was increased. Additional seeding at 24 hour and 48 hours did not enhance the percentage of BOD removal significantly. Initial seeding was adequate for the treatment of EG.

6.2 Recommendations

1) The temperature of the wastewater in the experimental setup was controlled by the use of a cooling coil that was put in the storage wastewater tank. It was very difficult to continuously monitor the temperature manually during the entire run of 72 hours. An automatic temperature control should be used to maintain the constant temperature of the wastewater.

2) The glass collars around the cap of the bottle were not always covered with water. An over cap should always be use to prevent evaporation of the water seal during incubation.

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APPENDIX – A

Summary of Experimental data:

Table A-1

Run-1: 0.0069 kg $m^{-2}s^{-1}$ air flow rate, 2 Capsules at 0-hour, with 5.5 kg $m^{-2}s^{-1}$ liquid flow rate

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	8.5	2.4	9.4	9.1	82.85	82.13	0	0	2
		8.6	2.6			81.42				
2	24	9.0	6.4	9.4	9.1	32.85	34.99	47.14	57.39	0
		9.1	6.2			37.14				
3	48	9.3	7.3	9.4	9.1	24.28	24.99	57.14	69.57	0
		9.2	7.1			25.71				
4	72	9.0	7.5	9.4	9.1	17.14	16.42	65.71	80.01	0
		9.1	7.7			15.71				

Table A-2

Run-2: 0.0069 kg $m^{-2}s^{-1}$ air flow rate, 6 Capsules at 0-hour, with liquid flow rate of 5.5 kg $m^{-2}s^{-1}$

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	8.6	3.1	9.1	8.9	75.71	74.99	0	0	6
		8.3	2.9			74.28				
2	24	8.9	7.4	9.1	8.9	18.57	20.71	54.28	72.38	0
		9.1	7.3			22.85				
3	48	9.2	7.5	9.1	8.9	21.42	18.56	56.43	75.25	0
		9.0	7.7			15.71				
4	72	9.3	8.6	9.1	8.9	7.41	12.85	62.14	82.86	0
		9.1	8.5			5.71				

Table A-3

Run-3: 0.0069 kg $m^{-2}s^{-1}$ air flow rate, without seeding, with liquid flow rate of 5.5 kg $m^{-2}s^{-1}$

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	9.2	3.8	9.3	9.2	75.71	75.64	0	0	0
		9.3	3.9			75.57				
2	24	9.4	4.7	9.3	9.2	65.42	65.35	10.29	20.23	0
		9.3	4.6			65.28				
3	48	9.6	5.3	9.3	9.2	59.02	58.98	16.74	25.01	0
		9.6	5.4			58.42				
4	72	9.5	5.6	9.3	9.2	54.14	53.14	22.50	29.36	0
		9.5	5.9			52.71				

Table A-4

Run-4: 0.0069 kg $m^{-2}s^{-1}$ air flow rate, 2 Capsules at 0, 24, and 48 hour, with liquid flow rate of 5.5 kg $m^{-2}s^{-1}$

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	8.8	3.8	9.6	9.3	66.71	65.14	0	0	2
		8.7	3.9			63.57				
2	24	9.4	6.7	9.6	9.3	34.28	31.42	33.72	51.71	2
		8.9	6.6			28.57				
3	48	8.8	7.1	9.6	9.3	20.0	21.21	43.93	67.41	2
		9.0	7.1			22.42				
4	72	8.8	7.5	9.6	9.3	14.7	13.27	51.87	79.62	
		8.9	7.6			11.85				

Table A-5

Run-5: 0.0138 kg $m^{-2}s^{-1}$ air flow rate, 2 Capsules at 0, 24 and 48 – hour, with liquid flow rate of 5.5 kg $m^{-2}s^{-1}$

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	8.2	2.5	9.3	9.0	78.2	79.06	0	0	2
		8.3	2.4			79.8				
2	24	9.0	6.9	9.3	9.0	27.42	29.58	49.48	62.32	2
		8.8	6.4			31.71				
3	48	10.1	8.5	9.3	9.0	19.28	18.85	60.21	76.12	2
		9.9	8.4			18.42				
4	72	9.3	7.9	9.3	9.0	15.71	12.85	69.06	87.31	
		9.4	8.4			10.00				

Table A-6

Run-6: 0.0207 kg $m^{-2}s^{-1}$ air flow rate, 2 Capsules at 0, 24, and 48 –hour, with liquid flow rate of 5.5 kg $m^{-2}s^{-1}$

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	8.5	4.8	8.9	8.6	49.14	51.14	0	0	2
		8.6	4.6			53.14				
2	24	9.0	6.9	8.9	8.6	26.28	25.56	25.58	57.92	2
		9.1	7.1			24.85				
3	48	9.8	8.6	8.9	8.6	14.01	13.79	37.35	73.18	2
		9.6	8.4			13.57				
4	72	9.8	9.2	8.9	8.6	5.0	5.4	45.74	89.41	
		9.7	9.1			5.8				

Table A-7

Run-7: 0.0276 kg $m^{-2}s^{-1}$ air flow rate, 2 Capsules at 0, 24, and 48-hour, with liquid flow rate of 5.5 kg $m^{-2}s^{-1}$

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	8.5	3.1	9.1	8.9	74.14	71.42	0	0	2
		8.4	3.4			68.71				
2	24	10.2	7.9	9.1	8.9	29.85	31.99	39.43	64.12	2
		10.4	7.8			34.14				
3	48	10.4	8.8	9.1	8.9	20.14	18.21	53.21	74.51	2
		10.1	8.8			16.28				
4	72	9.5	8.4	9.1	8.9	5.72	5.71	65.71	92.01	
		9.4	8.6			5.71				

Table A-8

Run-8: 0.0345 kg $m^{-2}s^{-1}$ air flow rate, 2 Capsules at 0, 24, and 48-hour. with liquid flow rate of 5.5 kg $m^{-2}s^{-1}$

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	9.5	7.1	9.4	9.2	84.14	80.28	0	0	2
		9.3	7.2			80.28				
2	24	9.2	7.2	9.4	9.2	26.71	26.14	54.14	65.41	2
		9.2	7.3			25.57				
3	48	9.3	8.4	9.4	9.2	11.28	13.21	67.07	79.52	2
		9.4	8.2			15.14				
4	72	9.7	8.8	9.4	9.2	5.19	5.47	74.88	93.21	
		9.6	8.9			5.71				

Table A-9

Run-9: 0.0414 kg $m^{-2}s^{-1}$ air flow rate, 2 Capsules at 0, 24, and 48-hour, with liquid flow rate 5.5 kg $m^{-2}s^{-1}$

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	10.1	6.5	9.0	8.9	48.85	40.92	0	0	2
		9.8	6.9			33.0				
2	24	10.2	8.5	9.0	8.9	21.57	20.28	20.64	67.41	2
		10.1	8.6			19.0				
3	48	9.6	8.9	9.0	8.9	8.57	8.56	32.35	83.22	2
		9.5	8.8			8.55				
4	72	9.2	8.9	9.0	8.9	1.71	2.42	38.51	94.71	
		9.3	8.8			3.14				

Table A-10

Run-10: 5.5 kg $m^{-2}s^{-1}$ liquid flow rate, 2 Capsules at 0, 24, and 48 –hour, with 0.0069 kg $m^{-2}s^{-1}$ air flow rate

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	8.5	3.5	9.5	9.3	68.57	70.71	0	0	2
		8.6	3.3			72.85				
2	24	9.1	6.6	9.5	9.3	32.85	32.13	38.58	54.56	2
		9.2	6.8			31.42				
3	48	9.4	7.9	9.5	9.3	18.57	17.85	52.86	74.74	2
		9.2	7.8			17.14				
4	72	9.4	8.4	9.5	9.3	11.42	9.99	60.72	85.87	
		9.3	8.5			8.57				

Table A-11

Run-11: 11 kg $m^{-2}s^{-1}$ liquid flow rate, 2 Capsules at 0, 24, and 48-hour, with 0.0069 kg $m^{-2}s^{-1}$ air flow rate

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	8.5	3.3	9.4	9.2	71.42	69.28	0	0	2
		8.3	3.4			67.14				
2	24	9.2	6.1	9.4	9.2	41.42	39.99	29.29	42.27	2
		9.3	6.4			38.57				
3	48	9.8	7.8	9.4	9.2	22.85	23.56	45.72	65.99	2
		9.4	7.5			24.28				
4	72	9.2	8.4	9.4	9.2	8.57	7.85	61.43	88.66	2
		9.3	8.6			7.14				

Table A-12

Run-12: 16.5 kg $m^{-2}s^{-1}$ liquid flow rate, 2 Capsules at 0, 24, and 48 –hour, with 0.0069 kg $m^{-2}s^{-1}$ air flow rate

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	8.8	4.5	9.3	8.9	55.71	53.56	0	0	2
		8.6	4.6			51.42				
2	24	9.3	6.9	9.3	8.9	28.57	29.28	24.28	45.33	2
		9.4	6.9			30.08				
3	48	9.1	7.1	9.3	8.9	22.85	23.56	30.0	56.01	2
		9.3	7.2			24.28				
4	72	9.5	8.5	9.3	8.9	8.57	9.28	44.28	82.67	2
		9.4	8.3			10.0				

Table A-13

Run-13: 27.5 kg $m^{-2}s^{-1}$ liquid flow rate, 2 Capsules at 0, 24, and 48-hour with 0.0069 kg $m^{-2}s^{-1}$ air flow rate

Sample	Time (hours)	DO_1 (mg/L)	DO_2 (mg/L)	B_1 (mg/L)	B_2 (mg/L)	BOD_5 (mg/L)	$BOD_{5,ave}$ (mg/L)	ΔBOD_5 (mg/L)	$\%BOD_5$ (mg/L)	Seeding
1	0	8.4	4.4	9.5	9.3	54.28	56.42	0	0	2
		8.6	4.3			58.57				
2	24	8.8	6.2	9.5	9.3	34.28	34.99	21.43	37.98	2
		9.0	6.3			35.71				
3	48	9.3	7.0	9.5	9.3	30.0	29.28	27.14	48.10	2
		9.4	7.2			28.57				
4	72	9.8	8.6	9.5	9.3	14.21	12.81	43.61	77.29	2
		9.7	8.7			11.42				

APPENDIX- B

Calculating Biochemical Oxygen Demand (BOD)

$$BOD_5 = \frac{[(D_1 - D_2) - (B_1 - B_2)]f}{p}$$

Where

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

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

P = Decimal volumetric fraction of sample used

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

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

f = Ratio of the seed in the sample to seed in control(%seed in D_1 / % of seed in B_1)

The experimental values for all thirteen runs can be found in Appendix A. A sample calculation for Run 4 is given below [55].

At 0 hour of treatment, the BOD_5 values for Run 4 of the two trials can be calculated by equation (a):

$$BOD_{5,1} = \frac{[(8.8-3.8)-(9.6-9.3)]1}{0.07} = 66.71$$

$$BOD_{5,2} = \frac{[(8.7 - 3.9) - (9.6 - 9.3)]1}{0.07} = 63.57$$

Therefore the average BOD_5 can then be calculated as:

$$BOD_{5avg} = \frac{BOD_{5,1} + BOD_{5,2}}{2}$$

$$BOD_{5avg} = \frac{66.71 + 63.57}{2} = 65.14$$

At 24 hours of treatment, the BOD_5 values for the two trials can be calculated by:

$$BOD_{5,1} = \frac{[(9.4 - 6.7) - (9.6 - 9.3)]1}{0.07} = 34.28$$

$$BOD_{5,2} = \frac{[(8.9 - 6.6) - (9.6 - 9.3)]1}{0.07} = 28.57$$

$$BOD_{5avg} = \frac{34.57 + 28.57}{2} = 31.42$$

At 48 hours of treatment, the BOD_5 values for the two trials can be calculated by:

$$BOD_{5,1} = \frac{[(8.8-7.1)-(9.6-9.3)]1}{0.07} = 20.0$$

$$BOD_{5,2} = \frac{[(9.0-7.1)-(9.6-9.3)]1}{0.07} = 22.42$$

$$BOD_{5avg} = \frac{20 + 22.42}{2} = 21.21$$

At 72 hours of treatment, the BOD_5 values for the two trials can be calculated by:

$$BOD_{5,1} = \frac{[(8.8-7.5)-(9.6-9.3)]1}{0.07} = 14.7$$

$$BOD_{5,2} = \frac{[(8.9-7.8)-(9.6-9.3)]1}{0.07} = 11.85$$

$$BOD_{5avg} = \frac{14.7 + 11.85}{2} = 13.27$$

Therefore, the BOD_{5avg} at 0, 24, 48, and 72 hours of treatment are 65.14, 31.42, 21.21, and 13.27 mg/l respectively. The calculated BOD_{5avg} for each of the runs are listed in Appendix A.

The percentage of BOD removal for Run 4 is calculated below:

At 0 Hours, the percentage of BOD removal is 0 mg/l.

At 24 hours, the percentage of BOD removal is:

$$\%BOD\,Removal = \frac{(65.14 - 31.42)mg/l}{65.14mg/l} x100 = 51.7\%$$

At 48 hours, the percentage of BOD removal is:

$$\%BOD\,Removal = \frac{(65.14 - 21.21)mg/l}{65.14mg/l} x100 = 67.4\%$$

At 72 hours, the percentage of BOD removal is:

$$\%BOD\,Removal = \frac{(65.14 - 13.27)mg/l}{65.14mg/l} x100 = 79.62\%$$

APPENDIX-C

Calculating Rate Constant using Log – Differential Method

Referring to Appendix A.

We know that (from Equation 15): $\log (L) = \log (L_0 e^{-kt})$

$$\text{Log } (L) = -kt \ (\log e) + \log (L_0)$$

$$\therefore \text{ Slope} = -k \log e$$

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

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

Using Excel, a linear regression equation can be found.

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

Therefore from Figure D.1, Rate Constant Run 1, the equation was found to be

$y = -0.0089x + 1.8462$

$k = 0.0089 / 0.4343$

$k = 0.0204/ \text{ hr}$

Similarly, all the rate constant can be found in Run 1 to Run 13 in rate constant figures.

APPENDIX – D

Graphs of Log (BOD_5) vs. Treatment time.

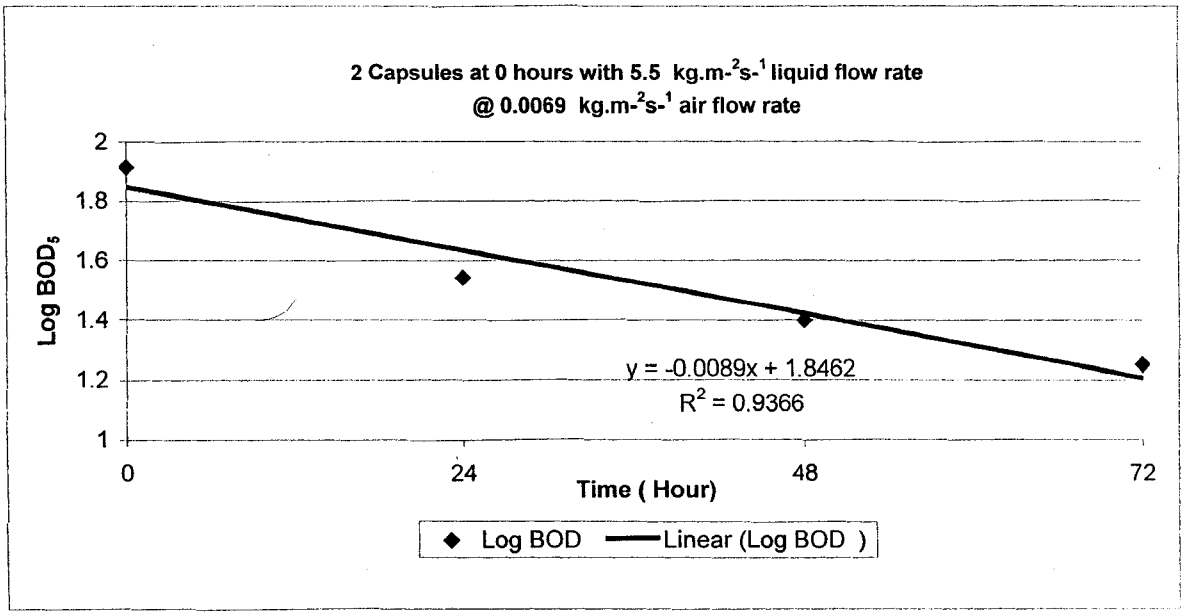

Figure D.1 - Rate Constant For Run -1

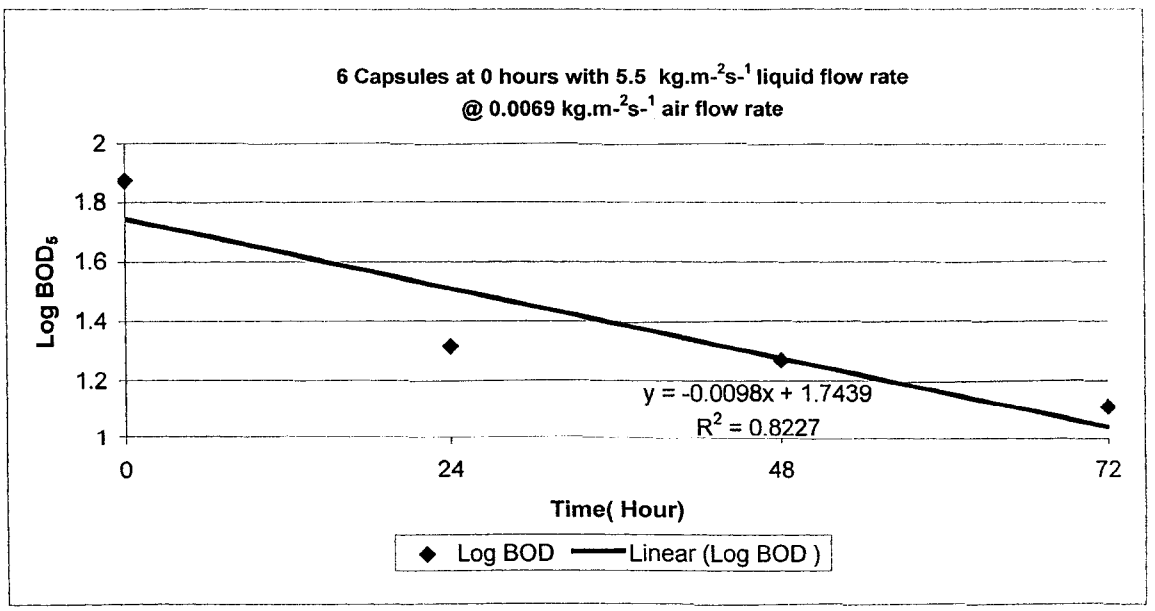

Figure D.2 - Rate Constant For Run -2

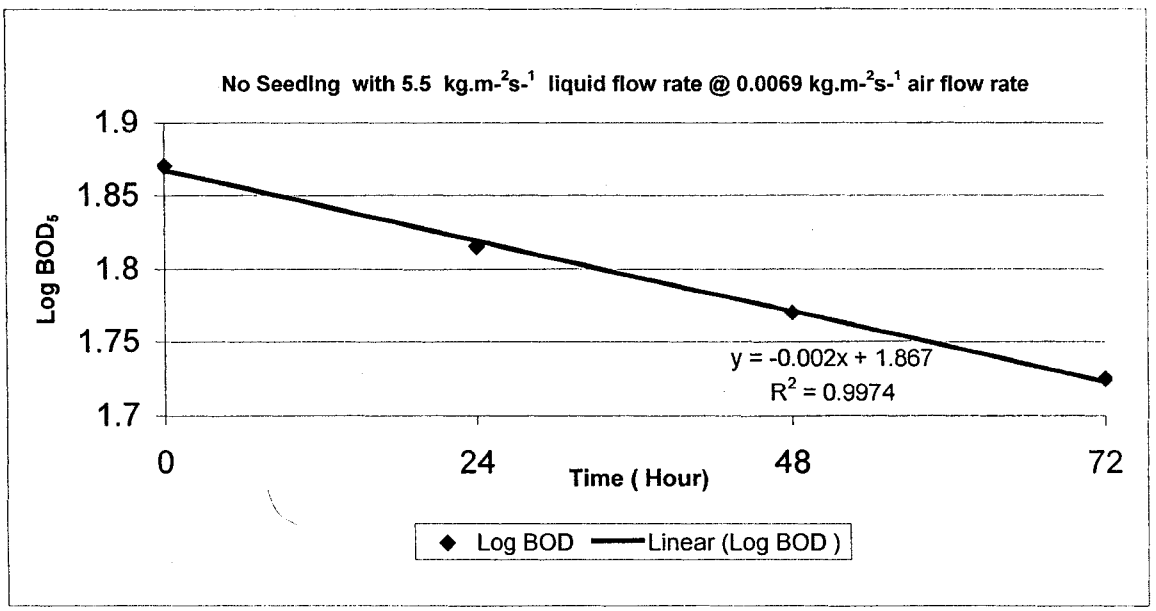

Figure D.3 - Rate Constant For Run -3

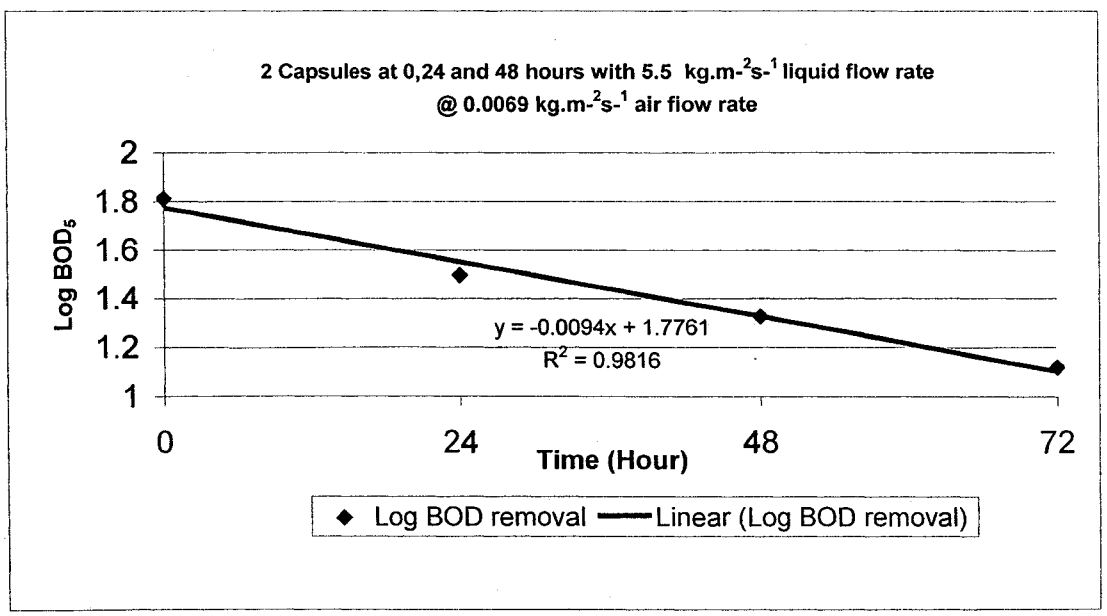

Figure D.4 - Rate Constant For Run -4

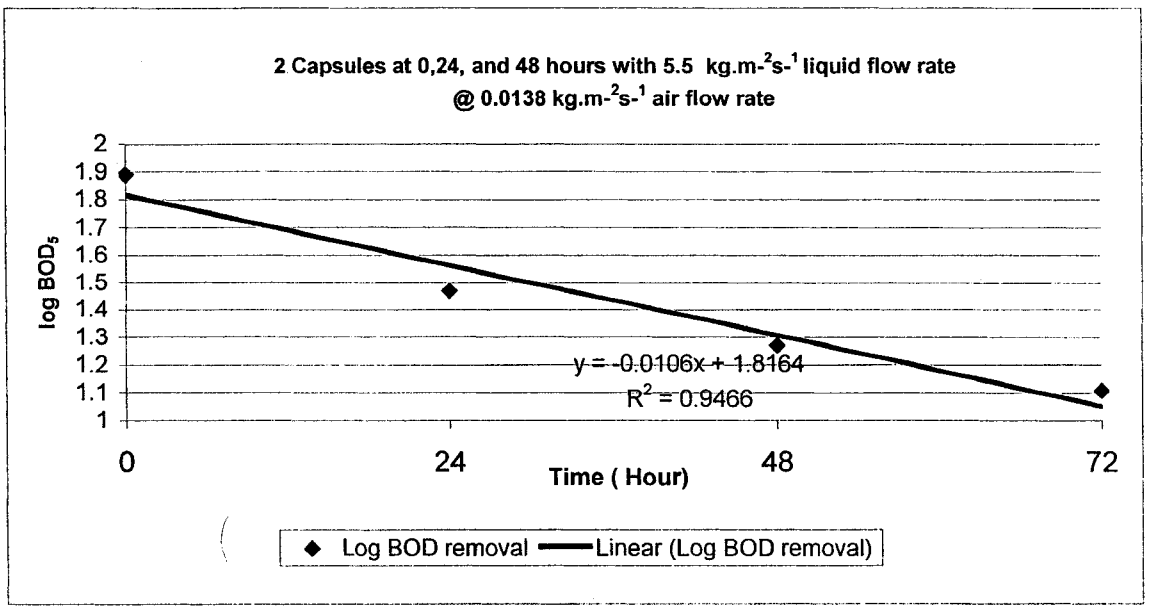

Figure D.5 - Rate Constant For Run -5

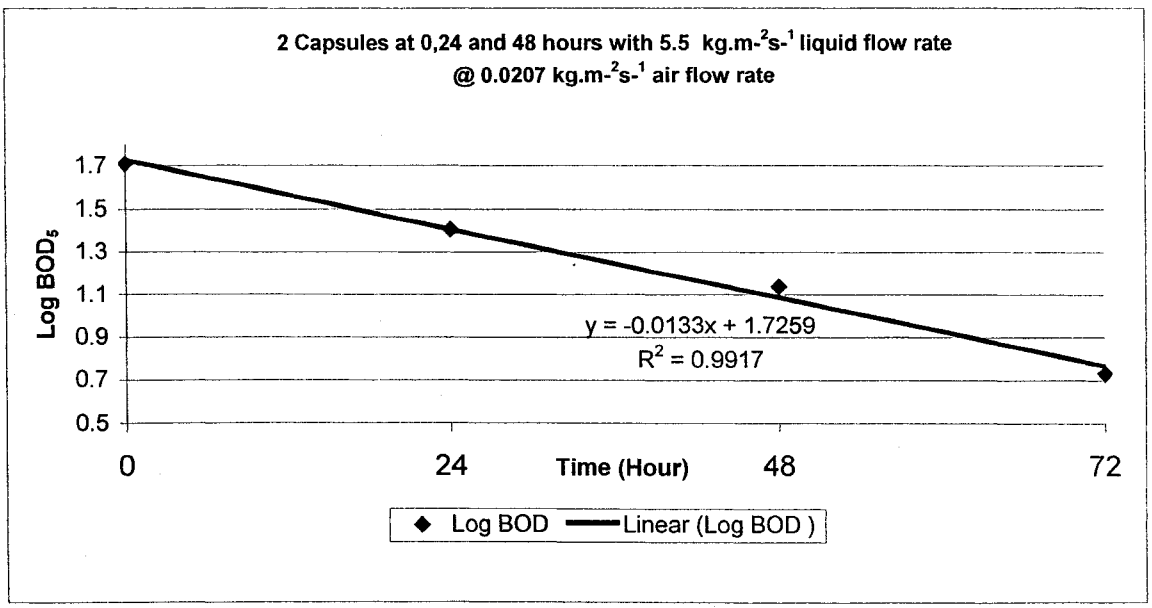

Figure D.6 - Rate Constant For Run -6

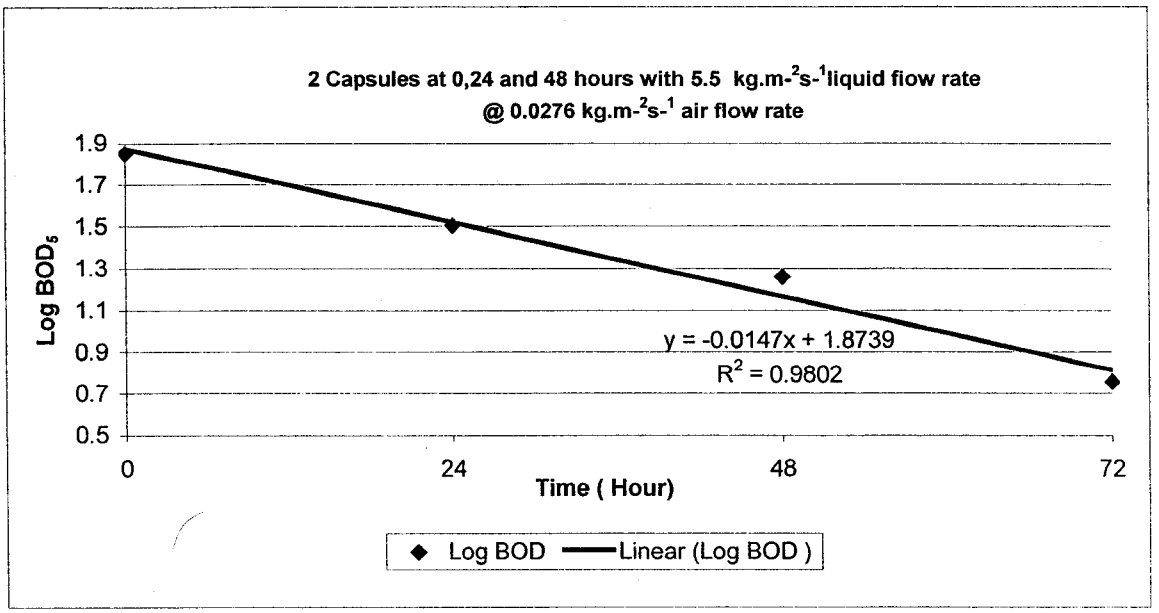

Figure D.7 - Rate Constant For Run -7

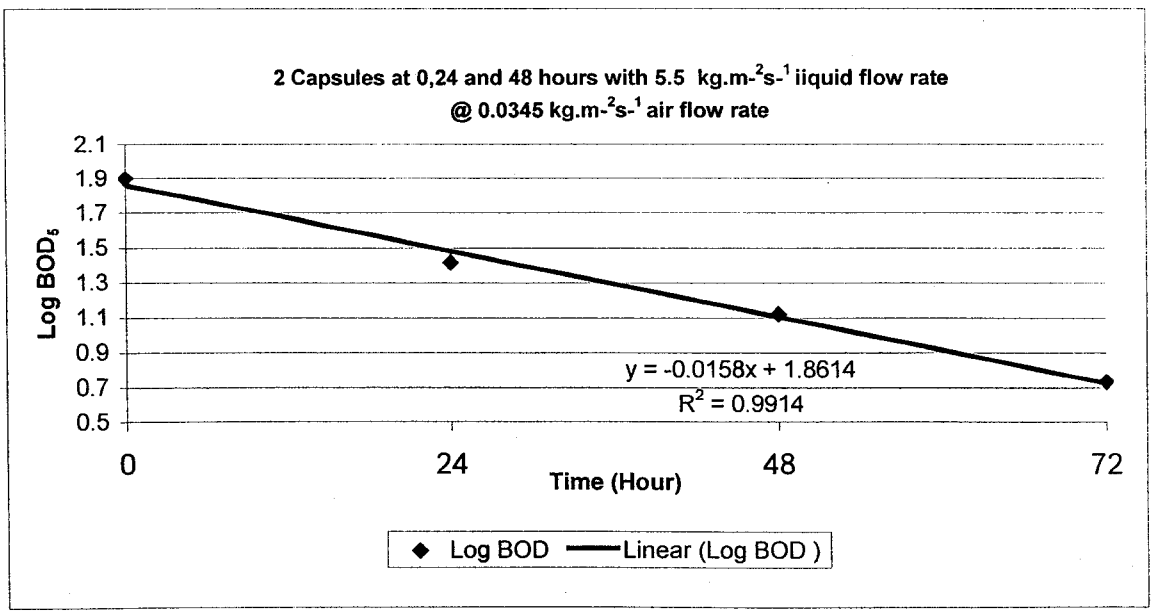

Figure D.8 - Rate Constant For Run -8

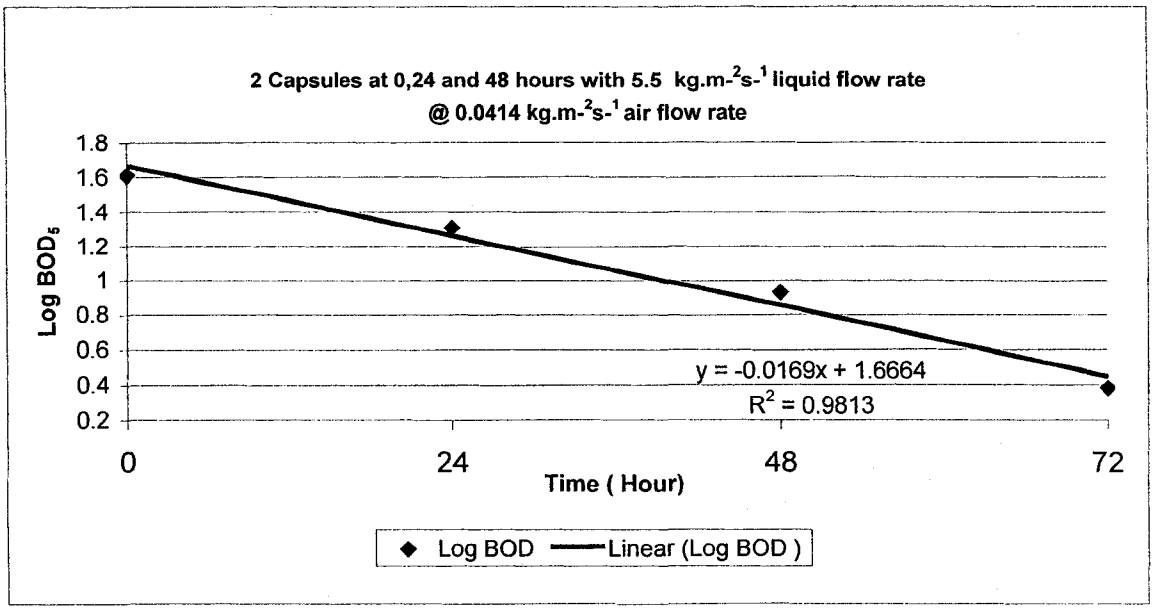

Figure D.9 - Rate Constant For Run -9

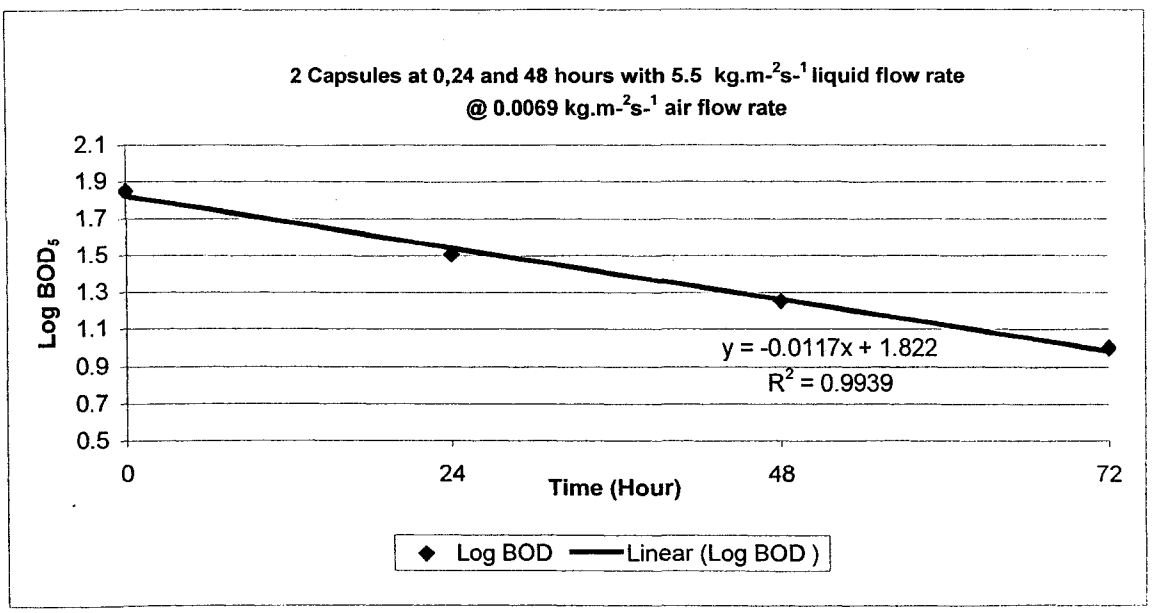

Figure D.10 - Rate Constant For Run -10

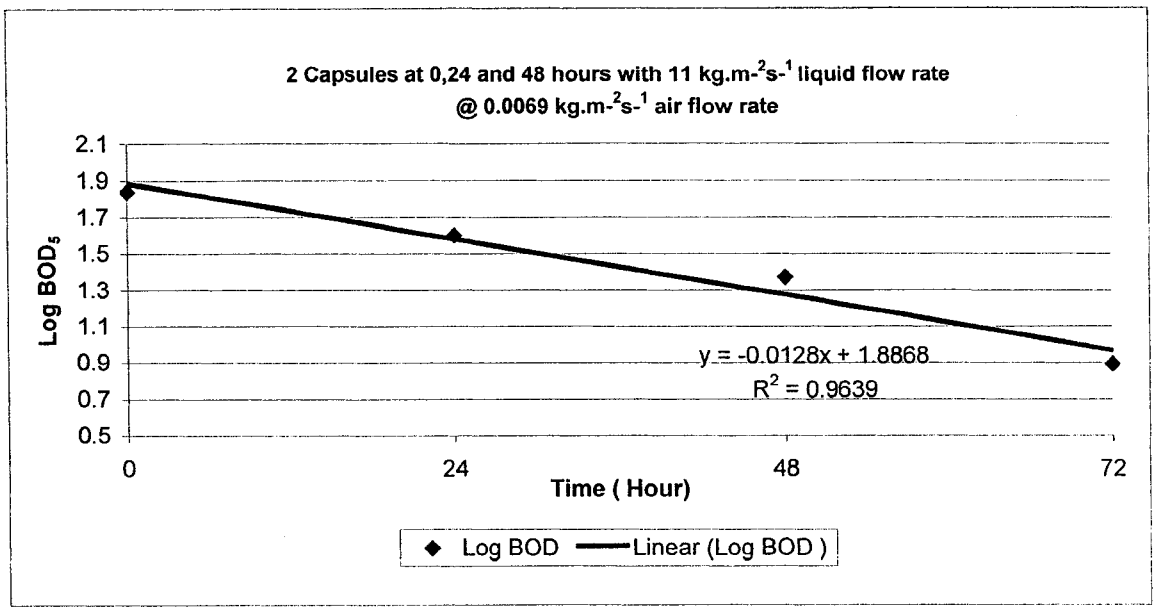

Figure D.11 - Rate Constant For Run -11

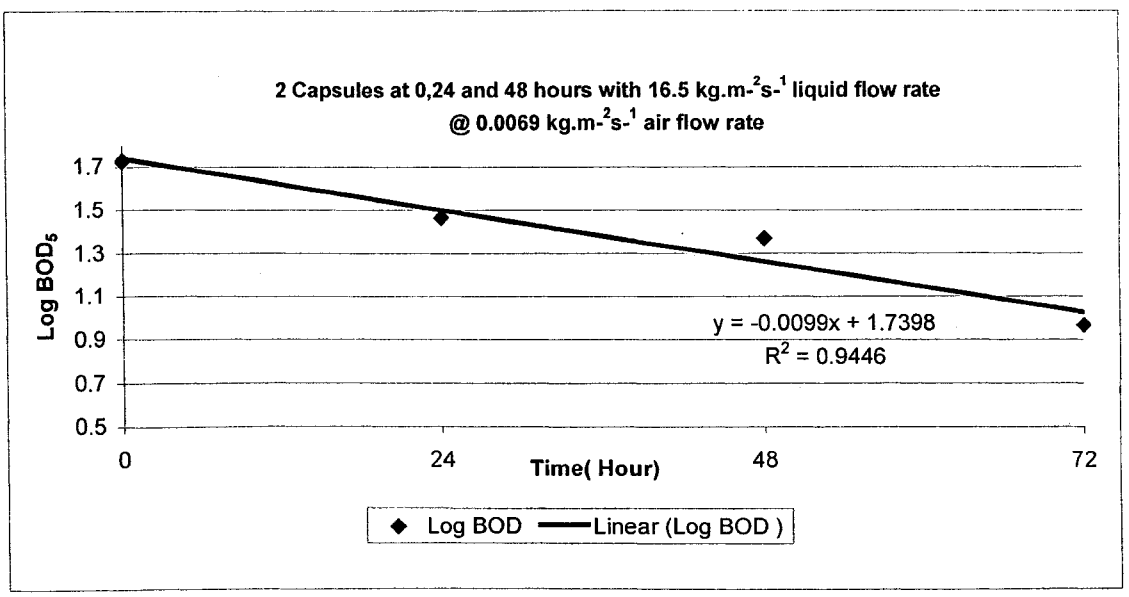

Figure D.12 - Rate Constant For Run -12

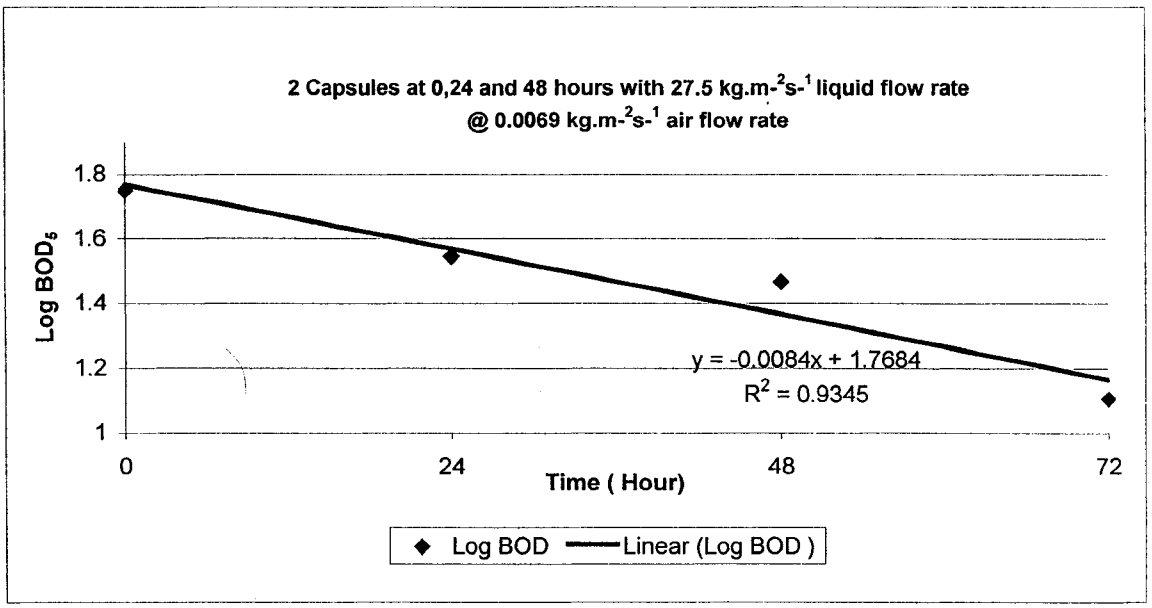

Figure D.13 - Rate Constant For Run –13

APPENDIX-E

Errors 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 be taken as the possible value the error may have. This 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 [56]:

$$BOD = (DO_1 - DO_2) \times f \qquad (19)$$

$$\omega_{BOD} = \left\{ \left(\frac{\partial BOD}{\partial X_1} \omega_{DO_1} \right)^2 + \left(\frac{\partial BOD}{\partial X_2} \omega_{DO_2} \right)^2 \right\}^{\frac{1}{2}} \quad (20)$$

Where, ω_{BOD} is uncertainty in result, ω_{DO_1} and, ω_{DO_2} are the uncertainties in the independent variables, X_1 and X_2 are independent variables (X_1=DO_1, X_2=DO_2).

By using data from Appendix A.

$\omega_{DO_1} = 0.1$

$\omega_{DO2} = 0.1$

$\frac{\partial BOD}{\partial x_1} = 14$

$\frac{\partial BOD}{\partial x_2} = -14$

$\omega_{BOD} = \left\{ \left(14 \times \omega_{DO_1}\right)^2 + \left(-14 \times_{DO_2}\right)^2 \right\}^2 = 1.98$

$\omega_{BOD} = 1.98 = 2.0$

$BOD_5 = 82.1 \pm 2.0$

Therefore, the expected uncertainty/errors in this project was approximately $\pm$ 2.0 mg/L.