BIOLOGICAL DENITRIFICATION SYSTEM FOR INDUSTRIAL WASTEWATER

By

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A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

2009

To my parents and family members

ACKNOWLEDGMENTS

I gratefully acknowledge my advisor, Dr. Spyros Svoronos, for his guidance and support. I thank my co-chair, Dr. Ben Koopman, for his valuable advice through the course of the experiments. I also acknowledge Kiranmai Durvasula and Vijay Krishna for their guidance and advice in experimental work. I am also grateful to Chris Buechler and Darrick Elmore for their guidance and providing industrial samples and material used in the experiments. I thank 'Solutions Defined' team members, Danyal Turkoglu, Sergio Posada, Eric Staunton, Julie Mammino, Cherona Levy, Paul Lang, Kelly Hodoval, Rosalynn Gaffney and Allen Tam, for working with me on this project. Finally, I thank my parents and family members for their endless support and advice throughout my studies.

TABLE OF CONTENTS

page

LIST OF FIGURES

Abstract of Thesis Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Master of Science

BIOLOGICAL DENITRIFICATION SYSTEM FOR INDUSTRIAL WASTEWATER

By

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August 2009

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Major: Chemical Engineering

The purpose of this project was to investigate the suitability of a biological system for treating a high nitrate industrial process stream (IPS). The main focus will be on the required pretreatment of the IPS. Earlier research carried out by a graduate student 'Sherin Peter' on denitrification of the IPS has proved that VOCs present in it hinder bacterial growth. During this project, attempts were made to minimize the VOC content of the IPS so that denitrification process is not hindered. Aeration with compressed air was used as a method of stripping VOCs out of the IPS. Experiments to find out the optimized method of aeration were carried out during this project.

Presence of metal ions was also found to be a hindering factor in previous research carried out on the IPS and ion-exchanging the IPS was found to be effective in dealing with this problem. However the large volumetric flow rate of the IPS makes ion-exchanging cost prohibitive. It was ascertained that ion-exchanging certainly helps but is not essential.

Denitrifying bacteria require carbon for their growth and adequate quantities of carbon are absolutely essential. Carbon contained in the IPS was first choice since it eliminates the extra cost external carbon source. It was found that carbon in the IPS is sufficient for significant nitrate

removal (around 70%). Effectiveness of the two waste carbon process streams (CPS) available at the industry manufacturing site was also checked as probable additional carbon sources.

Performance of an attached growth bioreactor for denitrification of nigh nitrate content wastewater was also studied during this project. It was found that the attached growth bioreactor is able to obtain 100% denitrification of synthetic nitrate sample but the pH in the bioreactor often falls below 7 during continuous operation which has a potential of killing all the bacterial culture and therefore the bioreactor. pH drop results because the feed of synthetic sample used was at pH 5. Using synthetic feed at pH 7 could eliminate this problem but at a considerable expense.

CHAPTER 1
INTRODUCTION

Need for Denitrification

Nitrate present in water can act as a fertilizer to aquatic weeds, grasses and algae. High nitrate levels in water reservoirs can lead to their excessive growth. This leads to eutrophication and reduced oxygen level which is harmful to fish present in aquatic biosphere and hence can be a cause of ecological imbalance. It is, therefore, essential to ensure sufficient removal of nitrate [1]. EPA has strict regulations to avoid high nitrate wastes being discharged in water reservoirs. Availability of nitrate can be minimized by discharging it as nitrogen gas through the application of biological denitrification. [2]

Domestic wastewater contains 0-20 mg/lit of NO_3^-- N. [6] Industrial wastewater, on the other hand, can contain much more concentration of NO_3^-- N. Metal processing industries and industries manufacturing plastics and resins, explosives and fertilizers produce high nitrate content waste. [3]

Description of Denitrification Systems

Denitrification involves reduction of nitrate nitrogen (NO_3^-- N) which acts as a terminal electron acceptor. The process takes place in anaerobic conditions and is alternative to reduction of oxygen. Microorganisms responsible for denitrification are facultative anaerobes. The process can be carried out by a large number of microbial genre commonly found in wastewater treatment system. This includes Achromobacter, Aerobacter, Alcaligenes, Bacillus, Flavobacterium, Micrococcus, Proteus and Pseudomonas. [2]

There are 2 types of enzyme systems involved with the reduction of NO_{3-}-N. [2]

1. Assimilatory: nitrate nitrogen is converted to ammonia nitrogen
2. Dissimilatory: nitrate nitrogen is converted to nitrogen gas.

The Steps in the Reduction of Nitrate are given as [2]:

$NO_{3-} \rightarrow NO_{2-} \rightarrow NO \rightarrow N_2O \rightarrow N_2$

Any one of Nitric Oxide (NO), Nitrous Oxide (N_2O) and nitrogen gas (N_2) can be released as a gaseous end product of the process. Final end product formed depends on the type of organism and pH. N_2 is the major product formed by the mixed cultures used in wastewater treatment. [2]

The process uses nitrate nitrogen as the nitrogen source for bacterial cell synthesis and as the terminal electron acceptor. Proteins, Carbohydrates, Acetate, Propionate and Benzoate etc. can be used as a carbon source. [2]

Advantages and Disadvantages of Biological Denitrification

Biological denitrification is a stable, highly efficient and reliable method of nitrate removal. The process has easy process control and can be run on a continuous basis and is thus useful in dealing with large quantities of process streams to be treated. [2] Generation of non hazardous residues is one of the most important features of biological denitrification. [4]

Denitrification process can be carried out either in slurry reactors or fixed film reactors. Both types of reactors have capability of producing quality effluents in a cost effective manner. Attached film bioreactors allow for short hydraulic residence times with high solids retention times and low solids waste after denitrification. Slurry reactors give better process control and possess greater adaptive potential. [2]

Selection of proper media size and minimization of increase in head loss throughout the system are two important problems faced in designing of attached film reactors. On the other hand, ensuring reliable settling in CSTRs with cell recycle is the problem associated with the use of slurry reactors. [2]

Studies on denitrification process carried out in attached growth bioreactors showed that biomass of denitrifying bacteria grows on the packing media. Increase in nitrate content of the wastewater fed to the bioreactor leads to increase in the biomass that gets developed on the media. This phenomenon is accompanied by the increase in pressure drop which indicates accumulation of excessive biomass on the packed media. Increase in the pressure drop adversely affects the performance of the reactor and thus needs to be avoided. One way of regaining efficiency is to flush out the biomass using high water flow. [4]

Typical values of effluent pH observed in this type of bioreactors are in 7 to 8. This pH range does not have any significant effect on rate of denitrification. High rates of denitrification were observed up to effluent pH above 9 but effluent pH more than 9.5 seem to adversely affect the denitrification process. Use of external carbon source has proved to be effective in obtaining high nitrate removal rates for synthetic nitrate solutions. 70-80% nitrate reduction is claimed by this process. [4]

Denitrification Chemical Equation [2]

1] Reaction for bacterial cell synthesis (R_c):

$$\frac{1}{28}NO_3^- + \frac{5}{27}CO_2 + \frac{29}{28}H^+ + e^- = \frac{1}{28}C_5H_7O_2N + \frac{11}{28}H_2O$$

2] Reaction for electron acceptor with nitrate as the terminal electron acceptor (R_a):

$$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2 + \frac{3}{5}H_2O$$

3] Reaction for electron donor with acetate as the carbon source (R_d):

$$\frac{1}{8}CH_3COO^- + \frac{3}{8}H_2O = \frac{1}{8}CO_2 + \frac{1}{8}HCO_3^- + H^+ + e^-$$

The overall molar-based equation for bacterial growth can be obtained as,

$R = R_d + f_e \times R_a + f_s \times R_c$

Where,

f_e = fraction of electrons used for energy

and

f_s = fraction of electrons used for biosynthesis

and $f_e + f_s = 1$

Calculation of f_s:

f_s = (growth yield) x (appropriate conversion factor)

Denitrification with acetate as electron donor yields about 15 to 18 g dry matter per mole acetate. [5] We will consider 16.5 g dry matter per mole of acetate for our calculation.

That is, 16.5 g dry matter per 98 g of acetate (potassium acetate is considered here)

From equation R_c, it can be said that (1/28) moles of biomass = 4.0357 grams of biomass is produced per e^- equivalent.

From equation R_d, 8 g COD = 1 e^- equivalent.

Therefore,

$$fs = \frac{16.5 gVSS}{98 gCOD} x \frac{8 gCOD}{e - equivalent} x \frac{e - equivalent}{4.0357 gVSS}$$

Therefore,

$f_s = 0.33$

Therefore, $f_e = 0.67$

Final equation fir denitrification can be obtained by putting values of f_s and f_e in the formula for overall rate equation (R) stated above.

Previous Research on Denitrification of the Industrial Process Stream (IPS)

A graduate student, 'Sherin Peter', proved in her research that biological denitrification of the IPS is possible after removal of VOCs present in it by aeration of the IPS. She also proved that, higher denitrification rates can be obtained by cation exchanging the IPS and thereby minimizing the metal ions present in it. Desired rate of denitrification of the IPS can be obtained after providing it with pretreatment of aeration (to remove VOCs) and ion-exchange (to minimize metal ions) and with the use of external carbon source in the form of Potassium Acetate. It was possible to get denitrification rate of around 2 mg NO_3-N/L/min and an overall denitrification of 98%. Investigation of available carbon process streams (CPS) with the industry as alternate carbon sources was not done. It was found that micronutrients should be directly added to the reactor since precipitation of micronutrients in feed creates deficiency of micronutrients in the reactor which affects the rate of denitrification.

Goal of This Project

The main focus of this research work was to determine and optimize a pretreatment to the IPS which can be implemented on an industrial scale. This included optimization of aeration required to strip off the VOCs present in the IPS and investigation of the necessity of ion exchanging the IPS. Selection of cost efficient carbon source was also an important area to be researched. Performance of attached film bioreactor for denitrification of high nitrate synthetic wastewater was also studied.

CHAPTER 2
BIOTREATABILITY TEST

Introduction

Earlier research on denitrification on the industrial process stream (IPS) has proved that presence of Volatile Organic Compounds (VOCs) and metal ions present in the IPS affect the growth of denitrifying bacteria. Designing of pretreatment which makes IPS more suitable for denitrifying bacteria was essential. To verify if pretreatment provided to the IPS is good enough to sustain bacterial growth in it, a batch test was developed during previous research.

This test provides us with Biological Treatability Index (BI) which is a comparison of the maximum specific growth rate (μ_{max}) of denitrifying bacteria grown in an IPS sample to that of denitrifying bacteria grown in a synthetic nitrate sample of the same nitrate-nitrogen concentration:

$$BI = \frac{\mu_{max}^{sample}}{\mu_{max}^{synthetic}}$$

Treatable nitrate solutions will have a value close to 1. While BI of 0 indicates that the sample cannot be denitrified biologically.

Procedure

1] NO_3-N content of the IPS sample is measured using HACH® NitraVer Test 'N Tube test kits.

2] A synthetic nitrate solution of about the same NO_3-N content is prepared by adding concentrated nitric acid to DI water. Approximately 250 ml of synthetic nitrate solution is prepared to carry out each test.

3] 4:1 ratio of carbon to NO_3-N is used in all the samples used in this test. Potassium acetate is used as a carbon source.

4] Following chemicals are added to support bacterial growth and metabolism:

a. 0.5 g/L potassium phosphate as phosphorus source

b. 0.1 g/L magnesium sulfate heptahydrate as magnesium source

c. 0.3 g/L ammonium chloride as the ammonium source

5] Synthetic nitrate solution and the IPS sample are neutralized to pH 8 using NaOH pallets.

6] Well stirred samples of synthetic nitrate solution and the IPS separated in three parts of volume 60 ml each are put in three125 ml Erlenmeyer Flasks.

7] 10 ml of denitrifying bacterial culture, grown in a high synthetic nitrate stream, is added to each flask.

8] 0.2 ml micronutrient solution (prepared using instructions for trace element solution by Vishniac & Santer) is also added to each flask. Addition of micronutrient solution is critical for bacterial growth during the experiment.

9] 5 ml sample is collected from each flask and flasks are stoppered immediately with solid rubber stoppers. Initial (time = 0 hrs) readings of NO_{3}-N, pH, and absorbance are obtained using 5 ml samples drawn out.

The NO_{3}-N concentration is measured after filtering the sample from each flask using 0.45 μm filters, and diluting the samples to appropriate concentrations.

10] All the flasks are kept in a shaking incubator set at 37°C and 250 rpm.

11] pH, and absorbance readings of one flask of each sample (Synthetic nitrate solution and IPS) are measured at around 3-4 and 7-8 hrs.

12] Final NO_{3}-N concentration, pH and absorbance are measured at 22-24 hrs.

13] To calculate maximum specific growth rate of denitrifying bacteria in a sample, a graph of [ln (absorbance)] vs. time was plotted. It was proved in earlier research that, the slope of a trend

line which shows the best fit of the data points gives the maximum specific growth rate for the sample. Final value of BI was then calculated as

$(\mu\_max)_{sample} / (\mu\_max)_{synthetic\ solution}$

CHAPTER 3
PRETREATMENT TO THE INDUSTRIAL PROCESS STREAM

Aeration

Introduction

Previous studies on the industrial process stream (IPS) proved that presence of volatile organic compounds (VOCs) present in it hinder the growth of denitrifying bacteria and aeration of the IPS can be used as a pretreatment before it is used for the process of denitrification. It was essential to optimize the pretreatment so that it can be implemented on industrial scale in a cost effective way.

Various factors which affect the performance of aeration pretreatment were considered. Aeration of the IPS at different pH, different time durations and air flow rate were tried to find out the best trade-off between the cost and the effectiveness of the pretreatment. Packed column aeration was also used in order to achieve efficient removal of VOCs.

Experimental Set-up for Aeration Pretreatment

1] Aeration was performed in stirred vessel.

Specifications: Made by ‘New Brunswick Scientific Co., Inc’, and the specific machine used was ‘BIOFLO 110 Fermentor/Bioreactor’.

2] The aeration pretreatment to the IPS was carried out in a chemical hood. This is because VOCs getting stripped out of the IPS were assumed to be harmful to the human body.

3] Five hundred milliliters of sample is poured into the vessel. Agitation is set to 550 rpm.

4] Air from a compressed air tank is passed through a flowmeter and then sent into vessel right below the rotating blades. Air flow rate was adjusted as per the pretreatment requirements of individual experiment. Air flow rate was measured by the flowmeter.

5] Duration of the aeration was also determined by the pretreatment requirements of individual experiment. Samples obtained after this pretreatment were used in biotreatability tests.

Figure showing air tank, vessel used for aeration is shown below.

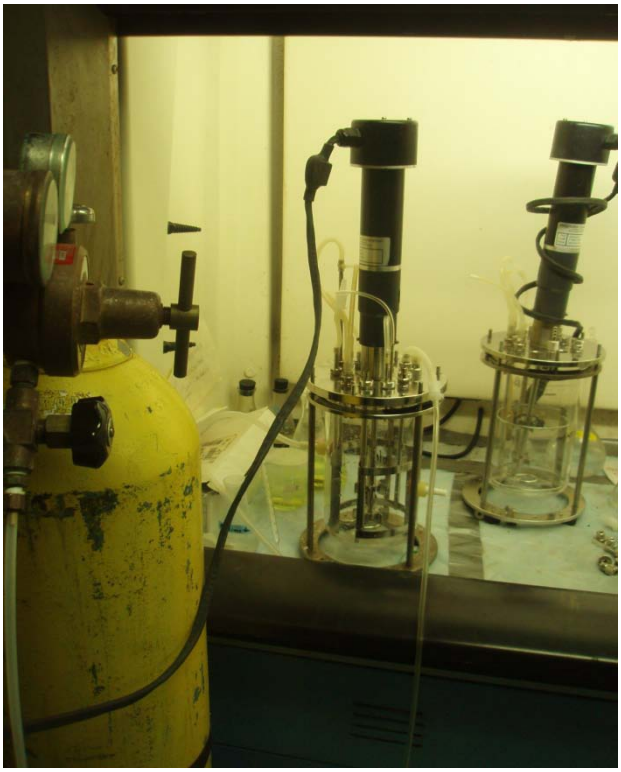

Figure 3-1. Assembly for aeration of the IPS

Biotreatability Tests to Optimize Pretreatment

1] Aeration of IPS at pH 2 and at pH 2 & 8

In order to remove weakly acidic VOCs, it was essential to aerate the IPS at low pH. IPS was therefore aerated at pH 2. It was also hypothesized that the IPS may contain some basic VOCs. To get rid of those VOCs, IPS was aerated at pH 8. First biotreatability test conducted used following three different IPS samples:

1] Aeration at pH 2 for 2 hours and at air pressure of 1.6 lpm. 10 corresponds to 1.6 L/min and the volume of the sample aerated was 500 ml.

2] Aeration at pH 2 and 8 for 2 hours each and at air pressure of 1.6 lpm.

3] No pretreatment.

Results of the experiment are shown in graphs below:

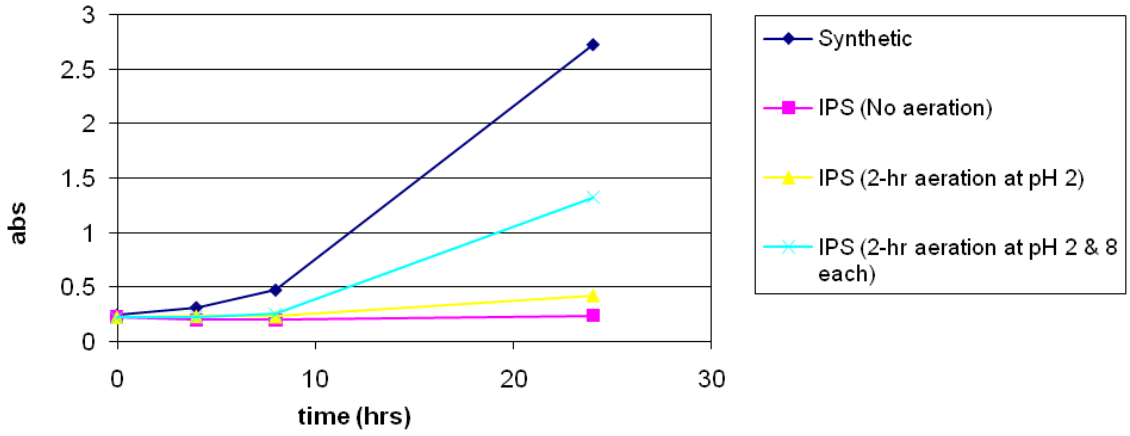

Figure 3-2. Absorbance results for no aeration, aeration at pH 2 and pH 2 & 8

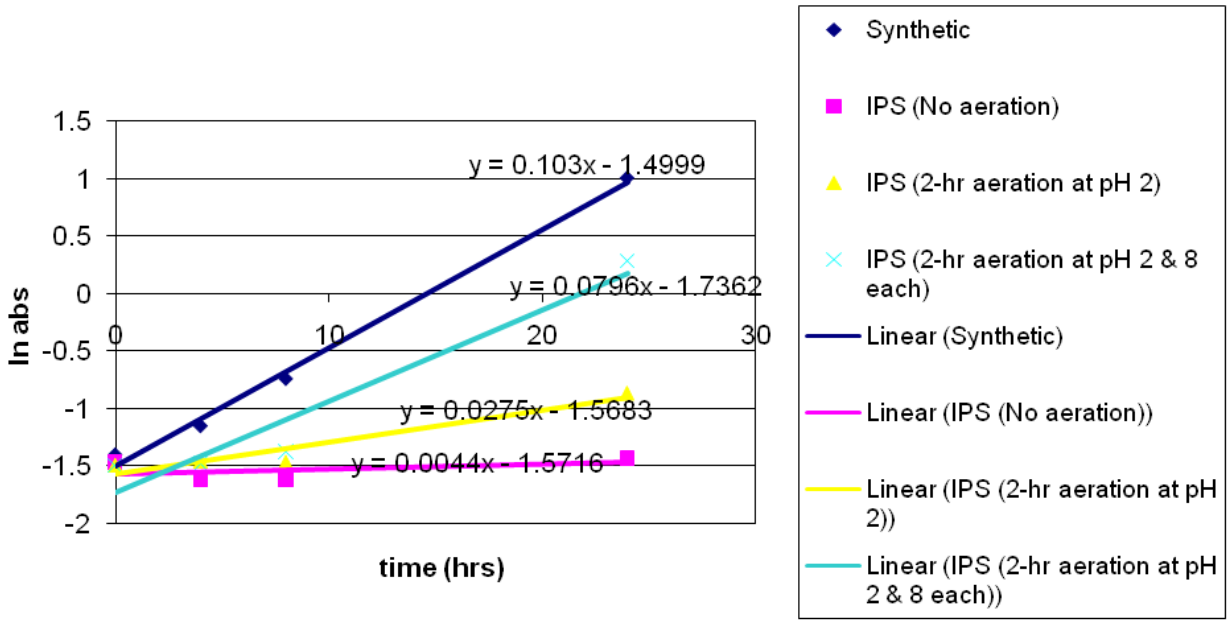

Figure 3-3. BI of IPS with no aeration, aeration at pH 2 and pH 2 & 8

1] Aeration at pH 2 for 2 hours = 0.27

2] Aeration at pH 2 & 8 for 2 hours each = 0.77

3] No pretreatment, BI = 0.04

Low BI value for the sample without any pretreatment ascertained previous findings that pretreatment of the IPS is certainly required. It was also found that aeration of the IPS at pH 2 and pH 8 is more effective than aeration at pH 2.

2] Aeration of IPS at pH 5 and at pH 8

Raising pH of the IPS to 8 is cost prohibitive and therefore it was decided to find out the BI value of the IPS at slightly lower pH.

Another experiment was carried out in which following pretreatments were considered:

1] Aeration at pH 5 for 2 hours and at air pressure of 1.6 lpm
2] Aeration at pH 8 for 2 hours and at air pressure of 1.6 lpm

Results of the experiment are shown in graphs below:

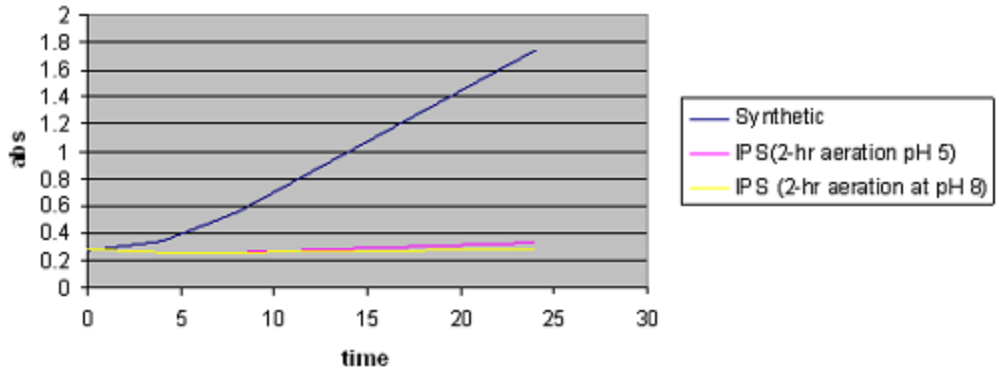

Figure 3-4. Absorbance results for aeration of pH 5 and pH 8.

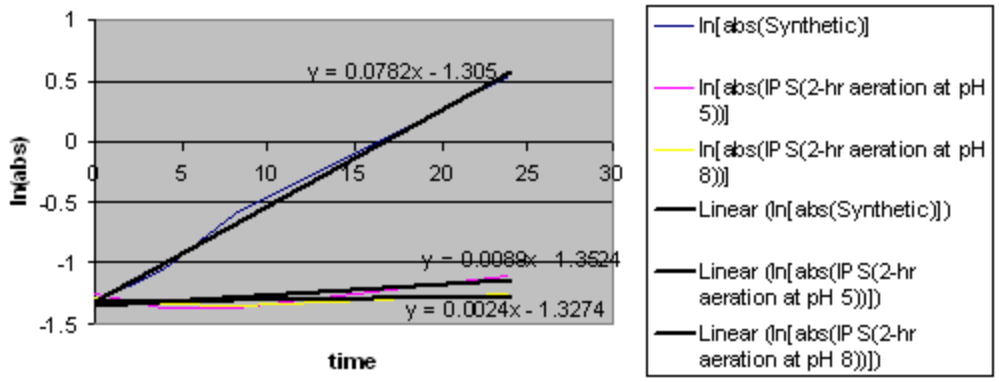

Figure 3-5. BI of IPS with aeration at pH 5 and pH 8

1] Aeration at pH 5 for 2 hours, BI = 0.11
2] Aeration at pH 8 for 2 hours, BI = 0.03

Low BI values from this experiment proved that it is essential to aerate the IPS at pH 2 to remove acidic VOCs. But last experiment showed low BI value for aeration the IPS sample aerated at pH 2. Therefore it was concluded that aeration for 2 hours at 1.6 lpm of air flow pressure is not enough pretreatment to the IPS and it is essential to find out a better way to aerate the IPS more efficiently.

3] 6 Hours of Aeration at pH 2 & 5

In order to achieve more efficient aeration, the IPS sample was aerated for 6 hours at pH 2 and 5 each. The air flow pressure was set at 1.6 lpm.

Following graphs show the result of this experiment.

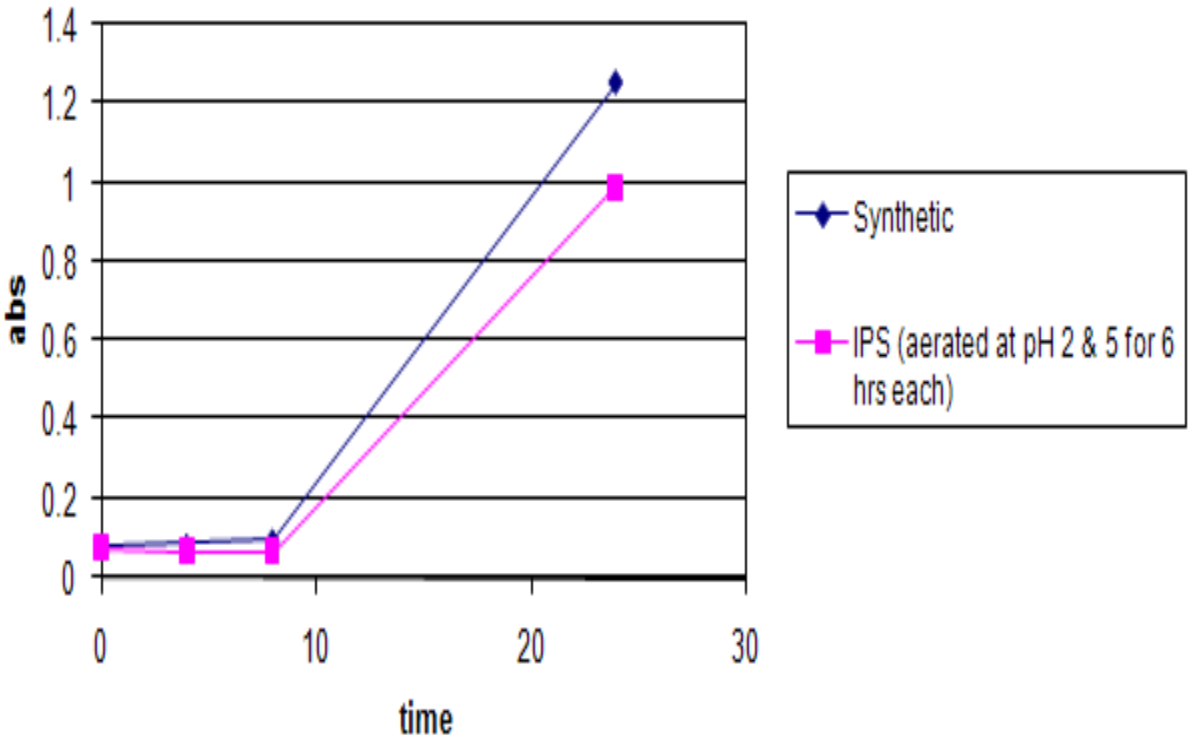

Figure 3-6. Absorbance results for aeration at pH 2 & 5 for 6 hours each

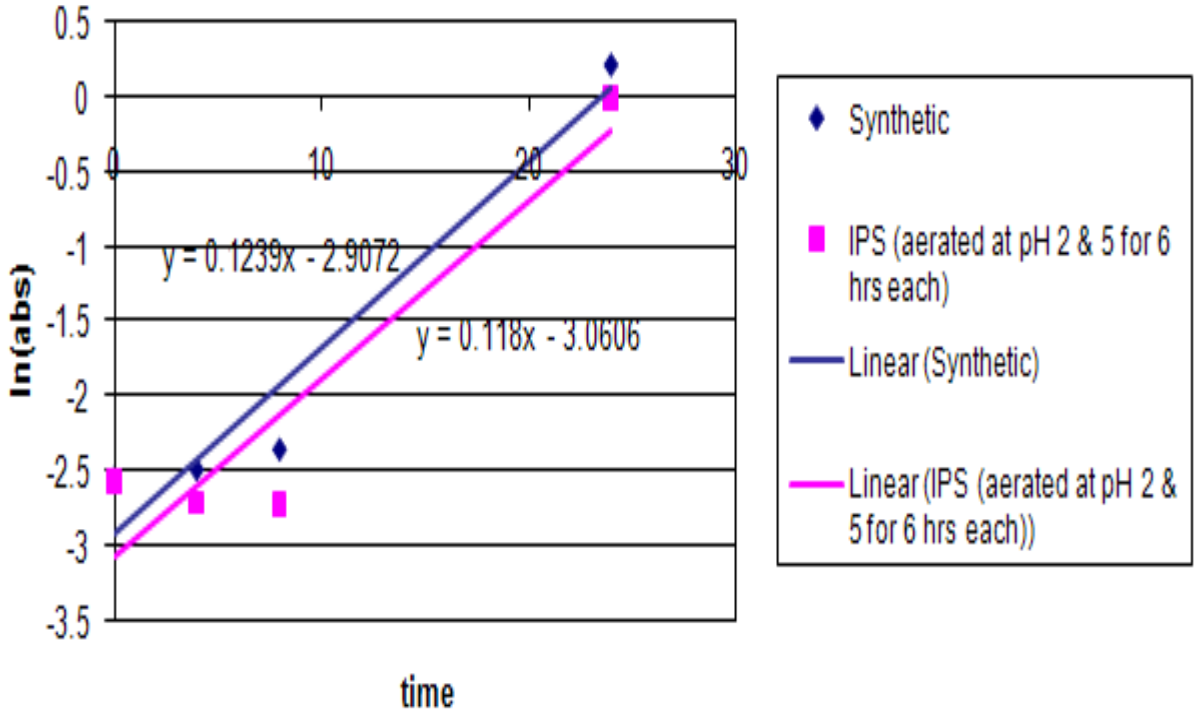

Figure 3-7. BI of IPS with aeration at pH 2 & 5 for 6 hrs each

BI value in this case was found to be equal to 0.85. This is significantly greater than previous BI values obtained for aeration of the IPS for 2 hours. High BI value obtained from this experiment showed that pretreatment of the IPS was successful.

But again, raising pH of the IPS to 5 is not cost efficient as far as implementing it on the industrial scale is concerned. It was thus essential to examine if aeration at pH 2 can give good BI values.

4] 1-hr Aeration at pH 2 and at Air Flow Pressure of 16 Lpm

In an attempt to get high BI value (i.e. efficient pretreatment) to the IPS at pH 2, an experiment was carried out in which the IPS was aerated for 1 hour at pH 2 and at air flow pressure of 16 lpm.

Following graphs show the result of this experiment.

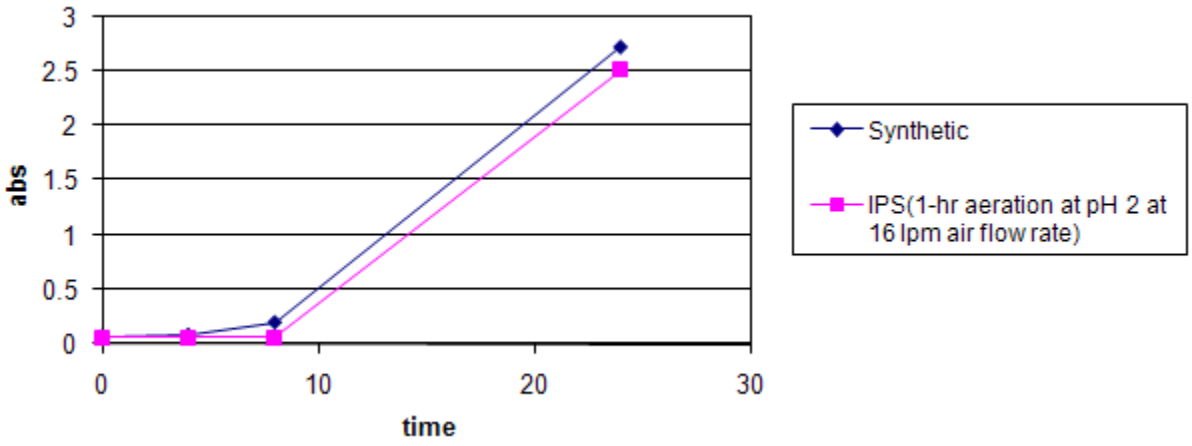

Figure 3-8. Absorbance results for aeration at pH 2 at 16 lpm for 1 hour

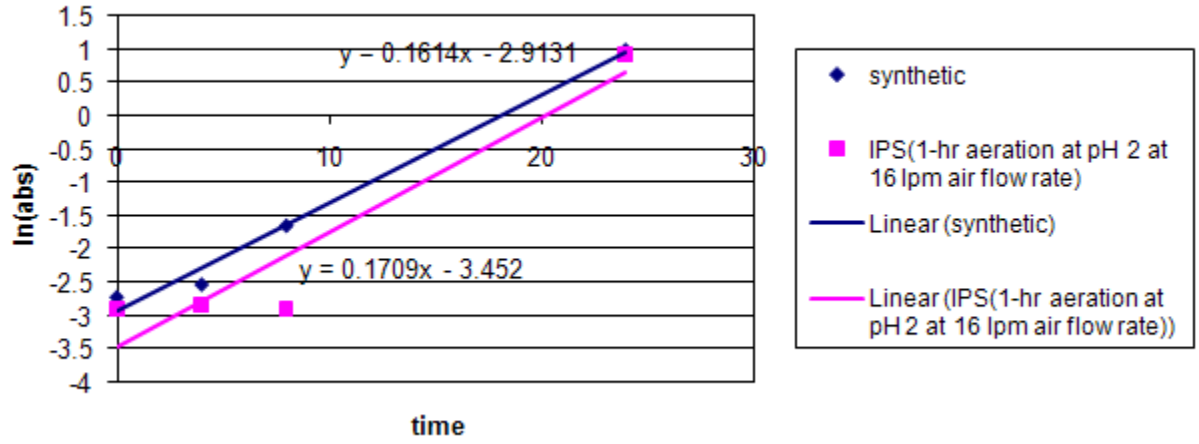

Figure 3-9. BI of IPS with aeration for 1 hr at pH 2 and at 16 lpm

BI for this experiment is 1.06 which is in the limits of experimental error. This result shows that 1-hr aeration to the IPS at pH 2 and at air flow pressure of 16 lpm makes the IPS treatable by the denitrifying bacteria. Air flow rate was measured as 16 liters/min.

5] Aeration at pH 2 at 16 Lpm for Different Time Intervals

Having found that aeration at pH 2 can work great with higher air flow rates, it was essential to figure out if aeration conducted for lesser period of time can serve as a sufficient pretreatment for the practical applications.

An experiment was therefore conducted to optimize aeration. Pretreatment conditions are as listed below:

1] Aeration at pH 2 at 100 for 10 minutes
2] Aeration at pH 2 at 100 for 60 minutes

Following graphs show the result of this experiment.

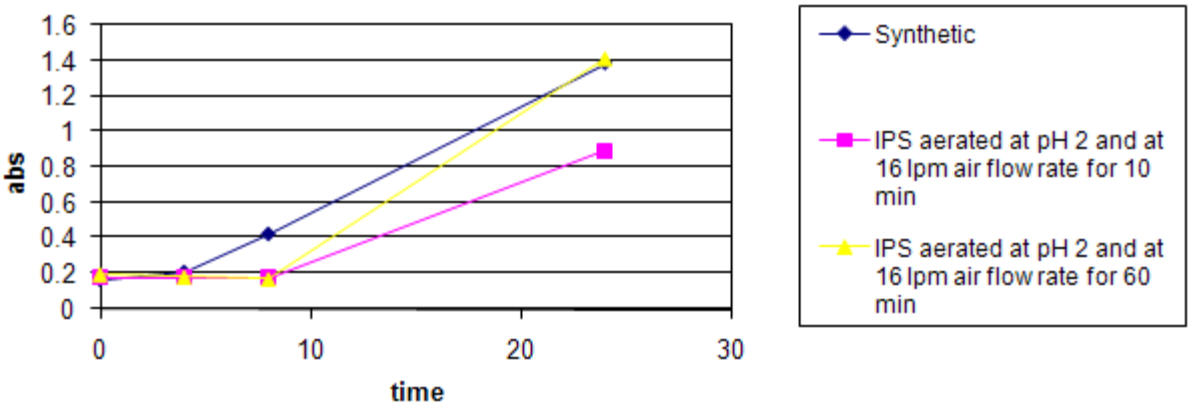

Figure 3-10. Absorbance results for aeration at pH 2 for 10 and 60 minutes.

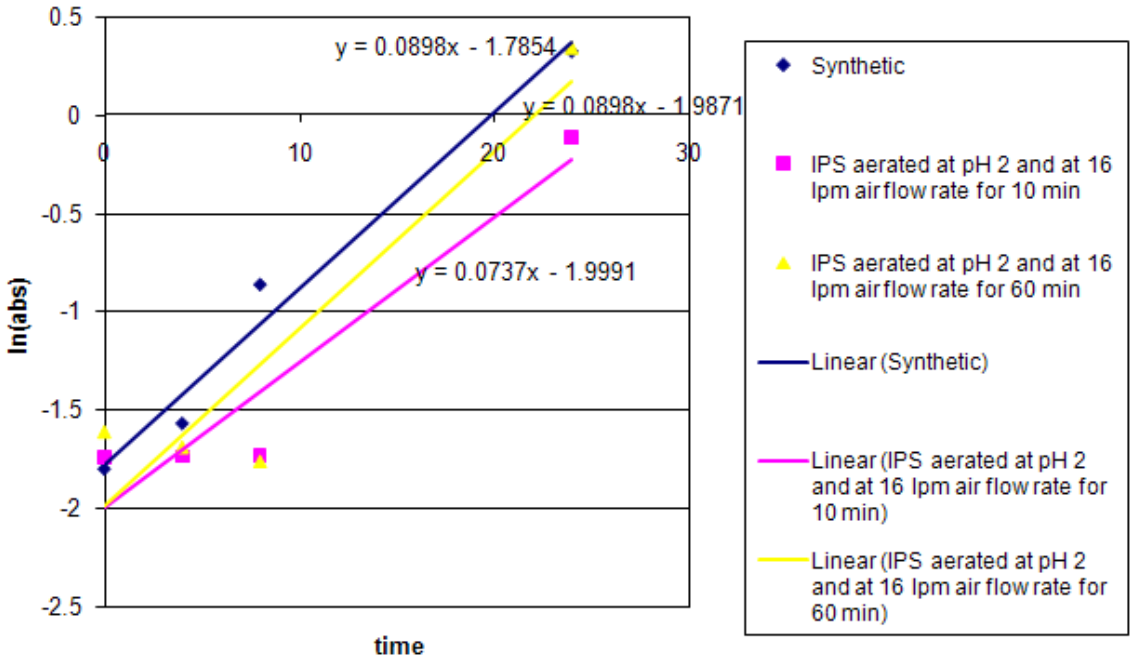

Figure 3-11. BI of IPS with aeration for different time intervals at pH 2 and at 16 lpm

BI for the IPS sample aerated for 10 minutes was found to be equal to 0.27 and that of the IPS sample aerated for 1 hr was found to be equal to 0.77.

All the experiments performed till now were performed on sample 1. It was known that the IPS has variability in its composition. Sample 3 had NO_3--N of approximately 2600 mg/lit. To verify if the method of biological denitrification works at such a high nitrate level, a biotreatability test conducted was conducted on

1] Sample 2 with NO_3--N content of 1100 mg/lit
and
2] Sample 3 with NO_3--N of 2600 mg/lit

Both the samples were aerated at pH 2 for 1 hour and at 16 lpm. It should be noted that the ratio of potassium acetate to nitrate nitrogen used for the IPS sample 3 is maintained between 2.5 to 3 is to 1. This is done because high levels of carbon corresponding to exceptionally high NO_3—N levels in IPS sample 3 were assumed to be harmful for the growth of denitrifying bacteria. The same ratio is used whenever IPS sample 3 during an experiment.

Following graphs show the result of this experiment.

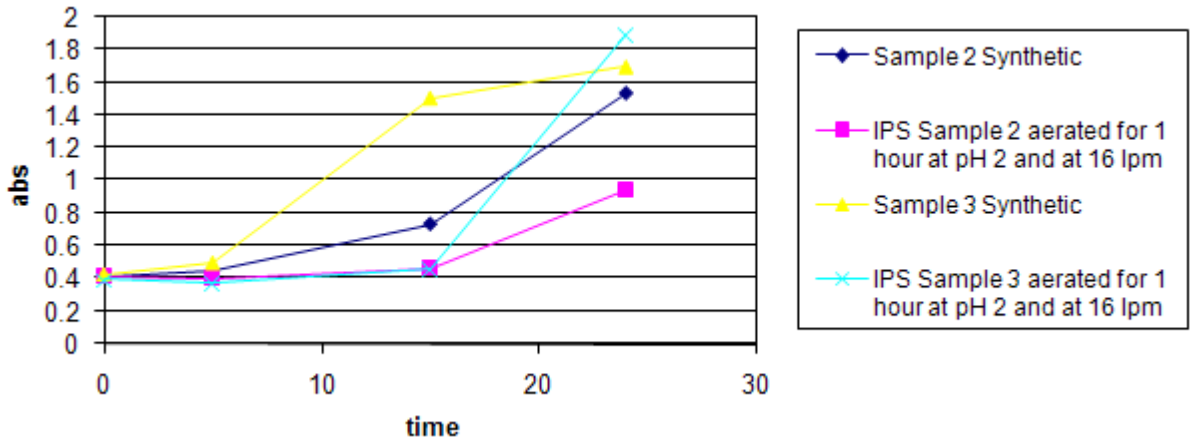

Figure 3-12. Absorbance results for aeration IPS samples 2 and 3

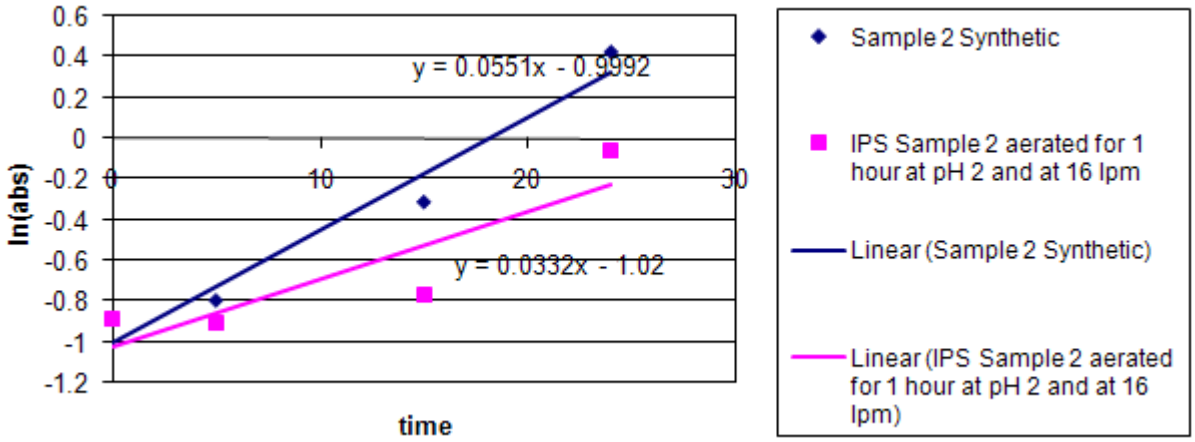

Figure 3-13. BI for aeration IPS samples 2

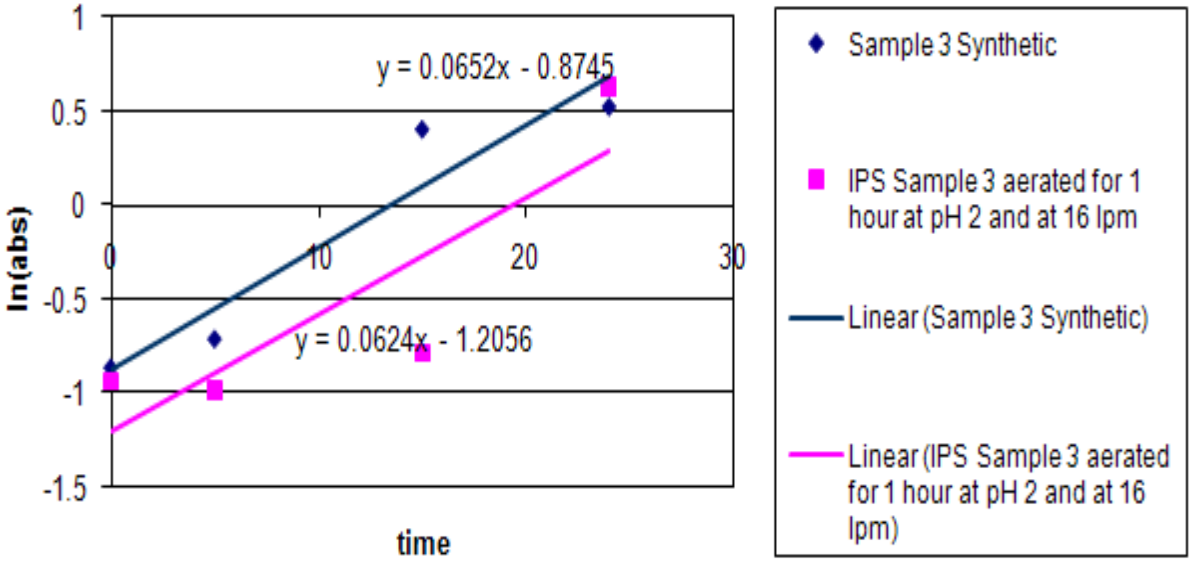

Figure 3-14. BI for aeration IPS samples 3

BI of sample 2 was found to be approxmitely equal to 0.6 and that of sample 3 was 0.96. There results proved that the denitrifying bacteria work well even at very high nitrate content. These results also conclude that, variability of the IPS will not have adverse effect on the process of denitrification if the IPS is pretreated properly.

Ion-exchange

Introduction

Previous studies on the IPS have proved that ion-exchanging the IPS helps to increase the rate of denitrification. Although it was a useful finding, it was impractical to implement it on a industrial scale. It was therefore necessary to find out if ion-exchanging IPS is absolutely essential.

Biotreatability Tests

1] Ion Exchanged vs. Non Ion Exchanged Sample 2

Ion-exchanged sample 2 and non-ion exchanged sample 2 were used to carry out biotreatability test. Both the samples were aerated for 1 hr at pH 2 at 16 lpm.

Following graphs show the result of this experiment.

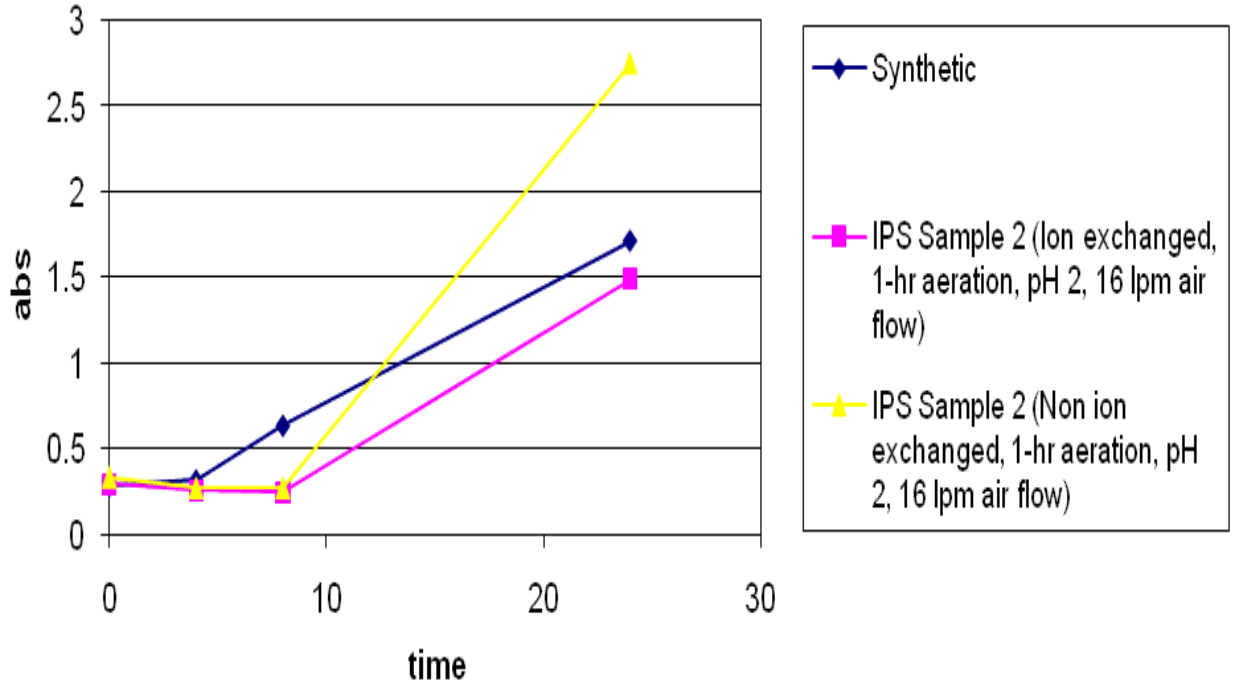

Figure 3-15. Absorbance results ion exchanged and non ion exchanged sample 2

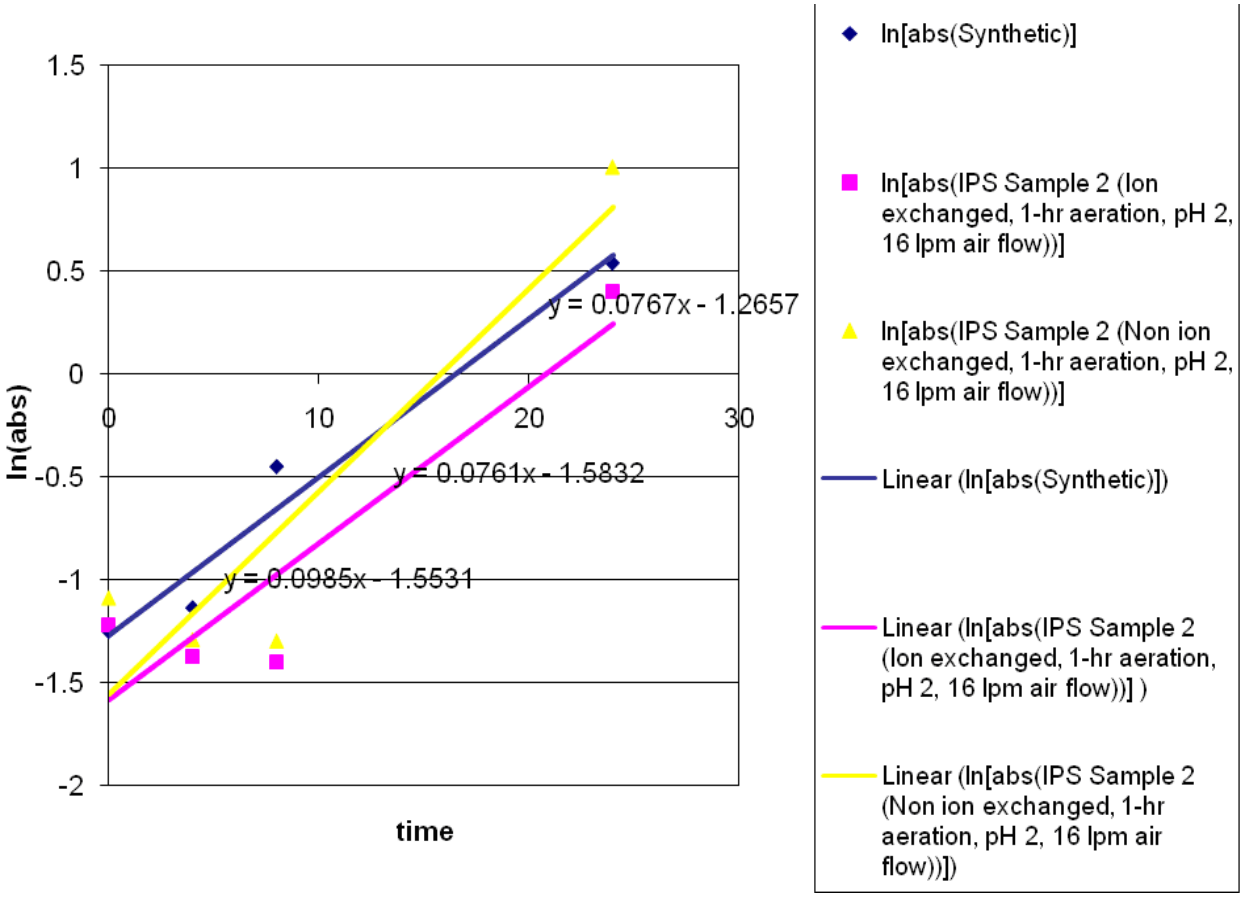

Figure 3-16. BI for ion exchanged and non ion exchanged sample 2

Results of the biotreatability test showed that BI of the ion-exchanged sample is 0.99 and that of non ion-exchanged sample is 1.28. Although a BI value of 1.28 is on a higher side, it is within the limits of experimental error. But this experiment proves that both the samples are well treated and are good to be used for the process of denitrification and non ion-exchanged sample is certainly treatable.

2] Ion Exchanged vs. Non Ion Exchanged Sample 3

Ion-exchanged and non ion exchanged sample 3 were used to in a biotreatability test to account for the variability in constitution of the IPS. Sample 3 has exceptionally high nitrate content. Both the samples were aerated for 1 hr at pH 2 at 16 lpm.

Following graphs show the result of this experiment.

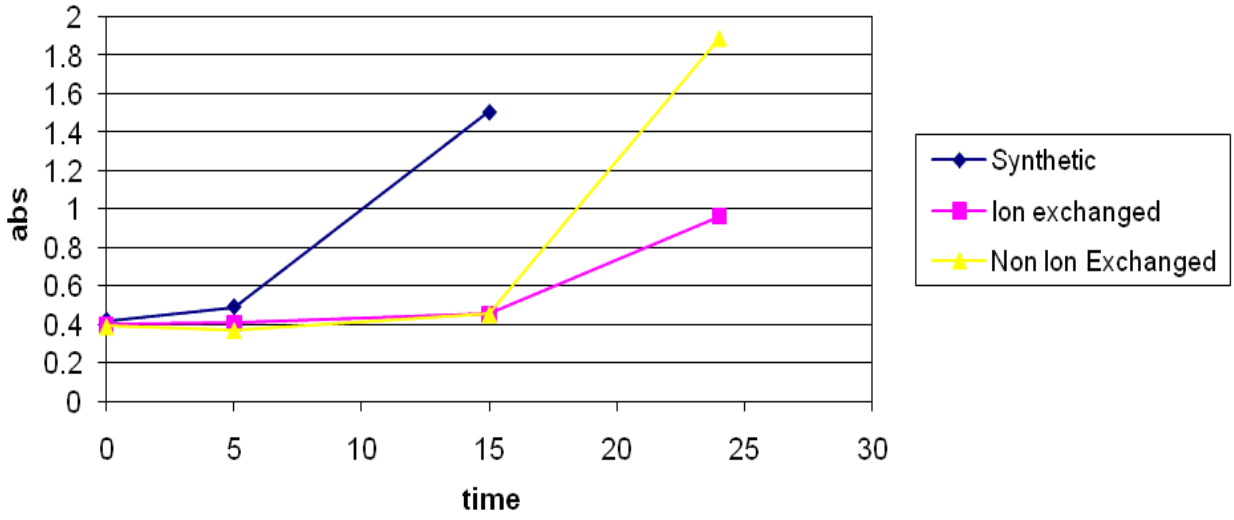

Figure 3-17. Absorbance results ion exchanged and non ion exchanged sample 3

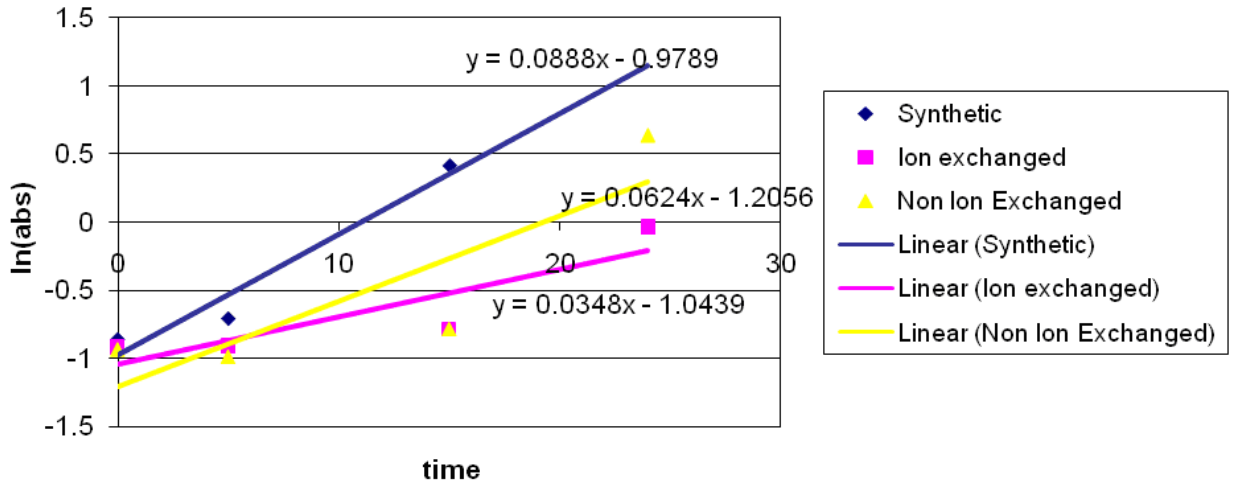

Figure 3-18. BI for ion exchanged and non ion exchanged sample 3

The BI of the ion exchanged sample was found to be equal to 0.4 and that of non ion exchanged sample was found to be equal to 0.7. Therefore, it is confirmed that non ion exchanged sample can work well.

CHAPTER 4
CARBON SOURCE FOR DENITRIFICATION

Introduction

After pretreatment was designed and optimized, it was essential to find out if the carbon content of the IPS is enough carbon source for the process of denitrification. Carbon contained in the IPS was the first choice because it eliminates the cost associated with using external carbon source. Biotreatability tests were thus performed on the samples of the IPS to figure out if the use of external carbon source can be avoided.

It should be noted that the use of external carbon source is essential in case of the synthetic nitrate sample used in the biotreatability test. Synthetic nitrate solution is made by adding small amount of conc. nitric acid to water and thus can not possibly have carbon present in it.

Biotreatability Tests

1] Ion Exchanged vs. Non Ion Exchanged Sample 2 without External Carbon Source

All the procedure of biotreatability test previously described remains the same except that no potassium acetate is added to the IPS samples.

Ion-exchanged sample 2 and non-ion exchanged sample 2 were aerated at pH 2 at 100 lpm. Both these samples are devoid of external carbon source.

Following graphs show the result of this experiment.

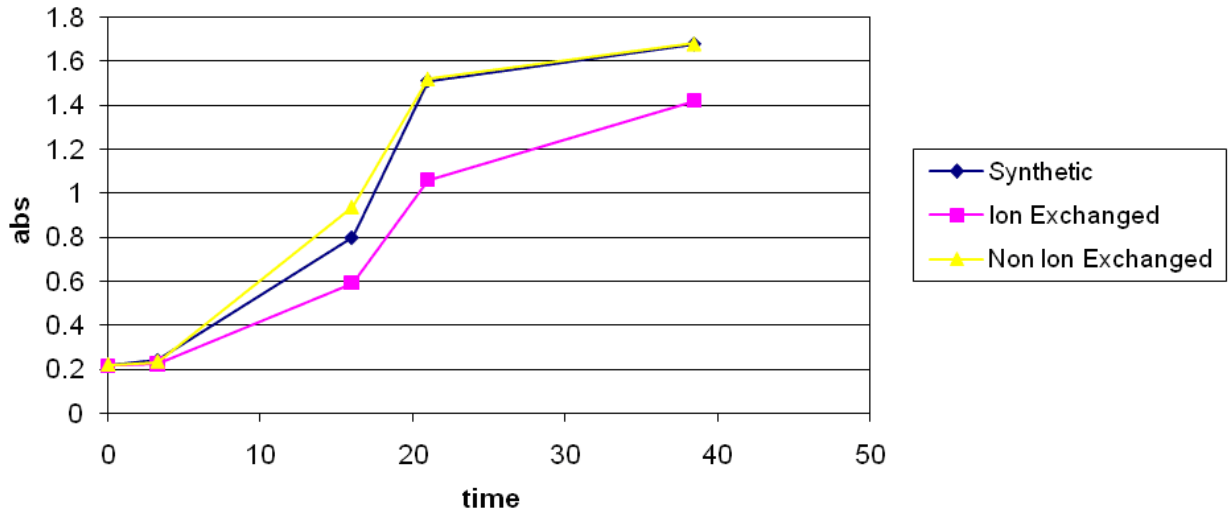

Figure 4-1. Absorbance values of ion exchanged and non ion exchanged sample 2 without external carbon

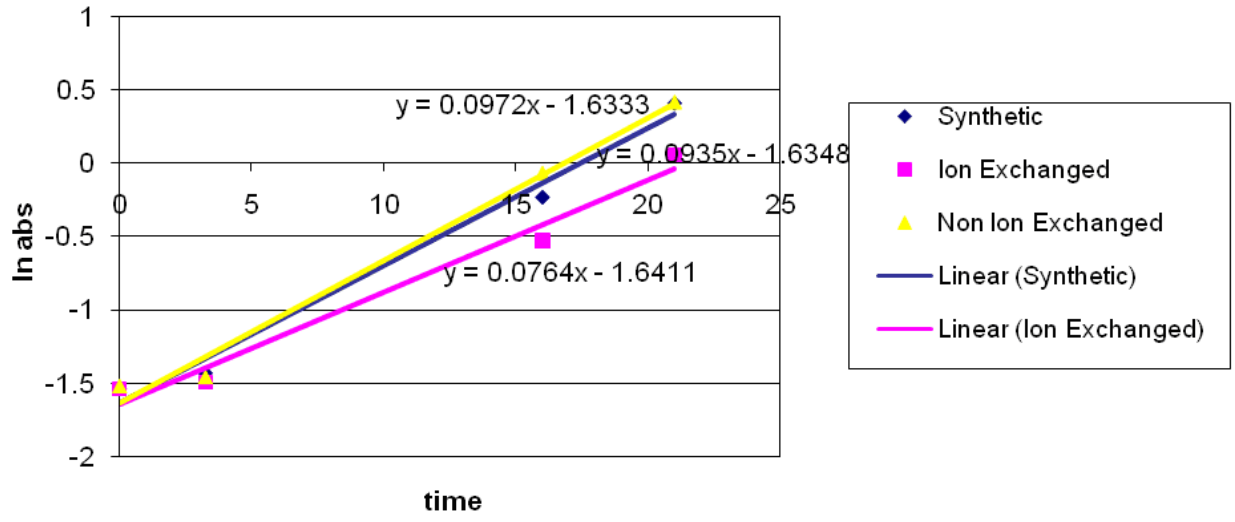

Figure 4-2. BI of ion exchanged and non ion exchanged sample 2 without external carbon

IPS without external Carbon has initial nitrate nitrogen of 820 mg/lit and final nitrate nitrogen of 246 mg/lit. This is 70% reduction. When synthetic sample had 730 mg/lit of initial nitrate nitrogen and 20 mg/lit of final nitrate nitrogen. This is 97.3 % reduction.

Nitrate nitrogen reduction obtained at the end of BI test (24 hrs) on sample 2 gave 70% nitrate reduction. The BI value of ion exchanged sample is 0.82 and that of non ion exchanged

sample is around 1. The excellent BI does indicate that the carbon is available. Also the fact that synthetic and IPS stopped being exponential at the same time indicates that the carbon contained in the IPS may be sufficient.

These ion exchanged and non ion exchanged sample BI values seem to refute previous findings that metal ions hinder the growth of denitrifying bacteria. But the laboratory analysis of ion exchanged and non ion changed IPS sample 2 shows that there is little difference between metal ion content of both the samples and both the samples have very low copper content.

2] Ion Exchanged vs. Non Ion Exchanged Sample 3 Without External Carbon Source

The same experiment was carried out on ion-exchanged sample 3 and non-ion exchanged sample 3. Pretreatment used was aeration at pH 2 for 1 hour at 16 lpm

Following graphs show the result of this experiment.

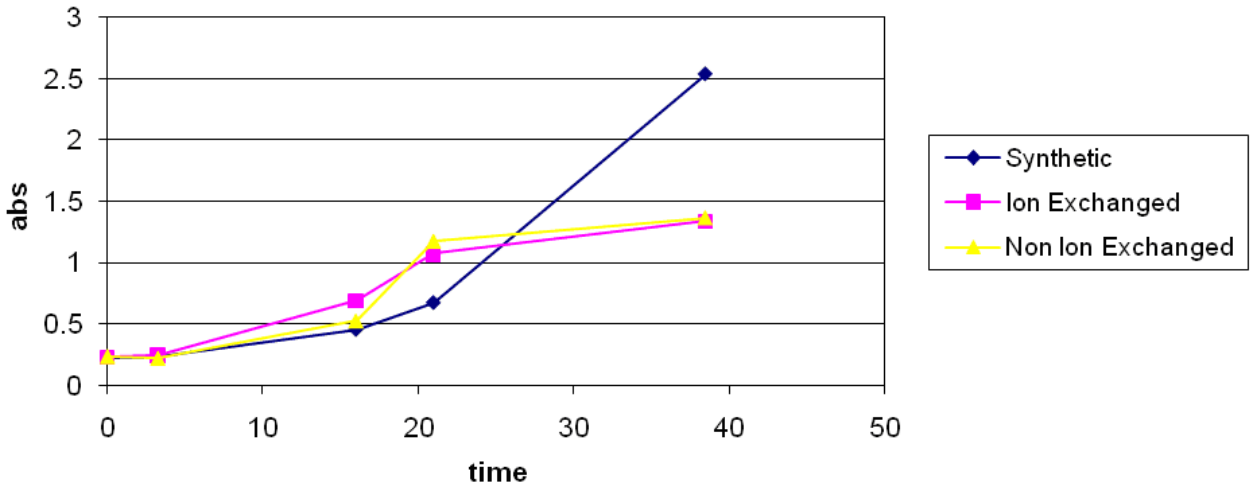

Figure 4-3. Absorbance values of ion exchanged and non ion exchanged sample 3 without external carbon

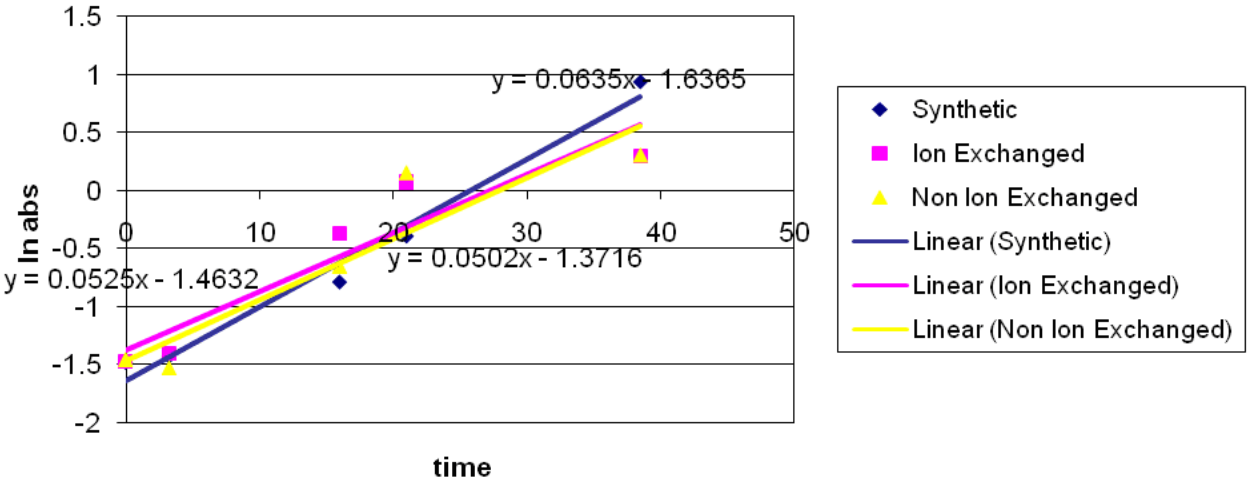

Figure 4-4. BI of ion exchanged and non ion exchanged sample 3 without external carbon

Since the IPS sample 3 had exceptionally high nitrate content, final reading of the experiment was taken at 38.5 hrs. In general, last reading was taken at around 36-39 hrs in all those experiments in which sample 3 was used. But in some cases it was observed that absorbance of synthetic nitrate solution started dropping after 24 hrs which as indicated by the nitrate test showed that the NO_3-N of the synthetic nitrate sample got eaten up by the bacteria and hence bacteria started dying. In such cases, therefore, final reading of 36-39 hrs had to be dropped and results are based on reading obtained after 24 hrs.

The BI of ion-exchanged and non ion-exchanged sample was measured to be 0.79 and 0.82. This experiment shows that the IPS without external carbon exhausted carbon much earlier than the synthetic sample. Therefore, when nitrate nitrogen levels are very high, addition of external carbon will be beneficial.

Again, these ion exchanged and non ion exchanged sample BI values seem to refute previous findings that metal ions hinder the growth of denitrifying bacteria. But the laboratory analysis of ion exchanged and non ion changed IPS sample 3 shows that there is little difference

between metal ion content of both the samples and both the samples have very low copper content.

Investigation on Other Waste Streams as Probable Carbon Sources

It may be questioned that if carbon present in the IPS is found to be sufficient for carrying out denitrification process then investigation on other carbon sources is not justified. Reasons to investigate CPS are as follows:

1] 2 Waste Carbon Process Streams are available and need treatment. If one or both of those can be used in this process and treated then cost of treating them separately may be avoided. Results obtained from these experiments can serve as data for the cost-benefit optimization problem.

2] The IPS is highly variable in NO_3-N content and contents of other constituents like the carbon source. It will be therefore worth investigating if CPS available can be used as additional carbon source so that the denitrification process under consideration is invulnerable against changes in composition of the IPS.

It should be noted that, these experiments were carried out considering constraints on availability of waste carbon process streams. In all the experiments performed on CPS 1 and CPS 2, therefore, the ratio of volume of CPS used to that of IPS used is maintained the same as per those constraints and carbon to NO_3-N ratio is not guaranteed as 4:1.

Two industrial waste streams were available as probable carbon sources. It was required to find out if any of those can be used as a carbon source for denitrification process. A biotreatability experiment was therefore conducted with the first carbon source. Following four samples were used to carry out the test:

1] Synthetic
2] IPS (aerated at pH = 2 at 100 for 1 hour) + Synthetic Carbon
3] CPS 1 (aerated at pH = 4.75 at 16 lpm for 1 hour) + synthetic nitrate

4] IPS (aerated at pH = 2 at 100 for 1 hour) + CPS 1 (aerated at pH = 4.75 at 16 lpm for 1 hour)

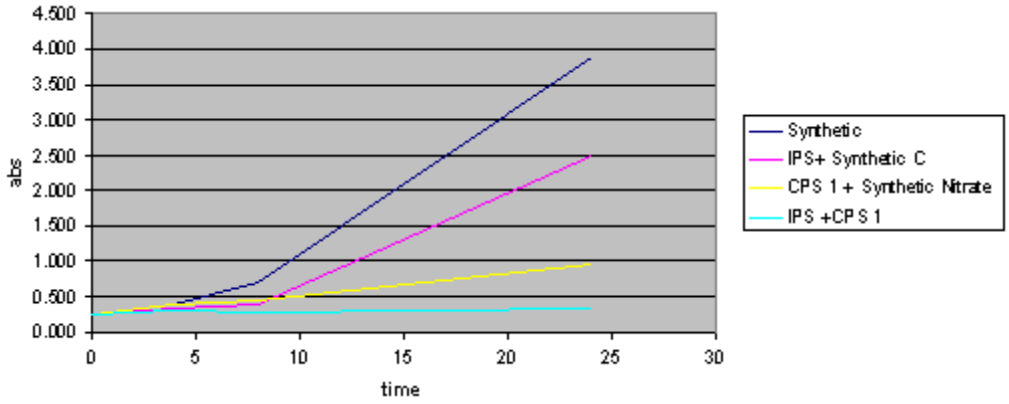

Figure 4-5. Absorbance values during biotreatability of investigation on other waste streams as probable carbon sources

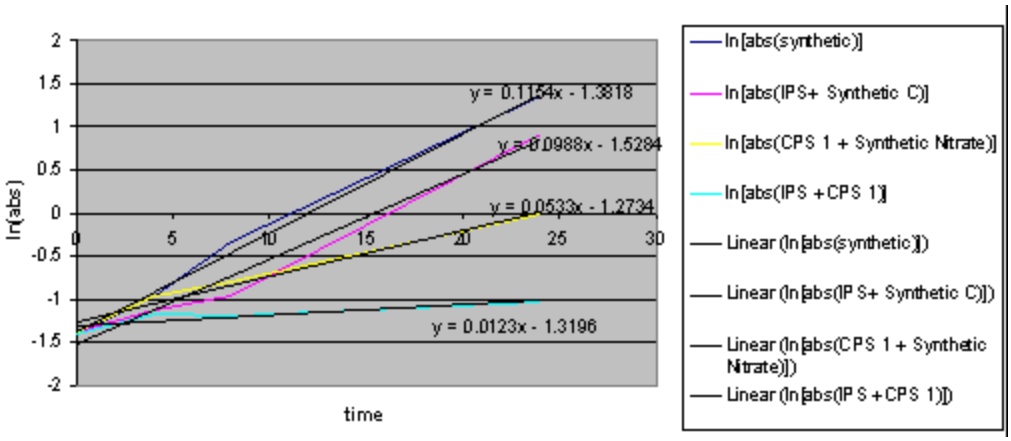

Figure 4-6. BI values during biotreatability of investigation on other waste streams as probable carbon sources

Results of the experiment are:

1] IPS + synthetic carbon, BI = 0.86
2] CPS 1 + synthetic nitrate, BI = 0.46
3] IPS + CPS 1, BI = 0.11

The experiment shows that CPS1 can not be used as a carbon source since BI is very low. Another experiment was carried out in which CPS1 was used as a carbon source and synthetic nitrate was used as a NO_3-N source. Results of the experiment are shown in the figure.

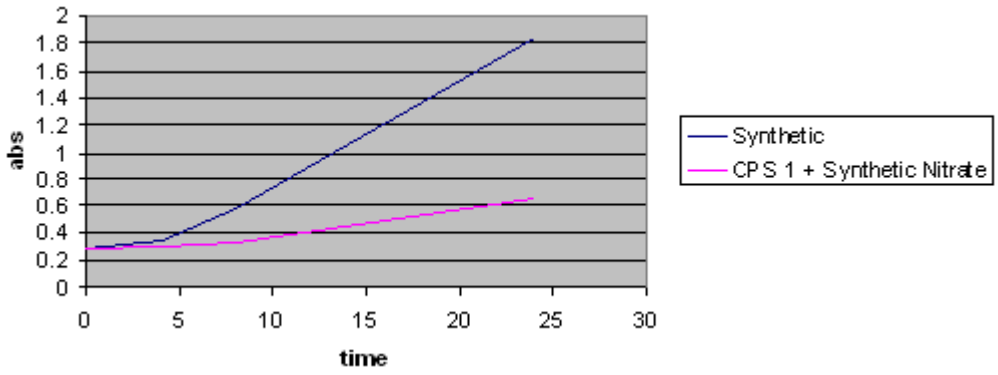

Figure 4-7. Absorbance values during biotreatability of CPS1 as a Carbon Source

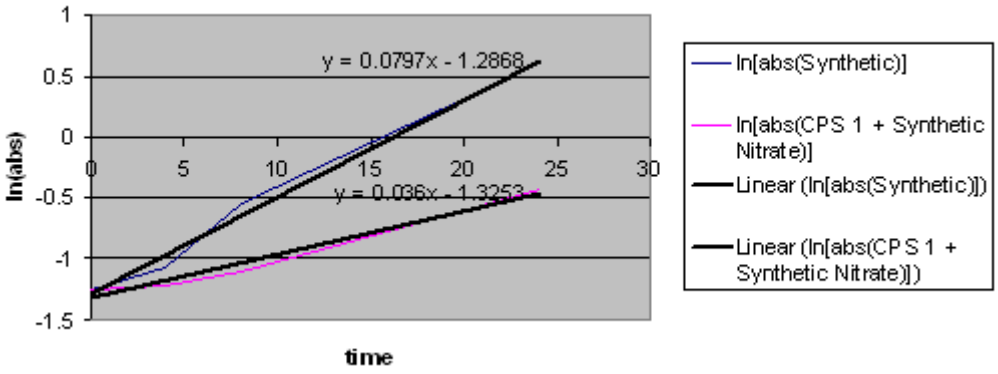

Figure 4-8. BI values during biotreatability of CPS1 as a Carbon Source

From the graph, it can be seen that the BI of CPS1+ Synthetic Nitrate solution is 0.45. It can be concluded from this experiment that CPS1 (without pretreatment) is not a good carbon source for the denitrification process.

To check if CPS1 can serve as a good carbon source after aeration as a pretreatment, an experiment was performed in which an aerated sample of CPS1 was compared to the non-aerated sample of CPS1. 500 ml of CPS1 was aerated for 1 hour.

Results of the experiment are shown in the graphs below:

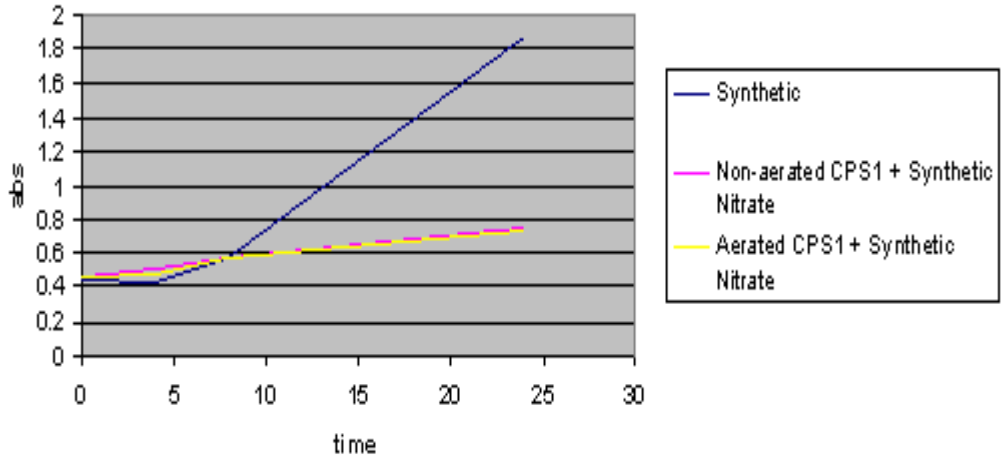

Figure 4-9. Absorbance values during biotreatability of CPS1 as a Carbon Source with and without pretreatment

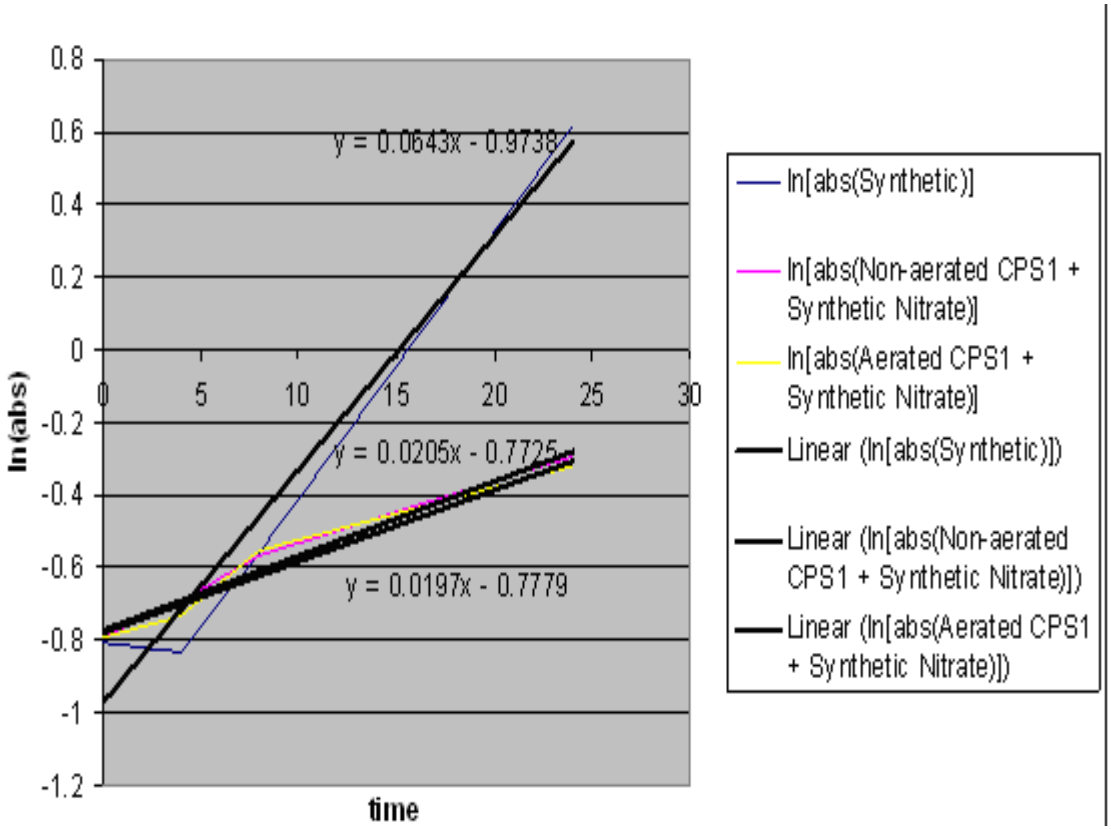

Figure 4-10. BI values during biotreatability of CPS1 as a Carbon Source with and without pretreatment

Results are:

1] Non-aerated CPS1 + synthetic nitrate, BI = 0.32

2] Aerated CPS1 + synthetic nitrate, BI = 0.31

It can be seen that there is no significant difference in performance of aerated and non-aerated CPS1 as a carbon source. Also, both the samples showed low value of BI. It can be concluded that the CPS1 is not a good carbon source of the denitrification process under consideration.

Investigation of CPS2 as a carbon source for denitrification process:

500ml of CPS2 was aerated at pH = 1.5 at 16lit/min for 2 hours. The sample obtained after this pretreatment is used as a carbon source for the biotreatability experiment.

Following samples are used in this experiment:

1] IPS (aerated for 1 hr at pH =2 and at 16 lit/min) + Synthetic carbon

2] CPS 2 (aerated for 2 hrs at pH = 1.6 and at 16 lit/min) + Synthetic Nitrate

3] IPS (aerated for 1 hr at pH =2 and at 16 lit/min) + CPS 2 (aerated for 2 hrs at pH = 1.6 and at 16 lit/min)

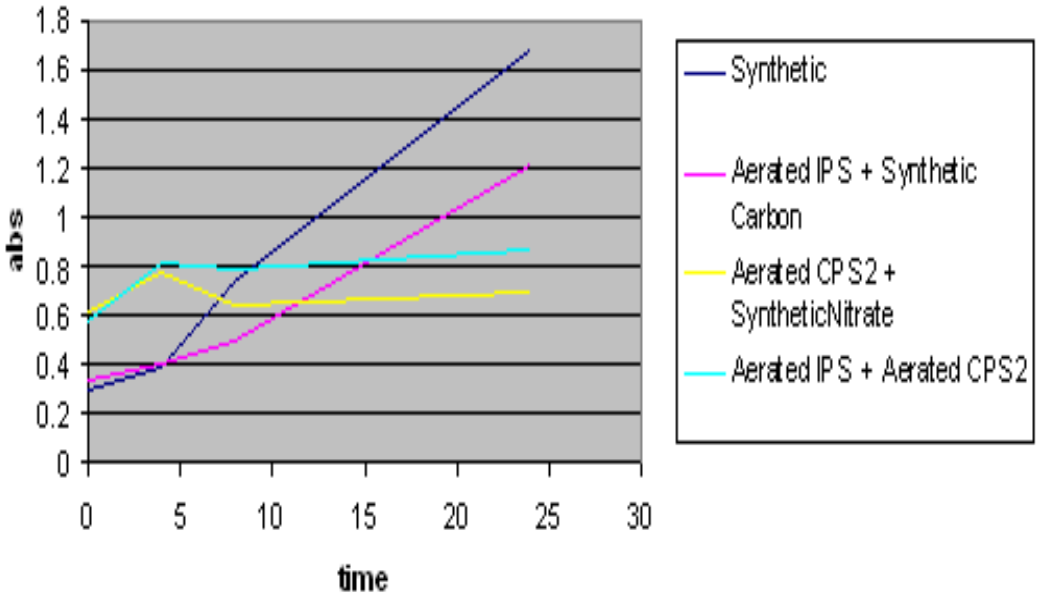

Figure 4-11. Absorbance during biotreatability of CPS2 as a Carbon Source

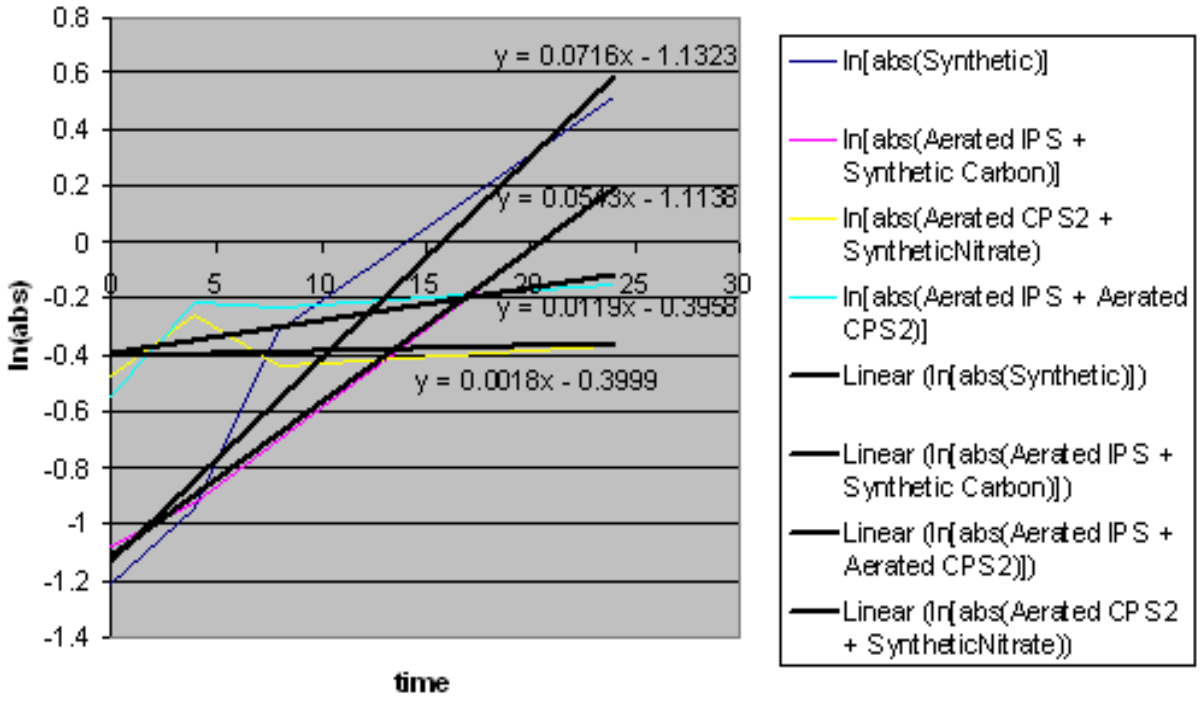

Figure 4-12. BI during biotreatability of CPS2 as a Carbon Source

Results are given below:

1] Aerated IPS + Synthetic Carbon, BI = 0.745
2] Aerated CPS 2 + Synthetic Nitrate, BI = 0.166
3] Aerated IPS + Aerated CPS 2, BI = 0.021

Since BI values of all the samples in which CPS 2 was used as a carbon source are low, we can conclude that CPS 2 is not a good carbon source for the denitrification process under consideration.

CHAPTER 5
OPTIMIZATION OF AERATION PRETREATMENT

Packed Column Aeration

Introduction

In order to achieve aeration in more efficient manner, packed column aeration was used. Packing increase the contact area between air and the IPS and the air residence time; leading to more efficient VOC removal. In order to maintain safe working conditions in the lab, counter current aeration was avoided. Air was passed from the bottom to the top of the packed column against the stagnant volume of IPS.

Figure 5-1. Packed column for aeration experiments

Aeration Experiment to Optimize Aeration Pretreatment

To optimize aeration, an experiment was performed in which the IPS was pretreated using the packed column. 500 ml of non-ion exchanged sample 3 was used in each of the following samples of this experiment:

1] Aeration for 15 min at 16 lpm
2] Aeration for 30 min at 16 lpm

3] Aeration for 60 min at 16 lpm
4] Aeration for 60 min at 8 lpm
5] Aeration for 60 min at 4 lpm

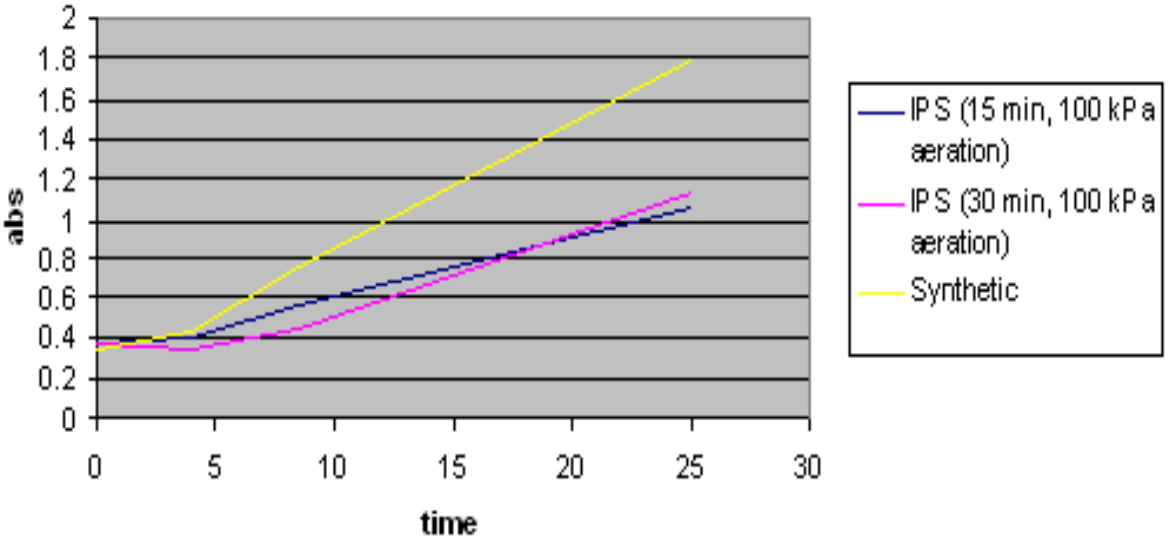

Figure 5-2. Absorbance during biotreatability of aeration experiment to optimize aeration pretreatment

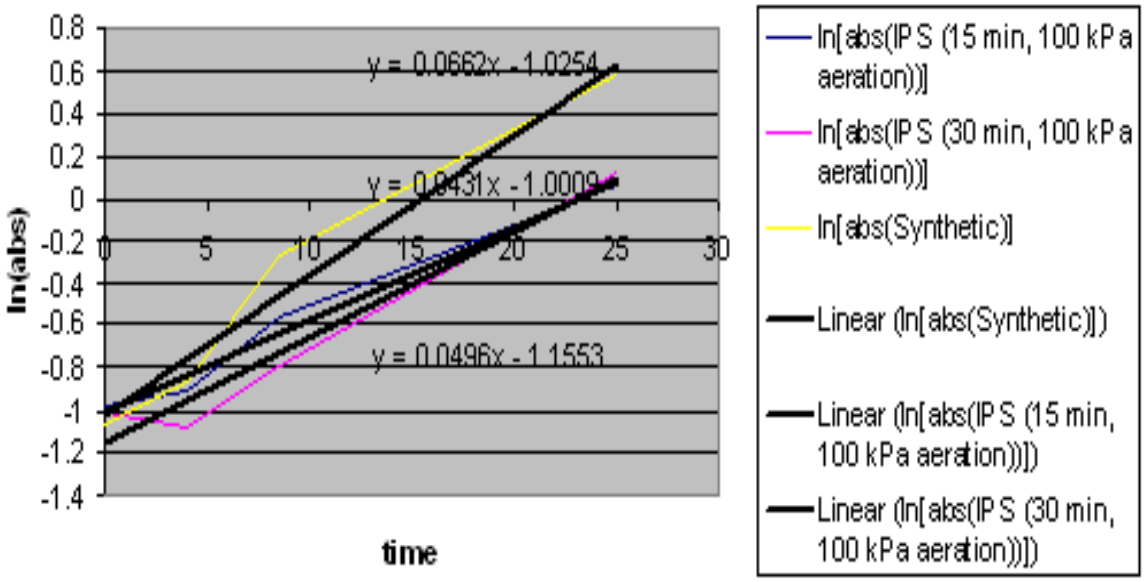

Figure 5-3. BI during biotreatability of aeration experiment to optimize aeration pretreatment

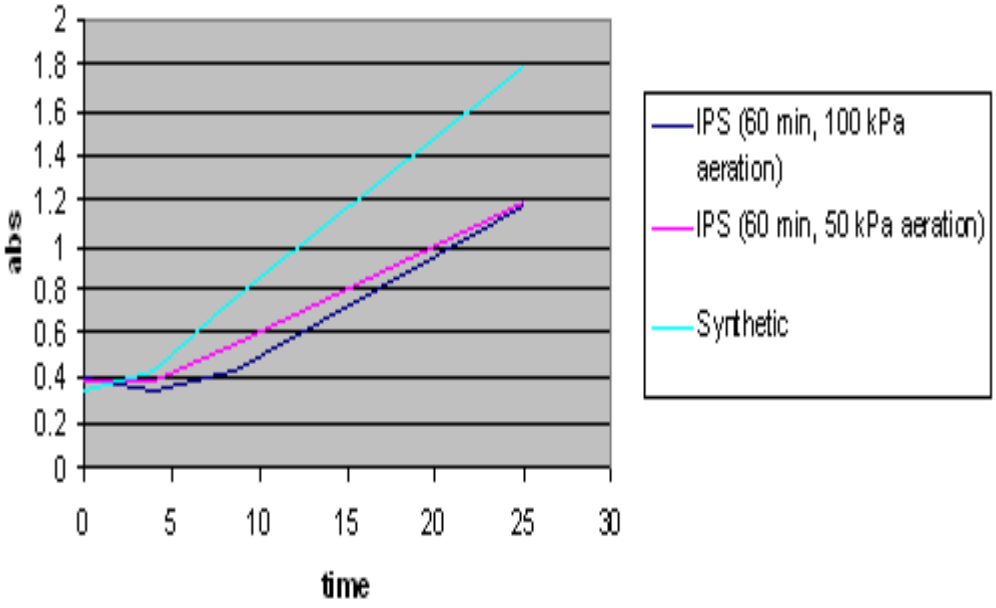

Figure 5-4. Absorbance during biotreatability of aeration experiment to optimize aeration pretreatment

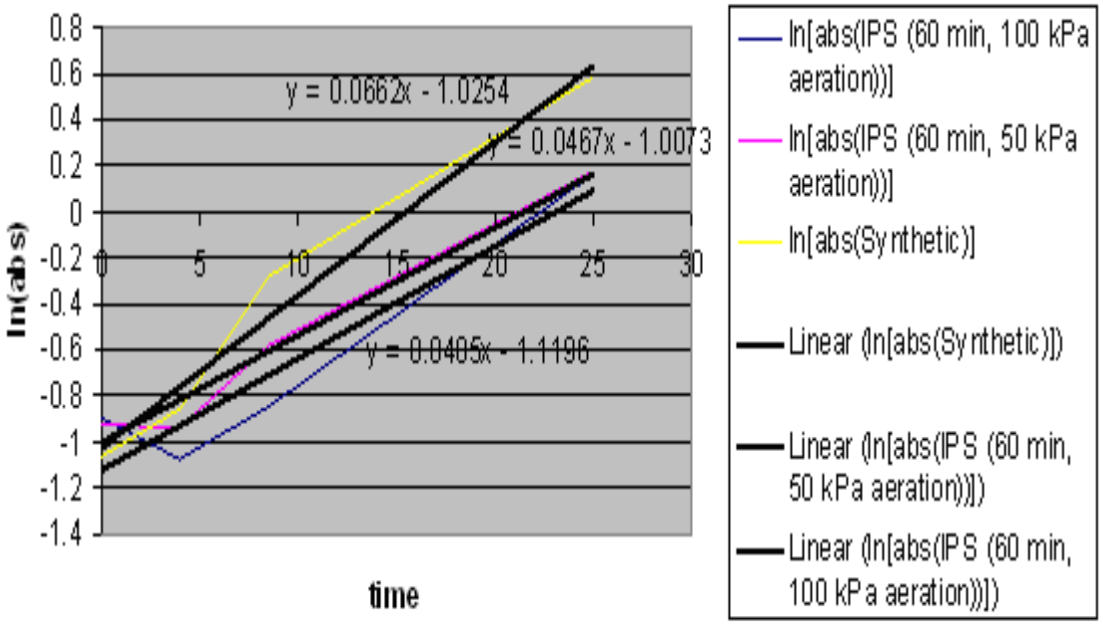

Figure 5-5. BI during biotreatability of aeration experiment to optimize aeration pretreatment

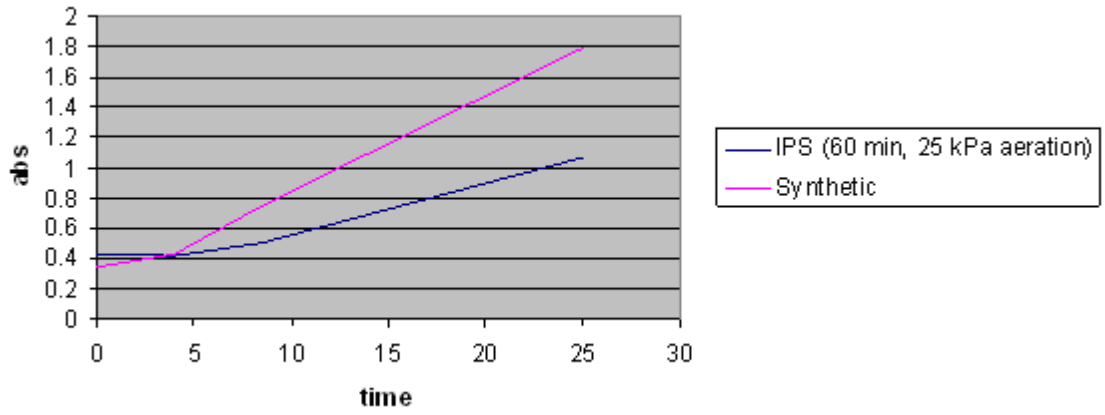

Figure 5-6. Absorbance during biotreatability of aeration experiment to optimize aeration pretreatment

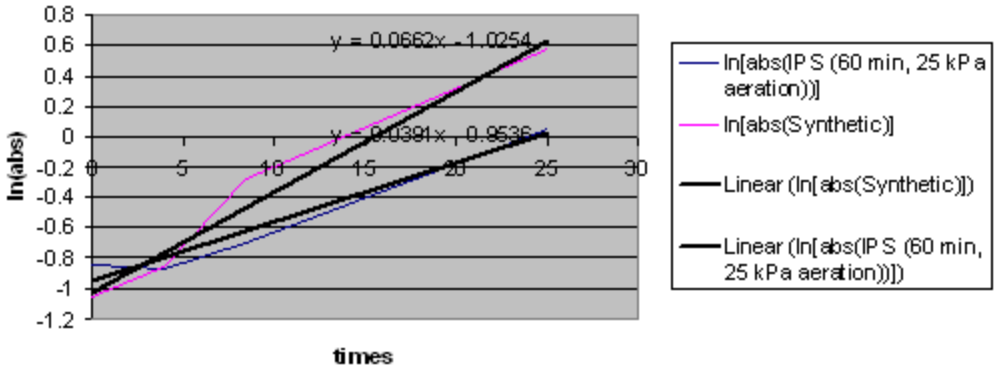

Figure 5-7. BI during biotreatability of aeration experiment to optimize aeration pretreatment

The results of biotreatability of these samples are:

1] Aeration for 15 min at 16 lpm (100 kPa), BI = 0.65
2] Aeration for 30 min at 16 lpm (100 kPa), BI = 0.75
3] Aeration for 60 min at 16 lpm (100 kPa), BI = 0.73
4] Aeration for 60 min at 8 lpm (50 kPa), BI = 0.70
5] Aeration for 60 min at 4 lpm (25 kPa), BI = 0.59

This experiment proved that packed column aeration for lesser period of time and at lesser pressure of air flow provide good pretreatment to the IPS. These results provide useful data for optimization during process designing.

But as a result of packed column aeration, it was concluded that efficient aeration method can reduce the time duration of the pretreatment and air flow rate required to achieve efficient aeration.

CHAPTER 6
ATTACHED GROWTH BIOREACTOR

Introduction

Attached growth bioreactors are reactors in which bacteria attach on solid immobile packing medium like rock, slag, ceramic or plastic. In order to maintain anoxic conditions in the reactor, media is kept submerged. Recirculation makes the system homogeneous. Attached growth bioreactors allow for short hydraulic residence times with high solids retention times and low solids waste after denitrification.

Materials and methods

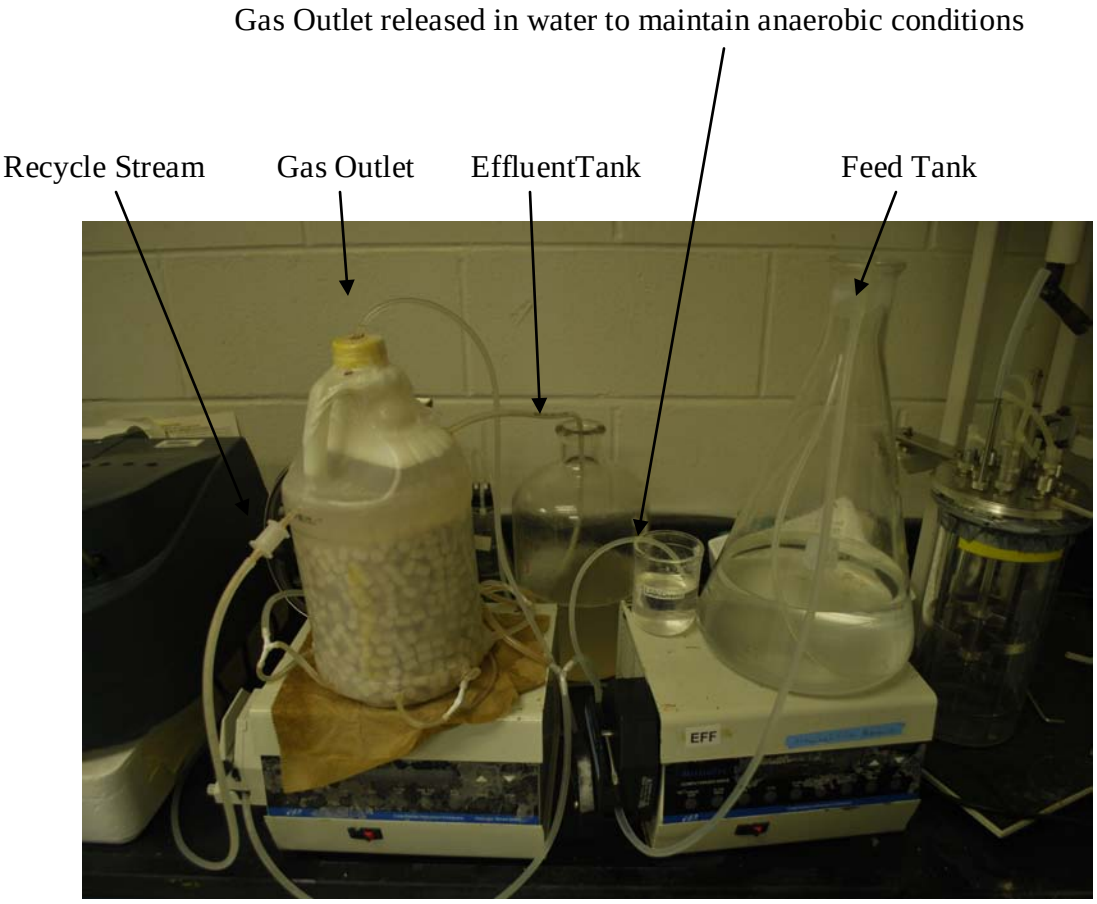

Figure 6-1. Experiment setup for attached growth reactor

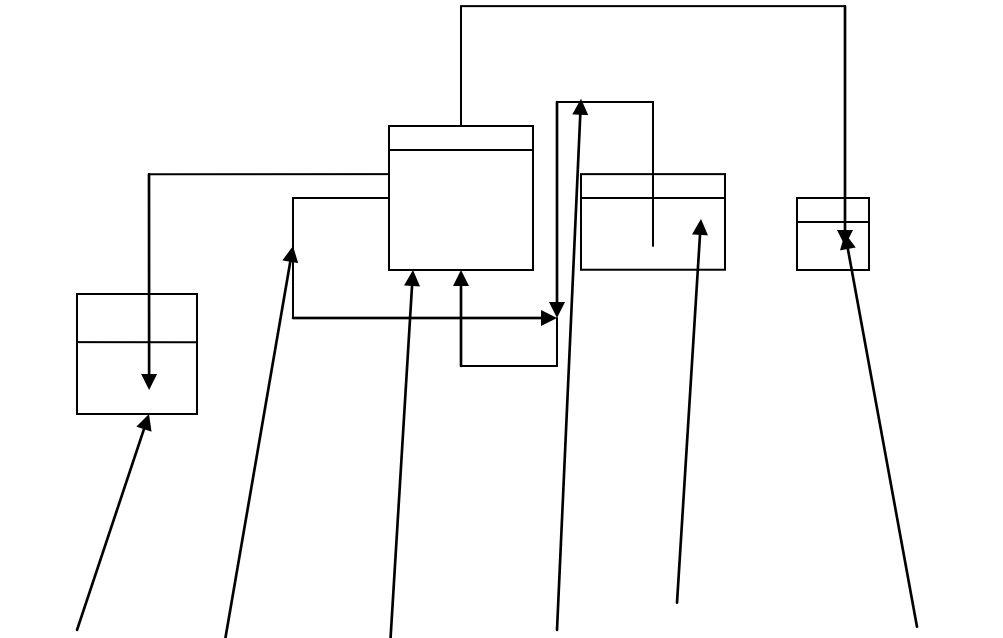

Figure 6-2. Block diagram of the attached growth reactor assembly

A 3.78 L HDPE bottle was used to construct the attached growth bioreactor. The set-up of the bioreactor is shown in figure 6.1. It was filled to $3/4^{th}$ of its volume by rock media from Biomax and a culture of denitrifying bacteria grown on high synthetic nitrate stream. About 2 liters of denitrifying bacterial culture was used. The working volume of the bioreactor was around 3.5 liters. This media provided high surface area for the attached growth of bacterial cells. Denitrifying bacteria were allowed to attach to the rock media by not starting either recycle or fresh feed pump for the first day. The reactor content was just recirculated on the second day. This was done to homogenize the reactor content. Fresh feed pump was kept off for first couple of days.

The bioreactor was provided with 8 inlet ports at the bottom to avoid channeling of the inlet feed. An outlet port was provided at a level of upper end of the rock packings. Bioreactor content was pumped out of this end (recycled) and was mixed with a stream of high synthetic

nitrate content. Flow rates of the recycled bioreactor effluent and the synthetic nitrate feed stream were adjusted such that the pH of the combined stream is around 7. Flow rate of the recycled stream was maintained at 9.45 ml/min and that of the synthetic nitrate feed stream was maintained at 0.7 ml/min. The reactor was therefore operated at a recycle rate of 13.5. The combined feed stream was pumped from the bottom of the bioreactor to its top.

Effluent outlet was provided at a level slightly higher than the recycle outlet. This means that, a small volume of the reactor in its upper portion does not have any rock media. This ensures the maintenance of anaerobic conditions in the reactor volume. Effluent receiving tank was adjusted in such a way that the effluent moves to the receiving tank under gravity. One end of the effluent tube was inserted into the effluent port while the other end was place in water to prevent air entering into the bioreactor through effluent tube. Denitrification process produces carbon dioxide (CO_2) and Nitrogen (N_2) gases. It is, therefore, essential to provide a bioreactor with a gas outlet. One end of the gas outlet was provided at the top of the bioreactor while the other end of the gas outlet was placed in a beaker filled with water. This was done to maintain anoxic conditions into the bioreactor.

Feed Preparation and Sampling

Synthetic nitrate solution with high NO_3^--N content was made by adding concentrated nitric acid to DI water. Concentration of NO_3^--N in the synthetic nitrate feed was set to around 1000 mg/lit of NO_3^--N. Potassium acetate was added as a carbon source. A carbon to nitrate nitrogen ratio of 4:1 was maintained in the feed. 0.024 g/lit of potassium phosphate was added as a source of phosphorus. 0.01 g/lit of yeast extract and 0.03 ml/lit of molybdic acid solution prepared by adding 1.1 g of molybdic acid dissolved in 1000 ml of DI water. 4 drops/lit of micronutrients were added to the feed. The resulting synthetic nitrate solution has a pH of around 5.

Sample of the bioreactor content were obtained from the effluent outlet tube. pH and NO_3^--N were measured once a day. NO_3^--N was measured using HACH® NitraVer test kits and a spectrophotometer.

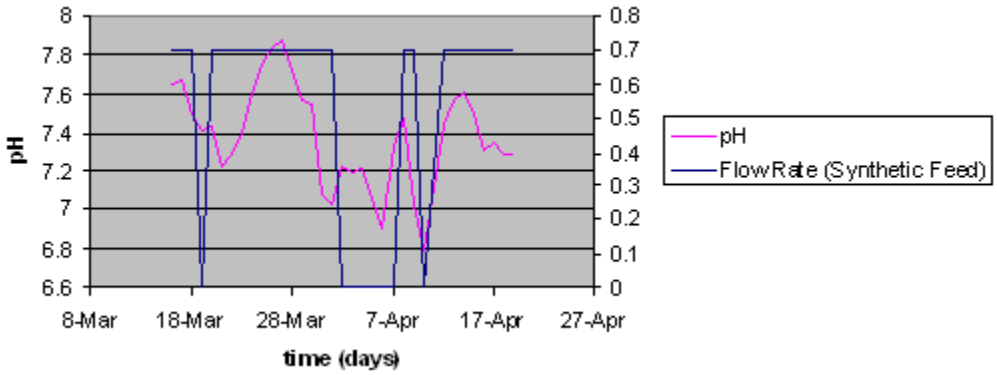

Figure 6-3. Performance of attached growth bioreactor (pH vs. time)

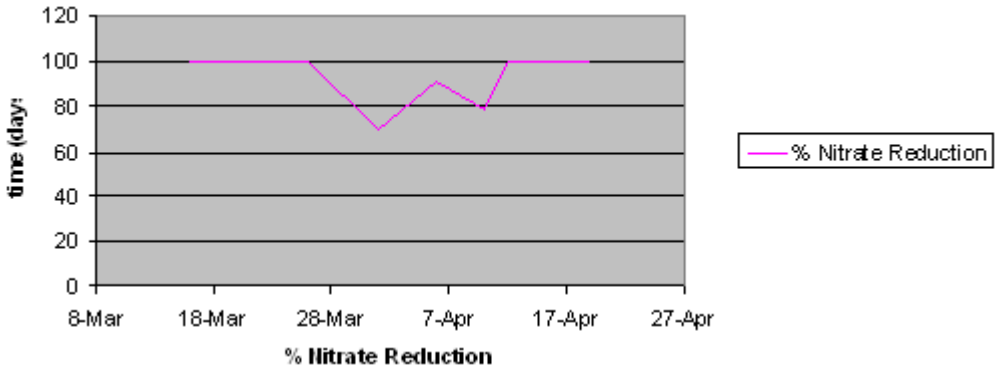

Figure 6-4. Performance of attached growth bioreactor (% nitrate reduction vs. time)

Results ad Conclusion

It was observed that the pH of the effluent of attached growth bioreactor remains in the range of 7 to 8. Even though optimal growth of denitrifying bacteria is observed in the pH range of 8 to 9.5, 100% reduction of NO_3^--N was noted even in this pH range. The reactor was run for around 5 weeks and maximum NO_3^--N reduction of 0.7 mg/min i.e. 0.35 mg/ (lit.min) was obtained.

Previous research carried out by a graduate student 'Sherin Peter' studied denitrification of synthetic nitrate solution in a suspended growth bioreactor run as a CSTR. It was found that, NO_3^--N reduction of 4 mg/ (lit. min) is achievable on a synthetic nitrate solution. This rate of denitrification is much higher than the rate of denitrification obtained by an attached growth reactor. Fluctuating values of pH was the most important reason why higher flow rates of fresh nitrate feed were not opted for. pH of the reactor below 7 has the ability of killing the bacterial culture and thereby entire reactor. Feed at pH 7 can be used to keep the bioreactor operational in pH level of 7 to 9.5.

In conclusion, 100% denitrification obtained in the attached growth bioreactor was an encouraging fact about the performance of this reactor. Difficulty in controlling the pH fluctuations was a hindering factor in achieving higher rates of nitrate reduction.

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BIOGRAPHICAL SKETCH

Author, Shourie Kapadi, has completed his Bachelor's Degree in Chemical Engineering at the University of Mumbai. He then pursued his master's degree in Chemical Engineering at the University of Florida. He received his degree in August 2009.

This thesis was a part of his research work conducted while studying as a graduate student at the University of Florida. The inspiration to pursue work on denitrification came from his interest in the area of Biological Wastewater Treatment.