

# Optimizing Denitrification at City of Austin's Walnut Creek Wastewater Treatment Plant

Øystein Sveum Moen

NORWEGIAN UNIVERSITY OF LIFE SCIENCES  
DEPARTMENT OF MATHEMATICAL SCIENCES AND TECHNOLOGY (IMT)  
MASTER THESIS 30 CREDITS 2010



## Abstract

The purpose of this project was to explore ways to optimize denitrification at City of Austin's Walnut Creek Wastewater Treatment Plant (WWTP), by ensuring good denitrification all year while maintaining a low effluent ammonia concentration. Another aim was to seek ways to keep high alkalinity through the treatment process to maintain good pH control. The experiments were conducted using laboratory scale reactors fed with wastewater from the WWTP.

The project used standardized methods to determine chemical and biochemical oxygen demand (COD, BOD), total nitrogen, nitrate, and ammonia. Other methods include trend measurements of nitrate, dissolved oxygen (DO), and pH; titrating to determine the wastewater's alkalinity; and making chemical solutions

It was discovered that denitrification was happening in reactor 3 with 67% nitrogen removal. The significance of the solids retention time (SRT) for denitrification was established: longer is better. Unusual COD/BOD ratios were discovered as  $COD < BOD$ . High alkalinity was maintained throughout the treatment process, an average of  $105 \frac{mg \text{ CaCO}_3}{L}$  in the effluent, without adding chemicals. Effluent ammonia concentrations were maintained at a level below Walnut Creek's discharge permit of  $2.0 \frac{mg}{L}$ . The pH was maintained within the WWTP's requirements of  $6.0 < pH < 9.0$  with operating values ranging from  $7.1 < pH < 7.8$ .

## **Preface**

This report is the result of a Master's thesis at the University of Texas at Austin on behalf of the Norwegian University of Life Sciences. The Master's thesis is mandatory and constitutes the 10<sup>th</sup> and final semester of the degree in Water and Environmental Technology. The report contains work done between January and May 2010.

I wish to thank Dr. Desmond Lawler at the University of Texas at Austin for giving me the chance to take part in an on-going project for the City of Austin regarding optimizing denitrification for the city's Walnut Creek Wastewater Treatment Plant, and for his good advice toward the end of the writing period. I would also like to thank MS student Mark Hughes for the laboratory collaboration and his help in locating good sources.

I also wish to thank Prof. Jarle Bjerkholt at the Norwegian University for Life Sciences.

This report is written using Microsoft Office Word and Excel 2007.

## Table of Contents

Abstract .....	ii
Preface .....	iii
1 Introduction.....	1
1.1 Outline .....	1
2 Background and Motivation .....	2
2.1 Walnut Creek Wastewater Treatment Plant .....	2
2.2 Nitrification .....	2
2.3 Denitrification.....	3
2.4 Similar Research.....	5
3 Materials and Methods .....	6
3.1 Laboratory Reactor Setup.....	6
3.2 Nitrogen.....	8
3.2.1 Nitrate.....	9
3.2.2 Ammonia.....	11
3.2.3 Total Nitrogen .....	12
3.3 Wastewater Conditions.....	14
3.3.1 pH.....	14
3.3.2 Alkalinity .....	15
3.3.3 Dissolved Oxygen (DO).....	15
3.4 Oxygen Demand.....	16
3.4.1 Chemical Oxygen Demand (COD) .....	17
3.4.2 Biochemical Oxygen Demand (BOD <sub>5</sub> ).....	18
3.5 Solids .....	19
3.5.1 Total Suspended Solids (TSS) .....	19
3.5.2 Fixed and Volatile Suspended Solids (VSS).....	20
4 Results and Discussion .....	21
4.1 Experimental work .....	21
4.2 Results .....	23
4.2.1 Nitrate, Ammonia, and Total Nitrogen .....	23
4.2.2 pH, Alkalinity, and Dissolved Oxygen .....	29
4.2.3 Chemical and Biochemical Oxygen Demand .....	33
4.2.4 Solids.....	35
5 Future Work.....	37
6 Conclusion .....	38
Bibliography.....	39
Appendix .....	41

## 1 Introduction

The City of Austin's Walnut Creek Wastewater Treatment Plant (WWTP) struggles to maintain efficient year-round treatment, especially during the winter. The reduced temperature of the wastewater this time of the year brings about problems related to a drop in alkalinity and subsequent difficulties in regards to pH control. This difficulty causes the biological steps of the treatment process to be less efficient.

This thesis deals with a project conducted at the University of Texas at Austin (UT), department of Environmental and Water Resources Engineering (EWRE), that seeks to find a solution to these problems by emulating current conditions at the WWTP and experimenting with alternatives to improve the situation. These alternatives include, but are not limited to, varying the anoxic periods and solids retention times (SRT). The goal is to optimize denitrification at the Walnut Creek WWTP.

Three small laboratory scale reactors of 6 L were operated over an extended period, each representing a different treatment cycle with regards to aeration, mixing, anoxic, and settling periods. Varying drawing and filling periods were set by timer, and different wastewater exchange volumes were used to create different conditions in each reactor. The reactors are filled with real wastewater from the WWTP that is collected once a week from the WWTP's primary effluent to emulate the conditions as closely as possible. Samples are taken from the reactors every day and their contents are measured, recorded, and analyzed for several constituents: pH, nitrate ( $NO_3^-$ ), ammonia ( $NH_3$ ), dissolved oxygen (DO), total nitrogen, total suspended solids (TSS), volatile suspended solids (VSS), chemical oxygen demand (COD), and biochemical oxygen demand ( $BOD_5$ ). Nitrite ( $NO_2^-$ ) is left out due to its presumed insignificance in relation to the whole.

### 1.1 Outline

First, in chapter 2, I provide an overview of the project; City of Austin's WWTP's background, general information about nitrification and denitrification. Next, in chapter 3, the reactor setup and methods are presented. Chapter 4 describes the experimental results and the interpretation of those results. In chapter 5, I present what future work needs to be done for things to work out as planned. The thesis is concluded in chapter 6.

## 2 Background and Motivation

### 2.1 Walnut Creek Wastewater Treatment Plant

The City of Austin has over the past ten years experienced a decreasing trend for the wastewater's alkalinity. Back in 2007 the alkalinity dropped to the point where the operators had difficulties sustaining the pH through the aeration basins. In order to meet effluent requirements of pH 6.0, operators were forced to add sodium hydroxide. The costs and hazards of working with sodium hydroxide made the Austin Water Utility seek an alternative. Engineers at the city suggested turning off the air valves at the influent of the aeration basin to create anoxic zones. The theory was that denitrification in the anoxic zones would increase alkalinity. The anoxic zone at the WWTP keeps a DO concentration of 0.9-1.3  $\frac{mg O_2}{L}$ , anoxic zones' DO concentration is normally  $<0.5 \frac{mg O_2}{L}$ . The solution turned out to be a success and sodium hydroxide was no longer required. In addition, less air was needed in the aeration basins, which saves both energy and money. However, occasional problems ensuring good denitrification during the winter and maintaining low effluent ammonia persist. The wastewater's temperature varies between 17°C in the winter to 30°C in the summer. This project explores ways to optimize denitrification at Walnut Creek by ensuring good denitrification all year while maintaining a low effluent ammonia concentration (Lawler & Hughes, 2009).

### 2.2 Nitrification

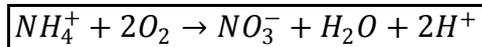
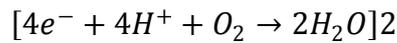
Nitrification is a biological two-step process in which nitrogen as ammonia is initially oxidized to nitrite by a group of bacteria called *Nitrosomonas*, and then quickly oxidized to nitrate with help from the *Nitrobacter* bacteria group. Nitrifying bacteria range in size from 0.3-11.7  $\mu m$ . Nitrification can be a necessity for a number of reasons: reducing ammonia concentrations in the effluent to allow higher DO concentrations and reduce fish toxicity, controlling eutrophication in receiving water, and controlling the concentrations of nitrogen with regards to water-reuse applications (Tchobanoglous et al., 2003).

The nitrification process is highly temperature dependent. Nitrifying bacteria operate much more slowly in low temperatures and therefore require a longer SRT during winter to sustain nitrification. Short SRTs during cold periods could lead to nitrifying bacteria being washed out and thus halt the nitrification (Wang et al., 2008). According

to Grady et al. (1999) a temperature difference of 30°C to 17°C would effectively mean an increase in the minimum required SRT of 300%; from 12.5 hours during the summer to 50 hours during the winter. For every  $\frac{mg\ NH_3-N}{L}$  oxidized during nitrification,  $4.6\ \frac{mg\ O_2}{L}$  is consumed.

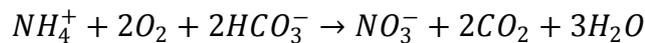
The nitrification reaction is shown in Equation 1.

**Equation 1 -- Nitrification**



Nitrification decreases alkalinity by  $7.1\ \frac{mg}{L}$  for every  $\frac{mg}{L}$  of ammonia converted to nitrate. See Equation 2. For every  $NH_4^+$  converted, two  $HCO_3^-$  are consumed.

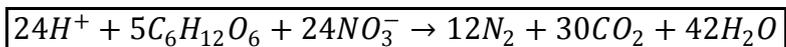
**Equation 2 -- Nitrification and alkalinity**



### 2.3 Denitrification

The denitrifying process reduces nitrate to nitrogen gas (N<sub>2</sub>-N) which is then expelled to the atmosphere. Denitrification is made possible by a number of different types of bacteria that are common to municipal wastewater and come in large quantities (Rusten et al., 2005). Denitrification can only happen under anoxic conditions as a result of nitrate substituting for oxygen as the electron acceptor. If the conditions are not anoxic, potential oxygen entering the reactors will be consumed before the nitrate and thus slow down the denitrifying process. The denitrification reaction is shown in Equation 3.

**Equation 3 -- Denitrification**



Denitrification increases alkalinity by  $3.6 \frac{mg}{L}$  for every  $\frac{mg}{L}$  of nitrate converted to nitrogen gas. See Equation 4. For every  $NH_4^+$  converted, one  $HCO_3^-$  is produced.

Equation 4 -- Denitrification and alkalinity

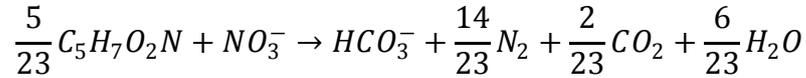


Figure 1 shows a commonly used denitrification process. Nitrification takes place in the aerobic zone whereas denitrification occurs in the anoxic zone. Return Activated Sludge (RAS) is recycled from both the aerobic zone and the secondary clarifier. Recycling nitrates from the aerobic zone ensures that the nitrogen removal will be greater than with RAS alone, giving the denitrifying bacteria more to consume. The figure shown is different from the situation at Walnut Creek WWTP which does not have a physical wall separating the two zones, or a nitrate feed going from the aerobic to the anoxic zone. The lack of a physical separation wall between the two zones hinders the anoxic zone from becoming truly anoxic. Zone separation is accomplished solely by turning off the blowers in the now anoxic zone.

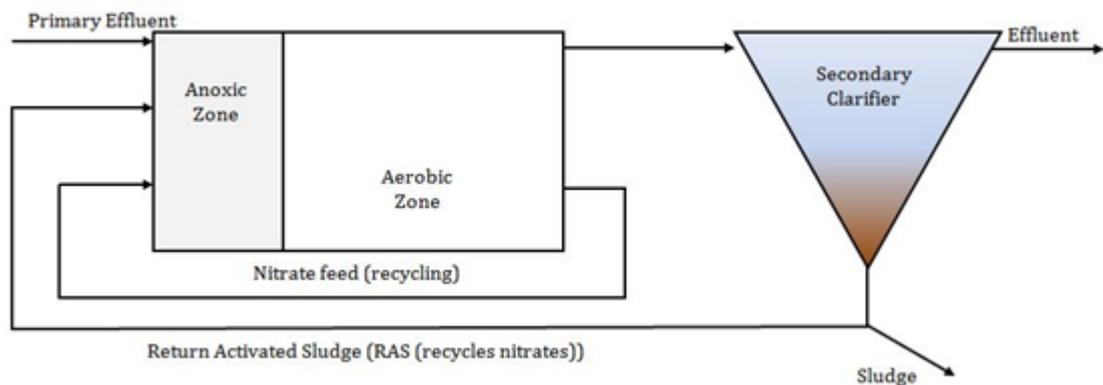


Figure 1 -- Traditional denitrification process

Figure 2 more closely depicts the situation at Walnut Creek. The lack of internal recycle from the aerobic to anoxic zone means that the only nitrified water that is returned is that associated with the RAS, and that is about 40-50% of the total flow. This fact limits the amount of denitrification that can be achieved at Walnut Creek.

By turning off the blower in the influent end of the aeration basin, the operators were able to create a partially anoxic zone. As an additional bonus, shutting off a blower saves the City of Austin a lot of money and conserves energy.

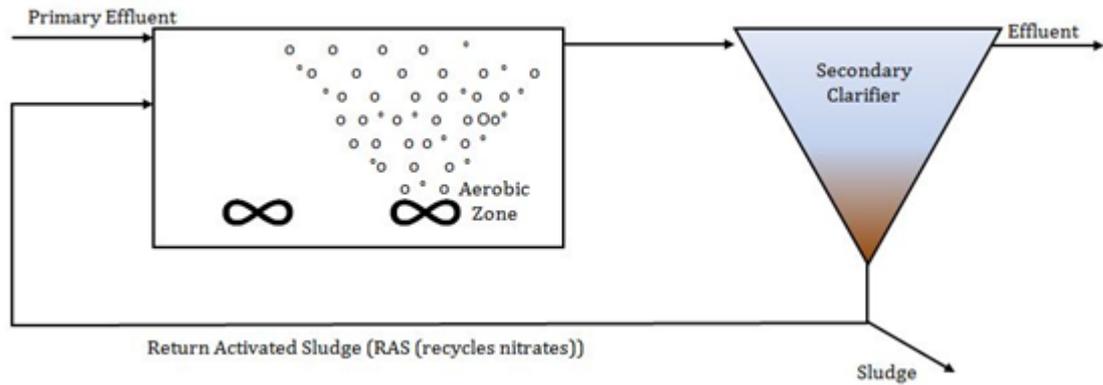


Figure 2 -- Walnut Creek situation

## 2.4 Similar Research

Research on sequencing batch reactors (SBR) and their ability to simultaneously perform nitrification, denitrification, ammonia, and phosphorous removal has been done before (Akin & Ugurlu, 2005). Akin & Ugurlu's SBR project was, however, conducted using synthetic wastewater. Synthetic wastewater will provide more consistent results and simplifies the process of reaching steady-state, but it does not replicate the exact conditions of a WWTP, which one can only achieve by using real wastewater.

### 3 Materials and Methods

#### 3.1 Laboratory Reactor Setup

The laboratory setup consists of three laboratory scale sequencing batch reactors that are located on the 8<sup>th</sup> floor of Ernest Cockrell Jr. Hall (ECJ) at UT. Each reactor has a volume of 6 L. The choice of reactor volume was made with practicality in mind; it was important that the reactors were neither too small, as that would make it difficult to emulate real world conditions, nor too big, as this would cause logistical problems in the laboratory based on their size and with regards to collecting wastewater from the WWTP.

Each reactor (R#) is controlled by a total of four ordinary, electronic timers. They control when to start and stop influent (In #), effluent (Eff #), and aeration (Air #) pumps, and mixing (Mix #) motors. The initial timer schedule through April 5<sup>th</sup> is rendered in Table 1. On April 5<sup>th</sup> all reactors were set to run by the same schedule, R1’s initial cycle, with the exception of the aeration timer for R3.

The aeration settings printed below are actually reversed; i.e., when the schedule says *On* the air is really turned off, and when the schedule says *Off* the air is turned on. This is done so that, in case of the timers being unplugged, the reactors will still get their air and the bacteria culture will remain active.

**Table 1 -- Initial reactor operating schedule**

	Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5		Cycle 6	
	On	Off	On	Off								
<b>Reactor 1</b>												
In 1	8:00 AM	8:10 AM	2:00 PM	2:10 PM	8:00 PM	8:10 PM	2:00 AM	2:10 AM				
Eff 1	1:50 PM	2:00 PM	7:50 PM	8:00 PM	1:50 AM	2:00 AM	7:50 AM	8:00 AM				
Mix 1	8:00 AM	12:50 PM	2:00 PM	6:50 PM	8:00 PM	12:50 AM	2:00 AM	6:50 AM				
Air 1	12:50 PM	3:15 PM	6:50 PM	9:15 PM	12:50 AM	3:15 AM	6:50 AM	9:15 AM				
<b>Reactor 2</b>												
In 2	8:00 AM	8:10 AM	12:48 PM	12:58 PM	5:36 PM	5:46 PM	10:24 PM	10:34 PM	3:12 AM	3:22 AM		
Eff 2	12:38 PM	12:48 PM	5:26 PM	5:36 PM	10:14 PM	10:24 PM	3:02 AM	3:12 AM	7:50 AM	8:00 AM		
Mix 2	8:00 AM	11:50 AM	4:38 PM	4:38 PM	5:36 PM	9:26 PM	10:24 PM	2:14 AM	3:12 AM	7:02 AM		
Air 2	11:50 AM	1:48 PM	6:36 PM	6:36 PM	9:26 PM	11:24 PM	2:14 AM	4:12 AM	7:02 AM	9:00 AM		
<b>Reactor 3</b>												
In 3	8:00 AM	8:10 AM	12:00 PM	12:10 PM	4:00 PM	4:10 PM	8:00 PM	8:10 PM	12:00 AM	12:10 AM	4:00 AM	4:10 AM
Eff 3	11:50 AM	12:00 PM	3:50 PM	4:00 PM	7:50 PM	8:00 PM	11:50 PM	12:00 AM	3:50 AM	4:00 AM	7:50 AM	8:00 AM
Mix 3	8:00 AM	11:10 AM	12:00 PM	3:10 PM	4:00 PM	7:10 PM	8:00 PM	11:10 PM	12:00 AM	3:10 AM	4:10 AM	7:10 AM
Air 3	11:10 AM	12:50 PM	3:10 PM	4:50 PM	7:10 PM	8:50 PM	11:10 PM	12:50 AM	3:10 AM	8:50 AM	7:10 AM	8:50 AM

All reactors have a hydraulic retention time (HRT) of 10 hours, meaning that the aerobic and anoxic periods together last for 10 hours. An HRT of 10 hours was chosen to closely emulate the WWTP’s conditions. Each reactor treats  $12 \frac{L}{day}$ . The initial SRT

of the reactors was 12 days. An SRT of 12 days means that  $\frac{1}{12}$  of the biomass of the reactor is wasted each day; a full biomass exchange is complete in 12 days. Biomass is removed from the reactors after the aerobic period, but before the mixing period ends and the settling period begins. This provides a sample of well-mixed mixed liquor suspended solids (MLSS). The SRT for R2 and R3 has later been increased to 20 days; 300 mL of biomass is wasted every day compared to R1's  $500 \frac{mL}{day}$ .

The reactors all maintain about 18°C, which represents the WWTP's worst conditions over the year. Table 2 shows the initial individual reactor settings.

**Table 2 -- Individual reactor setup**

	Recycle ratio	Cycle time	Settling time
Reactor 1	1.0	5.0 hours	1.0 hours
Reactor 2	1.5	4.0 hours	0.8 hours
Reactor 3	2.0	3.3 hours	0.7 hours

A recycle ratio of 1.0 means that the amount of wastewater left in the reactor after the effluent has been drawn, is the same as the amount of new wastewater added to the reactor. A ratio of 1.5 (R2) in this case refers to 3.6 L being left in the reactor and 2.4 L being added. The cycle time is the duration between two effluent drawings, minus the settling time.

See Figure 3 for a simplified view of a reactor's composition. The effluent timers tell the effluent pumps when to empty the reactors. The reactors are set to empty after the settling period. The pumps will then run until the bottom float switches turn the pumps off. The influent pumps start a few minutes after the emptying has ended so that these will not risk overlapping. The pumps then fill the reactors until the top float switches reach their upper position and subsequently turn the pumps off. The mixing motors start mixing the content of the reactors and the air diffusion stones begin supplying air to the reactors, which marks the beginning of the aerobic period. When the air turns off the reactors begin their anoxic period, and the mixing motors' ending starts the settling period that allows the suspended solids to settle before initiating the emptying sequence.

Once a week approximately 200 L of fresh wastewater are collected from the WWTP's primary effluent and stored in a room maintaining a steady temperature of 4°C. All three reactors get their influent wastewater from the same 50 L tank. The tank is given

time to reach a higher temperature in the laboratory before the reactors are fed. This procedure happens to emulate winter conditions at the WWTP quite well as the reactors maintain about 18°C throughout the cycle. As of mid-April the reactors are heated using fish tank heaters to simulate more optimal conditions.

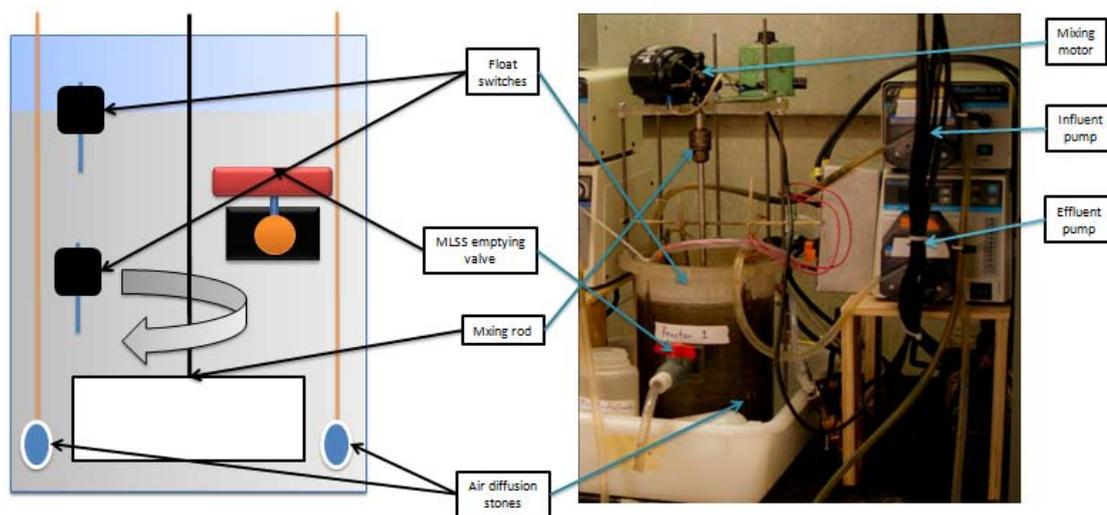


Figure 3 -- Reactor setup

The reactors themselves are transparent acrylic containers with a volume of 7.6 L (D=19.05 cm, H=26.67 cm), of which 6 L are filled in this setup. In the side they have a hole with a connected valve and tube so that samples can be taken at any given time (fig.: *MLSS emptying valve*). Two float switches control the water level of the reactors; one stops the influent pumps when the level reaches the maximum point (6 L) and the other stops the effluent pump when the minimum level is approached (~3 L). Two air diffusion stones supply the reactors with air and the amount of air is regulated using valves connected to each reactor. A mixing rod is connected to a motor sitting on top of the reactors, this ensures that the content of the reactors are well mixed as long as the settling periods are not in effect. The wastewater is fed to the reactors through rubber tubing leading from the 50 L influent tank. The influent water contains practically no nitrates; nitrogen exists mainly as ammonia.

### 3.2 Nitrogen

Removal of nitrogen through denitrification is the goal of this project. Nitrogen in the reactors exists mainly as nitrate and ammonia. Ammonia can, in addition to phosphorous, cause significant problems in regards to water quality if present in great amounts. This includes an increase in aquatic growth such as algae which, subsequently,

will affect dissolved oxygen, temperatures, etc. and cause problems for aquatic life. Through the nitrifying process ammonia is oxidized to nitrite, which very quickly is oxidized to nitrate; nitrite is therefore not considered of importance in our experiments and will not be measured in any way.

### 3.2.1 Nitrate

To measure the nitrate concentration of samples, two methods were used; one involving the use of vials and the other involving the utilization of a pH meter and a nitrate electrode probe.

When measuring nitrate using vials, samples of 1 mL are added to vials containing the *NitraVer*<sup>®</sup> X Test 'N Tube<sup>™</sup> Reagent. The vials are then placed in the UV/vis spectrophotometer (UV/vis) and their absorbance before digestion ( $\alpha_1$ ) is measured at a wavelength  $\lambda = 410$  nm. After this the *NitraVer*<sup>®</sup> X Nitrogen, Nitrate Reagent B is added and the sample shaken for 15 seconds. The sample is allowed a 5 minute reaction time before being placed in the UV/vis once again where the absorbance after digestion ( $\alpha_2$ ) is measured.

The content of the reagents is a chromotropic acid that reacts with the nitrate, yielding a yellow color making it measurable in the UV/vis with a maximum absorbance at 410 nm. The actual nitrate concentrations are thereafter calculated as the difference before and after digestion using a linear equation based on a standard curve like the one shown in Figure 4, see Equation 5. When measuring nitrate using vials, it is of great importance that the sample be filtered before adding it to the vial as biomass residue *will* cause problems for the UV light refraction and thus yield erroneous results. The standard curve is based on standards of 1, 10, 20, and 30  $\frac{mg NO_3-N}{L}$ .

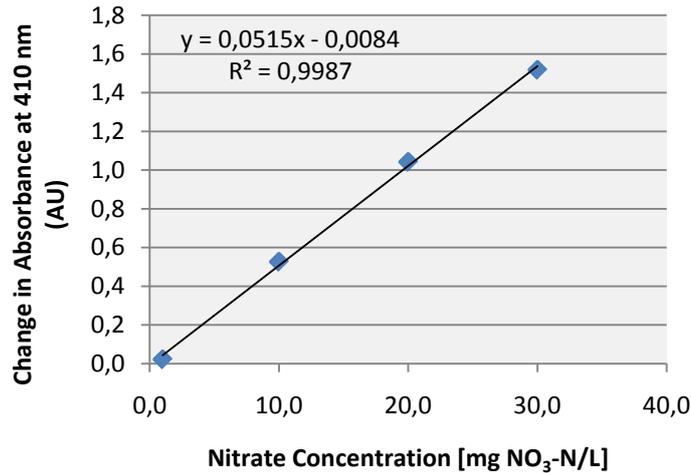


Figure 4 -- Nitrate standard curve (vials)

Equation 5 -- Nitrate calculation from absorbance

$$(\alpha_1 - \alpha_2) = ax + b$$

$$x = \frac{(\alpha_1 - \alpha_2) - b}{a}, \left( \frac{mg NO_3^- - N}{L} \right)$$

Nitrates are also measured using a pH meter (i.e., millivolts meter) with the addition of a nitrate electrode. The nitrate electrode is equipped with a probe with a sensor that measures nitrate activity in the water. The nitrate activity in the water then affects the electronic potential of a solution in the probe; the change in electronic potential of the solution is converted into a voltage scale by the meter which gives us the result as millivolts (mV).

To simplify things we decided to measure conductivity as opposed to measuring concentration directly. The latter requires calibration to give consistently correct results whereas the former provides correct measurements without calibration. Standardized curves are made based on prepared nitrate standards of 1, 3, 10, 30, and 100  $\frac{mg NO_3-N}{L}$  based on a 1 000  $\frac{mg}{L}$  stock solution. An example curve is shown in Figure 5. The voltage readings from the measurements ( $\alpha_1$ ) are converted to  $\frac{mg}{L}$  concentrations based on said curves. Samples are grabbed from either the reactors themselves or from the effluent, as volumes of 20 mL or 100 mL, depending on how much of the reactors' MLSS have been wasted for TSS. An ionic strength adjuster (ISA) is added to the samples at a rate of 2%.

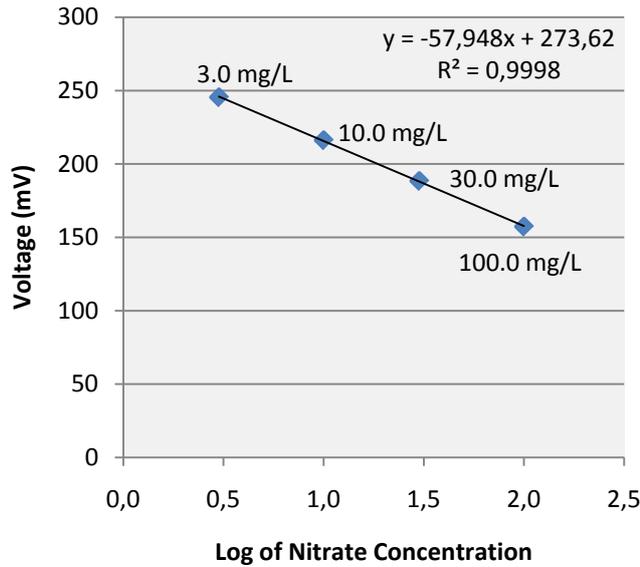


Figure 5 -- Nitrate standard curve (probe)

The addition of an ISA is important to ensure that all samples and standards have similar ionic strengths. By doing so, the effect of variable ionic strength on the measuring apparatus' activity is overcome (Fondriest Environmental).

Conversions from standard curve to nitrate concentrations are done using Equation 6.

Equation 6 -- Concentration from voltage

$$\log(\alpha_1) = ax + b$$

$$x = 10^{\left(\frac{\alpha_1 - b}{a}\right)}, \frac{mg\ N}{L}$$

### 3.2.2 Ammonia

Nitrogen as ammonia is measured using an ammonia electrode probe connected to a pH meter. Ammonia standards are made every week to control the consistency of the results. A 1 000  $\frac{mg\ NH_4-N}{L}$  standard solution is made using 4 720  $\frac{mg\ (NH_4)_2SO_4}{L}$ . This standard is then diluted to 3, 10, 30, and 100  $\frac{mg\ NH_4-N}{L}$  to generate a standard curve. The ammonia probe is, like the nitrate probe, set to give the measurements as mV so that the uncertainty in conjunction with calibration is ruled out.

Measuring ammonia takes a lot longer than nitrate or pH measurements. Whereas measuring pH provides results almost instantly, ammonia readings can take many minutes.

An ISA is added to the samples so that the electrode measurements can be conducted. The addition of ISA to the standards – and the samples for that matter – causes the samples to degrade to the point where they will no longer serve their function. This is why new ammonia standards must be made when creating new standard curves. A major potential source of error before measuring ammonia lies in the making of the ISA, the human factor. The same amount of ISA is added both to the standards and samples; 2% of the sample volume.

The sample ammonia concentrations are found the same way as nitrate concentrations; by the use of standard curves. Figure 6 shows an example of an ammonia standard curve.

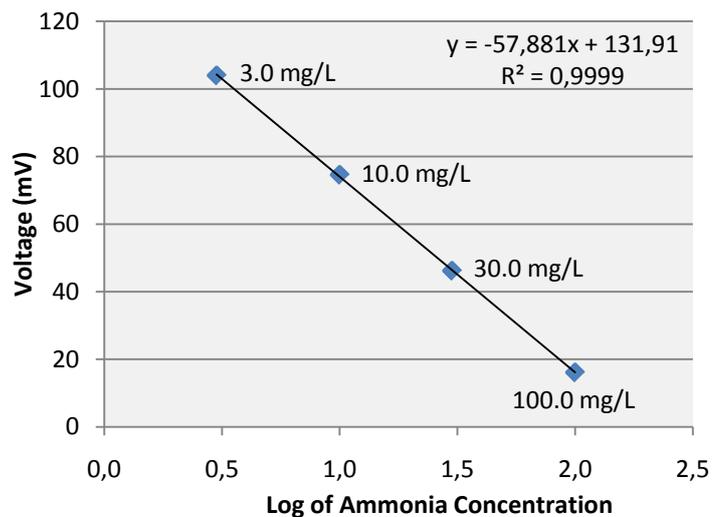


Figure 6 -- Ammonia standard curve

The ammonia concentration is calculated using Equation 6.

### 3.2.3 Total Nitrogen

Total nitrogen is measured using either vials or, as of April 20<sup>th</sup>, the *Aurora 1030C TOC Analyzer*. Samples are taken from the reactors' effluent using a pipette and then added to vials that go through a series of reactions.

The vials used for total nitrogen contain a hydroxide reagent. The procedure starts with adding a persulfate reagent and a 2 mL sample to each vial; one blank with DI, one

influent with a dilution factor of 4, and one sample from each reactor's effluent with a dilution factor of 2.

*An alkaline persulfate digestion converts all forms of nitrogen to nitrate. Sodium metabisulfite is added after the digestion to eliminate halogen oxide interferences. Nitrate then reacts with chromotropic acid under strongly acidic conditions to form a yellow complex with an absorbance maximum at 410 nm.*

The rest of the procedure is described in DR/4000 Procedure (2005).

After the procedure, the vials are placed in the UV/vis. The absorbance units (AU) measured at 410 nm ( $\alpha_1$ ) are then converted using a slightly modified Equation 5 seen in Equation 7.  $\alpha_{\text{blank}}$  represents the blank samples AU and  $\beta$  represents the dilution factor of the sample.

**Equation 7 -- Total Nitrogen calculation**

$$x = \left( \frac{\alpha_1 - b}{a} - \alpha_{\text{blank}} \right) \times \beta, \frac{\text{mg N}}{\text{L}}$$

The final step is to measure the total nitrogen absorbance in the UV/vis at 410 nm. The absorbance units (AU) at 410 nm are then converted to a total nitrogen concentration using Equation 7.

Total nitrogen can also be measured with the help from the *Aurora 1030C TOC Analyzer* by utilizing the total bound nitrogen (TN<sub>b</sub>) module, which can detect TN<sub>b</sub> in the range from 100  $\frac{\mu\text{g}}{\text{L}}$  level to 1 000  $\frac{\text{mg}}{\text{L}}$  undiluted, but can theoretically measure indefinite amounts of TN if diluted (OI Analytical, 2009). Using the *Aurora 1030C TOC Analyzer* takes a bit more effort to set up but is essentially better for this purpose as one eliminates the need to supervise the procedure and do not risk human error after starting the analyzer.

Bound nitrogen is converted into NO<sub>x</sub> compounds at temperatures over 700°C. The high temperature is necessary for the reaction to go smoothly and avoid explosive reactions which can happen at cooler temperatures. The samples are placed in a sampling wheel and each sample's position in the wheel is entered into the connected computer. The wheel is prepared with nitrogen standards, blanks, wastewater samples, and cleaning water. A sampling sequence is set up with a desired number of repetitions per sample

and when to clean the probe. We run the machine at 3 repetitions per sample and clean the probe between each sample as we are dealing with wastewater. The machine has the ability to create its own standards, but we choose to feed it with pre-made standards to make sure the results come out correctly.

Nitrogen compounds are measured by electrochemically detecting nitric oxide. The machine is set to run at a temperature of 720°C and a pressure of 110.3 kPa. These settings are chosen as the nitrogen concentration is in the area between 1-80  $\frac{mg\ N}{L}$ , which requires a pressure of 110.3-137.9 kPa and a suggested injection volume of 0.1 mL.

### 3.3 Wastewater Conditions

pH and alkalinity are both important factors concerning how nitrification and denitrification are carried out in the reactors. While pH is important for maintaining consistency with regards to the biological processes in the treatment, alkalinity is important for maintaining control over the pH. Higher alkalinity will make the water less susceptible to change in pH by the addition of acid. As the nitrifying process uses alkalinity, one should be aware that the alkalinity within a sludge floc will be lower than that observed in the water. The amount of DO in the reactors decides whether or not denitrification will occur.

#### 3.3.1 pH

Growth rate for nitrifying bacteria is strongly related to pH. The optimal pH range for nitrification is in the range 7.5<pH<8.0, and nitrification is reduced significantly when pH drops below 6.8. For example, nitrification can at a pH of 5.8-6.0 be as low as 10-20% of that at pH 7.0 (Tchobanoglous et al., 2003). In addition to the pH's significance for nitrification, the wastewater must also meet the effluent pH requirements of 6.0<pH<9.0.

pH is measured using an *Orion 720A+* pH meter with a probe. The pH meter is initially calibrated every day using three buffers before measuring the actual samples; the buffers' pH is 4.01, 7.0, and 10.0. pH is measured either directly in the reactors continuously through their cycle, at specific periods during the cycle, or when titrating. This is done by simply placing the probe in the fluid that one wishes to measure and reading the display of the pH meter.

### 3.3.2 Alkalinity

Alkalinity is a measure for how resistant the wastewater is to change in pH by addition of acids. The amount of acid needed to reduce pH in the wastewater helps determine the wastewater's alkalinity as  $\frac{mg\ CaCO_3}{L}$ . The alkalinity of the wastewater is determined through titration with the use of hydrochloric acid (HCl). The HCl is diluted to 0.25N before titrating.

The acid is added at a rate of 0.5-5.0  $\frac{mL}{load}$  to a wastewater sample of 100 mL through a burette, while being stirred on a magnetic stir plate to create a well mixed sample. pH is measured initially before adding any acid and then tracked through the titrating process. The values are written down for each acid addition and the amount of added acid is adjusted depending on how great the change of pH was after the last addition. The pH values are then typed into a spreadsheet and the alkalinity is determined by the change in pH per mL of added HCl; the biggest slope represents the endpoint of the titration and the alkalinity of the sample. For example, inflection point hit after adding 15 mL HCl to the sample. Equation 8 and Equation 9 explain the calculation of alkalinity.

Equation 8 -- Alkalinity as CaCO<sub>3</sub>  
(Standard Methods, 2005)

$$\frac{A \times N \times 50\ 000}{mL\ sample} , \frac{mg\ CaCO_3}{L}$$

Where A = mL standard acid used and N = normality of standard acid.

Equation 9 -- Example calculation

$$\frac{15\ mL\ HCl \times 0.025N \times 50\ 000\ mg\ CaCO_3/eq}{100\ mL} = 187.5\ \frac{mg\ CaCO_3}{L}$$

### 3.3.3 Dissolved Oxygen (DO)

Dissolved oxygen must be present for nitrification to happen. The nitrifying bacteria's growth rate is greatly influenced by the amount of DO down to a certain point. Figure 7 shows that a DO concentration higher than 2  $\frac{mg\ O}{L}$  makes little difference to the minimum required SRT.

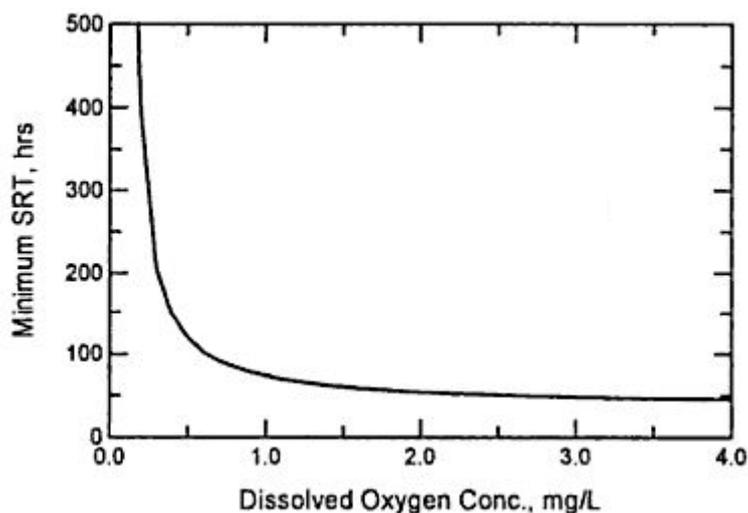


Figure 7 -- DO conc. vs. min. SRT  
(Grady et al., 1999)

To measure DO, a DO meter with a probe is utilized. The probe has a permeable membrane that selectively lets DO pass through; the probe then sends the signal to the meter. The DO meter converts the probe's readings into  $\frac{mg\ O}{L}$ .

The meter has to run for 30 minutes to warm up and for calibration to be exact. The meter and probe is calibrated to 98.5% oxygen saturation. With a water temperature of 20°C, this would mean a concentration of  $8.87 \frac{mg\ O}{L}$ . DO measurements are taken in the reactors during the treatment cycles and before and after BOD<sub>5</sub> incubation.

For DO measurements in the reactors, the probe is lowered into the wastewater and safely secured. Measuring DO directly in the reactors is done to have better control over the reactors' working conditions and to create DO trend curves. Measuring DO is also a measure to make sure the air diffusion stones are supplying the correct air flow. DO is also measured in BOD<sub>5</sub> experiments. The DO is then measured in a prepared BOD<sub>5</sub> bottle both before and after a five day incubation period. The probe is submerged in the sample and it takes about 15-45 seconds for the reading to stabilize. See chapter 3.4.2 for more on BOD<sub>5</sub>.

### 3.4 Oxygen Demand

Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD<sub>5</sub>) are different ways of measuring how much oxygen the water consumes once it reaches the recipient after treatment. Major differences include two hour incubation time for COD samples versus five days for BOD. COD is a more stable measurement method as one

uses chemicals to determine the oxygen demand rather than relying on microorganisms. A result of this is that oxidation efficiency of a BOD test depends on water conditions such as pH and temperature etc. as the organisms are susceptible to these variables. The COD tests will oxidize regardless of water conditions due to the potassium dichromate ( $K_2Cr_2O_7$ ) used in the vials.

### 3.4.1 Chemical Oxygen Demand (COD)

Vials are used for measuring the concentration of COD in the wastewater. Using a pipette, samples of 2 mL are added to the vials. This includes samples from, respectively, the influent water from the feeder tank and effluent water from each reactor. As the influent keeps a higher concentration of COD than the effluent it has to be diluted in order to get applicable results using vials with a low range solution, which can detect COD in the range from 1-150  $\frac{mg\ O}{L}$ . In addition to the wastewater samples a blank is always run; this is a vial where 2 mL of distilled de-ionized water (DI) is added as a reference. After adding the sample volumes, the vials are inverted 10-15 times to mix the contents and then placed in a heater at 150°C for 2 hours. The vials need to cool to less than 120°C before being analyzed in the UV/vis at a wavelength of 420 nm. The AU ( $\alpha_x, \alpha_{blank}$ ) is recorded.

A COD standard curve of 25, 50, 75, 100, 125, and 150  $\frac{mg\ O_2}{L}$  is made for sample concentration calculation. See Figure 8 for an example curve.

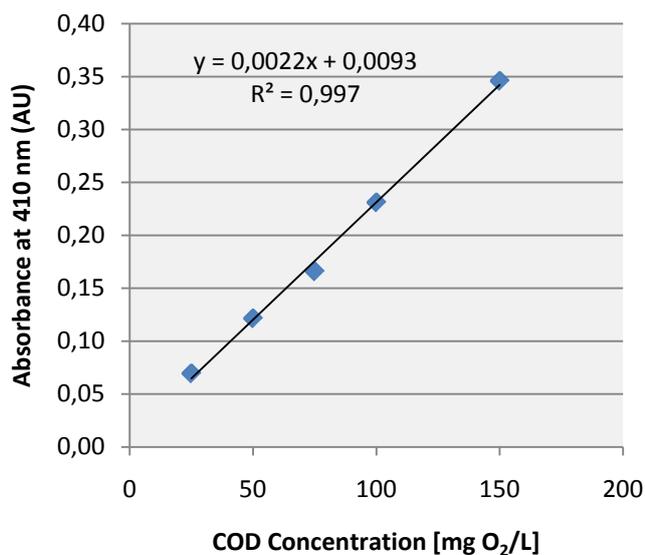


Figure 8 -- COD standard curve

To convert AU to  $\frac{mg\ O_2}{L}$ , Equation 10 is utilized.

**Equation 10 -- COD calculation**

$$\frac{(\alpha_{blank} - \alpha_1) - b}{a} \times \beta, \frac{mg\ O_2}{L}$$

Where  $\beta$  represents the dilution factor of the sample.

In addition to running COD tests with pre-made solutions, laboratory made reagent solutions and COD standards were prepared. The vials are prepared with 1.5 mL digestion solution, 3.5 mL sulfuric acid reagent, and 2.5 mL of sample. COD standard concentration samples of 25, 50, 75, 100, 125, and 150  $\frac{mg\ O_2}{L}$  are used for creating standard curves. The low and high range solutions described in Standard Methods (2005) are not optimal for the COD concentrations in the wastewater. See appendix A.2 for mid-range digestion solution. This self-made solution is a modification of the solutions mentioned in Standard Methods (2005).

### **3.4.2 Biochemical Oxygen Demand (BOD<sub>5</sub>)**

BOD<sub>5</sub> tests are done twice every week to ensure consistency and to work out the trend. The BOD<sub>5</sub> test consists of ten 300 mL bottles with flared mouths and ground-glass stoppers; two blanks, two influent samples, and two effluent samples from each reactor. The BOD<sub>5</sub> bottles are prepared with 1 mL of seed which is concentrated MLSS from R1. Six of the bottles are then filled with 100 mL of effluent sample, and two are filled with 5 mL of influent sample because of the higher concentration. The bottles are then topped off with oxygen saturated dilution water. The dilution water is prepared by adding 1  $\frac{mL}{L}$  each of phosphate buffer, magnesium sulfate, calcium chloride, and ferric chloride solution (Standard Methods, 2005) to DI, see appendix A.1. The dilution water is aerated to a DO concentration of at least 7.5  $\frac{mg\ O_2}{L}$ . The blank samples contain only seed and dilution water. The DO of each BOD<sub>5</sub> bottle is measured before they are placed in a dark cabinet maintaining approximately 20°C. It is important to keep them in the dark to avoid photosynthesis happening. Over a period of five days the biological organisms in the water will oxidize organics and consume oxygen in the process. After five days the bottles are removed from the cabinet and once again checked for DO. The

change in DO relative to the blank samples tells us how much BOD<sub>5</sub> is present in the wastewater as  $\frac{mg\ O_2}{L}$ , after accounting for the dilution of the samples.

### 3.5 Solids

Mixed Liquor (MLSS), Total (TSS), and Volatile (VSS) Suspended Solids are all related to the solids in the wastewater. MLSS is the term used to define the mixture of solids resulting from combining recycled sludge with influent wastewater (Tchobanoglous et. al, 2003), TSS are the total weight of suspended solids after evaporation and drying and VSS are the solids that are burned off when igniting the TSS. Filters are weighed to have their initial weight before any of the above mentioned factors are sampled and then re-weighed after their period of preparation.

#### 3.5.1 Total Suspended Solids (TSS)

TSS is measured using an apparatus where MLSS, influent, and effluent are filtered through a fine filter, 934-AH filters with a pore size of 1.7  $\mu\text{m}$ , which later is weighed.

The filters are initially prepared by burning off any organic material in a 550°C oven for about 30 minutes so that this will not affect the end results. The filter is then weighed before filtering. A filter is placed on a perforated marble pad and vacuum is applied to drain the water more quickly through the filter. The top jar is clamped to the filter holder and sample is added into the jar. Deciding the filter volume of each sample depends on how much suspended solids they seem to contain and how quickly they drain through the filters. No sample should take longer than 10 minutes to drain through the filter. MLSS containing a lot of suspended solids will take much longer to filter than effluent water from one of the reactors which, in comparison, contains very little suspended solids. The amount of suspended solids in the influent water is somewhere in between the MLSS and the effluents. Based on knowledge and experience, we worked out set volumes for TSS filtration; the MLSS have a filtered volume of 20 mL as the filters are bound to pack relatively quickly based on the amount of TSS, the effluents have a filtered volume of 1 L as they contain very little TSS and the water drains through the filters quickly, and the influent has a filtered volume of 300 mL.

After the filtration, the filters are placed in an oven at 103°C for more than 1 hour. This is done to be certain that the filters are dried out so that water will not be part of the filters' mass. When drying is completed, the filters are placed in a desiccator to cool and

keep the filters from absorbing humidity from the air. See Equation 11 for TSS calculation.

**Equation 11 -- TSS calculation  
(Standard Method, 2005)**

$$\frac{mg\ TSS}{L} = \frac{(A - B) \times 1\ 000\ mL/L}{mL\ sample}$$

Where A = mass of dried residue + filter and B = mass of filter, both in mg.

### **3.5.2 Fixed and Volatile Suspended Solids (VSS)**

The VSS are measured by placing the filters from the TSS process in an oven maintaining 550°C for a period of 30 minutes. In this process all the organic matter of the TSS samples will burn off. The fixed solids are the remaining solids on the filter while the VSS are represented by the weight lost on ignition (Standard Methods, 2005).

VSS are calculated using Equation 11. The only difference is that A and B represent weight of filter before and after ignition.

## **4 Results and Discussion**

Most measurements involving effluent contents are done using the 8 a.m. effluents for practical reasons; it is the only time the reactors' effluent pumps are in effect at the same time. Up until mid-March, R3 was showing effluent results that were hard to understand. As twelve timers are utilized to control the setup, errors were bound to happen. Until mid-March the aeration period between cycle 4 and 5 was not in effect. This is likely to have colored the results in some way and might very well be the reason why R3's nitrate concentrations were as low as recorded in the period preceding this discovery.

### **4.1 Experimental work**

From my joining the project on January 18<sup>th</sup> through April 5<sup>th</sup> the reactors were operated as shown in Table 1. Small, insignificant changes were made from time to time including fiddling with the SRT. Individual control over aeration to each reactor was not implemented until mid-February. The initial individual air control did not work sufficiently and was later improved by more precise valves.

It was decided that some changes had to be made in order to be able to meet deadlines. Significant changes were made to the reactors' operating conditions in early April so that chances to reach steady state would improve.

On April 5<sup>th</sup> the timers of reactors 2 and 3 were reconfigured so that they now are on the same cycle regarding aeration, mixing, and settling periods and influent and effluent wastewater as R1. This leads to our ability to monitor more closely how the reactors are doing in relation to each other and the WWTP.

On April 7<sup>th</sup> certain conditions under which the reactors operate were modified. There is a thought that modifying the reactors' SRT and/or anoxic periods will provide the desired results; more consistent denitrification with higher nitrate removal. The increased SRT will increase the amount of denitrifying bacteria. The WWTP cannot increase their SRT much due to the type of pump they are using, a screw pump. See Table 3 for new schedule.

Table 3 -- Schedule as of April 7<sup>th</sup>

	Cycle 1		Cycle 2		Cycle 3		Cycle 4	
	On	Off	On	Off	On	Off	On	Off
<b>R 1</b>								
In 1	8:00 AM	8:10 AM	2:00 PM	2:10 PM	8:00 PM	8:10 PM	2:00 AM	2:10 AM
Eff 1	1:50 PM	2:00 PM	7:50 PM	8:00 PM	1:50 AM	2:00 AM	7:50 AM	8:00 AM
Mix 1	8:00 AM	12:50 PM	2:00 PM	6:50 PM	8:00 PM	12:50 AM	2:00 AM	6:50 AM
Air 1	12:50 PM	3:15 PM	6:50 PM	9:15 PM	12:50 AM	3:15 AM	6:50 AM	9:15 AM
<b>R 2</b>								
In 2	8:00 AM	8:10 AM	2:00 PM	2:10 PM	8:00 PM	8:10 PM	2:00 AM	2:10 AM
Eff 2	1:50 PM	2:00 PM	7:50 PM	8:00 PM	1:50 AM	2:00 AM	7:50 AM	8:00 AM
Mix 2	8:00 AM	12:50 PM	2:00 PM	6:50 PM	8:00 PM	12:50 AM	2:00 AM	6:50 AM
Air 2	12:50 PM	3:15 PM	6:50 PM	9:15 PM	12:50 AM	3:15 AM	6:50 AM	9:15 AM
<b>R 3</b>								
In 3	8:00 AM	8:10 AM	2:00 PM	2:10 PM	8:00 PM	8:10 PM	2:00 AM	2:10 AM
Eff 3	1:50 PM	2:00 PM	7:50 PM	8:00 PM	1:50 AM	2:00 AM	7:50 AM	8:00 AM
Mix 3	8:00 AM	12:50 PM	2:00 PM	6:50 PM	8:00 PM	12:50 AM	2:00 AM	6:50 AM
Air 3	12:50 PM	4:30 PM	6:50 PM	10:30 PM	12:30 AM	4:30 AM	6:50 AM	10:30 AM

The table shows that R1 now operates as it always has with the same aeration periods and the same amount of MLSS drawn for TSS measurements of  $500 \frac{mL}{day}$  giving an SRT of 10 days. R2 now operates under the same conditions as R1, but instead of the  $500 \frac{mL}{day}$ , we extract  $300 \frac{mL}{day}$  giving an SRT of 20 days. R3 is also deprived of  $300 \frac{mL}{day}$ . In addition to this, R3's anoxic period is modified so that it can be determined whether an increased SRT or a combination of increased SRT and increased anoxic period will prove best for the reactors with regards to the denitrifying process. The recycle ratio is changed to 1.0 for all reactors to maintain an HRT of 10 hours.

On April 15<sup>th</sup> a discovery was made, the COD concentration of wastewater influent to the WWTP varies throughout the day. The results have consistently shown low COD concentrations compared to BOD concentrations. The solution to this problem is the time of day wastewater is collected from the WWTP. This is done every week at the same time, Friday mornings, which happens to be the time of day when the COD concentrations are at their lowest.

On April 19<sup>th</sup> wastewater was collected after noon to make sure that higher amounts of COD would be present. More COD can potentially lead to the reactors improving their ability to denitrify. An alternative solution would be to preheat the wastewater before

filling the reactors and to simulate more optimal conditions, and make modifications once we know the reactors are working as desired.

On April 27<sup>th</sup> fish tank heaters were acquired. The heaters are used to heat the influent wastewater from 4°C (from being stored in the cold) to about 25°C to more accurately simulate optimal operating conditions. This is done to ensure that the biological processes are functioning as expected.

## 4.2 Results

### 4.2.1 Nitrate, Ammonia, and Total Nitrogen

Nitrification is working well at the WWTP, while the denitrification process is not optimal. Figure 9 shows ammonia in the influent versus nitrate in the effluent from the WWTP. Ammonia concentrations in the effluent are less than  $1.0 \frac{mg}{L}$  and have not been plotted.

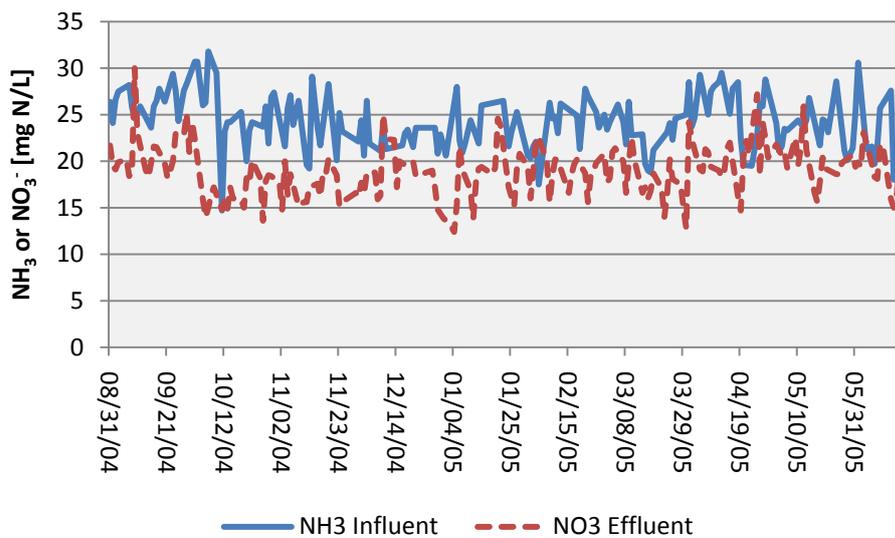


Figure 9 -- Ammonia vs. nitrate WWTP

Denitrification in the reactors is working better than that of the WWTP. Figure 10 shows a gap in between ammonia and nitrate, implicating denitrification has occurred. Effluent ammonia has not been plotted due to the concentrations being below  $1.0 \frac{mg}{L}$ , which meets the WWTP's effluent requirements.

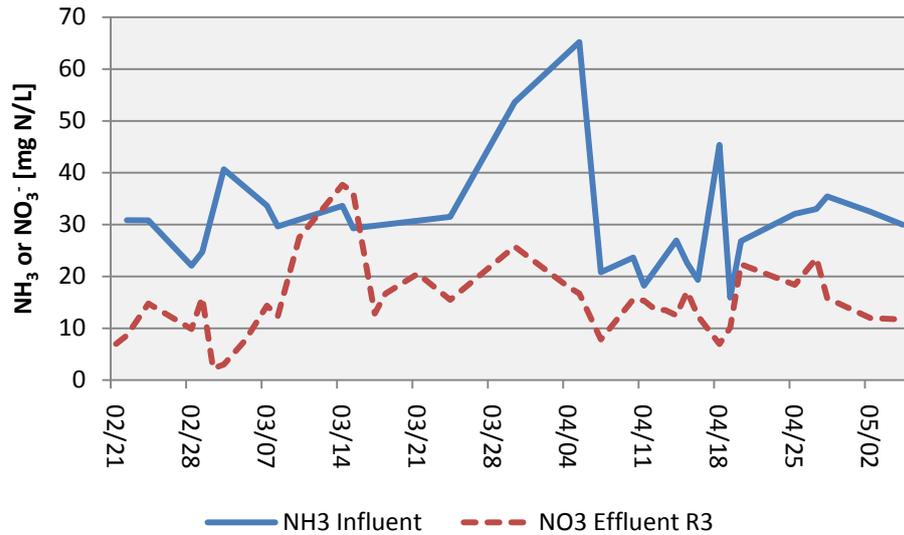


Figure 10 -- Ammonia vs. nitrate reactor

The amount of nitrate in the effluent tells us whether or not denitrification has taken place on a significant scale. From March 26<sup>th</sup> to March 28<sup>th</sup> the nitrate concentration of each reactor was logged through a cycle; R1 the 26<sup>th</sup>, R2 the 27<sup>th</sup>, and R3 the 28<sup>th</sup>.

Figure 11 shows the nitrate trend from the above-mentioned dates before the reactors started operating by the same schedule. One can see that the nitrate concentrations start out at  $15-20 \frac{mg NO_3-N}{L}$ , experiencing a small reduction due to denitrification during the anoxic period, and increase to about  $25-30 \frac{mg NO_3-N}{L}$  after approximately 80% of the cycle. This is when the reactors' mixing and aeration periods come to an end and the settling period begins.

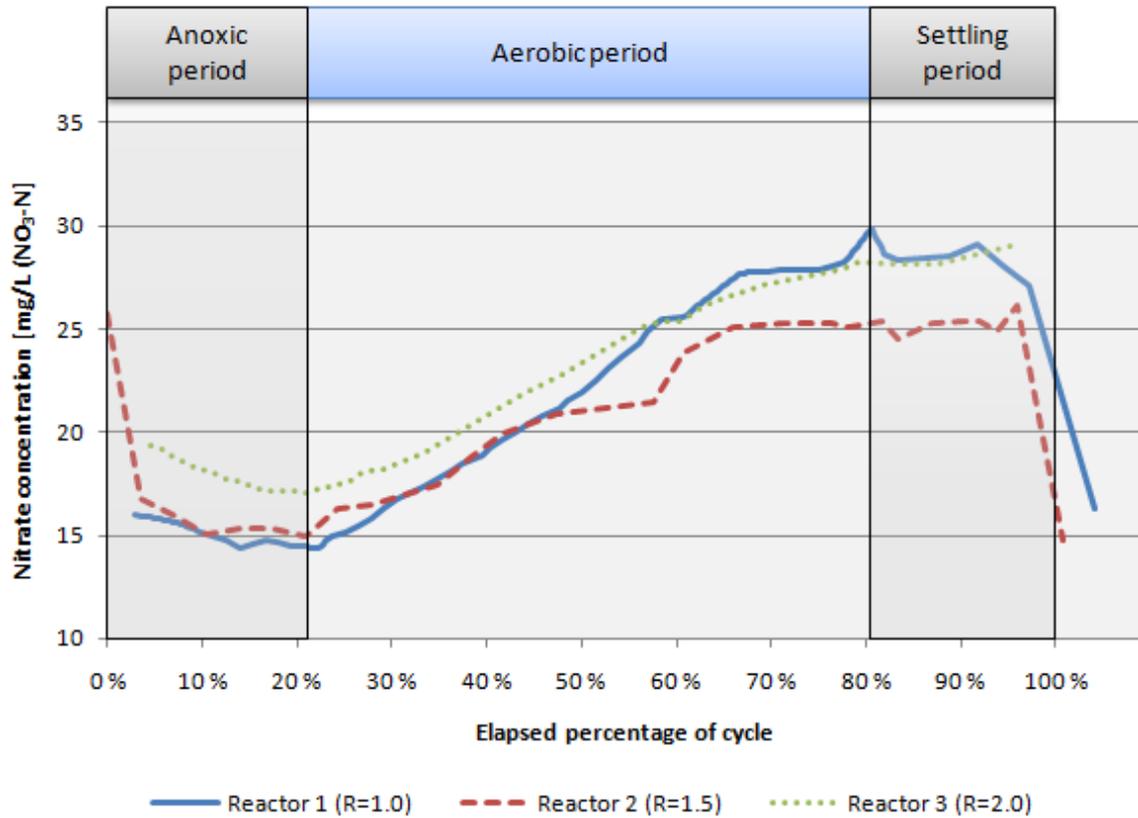


Figure 11 -- Nitrate trend late March

After settling, the effluent pumps start running and, subsequently, influent water is added. The new wastewater is practically free of nitrates as the nitrogen in the influent mainly exists as ammonia, which reduces the nitrate concentration of the reactor.

The figure shows that some denitrification is happening. During the anoxic period the nitrate concentration is reduced by 2-3  $\frac{mg NO_3-N}{L}$  before increasing as nitrification commences when the aerobic period begins.

On May 5<sup>th</sup> nitrate values were tracked through the first 35% of the cycle including the anoxic period. This can be seen in Figure 12. The initial drop in nitrate concentration is a result of ammonia rich influent being added within the first 10 minutes of the cycle. After that, the reactors follow each other with the nitrate reduction until about 20% of the cycle is completed.

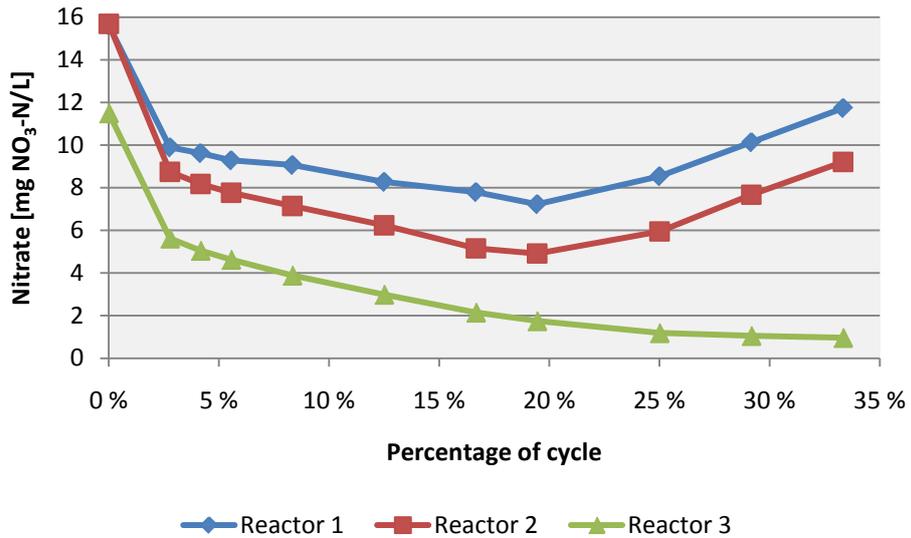


Figure 12 -- Nitrate trend May 5<sup>th</sup>

This is where the aerobic period starts for R1 and R2; R3 operates with an anoxic period of 2 hours compared to 1 hour for the others. This extended anoxic period increases the denitrification.

The difference between R1 and R2 is probably caused by the difference in SRT. As more MLSS is removed from R1 than R2, there is less *food* available to the denitrifying bacteria in R1, which causes less denitrification.

Figure 13 shows the relation between DO and nitrate concentrations in R3. One can see that denitrification is barely happening during the anoxic period of the cycle.

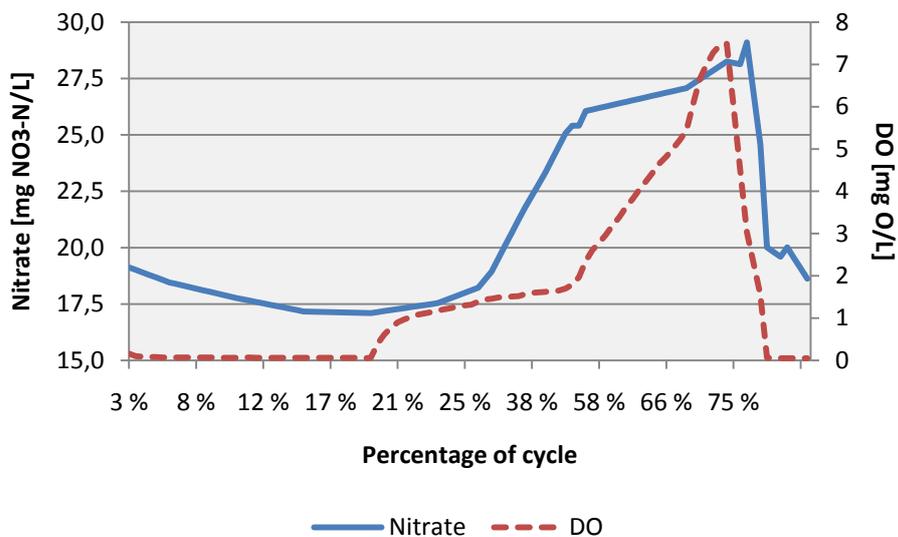


Figure 13 -- Dissolved Oxygen vs. Nitrate concentration in reactor 3

The trend depicted in the figure was recorded late March when the reactors were still operating with quite high nitrate concentrations. Effluent nitrate levels after April 5<sup>th</sup> have not been above  $25 \frac{mg}{L}$ . The reason for this may be the reduced ammonia concentration of the collected wastewater. Denitrification is occurring, but not on a big scale.

The figure also shows that the conversion from ammonia to nitrate takes place when the DO concentration increases after the anoxic period. The sudden drops in both DO and nitrate at the end of the cycle is due to drawing of effluent and subsequent filling of the reactor with ammonia rich influent. DO is a parameter that proves difficult to control in laboratory scale reactors.

Nitrification is the oxidation of ammonia to nitrate. Since both nitrate and ammonia are expressed in terms of N, complete nitrification results in a nitrate concentration equal to the original ammonia concentration. Walnut Creek WWTP's primary effluent has an average ammonia concentration of  $22.5 \frac{mg NH_3-N}{L}$  (June 2007-June 2009) that through the treatment process is reduced to less than  $0.30 \frac{mg NH_3-N}{L}$ .

The laboratory reactors start out with an average  $NH_3$  concentration of  $28 \frac{mg NH_3-N}{L}$ . Through a cycle the wastewater's  $NH_3$  concentration is reduced to less than Walnut Creek's discharge permit of  $2.0 \frac{mg NH_3-N}{L}$ , see Figure 14. This proves the reactors are capable of maintaining a low ammonia concentration in the effluent even in periods where the wastewater keeps a low temperature. The spikes might be a result of erroneous measurements.

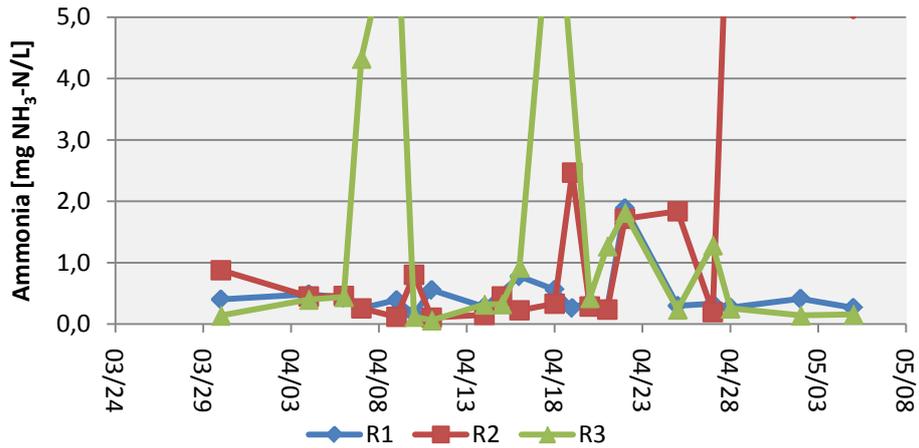


Figure 14 -- Ammonia concentration effluent

Total nitrogen (TN) removal development from April 15<sup>th</sup>–May 6<sup>th</sup> is shown in Figure 15. From the figure one can see that R3 has had the best removal percentage all along, starting with 38% removal on April 15<sup>th</sup> and ending up with 67% removal on May 6<sup>th</sup>.

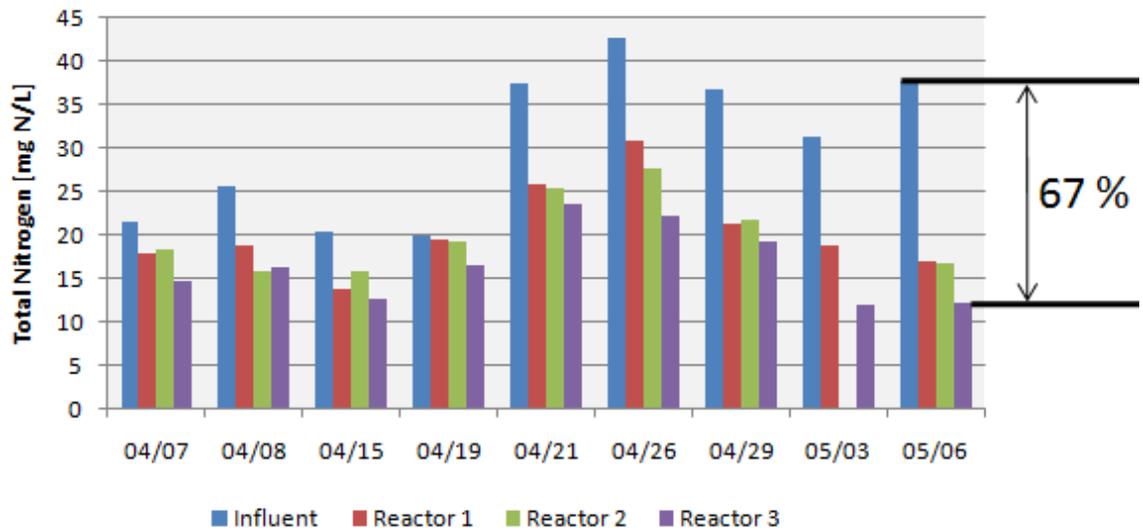


Figure 15 -- Total Nitrogen

TN concentration in the influent has increased from  $21 \frac{mg\ N}{L}$  to  $38 \frac{mg\ N}{L}$  while the TN concentration in R3’s effluent has decreased from  $15 \frac{mg\ N}{L}$  to  $12 \frac{mg\ N}{L}$ . The overall removal improvement of 76% for R3 shows that the implemented changes have made a difference.

#### 4.2.2 pH, Alkalinity, and Dissolved Oxygen

Average primary effluent and effluent pH at the WWTP is shown in Figure 16. Walnut Creek WWTP has an effluent pH requirement of  $6.0 < \text{pH} < 9.0$  and began having problems maintaining this in 2007 due to decreasing influent alkalinity. Their operators saw no other solution than adding sodium hydroxide (NaOH) to increase the effluent pH.

Figure 16 shows that the operators at the WWTP were able to keep the pH from dropping below the minimum requirement of pH 6.0 as a result of their NaOH supplements.

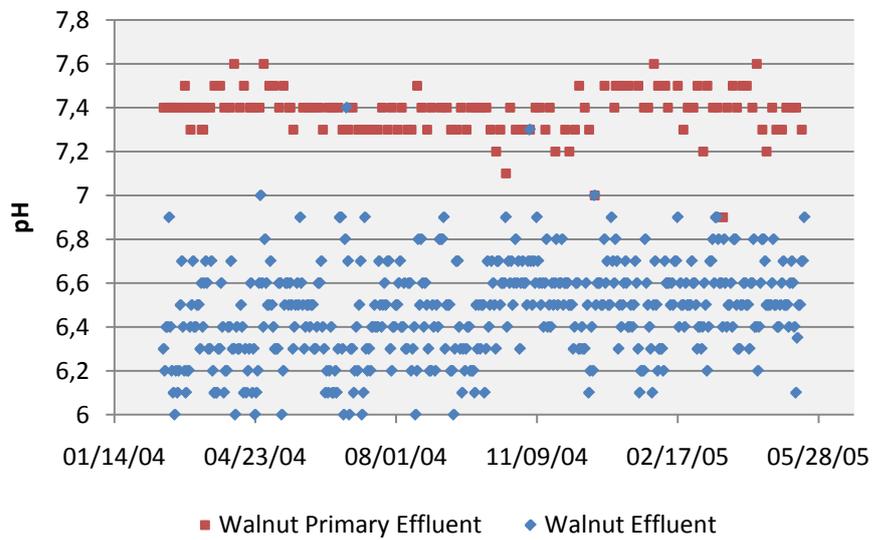


Figure 16 -- WWTP pH

Figure 17 shows the pH trend for the three reactors. As the figure shows, the pH never drops below the above mentioned requirement.

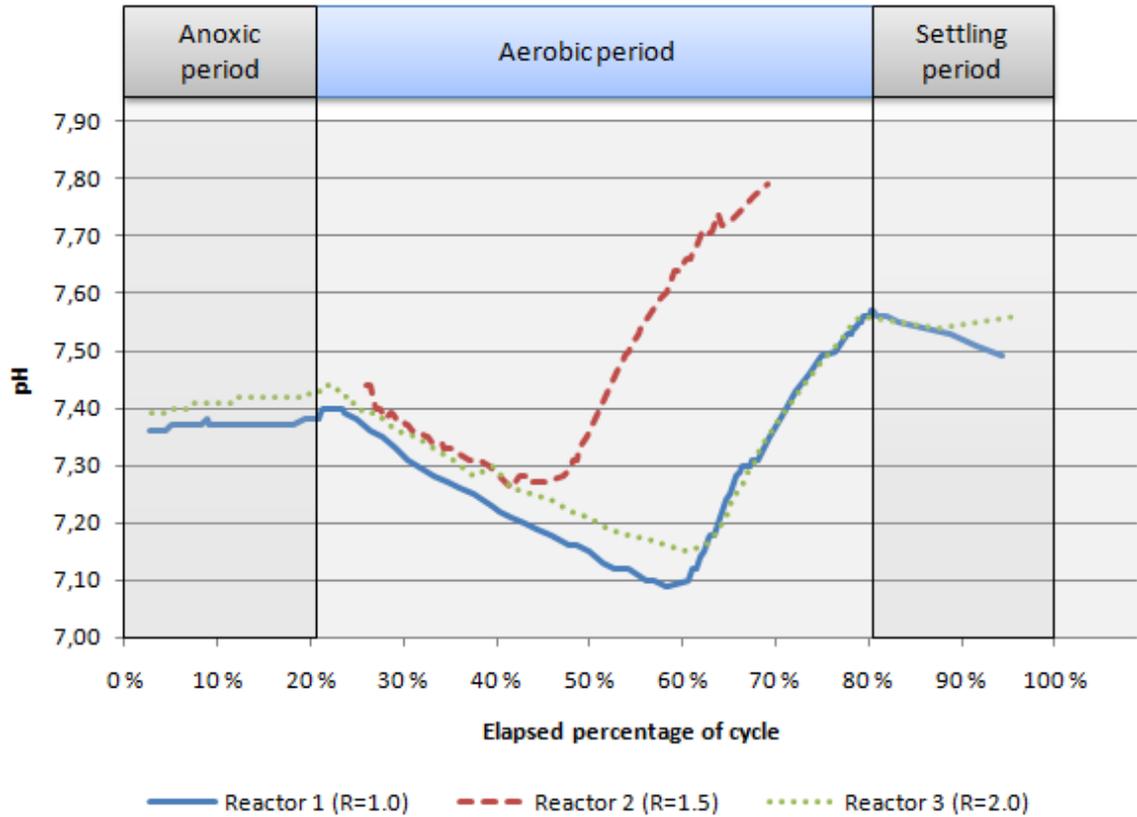


Figure 17 -- pH trend

The Walnut Creek WWTP maintains an average alkalinity of  $204 \frac{mg \text{ CaCO}_3}{L}$  in the primary effluent. Figure 18 shows both the primary effluent and effluent alkalinity at the WWTP.

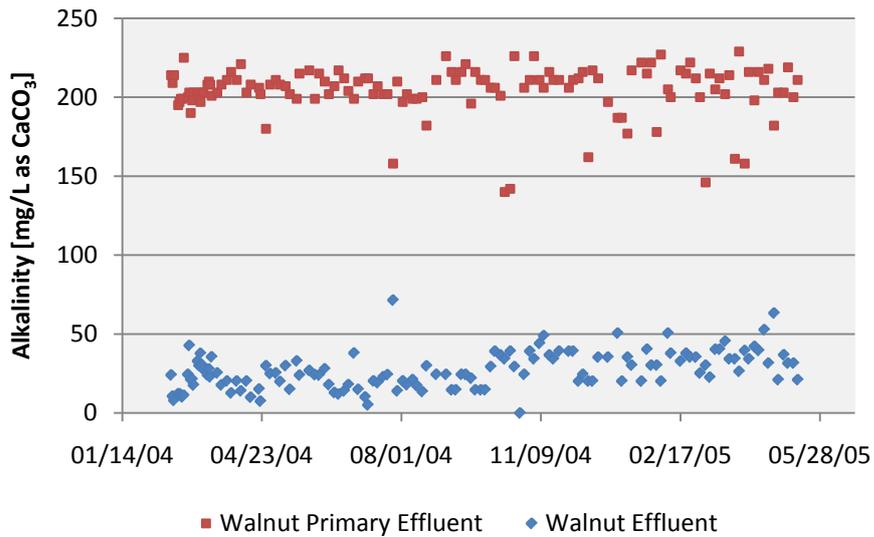


Figure 18 -- WWTP alkalinity

The nitrifying process uses alkalinity, while the denitrifying process produces alkalinity. This can be seen from the alkalinity measurements taken of the effluent. In the effluent, the alkalinity has dropped to an average of about  $29 \frac{mg \text{ CaCO}_3}{L}$ . This drop in alkalinity results in a drop in effluent pH.

An interesting point is the difference in effluent alkalinity before and after the operators decided to turn off the blower. Figure 19 shows the reduction in energy use by the WWTP after they decided to implement their solution. The effluent alkalinity averaged  $21.3 \frac{mg \text{ CaCO}_3}{L}$  before turning off the blower. This increased to an average of  $34.5 \frac{mg \text{ CaCO}_3}{L}$  after the experiment was started; an improvement of 62%. An article in the *Austin Chronicle* mentions that this solution yields energy savings of  $2\,500 \frac{MWh}{year}$ , which in addition saves a lot of money (Gregor, 2009).

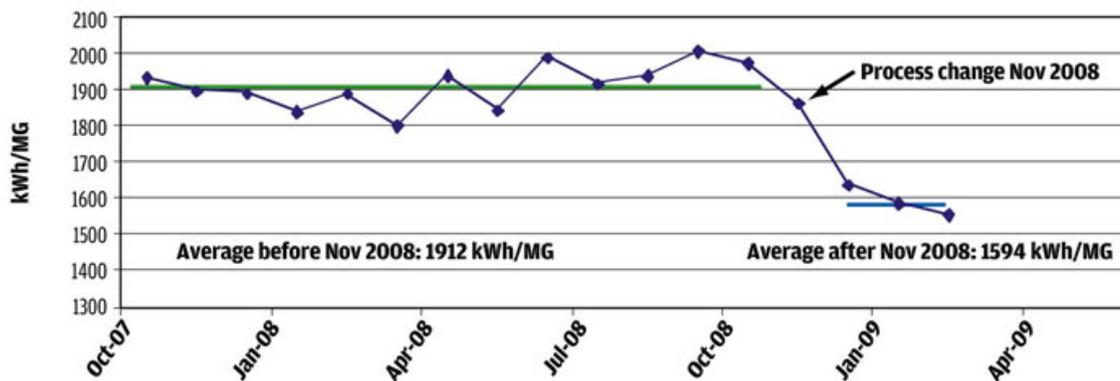


Figure 19 -- WWTP energy use (Austin Chronicle)

The laboratory reactors get their influent from the WWTP’s primary effluent. Influent alkalinity has an average of about  $270 \frac{mg \text{ CaCO}_3}{L}$ . The increase in alkalinity from the time the wastewater gets collected at the WWTP until it is used as influent can be caused by dissolution of  $\text{CaCO}_3$  or other anaerobic activity. See Figure 20 for alkalinity titration results from the influent and reactors’ effluent. The influent alkalinity varies depending on the WWTP’s alkalinity at the time of wastewater collection and how long the wastewater has been sitting in the 50 L tank prior to titration taking place.

Through nitrification,  $7.1 \frac{mg}{L}$  of alkalinity are depleted for every  $\frac{mg}{L}$  of ammonia being converted to nitrite and then nitrate, and through denitrification,  $3.6 \frac{mg}{L}$  of alkalinity are

recovered for every  $\frac{mg}{L}$  of nitrate being removed (Scott). This difference causes the reduction of alkalinity through each cycle.

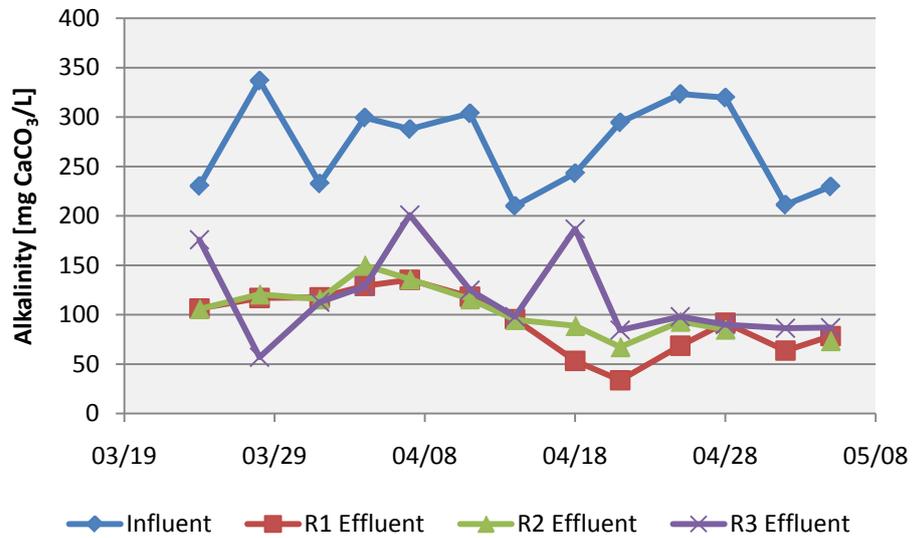


Figure 20 -- Reactor alkalinity

Through the nitrifying process, ammonia is oxidized to nitrate, decreasing pH and consuming more alkalinity than what is recovered by the denitrifying process (Tchobanoglous et al., 2003). The effluents contain on average  $93 \frac{mg CaCO_3}{L}$  for R1,  $104 \frac{mg CaCO_3}{L}$  for R2, and  $118 \frac{mg CaCO_3}{L}$  for R3. From these numbers and Figure 20, one can derive that the reactors are in fact capable of maintaining a higher effluent alkalinity than that of the WWTP even during the coldest conditions. Problems maintaining pH control do not arise until the effluent alkalinity drops to  $<50 \frac{mg CaCO_3}{L}$ .

Figure 21 shows the DO trend over the course of one cycle for each of the three reactors. R1 and R3 have a DO concentration of less than  $0.5 \frac{mg O_2}{L}$  after less than 10 minutes. R2 needed less than 25 minutes to get below  $1.0 \frac{mg O_2}{L}$ .

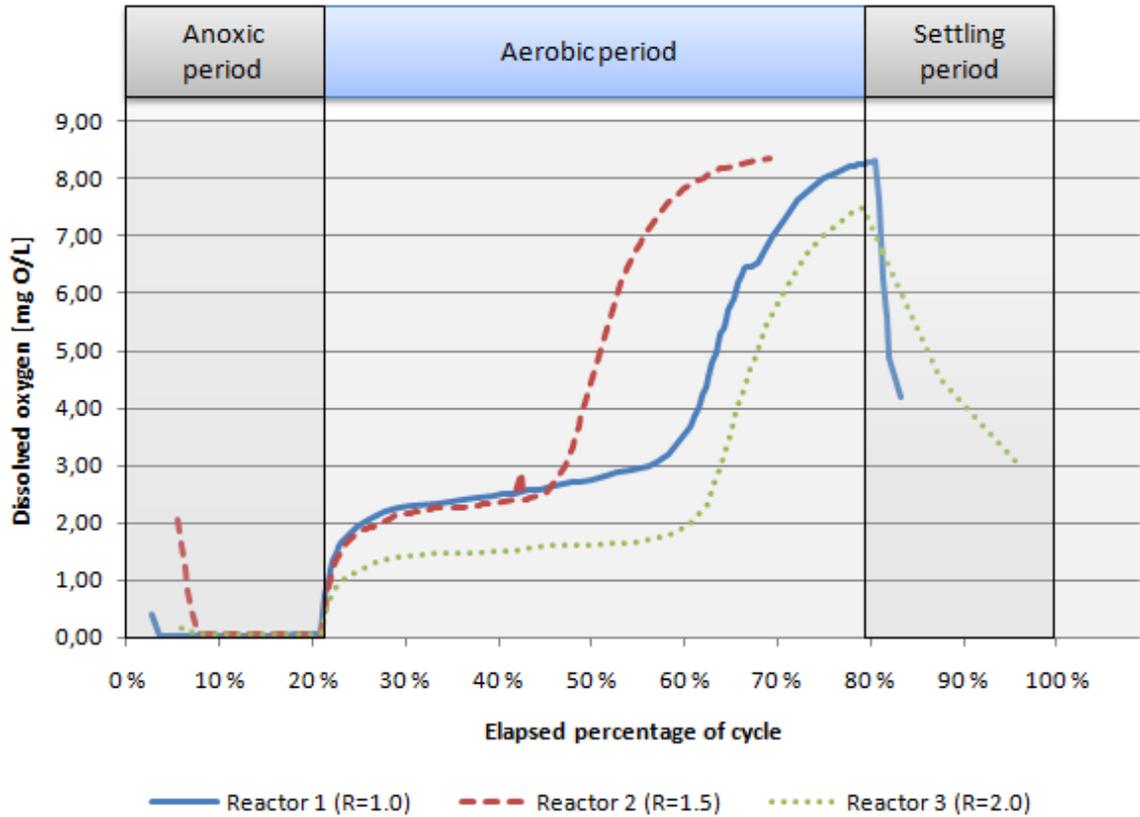


Figure 21 -- Dissolved Oxygen trend

The reactors are filled before the anoxic period and emptied after the settling period; emptying after settling is a measure to be able to exchange the water without removing the bacteria.

#### 4.2.3 Chemical and Biochemical Oxygen Demand

The COD concentrations of the collected wastewater were generally low as the wastewater collecting was done in the morning when the concentrations are at their lowest. COD removal in the reactors is shown in Figure 22. The reactors achieved an average COD removal of 72-79% until April 7<sup>th</sup>, which is when the reactors all got the same operating schedule, but slightly different SRTs and aeration periods. After modifying the schedule, average COD removal increased to 85-88%.

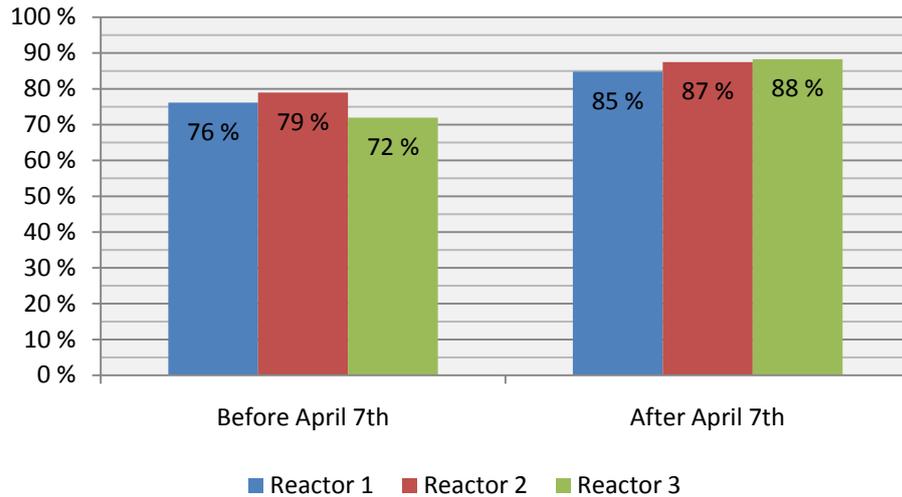


Figure 22 -- COD removal

From the figure one can see that R3 with an SRT of 20 days and increased anoxic period, improved its COD removal by 16%, R2 improved by 8%, and R1 improved by 9%. The changes made on April 7<sup>th</sup> have improved COD removal in R3, but not in R1 and R2. R1 acts as a reference in this matter as the schedule was not altered for this reactor. The average of 11% increase in COD removal might not be a direct result of the changes made to the reactors.

The COD concentrations were much lower than the BOD concentrations, which seemed strange as BOD in municipal wastewater normally is about 65% of COD (Suthersan, 1996). Some research on the matter was conducted and a possible solution found; the COD seems to vary throughout the day. Based on these discoveries, wastewater collection was re-scheduled to the afternoon.

The BOD concentrations of the WWTP decrease from an average of  $172.6 \frac{mg\ O}{L}$  to an average of  $3.2 \frac{mg\ O}{L}$  in the effluent. This gives an average BOD removal of 98%. Figure 23 shows the reactors’ effluents versus the influent’s BOD concentrations; average BOD removal in the reactors is also 98%. The reason why R3 does not show consistently on the chart is that the DO concentrations after five days of incubation were less than  $1.0 \frac{mg\ O}{L}$ . For a BOD<sub>5</sub> test to be valid the value must be greater than that.

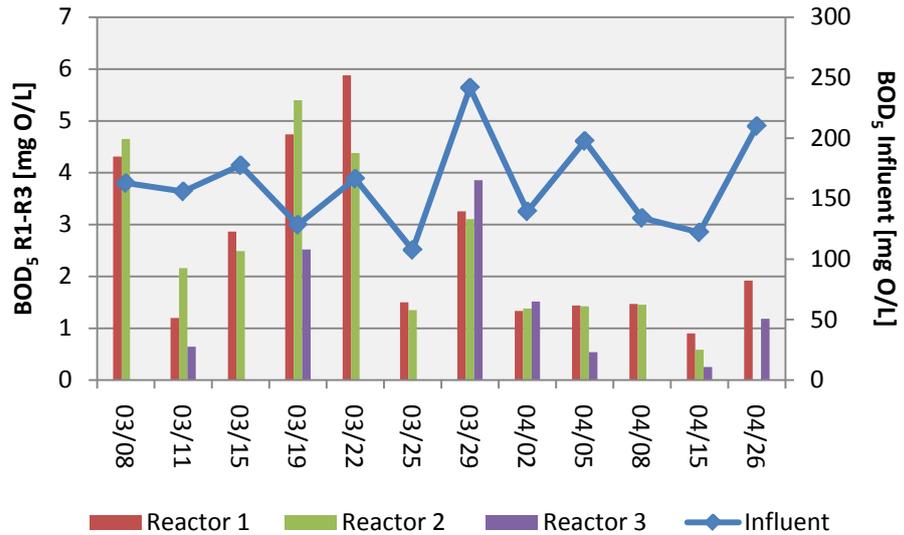


Figure 23 -- BOD<sub>5</sub> removal

Figure 24 shows the correlation between COD and BOD<sub>5</sub> in the influent. The COD concentrations are normally higher than the BOD concentrations, but not in this laboratory experiment. The reason this is occurring is unknown, and COD measurements were not provided by the WWTP operators.

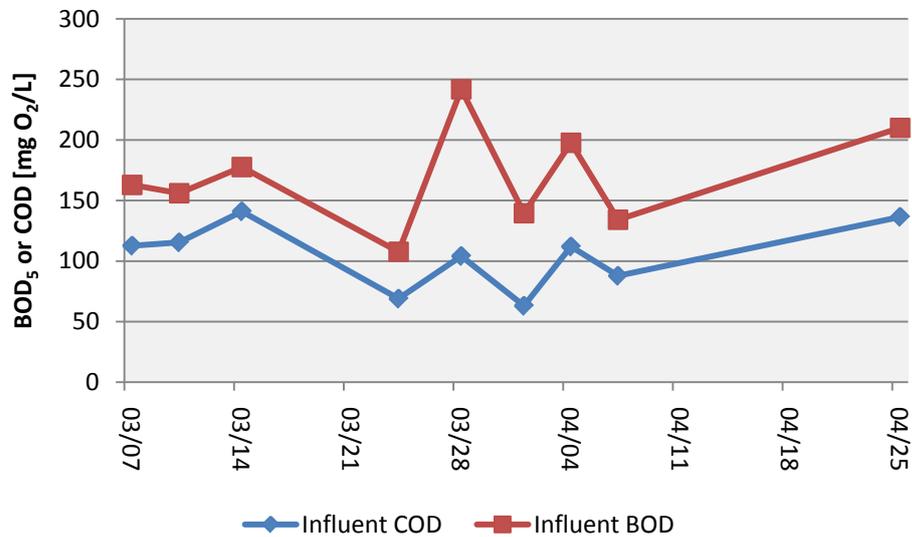


Figure 24 -- Influent COD vs. BOD<sub>5</sub>

#### 4.2.4 Solids

Walnut Creek WWTP operates within a TSS range of approximately 1 000-1 500  $\frac{mg\ TSS}{L}$ . The WWTP's operating area is shown in the lighter area of Figure 25. From the figure one can see that the reactors' TSS have varied throughout the measuring period.

Possible reasons for varying TSS include heavy precipitation the day of or the day before collecting wastewater at the WWTP.

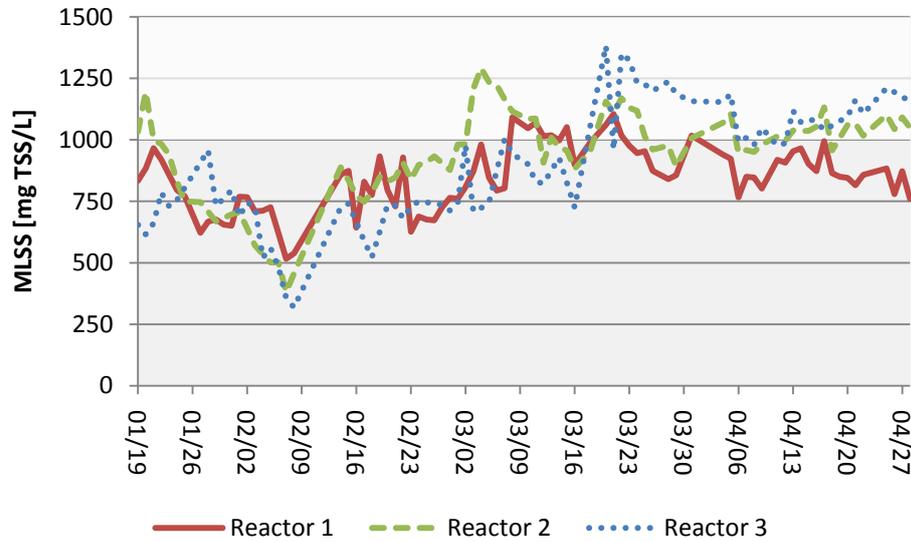


Figure 25 -- TSS reactor development

The increased flow leading to the WWTP would lead to less concentrated wastewater with regards to all constituents. Figure 26 shows the relation between TSS and nitrate concentration. The two parameters follow each other closely with the exception of a couple of nitrate spikes that might be caused by erroneous measurements. Nitrification relies on the presence of available inorganic compounds in order to occur.

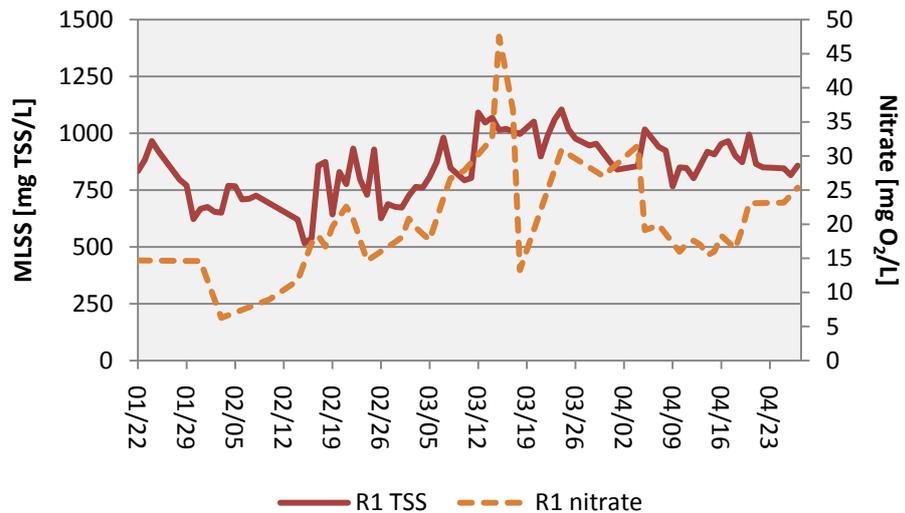


Figure 26 -- TSS vs. nitrate

VSS preparations of TSS filters were not made often enough to create representative data.

## 5 Future Work

There are a few changes that need to be made in order for the reactors to perform their best.

COD samples should be taken at the beginning, middle, and end of each period of the reactors' cycles to show where the greatest reductions take place. Wastewater collection should be re-scheduled to always occur at a time with higher COD concentrations than what has been prevalent.

One could consider making synthetic wastewater to get more consistent results week after week knowing that the wastewater constituents are the same at all times. The drawback of this method would be that the reactors are no longer able replicate the conditions at the WWTP.

Nitrite measurements should have priority in future work. Even though nitrite might exist in small amounts and does not influence the total nitrogen concentration significantly, it should be measured to add to the credibility of the total nitrogen, nitrate, and ammonia experiments. Measuring nitrite will potentially tell whether or not the nitrate and ammonia measurements are in fact correct. Any nitrite concentration above  $0.5 \frac{mg NO_2-N}{L}$  is considered high.

Measuring the expulsion of nitrogen gas (N<sub>2</sub>) above the reactors is a possibility to monitor how the denitrifying is progressing. This would also potentially reveal how much of the converted nitrate ends up as environmentally unfriendly nitrous oxide (N<sub>2</sub>O).

## 6 Conclusion

The goal of this project was to explore ways to optimize denitrification at City of Austin's Walnut Creek WWTP, to maintain low ammonia concentrations in the effluent, and to maintain high alkalinity throughout the treatment process to prevent the pH from dropping below the requirement of  $6.0 < \text{pH} < 9.0$ .

The reactor setup worked well, but it was time consuming to maintain accuracy for every parameter. Even though the setup did not reach steady state during the four month period from January until May, the results are still considered credible.

Measuring parameters requiring the usage of additional chemical solutions, such as ISAs for nitrate or ammonia, has a potential of yielding erroneous results. The uncertainties lie in attempting to prepare identical solutions each time and following an identical procedure whenever these parameters are to be measured.

Alkalinity was maintained at a higher level than the WWTP was able to achieve, averaging at  $105 \frac{\text{mg CaCO}_3}{\text{L}}$  for the three reactors. This, in addition, helped maintain a pH within the requirements of  $6.0 < \text{pH} < 9.0$ . The reactors' pH stayed between 7.1 and 7.8. Controlling the DO of the laboratory scale reactors proved difficult.

Ammonia in the effluent was kept at a level below  $2.0 \frac{\text{mg}}{\text{L}}$ , which means nitrification has been successful and Walnut Creek's effluent requirements have been met. R3 achieved a nitrogen removal of 67% after extending its SRT. Extending the SRT might not be possible at the WWTP, but proves to be an effective way to increase denitrification where applicable. In addition to this, the WWTP should seek ways to implement nitrate recycling from the aerobic to the anoxic zone.

## **Bibliography**

Akin, B. S., & Ugurlu, A. (2005). *The effect of sludge retention time on phosphate removal in a simultaneous feeding and decanting sequencing batch reactor*. Freising, Germany.

American Public Health Association/American Water Works Association/Water Environment Federation. (2005). *Standard Methods for the Examination of Water & Wastewater* (21st ed.). Washington, DC: American Public Health Association.

Fondriest Environmental. (n.d.). Retrieved May 15, 2010, from Fondriest Environmental: [http://www.fondriest.com/products/nexsens\\_aj0n31-125.htm](http://www.fondriest.com/products/nexsens_aj0n31-125.htm)

Grady, C. L., Daigger, G. T., & Lim, H. C. (1999). *Biological wastewater treatment* (2nd ed.). New York, NY: Marcel Dekker, Inc.

Gregor, K. (2009, June 19). Retrieved May 15, 2010, from Austin Chronicle: <http://www.austinchronicle.com/gyrobase/Issue/story?oid=oid:795602>

Hach Company. (2005). *DR/4000 Procedure, Nitrogen, total*. Hach Company.

Lawler, D. F., & Hughes, M. P. (2009). *Optimizing Denitrification at Austin's Walnut Creek Wastewater Treatment Plant to Improve Plant Performance*. University of Texas, Austin.

OI Analytical. (2009). *Aurora 1030 Combustion TOC Analyzer Operator's Manual*. College Station, TX: OI Analytical.

Rusten, B., Hem, L. J., & Storhaug, R. (2005). *Nitrifikasjonshemming på biologiske renseanlegg*. Oslo, Norway: Aquateam.

Scott, R. (n.d.). (Atlantic States Rural Water & Wastewater Association) Retrieved 5 8, 2010, from <http://www.cwpaa.org/Basic%20Nitrogen.htm>

Suthersan, S. S. (1996). *Remediation Engineering: Design Concepts* (1st ed.). Boca Raton, FL: CRC Press LLC.

Tchobanoglous, G., Burton, F. L., & Stensel, H. D. (2003). *Wastewater Engineering: Treatment and reuse* (4th ed.). New York, NY: McGraw-Hill.

Wang, L. K., Pereira, N. C., & Hung, Y. (2008). *Biological Treatment Processes: Volume 8* (1st ed.). New York, NY: Humana Press.

**Appendix**

Appendix A.....Chemical solutions

Raw data is available in the included files.

## Appendix A: Chemical solutions

### A.1. Preparation of BOD<sub>5</sub> dilution water

#### a) Phosphate buffer solution

Dissolve 42.5 g KH<sub>2</sub>PO<sub>4</sub> and 1.7 g NH<sub>4</sub>Cl in about 700 mL DI. Adjust pH to 7.2 with 30% NaOH and dilute to 1 L.

#### b) Magnesium sulfate solution

Dissolve 22.5 g MgSO<sub>4</sub>·7H<sub>2</sub>O in DI and dilute to 1 L.

#### c) Calcium chloride solution

Dissolve 27.5 g CaCl<sub>2</sub> in DI and dilute to 1 L.

#### d) Ferric chloride solution

Dissolve 0.25 g FeCl<sub>3</sub>·6H<sub>2</sub>O in DI and dilute to 1 L.

### A.2. Preparation of COD vial solution

#### a) Digestion solution, mid range

Add to about 500 mL DI 5.62 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, primary standard grade, previously dried at 150°C for 2 h, 167 mL concentrated H<sub>2</sub>SO<sub>4</sub>, and 33.3 g HgSO<sub>4</sub>. Dissolve, cool to room temperature, and dilute to 1 L.

#### b) Sulfuric acid reagent

Add Ag<sub>2</sub>SO<sub>4</sub>, technical grade powder, to concentrated H<sub>2</sub>SO<sub>4</sub> at the rate of  $5.5 \text{ g} \frac{\text{AgSO}_4}{\text{kg H}_2\text{SO}_4}$ . Let stand 1 to 2 d to dissolve. Mix.