

5-2010

ENERGY AND NUTRIENT RECOVERY FROM ANAEROBIC TREATMENT OF ORGANIC WASTES

Christian-dominik Henrich
Clemson University, henrichc@web.de

Follow this and additional works at: https://tigerprints.clemson.edu/all_dissertations

 Part of the [Environmental Engineering Commons](#)

Recommended Citation

Henrich, Christian-dominik, "ENERGY AND NUTRIENT RECOVERY FROM ANAEROBIC TREATMENT OF ORGANIC WASTES" (2010). *All Dissertations*. 551.
https://tigerprints.clemson.edu/all_dissertations/551

This Dissertation is brought to you for free and open access by the Dissertations at TigerPrints. It has been accepted for inclusion in All Dissertations by an authorized administrator of TigerPrints. For more information, please contact kokeefe@clemson.edu.

ENERGY AND NUTRIENT RECOVERY FROM ANAEROBIC TREATMENT OF ORGANIC WASTES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Biosystems Engineering

By
Christian-Dominik Henrich
May 2010

Accepted by:
Dr. Charles V. Privette III, Committee Chair
Dr. David E. Brune, Major Advisor
Dr. Young Jo Han
Dr. Arnold G. Eversole

ABSTRACT

The objective of the research was to develop a complete systems design and predictive model framework of a series of linked processes capable of providing treatment of landfill leachate while simultaneously recovering nutrients and bioenergy from the waste inputs. This proposed process includes an “Ammonia Recovery Process” (ARP) consisting of: 1) ammonia de-sorption requiring leachate pH adjustment with lime or sodium hydroxide addition followed by, 2) ammonia re-absorption into a 6-molar sulfuric acid spray-tower followed by, 3) biological activated sludge treatment of soluble organic residuals (BOD) followed by, 4) high-rate algal post-treatment and finally, 5) an optional anaerobic digestion process for algal and bacterial biomass, and/or supplemental waste fermentation providing the potential for additional nutrient and energy recovery. In addition, the value provided by the waste treatment function of the overall processes, each of the sub-processes would provide valuable co-products offering potential GHG credit through direct fossil-fuel replacement, or replacement of products requiring fossil fuels. These valuable co-products include, 1) ammonium sulfate fertilizer, 2) bacterial biomass, 3) algal biomass providing, high-protein feeds and oils for biodiesel production and, 4) methane bio-fuels. Laboratory and pilot reactors were constructed and operated, providing data supporting the quantification and modeling of the ARP. Growth parameters, and stoichiometric coefficients were determined, allowing for design of the leachate activated sludge treatment sub-component. Laboratory and pilot algal reactors were constructed and operated, and

provided data that supported the determination of leachate organic/inorganic-nitrogen ratio, and loading rates, allowing optimum performance of high-rate algal post-treatment. A modular and expandable computer program was developed, which provided a systems model framework capable of predicting individual component and overall performance. The overall systems model software, ENRAT, predicted that a full-scale operation to treat 18,750 L leachate/day would need an Ammonia Recovery process consisting of 88,300 L of total gas transfer column volume, an activated sludge system of 74,417 L, and an algal post treatment raceway of 683 m² (30 cm depth). The ARP would consume 262.5 L/day of 6N sulfuric acid and produce 16.12 kg-N/day ammonium sulfate. The activated sludge system and algal post treatment would produce 900 g-VS/day (or 44.6 L 2% sludge) and 6.83 kg-VS/day (or 341.6 L 2% sludge) of bacterial and algal biomass.

DEDICATION

I dedicate this work to my godfather, Heinrich Gröner.

May he rest in peace.

ACKNOWLEDGEMENTS

I would like to express my appreciation to my advisor, Dr. David Brune, for his guidance and ensuring my graduate work was rewarding and enjoyable. Thanks to the members of my committee, Dr. Charles Privette III, Dr. Thomas Schwedler, Dr. Arnold Eversole, and Dr. Young Jo Han for their advice, insights and review of my manuscript. My thanks goes to Lance Beecher for conducting initial experiments and for his great support at any time. Special thanks goes to Kent Bioenergy for the financial support, cooperative behavior, and for a pilot plant which implemented the majority of this work. This work would not have been possible without your efforts.

I would also like to thank Vickie Byko and Christy Leard for their assistance during the years I studied at Clemson University. Last but not least, I want to thank my family and friends, especially Eva, Bianca, Ernie, Peter, and Andrew for all their encouragement and support.

- Thank you

TABLE OF CONTENTS

	Page
TITLE PAGE.....	I
ABSTRACT	II
DEDICATION.....	IV
ACKNOWLEDGEMENTS	V
LIST OF TABLES	X
LIST OF FIGURES	XIII
1 INTRODUCTION.....	1
1.1 Waste Recycle, Avoidance, and Energy Recovery	1
1.2 Research Objectives	2
2 METHODS	5
2.1 Experimental Design.....	5
2.2 Leachate Composition	6
2.3 Laboratory Water Quality Determination.....	7
2.4 Ammonia Recovery Process	10

2.4.1	Laboratory Scale	10
2.4.2	Pilot Plant.....	12
2.5	Activated Sludge Treatability Study Experimental Apparatus	16
2.6	Algal Post Treatment	17
2.6.1	Laboratory Scale	17
2.6.2	Pilot Plant.....	19
3	AMMONIA RECOVERY PROCESS (ARP).....	20
3.1	Introduction.....	20
3.2	Theoretical Background.....	21
3.2.1	Basification.....	21
3.2.2	De-sorption	23
3.2.3	Absorption.....	29
3.3	Results and Discussion.....	38
3.3.1	De-sorption	38
3.3.2	Absorption.....	48
3.4	Model Equations as used for Computation.....	59
4	ACTIVATED SLUDGE SYSTEM.....	62
4.1	Introduction.....	62
4.2	Treatability Study and Determination of Growth Parameters	64
4.2.1	BOD and Biomass Yield.....	64
4.2.2	Monod Kinetics K_s , μ_{max} , and b_H	67
4.3	Wastewater Characteristics	71
4.3.1	Characteristics of Domestic Wastewater	71
4.3.2	Characteristics of Pretreated Landfill Leachate	73
4.4	Activated Sludge Modeling.....	75
4.4.1	Simple CSTR Mass Balance.....	75

4.4.2	Activated Sludge Model No. 1 (ASM1).....	77
4.5	Model Equations as used for Computation.....	88
4.6	Proposed Activated Sludge Design.....	92
5	ALGAE POST TREATMENT	95
5.1	Introduction.....	95
5.2	Lab Scale Algae Growth Results	96
5.3	Algae Pilot Plant Operation	104
5.4	Model Equations Used for Computation	110
6	OVERALL SYSTEMS MODEL FRAMEWORK ENRAT v1.0	112
6.1	Introduction.....	112
6.2	Model Results	115
7	SUMMARY	124
8	CONCLUSIONS	132
	APPENDICES.....	136
A.	Abbreviations	137
B.	Symbols.....	139
C.	Algae Culture Apparatus.....	142
D.	ENRAT Model Software; ENRAT.JAR	144

LITERATURE CITED146

LIST OF TABLES

Table	Page
1 Sources of experimental data.	5
2 Representative characteristics of landfill site I and II leachate.	6
3 Artificial leachate recipe.	6
4 Algal culture feed composition at varying VFA/NH ₃ -N ratios.	18
5 Dissociation fractions α_0 for the acid-base pair ammonium/ammonia at different ph values.	21
6 Overall gas transfer system parameters.	28
7 Overall gas transfer fluid parameters.	28
8 Ammonium sulfate salt concentrations after neutralization of sulfuric acid by ammonia.	31
9 Reactions, equilibria and rates of the absorption process of ammonia by sulfuric acid.	32
10 Pilot plant de-sorption overall gas transfer coefficients for ammonia.	42
11 Comparison of different air stripping systems and obtained overall gas transfer coefficients.	47
12 Pilot plant overall gas transfer coefficients for ammonia absorption.	57
13 Overall gas transfer coefficients of different ammonia absorption systems.	58
14 Determination of $Y_{H,V/5B}$ and BOD_L for selected samples.	66
15 Kinetic parameters and stoichiometric coefficients measured or assumed for low strength pretreated landfill leachate.	70

Table	Page
16 Characteristics of domestic wastewater, after primary sedimentation.....	71
17 Characteristics of municipal wastewater (in COD and nitrogen-N units).....	72
18 Representative characteristics of landfill site II pretreated leachate in conventional units.....	74
19 Representative characteristics of pretreated leachate (in COD and nitrogen-N units).....	74
20 Model input parameters for a leachate treatment facility treating 500 gal/day of leachate.	115
21 Model output parameters for a leachate treatment facility treating 500 gal/day of leachate.	115
22 Inflows for a leachate treatment facility treating 500 gal/day of leachate.....	116
23 Outflows for a leachate treatment facility treating 500 gal/day of leachate.....	117
24 Model input parameters for a leachate treatment facility treating 5,000 gal/day of leachate.	117
25 Model output parameters for a leachate treatment facility treating 5,000 gal/day of leachate.	118
26 Inflows for a leachate treatment facility treating 5,000 gal/day of leachate.....	118
27 Outflows for a leachate treatment facility treating 5,000 gal/day of leachate.....	119
28 Model input parameters for a leachate treatment facility treating 5,000 gal/day of leachate and one ton/day MOW.	120

Table	Page
29 Model output parameters for a leachate treatment facility treating 5,000 gal/day of leachate and one ton/day MOW.	120
30 Inflows of a leachate treatment facility treating 5,000 gal/day of leachate and one ton/day MOW.	121
31 Outflows of a leachate treatment facility treating 5,000 gal/day of leachate and one ton/day MOW.	121
32 Abbreviations.	137
33 Symbols.	139
34 Indices.	141
35 Materials needed to construct the algal culture apparatus.	142

LIST OF FIGURES

Figure	Page
1 Proposed system design for treatment of landfill leachate.	2
2 Laboratory de-sorption column at Clemson University.	11
3 Laboratory absorption column with acid recycle pump, spray nozzles from top, acid trap on top.	11
4 Laboratory absorption column with acid recycle pump, gas inlet on bottom.	11
5 Laboratory absorption column, flowchart.	11
6 Ammonia Recovery Process pilot plant flowchart.	13
7 Ammonia Recovery Process at "landfill site II", showing green de- sorption and absorption columns on the left and the blue leachate storage tank in the back.	14
8 Ammonia Recovery Process at "landfill site II", showing green de- sorption and absorption columns.	14
9 Internal view of absorption column showing spray nozzles.	15
10 Internal view of de-sorption column showing spray nozzles.	15
11 Ammonia Recovery Process at "landfill site II", showing green absorption columns and acid spray pumps.	15
12 Ammonia Recovery Process at "landfill site II", showing green de- sorption columns and leachate recycle pumps.	15
13 Two liter aerated flasks in temperature controlled greenhouse enclosure.	17

Figure	Page
14 Temperature controlled algal culture apparatus with A/C unit.....	17
15 Pilot plant high-rate algal post treatment units operated by Kent Bioenergy located at landfill site II.	19
16 Proposed system design for treatment of landfill leachate; ARP is highlighted.....	20
17 Ammonia de-sorption from raw and synthetic leachate.	38
18 Leachate ammonia concentration vs. time obtained from lab scale stripping column at room temperature.	39
19 Leachate ammonia concentration vs. time obtained from lab scale stripping column at room temperature.	40
20 Leachate ammonia concentration vs. time obtained from lab scale stripping column at room temperature.	40
21 Predicted leachate retention time versus removal efficiency for air stripping at k_La ranging from 0.001 to 0.040 min^{-1}	41
22 Leachate ammonia concentration vs. time obtained from pilot plant stripping columns.	43
23 Leachate ammonia concentration vs. time obtained from pilot plant stripping columns.	43
24 Leachate ammonia concentration vs. time obtained from pilot plant stripping columns.	44
25 Leachate ammonia concentration vs. time obtained from pilot plant stripping columns in November 2009 through January 2010.....	45
26 Ammonia removal in % from raw leachate vs. time obtained from pilot plant stripping columns in November 2009 through January 2010.....	46

Figure	Page
27 Ammonia absorption rate vs. ammonia concentration in gas phase in laboratory absorption column.....	49
28 Ammonium in sulfuric acid solution vs. time in laboratory absorption column.	49
29 Ammonia absorption rate vs. ammonia concentration in gas phase in laboratory absorption column.....	50
30 Ammonium in sulfuric acid solution vs. time in laboratory absorption column.	50
31 Ammonium in sulfuric acid solution vs. time in laboratory absorption column, constant ammonia inflow of 1.5 ppm, at room temperature.....	52
32 Ammonium in sulfuric acid solution vs. time in laboratory absorption column, constant ammonia inflow of 220 ppm, at ~80°C.....	52
33 Acid neutralization, batch simulation.....	53
34 Predicted gas retention time versus removal efficiency for ammonia absorption at k_{La} ranging from 5 to 50 min^{-1}	55
35 Ammonium in sulfuric acid solution vs. time obtained from pilot plant stripping columns in November 2009 through January 2010 for column 7 and 9.	56
36 Ammonium in sulfuric acid solution vs. time obtained from pilot plant stripping columns in November 2009 through January 2010 for column 8 and 10.	56
37 Proposed system design for treatment of landfill leachate; Activated Sludge treatment is highlighted.	62
38 BOD vs. time of Landfill site I leachate.	65

Figure	Page
39 BOD vs. time of Landfill site II leachate.	65
40 Bacterial growth vs. time on landfill site I leachate.	68
41 Bacterial growth vs. time on landfill site II leachate.	68
42 Schematic diagram of a CSTR, with biomass withholding (SRT \neq HRT) (adopted from Grady et al., 1999).....	75
43 Schematic diagram of biomass growth, including death and lysis of biomass, and hydrolysis of particulate organic matter (adopted from Grady et al., 1999).	77
44 Activated sludge CSTR design for a system treating landfill site II leachate; oxygen input, heterotrophic biomass, autotrophic biomass, ammonia, nitrate, and soluble substrate vs. SRT; with and without nitrification inhibitor input; HRT=3 hr, V=7500 L.	93
45 Proposed landfill leachate treatment system with algal post treatment highlighted.	95
46 Algal culture average start biomass vs. time, with feed VFA/NH ₃ -N ratios of 0.75, 1.35, 2.73, and 4.0 and 20 mg/L-day NH ₃ -N.	97
47 Algal culture average productivity vs. time, with feed VFA/NH ₃ -N ratios of 0.75, 1.35, 2.73, and 4.0 and 20 mg/L-day NH ₃ -N.	97
48 Algal culture average nitrogen uptake vs. time, with feed VFA/NH ₃ -N ratios of 0.75, 1.35, 2.73, and 4.0 and 20 mg/L-day NH ₃ -N.	98
49 Algal culture average nitrogen uptake and biomass gain vs. feed VFA/NH ₃ -N ratio.....	98
50 Algal cultures average nitrogen balance vs. feed VFA/NH ₃ -N ratio.	101

Figure	Page
51 Drawings of algal culture appearance in a microscope for different feed VFA/NH ₃ -N ratios of 0.75(1), 1.35(2), 2.73(3), 4(4) compared to observed cell health.....	102
52 Algae in pilot plant post treatment tank during start-up phase, 40x*10x.....	104
53 Algae in pilot plant post treatment tank during exponential and maturation phase, 40x*10x.....	105
54 Algae in pilot plant post treatment tank during decay phase, 40x*10x	106
55 Pilot plant algal post treatment at landfill site II end of February 2010, Unit #1 through #8 (from left to right); directly after sampling (Kent Bioenergy).....	107
56 Pilot plant algal post treatment at landfill site II end of February 2010, Unit #1 through #8 (from left to right); five minutes after sampling (Kent Bioenergy).....	107
57 Pilot plant algal post treatment at landfill site II beginning of March 2010, Unit #1 through #8 (from left to right); directly after sampling (Kent Bioenergy).	108
58 Pilot plant algal post treatment at landfill site II beginning of March 2010, Unit #1 through #8 (from left to right); ten minutes after sampling (Kent Bioenergy).	108
59 Flow diagram of unit operations described by the model "ENRAT".	113
60 Schematic drawing of the algae algal culture apparatus.	143
61 Algal culture apparatus.....	143
62 Heating chamber of the algal culture apparatus.....	143
63 Graphical Interface of ENRAT v1 in MainWindow.java.....	144

1 INTRODUCTION

1.1 Waste Recycle, Avoidance, and Energy Recovery

The Industrial Revolution of the mid-19th century has dramatically changed the volume and decomposability of wastes produced by modern society. Prior to the 20th century most people reused, repaired, or recycled personal possessions both out of necessity and as a part of a greater appreciation of family legacy and heirloom valuation. Mass production in the second half of the 20th century has been resulting in massive increases in product consumption and consequently, waste production, since items now designed to last a limited period of time are thrown away rather than reused. As a result of practices of a “throw-away society” combined with exponentially expanding population, energy resources and raw materials are becoming increasingly scarce. Environmentally threatening landfills are increasing, being filled and/or closed down. Modern engineered landfills are being built on more limited footprints increasing waste disposal costs. As costs rise and availability of space for new landfills declines, attitudes towards "garbage" are rapidly changing with the focus shifting to view trash as a raw material to be reclaimed and converted into useful products or for energy recovery as opposed to disposal and entombment. Long term sustainability has become the mandate of the 21st century with sustainability defined as:

"Development, meeting the needs of the present, without compromising the ability of future generations to meet their needs"(WSDE, 2008)"

In the specific case of landfills and leachate generation associated with landfills, this approach implies a search for improved methods for disposal avoidance, or wastes recycling and energy recovery. This research focused on development of systems and processes supporting the goal of moving towards a more sustainable society.

1.2 Research Objectives

The primary objective of this research was to develop a total systems design and predictive model framework of a series of linked processes capable of providing complete treatment of landfill leachate while simultaneously recovering nutrients and bioenergy from the waste inputs. The proposed system flowchart is illustrated below (Figure 1).

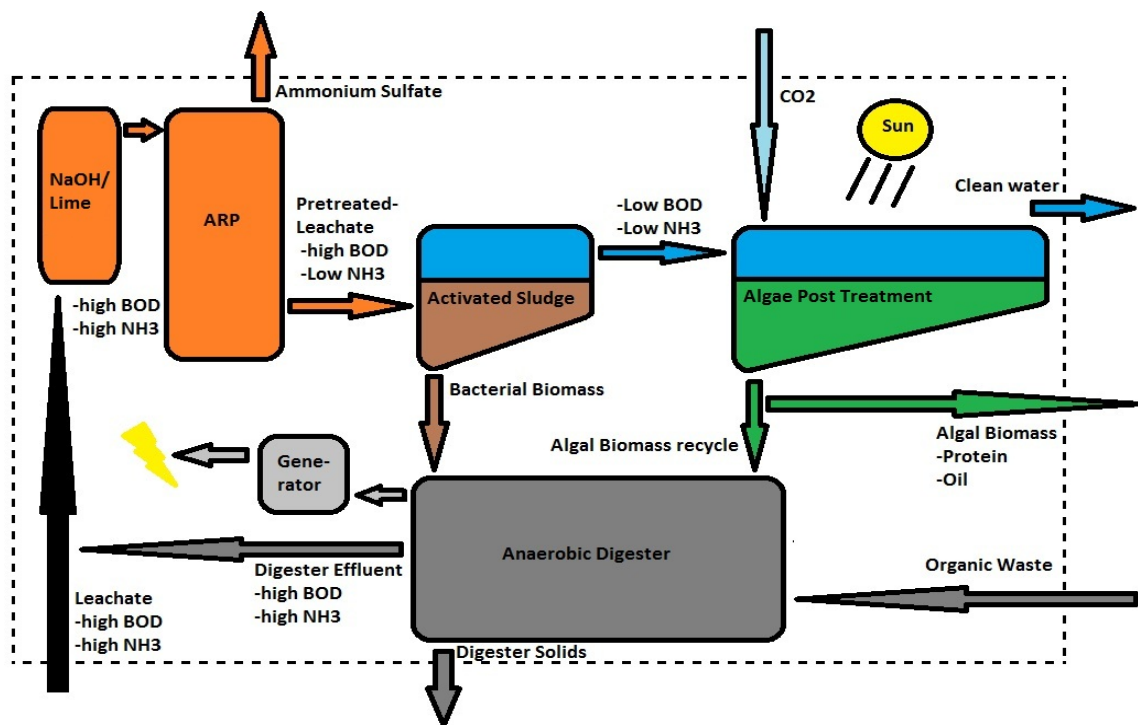


Figure 1: Proposed system design for treatment of landfill leachate.

This proposed process includes an “Ammonia Recovery Process” (ARP) consisting of: 1) ammonia de-sorption requiring leachate pH adjustment with lime or sodium hydroxide addition followed by, 2) ammonia re-absorption into a 6 N sulfuric acid spray-tower followed by, 3) biological activated sludge treatment of soluble organic residuals (BOD) followed by, 4) high-rate algal post-treatment and finally, 5) an optional anaerobic digestion process for algal and bacterial biomass, and supplemental waste fermentation providing the potential for additional nutrient and energy recovery.

In addition to the value provided from the waste treatment function of the overall processes, each of the sub-processes would provide valuable co-products offering potential GHG-credit through direct fossil-fuel replacement, or replacement of products requiring fossil-fuels. These valuable co-products include, 1) ammonium sulfate fertilizer, 2) bacterial biomass, 3) algal biomass providing, high-protein feeds and oils for biodiesel production and, 4) methane bio-fuels.

Specific sub-objectives of this research included:

- a) Construction and operation of laboratory and pilot scale reactors, providing data supporting the quantification and modeling of the “Ammonia Recovery Process.”
- b) Determination of growth parameters, and stoichiometric coefficients, allowing for design development of the leachate activated sludge treatment sub-component.
- c) Construction and operation of laboratory and pilot-scale algal reactors providing data supporting the determination of leachate organic/inorganic-nitrogen ratios,

- and loading rates allowing optimum performance of high-rate algal post-treatment.
- d) Development of a modular, expandable computer program (using Java) providing a systems model framework capable of predicting individual component and overall system performance.

2 METHODS

2.1 Experimental Design

Lab scale experiments were conducted at Clemson University using landfill leachate coming from two different landfill sites. Locations of these two landfills are not disclosed at request of the research sponsor. The first landfill site will be referred to as landfill site I, producing a high strength leachate, and the second landfill, will be referred to as landfill site II, producing a low strength leachate. The leachate treatment pilot plant was installed and operated at landfill site II during summer 2009. The source of experimental data is shown below.

Table 1: Sources of experimental data.

Process	Scale	Leachate/ ammonia source	Date	Location
Ammonia Recovery				
De-sorption	Laboratory	Synthetic	Fall 2008	Clemson U.
	Laboratory	Landfill site I	Spring 2009	Clemson U.
	Pilot plant	Landfill site II	Nov. 2009 - Jan. 2010	Landfill site II
Absorption	Laboratory	Synthetic	Fall 2008	Clemson U.
	Laboratory	Landfill site I	Spring 2009	Clemson U.
	Laboratory	Cylinder	Summer 2009	Clemson U.
	Pilot plant	Landfill site II	Nov. 2009 - Jan. 2010	Landfill site II
Activated sludge				
	Laboratory	Landfill site II	Fall 2009 - Spring 2010	Clemson U.
Algal post treatment				
	Laboratory	Digester effluent	Spring 2007	Clemson U.
	Pilot plant	Landfill site II, synthetic	Fall 2009 and Spring 2010	Landfill site II

2.2 Leachate Composition

Table 2 shows a comparison of representative characteristics of leachate from landfill site I and II (high and low strength) leachate.

Table 2: Representative characteristics of landfill site I and II leachate.

Symbol	Name	Landfill site I (high strength)	Landfill site II (low strength)	Unit
TSS	Total Suspended Solids	1,900	500	mg/L
VSS	Volatile Suspended Solids	600	230	mg/L
BOD ₅	Five day Biological Oxygen Demand	3,500	500	mg-O ₂ /L
COD _t	Total Chemical Oxygen Demand	12,000	1,000	mg/L
TAN	Total Ammonia Nitrogen	2,300	900	mg-N/L
TKN	Total Kjeldahl Nitrogen	2,600	1,000	mg-N/L
NO _x	Nitrate-Nitrite Nitrogen	0	0	mg-N/L
ALK	Alkalinity	12,500	6,900	mg- CaCO ₃ /L

For initial experimental trials an artificial leachate was produced. This artificial leachate was designed to simulate a high strength landfill leachate (Table 3).

Table 3: Artificial leachate recipe.

Reagent	Concentration
ammonium acetate	128 meq/L
ammonium bicarbonate	72 meq/L
sodium bicarbonate	51 meq/L
Yielding:	
NH ₃ -N	2800 mg/L
Alkalinity	12,556 mg/L (as CaCO ₃)
Volatile Fatty Acids	7680 mg/L (as HAC)

(Empirical recipe, based on D.E. Brune and L. Beecher)

2.3 Laboratory Water Quality Determination

Water quality determinations included temperature, pH, alkalinity, total phosphorous, dissolved oxygen, ammonia nitrogen, total nitrogen, TSS, VSS, FS, and metals with procedures and material requires as listed below.

Temperature

Temperature measurements were obtained using a HACH HQ40D multimeter with a HACH LDO 101 probe (1 to 200% saturation; 0.1-20 mg/L; ± 0.1 mg/L for 0-8 mg/L, ± 0.2 mg/L for >8 mg/L) integrated temperature meter.

PH

PH measurements were obtained using a HACH HQ40D multimeter with a HACH PHC101 pH probe (2.0-14.0 pH $\pm 0.5\%$).

Alkalinity

Water Alkalinity was determined using a HACH sulfuric acid digital titrator with bromocresol green-methyl red packets for colorimetrically determination of alkalinity.

Total Phosphorous

To measure total phosphorous the HACH Phosphorous, total reagent set (test n tube) PhosVer^(TM) 3 Acid Persulfate Digestion method(0.01 -3.50 mg-P/L) was used.

Dissolved Oxygen (DO)

DO measurements were obtained using a HACH HQ40D multimeter with a HACH LDO 101 probe (1 to 200% saturation; 0.1-20 mg/L; ± 0.1 mg/L for 0-8 mg/L, ± 0.2 mg/L for >8 mg/L) integrated temperature meter.

TAN (Total Ammonia Nitrogen)

During laboratory experiments TAN measurements were obtained using the HACH AmVer High Range Ammonia (0-50 mg-N/L) kit, Reagent set 26069-45. Pilot plant ammonia measurements were conducted using an Oakton Ion6 Acorn Series Ion meter for measuring ammonia (1×10^{-6} M - 1M $\text{NH}_3\text{-N}$).

Total Solids(TS), Volatile Solids(VS), and Total non Volatile Solids(TNVS)

TSS, VSS and TNVS analysis were performed by using methods outlined in APHA (1995) were, 90 mL of raw sample were centrifuged at 14,000 rpm for 7 minutes, the supernatant was disposed, the precipitant was re-suspended in de-ionized-water, filled into a weighted crucible and dried for 24 hours in the 105°C oven, and then weighted again. Finally the crucible with dried sample was burned for 2 hours in the 500°C oven and weighted again. Total solids, non volatile solids and volatile solids were calculated using equation (1).

$$\text{Total solids} = \text{weight}(\text{crucible with dried sample}) - \text{weight}(\text{crucible})[\text{g}] \quad (1)$$

$$\text{Non volatile s.} = \text{weight}(\text{crucible with burned sample}) - \text{weight}(\text{crucible})[\text{g}]$$

$$\text{Volatile solids} = \text{Total solids} - \text{Non volatile solids}[\text{g}]$$

Total Kjeldahl Nitrogen (TKN)

If located at landfill site II, samples were sent to Mid-Atlantic Laboratories, 224 Main St., Port Royal, VA 22535, (804) 742-5577 for determination of the Total Kjeldahl Nitrogen. Samples from laboratory experiments originating from activated sludge treatability studies at Clemson University were brought to the Agricultural Service

Laboratory, 171 Old Cherry Rd, Clemson, SC, 29634, for determination of the Total Kjeldahl Nitrogen using method described in UW-Extension (2003).

Five-day Biological Oxygen Demand (BOD₅)

The five-day Biological Oxygen Demand was measured using a respirometer obtained from Challenge technology, Inc, entitled the "Quick Scan BOD Analyzer" over a period of five days. Nitrification inhibitor (Cat. 2533-35) obtained from HACH Chemical Co. was used to suppress nitrifying organisms. If located at landfill site II, samples were sent to Mid-Atlantic Laboratories, 224 Main St., Port Royal, VA, 22535, (804) 742-5577, for the BOD measurement.

Volatile Fatty Acids (VFA)

Volatile fatty acids were adsorbed on a column of silicic acid, followed by elution with n-butanol in chlorophorm. The eluate was collected and titrated with standard base. All short-chain (C₁-C₆) organic acids eluted by this solvent system were reported collectively as total volatile fatty acids.

2.4 Ammonia Recovery Process

2.4.1 Laboratory Scale

De-sorption

A laboratory-scale ammonia de-sorption column was designed, constructed and operated at Clemson University. This column was built out of PVC pipe with a diameter of 12 inches (30 cm). The column was filled with 8 L of synthetic leachate and ~20 mL/L 10N sodium hydroxide was added for basification. To start the de-sorption process air at 1 to 5 ft³/min (28 to 140 L/min) (depending on experiment) was blown through the liquid (Figure 2). Lab scale de-sorption data were used to develop and confirm the model equations under small scale conditions.

Absorption

The absorption column at Clemson University was built out of acrylic in a rectangular shape. The column was 3.5 ft (1.05 m) high and its volume was 21 gallons (79 L). The column sump contained 4 L of 6 N sulfuric acid. A pressure pump from SHURflow (Model No. 8000-543-238) recycled acid from the sump through three spray nozzles (Uni Jet Tx size 4 at 75 PSI, with 3.9 gal/hr (14.6 L/hr) each from Spraying Systems Co.) (Figure 3 to Figure 5). The ammonia laden entered from the bottom, passed by the acid mist and exited through an acid trap at the top. Lab scale absorption data was used to develop and confirm the model equations under small scale conditions.



Figure 2: Laboratory de-sorption column at Clemson University.



Figure 3: Laboratory absorption column with acid recycle pump, spray nozzles from top, acid trap on top.



Figure 4: Laboratory absorption column with acid recycle pump, gas inlet on bottom.

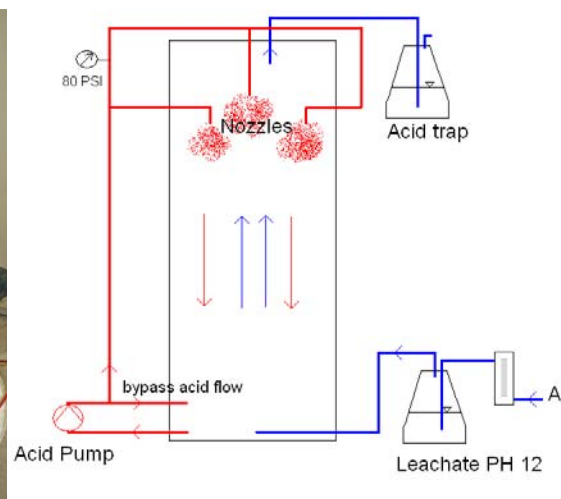


Figure 5: Laboratory absorption column, flowchart.

2.4.2 Pilot Plant

De-sorption Columns

The pilot plant de-sorption columns at landfill site II contain spray-nozzles spraying the leachate from the top, while air enters from the bottom (Figure 6 to Figure 12). These columns are 9 ft (2.7 m) high and 24 inch (60 cm) in diameter. Five spray nozzles (1" FullJet, size 4.2 from Spraying systems Co.) allow a flow of 4.9 gallons per minute (18.4 L/min) at 10 PSI each. Therefore, the total internal leachate recirculation was about 30 gal/min (112 L/min) (with 100 L leachate per column, leachate was recirculated about once per minute). The airflow was 3700 L/min, resulting in a residence time of 0.12 minutes (5 seconds) per column. Six columns are setup in a row where raw leachate is entering at column 1 and air is entering in column 6 in countercurrent flow (Figure 6). Each column operated for 60 minutes before the leachate was passed to the next column, and pretreated leachate exiting column 6 was neutralized and moved to a storage tank for further treatment (semi-batch process total treatment of 6x60 minutes). About 15 g/L of 50% sodium hydroxide solution was added to column 1 when raw leachate was filled in. The ammonia laden gas was routed to the absorption columns.

Absorption Columns

Pilot scale absorption columns at landfill site II are 9 ft (2.7 m) high and 24 inch (60 cm) in diameter. Ten spray nozzles (1/8" FullJet, size 1 from Spraying systems Co.) allow a flow of 0.29 gallons per minute (1 L/min) at 100PSI each (Figure 6 to Figure 12).

The absorption side of the ARP at landfill site II was setup in two rows of 3 columns each. Therefore, ammonia laden gas at 3700 L/min from the de-sorption process was divided into two streams of 1850 L/min per set of columns. The first two columns in each set were spraying sulfuric acid, and the third column was spraying water to wash air of possible exiting acid drops. Acid or water (100 L) was placed in each column, and with a total of 10.8 L/min spray, recirculated about once every 10 minutes.

Pilot scale setup data from operation at landfill site II in November 2009 through January 2010 were used to confirm the developed model equations and evaluate process for a full scale operation.

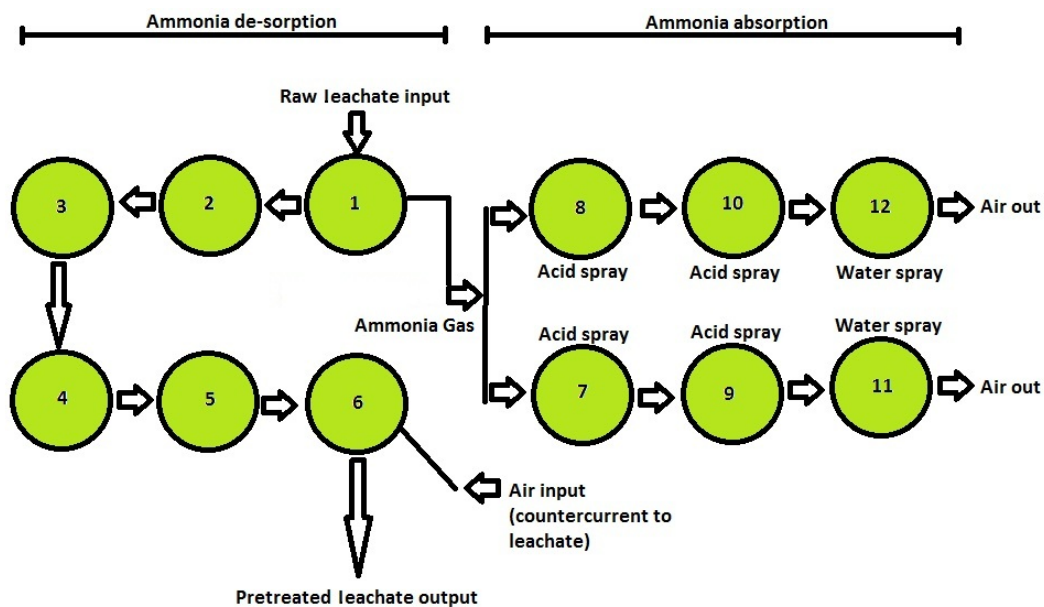


Figure 6: Ammonia Recovery Process pilot plant flowchart.



Figure 7: Ammonia Recovery Process at "landfill site II", showing green de-sorption and absorption columns on the left and the blue leachate storage tank in the back.



Figure 8: Ammonia Recovery Process at "landfill site II", showing green de-sorption and absorption columns.



Figure 9: Internal view of absorption column showing spray nozzles.



Figure 10: Internal view of de-sorption column showing spray nozzles.



Figure 11: Ammonia Recovery Process at "landfill site II", showing green absorption columns and acid spray pumps.



Figure 12: Ammonia Recovery Process at "landfill site II", showing green de-sorption columns and leachate recycle pumps.

2.5 Activated Sludge Treatability Study Experimental Apparatus

Heterotrophic growth curves were determined using a respirometer obtained from Challenge technology, Inc, entitled the "Quick Scan BOD Analyzer" over a period of five days. Nitrification inhibitor (Cat. 2533-35) obtained from HACH Chemical Co. was used to suppress nitrifying organisms. After quantification of oxygen demand of leachate, the yield coefficient was determined by dividing accumulated biomass after 5 days by the 5-day biological oxygen demand as mg-VS/mg-BOD₅. Bacterial biomass over time was calculated by multiplying the measured oxygen demand with the yield coefficient.

2.6 Algal Post Treatment

2.6.1 Laboratory Scale

Algal Culture Apparatus

Algae growth trials were conducted in a temperature controlled 1.2 x 1.2 m greenhouse, covered by light penetrable covering. Algae cultures were grown at 25°C. Flasks were individually aerated and supplied with carbon dioxide to control pH. The greenhouse provided space for 16 2-L Erlenmeyer flasks (Figure 13 and Figure 14).

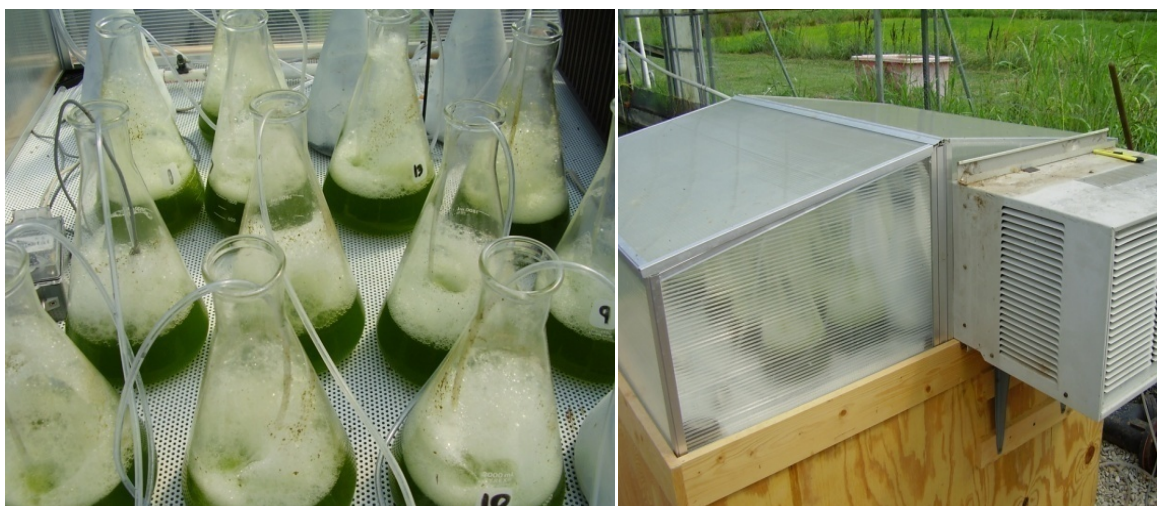


Figure 13: Two liter aerated flasks in temperature controlled greenhouse enclosure.



Figure 14: Temperature controlled algal culture apparatus with A/C unit.

In appendix C the setup is described in more detail.

Experimental Setup

The ratio of volatile fatty acid concentration (VFA) to ammonia concentration in the modified digester effluent used as a nutrient feed source for growing the algae was varied from a range of 0 to 4. The temperature was held at 25°C. A carbon dioxide/air mixture was supplied to the culture by air diffusers to maintain pH at pH7 and to mix algal cultures. Table 4 illustrates algal growth trial feed compositions, VFA/NH₃-N ratios, and BOD equivalents. Four flasks were setup for each feed composition, one of each was painted black as control to allow a comparison of heterotrophic vs. photoautotrophic growth.

Table 4: Algal culture feed composition at varying VFA/NH₃-N ratios.

Parameter	Feed ratio: 0.75	1.35	2.73	4
Ammonia, mg/L	1607	1445	1571	1489
Fatty acid, mg/L	1173	1951	4370	5958
BOD₅, mg/L	1450	2418	5418	7388
BOD₅/ Ammonia ratio	0.90	1.67	3.45	4.96
BOD₅/ VFA	1.24			

During an initial “acclimation phase” the algal cultures were fed with an ammonium chloride solution supplying 20 mg-N/L and 0.5 mL of digester effluent supplying minor nutrients. After the acclimation phase, feed VFA to ammonia-N ratios were adjusted to: 0.75, 1.35, 2.73, and 4.0 with 20 mg-N/L-day ammonia added to each reactor. The cell and hydraulic age was maintained at 3 days by one third water exchange per day.

2.6.2 Pilot Plant

At landfill site II, eight algal raceways were set up for algal post treatment of pretreated leachate; each containing 8000 L of water at 40 cm depth. The reactors were constructed from carbon fiber and the liquid was mixed with stainless steel paddle wheels (Figure 15). These algal reactors were operated by Kent Bioenergy at landfill site II, and data were provided for integration into this work.



Figure 15: Pilot plant high-rate algal post treatment units operated by Kent Bioenergy located at landfill site II.

3 AMMONIA RECOVERY PROCESS (ARP)

3.1 Introduction

The proposed ARP is a three step process.

- 1) Adjustment of leachate-pH to > 11.0 (referred to as “basification”) with addition of 20 ml/L of 10 N sodium hydroxide converting ammonium-N to volatile ammonia-N.
- 2) Ammonia-N de-sorption using air stripping.
- 3) Ammonia recapture/ absorption by routing ammonia laden gas through 6 N sulfuric acid spray resulting in an ammonium sulfate solution suitable for use as plant fertilizer.

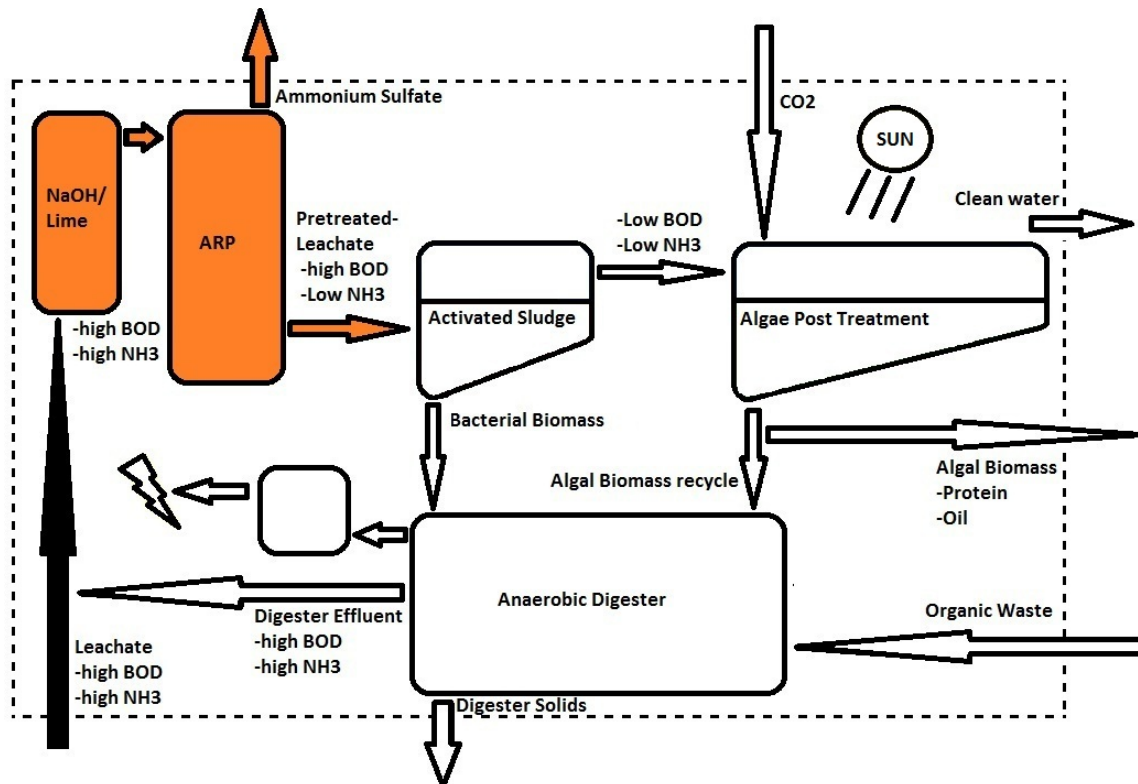


Figure 16: Proposed system design for treatment of landfill leachate; ARP is highlighted.

3.2 Theoretical Background

3.2.1 Basification

Transferring soluble ammonium (NH_4^+) from wastewater to air and then to another liquid (sulfuric acid solution), requires that the ammonium first be converted into its volatile form, ammonia (NH_3). Ammonium/Ammonia is a weak acid/base-pair and dissociates in water according to the pH of the solution and its acid constant K_a (Körner et al., 2001).

For acids and bases the dissociation fraction is defined as:

$$\alpha_{0,i} = \frac{[H^+]}{[H^+] + K_{a,i}} \quad (\text{Weak acids and bases}) \quad (2)$$

$$\alpha_0 = 1 \quad (\text{Strong acids and bases})$$

Where α_0 is the dissociation fraction, $[H^+]$ is the concentration of hydrogen-ions, and $K_{a,i}$ is the acid dissociation constant of the component i.

In case of ammonium/ammonia, with at a pka of 9.3 and using equation (2) the dissociation fraction at various pH values can be calculated and are given in Table 5.

Table 5: Dissociation fractions α_0 for the acid-base pair ammonium/ammonia at different pH values.

pH [-]	α_0 [-]	pH [-]	α_0 [-]
14	0.000020	7	0.995013
13	0.000199	6	0.999499
12	0.001991	5	0.999950
11	0.019562	4	0.999995
10	0.166338	3	0.999999
9	0.666139	2	1.000000
8	0.952273	1	1.000000

This suggests that at a pH of 9.3 50% of ammonia in water is present in its protonated form as ammonium and 50% in its de-protonated form as ammonia. At pH >11 essentially 100% of ammonium-N is present in its de-protonated form of free ammonia, which is a gas and if allowed it will volatilize from the solution.

Leachate “basification” can be achieved using a variety of strong bases, for example sodium hydroxide or calcium hydroxide (lime). If lime is used to raise the pH of the ammonium enriched wastewater, the calcium ion may form insoluble complexes with metals or other molecules, yielding a precipitate. This precipitate needs to be removed before the leachate moves downstream to avoid scaling and fouling of equipment. (Abbas et al., 2009, Marttinen et al., 2002). The primary advantage of using lime as the basification agent is its low cost and its ability to remove heavy metals from the wastewater. Sodium hydroxide provides more rapid pH adjustment, and does not form an insoluble precipitant; the major disadvantage being the higher price. For modeling and lab scale experimental purposes sodium hydroxide was used, to avoid precipitant formation.

3.2.2 De-sorption

De-sorption means the use of ammonia-N air stripping. Unlike conventional air stripper systems ammonia is not released into the atmosphere. Rather, it is re-captured in a subsequent acid absorption unit.

In this proposed process the leachate, having previously been adjusted to a pH > 11, is either bubbled with air at flow-rates of 1 to 18 ff³/min or is sprayed in a countercurrent air/leachate column. During the contact period ammonia-N transfers from the liquid phase into the gas phase. In the pilot-scale system, the process is carried out in a spray column, where the leachate was sprayed from the top of the column, and air is entered from the bottom of the column. The rate-limiting step in ammonia transfer from the liquid phase to the gas phase occurs at the gas/liquid boundary layer resisting the gas transfer. If the concentration of ammonia-N in gas phase is assumed to be in equilibrium with the concentration of the ammonium-N in the liquid phase, then gas transfer rate in a batch air-stripper system can be predicted using the equations developed by Mutter-Müller et al. (1981);

$$-\ln\left(\frac{C_{i,t}}{C_{i,0}}\right) = \frac{Q_{gas} * K_{H,i}}{V_{Liquid}} \left[1 - e\left(\frac{-k_L a * V_{Liquid}}{K_{H,i} * Q_{gas}}\right) \right] * t \quad (3)$$

where $C_{i,t}$ and $C_{i,0}$ are the liquid phase concentrations of compound i initially and at time t in mg/L, $K_{H,i}$ is the Henry's law constant for compound i, $k_L a$ is the overall gas

transfer coefficient in min^{-1} , V_{Liquid} is the volume of the liquid in L, Q_{gas} is the gas flow in L/min, and t is the stripping time in min.

However, if the concentration of compound i in effluent gas is far from its saturation concentration ($k_L a V_{Liquid} / K_{H,i} Q_{gas} \ll 1$), then equation (3) reduces to:

$$-\ln\left(\frac{C_{i,t}}{C_{i,0}}\right) = k_L a * t \quad \text{or} \quad \frac{C_{i,t}}{C_{i,0}} = e^{-k_L a * t} \quad (4)$$

At very short residence times of gas inside the stripping tower (when the concentration of ammonia in the gas phase approaches zero), and ammonia being an highly soluble gas, equation (4) best describes the rate of transfer for the proposed system. Therefore the ammonia-N transfer rate could be described as:

$$\frac{dC}{dt} = k_L a * (\Delta C) = k_L a * (C_{liquid} - C_{gas}) \quad (5)$$

Where dC/dt is the change of ammonia over time in mg/L-min, $k_L a$ is an overall gas transfer coefficient in min^{-1} , and ΔC is the ammonia concentration gradient in mg/L.

At sufficiently high air flow rates, the concentration of ammonia in the gas phase approaches zero, and equation (5) reduces to:

$$-r = k_L a * C_{liquid} \quad (6)$$

Where r is the rate of mass transfer out of the liquid in [mg/L-min] at a limiting $C_{gas} \sim 0$ (mg/L).

Under such conditions where the gas has a relatively short residence time in the column and ammonia being a relatively soluble gas, equation (6) would best describe the rate of nitrogen transfer.

Furthermore, the gas and liquid flow through the stripping column can be represented as a continuous plug flow system. Under this assumption the column can be represented as a series of infinitesimally small sections, and applying a nitrogen mass balance yields:

$$Ac * \frac{\partial C}{\partial t} = -\frac{\partial(Q * C)}{\partial x} + r + Ac \quad (7)$$

Where x is the length of an infinitesimal small segment of the column, $\frac{\partial C}{\partial t}$ is the change in ammonia-N concentration over time, $\frac{\partial C}{\partial x}$ is the change of the ammonia-N concentration along the column in the x direction, and Ac is the cross sectional area.

At steady state, equation (7) reduces to:

$$0 = -Q \frac{d(C)}{dx} + r + Ac \quad (8)$$

Where $\frac{d(C)}{dx}$ is the change of ammonia-N concentration in x direction.

If the gas transfer rate from equation (6) is substituted into equation (8) the result is:

$$0 = -Q_{liquid} \frac{d(C_{liquid})}{dx} - k_L a * C_{liquid} + Ac \quad (9)$$

Rearranging and integrating equation (9), yields:

$$\frac{Ac * H}{Q_{liquid}} = \tau_{liquid} = -\frac{1}{k_L a} * (\ln(C_{NH_3 in}) - \ln(C_{NH_3 out})) \quad (10)$$

Where τ_{liquid} is the retention time of the liquid inside the column in min, $C_{NH_3 in}$ and $C_{NH_3 out}$ represent the ammonia concentrations of the liquid entering and exiting the column in mg/L, H is the height of the column in dm, Q_{liquid} is the liquid flow-rate in

L/min, A_c is the cross sectional area in dm^2 , and $k_L a$ is an overall gas transfer coefficient in min^{-1} .

However, in actual practice, the ammonia laden-leachate is recirculated inside the de-sorption column. Recirculation shifts reactor behavior from a plug - flow pattern to that of a completely mixed system. However, equations (3)-(10) remain applicable. The effect of recirculation reduces theoretical height of the column (H in equation (10)) to an “effective” lower column height. For practical purposes the recirculation is considered to be internal, therefore will not be included into the overall mass balance of the system, but its influence is included into the overall gas transfer coefficient. Thus, the retention time in equation (10) represents the time required for the leachate ammonia nitrogen to reach the concentration $C_{NH_3 \text{ out}}$.

The general mass balance for compound i present in the liquid phase, for a completely mixed system, can be written as follows:

$$V * \frac{dC_i}{dt} = Q_{in} * C_{i,in} - Q_{out} * C_{i,out} + r_i * V \quad (11)$$

Where dC_i/dt is the change in concentration of compound i over time in mg/L-min , $C_{i,in}$ and $C_{i,out}$ represents the initial concentration of compound i and concentration of compound i at time t in mg/L , V is the Volume of the reactor in L , and r is the sum of reaction rates of compound i in mg/L-min .

In case of ammonia air-stripping, if gas transfer is assumed as the only rate-limiting reaction, and combining with the relationship representing column liquid retention time:

$$\tau = \frac{V}{Q} \quad (12)$$

the mass balance equation for ammonia-N in the liquid phase can be written as:

$$\frac{dNH_3L}{dt} = (C_{NH_3LO} - C_{NH_3L}) * \frac{1}{\tau_{Liquid}} - k_L a_{desorb} * C_{NH_3L} \quad (13)$$

Where τ_{Liquid} is the residence time of the liquid inside the column in min, $k_L a_{desorb}$ is an overall gas transfer coefficient in min^{-1} , dNH_3L/dt is the change of ammonia concentration in the leachate over time in mg/L-min , and C_{NH_3LO} and C_{NH_3L} are the initial ammonia-N concentration and the ammonia-N concentration at time t in mg/L .

The mass balance for ammonia-N in the gas phase can be written as:

$$\frac{dNH_3GD}{dt} = (C_{NH_3GDO} - C_{NH_3GD}) * \frac{1}{\tau_{Gas}} + (C_{NH_3LO} - C_{NH_3L}) * \frac{1}{\tau_{Liquid}} \quad (14)$$

Where τ_{Gas} is the residence time of the gas inside the column in min, dNH_3GD/dt is the change of ammonia concentration in the gas over time in mg/L-min , and C_{NH_3GDO} and C_{NH_3GD} are the initial ammonia-N concentration and the ammonia-N concentration at time t of the gas phase in mg/L .

The overall gas transfer is dependent on stripper geometry, flow rates, contact time, the gas/liquid interfacial area, and diffusion rate of the gas through the liquid and the gas layers at the interface. The diffusion coefficient is affected by the viscosity of the

liquid, the molecular diameter, and especially the temperature (Saracco and Genon, 1994). Therefore, when a system $k_L a$ has been determined, it is only valid for the system configuration as measured and combines all effects in one overall coefficient. The main design parameters impacting the $k_L a$ will be air/liquid surface area and volume ratio of the gas/liquid interface (smaller drops) and degree of mixing. A change in retention time of the gas will change the $k_L a$ in both ways, since it changes the contact time and the degree of mixing, or turbulence, within the system. System properties and fluid parameters impacting gas transfer rates are summarized in Table 6 and Table 7.

Table 6: Overall gas transfer system parameters.

Parameter	Increasing $k_L a$	Decreasing $k_L a$
Transfer system(i.e., spray, plates, media)	Increasing surface area	Dec. surface area
Gas flow	Higher Turbulence	Lower turbulence
Recirculation of liquid	Multiple effects	Multiple effects
Dead zones and short circuit	Reduced	Increased

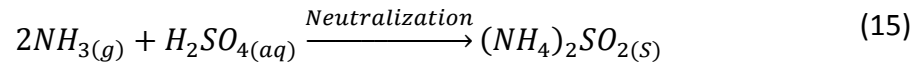
Table 7: Overall gas transfer fluid parameters.

Parameter	Increasing $k_L a$	Decreasing $k_L a$
Temperature	Increased diffusion	Decreased diffusion
Turbulence	Dec. layer thickness	Inc. layer thickness
Viscosity	Dec. layer thickness	Inc. layer thickness

Modeling and predicting the influence of each system geometry and dynamic properties would be extremely complicated, and essentially impossible task. Rather, an overall $k_L a$ value is field determined for each specific system configuration.

3.2.3 Absorption

The absorption process uses a 6 normal sulfuric acid solution to capture the ammonia gas produced by the de-sorption unit yielding an ammonium sulfate salt. Air-ammonia gas mixture passes through a sulfuric acid spray-tower or reactor. During the contact period, ammonia gas is absorbed into the acidic liquid phase neutralizing the sulfuric acid to forming ammonium sulfate salt. The overall neutralization reaction is given as:



Two mole of ammonia neutralizes one mole of sulfuric acid producing one mole of ammonium sulfate. The kinetics of the neutralization reaction may be represented as 5 separate reactions. The reactions include gas transfer, acid-base dissociation, ionic attraction and salt precipitation. The first reaction is the transfer of ammonia in gas phase into the liquid acid phase, with ammonia molecules moving gas bulk phase through the gas/liquid boundary layer into the bulk liquid phase. This rate of transfer is given by:

$$\frac{dC}{dt} = k_L a * \Delta C \quad (16)$$

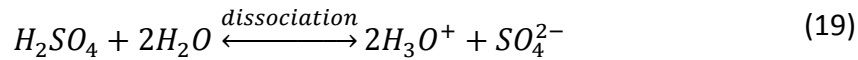
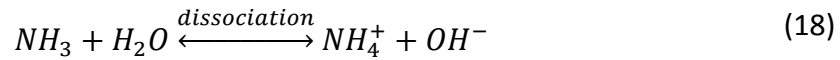
Where dC/dt is the change of ammonia concentration over time in mg/L-min, $k_L a$ is the overall gas transfer coefficient in min^{-1} , and ΔC is the ammonia concentration gradient between gas and liquid phase in mg/L.

The equilibrium concentration of ammonia in the liquid phase in contact with the gas phase is described by Henry's law:

$$P = K_H * C_{liquid} \quad (17)$$

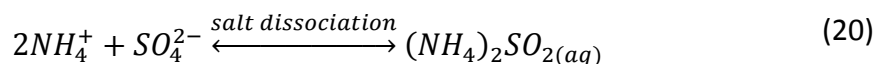
Where C_{liquid} is the ammonia concentration in the liquid phase in mol/L, K_H is the Henry's law constant for ammonia in water at constant temperature in L*atm/mol, and P is the partial pressure of ammonia above the liquid in atm.

The second reaction is acid-base dissociation in water, where sulfuric acid dissociates into hydrogen and sulfate ions, with ammonia dissociation into ammonium and hydroxyl-ions.

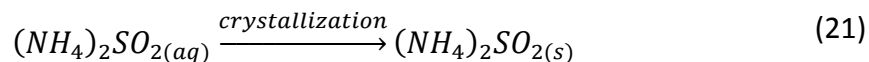


The rate at which this occurs is relatively rapid, since acid-base dissociation is an exothermal process. For this application these reactions are considered to be non-rate limiting. At a solution pH <6, the fraction of NH_4^+ (α_0 would be essentially 100%, therefore the ammonia-N concentration in the acid solution is assumed to be zero). The system will typically operate at pH values < 2, therefore ammonia can be modeled as if it is a strong base.

The third reaction is the formation of salt in solution. The reaction type is ionic attraction represented as:.



This step is also not considered rate limiting, since the dissociated salt will already be in solution after the acid base dissociation process. The final reaction would include crystallization of the dissolved ammonium sulfate. The reaction is represented as:



The rate of this reaction depends upon the solubility product of the salt, defined as:

$$K_{sp,i} = [NH_4^+] * [SO_4^{2-}]^2 \quad (22)$$

Where $K_{sp,i}$ is the solubility product of ammonium sulfate, $[NH_4^+]$ is the molarity of ammonium, and $[SO_4^{2-}]^2$ is the molarity of sulfate to the power of its charge.

For ammonium sulfate the maximum solubility in water at 25°C is 745 g/L (Lide and Heynes, 2010). If the concentration in solution exceeds that maximum solubility, solid crystals will precipitate out of the solution. Table 8 shows the salt concentration appearing after a given sulfuric acid normality was neutralized.

Table 8: Ammonium sulfate salt concentrations after neutralization of sulfuric acid by ammonia.

Initial sulfuric acid concentration	Amount ammonia-N adsorbed per liter acid to be neutralized	Amount of ammonium sulfate produced	Percentage of solubility product reached
Normality	mol/L (g/L)	g/L	%
1	1 mole/L (14g/L)	132	17.6
6	6 mole/L (84g/L)	792	100 + 5% solid salt
18	18 mole/L (252g/L)	2376	100 + 217% solid salt

Therefore, the neutralization of 6 N sulfuric acid by ammonia will slightly be in excess of the maximum solubility of ammonium sulfate at 25 °C.

Processes included into the overall reaction and its rates and equilibria are summarized in Table 9.

Table 9: Reactions, equilibria and rates of the absorption process of ammonia by sulfuric acid.

Reaction	rate dC/dt	equilibrium C ₁ /C ₂
$NH_3(g) \xrightleftharpoons{\text{gas transfer}} NH_3(aq)$	Gas transfer $K_L a \Delta C$	Henry's law ($K_{i,H} * P_i$)
$H_2SO_4(aq) \xrightleftharpoons{\text{acid/base dissociation}} 2H^+ + SO_4^{2-}(aq)$	no resistance	Acid-base dissociation
$NH_3(aq) \xrightleftharpoons{\text{acid/base dissociation}} NH_4^+(aq)$		$\alpha_o = \frac{[H^+]}{[H^+] + [Ka]}$
$2NH_4^+(aq) + SO_4^{2-}(aq) \xrightleftharpoons{\text{ionic attraction}} (NH_4)_2SO_4(aq)$	no resistance	Ionic charge balance
$(NH_4)_2SO_4(aq) \xrightleftharpoons{\text{solid salt formation}} (NH_4)_2SO_4(s)$	no resistance	Solubility product K_{sp}

Henry's law does not control the overall reaction since the equilibrium concentration of ammonium-N in the solution will be essentially zero. Ignoring all non-rate limiting steps the rate of ammonia-gas absorption into the acid solution can be written as:

$$\frac{dC}{dt} = k_L a * (\Delta C) = k_L a * (C_{gas} - C_{liquid}) \quad (23)$$

Where dC/dt is the change of ammonia-N concentration over time in mg/L-min, $k_L a$ is an overall ammonia transfer coefficient in min^{-1} , and ΔC is the ammonia-N concentration gradient in mg/L. Furthermore, the concentration gradient at $\text{pH} \ll \text{pKa}$ is

equal to the concentration of ammonia in the gas phase, since the dissociation of ammonia to ammonium in the liquid phase is essentially 100% complete.

Thus, equation (23) reduces to

$$\frac{dC}{dt} = k_L a * C_{gas} \quad (24)$$

With the limitation of $\text{pH} \ll \text{pKa}$ (or 9.3 for ammonia).

In the acid-column, acid is sprayed from the top, falling to the bottom as a fine acid mist collecting in the column sump. The air, carrying ammonia-gas from the desorption process enters at the bottom of the column rising up the column exiting at the top. Ammonia gas passes the acid mist in a countercurrent flow, providing contact-time between gas-phase and liquid. This flow pattern is represented as a continuous plug flow system. The general mass balance is defined as:

$$Ac * \frac{\partial C}{\partial t} = - \frac{\partial(Q * C)}{\partial x} + r + Ac \quad (25)$$

Where x is the length of an infinitesimally small segment of the column, $\frac{\partial C}{\partial t}$ is the change of ammonia concentration over time, $\frac{\partial C}{\partial x}$ is the change of the ammonia concentration with respect to column height (in x direction), and Ac is the cross sectional area.

At steady state equation(25) reduces to:

$$0 = -Q \frac{d(C)}{dx} + r + Ac \quad (26)$$

Where $\frac{d(C)}{dx}$ is the change of concentration with respect to column height (x direction).

Substitution of the reaction rate, r from equation (24) into equation (26) yields:

$$0 = -Q_{gas} \frac{d(C_{gas})}{dx} + k_L a * C_{gas} + Ac \quad (27)$$

Rearranging and integrating equation (27) produces:

$$\frac{Ac * H}{Q_{gas}} = \frac{V}{Q_{gas}} = \tau_{gas} = \frac{1}{k_L a} * \left(\ln(C_{NH_3 gas in}) - \ln(C_{NH_3 gas out}) \right) \quad (28)$$

Where τ_{gas} is the retention time of the gas inside the column in min, $C_{NH_3 gas in}$ and $C_{NH_3 gas out}$ represent the ammonia concentrations of the gas entering and exiting the column in mg/L, H is the height of the column in dm, Q_{gas} is the gas flow-rate in L/min, Ac is the cross sectional area in dm², and $k_L a$ is an overall gas transfer coefficient in min⁻¹.

Equation (28) can be rewritten to solve for the concentration of ammonia in the gas phase, dependent on the residence time of the gas, and the overall gas transfer coefficient:

$$C_{NH_3 GA} = e^{-k_L a_{absorb} * \tau_{gas}} * C_{NH_3 GAO} \quad (29)$$

Where $C_{NH_3 GAO}$ and $C_{NH_3 GA}$ represent the initial concentration of ammonia-N and the ammonia-N concentration at time t of the gas in mg/L, τ_{gas} is the residence time of the gas in the system in min, and $k_L a_{absorb}$ is an overall gas transfer coefficient in min⁻¹.

However, in actual practice, the sulfuric acid solution is recirculated inside the absorption column. Recirculation shifts reactor behavior from a plug - flow pattern to

that of a completely mixed system. The effect of recirculation reduces theoretical height of the column (H in equation (28)) to an “effective” lower column height. For practical purposes the recirculation is considered to be internal, therefore will not be included into the overall mass balance of the system, but its influence is included into the overall gas transfer coefficient. Thus, the retention time in equation (28) represents the time required for the gas effluent ammonia-N concentration to reach $C_{NH_3\ gas\ out}$. The general mass balance for compound i present in the liquid phase, for a completely mixed system, can be written as follows:

$$V * \frac{dC_i}{dt} = Q_{in} * C_{i,in} - Q_{out} * C_{i,out} + r_i \quad (30)$$

Where dC_i/dt is the change in concentration of compound i over time in mg/L-min, $C_{i,in}$ and $C_{i,out}$ represents the initial concentration of compound i and concentration of compound i at time t in mg/L, V is the volume of the reactor in L, and r is the sum of reaction rates of compound i in mg/L-min.

A mass balance around ammonium sulfate in solution yields (applying equation (30)):

$$\begin{aligned} \frac{dNH_3A_{(aq)}}{dt} = & (C_{NH_3AO} - C_{NH_3A(aq)}) * \frac{1}{\tau_{Liquid}} \quad (31) \\ & + \left((C_{NH_3GAO} - C_{NH_3GA}) * \frac{1}{\tau_{gas}} \text{ for } NH_3A_{(aq)} \right. \\ & \left. < K_{sp}; \text{ and } 0 \text{ for } NH_3A_{(aq)} < K_{sp} \right) \end{aligned}$$

Where $dNH_3A_{(aq)}/dt$ is the change of ammonium sulfate concentration in the liquid versus time in mg-N/L-min, C_{NH_3AO} and $C_{NH_3A(aq)}$ represent the initial concentration of

ammonium sulfate-N and the ammonium sulfate-N concentration at time t of the liquid in mg/L, C_{NH_3GAO} and C_{NH_3GA} represent the initial concentration of ammonia-N and the ammonia-N concentration at time t of the gas in mg/L, and τ_{gas} is the residence time of the gas in the system in min.

Equation (31) shows, that once the ammonium sulfate solution reaches its maximum solubility, solid ammonium sulfate crystallizes out of solution. If a crystal separation unit operation is included in the process, flow of solid salt from the column can be produced. However, here it is assumed that solid salt accumulates in the column sump.

A mass balance around solid ammonium sulfate accumulating in the column sump yields :

$$\frac{dNH_3A_{(s)}}{dt} = 0 \quad \text{for } NH_3A_{(aq)} < K_{sp} \quad (32)$$

$$(C_{NH_3GAO} - C_{NH_3GA}) * \frac{1}{\tau_{gas}} \quad \text{for } NH_3A_{(aq)} > K_{sp}$$

Where $dNH_3A_{(s)}/dt$ is the change of solid ammonium sulfate concentration accumulating versus time in mg-N/L-min, C_{NH_3GAO} and C_{NH_3GA} represent the initial concentration of ammonia-N and the ammonia-N concentration at time t of the gas in mg/L, and τ_{gas} is the residence time of the gas in the system in min.

A mass balance around the sulfuric acid in the column yields:

$$\frac{dH_2SO_4}{dt} = (C_{H_2SO_4O} - C_{H_2SO_4}) * \frac{1}{\tau_{Liquid}} - (C_{NH_3GAO} - C_{NH_3GA}) * \frac{1}{14 * \tau_{gas}} \quad (33)$$

Where dH_2SO_4/dt is the change of sulfuric acid normality in the liquid versus time in Normality/min, $C_{H_2SO_4O}$ and $C_{H_2SO_4A}$ represent the initial sulfuric acid normality and the sulfuric acid normality at time t of the acid solution in Normality, C_{NH_3GAO} and C_{NH_3GA} represent the initial concentration of ammonia-N and the ammonia-N concentration at time t of the gas in mg/L, τ_{liquid} is the residence time of the acid solution in the system in min, and τ_{gas} is the residence time of the gas in the system in min.

As can be seen from equation (28) that the acid flow-rate through the column has no impact on the rate of ammonia recapture, however, it does indirectly influence it by impacting the $k_L a$. Since the $k_L a$ is directly affected by the amount of surface area and the ratio of the liquid volume to its surface area, changing the acid flow rate will change the overall gas transfer. If the acid spray flow is too low, the liquid contact surface area may be decreased, thereby decreasing the effective gas $k_L a$, conversely, if the acid spray is too high, drops of acid will impinge upon each other more often, leading to formation of larger droplets, decreasing the volume to surface area ratio and the gas transfer coefficient.

3.3 Results and Discussion

3.3.1 De-sorption

Preliminary air stripping experiments were conducted in the laboratory at Clemson University prior to the pilot plant setup at landfill site II. Artificial and real landfill leachate was investigated and the de-sorption model applied. Figure 17 shows the comparison between stripping experiments where artificial and real landfill leachate were run side by side. It can be seen that the behavior is nearly identically in terms of ammonia air stripping.

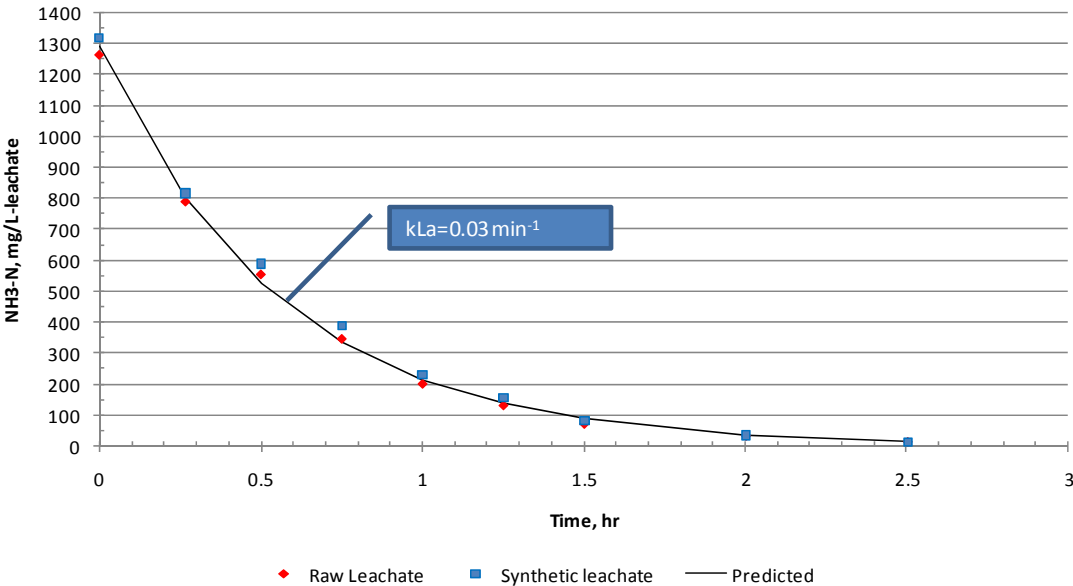


Figure 17: Ammonia de-sorption from raw and synthetic leachate.

In Figure 18 to Figure 20 6 air stripping experiments that were conducted at Clemson University are shown together with the application of equation (6). The data points represent the experimental values, the solid line represents the calculated stripping process when using the experimental overall gas transfer coefficient $k_L a$. The model gives a good representation of the experimental air stripping process of ammonia. Experimental determined $k_L a$'s were in the range of 0.0001 to 0.0007 min^{-1} . Synthetic leachate was used in experiments 1-5, landfill I leachate was used in experiments 6 and 7, respectively.

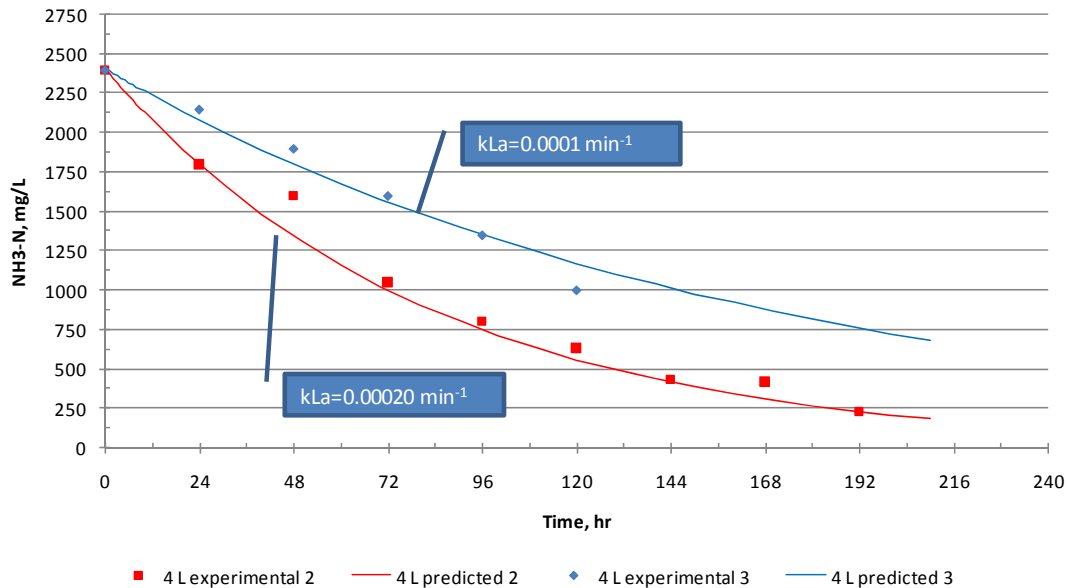


Figure 18: Leachate ammonia concentration vs. time obtained from lab scale stripping column at room temperature.

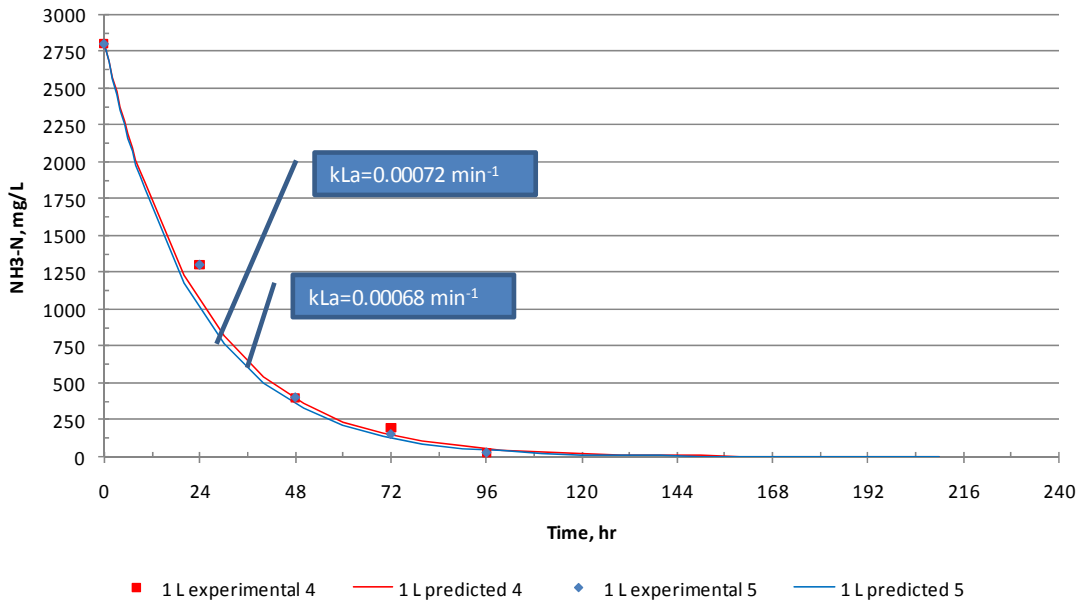


Figure 19: Leachate ammonia concentration vs. time obtained from lab scale stripping column at room temperature.

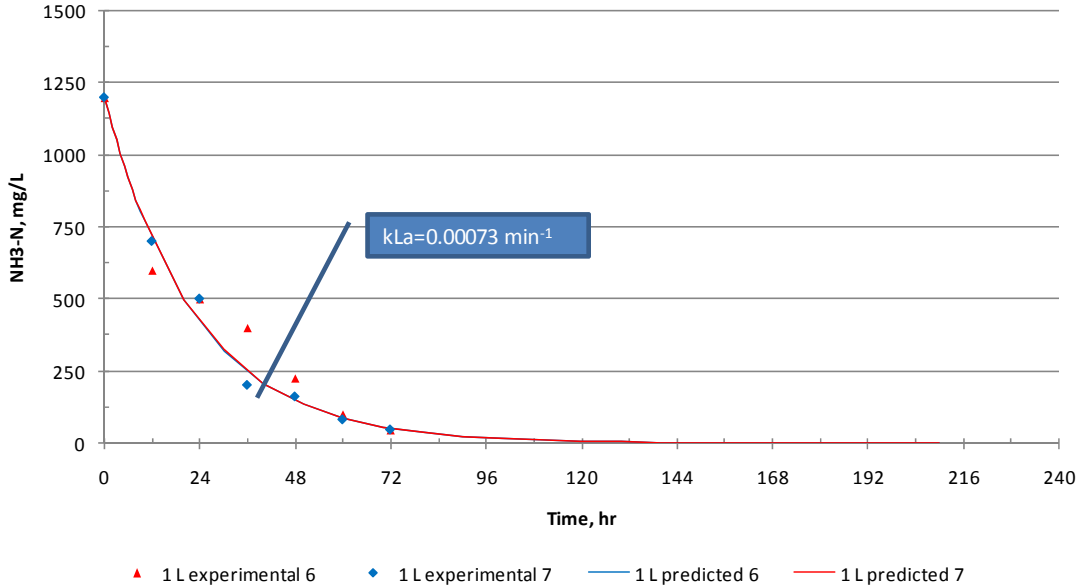


Figure 20: Leachate ammonia concentration vs. time obtained from lab scale stripping column at room temperature.

Applying equation (10), a series of plots could be generated (Figure 21), that show the calculated retention times of leachate inside an air stripper column to reach a certain removal of ammonia. Figure 21 shows the retention time of leachate inside a stripping system versus the removal efficiency for different gas transfer coefficients of the system.

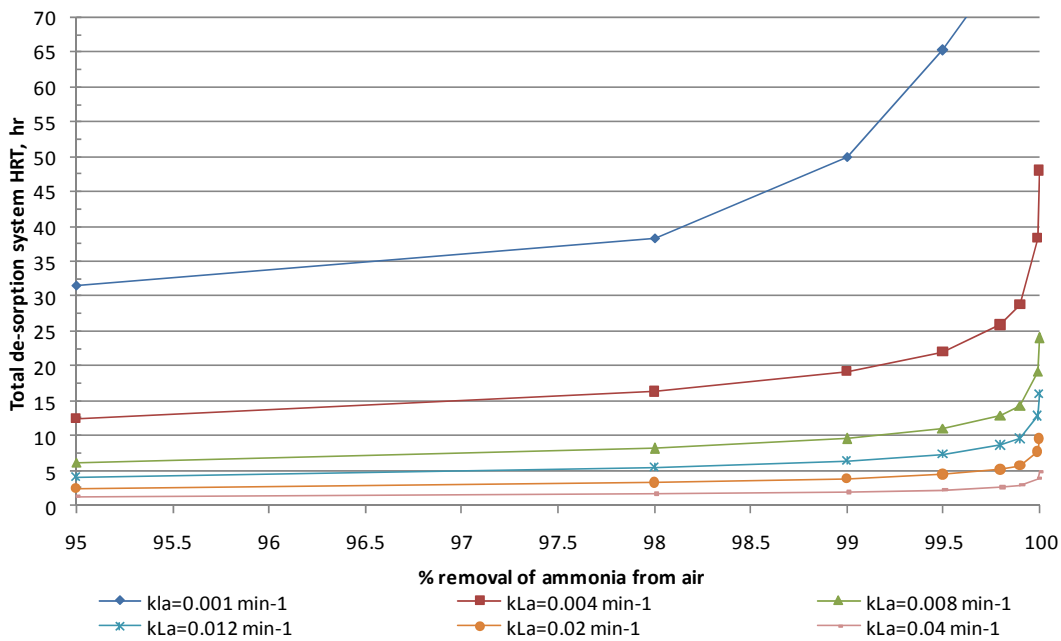


Figure 21: Predicted leachate retention time versus removal efficiency for air stripping at k_La ranging from 0.001 to 0.040 min^{-1} .

For example if the system has a k_La of 0.008 min^{-1} , to achieve 95% removal of the influent ammonia, the wastewater would have to be stripped for about 6 hours, whereas for 99% removal it would be about 10 hours. The higher the ammonia removal desired, the longer the treatment will have to be, being infinity for 100% removal.

The following paragraphs investigate the results obtained at the pilot plant facility at landfill site II. The way the pilot plant is setup, the process has to be modeled as a semi batch process, since the de-sorption process is divided into 6 individual stripping columns. The leachate stream is handed down from column to column, and moved every 60 minutes. The air enters the last column and exits the first column in countercurrent flow to the leachate. Table 10 shows a comparison between the overall gas transfer coefficients determined in each column. Even though every column is built the same way, they are operating at different temperatures due to a difference in exposure to closely located landfill flares (Column 4-6 direct exposure, Column 1-3 in shade).

Table 10: Pilot plant de-sorption overall gas transfer coefficients for ammonia.

Column	$k_L a$ [min ⁻¹]	Column surface temperature [°C]
Column 1	0.0063	17.5
Column 2	0.0066	17
Column 3	0.0054	16
Column 4	0.0089	29
Column 5	0.0092	28.5
Column 6	0.012	27.5

Increasing the temperature increases the gas transfer, most likely due to enhanced molecular diffusion of ammonia in the gas phase. Pilot plant batch experiments at overall gas transfer coefficients ranging from 0.006 to 0.008 min⁻¹ are shown in Figure 22 to Figure 24.

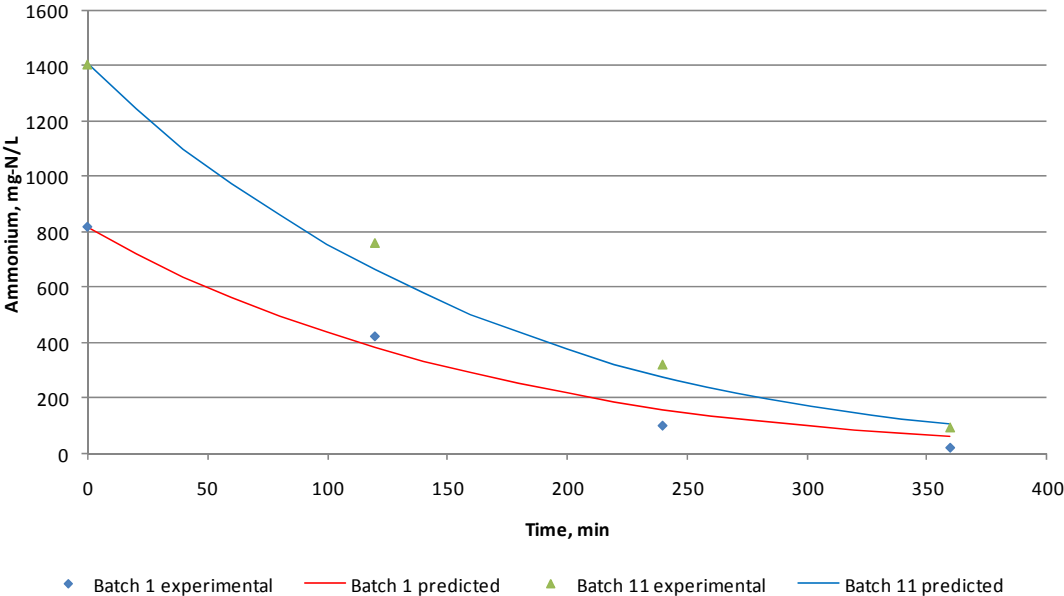


Figure 22: Leachate ammonia concentration vs. time obtained from pilot plant stripping columns.

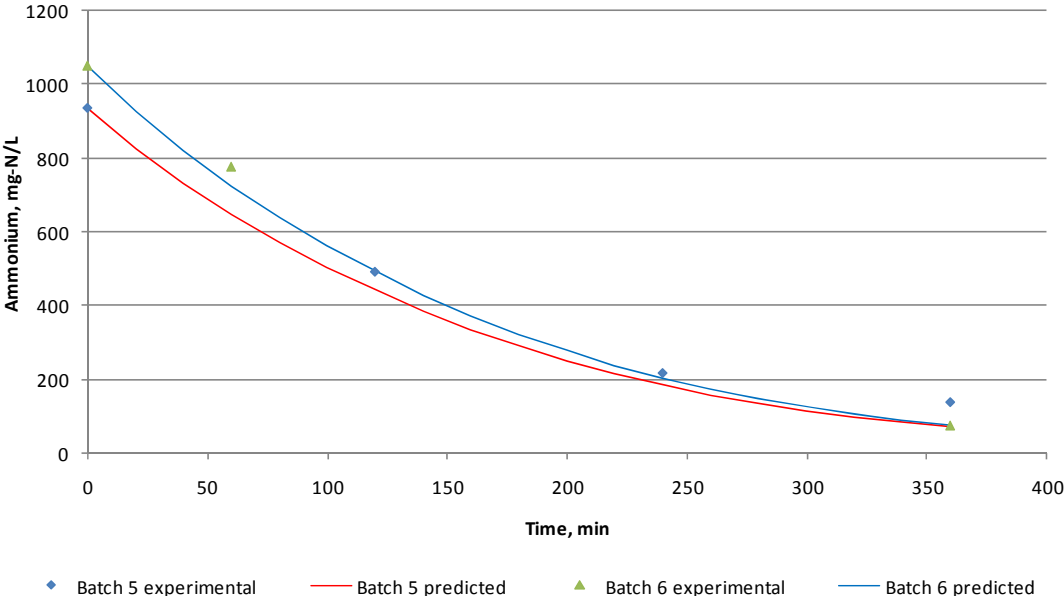


Figure 23: Leachate ammonia concentration vs. time obtained from pilot plant stripping columns.

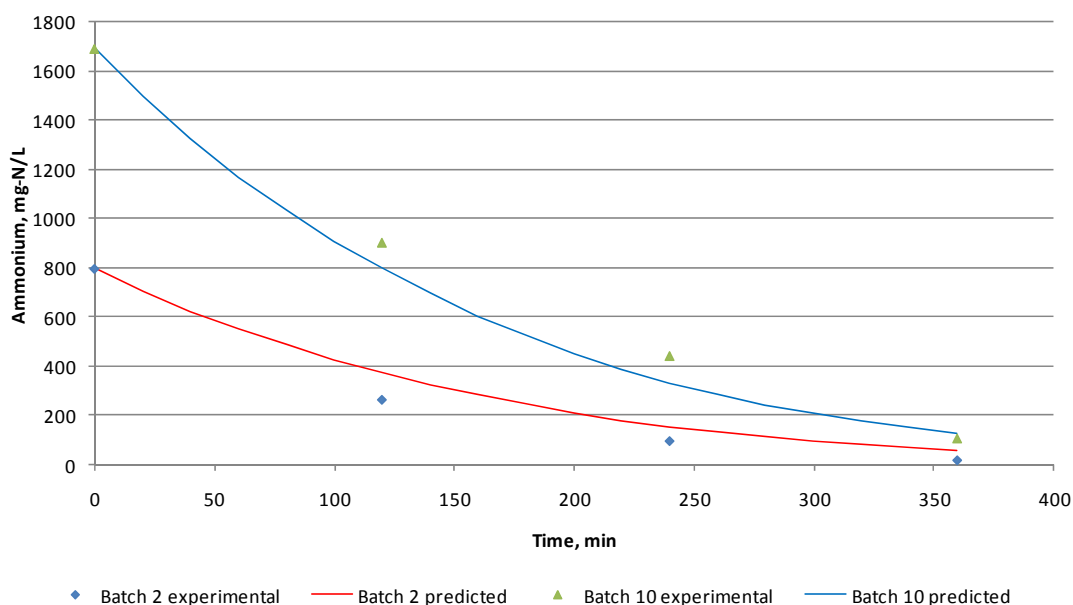


Figure 24: Leachate ammonia concentration vs. time obtained from pilot plant stripping columns.

The model represents the experimental data. Variance in the experimental data is most likely due to leachate handling from column to column and variable sampling time (± 10 min).

De-sorption experiments conducted at landfill site II from November 2009 through January 2010 were combined (Figure 25). The effluent ammonia concentration of each stage was plotted versus the time of reaction beginning with raw leachate addition at time zero. The leachate recycled in each column for 60 minutes and then was transferred to the next column. Raw leachate was filled into the first column and the effluent from the last column (number 6) was moved to further treatment. The ammonia stripped by an airflow of 3700 L/min was routed to the acid absorption columns.

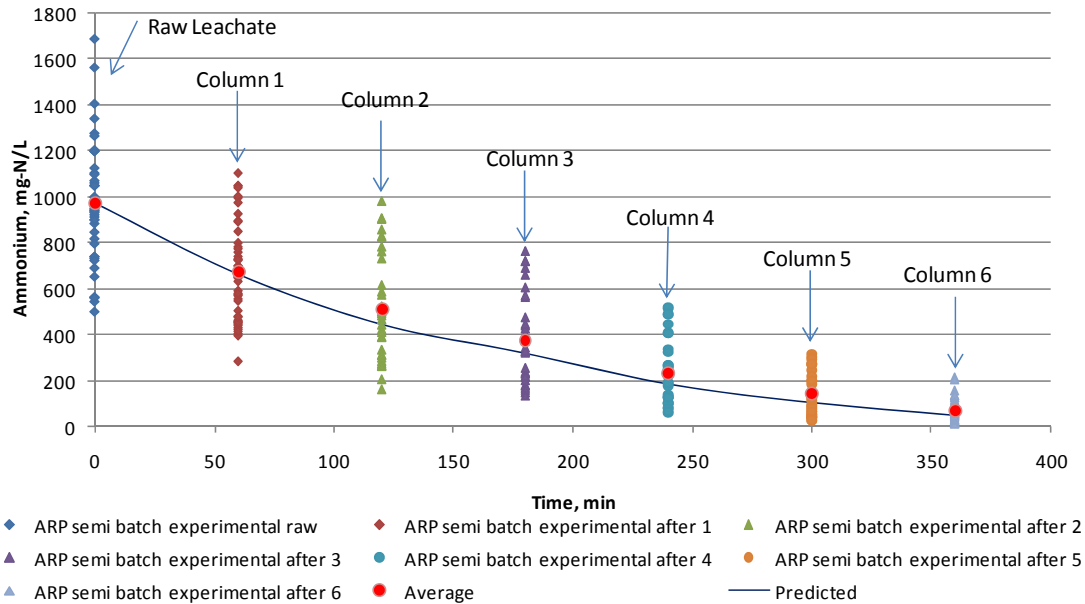


Figure 25: Leachate ammonia concentration vs. time obtained from pilot plant stripping columns in November 2009 through January 2010.

The red circles in Figure 25 represent the average of the effluent concentrations in each column, after one hour of treatment. The solid line represents the calculated stripping process, when the initial average raw leachate was 969 mg-N/L (average of experimental). The $k_L a$'s for the simulation were those found for each column (Table 10). The model represents the average of the experimental data. With an air inflow of about 3700 L/min an average ammonia-N concentration in the air of 0.385 ppm could be calculated. The range of data points may be explained by the fact that the initial raw leachate ammonia concentration ranging from about 500 mg-N/L to about 1700 mg-N/L, leading to a variation in the data for the other columns. From column 1 through 6 the range of the effluent concentrations decreased with each column. This can be

explained by the model, since removal efficiency is a function of the $k_L a$, not the inflow concentration. Data shown in Figure 25 was converted into percent ammonia removal from raw leachate, a variance of $\pm 5\%$ to $\pm 10\%$ was calculated (Figure 26).

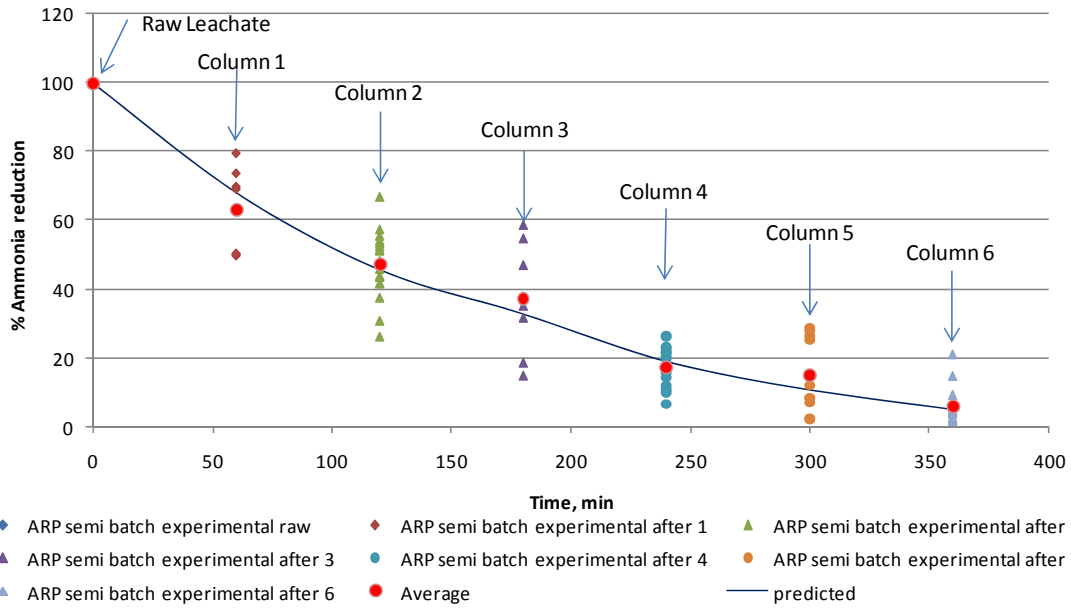


Figure 26: Ammonia removal in % from raw leachate vs. time obtained from pilot plant stripping columns in November 2009 through January 2010.

Table 11 compares different air stripping systems and their achieved overall gas transfer coefficients with the one used in this work. The system investigated in this work outperformed the packed tower worked with by Le et al. (2006), as the only other system > 1000 L. The aerocyclone by Quan et al. (2009) had a higher $k_L a$, probably because low quantities of leachate were sprayed in a fine droplet mist, creating a higher surface area for gas transfer.

Table 11: Comparison of different air stripping systems and obtained overall gas transfer coefficients.

System	$k_L a$ [min-1]	Notes	Source
Simple stripping column	0.00073	Only one hose introduced air to liquid (5 L)	Lab scale
Packed tower	0.007	Tower packed with porous media to add surface area (1000 L)	Le et al. (2006)
Stripping tank	0.008	Aerated tank (50 mL)	Basakcildan et al. (2007)
Ammonia Recovery Process (ARP)	0.0119	Leachate course spray, air in countercurrent, (2000 L/day)	Pilot-plant
Water-Sparged Aerocyclone (WSA)	0.016	Fine leachate spray, air introduced tangentially into aerocyclone (10 L)	Quan et al. (2009)

3.3.2 Absorption

Prior to the pilot-plant installation of absorption columns at landfill site II, a lab scale ammonia capture unit was built at Clemson University and operated to confirm model equations. Absorption batch experiments were conducted with ammonia being supplied by a separate air stripping column, and then routed through the acid spray unit. Here the ammonia-air mixture was contacted with a fine spray of sulfuric acid. The overall gas transfer coefficient of the system was determined using a linear regression of the ammonia uptake rate versus ammonia concentration in the air. Airflow, nozzle pressure, nozzle count (and therefore acid flow and droplet size) were varied. A second acid trap was setup after the spray column to catch possible ammonia exiting the system. Figure 27 and Figure 29 show the rate of ammonia transfer versus the ammonia in the airflow to determine the $k_L a$. Figure 28 and Figure 30 show the evolution of the ammonium concentration in the acid. The data points represent the experimental values, the solid lines represent the model applied, using the determined $k_L a$ and the measured inflow ammonia concentrations. The acid used in each experiment was 6 Normal sulfuric acid, with a maximum $NH_4 - N$ concentration of 82000 mg-N/L at standard conditions.

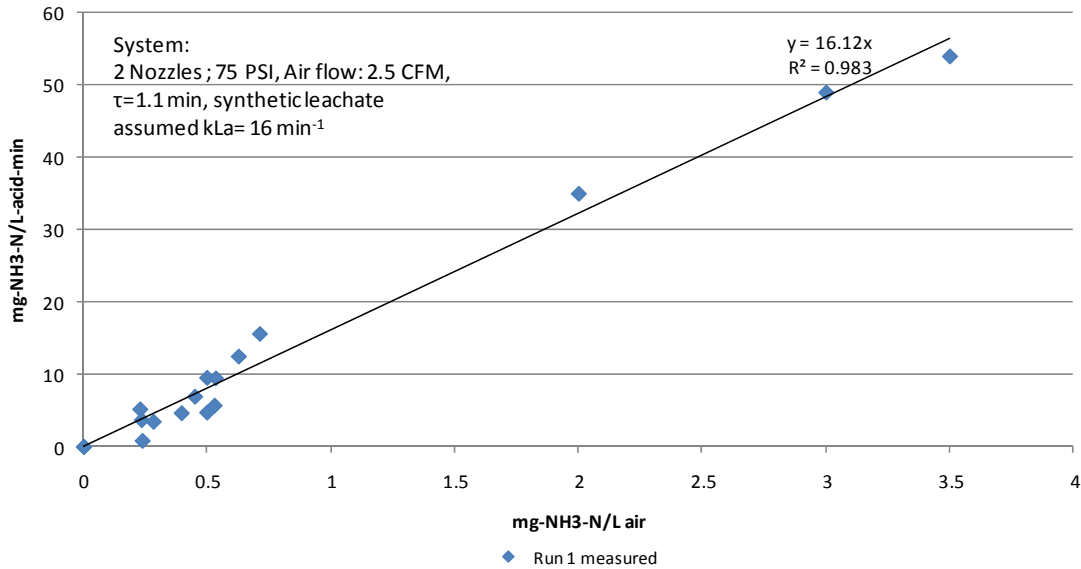


Figure 27: Ammonia absorption rate vs. ammonia concentration in gas phase in laboratory absorption column.

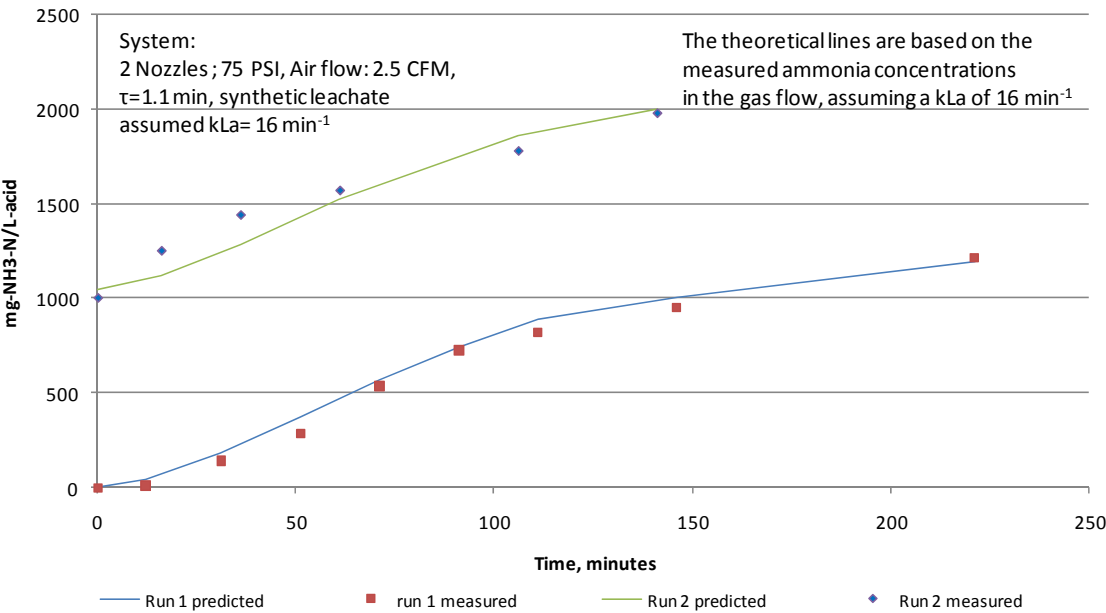


Figure 28: Ammonium in sulfuric acid solution vs. time in laboratory absorption column.

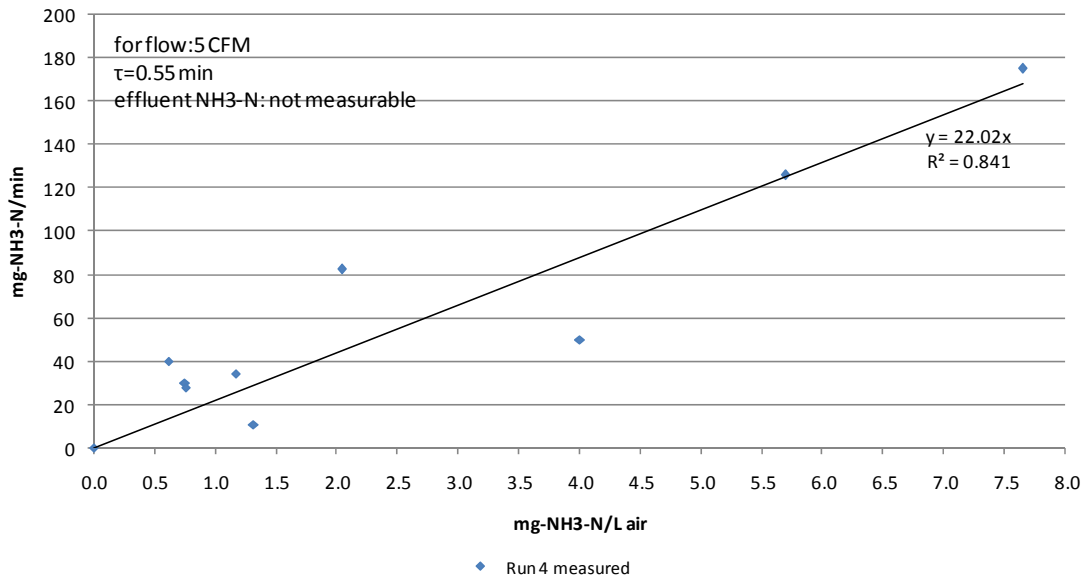


Figure 29: Ammonia absorption rate vs. ammonia concentration in gas phase in laboratory absorption column.

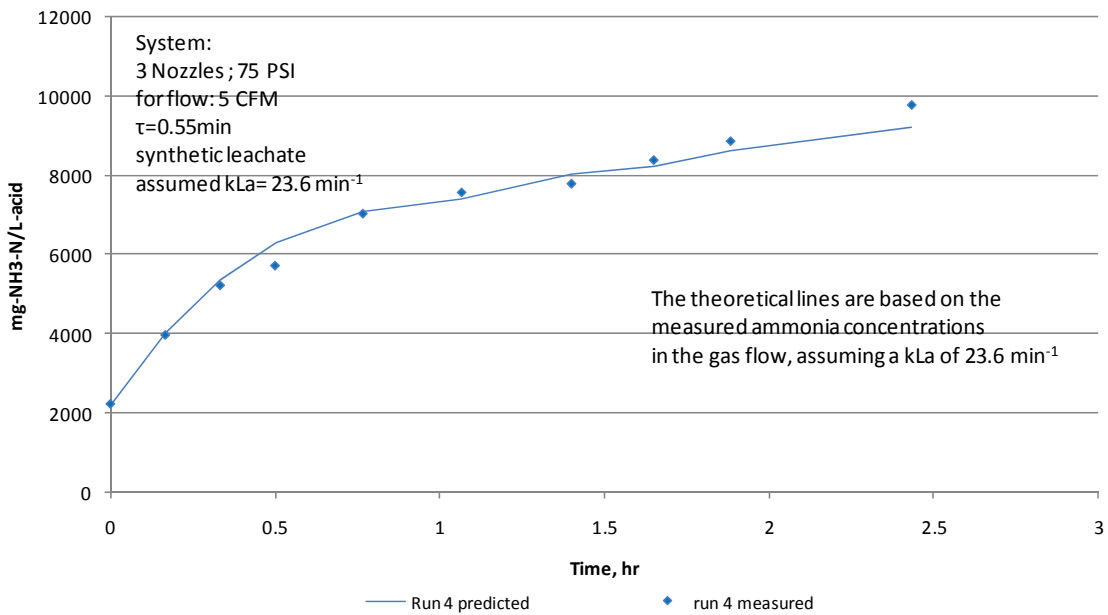


Figure 30: Ammonium in sulfuric acid solution vs. time in laboratory absorption column.

Increasing the airflow rate (from 2.5 to 5 ft³/min) and the amount of spray nozzles (from 2 to 3) lead to an increase of the ammonia transfer (Figure 27 to Figure 30). By increasing nozzles number, and therefore the amount of acid drops, the transfer surface between the gas and the liquid phase could be increased, changing the $k_L a$ of the system from initial 16 to 22 min⁻¹. When doubling the airflow from 2.5 to 5 ft³/min it was observed that the turbulence inside the spray column was increased. Raising the turbulence in the system raises the $k_L a$ also. This effect is associated with the gas-liquid film between the two phases. A higher turbulence reduces the gas film thickness, therefore reducing gas transfer resistance.

To create a more reproducible experimental environment, the variable ammonia inflow concentration created by a batch air stripping column was replaced by a constant ammonia inflow stream. An ammonia cylinder was setup to supply a constant ammonia inflow to the acid capture unit. Figure 31 and Figure 32 show two experiments, one with an inflow of 1.5 ppm ammonia and one with 220 ppm ammonia. Both experiments confirmed the applied model. The only difference was the overall gas transfer coefficient, which was 24.5 min⁻¹ for the 1.5ppm inflow concentration and 33 min⁻¹ for the 220 ppm inflow due to temperature increase from 25°C to 80 °C.

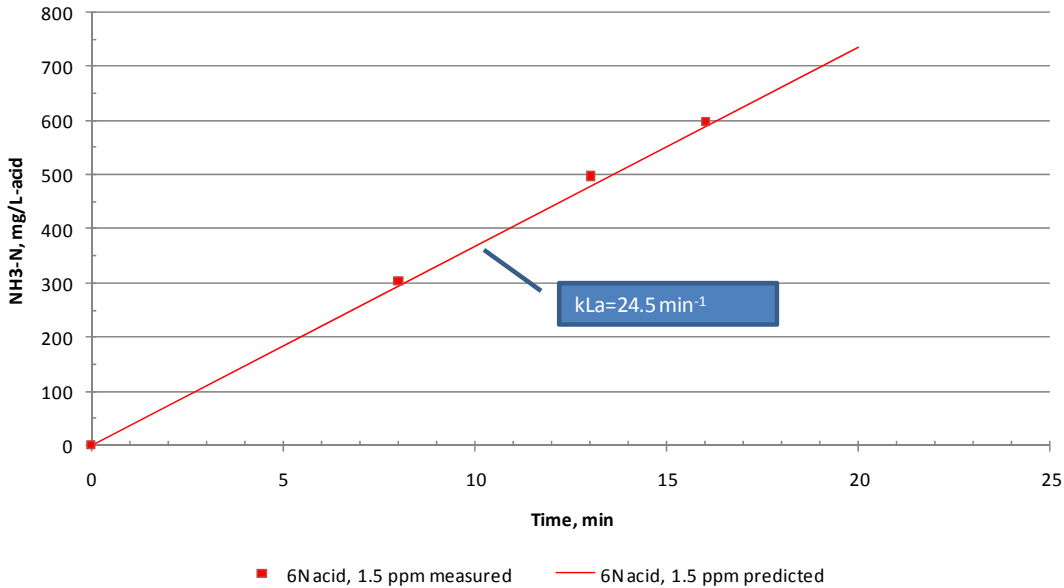


Figure 31: Ammonium in sulfuric acid solution vs. time in laboratory absorption column, constant ammonia inflow of 1.5 ppm, at room temperature.

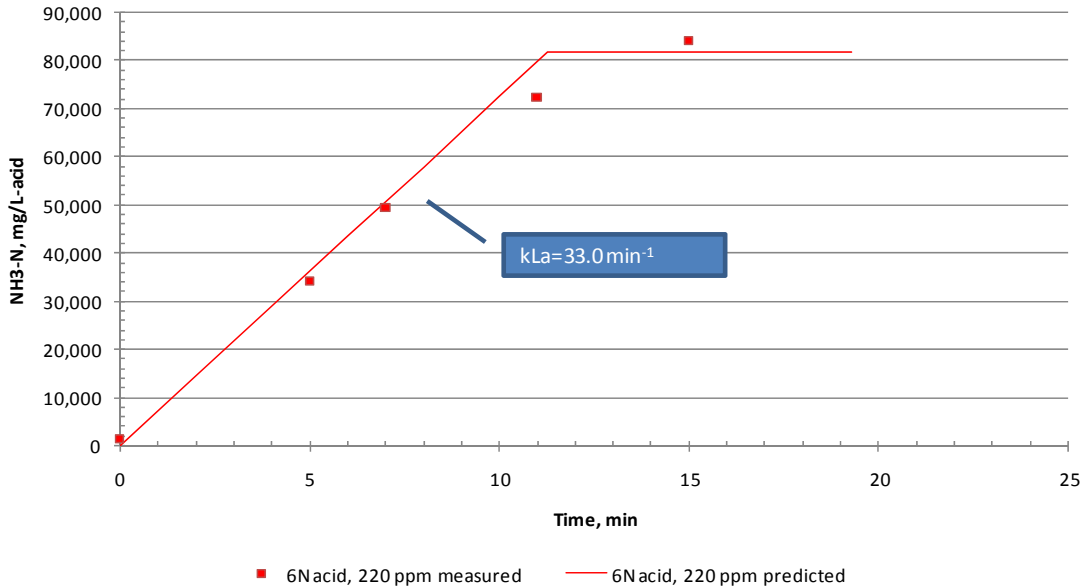


Figure 32: Ammonium in sulfuric acid solution vs. time in laboratory absorption column, constant ammonia inflow of 220 ppm, at ~80°C.

When 220 ppm was used as ammonia inflow, saturation was seen after approximately 11 minutes (this was 7260 mg/min ammonia uptake rate, versus 36 mg/min uptake rate for 1.5ppm inflow). Since the reaction was very fast, the neutralization energy was set free within a short amount of time, heating the sulfuric acid solution to about 80°C. The increased heat increased the overall gas transfer coefficient, since all other parameters were kept the same. Increasing the temperature increases the gas transfer due to enhanced molecular diffusion of ammonia in the gas phase. After saturating the acid (after approximately 11 minutes; the model suggested 11.21 minutes) ammonium sulfate could be seen precipitating inside the spray column, after the solution was cooled.

A batch acid neutralization experiment using a k_{La} of 16 min^{-1} and an inflow ammonia of 0.385 ppm was predicted as it developed over time (Figure 33).

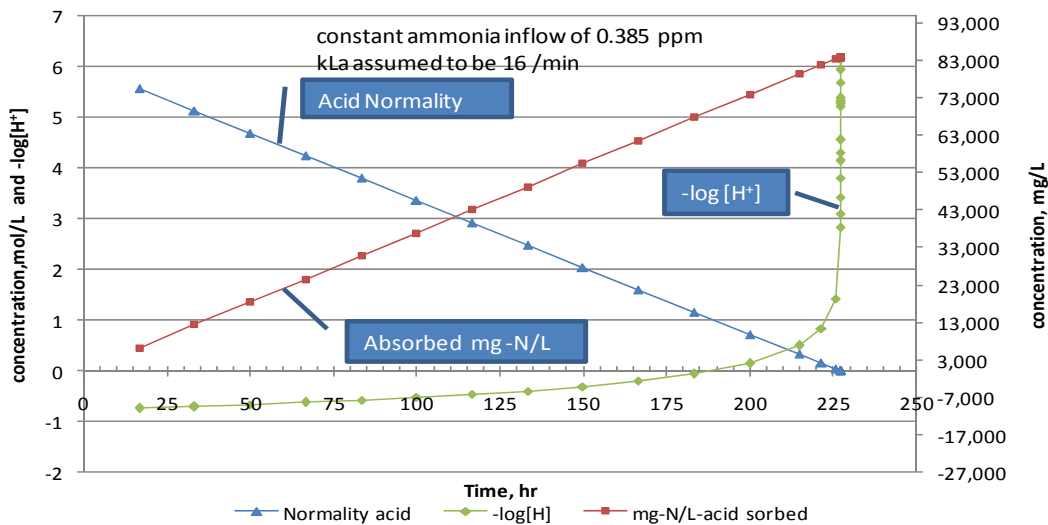


Figure 33 Acid neutralization, batch simulation.

In Figure 33 the negative logarithm of the hydrogen-ion concentration of the acid solution is shown together with the acid normality and the ammonium sulfate concentration until the acid is completely neutralized. This plot is relevant when such a spray column is needed to be operated in continuous mode. An optimum operating pH would need to be determined to minimize the acid waste and maximize ammonium sulfate concentration in the effluent. The model suggests an operating pH between 0.5 and 1.5. If the pH is higher than 1.5, only a small amount of ammonia would neutralize the acid which would disable the uptake capacity of the spray column whereas at $\text{pH} < 0.5$ the effluent would contain unneutralized acid.

After applying a continuous flow model for the absorption process, the relationship between the gas retention time, the overall gas transfer coefficient, and the removal efficiency could be predicted. Figure 34 shows the gas retention time versus the removal efficiency for different $k_L a$'s. As an example, if an ammonia removal of 95% with a system $k_L a$ of 5 min^{-1} had to be achieved, the gas retention time had to be 0.6 minutes, or 0.95 minutes for 99% removal respectively. The airflow influences the $k_L a$. Therefore, after setting the retention time a new $k_L a$ has to be determined. One constraint of increasing the airflow would be the possibility of carrying out acid drops with the effluent gas.

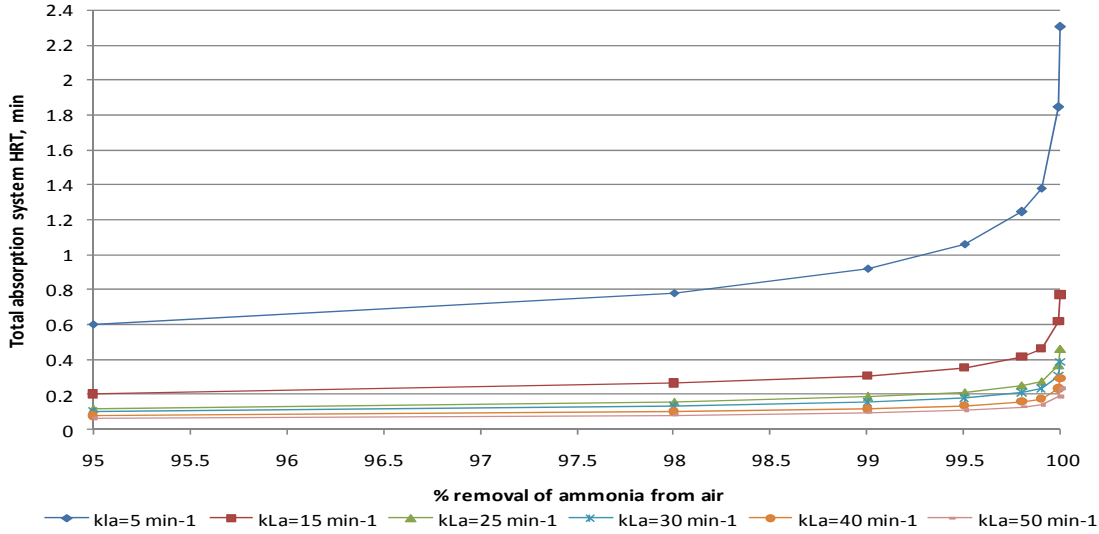


Figure 34: Predicted gas retention time versus removal efficiency for ammonia absorption at $k_L a$ ranging from 5 to 50 min^{-1} .

The absorption side of the pilot plant at landfill site II is setup the way that the effluent ammonia gas from the de-sorption process is divided up into two tracks of two acid spray columns. This reduces the chance of acid carryover into the final effluent air, however, each track has a third spray column, where only water is sprayed to catch possible exiting acid. The ammonia concentration versus time of track one (Column 7 and 9) is shown in Figure 35, and track two (Column 8 and 10) in Figure 36, respectively. The experimental data were from November 2009 to January 2010 and are represented by data points, whereas model calculations are represented by a solid line. Parameters applied to the model were the measured average $k_L a$'s of 18 and 16.3 min^{-1} , and the average measured ammonia concentration in the air inflow stream of 0.385 ppm, and an airflow of 1850 L/min for each track.

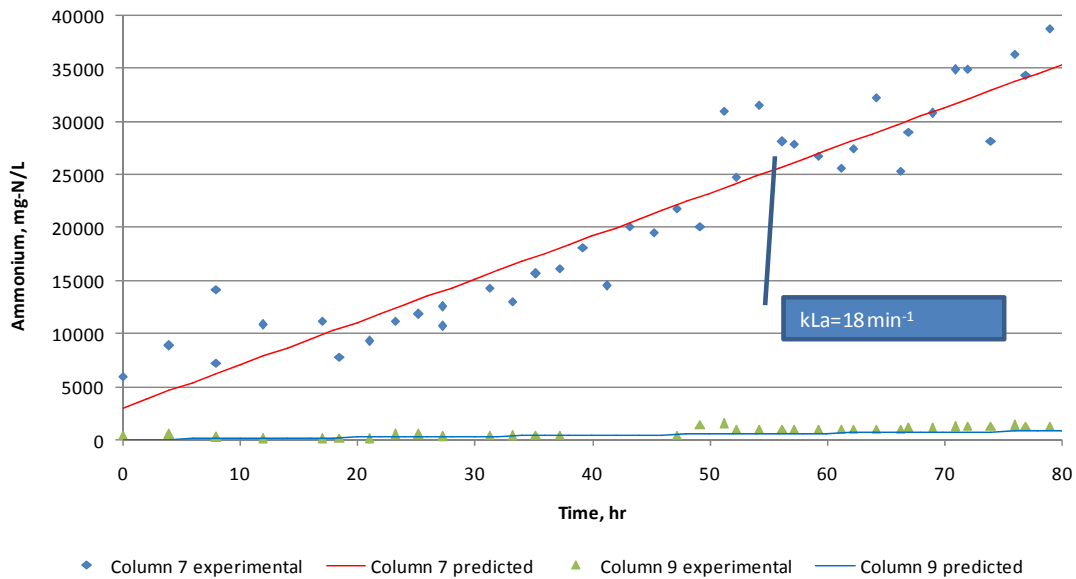


Figure 35: Ammonium in sulfuric acid solution vs. time obtained from pilot plant stripping columns in November 2009 through January 2010 for column 7 and 9.

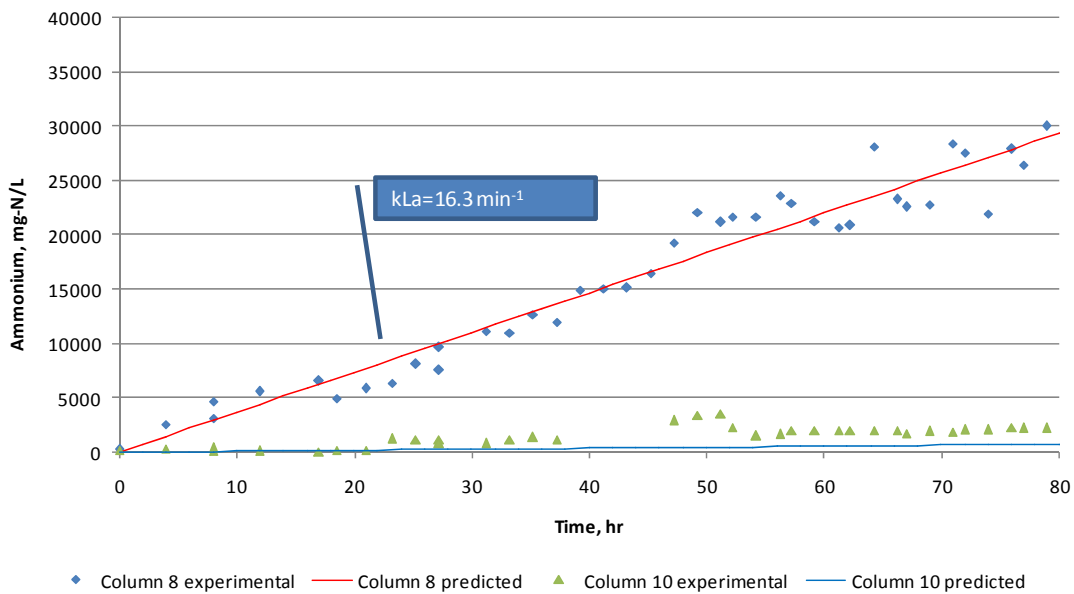


Figure 36: Ammonium in sulfuric acid solution vs. time obtained from pilot plant stripping columns in November 2009 through January 2010 for column 8 and 10.

The experimental data are very well represented by the model for track one and two. Some of variation may be due to measurement errors at high concentrations, and different leachate inflow ammonium concentrations leading to fluctuations of the ammonium laden gas inflow. After about 60 hours of operation, the uptake in column 8 leveled, indicating less increase of ammonium sulfate and therefore less ammonia uptake than anticipated. This may be explained by the fact that by inspecting the column after 79 hours of operation, 6 of the 10 acid spray nozzles were clogged because of a destroyed filter, leading to a decrease in acid droplets and therefore less ammonium transfer. This could also be the reason why experimental values for the ammonia uptake for column 10 were higher than anticipated, because of column 8 passing through un-captured ammonia.

The average $k_L a$ for column 8 and 10 was 16.3 min^{-1} and 18 for column 7 and 9 respectively, as shown in Table 12.

Table 12: Pilot plant overall gas transfer coefficients for ammonia absorption.

Column	$k_L a$ [min-1]	Column Surface Temperature [°C]
Column 7	18	28
Column 9	18	29
Column 8	16.3	16
Column 10	16.3	17
average	17.2	22

The difference in overall gas transfer coefficient could be explained by the lower temperature of column 8 and 10 compared to 7 and 9. A comparison of obtained overall ammonia gas transfer coefficients is given in Table 13.

Table 13: Overall gas transfer coefficients of different ammonia absorption systems.

System	$k_L a$ [min⁻¹]	Notes	Source
Lab acid spray column 2 nozzles	16	Minimum gas HRT of 0.29 minutes***(one column) (0-5ppm** and HRT=1-1.5) 4L acid	lab scale
Lab acid spray column 3 nozzles	18-25	Minimum gas HRT of 0.211 minutes***(one column) (5-10ppm** and HRT=0.55) 4L acid	lab scale
Lab acid spray column 3 nozzles	30-35	Boiling due to neutralization energy, minimum gas HRT of 0.15 minutes*** (one column) (220ppm** and HRT=0.55) 4L acid	lab scale
ARP Absorption side 10 nozzles	16-18	Minimum gas HRT of 0.22 minutes* or 0.166 minutes *** (0.4 ppm** and HRT~0.24) 100L acid (two columns in series)	pilot scale

*Minimum HRT for 99.9% recapture **Ammonia concentration in the influent gas stream

***Minimum HRT for 99.5% recapture

3.4 Model Equations as used for Computation

For general mass balances discussed above dC_i/dt can be substituted by $\Delta C_i/\Delta t$ to be able to solve the equations simultaneously by looking at finite element differences for the time step Δt .

1) Ammonia in Leachate for De-sorption(NH_3L)

$$NH_3L_2 = \left\{ \left[(NH_3LO - NH_3L_1) * \frac{1}{\tau_{Liquid}} - k_L a_{desorb} * NH_3L_1 \right] * \Delta t \right\} + NH_3L_1 \quad (34)$$

Where $NH_3L_{1,2}$ are the ammonia concentrations in the liquid at time one and two respectively in mg-N/L, and all other parameters are previously defined.

2) Ammonia in Gas Phase for De-sorption(NH_3GD)

$$NH_3GD_2 = \left\{ \left[(NH_3GDO - NH_3GD_1) * \frac{1}{\tau_{Gas}} + (NH_3LO - NH_3L_1) * \frac{1}{\tau_{Liquid}} \right] * \Delta t \right\} + NH_3GD_1 \quad (35)$$

Where $NH_3GD_{1,2}$ are the ammonia concentrations in the de-sorption gas at time one and two respectively in mg-N/L, and all other parameters are previously defined.

3) Ammonia in Gas Phase for Absorption (NH_3GA)

$$NH_3GA_2 = e^{-k_L a_{absorb} * \tau_{gas}} * NH_3GAO \quad (36)$$

Where NH_3GA_2 is the ammonia concentrations in the absorption gas at time two in mg-N/L, and all other parameters are previously defined.

4) Ammonia in Acid Solution for Absorption ($NH_3A_{(aq)}$)

if $NH_3A_{(aq)} < K_{sp}$ then (37)

$$NH_3A_{2(aq)} = \left\{ \left[(NH_3AO_{(aq)} - NH_3A_{1(aq)}) * \frac{1}{\tau_{Liquid}} + (NH_3GAO - NH_3GA_1) * \frac{1}{\tau_{Gas}} \right] * \Delta t \right\} + NH_3A_{1(aq)}$$

if $NH_3A_{(aq)} > K_{sp}$ then (38)

$$NH_3A_{2(aq)} = \left\{ \left[(NH_3AO_{(aq)} - NH_3A_{1(aq)}) * \frac{1}{\tau_{Liquid}} + 0 \right] * \Delta t \right\} + NH_3A_{1(aq)}$$

Where $NH_3A_{1,2(aq)}$ are the ammonium sulfate concentrations in the absorption liquid at time one and two in mg-N/L, K_{sp} is the ammonium sulfate saturation constant in mg/L, and all other parameters are previously defined.

5) Ammonia in Acid Solution for Absorption ($NH_3A_{(s)}$)

if $NH_3A_{(aq)} < K_{sp}$ then (39)

$$NH_3A_{2(s)} = \{ [+0] * \Delta t \} + NH_3A_{1(s)}$$

if $NH_3A_{(aq)} > K_{sp}$ then (40)

$$NH_3A_{2(s)} = \left\{ \left[+(NH_3GAO - NH_3GA_1) * \frac{1}{\tau_{Gas}} \right] * \Delta t \right\} + NH_3A_{1(s)}$$

Where $NH_3A_{1,2(s)}$ are the solid ammonium sulfate concentrations in the absorption column at time one and two in mg-N/L, and all other parameters are previously defined.

6) Normality of acid in solution (H_2SO_4)

$$H_2SO_{4,2} = \left\{ \left[(H_2SO_{4,0} - H_2SO_{4,1}) * \frac{1}{\tau_{Liquid}} - (NH_3GA_0 - NH_3GA_1) * \frac{1}{14 * \tau_{Gas}} \right] * \Delta t \right\} + H_2SO_{4,1} \quad (41)$$

Where $H_2SO_{4,1,2}$ are the acid normalities in the absorption column at time one and two in Normality, and all other parameters are previously defined.

4 ACTIVATED SLUDGE SYSTEM

4.1 Introduction

Algal growth experimental trials conducted at Clemson’s aquaculture facility suggest that at BOD/NH₃-N feed ratios in excess of 1/1 lead to culture instability. Therefore, it was concluded that VFA reduction to a level of BOD/NH₃-H <1 prior to algal post treatment is required to avoid bacterial dominance of the culture. Consequently, the proposal includes an activated sludge unit prior to algal post treatment, the system flow chart is illustrated below.

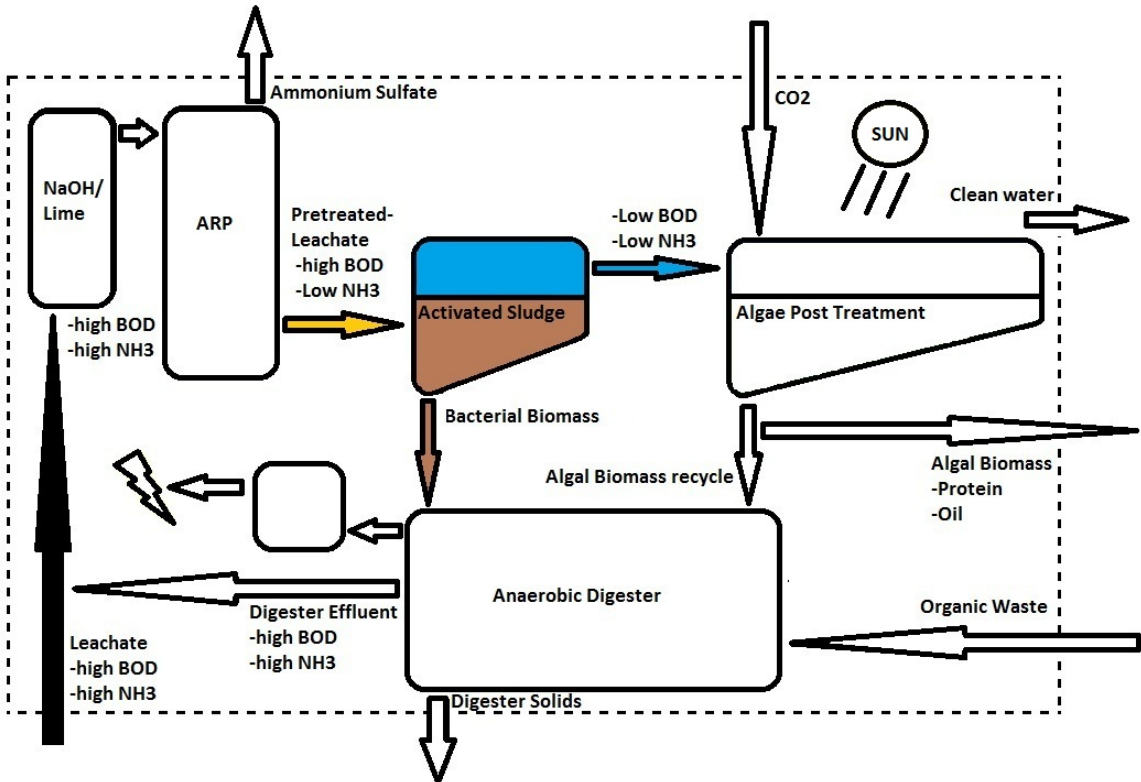


Figure 37: Proposed system design for treatment of landfill leachate; Activated Sludge treatment is highlighted.

Waste activated sludge could be loaded into an optional digester for energy recovery. Activated sludge process design and operation are well understood from conventional wastewater treatment designs and models such as Activated Sludge Model No1 (ASM-1) are available (Greedy et al., 1999). Possible systems include a single-stage aerated Completely Stirred Tank Reactor (CSTR) with sludge settling unit and sludge recycle, or sequencing batch reactors neglecting the need for a separate settling tank.

A landfill leachate laboratory treatability study was conducted, and the Activated Sludge Model No.1 was used to propose a simple CSTR activated sludge design for the pilot plant treatment facility. Batch growth trials were conducted to obtain kinetic parameters such as maximum growth rate, and decay rate or stoichiometric coefficients such as yield and half saturation constant for pretreated landfill leachate. These parameters and coefficients were then used to model the activated sludge process.

4.2 Treatability Study and Determination of Growth Parameters

4.2.1 BOD and Biomass Yield

The BOD of a sample is defined as the amount of oxygen a bacterial community would need to oxidize biodegradable organic compounds (Grady et al., 1999). The time dependent BOD relationship is represented as:

$$BOD_t = BOD_L * (1 - 10^{(-k*t)}) \quad (Base\ 10) \quad (42)$$

Where BOD_t is the biological oxygen demand until time t in $mg-O_2/L$, BOD_L is the ultimate biological oxygen demand of the sample in $mg-O_2/L$, k is the BOD rate constant in day^{-1} , and t is the time t in days.

The BOD constant k was determined by fitting a BOD curve to observed growth data. Note that the BOD curve, a first order approximation, does not reflect the s-shaped bacterial growth curve. Figure 38 shows BOD curves for heterotrophic bacterial growth on landfill site I leachate. Figure 39 shows BOD curves of landfill site II leachate. The BOD constants determined for landfill site I leachate were 0.23 to 0.27 day^{-1} (base 10), and 0.32 to 0.4 day^{-1} for landfill site II leachate, respectively. BOD constants for standard domestic wastewater are typically 0.3 day^{-1} (base 10) (Grady et al., 1999).

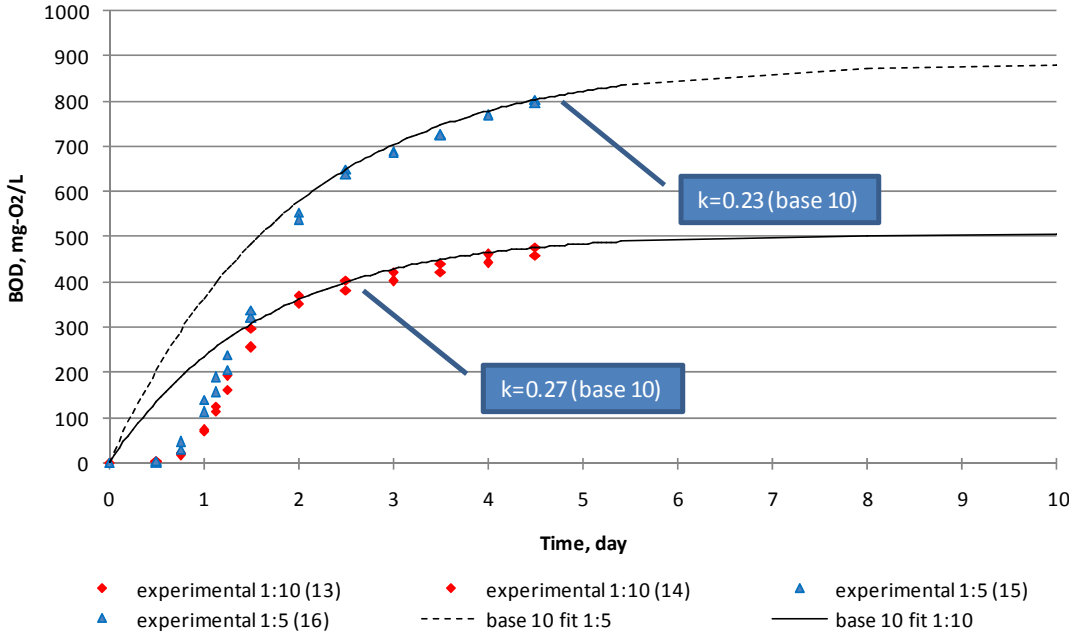


Figure 38: BOD vs. time of Landfill site I leachate.

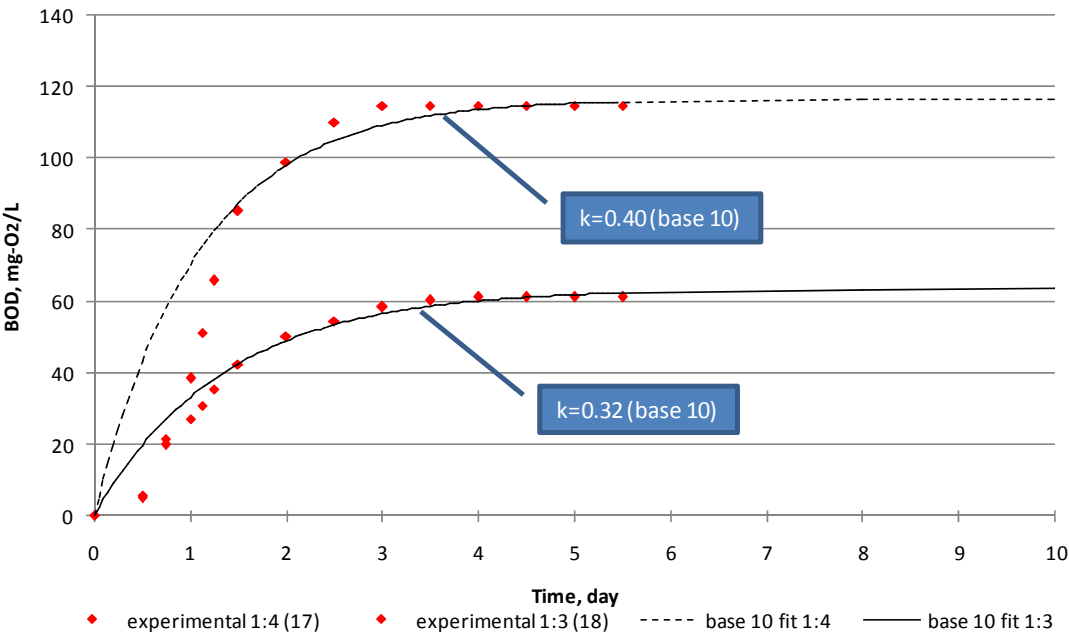


Figure 39: BOD vs. time of Landfill site II leachate.

To determine the bacterial biomass yield for growth on leachate as substrate, the biomass concentration was measured after BOD consumption. The yield is expressed in units of mg-VS biomass produced per mg-O₂ used.

BOD₅, BOD_L and yield coefficients of heterotrophic bacteria growing on pretreated landfill leachate are shown in Table 14. The average biomass yield observed was 0.476 mg-VSS/mg-BOD₅. For standard municipal wastewater the literature suggests an heterotrophic yield of 0.5 mg-VSS/mg-BOD₅ (Grady et al., 1999).

Table 14: Determination of $Y_{H,V/5B}$ and BOD_L for selected samples.

System	Dilution [1:]	BOD₅ sample [mg-O₂/L]	BOD_L Sample [mg-O₂/L]	VS Biomass [mg-VS/L]	$Y_{H,V/5B}$ [mg-VS/mg-BOD₅]
Sample 13	10	470	489.1	331.2	0.417
Sample 14	10	453	471.1	418.4	0.511
Sample 15	5	793	825.3	619.2	0.445
Sample 16	5	786	818.3	592.8	0.389
Average	-				0.476

4.2.2 Monod Kinetics K_s , μ_{max} , and b_H

The standard approach to model bacterial growth is the basic Monod model for growth on a single substrate (Grady et al., 1999). The Monod equation is shown below:

$$\mu_{max} = \mu * \frac{S}{K_s + S} - b_H \quad (43)$$

Where μ_{max} is the maximum growth rate in day^{-1} , μ is the specific growth rate in day^{-1} , S is the substrate concentration in mg/L , b_H is the decay rate in day^{-1} , and K_s is the half saturation constant for the substrate in mg/L .

μ_{max} and b_H , are constants of the bacterial population, K_s is a constant of the substrate used by that bacterial population. These parameters can be determined by analyzing the bacterial growth over time. The standard approach is to rewrite equation (43) to generate a linear relationship (Grady et al., 1999). An example would be the Lineweaver Burk linearization, as shown below:

$$\frac{1}{\mu} = \frac{K_s}{\mu_{max}} * \frac{1}{S} + \frac{1}{\mu_{max}} \quad (44)$$

When plotting $1/S$ vs $1/\mu$ the slope of line would be K_s/μ_{max} and the intercept would be $1/\mu_{max}$. However, this approach was attempted but was non revealing, mainly because the plot of inverse experimental data adds most weight to the weakest data. Thus, a non linear fit using the Monod equation was conducted to determine growth parameters. Non linear fits for bacterial growth on landfill site I and II leachate are shown in Figure 40 and Figure 41.

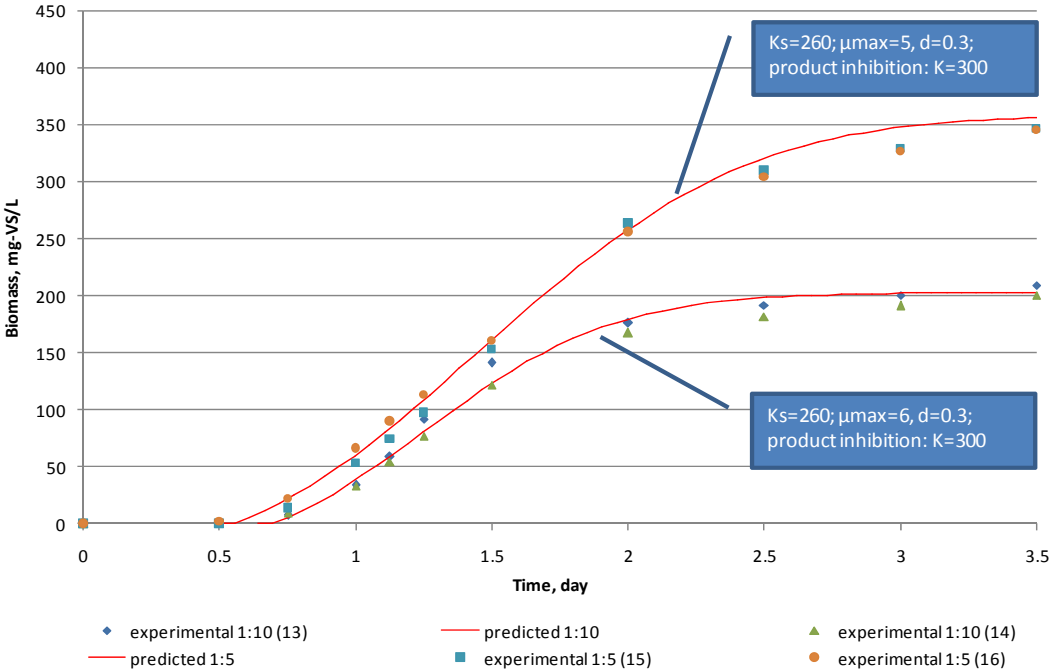


Figure 40: Bacterial growth vs. time on landfill site I leachate.

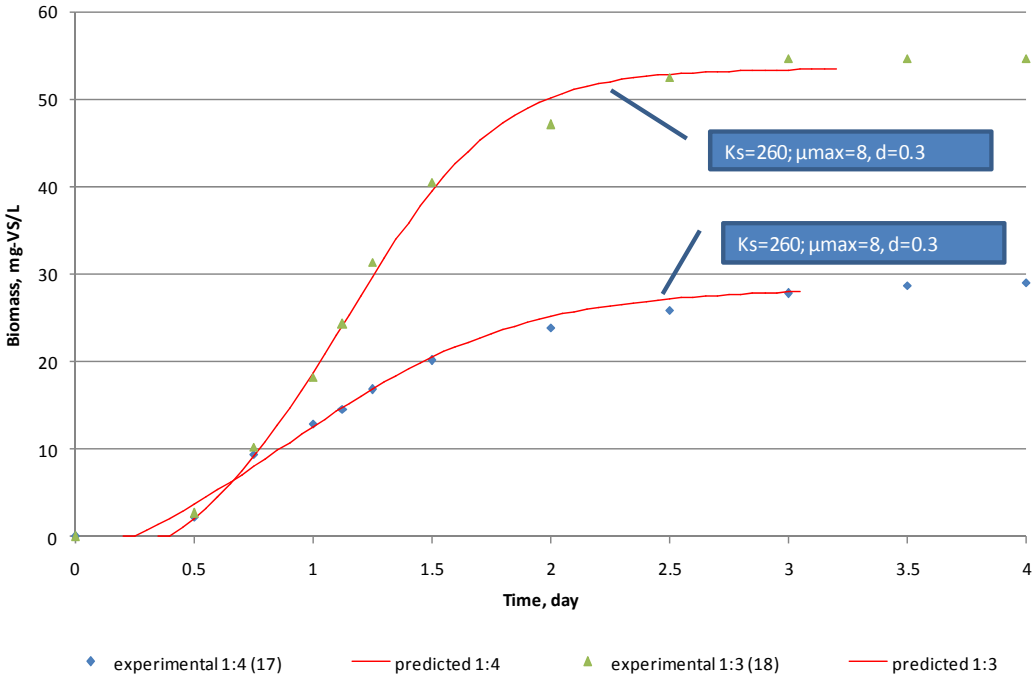


Figure 41: Bacterial growth vs. time on landfill site II leachate.

The maximum growth rate μ_{\max} for landfill site I pretreated leachate ranged from 5 to 6 day^{-1} depending on dilution of initial leachate. The dependence of the initial leachate concentration suggests the presence of inhibitory substances. Furthermore an product inhibition term with a constant of 300 mg/L was added to fit the data. For landfill site II pretreated leachate the average maximum heterotrophic growth rate was 8 day^{-1} independent of the leachate dilution, and without an inhibition term. For all samples the K_s for pretreated leachate was 260 mg BOD₅/L, and the decay rate was 0.3 day^{-1} . The kinetic parameters for standard activated sludge and domestic wastewater are $\mu_{\max} = 6 \text{ day}^{-1}$, $b_H = 0.18 \text{ day}^{-1}$, and $K_s = 20 \text{ mg-BOD/L}$ (Grady et al., 1999). It can be concluded, that the Monod model gives a good representation of observed bacterial growth on pretreated landfill leachate II. Therefore, Monod based activated sludge models, as used for domestic wastewater activated sludge, can be used to model bacterial growth on pretreated landfill leachate II (low strength leachate). However, ASM-1 cannot be used to model landfill leachate I (high strength leachate), because of an unknown inhibition.

Autotrophic growth parameters have not been determined for pretreated landfill leachate. But after concluding that heterotrophic growth is similar to standard wastewater activated sludge, all autotrophic growth parameters were assumed to be similar. Furthermore the oxygen and ammonia half saturation constants for autotrophic growth will be the same. Modern wastewater data are expressed on a COD or nitrogen-N basis, therefore all determined, or assumed parameters for bacterial growth on

pretreated leachate are expressed in COD or nitrogen-N units and presented in Table 15. Assumed values were adopted from Grady et al., (1999).

Table 15: Kinetic parameters and stoichiometric coefficients measured or assumed for low strength pretreated landfill leachate.

Symbol	Name	Unit	Value
Y_H	Heterotrophic biomass yield	mg b. COD/mg COD used	0.476 ^c
f'_D	Fraction of debris in biomass	mg debris COD/mg b. COD	0.08 ^a
$i_{N/XB}$	Nitrogen in active biomass	mg-N/mg COD in active b.	0.086 ^a
$i_{N/XD}$	Nitrogen in biomass debris	mg-N/mg COD in b. debris	0.06 ^a
Y_A	Autotrophic biomass yield	mg b. COD/mg N oxidized	0.24 ^a
μ_H	Heterotrophic maximum growth rate	hr ⁻¹	0.333 ^c
K_s	Het. substrate half saturation constant	mg-COD/L	260 ^c
$K_{O,H}$	Het. oxygen half saturation constant	mg-O ₂ /L	0.1 ^a
K_{NO}	Het. anoxic nitrate half sat. constant	mg-N/L	0.2 ^a
$b_{L,H}$	Heterotrophic decay constant	hr ⁻¹	0.0083 ^c
η_g	Anoxic growth factor	dimensionless	0.8 ^a
η_h	Anoxic hydrolysis factor	dimensionless	0.4 ^a
k_a	Ammonification rate coefficient	L/(mg Biomass-hr)	0.0067
k_h	Hydrolysis coefficient	mg COD/(mg Biomass-hr)	0.092 ^a
K_x	Half saturation coefficient of hydrolysis of slowly biodegradable substrate	mg-COD/mg-Biomass COD	0.15 ^a
μ_A	Maximum Autotrophic growth rate	hr ⁻¹	0.032 ^a
K_{NH}	Autotrophic ammonia half sat. constant	mg-N/L	1.0 ^a
$K_{O,A}$	Autotrophic oxygen half sat. constant	mg-O ₂ /L	0.75 ^a
$b_{L,A}$	Autotrophic decay rate	hr ⁻¹	0.004 ^a

a) assumed b)calculated c)measured

4.3 Wastewater Characteristics

4.3.1 Characteristics of Domestic Wastewater

The conventional parameters describing a wastewater are BOD₅, TKN, ammonia-N, nitrate-N, total COD, VSS, TSS, and alkalinity (Table 16).

Table 16: Characteristics of domestic wastewater, after primary sedimentation.

Symbol	Name	Value	Unit
TSS	Total Suspended Solids	82	mg/L
VSS	Volatile Suspended Solids	61.5	mg/L
BOD ₅	Five day Biological Oxygen Demand	155	mg-O ₂ /L
COD _t	Total Chemical Oxygen Demand	325	mg/L as COD
TAN	Total Ammonia Nitrogen	25	mg-N/L
TKN	Total Kjeldahl Nitrogen	43.5	mg-N/L
NO _x	Nitrate-Nitrite Nitrogen	0.0	mg-N/L
ALK	Alkalinity	200	mg-CaCO ₃ /L

(Grady et al., 1999)

For wastewater modeling a more fractionated wastewater characterization is required. For example total COD is divided into particulate and soluble inert COD, and slowly and readily biodegradable substrate. The wastewater characteristics needed for the Activated Sludge Model No.1 (ASM-1, International Association on Water Quality) are shown in Table 17 together with typical values for domestic wastewater.

It is possible to convert traditional parameters into COD and nitrogen based parameters using equations (45) to (52) according to Grady et al.(1999).

Table 17: Characteristics of municipal wastewater (in COD and nitrogen-N units)

Symbol	Name	Value	Unit
X _{IO}	Particulate inert organic matter	35	mg-COD/L
S _{IO}	Soluble inert organic matter	25	mg-COD/L
X _{SO}	Slowly biodegradable substrate	150	mg-COD/L
S _{SO}	Readily biodegradable substrate	115	mg-COD/L
S _O	Oxygen	0	mg-O ₂ /L
S _{NOO}	Soluble nitrate nitrogen	0	mg-N/L
S _{NHO}	Soluble ammonia nitrogen	25	mg-N/L
S _{NSO}	Soluble biodegradable organic nitrogen	6.5	mg-N/L
X _{NSO}	Particulate biodegradable organic nitrogen	8.5	mg-N/L
S _{NIO}	Soluble inert organic nitrogen	1.5	mg-N/L
X _{NIO}	Particulate inert organic nitrogen	2.1	mg-N/L
S _{ALKO}	Alkalinity	2	mmol/L

(Grady et al., 1999)

$$COD_{total,measured} = COD_{BO} + COD_{IO} \quad (45)$$

Where COD_{BO} is the total biodegradable fraction, and COD_{IO} is the total inert fraction of organic matter.

$$COD_{BO} = \frac{BOD_L}{(1 - f_D * Y_H)} = S_{SO} + X_{SO} \quad (46)$$

The parameters are defined in Table 15 and Table 19. S_{SO} and X_{SO} have to be assumed according to experience or other indicators.

$$COD_{IO} = S_{IO} + X_{IO} \quad (47)$$

The parameters are defined in Table 15 and Table 19. S_{IO} and X_{IO} have to be assumed according to experience or other indicators.

$$TKN_{measured} = ON_{TO} + S_{NHO,measured} \quad (48)$$

Where ON_{TO} is the total organic nitrogen fraction of the total Kjeldahl nitrogen.

$$S_{NSO} + X_{NSO} = ON_{TO} - S_{NIO} - X_{NIO} \quad (49)$$

The parameters are defined in Table 15 and Table 19.

$$X_{NIO} \sim i_{N/XD} * X_{IO} \quad (50)$$

The parameters are defined in Table 15 and Table 19.

$$S_{NIO} \sim 1.5 \left[\frac{mg - N}{L} \right] \quad (51)$$

The parameters are defined in Table 15 and Table 19.

$$S_{NSO} = (S_{NSO} + X_{NSO}) * \frac{S_{SO}}{X_{SO} + S_{SO}} \quad (52)$$

The parameters are defined in Table 15 and Table 19.

Equation (52) shows that the ratio of particulate to soluble organic nitrogen is usually the same as for particulate to soluble organic matter.

4.3.2 Characteristics of Pretreated Landfill Leachate

The BOD₅, total COD, VSS, TSS, TAN, TKN, and alkalinity of landfill site II pretreated landfill leachate were determined and are shown in Table 18. Pretreated leachate is the effluent from the Ammonia Recovery Process, where most ammonia was removed.

Table 18: Representative characteristics of landfill site II pretreated leachate in conventional units.

Symbol	Name	Value	Unit
TSS	Total Suspended Solids	500	mg/L
VSS	Volatile Suspended Solids	230	mg/L
BOD ₅	Five day Biological Oxygen Demand	290	mg-O ₂ /L
COD _t	Total Chemical Oxygen Demand	560	mg/L as COD
TAN	Total Ammonia Nitrogen	8	mg-N/L
TKN	Total Kjeldahl Nitrogen	35	mg-N/L
NO _x	Nitrate-Nitrite Nitrogen	3	mg-N/L
ALK	Alkalinity	5500	mg-CaCO ₃ /L

For modeling the activated sludge process, parameters in conventional units as shown in Table 18 were to be converted to COD based units. The conversions were done based on equations (45) to (52). All wastewater characteristics used for modeling the activated sludge process are summarized in Table 19.

Table 19: Representative characteristics of pretreated leachate (in COD and nitrogen-N units).

Symbol	Name	Representative value	Unit
X _{IO}	Particulate inert organic matter	156 ^{*b}	mg-COD/L
S _{IO}	Soluble inert organic matter	78 ^{*b}	mg-COD/L
X _{SO}	Slowly biodegradable substrate	108.7 ^{**b}	mg-COD/L
S _{SO}	Readily biodegradable substrate	217.3 ^{***b}	mg-COD/L
S _O	Oxygen	0 ^a	mg-O ₂ /L
S _{NOO}	Soluble nitrate nitrogen	3 ^c	mg-N/L
S _{NHO}	Soluble ammonia nitrogen	8 ^c	mg-N/L
S _{NSO}	Soluble biodegradable organic nitrogen	13.9 ^{*b}	mg-N/L
X _{NSO}	Particulate biodegradable organic nitrogen	4.7 ^{*b}	mg-N/L
S _{NIO}	Soluble inert organic nitrogen	1.5 ^{*b}	mg-N/L
X _{NIO}	Particulate inert organic nitrogen	6.9 ^{*b}	mg-N/L
S _{ALKO}	Alkalinity	55 ^c	mmol/L

a) assumed b)calculated c)measured, **30% of BOD_L, ***70% of BOD_L, * 30% to 70% particulate to soluble matter.

4.4 Activated Sludge Modeling

4.4.1 Simple CSTR Mass Balance

To describe a simple continued stirred tank reactor (CSTR) and model microbial growth, a mass balance around the reactor for all components of interest were to be developed. In this case the control volume is a single CSTR with inflow, outflow, and biomass waste as shown in Figure 42.

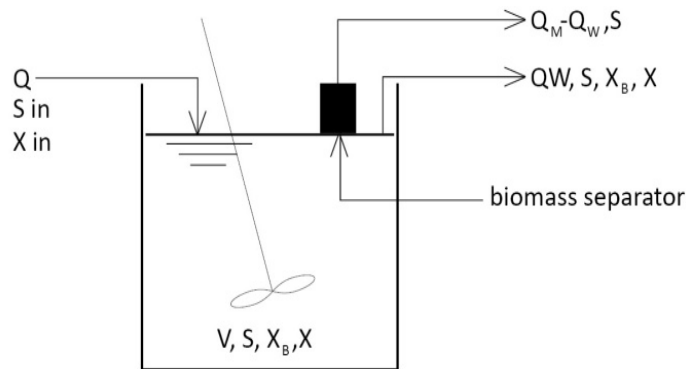


Figure 42: Schematic diagram of a CSTR, with biomass withholding (SRT \neq HRT) (adopted from Grady et al., 1999).

The general mass balance can be written as following:

$$\frac{dC_i}{dt} * V = Q_{in} * C_{i,in} - Q_W * C_i - Q_{out} * C'_{i,out} + r_i * V \quad (53)$$

Where dC/dt is the change in concentration over time, V is the reactor volume in L, Q_{in} is the reactor inflow in L/day, Q_w is the waste flow in L/day, Q_{out} is the reactor outflow in L/day, C_{in} and C_w are the concentrations of component i in the inflow and the waste flow respectively in mg/L, $C'_{i,out}$ is the concentration of component i in the outflow of

the reactor passing through the biomass separator in mg/L (it is zero for particulate matter), and r_i is the sum of all reaction rates of component i in mg/L-day.

At steady state, equation (53) equals zero and can be rewritten:

$$0 = \left(\frac{Q_{in}}{V} * C_{i,in} \right) - \left(\frac{Q_w}{V} * C_i \right) - \left(\frac{Q_{in} - Q_w}{V} * C'_{i,out} \right) + r_i \quad (54)$$

4.4.2 Activated Sludge Model No. 1 (ASM1)

ASM1 involves death and lysis of biomass into particulate substrate and inert biomass debris. The particulate substrate will undergo hydrolysis by active heterotrophic bacteria and turned into soluble substrate, on which new biomass can grow on (Figure 43).

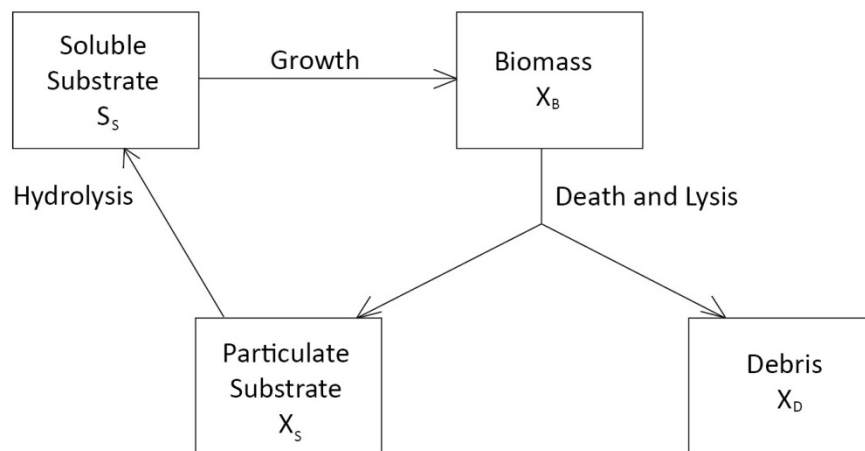


Figure 43: Schematic diagram of biomass growth, including death and lysis of biomass, and hydrolysis of particulate organic matter (adopted from Grady et al., 1999).

Following processes were included into ASM1: Aerobic and anoxic growth of heterotrophic bacteria, aerobic growth of autotrophic bacteria, death and lysis of heterotrophs, death and lysis of autotrophs, ammonification of soluble organic nitrogen, hydrolysis of particulate organic matter, hydrolysis of particulate organic nitrogen.

Process rates and mass balance equations for each component of Table 19 are presented in equations (55) to (80). The derivation of the shown reaction rates are described by Henze et al. (1987), Grady et al. (1999).

1) Particulate Inert Organic Matter (X_I) (COD or Nitrogen)

Particulate inert organic matter is not be participating in any biological reaction, therefore following applies:

$$r_{X_I} = 0 \quad (55)$$

Where r_{X_I} is the sum of reactions of particulate inert organic matter.

The dynamic mass balance equation for particulate inert organic matter in a simple CSTR process is shown below:

$$\frac{dX_I}{dt} = \left(\frac{Q_{in}}{V} * X_{IO} \right) - \left(\frac{Q_w}{V} * X_I \right) \quad (56)$$

The parameters are defined in Table 15 and Table 19.

2) Slowly biodegradable substrate (X_S)

Particulate slowly biodegradable substrate will be formed by the death and lysis of heterotrophic and autotrophic biomass, and destroyed by hydrolysis of particulate organic matter carried out by heterotrophic biomass. The sum of reactions for slowly biodegradable substrate is shown below:

$$r_{XS} = (1 - f_D') * (b_{L,H} * X_{B,H}) + (1 - f_D') * (b_{L,A} * X_{B,A}) - k_h * \frac{\frac{X_S}{X_{B,H}}}{K_x + \left(\frac{X_S}{X_{B,H}}\right)} \quad (57)$$

$$* \left[\left(\frac{S_O}{K_{O,H} + S_O} \right) + \eta_h * \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) * \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) \right] * X_{B,H}$$

Where r_{XS} is the sum of reactions of slowly biodegradable substrate, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for slowly biodegradable substrate in a simple CSTR process is shown below:

$$\frac{dX_S}{dt} = \left(\frac{Q_{in}}{V} * X_{S0} \right) - \left(\frac{Q_W}{V} * X_S \right) + r_{XS} \quad (58)$$

The parameters are defined in Table 15 and Table 19.

3) Heterotrophic Biomass ($X_{B,H}$)

Heterotrophic biomass is formed by aerobic and anoxic heterotrophic growth, and destroyed by death and lysis. The sum of reactions for heterotrophic biomass is shown below:

$$r_{XB,H} = \left(\mu_{H,max} * \left(\frac{S_S}{K_S + S_S} \right) * \left(\frac{S_O}{K_{O,H} + S_O} \right) * X_{B,H} \right) \quad (59)$$

$$+ \left(\mu_{H,max} * \left(\frac{S_S}{K_S + S_S} \right) * \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) * \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) * \eta_g * X_{B,H} \right) - (b_{L,H} * X_{B,H})$$

Where $r_{XB,H}$ is the sum of reactions of heterotrophic biomass, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for heterotrophic biomass in a simple CSTR process is shown in equation (60). Note that it is assumed that no biomass is present in the influent.

$$\frac{dX_{B,H}}{dt} = -\left(\frac{Q_W}{V} * X_{B,H}\right) + r_{XB,H} \quad (60)$$

The parameters are defined in Table 15 and Table 19.

4) Autotrophic Biomass ($X_{B,A}$)

Autotrophic biomass is formed by aerobic autotrophic growth, and destroyed by death and lysis. The sum of reactions for heterotrophic biomass is shown below:

$$r_{XB,A} = \left(\mu_{A,max} * \left(\frac{S_{NH}}{K_{NH} + S_{NH}}\right) * \left(\frac{S_O}{K_{O,A} + S_O}\right) * X_{B,A}\right) - (b_{L,A} * X_{B,A}) \quad (61)$$

Where $r_{XB,A}$ is the sum of reactions of autotrophic biomass, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for autotrophic biomass in a simple CSTR process is shown in equation (62). Note that it is assumed that no biomass is present in the influent.

$$\frac{dX_{B,A}}{dt} = -\left(\frac{Q_W}{V} * X_{B,A}\right) + r_{XB,A} \quad (62)$$

The parameters are defined in Table 15 and Table 19.

5) Biomass Debris (X_D)

Biomass debris is produced by death and lysis of heterotrophic and autotrophic biomass only. The sum of reactions for biomass debris is shown below:

$$r_{XD} = f'_D * (b_{L,H} * X_{B,H}) + f'_D * (b_{L,A} * X_{B,A}) \quad (63)$$

Where r_{XD} is the sum of reactions of biomass debris, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for biomass debris in a simple CSTR process is shown in equation (64). Note that it is assumed that no biomass debris is present in the influent.

$$\frac{dX_D}{dt} = -\left(\frac{Q_W}{V} * X_D\right) + r_{XD} \quad (64)$$

The parameters are defined in Table 15 and Table 19.

6) Soluble Inert Organic Matter (S_I) (COD or Nitrogen)

Soluble inert organic matter will not be participating in any biological reaction, therefore following applies:

$$r_{SI} = 0 \quad (65)$$

Where r_{SI} is the sum of reactions of soluble inert organic matter.

The dynamic mass balance equation for soluble inert organic matter in a simple CSTR process is shown below:

$$\frac{dS_I}{dt} = \left(\frac{Q_{in}}{V} * S_{Io}\right) - \left(\frac{Q_W}{V} * S_I\right) - \left(\frac{Q_{in} - Q_W}{V} * S_I\right) \quad (66)$$

The parameters are defined in Table 15 and Table 19.

7) Readily Biodegradable Substrate (S_S)

Readily biodegradable substrate is reduced by aerobic and anoxic heterotrophic growth, and produced by hydrolysis of particulate organics. The sum of reactions for readily biodegradable substrate is shown below:

$$\begin{aligned}
 r_{SS} = & - \left(\frac{\mu_{H,max}}{Y_H} * \left(\frac{S_S}{K_S + S_S} \right) * \left(\frac{S_O}{K_{O,H} + S_O} \right) * X_{B,H} \right) \\
 & - \left(\frac{\mu_{H,max}}{Y_H} * \left(\frac{S_S}{K_S + S_S} \right) * \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) * \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) \right. \\
 & \left. * \eta_g * X_{B,H} \right) + k_h * \frac{\frac{X_S}{X_{B,H}}}{K_x + \left(\frac{X_S}{X_{B,H}} \right)} \\
 & * \left[\left(\frac{S_O}{K_{O,H} + S_O} \right) + \eta_h * \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) * \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) \right] * X_{B,H}
 \end{aligned} \tag{67}$$

Where r_{SS} is the sum of reactions of readily biodegradable substrate, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for readily biodegradable substrate in a simple CSTR process is shown below:

$$\frac{dS_S}{dt} = \left(\frac{Q_{in}}{V} * S_{S0} \right) - \left(\frac{Q_W}{V} * S_S \right) - \left(\frac{Q_{in} - Q_W}{V} * S_S \right) + r_{SS} \tag{68}$$

The parameters are defined in Table 15 and Table 19.

8) Oxygen (S_O)

Oxygen will be used in aerobic growth of heterotrophic and autotrophic biomass, and supplied by aeration. For the simplicity of the model the oxygen concentration of the mixed suspension will be set to a constant value, assuming a constant supply to match the need for aerobic growth. If the oxygen concentration is set to be zero, aerobic growth will not occur. The sum of oxygen needed for heterotrophic and autotrophic growth is shown below:

$$r_{SO} = \frac{1 - Y_H}{Y_H} * \left(\mu_{H,max} * \left(\frac{S_S}{K_S + S_S} \right) * \left(\frac{S_O}{K_{O,H} + S_O} \right) * X_{B,H} \right) + \frac{4.57 - Y_A}{Y_A} \quad (69)$$

$$* \left(\mu_{A,max} * \left(\frac{S_{NH}}{K_{NH} + S_{NH}} \right) * \left(\frac{S_O}{K_{O,A} + S_O} \right) * X_{B,A} \right)$$

Where r_{SO} is the sum of reactions of oxygen, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for oxygen in a simple CSTR process is shown below. Note that the CSTR is set to operate at a constant oxygen concentration.

$$\frac{dRO}{dt} = -r_{SO} * V \quad (S_O \text{ is constant}) \quad (70)$$

Where RO is the oxygen supply in [mg], other parameters are defined in Table 15 and Table 19.

9) Nitrate Nitrogen (S_{NO})

Nitrate nitrogen is produced by aerobic autotrophic growth and used for anoxic heterotrophic growth. The sum of reactions for nitrate nitrogen is shown below:

$$r_{SNO} = \left(\frac{\mu_{A,max}}{Y_A} * \left(\frac{S_{NH}}{K_{NH} + S_{NH}} \right) * \left(\frac{S_O}{K_{O,A} + S_O} \right) * X_{B,A} \right) - \frac{1 - Y_H}{2.86 * Y_H} \quad (71)$$

$$* \left(\mu_{H,max} * \left(\frac{S_S}{K_S + S_S} \right) * \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) * \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) * \eta_g * X_{B,H} \right)$$

Where r_{SNO} is the sum of reactions of nitrate nitrogen, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for nitrate nitrogen in a simple CSTR process is shown below:

$$\frac{dS_{NO}}{dt} = \left(\frac{Q_{in}}{V} * S_{NOO}\right) - \left(\frac{Q_W}{V} * S_{NO}\right) - \left(\frac{Q_{in} - Q_W}{V} * S_{NO}\right) + r_{SNO} \quad (72)$$

The parameters are defined in Table 15 and Table 19.

10) Ammonia Nitrogen (S_{NH})

Ammonia nitrogen will be used for anoxic and aerobic heterotrophic growth, for aerobic autotrophic growth, and produced by ammonification of soluble organic nitrogen. The sum of reactions for ammonia nitrogen is shown below:

$$\begin{aligned} r_{SNH} = & -i_{N/XB} * \left(\mu_{H,max} * \left(\frac{S_S}{K_S + S_S} \right) * \left(\frac{S_O}{K_{O,H} + S_O} \right) * X_{B,H} \right) - i_{N/XB} \quad (73) \\ & * \left(\mu_{H,max} * \left(\frac{S_S}{K_S + S_S} \right) * \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) * \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) \right. \\ & * \eta_g * X_{B,H} \left. \right) - \left(i_{N/XB} - \frac{1}{Y_A} \right) \\ & * \left(\mu_{A,max} * \left(\frac{S_{NH}}{K_{NH} + S_{NH}} \right) * \left(\frac{S_O}{K_{O,A} + S_O} \right) * X_{B,A} \right) + (k_a * S_{NS} \\ & * X_{B,H}) \end{aligned}$$

Where r_{SNH} is the sum of reactions of ammonia nitrogen, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for ammonia nitrogen in a simple CSTR process is shown below:

$$\frac{dS_{NH}}{dt} = \left(\frac{Q_{in}}{V} * S_{NH0} \right) - \left(\frac{Q_W}{V} * S_{NH} \right) - \left(\frac{Q_{in} - Q_W}{V} * S_{NH} \right) + r_{SNH} \quad (74)$$

The parameters are defined in Table 15 and Table 19.

11) Soluble Biodegradable Organic Nitrogen (S_{NS})

Soluble biodegradable organic nitrogen will be destroyed by ammonification, and produced by hydrolysis of particulate organic nitrogen. The sum of reactions for soluble biodegradable organic nitrogen is shown below:

$$r_{SNS} = \left(\frac{X_{NS}}{X_S} \right) * \left\{ k_h * \frac{\frac{X_S}{X_{B,H}}}{K_x + \left(\frac{X_S}{X_{B,H}} \right)} * \left[\left(\frac{S_O}{K_{O,H} + S_O} \right) + \eta_h * \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) * \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) \right] * X_{B,H} \right\} - (k_a * S_{NS} * X_{B,H}) \quad (75)$$

Where r_{SNS} is the sum of reactions of soluble biodegradable organic nitrogen, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for soluble biodegradable organic nitrogen in a simple CSTR process is shown below:

$$\frac{dS_{NS}}{dt} = \left(\frac{Q_{in}}{V} * S_{NS0} \right) - \left(\frac{Q_W}{V} * S_{NS} \right) - \left(\frac{Q_{in} - Q_W}{V} * S_{NS} \right) + r_{SNS} \quad (76)$$

The parameters are defined in Table 15 and Table 19.

12) Particulate Biodegradable Organic Nitrogen (X_{NS})

Particulate biodegradable organic nitrogen will be produced by death and lysis of autotrophic and heterotrophic biomass and destroyed by hydrolysis to soluble organic nitrogen. The sum of reactions for particulate biodegradable organic nitrogen is shown below:

$$\begin{aligned}
 r_{X_{NS}} = & (i_{N/XB} - f'_D * i_{N/XD}) * (b_{L,H} * X_{B,H}) + (i_{N/XB} - f'_D * i_{N/XD}) \\
 & * (b_{L,A} * X_{B,A}) \\
 & - \left(\frac{X_{NS}}{X_S} \right) \left\{ k_h * \frac{\frac{X_S}{X_{B,H}}}{K_x + \left(\frac{X_S}{X_{B,H}} \right)} \right. \\
 & \left. * \left[\left(\frac{S_O}{K_{O,H} + S_O} \right) + \eta_h * \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) * \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) \right] * X_{B,H} \right\}
 \end{aligned} \tag{77}$$

Where $r_{X_{NS}}$ is the sum of reactions of particulate biodegradable organic nitrogen, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for particulate biodegradable organic nitrogen in a simple CSTR process is shown below:

$$\frac{dX_{NS}}{dt} = \left(\frac{Q_{in}}{V} * X_{NSO} \right) - \left(\frac{Q_W}{V} * X_{NS} \right) + r_{X_{NS}} \tag{78}$$

The parameters are defined in Table 15 and Table 19.

13) Alkalinity (S_{ALK})

Alkalinity is destroyed by growth of aerobic heterotrophic and autotrophic bacteria, produced by anoxic growth of heterotrophic bacteria and ammonification of soluble organic nitrogen. The sum of reactions for alkalinity is shown below:

$$\begin{aligned}
 r_{SALK} = & -\frac{i_{N/XB}}{14} * \left(\mu_{H,max} * \left(\frac{S_S}{K_S + S_S} \right) * \left(\frac{S_O}{K_{O,H} + S_O} \right) * X_{B,H} \right) & (79) \\
 & + \left(\frac{1 - Y_H}{14 * (2.86 * Y_H)} - \frac{i_{N/XB}}{14} \right) \\
 & * \left[\mu_{H,max} * \left(\frac{S_S}{K_S + S_S} \right) * \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) * \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) \right. \\
 & * \eta_g * X_{B,H} \left. \right] - \left(\frac{i_{N/XB}}{14} - \frac{1}{7 * Y_A} \right) \\
 & * \left(\mu_{A,max} * \left(\frac{S_{NH}}{K_{NH} + S_{NH}} \right) * \left(\frac{S_O}{K_{O,A} + S_O} \right) * X_{B,A} \right) + \frac{1}{14} (k_a * S_{NS} \\
 & * X_{B,H})
 \end{aligned}$$

Where r_{SALK} is the sum of reactions of alkalinity, and other parameters are defined in Table 15 and Table 19.

The dynamic mass balance equation for alkalinity in a simple CSTR process is shown below:

$$\frac{dS_{ALK}}{dt} = \left(\frac{Q_{in}}{V} * S_{ALKO} \right) - \left(\frac{Q_W}{V} * S_{ALK} \right) - \left(\frac{Q_{in} - Q_W}{V} * S_{ALK} \right) + r_{SALK} \quad (80)$$

The parameters are defined in Table 15 and Table 19.

4.5 Model Equations as used for Computation

The retention time is defined as the time fluid is inside the reactor:

$$HRT = \frac{V}{Q_{in}} = \theta \quad (81)$$

Where θ is the hydraulic retention time in days, and all parameters are defined elsewhere.

The solids retention time is defined as the time solids stay inside the reactor:

$$SRT = \frac{V}{Q_w} = \theta_c \quad (82)$$

Where θ_c is the hydraulic retention time in days, and all parameters are defined elsewhere.

For general mass balances discussed above the efficiency of the biomass separator was set to be 100%. In reality that will not be the case, therefore there will be residual solids in the effluent according to an experimental determined efficiency coefficient η_c of the separating system. Inserting the HRT, SRT, and the efficiency factor for solids retardation into the individual mass balances and substituting dC_i/dt by $\Delta C_i/\Delta t$ yields following equations:

1) *Particulate Inert Organic Matter (X_I) (COD or Nitrogen)*

$$X_{I,2} = \left\{ \left[\left(\frac{1}{\theta} * X_{I0} \right) - \left(\frac{1}{\theta_c} * X_I \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_c} \right) * X_I * \eta_c \right) \right] * \Delta t \right\} + X_{I,1} \quad (83)$$

Where all parameters are defined elsewhere.

2) Slowly Biodegradable Substrate (X_S)

$$X_{S,2} = \left\{ \left[\left(\frac{1}{\theta} * X_{SO} \right) - \left(\frac{1}{\theta_C} * X_S \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_C} \right) * X_S * \eta_C \right) + r_{XS} \right] * \Delta t \right\} + X_{S,1} \quad (84)$$

Where all parameters are defined elsewhere.

3) Heterotrophic Biomass ($X_{B,H}$)

$$X_{B,H,2} = \left\{ \left[- \left(\frac{1}{\theta_C} * X_{B,H} \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_C} \right) * X_{B,H} * \eta_C \right) + r_{XB,H} \right] * \Delta t \right\} + X_{B,H,1} \quad (85)$$

Where all parameters are defined elsewhere.

4) Autotrophic Biomass ($X_{B,A}$)

$$X_{B,A,2} = \left\{ \left[- \left(\frac{1}{\theta_C} * X_{B,A} \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_C} \right) * X_{B,A} * \eta_C \right) + r_{XB,A} \right] * \Delta t \right\} + X_{B,A,1} \quad (86)$$

Where all parameters are defined elsewhere.

5) Biomass Debris (X_D)

$$X_{D,2} = \left\{ \left[- \left(\frac{1}{\theta_C} * X_D \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_C} \right) * X_D * \eta_C \right) + r_{XD} \right] * \Delta t \right\} + X_{D,1} \quad (87)$$

Where all parameters are defined elsewhere.

6) Soluble Inert Organic Matter (S_I)(COD or Nitrogen)

$$S_{I,2} = \left\{ \left[\left(\frac{1}{\theta} * S_{IO} \right) - \left(\frac{1}{\theta_C} * S_I \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_C} \right) * S_I \right) \right] * \Delta t \right\} + S_{I,1} \quad (88)$$

Where all parameters are defined elsewhere.

7) Readily Biodegradable Substrate (S_s)

$$S_{s,2} = \left\{ \left[\left(\frac{1}{\theta} * S_{s0} \right) - \left(\frac{1}{\theta_c} * S_s \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_c} \right) * S_s \right) + r_{ss} \right] * \Delta t \right\} + S_{s,1} \quad (89)$$

Where all parameters are defined elsewhere.

8) Oxygen (S_o)

$$RO_2 = \{ [-r_{sO} * V] * \Delta t \} + RO_1 (S_o \text{ is constant}) \quad (90)$$

Where R_{sO} is the mass of oxygen that has to be supplied mg/day, and all other parameters are defined elsewhere.

9) Nitrate Nitrogen (S_{NO})

$$S_{NO,2} = \left\{ \left[\left(\frac{1}{\theta} * S_{NO0} \right) - \left(\frac{1}{\theta_c} * S_{NO} \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_c} \right) * S_{NO} \right) + r_{SNO} \right] * \Delta t \right\} + S_{NO,1} \quad (91)$$

Where all parameters are defined elsewhere.

10) Ammonia Nitrogen (S_{NH})

$$S_{NH,2} = \left\{ \left[\left(\frac{1}{\theta} * S_{NH0} \right) - \left(\frac{1}{\theta_c} * S_{NH} \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_c} \right) * S_{NH} \right) + r_{SNH} \right] * \Delta t \right\} + S_{NH,1} \quad (92)$$

Where all parameters are defined elsewhere.

11) Soluble Biodegradable Organic Nitrogen (S_{NS})

$$S_{NS,2} = \left\{ \left[\left(\frac{1}{\theta} * S_{NS0} \right) - \left(\frac{1}{\theta_c} * S_{NS} \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_c} \right) * S_{NS} \right) + r_{SNS} \right] * \Delta t \right\} + S_{NS,1} \quad (93)$$

Where all parameters are defined elsewhere.

12) Particulate Biodegradable Organic Nitrogen (X_{NS})

$$X_{NSO,2} = \left\{ \left[\left(\frac{1}{\theta} * X_{NSO} \right) - \left(\frac{1}{\theta_C} * X_{NS} \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_C} \right) * X_{NS} * \eta_C \right) + r_{XNS} \right] * \Delta t \right\} \quad (94)$$

$$+ X_{NSO,1}$$

Where all parameters are defined elsewhere.

13) Alkalinity (S_{ALK})

$$S_{ALK,2} = \left\{ \left[\left(\frac{1}{\theta} * S_{ALKO} \right) - \left(\frac{1}{\theta_C} * S_{ALK} \right) - \left(\left(\frac{1}{\theta} - \frac{1}{\theta_C} \right) * S_{ALK} \right) + r_{SALK} \right] * \Delta t \right\} \quad (95)$$

$$+ S_{ALK,1}$$

Where all parameters are defined elsewhere.

4.6 Proposed Activated Sludge Design

A computer software was developed implementing the Activated Sludge Model No1 to model and design an activated sludge completely mixed reactor as part of a 500 gal/day leachate treatment facility. The computer code and user interface are shown in appendix **Fehler! Verweisquelle konnte nicht gefunden werden..** Kinetic parameters and stoichiometric coefficients used are shown in Table 15 and pretreated leachate characteristics used are shown in Table 19. Other model input parameters where the hydraulic retention time (HRT), which was set to be 3 hrs, and the oxygen concentration inside the tank, which was set to be constant at 2.0 mg-O₂/L. With 500 gal/day pretreated leachate input and an HRT of 3 hrs, the tank volume is calculated to be 7,500 L.

Two scenarios have been modeled, one where nitrification inhibitor is used to suppress nitrification, and one without nitrification inhibitor. It is assumed that the clarifier of the activated sludge system is 100% efficient, therefore the effluent will be free of particulates, including biomass and other particulate organic matter. Figure 44 represents the model results for heterotrophic biomass, autotrophic biomass, soluble substrate, nitrate, and ammonia in mg-COD or mg-N /L inside the reactor, and oxygen input in g-O₂/day, versus varying solids retention time (SRT).

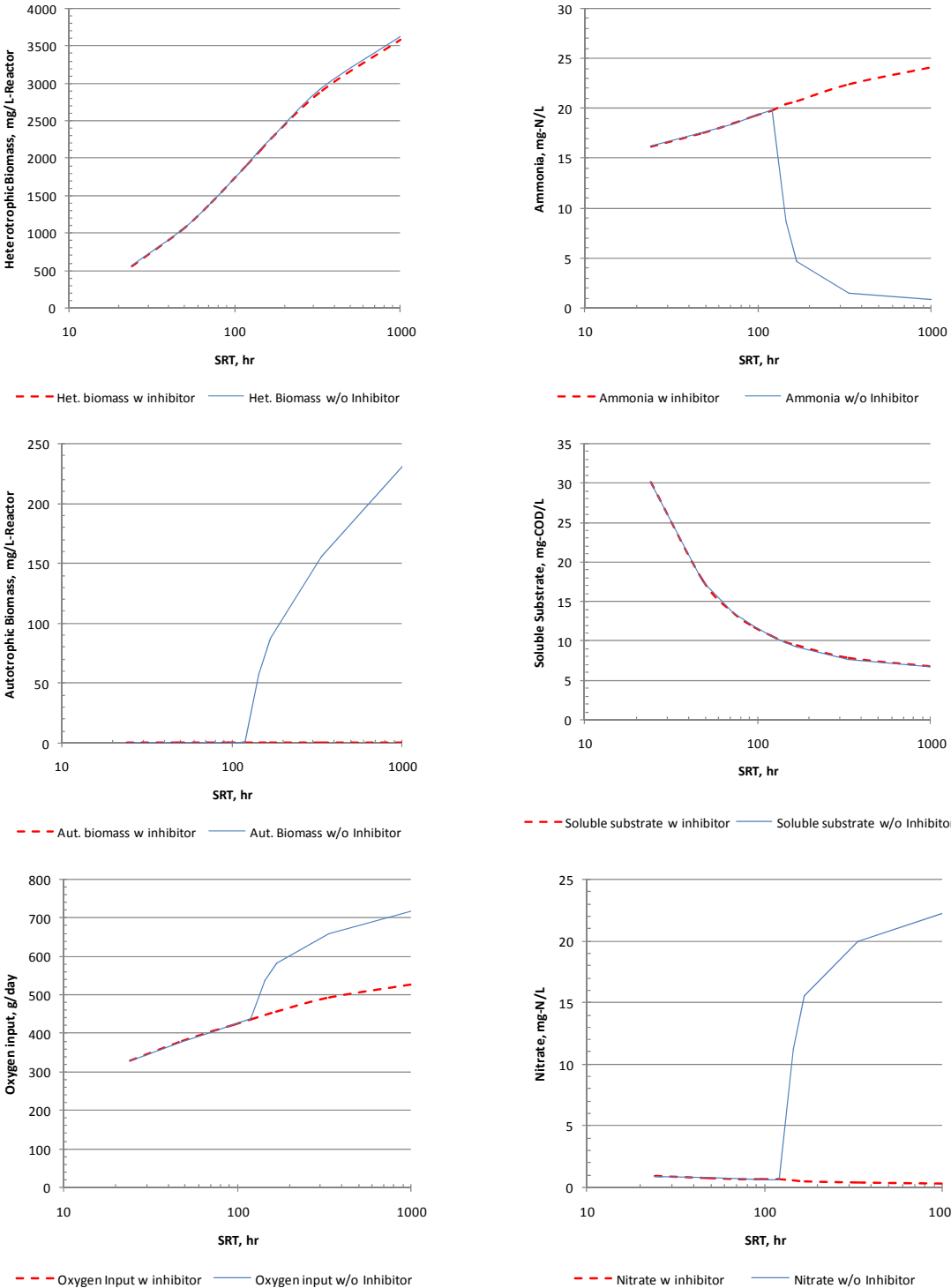


Figure 44: Activated sludge CSTR design for a system treating landfill site II leachate; oxygen input, heterotrophic biomass, autotrophic biomass, ammonia, nitrate, and soluble substrate vs. SRT; with and without nitrification inhibitor input; HRT=3 hr, V=7500 L.

At an SRT of < 120 hrs nitrification inhibitor does not have an effect, because nitrifying biomass cannot accumulate inside the reactor due to its slow growth and therefore washout. At an SRT of > 120 hrs, however, nitrifying bacteria accumulates inside the system and nitrification takes place if no nitrification inhibitor is used. At an SRT of 100 hrs the effluent ammonia concentration would be 19 mg/L (8 mg/L in influent) with or without nitrification inhibitor, the increase is due to hydrolysis and ammonification of soluble and particulate organic nitrogen. The soluble substrate concentration would be 11 mg-COD/L (217 mg-COD/L in influent) with a COD to BOD₅ ratio of 2/1 the effluent BOD₅ would be 5.5 mg-BOD₅/L, resulting in a NH₄ to BOD ratio of 1/3. With an NH₄ to BOD ratio below 1/1 this effluent would be suitable for algal post treatment. Nitrification inhibitor to suppress nitrification would not be needed since SRT would be below 120 hr.

5 ALGAE POST TREATMENT

5.1 Introduction

The cultivation of microalgae offers the potential to use solar-energy to assist in leachate final treatment providing opportunity for an increased green house gas (GHG) reduction from the overall process.

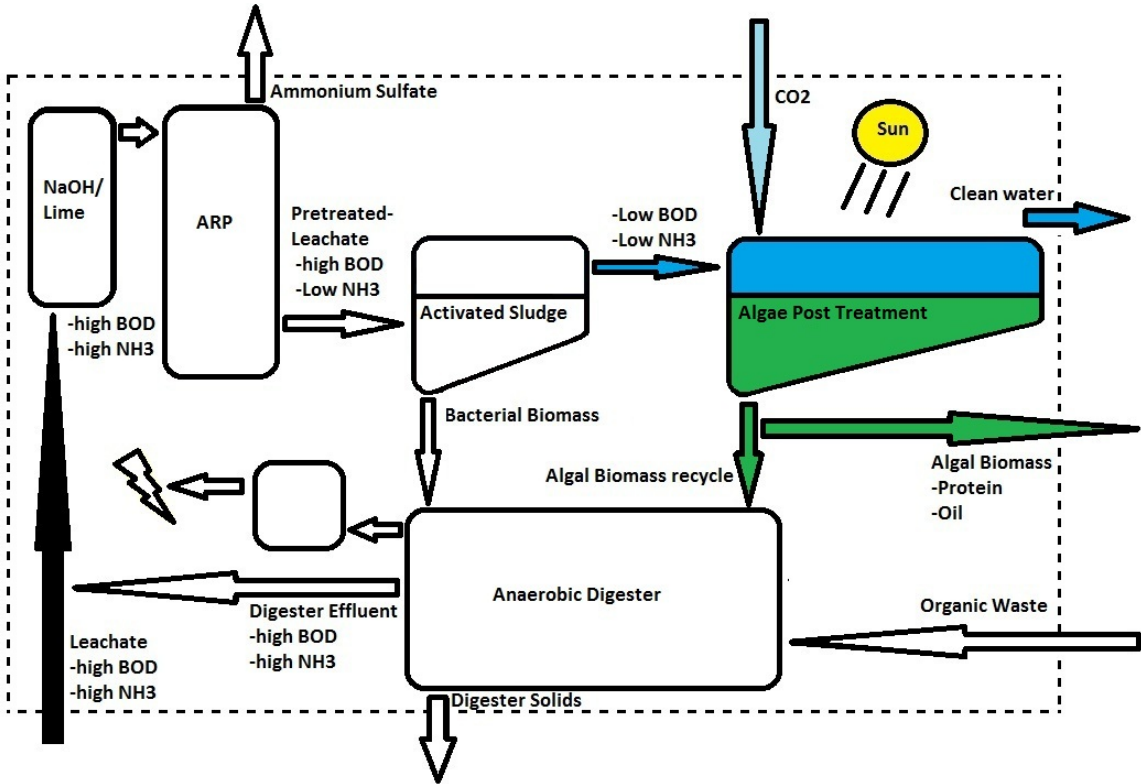


Figure 45: Proposed landfill leachate treatment system with algal post treatment highlighted.

Algae post treatment is realized using high-rate, paddlewheel driven algal ponds as used in the Controlled Eutrophication Process (CEP) (Benemann et al., 2002)

5.2 Lab Scale Algae Growth Results

The objective of algal growth trials conducted at Clemson University aquaculture facility was to evaluate algal growth potential using anaerobic digester effluent as a nutrient supply, in particular to determine the impact of digester VFA concentration on algal performance. Nitrogen as ammonia is a valuable nutrient needed by algae to form biomass. Using digester effluent as nutrient source for microalgae growth, nitrogen could be recycled as an agricultural fertilizer, or algae oil could be produced and turned into biofuels rather than being dissipated as nitrogen gas during an energy consuming aerobic treatment.

The average algal reactor initial biomass concentration and the average biomass gain vs. time is shown in Figure 46 and Figure 47, respectively. The average nitrogen uptake rate vs. time is shown in Figure 48.

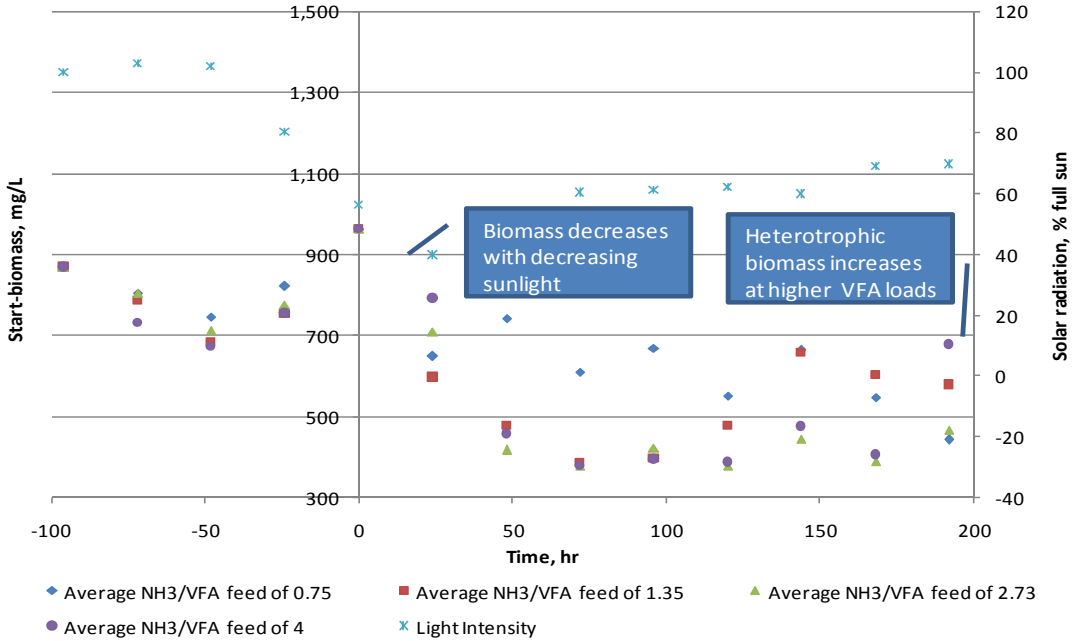


Figure 46: Algal culture average start biomass vs. time, with feed VFA/NH₃-N ratios of 0.75, 1.35, 2.73, and 4.0 and 20 mg/L-day NH₃-N.

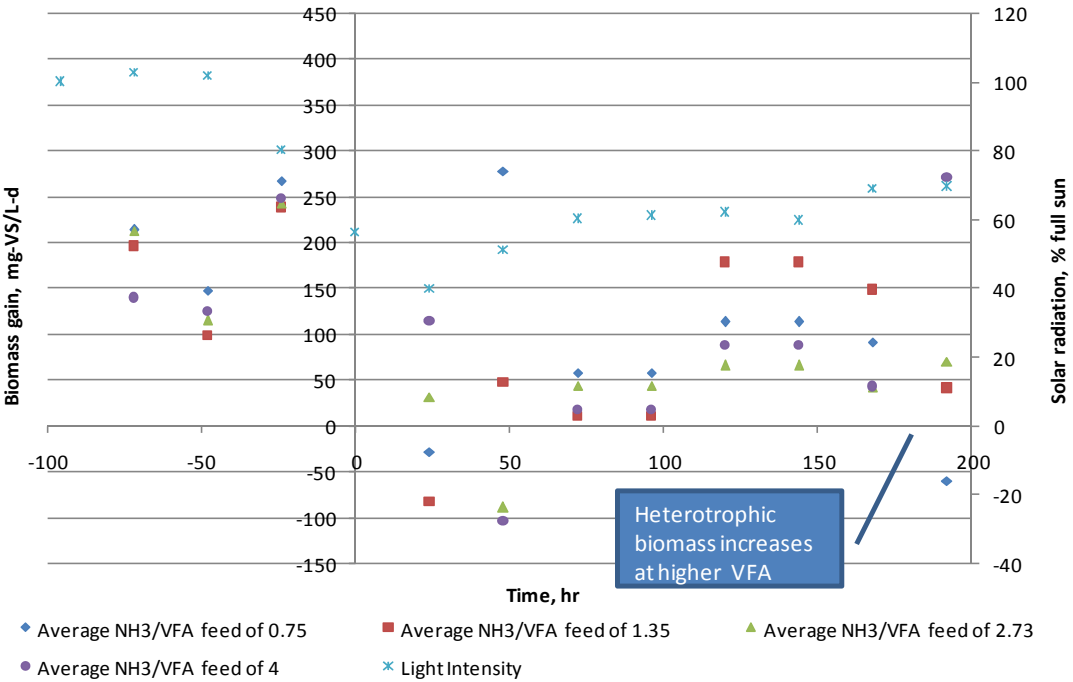


Figure 47: Algal culture average productivity vs. time, with feed VFA/NH₃-N ratios of 0.75, 1.35, 2.73, and 4.0 and 20 mg/L-day NH₃-N.

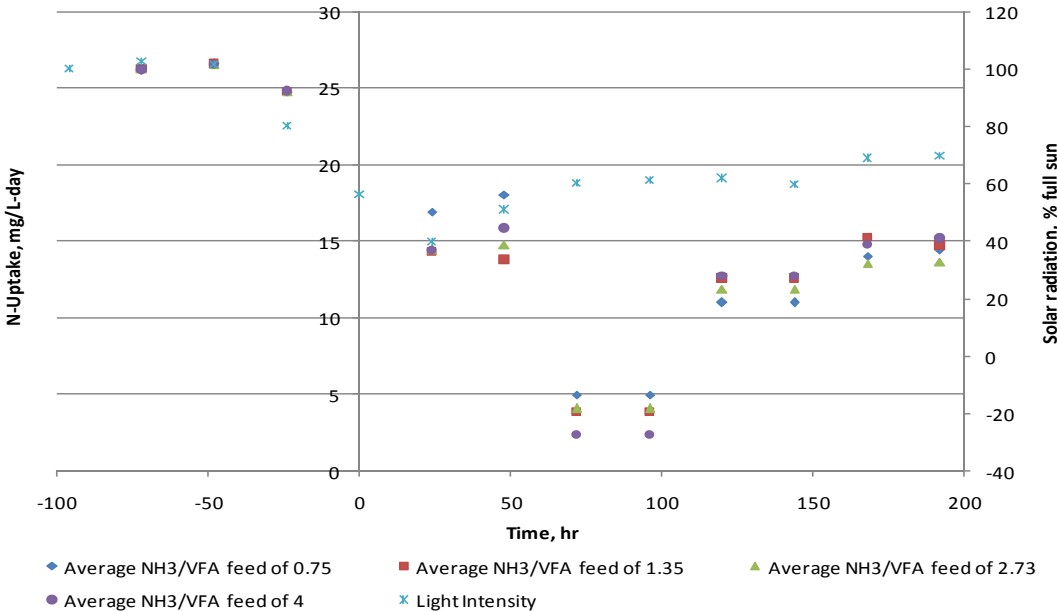


Figure 48: Algal culture average nitrogen uptake vs. time, with feed VFA/NH₃-N ratios of 0.75, 1.35, 2.73, and 4.0 and 20 mg/L-day NH₃-N.

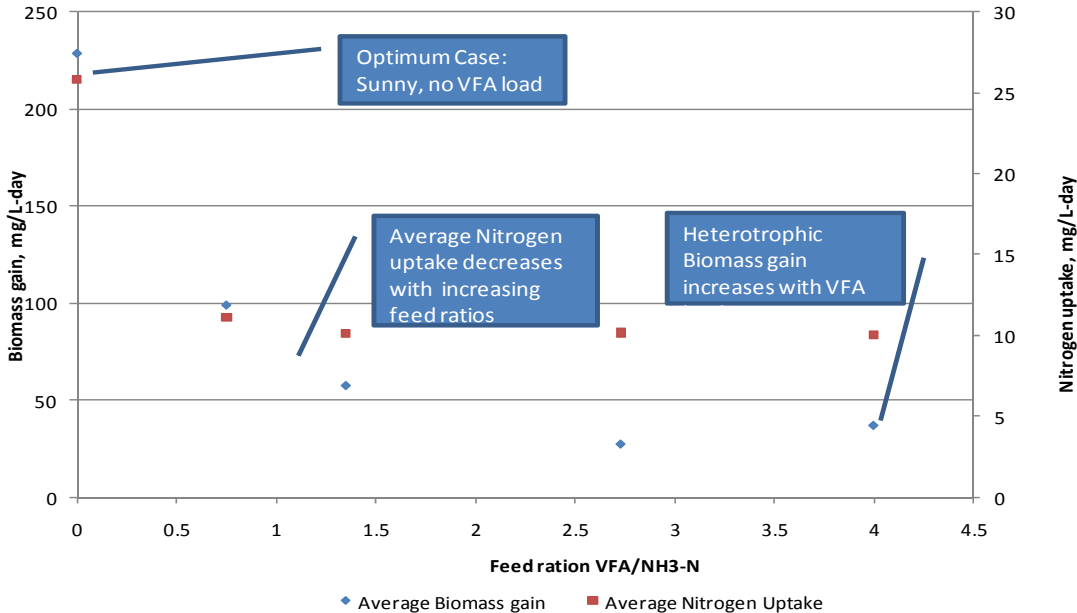


Figure 49: Algal culture average nitrogen uptake and biomass gain vs. feed VFA/NH₃-N ratio.

During the acclimation phase solar radiation was high, and none of the cultures were receiving a BOD load that influenced algal growth. The average algal biomass concentration ranged from 700 to 900 mg/L yielding a distinct dark green color. Average nitrogen uptake rates were 25 mg-N/L-day, and the average biomass gain was 230 mg-VS/L-day. This productivity translates to 23 g-VS/m²-day (10 cm depth), and 69 g-VS/m²-day (30 cm depth), suggesting optimal growth conditions. A productivity of 20 g-VS/m²-day for a 30 cm deep high rate algal production system was suggested by Brune et al. (2008), Henrich (2008), and Brune et al. (2003), to be representative for practical full scale applications.

The algal biomass gain for a VFA/NH₃-N feed ratio of 0.75 averaged 98.7 mg/L-day (9.9 g-VS/m²-day; 10cm depth or 29.6 g-VS/m²-day; 30cm depth). For a feed ratio of 1.35 the average biomass gain was 57.2 mg/L-day (5.7 g-VS/m²-day; 10cm depth or 17.2 g-VS/m²-day; 30cm depth), and 27 mg/L-day (2.7 g-VS/m²-day; 10cm depth or 8 g-VS/m²-day; 30cm depth) for a VFA/NH₃-N feed ratio of 2.73, respectively. For a VFA/NH₃-N feed ratio of 4.0 the average growth was 36.6 mg/L-day, including bacterial biomass. With approximately half of the biomass consisting of bacteria the productivity was < 1.5 g-VS/m²-day (10cm depth) or 4.5 g-VS/m²-day (30cm depth). The decline of algal productivity was enhanced by mixed weather conditions (only 50% of full sun). After two days of digester effluent supplemented feed, cultures receiving VFA/NH₃-N ratios of 0.75 and 1.35 began to recover. Algal cultures receiving VFA/NH₃-N ratios of above 1.35 did not recover, and stayed bacterial. The density of algal cells decreased

with increasing VFA input, increasing the amount of bacterial sludge. After 4 days of digester effluent supplemented feed, algal cultures receiving a VFA/NH₃-N ratio > 0.75 mainly consisted of bacterial flocks and decaying algal cells. At a VFA/NH₃-N feed ratio of 0.75 however, mainly live algal cells were observed microscopically

Despite the failure of the algal cultures, nitrogen uptake remained at an average of 10 mg/L-day (Figure 49). The unchanged nitrogen uptake is likely the result of increased bacterial growth in those cultures receiving high VFA loads. Low levels of nitrate could be seen during the fourth day of operation, suggesting increasing autotrophic activity. Even though cultures were aerated, it is possible that denitrifying biomass was present in oxygen depleted dead zones, and could explain the increased amount of unaccounted for nitrogen (Figure 50). The amount of nitrogen unaccounted for was higher (> 50% unaccounted for) for cultures receiving levels of organic carbon in excess of VFA/NH₃-N of 0.75 than for cultures receiving levels of organic carbon < VFA/NH₃-N of 0.75 (< 20% unaccounted for).

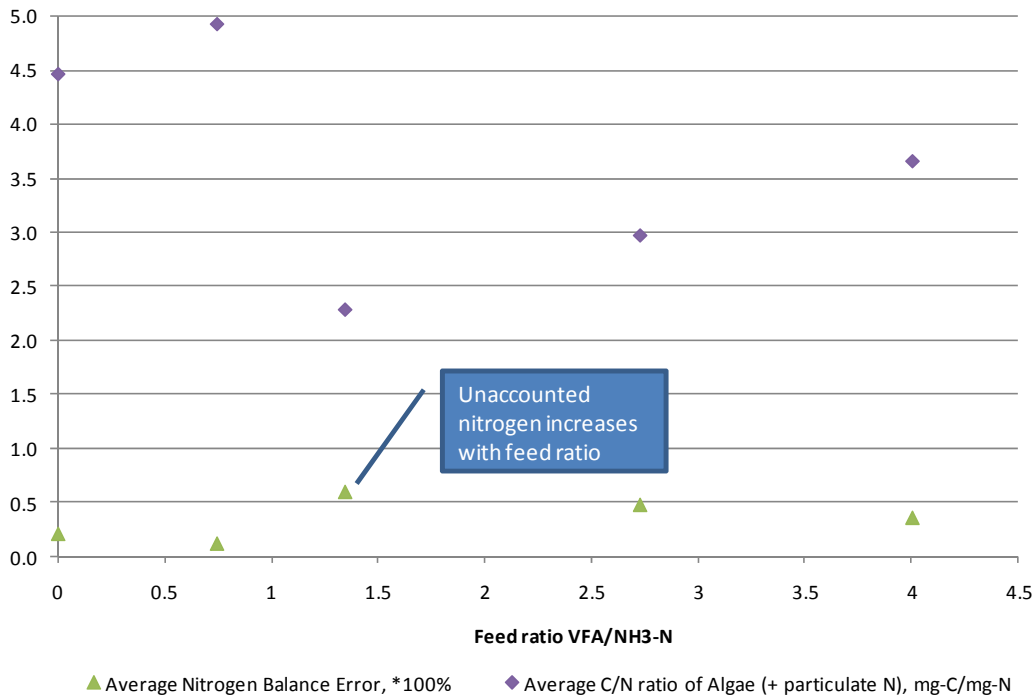


Figure 50: Algal cultures average nitrogen balance vs. feed VFA/NH₃-N ratio.

Figure 51 shows a representation of cultures. Increasing VFA load cultures contained more dead algal cells and an increasing amount of bacterial sludge. Also, with increasing VFA load the color of the culture become brown due to excessive bacterial growth, whereas cultures receiving VFA/NH₃-N < 0.75 stayed green and contained more healthy algae cells.

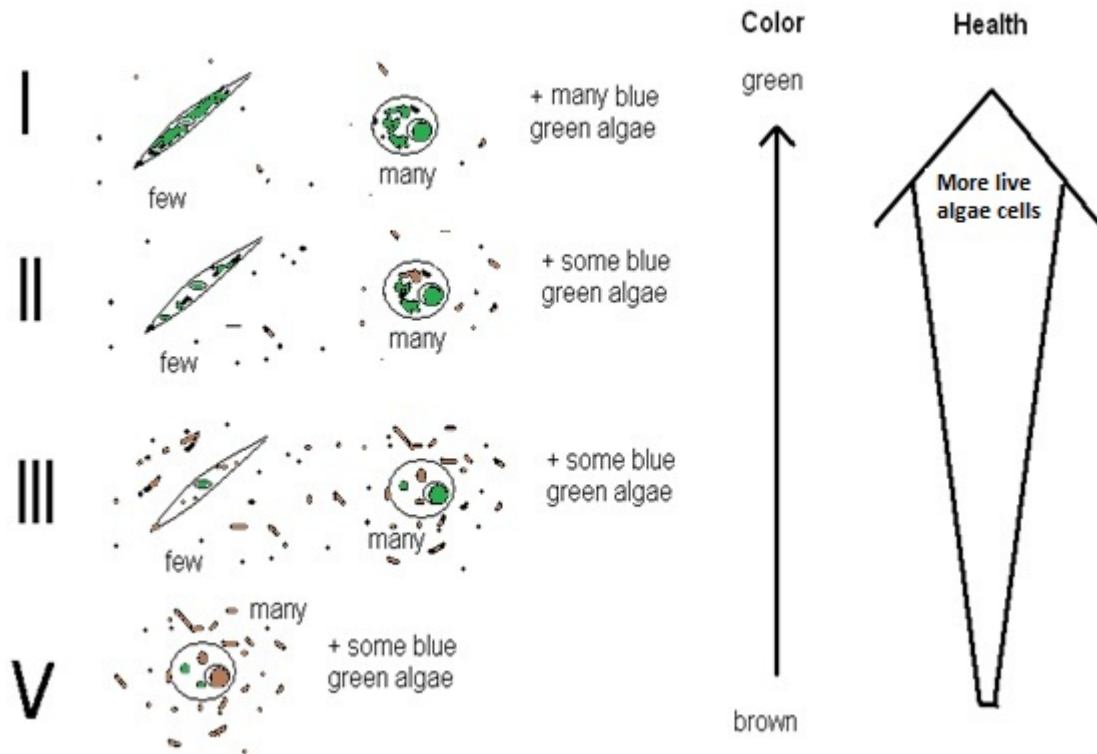


Figure 51: Drawings of algal culture appearance in a microscope for different feed VFA/NH₃-N ratios of 0.75(1), 1.35(2), 2.73(3), 4(4) compared to observed cell health.

In summary algal cultures receiving modified digester effluent without VFA can produced an average of 230 mg/L-day translating to 23 g-VS/m²-day (10cm depth) or 69 g-VS/m²-day (30cm depth) with a cell age of 3 days. Algal cultures receiving modified digester effluent with VFA were more susceptible to environmental influences, such as light inhibition and temperature. Algal cultures receiving a feed with a VFA/NH₃-N ratio of > 0.75 (or BOD/NH₃-N ratio of 0.9) did not recover from light limiting stress and failed. In contrast, algal cultures receiving a VFA/NH₃-N ratio of ≤ 0.75 did suffer from light limitation, but were not outgrown by bacteria and recovered after solar radiation increased.

The algal biomass gain under mixed weather conditions (50% full sun) for a VFA/NH₃-N feed ratio of 0.75 averaged 98.7 mg/L-day (9.9 g-VS/m²-day; 10cm depth or 29.6 g-VS/m²-day; 30cm depth). For a feed ratio of 1.35 the average biomass gain was 57.2 mg/L-day (5.7 g-VS/m²-day; 10cm depth or 17.2 g-VS/m²-day; 30cm depth), and 27 mg/L-day (2.7 g-VS/m²-day; 10cm depth or 8 g-VS/m²-day; 30cm depth) for a VFA/NH₃-N feed ratio of 2.73. For a VFA/NH₃-N feed ratio of 4.0 the average growth was 36.6 mg/L-day, including bacterial biomass. Where approximately half of the biomass consisted of bacteria the productivity was less than 1.5 g-VS/m²-day (10cm depth) or 4.5 g-VS/m²-day (30cm depth).

This data suggest that algal cultures for treatment digester effluent or pretreated landfill leachate would require an additional pretreatment to remove or reduced volatile fatty acids to a VFA to ammonia ratio in the input stream < one (BOD/NH₃-H <1) with ammonia loadings within the algal assimilation capacity (20 mg-N/L at 23 mg-VS/m²-day algal productivity), to avoid instability of the algal culture and bacterial dominance under maximum load.

5.3 Algae Pilot Plant Operation

Startup

During start-up of the algal post treatment stage, the raceway was filled up with clean water and injected with a local source of algae species.

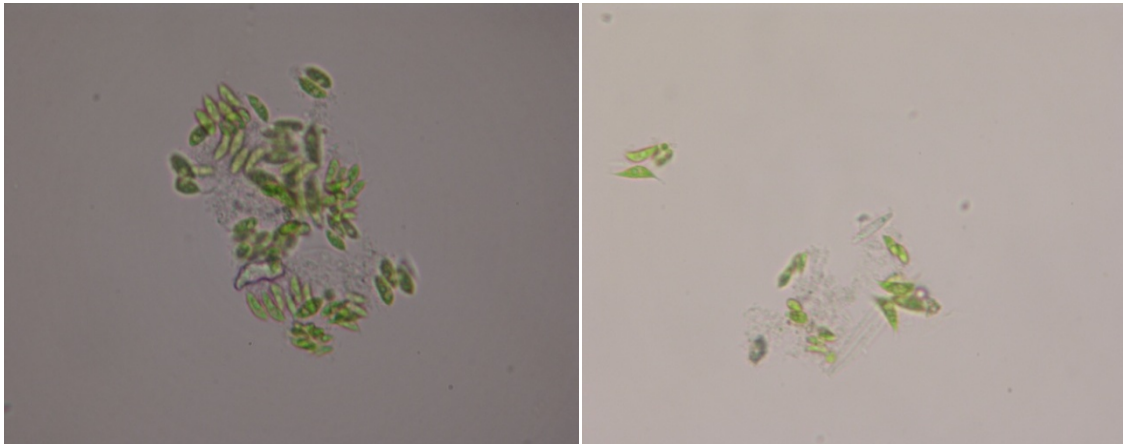


Figure 52: Algae in pilot plant post treatment tank during start-up phase, 40x*10x

At landfill site II, the dominant algae species developing were *Oscillatoria* (filamentous) and *Scenedesmus* (single/multi cell green algae), well suspended with some coagulated cells around debris (Figure 52).

Exponential Growth Phase

Characteristic of exponential growth phase was light green color, high net oxygen production, high respiration at night, and increasing of the average pH over time due to increased CO₂ uptake (AM DO 6-7 mg/L, PM DO 18-22 mg/L, AM pH 9.0-9.5, PM pH 9.5-10.0, Secchi disc 25-35 cm, increasing N-uptake).

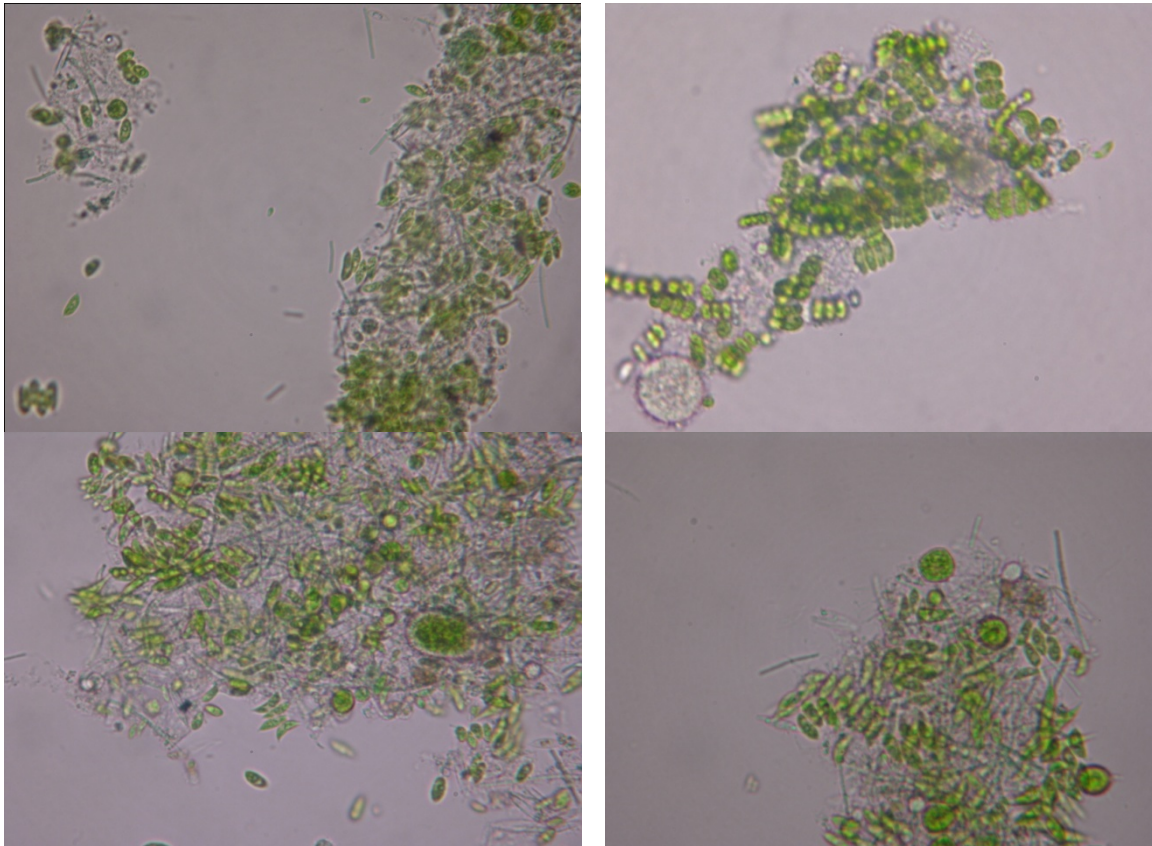


Figure 53: Algae in pilot plant post treatment tank during exponential and maturation phase, 40x*10x.

The community mainly consists of *Scenedesmus* and *Oscillatoria*, some were coagulated in flocks and held in suspension by paddle wheels (Figure 53). (AM DO 8-10 mg/L, PM DO 13-16 mg/L, AM pH 8.5-9.0, PM pH 9.5-10.0, Secchi disc 12-18 cm, high N-utilization).

Decay

When solids were not removed, the decay phase starts, pH and DO drop down as bacteria break down and assimilate dead algae biomass (AM DO 3-5 mg/L, PM DO 8-11 mg/L, AM pH 7-8, PM pH 8-9, Secchi disc 12-15 cm, low N-utilization). The color turns brown (Figure 54).

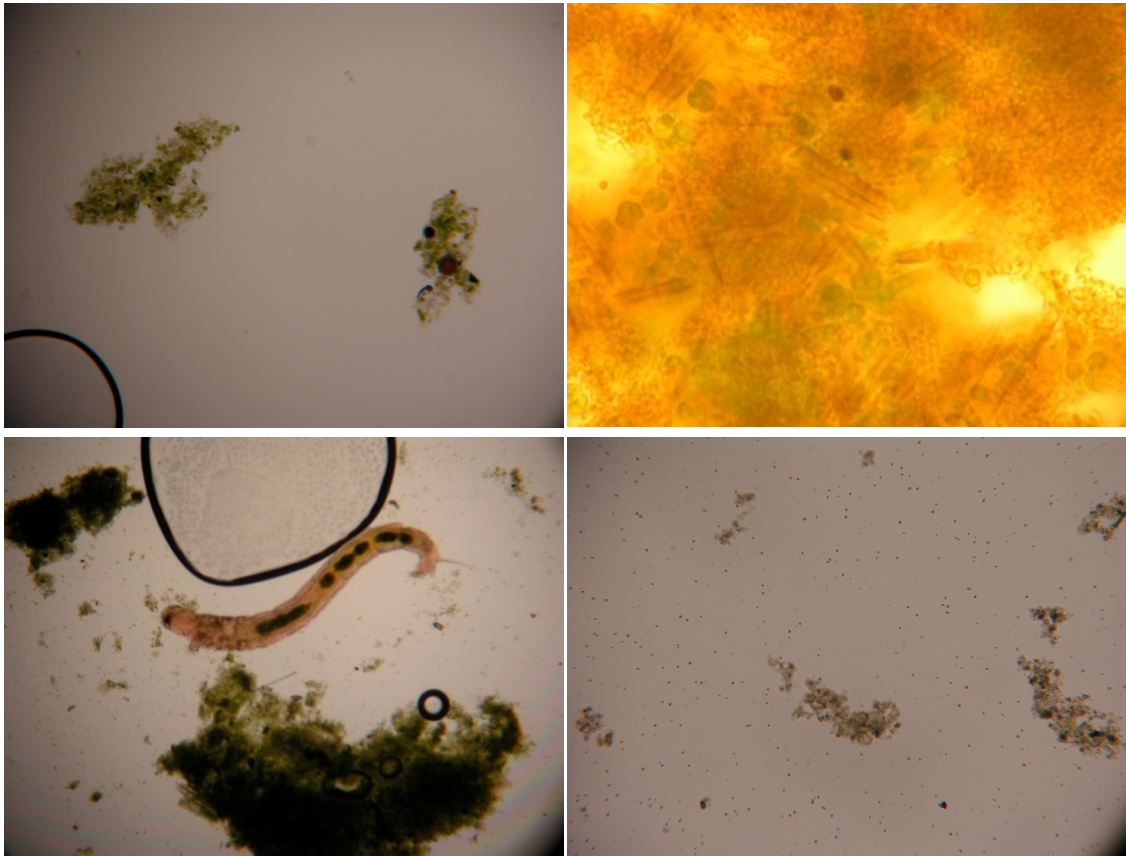


Figure 54: Algae in pilot plant post treatment tank during decay phase, 40x*10x

With cell-ages > 20 days small invertebrates start to occur in the system and consume algae. Units where cell age was approximate 3 days by removing solids, these invertebrates were rarely seen.

Pilot Scale Observations and Conclusions

The research on continuous algal cultures at landfill site II was done while only fertilizing the units with artificial fertilizer to establish algal cultures, however, some trials were conducted with substituting artificial fertilizer by pretreated leachate after

neutralizing without prior BOD-removal. Algal cultures decayed due to bacterial growth on BOD present in pretreated leachate, similar to laboratory algal growth trials.

Figure 55 shows a comparison of algal cultures from each tank at sampling in February. Figure 56 shows the samples allowed to be settled for 5 minutes. Algal culture tanks #1, #3, #5, #7, and #8 contained flocculating biomass (cultures altered with a proprietary process from Kent Bioenergy), #5 and #7 settled >90% of biomass. These two cultures did not receive pretreated leachate and were therefore non-bacterial. Units #2, #4 and #6 however received pretreated leachate and were beginning to shift bacterial.



Figure 55: Pilot plant algal post treatment at landfill site II end of February 2010, Unit #1 through #8 (from left to right); directly after sampling (Kent Bioenergy).



Figure 56: Pilot plant algal post treatment at landfill site II end of February 2010, Unit #1 through #8 (from left to right); five minutes after sampling (Kent Bioenergy).

Figure 57 and Figure 58 show samples from the same raceways 2 weeks later. Due to low temperatures and pretreated leachate BOD load, most of the cultures started to shift bacterial, or ceased growing. However, unit #1, #3, #5, #7 still contained flocculating biomass, with unit #5 and #7 settling >90% of biomass in 10 minutes.



Figure 57: Pilot plant algal post treatment at landfill site II beginning of March 2010, Unit #1 through #8 (from left to right); directly after sampling (Kent Bioenergy).



Figure 58: Pilot plant algal post treatment at landfill site II beginning of March 2010, Unit #1 through #8 (from left to right); ten minutes after sampling (Kent Bioenergy).

The experiments fail to show if the algal post treatment was effective in treating the activated sludge effluent combined with bio-flocculation. Also, cell retention times

were very long (15 - 20 days), for better control and performance purposes, algal cultures should be operated at a cell retention time of about 3 days. The system has yet to prove bio-flocculation at maximum productivity of 20 g-VS/m²-day and ammonia load of 10 mg/L-day. However, the algal cell age has to be controlled to limit algal density. Removing 30% of the algae biomass per day will reduce cell-age to 3 days and improves productivity. The two ways to remove algal biomass economically, are bio flocculation or algal harvest by filter feeding organisms like tilapia or brine shrimp (Henrich, 2008, Beecher and Brune, 2007, Yen, 2004, Turker et al., 2003, Brune et al., 2001). Experiments at landfill site II showed that algae bio flocculate sporadically, but this has yet to be consistent enough to be relied on during full scale algal post treatment of pretreated landfill leachate. Therefore biomass removal using filter feeding organisms may be needed. Additionally for species control filter feeding fish have been inevitable for Clemson's Partitioned Aquaculture processes. Without animals feeding on zooplankton, algal cultures may not be possible in an open raceway system.

5.4 Model Equations Used for Computation

In order to integrate a preliminary design of an algal post treatment system, mass balance equations using productivity and conversion factors were used for computation.

The algal post treatment system was modeled assuming that biomass can be removed with bio flocculation or animals filtering biomass directly from the raceways. This allows the disconnection of the HRT from the SRT. Equations (96) to (104) are used for preliminary design, when SRT is not equal to HRT.

Assumptions:

- SRT \neq HRT; harvest by settling of algae
- Nitrate and soluble organic nitrogen unchanged in effluent
- Particulate matter will be harvested with algal sludge
- BOD remains unchanged
- Effluent is free of biomass

$$\text{standing crop} = \text{productivity} * \theta_c \left[\frac{g - C}{m^2} \right] \quad (96)$$

$$\text{algal density} = \frac{\text{standing crop} * A}{V} \left[\frac{g - C}{L} \right] \quad (97)$$

$$\text{total carbon uptake} = C_{NH_3-N, in} * Q_{in} * \frac{C}{N} \left[\frac{g - C}{day} \right] \quad (98)$$

$$A = \frac{\text{total carbon uptake}}{\text{productivity}} [m^2] \quad (99)$$

$$V = A * \text{depth} [m^3] \quad (100)$$

$$\text{biomas in effluent} = 0 \left[\frac{g - C}{L} \right] \text{ (perfect settling asumed)} \quad (101)$$

$$\text{total biomas in reactor} = \text{algal density} * V [g - C] \quad (102)$$

$$\text{excess biomas} = \frac{\text{total biomas in reactor}}{\theta_c} \left[\frac{g - C}{day} \right] \quad (103)$$

$$\theta = \frac{V}{Q} [day] \quad (104)$$

6 OVERALL SYSTEMS MODEL FRAMEWORK ENRAT v1.0

6.1 Introduction

A modular, expandable computer program (using Java) was developed providing a systems model framework capable of predicting individual components and overall system performance. The overall system model includes the ammonia recovery process, activated sludge system, algal post treatment, and anaerobic digester. Individual unit operations may be activated or deactivated, or external inputs may be added depending on user needs. The program, entitled "ENRAT" (Energy and Nutrient Recovery from Anaerobic Treatment) consists of user interface and programming code (appendix D). Sub models may be adjusted as needed in later versions. The master file contains the user interface and adjustable flow-rates and configures transfers of flow from one unit operation to another. The master file also contains a save mechanism, which saves all streams and operational parameters into a text-file called "ModelData.txt" (each click on the "calculate" button will add data at the end of that file). Columns and rows in the text-file are divided by semicolons (;), and can be imported into programs such as Microsoft Excel. The output is displayed in pop-up table and in text fields embedded in the user interface flow diagram. A schematic representation of ENRAT is illustrated in Figure 59.

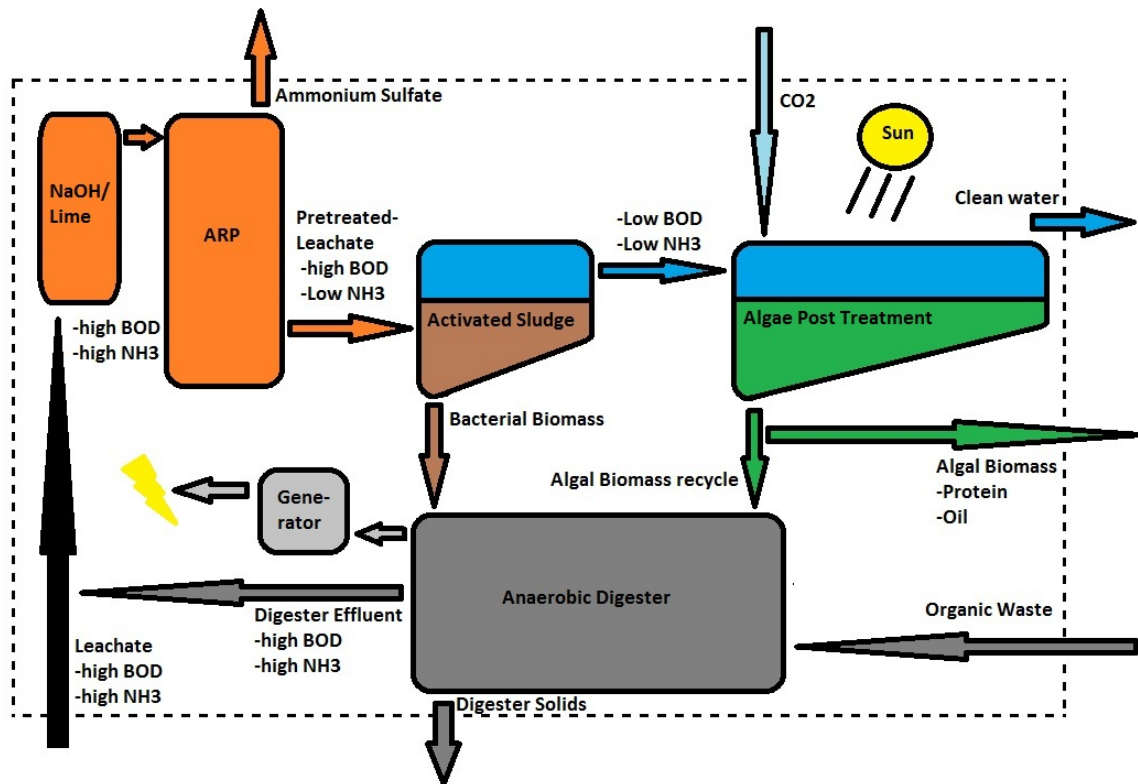


Figure 59: Flow diagram of unit operations described by the model "ENRAT".

ENRAT was used to calculate the nitrogen and carbon transformation and energy yields for three case studies representing 1) treatment of 500 gal leachate per day, 2) treatment of 5,000 gallons per day, and 3) treatment of 5,000 gallons per day plus 1 ton per day of organic waste. Specifically, the three cases represent simulations consisting of:

Case I: Treatment of 500 gal leachate per day (178,000 gal/yr); this model trial includes the ARP, activated sludge reactor, and algal post-treatment, representing a proposed pilot-plant operation at landfill site II. The system is represented to operate on a 24 hrs per day basis.

Case II: Treatment of 5,000 gal leachate per day (1,780,000 gal/yr); this model trial includes ARP, activated sludge reactor, and algal post-treatment, representing full scale operation at landfill site II. The system is modeled to operate 24 hrs per day.

Case III: Treatment of 5,000 gal Leachate per day (1,780,000 gal/yr) along with an additional 1 ton of organic waste per day (365 ton/yr); this model trial includes ARP, activated sludge reactor, algal post-treatment, and anaerobic digester for energy production with sludge recycle. The system is modeled to operate 24 hrs per day.

6.2 Model Results

Results of model simulations for the three cases are given in Table 20 to Table 31.

Case I: Treatment of 500 gal Leachate per Day

Table 20 and Table 21 show model input and output parameters for a proposed 500 gal/day leachate treatment facility, including ammonia recovery process, activated sludge unit, and algal post treatment.

Table 20: Model input parameters for a leachate treatment facility treating 500 gal/day of leachate.

ARP		Activated Sludge		Algal Raceway	
De-sorption Column		SRT, day	6	SRT, day	5
kLa, min⁻¹	0.01	Biomass, mg/L	3,000	Recycle, %	0
HRT-Gas, min	0.12	μmax, day⁻¹	8	Pr., g-C/m²-day	5
HRT-Leachate, min	70	Ks, mg/L	260	Depth, m	0.3
Absorption Column		b, day⁻¹	0.3		
kLa, min⁻¹	16	Y, mg-VSS/mg-BOD₅	0.476		
HRT-Gas, min	0.24				
HRT-Acid, min	10,000				

Table 21: Model output parameters for a leachate treatment facility treating 500 gal/day of leachate.

ARP		Activated Sludge		Algal Raceway	
De-sorption Column		Volume, L	7,442	Volume, L	20,495
Removal Efficiency	95.9	HRT, day	0.095	HRT, day	10.96
ARP Volume, L	8,830			Area, m²	68.3
Number of Column Set's	0.91				
Absorption Column					
Recapture Efficiency	99.95				
ARP Volume, L	8,830				
Number of Column Set's	0.91				

Table 22 shows system inflows for the proposed 500 gal/day leachate treatment facility, including leachate and acid inflow. Table 23 shows system outflows for the proposed 500 gal/day leachate treatment facility, including adsorption outflow (ammonium sulfate solution), algal waste sludge, waste activated sludge, and treated leachate outflow.

Table 22: Inflows for a leachate treatment facility treating 500 gal/day of leachate.

Parameter↓	Stream→	Leachate Input	Acid Inflow
Flow	L/day	1,875	26.25
VS Load	g/day	431.25	
Total C. Load	g/day	225	
VFA Load	g/day	440.65	
Total N. Load	g/day	1,875	
Ammonia Load	g/day	1,687.5	
Organic N. Load	g/day	187.5	
VS Conc.	mg/L	230	
Total C. Conc.	mg-C/L	120	
VFA Conc.	mg-C/L	235	
Total N. Conc.	mg-N/L	1,000	
Ammonia Conc.	mg-N/L	900	
Organic N. Conc.	mg-N/L	100	
C/N Ratio	-	0.12	
BOD	mg-O ₂ /L	290	

Table 23: Outflows for a leachate treatment facility treating 500 gal/day of leachate.

Parameter↓	Stream→	Adsorption Outflow	Algae Waste Sludge	Algae Tank Outflow	AS Waste Sludge
Flow	L/day	26.25	34.16	1,870.5	4.47
VS Load	g/day		683.18	56.12	90.1
Total C. Load	g/day		341.59	28.06	45.05
VFA Load	g/day		0	0	0
Total N. Load	g/day	1,616.8	61.0	18.71	177.7
Ammonia Load	g/day	1,616.8	0	0	0
Organic N. Load	g/day		61.0	18.71	177.7
VS Conc.	mg/L		20,000	30	20,174
Total C. Conc.	mg-C/L		10,000	15	10,087
VFA Conc.	mg-C/L		0	0	0
Total N. Conc.	mg-N/L	61,621	1,785.7	10	39,796
Ammonia Conc.	mg-N/L	61,621	0	0	0
Organic N. Conc.	mg-N/L		1,785.7	10	39,796
C/N Ratio	-		5.6	1.5	0.25
BOD	mg-O ₂ /L		0	9.79	0

Case II: Treatment of 5,000 gal Leachate per Day

Table 24 and Table 25 show model input and output parameters for a proposed 5,000 gal/day leachate treatment facility, including Ammonia Recovery process, activated sludge unit, and algal post treatment.

Table 24: Model input parameters for a leachate treatment facility treating 5,000 gal/day of leachate.

ARP		Activated Sludge		Algal Raceway	
De-sorption Column		SRT, day	6	SRT, day	5
kLa, min ⁻¹	0.01	Biomass, mg/L	3,000	Recycle, %	0
HRT-Gas, min	0.12	μmax, day ⁻¹	8	Pr., g-C/m ² -day	5
HRT-Leachate, min	70	Ks, mg/L	260	Depth, m	0.3
Absorption Column		b, day ⁻¹	0.3		
kLa, min ⁻¹	16	Y, mg-VSS/mg-BOD ₅	0.476		
HRT-Gas, min	0.24				
HRT-Acid, min	10,000				

Table 25: Model output parameters for a leachate treatment facility treating 5,000 gal/day of leachate.

ARP		Activated Sludge		Algal Raceway	
De-sorption Column		Volume, L	74,416	Volume, L	204,952
Removal Efficiency	95.9	HRT, day	0.095	HRT, day	10.96
ARP Volume, L	88,300			Area, m²	683.18
Number of Column Set's	9.1				
Absorption Column					
Recapture Efficiency	99.95				
ARP Volume, L	88,300				
Number of Column Set's	9.1				

Table 26 shows system inflows for the proposed 5,000 gal/day leachate treatment facility, including leachate and acid inflow. Table 27 shows system outflows for the proposed 5,000 gal/day leachate treatment facility, including Adsorption outflow algal waste sludge, waste activated sludge, and treated leachate outflow.

Table 26: Inflows for a leachate treatment facility treating 5,000 gal/day of leachate.

Parameter↓	Stream→	Leachate Input	Acid Inflow
Flow	L/day	18,750	262.5
VS Load	g/day	4,312.5	
Total C. Load	g/day	2,250	
VFA Load	g/day	4,406.2	
Total N. Load	g/day	18,750	
Ammonia Load	g/day	16,875	
Organic N. Load	g/day	1,875	
VS Conc.	mg/L	230	
Total C. Conc.	mg-C/L	120	
VFA Conc.	mg-C/L	235	
Total N. Conc.	mg-N/L	1,000	
Ammonia Conc.	mg-N/L	900	
Organic N. Conc.	mg-N/L	100	
C/N Ratio	-	0.12	
BOD	mg-O ₂ /L	290	

Table 27: Outflows for a leachate treatment facility treating 5,000 gal/day of leachate.

Parameter↓	Stream→	Adsorption Outflow	Algae Waste Sludge	Algae Tank Outflow	AS Waste Sludge
Flow	L/day	262.5	341.6	18,705	44.66
VS Load	g/day		6,831.7	561.2	901
Total C. Load	g/day		3,415.9	280.58	450.5
VFA Load	g/day		0	0	0
Total N. Load	g/day	16,168	609.98	187.1	1,777
Ammonia Load	g/day	16,168	0	0	0
Organic N. Load	g/day		609.98	187.1	1,777
VS Conc.	mg/L		20,000	30	20,174
Total C. Conc.	mg-C/L		10,000	15	10,087
VFA Conc.	mg-C/L		0	0	0
Total N. Conc.	mg-N/L	61,621	1,785.7	10	39,796
Ammonia Conc.	mg-N/L	61,621	0	0	0
Organic N. Conc.	mg-N/L		1,785.7	10	39,796
C/N Ratio	-		5.6	1.5	0.25
BOD	mg-O2/L		0	9.79	

Case III: Treatment of 5,000 gal Leachate per Day plus 1 ton/day Organic Waste

Table 28 and Table 29 show model input and output parameters for a proposed 5,000 gal/day leachate treatment facility including an additional 1 ton/day of organic waste treatment, including Ammonia Recovery process, activated sludge unit, algal post treatment, and anaerobic digester.

Table 28: Model input parameters for a leachate treatment facility treating 5,000 gal/day of leachate and one ton/day MOW.

ARP	Activated Sludge	Algal Raceway	Anaerobic Digester
De-sorption	SRT, day 6	SRT, day 5	HRT, day 20
kLa, min ⁻¹ 0.01	Biomass, mg/L 3,000	Recycle, % 100	Loading, g-VS/L-d 4
HRT-Gas, min 0.12	μmax, day ⁻¹ 8	Pr., g-C/m ² -d 5	VS-Dest., % 50
HRT-Liquid, min 70	Ks, mg/L 260	Depth, m 0.3	
Absorption	b, day ⁻¹ 0.3		
kLa, min ⁻¹ 16	Y, mg-VSS/mg-BOD5 0.476		
HRT-Gas, min 0.24			
HRT-Acid, min 10,000			

Table 29: Model output parameters for a leachate treatment facility treating 5,000 gal/day of leachate and one ton/day MOW.

ARP	Activated Sludge	Algal Raceway	Anaerobic Digester
De-sorption	Volume, L 200,542	Volume, L 286,472	Volume, L 113,865
Removal Eff. 95.9	HRT, day 0.204	HRT, day 12.221	Biogas, L/Reactor-L 1.81
ARP Volume, L 110,000		Area, m ² 954.9	Energy, kWh/day 460
Column Set's 11.45			
Absorption			
Recapture Eff. 99.95			
ARP Volume, L 110,000			
Column Set's 11.45			

Table 30 shows system inflows for the proposed 5,000 gal/day leachate treatment facility with an additional 1 ton/day of organic waste treatment, including leachate, organic waste, and acid inflow. Table 31 shows system outflows for the proposed 5,000 gal/day leachate treatment facility with an additional 1 ton/day of organic waste treatment, including adsorption outflow (ammonium sulfate solution), digester waste sludge, and treated leachate outflow. Additionally Table 31 shows two internal flows, digester inflow and de-sorption column inflow.

Table 30: Inflows of a leachate treatment facility treating 5,000 gal/day of leachate and one ton/day MOW.

Parameter↓	Stream→	Leachate Input	Acid Inflow	Organic Waste Input
Flow	L/day	18,750	329.86	8,340
VS Load	g/day	4,312.5		435,840
Total C. Load	g/day	2,250		217,920
VFA Load	g/day	4,406.3		0
Total N. Load	g/day	18,750		10,448
Ammonia Load	g/day	16,875		0
Organic N. Load	g/day	1,875		0
VS Conc.	mg/L	230		52,259
Total C. Conc.	mg-C/L	120		26,129
VFA Conc.	mg-C/L	235		0
Total N. Conc.	mg-N/L	1,000		1,252.8
Ammonia Conc.	mg-N/L	900		0
Organic N. Conc.	mg-N/L	100		0
C/N Ratio	-	0.12		20.86
BOD	mg-O2/L	290		0

Table 31: Outflows of a leachate treatment facility treating 5,000 gal/day of leachate and one ton/day MOW.

Parameter↓	Stream→	Adsorption Outflow	(Digester Inflow)	Algae Tank Outflow	Dig. Waste Sludge	(De-sorption Inflow)
Flow	L/day	329.86	5,693.3	23,440	882.06	23,561
VS Load	g/day		455,463	703.23	220,514	18,746
Total C. Load	g/day		227,731	351.61	110,257	9,466
VFA Load	g/day		0	0	0	11,623
Total N. Load	g/day	25,276	17,256	234.41	3,675	32,330
Ammonia Load	g/day	25,276	0	0	0	26,381
Organic N. Load	g/day		6,808	234.41	0	5,949
VS Conc.	mg/L		50,959	30	250,000	795.64
Total C. Conc.	mg-C/L		25,479	15	125,000	401.80
VFA Conc.	mg-C/L		0	0	0	493.32
Total N. Conc.	mg-N/L	76,664	1,930	10	4,166	1,372.2
Ammonia Conc.	mg-N/L	76,664	0	0	0	1,119.7
Organic N. Conc.	mg-N/L		761.72	10	0	252.50
C/N Ratio	-		13.2	1.5	30	0.293
BOD	mg-O2/L		0	9.79	0	610.60

Summary

The model predicts that a pilot scale operation to treat 500 gal/day of leachate would need an ARP unit 0.91 times the size of the ARP present on landfill site II or 8,830 L total column volume, an activated sludge system of 7,442 L, and an algal post treatment raceway of 68.3 m² at a depth of 30 cm. The ARP would consume 26.25 L of 6N sulfuric acid per day to produce 1.6 kg-N ammonium sulfate per day. The activated sludge system and the algal post treatment would produce 90 g-VS (or 4.5 L 2% sludge) and 683 g-VS (or 34.2 L 2% sludge) of bacterial and algal biomass per day. If solids would be loaded into a digester 0.9 kWh/day could be recaptured.

A full scale operation to treat 5,000 gal/day of leachate would need an ARP unit 9.2 times the size of the ARP present on landfill site II or 88,300 L total column volume, an activated sludge system of 74,417 L, and an algal post treatment raceway of 683 m² at a depth of 30 cm. The ARP would consume 262.5 L of 6N sulfuric acid per day to produce 16.12 kg-N ammonium sulfate per day. The activated sludge system and the algal post treatment would produce 900 g-VS (or 44.6 L 2% sludge) and 6.83 kg-VS (or 341.6 L 2% sludge) of bacterial and algal biomass per day. If solids would be loaded into a digester 9 kWh/day could be recaptured.

A full scale operation to treat 5,000 gal/day of leachate along with an additional 1 ton of organic waste per day would need an ARP unit 11.45 times the size of the ARP present on landfill site II or 110,000 L total column volume, an activated sludge system of 200,542 L, an algal post treatment raceway of 955 m² at a depth of 30 cm, and an

anaerobic digester with 113,865 L volume. The ARP would consume 329.86 L of 6N sulfuric acid per day to produce 25.3 kg-N ammonium sulfate per day. Biomass produced by the activated sludge system and the algal post treatment would be mixed with the inflow organic waste and loaded to the anaerobic digester. The mass loaded would have a C/N ratio of 13.2 and a VS content of 455.5 kg/day. 882 L/day 25% waste digester sludge would have to be disposed of. The energy yield from biogas produced would be approximately 460 kWh/day.

7 SUMMARY

The objective of this research was to develop a total systems design and predictive model of a series of linked processes capable of providing complete treatment of landfill leachate while simultaneously recovering nutrients and bioenergy from waste inputs. The process includes an “Ammonia Recovery Process” (ARP) consisting of: 1) ammonia de-sorption requiring leachate pH adjustment with lime or sodium hydroxide addition followed by, 2) ammonia re-absorption into a 6-molar sulfuric acid spray-tower followed by, 3) biological activated sludge treatment of soluble organic residuals (BOD) followed by, 4) high-rate algal post-treatment, and finally, 5) an optional anaerobic digestion process for algal and bacterial biomass, and/or supplemental waste fermentation providing the potential for additional nutrient and energy recovery. In addition to the value provided from the waste treatment function of the overall processes, each of the sub-processes would provide valuable co-products offering potential GHG-credit through direct fossil-fuel replacement, or replacement of products requiring fossil-fuels. These valuable co-products include 1) ammonium sulfate fertilizer, 2) bacterial biomass, 3) algal biomass providing, high-protein feeds and oils for biodiesel production and 4) methane bio-fuels.

Ammonia Recovery Process (ARP)

Using lab and pilot scale de-sorption columns gas transfer rates from leachate to air were determined. Based on this data and literature sources a quantitative model for

the de-sorption process was developed. The model was confirmed with pilot-scale ammonia recovery process (ARP) data taken from operation at landfill site II. Adjustment of leachate to pH 12 prior to ammonia de-sorption and recapture was done using sodium hydroxide at 15 g/L-leachate addition. Gas transfer was the rate-limiting process for the de-sorption process. The concentration of ammonia in the air stream can be considered to be negligible, as ammonia transfer was not influenced by Henry's law. The k_{La} represents the overall gas transfer coefficient, impacted primarily by air/water surface area, temperature, and air/water turbulence.

An artificial landfill leachate was produced consisting of 128 meq/L ammonium sulfate, 72 meq/L ammonium bicarbonate, and 51 meq/L sodium-bicarbonate. This synthetic leachate behaved similarly to actual landfill leachate in ammonia de-sorption trials. Lab-scale de-sorption experiments were performed with both actual leachate and artificial leachate. It was demonstrated that the de-sorption k_{La} could be increased from 0.0001 min^{-1} (lab-scale, simple air bubbling) to 0.006 min^{-1} (pilot scale, coarse leachate spray). The de-sorption model was verified with pilot- scale ARP data.

Increased temperature increased gas diffusion through gas/liquid boundary layers and therefore increased the k_{La} . An average k_{La} of 0.008 min^{-1} for pilot scale de-sorption columns was observed at average winter temperature of $22 \text{ }^{\circ}\text{C}$, whereas, an average k_{La} for columns facing landfill flares was 0.01 min^{-1} at $27 \text{ }^{\circ}\text{C}$ and for columns not facing flares average winter k_{La} was 0.006 min^{-1} at $17 \text{ }^{\circ}\text{C}$. Assuming an overall k_{La} of 0.008 min^{-1} the minimum column required retention time was determined to be 10 hrs

for 99% ammonia removal, and 6 hrs for 95% removal, respectively. Initial ammonia concentration in leachate did not influence the overall ammonia removal efficiency.

Lab and pilot- scale absorption columns data were used to determine gas transfer rates of ammonia from the gas to the liquid phase. An absorption-model was developed and results confirmed with pilot-scale ARP operation at landfill site II. Gas transfer was the rate limiting process for the absorption reaction. The concentration of ammonia in the liquid stream can be considered to be zero. The low pH of sulfuric acid solution immediately converts ammonia into ammonium, and once again gas transfer was not influenced by Henry's law. The k_{La} represented an overall gas transfer coefficient, influenced primarily by surface area, temperature and turbulence. By increasing gas transfer area the absorption k_{La} was increased from 16 min^{-1} (using 2 nozzle acid spray) to 25 min^{-1} (using 3 nozzle acid spray). Increased temperature increased gas diffusion through gas and liquid boundary layers and therefore increased the k_{La} . By increasing temperature from 25°C to $> 80^{\circ}\text{C}$, the lab scale absorption k_{La} increased from 25 min^{-1} to 35 min^{-1} . An average k_{La} of 17.2 min^{-1} for the pilot scale absorption columns in winter was observed at 22°C . The average k_{La} for columns facing hot landfill flares was 18.0 min^{-1} at 27°C and for columns not facing flares the average winter k_{La} was 16.3 min^{-1} at 17°C . Initial ammonia concentration in influent gas did not influence the overall ammonia recapture efficiency. The gas transfer model was confirmed with pilot scale ARP data. Assuming a k_{La} of 16 min^{-1} minimum air retention

time inside a series of two columns was determined to be 0.22 min for 99.9% ammonia recapture, and 0.166 min for 99.5% recapture respectively.

Activated Sludge System

Bacterial growth on pre-treated leachate from landfill site I and II was studied and kinetic parameters and stoichiometric coefficients were determined. Pre-treated leachate behaved (and was modeled) in a manner similar to high-strength domestic wastewater. Characteristics of pretreated leachate and growth kinetics were used to model an activated sludge unit for leachate BOD treatment.

BOD rate constants obtained from landfill site I pretreated leachate were 0.23-0.27 day⁻¹ and 0.32-0.40 day⁻¹ for landfill site II. The average biomass yield of heterotrophic bacterial growth on pretreated leachate was 0.476 mg-VS/mg-BOD₅. The average half saturation constant (K_s) for BOD in pretreated landfill leachate was 260 mg-BOD₅/L for both landfill sites. Monod growth parameters for heterotrophic bacterial growth on landfill site I pretreated landfill leachate were $\mu_{max} = 5-6 \text{ day}^{-1}$ and $b = 0.3 \text{ day}^{-1}$, and $\mu_{max} = 8 \text{ day}^{-1}$ and $b = 0.3 \text{ day}^{-1}$ for landfill site II pretreated leachate. Since bacterial growth on pretreated landfill leachate was similar to high strength domestic wastewater, it was determined that the Standard Activated Sludge Model No. 1 (ASM-1) can be used for modeling. A computer software was developed implementing ASM-1 to model and design an activated sludge completely mixed reactor as part of a 500 gal/day (1875 L/day) leachate treatment facility. With an HRT of 3 hrs, a CSTR volume of 7,500 L and an SRT of 100 hrs the effluent ammonia concentration would be 19 mg/L (8 mg/L in

influent) and the effluent BOD₅ concentration would be 5.5 mg-BOD₅/L resulting in a BOD/NH₃-H ratio of 0.3 which is < 1/1 and therefore effluent may be suitable for algal post treatment. No nitrification inhibitor would be needed to suppress nitrification, if SRT is set < 120 hrs.

Algal Post Treatment

Algal growth on synthetic leachate and digester effluent was investigated to quantify the impacts of biodegradable organic compounds on algal growth. Continuous 2-L algal cultures were fertilized at VFA to ammonia input ratios ranging from 0.05 to 4. Algal cultures did not tolerate high loads of VFA (> VFA/NH₃-N of 1/1) and algae cultures were dominated by bacteria.

Productivity of lab-scale algal cultures grown at reduced solar radiation levels of 50% full sun at VFA/NH₃-N feed ratio of 0.75 averaged 98.7 mg/L-day (9.9 g-VS/m²-day; 10cm depth or 29.6 g-VS/m²-day; 30cm depth). At a ratio of 1.35 the average biomass gain was 57.2 mg/L-day (5.7 g-VS/m²-day; 10cm depth or 17.2 g-VS/m²-day; 30cm depth), and 27 mg/L-day (2.7 g-VS/m²-day; 10cm depth or 8 g-VS/m²-day; 30cm depth), for a VFA/NH₃-N feed ratio of 2.73, respectively. At a ratio of 4.0, productivity was < 1.5 g-VS/m²-day (10cm depth) or 4.5 g-VS/m²-day (30cm depth). It was concluded that VFA removal prior to algal post treatment to a level of BOD/NH₃-H <1 within the algal assimilation capacity of 20 mg-N/L-day at (23 mg-VS/m²-day algal productivity) is necessary to insure algal culture stability.

Pilot-scale algal post-treatment systems operating at landfill site II were observed to bio-flocculate and settle, with cultures settling >90% of biomass in 5 - 10 minutes. Cultures fertilized by pretreated leachate (without prior BOD removal) were observed to shift to bacterial dominance as suggested by lab-scale results. Pilot-scale algal post treatment has not yet proven bio-flocculation at maximum productivity of 20 g-VS/m²-day. Biological filter feeders may be required for algal biomass removal.

Overall System Model Framework ENRAT

A modular, expandable computer program (using Java) was developed providing a systems model capable of predicting individual components and overall system performance. The overall system model development included the ammonia recovery process, activated sludge system, algal post treatment, and anaerobic digester. Individual unit operations may be activated or deactivated, or external inputs may be added depending on user needs. The program, entitled "ENRAT" (Energy and Nutrient Recovery from Anaerobic Treatment) was used to calculate the nitrogen transformation and energy yields for three case studies representing 1) treatment of 500 gal (1875 L) Leachate per day, 2) treatment of 5,000 gal (18750 L) per day, and 3) treatment of 5,000 gal (18750 L) leachate per day plus 1 ton per day of organic waste.

The model predicted that a pilot operation to treat 500 gal leachate per day would require an ARP unit 0.91 times the size of the ARP present on landfill site II (8,830 L total volume), an activated sludge system of 7,442 L, and an algal post treatment raceway of 68.3 m² at a depth of 30 cm. The ARP would consume 26.25 L of 6N sulfuric

acid per day to produce 1.6 kg-N ammonium sulfate per day. The activated sludge system and the algal post treatment would produce 90 g-VS (or 4.5 L 2% sludge) and 683 g-VS (or 34.2 L 2% sludge) of bacterial and algal biomass per day. If solids would be loaded into a digester 0.9 kWh/day could be recaptured.

A full scale operation to treat 5,000 gal of leachate per day would require an ARP unit 9.2 times the size of the ARP present on landfill site II (88,300 L total volume), an activated sludge system of 74,417 L, and an algal post treatment raceway of 683 m² at a depth of 30 cm. The ARP would consume 262.5 L of 6N sulfuric acid per day to produce 16.1 kg-N ammonium sulfate per day. The activated sludge system and the algal post treatment would produce 900 g-VS (or 44.6 L 2% sludge) and 6.83 kg-VS (or 341.6 L 2% sludge) of bacterial and algal biomass per day. If solids would be loaded into a digester 9 kWh/day could be recaptured.

A full scale operation to treat 5,000 gal leachate per day along with an additional 1 ton of organic waste per day would require an ARP unit 11.45 times the size of the ARP present on landfill site II (110,000 L total volume), an activated sludge system of 200,542 L, an algal post treatment raceway of 954.91 m² at a depth of 30 cm, and an anaerobic digester with 113,865 L volume. The ARP would consume 329.9 L of 6N sulfuric acid per day to produce 25.3 kg-N ammonium sulfate per day. Biomass produced by the activated sludge system and the algal post treatment would be mixed with the inflow organic waste and loaded to the anaerobic digester. The mass loaded would have a C/N ratio of 13.2 and a VS content of 455.5 kg/day. A 25% waste digester

sludge (882 L/day) would have to be disposed of. The energy yield from biogas produced would be approximately 460 kWh/day.

8 CONCLUSIONS

1) Ammonia Recapture Process (ARP)

- 1) Gas Transfer is the rate limiting process for the de-sorption process. The transfer coefficient (kLa) is influenced primarily by surface area, temperature, and turbulence.
- 2) An artificial landfill leachate was fabricated using 128 meq/L ammonium sulfate, 72 meq/L ammonium bicarbonate, and 51 meq/L sodium-bicarbonate and behaved similarly to actual landfill leachate in ammonia de-sorption trials.
- 3) The de-sorption kLa increases from 0.0001 min⁻¹ (with air bubbling) to 0.006 min⁻¹ (using leachate spray nozzles).
- 4) The de-sorption model was verified by pilot scale ARP data.
- 5) At 22 degrees an average kLa of 0.008 min⁻¹ was observed for pilot-scale de-sorption columns. At temperature of 17 vs. 27 °C average kLa were observed to increase from 0.006 min⁻¹ to 0.01 min⁻¹.
- 6) At an average de-sorption kLa of 0.008 min⁻¹ the minimum liquid retention time was determined to be 10 hrs for 99% ammonia removal, and 6 hrs for 95% removal respectively.
- 7) Initial ammonia concentration in leachate did not influence the overall ammonia removal efficiency.
- 8) Gas Transfer was the rate limiting process for the ammonia absorption. The kLa is influenced by surface area, temperature, and turbulence.
- 9) The lab scale absorption kLa was observed to increase from 16 min⁻¹ with 2 nozzle acid spray) to 25 min⁻¹ with 3 nozzle acid spray.

- 10) By increasing temperature from 25°C to > 80°C, the lab scale absorption kLa increased from 25 min^{-1} to 35 min^{-1} .
- 11) The absorption model was successfully confirmed with pilot-scale ARP data.
- 12) The average pilot scale absorption kLa increased from 16.3 min^{-1} to 18.0 min^{-1} at increasing operating temperatures of 17 to 27 °C.
- 13) Initial ammonia concentration in influent gas did not influence the overall ammonia recapture efficiency.
- 14) Assuming an absorption kLa of 16 min^{-1} the minimum air retention time was determined to be 0.22 min for 99.9% ammonia recapture, and 0.166 min for 99.5% recapture respectively.

3) Activated Sludge System

- 15) BOD rate constants of bacteria using landfill site I pretreated leachate were 0.23-0.27 day^{-1} and 0.32-0.40 day^{-1} for landfill site II pretreated leachate.
- 16) The average biomass yield of heterotrophic bacterial growth on pretreated leachate was 0.476 mg-VS/mg-BOD_5 .
- 17) The average half saturation constant (K_s) for BOD in pretreated landfill leachate was 260 $\text{mg-BOD}_5/\text{L}$.
- 18) Monod growth parameters for heterotrophic bacterial growth on landfill site I pretreated landfill leachate were; $\mu_{\text{max}}=5\text{-}6 \text{ day}^{-1}$ and $b=0.3 \text{ day}^{-1}$, and $\mu_{\text{max}}=8 \text{ day}^{-1}$ and $b=0.3 \text{ day}^{-1}$, for landfill site II pretreated leachate respectively.
- 19) Bacterial growth on pretreated landfill leachate is similar to high strength domestic wastewater, therefore the Standard Activated Sludge Model No. 1 (ASM-I) can be used for modeling.

-
- 20) A computer software was developed implementing ASM-1 to model and design an activated sludge CSTR as part of a 500 gal/day leachate treatment facility. With a volume of 7,500 L, HRT of 3 hrs, and an SRT of 100 hrs the effluent BOD/NH₃-H ratio was 5.5 mg-BOD₅/19 mg-N or 0.3, and therefore suitable for algal post treatment without the need of nitrification inhibitor.

2) Algal Post Treatment

- 21) Lab-scale algae cultures were unstable at VFA/NH₃-N ratios in excess of 1/1).
- 22) Algal productivity in 2 liter lab-scale cultures at reduced light levels (of 50%) at VFA/NH₃-N feed ratio of 0.75 averaged 98.7 mg/L-day (9.9 g-VS/m²-day; 10cm depth or 29.6 g-VS/m²-day; 30cm depth). For a feed ratio of 1.35 the average biomass gain was 57.2 mg/L-day (5.7 g-VS/m²-day; 10cm depth or 17.2 g-VS/m²-day; 30cm depth), and 27 mg/L-day (2.7 g-VS/m²-day; 10cm depth or 8 g-VS/m²-day; 30cm depth) for a VFA/NH₃-N feed ratio of 2.73, respectively. For a VFA/NH₃-N feed ratio of 4.0, productivity was < 1.5 g-VS/m²-day (10cm depth) or 4.5 g-VS/m²-day (30cm depth).
- 23) VFA removal to a level of BOD/NH₃-H <1 within the algal assimilation capacity of 20 mg-N/L-day at (23 mg-VS/m²-day algal productivity) prior to algal post treatment was necessary to avoid bacterial dominance of algal cultures
- 24) Biological filter feeders may be necessary to remove algae biomass, since bio-flocculation of algae has yet to be consistent.

4) Overall Model Development of the Landfill Leachate Treatment System

- 25) A modular, expandable computer program (using Java) was developed providing a systems model framework capable of predicting individual components and overall system performance, called "ENRAT" (Energy and Nutrient Recovery from Anaerobic Treatment).
- 26) "ENRAT" predicted that a pilot operation to treat 500 gal-leachate/day would require an ARP unit 0.91 times the size of the ARP present on landfill site II (8,830 L total volume), an activated sludge system of 7,442 L, and an algal post treatment raceway of 68.3 m² (30 cm depth). The ARP would consume 26.25 L/day of 6N sulfuric acid and produce 1.6 kg-N/day ammonium sulfate. The

activated sludge system and algal post treatment would produce 90 g-VS/day (or 4.5 L 2% sludge) and 683 g-VS/day (or 34.2 L 2% sludge) of bacterial and algal biomass (equivalent to 0.9kWh/day recovery).

27) "ENRAT" predicted that a full-scale operation to treat 5,000 gal-leachate/day would require an ARP unit 9.2 times the size of the ARP present on landfill site II (88,300 L total volume), an activated sludge system of 74,417L, and an algal post treatment raceway of 683 m² (30 cm depth). The ARP would consume 262.5 L/day of 6N sulfuric acid and produce 16.1 kg-N/day ammonium sulfate. The activated sludge system and algal post treatment would produce 900 g-VS/day (or 44.6 L 2% sludge) and 6.83 kg-VS/day (or 341.6 L 2% sludge) of bacterial and algal biomass (equivalent to 9kWh/day recovery).

28) "ENRAT" predicts that a full-scale operation to treat 5,000 gal-leachate/day along with 1 ton/day of organic waste would require an ARP unit 11.45 times the size of the ARP present on landfill site II (110,000 L total volume), an activated sludge system of 200,542 L, an algal post treatment raceway of 955 m² (30 cm depth), and an anaerobic digester with 113,865 L volume. The ARP would consume 329.86 L/day of 6N sulfuric acid and produce 25.3 kg-N/day ammonium sulfate. The mass loaded to the anaerobic digester would have a C/N ratio of 13.2 and a VS content of 455.5 kg/day. A 25% digester waste sludge of 882 L/day would have to be disposed of. The energy yield from biogas produced would be 460 kWh/day.

APPENDICES

A. Abbreviations

Table 32: Abbreviations.

Abbreviation	Meaning
PAS	Partitioned Aquaculture System
SBR	Sequence Batch Reactor
N	Nitrogen
C	Carbon
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
VFA	Volatile Fatty Acids
gpm	Gallon per minute
DO	Dissolved Oxygen
TSS	Total Suspended Solids
VSS	Volatile Suspended Solids
TNVS	Total Non Volatile Solids
TKN	Total Kjeldahl Nitrogen
TAN	Total Ammonia Nitrogen
DI	De-Ionized
ABS	Absorption
Trans	Transmission
ARP	Ammonia Recovery Process
AS	Activated Sludge
HAC	Acedic Acid
ALK	Alkalinity
rpm	Rounds per minute
hrs	hours
BOD ₅	Five day Biological Oxygen Demand
CSTR	Completely stirred tank reactor
SCFM or CFM	Standard Cubic Feet per Minute
lime	Calcium hydroxide
k _L a	Overall gas transfer coefficient
Decr.	Decreased
Conc.	Concentration
HRT	Hydraulic retention time
SRT	Solids retention time
ppm	Parts per million
SD	Secchi depth
ALK	Alkalinity
C/N	Carbon – Nitrogen ratio
inf.	Infinite
ASM-1	Activated Sludge Model number one
No.	Number
b.	biomass

(Table 32 cont.)

Abbreviation	Meaning
sat.	saturation
NO _x	Nitrite, Nitrate nitrogen
CEP	Controlled Eutrophication Process
Pr.	Productivity

B. Symbols

Table 33: Symbols.

Identifier	Name	Unit
μ	Growth rate	[day ⁻¹]
μ_A	Maximum Autotrophic growth rate	[hr ⁻¹]
μ_H	Heterotrophic maximum growth rate	[hr ⁻¹]
μ_{max}	Maximum growth rate	[day ⁻¹]
A	Area	[m ²]
A _c	Cross sectional area	[dm ²]
ALK	Alkalinity	[mg-CaCO ₃ /L] or [meq/L]
b_H	Heterotrophic decay rate	[day ⁻¹]
$b_{L,A}$	Autotrophic decay rate	[hr ⁻¹]
$b_{L,H}$	Heterotrophic decay constant	[hr ⁻¹]
c	Concentration	[mg/L]
COD _t	Total Oxygen Demand	[mg-O ₂ /L]
f'_D	Fraction of debris in biomass	[mg-COD/mg COD]
H	Theoretical column height	[dm]
H ⁺	Hydrogen concentration	[mol/L]
H ₂ SO ₄	sulfuric acid concentration	[N]
HRT	Hydraulic retention time	[min]
$i_{N/XB}$	Nitrogen in active biomass	[mg-N/mg-COD]
$i_{N/XD}$	Nitrogen in biomass debris	[mg-N/mg-COD]
k	BOD constant (base 10)	[day ⁻¹]
K_a	Acid dissociation constant	[mol/L]
k_a	Ammonification rate coefficient	[L/mg-hr]
K_H	Henry's Law constant	[-] or [L*atm/mol]
k_h	Hydrolysis coefficient	[mg COD/mg-b*hr]
k_{La}	Overall gas transfer coefficient	[min]
K_{NH}	Autotrophic ammonia half sat. constant	[mg-N/L]
K_{NO}	Het. anoxic nitrate half sat. constant	[mg-N/L]
$K_{O,A}$	Autotrophic oxygen half sat. constant	[mg-O ₂ /L]
$K_{O,H}$	Het. oxygen half saturation constant	[mg-O ₂ /L]
K_s	Substrate half saturation constant	[mg/L]
K_s	Het. substrate half saturation constant	[mg-COD/L]
K_{sp}	Solubility product	[mol ³ /L ³]
K_x	Half saturation coefficient of hydrolysis of slowly biodegradable substrate	[mg-COD/mg-b.-COD]
NH ₃ A	Ammonium sulfate in absorption acid solution	[mg-N/L]
NH ₃ GA	Ammonia conc. in absorption gas phase	[mg-N/L]
NH ₃ GD	Ammonia conc. in de-sorption gas phase	[mg-N/L]
NH ₃ L	Ammonia concentration in leachate	[mg-N/L]

(Table 33 cont.)

Identifier	Name	Unit
NO _x	Nitrate-Nitrite concentration	[mg-N/L]
ON _{TO}	Organic nitrogen	[mg-N/L]
P	Partial pressure	[atm]
Q	Flow rate	[L/min]
r	Rate per volume	[g/L-day] or [g/L-min]
S	Substrate	[mg/L]
S	Soluble matter	[mg-N/L] or [mg-COD/L]
SALKO	Alkalinity	[mmol/L]
SIO	Soluble inert organic matter	[mg-COD/L]
SNHO	Soluble ammonia nitrogen	[mg-N/L]
SNIO	Soluble inert organic nitrogen	[mg-N/L]
SNOO	Soluble nitrate nitrogen	[mg-N/L]
SNSO	Soluble biodegradable organic nitrogen	[mg-N/L]
SO	Oxygen	[mg-O ₂ /L]
SRT	Solids retention time	[min]
SSO	Readily biodegradable substrate	[mg-COD/L]
T	Temperature	[°C]
TAN	Total Ammonia Nitrogen	[mg-N/L]
V	Volume	[L]
x	length	[m]
X	Particulate matter	[mg-N/L] or [mg-COD/L]
XIO	Particulate inert organic matter	[mg-COD/L]
XNIO	Particulate inert organic nitrogen	[mg-N/L]
XNSO	Particulate biodegradable organic nitrogen	[mg-N/L]
XSO	Slowly biodegradable substrate	[mg-COD/L]
Y _A	Autotrophic biomass yield	[mg-COD/mg-N]
Y _H	Heterotrophic biomass yield	[mg-COD/mg COD]
Y _{H,V/5B}	Heterotrophic biomass yield	[mg-VS/mg-BOD ₅]
α ₀	Acid dissociation fraction	[-]
ΔC	Concentration gradient	[mg/L]
Δt	Time Interval	[min]
η _c	Clarifier efficiency	[-]
η _g	Anoxic growth factor	[-]
η _h	Anoxic hydrolysis factor	[-]
θ	Hydraulic retention time	[day]
θ _c	Solids retention time	[day]
ρ	Density	[kg/m ³]
τ	Retention time	[min]

Table 34: Indices.

Indices	Meaning
(aq)	In solution
(s)	solid
0	Initial
1	At time 1
2	At time 2
3	At time 3
5	At day five
absorb	Applying to the absorption process
ALK	Alkalinity
B	biomass
BO	Biodegradable
D	Biomass debris
desorb	Applying to the de-sorption process
gas	Valid for the gaseous phase
i	Compound i
I	Inert
in	Inflow
IO	Inert
L	ultimate
Liquid	Valid for the liquid phase
NH	Ammonia nitrogen
NI	Inert organic nitrogen
NO	Nitrate nitrogen
NS	Biodegradable organic nitrogen
out	Outflow
S	Substrate
t	At time t
w	Waste flow

C. Algae Culture Apparatus

Table 35: Materials needed to construct the algal culture apparatus.

#	Name	Size(L*W*H)	Count	Misc
1	Press board	1.20*0.02*1m	2	Sides
2	Press board	1*1*0.02m	2	Door/side
3	Press board	1:20*0.02*1m	2	Top/bottom
4	Balks	1*0.1*0.1m	4	
5	Screws/ Nails		plenty	
6	Wood glue	~250mL	2	
7	Cover panel	1.20*0.005*1m		White, perforated
8	Clear coat	~1L	1	To protect the wood
9	Greenhouse	1.20*1*0.6m	1	
10	Hinges	10*5	2	Zinc covered
11	Door latch		1	Zinc covered
12	Styrofoam	(as Board)	6-12	To insulate the inside
13	Shelves	H: ~10 cm	4	Length as the side boards
14	Laths	H: ~1 in	~4	As cover panel support
15	Fan	15*15 cm	1	At least 120 rpm
16	Plastic pipe	d=0.5-1 cm		Different lengths
17	Thermostat	-	1	
18	Heater	-	1	
19	Flexible tube	Small dia.	plenty	For aeration
20	Air stones	L: ~2 in	16	For aeration
21	Valves	Fit the tube	plenty	For aeration
22	Air conditioner unit	Window unit	1	

Assembly

- (1) The greenhouse
- (2) Chamber with heater
- (3) Door (with hinges and door latch)
- (4) Side press board
- (5) Cover Panel (between the greenhouse and the ceiling of the box laths underneath the cover panel to hold it)
- (6) two by four

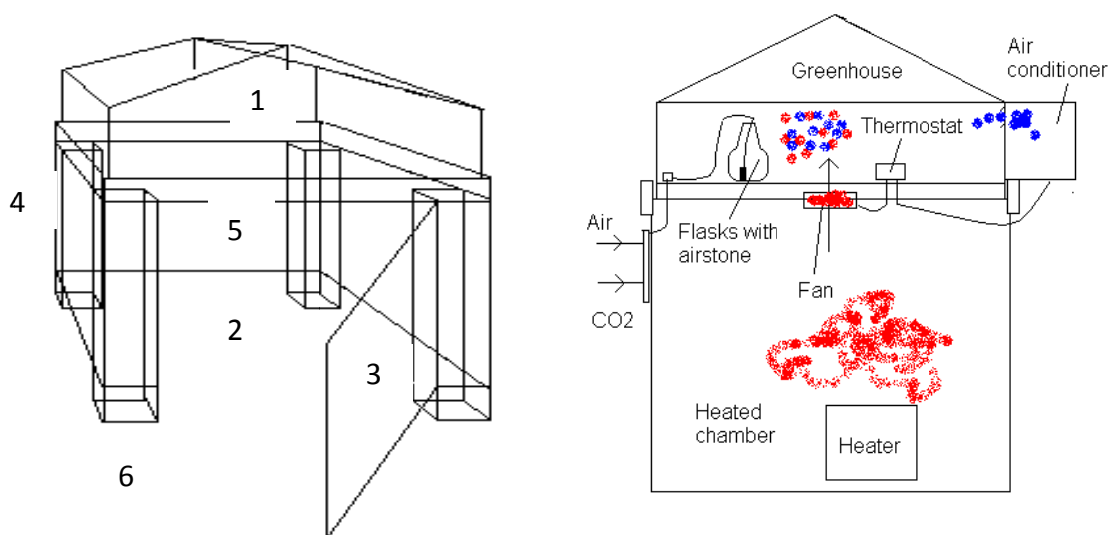


Figure 60: Schematic drawing of the algae algal culture apparatus.

The thermostat controls the fan and the air conditioner to keep the temperature constant at 85°F. The air for aeration of the cultures is mixed with CO₂ (from a cylinder) outside the box (air is provided by an air-pump) and then routed to each flask for individual air supply.



Figure 61: Algal culture apparatus.



Figure 62: Heating chamber of the algal culture apparatus.

D. ENRAT Model Software; ENRAT.JAR

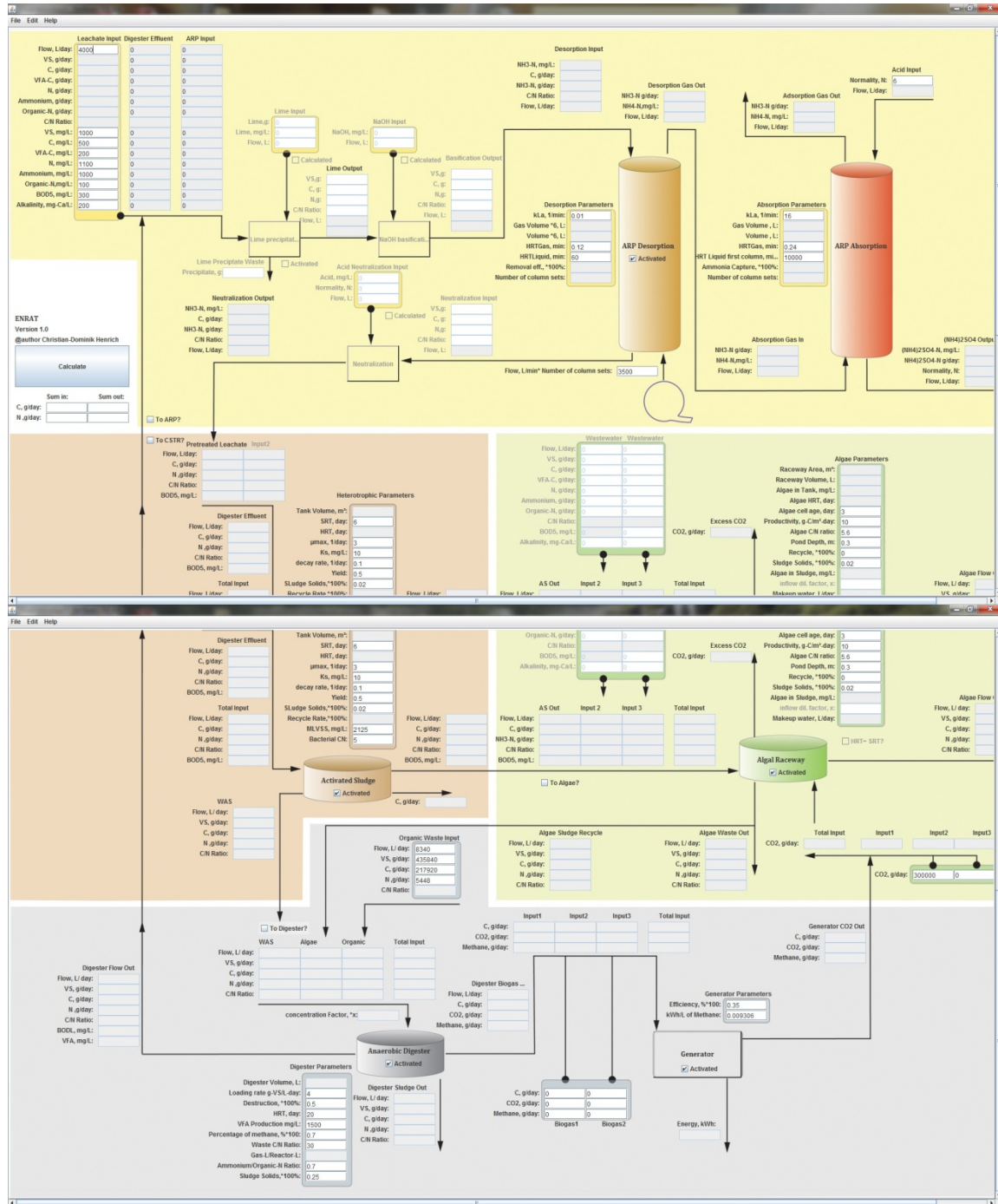


Figure 63: Graphical Interface of ENRAT v1 in MainWindow.java.

The program code can be found on supplemental CD. The executable ENRAT.Jar file contains all source code files. Java software which is needed to run ENRAT.Jar, can be found on www.sun.com for download.

LITERATURE CITED

- Abbas, A. A., G. Jingsong, L. Zhi Ping, P. Y. Ya, and W. S. Al-Rekabi, (2009). "Review on Landfill Leachate Treatments." *J. App. Sci. Res.*, 5 (5): pp. 535-545.
- APHA, (1995). Standard Methods For The Examination of Water and Wastewater. Editor: A. D. Eaton, L. S. Clesceri, and A. E. Greenberg. Washington DC.
- Basakcildan-kabakci, S., A. N. Ipekoglu, and I. Talinli, (2007). "Recovery of ammonia from urine by stripping and absorption." *Environmental Eng. Sci.*, 24 (5): pp. 615-624.
- Beecher, L. E. and D. E. Brune,(2007). "Brine shrimp patent Concentration and Separation of Lipids from Renewable Resources." Clemson University, US Patent Application 20090181436.
- Benemann, J. R., J. C. Van Olst, M. J. Massingill, J. C. Weissman, and D. E. Brune, (2002). "The controlled Eutrophication Process: Using Microalgae for CO₂ Utilization and Agricultural Fertilizer Recycling."
- Brune, D. E., J. A. Collier, and T. E. Schwedler, (2001). "Partitioned Aquaculture System." U.S. Patent 6192833.
- Brune, D. E., T. J. Lundquist, and J. R. Benemann (2009). "Microalgal Biomass for Greenhouse Gas Reductions; Potential for Replacement of fossil-Fuels and Animal feeds." *J. Envir. Engineering*, 135 (11): pp. 1136-1144.
- Brune, D.E., G. Schwartz, A.G. Eversole, J.A. Collier, and T.E. Schwedler, (2003). "Intensification of pond aquaculture and high rate photosynthetic systems." *Aquacultural Engineering* 28, 65-86.
- Brune, D.E., K. Kirk, and C.-D. Henrich, (2008). "Shrimp Production in a Zero-discharge Photoautotrophic-Chemoautotrophic Partitioned Aquaculture System." World Aquaculture Society Meeting, Orlando, FL.
- Grady, C. L. P. Jr, G.T. Daigger, and H. C. Lim, (1999). Biological Wastewater Treatment, 2nd ed., Merce Dekker, Inc. New York.
- Guo, X., J. K. Tak, and R. L. Johnson, (2009). "Ammonia removal from air stream and biogas by a H₂SO₄ impregnated adsorbent originating from waste wood-shavings and biosolids." *Journal of Hazardous Materials*, 166: pp. 372-376.

-
- Henrich, C.-D., (2008). "Algal and Bacterial Nitrogen Processing in a Zero-Discharge Suspended-Culture Shrimp Production System." Master's Thesis, Clemson University, Clemson, South Carolina.
- Henze, M., C. P.L. Grady, Jr., W. Gujer, G. v. R. Marais, and T. Matsuo, (1987). "A general model for single-sludge wastewater treatment systems." *Water Research*, 21: pp. 505-515.
- Körner, S., S. K. Das, S. Veenstra, and J. E. Vermaat, (2001). "The effect of pH variation at the ammonium/ammonia equilibrium in wastewater and its toxicity to *Lemna gibba*." *Aquatic Botany*, 71.
- Le, L., H. W. Wang, and H. H. Lu, (2006). "Nitrogen removal using an air stripper tower in an urban wastewater treatment plant." *China Water Wastewater*, 17: pp. 92-95.
- Lide, D. R., W.M. Haynes,(ed.) (2010). Handbook of Chemistry and Physics. 90th ed., Internet Version, http://www.hbcnetbase.com/toc/default.asp?exp=*toc*, as of 03.24.10.
- Marttinen, S. K., R. H. Kettunen, K. M. Sormunen, R. M. Soimasuo, and J. A. Rintala, (2002). "Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates." *Chemosphere*, 46, pp. 851-858.
- Matter-Müller, C., W Gujer, and W. Giger, (1981). "Transfer of volatile substances from water to the atmosphere." *Water Resources*, 15: pp. 1271-1279-
- Quan, X. J., F. P. Wang, Q. H. Zhao, T. T. Zhao, and J. X. Xiang, (2009). "Air stripping of ammonia in a water-sparged aerocyclone reactor." *Journal of Hazardous Materials*, 170: pp. 983-988.
- Saracco, G. and G. Genon, (1994). "High temperature ammonia stripping and recovery from process liquid wastes." *Journal of Hazardous Materials* 37: pp. 191-206.
- Turker, H., A. G. Eversole, and D. E. Brune, (2003). "Filtration of Green Algae and Cyanobacteria by Nile Tilapia, *Oreochromis niloticus*, in the Partitioned Aquaculture System." *Aquaculture*, 215: pp. 93-101.
- UW-Extension, (2003). Recommended Methods of Manure Analysis(A3769), Peters, J. (ed.), University of Wisconsin, <http://learningstore.uwex.edu/Assets/pdfs/A3769.pdf>.

Washington State Department of Ecology (WSDE), (2008). "Toward a Sustainable Washington", <http://www.ecy.wa.gov/sustainability/definition.htm>, as of 04.15.08.

Yen, H., (2004). "Anaerobic bioassay of methane potential of microbial biomass." PHD Dissertation, Clemson University, Clemson, South Carolina.