

Biological Process Design and Pilot Testing for a Carbon Oxidation, Nitrification, and Denitrification System

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In response to a new NPDES permit incorporating Organic Chemical, Plastic, and Synthetic Fiber (OCPSF) effluent limits for BOD (carbonaceous and nitrogenous), TSS, and priority pollutants, a treatability study was conducted to establish design criteria for a new process wastewater treatment plant for DSM Chemicals North America, Inc. The permit also requires partial removal of total nitrogen. Based on the discharge criteria, a two-stage biological process configuration was selected. The configuration consisted of an anoxic followed by an aerobic reactor with mixed liquor recirculation. To establish design criteria, a two-phase study was conducted. The first phase involved determining wastewater characteristics and kinetic and stoichiometric coefficients. These values were used as input to "Simulation of Single-Sludge Processes" (SSSP), a computer model that was used to evaluate potential process configurations. In the second phase, a pilot-scale system was operated to verify performance. With a volume distribution of 40 percent anoxic and 60 percent aerobic and a recirculation ratio of 2, BOD, COD, and total nitrogen removal efficiencies of 99, 88, and 80 percent were obtained, respectively. Approximately 84 percent of the biodegradable COD was removed through denitrification.

INTRODUCTION

Background

DSM Chemicals North America, Inc., Augusta, Georgia, manufactures caprolactam and generates process wastewater containing 3,400 mg/l of chemical oxygen demand (COD) and 660 mg/l of total nitrogen. The new process wastewater NPDES permit will incorporate stringent Organic Chemical, Plastics,

and Synthetic Fibers (OCPSF) industrial subcategory effluent limits for biochemical oxygen demand (BOD) (carbonaceous and nitrogenous), total suspended solids (TSS), and priority pollutants. In addition to OCPSF requirements, the permit requires partial removal of total nitrogen. Because the existing single-stage aerobic biological treatment system could not be upgraded to meet the new permit requirements cost effectively, a new system will be constructed. A two-stage single-sludge carbon oxidation, nitrification, and denitrification system was

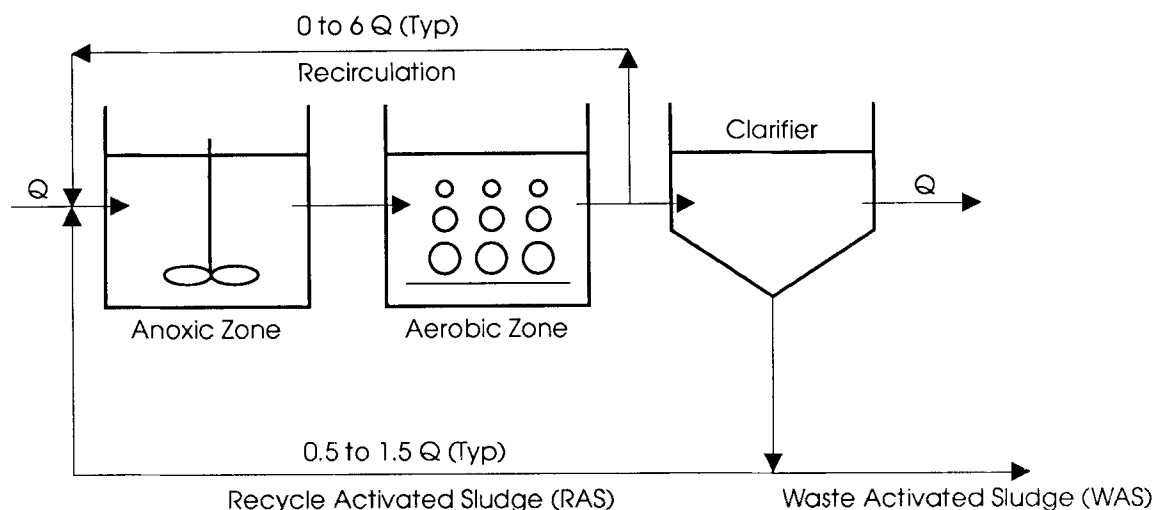


FIGURE 1. Two stage single-sludge anoxic/aerobic configuration for carbon oxidation, nitrification and denitrification.

selected based on the need to reduce total nitrogen and the desire to minimize oxygen and alkalinity requirements. The system will consist of an anoxic reactor followed by an aerobic reactor with mixed liquor recirculation as presented in Figure 1.

To develop design criteria, a treatability study was conducted. The study included lab-scale testing, computer-aided process simulation, and pilot-scale testing. Simulation was an integral part of the study program because of the complexity of the biological system. It was performed with SSSP [1], a program based on the mathematical model for single sludge systems developed by a task group of the International Association for Water Pollution Research and Control (IAWPRC) [2] SSSP was chosen because it has been shown to accurately describe the performance of systems incorporating carbon oxidation, nitrification, and denitrification [3].

The IAWPRC model incorporates eight reactions operating on 13 components. With respect to microorganism growth and decay, reactions include the aerobic and anoxic growth of heterotrophs, aerobic growth of autotrophs, and decay of heterotrophs and autotrophs. Biochemical reactions include ammonification of soluble organic nitrogen, hydrolysis of

entrapped organics, and hydrolysis of entrapped organic nitrogen. Components are classified as organics, microorganisms, nitrogen, oxygen, and alkalinity. Organics include soluble organics (readily biodegradable), particulate organics (slowly biodegradable), particulate products, and inert particulates. Microorganisms are either heterotrophs or autotrophs. Nitrogen includes soluble ammonia, nitrate/nitrite, soluble organic nitrogen (readily biodegradable), and biodegradable particulate organic nitrogen (slowly biodegradable). All nitrogen species are expressed as nitrogen equivalents. Both organic and microorganism components are expressed as equivalent amounts of COD to facilitate development of mass balance equations. All components are linked through the appropriate kinetic and stoichiometric relationships using a matrix format [2,4].

An important aspect of the IAWPRC model is the focus on prediction of activated sludge concentrations and electron acceptor (oxygen and nitrate) requirements rather than substrate removal. The rationale of the IAWPRC task group was that because of the long solids retention time (SRT) incorporated into the design of most biological treatment systems, differences in effluent soluble biodegradable substrate concentration

Table 1 Historical Wastewater Characteristics

Parameter	Average Day Concentration (mg/l)	Maximum/Average Ratio
COD	3,390	2.00
BOD	1,695	2.53
TKN	362	3.72
NH ₃ -N	226	4.18
NO ₃ -N	299	2.14
Total Nitrogen	662	3.01
PO ₄ -P	49	3.76
Benzene	54	— ^b
Toluene	39	— ^b
Phenol	3.2	— ^b
TSS	22	— ^b
VSS	10	— ^b
Alkalinity (as CaCO ₃)	200	— ^b
pH ^a	6.1	11.8

^apH units, S.U.

^bInsufficient data to establish meaningful ratio

Table 2 New NPDES Permit Requirements

Parameter	Maximum Monthly Average (mg/l)	Maximum Day (mg/l)
BOD	34 ^a	92 ^a
TSS	49	159
Total Nitrogen	330	826
Benzene	0.037	0.136
Toluene	0.026	0.080
Phenol	0.015	0.026

^aIncludes carbonaceous and nitrogenous BOD

between different system configurations are relatively small. Conversely, large differences in activated sludge concentrations and electron acceptor (oxygen and nitrate) requirements are common [2]. Furthermore, nitrogen removal is greatly influenced by activated sludge concentration and electron acceptor requirements, but influenced little by effluent soluble biodegradable substrate concentration.

OBJECTIVE AND APPROACH

A phased and iterative approach was taken. In the first phase, the pilot plant was started and selected wastewater characteristics and kinetic and stoichiometric coefficients were determined in lab-scale experiments.

In the second phase, SSSP simulations were performed using experimentally determined wastewater characteristics and kinetic and stoichiometric coefficients. These simulations were used to aid in the selection of the pilot plant configuration to be tested. The pilot plant was reconfigured and a 30-day test run was conducted.

The first-phase objective was to determine the following parameters:

- Heterotrophic yield
- heterotrophic decay coefficient
- Anoxic growth and hydrolysis factors
- Maximum specific growth rate coefficient of nitrifiers
- Readily biodegradable COD concentration

The second-phase objective was to verify the performance of the pilot plant.

WASTEWATER CHARACTERISTICS AND PERMIT REQUIREMENTS

Table 1 presents the historical average process wastewater characteristics and the ratios of maximum to average day load for each parameter. The COD to total nitrogen ratio is approximately five, indicating that a substantial portion of the COD could be removed through denitrification. The maximum-to-average day ratios indicate that the reduced nitrogen (TKN) load is highly variable compared to the COD load.

The new NPDES permit requirements are presented in Table 2. Based on the wastewater characteristics, monthly average BOD and total nitrogen removals of greater than 98 and 50 percent are required, respectively. Benzene and toluene removals of greater than 99.9 percent are required. Phenol removal of greater than 99.5 percent is required.

DESCRIPTION OF EXPERIMENTS AND DISCUSSION OF RESULTS

Initial Simulations and Pilot Plant Startup

Simulations

Because the lab-scale experiments require a stable nitrifying and denitrifying sludge acclimated to the wastewater to be

Table 3 Definition of Kinetic and Stoichiometric Parameters

Symbol	Definition
Y_A	Yield of autotrophic biomass
Y_H	Yield of heterotrophic biomass
f_p	Fraction of biomass leading to particulate products
i_{XB}	Mass of nitrogen per mass of COD in biomass
i_{XP}	Mass of nitrogen per mass of COD in products from biomass
μ_{Hm}	Maximum specific growth rate for heterotrophic biomass
K_S	Half-saturation coefficient for heterotrophic biomass
$K_{O,H}$	Oxygen half-saturation coefficient for heterotrophic biomass
K_{NO}	Nitrate half-saturation coefficient for denitrifying heterotrophic biomass
b_H	Decay coefficient for heterotrophic biomass
η_b	Correction factor for μ_{Hm} under anoxic conditions
η_h	Correction factor for hydrolysis under anoxic conditions
k_a	Ammonification rate
k_h	Maximum specific hydrolysis rate
K_X	Half-saturation coefficient for hydrolysis of slowly biodegradable substrate
μ_{Am}	Maximum specific growth rate for autotrophic biomass
K_{NH}	Ammonia half-saturation coefficient for autotrophic biomass
$K_{O,A}$	Oxygen half-saturation coefficient for autotrophic biomass
b_A	Decay coefficient for autotrophic biomass

Table 4 Typical Parameter Values at Neutral pH and 20°C for Domestic Wastewater [1]

Symbol	Units	Default Value	Assumed Value
Stoichiometric Parameters			
Y_A	g cell COD formed (g N oxidized) ⁻¹	0.24 ^a	
Y_H	g cell COD formed (g COD oxidized) ⁻¹	0.67	0.45
f_p	dimensionless	0.08 ^a	
i_{XB}	g N(g COD) ⁻¹ in biomass	0.086 ^a	
i_{XP}	g N(g COD) ⁻¹ in products from biomass	0.06 ^a	
Kinetic Parameters			
μ_{Hm}	day ⁻¹	4.0	
K_S	g COD m ⁻³	10	
$K_{O,H}$	g O ₂ m ⁻³	0.10 ^a	
K_{NO}	g NO ₃ -N m ⁻³	0.20 ^a	
b_H	day ⁻¹	0.62	0.10
η_g	dimensionless	0.8	
η_h	dimensionless	0.4	
k_a	m ³ (g cell COD·day) ⁻¹	0.16	
k_h	g slowly biodegradable COD (g cell COD·day) ⁻¹	2.2	
K_X	g slowly biodegradable COD (g cell COD) ⁻¹	0.15	
μ_{Am}	day ⁻¹	0.65	0.30
K_{NH}	g NH ₃ -N	1.0	
$K_{O,A}$	g O ₂ m ⁻³	1.0 ^a	
b_A	day ⁻¹	0.12	0.03

^aCan be considered constant [2]

treated, it was necessary to start the pilot plant before the actual configuration to be tested was selected. To aid in the selection of the initial pilot plant configuration, simulations were performed using historical wastewater characteristics and assumed kinetic and stoichiometric coefficients.

Table 3 defines the kinetic and stoichiometric parameters used in the model. Table 4 presents the units and default values for these parameters [1]. For the initial simulations, default values were used with the exceptions of the assumed values listed in Table 4. It was believed that the assumed values would be more accurate than the default values for DSM wastewater. Historical data were used to define the initial simulation wastewater characteristics as presented in Table 5. It was assumed that 80 percent of the COD was biodegradable and that of the biodegradable COD, 25 percent was soluble (readily biodegradable) and 75 percent was particulate (slowly biodegradable). Similarly, organic nitrogen was assumed to be 80 percent biodegradable with 25 percent soluble and 75 percent particulate.

Several alternative process configurations were evaluated at a 30-day SRT. This relatively long SRT was selected because the effect of wastewater constituents on nitrification were unknown and a stable nitrifier population was required. A feed flow rate of 52 l/day was selected based on a target reactor mixed liquor volatile suspended solids (MLVSS) of approximately 4,500 mg COD/l (approximately 3,000 mg VSS/l). Figure 2 presents SSSP input and output for the initial pilot plant configuration chosen. The reactor volumes and flow rates presented are 1,000 times greater than the pilot plant values because SSSP accepts only whole numbers. Under the section entitled "Steady-State Solution" the column headed by the number 1 describes the anoxic reactor contents, and the column headed by number 2 describes the aerobic reactor contents (or unclarified effluent). A small anoxic reactor volume relative to the aerobic reactor volume was selected for startup to promote development of a stable nitrifier population. Recirculation was not required with this configuration because of the excess nitrate concentration in the anoxic reactor. A recycle

Table 5 Wastewater Constituents Used for Initial Simulations

Symbol	Constituent Definition	Units	Historical Value
$X_{B,H}$	Heterotrophic organisms	g COD m ⁻³	0
$X_{B,A}$	Autotrophic organisms	g COD m ⁻³	0
X_P	Particulate organics	g COD m ⁻³	0
X_I	Inert particulates (organics)	g COD m ⁻³	0
X_S	Particulate organics	g COD m ⁻³	2034
S_S	Soluble organics	g COD m ⁻³	678
S_{NH}	Soluble ammonia N	g N m ⁻³	226
S_{NO}	Soluble nitrate/nitrate N	g N m ⁻³	299
S_{ND}	Soluble organic N	g N m ⁻³	27
X_{ND}	Biodegradable particulate organic N	g N m ⁻³	82
S_O	Oxygen	g O ₂ m ⁻³	0
S_{ALK}	Alkalinity	mole m ⁻³	100

PROCESS CONFIGURATION AND FLOW DISTRIBUTION

OVERALL PLANT SPECIFICATIONS:

Number of Reactors (up to 9) = 2
 Solids Retention Time (days) = 30.0
 Average Flow Rate (m³/day) = 52

INDIVIDUAL REACTOR SPECIFICATIONS:

	1	2
Reactor Volume (m ³)	= 30	170
Feed Fraction (0 to 1)	= 1.00	0.00
O ₂ Concentration (g O ₂ /m ³)	= 0.00	2.00
Recycle Input (m ³ /day)	= 52	0
Recirculation Input (m ³ /day)	= 0	0
Recirculation originated from reactor	= *	*

STEADY-STATE SOLUTION

CONSTITUENTS		FEED	1	2
Heterotrophic Organisms	g cod m-3	= 0.0	3509.0	3456.4
Autotrophic Organisms	g cod m-3	= 0.0	261.4	281.8
Particulate Products	g cod m-3	= 0.0	810.3	857.1
Inert Particulates	g cod m-3	= 0.0	0.0	0.0
Particulate Organics	g cod m-3	= 2034.0	666.1	54.0
Soluble Organics	g cod m-3	= 678.0	1.3	0.2
Soluble Ammonia N	g n m-3	= 226.0	116.8	0.6
Soluble Nitrate/Nitrite N	g n m-3	= 299.0	112.6	247.2
Soluble Organic N	g n m-3	= 27.0	0.2	0.1
Biodegrad Part Organic N	g n m-3	= 82.0	30.2	3.5
Oxygen	g o ₂ m-3	= 0.0	0.0	2.0
Alkalinity	mole m-3	= 1.0	6.5	-11.4
MLVSS	g cod m-3	=	5246.8	4649.2
O ₂ Consumed	g o ₂ m-3 d-1	=	0.0	744.0
Nitrate Consumed	g no ₃ -n m-3 d-1	=	556.3	5.2

FIGURE 2. Simulation for initial pilot plant configuration (20°C).

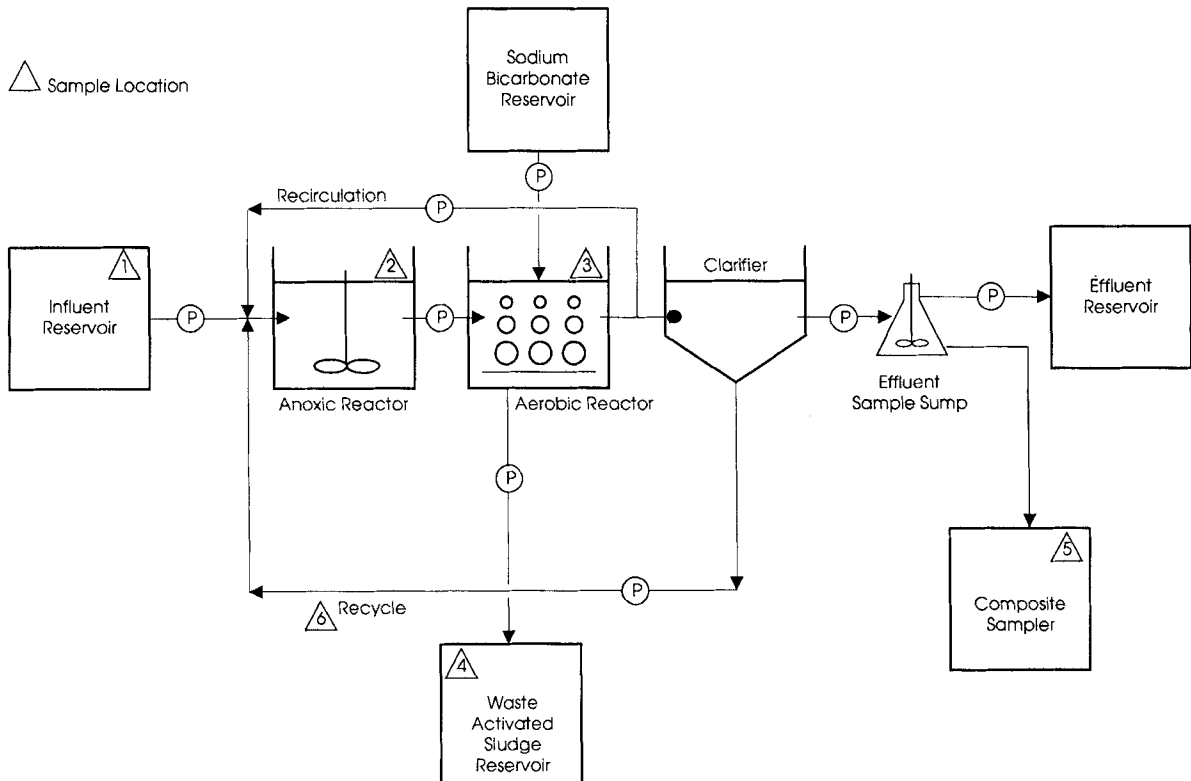


FIGURE 3. Pilot plant process flow diagram.

Table 6 Pilot Plant Analytical Schedule

Parameter	Sample Location						Testing Frequency			Analytical Method [5,6]
	Influent (1)	Anoxic Reactor (2)	Aerobic Reactor (3)	Waste Sludge (4)	Effluent (5)	Recyle (6)	Daily	Alternate Days	Bi-Weekly	
COD	X			X ^a	X		X			EPA 410.1
SCOD	X	X			X			X		EPA 410.1
BOD					X			X		EPA 405.1
CBOD	X				X			X		EPA 405.1
SBOD					X			X		EPA 405.1
TKN	X	X		X ^a	X		X			EPA 351.3
NH ₃ -N	X	X			X		X			SM 417E
NO ₂ -N		X			X	X	X			EPA 354.1
NO ₃ -N	X	X			X	X	X			EPA 353.3
PO ₄ -P	X				X				X	EPA 365.3
TSS	X	X	X	X	X		X			EPA 160.2
VSS	X		X						X	EPA 160.4
Alkalinity	X	X	X		X		X			EPA 310.1
pH	X	X	X		X		X			EPA 150.1
OUR			X				X			SM 213A
SVI			X					X		SM 213C
DO		X	X				X			EPA 360.1
Temperature			X				X			EPA 170.1
Benzene	X				X _b			X		EPA 602
Toluene	X				X ^b			X		EPA 602
Phenol	X				X			X		EPA 604
Microscopic Observation			X						X	—

^aBi-weekly

^bAnalyzed during startup only

flow rate equal to the feed flow rate was used throughout the study.

Materials

Figure 3 presents the pilot plant process flow diagram. The anoxic and aerobic reactors were 55-gallon cylindrical polyethylene tanks. The anoxic reactor had a liquid volume of 30 liters and was mixed using a variable speed mixer. The aerobic reactor had a volume of 170 liters and was mixed and aerated with compressed air. The secondary clarifier consisted of an inverted, open-top, 20-liter cylindrical carboy. The clarifier was fitted with a 4-inch-diameter stilling well which received mixed liquor; a polypropylene funnel which served as the overflow weir; and a rake arm driven by a variable speed motor. All pumping was performed with peristaltic pumps. Waste sludge was automatically pumped from the aerobic reactor on a 1-hour cycle. Alkalinity was supplied to the aerobic reactor with a manually controlled piston metering pump when required. Clarifier effluent was pumped to a mechanically mixed 1-liter Erlenmeyer flask which served as a composite sample sump. A refrigerated ISCO sampler was used to collect an effluent sample on a 15-minute cycle. Flask overflow was pumped to an effluent tank for daily volume measurement.

Methods

The pilot plant was seeded with biomass from the existing WWTP and operated for approximately 10 weeks before the

test run began. A 24-hour composite process wastewater sample was collected daily in a 55-gallon drum to serve as the pilot plant influent. The influent flow rate was constant during each run. Dynamic pollutant loadings were the result of daily variations in pollutant concentrations. The reactor temperatures were targeted for the anticipated full-scale minimum monthly average temperature of approximately 20°C. Provisions were not made to cool the reactors when slightly higher temperatures were periodically encountered. Table 6 presents the pilot plant analytical schedule during startup and testing. Analyses were performed in accordance with established procedures [5,6].

WASTEWATER CHARACTERISTIC AND KINETIC AND STOICHIOMETRIC COEFFICIENT DETERMINATION

Because most of the kinetic and stoichiometric parameters presented in Table 4 are either near constants (Y_A , f_p , i_{XB} , i_{XF} , K_{NO} , $K_{O,H}$, $K_{O,A}$) or have minimal influence in predicting sludge generation and oxygen requirements (K_S , k_a , k_b , K_X , K_{NH} , b_A), determination of a relatively small number of parameter coefficients will result in reasonably accurate model calibration. The following parameters are greatly influenced by wastewater composition and were determined experimentally:

Y_H —Heterotrophic yield (g COD/g COD)

b_H —Heterotrophic decay coefficient (day⁻¹)

η_g —Anoxic growth factor (dimensionless)

Table 7 Test Run Data for Heterotrophic Yield Determination

Time (hr)	VSS (mg/l)	SCOD (mg/l)
0	396	2,882
21	597	2,186
45	883	1,085
69	730	784
93	620	749

η_h —Anoxic hydrolysis factor (dimensionless)

μ_{Am} —Maximum specific growth rate coefficient of nitrifiers (day^{-1})

S_s —Readily biodegradable COD concentration (g COD m^{-3})

Heterotrophic Yield

Theory. The true heterotrophic yield (Y_H) is required to estimate the concentration of readily biodegradable COD in the influent wastewater, and to predict sludge production and oxygen requirements. This value is estimated by determining the increase in volatile suspended solids (VSS) and decrease in soluble COD (SCOD) in a batch reactor. The true heterotrophic yield is calculated using the following equation:

$$Y_H = \frac{\Delta \text{VSS}}{\Delta \text{SCOD}} \quad (1)$$

Materials. A 13-liter batch reactor with diffused aeration was used.

Methods. An aliquot of filtered influent wastewater and acclimated biomass (approximately 400 mg VSS/l) obtained from the pilot plant was placed in the reactor. The reactor VSS and SCOD concentrations were measured daily until the SCOD concentration became limiting.

Results. One test run was conducted to determine Y_H . Results are presented in Table 7. The increase in VSS over the first 45 hours was 487 mg/l while the decrease in COD was 1797 mg/l. The resulting yield is 0.27 mg VSS/mg COD. Assuming 1.48 mg COD/mg VSS, Y_H is 0.40 mg COD/mg COD. After 45 hours, the supply of biodegradable COD was exhausted and cell decay began to occur as the data for hours 69 and 93 indicate.

Heterotrophic Decay

Theory. The heterotrophic decay coefficient is affected by the nature of the wastewater being treated. Therefore, it should be determined to estimate sludge production and oxygen requirements [2,7]. An indirect determination was used for this study, requiring that the true yield, observed yield, and SRT of a system operating under steady-state conditions be known. The traditional decay coefficient b'_H may then be calculated using:

$$Y_{obs} = \frac{Y_H}{1 + b'_H \theta_X} \quad (2)$$

where:

Y_{obs} = observed (net) yield

θ_X = solids retention time

As described by the IAWPRC task group [2], traditional modeling of biological systems does not incorporate the recycling of substrate from decay. Therefore, the traditional decay coefficient must be modified for use in SSSP. The modified decay

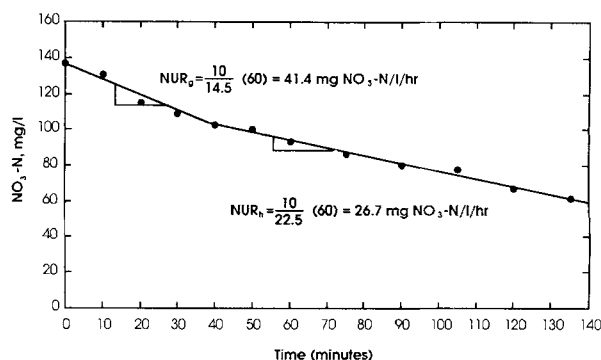


FIGURE 4. Nitrate concentration versus time for the determination of anoxic growth and hydrolysis factors.

coefficient (b_H) is calculated using:

$$b_H = \frac{b'_H}{1 - Y_H(1 - f_p)} \quad (3)$$

Results. The observed yield in the pilot plant at a 30-day SRT was 0.12 mg VSS/mg COD removed at an average temperature of 19°C. Based on the experimentally determined true yield of 0.27 mg VSS/mg COD, the traditional heterotrophic decay (b'_H) calculated using equation 2 is 0.042 day^{-1} . The modified decay coefficient calculated from equation 3 is 0.066 day^{-1} .

Anoxic Growth and Hydrolysis Factors

Theory. The anoxic growth factor (η_g) and anoxic hydrolysis factor (η_h) are used to predict denitrification performance [2,8]. The anoxic growth factor adjusts for either the change in growth of heterotrophic bacteria when using nitrate as the electron acceptor, or for the fact that not all heterotrophs can denitrify [2]. The anoxic hydrolysis factor adjusts for the hydrolysis of slowly biodegradable COD by heterotrophs when using nitrate as the electron acceptor.

To determine these factors, nitrate utilization rate (NUR) and oxygen utilization rate (OUR) are measured in parallel anoxic and aerobic batch reactors, respectively. When the biomass is brought into contact with the influent wastewater, the initial growth of heterotrophs results from the removal of readily biodegradable COD. When the readily biodegradable COD has been removed, the growth of heterotrophs results from the hydrolysis of slowly biodegradable COD to readily biodegradable COD. The anoxic growth and hydrolysis factors are calculated from the ratio of NUR to OUR using the following equations:

$$\eta_g = \frac{2.86 \times \text{NUR}_g}{\text{OUR}_g} \quad (4)$$

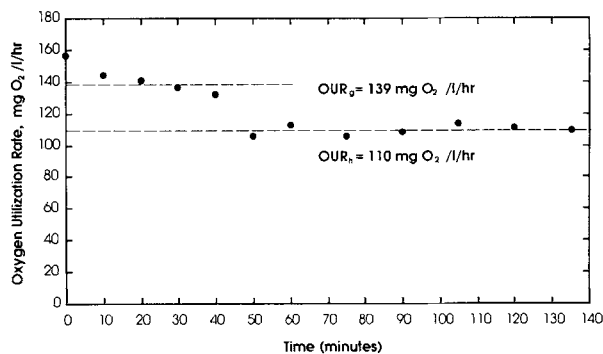


FIGURE 5. Oxygen utilization rate versus time for the determination of anoxic growth and hydrolysis factors.

Table 8 Summary of Test Run Data for Anoxic Growth and Hydrolysis Factor Determination

Run	Growth		η_g^a	Hydrolysis		η_h^a
	NUR _g (mg NO ₃ -N/1/hr)	OUR _g (mg O ₂ /1/hr)		NUR _h (mg NO ₃ -N/1/hr)	OUR _h (mg O ₂ /1/hr)	
1	41	139	0.84	27	110	0.70
2	60	176	0.98	31	138	0.64
3	60	148	1.0 ^b	25	100	0.72
Average			0.94			0.69

^a $\eta = 2.86 \times \text{NUR}/\text{OUR}$

^bCalculated value equals 1.16, however, maximum theoretical value 1.0.

$$\eta_h = \frac{2.86 \times \text{NUR}_g}{\text{OUR}_g} \quad (5)$$

Materials. Two 9.0-liter mechanically mixed batch reactors were used. The anoxic reactor was sealed and nitrogen gas was continually added to the reactor headspace and vented to assure that oxygen was not present. Compressed air was delivered through two gas diffusing stones in the aerobic reactor.

Methods. The reactors were seeded with 5 liters of biomass from the pilot plant anoxic reactor before each test. The biomass was then contacted with influent wastewater volumes ranging from 0.75 to 1.5 liters. Depending on the wastewater nitrate concentration, 0.1 or 0.2 liter of 1,000 mg/l NO₃-N standard was also added to maintain nonlimiting NO₃-N concentrations. DO was continuously monitored in the anoxic reactor to verify that none was present. Samples were obtained from each reactor at 10- to 15-minute intervals for 2 to 3 hours. The samples were filtered before analysis. Anoxic reactor pH, temperature, and MLVSS, NO₃-N, NO₂-N, SCOD, and alkalinity concentrations were determined at various intervals. Only OUR was determined in the aerobic reactor.

Results. Plots of NO₃-N and OUR versus time for one test run are presented in Figures 4 and 5, respectively. The plots indicate that the readily biodegradable COD in both reactors was removed after approximately 40 minutes, after which there was a distinct decrease in both NUR and OUR. Table 8 presents a summary of the results for the three test runs. The average anoxic growth and hydrolysis factors were 0.94 and 0.69, respectively.

Maximum Specific Growth Rate Coefficient of Nitrifiers

Theory. The maximum specific growth rate coefficient of nitrifiers (μ_{Am}) is highly dependent on constituents in the wastewater and must be determined to predict nitrification performance [2]. Since nitrifying bacteria grow at a much slower rate than heterotrophic bacteria, the minimum SRT in

nitrifying systems is dependent on μ_{Am} . Once μ_{Am} is determined, an appropriate SRT with a reasonable factor of safety can be selected. To determine μ_{Am} , nitrifying biomass from a system treating the wastewater is placed in a batch reactor and diluted with system effluent. Nonlimiting NH₃-N concentrations should be maintained for several days. In an environment with a relatively low concentration of nitrifying bacteria and nonlimiting NH₃-N concentrations, the nitrifying bacteria will grow at their maximum rate, making oxidized nitrogen production (NO₂-N + NO₃-N) proportional to the mass of nitrifying bacteria. A plot of the natural logarithm of the oxidized nitrogen concentration versus time will give a straight line with a slope equal to $\mu_{Am}(2)$.

Materials. A 12-liter batch reactor with diffused aeration was used. An automatic pH controller was used to maintain reactor pH. Alkalinity was supplied using a peristaltic pump.

Methods. An aliquot of pilot plant effluent and acclimated pilot plant biomass (approximately 400 mg VSS/l) was placed in the reactor. Ammonium chloride was added to provide an initial NH₃-N concentration of approximately 300 mg/l. The reactor DO was maintained at 4 mg/l. Reactor pH was monitored continuously, and a concentrated stock solution of sodium bicarbonate was automatically delivered to the reactor when the pH fell below 7.2. Dry sodium bicarbonate was added directly to the reactor as needed to meet major alkalinity requirements. Reactor temperature, pH, and soluble TKN (STKN), NH₃-N, NO₂-N, NO₃-N, and SCOD concentrations were measured daily until the NH₃-N concentration became limiting.

Results. High NH₃-N concentrations in the reactor resulted in inhibition of *Nitrobacter* and a buildup of NO₂-N. This did not interfere with μ_{Am} determination since the growth rate of *Nitrosomonas* is the rate-limiting step in the conversion of ammonia to nitrate. The plot of the natural log of NO₂-N concentration versus time for the single test run conducted is presented in Figure 6. The slope of the line is 0.36 day⁻¹ at 20°C. This value agrees with reported literature values ranging from 0.34 to 0.65 day⁻¹ [2].

Readily Biodegradable COD

Theory. An estimate of readily biodegradable COD in the influent wastewater is required to predict sludge production, oxygen requirements, and organic and nitrogen removals. The concentration of readily biodegradable COD (S_r) is estimated by measuring the change in OUR in a completely mixed reactor with a square wave loading condition. The reactor is operated at an SRT of approximately 2 days, and the square wave loading condition consists of an alternating 12-hour on/off feed. The change in OUR shortly after feed termination is associated with the removal of readily biodegradable COD. A detailed theoretical discussion of the readily biodegradable COD test is presented by Ekama *et al* [9]. The concentration of readily biodegradable COD is calculated using the following equation:

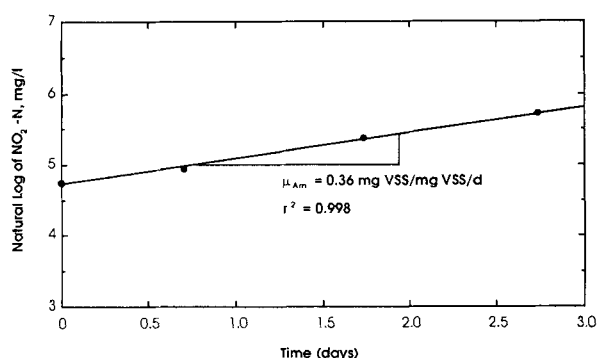


FIGURE 6. Natural logarithm of NO₂-N versus time for the determination of maximum specific growth rate of *Nitrosomonas*.

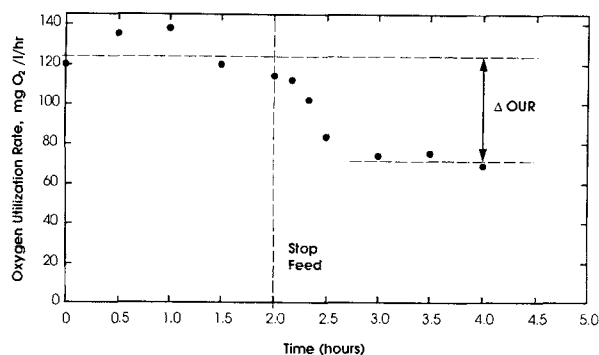


FIGURE 7. Response of completely mixed reactor to a 12-hour square wave load for the determination of readily biodegradable COD.

$$\text{Readily Biodegradable COD (mg/l)} = \frac{\Delta \text{OUR} V}{Q(1 - Y_H)} \quad (6)$$

where:

ΔOUR = change in OUR after feed termination (mg/l/hr)
 V = reactor volume (l)
 Q = feed flow rate prior to termination (l/hr)

Materials. A 9.8-liter completely mixed reactor with an internal clarifier and solids recycle was used. Influent wastewater delivery and solids wasting were performed using variable-speed peristaltic pumps operated by a programmable controller. Compressed air was delivered through two gas diffusing stones.

Methods. A 24-hour composite sample of influent wastewater was collected daily and used as feed to the reactor. The reactor was seeded with biomass from the existing WWTP and operated under constant flow and load conditions for approximately 3 SRTs. The targeted SRT was 2.5 days. After stable OURs and VSS concentrations were obtained, a square wave loading condition was established (12-hour on/off feed). The reactor was operated under these conditions for 2 SRTs before testing began. OURs were determined every half hour for 2 hours before feed termination to obtain an average OUR. After feed termination, OURs were determined every 10 minutes for the first 30 minutes and every 30 minutes thereafter until the OUR stabilized (approximately 2 to 3 hours). The influent flow rate, reactor pH, temperature, and COD, TSS, VSS, and $\text{NH}_3\text{-N}$ concentrations were determined daily in addition to the OUR measurements.

Results. A plot of OUR versus time for one test run is presented in Figure 7. The plot illustrates the dramatic decrease in OUR resulting from the removal of readily biodegradable COD. Table 9 summarizes the COD data from each test run. Based on the heterotrophic yield of 0.40 mg COD/mg COD and an 88 percent biodegradable COD fraction, the average readily biodegradable COD concentration from eight test runs was 951 mg/l. This concentration represents 24 percent of the total feed COD and 28 percent of the biodegradable COD. The readily biodegradable fraction varied significantly between test runs, ranging from 6 to 51 percent of the biodegradable COD.

SECOND PHASE

Simulations and Pilot Plant Reconfiguration

Simulations

Two sets of simulations were performed using the experimentally determined coefficients and the wastewater characteristic data obtained during initial pilot plant operation. The first set of simulations involved varying the anoxic reactor volume, reported as a fraction of total reactor volume, while holding the recirculation ratio constant at three times the feed flow rate. The second set of simulations involved varying the recirculation ratio while holding the reactor volumes constant. These simulations were used to aid in the selection of reactor volumes and a recirculation flow rate.

Initial pilot plant effluent BOD data indicated that a soluble carbonaceous BOD (SCBOD) of less than 15 mg/l would be

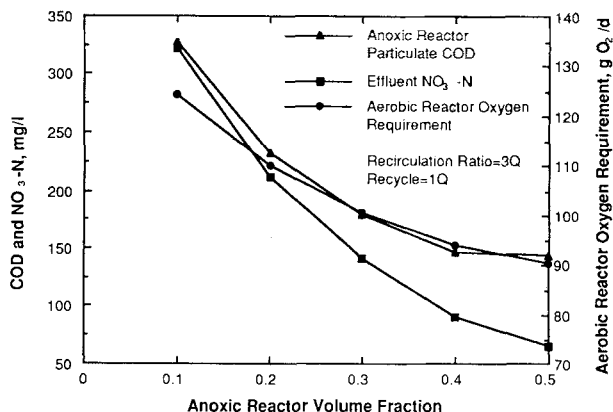


FIGURE 8. Effect of anoxic reactor volume fraction on anoxic reactor particulate COD, effluent $\text{NO}_3\text{-N}$ and aerobic reactor oxygen requirement.

Table 9 Summary of COD Data from Readily Biodegradable COD Tests

Run	Influent COD (mg/l)	Biodegradable COD ^a (mg/l)	Readily Biodegradable COD ^b (mg/l)
1	4,412	4,323	1,630
2	3,769	3,317	436
3	5,318	4,680	1,197
4	4,104	3,612	217
5	4,030	3,546	712
6	2,825	2,486	1,272
7	3,059	2,692	1,058
8	3,059	2,692	1,089
Average	3,885	3,419	951

^aThe biodegradable COD was assumed to be equal to 88 percent of the influent COD based on preliminary pilot data

^bCalculated using equation 6

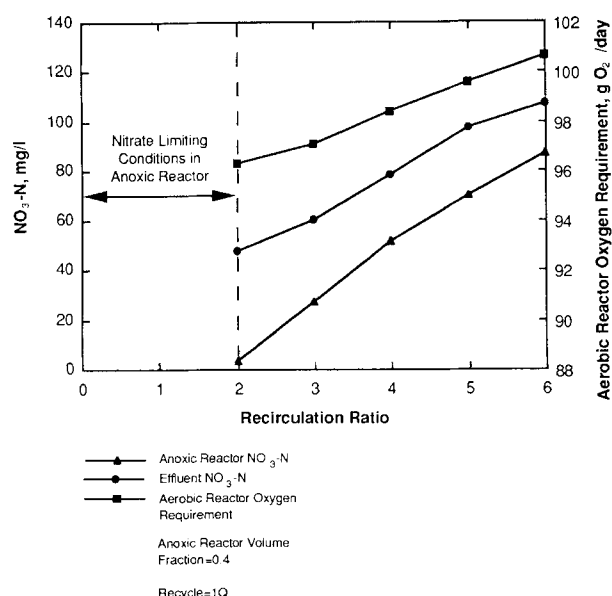


FIGURE 9. Effect of recirculation ratio on anoxic reactor NO₃-N, effluent NO₃-N and aerobic reactor oxygen requirement.

required to meet the 34 mg/l total BOD limit. Since the pilot plant SCBOD had averaged 10 mg/l, it was apparent that reducing the SRT could cause the SCBOD concentration to quickly approach or exceed the 15 mg/l target. Thus, a 30-day SRT was selected for the additional pilot plant studies.

Simulation results showing the effect of varying anoxic reactor volume fraction on particulate organics (slowly biodegradable COD), effluent NO₃-N, and aerobic reactor oxygen requirements at a recirculation ratio of three are presented in Figure 8. Anoxic fractions greater than 0.5 were not evaluated because sludge settleability is reported to deteriorate at higher ratios [10,11]. As the anoxic fraction approaches the maximum of 0.5, the rate of decrease in the three dependent variables declines significantly. This is the result of a growth-limiting biodegradable COD concentration in the anoxic reactor.

Selecting an anoxic and aerobic reactor volume distribution required a compromise between nitrification stability and total nitrogen removal. During startup, the pilot plant had shown slight instability with respect to nitrification, resulting in high nitrogenous BOD (NBOD). Conversely, historical data indicated that maximum month average day total nitrogen loads could be 30 percent higher than average month average day loads. High total nitrogen loads without a concurrent increase in process or supplemental wastewater COD would result in high effluent total nitrogen as nitrate. Based on these considerations, a volume distribution of 40 percent anoxic and 60 percent aerobic was selected. At this distribution the predicted effluent NO₃-N concentration of 91 mg/l would result in a factor of safety of greater than 200 mg/l with respect to the effluent total nitrogen limit. With respect to nitrification, the aerobic SRT would be 18 days (0.6 × 30 days). Based on $\mu_{A,n}$ of 0.36 day⁻¹, the theoretical minimum SRT for nitrification is 2.8 days (1/0.36 day⁻¹). Therefore, a sixfold factor of safety would be achieved for nitrification. The large factor of safety is necessary because of the highly variable TKN load and the potential for nitrifier inhibition.

Table 10 Pilot Plant Process Parameters

Parameter	Value
Overall System	
Solids Retention Time (θ_x)	30 days
Hydraulic Retention Time	4.44 days
Influent Flow Rate	45 l/d
Organic Loading Rate (F_a/M_v) (average)	0.27 mg COD/mg MLVSS/d
Organic Removal Rate (F_r/M_v) (average)	0.24 mg COD/mg MLVSS/d
Anoxic Reactor	
Solids Retention Time	12 days
Volume	80 liters
Recycle Flow Rate	45 l/d
Recirculation Flow Rate	90 l/d
Actual Hydraulic Retention Time	0.44 days
Nominal Hydraulic Retention Time	1.78 days
MLSS (average)	2,771 mg/l
MLVSS (average)	2,466 mg/l
Organic Loading Rate (F_a/M_v) (average)	0.71 mg COD/mg MLVSS/d
Organic Removal Rate (F_r/M_v) (average)	0.55 mg COD/mg MLVSS/d
Dissolved Oxygen (average)	0 mg/l
Aerobic Reactor	
Solids Retention Time	18 days
Volume	120 liters
Actual Hydraulic Retention Time	0.67 days
Nominal Hydraulic Retention Time	2.67 days
MLSS (average)	2,830 mg/l
MLVSS (average)	2,519 mg/l
SVI (average)	68 ml/g
Organic Loading Rate (F_a/M_v) (average)	0.11 mg COD/mg MLVSS/d
Organic Removal Rate (F_r/M_v) (average)	0.05 mg COD/mg MLVSS/d
Air Flow Rate (average)	283 l/hr
Dissolved Oxygen (average)	2.9 mg/l
Oxygen Utilization Rate (average)	22 mg/l/hr
Temperature (average)	21°C

Table 11 Pilot Plant Average Influent and Effluent Characteristics

Parameter	Influent (mg/l)	Anoxic Reactor (mg/l)	Effluent (mg/l)
COD	3,101	—	406
SCOD	—	463	381
Total BOD	1,511	—	19
SCBOD	—	—	5
NBOD	—	—	6
BOD _{TSS}	—	—	8
TKN	322	81 ^b	30
NH ₃ -N	240	63	8
NO ₂ -N	0	0.2	3
NO ₃ -N	436	67	116
Total Nitrogen	758	148 ^b	149
PO ₄ -P	44	—	40
TSS	21	2,771	23
VSS	10	2,466	20
Benzene	27	—	— ^a
Toluene	60	—	— ^a
Phenol	2.4	—	<0.01
Acidity	100	—	—
Alkalinity (as CaCO ₃)	—	662	270
pH	4.11	7.8	7.5

^aNot analyzed during the test run. Less than 0.01 mg/l during startup.

^bSoluble.

Simulation results showing the effect of recirculation ratio on anoxic reactor NO₃-N, effluent NO₃-N, and aerobic reactor oxygen requirement at an anoxic fraction of 0.4 are presented in Figure 9. Below a recirculation ratio of two, NO₃-N is limiting in the anoxic reactor. As the recirculation ratio increases,

effluent NO₃-N and aerobic reactor oxygen requirements increase.

The recirculation ratio plays an important role in maintaining the proper pH in each reactor, which is particularly critical when treating high-strength nitrogenous wastewaters. At low

PROCESS CONFIGURATION AND FLOW DISTRIBUTION

OVERALL PLANT SPECIFICATIONS:

Number of Reactors (up to 9) = 2
 Solids Retention Time (days) = 30.0
 Average Flow Rate (m³/day) = 45

INDIVIDUAL REACTOR SPECIFICATIONS:

	1	2
Reactor Volume (m ³)	= 80	120
Feed Fraction (0 to 1)	= 1.00	0.00
O ₂ Concentration (g O ₂ /m ³)	= 0.00	2.00
Recycle Input (m ³ /day)	= 45	0
Recirculation Input (m ³ /day)	= 90	0
Recirculation originated from reactor	= 2	*

STEADY-STATE SOLUTION

CONSTITUENTS		FEED	1	2
Heterotrophic Organisms	g cod m-3	= 0.0	3215.9	3166.7
Autotrophic Organisms	g cod m-3	= 0.0	178.1	188.3
Particulate Products	g cod m-3	= 0.0	542.5	554.9
Inert Particulates	g cod m-3	= 0.0	0.0	0.0
Particulate Organics	g cod m-3	= 1965.0	136.2	27.2
Soluble Organics	g cod m-3	= 764.0	0.5	0.1
Soluble Ammonia N	g n m-3	= 240.0	58.0	0.8
Soluble Nitrate/Nitrite N	g n m-3	= 436.0	57.9	118.3
Soluble Organic N	g n m-3	= 17.0	0.1	0.0
Biodegrad Part Organic N	g n m-3	= 43.0	4.6	1.7
Oxygen	g o ₂ m-3	= 0.0	0.0	2.0
Alkalinity	mole m-3	= -0.5	13.5	5.1
MLVSS	g cod m-3	=	4072.8	3937.1
O ₂ Consumed	g o ₂ m-3 d-1	=	0.0	615.2
Nitrate Consumed	g no ₃ -n m-3 d-1	=	314.7	3.5

FIGURE 10. Simulation for pilot plant test run (21°C).

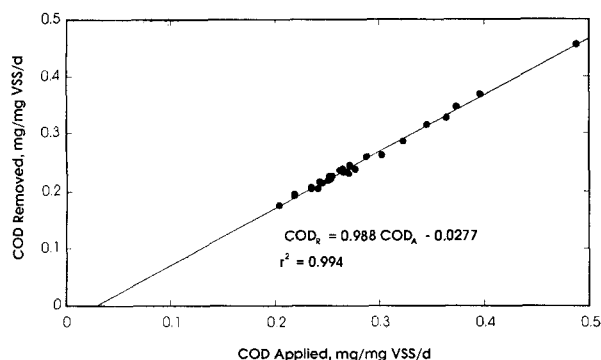


FIGURE 11. COD removed per unit biomass per unit time versus COD applied per unit biomass per unit time.

recirculation ratios, anoxic reactor alkalinity concentrations are typically high because of the production and buildup of alkalinity. Likewise, aerobic reactor alkalinity concentrations are typically low because of the consumption and depletion of alkalinity. This situation can result in a very high anoxic reactor pH and a very low aerobic reactor pH. By increasing the recirculation ratio, the transfer of alkalinity from the anoxic reactor to the aerobic reactor is increased, bringing the reactor alkalinity concentrations and pHs closer together. This reduces the pH-induced stress on the microorganisms as they pass from one environment to the other.

Based on considerations of wastewater variability with respect to nitrogen, COD, and alkalinity, and given fixed anoxic and aerobic reactor volumes, it is apparent that the recirculation ratio is an important operational parameter. Based on the results of the simulations presented in Figure 9, a recirculation ratio of three was initially selected for the pilot test run. However, influent $\text{NO}_3\text{-N}$ concentration increased prior to the start of the test run and a recirculation ratio of two was used.

Based on the SSSP simulations, the pilot plant was reconfigured to have an anoxic volume of 80 liters, an aerobic volume of 120 liters, and a recirculation ratio of two. Furthermore, the influent flow was reduced to 45 l/d. This change was made to provide an MLVSS concentration of 3,000 mg/l (4,500 mg/l as COD) based on updated COD load and yield data. After these changes were made, the system was operated for approximately 2 weeks prior to the start of the test run.

Pilot Plant Test Run

Pilot plant process parameters are summarized in Table 10. Average influent, anoxic reactor, and effluent characteristics are presented in Table 11. SSSP input and output for the actual test run conditions are presented in Figure 10. This simulation was run using the measured parameter values reported earlier.

Organic Removal

A COD balance around the system accounted for 98 percent of the influent COD, indicating that the data should be acceptable [9]. A plot of COD removed per unit biomass per unit time versus COD applied per unit biomass per unit time for the overall system during the pilot plant run is presented in Figure 11. The line of best fit indicates that 98.8 percent of the biodegradable COD was removed and no decrease in COD removal was observed at the highest loading rates. The intersection of the line of best fit with the x-axis represents a non-biodegradable SCOD of 310 mg/l.

A chronological plot of effluent total BOD, SCBOD, NBOD, and BOD exerted by total suspended solids (BOD_{TSS}) is pre-

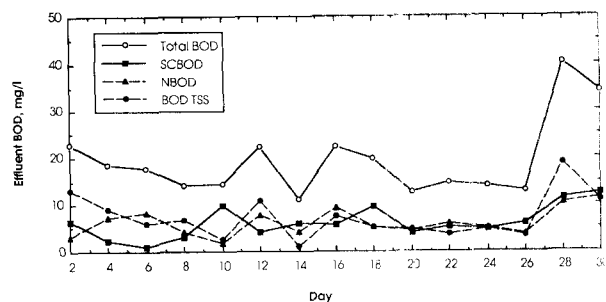


FIGURE 12. Chronological plot of effluent total BOD, SCBOD, NBOD, and BOD of suspended solids.

sented in Figure 12. The plot and the effluent BOD data presented in Table 11 indicate that the majority (74 percent) of effluent total BOD was attributable to NBOD and BOD_{TSS} . Because BOD_{TSS} is a function of sludge settleability, which is inherently variable, tertiary filtration will be incorporated into the full-scale system. This will provide a greater margin of safety should effluent SCBOD or NBOD concentrations increase periodically in the full-scale system.

Effluent benzene and toluene were not analyzed during the test run because they were not detected in any of the analyses performed during startup. Effluent phenol concentrations were less than 0.01 mg/l during the test run. SSSP does not model removal of individual organic compounds.

Nitrogen Removal

A nitrogen balance around the system accounted for 91 percent of the influent total nitrogen. A plot of TKN removed per unit biomass per unit time versus TKN applied per unit biomass per unit time is presented in Figure 13. The plot indicates no decrease in removal at the highest TKN loading encountered. The intersection with the x-axis corresponds to a nonbiodegradable soluble TKN concentration of 28 mg/l. This value is equal to the average effluent concentration of 30 mg/l, less 2 mg/l nitrogen associated with effluent VSS.

Based on SSSP, the average effluent $\text{NH}_3\text{-N}$ concentration was expected to be approximately 1 mg/l; however, 8 mg/l was obtained. To determine if growth-limiting conditions existed with respect to variables other than substrate and oxygen, a micronutrient analysis of the influent wastewater and biomass was performed at the midpoint of the test run. The analyses indicated that both the influent and biomass were deficient in calcium, magnesium, and potassium. The absence of these micronutrients may explain the incomplete nitrification. Although no additional pilot testing was performed to confirm this theory, provisions for addition of these micronutrients will be provided in the full-scale system. Assuming that the remaining 8 mg/l $\text{NH}_3\text{-N}$ could have been removed,

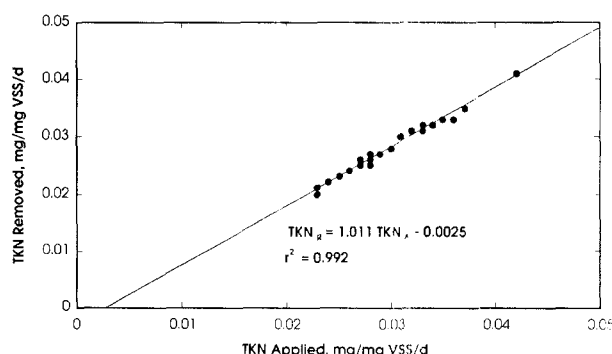


FIGURE 13. TKN removed per unit biomass per unit time versus TKN applied per unit biomass per unit time.

Table 12 Summary of Pilot Plant Oxygen Requirements and Comparison with SSSP Predictions

Parameter	Anoxic Reactor		Aerobic Reactor		Overall System	
	Pilot Plant	SSSP	Pilot Plant	SSSP	Pilot Plant	SSSP
Total COD removed (g/d)	106	98	18	23	124	121
COD oxidized (g/d)	83 ^a	75	14	19	97	94
COD removed by cell synthesis	23 ^a	23	4	4	27	27
Nitrate consumed (g/d)	23	25	—	0.4	23	25
Nitrate consumed expressed as oxygen (g/d) ^b	65	72	—	1.1	65	73
Oxygen consumed as oxygen (g/d)	0	0	63	72	63	72
Nitrogenous oxygen demand (g/d) ^c	0	0	40	49	40	49
Carbonaceous oxygen demand (g/d) ^d	65	72	23	23	88	95
Total oxygen demand (g/d)	65	72	63	72	128	144

^aBased on overall system yield of 0.14 mg VSS/mg COD and 1.54 mg COD/mg VSS.

^b2.86 mg O₂/mg NO₃-N

^cAssumes 4.57 mg O₂/mg NH₃-N oxidized to nitrate

^dDifference between oxygen consumed and nitrogenous oxygen demand

the actual nonbiodegradable TKN concentration would be 20 mg/l.

Oxidized nitrogen removal was directly related to daily COD loading. SSSP's prediction of oxidized nitrogen removal was nearly equal to pilot plant removal. Overall, the effluent NO₂/NO₃-N concentration averaged 119 mg/l, while SSSP predicts 118 mg/l. In the anoxic reactor, the NO₂/NO₃-N concentration averaged 67 mg/l, while SSSP predicts 58 mg/l.

An alkalinity balance around the reactors indicates that 3.40 mg alkalinity/mg NO₃-N removed was recovered in the anoxic reactor and 7.29 mg alkalinity/mg NH₃-N converted to nitrate was consumed in the aerobic reactor. These values are very close to theoretical stoichiometric coefficients for alkalinity recovery and consumption. With respect to reactor alkalinity concentrations, SSSP predictions and actual concentrations were nearly equal. The anoxic and aerobic reactor alkalinity concentrations averaged 662 and 270 mg/l as CaCO₃, respectively. SSSP predicted anoxic and aerobic reactor alkalinity concentrations of 675 and 255 mg/l, respectively, when expressed as CaCO₃.

Sludge Production

The average MLVSS concentration in the anoxic and aerobic reactors was 2,466 and 2,519 mg/l, respectively. The measured COD/VSS ratio was 1.54 g COD/g VSS. Based on this ratio, SSSP predicted anoxic and aerobic reactor concentrations of 2,645 and 2,557 mg/l, respectively. These values represent very accurate predictions of sludge production. The net solids yield was 0.14 mg VSS/mg COD removed, and cell nitrogen content was 13 percent by weight. The mixed liquor VSS/TSS ratio was 0.89.

Oxygen Requirements

Table 12 presents a summary of oxygen requirements for each reactor, and compares these values with SSSP predictions. Again, actual and predicted values compare very well. A significant point to note is that the use of a single sludge system reduces the oxygen consumption by about half for this wastewater. This follows from the fact that the nitrate consumption, expressed as oxygen, is approximately equal to the oxygen consumption. If denitrification had not been employed, it would have been necessary to supply the total electron acceptor as oxygen.

CONCLUSIONS

Pilot test results indicate that DSM process wastewater can be treated to the required permit limits using a two-stage single-sludge carbon oxidation, nitrification, and denitrification process. The process was stable over a wide range of pollutant loadings and provided a reasonable level of safety for each permit parameter.

SSSP was a very useful tool for process design. Once calibrated for DSM wastewater, SSSP was used to evaluate many alternative process configurations in a relatively short time. The ability to experiment with various process parameters also enhances an engineer's understanding of the importance of these parameters with respect to system design. Although SSSP is a powerful modeling tool, it should be used by engineers as a guide to process design. Many factors influencing process

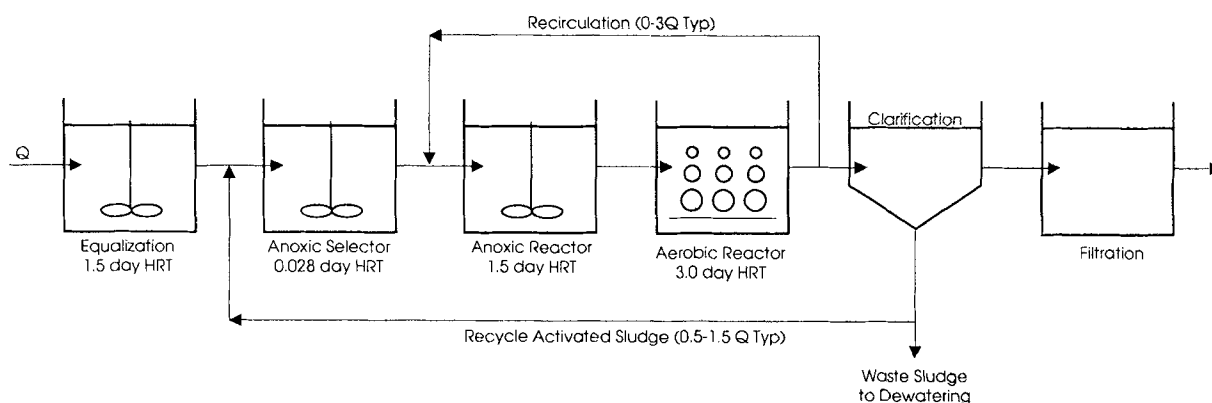


FIGURE 14. Full scale process flow diagram.

design (microorganism inhibition, thermodynamic influences, priority pollutant removal, etc.) are not incorporated in the model and must be accounted for by the engineer.

SSSP predictions of anoxic and aerobic reactor MLVSS, COD, $\text{NH}_3\text{-N}$, and $\text{NO}_3\text{-N}$ concentrations, sludge production, and oxygen and alkalinity requirements were very close to actual pilot plant values. These results indicate that the model can be calibrated with a reasonable degree of certainty by determining a few key wastewater and kinetic and stoichiometric parameters.

RECOMMENDATIONS

The recommended full-scale configuration showing major equipment sizes is presented in Figure 14. Fixed volume equalization was selected and sized to reduce the peak to average day oxygen demand ratio to approximately two. An anoxic selector was incorporated to control potential filamentous bacterial growth, although none was encountered in the pilot study. The distribution of anoxic to aerobic volume tested in the pilot study was altered slightly so that four equal-size tanks could be used (one equalization, one anoxic, two aerobic). A pumping capacity of up to three times the influent flow rate was selected for the recirculation system to provide flexibility. Centrifugal blowers and a coarse bubble diffuser system were selected for aeration. A pumping capacity of up to 1.5 times the influent flow rate was selected for the sludge recycle system.

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