To the Graduate Council:

I am submitting herewith a thesis written by Tee-Meng Poon entitled "ANALYSIS OF ADVANCED PROCESS MEASUREMENT PARAMETERS FOR A BIOLOGICAL WASTEWATER TREATMENT PROCESS." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Robert M. Counce

Robert M. Counce, Major Professor

We have read this thesis
and recommend its acceptance:

Jerry Wang

Duane D Bruns

Moonis Raza Ally

Thomas V Rebottis

Accepted for the Council:

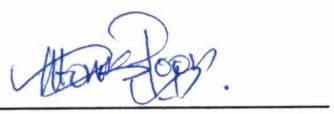
C. W. Winkel

Associate Vice Chancellor
and Dean of The Graduate School

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a Master's degree at The University of Tennessee, Knoxville, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledge of the source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Head of Interlibrary Services when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature 

Date NOVEMBER 14, 1994

ANALYSIS OF ADVANCED PROCESS MEASUREMENT PARAMETERS FOR A BIOLOGICAL WASTEWATER TREATMENT PROCESS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Tee-Meng Poon

December 1994

DEDICATION

To my father Mr. Kng-Guan Poon

and

my mother Mrs. Siew-Eng Poon

I dedicate this Thesis.

Their words of motivation and unlimited patience helped to transform an idea into reality.

ACKNOWLEDGMENT

I would like to thank all those who have contributed in one way or another to the completion of this Thesis, but in particular I would like to express my sincere thanks to the following people for their special contributions: Dr. R. M. Counce (major advisor) for his guidance and intellectual stimulation, as well as for other invaluable behind-the-scenes assistance; Dr. T. W. Wang and Dr. D. D. Bruns (Committee members) for their comments and assistance on the subject of process control, especially Dr. T. W. Wang for her contributions in bioreactor control strategy; T. V. Schulte (Committee member) for increasing my knowledge in biological wastewater treatment processes and defining the objectives of this research, as well as for his direction on designing the bio-treatment model; Dr. M. Ally (Committee member) and Dr. J. M. Holmes for their constructive advice and reviews on the research work.

In addition, I would like to thank many others who have provided practical advice, reviews, and other forms of assistance: Dr. A. Bhattacharyya, A. F. Brunn, Dr. C. F. Moore, Dr. C. J. Perilloux, Dr. G. D. Reed, Dr. R. A. Reiche, and R. A. Reimer. I would also like to acknowledge the Department of Environmental System Engineering at Clemson University for its development of SSSP biological simulation program.

The support for this project was provided by the Department of Energy (DOE) cooperating agreement DE-FC05-920R22056 and by the E. I. du Pont de Nemours and Company (DuPont). This support does not constitute an endorsement by DOE or by DuPont of the views expressed herein.

Finally, the encouragement and support of my family and my friend Junko were truly invaluable.

ABSTRACT

This investigation attempts to show the potential of advanced process measurement parameters for the control of a biological wastewater treatment process. The research first reviews the status of instrumentation and control strategy for wastewater treatment operations, presenting recent developments in sensor technology and their applications. The problems associated with the development of a wastewater control strategy are then discussed and a problem-driven methodology is presented for developing a control strategy for a wastewater treatment plant. Advanced parameters for biological process control in wastewater treatment are identified and evaluated. By utilizing a typical biological process treating a hypothetical waste stream, an analysis is performed of the steady-state responses of these process parameters.

A two-stage Bardenpho wastewater treatment model is used in the study of the sensitivity of process measurement parameters to variations in input conditions. The first reactor zone in the Bardenpho model is for nitrate removal and the subsequent zone is designed for carbon oxidation and nitrification. The influent variables are chemical oxygen demand (COD), ammonium-nitrogen, nitrate, and hydraulic loadings. The process parameters analyzed are oxidation reduction potential (ORP), uptake rates for oxygen, nitrate, and ammonium-nitrogen (OUR, NUR, and AUR, respectively), and their specific uptake rates (SOUR, SNUR, and SAUR, respectively).

All these parameters (ORP, OUR, NUR, and AUR) are sensitive to influent changes, but to different extents. For specific uptake rates (SOUR, SNUR, and SAUR), the influent COD changes have the greatest effects, followed by the effects of influent ammonium and nitrate and the inlet flow rate. The substrate uptake rates (OUR, NUR, and AUR), however, have the greatest sensitivity to influent COD variations, following

changes in inlet ammonium and nitrate and the influent flow rate. The greatest single effect on ORP values is influent nitrate concentration, followed by ammonium, COD, and the flow rate.

Monitoring of the anoxic zone in the Bardenpho model suggests that, by manipulating the recirculation rate, the SNUR and ORP are applicable as measurement parameters for monitoring the denitrification process. The two hypothesized measurement parameters are analyzed with two different mathematical models, one for SNUR and one for ORP. The responses of SNUR and ORP to input variations are used as measurement variables to the empirical model that is used to predict the required recirculation rate. Manipulation of recirculation rate is implemented based on the measurements of influent COD, ammonium, and nitrate; the inlet flow rate; and the nitrate content in the aerobic zone outlet.

PREFACE

The ultimate goal of biological wastewater treatment is to treat the wastewater so that the effluent quality complies with environmental regulations. Some important factors that directly affect the design and performance of wastewater treatment units include the flexibility of the treatment system, the reliability of sensors and measurement methods, and the effectiveness of the process control strategy. This research is a review of instrumentation and control strategy for biological wastewater treatment systems and an investigation of biological process parameters for process control applications.

The research involved are literature review and discussions with knowledgeable individuals, clearly establishing basic needs in instrumentation and control strategy. Further review of the literature established the state-of-the-art in applicable instrumentation and determined which instrumentation is likely to be available for industrial use in the near and long terms. A problem-driven method for addressing control strategy problems in industrial wastewater biological treatment was then developed. A steady-state analysis of process measurement parameters was evaluated to study their application to process control in bioreactors.

In order to determine useful process measurement parameters for process control and monitoring, the overall study approach utilized a computer model of a biological wastewater treatment system treating a hypothetical waste stream. The focus of this study was the simulation of the complete bio-treatment system following the analysis of useful process measurement parameters. Finally, a recirculation model for the denitrification zone was developed to demonstrate the applications of process parameters as controlled and manipulated variables. Rather than developing the control system, this research activity is intended to establish the critical aspects important to the control of a biological

treatment process. This study provides the principles of such a control strategy as well as a functional analysis of potential process control parameters.

TABLE OF CONTENTS

CHAPTER **PAGE**

1. INTRODUCTION 1
   1.1 OBJECTIVES 1
   1.2 DELIVERABLES 3

2. BACKGROUND 4
   2.1 LITERATURE REVIEW 4
      2.1.1 Classification of Biological Treatment Process 4
      2.1.2 Anaerobic and Aerobic Treatment 7
      2.1.3 Fundamentals of Microbiology 9
      2.1.3.1 Types and Role of Microorganism 9
      2.1.3.2 Enzyme Kinetics 11
      2.1.3.3 Kinetics of Microorganism Growth 14
      2.1.3.4 Factors Affecting Growth 15
      2.1.4 Industrial Wastewater Characterization 18
      2.1.4.1 Typical Wastewater Analysis 21
      2.1.5 Discussion of Bioreactor Processes 25
      2.1.5.1 Activated Sludge Process 26
         Process Description 26
         Applications 28
         Control and Instrumentation Concerns 29
      2.1.5.2 Aerated Lagoon 30
         Process Description 30
         Applications 31
         Control and Instrumentation Concerns 32
      2.1.5.3 Aerobic Digestion 33
         Process Description and Microbiology 33
         Applications 34
         Control and Instrumentation Concerns 36
      2.1.5.4 Trickling Filter 36

CHAPTER **PAGE**

Process Description 36
Applications 38
Control and Instrumentation Concerns 39
2.1.5.5 Rotating Biological Contactor 39
Process Description 40
Control and Instrumentation Concerns 40
2.1.5.6 Nitrification 42
Process Microbiology and Biochemistry 42
Applications 43
Control and Instrumentation Concerns 44
2.1.5.7 Denitrification 46
Process Microbiology and Design 46
Bardenpho Process 50
2.1.5.8 Anaerobic Digestion and Anaerobic Contactor 52
Process Description and Microbiology 52
Anaerobic Contact Process 54
Applications 54
Control and Instrumentation Concerns 56
2.1.5.9 Advanced Anaerobic Digester 58
Upflow Anaerobic Sludge Blanket 58
Fluidized Bed Anaerobic Reactor 60
Anaerobic Biofilter Reactor 62
2.1.5.10 Sequencing Batch Reactor 64
Process Description 65
Applications 67
2.1.5.11 Biological Aerated Filter 71
Process Description 71
Applications 72
2.1.5.12 Concluding Remarks 75

2.2 INSTRUMENTS AND MEASUREMENTS OF BIOREACTOR 79

CHAPTER **PAGE**

2.2.1 Instrumentation 80
2.2.2 Recent Developments in Instruments Technology 83
2.2.2.1 Optical Measurement Methods 84
2.2.2.2 Microbial Sensors 86
2.2.2.3 Microbial BOD Sensors 91
2.2.3 Biological Activity Measurement 96
2.2.3.1 Biomass Detection Method 96
2.2.3.2 TTC-Dehydrogenase Method 102
2.2.3.3 Methylene Blue Reduction Method 103
2.2.3.4 Adenosine Triphosphate (ATP) Method 104
2.2.3.5 Microcalorimetric Method 108
2.2.3.6 Oxidation-Reduction Potential Method 109
2.2.3.7 Oxygen Utilization Rate - Activated Sludge Process 111
2.2.3.8 Immediate Maximum Specific Oxygen Uptake Rate 117
2.2.4 Chemical and Physical Variables Measurement 119

2.3 CONTROL STRATEGY OF BIOREACTOR SYSTEMS 122
2.3.1 Aspects of Process Control 124
2.3.2 Process Control Parameters in Bioreactor 126
2.3.3 Development of Control Strategy 128
2.3.3.1 Treatment Objectives: Stage One 129
2.3.3.2 Importance of Wastewater Characteristics: Stage Two 131
2.3.3.3 Bioreactors Selection and Characteristics: Stage Three 132
2.3.3.4 Biological Phenomena: Stage Four 133
2.3.3.5 Dynamic Behavior of Treatment Process: Stage Five 134
2.3.3.6 Controllability of Process Variables: Stage Six 136
2.3.3.7 On-line Instrumentation and Treatment Plant Data Analysis: Stage Seven 137
2.3.3.8 Control Schemes Selection: Stage Eight 139
2.3.3.9 Data Management System: Stage Nine 141
2.3.3.10 Evaluation of Control Strategy: Stage Ten 142

CHAPTER **PAGE**

3. STUDY APPROACH 144
   3.1 BIOLOGICAL TREATMENT MODEL 145
   3.2 PREDICTIVE EQUATIONS DEVELOPMENT 149
      3.3.1 Oxidation Reduction Potential 149
      3.3.2 Specific Ammonium-nitrogen, Nitrate, and Oxygen Uptake Rates 158
   3.3 ANOXIC ZONE RECIRCULATION MODEL 161

4. METHOD OF ANALYSIS 167
   4.1 BIO-SIMULATOR PROGRAM 167
   4.2 DESIGN SPECIFICATIONS OF TREATMENT MODEL 167

5. RESULTS AND DISCUSSIONS 172
   5.1 SINGLE VARIABLE ANALYSIS 172
   5.2 ANOXIC ZONE RECIRCULATION MODEL EVALUATION 194

6. SUMMARY AND CONCLUSION 222

7. RECOMMENDATIONS 227

REFERENCES 228

APPENDIX 243

VITA 248

LIST OF TABLES

TABLE			PAGE
2.1	-	Major Biological Wastewater Treatment Processes	6
2.2	-	Comparison of anaerobic and Aerobic Treatments	8
2.3	-	Summary of Useful Microorganism and Uses	12
2.4	-	Physical and Chemical Characteristics of Wastewater	20
2.5	-	Comparison of Features of Various Anaerobic Reactor	77
2.6	-	Typical Features of Various Aerobic Bio-treatment Processes	78
2.7	-	Ion-sensitive Electrodes	81
2.8	-	Characteristic of Microbial Sensors	90
2.9	-	Properties of an Ideal Biomass Detector	98
2.10	-	Analytical Parameters of Non-bioelectrochemical Biomass Detection Methods	99
2.11	-	Analytical Parameters of Selected Bioelectrochemical Biomass Detection Methods	100
2.12	-	Sensors for Control and Monitoring of the Chemical Variables in Bio-treatment Process	120
2.13	-	Sensors for Monitoring and Control of the Physical Environment in Bio-treatment Process	121
2.14	-	Basic Important Control Variables in Bioreactor	127
3.1	-	Standard Redox Potential of Some Redox Pairs in Various Biochemical Reactions	151
4.1	-	Design Specifications of the Simulated Biological Treatment Model	168
4.2	-	Biokinetic Constants for Heterotrophic and Autotrophic Microorganisms	170
5.1	-	Effluent Variables in Anoxic (Denitrification) Zone for COD Single Variable Analysis	174
5.2	-	Single Variable Analysis for COD in Aerobic (carbon oxidation and nitrification) Zone	175

TABLE **PAGE**

5.3 - Effluent Variables in Anoxic (Denitrification) Zone for NH_4 Single Variable Analysis 176

5.4 - Single Variable Analysis for NH_4 in Aerobic (carbon oxidation and nitrification) Zone 177

5.5 - Effluent Variables in Anoxic (Denitrification) Zone for Q_i Single Variable Analysis 178

5.6 - Single Variable Analysis for Q_i in Aerobic (carbon oxidation and nitrification) Zone 179

5.7 - Effluent Variables in Anoxic (Denitrification) Zone for NO_3 Single Variable Analysis 180

5.8 - Single Variable Analysis for NO_3 in Aerobic (carbon oxidation and nitrification) Zone 181

5.9 - Combinations of Input Variables for the Bio-treatment Model Simulations 196

5.10 - Anoxic (Denitrification) Zone Effluent Variables for Control Model Evaluations 197

5.11 - Aerobic (carbon oxidation and nitrification) Zone Effluent Variables for Control Model Evaluations 198

5.12 - Comparison Between Predicted and Simulated Results 199

5.13 - Analysis of Recirculation Rate Model Using SNUR as a Process Parameter. 206

5.14 - Analysis of Recirculation Rate Model Using ORP as a Controlled Variable. 211

LIST OF FIGURES

FIGURE			PAGE
2.1	-	Partition of Organic Constituents of a Wastewater	22
2.2	-	Simplified Diagram of Conventional Activated Sludge Process	27
2.3	-	Typical Layout of Aerated Lagoon Treatment System	31
2.4	-	Cutaway View of a Spherical Trickling Filter	38
2.5	-	A Typical Rotating Biological Filter	41
2.6	-	A Single-sludge Four-stage Bardenpho Process	51
2.7	-	Conventional Single-stage Anaerobic Digester	55
2.8	-	Upflow Anaerobic Sludge Blanket	60
2.9	-	Typical Fluidized-bed Reactor System	61
2.10	-	Anaerobic Biofilter Reactor System	63
2.11	-	Typical SBR Operation for One Cycle	66
2.12	-	Schematic of a Biological Aerated Filter Cell	73
2.13	-	Construction of a Microbial Electrode (Biosensor)	89
2.14	-	Wastewater Treatment Control is an Interdisciplinary Field	123
2.15	-	A Problem-driven Methodology for Developing Control Strategy in Wastewater Treatment Plant	130
2.16	-	The Metabolic Process of Aerobic Microorganisms	134
3.1	-	A Typical Activated-Sludge Two-Stage Biological Nitrification-Denitrification Process	146
3.2	-	ORP Profile of Denitrification in the Anoxic Zone	157
5.1	-	Oxidation Reduction Potential as a Function of Influent Variables in Anoxic Zone	184
5.2	-	Oxygen Uptake Rate as a Function of Influent Variables in Aerobic Zone	185
5.3	-	Specific Oxygen Uptake rate as a Function of Influent Variables in Aerobic Zone	186
5.4	-	Nitrate Utilization Rate as a Function of Influent Variables in Anoxic Zone	187

FIGURE PAGE

5.5 - Specific Nitrate Utilization Rate as a Function of Influent Variables in Anoxic Zone 188

5.6 - Ammonium-nitrogen Uptake Rate as a Function of Influent Variables in Aerobic Zone 189

5.7 - Specific Ammonium-nitrogen Uptake Rate as a Function of Influent Variables in Aerobic Zone 190

5.8 - Specific Nitrate Uptake Rate Changes with Recycling Ratio 200

5.9 - The Double Reciprocal Plot for Determination of Biokinetic Constants 201

5.10 - Comparison between Predicted Recycling Ratio and Experimental Recycling Ratio 202

5.11 - Comparison Profile of Predicted and Simulation Recirculation Rate 203

5.12 - Redox Potentials in the Anoxic Zone as a Function of Recycling Ratio 208

5.13 - Comparison of Recirculation Rate Predictions Based on SNUR and ORP Parameters 210

5.14 - Specific Oxygen Uptake Rate Variations with Overall Recycling Ratio 214

5.15 - Overall Removal Efficiency with Respect to Redox Potential in the Denitrification Zone 215

5.16 - Variations of Overall Removal Efficiency with Overall Recycling Ratio 216

5.17 - Overall Removal Efficiency Variations with Residual Nitrate Concentration in the Anoxic Zone 217

5.18 - Overall Removal Efficiency Changes with Residual Nitrate Concentration in the Aerobic Zone 218

LIST OF ABBREVIATIONS

ATP	-	adenosine triphosphate
AUR	-	ammonium-nitrogen uptake rate (M/L^3-t)
BOD	-	biological oxygen demand
C	-	DO concentration (M/L^3)
C^*	-	saturation DO concentration (M/L^3)
C_{in}	-	inlet DO concentration (M/L^3)
COD	-	chemical oxygen demand or soluble organic
DO	-	dissolved oxygen
E_{all}	-	overall removal efficiency
F	-	Faraday's constant (23.07 cal/mV)
k	-	maximum specific substrate uptake rate (t^{-1})
k_d	-	decay constant for heterotrophs (t^{-1})
$k_{d,N}$	-	decay constant for nitrifier (t^{-1})
K_c	-	saturation constant (M/L^3)
K_{den}	-	nitrate saturation constant (M/L^3)
K_La	-	overall mass (oxygen) transfer coefficient (t^{-1})
K_N	-	saturation constant for nitrifier (M/L^3)
K_r	-	recyling ratio when SNUR = 0.5 S_{max} (dimensionless)
K_s	-	saturation constant for heterotrophs (M/L^3)
l	-	liter
L	-	length (m)
M	-	mass (g)
MLVSS	-	mixed-liquor volatile suspended solids (M/L^3)
MLSS	-	mixed-liquor suspended solids (M/L^3)
NUR	-	nitrate uptake rate (M/L^3-t)
ORP	-	oxidation reduction potential or redox potential or E_h (mV)
OUR	-	oxygen uptake rate (M/L^3-t)
$(q)_{DN}$	-	specific denitrification rate (t^{-1})
Q	-	flow rate (L^3/t)
R	-	gas law constant (8.314 J/mol-K)
R_{all}	-	overall recycling ratio (dimensionless)

R_r	-	nitrate recycling ratio or recycling ratio (dimensionless)
S	-	growth limiting substrate concentration (M/L^3)
S_{max}	-	maximum specific nitrate uptake rate (t^{-1})
SAUR	-	specific ammonium-nitrogen uptake rate (t^{-1})
SF	-	safety factor
SNUR	-	specific nitrate uptake rate (t^{-1})
SOUR	-	specific oxygen uptake rate (t^{-1})
$SOUR_{im}$	-	immediate maximum specific oxygen uptake rate (t^{-1})
T	-	temperature (°C)
TTC	-	triphenyltetrazolium chloride
t	-	time (day)
VSS	-	volatile suspended solids (M/L^3)
V	-	volume (L^3)
X	-	biomass concentration (M/L^3)
Y_H	-	heterotrophs yield coefficient (M/M)

Greek letter

μ	-	specific growth rate (t^{-1})
μ_{max}	-	maximum specific growth rate (t^{-1})
$\mu_{m,den}$	-	denitrifying bacteria maximum specific growth rate (t^{-1})
$\mu_{m,n}$	-	nitrifier maximum specific growth rate (t^{-1})
μ_m	-	heterotrophs maximum specific growth rate (t^{-1})
θ_c^m	-	minimum sludge age (t)
θ_c	-	sludge age or solids retention time (t)
θ	-	hydraulic residence time (t)

Subscript

e	-	effluent
i	-	influent
re	-	recirculation
rs	-	return or recycle sludge
aerobic	-	aerobic zone or reactor
anoxic	-	anoxic zone or reactor

CHAPTER 1

INTRODUCTION

The focus of this project is to provide a study of control strategies and instrumentation required to maintain near-optimal operation of industrial biological wastewater treatment units. There is need for such units to operate in a continuous "in-line" mode where any interruption in continuous availability will interrupt production operations. An example of the need for this type of waste treatment is as an alternative to disposal options such as deep-well injection of aqueous wastes. Consideration of other waste disposal technologies would be greatly simplified if continuous biological processes could be relied upon for high-availability service. This study is directed toward maintaining the in-line availability of biological wastewater treatment systems operating with near-optimal performance at an availability compatible with production processes, that are typically greater than 90%. This study involved the participation of individuals at the University of Tennessee, the Oak Ridge National Laboratory and E. I. du Pont de Nemours and Company.

1.1 OBJECTIVES

The study was initiated with an extensive review of the related literature, which is reported in Chapter 2. Wastewater streams in wastewater treatment units serving integrated chemical process facilities may contain organic, as well as inorganic contaminants, some of which may be toxic or inhibitory to biological organisms; both the total flow rate and the individual component flow rates are subject to variation. From the review of the literature and pertinent discussions, the critical aspects of the control of

biological wastewater treatment units are established. The identification of critical issues serves as a basis for establishing sensor and instrumentation needs as well as control strategies. Currently available sensors and instrumentation are identified and priorities established for future research and development activities in this area. The study addresses process measurement parameters that provide advance warning of impending loss of biological activity so that proper actions may be initiated. These prospective process measurement parameters for bioreactor process control applications are identified and analyzed. However, emphasis is placed on those parameters that may be used for on-line applications. A model demonstrating advanced monitoring of biological wastewater units using those measurement parameters is developed to confirm and illustrate the features of the approaches developed in this activity. The primary objectives of this research activity are summarized as follow:

Part I: Chapter 2
Review of strategies and instrumentation for control of industrial biological treatment systems.
- Introduction of industrial biological wastewater treatment processes.
- Measurements and instrumentation of bioreactor.
- Process control of bioreactor.

Part II: Chapters 3-5
Modeling and steady-state characterization of process measurement parameters for control of bioreactors.
- Single variable analysis of process parameters.
- Monitoring of bio-treatment process.

The main objective of part II is the study of the responses of process measurement parameters to input variations. With this sensitivity information, the monitoring of a

typical bio-treatment process is developed to illustrate the potential use of process measurement parameters as control variables. The analyses will provide some insight of process control in biological wastewater treatment process.

1.2 DELIVERABLES

The output of this activity is (1) a review of strategy for control of biological wastewater treatment units and identification of accompanying instrumentation and sensor availability and needs; (2) methodology addressing the development of control strategy for wastewater treatment plant and an investigation of process measurement parameters for process control applications; and (3) steady-state analysis of a typical bio-treatment model to promote the use of more efficient process parameters for monitoring biological wastewater treatment systems.

CHAPTER 2

BACKGROUND

2.1 LITERATURE REVIEW

Biochemical operations, in which chemical and physical transformations are carried out by living microorganisms, have many diverse uses. One of the major uses is the biological treatment of wastewater. This section provides an introduction to biological wastewater treatment processes through a review of the current literature.

2.1.1 CLASSIFICATION OF BIOLOGICAL TREATMENT PROCESSES

There are four major groups of biological processes: aerobic processes, anaerobic processes, anoxic processes, and combination of aerobic and anoxic or anaerobic processes. Usually, it is convenient to divide biological treatments into aerobic and anaerobic treatments. An aerobic process is a biological treatment process that occurs in the presence of oxygen, whereas an anaerobic process occurs in the absence of oxygen. The primary differences between the two processes result from the different terminal electron acceptors used by the microorganisms and by the system configuration. Aerobic microorganisms use oxygen as the final electron acceptor for formation of adenosine triphosphate (ATP), a high-energy phosphate complex that serves as an energy source for the aerobes. On the other hand, anaerobic microbes use alternative electron acceptors such as nitrate (NO_3^-), which can act as the final electron acceptor. Its product, nitrous oxide (N_2O^-), is also an acceptor leading to formation of dinitrogen (N_2). This process is called denitrification, which is an important biological waste treatment process. Anoxic denitrification is defined as the process by which nitrate nitrogen is converted biologically

to nitrogen gas with oxidized nitrogen serving as an electron acceptor, provided that the oxygen is absent in the system.

The individual processes are further divided, depending on whether treatment is accomplished in the fixed-growth (fixed-film) system, dispersed-growth system, or a combination of both. In the fixed-film processes, the biomass is attached to a bed of fixed medium, and the wastewater percolates through the bed, contacting the microorganisms during this passage. In the dispersed-growth bioreactors, biodegradation is carried out by microorganisms that are suspended in the liquid phase of the reactors.

The advantages of fixed-film processes are simplicity and ease of operation. They are ideal for remote and small industrial streams and are capable of handling high loads per unit volume of reactor because of the relatively high concentration of the biomass attached to the surface of the fixed media. The disadvantages are less flexibility in operation, difficulty in achieving high removal efficiencies, and greater sensitivities to cold weather conditions (Eckenfelder et al., 1989).

The major biological treatment processes are identified in Table 2.1. The aerobic, anaerobic, and anoxic treatment processes are classified according to whether they are fixed- or dispersed-growth systems. The combined processes include facultative lagoons and anaerobic-facultative-aerobic lagoons.

Table 2.1 Major Biological Wastewater Treatment Processes (Metcalf & Eddy Inc., 1979).

Type	Common name	Purposes
Aerobic Process		
Dispersed-growth	Activated Sludge:	
	• conventional (plug flow)	carbonaceous BOD removal
	• pure oxygen system	nitrification
	• extended aeration	
	• contact stabilization	
	• continuous-flow stirred	
	Nitrification	nitrification
	Aerobic Digestion	stabilization
		carbonaceous BOD removal
	Aerated Lagoons	carbonaceous BOD removal
Fixed-growth	Trickling Filter	carbonaceous BOD removal
		nitrification
	Rotating Biological	carbonaceous BOD removal
	Contactors	nitrification
	Packed-bed Reactor	nitrification
Anaerobic Process		
Dispersed-growth	Anaerobic Digestion:	stabilization
	• standard-rate, single stage	carbonaceous BOD removal
	• two stage	
	Anaerobic Contact Process	carbonaceous BOD removal
	Upflow Activated Sludge Blanket	carbonaceous BOD removal
Fixed-growth	Anaerobic Filter	carbonaceous BOD removal
		stabilization
		nitrification
	Anaerobic Lagoons	carbonaceous BOD removal
		stabilization
	Fluidized Bed	
	Packed-bed	
Anoxic Process		
Dispersed-growth	Suspended-growth	denitrification
Fixed-growth	Fixed-film denitrification	denitrification

2.1.2 ANAEROBIC AND AEROBIC TREATMENT

Soluble organic matter can be converted to carbon dioxide and other end products by aerobic pathway or anaerobic pathway. Under aerobic conditions (presence of oxygen), the reduced soluble organic compounds are oxidized to carbon dioxide and water:

Aerobic: $\text{Organics} + \text{oxygen} \rightarrow CO_2 + H_2O + \text{energy}$

However, under anaerobic conditions (absence of oxygen), the soluble organics are decomposed to intermediate end products, such as organics acids and alcohols, and ultimately to methane gas, carbon dioxide and water:

Anaerobic: $\text{Organics} \rightarrow \text{intermediates} + CO_2 + H_2O + \text{energy}$

$\text{Organic acid intermediates} \rightarrow CH_4 + CO_2 + \text{energy}$

A general comparison of aerobic and anaerobic treatment processes is listed in Table 2.2. The major disadvantages of aerobic processes are the higher sludge yield and energy requirement. On the other hand, the disadvantages of anaerobic process are more sensitivity to environmental conditions such as pH, temperature and toxic shock and inability to achieve economically high performance levels such as an effluent BOD of 20 mg/l or very high BOD removal (Grady and Lim, 1980). The slow growth of anaerobic microorganisms also results in low performance in the stirred tank reactor and time consuming start-up procedure. However, anaerobic processes can be cost effective, especially if employed as a pretreatment before aerobic polishing of high-strength

Table 2.2 Comparison of Anaerobic and Aerobic Treatments (Eckenfelder et al. 1989).

Parameter	Anaerobic	Aerobic
Energy requirement	low	high
Treatment degree	moderate(60-90%)	high (95%+)
Sludge production	low	high
Process stability (to toxic compounds and load changes)	low to moderate	moderate to high
Start-up time	2 to 4 months	2 to 4 weeks
Nutrient requirement	low	high for certain industrial wastes
Odor	potential odor problems	less opportunity for odors
Sensitivity:		
Temperature	high	low
pH	high	low
Alkalinity requirement	high for certain industrial waste	low
Biogas production	yes (net benefit is contingent on the need for reactor heating)	no

industrial wastewater and treatment of sludge produced by aerobic processing of sewage. Furthermore, there is a possibility of recovering energy in the form of methane gas in anaerobic systems.

2.1.3 FUNDAMENTALS OF MICROBIOLOGY

Living microorganisms can be found almost anywhere water is in liquid state. With the exception of certain industrial wastes, wastewater provides an ideal growth medium for a large number of diverse living microorganisms, and these microorganisms can play a major role in all stages of biological wastewater treatment. Chapter 2.1.3 provides the basic concepts underlying the microbiology of biological wastewater treatment processes.

2.1.3.1 TYPES AND ROLE OF MICROORGANISMS

Basic to the design of a biological treatment process or to the selection of the type of process to be used and the appropriate control and instrumentation of the system is an understanding of the form, structure and biochemical activities of the important microorganisms. In this chapter the physiology and cytology of the microorganisms will be briefly introduced and discussed.

In biological wastewater treatment, the most widely occurring and abundant group of microorganisms is the bacteria, which are the most important in terms of utilizing the organic matter present in wastewater (Gray, 1989). Other microorganisms such as fungi, protozoa, algae, and a range of other invertebrate organisms also play important but comparatively minor roles. In this report two types of microorganism are introduced. For

further understanding of microbiology, references by Metcalf and Eddy (1979) and Gray (1989) are recommended.

Bacteria are classified as heterotrophic or autotrophic bacteria based on nutritive requirements, but several species may function both heterotrophically and autotrophically. Heterotrophic bacteria use organic compounds as an energy and carbon source for synthesis. Aerobes, anaerobes, and falcultative bacteria are subgroups of heterotrophic bacteria. Facultative bacteria use free dissolved oxygen when available but can also respire and multiply in the absence of oxygen. Autotrophic bacteria use carbon dioxide as a carbon source and oxidized inorganic compounds for energy. Autotrophs of greatest significance in wastewater treatment are nitrifying, sulfur, and iron bacteria (Viessman and Hammer, 1993). The dominant bacteria are the aerobic heterotrophs that degrade and eventually mineralize organic compounds present in wastewater into carbon dioxide and water. The bacterial communities found in wastewater treatment plants are complex, with a variety of genera present. The dominant genera are usually aerobic, heterotrophic and so forth. Bacteria reproduce by binary diffusion (the mature cell divides into two new cells). In most of species, the reproduction process occurs in 20 to 30 minutes under ideal environmental conditions.

The other important type of microorganisms in wastewater treatment units are the fungi, including yeast and mold (nonphotosynthetic plants). The heterotropic fungi can be as efficient as heterotrophic bacteria for the removal of organic compounds from wastewater. The ability of the fungi to survive under low pH and nitrogen-limiting conditions makes them very important in the biological treatment of some industrial waste and in the composting of solid organic waste (Metcalf & Eddy, 1979). A disadvantage of fungi is that they produce a greater biomass per unit weight of substrate utilized than many of the important bacteria in wastewater treatment units, resulting in more film and

sludge production per unit mass of BOD removed. The summary of useful organisms and reactions is provided in Table 2.3.

2.1.3.2 ENZYME KINETICS

The organic matters in wastewater are metabolized by microorganisms in a series of enzymatic reactions. Enzymes are proteins, or combinations of either an inorganic or low-molecular-weight organic molecules. Enzymes are specific, versatile, and very effective biological catalysts, resulting in much higher reaction rates as compared to chemically catalyzed reactions under ambient conditions (Shuler and Kargi, 1992). There are two general types of enzyme, extracellular and intracellular. The extracellular enzyme converts the substrate or nutrient to a form that can be transported into the cell, and intracellular enzyme is involved in the synthesis and energy reactions within the cell (Gray, 1989). Enzymes lower the activation energy of the reaction, which is catalyzed by binding the substrate and forming an enzyme-substrate complex for conversion to a specific product, releasing the original enzyme to repeat the reaction. Different types of enzymes must be produced by the cell or microorganism for each specific substrate utilized. An enzyme reaction can be represented by the following equation:

$$\text{Enzyme (E)} + \text{Substrate (S)} \rightarrow \text{Enzyme-substrate complex (ES)} \rightarrow \text{Product (P)} + \text{Enzyme (E)}$$

or by notations:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} P + E \qquad (2.1\text{-}1)$$

where *k*s are the equilibrium constants. The activity of enzymes is substantially affected

Table 2.3 Summary of Useful Microorganism and Uses (Gray, 1989 and Cheremisinoff, 1987).

Microorganism	Uses/reaction	Oxygen Requirement	pH	Temp. (°C)
A. Organic Degraders				
Zooglea ramigera[1]	Organics to CO_2 and H_2O	Facultative	6-8	10-30
Sphaerotilus natans[1]	"	"	"	"
Pseudomonas sp.[1]	"	"	"	"
Clostridia sp.	"	Anaerobic	7-8	20+
Bacillus sp.	"	Facultative		
B. Nitrogen Users				
Nitrosomonas[2]	$NH_4^+ \rightarrow NO_2^-$	Aerobic	7-8	10-25
Nitrobacter[2]	$NO_2^- \rightarrow NO_3^{2-}$	"	"	"
Thiobacillus Denitrificans	$NO_3^{2-} + 2S + H_2O \rightarrow HSO_4^- + SO_4^{2-} + N_2$	"		
Psedomonas	$NO_3^{2-} \rightarrow N_2$	"		
C. Sulfur Bacteria				
Beggiatoa	$2H_2S + O_2 \rightarrow 2S + H_2O$	Aerobic	Low	
Desulfovibrio[3]	$CH_3COOH + SO_4^{2-} \rightarrow 2CO_2 + H_2S + 2OH^-$	Anaerobic	"	
D. Methane Bacteria				
Methanococcus vanieli[4]	Formate + $H_2 \rightarrow CH_4$	Anaerobic	6.4-7.2	35
Methanobacterium sohngeni	Acetate Butyrate $\rightarrow CH_4$			
Methanomonas	$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$	Aerobic		
E. Others				
Thiocyanoxidans	oxidize cyanide		7	
Cellulomonas sp.	cellulose-protein			35
Penicillium (fungus)	degrade DDT			
Zylerion xylestrix	pesticides/herbicides			

1. utilizes polysacharides and carbohydrates, degrade kepone, piperonylic acid, and pentachlorophenol
2. nitrification
3. consumed organic in reaction
4. digestion and other anaerobic treatment processes

by pH and temperature, as well as substrate concentration. Enzymes are also irreversibly inhibited by certain compounds that act as inhibitors; that is, heavy metals such as lead, mercury, and cadmium (Gray, 1989). The inhibitors bind to the enzyme and/or enzyme-substrate complex to inhibit or reduce the activity of the enzyme. Generally, there are four types of enzyme inhibition kinetics (Shuler and Kargi, 1992):

1. *Competitive inhibition*: the inhibitor is substrate analogs and competes with the substrate for the active site of the enzyme, therefore reducing the enzyme activity. The inhibition can be overcome by high substrate concentrations.
2. *Noncompetitive inhibition*: inhibitor is not substrate analogs and binds to a site distinct from the active site which binds the substrate, thus reducing the enzyme affinity to the substrates. The inhibition can be controlled by manipulating the enzyme to inhibitor ratio (E:I).
3. *Uncompetitive inhibition*: inhibitors bind to only the ES complex and no affinity for the enzyme itself. The result is the reduction in enzyme reaction rate.
4. *Substrate inhibition*: high substrate concentration may cause inhibitions in some enzymatic reactions.

Other inhibitions include feedback inhibition where the enzyme that catalyzes the first step in the metabolic pathway is inhibited by the end product of the reaction (Baily and Ollis, 1986). Enzymes are chemical components released by microorganisms for metabolic activity (for example reaction with substrate). Hence if the enzymes are inhibited, the life support processes become increasingly weak until the microorganisms eventually die and lyse. In general, the understanding of enzyme inhibition mechanisms are important for

control and maintaining a healthy environment for the optimum growth of microorganisms.

2.1.3.3 KINETICS OF MICROORGANISM GROWTH

Microorganisms can grow under a variety of physical, chemical and nutritional conditions. Growth is a result of both replication and changes in cell sizes. Thus in a suitable physiochemical environment, the rate of microbial growth is directly proportional to cell concentration. The overall rate of biological reaction within the reactor is dependent on the catalytic activity of the enzymes in the prominent reactions. To ensure that the microbes grow, they must be allowed to remain in the system long enough to reproduce. This period depends on their growth rate, which is directly proportional to the rate at which they metabolize or utilize the waste. In a suitable nutrient environment, microbial mass increases with time and can be described simply by:

$$\text{substrate} + \text{cells} \rightarrow \text{extracellular products} + \text{more cells}$$

$$\sum S + X \rightarrow \sum P + nX \qquad (2.1\text{-}2)$$

where S is substrate or nutrient , X is microorganisms or cells, and P is the extracellular products. The rate of microbial growth is characterized by the specific growth rate, which is defined as (Shuler and Kargi, 1992):

$$\mu \equiv \frac{1}{X}\frac{dX}{dt} \qquad (2.1\text{-}3)$$

where X is cell mass concentration, t is time, and μ is specific growth rate. A functional relationship of specific growth rate to substrate concentration was proposed by Monod in 1942. He assumed a single chemical species, substrate (S), is growth rate limiting. This assumption implied that an increase in S influences growth rate, while changes in other concentrations are negligible. The specific growth rate can be represented by the Monod equation (Bailey and Ollis, 1986):

$$\mu = \frac{\mu_{max} S}{K_s + S} \qquad (2.1\text{-}4)$$

where μ_{max} is the maximum growth rate when $S >> K_s$. The constant K_s is known as the saturation constant or half velocity constant and is equal to the limiting substrate (S) concentration at which the specific growth rate is half its maximum value. The above mentioned specific growth rate model (Eq. 2.1-4) is just one type of many microbial growth kinetic models. There are other types of kinetic models, which in particular instances give better description of microbial growth, such as Blackman, Tessier, and Moser models. Reader is referred to Gaudy and Gaudy (1980), Benefield and Randall (1980), Bailey and Ollis (1986), Gray (1989), and Shuler and Kargi (1992) for more details in specific microbial growth rate models.

2.1.3.4 FACTORS AFFECTING GROWTH

A number of environmental factors affect the activity of wastewater microbial populations and the rate of biochemical reactions in general. Of particular importance are temperature, pH, dissolved oxygen concentration, nutrient concentration, and toxic

pollutants inhibition. It is possible to control all these factors within a biological treatment system to ensure that microbial growth continues under optimum conditions.

The majority of biological wastewater treatment units operate in the mesophilic temperature range, microorganisms growing best in the temperature range 20°-40°C (Gray, 1989). The temperature dependence of the biological reaction rate constant is very important in assessing the overall efficiency of a biological treatment system. Temperature not only affects the metabolic activities of the microbial population, but also has a profound effect on such factors as gas transfer rates and the settling characteristic of the biological solids. Higher temperature results in an increased increment of biological activity that in turn increases the rate of substrate removal; the increased metabolism at higher temperature can also contribute to the problem of oxygen limitation. To account for the temperature effect on the biological reactions, the most useful equation is the Arrhenius form relating temperature to growth and death rate constants (Shuler and Kargi, 1992).

$$\mu = Ae^{-E_a/RT} \qquad (2.1\text{-}5)$$

$$k_d = A'e^{-E_d/RT} \qquad (2.1\text{-}6)$$

where
- A, A' - frequency factor
- R - gas law constant
- T - temperature
- E_a, E_d - activation and deactivation energies

The growth activation energy is typically 10 to 20 kcal/mol and for deactiviation energy (thermal death), 60 to 80 kcal/mol. Therefore, thermal death is more sensitive to temperature changes than microbial growth. According to Equations 2.1-5 and 2.1-6, the net growth rate (for temperature above optimal level) can be expressed by:

$$\frac{dX}{dt} = (\mu - k_d)X \qquad (2.1\text{-}7)$$

According to the microorganisms temperature optima (T_{opt}), they can be classified into three groups (Shuler and Kargi, 1992): (1) psychrophiles ($T_{opt} < 20^{\circ}C$), (2) mesophiles ($20^{\circ}C < T_{opt} < 50^{\circ}C$), and (3) thermophiles ($T_{opt} \geq 50^{\circ}C$). If the temperature increases towards the optimal temperature, the growth rate increases. Above the optimal temperature range, the growth decreases and thermal death may occur.

Hydrogen ion concentration (pH) affects the activity of enzymes and therefore the microbial growth rate. The optimal pH for growth varies from one genus to the other, and usually pH in a bioreactor can be controlled by the operator. For carbonaceous oxidation, the optimum pH range lies between 6.5 and 8.5. Microbial activity is inhibited at pH greater than 9.0, whereas at pH less than 6.5 fungi dominate over the bacteria in the competition for the substrate (Gray, 1989). In order to minimize the fluctuation of influent pH, completely mixing aeration reactors with buffering capacity is useful. If the buffering capacity is insufficient, then pH adjustment will be needed. Anaerobic bacteria have less pH tolerance, ranging from pH 6.7 to 7.4 with optimum growth at pH 7.0 to 7.1 (Gray, 1989). For active aerobic heterotrophic microbial activity, a dissolved oxygen concentration between 1 and 2 mg/l is required, even though optimum growth is also dependent on sufficient essential nutrients and trace elements being present (Gray, 1989).

Besides organic carbon, nitrogen, and phosphorus, other elements such as sulfur, iron, calcium, magnesium, potassium, manganese, copper, zinc, and molybdenum must also be available for metabolism to occur. For industrial wastewater, nitrogen and phosphorus may be present in low concentrations. Therefore these nutrients usually have to be supplemented. It is desirable to maintain a BOD_5:Nitrogen:Phosphorus ratio of 100:5:1 in order to ensure maximum microbial growth (Gray, 1989).

Toxic substances such as phenol, cyanide, ammonia, sulfide, heavy metals (such as copper and mercury), and trace organics can totally inhibit the microbial activity of a biological treatment process if the concentration exceeds threshold limits for the microorganism. However, constant exposure to low concentrations of these compounds results in the microbial community becoming acclimatized, thus permitting increases in the concentrations that they can tolerate. Furthermore, salt concentration of 30 g/l will severely inhibit the activated sludge process due to osmotic stress, although shock loads of sodium chloride have little effect on the microorganism developing the film in percolating filters (Gray, 1989).

In order to obtain maximum growth of biomass, environmental factors must be controlled and optimized such that the appropriate physiochemical environment is achieved within the biological wastewater treatment system. This task requires skill, appropriate control strategy and reliable instrumentation.

2.1.4 INDUSTRIAL WASTEWATER CHARACTERIZATION

Understanding the nature of wastewater is essential in the design and operation of biological wastewater units. Selection of biological treatment processes is based primarily on the wastewater characteristics and treatment objectives. The information in this chapter deals with characterization of industrial wastewater.

Water discharged from manufacturing industries, known as industrial wastewater, may contain a large number of potentially harmful compounds. Waste characteristics vary greatly from one industry to another; industrial wastewater typically contains such components as hydrocarbons, carbohydrates, alcohols, lipids, aromatics organics and inorganic material. The purpose of wastewater characterization (Metcalf and Eddy, 1979) is to :

- determine the physical, chemical, and biological characteristics;
- determine the concentrations of constituents in the wastewater; and
- determine the best means of reducing the pollutant concentrations.

The primary physical properties and the chemical constituents of industrial wastewater are listed in Table 2.4. The biodegradable organic matter in wastewater is generally classified in three categories: carbohydrates, proteins, and fats. Approximately 20% to 40% of the organic matter in wastewater such as polymeric non-carbohydrate material appears to be non-biodegradable (Viessman and Hammer, 1993). On the other hand, the inorganic materials generally consist of nitrogenous, phosphorus, and sulfur compounds, as well as heavy metals. The most common forms of phosphorus are organic phosphorus, orthophosphates, and polyphosphate. All polyphosphates progressively hydrolyze in aqueous solution and revert to the ortho form (Viessman and Hammer, 1993). However, the common forms of nitrogen are organic, inorganic, and gaseous nitrogen. The wastewater characteristics of concern in biological treatment system include pollutants concentration, presence of nutrients, toxicants, total suspended and dissolved solids, and other compounds inhibitory to the growth of microorganisms.

Table 2.4 Physical and Chemical Characteristics of Wastewater (Sundstrom and Klei, 1979).

Physical Characteristics:	Properties
	Color
	Odor
	Solids (suspended and dissolved solids)
	Temperature
	pH
Chemical Characteristics:	**Constituents**
Organics:	Carbohydrates
	Fats, oils, and grease
	Pesticides
	Phenols
	Proteins
	Surfactants
Inorganics:	Chlorides
	Nitrogenous compounds $\left(NH_4^+, NO_2^-, NO_3^-\right)$
	Phosphorous compounds $\left(PO_4^{3-}, HPO_4^{2-}, H_2PO_4^{2-}, Na_3(PO_3)_6, Na_4P_2O_7\right)$
	Sulfur compounds $\left(SO_4^{2-}, S^{2-}, S, SO_3^{2-}\right)$
	Heavy metals $\left(Ni^{2+}, Pb^{2+}, Cd^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}\right)$
Dissolved gases:	Hydrogen sulfide
	Hydrogen cyanide
	Methane
	Oxygen

The organic content of a wastewater stream can be partitioned into various fractions based on amenability to biological treatment as shown in Figure 2.1. The soluble organics that are sorbed to biomass are removed with relative ease, although part of such organics may degrade rather slowly. However, the non-sorbable portion of soluble organics may degrade through the activity of extracellular enzymes; the remaining non-degradable portion will be left in the effluent (Eckenfelder et al., 1989). On the contrary, the insoluble organics (volatile suspended solids) are more easily removed in any biological treatment process because such organics are enmeshed in the biomass and either degrade or physically separate from the liquid.

The biological components of wastewater include a wide variety of microorganisms such as bacteria, fungi, protozoa, and viruses. These microbes occur in very large numbers, typically the bacteria for which total counts in the range of 1 to 38 x 10^6 ml^{-1} are routinely recorded (Horan, 1990). However, the survival of microbes depends on the wastewater characteristics and the environment; for instance the industrial wastewater that contains toxins is particularly hostile to microorganisms.

2.1.4.1 TYPICAL WASTEWATER ANALYSIS

Total solids content is one of the most important physical characteristics of wastewater. Total solids include both the suspended solids and the dissolved solids that are determined by separations of solid and liquid phase through evaporation. Suspended solids are a combination of settleable solids and non-settleable (colloidal) solids, which are usually estimated by filtering a waste water sample through a membrane filter (Benefield and Randall, 1980). Solids remaining after filtration are dried, weighed, and then ignited.

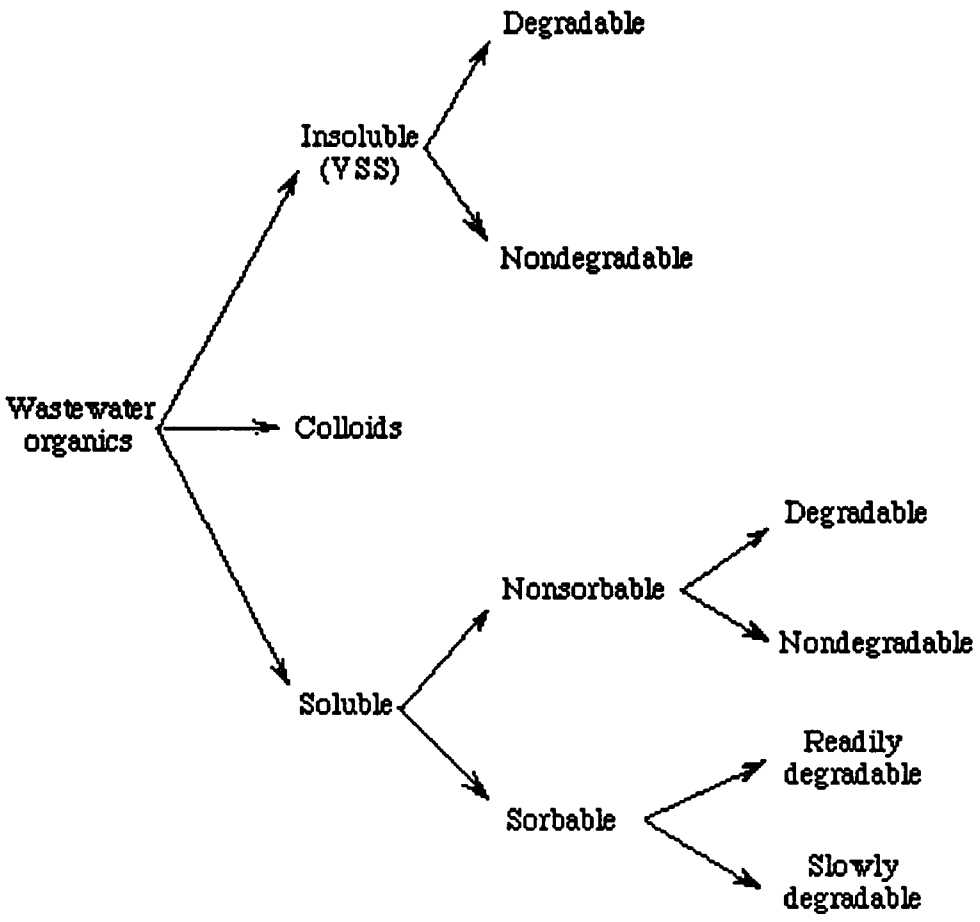


Figure 2.1 Partition of organic constituents of a wastewater (Eckenfelder, 1989)

The weight loss after ignition at 600 °C is a measure of the volatile solids, which are categorized as organic material. The remaining solids are the fixed solids, which are considered as inorganic (mineral) material. Usually the term volatile suspended solids (VSS) refers to the suspended solids associated with the volatile fraction of the suspended solids. On the other hand, the suspended solids associated with the mineral fraction are termed fixed suspended solids (FSS).

The carbon content of wastewater can be tested in several different off-line methods. The commonly used laboratory methods are: biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), permanganate value (PV), and total oxygen demand (TOD).

The most widely used parameter of organic pollution applied to both industrial wastewater and surface water is the 5-day BOD (BOD_5). The BOD_5 test exploits the ability of microorganism to oxidize organic material to carbon dioxide and water using molecular oxygen as an oxidizing agent. Thus the BOD_5 is the amount of dissolved oxygen consumed when a wastewater sample is seeded with active bacteria and is incubated at 20°C for 5 days (Horan, 1990). The disadvantages of BOD_5 measurement are that it is only applicable to biodegradable, soluble organics and requires a high concentration of active bacteria pre-adapted to the type of waste. Moreover, long periods of incubation are needed for refractory organic wastes.

The COD test utilizes potassium dichromate in boiling concentrated sulfuric acid (150°C), in the presence of a silver catalyst, to serve as a strong oxidizing agent (Horan, 1990). Under these conditions most of the carbon content in the wastewater sample is oxidized to carbon dioxide, and the hydrogen present is oxidized to water. In short, COD is a measure of the concentration of chemically oxidizable organic compounds present in wastewater and is less expensive than BOD measurements. The shortcomings of this

method are that it does not oxidize ammonia and is subject to interference from high concentrations of chloride ions (Horan, 1990). Other disadvantages include: certain organic compounds such as straight-chain, saturated aliphatic acids, and alcohols are not efficiently oxidized by dichromate; and certain inorganics (for example sulfides, sulfites, thiosulfites, nitrites and ferrous iron) create an inorganic COD when oxidized by dichromate, which results in inaccuracy for estimation of the organic content of the wastewater (Adams et al., 1981).

The TOC method is especially applicable to small concentrations of organic matter. A known quantity of wastewater sample is injected to a high temperature furnace, where the organic carbon is oxidized to CO_2 in the presence of a catalyst (Metcalf & Eddy, 1979). The CO_2 produced is quantitatively measured by an infrared analyzer. This test can be performed very rapidly and is increasing in popularity; however, certain resistant organic compounds may not be oxidized.

The principles of the PV test are very similar to the COD test in that the organic material in the wastewater is oxidized chemically, and the remaining oxidizing agent after the reaction is analyzed by titration (Horan, 1992). In this test potassium permanganate acts as an oxidizing agent in the presence of dilute sulfuric acid as the sample is boiled for 30 minutes. Because of the mild oxidizing conditions, many organic compounds are not oxidized. However, this method is rapid and requires inexpensive equipment.

The TOD is a rapid, automated test that oxidizes a waste in an air stream in the presence of a platinum catalyst at 900°C (Horan, 1992). Under these conditions all the carbon in the sample will be oxidized to CO_2, and the oxygen demand is estimated from the difference in oxygen content of the air before and after reaction.

2.1.5 DISCUSSION OF BIOREACTOR PROCESSES

In the preceding sections, several types of biological wastewater treatment systems are presented. This section deals with the application, operation and theory of each of the biological treatment processes listed below:

1. Activated Sludge
2. Aerobic Digestion
3. Aerated Lagoon
4. Trickling Filter
5. Rotating Biological Contactor
6. Nitrification
7. Denitrification
8. Anaerobic Contact
9. Anaerobic Digestion
10. Advanced Anaerobic Digesters
11. Sequencing Batch Reactor
12. Biological Aerated Filter

The aerobic dispersed-growth systems include activated sludge, aerobic digestion, and aerated lagoon processes, whereas the aerobic fixed-bed systems are the trickling filter and biological rotating contactor. On the other hand, both the anaerobic digestion and anaerobic contact are dispersed-growth processes. This section is intended to serve only as an overview of the basic concepts of biological treatment processes. The design Equations are excluded in the following discussion of bio-treatment processes; however the reader is referred to the cited literature for details.

2.1.5.1 ACTIVATED SLUDGE PROCESS

The activated sludge process is the most widely used biological wastewater treatment process today, treating both domestic waste and industrial wastewater. The process is more than simply a refinement of the percolating filter process; it is conceptually a very different treatment system (Gray, 1989). The activated sludge process utilizes the dispersed bacterial flocs and free-living microorganisms that are suspended in the water. The microorganisms generally found in an activated sludge consist of bacteria, fungi, and protozoa.

Process Description

The activated sludge (AS) process is a dispersed-growth system in which microorganisms are constantly supplied with organic matter and oxygen. The microorganisms grow in flocs made up of aggregates of microbes, inorganic and organic colloidal material and larger particulate material. These flocs are responsible for the decomposition of the organic material into carbon dioxide and water. The major components of an AS system include a well-agitated and aerated, continuous flow reactor with a settling tank. A simplified flowsheet of an AS process is shown in Figure 2.2. The aerobic environment in the reactor is achieved by the use of diffused or mechanical aeration, which also serves to maintain the mixed liquor in a completely mixed regime. The mixture of new cells and old cells is continuously passed into a settling tank where the cells are separated from the treated wastewater. A portion of the settled cells is recycled to maintain the desired concentration of microbes in the reactor, and a portion is discharged. Usually, a mixed culture of organisms is utilized in the bioreactor.

The different types of activated sludge processes are categorized by their system configurations, which are listed below:

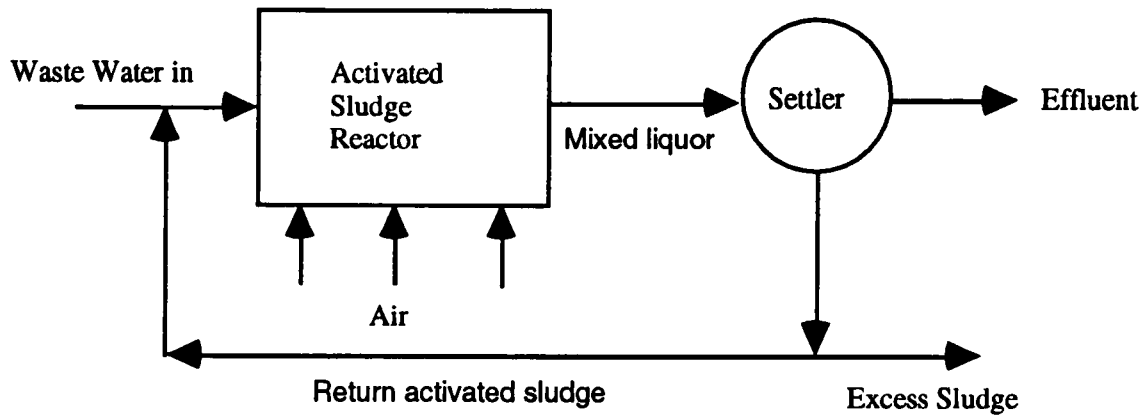


Figure 2.2 Simplified diagram of conventional activated sludge process.

- Conventional Activated Sludge
- Tapered Aeration Activated Sludge
- Step Aeration Activated Sludge
- Contact Stabilization Activated Sludge
- Completely Mixed Activated Sludge
- Extended Aeration Activated Sludge
- Pure Oxygen Activated Sludge

For the application and theory of various types of activated sludge processes, the references Gray (1989), Grady and Lim (1980), and Benefield and Randall (1980) are recommended. Regardless of the reactor configuration, all the activated sludge systems have four common characteristics:

1. They employ aerobic flocculent slurries containing microorganisms.
2. They separate the microorganisms from the effluent by sedimentation of the solid.

3. They recycle the microorganisms from the settler to the reactor.
4. Their performance is dependent on mean cell residence time.

The primary objective of the activated sludge process is the removal of soluble organic matter, but if the concentration of soluble organic matter is less than 50 mg/l of biodegradable COD, AS treatment is not recommended because physical-chemical means are usually more economic. One example of the physical-chemical process is a combination of flocculation, sedimentation, and filtration treatment systems. If the concentration of soluble COD is greater than 4000 mg/l, it is likely to be more economic to use an anaerobic biochemical operations. The activated sludge process is capable of producing high-quality effluent because the cells are removed prior to discharge. Thus it is often used as the primary means of industrial wastewater treatment.

Applications

The primary merit of AS treatment is that it can attain an effluent of high quality at a reasonable cost. Compared to an aerated lagoon, it is capable of achieving equal reductions in soluble substrate in vessels of much smaller volume while producing an effluent relatively free of suspended solids. In addition, the mean cell residence time is regulated by adjusting the amount of sludge discharged in order to obtain desired effluent quality. The AS reactor is controllable, relatively resistant to shock loads, and able to achieve acceptable effluents in spite of variable input conditions. However, the AS process perform better under more stable conditions.

The main defect of the activated sludge process is the direct result of its controllability; it is a complicated process that requires relatively sophisticated operation in order to achieve the desired results. It is, however, relatively sluggish in response to

transient changes, which limits the applicability of some automatic control techniques (Grady and Lim, 1980). Furthermore, the activated sludge system is sensitive to fluctuations in the organic strength of wastewater, thus increasing the difficulty of control. Other disturbances in input parameters, such as waste flow and composition, can lead to system failure.

A list of wastewater treated by the activated sludge process includes almost all biodegradable wastewater, which is why this biological treatment is by far most widely used of all. Furthermore, its ability to produce an effluent of excellent quality makes it very useful in the field of industrial wastewater treatment.

Control and Instrumentation

The main objective of the AS process is to produce a high-quality effluent at a minimal operating cost. The variation in effluent quality is affected by a number of factors that must be properly controlled to maintain stability and efficient performance. The most important factors are (Horan, 1990):

1. Influent variables: variations in the flow rate, BOD and suspended solids concentration, toxic materials.
2. Plant operational parameters: fluctuations in sludge age, food to microorganism (F/M) ratio, mixed liquor solids concentration, recycle ratio and solids concentration, and solid discharge rate.
3. Oxygen requirements for the waste.
4. Settling characteristic: stirred sludge variation.
5. Environment factors: temperature, pH, and wind.

Effective control of the above parameters results in decrease of effluent variability and increase of efficiency of AS performance.

2.1.5.2 AERATED LAGOON

The aerated lagoon is a relatively shallow basin with a large surface area, generally several acres, which operates on a flow-through basis and requires mechanical aeration units. There are several types of lagoons, with classification into specific types being based upon such factors as the complexity of the microbial community employed, the degree of mixing, and the reaction environment. In this section the completely mixed aerated lagoon (Grady, 1980), which is the simplest from both a physical and ecological point of view, is the subject of discussion.

Process Description

The completely mixed aerated lagoon (CMAL) is generally round or square with a depth of several meters and a large surface area. In the past, these have generally been earthen basins with mechanical aeration. The concept underlying this process resembles a completely mixed reactor. However, the shape of the lagoon is important in achieving a completely mixed condition. The mixing energy supplied to a CMAL must be sufficient to keep all solids in a uniform suspension and to provide an adequate supply of oxygen throughout the basin. Occasionally, in deeper lagoons, submerged turbines must be provided in order to obtain completely mixed condition. Because of the stringent environmental requirements, many aerated lagoons are now used in conjunction with settling facilities and incorporate the recycle of biological solids. A schematic diagram of CMAL is depicted in Figure 2.3.

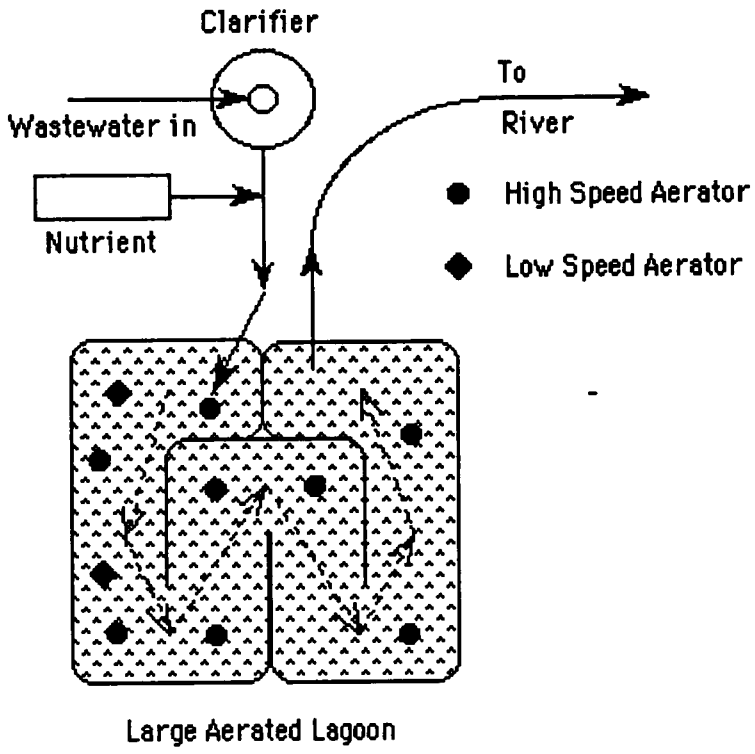


Figure 2.3 Typical layout of aerated lagoon treatment system.

The microbial population in a CMAL is predominately heterotrophic; metabolism is carried out by aerobic respiration as long as the oxygen supply is sufficient. However, the ecology of the microbial community is quite complex with many interactions among the species that are beyond the scope of this report.

Applications

There are two major uses of completely mixed aerated lagoons: conversion of soluble organic matter into insoluble microbial cells and stabilization of the organic material. The first use has two applications:

1. Pretreatment of industrial wastewater prior to discharge to municipal sewer. This makes the characteristics of the wastewater entering the municipal plant more uniform, therefore alleviating the problems associated with a diversity of organic compounds from any sources.
2. Prior to sedimentation as the major total treatment system for a small community.

The second use of the CMAL is as a stabilization pond for organic matter. Stabilization occurs when sufficient time is provided to allow a large portion of the microbial cells to undergo decay. This application allows the reduction of sludge that must be discharged.

Control and Instrumentation Concerns

One of the major advantages of CMALs is their ease of operation, which makes them attractive for low-cost installation (Grady, 1980). CMALs are relatively resistant to upsets by organic and pH shock and are also capable of handling high-strength waste because the large reactor volume reduces the problem of oxygen transfer. Finally, lagoons also act as a cooling ponds, so that waste with a high temperature can be treated without additional cooling requirements.

Unfortunately, some of the merits associated with CMAL become defects under certain conditions. For example, during winter when the cooling characteristics of the lagoon reduces the waste temperature, the degree of treatment will also be reduced. Coupled with this is the fact that no operational control can be exerted over the values of the kinetic parameters. This problem has served as a major consideration of aerated lagoon design. Other problems such as short circuiting (resulted in stagnant zones created

within the pond), solids deposition and freezing of aerators can be overcome by modification of facility. The BOD removal rate for CMAL is a function of hydraulic (or solid) detention time, temperature, and the nature of the wastewater (Viessman and Hammer, 1993). For further reading of design considerations, reference Horan (1990) is recommended. In general, properly designed completely mixed aerated lagoons offer a reasonable alternative for the treatment of readily biodegradable wastewater.

2.1.5.3 AEROBIC DIGESTION

Aerobic digestion (AD) is an alternative method of treating the organic sludge produced from various treatment operations. AD has been defined as "a process wherein thickened sludge separated from their associated liquors undergo stabilization during prolonged aeration" (Barnhart, 1961). The aerobic digester can be used to treat a) only waste activated or trickling filter sludge, b) mixtures of primary sludge and waste activated or trickling filter sludge, and c) waste sludge from the activated sludge treatment without settling.

Process Description and Microbiology

Two types of aerobic digestion are commonly used today: conventional and pure oxygen. In conventional AD, the sludge is aerated for an extended period of time in an open, unheated tank using conventional air diffusers or surface aeration equipment (Metcalf & Eddy Inc., 1979). This process can be either continuous or batch. Pure oxygen AD is a modification of the aerobic digestion process in which pure oxygen is used instead of air.

AD is similar to activated sludge process; as the supply of available substrate food is depleted, the microbes begin to consume their own protoplasm to obtain energy for cell-maintenance reaction (Metcalf & Eddy Inc., 1979). When this occurs, cell tissue is oxidized aerobically to carbon dioxide, water, and ammonia. Actually only about 75% to 80% of the cell tissue can be oxidized; the remaining is composed of inert components and organic matter that are not biodegradable. The ammonia in this process is subsequently oxidized to nitrate in further digestion.

Applications

AD is a viable alternative to anaerobic digestion for sludge stabilization. As mentioned earlier, the primary function of AD is treating organic sludge produced from other treatment processes. Moreover, AD can be considered as a means of conditioning sludge prior to dewatering. The advantages of AD are summarized as follows (Benefield and Randall, 1980 and Grady and Lim, 1980):

- Aerobic digestion produces an odorless, humus-like, biologically stable end product that can be disposed of easily.

- Aerobic digestion produces a supernatant that contains little soluble biodegradable organic matter.

- The digested sludge usually has good dewatering properties, although this should be qualified by noting that the dewatering characteristics depend upon the digestion time.

- Aerobic digestion can economically handle low waste sludge concentrations, thereby eliminating the need for sludge thickening devices associated with anaerobic digestion of secondary sludge.

- When applied to secondary sludge (from secondary treatment), aerobic digestion can achieve organic solids reductions similar to those of anaerobic systems (that is, around 45% to 50%).

- In comparison to anaerobic digestion, more of the sludge's basic fertilizer value is retained, making it beneficial for land application.

- Capital costs for aerobic digesters are less than for anaerobic digesters because the construction is simple.

- Aerobic digesters experience fewer operational problems than anaerobic ones because the system is more stable; therefore lower maintenance cost will be required and less skilled labor can be used to operate the facility.

The disadvantages most often claimed for aerobic digestion are listed below (Benefield and Randall, 1980, and Grady and Lim, 1980):

- Energy must be expended to supply oxygen to the system; thus operating costs are higher than for anaerobic digestion.

- There is no recovery of energy in the form of methane.

- Aerobically digested sludges do not always clarify well; consequently, the supernatant may be high in suspended solids.

- Aerobic digestion of primary sludge produces more residual sludge than anaerobic digestion.

- The efficiency is dependent upon temperature, and therefore good temperature control is necessary.

Control and Instrumentation Concerns

The important environmental factors governed in the operation of the AD process are temperature and pH. It has been observed that the AD operation is temperature dependent, especially at temperatures below 20°C (Metcalf & Eddy, 1979). Thus, in extremely cold weather, consideration should be given to heating the sludge or the air supply, covering the tank, or both. It is critical that the pH in the AD process remain above 5.5. Thus pH has to be checked periodically and adjusted if it drops too low. Other factors need to be controlled are hydraulic residence time, loading criteria, oxygen requirements for complete oxidation of cell tissue, dewatering characteristics, and energy required for mixing. These factors have to be controlled properly to achieve high efficiencies in AD. Nevertheless, it is apparent that AD can bring about the stabilization of primary sludge, trickling filter humus, and waste activated sludge as well as various mixtures of the three.

2.1.5.4 TRICKLING FILTER

Trickling filter (TF) is an attached (fixed) growth system in a shape of packed tower used to removed organic matter by aerobic process. Because of the advancement in polymeric material, the efficiency of trickling filter has been improved. As a result, TF has been used as a pretreatment device preceding other biological treatment operations.

Process Description

A trickling filter (also referred to as a biofilter, bacteria bed or percolating filter) is a reactor of rectangular or circular cross section filled with a permeable media. Wastewater is distributed mechanically over the top surface of the media and percolates

down through the filter to collect in an underdrain system at its base (Horan, 1990). The bacteria and microorganisms grow as a thin film on the solid media while metabolizing the soluble organic matter from the wastewater flowing over them. Thus, the detachment of microbial solids from the film surface results in suspended solids at the effluent. Although a large number of materials have been tested for filter media, the most successful have been plastic and crushed granite or limestone (Grady and Lim, 1980).

The major components of TF are a rectangular or spherical tank, filter media, distributor, and underdrain system. The function of a distributor is to provide an even hydraulic load (flow per unit cross-sectional area) over the entire surface. Usually, rotary or fixed types are used. The rotary distributor has either one or two arms or more, which are driven by the reaction of the wastewater flowing out of them. Many types of distribution systems are available; a consideration is that the distributor and media must be compatible so that the surface media are properly cover with wastewater. The underdrain system must provide three important functions (Grady, 1980):

- support the media;
- provide an uninterrupted path of flow for the liquid to the floor drain; and
- allow access of air to the bottom of the filter so that a continuous supply of oxygen may be brought to the microorganism.

Filter media should provide both a large surface area for the growth of a slime layer and also a large void space for supplying oxygen and facilitating liquid flow. A simplified diagram of a sphere TF is shown in Figure 2.4.

Recirculation provides a recycle of a portion of treated effluent for mixture with the influent. One purpose of recirculation is to reduce the proportionality of organic and

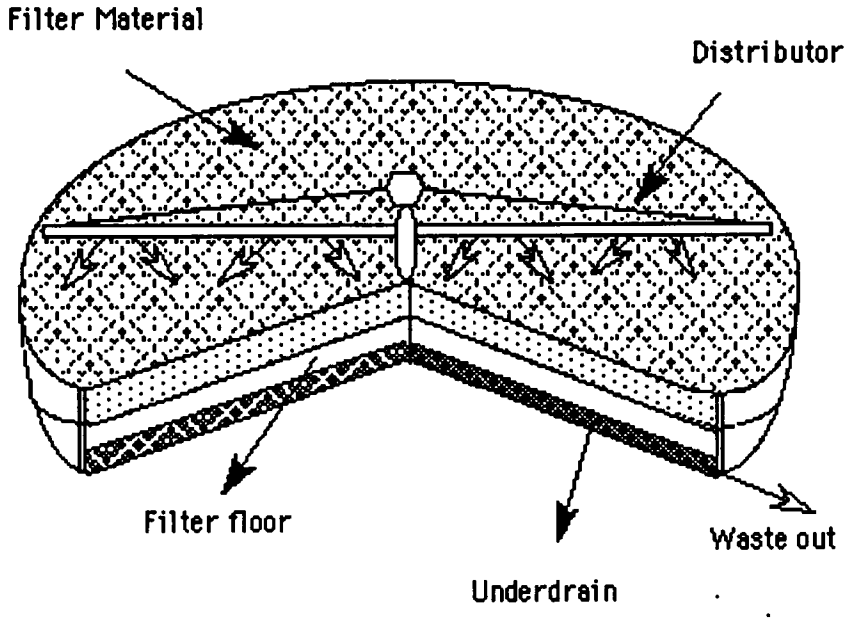


Figure 2.4 Cutaway view of a spherical trickling filter.

hydraulic loads. Otherwise a change in hydraulic load will result in a proportional change in the organic loading, and vice versa (Grady, 1980).

Applications

The major advantage of trickling filters is that they are comparatively simple to operate and have low operating costs, thus making them ideal for remote sites or for small communities. In addition, because large masses of microbes must be present for trickling filters to achieve a high-quality effluent, they posses substantial reserve capacities, which make them very robust and tolerant to changes in the organic loading (Grady, 1980). Furthermore, they are able to tolerate shock and toxic loads owing to the short contact time of the wastewater with the slime layer. Because of the dense nature of microbial

film, which sloughs from the media, sludges relatively constant in character are produced and are easily removed by sedimentation.

One of the major disadvantages is the inability to control the effluent quality effectively, because the microbes growth when attached to a fixed surface provides little change in the mass in response to environmental changes. In addition, the space requirements for TFs are high, and TFs can only provide a limited treatment efficiency. In hot weather TFs are associated with odors and fly nuisances (Horan, 1990).

Control and Instrumentation Concerns

Recirculation is the only variable in the TF process that can be adjusted to accommodate the changes in the incoming wastewater flow rate and concentration. There is a minimum requirement of hydraulic loading to insure that all of the media is wetted and to prevent clogging due to excessive biofilm thickness. Currently, there are no TF control strategies for maintaining a constant effluent quality during changes in the organic loading (Horan, 1990).

2.1.5.5 ROTATING BIOLOGICAL CONTACTOR

Rotating biological contactors, or biodiscs, are another form of fixed-filmed bioreactor; thus they are similar to trickling filters in performance and utility. The primary difference is that the rotating biological contactor employs a rotating bed of attached bacteria (slime biomass) that is partially immersed in a tank of wastewater.

Process Description

A rotating biological contactor (RBC) is composed of a series of closely spaced circular disks of wood, metal, polystyrene or polyvinyl chloride (usually depending on the manufacturer), which is partially submerged (about 40%) in wastewater and rotates slowly through it. The rotation exposes the surface of the RBC to the atmosphere, permitting aeration followed by resubmergence into the wastewater. In operation, biomass growth becomes attached to the surfaces of the disks and eventually forms a slime layer over the entire wetted surface area of the disk. This biofilm is responsible for BOD removal. As the film accumulates, sloughing occurs in an identical manner to that of a trickling filter. The rotation also allows the biomass to obtain oxygen from the air and maintain aerobic conditions. In summary, rotation of the disc provides aeration, keeps the tank content mixed and helps produce the shear forces necessary for sloughing (Horan, 1990). A simplified diagram of an RBC is depicted in Figure 2.5.

The major application of RBC is the removal of soluble organic matter through its conversion to insoluble microbial cells, which can be removed by sedimentation, therefore yielding high-quality effluent. Consequently, RBC can be used as a prime means of municipal and industrial wastewater treatment or pretreatment of industrial wastewater.

Control and Instrumentation Concerns

The advantages associated with RBC resemble those of the trickling filter. The difference between the two is that the biomass is passed through the wastewater rather than passing the wastewater over the biomass. The RBC provides assurance of adequate wetting of all of the microorganism film regardless of the influent flow rate, therefore eliminating the need for recirculation. In addition, the ease of operation and low land

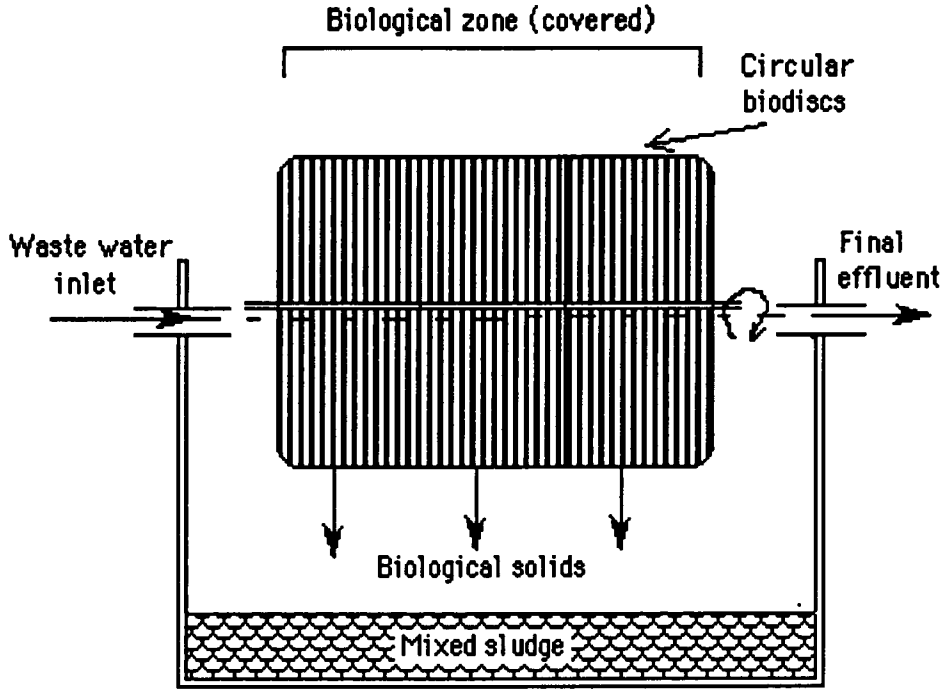


Figure 2.5 A typical rotating biological filter.

requirements also make RBC particularly suitable for small sites. Several other advantages include (Horan, 1990):

- Low power requirements and maintenance costs.
- Stability against hydraulic shock loading.
- Direct control of the film thickness by adjusting rotational speeds.
- Capability of achieving high degree of carbonaceous and nitrogenous BOD removal.
- Ponding of the bed and clogging of filter nozzles is alleviated.

The major problems associated with the RBC are the lack of reserve capacity and the absence of operational controls (Grady and Lim, 1980). Once the RBC is installed, there is little that can be done to accommodate the changes in the influent character or the effluent criteria. The only control options available are the speed of rotation and the depth of immersion of the discs. Other problems include breaking or cracking of the discs and shaft bearing failure. Regular maintenance of the rotating gear is mandatory. In general, the factors affecting the performance of RBC include temperature, oxygen transfer, media rotational speed, and depth of immersion of disks. However, regardless of their defects, RBCs are ideal biological treatment units for small communities that may have only a minimal operations staff.

2.1.5.6 NITRIFICATION

Nitrification, a type of reaction rather than a distinct biochemical operation, occurs when ammonia nitrogen in a wastewater is converted to the nitrate by microorganisms. Nitrification can be performed in nearly any type of the biological treatment system (suspended growth and attach growth systems); the most common are single-stage or two-stage activated sludge processes, biological rotating contactors, and trickling filters.

Process Microbiology and Biochemistry

Nitrification involves a group of aerobic, chemoautotrophic bacteria, collectively known as nitrifiers. *Nitrosomonas* oxidize ammonium nitrogen to nitrite nitrogen (NO_2^-) and *Nitrobacter* further oxidized the nitrite to nitrate (NO_3^-). Both utilize inorganic carbons including carbon dioxide (CO_2), bicarbonate (HCO_3^-), and carbonates (CO_3^{2-}) as

their energy source for biomass synthesis. Each individual chemical reaction and the overall nitrification are represented by the following equations:

$$2NH_4^+ + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_2^- + NH_4^+ + 2H_2O \qquad (2.1\text{-}8)$$

$$2NO_2^- + O_2 \xrightarrow{\text{Nitrobacter}} 2NO_3^- \qquad (2.1\text{-}9)$$

$$NH_4^+ + 2O_2 \xrightarrow{\text{Nitrifiers}} NO_3^- + 2H^+ + H_2O \qquad (2.1\text{-}10)$$

Because the nitrification may be performed in any of the processes mentioned above, the physical characteristics and operation of the bioreactors are similar to those for activated sludge, biological rotating contactor, and trickling filter processes.

Applications

In some cases carbon oxidation and nitrification are performed together to remove soluble organic matter and nitrogenous compounds. Nitrification systems are designed to meet one objective, conversion of ammonia nitrogen to nitrate so that the concentration of ammonia is reduced. If the application is for wastewater where the discharge of nitrate would cause a problem, then nitrification is coupled with denitrification to provide complete nitrogen removal (Grady and Lim, 1980). The reduction of nitrate to nitrogen or denitrification reaction is shown below:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

The process of denitrification is further discussed in Chapter 2.1.5.7. However, for more in-depth information on denitrification, the reader is referred to Grady and Lim (1980) and Eckenfelder (1989).

Control and Instrumentation Concerns

In addition to temperature, pH and dissolved oxygen concentration are important parameters in nitrification kinetics studied by Wild, Sawyer, and McMahon (1971). Nitrification is also inhibited by high concentrations of free ammonia and nitrite. Free ammonia concentrations in the range of 10 to 150 mg/l inhibit *Nitrosomonas*, and free ammonia concentrations of 0.1 to 1.0 mg/l are inhibitory to *Nitrobacter*. *Nitrobacter* are more sensitive to low free ammonia concentration and when inhibited, a build-up of nitrites will occur, resulting in further inhibition of *Nitrobacter*. Both genera are sensitive to low concentrations of free nitrous acid.

Above 10°C the rate of nitrification reduces by about one half for every 10°-12°C temperature drop, but the rate reduces more rapidly in cold wastewater so that lowering the temperature from 10° to 5°C halves the rate of ammonia oxidation (Viessman and Hammer, 1993). Eckenfelder (1989) reported that nitrification occurs over a temperature range of 5° to 45°C with the optimum temperature range from 25° to 35°C. Sludge age (solid retention time) and temperature are interrelated factors in establishing and maintaining healthy nitrifier populations. The relationship can be expressed by (Eckenfelder, 1989):

$$\theta_c = 2.13e^{0.098(15-T)} \qquad (2.1\text{-}11)$$

where: θ_c - sludge age, time

T - temperature, °C

For design purposes, the U.S. EPA recommended a safety factor in the order of 2.5[26] to the sludge age (determined by Equation 2.1-11) to ensure that ammonia breakthrough does not occur during diurnal peaks in loads (Eckenfelder, 1989).

The nitrification rate is also a function of pH. Viessman and Hammer (1993) reported the optimum pH for nitrification is $8.2 \leq pH \leq 8.6$, with 90% of the maximum occurring at pH 7.8 and 8.9. However the rate decreases 50% of the maximum at $pH < 7.0$ and $pH > 9.8$.

Oxygen Requirements

Dissolved oxygen (DO) concentration is an important parameter that must be controlled for effective nitrification. It was recommended that nitrification systems be designed at DO levels of 2.5-3.0 mg/l under winter conditions (Eckenfelder, 1989). Oxygen requirements for substrate biooxidation are determined by the nitrogen concentration relative to the carbon source and are inversely affected by mean cell residence time. Total oxygen requirements for activated sludge processes are dependent on COD:TKN (chemical oxygen demand:total kjeldahl demand) ratio of the wastewater and also the mean cell residence time of the system. In general, DO in nitrification systems must be effectively controlled for complete nitrification because low DO concentrations will eventually lead to incomplete nitrification.

Another important factor to be considered is that autotrophs are out-competed for oxygen by heterotrophs. Therefore, ammonium oxidizers (*Nitrosomonas*) may out-compete nitrite oxidizers (*Nitrobacter*) to the point of completely inhibiting them. This observation suggests that nitrite accumulation could result.

2.1.5.7 DENITRIFICATION

As noted earlier, nitrification is the oxidation of ammonia nitrogen to nitrate therefore reduces the ammonia nitrogen discharged to a receiving body of water. However, nitrification does not reduce the mass of nitrogen discharged; it merely changes its state. As a result, highly nitrified effluents can still accelerate the algae bloom-eutrophication. One way of minimizing the availability of nitrogen is to discharge it to the atmosphere as nitrogen gas through the application of biological denitrification. In other words, nitrate are bacterially reduced to gaseous nitrogen by facultative heterotrophs in an anoxic environment.

There are two types of denitrification processes, anoxic-suspended and anoxic-attached growth. The term anoxic is used rather than anaerobic because the principal biochemical pathways are not anaerobic, but only the modifications of aerobic pathways (Metcalf and Eddy, 1991). The discussion is concentrated on a combined carbon oxidation-nitrification/denitrification (single-sludge) suspended-growth system using internal and endogenous carbon source.

Process Microbiology and Design

In denitrification, an organic carbon source such as methanol, acetic acid, ethanol, or sugar is needed to act as an electron donor and to supply carbon for biological synthesis. Nitrate is used by the heterotrophic microorganisms as an electron acceptor for energy metabolism (Benefield and Randall, 1980). Denitrification can be described by:

$$NO_3^- + \text{substrate} \rightarrow N_2 + CO_2 + H_2O + OH^- + \text{cells} \qquad (2.1\text{-}12)$$

Nitrate nitrogen is converted to reduced forms such as nitrogen, nitrous oxide, and nitrite oxide, as shown by the reduction reaction with the redox state of each intermediate:

$$\underset{\text{Nitrate}}{\overset{+5}{NO_3^-}} \rightarrow \underset{\text{Nitrite}}{\overset{+3}{NO_2^-}} \rightarrow \underset{\text{Nitric oxide}^*}{\overset{+2}{NO}} \rightarrow \underset{\text{Nitrous oxide}^*}{\overset{+1}{N_2O}} \rightarrow \underset{\text{Nitrogen}^*}{\overset{0}{N_2}}$$

where the asterisk denotes gaseous end-products. The redox state of the intermediates in denitrification shows that the reaction proceeds associated with the gain of electrons in each step. Although the wastewater itself can serve as an electron donor and as a carbon source, in separate stage nitrification/denitrification systems the available carbon is usually inadequate. Therefore, an external carbon source must be supplied, frequently achieved by providing methanol. The stoichiometry of the overall nitrate removal reaction using methanol as carbon source can be represented by the following empirical equation (Benefield and Randall, 1980):

$$NO_3^- + 1.08CH_3OH + H^+ \rightarrow 0.065C_5H_7O_2N + 0.47N_2 + 0.76CO_2 + 2.44H_2O \qquad (2.1\text{-}13)$$

The two important factors that affect the rate of denitrification are substrate (electron donor) concentration and the nitrate concentration. Both these effects can be modeled by standard Monod kinetics (Horan, 1990):

$$\frac{d[NO_3]}{dt} = \mu_{m,den} \frac{[NO_3]}{K_{den} + [NO_3]} X \qquad (2.1\text{-}14)$$

where $\frac{d[NO_3]}{dt}$ - denitrification rate, M/L^3-t

$\mu_{m,den}$ - maximum specific growth rate of denitrifying bacteria, t^{-1}

K_{den} - NO_3 saturation constant, M/L^3

X - biomass concentration, M/L^3

$[NO_3]$ - NO_3 concentration, M/L^3

The values for the nitrate saturation coefficient are generally very low, and thus $[NO_3] >> K_{den}$. Consequently, the denitrification rate follows zero-order kinetics with respect to nitrate concentration and carbon content, but first-order kinetics with respect to biomass concentration. The first-order reaction can be written as:

$$\frac{d[NO_3]}{dt} = \mu_{m,den} X \qquad (2.1\text{-}15)$$

For a completely mixed reactor with sludge recycle, a material balance equation for nitrate entering and leaving the denitrification tank is provided by (Benefield and Randall, 1980):

$$\left(\frac{d[NO_3]}{dt}\right) V_{anoxic} = Q_i[NO_3]_i + Q_{rs}[NO_3]_e - \mu_{m,den} X V_{anoxic} - (Q_i + Q_{rs})[NO_3]_e \qquad (2.1\text{-}16)$$

where V_{anoxic} - denitrification tank volume, L^3

Q_i - inlet wastewater flow rate, L^3/t

Q_{rs} - sludge recycle flow rate, L^3/t

$[NO_3]_i$ - influent nitrate concentration, M/L^3

$[NO_3]_e$ - effluent nitrate concentration, M/L^3

Substituting for $\mu_{m,den}X$ from Equation 2.1-15 and assuming steady state, Equation 2.1-16 becomes:

$$\frac{Q_i\left([NO_3]_i - [NO_3]_e\right)}{V_{anoxic}X} = \mu_{m,den} = (q)_{DN} \tag{2.1-17}$$

The term $\mu_{m,den}$ is often referred to as the specific denitrification rate, $(q)_{DN}$, and has the unit time^{-1}. It is related to the temperature by (Horan, 1990):

$$(q)_{DN,T} = 0.07(1.06)^{T-20°C} \tag{2.1-18}$$

where T(°C) is the operating temperature. As reported by Metcalf and Eddy (1991), the effect of dissolved oxygen concentration on the overall denitrification rate can be formulated as:

$$R'_{DN} = R_{DN(20°C)} \times 1.09^{(T-20°C)}(1 - DO) \tag{2.1-19}$$

where R'_{DN} - overall denitrification rate, t^{-1}

$R_{DN(20°C)}$ - specific denitrification rate, t^{-1} (mg NO_3/mg MLVSS-d)

DO - dissolved oxygen concentration in wastewater, M/L^3

Equation 2.1-19 indicates that the rate of denitrification reduces linearly to zero when DO concentration approaches to 1.0 mg/l. The typical specific denitrification rates with various carbon sources are provided by Metcalf and Eddy (1991) and Eckenfelder

(1989). The important factors that influence the denitrification or nitrate reduction rate include (Londong, 1992; and Abeling and Seyfried, 1992):

- Dissolved oxygen concentration.
- Substrate (carbon) concentration.
- Mixture quality of influent wastewater, return sludge and recycled nitrate.
- Temperature and pH.
- Nitrous acid concentration (inhibition limit of 0.13 mg HNO_2/l).

Bardenpho Process

Several processes have been proposed for biological nitrification-denitrification in separate and combined systems. The single-sludge, four-stage, proprietary Bardenpho process as shown in Figure 2.6 is one of the combined bio-treatment systems. The Bardenpho process (four reaction zones) relies on an aerobic zone for nitrification and an anoxic zone for denitrification. It uses the organic carbon in the wastewater as the electron donor to achieve nitrate reduction. The untreated wastewater mixes with the nitrified recirculation from the subsequent aerobic zone (second reaction zone), and then this mixture enters the anoxic zone (first reaction zone) for denitrification. Both zones reduce the soluble organic content of the wastewater, but the major carbon oxidation occurs in the aerobic reaction zone. The ammonia-nitrogen in the wastewater is nitrified to nitrate in the aeration basin (second reaction zone). Usually, a smaller anoxic stage (third reaction zone) is added following the aerobic stage for further denitrification using an endogenous carbon source. A relatively small aerobic zone (fourth reaction zone) is also added for

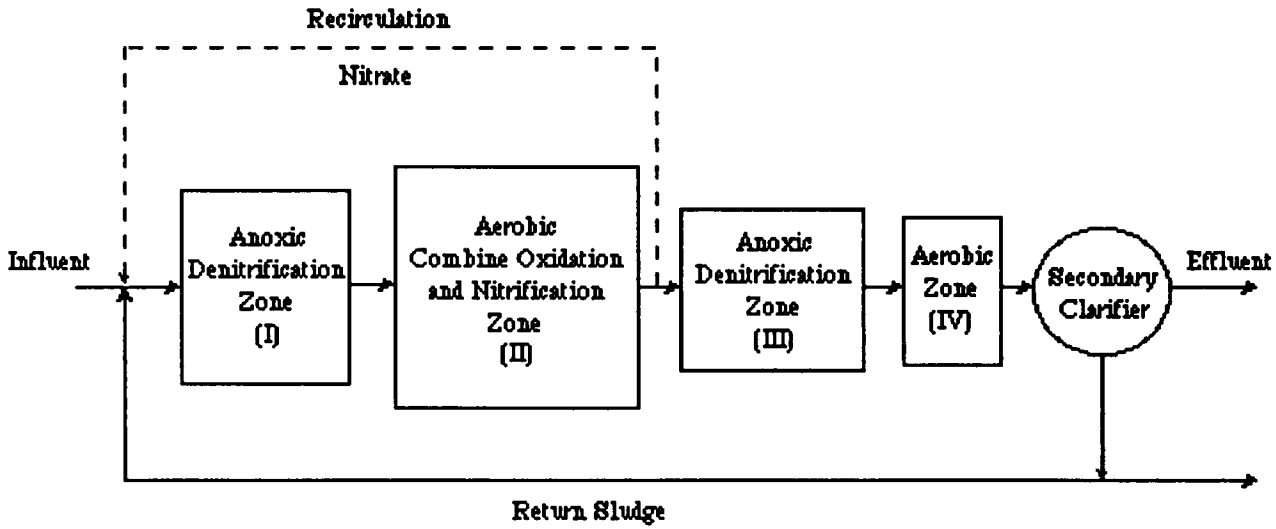


Figure 2.6 A single-sludge four-stage Bardenpho process.

stripping entrained nitrogen gas prior to clarification. Nitrogen removal in excess of 90% is possible in the Bardenpho process without the addition of any chemicals (Barnard, 1978).

2.1.5.8 ANAEROBIC DIGESTION AND ANAEROBIC CONTACT

All of the biochemical operations discussed so far have been aerobic and anoxic. However, not all microbes utilize oxygen; metabolism in the absence of oxygen is called anaerobic. The two most common anaerobic, dispersed-growth processes used for biological wastewater treatment are the anaerobic digestion and the anaerobic contact processes. The latter has been used to remove soluble organic matters by anaerobic microorganisms. In this section, anaerobic digestion is emphasized because of its important role in organic material and biological solids stabilization. Regardless of the type of anaerobic process, all anaerobic biochemical operation share a unique feature — the formation of methane (Grady and Lim, 1980).

Process Description and Microbiology

In Anaerobic Digestion (ANA) process, the organic material in mixtures of primary settled and biological sludges under anaerobic conditions is biologically converted to CH_4 and CO_2. The biological conversion involving multiple stages of anaerobic conversion that describes as follow (Grady and Lim, 1980):

1. Insoluble complex organics in sludges are solubilized by hydrolysis (catalyzed by enzymes that are released from bacteria) into simple soluble organics.

2. Acid-producing bacteria oxidized the small molecules of soluble organic to acidic end products (such as formic and acetic acids, and volatile acids), bacterial cells, and other products.

3. Some of the volatile acids (larger than acetic acid) are utilized by hydrogen-producing bacteria (posses a specialized enzyme system) to produce acetic acid, carbon dioxide and hydrogen.

4. The acid end products are utilized by methanogenic bacteria to produce methane gas and carbon dioxide.

Because of the diverse nature of anaerobic bacteria, a large number of end products can result from their metabolism.

Anaerobic digester may be operated on a batch or a continuous basis; in most circumstances, continuous processes are favored because the waste is usually produced continuously and there is a steady demand for the gas. The classic design for a digester is a variant of the continuously stirred tank reactor (CSTR). Because the contents of this type of digester are completely mixed, the effluent will contain some fraction of freshly added, undigested feed compound, and will also include some of the still active microbial population. The alternatives to the CSTR seek to overcome these problems, and these alternatives are discussed in Chapter 2.1.5.9. However, digesters are usually covered (fixed or moving), circular concrete tanks with vertical side-walls and a sloped bottom (Grady and Lim, 1980). The sludge is introduced continuously or intermittently and retained in the reactor for varying periods of time. The effluents are withdrawn at any of several levels within the reactor to ensure that the system is homogeneously mixed. The effluent is routed to a settler, depending upon the sludge disposal method. A typical

conventional anaerobic digester without mixer, heater, and recycle for sludge digestion is depicted in Figure 2.7.

Anaerobic Contact Process

Contact anaerobic systems are specifically designed to treat weaker sludges with low solids concentrations and high strength effluents. The four major contact systems are: 1) anaerobic contact reactor, 2) anaerobic sludge blancket, 3) fluidized bed anaerobic reactor, and 4) fixed (static) media reactor. The latter three contact systems are further discussed in Chapter 2.1.5.8. In the anaerobic contact reactor, untreated high-strength wastes are mixed with recycle sludge solids and then digested in an air-tight reactor where the mixture is completely mixed. After the digestion process, the mixture is separated in a clarifier and the supernatant is released as effluent, usually for further treatment; the anaerobic sludge is recycled to seed the incoming wastewater. This process has been practiced successfully for stabilization of high-strength soluble waste (Metcalf and Eddy, 1979).

Applications

The advantages associated with anaerobic waste treatment are directly attributable to the special characteristics of anaerobic bacteria. "Anaerobic metabolism yields little energy for growth, and because much of the energy in the original substrate is released as product gases, only small amount of the original waste is converted to new cells" (Grady and Lim, 1980). The product methane produced by the anaerobic process is a valuable energy source. The fact that no oxygen is required is also useful. Anaerobic processes are particularly beneficial and effective in biological wastewater treatment, especially if the

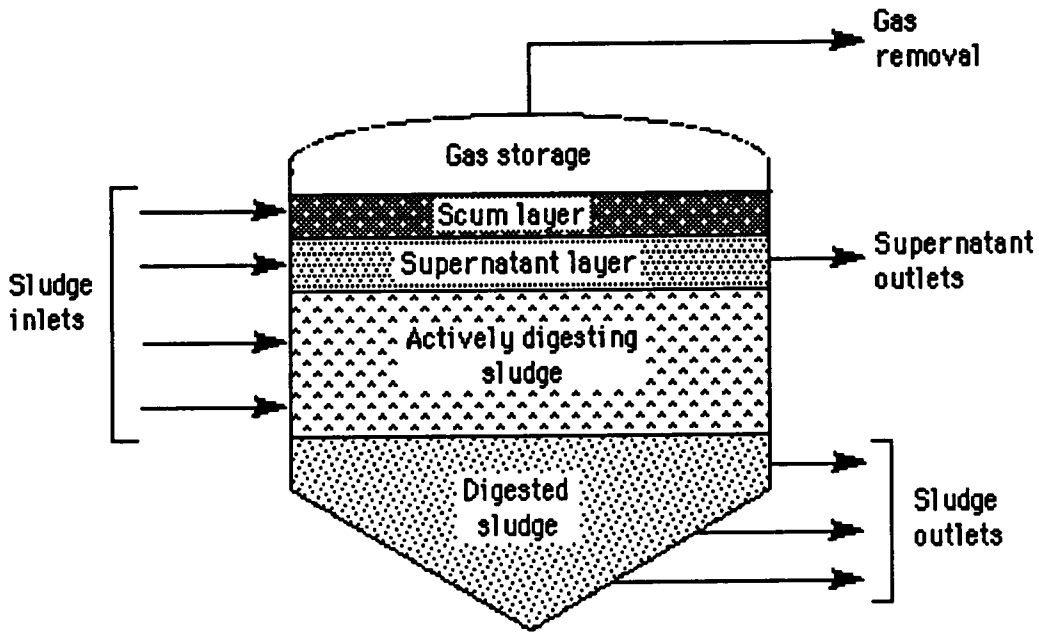


Figure 2.7 Conventional single-stage anaerobic digester.

wastewater has a high concentration of suspended solids, or the wastewater treatment system has sludge bulking problems, inability to withstand high BOD or COD loadings, high operational and energy cost, and high production of biomass as wasted sludge that requires subsequent disposal (Gray, 1989). In summary, the advantages of the anaerobic process for treating high-strength organic wastes are 1) a high degree of purification, 2) the ability to treat high-organic loads, 3) production of small amounts of sludge, 4) process stability, 5) production of combustible methane gas, and 6) a final effluent that contains soluble organic matter that may be readily fed to aerobic treatment.

The major disadvantage concerns the microbial population which is inherently unstable, hence requiring that the system to be closely controlled and monitored.

Furthermore, some synthetic organic chemicals are resistant to anaerobic biodegradation, thereby limiting the applicability of these operations. The slow growth rate of the cells requires that the anaerobic digester be designed with longer mean cell residence time (Grady and Lim, 1980).

Control and Instrumentation Concerns

Temperature is a parameter requiring special control because a small increase in temperature will result in a significant increase in specific growth rate of the microbes. Therefore, the warmer the reactor, the shorter the mean cell residence time for complete digestion (Gray, 1989). The temperature ranges for effective anaerobic process are: mesophilic range of 85 to 100°F (29 to 38°C) and the thermophilic range of 120 to 135°F (49 to 57°C) (Eckenfelder 1989).

Most of the anaerobic treatment systems have problems with pH control that arise from differences in the growth rate of the bacterial populations with pH. For example, methanogenic bacteria are quite sensitive to pH, which affects the population growth (Grady and Lim, 1980). Usually, the methane microorganisms function over a pH range of 6.6 to 7.6 with an optimum near pH 7.0 (Eckenfelder 1989). The digesting sludge has a tendency to become acidic, which will inhibit the methanogenic bacteria. As reported by Gray (1989), under these conditions, if the buffering capacity is exceeded, the pH may rapidly decrease to 6.0, causing the process to fail. Generally, an optimum pH of approximately 7.0 is necessary for the anaerobic system to function (Grady and Lim, 1980). Lime is commonly used to raise the pH of an anaerobic system when there is a process imbalance, but precaution must be taken to avoid precipitation of calcium carbonate due to excess dosage of lime. Sodium bicarbonate can alternatively be used for pH adjustment. It is desirable to have a bicarbonate alkalinity in the range of 2500 to 5000

mg/l to provide a buffer capacity to handle an increase in volatile acids with a minimal decrease in pH (Eckenfelder 1989). The alkalinity in anaerobic process can be controlled by varying the feed rate or adjusting alkalinity dosage to the wastewater.

The concentration of volatile fatty acids (chiefly acetate, propionate, and butyrate) has been proposed as an indicator of digester performance (Hawkes and Hawkes, 1987). The concentrations of these acids in a stable digester are usually between 100 and 2000 ppm unless a fluctuation occurs in digester operating conditions, such as feed composition or temperature. Any decrease in the activity of the methanogenic microbial population may be followed by an increase in the volatile fatty acid concentration, thus increasing the acidity of the digester, which may cause methanogen inhibition.

Other factors influencing the performance of anaerobic process include (Grady and Lim, 1980):

1. The presence of ammonia (either ammonium ion or free ammonia produced from digestion of protein) that can be very toxic to bacteria. Inhibition occurs at concentrations greater than 1500 mg/l (Eckenfelder 1989).

2. An increase of volatile acid concentrations (released from anaerobic metabolism) can drop the pH below 6.0, which inhibits the microorganisms.

3. The additions of base resulting in addition of light metal cations (such as sodium, potassium, calcium, and magnesium), which also exhibit toxic effects when concentrations are high.

4. Concentrations of sulfide (from reduction of sulfates and degradation of proteins) greater than 200 mg/l will cause the metabolic activity of methanogenic bacteria to cease.

5. Heavy metals such as iron, zinc, cadmium, nickel, and copper are toxic to the anaerobic microorganism population even at low concentration.

6. Rapid environmental changes affect the proper functioning of methanogenic culture.

7. Improper loading of waste-containing protein will cause the concentration of ammonia to increase, subsequently causing inhibition.

2.1.5.9 ADVANCED ANAEROBIC DIGESTER

Anaerobic processes can be operated in several types of digester. The most common are the continuously stirred tank and batch digesters. In the continuous stirred tank digester, problems in digestion may occur, as the contents of this type of reactor are completely mixed. As a result, the sludge effluent will contain some fraction of freshly added, undigested feed materials and will also include some of the still-active microbial population. The alternative is to prevent large amounts of active microbial population from being washed out in the effluent, such as digester involving microorganism retention. One of the most successful alternatives in microorganism retention is the upflow anaerobic sludge blanket reactor. A brief summary of various alternative reactor systems is discussed below. However, the primary differences are in the reactor used for the anaerobic process and in the system configurations.

Upflow Anaerobic Sludge Blancket

The upflow anaerobic sludge blanket (UASB) was originally developed in The Netherlands in 1978 and has been installed for wastewater treatment in 300 sites worldwide (Caruana, 1994). In the UASB system, wastewater is directed to the bottom of the reactor where it is distributed uniformly. The wastewater flows upward through a blanket of biologically formed granules that digest the waste as it passes through the blanket. Methane and carbon dioxide gas bubbles rise and are captured in the gas dome.

Liquid passes into the settling portion of the reactor where solids separate from liquids. The solids return to the blanket area while the liquid exits over the weir. In order to keep the blanket in suspension, an upflow velocity of 2 to 3 ft/h (0.6 to 0.9 m/h) has been used (Eckenfelder 1989). The design provides for an even distribution of the entering wastewater over the base of the digester. A simplified configuration of UASB is depicted in Figure 2.8.

The UASB process is characterized by very high mean cell residence time (higher than the anaerobic biofilters), and the difficulty in maintaining and operating the structure of the sludge blanket (Gray, 1989). This type of digester is particularly suited to treating low-strength (~1% dry matter) soluble waste. The limitations inherent in the UASB digester are (Hawkes and Hawkes, 1987):

1. The bed can be disrupted if the influent flow rate is too fast, or if gas production is too vigorous.

2. It may not treat particulate waste effectively as particles appear to interfere with flocculation and may also accumulate in the bed thus reducing its effectiveness per unit volume.

3. Unsuccessful or inefficient operations may occur if the influent forces channels through the sludge blanket instead of passing uniformly through the whole volume of the bed.

In addition, Caruana (1994) reported a study conducted by University of Hong Kong that showed that when UASB is employed under careful acclimation and proper conditions, each liter of volume of a UASB reactor could remove up to 160 grams of COD daily — a loading rate over 60% more than those ever reported. However, "effectiveness of the

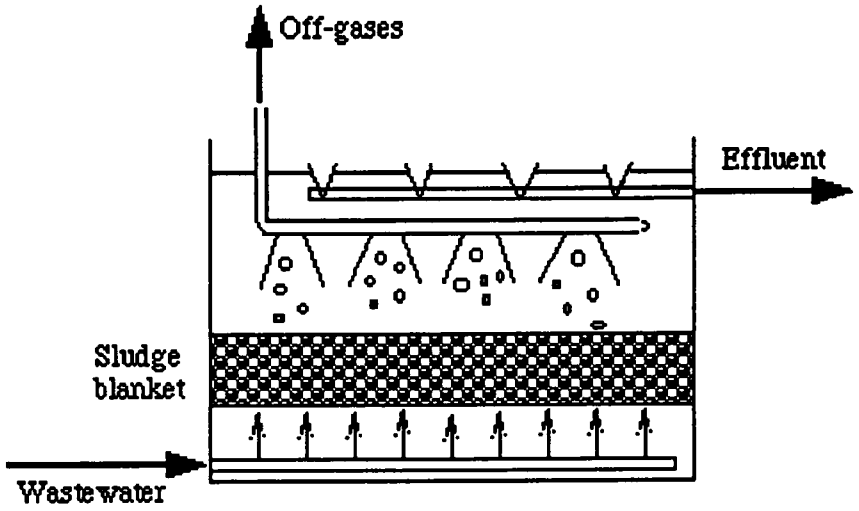


Figure 2.8 Upflow anaerobic sludge blanket (UASB).

process is reduced if the wastewater contains large amounts of suspended solids that have to be hydrolyzed by enzymatic reaction before biodegradation can take place" (Caruana, 1994).

Fluidized Bed Anaerobic Reactor

The Fluidized Bed Anaerobic Reactor (FBAR), which uses small, fluidized media for cell immobilization and retention, is a recent process innovation in industrial wastewater treatment. The classifications of FBAR depend on the system configurations and fluidized media used for microbial growth. In the FBAR, wastewater is generally pumped upward through a fluidized media (bed) such as sand on which microbial growth has been developed. The suspended particles are in constant motion; channeling or clogging should be prevented to achieve efficient substrate transfer. The support granules

should be of low density to minimize energy requirements for fluidization. The recycle effluent is returned to mix with the feed in quantities dictated by the strength of the wastewater and the fluidized velocity. A typical fluidized-bed reactor system is illustrated in Figure 2.9.

The fluidized bed media (growth media for anaerobic microorganisms) play an important role in treatment efficiency of the reactor. Biofilm formation on the fluidized media enables the attainment of a highly active and concentrated microbial population as well as a characteristically long mean cell residence time in the reactor (Boening and Larsen, 1982 and Chen et al., 1985).

An evaluation study of anaerobic fluidized bed treatment of industrial wastewater was conducted by Chen et al. (1988). The reactor is called an anaerobic fluidized bed biofilm reactor (AFBBR) and granular activated carbon (GAC) was used as the growth

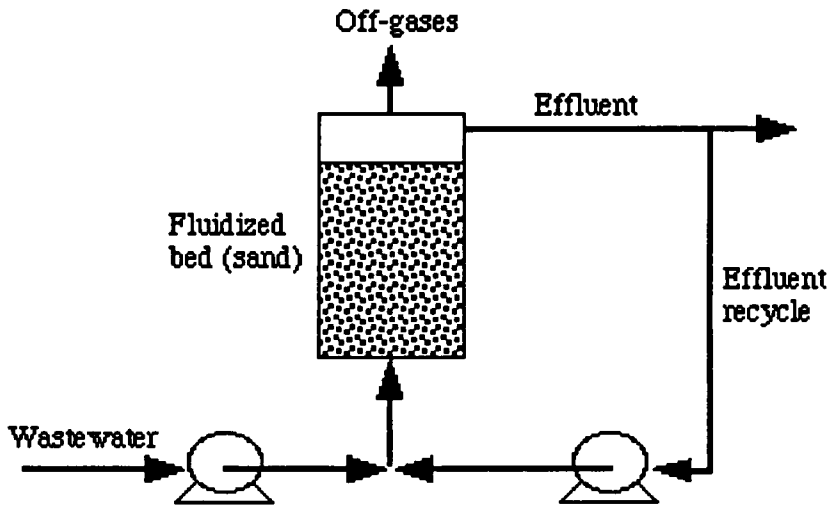


Figure 2.9 Typical fluidized-bed reactor system.

media for cell immobilization and retention. The objective of the laboratory investigation was to evaluate the AFBBR technology as a mean of pretreatment of concentrated industrial wastewater in Taiwan. The wastewater used contained COD (4100-9100 mg/l), BOD (2410-5840 mg/l), nitrogen, phosphorus, solids and volatile solids. They reported over 70% of COD removal have been achieved with 15 l/day of methane produced at high food:microorganism ratios.

In AFBBR, operating problems commonly associated with cell wash-out phenomena are absent, because virtually all active cells are immobilized in the biofilms. The condition of loss of all cell is termed wash-out therefore no growth will occur in the reactor. Furthermore, reactor biomass holdup in the range of 15 to 30 g/l volatile solids are common in AFBBRs designed to treat concentrated, but biodegradable, industrial wastewater (Hakulinen and Salkinoja-Salonen 1982, Schraa and Jewell 1984, and Switzenbaum 1985). Therefore, an AFBBR can function properly under extreme loading conditions because the resulting food:microorganism (F:M) ratios are usually in the range desirable for anaerobic biological wastewater treatment systems. AFBBR technology has advanced because it promotes the recovery of usable energy with good process efficiency and stability. The potential applications of AFBBR for hazardous waste treatment with inhibitory/recalcitrant compositions have also been reported (Fox et al., 1988 and Wang et al., 1986).

Anaerobic Biofilter Reactor

Anaerobic reactors using inert stationary support media to retain the active biomass are generally known as anaerobic biofilters. The biofilter reactors can be operated either in up-flow mode as shown in Figure 2.10 or in down-flow mode (Eckenfelder, 1989). In design, the biofilters are submerged percolating filters, full of

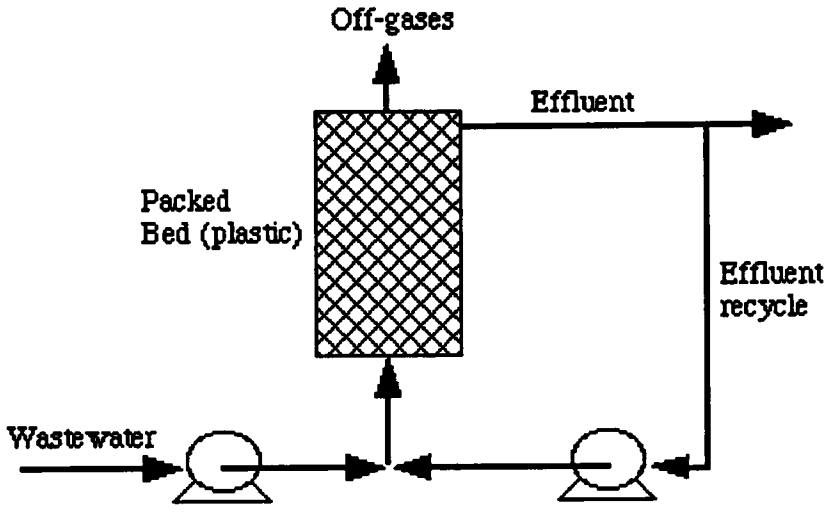


Figure 2.10 Anaerobic biofilter reactor system.

wastewater so that no oxygen can diffuse into the reactor, and are operated using a wide variety of media, ranging from mineral to random-pack plastic filter media (Gray, 1989). Particularly, mineral media such as porous stone, gravel, and pottery fragments are of the favorites. In contrast, most anaerobic biofilters use plastic media because the media have much greater specific surface area and a lower density compared to the mineral media (Anderson et al., 1984). The primary functions of packed media are to retain the biological solids and allow a mechanism for separating the solids and the gas produced in the digestion process. The shape and diameter of both the media and reactor are important factors that affect the stability of attached film (Berg and Lentz, 1979 and 1980). Different support material arrangements result in significant different performance characteristics. Thus, the nature and arrangement of the support media greatly affect the process, and an optimal support medium has not yet been found (Hawkes and Hawkes, 1987). This

subject is discussed by Young and Dahab (1983); Wilkie et al. (1983); and Berg and Kennedy (1981). Other factors such as gas production can also dislodge the film, although the gas flow may also reduce the risk of filter medium clogging.

Anaerobic biofilters are ideal for relatively cold and dilute wastes because they have an extremely high mean cell residence time to hydraulic retention time ratio. This characteristic renders the process a high degree of stability, an excellent resistance to inhibitory compounds, and a satisfactory performance even at low temperature (Gray, 1989). The applications of biofilters include treating sewage, starch, whey, cellulose, distillery, pharmaceutical, and fish processing waste, with an average COD reduction rate between 80% and 90% at a typical organic loading of 3.5 kg/m^3-d (Gray, 1989). At present, the major use of anaerobic biofilters has been removing nitrates from sewage effluents (denitrification). Biofilter reactors have advantage over UASB reactors in that they are not susceptible to washout by high hydraulic-shock loads. However, the limitation of biofilter systems is treating wastewater with relatively low suspended solids, as the high concentrations of solids may blocked the filter medium. Therefore, a pretreatment step is included to remove excess suspended solids prior to entering the biofilter reactor or the biofilter is coupled with other bioreactor systems (for example, an anaerobic contact reactor because the effluents from this process are largely free from suspended solids).

2.1.5.10 SEQUENCING BATCH REACTOR

The sequencing batch reactor (SBR) (or semi-batch biological reactor) is not new. In fact, it preceded the development of continuous-flow activated sludge technology. Barth (1981) traced the history of SBR technology to the modern era of continuous flow

activated sludge. The SBR is actually a fill-and-draw activated sludge system operated in a batch process. Each tank in the SBR system is filled with wastewater during a discrete period of time and then operated in a batch treatment mode. After treatment, the mixed liquor is allowed to settle for a predetermined amount of time, and then the clarified supernatant is withdrawn from the tank.

Process Description

The SBR system may be composed of one or more tanks. In biological waste treatment, each tank in the system has five basic operating modes or periods, each of which is named according to its primary function. These operating modes are fill, react, settle, draw, and idle and occur in a time sequence. Figure 2.11 illustrates the single tank SBR operation during a single cycle. During the fill mode, the raw wastewater is received. The react portion of the cycle provides the time to complete desired reactions with aeration. The settle mode provides the time to separate the microorganisms from the treated effluent. The draw portion of the cycle provides for the discharge of treated effluent, and, finally, the idle mode is the time after discharging the tank and before refilling. The settling characteristics for microorganisms developed in the SBR depend upon the fill:react time ratio, which in turn affects the maximum substrate concentrations in the reactor.

A study pertaining to the effect of fill:react ratio on SBR performance was conducted by Dennis and Irvine (1979). The single tank system is applicable for a non-continuous flow situation, but a multiple-tank system is required to accommodate a continuous flow of wastewater. In a multiple-tank system, the reactors fill in sequence, the criterion being that one reactor must have completed the draw mode prior to another

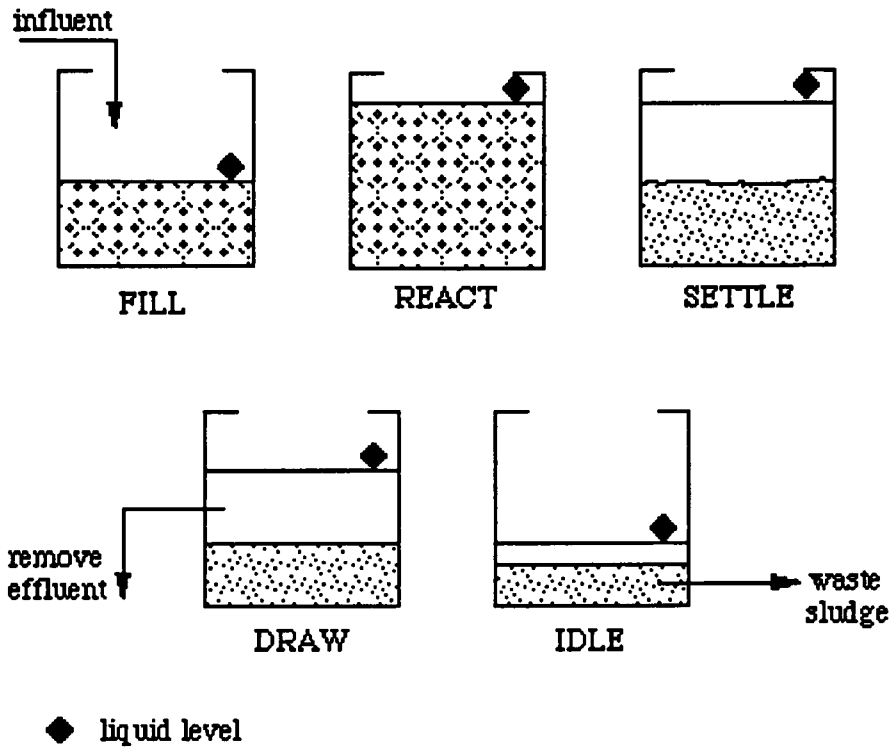


Figure 2.11 Typical SBR operation for one cycle.

completing fill. The microorganisms remain in each reactor until wasting is necessary. Wasting is a process of removing the activated-sludge from the system. The time between wasting may range from bimonthly in a low-yield single-tank system to once during each cycle in a high-yield multiple-tank system.

Each tank in the SBR system is operated such that either plug-flow or completely mixed behavior is promoted. The degree of soluble substrate accumulation in the mixed liquor during fill and the time provided for the react mode determine the extent to which a SBR system simulates an ideal plug-flow CFS (continuous flow system). However, an

SBR system with an extended fill period with little accumulation of soluble substrate resembles a completely mixed CFS (Irvine & Busch 1979).

One modification of the SBR process, the intermittent cycle extended aeration system (ICEAS), operates on the principle of continuous feed as in a continuous-flow activated sludge system, but with intermittent withdrawal as in the SBR system. The ICEAS system has been used extensively in Australia.

Applications

Reviews indicated that the SBR system has advantages over other biological reactors in wastewater treatment applications. In the past decade, SBR has been shown in full-scale operation to be capable of achieving biochemical oxygen demand (BOD) and suspended solids (SS) reductions, and nitrogen and biological phosphorus removals. SBR is also feasible for the treatment of hazardous waste (Irvine Ketch et al., 1985). Effluents limits of 10 mg/l BOD and SS are attainable. Excellent effluent quality can be achieved in both high and low loading, and biological phosphorus removal is easily attained in both cases. Irvine et al (1979), Alleman and Irvine (1980), and Irvine et al (1983) showed that SBRs provide a viable treatment alternative for nitrogen removal without supplemental carbon addition. In addition, Palis and Irvine (1985) conducted a bench-scale study of nitrogen removal in a low-loaded single tank sequencing batch reactor. Their results showed approximately 90% total nitrogen removal in low-loaded (0.02 to 0.05 kg BOD_5/d-kg MLSS) SBR operation. Another study conducted by Manning and Irvine (1985) showed that biological phosphorus removal can be achieved in an SBR with a relatively low ratio of chemical oxygen demand and total kjeldahl nitrogen (COD/TKN). The process produced a highly nitrified effluent and a sludge with

excellent settling characteristics. Furthermore, the SBR can be designed to operate as non-nitrifying system and still be capable of biological phosphorus removal.

Pilot-scale experiments were conducted to investigate the feasibility of a three-stage SBR system process for carbon and nitrogen removal (Jones et al., 1990). Stage 1 accomplished carbon removal in an SBR operated under high loading conditions. The function of stage 1 is to rapidly uptake organic material at initially high concentrations, without complete metabolism of the organic wastewater constituents (that is, incomplete conversion to carbon dioxide and cellular end products). The substrates that are not completely metabolized within the time frame provided remain available, and these sequestered organic substances are further use by microorganisms during denitrification. Stage 2 performs the nitrification process in a fixed-film reactor, and the last or third stage does denitrification using "sequestered" organic substrates (more rapid than under "endogenous" conditions). The overall nitrogen removal capacity of the system is limited to about 75%, not as a result of kinetic limitations but because of the necessity of retaining influent nitrogen in the settled sludge from the first stage.

Flexibility is one of the main reasons this process is preferred over other biological treatment processes. The advantages of SBR system over other treatment processes has been frequently compared in the literature. Among the prominent points are (Arora et al 1985):

- An SBR serves as an equalization basin during fill and therefore can easily tolerate peak flows and shock loads of BOD without degradation in effluent quality.

- Because of the periodic nature of SBR, effluent discharge can be controlled until specific requirements are met.

- Mixed liquor solids cannot be washed out by hydraulic surges because they can be held in the tank as long as necessary.

- Return activated sludge pumping is not required, because the mixed liquor is always in the reactor.

- Solid-liquid separation occurs under nearly ideal quiescent conditions. Thus, during the settling period, no short-circuiting will exist.

- Because the dissolved oxygen concentration is zero or near zero during anoxic fill, it provides for a greater oxygen-driving gradient during the react period.

- Filamentous growth can be easily controlled by varying the operating strategies during fill.

- An SBR can be operated to achieve nitrification, denitrification, or biological phosphorus removal without chemical addition.

- The ribonucleic acid (RNA) content of the microorganism in the SBR is three to four times greater than would be expected in the conventional continuous-flow system.

Arora et al (1985) also reported that all the plants evaluated for that study are producing acceptable quality effluent, and different water quality objectives (carbon, nitrogen, and phosphorus removals) are frequently achieved in an SBR by appropriate changes in the operating strategy; such changes can be made easily by the microprocessor settings at the control panel. A problem encountered by all U.S. SBR plants examined was the operation of the decanter mechanism. The problem, which stems from mixed liquor suspended solids entering the decanter piping during fill, react, and settle periods, has

been corrected. It is very desirable that improvement of decanter equipment is encouraged, because this device is crucial to the successful SBR operation.

A major difficulty encountered in consideration of any new process is development of realistic cost estimates for the proposed system. The approach for promoting a new process often overstates the advantages of the system and underestimates its cost. Kethhum et al (1979) did a cost analysis of sequencing-batch reactors. He made an initial investment cost comparison among sequencing batch, activated-sludge, non-aerated lagoon, and aerated-lagoon systems to treat wastewater from small rural communities. The analysis showed that the sequencing-batch system using a single-cell lagoon required the least cost of the alternatives considered.

Recently, results from bench-scale studies indicated that the SBR can provide substantial savings in energy and cost by biologically removing organic compounds found in hazardous waste, rather using with activated carbon (Irvine et al., 1984). Based on these SBR capabilities, the New York State Energy Research and Development Authority (NYSERDA) and CECOS International agreed to co-fund a full-scale SBR study to demonstrate the SBR for biological treatment of hazardous wastes at CECOS (Herzbrun et al., 1985). Various operating strategies (different detention times, feed volume, cycles per day etc.) were deployed to determine the SBR limitations. Furthermore, cold weather simulation was conducted to test the viability of full-scale SBR operation during extended winter periods. Herzbrun stated that a 1900 m^3 SBR was constructed and tested for a month. The results achieved were TOC degradation of 76% and Phenol removal of 99.0% during the first month of operation; all other data indicated proper performance.

2.1.5.11 BIOLOGICAL AERATED FILTER

Many efforts have been made to develop high-rate, biological, fixed-film processes that reduce reactor volume and land area requirements. Examples of such processes reported in the literature are an upflow fluidized bed reactor with preoxygenation of the influent (Jeris, 1977); an upflow granular media reactor with air sparging from the bottom of the media (Young and Steward, 1979); and upflow plastic media reactors or aerated submerged biological filter with air sparging from the bottom of the reactor (Rusten, 1984; Iida and Teranishi, 1984).

A recent development in high-rate, biological, fixed-film process treatment is the Biological Aerated Filter (BAF) or Biocarbone. BAF is an innovative technology that combines aerobic degradation of pollutants and physical retention of suspended solids in one reactor. High concentrations of active biomass attach to the expanded medium in an aerated, packed-bed filter resulting in high removal efficiency of BOD. High-rate biological treatment and in-situ removal of suspended solids are claimed as advantages of the process (Dillon and Thomas, 1990). This technology is used on a large scale at about fifty installations worldwide (Rogalla et al. 1990).

Process Description

The BAF system is similar to the conventional rapid sand filters (refer to Viessman and Hammer, 1993 for sand filters), except that air is sparged into the lower portion of the filter bed, and a coarser filter medium is used (granular media). The filter grains retain the suspended solids and provide a surface for biofilm development. The filter medium is supported by an underdrain that contains plastic nozzles to receive treated wastewater. The process air header is located in the media about 30 cm (1 ft) above the underdrain. Wastewater is fed into the mixing zone from above the filter and flows

downwards, counter-current to the flow of process air. The downflow immersed granular bed is designed for high oxygen-transfer by counter-current aeration (Rogalla 1990). A schematic diagram of biological aerated filter is shown in Figure 2.12.

Backwashing is an integral part of the BAF process in order to flush out the solids removed by filtration and the excess biological solids produced. In addition, counter-current backwash rinses the top of the filter bed, where the solids retention is greatest and where the most intensive rinsing is required (Rogalla et al. 1990). Filtration efficiency decreases because of a low rate of filtration and passage of excess turbidity through the bed. Therefore, backwashing is necessary for process cleaning of the bed.

The backwash frequency requirement is determined by the influent total suspended solid concentration as well as the hydraulic application rate and the solids accumulation capacity of the granular medium. Under average operating conditions, granular-media filters are backwashed about once every 24 hours (Viessman and Hammer, 1993). In BAF, backwashing is initiated either by a high water level or on a timed basis. The backwash sequence has been completely automated by the use of a microprocessor and automated valves on the influent, effluent, process air, back wash air, and water lines. The sequence includes air scour, followed by combined air scour and water backwash (Stensal et al. 1988). For different types of filtration backwashing systems, the reader is referred to Metcalf and Eddy, Inc. (1979).

Applications

The BAF is a relatively new innovative process for wastewater treatment; thus limited information is available describing design criteria and treatment performance. However, the application and performance of the BAF have been evaluated by numerous government agencies (Stensel and Lee, 1983; Stensel et al., 1984; Stensel et al., 1988;

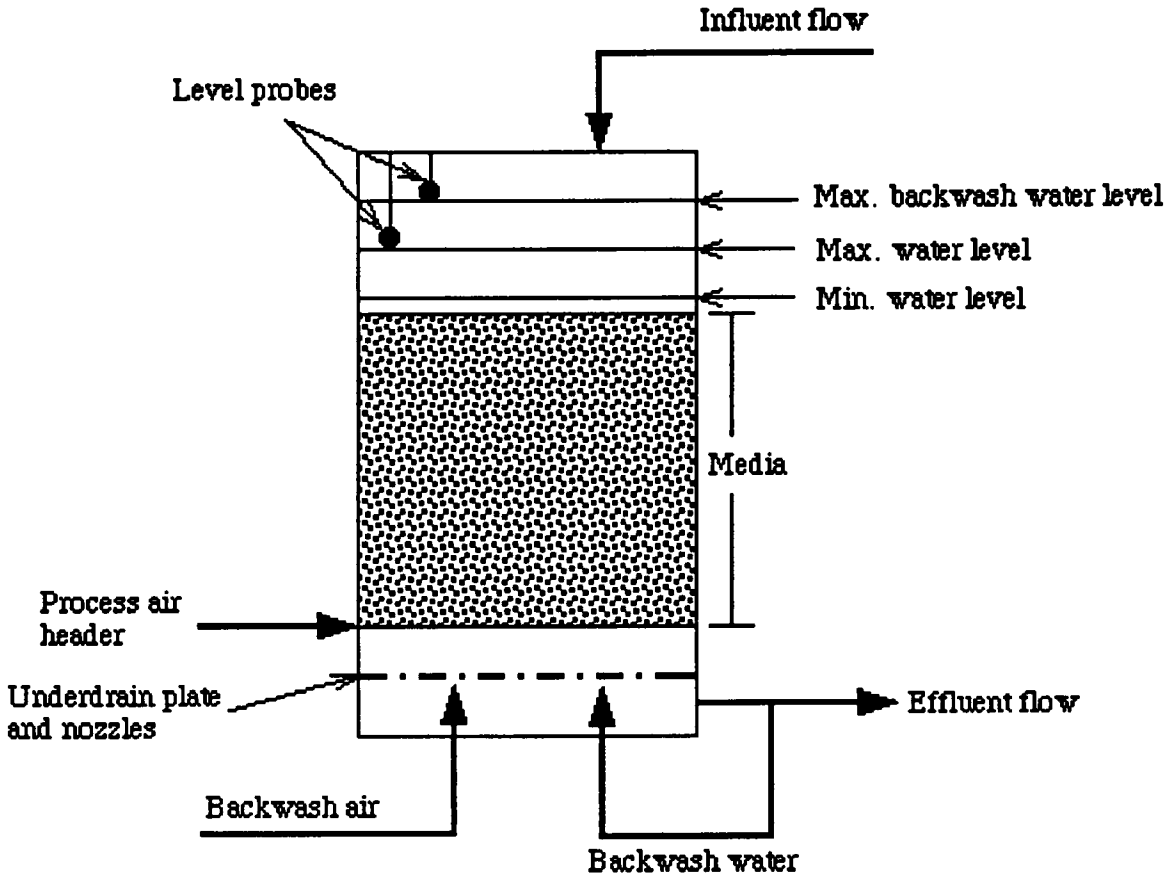


Figure 2.12 Schematic of a biological aerated filter cell.

EPA, 1988). Examples are the two year evaluation of a two-cell, full-size BAF wastewater treatment unit (Stensel et al. 1988). The two BAF units are operated at different loading rates: a higher loading rate for biochemical oxygen demand (BOD) removal only and a lower loading rate for combined BOD removal and nitrification. Their investigations include the effects of media size and backwash frequency; effects of organic loading and wastewater temperature on effluent quality; nitrification performance; sludge production; oxygen utilization efficiency; and oxygen requirements. Their study

concluded that the backwash frequency and media size are important operating and design parameters for the BAF system. The effluent BOD and suspended solids concentration are related to the soluble BOD volumetric loading and reactor temperature. The oxygen utilization efficiency is related to the amount of air supplied per unit of BOD applied to the BAF unit. Mathematical relationships are also developed to predict oxygen consumption and sludge production as a function of influent soluble BOD and suspended solids to influent total BOD ratios.

Another study conducted by Rogalla et al. (1990) evaluates the application of BAF for the nitrification and phosphorus precipitation processes. The objective of their study is to optimize a compact nutrient (phosphorus and nitrogen compounds) removal system by combining a settler and the BAF. A full-scale case study by Rogalla et al. (1990) verified that the nitrification and effluent objectives of less than 10 mg/l for BOD, suspended solids and TKN can be achieved with empty bed contact times of about 2.5 hours.

A mathematical biofilm model has been developed to describe substrate and oxygen utilization as well as various oxygen transfer pathways for the BAF reactor (Lee and Stensel 1986). Several assumptions made in the biofilm model development are:

1. Even distribution of biofilm throughout the entire supporting media.
2. Constant oxygen and substrate diffusion coefficients within the biofilm.
3. Plug flow and steady-state operation.
4. Biological kinetics of oxygen and substrate utilization within the biofilm that can be described by the Monod kinetic model.

The reader is referred to Lee and Stensel (1986) for the mathematical equations describing the biofilm model. The validity of the biofilm model is verified by a comparison of model simulations with experimental data. Their findings show that the biofilm model can provides information for substrate removal, oxygen utilization, and oxygen transfer in the BAF reactor. Furthermore, the accuracy of the biofilm model simulation is affected by the biofilm thickness and distribution assumptions. The proportion of biofilm surface area in contact with air bubbles is another important parameter that is critical in biofilm model simulations.

Other research concerning BAF applications include aerated biofilters for nitrification and effluent polishing (Paffoni et al. 1990), a pilot-scale evaluation of BAF for complete treatment of settled sewage (Dillon and Thomas 1990), and BAF evaluation coupled with on-line pollution sensors based on UV absorption for measuring influent and effluent COD concentration (Rogalla 1990).

Since the newly developed BAF system was introduced in the early 1980s, many efforts has been made in the past few years to evaluate the applications of BAF for sewage wastewater applications. Unfortunately, there is not much work pertaining to industrial wastewater applications.

2.1.5.12 CONCLUDING REMARKS

In Chapter 2.1.5, the biological treatment processes and bioreactor design principles that enjoy current applications and that will likely be used in the future for industrial wastewater treatment are discussed. The advantages and disadvantages, and some control problems associated with various treatment processes, are also presented.

The basic features of anaerobic reactors are compared in Table 2.5. The major control parameter for the anaerobic processes is pH, because the methanogenic bacteria are very sensitive to pH changes (Chapter 2.1.5.8). An alkaline addition system is usually incorporated to reduce the acidity of the wastewater.

A summary of those aerobic systems with fixed- and dispersed-growth processes is provided in Table 2.6. The "control parameters" defined in Table 2.6 are those variables that have more impact on the process. Therefore, the basic control parameters such as dissolved oxygen, suspended solids, and inhibitor concentrations are not included. The "control concerns" feature the problems associated with the bio-treatment process. On the other hand, sensitivity is defined as the degree of effect those variables (temperature, pH, toxins, and organic loading) have upon the process. The operating costs are not included, but some fixed-film processes such as RBC and TFP usually have higher capital costs and lower operating costs. Furthermore, the energy requirement for percolating filtration (fixed-film process) are low compared to dispersed-growth reactors such as activated sludge (Gray, 1989). Although the SBR and BAF processes are tested in full-scale operation (refer to Chapter 2.1.5.10 and 2.1.5.11), the information regarding design, kinetic, and control principles are still under investigation and are not well-documented in the literature. These advanced treatment processes, however, are more robust compared to those conventional treatment processes. For example, SBR can achieve nitrification, denitrification, or biological phosphorus removal without chemical addition and is even feasible for hazardous waste reduction.

Finally, the information provided in Chapter 2.1.5 is an attempt to provide knowledge regarding reactor designs, their applications, and some control and instrumentation concerns. For more detailed information, the reader is referred to the cited references.

Table 2.5 Comparison of features of various anaerobic reactors[1] (Gray, 1989).

Feature	ANWR[2]	ANCR[3]	UASB[4]	FBAR[5]	ANBR[6]
Commercial Applications	stabilization	stabilization BOD removal	BOD removal	BOD removal toxic removal	BOD removal nitrification
Ease of start-up	1	5	4	3	2
Ease of operation after proper acclimatization	2	2	5	3	3
Good process control possible under transient influent conditions	1	5	3	3	3
Shocks resistance due to:					
Temperature	1	3	5	5	5
toxics	1	3	5	5	5
high organic load	1	4	5	5	5
Tolerance for influent quality variations	1	4	2	4	5
Tolerance of high influents solids fluctuations	4	3	1	2	2
Incorporation of sludges from pretreatment and aerobic polishing	5	4	1	1	1
Reference (Chapter)	2.1.5.8	2.1.5.8	2.1.5.9	2.1.5.9	2.1.5.9

1. Efficacy rating from 1 to 5 (1=lowest and 5=highest)
2. ANWR - anaerobic flow-through digester without recycle
3. ANCR - anaerobic digester with recycle
4. UASB - upflow anaerobic sludge blanket reactor
5. FBAR - fluidized bed anaerobic reactor
6. ANBR - anaerobic biofilter reactor

Table 2.6 Typical features of various aerobic bio-treatment processes.

Features	ASP	CMAL	ADP	TFP	RBC	SBR	BAF
Commercial applications	BOD removal nitrification denitrification nutrient removal	BOD removal stabilization	sludge digestion	BOD removal nitrification	BOD removal nitrification	BOD removal SS removal nutrient removal toxins removal	BOD removal nitrification nutrient removal
Control concerns	sophiscated control bulking problems settling problems	limited control short circuting solids deposition aerators problems weather	temperature dependent dewatering problems	limited control recirculation clogging oxygen transfer	limited control oxygen transfer no recirculation	limited info. decanter problems fill to react ratio	limited info. oxygen transfer
Control parameters	influent flow rate sludge recycle rate sludge wasting rate aeration rate F/M ratio temperature pH	influent flow rate aerator speed detention time	temperature pH influent flow rate aerator speed	rotational speed influent flow rate temperature contact time	depth of immersion rotational speed temperature influent flow rate	fill time react time aeration rate influent flow rate	limited info. temperature
Sensitivity to:							
temperature	moderate	moderate	high	high	high	moderate	moderate
pH	na	low	high	na	na	na	na
toxic shocks	high	low	na	low	low	low	na
organic loading	high	low	na	low	low	low	na
Capital cost	low	low	low	high	na	low	na
Odour	low	yes	no	moderate	moderate	na	no
Fly	no	yes	no	high	high	na	no
Chapter (ref.)	2.1.5.1	2.1.5.2	2.1.5.3	2.1.5.4	2.1.5.5	2.1.5.10	2.1.5.11

na - information not available
ASP - activated sludge process; CMAL - completely mixed aerated lagoon; ADP - aerobic digestion process;
TFP - trikling filter process; RBC - rotating biological contactor; SBR - sequencing batch reactor; BAF - biological aerated filter

2.2 INSTRUMENTS AND MEASUREMENTS OF BIOREACTOR

The maintenance of optimal conditions for wastewater treatment in the complex environment of a bioreactor requires the control and measurement of several important parameters. Actual process control strategies for industrial biological treatment units are primitive in comparison to those used in the chemical industry, both because of the lack of biosensors for on-line measurements and the lack of reliable, quantitative, dynamically accurate models. In this chapter an attempt is made to classify different sensors with respect to their function and their reliability for on-line use.

Control of a process involves measurement and control of key variables. In general, the number of key variables for control of a biological process is larger than those for control of ordinary chemical processes. Key variables for control of biological processes include physical, chemical and biological parameters. Examples of physical parameters are temperature, flow rates, liquid level and impeller speed. Measurements of physical variables connected with biological processes is not the focus of this study, and the reader is referred to Onken et al. (1985) for further information on this subject. Measurement of chemical and biological variables receive the major emphasis in this study. However, some of common sensors for physical-variables measurement are provided in Chapter 2.2.4.

Analysis of the exhaust gas from biological processes is relative straightforward and is not included in this study. Again, the reader is referred to Onken et al. (1985). On-line techniques are preferable for real time measurement and control, but both on-line and off-line techniques are discussed. Thus, this section will briefly introduce some perspective and opportunities for instrumentation in bioreactors. In addition, it will serve as a background for the research of advanced control strategies and instrumentation of bioreactors for industrial wastewater treatment.

2.2.1 INSTRUMENTATION

Instrumentation and automation play an increasingly significant role in the overall control of biological treatment plants. A major portion of this study centers on measurements associated with the aqueous feed and effluent streams as well as those measurements associated with the active biological medium. Typically, biological treatment systems for industrial wastewater have on-line monitors for temperature, pH, dissolved O_2 and TOC and off-line monitors for BOD, COD, total suspended solids and settleable solids. Some of these measurements are discussed in Chapter 2.1.4.1. Other measurements may be required by permit, such as tests for nutrients and whole effluent methods that involve exposure of living organisms to the wastewater. Still other measurements are for the protection of the microorganisms in the bioreactor; these measurements are to monitor the presence of species that may be toxic or inhibitory to the microorganisms or to assess the vitality of these organisms.

The pH of the biological process is an important variable; measurement is usually done electrochemically. Dissolved gases, O_2, CO_2 and volatile organic compounds (VOCs) are important variables in biological processes. While O_2 and CO_2 may be measured electrochemically, mass spectrometry may be used for these analyses as well as provide analysis for the VOCs (Onken et al., 1985). The use of ion-specific electrodes also enables measurement of many other dissolved inorganic ions. Examples of some commercially available, ion-specific electrodes are presented in Table 2.7. Little is known about the on-line use of ion-specific electrodes, and reader is referred to Phillips (1990).

Several methods exist for measurements relevant to biomass concentration and activity. Turbidity measurements may be done on line. As the biomass concentration decreases, the optical transmittance increases. Hence its turbidity decreases because the

Table 2.7 Ion-sensitive electrodes (Onken et al., 1985).

Ion	Lowest Concentration Range (mol/l) of Application	Interference by Other Ions
NO_3^-	10^{-5}	$Cl^-, Br^-, F^-, NO_2^-, SO_4^{2-}, CH_3COO^-$
S^{2-}	10^{-15}	Hg^{2+}
Cl^-	10^{-5}	Br^-, I^-, CN^-, S^{2-}
I^-	10^{-7}	S^{2-}
K^+	10^{-5}	$Na^+, NH_4^+, Cs^+, H^+, Li^+$
Ca^{2+}	10^{-5}	$Na^+, Mg^{2+}, Pb^{2+}, Fe^{3+}, Zn^{2+}, Cu^{2+}$
Cu^{2+}	10^{-10}	$S^{2-}, Ag^+, Hg^{2+}, Cl^-, Br^-, I^-, Fe^{3+}, Cd^{2+}$

indirect nature of this analysis is subject to interference. Light scattering is another on-line indirect measurement for the biomass concentration. The light scattering can be correlated with biomass concentration (Onken et al., 1985) and is subject to an error of ±10%. Other on-line methods for determining the biomass concentration, such as particle counters, fluorescent measurements, and redox potential measurements, are suggested by Onken et al. (1985).

Enzymatic analysis for many organic and inorganic species is available either on- or off-line. Enzymatic analysis relies on the ability of enzymes to react selectively with some well-defined compounds or substrates. For example, lactose (substrate) analyzes by β-galactosidase (enzyme), β-D-glucose analyzes by glucose oxidase, and primary short-chain alcohols analyze by alcohol oxidase (Onken et al., 1985). Mostly immobilized enzymes on a carrier (such as ion-exchange resin) are used (Onken et al., 1985). Thus

reliable biosensors or indicators of bioactivity are important for successful control strategy.

The problems to be solved in the development of an on-line biosensor (probe) include (Wise, 1990):

- microbial fouling of probes;
- (bio)chemical interference with sensor response in complex analyte (substance to be analyzed) mixtures;
- electrical interference;
- analyte chelation, binding and buffer effects;
- operation under a wide variety of aqueous physiochemical and physiological environment;
- calibration of sensors and routine maintenance of error free calibration;
- poor mixing of large bioreactors; and
- inexpert handling of sensors.

Nevertheless, it is likely that reliable biosensors or other indicators of bioactivity will be available in the near future. For example, optical measurement technology and the use of optic fibers may result in the development of more reliable biosensors (Halme, 1985). "The new technologies which may lead to new breakthroughs in the near future are optics and especially the use of optical fibers, 'on chip' sensors and the enzyme and microbe sensors". Additionally, Ramsey et al. (1985) conclude that both poised potential and fuel cell bioelectrochemical techniques provide simple, rapid, inexpensive and moderately sensitive means for detecting viable biomass. "Such techniques could be cost effective in detecting microbial contamination in samples such as . . . industrial wastewater . . . .".

Considerable effort is now being devoted to the development of more suitable instruments that can provide more detailed information about biological processes, the

need for on-line measurements, and continued improvements in process yields and productivity. Unfortunately, few ideas or developments have yet been realized on a commercial scale, but hopefully it is only a matter of time before this will change.

The following section concentrates on development and innovation in measurement methods and biosensors in the past, present and future. This section does not intend to judge which methods or biosensors being developed are best, but rather to serve as a literature review of development of biosensors or measurement techniques for wastewater treatment applications.

2.2.2 RECENT DEVELOPMENTS IN INSTRUMENTS TECHNOLOGY

Frequently, environmental or process conditions are such that there is a requirement for non-contact sensors or, at the very least, intrinsically safe sensors such as those deploying fiber optics for measurement of a range of physical variables. Unfortunately, non-contact sensing techniques are not yet practicable when monitoring such variables as treatability, toxicity and concentrations of nutrient/substrate, heavy metal ions and trace organics that would be required, for example, in certain wastewater applications. However, recent developments in advanced measurement techniques, microbial electrodes, and fiber optic technologies reveal significant improvement in instrumentation. For example, the newly developed respirometer is capable of indicating of the arrival of toxic substances at the inlet to a treatment works (Meredith, 1990). This respirometric technique enables the plant operator to continuously monitor the respiration rate of the biomass; therefore, it can rapidly identify the presence of an inhibitor as the respiration rate decreases. In addition, there is an innovative chemical oxygen demand

(COD) rapid tester for continuous measurement of COD in a treatment stream (Meredith, 1990).

One of the methods to monitor heavy metal or trace organics concentrations is the deposition of appropriate sensitive materials on the gates of an array of metal oxide field effect transistors (MOSFETS), which are integrated with a microprocessor onto a single chip. For example, soluble phosphate and/or borate glasses containing oxides of the heavy metals of interest are deposited onto the gate of a MOSFETS, forming an ion-selective electrode for monitoring toxic metal concentrations (Briggs and Grattan, 1990). Other techniques for measurement of trace organics, toxicity, and treatability include an enzyme modified field effect transistor (FET) sensor (Sibbald 1986, 1985) and an immobilized enzyme thermistor based on measurement of the heats of reaction (Mosbach and Dannielson 1987). In principle, these are cheaper to fabricate and install, frequently more useful and of more general applicability than current conventional sensors.

Some of the recent innovations in measuring or monitoring techniques are worthy of mention. Thus, this section provides the information of some exciting developments in instrumentation. The principles and applications of fiber-optic sensors and microbial sensors for biological treatment processes are also discussed.

2.2.2.1 OPTICAL MEASUREMENT METHODS

An attractive solution to many measurement problems in the wastewater industry is the use of optical fibers and electro-optics coupled with microprocessors, particularly where inherent safety considerations are paramount. Examples are applications such as in a sewer system where the environment is particularly hostile and in the monitoring of a flammable fluid. Optical sensors may be defined as those devices which use

IR/visible/UV radiation to detect a change in a variable to be measured, regardless of the nature of the interaction of the light with the measurand or variable to be measured (Briggs and Grattan, 1990). Fiber optic sensors can be classified as "intrinsic" and "extrinsic" types. The extrinsic fiber sensors use the fiber primarily as a means of guiding light through the fiber to the measurand region, where its polarisation, wavelength, phase or intensity is modulated by the measurand and then guided to a receiver where signal processing occurs. In an intrinsic fiber optic sensor, the fiber itself acts as the sensor, and the propagation of light within the fiber is disturbed in a measurable way. For further information on fiber optic biosensors, the reader is referred to Schaffar et al. (1991) and Arnold (1991). The merits and applications of fiber optic techniques may be summarized as having inherent electrical safety and freedom from interference from electromagnetic "noise". Furthermore, they are small, light and largely free from cross-talk. This new technology is becoming accepted for measurement applications.

It is beyond the scope of this report to discuss the very wide range of optic phenomena used in optical sensors; however, there are a number of review texts (Wolfbeis, 1990; Grattan, 1987; Culsaw, 1986; and Pitt et al. 1985) contain opinions of a large number of experts in the field of fiber optic chemical sensors. Summary descriptions of various fiber optic sensor technologies are provided in subsequent paragraphs.

A significant application of lasers and fiber optics concerns flow measurement through the use of the laser (Doppler) anemometer, which has been commercially available for some years, but at a significant cost (Briggs and Grattan, 1990). Laser anemometers are non-contact optical instruments used for fluid flow structure (gases and liquids) investigation. The unique advantages over other fluid flow instrumentation are (Briggs and Grattan, 1990):

- non contact optical measurement;
- no calibration (no drift);
- well defined directional response;
- high spatial and temporal resolution; and
- multi-component directional measurements.

Medlock (1986) proposed and discussed other fiber optic instruments such as vortex shedding devices. Blum and Gautier (1991) studied the bioluminescence- and chemiluminescence-based fiber-optic sensors for adenosine triphosphate (ATP) and other analytes including ammonia, ethanol, and phosphate. Bioluminescence, or "living light," is a very diverse and unique natural phenomenon and is the emission of light by living organisms (e.g. firefly). Chemiluminescence refers to a synthetic chemical compound such as luminol which can undergo oxidation in the presence of hydrogen peroxide to produce light. Blum and Gautier (1991) also developed a continuous-flow bioluminescent method using a specially designed flow cell to facilitate automation. Fiber optic sensor technology offers a great analytical potential that is far from being completely exploited.

2.2.2.2 MICROBIAL SENSORS

Effective control of biological treatment processes is essential for maintaining high quality effluent that meets the more stringent requirements of pollution control. Hence, effective control calls for a biosensor that is capable of performing rapid, continuous, and sensitive on-line monitoring and/or measurements of biological processes. Recent developments in biosensors include enzymatic sensors and microbial sensors. These

developments have predominantly utilized enzyme-catalyzed reactions and microbially-catalyzed reactions. The enzyme sensor may be highly specific for the substrates of interest, but the enzymes employed are generally expensive and unstable. Therefore, the microbial sensor is considered to be more suitable for on-line monitoring and control of biochemical processes. The advantages of microbial sensors are (Karube and Chang, 1991):

- less sensitive to inhibition by solutes and are more tolerant to sub-optimal pH and temperature values than enzyme probes;
- longer lifetime than enzyme electrodes; and
- cheaper, because an active enzyme in a microorganism need not be isolated.

The disadvantages are (Karube and Chang, 1991):

- require longer time to return to baseline signal (original set-point) after use;
- some have longer response time than enzyme electrodes; and
- because microorganisms contain many enzymes, care must be taken to assure a degree of activity (e.g., by optimizing storage conditions or adding specific enzyme reactions).

Microbial sensors are devices incorporating a biological sensing element (a microorganism) that can specifically recognize species of interest, either intimately connected to or integrated within a suitable transducing system [dissolved oxygen (DO) electrode]. The function of the transducer is to quantitatively convert the biochemical signal into an electronic signal that can be suitable processed for output. The transducer

system can be a potentiometric, amperometric, thermometric, optical, or other measurement system. The operations of microbial sensor are described by Karube and Chang (1991) as five-step processes:

1. The substrate is transported to the surface of the sensing system in a vessel.
2. The substrate diffuses through the membrane to the immobilized microorganism.
3. The reaction occurs at the immobilized microorganism.
4. The products are formed in the microorganism and are transported through the teflon-membrane to the surface of the detector.
5. The products are measured at the detector surface.

A simplified construction of a microbial electrode (biosensor) is shown in Figure 2.13. This oxygen electrode consists of a Teflon membrane, a platinum cathode, an aluminum anode, and a saturated potassium chloride electrolyte. The microorganism-immobilized membrane is placed on the Teflon membrane and fixed in place using either a bored cap or a dialyzed membrane o-ring.

Many kinds of microbial biosensors have been developed, some of which have already been used for wastewater and environmental monitoring. The characteristics of these microbial sensors are summarized in Table 2.8. The on-line uses of these biosensors are still to be investigated.

The performance characteristics of any individual microbial biosensor depends on its components. The selectivity of the biosensor is determined by the nature of the biological element, for example, immobilized microorganisms. The response time is determined by the characteristics of the membrane separating the biological element from

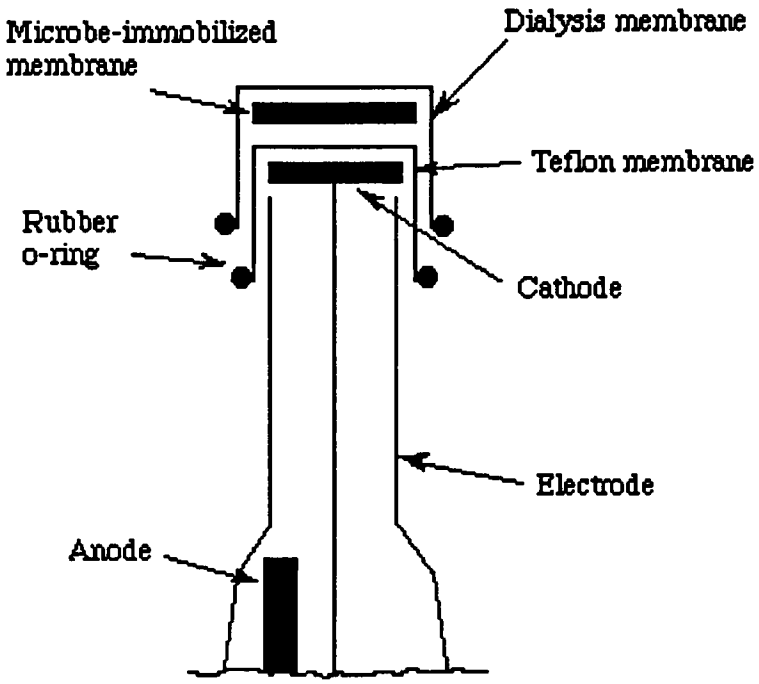


Figure 2.13 Construction of a microbial electrode (biosensor).

Table 2.8 Characteristic of microbial sensors (Karube and Chang, 1991).

Sensor	Immobilized Cells	Type of Electrode	Range (mg/l)	Response (min)	Stability (days)
Glucose	*Pseudomonas fluorescens*	Oxygen	3-20	10	14
Acetic acid	*Trichosporon brassicae*	Oxygen	10-200	15	30
Ammonia	*Nitrifying bacteria*	Oxygen	3-45	5	20
Methanol	*Unidentified bacteria*	Oxygen	3-22	15	30
Ethanol	*T. Brassicae*	Oxygen	3-30	15	30
Nystatin	*Saccharomyces cerevisiae*	Oxygen	1.2-800	60	-
Carcinogen	*Bacillus subtilis*	Oxygen	1-10	60	-
BOD	*Trichosporon cutaneum*	Oxygen	3-30	10	30
Cell population	-	Fuel cell	10^6-10^{11}	15	60
Formic acid	*Clostridium butyricum*	Fuel cell	1-1000	10	30
Glutamic acid	*Escherichia coli*	CO_2	8-800	5	20
Lysine	*E. coli*	CO_2	10-100	5	20
Nicotinic acid	*Lactobacillus coli*	pH	10^{-2}-5	60	30

the external environment. The stability and operational life of biosensors are determined by the inherent stability of the biological element and the method used to immobilized it. And finally, the sensitivity and dynamic range are determined by the transducer (Phillips 1990).

2.2.2.3 MICROBIAL BOD SENSORS

Biochemical oxygen demand (BOD) is one of the most widely used measurements of aquatic pollution. It has long been used to measure the relative oxygen requirements of wastewater and the quality of receiving waters and was discussed in Chapter 2.1.4.1. Its application may also be extended to process control and optimization of wastewater treatment facilities. The conventional BOD test takes 5 days, which is too long for use in process control. The five-day BOD test should be used only as a check or confirmation method. Total organic carbon (TOC) and chemical oxygen demand (COD) assays measure total organic matter, but they do not provide a valid measure of biologically degradable organic matter (Sherrard et al., 1979), therefore reducing their importance in real-time control of a particular treatment system. A method for rapidly and continuously measuring biodegradable organic matter would be useful in control of biological wastewater treatment processes.

Reviews indicate that the use of a biofilm electrode can provide measurement of BOD in less than 20 minutes. The first report of rapid BOD measurement with biofilms was by Karube et al.(1977), who developed a sensor for BOD using a microbial electrode. The microbial electrode consisted of a bacteria-collagen membrane (biofilm) and an oxygen (dissolved oxygen) electrode. The biofilm was prepared from an aerobic enrichment culture of soil microorganisms and was applied to the teflon-covered surface

of a DO electrode. It is known that oxygen is consumed by the respiration of aerobic microbes. Thus, dissolved oxygen is consumed by the microbes in the collagen membrane immersed in the wastewater sample solution until a steady state is reached with respect to the diffusion of oxygen from the solution. The respiration rate of microbes is measured by the DO electrode; as the content of microbes is high in the membrane, the respiration rate is dependent on the concentration of nutrients in the sample solution. This result provides an estimation of BOD in wastewater. The BOD of industrial wastewater can be estimated within 15 minutes by using the microbial electrode. The immobilized microbes are stable against heavy metals ions such as Hg^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, and Pb^{2+} but are inactivated in the collagen membrane at $6.5 < pH > 8.0$, as well as temperatures above 50°C.

Karube et al (1977) also developed a biofuel cell utilizing a microbial electrode that consists of a single species of bacteria. In contrast, the microbial electrode uses many species of microorganism obtained from soil. In spite of using only a single species, the biofuel cell was capable of giving reproducible results for the estimation of BOD.

The development of a BOD sensor utilizing yeast microorganisms was reported by Kulys and Kadziauskine (1980). The sensor consisted of yeast cells (*Hansenula anomula*) immobilized on the surface of a DO electrode and was tested on a substrate solution comprised of L-lactate, sodium pyruvate, D-glucose, sucrose and distilled ethanol. No wastewater samples were examined and the data were not standardized with respect to BOD.

Microbial BOD sensors appear promising and attractive in controlling biological wastewater treatment units. Laboratory studies have been conducted to expand the application of microbial BOD sensor to industrial uses. Harita et al (1985) developed a BOD quick estimating system utilizing a microbial electrode. They used the technology

developed by Hikuma et al (1979). who found a sensor that consisted of yeast cells (*Trichosporon cutaneum*) immobilized on the surface of an oxygen probe for estimation of BOD. The BOD quick-estimating system made by Harita et al (1985) utilized the responsiveness (current signal) of microbial electrodes towards samples of wastewater and rinsing water. The response of this signal was proportional to the concentration of BOD in the wastewater and is calibrated with respect to a reference water. Harita et al (1985) concluded that this system can be used successfully for wastewater containing sucrose, hisidine, glycerol, fructose, glycine, lactic acid, glutamic acid, and glucose.

Strand and Carlson (1984) conducted a study comparing the response of a biofilm (immobilized microbial membrane) BOD electrode with the conventional 5-day BOD for samples of untreated, primary-settled, and secondary-treated municipal wastewater. The construction of the biofilm BOD electrode is similar to that of Karube et al. (1977). The wastewater samples were obtained from a conventional activated sludge plant. Their results indicated that the biofilm BOD probe provided a signal within 20 minutes that was proportional to the conventional 5-day BOD for soluble organics in primary-settled wastewater and secondary-treated wastewater. The biofilm BOD probe did not respond to the particulate organic matter in untreated municipal wastewater. Biofilm electrodes are more reliable than other techniques because anaerobic conditions can be detected as soon as they develop. Strand and Carlson further stated that more observations over a greater range of sample BOD variations are needed to further clarify the relationship between the biofilm BOD and the conventional BOD analysis. The biofilm BOD probe may eventually be used to assist in the control and monitoring of biological treatment processes.

The continuous short-time BOD-measurement BOD-M3 is a measuring device that has been developed by STIP Siepmann und GmbH in Reinheim; this device has met with

general approval in more than 200 local and industrial applications up to now. The features of a BOD-M3-measuring unit for determining BOD are (Kalte 1990):

- complete, continuous measuring of BOD;
- a measuring delay of 3 minutes;
- a measuring range from 2 - 10,000 mg BOD/l; and
- BOD available as an output signal.

The BOD-M3 unit consists of a weather-proof aluminum cabinet. The major components of the measuring device are: (1) a small bioreactor consisting of a plastic ring which offers the growth surface for microorganisms; (2) an automatic control system for diluting the incoming wastewater with dilution water up to a point where a constant low supply of nutritive substance for the microorganisms is obtained; (3) two oxygen probes for controlling the oxygen consumption of the reaction between the bioreactor supply and discharge; and (4) a microprocessor for BOD pollution calculation based on the dilution rate of the wastewater. The measuring unit of the BOD-M3 can attain a reproducibility of 98% and is ten times more accurate than the conventional 5-day BOD based on the DIN-methodology (Köhne et al. 1986). Because of its short time delay of 3 minutes, the BOD-M3 is being used more and more for monitoring and control of wastewater treatment processes. Kalte (1990) demonstrated the effective application of BOD-M3 measurement in nitri-denitrification sewage treatment plant and also an activated sludge wastewater treatment plant.

An amperometric BOD measuring probe and analyzer were developed by Princz and Olah (1990). The basic sensor was an oxygen membrane probe equipped with a "sandwich" membrane which contained microbes (aerobic enrichment) obtained from the activated sludge of a sewage treatment plant. The sandwich membranes are freeze-dried

for conservation, and prior to measurement the membranes are reactivated. Reproducibility and time delays for BOD measurement are improved and decreased, respectively, in comparison to conventional 5-day BOD measurement. The microbial probe is capable of determining BOD concentrations in non-toxic wastewater. No significant conclusion has been made for the lifetime of the membrane.

Hikuma et al. (1992) demonstrated the use of microbial electrodes for monitoring of the microbiology of the nitrogen elimination processes. In the nitrification and denitrification processes, the nitrifying bacteria have extremely low-growth rates compared to those of organotrophic bacteria (Hikuma et al., 1992). The biomass tends to decrease during various operating circumstances, and, once decreased, much time is required to return to the original state. Therefore, process monitoring is strongly beneficial for rapid detection of abnormal conditions, should they arise. On-line measurements of ammonia and BOD in the nitrification and denitrification process are carried out by the ammonia electrode and BOD electrode. The ammonia probe was constructed with a microbial membrane and an oxygen electrode. The membrane was prepared by using an acetycellulose membrane and nitrifying bacteria obtained from an activated sludge. The microbial probe for BOD estimation was constructed with an oxygen probe and a membrane containing the yeast, *Trichosporon cutaneum*. The wastewater samples were obtained from an amino acid fermentation factory. Their experimental results showed that the nitrification and denitrification rates of the activated sludge were efficiently measured by the microbial electrodes. These techniques made it possible to monitor the plant and estimate important parameters for the control of nitrogen and BOD loadings. In addition, the experimental results indicate the possibility of an automation system that would include microbial electrodes coupled to a computer system for process control.

2.2.3 BIOLOGICAL ACTIVITY MEASUREMENT

To maintain optimal efficiency in biological wastewater treatment, it is desirable to measure the activity of microorganisms in the bioreactor. A rapid measure of the response of the microorganism to environment changes enables appropriate control actions to be undertaken. The evaluation of this situation requires instrumentation that measures overall microorganism activity (reaction rates) rapidly within minutes and without interference from variations in the physiochemical properties (viscosity, color, turbidity) of the biological media. Moreover, the techniques should be amenable to automation for continuous monitoring and control. Developments in biomass detection methods such as, standard measurement using ATP (adenosine triphosphate) assays, respirometric methods and calorimetric techniques reveal the full potential of automated devices for continuous measurement and control of bio-processes system.

2.2.3.1 BIOMASS DETECTION METHODS

The population of living microorganisms in a bioreactor is one of the indications of microbial activity. Generally, microbial concentrations in unfavorable conditions are much less than those in favorable conditions. The traditional method of determining cell concentration (biomass density) is by plate count. This method requires a large number of culture samples for a statistically reliable number. Rapid methods, such as turbidity or optical-density measurements of the culture medium, provide a fast, inexpensive, and simple way to estimate cell density in the absence of other solids or light-absorbing compounds (Shuler and Kargi, 1992). This method is based on the absorption of light by suspended cells in the sample culture media.

A number of reviews discuss the development of biomass detection methods. Table 2.9 shows the properties of an ideal biomass sensor. Table 2.10 lists the selected analytical parameters of the non-bioelectrochemical biomass detection methods. Among the selected methods, the acoustic resonance densitometry (ARD) and the piezoelectric membranes (PM) methods are considered to have potential for non-bioelectrochemical biomass detection. A list of selected analytical parameters for bioelctrochemical biomass detection methods are shown in Table 2.11. Ramsay et al. (1986) defined bioelectrochemical analysis as those in which the analytical signal is generated by the biomass producing or consuming electrical charges which are detected by electrodes. Luong and Guilbault (1991) reviewed the analytical application of piezoelectric crystal biosensors. The method exploits the piezoelectric effect, which was first discovered in 1880. The general approach is to coat a piezoelectric layer (crystal) onto a material (membrane) that interacts highly selectively with the target analyte. When the crystal is exposed to the particular substance of interest, adsorption occurs, causing frequency change that can be used to determine the amount of material adsorbed. The specificity and selectivity of the piezoelectric sensor are determined by the coating materials. Biologically active materials such as enzymes, antibodies, and antigens that are much more selective and specific than organic and inorganic coating materials have been subject to much research in the past decades. For further information on piezoelectric biosensors, the reader is referred to Luong and Guilbault (1991).

A piezoelectric membrane method for total mass detection was reported by Ishimori et al. (1981). In this procedure, an ultrasonic signal was generated and directed through the microbial sample onto a piezoelectric membrane. This membrane provided a measure of the intensity of the ultrasonic signal. Both yeast and bacterial cells could be

Table 2.9 Properties of an ideal biomass detector (Ramsay et al., 1986).

	Property
1.	Accuracy
2.	Reproducibility of response
3.	Rapid response
4.	Sensitivity (resolution of 10^7 viable cells ml^{-1})
5.	Large linear range
6.	On-line capability
7.	Autoclavability
8.	Low cost
9.	Ease of operation
10.	Durability
11.	Biological inertness
12.	Harmless to the biomass
13.	No added reagents
14.	No sample pre-treatment
15.	Operation in clear or opaque samples
16.	Differentiation between viable and non-viable biomass

Table 2.10 Analytical parameters of non-bioelectrochemical biomass detection methods (Ramsay et al., 1986).

Method	Detection Limit (cells/ml)	Analysis Time (hour)	Sample Pre-Treatment	Source of Analytical Signal	Reference
Bioluminescence	10^5	0.2	ATP extraction	Viable cells	Chappelle (1978)
Radiometry	1	8-16	Incubation	Viable cells	Waters (1972)
Direct microscopic counts	$5x10^7$	1	Staining	Viable cells	Pettipher (1951)
Epifluoresence	$5x10^3$	0.5	Staining	Viable cells	Pettipher (1951)
Viable Counts	10	24-72	Incubation	Viable cells	Postgate (1969)
Dry Weights	.02 mg/ml	8	Drying	Solid particles	Neufeld (1982)
Nephelometry	$2x10^5$	Real time	None	Suspended solids	Mallette (1969)
Turbidimetry	$2x10^6$	Real time	None	Suspended solids	Mallette (1969)
Fluorimetry	.4 mg/ml	Real time	None	Fluorophores	Zabriskie (1978)
Microcalorimetry	10^5	2	Incubation	Viable cells	Beezer (1978)
Filtration	-	0.5	Filtration	Solid particles	Nestaas (1983)
Electrical counting	-	0.1	None	Suspended solids	Dow (1979)
Piezoelectric membrane (PM)	10^6	Real time	None	Suspended solids	Ishimori (1981)
Acoustic resonance densitometry (ARD)	$1.0x10^8$	Real time	None	Suspended solids	Clarke (1985)

Table 2.11 Analytical parameters of selected bioelectrochemical biomass detection methods (Ramsay et al., 1986).

Method	Detection Range (cells/ml)	Analysis Time (hour)	Sample Pre-Treatment	Reference
Potentiometric	1 - $1x10^6$	7.5 - 17.0	Incubation	Wilkins (1978)
Fuel Cell	10^7 - 10^9	0.2	None	Matsunaga (1979)
Fuel Cell	$6x10^6$ - $4x10^9$	0.5	None	Turner (1982)
Fuel Cell	10^4 - 10^6	0.3	Preconcentration	Nishikawa (1982)
Amperometric	$3x10^8$ - $2x10^9$	0.1	None	Matsunaga (1980)
Amperometric	$7x10^5$ - $4x10^7$	0.2	Preconcentration	Matsunaga (1981)
Amperometric	$6x10^6$ - $6x10^8$	0.2	None	Ramsay (1983)
Amperometric	$3x10^6$ - $2x10^8$	0.1	None	Matsunaga (1984)

detected at concentrations above 10^6 cells/ml. In addition to providing real time analyses, the detection cell could be autoclaved, but not for extended periods, as the epoxy resin attaching the piezoelectric membrane tends to crack, requiring replacement.

The basis of acoustic resonance densitometry (ARD) is that, when a mass is at its resonant frequency, the frequency is inversely proportional to the mass. Thus, if a fixed volume of culture is made to resonate, the resonant frequency will be proportional to the specific gravity of the fluid. After calibrating the system, the specific gravity can be calculated. The weight per ml of suspended solids is then obtained by subtracting the specific gravity of the culture medium (Clarke et al., 1985 and Krakty and Leopald, 1968). The ARD device is extremely robust and autoclavable.

The principle of potentiometric analysis is the measurement of the potential developed at an electrode with respect to a reference electrode. No external poising potential is applied. Two studies (Wilkins, 1974, and Wilkins et al., 1978) involved

measuring the development of potential at a Pt electrode relative to a saturated calomel electrode. The potentiometric method is simple to operate, has low capital cost and detects a wide range of viable bacteria with a large dynamic range, but the lengthy analysis time is a disadvantage.

A fuel cell method of estimating microorganism concentration was reported by Matsunaga et al., (1979). In their work, a non-mediated fuel cell to detect microbial cells was used (a mediator is a small redox compound used to transfer electrons from biological material to an electrode or vice-versa). The background signal is provided by covering the anode of one of the two non-mediated fuel cells (only the anode side of the fuel cells are contacted with the analyte samples) with a dialysis membrane, thus excluding the microbes but allowing the oxidation of any interfering chemical species. Hence, the difference between the electrical currents from the two fuel cells is the analyte signal. Analysis time is less than 30 minutes and only viable cells produce a response. Other studies were conducted by Turner et al., (1982) and Nishikawa et al., (1982) using mediated fuel cells with different mediators to increase the analytical sensitivity for detecting bacterial species such as *E. coli*.

The methods based on measuring the current produced by the reaction of the analyte species at a working electrode are called amperometric methods. They can be categorized into two-or three-electrode systems. The three-electrode systems consists of a working electrode poised at a pre-set potential, a reference electrode and a counter electrode which completes the electrical circuit. In the two-electrode systems, the counter and reference electrodes are combined to yield simplicity in operation. However, the potential at the working electrode of the two-electrode systems is not maintained as accurately as in the three-electrode systems. Matsunaga et al. (1981) reported using a two-electrode biomass sensor with a filter pre-concentration step to increase analytical

sensitivity. The aerobic bacteria and yeast were detected at low concentrations, where the detection limits were approximately 10^6 cells/ml and 10^5 cells/ml, respectively.

Both the fuel cell and the amperometric methods have in common rapid response, applicability to both bacteria and yeast, low cost, medium sensitivity, and ease of operation. For these reasons, it is likely that these methods will be further developed.

2.2.3.2 TTC-DEHYDROGENASE METHOD

The TTC test was first proposed by Bucksteeg and Thiele (1959) and used to measure the activity of activated sludge (Bucksteeg, 1966; Ford et al., 1966; and Lenhard et al., 1964). In the TTC test, dehydrogenase activity is measured by using a tetrazolium salt (TriphenylTetrazolium Chloride, or TTC) as a hydrogen acceptor. Dehydrogenase is an enzyme involved in oxidation-reduction reactions. The dehydrogenase acts as a key enzyme in the biological oxidation of organic compounds. Thus, the dehydrogenase enzyme activity can be used as a measure of biological activity. The oxidation (respiration of microorganisms) of a substrate is coupled with the reduction of TTC to the red-colored triphenyl formazan (TF), which is insoluble in water. The intensity of the red color is taken as a measure of dehydrogenase activity. Since this discovery, the TTC-dehydrogenase determination method has found limited acceptance, partly in evaluating the "activity" of aerobic and anaerobic wastewater sludge and partly in evaluating the inhibitory effect of materials or composite materials on the activity of sludge.

A modified TTC test method was introduced by Klapwijk et al. (1974). With this modified method, they studied the correlation of TTC dehydrogenase with other parameters used to express activated sludge activity and biomass. The influence of toxic

substances on the dehydrogenase activity and the oxygen uptake of activated sludge was also examined. The results showed that the dehydrogenase activity measured by this modified TTC test correlates fairly well with oxygen uptake. In addition, the test gave better information about biomass activity than that based on mixed-liquor volatile suspended solids (MLVSS) and the nitrogen content of the sludge. Unfortunately, the TTC test is not a good indicator for the activity of activated sludge under toxic stress. The toxic substances tested were zinc, phenol, KCN, and 2,4-dichloro-phenoxyacetic acid.

Ryssov-Nielsen (1975) further tested the modified TTC-dehydrogenase test of Klapwijk et al. (1974) . In his study, the TTC-dehydrogenase determination was modified in such a way that it could be applied to indicate the effects of various inhibitors and substrate materials. By using lysozyme in the incubation medium, an improved reproducibility was achieved. Inhibition of activated sludge was shown by $HgCl_2$, KCN, $ZnCl_2$, and 2,4-dichloro-phenoxyacetic acid. The results obtained agreed fairly well with the results of short-time Warburg-test (refer to Metcalf and Eddy, Inc., 1979 for Warburg measurement procedure). The effect of the substrate pyruvate and lactate was also proved by the TTC test. As known from normal enzyme-substrate assays, very high substrate concentration provoked substrate inhibition, as a result lowering the reaction rate in activated sludge.

2.2.3.3 METHYLENE BLUE REDUCTION METHOD

If a method for measuring the activity of activated sludge system is to serve as a practical controlling measurement, it must express the total oxygen uptake capacity of well-conditioned, unpoisoned sludge, and of sludge under the influence of toxic compounds. The results of a study where the enzyme activity was determined by the

methylene blue reduction (MBR) method indicate that, for sludges containing toxic materials, the MBR has an advantage over traditional methods (Jorgensen, 1984). Jorgensen's (1984) work further develops the MBR method which was first developed by Halász (1972). The rate of MBR is a measure of the dehydrogenase activity of activated sludge and the time for reduction of methylene blue to the colorless leucomethylene blue. Halász (1972) stated that the MBR is about ten times as sensitive as the TTC method for sludge activity measurements. The advantages of MBR over the TTC test are:

1. The determination is simple and rapid.
2. No expensive equipment is required.
3. The response to toxic compounds is well correlated to the response of oxygen uptake rate.

2.2.3.4 ADENOSINE TRIPHOSPHATE (ATP) METHOD

Several traditional measurements such as total suspended solids (TSS) or biodegradable volatile suspended solids (BVSS) have been used to estimate the active biomass in biological systems. Unfortunately, they do not distinguish between living and dead organisms. These mass measurements have been generally assumed to be an indirect but accurate determination of active microbial mass in the mixed liquor. However increasing recognition of their limitations has led to the examination of several alternative measures of activity. The most frequently measurement methods are adenosine triphosphate (ATP), dissolved oxygen uptake rate, dehydrogenase enzyme activity, and plate counts. The use of these more advanced techniques yields a better indication of the

rate of substrate removal in growing cultures or in decaying cultures, which is a reflection of the rate of mass reduction through endogenous respiration as opposed to mass solubilization. Upadhyaya and Eckenfelder (1975) conducted bench-scale laboratory studies to test the model proposed by Barnard et al. (1972) and compared the results with other biological activity indicators such as adenosine triphosphate and dehydrogenase activity. The model estimates excess sludge production and organic removal parameters by incorporating biodegradable fraction as the measure of active mass in the activated sludge system.

Adenosine triphosphate (ATP) is a compound associated with the biochemical breakdown of substrate. The energy in biological systems is stored and transferred via ATP, which contains high-energy phosphate bonds. The ATP content of microbial cells can vary with age and physiological status. The specific ATP content of the cells varies between 1 to 6 mg ATP/g biomass for logarithmic growing cells, whereas ATP drops to 0.05 to 0.8 mg ATP/g biomass for the cells in the stationary phase (Van de Werf and Verstraete, 1984). The log-growth phase is defined as the period when the cells divide at a rate determined by their generation time and their ability to process food or substrate (usually there is always an excess amount of food surrounding the microorganisms). The stationary phase is the period when the population remains constant or stationary. This phenomenon can be explained as the point where the cells have exhausted the substrate or nutrients necessary for growth, and the growth of new cells is offset by the death of old cells (Metcalf and Eddy, 1979). ATP has a negligible existence time after cell death and the intracellular ATP concentration (mg ATP/mg cells) is approximately constant for a given microorganism. Thus, the ATP concentration in sludge may reflect the viable organism content of the sludge. Most of the studies pertaining to ATP are concentrated on using ATP as a control parameter for aerobic waste treatment systems such as the

activated sludge process. For example, Kucknerowicz et al (1979) found a linear relationship between ATP content and cell residence time, sludge loading rate, and specific substrate removal rate. Chiu et al. (1973) studied population dynamics in a continuous culture using ATP as a parameter. Weddle and Jenkins (1971) studied the viability and activity in activated sludge. Also, Kennicutt II (1980) proposed ATP as a control parameter for the activated sludge process.

Droste and Sanchez (1983) performed a critical evaluation of the most common measures of activity in aerobic sludge digestion process. These methods include: ATP content, plate counts, oxygen uptake rate, and the activity of dehydrogenase enzymes. Their findings concluded that: (1) ATP offers the best estimate of activity in a mixed microbial population; (2) the ATP content per active biodegradable cell mass was found to be constant with digestion time for a specific waste and set of operating conditions during aerobic batch digestion; and (3) plate counts do not provide a reliable estimation of activity in a mixed microbial population.

Most of the investigation indicated that ATP can be used to estimate bioactivity in an aerobic system; but how can one estimate biological activity in an anaerobic system where oxygen is absent? Conventional cell culturing is too slow to meet demands of anaerobic bioprocess monitoring. Furthermore, cell culturing techniques are impeded by other limitations such as cell aggregation and cell cultures and only detect those bacteria that are able to reproduce under specific culturing conditions. The use of ATP to monitor the microbial activity in an anaerobic sludge digester was investigated by Chung and Neethling (1988). A method was adapted to measure ATP levels in anaerobic sludges and used to monitor ATP levels in an laboratory scale anaerobic sludge digester. The results obtained were compared with other parameters such as gas production rate, volatile suspended solids, sludge age, and pH. They reported that ATP reflects the activity of

anaerobic digestion and responds similarly to other indirect activity measurements (pH and gas rate production). ATP also responds to the effect of an inhibitor; McCarty (1964) reported that large quantities of salt is inhibitory to anaerobic digester. ATP shows promise as a total activity indicator for anaerobic digesters but it cannot distinguish between the various microbial population groups in digestion.

Chung and Neethling (1989) extended the determination of microbial activity during anaerobic sludge digestion using the dehydrogenase measurement method. They stated that ATP concentration and dehydrogenase activity (DHA) are the most promising bioactivity parameters, as both are associated with metabolic pathways of the microorganism and are therefore able to distinguish between active and inactive biomass. In their study, DHA was used to monitor the microbial activity in an anaerobic digester. Their results indicate that the ATP and DHA content of the anaerobic digester correlate well with other indirect methods such as gas production rate. ATP and DHA respond rapidly to pulse feeding of the digester, indicate inhibition of the anaerobic bacteria, and reflected changes in the activity at various sludge age. It is postulated that this rapid response is a reflection of microbial activity rather than actual numbers of bacterial. Even though ATP and DHA are not directly related to biomass, they give a more direct measure of the bacterial numbers than traditional techniques for anaerobic sludge such as VSS or TSS. Furthermore, their high sensitivities to environmental changes can be used as an alarm for changes in metabolic activity. These methods appear to be the most direct way to detect a change in biochemistry of the anaerobic digester that potentially affects the stability of the process.

2.2.3.5 MICROCALORIMETRIC METHOD

An innovative technique which uses heat production (related to biological activity) is called flow microcalorimetric detection. In the work of Fortier et al. (1980), the influence of various chemical contaminants on a laboratory aerobic biological process were investigated using flow microcalorimetric detection. The technique, investigated by Beaubien and Jolicoeur (1985), addressed the applicability of dynamic microcalorimetry to industrial bioprocesses. The advantages of the flow microcalorimetry method are it allows rapid determination of organic loading of effluents and offers possibilities for complete automation. Very few methods permit these general advantages (e.g. continuous monitoring). Standard measurements of biological activity such as, dehydrogenase enzymes or ATP assays, allow batch quantitative measurements but usually require complex manipulations and cannot readily be automated (Beaubien and Jolicoeur 1985). Basically, a flow microcalorimeter is a twin cell calorimeter with counter-current heat exchangers and a modulated thermal detection device requiring a single thermistor sensor. The wastewater samples were circulated through the calorimeter where the heat flux was measured by the thermistor sensor. Results for this method were compared to those for the respirometric method which rely on measurement of oxygen consumption (refer to Chen et al. 1980, Haas 1979, and Olsson & Andrews 1978 for respirometric method). Beaubien and Jolicoeur (1985) conclude:

1. Microcalorimetric evaluation of microbial activity is a non-destructive method which permits (in a semi-continuous mode) a rapid (about 20 minutes) determination of the effluent organic loading.
2. Detection of toxic substances and the determination of the maximum concentration tolerated by the microbes can be achieved through this semi-continuous method.

3. Complete automation in either a continuous or semi-continuous mode is promising due to the dynamic nature of the flow microcalorimetry method.
4. Heat flux offers interesting possibilities as a measure of biological activity in anaerobic processes.

2.2.3.6 OXIDATION-REDUCTION POTENTIAL METHOD

The oxidation-reduction potential (ORP), or redox potential, is a measure of the activity of electrons involved in oxidation-reduction reactions within an aqueous environment. In most of the chemical and biological reactions that take place in biological treatment systems, the observed ORP cannot be interpreted thermodynamically. The observed ORP represents the net electron activity of all redox reactions taking place and thus indicates the general oxidative status of the system (Koch and Oldham 1985). An investigation conducted by Peddie et al. (1990), studied the use of ORP for monitoring and control of aerobic sludge digestion. A major characteristic of ORP as a monitoring parameter is that the ORP values observed are somewhat specific to the system in which they are measured. The exact values of the ORP reflect all of the factors attributed to electron activity such as chemical constituents in the system and varieties of biological activity, pH, and temperature, which may vary within the system over time (Peddie et al. 1990). ORP and pH are analogous in certain ways; real time ORP response in a different system is similar to a pH response in a system with varying buffer capacity.

Some of the advantages of ORP as a tool for monitoring oxidative conditions and biological activity are: (1) utility over the full range of redox conditions from highly reduced redox conditions to highly oxidized redox conditions; and (2) ease of measurement and minimal maintenance requirements. Recent interest in advanced

wastewater treatment processes including non-aerated zones, sequencing batch operations, and optimized oxygen usage have redeveloped the interest in ORP as a control and monitoring parameter. For example, Sekine et al. (1985) found a linear relationship between nitrification rate and ORP and proposed using ORP as an index of nitrification. Peddie et al. (1990) stated that real-time ORP profile offers the application of automated control strategies and optimization of biological process performance. It is relatively easy to program a controller to calculate the rate of change of the ORP and initiate process changes in response to peak positive or negative values. In addition, this control function could also incorporate inputs from other monitored parameters such as dissolved oxygen, pH, and on-line measurements of various chemical constituents. In their research Peddie et al. (1990) concluded that:

1. ORP has a great potential to serve as a real-time control parameter for biological systems, especially those that operate over more than one type of respiration cycle.
2. ORP is a useful monitoring parameter for biological systems, such as aerobic sludge digestion.
3. ORP can be used to accurately define the ranges of respiratory activity and indicate the presence or lack of various electron acceptors.
4. ORP technology holds promise to effect significant cost savings in daily operation of many conventional waste treatment plants through control of such variable as air supply.

A full-scale study of using ORP as a control parameter in an activated sludge system for biological nitrogen and phosphorus removal was performed by Menardiere et

al. (1991). The aim of the study was to show how the ORP parameter can be used to optimize biological nitrogen and phosphorus removal in a two-series reactor system. The plant studied consists of a non-aerated tank (first) followed by an aerated tank (second) and a settling tank. Sludge was recycled from the settling tank to the non-aerated tank. Controlling the air supply to the second aeration tank (for nitrification and denitrification) and monitoring the anaerobic environment in the first non-aerated tank, the ORP as a control parameter was verified. Their investigation confirmed that simultaneous nitrogen and phosphorus removal is possible in a two series reactor system. The ORP served a useful function as a control parameter. It helped to monitor anaerobic conditions in the non-aerated zone which permitted a better understanding of the operating conditions. Furthermore, in the aeration tank, ORP monitoring contributed successfully to the stability of effluent quality, regardless of large variations in the influent characteristics, flow rate and concentrations of carbon, nitrogen and phosphorus compounds.

2.2.3.7 OXYGEN UTILIZATION RATE - Activated Sludge Process

The oxygen utilization rate or oxygen uptake rate (OUR) has long been recognized as a valuable parameter for monitoring and control of the activated sludge process, since OUR is an important indicator of biological activity in the activated sludge reactor. In aerobic systems such as in the activated sludge process, the substrate is removed by biological oxidation, with oxygen as a final electron acceptor. Thus, the rate of substrate removal may be equivalent to the OUR. The development of oxygen electrodes has made OUR measurements much easier and time saving. A lot of work has been done to promote OUR as a valuable tool in activated sludge process control. OUR has been shown to provide information including (Goto and Andrews, 1985):

1. characteristics of the influent wastewater such as composition, concentration, and flow rate;
2. the "condition" (activity and degree of stabilization) of the sludge;
3. effluent quality; and
4. settling characteristics.

Because of the valuable information OUR can provide, much research has been conducted to develop control models for estimating OUR in the activated sludge process.

Haas (1979) examined the applicability of OUR as a control parameter and proposed a mathematical model involving the use of the OUR parameter in defining the activity of a biological treatment process. The control equation predicting steady state concentrations of effluent soluble substrate is:

$$S_e = S_i - (\theta \cdot OUR)\left(\frac{1}{f}\right)\left(1 + \frac{1}{\theta_c k_d}\right) \qquad (2.2\text{-}1)$$

where

S_e - effluent soluble substrate concentration, M/L^3

S_i - influent soluble substrate concentration, M/L^3

f - substrate oxygen demand, dimensionless

k_d - endogenous decay coefficient, t^{-1}

θ_c - solids retention time, t

θ - wastewater hydraulic retention time, t

Under conditions where the substrate is measured in units of oxygen consumption potential, such as BOD or COD, f is unity, resulting in the following simplification:

$$S_e = S_i - (\theta \cdot OUR)\left(1 + \frac{1}{\theta_c k_d}\right) \qquad (2.2\text{-}2)$$

where the terms in the above equations are:

$\theta \cdot OUR$ - may be considered as a parameter defining the activity of a treatment process at removing substrate.

$\frac{1}{f}$ - factor to convert substrate removal potential from oxygen based units to the actual units used.

$1 + \frac{1}{\theta_c k_d}$ - a constant for a fixed solid retention time , accounts for the removal of substrate by cell synthesis as well as respiration.

From the control Equations (2.2-1) and (2.2-2), the desired OUR for a specific hydraulic retention time, θ, and influent substrate concentration, S_i, is determined based on a target soluble effluent substrate concentration, S_e. The OUR calculated is compared to the measured OUR (measurable process variable); if the calculated OUR is greater than the OUR measured, then reduce the rate of sludge return, and vice versa. In this control technique, the OUR serves as a process control variable to indicate the biological activity of the sludge by manipulating the return sludge rate.

Another study pertaining to oxygen uptake in activated sludge processing was conducted by Giona et al. (1979). The goal of their study was to obtain analytical expressions for the calculation of the OUR essential for the biological process. Their investigation led to the formulation of a criterion for predicting specific oxygen consumption (as a function of consumed substrate) and the specific oxygen uptake rate (as a function of the biomass). The specific oxygen uptake rate is defined as the mass of oxygen utilized per unit mass of sludge per unit of time.

Chen et al. (1980) examined the response of an activated sludge process to transient organic loadings and evaluates the applicability of dissolved oxygen concentration and OUR as process control variables. The biological monitor system examined consisted of a contact chamber, cylindrical aeration basin, and clarifier. The feed and air go to the bottom of the contact chamber and flow to the top of aeration basin. Their results indicated that the response of the activated sludge system to organic transient loadings can be predicted rapidly by the use of the contact chamber which is operated at a much shorter hydraulic residence time than the aeration basin. Under transient conditions the changes in the dissolved oxygen concentration reflected the variation in the respiration of biomass. The DO changes are due to fluctuations in the influent waste characteristics. As a result, a correlation between the changes of the DO concentration and magnitude of shock loading is generated. This correlation showed that DO concentration and OUR parameters are good control indicators for the activated sludge process. Furthermore, the contact chamber showed potential for use in a control system because of its rapid and sensitive response and direct relationship to the influent characteristics.

In order to estimate OUR, it is first necessary to know the oxygen transfer rate coefficient, $K_L a$. The value of $K_L a$ depends on the hydrodynamics and turbulence at the interface between the air bubbles and the liquid. Therefore, in general, $K_L a$ depends on the aeration system, geometry of the aeration basin, liquid characteristics, and temperature. Many models have been developed to predict $K_L a$, for example, the plug-flow reactor model with Monod type kinetics (Olsson and Andrews, 1978). Furthermore, on-line methods of $K_L a$ determination have been the subject of much research, mostly concerned with control applications. Howell et al. (1984) developed a linear model of mass transfer rate which allows rapid calculation of the dissolved oxygen uptake rates for

process control. The model used for their study is based on the local mass balance for the dissolved oxygen (DO) in the liquid phase of an aerator.

$$\frac{dC}{dt} = K_L a \cdot (C^* - C) - OUR \qquad (2.2\text{-}3)$$

where C* and C are the saturation DO concentration and DO concentration, respectively.

One of the most common objections to on-line determination of $K_L a$ is the problem of respiration changes, because one can never know beforehand whether the plant load will change during a determination. A linear model by Howell et al. (1984), relating respiration rate changes is utilized for a continuous determination of $K_L a$. As a result, if $K_L a$ has been determined and the air flow rate is known, it become a simple matter to continuously estimates OUR from DO measurements.

In Goto and Andrews, (1985), the determination of $K_L a$ was not the primary concern but was needed only in order to predict OUR. Therefore, they designated $K_L a$ as a "plant specific oxygen transfer coefficient", K. Under continuous flow conditions for a continuous stirred tank reactor (CSTR), Equation (2.2-3) becomes:

$$\frac{dC}{dt} = \frac{Q_{i,rs}}{V} \cdot (C_{in} - C) - OUR + K(f_{air})(C^* - C) \qquad (2.2\text{-}4)$$

where

$Q_{i,rs}$ - flow rate (influent + recycle sludge)

V - reactor volume

C_{in} - DO concentration in the reactor influent

C - DO concentration in the reactor

and $K(f_{air})$ is the transfer coefficient as a function of air flow rate. By rearrangement of Equation (2.2-4) for OUR,

$$OUR = \frac{Q_{i,rs}}{V} \cdot (C_{in} - C) + K(f_{air})(C^* - C) - \frac{dC}{dt} \qquad (2.2\text{-}5)$$

If V and C^* are constant and known, and the air flow rate, $Q_{i,rs}$, C_{in} and C are available from on-line measurements, dC/dt can be adequately computed numerically, the OUR can be predicted by Equation (2.2-5). However, K must be known prior the determination of OUR. Hence, Goto and Andrews, (1985) used the least-square method with Equation (2.2-3) for estimation of K. Their study concluded that the K can be estimated on-line from measurements of DO, influent and return sludge flow rates, and air flow rate.

Since the above studies, much of the research has been concentrated on the direct and continuous measurement of OUR using either improved systems or instruments for activated sludge process control applications. For instance, an instrument which completely automates OUR determination in aerobic biological reactors has been developed by Randall et al. (1991). In addition, a continuous OUR analyzer has been developed, as well as ways to protect analyzers from slime (Kaneko et al., 1985). Their OUR analyzer consists of an air-bubble cleaning system for slime removal, continuous DO sensor membrane cleaning and an automatic air calibration system. They defined OUR as the decrease rate of the DO concentration which was consumed by the mixed-liquor suspended solid (MLSS) in an aeration tank. The OUR (unit of ppm/hr) can be expressed by the following equation:

$$OUR = \frac{C_a - C_b}{t} \qquad (2.2\text{-}6)$$

where C_a - DO concentration at the beginning of measurement, ppm

C_b - DO concentration after time t, ppm

t - time, hr

The developed analyzer measures OUR according to Equation (2.2-6). Field tests have been carried out to determine the feasibility of using the developed OUR analyzer in a wastewater plant for a period of 18 months. The results indicated that the OUR analyzer can operate in stability for 2 to 3 months without any maintenance. The results also agree very well with the results obtained by manual analysis. Sato et al. (1990) introduced an advanced control strategy for activated sludge process using a respiration rate meter. They have developed a ATU-respiration rate measuring system for more effective supervision and control in activated sludge processes. ATU (allylthiourea) is an inhibition agent for nitrification.

2.2.3.8 IMMEDIATE MAXIMUM SPECIFIC OXYGEN UPTAKE RATE

Some of the recent research regarding activated sludge processes are worth mentioning. Shamas and Englande (1992) studied the immediate maximum specific OUR as a potential process control parameter for an activated sludge system is an example. They indicate that most control strategies for the activated sludge process have made use of parameters that are closely related to bacterial growth kinetics. Such parameters include: sludge age or mean cell residence time, food to microorganism ratio, mixed liquor suspended solids concentration, specific substrate utilization rate, and OUR. Many disadvantages are associated with the use of the mentioned parameters. Consequently,

none of the above parameters are accepted universally as an effective plant control parameter. One of the major reasons underlying the failure of many of these control parameters is that they make no explicit acknowledgment of the physiological state of the bacterial cells. In other words, the control parameters must provide information concerning the biomass both quantitatively and qualitatively during transient environmental changes. Shamas and Englande (1992) introduced the immediate maximum specific oxygen uptake rate ($SOUR_{im}$) to provide such information. The objectives of their study were:

1. Establishment of $SOUR_{im}$ using correlation of physiological characteristics for an activated sludge culture under dynamic conditions.
2. Relationship between $SOUR_{im}$ and effluent quality changes measured in terms of chemical oxygen demand (COD).
3. Comparison of $SOUR_{im}$ to the traditional specific oxygen uptake rate (SOUR) relative to effluent quality under transient conditions.

Shamas and Englande (1992) concluded that $SOUR_{im}$ correlates very well with effluent COD in both the batch and continuous-feed activated sludge systems. In addition, $SOUR_{im}$ can also provides information regarding the physiological state of bacterial cultures. However, the validity of $SOUR_{im}$ as a process control parameter has not been established over a wide range of conditions and waste compositions.

2.2.4 CHEMICAL AND PHYSICAL VARIABLES MEASUREMENT

The applications and reliability of instruments for bio-activity detection are presented in Chapter 2.2.3, and those for microbial sensors are covered in Chapters 2.2.2.2 and 2.2.2.3. Most of the biological activity sensors are currently under development; however, the measurements regarding physical and chemical process variables such as flow, temperature, pH, and dissolved oxygen variables are well developed. Therefore, this section deals with some existing sensors for measurements of essential chemical and physical parameters. Since the viability of any monitoring and control system depends primarily on the commercial availability of robust and reliable sensors, progress with the development of basic process variable sensors are presented below.

A number of sensors for chemical system variables are summarized in Table 2.12, whereas the sensors for physical variables are shown in Table 2.13. The "area of applications" in both tables is defined as the prior applications for that particular process variable in bio-treatment plant operation. The "range" relates to the difference between the maximum and minimum values over which the sensor will operate (Flynn, 1990). The "accuracy" of a sensors is defined as the difference between the value produced by the instrument and some known or true value (Flynn, 1990). On the other hand, the "precision" of a measurement refer to the probability that repeated measurements will produce the same value (Flynn, 1990).

Generally, the information about these sensors can be categorized into three groups:

1. Commercially available sensors with satisfactory performance.
2. Commercially available sensors but have more or less limitations.
3. Sensors that only exist under development or in laboratory research.

Table 2.12 Sensors for control and monitoring of the chemical variables in bio-treatment process.

Chemical System Variables	Measuring Devices	Area of Applications	Range/units	Precision	Current Status	Comments	References
pH	Glass sensing and reference electrode	Digester Inlet to works Sludge thickening/ dewatering plants	1 to 12	±0.2	CA	calibration needed	Briggs (1985) Bailey & Ollis (1986) Flynn (1990)
Dissolved oxygen	Galvanic or polarographic electrodes	Aeration tanks Effluent channels Supernatant liquor	voltage or current	±5%	CA	sensitive to temperature	Schugerl (1991) Briggs (1985) Flynn (1990)
Redox potential	Amperometric or Potentiometric	Inlet to works Aeration tanks Digester 2nd settlement-tanks	0 to 100%	± 5%	CA and UD	slow response; drift, fouling and recalibration temperature dependence	Schugerl (1991) Briggs (1985) Flynn (1990) Shuler & Kargi (1992) Chapter 2.2.3.6
Dissolved carbon dioxide	pH probe + permeable membrane	Digester	1 to 1000 mbar	±2% to ±10%	CA	advanced electrode under lab research	Onken et al. (1985) Briggs (1985) Schugerl (1991)
Oxidized nitrogen	Ion selective electrode	Effluent channels Inlet to works Bio-filtration	0 to 50 mg N/L	±5%	CA	other ion specific electrode under lab research	Briggs (1985) Onken et al. (1985) Chapter 2.2.1
Ammonium nitrogen (total NH_3)	Ion selective electrode	Effluent channels Inlet to works Aeration tanks Sludge disposal	0 to 5, 10, or 50 mg N/L	±5%	CA	other ion specific electrode under lab research	Briggs (1985) Onken et al. (1985) Chapter 2.2.1
Organic matter	Ultraviolet adsorption	Inlet to works Effluent channels	0 to 10 or 0 to 100 mg C/L	±5%	UD	correlate well with TOC	Briggs (1985)
Metals Ag, Pb, Cu, Co Fe, Cd, Zn, Ni	Coulometry with platinum electrode	Inlet to works Effluent channels	< 1 mg/L	na	UD	others: MOSFET	Briggs (1985) Chapter 2.2.2

na - not available
CA - commercially available
UD - under development

Table 2.13 Sensors for monitoring and control of the physical environment in bio-treatment process.

Physical System Variables	Measuring Devices	Area of Applications	Range/units	Accuracy	Current Status	Comments	References
Temperature	Platinum resistance thermometers	Inlet to works Effluent channels Digester Aeration tanks	-10 to 40°C 20 to 130°C	± 0.5°C	CA	seldom a problem others: Thermocouples	Briggs (1985) Onken et al. (1985)
Flow	Magnetic-flow meter (MFM)	Inlet to works Effluent channels	2 - 10 m/s	±1% to ±1.5%	CA	MFM and LDA are costly	Schugerl (1991) Briggs (1985)
	Rotameter	Recycle sludge		±1% to ±3%	CA	LDA is non-contact optical instrument	Section 6.2.1
	Laser Doppler anemometer (LDA)		na	na	CA	others: Differential pressure Turbine flowmeter	
Liquid level	Level controller Floating bodies	Bio-filtration Aeration tank	depend on instrument	±2 to 4%	CA CA	others: Ultrasonic sensor Sight glass	Flynn (1990)
Viscosity	Couette Searle Capillary	Inlet to works	depend on instrument	na	UD UD UD	many estimation methods	Onken et al. (1985) Schugerl (1991)
Suspended solids (turbidity)	Absorptiometer Nephelometer	Inlet at works Sedimentation Aeration tank Effluent channels	5 to 500 or 5000 mg/L	±5%	CA CA	best mean is by gravimetrically filtration	Briggs (1985) Section 6.3.1
Pressure	Strain gauge	Bio-filtrations	Pascal	±0.1 to ±0.25%	CA	other:	Schugerl (1991)
		Tanks Decantation system	depend on instrument			Bourdon tube gauges	

na - not available
CA - commercially available
UD - under development

From the tables, the group 1 sensors are flow rates, liquid levels, pH, temperature, dissolved oxygen and carbon dioxide, suspended solids, viscosity, and pressure. The sensors associated with group 2 are oxidized nitrogen, ammonium nitrogen, redox potential, and BOD (Chapter 2.2.2.3). In group 3, there are sensors for organic matter, heavy metals, and treatability (Chapter 2.2.1).

2.3 CONTROL STRATEGY OF BIOREACTOR SYSTEMS

The ultimate goal of a biological wastewater treatment plant is to obtain a high-quality effluent that complies with environmental regulations. One of the reasons for lack of compliance is related to process control in biological treatment processes. The primary difficulties in process control are due to the wide variation in the quality and quantity of influent wastewater, which results in nonsteady-state conditions. The main objective of this research is to find methodologies and operations that will likely to maintain high quality performance under different external variations. This can be accomplished by combining the efforts of four interdisciplinary consortia (Olsson, 1992) which is illustrated by Figure 2.14.

A control system of a wastewater treatment plant can be considered to act on three different levels of ambition and complexity (Olsson, 1992):

1. maintain plant operation and avoid gross failures (e.g. bulking of activated sludge);
2. minimize operating costs while satisfying permit limits; and
3. improve effluent quality.

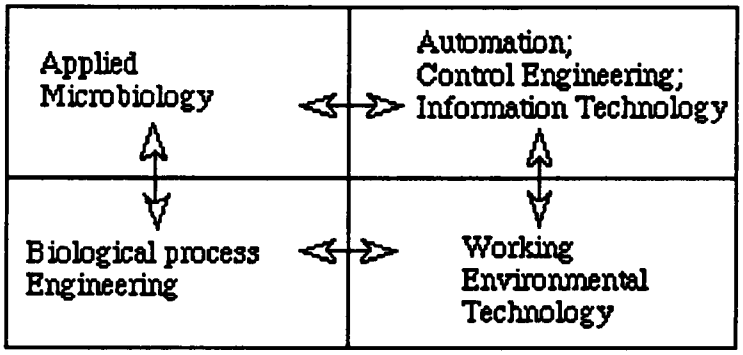


Figure 2.14 Wastewater treatment control is an interdisciplinary field.

Recent studies have found that failures in plant operational procedures are in many cases results of four top factors (Olsson 1992; Fioroni and Frais 1983; Arthur 1983, 1982; Huang 1981; and Hegg et al., 1978):

1. Lack of application of laboratory analysis to plant control - that is, a lack of utilization of test data in a logical sequence of reactions to modify and control the process.
2. Lack of understanding by operators of the basic biological treatment process - operator must have adequate knowledge of the biological process and hands-on experience on all equipment so that they can properly interpret data and utilize it through process control.
3. Lack of on-line instrumentation - the required process information is not instantly available for the operator to judge how effectively the process is functioning.
4. Lack of proper design of treatment plant - improperly designed expansions or new production facilities could cause an increase in hydraulic and/or pollutant loadings which results in changes in dynamic behavior of wastewater with respect to

composition, concentration, and flow rate. Therefore, the treatment plant must have a high degree of process flexibility incorporated during design.

Therefore, one can project that these problems can be overcome by an effective control strategy that can be efficiently and completely implemented. In reality there is no single "super" control strategy that is likely to solve all the treatment plant problems. However, this research is driven by the thought that an effective control strategy and associated system measurements can lead to substantial improvements in effluent quality and treatment efficiency, as well as maintaining process stability.

2.3.1 ASPECTS OF PROCESS CONTROL

Biological wastewater treatment process is a combination of biological, physical, and chemical operations which must be properly controlled to produce optimum results. In order to develop a control strategy and the instrumentation needed for a bioreactor or biological treatment process, it is important to know the answer to these questions:

1. What are the manipulatable parameters in the process? Some bioreactors have fixed parameters that are difficult to alter after they are built.
2. What are the manipulated variables and control variables? How are the manipulatable variables to be controlled to optimize the process?
3. What biosensors or other indicators of biological activity can be employed effectively for measuring physical, chemical, and biological variables?
4. How can the data needs for process control be handled? What are the means of data management?

The first two questions can be answered if the application, biological phenomena, and physical phenomena underlying the operation of bioreactors are reasonably well understood. For example, a conventional activated sludge process has three manipulable variables: rate of return sludge, rate of aeration and rate of wasting (Arthur 1983). The second question is associated with the control strategies employed to optimize the process. One objective to control the return sludge rate is stabilizing the food to microorganism (F:M) ratio. In this case, the return sludge rate is the manipulated variable and the F:M ratio is the control or measurable variable. The amount of food present is indicated by the respiration rate of the mixed liquor at the inlet to the aeration tank, and the concentration of viable microorganisms is indicated by the respiration rate of endogenously respiring return sludge. Measurement of these respiration rates can be used to indicate the concentrations of biological food, F, and viable microorganism, M. Consequently, the control of return sludge is dependent on the desired value of F:M ratio for a typical condition.

On the other hand, one objective of manipulating wasting rate is to stabilize the concentration of mixed liquor suspended solids (MLSS) in the aeration tank. When wasting is taking place, the quantity of microorganisms is reduced, placing a metabolic strain on those microorganisms still present in the system. Therefore a balance between food and microorganisms must be well maintained as the higher ratio of food will overloads the metabolite system and creates an imbalance in cellular growth phase. The purpose of manipulating rate of aeration is to maintain sufficient oxygen for the microorganisms to perform normal activity (that is, digesting the waste constituents). An effective control of aeration significantly reduces the energy costs required for aeration, as it is recognized that the energy requirements of aeration equal 60 to 80% of all energy required to operate the treatment plant (Arthur, 1983). The third question is more difficult

to answer because of the current lack of an ideal biosensor. For instance, the strategy discussed above for manipulating return sludge utilizes continuous measurements of respiration rate; therefore, sensors to measure these parameters must be reliable and precise. However, it is possible to identify the control strategy and instrumentation required without total regard to the availability of such instrumentation (further discussed in Section 2.3.3). Finally, it is necessary to have a well-designed plan for organizing, analyzing and utilizing the data to make them most effective in process control. The operating costs can be reduced significantly if proper data management systems are employed (Price, 1991).

2.3.2 PROCESS CONTROL PARAMETERS IN BIOREACTOR

Because of the large number of control parameters in bioreactors, it is convenient to classify them into three categories: physical, chemical, and biological (DiBiasio, 1989). Physical parameters include most physical characteristics of the system. Chemical parameters include those components of the extracellular environment that are indicators of biological activity. Biological parameters involve cell culture properties. Additionally, the control parameters vary considerably from one biological process to another. Table 2.14 indicates some of the common but essential parameters to be monitored in bioreactors. Some of these parameters are discussed in Chapters 2.2.2 and 2.2.3.

Table 2.14 Basic important control variables in bioreactor.

Parameters	Comments
PHYSICAL:	
Temperature	microbial growth
Influent and effluent flow rate	efficiency of process
Liquid level	in rotating bio-contactor
Pressure	in fluidized-bed reactor
Agitator speed	completely mixed conditions
Viscosity	high solids content present problems
Turbidity (indicate cell mass)	fouling and interference from gas bubbles and suspended solids
Aeration rate	provide oxygen for microbe
Liquid hold-up	avoid overfilling
CHEMICAL:	
Dissolved oxygen	for aerobic process
pH	toxic effect to microbe
Inhibitors	heavy metals toxic to microbes
Volatile organic acids	air pollution problems
Substrate concentrations	microbial growth
Oxygen uptake rate	indicates active microbes in aerobic zone
Ammonium uptake rate	substrate consumes in nitrification
Nitrate utilization rate	indicator of denitrification process
ORP (redox potential)	electrons transfer in chemical reaction
BIOLOGICAL:	
ATP	form of energy obtained from substrate
Food to microbe ratio	nutrient supply
Biomass	activity of cell

2.3.3 DEVELOPMENT OF CONTROL STRATEGY

Control strategy varies from one plant to another and depends on the various treatment objectives, wastewater characteristics and the type of biological treatment process. The most common and also the most difficult to control are effects due to hydraulic disturbances as evidenced by the operator's awareness of the dynamic behavior of the wastewater system (Andrews, 1974). The flow rate, composition, and concentration vary from time to time, and a control strategy should be able to accommodate large temporal variations in wastewater characteristics. The development of a control strategy is intimately related to the dynamic or transient behavior of the process. However, development of a control strategy is not solely dependent on the dynamic character of the wastewater, but also, is based on multi-interdisciplinary factors such as those described in Figure 2.14. "Control strategy" as used in this study means a strategy or a method used to control a wastewater treatment process to ensure high-quality effluent. Developing a control strategy for bio-treatment processes is not the main subject of this investigation, but the principles required for control strategy development are presented.

Other factors needed for consideration in developing control strategies include the physiology of microorganisms, performance of on-line instrumentation, and the means of data management. An understanding of biological phenomena provides the information for maintaining a healthy environment for growth of the microbes. If the limits of sensor capabilities are known, one can distinguish between the true and false alarms provided by the sensors. A wide variety of control algorithms are available for processing of the information necessary for process control: adaptive, proportional-integral-derivative (PID), cascade, feed-forward and ratio control algorithms. Therefore, effectiveness, reliability, and stability are the prime considerations in control model selection. A good

data management system allows proper data collection for the control scheme, which will eventually lead to an initiation of appropriate control actions. It is futile to discuss control strategies if controllability of plant parameters is severely limited or impossible. Figure 2.15 illustrates the procedure for formulating an effective control strategy. Stage one initiates the procedure by defining the treatment objectives and take into considerations all the factors that will lead to the development of an effective control strategy.

2.3.3.1 TREATMENT OBJECTIVES: STAGE ONE

Some of the considerations for designing a control strategy for biological wastewater treatment have been discussed in the preceding sections. A simplified diagram summarizing these considerations is presented in Figure 2.15. However, many actual cases encountered in practice will be considerable more complex. Thus, it would be a difficult task to try to cover all possible aspects in developing a control strategy for such a complicated bio-treatment process. It is believed, however, that the principles presented herein could help the practicing engineer to objectively and rationally develop a control strategy for a particular treatment system.

The first stage in developing an effective control strategy is defining treatment objectives and required effluent quality. The primary treatment objective in biological treatment systems is removal of biodegradable organics to levels specified by regulatory agencies. Additional objectives can include nutrient (nitrogen and phosphorus) removal, toxicity (heavy metals and toxic organics) reduction, and non-degradable organics removal.

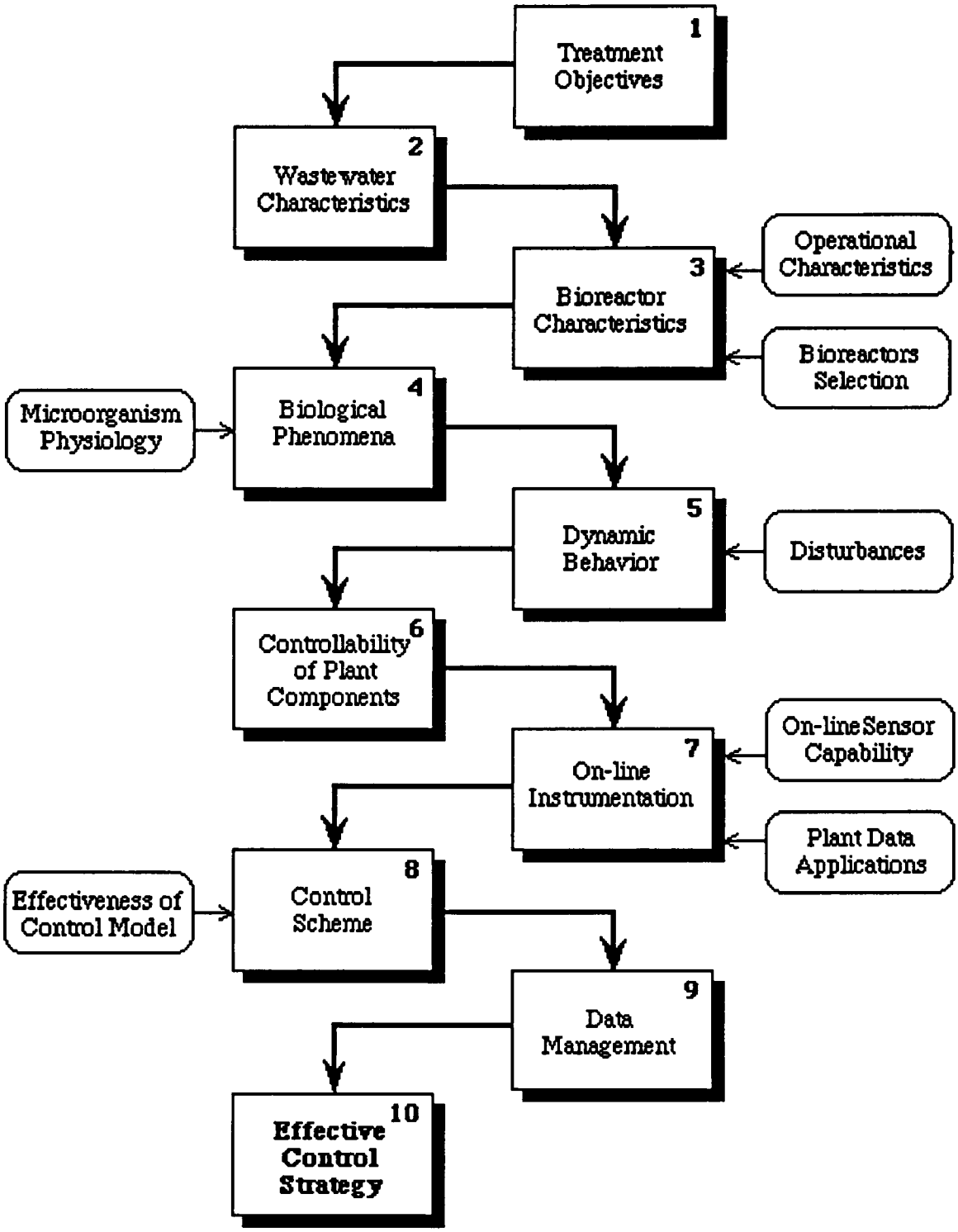


Figure 2.15 A problem-driven methodology for developing control strategy in wastewater treatment plant.

2.3.3.2 IMPORTANCE OF WASTEWATER CHARACTERISTICS: STAGE TWO

It is essential that the nature and characteristics of wastewater be evaluated with respect to the biological unit processes considered. Therefore, the second stage of control strategy development is the study of wastewater characteristics. The constituents and analysis methods of wastewater have been discussed in Chapter 2.1.4 and the effects of these components to the microorganisms are discussed in Chapter 2.1.3. Characterization of raw wastewater, which is the understanding of the biological, physical, and chemical components of wastewater, can provide helpful information for treatment process selection and design. The information that can be obtained in wastewater characterization are (Eckenfelder et al., 1989 and Eckenfelder, 1989):

1. biodegradability of wastewater (physical, chemical, and biological treatment);
2. strength of wastewater (high BOD);
3. inhibition effect (toxic to biomass);
4. non-biodegradable fractions (refractory substances such as alkyl benzene sulfonate);
5. flow and composition variations;
6. trace organics (e.g. phenol);
7. priority pollutants (heavy metals, cyanide, and toxic organics);
8. color and turbidity (aesthetic problems);
9. oil and floating materials (restricted by regulations);
10. volatile organics (e.g., hydrogen sulfide create air pollution problems);
11. nutrients contents (phosphorus and nitrogen, Chapter 2.1.3); and
12. alkalinity and acidity (affect the biomass, Chapter 2.1.3).

2.3.3.3 BIOREACTOR SELECTION AND CHARACTERISTICS: STAGE THREE

Particularly, the first five points of information characterizing wastewater listed above in stage two are essential in screening of bio-treatment process alternatives. Therefore, the prime objectives of the third stage in the development of control strategy are the selection of bioreactor types and analysis of the operational characteristics of the selected bio-treatment process. The typical characteristics of various types of biorectors are described in Chapter 2.1.5. For example, if the wastewater is high-strength waste, anaerobic treatments are preferable (Chapters 2.1.2, 2.1.5.8, and 2.1.5.9). On the other hand, if the wastes contain non-degradable components, then a physical and chemical treatment may be included. If the wastewater contains toxic materials to biomass then a pretreatment step is needed. Thus, it is crucial to understand the characteristics of wastewater (stage two) in order to arrive at a rational biological treatment process (stage three) that is able to meet the defined treatment objectives (stage one). The characteristics of a bioreactor depends on the biological system chosen. The system can be anaerobic, aerobic, anoxic or a combination, and either fixed-growth or dispersed-growth systems (refer to Chapters 2.1.1 and 2.1.2). For instance, if the system selected is an extended aerated activated sludge process, which is a suspended-growth system, the operational characteristics are (Chapter 2.1.5.1):

1. aeration requirement (intermittent interval);
2. mixing capacity (proper dispersion);
3. sludge wasting; and
4. sludge recycle.

In addition, an adequate understanding of mass transfer across gas/liquid interfacial areas is of importance for the characterization of a bioreactor. Especially in aerobic processes, the oxygen supply to microorganisms is one of the most essential limiting transport processes (Lubbert, 1991). Understanding the characteristics of the bioreactor can provide useful information such as the limitation and efficiency of the bioreactor, upsets of the bioreactor, and, most importantly, information that is essential for development of a control strategy.

2.3.3.4 BIOLOGICAL PHENOMENA: STAGE FOUR

The purpose of stage four is to comprehend the physiology of microorganisms, an important consideration in control strategy development. The factors affecting the microbes' growth are discussed in Chapter 2.1.3.4. The microorganisms used in biological treatment processes can be bacteria, algae, and/or protozoa, but most of the treatment systems employed mixed culture such as bacteria and algae (Chapter 2.1.3.1). The pattern of microbial growth and substrate utilization rate are influenced by environmental conditions such as temperature, pH, dissolved oxygen concentrations, and inhibitor concentrations. All microbes have optimum living conditions, for example, psychrophiles, whose optimum temperature is less than 20°C; similarly, the optimum pH for many bacteria ranges from a pH of 3 to 8. The metabolic process of aerobic cells or microorganisms is shown in Figure 2.16.

The biological systems of aerobic cells are similar to oxidation processes such as combustion. The microorganisms utilize food (substrates) and oxygen to creates energy and new organisms (product of metabolism), as well as production of carbon dioxide (Arthur, 1981). Therefore, a successful control strategy recognizes that the essential

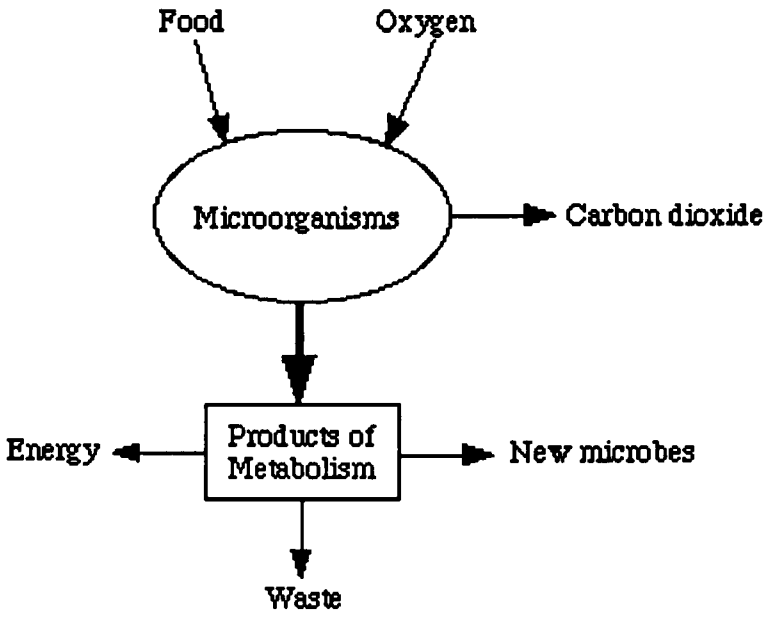


Figure 2.16 The metabolic process of aerobic microorganisms.

materials (food and oxygen) and optimal environmental conditions can provide support for optimum microbial growth, which is vital in process control.

2.3.3.5 DYNAMIC BEHAVIOR OF TREATMENT PROCESS: STAGE FIVE

The fifth stage in formulating the control strategy is the matter of analyzing the dynamic behavior of the wastewater treatment process. Influent disturbances to a wastewater treatment plant may vary significantly, both in amplitude and in frequency. Rainstorms can cause shock loads that upset the settler and clarifier systems, and this can seriously affect the whole plant system. Changes are always taking place in the inputs,

outputs or environment of a process as well as in the characteristics of the process itself. The time varying input to a treatment process included:

1. flow variations;
2. temperature and pH variations;
3. composition (nutrients, BOD and toxins); and
4. solid contents.

Some of the changes that occurs within the process are dissolved oxygen concentrations (in an aerobic process) or methane content (in an anaerobic process). BOD or COD is one of the output variations from the process. The quantity and quality of the effluent are influenced by the influent fluctuations; therefore, it is important to identify the nature of these changes and the rates at which they occur. Some may be so slow that they can be neglected for a typical process and some may be so rapid (very short duration) that they also have little appreciable effect on the process (Andrews, 1974). However, there are some transients which have a tremendous impact on the behavior of the treatment process, and these should be considered in process control design such as inlet flow variations. In addition, perceiving the dynamic behavior of the process allows one to correlate the relationship between input variables and output variables; most importantly, this information is required in stage seven—the correlation between temperature and BOD removal rate is one example. These correlations provide the insight into the actual changes that occur in the process.

2.3.3.6 CONTROLLABILITY OF PROCESS VARIABLES: STAGE SIX

Stage six in deriving control strategy is the determination of the controllability of treatment system variables that can be manipulated in order to control and monitor the process. The process-manipulated variables for activated sludge processes (including contact stabilization, extended air, and pure oxygen) are: rate of aeration, rate of return sludge, and rate of wasting. These manipulated variables have been discussed in Chapter 2.3.1. Additional manipulable components include storage of raw wastewater and microorganisms and wastewater feed and air flow distributions (Arthur, 1983, and Olsson and Andrews, 1977). For instance, raw wastewater storage is usually used when pH adjustment and nutrient addition are necessary or when toxic materials are commonly discharged to the plant. Since some toxins can be treated in certain concentrations, it is good to control the concentrations. The two major purposes of microorganisms storage as reported by Arthur (1983) are: (1) elimination of the solids washout during periods of high hydraulic loads; and (2) stabilization of the food to microorganism ratio. There are five problems in this stage:

1. What are the controlled/measured variables?
2. What are the disturbance variables?
3. What are the manipulable variables?
4. How do these manipulated variables relate to measured/controlled variables?
5. How are these manipulated variables to be manipulated to optimize the process?

The "controlled variable" is the output variable to be controlled and the "disturbance variable" is an input variable affecting the controlled variable through variation (Kristiansen, 1987). The "manipulable variable" is an input variable that can manipulate to optimized the process (Chapter 2.3.1).

The information obtained from Stage 2 through Stage 5 answers the first three questions. The remaining can be solved through Stages 7 and 8. An illustration of the way these variables are linked is given in Stage 8.

2.3.3.7 ON-LINE INSTRUMENTATION AND TREATMENT PLANT DATA ANALYSIS: STAGE SEVEN

Given the defined treatment objectives, the wastewater properties, the bioreactor operational characteristics, the necessary information on biological phenomena, the dynamic behavior of the process, and the known manipulated variables, the control strategy is ready to be developed, provided the process variables measurements are available and some of the correlations between these variables are known. Therefore, stage seven in control strategy derivation deals with the identification of an appropriate sensor for a typical measurement task and the application of plant data. The wastewater treatment environment is well-known for its hostility to instrumentation. Prolonged exposure of sensors to industrial wastewater and the products of the various treatment processes inevitably lead to a degradation in performance and reliability, especially of those sensors that are developed in the laboratory under favorable environmental conditions (Briggs, 1985). Various remedies exist, from good housekeeping practices to redesign of the whole system, but generally they add significantly to the cost and complexity of the instrumentation (Briggs, 1985). Dual-sensor systems with one on-stream and the other on standby to protect the intake to the water treatment plant in case of on-stream sensor failure is one of the remedies (Briggs, 1985). Some recent biosensor innovations for measuring biological activity are discussed in Chapters 2.2.2 and 2.2.3. The physical and chemical process variables are provided in Chapter 2.2.4.

The limitations of sensors should be well understood before one deploys the instruments for measurements in wastewater treatment process. Although, a number of advanced analytical tools such as fiber-optic detection (Chapters 2.2.2) have been developed in the past decade, instrumentation limitations need to be solved before there is widespread acceptance of these more advanced instruments by wastewater treatment plants. In general, the less complex the instrumentation, the higher the likelihood that its use is successful (Stephenson, 1985). A key factor to consider in this stage is the degree of accuracy actually required for measurement of process variables. The instruments may not meet the degree precision and accuracy stated by the manufacturer but may be adequate for monitoring and controlling plant operation to accomplish consistent results (Stephenson, 1985). White (1981) indicated that instrument accuracy of ±20% is appropriate if it is consistent.

Plant data applications also play a major role for developing process control strategy; therefore, another consideration in stage seven is the selection of proper plant data to provide information about the bio-treatment process. The plant data can be:

- BOD, COD, and TOC;
- dissolved oxygen concentrations, OUR, ATP, and ORP;
- pH and temperature;
- volatile suspended solids and total suspended solids;
- turbidity;
- mixed liquor suspended solid (MLSS) and MLVSS;
- flow rate;
- toxins;
- total nitrogen and phosphate concentrations;
- sludge volume index (SVI) and specific sludge volume index (SSVI); and
- level.

In most plants, a combination of several of these data points would be utilized, as each one tells the operator something slightly different about what is happening in the process (Kutcher and Ettel, 1983). The purposes of this step are to accomplish these objectives:

1. Identify the information (data) to provide insight on the conditions in the process.
2. Analyze the relationship of the data, for example, the variation of the effluent BOD concentrations with respect to the bioreactor temperature fluctuation.
3. Identify the type of information that are related to microbial activity, for instance, the dissolved oxygen concentration profile can lead to an understanding of the state of the microbial activity.
4. Identify the information that can be measured on-line and/or off-line.

Finally, with this information, the establishment of the on-line sensors needed for the measurement can be achieved.

2.3.3.8 CONTROL SCHEMES SELECTION: STAGE EIGHT

The primary objective of stage eight in development of overall control strategy is the selection of the right control algorithm for a particular control task. A wide variety of control schemes are available for control of process variables. One example is the regulation of dissolved oxygen by cascaded control system. Other control schemes include:

1. feedforward controls (opened-loop);
2. feedback controls (closed-loop);
2. ratio control; and
3. adaptive control.

The purpose of control is the manipulation of the control variables identified in stage six for (Lim and Lee, 1991):

1. Maintaining the desired outputs at a constant desired value by surpressing the influence of external disturbances and/or forcing the outputs to follow a desire profile, i.e., maintaining pH at a desired value by regulation of a valve which control the addition of alkaline solution.
2. Stabilizing unstable or potentially unstable processes.
3. Optimizing the performance of the process as defined by the measures such as effluent quality or yield.

These objectives are to be achieved under various constraints such as safety, limited resources, and operational constraints. The problems involved for design of a control system/scheme include (Lim and Lee, 1991):

1. What are the control objectives?
2. What should be manipulated? (Stage 6)
3. What should be measured? (Stage 7)
4. Which control variables should be paired with which measured outputs? (Stage 7) and what disturbances should be measured and used to manipulate the control variable (Stages 2, 6, and 5)?
5. How should the controllers (e.g. PID controller parameters) be tuned?
6. What are the best operating conditions?

Answering these questions can be illustrated by the example of a specific control problem such as controlling dissolved oxygen (DO) concentration in an activated sludge process. In this problem, the control objective is to (1) maintain a desired DO

concentration by (2) manipulating the aeration rate in the presence of external disturbances such as DO concentration in the return sludge and microbial growth rate, which can alter the oxygen demand; (3) DO concentration must be measured and (4) the pairing will be the DO measurement with the aeration rate so that the DO concentrations are controlled by aeration rate. The fifth question deals with the adjustment of the PID controller settings to obtain a satisfactory response to the control system, which is often done by trial and error (Lim and Lee, 1991); the controller tuning is dealt with in many references (Smith and Corripio, 1985; Shinskey, 1979; and Douglas, 1972). The sixth and final question is concerned with the optimal operating conditions or desired setpoint values; for an activated sludge process, the minimum critical oxygen concentrations range from 0.2-2.0 mg O_2/l (Gray, 1989). These operating conditions can be obtained from previous plant data, literature, or through an optimization procedure.

In some cases, the answers for the above six problems are not that obvious. With the information gathered from stages one to seven, however, they can be resolved in a systematic way, and one can arrive at a rational control system for any particular case.

2.3.3.9 DATA MANAGEMENT SYSTEM: STAGE NINE

The final stage of developing a wastewater treatment plant control strategy deals with the data logging system. For control systems to function properly, they require a good data collection and processing system that can provide a smooth flow of information from the sensors to the control units. Computers are useful tools in wastewater treatment plant. They assist in management, information processing, and quality control (Berthouex, 1992; Jones, 1985; Davis, 1983; Skrentner, 1983; and Chappel, 1981). The data obtained from the plant have to be tabulated and plotted by computer so that the

information are evaluated properly and appropriate actions can be undertaken. Data management is referred to as a building block for plant operations, because without proper, accurate and precise data, plant management becomes a guessing game (Boe, 1983). Therefore, a well planned and organized data management systems will circulate the information uninterruptedly from data collection (step 1) to results (step 7) as follows (Boe, 1983):

1. data collection;
2. analysis;
3. decisions;
4. direction;
5. action;
6. operations; and
7. results

When the results are stored as data, one can return to step 1 to begin the cycle again. Smooth circulation of information is important for the control systems to perform properly and efficiently.

2.3.3.10 EVALUATION OF CONTROL STRATEGY: STAGE TEN

Wastewater treatment plants are very complex by nature. They handle raw wastewater of varying quantity, quality and characteristic from day to day and even hour to hour and treat it through processes that involve mechanical, physical, chemical, and biological phases. Therefore, it is not an easy task to design a control strategy that is capable of coordinating such complex processes. Additionally, the control system must be even more sophisticated, because it must deal with the control of the entire treatment plant. The procedure (Figure 2.15) presented in this section considers the critical elements

(Stages one to nine) for the derivation of an effective control strategy such that the efficiency and effluent quality of an industrial biological wastewater treatment process are improved.

The process of developing a control strategy is summarized as follow:

Stage 1: Define the treatment objectives.

Stage 2: Analyze the nature and characteristics of wastewater.

Stage 3: Select the bio-treatment process and understand the characteristics of it.

Stage 4: Comprehend the critical aspects of biological phenomena.

Stage 5: Understand the dynamic behavior and it's impact upon the selected treatment process.

Stage 6: Identify the manipulable, output, and disturbance variables of the process.

Stage 7: Utilize the plant data effectively and identify the appropriate sensor for specific measurement task.

Stage 8: Define the control objectives and choose the appropriate control scheme.

Stage 9: Set-up the management system for information collection, storage, and processing.

Stage 10: Evaluate the derived control strategy.

If the control strategy generated through this methodology is not effective, then one may return to the stages with unresolved problems and correct the control strategy accordingly. This is a trial-and-error process until the desired objectives are met. The stages described above are to be used as a basic overall developmental procedure for deriving and evaluating a typical biological treatment process in the application part of this research activity, that is, the steady-state sensitivity analysis of process measurement parameters and evaluation of an anoxic zone monitoring strategy.

CHAPTER 3

STUDY APPROACH

One of the important considerations in developing an effective control strategy is identifying the proper measurement parameter or indicator that best describes the activity of the biological system (Figure 2.15 in Chapter 2.3). According to the literature reviewed for this investigation (Chapter 2.2), there are five measurement parameters other than conventional parameters such as MLVSS, sludge volume index, and dissolved oxygen that can be used in bioreactor control. These parameters are (1) TTC-dehydrogenase; (2) adenosine triphosphate (ATP); (3) oxidation reduction potential (ORP); (4) oxygen utilization rate (OUR); and (5) immediate maximum specific oxygen utilization rate ($SOUR_{im}$). The process parameters ORP, OUR, ammonium-nitrogen uptake rate (AUR), and nitrate utilization rate (NUR) were selected for this analysis. The major objective of this analysis is determining the steady-state sensitivity of the selected process measurement parameters for a biological treatment system treating a hypothetical industrial wastewater stream. The objective can be achieved using the research strategy shown below, which is partially based on Figure 2.15 in Chapter 2.3:

1. Define the treatment objectives: greater than 95% removal efficiency of COD, ammonium-nitrogen, and nitrate-nitrogen.
2. Characterize a hypothetical wastewater stream: the stream is composed of soluble COD, ammonium-nitrogen, and nitrate (the details are presented in Chapter 4), free of heavy metals and toxic or inhibitory materials.

3. Establish the biological treatment system: the Bardenpho process is a two-stage system, combining carbon oxidation and nitrification in an aerobic reactor (2^{nd} stage), and denitrification in an anoxic reactor (1^{st} stage).
4. Identify the process measurement parameters and derive their estimation methods: ORP, OUR, AUR, and NUR.
5. Analyze the steady-state characteristics of the response of process parameters to upsets of the biological treatment system: a bio-simulator is used to study the steady-state response of process parameters to changes in the input condition.

This strategy serves as the basic approach to the investigation into the sensitivity of the process measurement parameters for a typical bio-system model. The results obtained from this approach provide the bases for the derivation of a steady-state anoxic zone recirculation model.

3.1 BIOLOGICAL TREATMENT MODEL

The treatment objectives are focused on soluble organics (COD) and nitrogen removal. The bio-treatment model used is a two-stage Bardenpho, single-sludge system for simultaneous carbon oxidation, nitrification, and denitrification (Chapters 2.1.5.6 and 2.1.5.7). Figure 3.1 illustrates the schematic design of a single-sludge, two-stage system for the removal of organic carbon and nitrogen. Nitrate produced from oxidation of ammonium-nitrogen in the nitrification tank is recirculated and blended with the inlet raw wastewater before it flows into the denitrification zone for reduction to nitrogen gas. Aeration is required in the aerobic zone for soluble organic oxidation and nitrification.

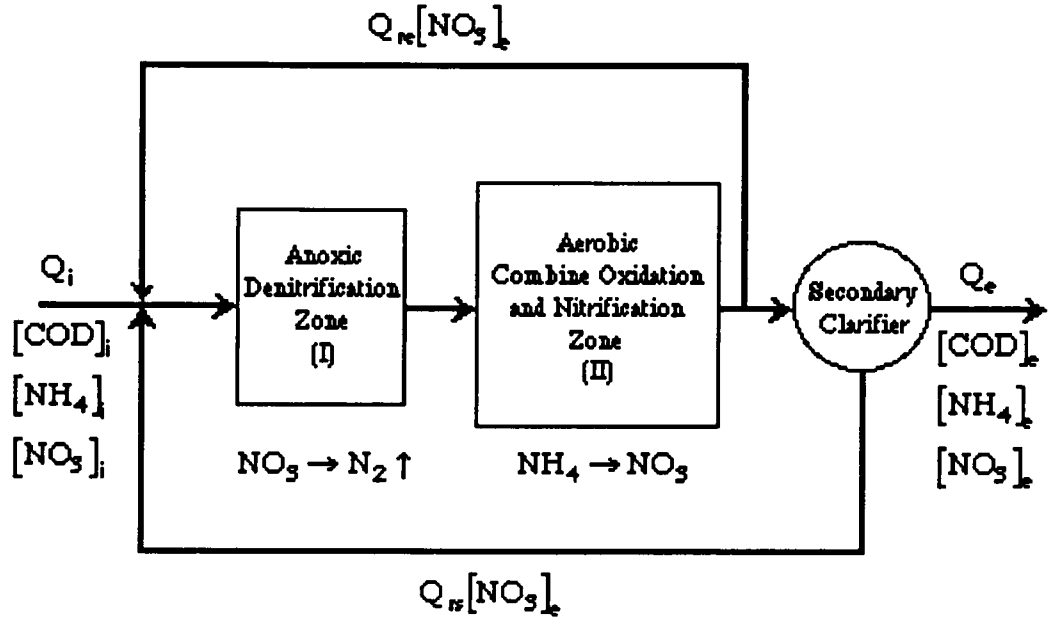


Figure 3.1 A typical activated-sludge two-stage biological nitrification-denitrification process.

For this typical process, the operating parameters are estimated using the design equations for activated sludge system. The minimum sludge age can be calculated by:

$$\frac{1}{\theta_c^m} = \frac{\mu_{m,n}[NH_4]_i}{K_N + [NH_4]_i} - k_{d,N} \qquad (3.1\text{-}1)$$

where $\mu_{m,n}$ - maximum specific growth rate of nitrifying bacteria, t^{-1}

K_N - saturation constant for nitrifier, M/L^3

$k_{d,N}$ - decay constant for nitrifier, t^{-1}

θ_c^m - minimum sludge age, t

$[NH_4]_i$ - influent ammonium-nitrogen concentration, M/L^3

The reader is referred to Metcalf and Eddy (1991) and Benefield and Randall (1980) for the biokinetic constants and temperature correction factors. The sludge age is estimated by assuming a safety factor (SF) in the range of 1.3 to 3.0 of the θ_c^m. Usually the safety factor is approximated by the ratio of the peak influent ammonium concentration to the average influent concentration:

$$SF = \frac{[NH_4]_{i,peak}}{[NH_4]_{i,average}} \tag{3.1-2}$$

Therefore the sludge age in unit time is:

$$\theta_c = (SF)\theta_c^m \tag{3.1-3}$$

Based on the substrate mass balance for the model described in Figure 3.1 (recycle system) and with the known microbial kinetics and the sludge age, the effluent ammonium concentration, $[NH_4]_e$, is determined by:

$$[NH_4]_e = \frac{K_N(1+k_{d,N}\theta_c)}{\theta_c(\mu_{m,n}-k_{d,N})-1} \tag{3.1-4}$$

On the other hand, the effluent organic carbon concentration, $[COD]_e$ (M/L^3), is calculated by a mathematical formula similar to Equation (3.1-4), but using the heterotrophic kinetic constants instead of autotrophic (nitrifiers) kinetics:

$$[COD]_e = \frac{K_s(1+k_d\theta_c)}{\theta_c(\mu_m - k_d)-1} \quad (3.1\text{-}5)$$

where K_s - saturation constant for heterotrophs, M/L^3

k_d - decay coefficient for heterotrophs, t^{-1}

μ_m - heterotrophs maximum specific growth rate, t^{-1}

The required aeration tank volume for carbon oxidation and nitrification is computed by:

$$V_{aerobic} = \frac{Y_H\theta_c Q_i([COD]_i - [COD]_e)}{X(1+k_d\theta_c)} \quad (3.1\text{-}6)$$

where Y_H - heterotrophs yield coefficient, M/M

X - biomass or mixed liquor suspended solids concentration, M/L^3

The aerobic volume can also be estimated based on aerobic hydraulic retention time, $\theta_{aerobic}$, in units time:

$$V_{aerobic} = \theta_{aerobic} Q_i \quad (3.1\text{-}7)$$

If the denitrification tank volume and influent flow rate are known, the anoxic retention time, θ_{anoxic}, is:

$$\theta_{anoxic} = \frac{V_{anoxic}}{Q_i} \quad (3.1\text{-}8)$$

The typical operating parameters for this investigation are provided in Table 4.1 and the biokinetic constants are summarized in Table 4.2. The bio-simulator used in this study is discussed in Chapter 4.

3.2 PREDICTIVE EQUATIONS DEVELOPMENT

The sensitivity of four measurement parameters (oxidation reduction potential, oxygen uptake rate, ammonium-nitrogen and nitrate uptake rate) are investigated for various loading conditions. The input variables are the loading rate of COD, ammonium, nitrate, and hydraulic. Therefore, this chapter deals with the development of a mathematical model for these measurement parameters. The backgrounds of the oxidation reduction potential and oxygen uptake rate are provided in Chapter 2.2.3.

3.2.1 OXIDATION REDUCTION POTENTIAL

Oxidation reduction (redox) reactions in biological reactions are normally defined in terms of the loss and gain of hydrogen or electrons. A couple (complete) reaction consists of an oxidation accompanied by a reduction, so that each couple has a tendency to either donate or accept reducing equivalents. This tendency is expressed as the oxidation reduction potential (ORP) or redox potential. The unit of measurement for this potential is either millivolt or volt. The larger the ORP of a substance, the stronger its oxidizing power; the smaller the ORP, the weaker the oxidizing power. The reader is referred to Chapter 2.2.3.6 for the applications of ORP as a control parameter in wastewater engineering.

Usually the redox reaction is written in "redox pair" (half reaction) form (for example, NO_3^-/NO_2^-), with the oxidized substance always written first. The typical ORP

values for various important biochemical reactions in the wastewater treatment process are presented in Table 3.1.

The concept of ORP derives from the science of thermodynamics; therefore, the standard ORP of chemical reactions can be calculated from their standard Gibbs free energies. That is, the amount of energy released by a redox pair (half reaction) is determined from the standard reduction potential of the half reaction and from the number of electrons transferred. The magnitude of energy released (the standard Gibbs free energy of formation) is expressed as (Brock, Smith, and Madigan, 1984):

$$G^\circ = -nE_h^\circ F \tag{3.2-1}$$

hence the standard redox potential is:

$$E_h^\circ = -\frac{G^\circ}{nF} \tag{3.2-2}$$

where E_h° - standard redox potential (ORP), millivolt (mV)

G° - standard Gibbs free energy, cal/mole

F - Faraday's constant, 23.066 cal/mV

n - number of electrons transferred

In order to calculate the redox potential, E_h, of a reduction half reaction over a range of concentrations and pressures, the relationship between the redox potential and standard redox potential, E_h°, is needed. From a thermodynamic point of view, redox potential is

Table 3.1 Standard redox potentials of some redox pairs in various biochemical reactions (Brock, Smith, and Madigan, 1984).

Biochemical Reactions	Redox Pair	E_h°(V)
Aerobic respiration	O_2/H_2O	+0.82
Nitrification	NO_3^-/NH_4^+	+0.33
	NO_3^-/NO_2^-	+0.43
Denitrification	NO_3^-/N_2	+0.74
	NO_2^-/NO	+0.36
	NO/N_2O	+1.18
	N_2O/N_2	+1.36
Sulphate reduction	SO_4^{2-}/H_2S	-0.22
Methanogenesis	CO_2/CH_4	-0.38

related to the chemical potentials of the substance in a chemical reaction (Levine, 1988):

$$\sum_i \nu_i \mu_i = -nFE_h \qquad (3.2\text{-}3)$$

where ν_i - stoichiometric coefficient for substance i

μ_i - chemical potential for substance i

The definition of activity, a_i, of substance i in chemical potential is (Levine, 1988):

$$\mu_i = \mu_i^\circ + RT\ln(a_i) \qquad (3.3\text{-}4)$$

where μ_i° - standard state chemical potential

R - gas constant (1.987 cal/K-mole)

T - temperature, K

Using Eq. (3.2-4) to express chemical potential in Eq. (3.2-3) in terms of activities yields:

$$\sum_i \nu_i \mu_i = \sum_i \nu_i \mu_i^\circ + RT \sum_i \nu_i \ln(a_i) \tag{3.2-5}$$

Since the first term in the right hand side of Eq. (3.2-5) is defined as the standard Gibbs energy for a typical chemical reaction (reactants and products, each in standard state), and the sum of logarithms equals the logarithm of the product, Eq. (3.2-5) becomes:

$$\sum_i \nu_i \mu_i = G^\circ + RT \ln\left[\prod_i (a_i)^{\nu_i}\right] \tag{3.2-6}$$

Substituting Eq. (3.2-6) into Eq.(3.2-3) and using the definition of Eq. (3.2-2) for standard Gibbs free energy of formation gives (Levine, 1988):

$$E_h = E_h^\circ - \frac{RT}{nF} \ln\left[\prod_i (a_i)^{\nu_i}\right] \tag{3.2-7}$$

Eq. (3.2-7) is the Nernst equation which relates redox potential (electron motive force in thermodynamics) to the activities a_i of the substances in the chemical reaction and to the standard redox potential, E_h°, of the reaction. The equilibrium position of a chemical reaction occurs when the activities are such that $\prod_i (a_i)^{\nu_i}$ equals the equilibrium constant K°. Thus the Nernst equation can be represented by:

$$E_h = E_h^\circ - \frac{RT}{nF} \ln[K^\circ] \tag{3.2-8}$$

and K° for a chemical reaction is expressed as:

$$K^\circ = \frac{[\text{product}]}{[\text{reactant}]} \tag{3.2-9}$$

where [] is in molar concentration.

To apply the concepts of thermodynamic discussed above for derivation of a redox potential (ORP) predictive equation, consider a denitrification half reaction which can be written as:

$$2NO_3^- + 12H^+ + 10e \rightarrow N_2 + 6H_2O \tag{3.2-10}$$

The equilibrium constant for this reaction using Eq. (3.2-9) is:

$$K^\circ = \frac{P_{N_2}[H_2O]^6}{[NO_3^-]^2[H^+]^{12}} \tag{3.2-11}$$

where P_{N_2} is the nitrogen gas partial pressure in units of atmosphere. Substituting Eq. (3.2-11) into Eq. (3.2-8) yields:

$$E_h = E_h^\circ - \frac{RT}{nF}\ln\left(\frac{P_{N_2}[H_2O]^6}{[NO_3^-]^2[H^+]^{12}}\right) \tag{3.2-12}$$

Expanding Eq. (3.2-12) gives:

$$E_h = E_h^o - \frac{RT}{nF}\left(\ln P_{N_2} + \ln[H_2O]^6 - \ln[NO_3^-]^2 - \ln[H^+]^{12}\right) \quad (3.2\text{-}13)$$

Assuming the activity of water (a_{H_2O}) in an aqueous system is constant at a molar concentration of 55 M, because in dilute aqueous solution the mole fraction (x_{H_2O}) and activity coefficient (γ_{H_2O}) are close to 1, the pH of the solution is also expressed as:

$$pH = -\log[H^+] = -\frac{\ln[H^+]}{2.303} \quad (3.2\text{-}14)$$

Using the above assumptions, the term $[H_2O]$ and $[H^+]$ can be eliminated in Eq. (3.2-13). The nitrogen partial pressure term is taken as 0.8 atm at temperature of 25°C (298 K) (Mosey, 1985). The standard redox potential (E_h^o), however, determined from Eq. (3.2-2) is 1245.4 mV, and, according to Eq. (3.2-10), there are 10 electrons transferred in the reaction. With this condition, Eq. (3.2-13) is reduced to the form of:

$$E_h = 1184.3 - 70.93pH + 5.134\ln[NO_3^-] \quad (3.2\text{-}15)$$

The redox equation (Eq. 3.2-15) expresses the ORP values of a denitrification chemical reaction as a function of nitrate concentration and pH. Similar redox equations for biochemical reactions such as nitrification can be derived using the concept presented above. The redox equation in logarithm base is:

$$E_h = 844 - 73.9pH + 7.39\log\left(\frac{[NH_4^+]}{[NO_3^-]}\right) \quad (3.2\text{-}16)$$

for a nitrification half reaction of:

$$NO_3^- + 10H^+ + 8e \rightarrow NH_4^+ + 3H_2O \qquad (3.2\text{-}17)$$

The reader is referred to Mosey (1985) for other redox equations. The correlations derived in this section depend heavily on well-defined chemical reactions, but the reactions occurring in the wastewater treatment process are complex and difficult to define, therefore reducing their potential usage. Mosey (1985) indicates that biochemical reactions, including sulphate reduction, methanogenesis, and nitrification, are sufficiently defined for estimation of their ORP.

Peddie et. al. (1990) derived an ORP empirical equation from their study of aerobic sludge digestion. They proposed the use of ORP as a monitoring and control parameter for the digestion process. They concluded that a linear relationship only exists for low concentrations of nitrate during the denitrification part of the cycle. At higher nitrate concentrations, the ORP shows a rapid increase. The empirical redox equation derived from their study is:

$$E_h \text{ (or ORP)} = 119.4 \log\left(NO_3^-\right) + 35.92 \qquad (3.2\text{-}18)$$

where () indicates mass concentration (mg/l). On the other hand, Koch and Oldham (1985) also studied the potential use of ORP as a control index for a biological nutrient removal system. Their findings conclude that the ORP values in the anoxic zone depend mainly on nitrate residual concentrations. The linear relationship of ORP and nitrate residual concentrations implies that the ORP can be used as a unique and effective means of monitoring and controlling process nitrate removal (Koch and Oldham, 1985). They

stated that an ORP control point of -100 mV would define a low nitrate concentration and the linear relationship. The ORP equation, derived from two months' operating data for an anoxic bioreactor, is (Koch and Oldham, 1985):

$$E_h \text{ (or ORP)} = \frac{(NO_3^-) - 1.08}{0.0081} \qquad (3.2\text{-}19)$$

In order to investigate the differences and effectiveness among the three predictive redox equations (Eq. 3.2-15, Eq. 3.2-18, and Eq. 3.2-19), an ORP profile of denitrification in the anoxic zone is presented in Figure 3.2. The theoretical ORP equation (Eq. 3.2-15) does not fit well with the experimental (empirical) redox equations (Eq. 3.2-18 and Eq. 3.2-19), because the theoretical equation is limited to well-defined chemical reactions. The reactions occurring in a wastewater treatment plant are less defined for ORP calculations. The ORP values are influenced by dissolved oxygen (DO) concentrations, pH values, and bacterial substrates present. For example, the DO concentration in the anoxic zone is not always zero during denitrification, and furthermore, the presence of NH_4-N and soluble organics also affect the ORP values in the anoxic zone. According to some experts (Koch and Oldham, 1985 and Peddie et al., 1990), the ORP control point is about -100 mV for optimal nitrate removal (denitrification). However, the optimal ORP control point has to be determined from experiment since the wastewater characteristics are different from plant to plant.

The plots in Figure 3.2 show that the ORP represented by Eq. (3.2-18) levels off when nitrate concentration exceeds a certain limit (1.0 mg/l). The ORP by Eq. (3.2-19), however, is directly proportional to nitrate concentration; that is, the ORP will be greater than thousands of millivolt if the nitrate concentration is greater than 10 mg/l. On the

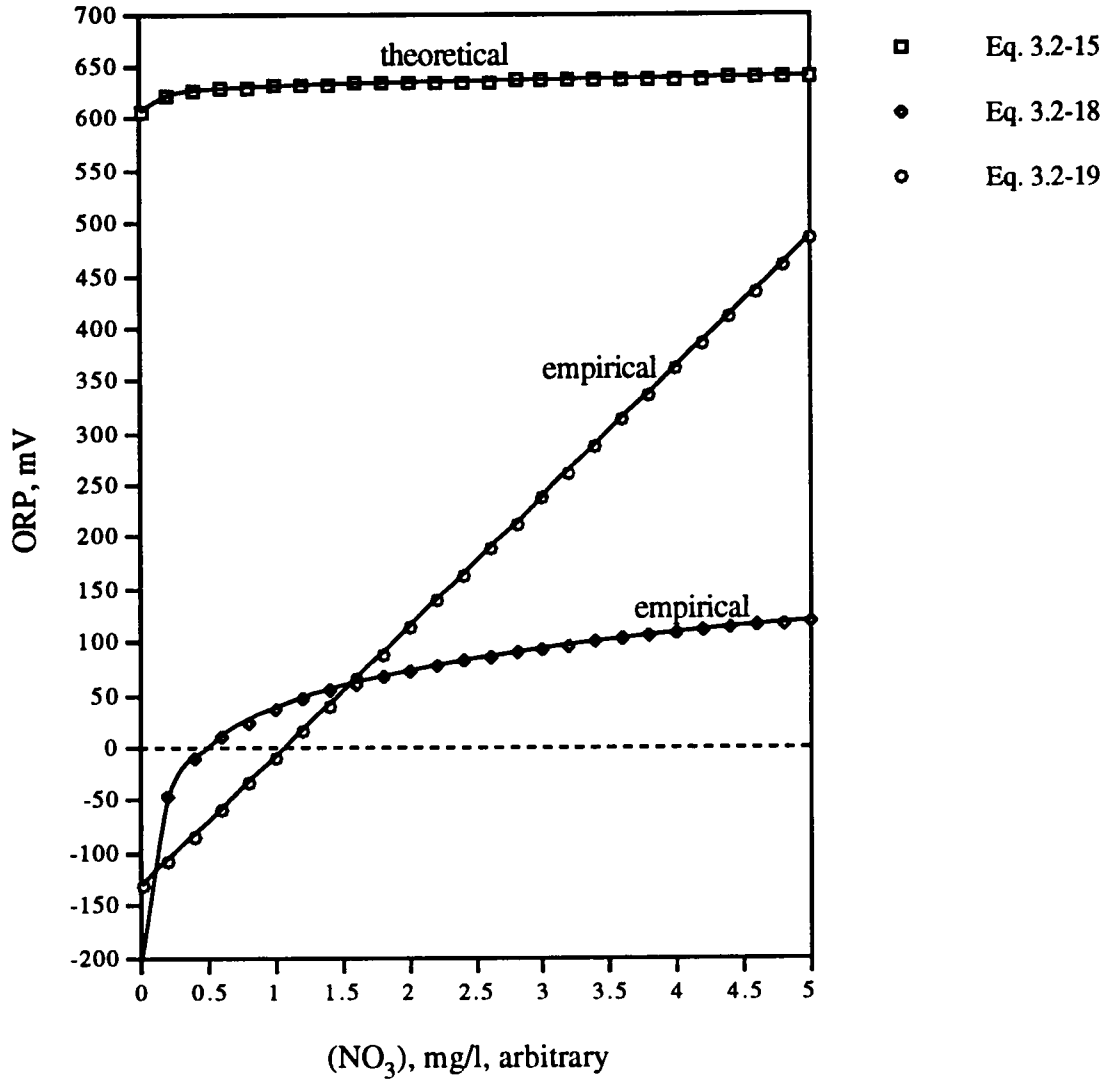


Figure 3.2 ORP profile of denitrification in the anoxic zone.

other hand, the nitrate concentration has no significant effect on the ORP predicted by Eq. (3.2-15). Again, this equation is based on well-defined chemical reactions, but one can observe that the general pattern of theoretical ORP is quite in agreement with the empirical ORP estimated by Eq. (3.2-18), that is, both ORPs begin to level-off at a certain nitrate concentration. The overall observations suggest that the best representative for ORP predictions is Eq. (3.2-18), hence it was used for the entire process parameter sensitivity analysis in this research.

3.2.2 SPECIFIC AMMONIUM-NITROGEN, NITRATE, AND OXYGEN UPTAKE RATES.

Design equations for many different types of bio-treatment processes can be developed by applying materials balances to the particular system of interest. Therefore, the derivative terms in these design equations depend upon a particular relationship to describe their derivative rate expressions. One form of this relationship, defined by Lawrence and McCarty (1970), is the substrate utilization (uptake) rate:

$$\left(\frac{ds}{dt}\right)_u = \frac{kXS}{K_c + S} \qquad (3.2\text{-}20)$$

where $\left(\frac{ds}{dt}\right)_u$ - overall substrate uptake rate, M/L^3-t

k - maximum specific substrate uptake rate, which is the maximum rate of substrate uptake per unit biomass, t^{-1}.

S - growth-limiting substrate concentration in solution, M/L^3

K_c - saturation constant, substrate concentration at one-half the maximum specific substrate uptake rate, M/L^3

X - active biomass concentration, M/L^3

Eq. (3.2-20) implies that the substrate uptake rate is continuous with respect to the substrate concentration. Eq. (3.2-20) is also related to the maximum specific growth rate defined by $k = \frac{\mu_m}{Y}$ (Y is the maximum yield coefficient), therefore the substrate utilization rate is also affected by the growth rate of microorganisms (Metcalf and Eddy, 1991). However, the specific substrate uptake rate is expressed as (Benefield and Randall, 1980):

$$\frac{\left(\frac{ds}{dt}\right)_u}{X} = \frac{kS}{K_c + S} = SSUR \qquad (3.2\text{-}21)$$

This particular expression, SSUR, has been investigated by many researches as a measurement parameter to indicate the activity of biomass in wastewater treatment processes. Because only the active biomass uses substrate during the course of living and growth, the measurement of SSUR reflects the extent of the microbial activity of a particular condition of a treatment system. Typical examples of using SSUR as a control parameter for this analysis are specific oxygen uptake rate, specific ammonium-nitrogen uptake rate, and specific nitrate uptake rate.

Ammonium-nitrogen utilization rate (AUR) is the ammonia consumed by the nitrifying bacteria in the aerobic zone. Using material balances, this rate is formulated as:

$$AUR = \frac{\left([NH_4]_i - [NH_4]_e\right)Q_i}{V_{aerobic}} \qquad (3.2\text{-}22)$$

where AUR in units of M/L^3-t (g N/m^3-d). The specific ammonium-nitrogen uptake rate is estimated using the definition of Eq. (3.2-21):

$$SAUR = \frac{AUR}{MLVSS} \tag{3.2-23}$$

where SAUR - specific ammonium-nitrogen uptake rate, g N/g VSS-d

MLVSS - steady-state active biomass concentration, g VSS/d

NUR - ammonium-nitrogen uptake rate, g N/m^3-d

The nitrate uptake rate (NUR) is the nitrate utilized by the heterotrophic microbes in the anoxic zone. This rate is provided in the SSSP solution; however, the specific nitrate uptake rate (SNUR) is estimated by:

$$SNUR = \frac{NUR}{MLVSS} \tag{3.2-24}$$

where SNUR - specific nitrate uptake rate, g NO_3/g VSS-d

NUR - nitrate uptake rate, g NO_3/m^3-d

The specific oxygen uptake rate is expressed as:

$$SOUR = \frac{OUR}{MLVSS} \tag{3.2-25}$$

where SOUR - specific oxygen uptake rate, g O_2/g VSS-d

OUR - oxygen uptake rate, g O_2/m^3-d

For details of OUR, the reader is referred to Chapter 2.2.3. Equations (3.2-22), (3.2-23), (3.2-24), and (3.2-25) are the estimation formulas for AUR, SAUR, SNUR, and SOUR, respectively. The OUR and NUR are provided in the SSSP simulations.

3.3 ANOXIC ZONE RECIRCULATION MODEL

Nitrate removal in the anoxic (denitrification) zone is dependent on the availability of a biodegradable organic substrate. Therefore, the maximum possible denitrification rate can be determined if a suitable on-line method of quantifying the biodegradable substrate can be found (Chapter 2.2, BOD and COD measurement methods). To achieve complete denitrification, the quantities of biodegradable organic carbon must sufficiently match the nitrate load (Figure 3.1, nitrate is recirculated from the aerobic zone to the anoxic zone). Therefore, if the recirculation rate is low, less nitrate is recycled into the anoxic zone. However, the recirculation rate has to be increased to prevent a peak nitrate concentration in the effluent. As a result, recirculation rate plays an important role in monitoring of nitrate concentrations at the aerobic zone effluent and anoxic zone effluent. This monitoring strategy uses the relationship between the influent content and the nitrate concentration at the aerobic zone outflow. This relationship is defined as overall recycling ratio, R_{all}:

$$R_{all} = \frac{(Q_{re} + Q_{rs})\left([NO_3]_e + [NH_4]_e + [COD]_e\right)}{Q_i\left([NO_3]_i + [NH_4]_i + [COD]_i\right)} \qquad (3.3\text{-}1)$$

Since the overall recycling ratio (Eq. 3.3-1) can be interpreted as the ratio of the effluent concentration to the influent concentration, the overall removal efficiency for the bio-treatment process is formulated as:

$$E_{all} = \frac{Q_i\left([NO_3]_i + [NH_4]_i + [COD]_i\right) - (Q_{re} + Q_{rs})\left([NO_3]_e + [NH_4]_e + [COD]_e\right)}{Q_i\left([NO_3]_i + [NH_4]_i + [COD]_i\right)} \tag{3.3-2}$$

or, in terms of the recycling ratio:

$$E_{all} = 1 - R_{all} \tag{3.3-3}$$

All the effluent variables in Eq. (3.3-1) are at the aerobic zone (carbon oxidation and nitrification) outflow. For this typical investigation, one can assume that both the effluent COD and ammonium-nitrogen concentrations are small compared to the effluent nitrate concentration. Hence Eq. (3.3-1) is reduced to:

$$R_r = \frac{(Q_{re} + Q_{rs})[NO_3]_e}{Q_i\left([NO_3]_i + [NH_4]_i + [COD]_i\right)} \tag{3.3-4}$$

where R_r is the dimensionless recycling ratio. The function of recirculation is to recycle nitrate from the aerobic to the anoxic zone; thus, the most important parameter in manipulating Q_{re} is the concentration of nitrate in the effluent aerobic zone . As a result, the neglect of the terms for the effluent COD and ammonium in Eq. (3.3-4) is reasonable. Moreover, this assumption also simplifies the control model analysis.

In order to manipulate the recirculation rate, Q_{re}, by Eq. (3.3-4), the required parameters are the concentration of influent variables, the effluent nitrate concentration (aerobic zone outflow), and the recycling ratio. The influent and effluent concentrations can be easily measured using the sensors and measurement methods discussed in Chapter

2.2. The nitrate concentration in the aerobic zone outflow is chosen in Eq. (3.3-4) because the measurement of nitrate content at the aerobic zone outflow is more reliable than that measured of the denitrification zone outflow. The nitrate concentration in the aerobic zone outflow is usually higher than the anoxic zone outflow nitrate concentration (< 1.0 mg/l); thus, the high nitrate content of the aerobic zone outflow favors the measurement.

The major objective of this study, to monitor the denitrification rate in the anoxic zone by manipulating the recirculation rate, requires the establishment of a relationship between the recycling ratio and the nitrate uptake rate in the anoxic zone. The nitrate concentration at the aerobic zone outflow depends on the nitrate consumption rate in the anoxic zone. Using these two bases and the definition of the specific substrate utilization rate (Eq. (3.2-21)), an association between the specific nitrate uptake rate in the anoxic zone and the nitrate recycling ratio can be formulated as:

$$\frac{\left(d[NO_3]_e/dt\right)_u}{X} = \frac{S_{max}R_r}{K_r + R_r} = SNUR \qquad (3.3\text{-}5)$$

where S_{max} - maximum specific nitrate uptake rate, g NO_3/g VSS-d

K_r - recycling ratio when $SNUR = \frac{1}{2}S_{max}$, dimensionless

Eq. (3.3-5) indicates that the relationship between the specific nitrate uptake rate and the recycling ratio resembles the relationship defined by either the Monod or Michaelis-Menten Equations [Baily and Ollis (1986), Benefield and Randall (1980), Shuler and Kargi (1992), Metcalf and Eddy (1991)]. This Monod assumption is based on the specific denitrification rate defined by Horan (1990). In Eq. (2.1-9) of Chapter 2.1.5.7, the SNUR is also referred to specific denitrification rate; however, in Eq. (2.1-9) the

nitrate concentration is used instead of the recycling ratio. For a low recycling ratio (K_r >> R_r), the SNUR reduces to the first order rate expression with respect to the recycling ratio; that is, the SNUR is directly proportional to recycling ratio, R_r.

$$SNUR = \frac{S_{max}}{K_r} R_r \qquad (3.3\text{-}6)$$

However, in a case when the recycling ratio is high (R_r >> K_r), then K_r can be neglected in the sum term of the denominator of Eq. (3.3-5). Under this condition, the specific nitrate uptake rate is zero-order with respect to the recycling ratio:

$$SNUR = S_{max} \qquad (3.3\text{-}7)$$

In order to determine the biokinetic constants R_r and K_r, Eq. (3.3-5) is linearized to double reciprocal form:

$$\frac{1}{SNUR} = \frac{K_r}{S_{max}} \frac{1}{R_r} + \frac{1}{S_{max}} \qquad (3.3\text{-}8)$$

A plot of the reciprocal of the specific nitrate uptake rate as a function of the reciprocal of the recycling ratio, R_r, will yield a straight line. Thus, the biokinetic constants can be found from the slope and intercept of the linear plot:

$$slope = \frac{K_r}{S_{max}} \qquad (3.3\text{-}9)$$

$$intercept = \frac{1}{S_{max}} \qquad (3.3\text{-}10)$$

Knowing the biokinetic constants permit the formulation of the recycling ratio, R_r, as a function of the specific nitrate uptake rate, SNUR, as follows:

$$R_r = \frac{SNUR \cdot K_r}{S_{max} - SNUR} \tag{3.3-11}$$

Eq. (3.3-11) defines the recycling ratio as a function of the specific nitrate uptake rate, whereas Eq. (3.3-4) defines the recycling ratio in terms of the influent and effluent concentrations. When the R_r parameter is known, by solving Q_{re} in Eq. (3.3-4), the anoxic zone can be monitored via the recirculation rate:

$$Q_{re} = \frac{R_r Q_i \left([NO_3]_i + [NH_4]_i + [COD]_i \right)}{[NO_3]_e} - Q_{ns} \tag{3.3-12}$$

where R_r is calculated by Eq. (3.3-11). The proposed model represented by Eq. (3.3-12) allows the control of the nitrate removal rate in the anoxic zone via manipulation of the recirculation rate based on the nitrate recycling ratio, which is a function of the content of the influent components and the concentration of nitrates in the aerobic zone outflow. Theoretically, Eq. (3.3-12) can predict the required recirculation rate with respect to different loading concentrations. The accuracy of the recirculation rate prediction, however, depends heavily on the recycling ratio represented by Eq. (3.3-11), as the assumption that the Monod equation applies to the relationship between the specific nitrate uptake rate and the recycling ratio is purely theoretical and overly simplified. Nevertheless, the major objective of the proposed empirical model is to analyze the

validity of using the specific nitrate uptake rate as an indicator of the removal efficiency in the anoxic zone.

In order to study the sensitivity of process parameters and the proposed control model, a number of simulations must be conducted at various loading conditions, with input variables that cover a wide range of variations. The simulation procedures are further discussed in Chapter 4.

CHAPTER 4

METHOD OF ANALYSIS

4.1 BIO-SIMULATOR PROGRAM

The computer program used for this wastewater treatment analysis was developed by the Department of Environmental Systems Engineering at Clemson University. The program is called the Simulation of Single-sludge Processes for Carbon Oxidation, Nitrification and Denitrification (SSSP) (Bidstrup and Grady, 1987). The SSSP is capable of simulating a bio-treatment model of up to nine completely mixed-activated sludge reactors. The user specifies the process flow sheet, influent variables and compositions, inlet flow rate, reactor volume, recycle flow rate, recirculation flow rate, and sludge age. Default biokinetic constants are included if others are not available. Based on the input specifications, the SSSP uses numerical techniques to calculate steady-state solutions for all the components' mass balances. For more information on the SSSP program, the reader is referred to the user manual (Bidstrup and Grady, 1987). The details and evaluations of the activated-sludge mathematical model are provided in Dold and Marias (1986); Grady et. al., (1986); Givens et al. (1991); and Gujer and Henze (1991).

4.2 DESIGN SPECIFICATIONS OF BIO-TREATMENT MODEL

The single-sludge simultaneous carbon oxidation, nitrification, and denitrification Bardenpho process is discussed in Chapters 2.1.5.6 and 2.1.5.7. The operating parameters for this Bardenpho model are shown in Table 4.1. The base case shown in Table 4.1 is referred to as the basic influent condition for designing the treatment model;

Table 4.1 Design specifications of the simulated biological treatment model.

Parameters	Notation	Unit	High	Base	Low
Organic	$[COD]_i$	g COD/m³	7500	5000	2500
Ammonium	$[NH_4]_i$	g N/m³	750	500	250
Nitrate	$[NO_3]_i$	g N/m³	150	100	50
Hydraulic	Q_i	m³/d	8177	5451	2726
Alkalinity	ALK	mole/m³		80	
MLVSS	X	g COD/m³		5000-6000	
Sludge age[1]	θ_c	days	5.0	3.5	
Reactor number	n			2	
<u>Anoxic Zone:</u>					
Volume I	V_{anoxic}	m³		1000	
Total flow fraction		0 to 1		1	
Dissolved oxygen	DO_{anoxic}	g O_2/m³		0	
Sludge recycle	Q_{rs}	m³/d		2500	
Recirculation	Q_{re}	m³/d	32700	21800	10900
<u>Aerobic Zone:</u>					
Volume II	$V_{aerobic}$	m³		7000	
Total flow fraction		0 to 1		0	
Dissolved oxygen	$DO_{aerobic}$	g O_2/m³		9	
Sludge recycle	Q_{rs}	m³/d		0	
Recirculation	Q_{re}	m³/d		0	

1. Sludge age of 3.5 days is used for single variable analysis but 5 days is employed for statistical factorial analysis.

that is, the sludge age (Eq. 3.1-3) is calculated based on the base-case condition, and the system is designed to achieve mixed liquor suspended solids in the range 5000-6000 g COD/m^3. The minimum sludge age calculated (Eq. 3.1-1) for complete nitrification is 1.89 days, and using a similar mathematical formula as Eq. (3.1-1), the minimum sludge age for denitrification is 0.33 days. Therefore, using a safety factor (Eq. 3.1-2) of 1.5, the required sludge age for the overall system is 3.5 days.

The volumes of the aerobic and anoxic zones are approximated by Eq. (3.1-7) and Eq. (3.1-8). The bio-treatment system is also designed to accomplish not less than 95% removals of COD, ammonium, and nitrogen. To confirm the SSSP program solution, the effluent COD and ammonium (NH_4) are estimated from Eq. (3.1-5) and Eq. (3.1-4) with the base case condition. The hand-calculated effluent concentrations for COD and NH_4 are 3.0 g/m^3 and 1.7 g N/m^3, respectively, in comparison to SSSP results of 3.6 g/m^3 and 2.0 g N/m^3, respectively. Once the base case condition is determined, the high and low cases are ±50% of the base case.

The steady-state sensitivity analysis of the process measurement parameters (Chapter 3.2.2) are performed using the SSSP program. The analysis method is called single variable analysis, in which one influent parameter varies from low to high and the rest of the parameters are held constant at base case. Since there are four influent variables, this investigation consists of 4 simulations with 11 runs in each simulation. Although this method does not provide the interaction effect among the input variables and the measurement parameters, the general profile of the effect can be observed. These analyses will serve as a basis for future research and development. Table 4.2 presents the partial biokinetic constants used in the SSSP simulations.

In order to verify the proposed recirculation rate predictive equation (Chapter 3.3), one additional input variable (recirculation rate) is added. Moreover, a wide range of

Table 4.2 Biokinetic constants for heterotrophic and autotrophic microorganisms.

Parameters	Unit	Value[1]	Value[2]
Heterotroph:			
μ_m	day^{-1}	4.0	4.0
K_s	g COD/m^3	10.0	10.0
Y_H	g COD/g COD	0.67	0.4
k_d	day^{-1}	0.62	0.62
Autotroph:			
$\mu_{m,n}$	day^{-1}	0.65	0.65
K_N	g N/m^3	1	1
Y_N	g COD/g N	0.24	0.15
$k_{d,N}$	day^{-1}	0.12	0.12

1. Default values from Bidstrup and Grady, (1987) for single variable analysis.
2. Assumed values from Dold and Marais (1986) for statistical factorial analysis.

variations from low to high is also needed for each input parameter. Thus, many simulations have to be performed to provide a wide coverage of input parameter variations. Each input parameter, for instance, has five variations which range from low to high; hence, for five input variables there are a total of 3125 combinations (factorial of 5^5). That is, more than 3000 simulations have to be performed just to provide a full study of the effects of the variables and to generate the data for the proposed recirculation rate analysis.

A statistical factorial method is introduced for this investigation that gives good estimates of the effects of variables from fewer simulations. In this proposed recirculation rate equation analysis, a two-level (high and low) and five-factor (five input variables) system is selected, which requires a total of 32 runs (2^5). Using the statistical factorial

method, the total runs are reduced to 20 runs plus 5 dummy runs (randomly set conditions). The details of this factorial statistical method can be found in Murphy (1977), Walpole and Myers (1989), and Davies (1992). The sludge age for this statistical factorial analysis is 5 days; thus, the assumed kinetic values (Table 4.2) are used in the SSSP simulations to generate a low-level of MLVSS concentration in the system—the length of the sludge age affects the concentration of the MLVSS concentration. The results generated from these activities are presented in Chapter 5 and the conclusions are summarized in Chapter 6.

CHAPTER 5

RESULTS AND DISCUSSIONS

In this study, the biological treatment model used for COD and nitrogen removals is a two-stage Bardenpho process. The SSSP program is used to simulate the bio-system model. The influent variables are COD, ammonia-nitrogen, nitrate, and hydraulic loadings. This bio-treatment model is derived to achieve nitrate removal in the anoxic zone and soluble organic (COD) and ammonium removals in the aerobic zone. The primary objective of the investigation is the steady-state analysis of the sensitivity of process measurement parameters under various influent conditions. The process parameters or control indexes are the oxidation reduction potential (ORP), oxygen uptake rate (OUR), ammonium-nitrogen utilization rate (AUR), and nitrate uptake rate (NUR). The specific oxygen, nitrate, and ammonium uptake rates (SOUR, SNUR, and SAUR) are also analyzed. The sensitivity of the process parameters is investigated through single variable analysis and statistical factorial analysis.

5.1 SINGLE VARIABLE ANALYSIS

The major purpose of the single variable analysis is to investigate the steady-state responses of process measurement parameters (ORP, OUR, NUR, and AUR) to variations in input conditions. There are four input variables: COD, ammonium, nitrate, and hydraulic loadings. Throughout the whole simulation, each input variable is varied from low to high while the others are held constant. All the steady-state solutions obtained from the simulations of the SSSP program in this single variable analysis are

summarized in Tables 5.1 through 5.8. For clarity, the solutions are presented in two categories: Tables 5.1, 5.3, 5.5, and 5.7 show the values of effluent parameters in the anoxic zone and; Tables 5.2, 5.4, 5.6, and 5.8 indicate results of effluent variables in the aerobic zone. In the anoxic zone category, the SNUR is calculated by Eq. (3.2-24) and the ORP is determined from Eq. (3.2-18), because, for this typical investigation, the ORP values are more adequately represented by Eq. (3.2-18) in comparison to Eq. (3.2-15) and Eq. (3.2-19). In the aerobic zone category, the ORP is estimated from Eq. (3.2-18), too, but the AUR, SOUR, and SAUR are estimated by Eq. (3.2-22), Eq. (3.2-25), and Eq. (3.2-23), respectively.

The influent COD concentration has a reverse effect on the residual nitrate content in the anoxic zone (Table 5.1); that is, when the soluble organic in the influent increases from 2500 to 7500 g/m^3, the soluble nitrate in the anoxic stage reduces from 219.4 to 0.2 g NO_3/m^3. Heterotrophs require a sufficient number of electron donors (organic matter) for nitrate removal, so, when the soluble organic is reduced, the nitrate concentration increases. Furthermore, the ORP values are reduced to negative potential when the nitrate concentration is less than 0.6 g/m^3. These behaviors agree with the findings from the literature (Chapters 2.2 and 3.1). Table 5.2 shows that the increase of inlet COD causes the reduction of aerobic zone effluent nitrate concentrations from 291.9 to 38.5 g NO_3/m^3 and the increase of effluent COD contents from 1.8 to 2.7 g COD/m^3. It can thus be concluded that the effect of influent COD on effluent COD is less than the effect of influent on effluent nitrate. The high nitrate concentration in the aerobic zone outlet suggests that an additional anoxic stage following the aerobic stage is required for further denitrification, which is usually the case in industrial applications (Chapter 2.1.5.7).

Table 5.1 Effluent variables in anoxic (denitrification) zone for COD single variable analysis[1,2].

Influent Organic $[COD]_i$ g COD/m^3	Soluble Organics $[COD]_e$ g COD/m^3	Ammonium Nitrogen $[NH_4]_e$ g N/m^3	Soluble Nitrate $[NO_3]_e$ g NO_3/m^3	Suspended[3] Solids MLVSS g COD/m^3	Nitrate Uptake Rate NUR g NO_3/m^3 · d	Redox[4] Potential ORP mV	Specific[4] Uptake rate SNUR g NO_3/g VSS · d
2500	154.1	77.7	219.4	2793.6	1113.4	315.46	0.562
3000	181.4	74.1	161.7	3311.0	1346.8	299.64	0.574
3500	208.7	70.5	104.1	3828.7	1580.1	276.80	0.582
4000	236.9	67.0	46.9	4345.5	1810.3	235.46	0.587
4500	287.6	64.7	4.3	4848.5	1959.0	111.56	0.570
5000	398.2	65.8	1.0	5311.1	1890.8	35.92	0.502
5500	513.3	67.1	0.5	5775.2	1809.3	-0.02	0.442
6000	632.0	68.6	0.4	6217.3	1719.5	-11.59	0.390
6500	742.5	69.7	0.3	6703.8	1642.3	-26.51	0.345
7000	858.2	71.0	0.2	7161.5	1556.6	-47.54	0.306
7500	972.3	72.3	0.2	7634.7	1475.7	-47.54	0.273

1. Fixed Parameters: $[NH_4]_i = 500$ g N/m^3; $[NO_3]_i = 100$ g N/m^3; $Q_i = 5451$ m^3/d; $\theta_c = 3.5$ d; $V_{anoxic} = 1000$ m^3; $Q_{rs} = 2500$ m^3/d; $Q_{re} = 21800$ m^3/d; $V_{aerobic} = 7000$ m^3; $DO_{aerobic} = 9.0$ g O_2/m^3.
2. The results are directly from SSSP program output unless otherwise noted.
3. Biomass conversion factor from g COD to g VSS is 1.41 g COD/g VSS.
4. ORP from eq. (3.2-18) and SNUR from eq. (3.2-24).

Table 5.2 Single variable analysis for COD in aerobic (carbon oxidation and nitrification) zone[1,2].

Influent Organic $[COD]_i$ g COD/m^3	Soluble Organics $[COD]_e$ g COD/m^3	Ammonium Nitrogen $[NH_4]_e$ g N/m^3	Soluble Nitrate $[NO_3]_e$ g NO_3/m^3	Suspended[3] Solids MLVSS g COD/m^3	Oxygen Uptake Rate OUR g O_2/m$^3 \cdot$d	Ammonia-N[4] Uptake Rate AUR g N/m$^3 \cdot$d	Redox[4] Potential ORP mV	Specific[4] Uptake Rate SOUR g O_2/g VSS$\cdot$d	Specific[4] Uptake Rate SAUR g N/g VSS$\cdot$d
2500	1.8	3.6	291.9	2811.3	1965.4	386.55	330.27	0.986	0.194
3000	1.8	3.6	231.0	3326.5	2026.2	386.55	318.14	0.859	0.164
3500	1.8	3.6	169.9	3841.9	2087.1	386.55	302.21	0.766	0.142
4000	1.8	3.6	109.4	4357.0	2149.1	386.55	279.38	0.695	0.125
4500	1.8	3.6	63.4	4873.0	2243.3	386.55	251.09	0.649	0.112
5000	2.0	3.6	56.7	5387.3	2422.6	386.55	245.30	0.634	0.101
5500	2.2	3.7	52.8	5906.6	2609.1	386.48	241.60	0.623	0.092
6000	2.3	3.7	49.3	6404.5	2799.2	386.48	238.05	0.616	0.085
6500	2.4	3.7	45.5	6944.9	2979.9	386.48	233.89	0.605	0.078
7000	2.6	3.7	42.0	7457.9	3166.4	386.48	229.74	0.599	0.073
7500	2.7	3.6	38.5	7986.3	3352.8	386.55	225.22	0.592	0.068

1. Fixed Parameters: $[NH_4]_i = 500$ g N/m^3; $[NO_3]_i = 100$ g N/m^3; $Q_i = 5451$ m^3/d; $\theta_c = 3.5$ d; $V_{anoxic} = 1000$ m^3; $Q_{rs} = 2500$ m^3/d; $Q_{re} = 21800$ m^3/d; $V_{aerobic} = 7000$ m^3; $DO_{aerobic} = 9.0$ g O_2/m^3.
2. The results are directly from SSSP program output unless otherwise noted.
3. Biomass conversion factor from g COD to g VSS is 1.41 g COD/g VSS.
4. AUR from eq. (3.2-22); ORP from eq. (3.2-18); SOUR from eq. (3.2-25); and SAUR from eq. (3.2-23).

Table 5.3 Effluent variables in anoxic (denitrification) zone for NH_4 single variable analysis[1,2].

Influent Ammonium-N $[NH_4]_i$ g N/m^3	Soluble Organics $[COD]_e$ g COD/m^3	Ammonium Nitrogen $[NH_4]_e$ g N/m^3	Soluble Nitrate $[NO_3]_e$ g NO_3/m^3	Suspended[3] Solids MLVSS g COD/m^3	Nitrate Uptake Rate NUR g NO_3/m$^3 \cdot$d	Redox[4] Potential ORP mV	Specific[4] Uptake rate SNUR g NO_3/g VSS$\cdot$d
250	701.3	36.9	0.1	5019.4	793.9	-83.48	0.223
300	640.7	42.7	0.2	5078.4	1014.2	-47.54	0.282
350	579.9	48.5	0.3	5137.2	1234.3	-26.51	0.339
400	520.0	54.3	0.4	5187.6	1450.9	-11.59	0.394
450	458.7	60.0	0.6	5253.1	1627.6	9.43	0.437
500	398.2	65.8	1.0	5311.1	1890.8	35.92	0.502
550	338.9	71.6	2.4	5373.6	2105.9	81.32	0.553
600	296.3	78.4	14.7	5421.8	2259.6	175.30	0.588
650	289.8	87.2	50.6	5448.1	2283.4	239.40	0.591
700	288.4	96.3	89.9	5471.0	2288.7	269.20	0.590
750	287.6	105.4	129.4	5493.7	2291.6	288.08	0.588

1. Fixed Parameters: $[COD]_i = 5000$ g COD/m^3; $[NO_3]_i = 100$ g N/m^3; $Q_i = 5451$ m^3/d; $\theta_c = 3.5$ d; $V_{anoxic} = 1000$ m^3; $Q_{rs} = 2500$ m^3/d; $Q_{re} = 21800$ m^3/d; $V_{aerobic} = 7000$ m^3; $DO_{aerobic} = 9.0$ g O_2/m^3.
2. The results are directly from SSSP program output unless otherwise noted.
3. Biomass conversion factor from g COD to g VSS is 1.41 g COD/g VSS.
4. ORP from eq. (3.2-18) and SNUR from eq. (3.2-24).

Table 5.4 Single variable analysis for NH_4 in aerobic (carbon oxidation and nitrification) zone[1,2].

Influent Ammonium $[NH_4]_i$ g N/m^3	Soluble Organics $[COD]_e$ g COD/m^3	Ammonium Nitrogen $[NH_4]_e$ g N/m^3	Soluble Nitrate $[NO_3]_e$ g NO_3/m^3	Suspended[3] Solids MLVSS g COD/m^3	Oxygen Uptake Rate OUR g O_2/m$^3 \cdot$d	Ammonia-N[4] Uptake Rate AUR g N/m$^3 \cdot$d	Redox[4] Potential ORP mV	Specific[4] Uptake Rate SOUR g O_2/g VSS$\cdot$d	Specific[4] Uptake Rate SAUR g N/g VSS$\cdot$d
250	2.8	3.7	10.4	5284.8	2030.0	191.80	157.35	0.542	0.051
300	2.6	3.6	19.5	5306.1	2108.3	230.81	189.95	0.560	0.061
350	2.5	3.6	28.7	5327.1	2186.6	269.75	209.99	0.579	0.071
400	2.3	3.7	37.9	5339.4	2265.2	308.60	224.41	0.598	0.081
450	2.2	3.7	47.2	5367.1	2344.0	347.54	235.79	0.616	0.091
500	2.0	3.6	56.7	5387.3	2422.6	386.55	245.30	0.634	0.101
550	1.9	3.6	67.1	5413.4	2503.8	425.49	254.03	0.652	0.111
600	1.8	3.6	88.5	5435.6	2608.4	464.43	268.39	0.677	0.120
650	1.7	3.6	133.5	5459.5	2764.5	503.36	289.70	0.714	0.130
700	1.7	3.6	181.7	5483.3	2927.8	542.30	305.69	0.753	0.139
750	1.7	3.6	230.3	5507.3	3092.1	581.23	317.98	0.792	0.149

1. Fixed Parameters: $[COD]_i = 5000$ g COD/m^3; $[NO_3]_i = 100$ g N/m^3; $Q_i = 5451$ m^3/d; $\theta_c = 3.5$ d; $V_{anoxic} = 1000$ m^3; $Q_{rs} = 2500$ m^3/d; $Q_{re} = 21800$ m^3/d; $V_{aerobic} = 7000$ m^3; $DO_{aerobic} = 9.0$ g O_2/m^3.
2. The results are directly from SSSP program output unless otherwise noted.
3. Biomass conversion factor from g COD to g VSS is 1.41 g COD/g VSS.
4. AUR from eq. (3.2-22); ORP from eq. (3.2-18); SOUR from eq. (3.2-25); and SAUR from eq. (3.2-23).

Table 5.5 Effluent variables in anoxic (denitrification) zone for Q_i single variable analysis[1,2].

Inlet Flow rate Q_i m^3/d	Soluble Organics $[COD]_e$ g COD/m^3	Ammonium Nitrogen $[NH_4]_e$ g N/m^3	Soluble Nitrate $[NO_3]_e$ g NO_3/m^3	Suspended[3] Solids MLVSS g COD/m^3	Nitrate Uptake Rate NUR g $NO_3/m^3 \cdot d$	Redox[4] Potential ORP mV	Specific[4] Uptake rate SNUR g NO_3/g VSS·d
2726	200.2	36.8	2.0	2664.7	1012.9	71.86	0.536
3271	203.2	40.8	6.9	3205.0	1305.4	136.08	0.574
3816	279.7	48.8	1.4	3725.7	1378.9	53.37	0.522
4361	319.4	54.6	1.2	4251.9	1553.2	45.37	0.515
4906	358.7	60.2	1.1	4783.2	1724.7	40.86	0.508
5451	398.2	65.8	1.0	5311.1	1890.8	35.92	0.502
5996	451.1	71.9	1.0	5760.8	2043.7	35.92	0.500
6541	475.8	76.4	0.9	6365.8	2211.0	30.46	0.490
7086	513.6	81.4	0.8	6879.3	2367.5	24.35	0.485
7631	551.3	86.4	0.8	7429.6	2520.5	24.35	0.478
8177	588.7	91.3	0.7	7958.6	2669.1	17.42	0.473

1. Fixed Parameters: $[COD]_i = 5000$ g COD/m^3; $[NH_4]_i = 500$ g N/m^3; $[NO_3]_i = 100$ g N/m^3; $\theta_c = 3.5$ d; $V_{anoxic} = 1000$ m^3; $Q_{rs} = 2500$ m^3/d; $Q_{re} = 21800$ m^3/d; $V_{aerobic} = 7000$ m^3; $DO_{aerobic} = 9.0$ g O_2/m^3.
2. The results are directly from SSSP program output unless otherwise noted.
3. Biomass conversion factor from g COD to g VSS is 1.41 g COD/g VSS.
4. ORP from eq. (3.2-18) and SNUR from eq. (3.2-24).

Table 5.6 Single variable analysis for Q_i in aerobic (carbon oxidation and nitrification) zone[1,2].

Inlet Flow rate Q_i m^3/d	Soluble Organics $[COD]_e$ $g\ COD/m^3$	Ammonium Nitrogen $[NH_4]_e$ $g\ N/m^3$	Soluble Nitrate $[NO_3]_e$ $g\ NO_3/m^3$	Suspended[3] Solids MLVSS $g\ COD/m^3$	Oxygen Uptake Rate OUR $g\ O_2/m^3 \cdot d$	Ammonia-N[4] Uptake Rate AUR $g\ N/m^3 \cdot d$	Redox[4] Potential ORP mV	Specific[4] Uptake Rate SOUR $g\ O_2/g\ VSS \cdot d$	Specific[4] Uptake Rate SAUR $g\ N/g\ VSS \cdot d$
2726	1.9	3.6	32.7	2694.0	1184.3	191.88	216.76	0.620	0.100
3271	1.8	3.6	43.0	3217.5	1377.7	191.88	230.96	0.604	0.084
3816	2.0	3.6	42.7	3772.2	1673.8	191.88	230.59	0.626	0.072
4361	2.0	3.6	47.4	4307.7	1921.1	191.88	236.01	0.629	0.063
4906	2.0	3.6	52.1	4849.0	2170.7	191.88	240.91	0.631	0.056
5451	2.0	3.6	56.7	5387.3	2422.6	191.88	245.30	0.634	0.050
5996	2.1	3.6	62.0	5851.2	2693.0	191.88	249.93	0.649	0.046
6541	2.0	3.7	65.2	6463.7	2930.2	191.80	252.54	0.639	0.042
7086	2.1	3.7	69.3	7006.8	3186.1	191.80	255.70	0.641	0.039
7631	2.1	3.7	73.3	7550.0	3444.2	191.80	258.61	0.643	0.036
8177	2.1	3.7	77.1	8091.5	3703.7	191.80	261.23	0.645	0.033

1. Fixed Parameters: $[COD]_i = 5000\ g\ COD/m^3$; $[NH_4]_i = 500\ g\ N/m^3$; $[NO_3]_i = 100\ g\ N/m^3$; $\theta_c = 3.5\ d$; $V_{anoxic} = 1000\ m^3$; $Q_{rs} = 2500\ m^3/d$; $Q_{re} = 21800\ m^3/d$; $V_{aerobic} = 7000\ m^3$; $DO_{aerobic} = 9.0\ g\ O_2/m^3$.
2. The results are directly from SSSP program output unless otherwise noted.
3. Biomass conversion factor from g COD to g VSS is 1.41 g COD/g VSS.
4. AUR from eq. (3.2-22); ORP from eq. (3.2-18); SOUR from eq. (3.2-25); and SAUR from eq. (3.2-23).

Table 5.7 Effluent variables in anoxic (denitrification) zone for NO_3 single variable analysis[1,2].

influent Nitrate $[NO_3]_i$ g NO_3/m^3	Soluble Organics $[COD]_e$ g COD/m^3	Ammonium Nitrogen $[NH_4]_e$ g N/m^3	Soluble Nitrate $[NO_3]_e$ g NO_3/m^3	Suspended[3] Solids MLVSS g COD/m^3	Nitrate Uptake Rate NUR g $NO_3/m^3 \cdot d$	Redox[4] Potential ORP mV	Specific[4] Uptake rate SNUR g NO_3/g VSS $\cdot$ d
50	472.9	69.9	0.5	5266.1	1618.5	-0.02	0.433
60	459.5	69.2	0.6	5270.6	1672.1	9.43	0.447
70	442.2	68.2	0.7	5282.1	1727.2	17.42	0.461
80	428.9	67.5	0.7	5290.8	1781.6	17.42	0.475
90	413.1	66.6	0.9	5304.1	1837.3	30.46	0.488
100	398.2	65.8	1.0	5311.1	1890.8	35.92	0.502
110	383.5	64.9	1.2	5316.9	1943.9	45.37	0.516
120	368.2	64.1	1.4	5332.8	2000.0	53.37	0.529
130	353.4	63.3	1.8	5342.2	2053.2	66.40	0.542
140	339.1	62.4	2.4	5351.3	2105.2	81.32	0.555
150	325.3	61.7	3.3	5359.7	2154.9	97.83	0.567

1. Fixed Parameters: $[COD]_i = 5000$ g COD/m^3; $[NH_4]_i = 500$ g N/m^3; $Q_i = 5451$ m^3/d; $\theta_c = 3.5$ d; $V_{anoxic} = 1000$ m^3; $Q_{rs} = 2500$ m^3/d; $Q_{re} = 21800$ m^3/d; $V_{aerobic} = 7000$ m^3; $DO_{aerobic} = 9.0$ g O_2/m^3.
2. The results are directly from SSSP program output unless otherwise noted.
3. Biomass conversion factor from g COD to g VSS is 1.41 g COD/g VSS.
4. ORP from eq. (3.2-18) and SNUR from eq. (3.2-24).

Table 5.8 Single variable analysis for NO_3 in aerobic (carbon oxidation and nitrification) zone[1,2].

influent Nitrate $[NO_3]_i$ g NO_3/m^3	Soluble Organics $[COD]_e$ g COD/m^3	Ammonium Nitrogen $[NH_4]_e$ g N/m^3	Soluble Nitrate $[NO_3]_e$ g NO_3/m^3	Suspended[3] Solids MLVSS g COD/m^3	Oxygen Uptake Rate OUR g $O_2/m^3 \cdot d$	Ammonia-N[4] Uptake Rate AUR g $N/m^3 \cdot d$	Redox[4] Potential ORP mV	Specific[4] Uptake Rate SOUR g O_2/g VSS·d	Specific[4] Uptake Rate SAUR g N/g VSS·d
50	2.2	3.6	56.0	5391.3	2528.8	386.55	244.65	0.661	0.101
60	2.2	3.7	56.2	5386.7	2510.3	386.48	244.84	0.657	0.101
70	2.1	3.6	56.1	5387.1	2484.1	386.55	244.75	0.650	0.101
80	2.1	3.7	56.4	5387.0	2466.6	386.48	245.02	0.646	0.101
90	2.0	3.6	56.5	5390.2	2444.2	386.55	245.11	0.639	0.101
100	2.0	3.6	56.7	5387.3	2422.6	386.55	245.30	0.634	0.101
110	2.0	3.6	56.9	5383.3	2401.0	386.55	245.48	0.629	0.101
120	1.9	3.6	57.2	5389.8	2380.1	386.55	245.75	0.623	0.101
130	1.9	3.6	57.5	5389.6	2359.1	386.55	246.02	0.617	0.101
140	1.9	3.6	58.1	5389.3	2338.6	386.55	246.56	0.612	0.101
150	1.8	3.6	59.1	5388.7	2319.0	386.55	247.45	0.607	0.101

1. Fixed Parameters: $[COD]_i = 5000$ g COD/m^3; $[NH_4]_i = 500$ g N/m^3; $Q_i = 5451$ m^3/d; $\theta_c = 3.5$ d; $V_{anoxic} = 1000$ m^3; $Q_{ra} = 2500$ m^3/d; $Q_{re} = 21800$ m^3/d; $V_{aerobic} = 7000$ m^3; $DO_{aerobic} = 9.0$ g O_2/m^3.
2. The results are directly from SSSP program output unless otherwise noted.
3. Biomass conversion factor from g COD to g VSS is 1.41 g COD/g VSS.
4. AUR from eq. (3.2-22); ORP from eq. (3.2-18); SOUR from eq. (3.2-25); and SAUR from eq. (3.2-23).

Table 5.3 shows that the inlet ammonium-nitrogen has a direct effect on nitrate concentration in the anoxic zone. This indicates that an increase of ammonium inlet (250 to 750 g N/m^3), expands the production of nitrate in the aerobic zone; hence, more nitrates are recirculated to the anoxic zone. Consequently, nitrate concentrations at the anoxic zone increase from 0.1 to 129.4 g NO_3/m^3, when the carbon source (COD) for microorganisms is insufficient at the anoxic zone . Table 5.4 shows that the effluent ammonium-nitrogen is fairly constant (about 3.6 g N/m^3) with respect to the changes in ammonia influent concentration. This tendency implies that the variations in influent substrate (COD and ammonium) concentration do not significantly affect the effluent substrate concentrations. This behavior is also observed throughout the whole single variable analysis, including inlet flow rate and inlet nitrate. According to the literature, the sludge age has a significant effect on effluent substrate concentration (Metcalf and Eddy, 1992 and Grady, 1980).

All the inlet components increase proportionally with increases in the inlet flow rate, which range from 2726 to 8177 m^3/d. As a result, the concentration of effluent components in the aerobic zone increase (Table 5.6). In the anoxic zone (Table 5.5), however, the soluble nitrate decreases from 2.0 to 0.7 g NO_3/m^3 while the nitrate concentration in the aerobic zone increases from 32.7 to 77.1 g NO_3/m^3. This occurs when the nitrate uptake rate increases significantly (1012.9 to 2669.1 g NO_3/m^3-d) with the inlet flow rate. As shown in Table 5.5, the second run has the highest ORP value (136.08 mV), which corresponds to a nitrate concentration of 6.9 g NO_3/m^3. Theoretically, the anoxic zone nitrate concentration should reduce according to the decrease of inlet flow rate. One explanation for this irregularity is that at this particular combination of input variables, the anoxic zone has failed to remove nitrate due to insufficient COD (as a carbon source) and high concentrations of ammonium and nitrate

at the inlet. Once again, the effluent COD (about 2.0 g COD/m^3) and ammonium concentration (about 3.6 g N/m^3) are not affected significantly by the increasing inlet flow rate (Table 5.6).

Table 5.7 shows that the nitrate concentration in the anoxic zone (change from 0.5 to 3.3 g NO_3/m^3) does not have much dependency on influent nitrate concentration (increase from 50 to 150 g/m^3). This phenomenon is even more noticeable in the aerobic zone outflow (change from 56.0 to 59.1 g NO_3/m^3), as indicated in Table 5.8. Both sets of changes in nitrate concentration imply that, within the influent nitrate range (50 to 150 g NO_3/m^3), the heterotrophs have sufficient soluble organics (inlet COD is constant) to remove nitrate in the anoxic zone. Additionally, the recycle of nitrate from the aerobic zone is quite uniform as the inlet ammonium is unchanged throughout the process. On the contrary, when inlet ammonium and COD are not constant (Tables 5.1 to 5.4), dramatic changes are observed in the anoxic and aerobic zones nitrate concentration.

To further illustrate the effect of input variations upon the process measurement parameters, the results obtained from this analysis are presented in graphical form, shown in Figures 5.1 to Figure 5.7.

Figure 5.1 shows the ORP in the anoxic zone as a function of input variables. These plots suggest that variations in the COD and ammonium influent have a major impact on ORP, that is, COD has a negative effect (varying ORP from 315 to -47 mV) and ammonium has a positive effect (changing ORP from -83 to 288 mV). Therefore, in order to maintain ORP in the anoxic zone at negative range (when the nitrate concentration is low), the inlet COD should be maintained at high loading, and the nitrate and ammonium should be kept at low loadings. This observation also indicates that, for a successful denitrification process (no nitrate build-up) in the anoxic zone, the process should operate at an ORP of less than -40 mV. The inlet flow rate, however, does not

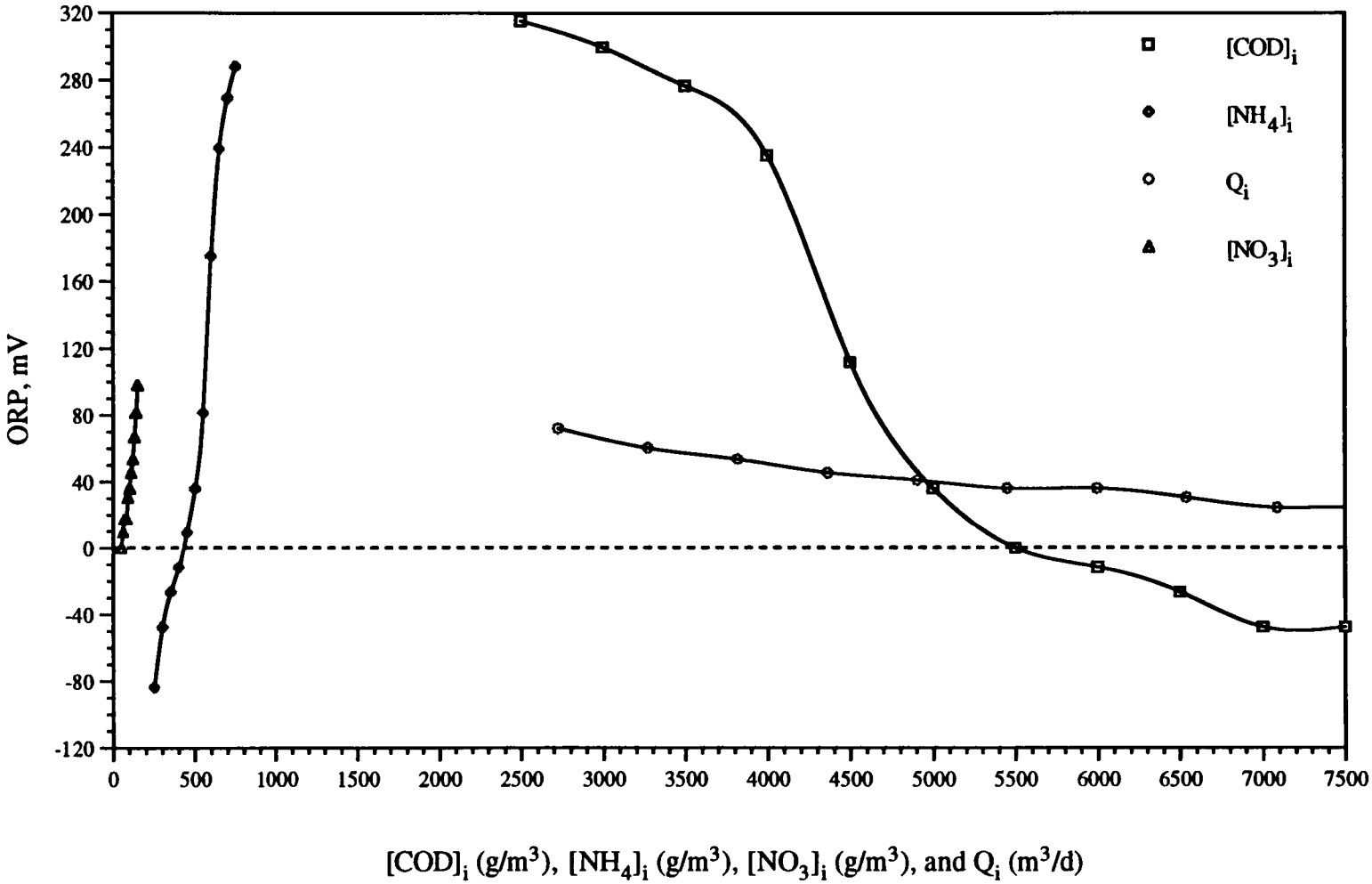


Figure 5.1 Oxidation reduction potential as a function of influent variables in anoxic zone.

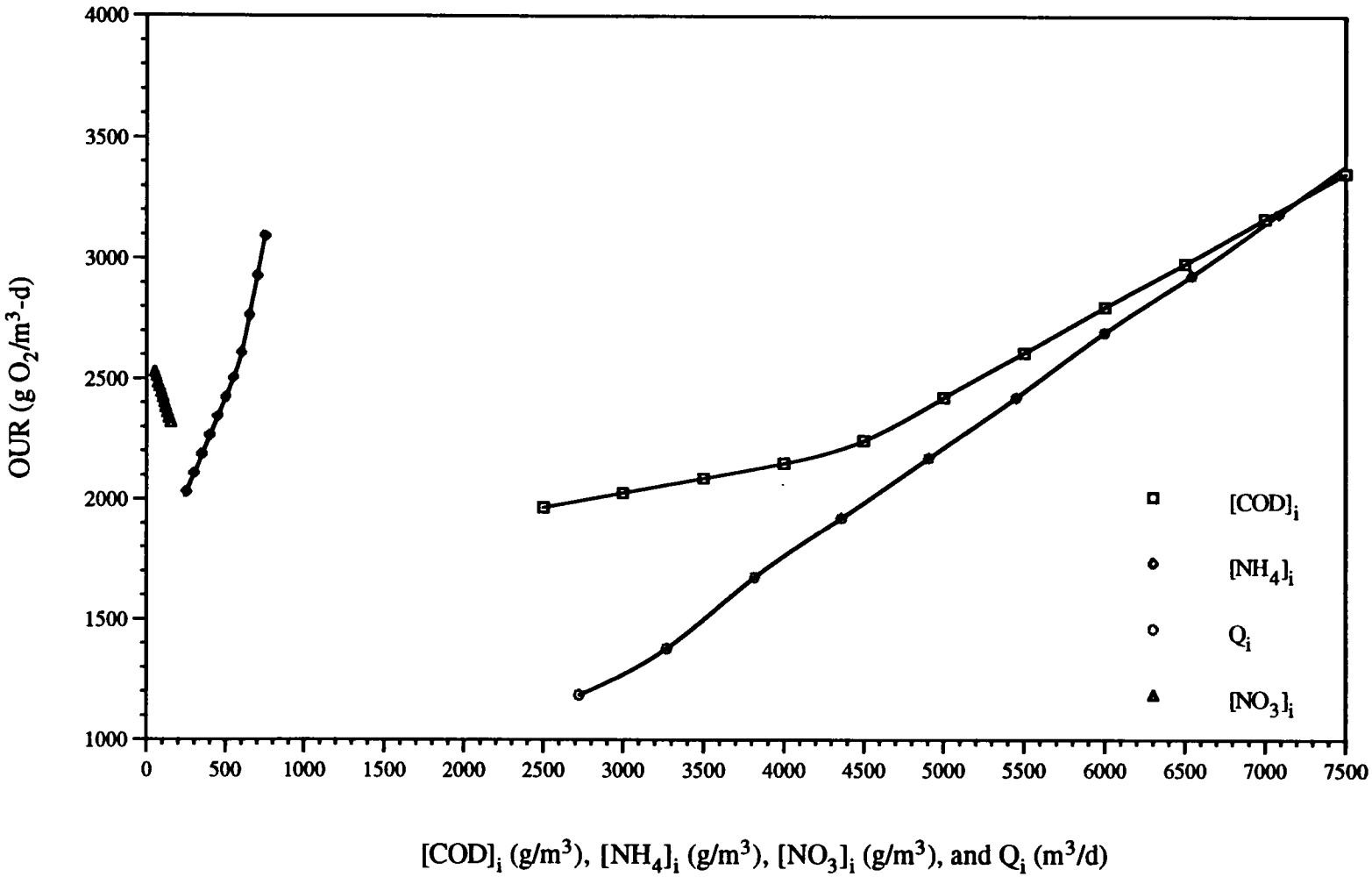


Figure 5.2 Oxygen uptake rate as a function of influent variables in aerobic zone.

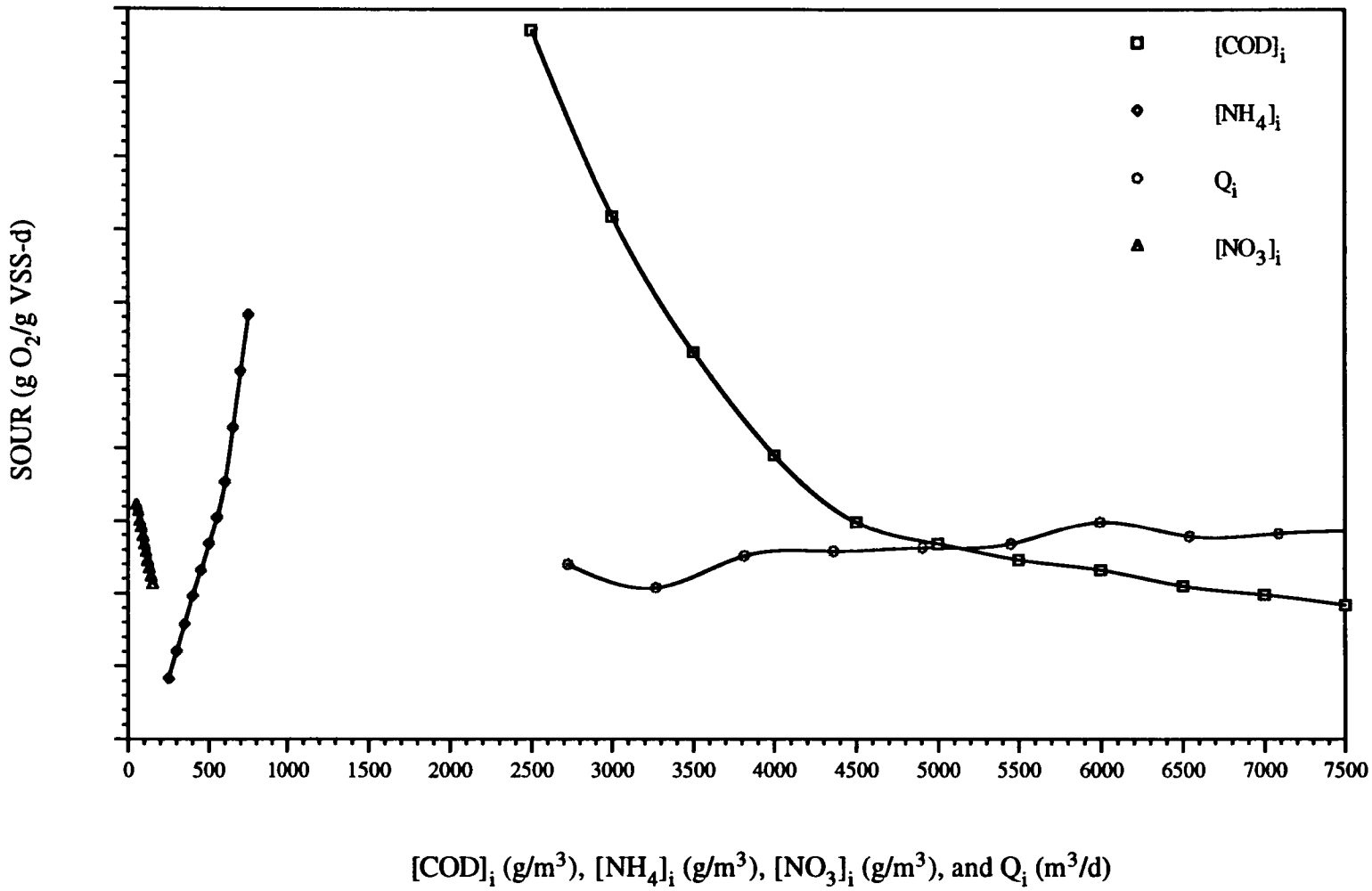


Figure 5.3 Specific oxygen uptake rate as a function of influent variables in aerobic zone.

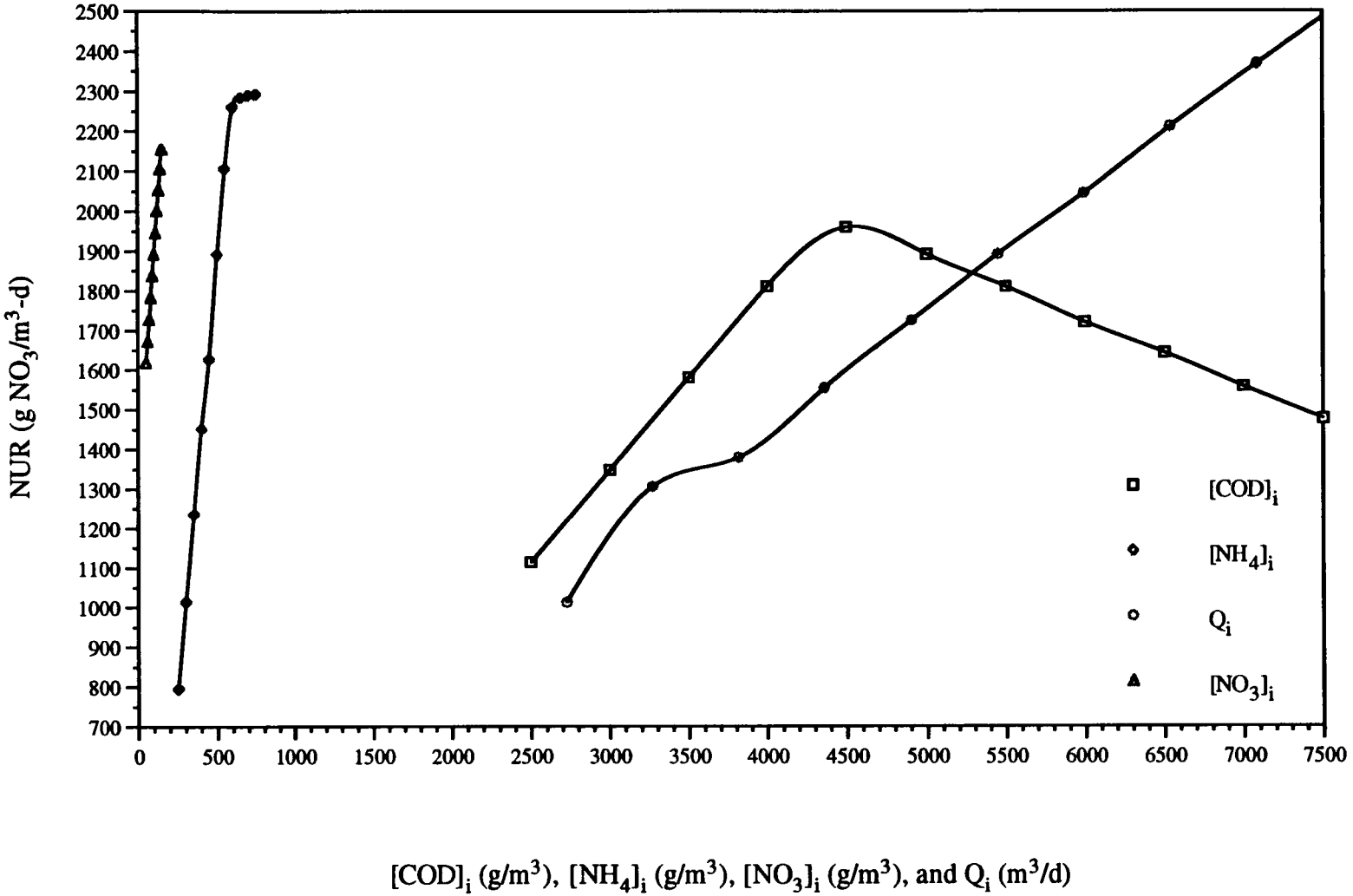


Figure 5.4 Nitrate utilization rate as a function of influent variables in anoxic zone.

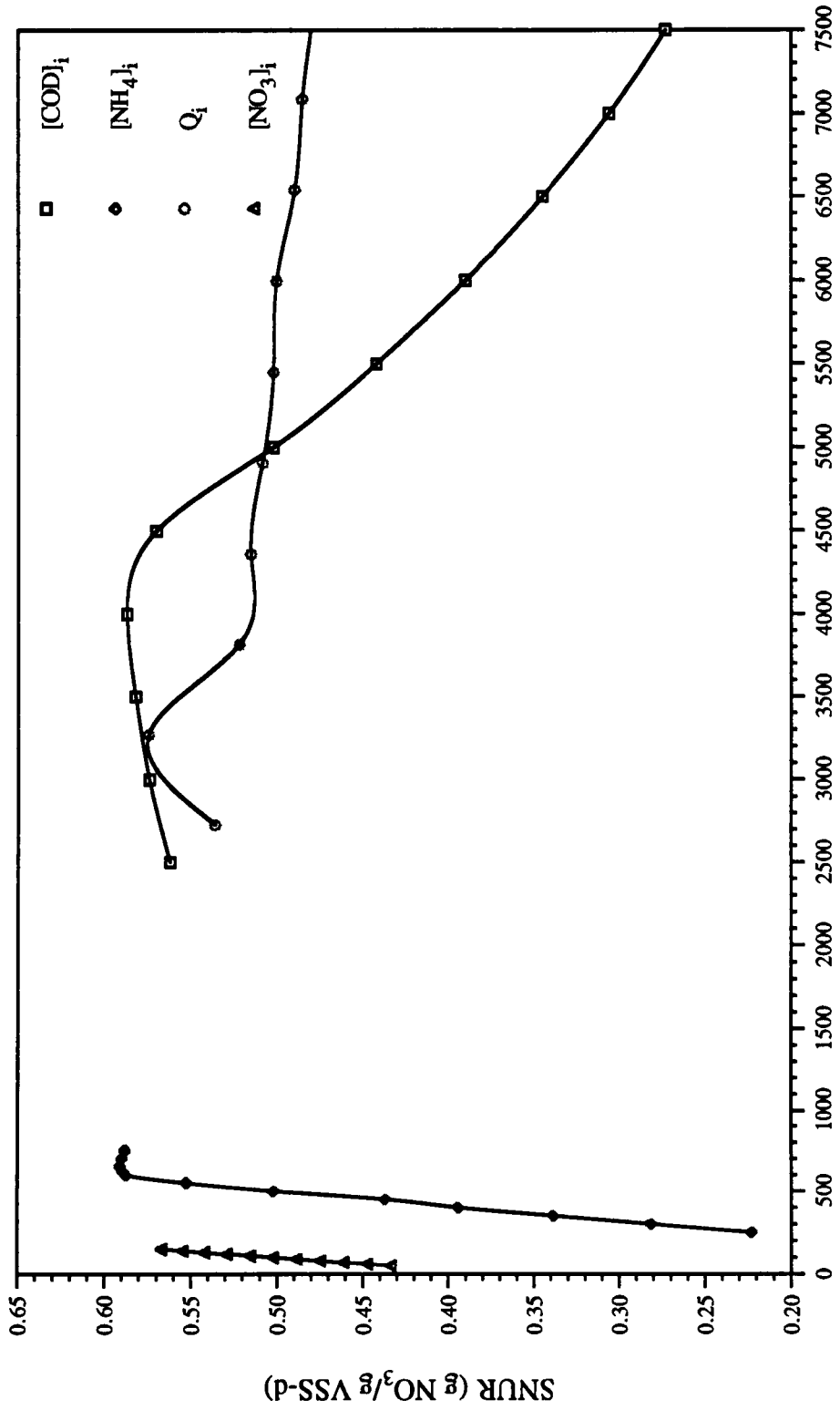


Figure 5.5 Specific nitrate utilization rate as a function of influent variables in anoxic zone.

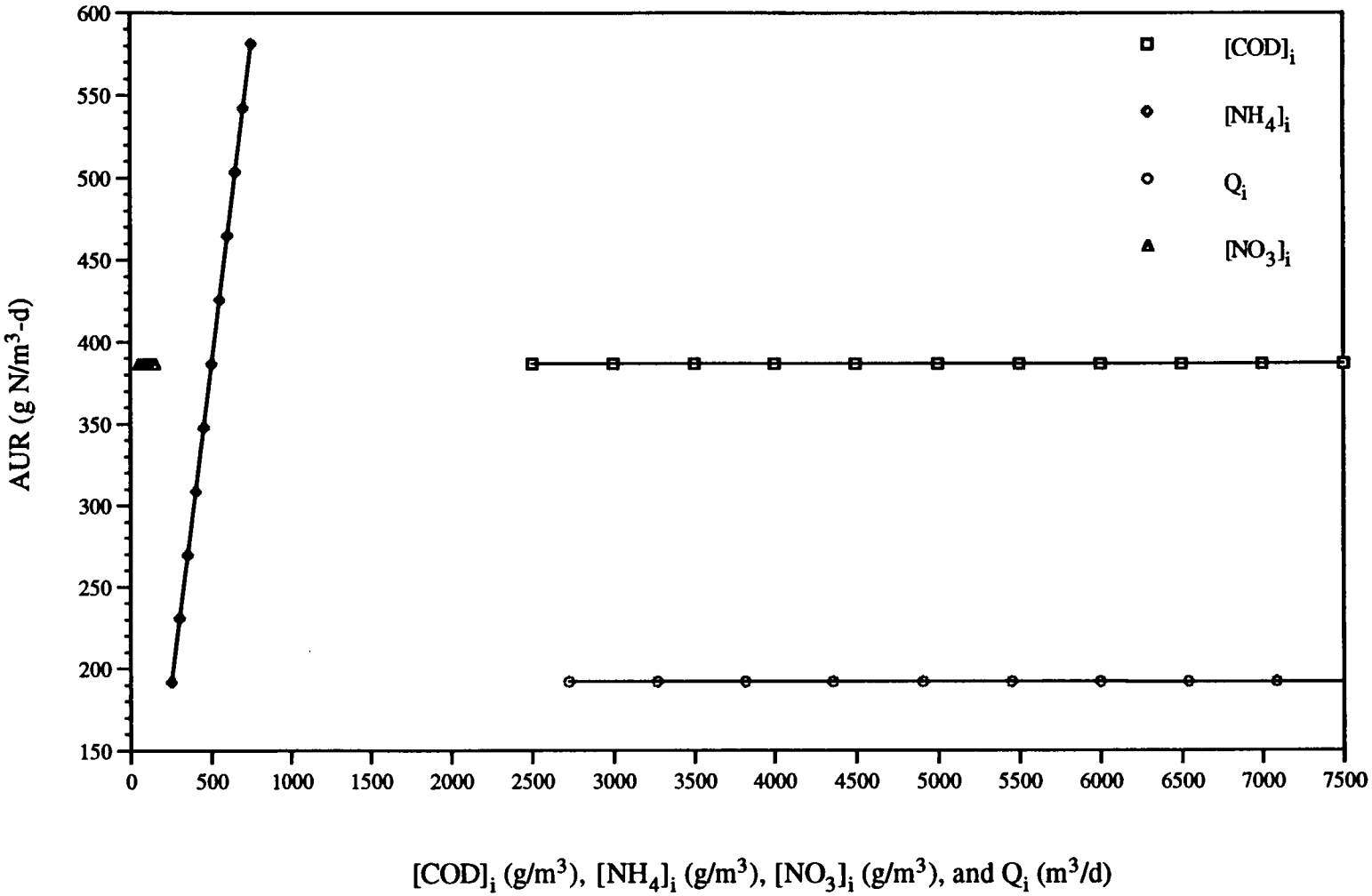


Figure 5.6 Ammonium-nitrogen uptake rate as a function of influent variables in aerobic zone.

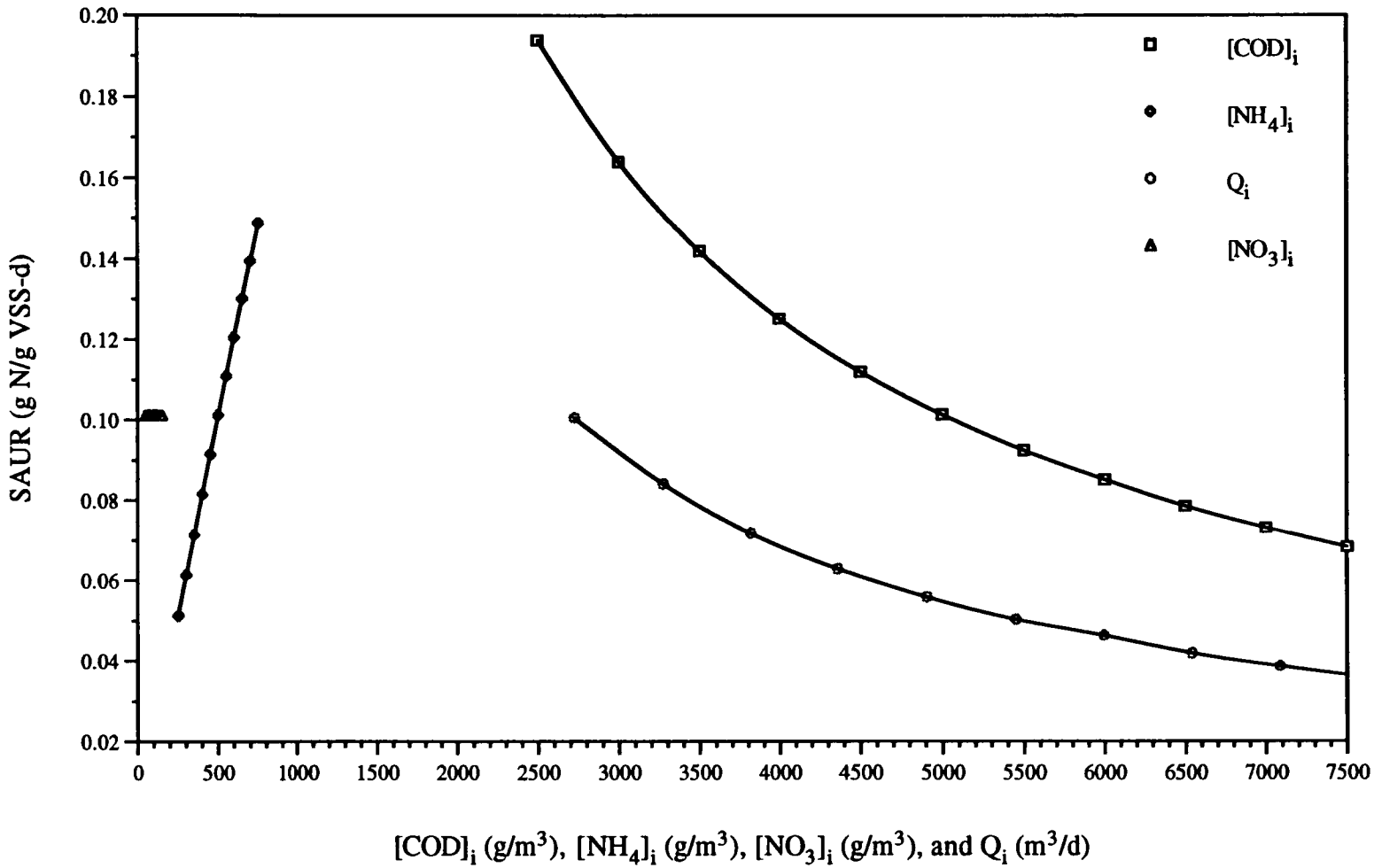


Figure 5.7 Specific ammonium-nitrogen uptake rate as a function of influent variables in aerobic zone.

have a great effect on the ORP (the variations of ORP are small within the range of the inlet flow rate changes). On the other hand, the influent nitrate effect is fairly significant as the ORP changes from 0 to 98 mV. Generally, the plots in Figure 5.1 show that ORP has a potential use as an indicator of activity in the anoxic zone. And since ORP can be measured on-line (Chapter 2.2.3 and 3.3.1), it further renders the ORP useful for process control in bioreactor.

The oxygen uptake rate (OUR) profile in the carbon oxidation and nitrification (aerobic) zone is depicted in Figure 5.2. The figure illustrates that, OUR is directly proportional to the changes in the influent COD, ammonium, and inlet flow rate. Among these three input variables, inlet flow rate (1184 to 3704 g O_2/m^3-d) has the greatest effect, followed by inlet COD and ammonium. Usually when the inlet concentration increases, more oxygen is utilized for the oxidation of carbon organic and ammonium. Figure 5.2 also indicates that, the least effect on OUR is the inlet nitrate variable because the reduction of nitrate occurs in the anoxic zone rather than the aerobic zone.

Figure 5.3 shows the specific oxygen uptake rate (SOUR) in the aerobic zone as a function of influent variables. SOUR is estimated by Eq. (3.2-25) which is the OUR divided by the biomass concentration. A decrease in SOUR (0.986 to 0.592 g O_2/g VSS-d) with an increase in inlet COD is due to the growth of microorganisms in the aerobic reactor, biomass growth depends on the sufficiency of substrate or food. The inlet flow rate does not affect the SOUR significantly as compared to the OUR parameter. The SOUR values only change from 0.62 to 0.645 g O_2/g VSS-d while the flow rate increases from 2726 to 8177 m^3/d. The inlet flow rate variations do not affect the SOUR dramatically, because of the different definitions of SOUR and OUR (Chapters 2.2.3.7 and 3.2.2). Both SOUR (0.542 to 0.792 g O_2/g VSS-d) and OUR (2030 to 3092 g O_2/m^3-d) have a similar response (directly proportional) to the ammonium inlet variations,

but the inlet nitrate variations have a reverse effect (indirect proportional) on both SOUR and OUR. This phenomenon suggests that the influent nitrate concentration does not influence the oxidation process in the aerobic zone.

In general, the analyses of Figures 5.2 and 5.3 suggests that the SOUR and OUR have the potential for indicating the activity of active microorganisms in the aerobic zone, as the rapid responses of OUR and SOUR to the changes can be observed in the input variations.

Figure 5.4 shows that a substantial increase in the nitrate uptake rate (NUR) takes place (794 to 2292 g NO_3/m^3-d) when the inlet ammonium concentration varies from 250 to 750 g N/m^3. A similar pattern is also observed in the effects of influent nitrate load and inlet flow rate; that is, NUR increases when the inlet nitrate and inlet flow rate increase. Figure 5.4 further shows that the NUR escalates to a peak (1959 g NO_3/m^3-d) at a COD inlet of 4500 g COD/m^3 and reduces accordingly with an increase of the COD inlet. This "peak" behavior suggests that, at an inlet COD range of 4000 to 5500 g COD/m^3, the substrate (COD) concentration matches the supply of nitrate from the aerobic zone. Hence, the heterotrophic microorganisms have sufficient carbon source for removal of nitrate in the anoxic zone. Another plausible cause for this "peak" behavior is the influent ammonium, nitrate and inlet flow rate are constant throughout the process, that is, the conversion of nitrate from ammonium is held stable. This "peak" behavior also suggests that an excess of substrate in the anoxic zone will affect the nitrate uptake rate.

As shown in Figure 5.5, the effect of the influent variables on SNUR has a pattern similar to their effect on NUR. The analyses of Figures 5.4 and 5.5 suggest that SNUR and NUR can serve as control indexes or process control parameters for the control of the denitrification rate in the anoxic zone. For example, when NUR is low and SNUR is high, the denitrification rate is reduced, and some control actions must be taken

to compensate for the failure. A possible corrective action is to increase the COD inlet. For industrial applications, the control point for the process parameters discussed so far must be determined by field experiment or pilot plant study.

The ammonium uptake rate (AUR) in the aerobic zone as a function of influent variables is illustrated in Figure 5.6. The plots in Figure 5.6 suggest that the COD and nitrate loads of the influent and the inlet flow rate have no efficacy on AUR, except for the inlet ammonium variable. The AUR changes from 192 to 581 g N/m^3-d when the inlet ammonium increases from 250 to 750 g N/m^3. This observation is predictable, as during analyses of the COD, inlet flow rate, and nitrate effects, the influent ammonium concentration is held constant.

Specific ammonium uptake rate (SAUR) as shown in Figure 5.7, is calculated by dividing AUR by the biomass concentration. As a result, when influent variables (COD and flow rate) increase, the growth of microorganisms also increases, thus reducing the SAUR. Furthermore, AUR and SAUR increase directly with an increase in influent ammonium concentration as, the more ammonium is in the aerobic zone, the greater the uptake of ammonium by the autotrophic microorganisms. One problem associated with the computation of SAUR is that the MLVSS used in the calculation should be autotrophic and not heterotrophic, as ammonium is oxidized to nitrate by autotrophic microorganisms.

The effects of the influent variables on each process parameter (Figures 5.1 to 5.7) are quite similar. This similarity can be seen especially in the effect of influent ammonium concentration on each process measurement parameter. The overall observation from this study shows that the influent COD has the greatest effect on the specific substrate uptake rate (SOUR, SNUR, and SAUR) followed by inlet ammonium, flow rate, and nitrate:

$$[COD]_i > [NH_4]_i > [NO_3]_i > Q_i$$

The substrate uptake rates (OUR, NUR, and AUR), however, have different responses to variations in input conditions:

$$[NH_4]_i > [COD]_i > Q_i > [NO_3]_i$$

The effects of influent variables on ORP are:

$$[NO_3]_i > [NH_4]_i > [COD]_i > Q_i$$

This single variable analysis also suggests that the specific substrate uptake rates (SOUR, SNUR, and SAUR), in contrast to the substrate uptake rates (OUR, NUR, and AUR), are better indicators of bioreactor performance, because the effects of some influent variables are not clearly observed using substrate uptake rates as indicators. The specific applications of these process parameters, however, depend on the biological treatment process as well as the nature of the wastewater being treated.

5.2 ANOXIC ZONE RECIRCULATION MODEL EVALUATION

The five input variables in this statistical factorial analysis are the influent COD, ammonium, and nitrate concentrations; the inlet flow rate; and recirculation rate. Their combinations used in the analysis are according to the factorial method described in Murphy (1977). The analysis totals 20 runs plus 5 randomly selected, dummy runs,

consisting of high and low cases of the input parameters in each individual run. The purpose of using the factorial method is to better record the effects of input variables from fewer simulations. For this investigation, a sludge age of 5 days and the yield coefficients of 0.4 (heterotroph) and 0.15 (autotroph) are used; all other biokinetic constants are similar to those in the first investigation (Tables 4.1 and 4.2). The combinations of input parameters for each individual run are summarized in Table 5.9. The effluent variables in the anoxic zone and in the aerobic zone are provided in Table 5.10 and Table 5.11, respectively. The effluent COD (1.4 to 2.8 g COD/m^3) and ammonium concentrations (1.6 g N/m^3) at the aerobic zone outflow are quite constant, regardless of the changes in the influent COD and ammonium concentrations. This observation is similar to the conclusion deduced from the single variable analysis (Chapter 5.1). As shown in Table 5.12, the recycling ratio, R_r, and overall recycling ratio, R_{all}, are calculated by Eq. (3.3-1) and Eq. (3.3-4), respectively. Since the most important parameter in the denitrification zone recirculation model is nitrate rather than COD or ammonium, the use of R_r instead of R_{all} is justifiable (Chapter 3.3). The overall removal efficiency, E_{all}, is estimated from Eq. (3.3-3).

The results generated from the evaluations of the proposed denitrification zone recirculation model are presented in Figures 5.8 through 5.11. Figure 5.8 shows the increases in the specific nitrate uptake rate (SNUR) and how it levels off with respect to the ascending recycling ratio (R_r). This finding indicates that the Monod assumption can be applied to the SNUR-R_r relationship (Chapter 3.3). Therefore, the plot of the reciprocal of the SNUR as a function of the reciprocal of the R_r is generated by Eq. (3.3-8), and, accordingly, the constants K_r and S_{max} are determined from Eq. (3.3-9) and Eq. (3.3-10). Figure 5.9 illustrates the double reciprocal plot with the slope of K_r/S_{max} and y-

Table 5.9 Combinations of input variables for the bio-treatment model simulations[1].

Run	Influent Organics $[COD]_i$ g COD/m^3	Influent Ammonium $[NH_4]_i$ g N/m^3	Influent Nitrate $[NO_3]_i$ g NO_3/m^3	Inlet Flow rate Q_i m^3/d	Recirculation Rate Q_{re} m^3/d
1	7500	750	50	2726	32700
2	7500	250	50	8177	32700
3	2500	250	150	8177	32700
4	2500	750	150	8177	32700
5	7500	750	150	8177	10900
6	7500	750	150	2726	32700
7	7500	750	50	8177	10900
8	7500	250	150	2726	32700
9	2500	750	50	8177	10900
10	7500	250	150	2726	10900
11	2500	750	50	2726	10900
12	7500	250	50	2726	10900
13	2500	250	50	2726	32700
14	2500	250	50	8177	32700
15	2500	250	150	8177	10900
16	2500	750	150	2726	32700
17	7500	750	50	8177	32700
18	7500	250	150	8177	10900
19	2500	750	150	2726	10900
20	2500	250	50	2726	10900
21	5000	500	100	5451	21800
22	7500	750	150	8177	32700
23	5000	750	50	5451	21800
24	2500	500	100	8177	21800
25	5000	250	50	2726	32700

1. Fixed parameter: $\theta_c = 5$ d; $V_{anoxic} = 1000$ m^3; $V_{aerobic} = 7000$ m^3; $Q_{rs} = 2500$ m^3/d; and $DO_{aerobic} = 9.0$ g O_2/m^3.

Table 5.10 Anoxic (Denitrification) zone effluent variables for control model evaluations.

Run	Soluble Organics $[COD]_e$ g COD/m^3	Ammonium Nitrogen $[NH_4]_e$ g N/m^3	Soluble Nitrate $[NO_3]_e$ g NO_3/m^3	Suspended Solids MLVSS g COD/m^3	Nitrate Uptake Rate NUR g $NO_3/m^3 \cdot d$	Redox Potential ORP mV	Specific Uptake rate SNUR g NO_3/g VSS $\cdot$ d
1	333.7	48.9	0.3	2329.4	1709.3	-26.51	1.035
2	1286.9	44.5	0.0	6600.2	1219.7	-322.28	0.261
3	196.8	39.6	3.0	2351.9	2586.7	92.89	1.551
4	175.8	133.2	378.6	2633.9	2796.7	343.75	1.497
5	1911.9	255.3	0.2	6879.9	4380.4	-47.54	0.898
6	300.2	47.8	0.5	2340.5	1983.9	-0.02	1.195
7	2087.5	261.0	0.2	6819.8	3558.2	-47.54	0.736
8	454.2	16.9	0.1	2201.8	721.1	-83.48	0.462
9	324.7	265.1	128.9	2653.5	2926.0	287.88	1.555
10	1074.8	37.6	0.1	2113.0	688.0	-83.48	0.459
11	153.1	119.5	295.7	884.6	951.3	330.94	1.516
12	1153.3	40.1	0.0	2084.9	411.8	-322.28	0.278
13	77.9	16.3	16.2	785.1	849.5	180.34	1.526
14	284.8	42.5	0.4	2332.9	1773.7	-11.59	1.072
15	464.7	80.2	0.8	2350.5	2270.6	24.35	1.362
16	76.2	52.2	496.9	874.3	867.4	357.85	1.399
17	935.0	127.3	0.2	6980.7	4530.2	-47.54	0.915
18	2451.1	83.3	0.1	6441.6	1850.6	-83.48	0.405
19	153.0	119.5	395.7	884.6	951.5	346.05	1.517
20	253.3	38.2	0.4	767.5	601.8	-11.59	1.106
21	548.7	81.2	0.4	3102.5	2387.9	-11.59	1.085
22	847.3	124.4	0.3	7010.0	5353.4	-26.51	1.077
23	419.3	122.7	1.1	3233.2	3220.7	40.86	1.405
24	229.1	114.2	94.5	2508.7	2832.8	271.79	1.592
25	294.9	17.6	0.1	1484.2	551.9	-83.48	0.524

Table 5.11 Aerobic (carbon oxidation and nitrification) zone effluent variables for control model evaluations.

Run	Soluble Organics $[COD]_e$ g COD/m^3	Ammonium Nitrogen $[NH_4]_e$ g N/m^3	Soluble Nitrate $[NO_3]_e$ g NO_3/m^3	Suspended Solids MLVSS g COD/m^3	Oxygen Uptake Rate OUR g $O_2/m^3 \cdot d$	Ammonia-N Uptake Rate AUR g $N/m^3 \cdot d$	Redox Potential ORP mV	Specific Uptake Rate SOUR g O_2/g VSS · d	Specific Uptake Rate SAUR g N/g VSS · d
1	2.0	1.6	45.0	2350.5	2784.5	291.45	233.31	1.670	0.175
2	2.8	1.6	23.1	6802.5	7357.4	290.17	198.74	1.525	0.060
3	1.5	1.6	42.1	2333.4	2419.4	290.17	229.86	1.462	0.175
4	1.4	1.6	511.1	2618.5	4911.5	874.24	359.32	2.645	0.471
5	2.1	1.6	235.7	7051.9	8621.8	874.24	319.18	1.724	0.175
6	1.8	1.6	45.3	2348.8	2674.3	291.45	233.66	1.605	0.175
7	2.3	1.6	235.3	7058.7	8949.4	874.24	319.09	1.788	0.175
8	2.6	1.6	8.9	2264.6	2324.8	96.73	149.28	1.447	0.060
9	1.4	1.6	395.3	2611.6	4839.8	874.24	345.99	2.613	0.472
10	2.6	1.6	20.9	2264.7	2321.9	96.73	193.55	1.446	0.060
11	1.4	1.6	414.5	869.0	1618.2	291.45	348.45	2.626	0.473
12	2.7	1.6	20.7	2266.2	2430.7	96.73	193.05	1.512	0.060
13	1.5	1.6	31.1	779.3	811.4	96.73	214.16	1.468	0.175
14	2.0	1.6	39.2	2348.6	2751.8	290.17	226.16	1.652	0.174
15	1.7	1.6	79.2	2341.6	2542.8	290.17	262.63	1.531	0.175
16	1.5	1.6	547.4	871.7	1661.9	291.45	362.87	2.688	0.471
17	2.1	1.6	117.4	7059.4	8598.7	874.24	283.04	1.717	0.175
18	2.6	1.6	46.7	6798.3	7072.0	290.17	235.24	1.467	0.060
19	1.4	1.6	514.5	869.0	1618.1	291.45	359.66	2.625	0.473
20	1.9	1.6	35.3	780.6	907.5	96.73	220.72	1.639	0.175
21	2.0	1.6	76.3	3131.7	3661.2	388.11	260.69	1.648	0.175
22	2.0	1.6	117.7	7055.2	8268.4	874.24	283.17	1.652	0.175
23	1.6	1.6	122.7	3217.9	4182.8	582.79	285.33	1.833	0.255
24	1.4	1.6	209.1	2479.0	3607.4	582.20	312.97	2.052	0.331
25	2.5	1.6	11.9	1523.5	1662.2	96.73	164.34	1.538	0.090

Table 5.12 Comparison between predicted and simulated results.

Run	Recycling Ratio R_r	Overall Recycling ratio R_{all}	Overall Removal Efficiency E_{all}	Calculated Recycling ratio R_r	% Differnece for R_r	Recirculation rate Q_{re}	Calculated Recirculation Q_{re}	% Difference for Q_{re}
1	0.070	0.076	92.44%	0.065	6.89%	32700	30276	7.41%
2	0.013	0.015	98.48%	0.008	33.55%	32700	20890	36.12%
3	0.062	0.067	93.29%	0.261	317.28%	32700	144383	341.54%
4	0.647	0.651	34.91%	0.215	66.84%	32700	9171	71.95%
5	0.046	0.047	95.33%	0.049	5.50%	10900	11638	6.77%
6	0.070	0.075	92.51%	0.093	34.24%	32700	44753	36.86%
7	0.046	0.047	95.28%	0.034	26.76%	10900	7314	32.90%
8	0.015	0.021	97.86%	0.017	18.06%	32700	39055	19.44%
9	0.196	0.198	80.22%	0.265	34.95%	10900	15583	42.96%
10	0.013	0.016	98.44%	0.017	31.04%	10900	15059	38.16%
11	0.617	0.622	37.81%	0.229	62.84%	10900	2479	77.26%
12	0.013	0.016	98.42%	0.009	29.81%	10900	6906	36.64%
13	0.143	0.158	84.23%	0.237	65.44%	32700	55736	70.45%
14	0.060	0.066	93.42%	0.071	17.39%	32700	38820	18.71%
15	0.045	0.047	95.34%	0.142	217.83%	10900	40089	267.79%
16	2.079	2.091	-109.07%	0.158	92.41%	32700	171	99.48%
17	0.061	0.063	93.72%	0.050	17.30%	32700	26609	18.63%
18	0.010	0.011	98.94%	0.014	49.45%	10900	17527	60.79%
19	0.744	0.748	25.18%	0.230	69.12%	10900	1638	84.98%
20	0.062	0.068	93.19%	0.076	22.97%	10900	13978	28.24%
21	0.061	0.064	93.64%	0.073	19.92%	21800	26640	22.20%
22	0.060	0.062	93.78%	0.071	18.52%	32700	39221	19.94%
23	0.094	0.097	90.32%	0.160	70.04%	21800	38820	78.07%
24	0.200	0.203	79.67%	0.309	54.21%	21800	34973	60.42%
25	0.029	0.039	96.10%	0.020	29.60%	32700	22282	31.86%

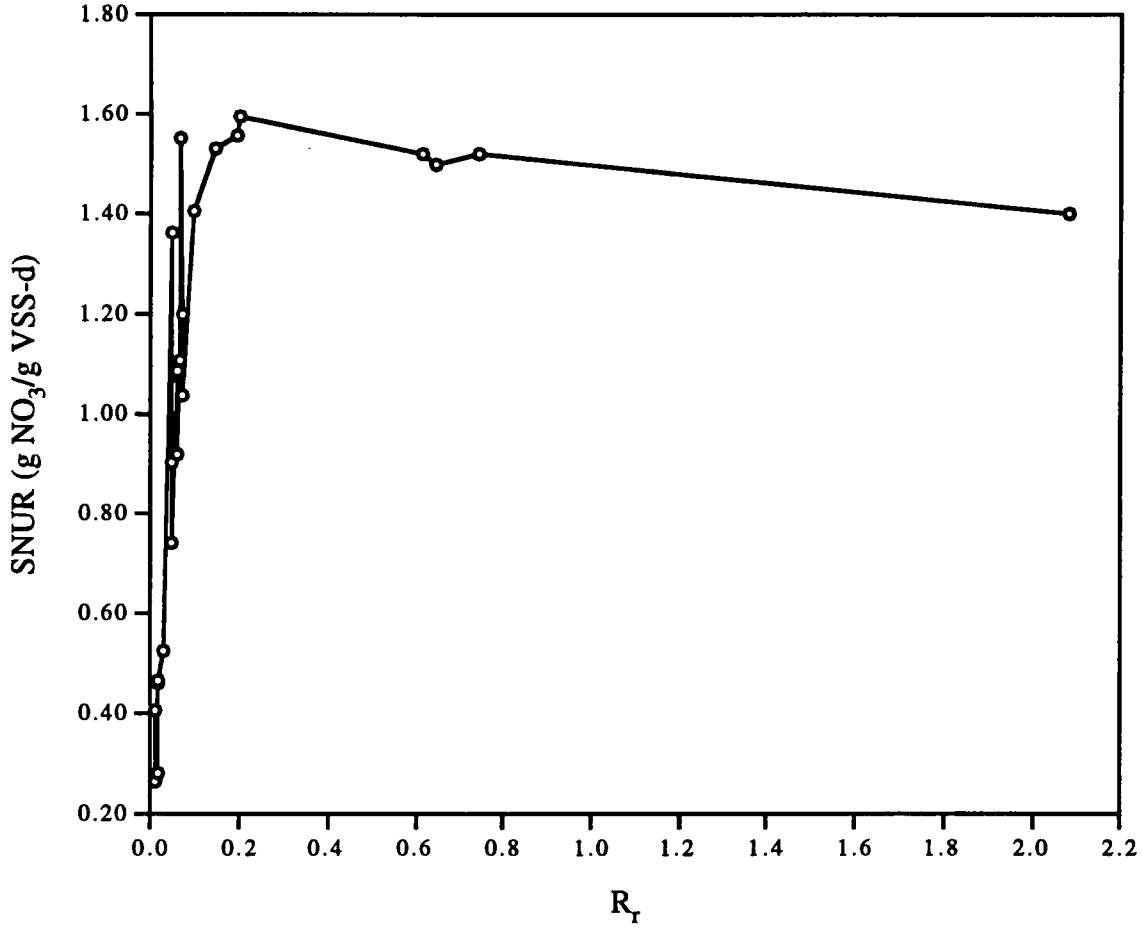


Figure 5.8 **Specific nitrate uptake rate changes with recycling ratio.**

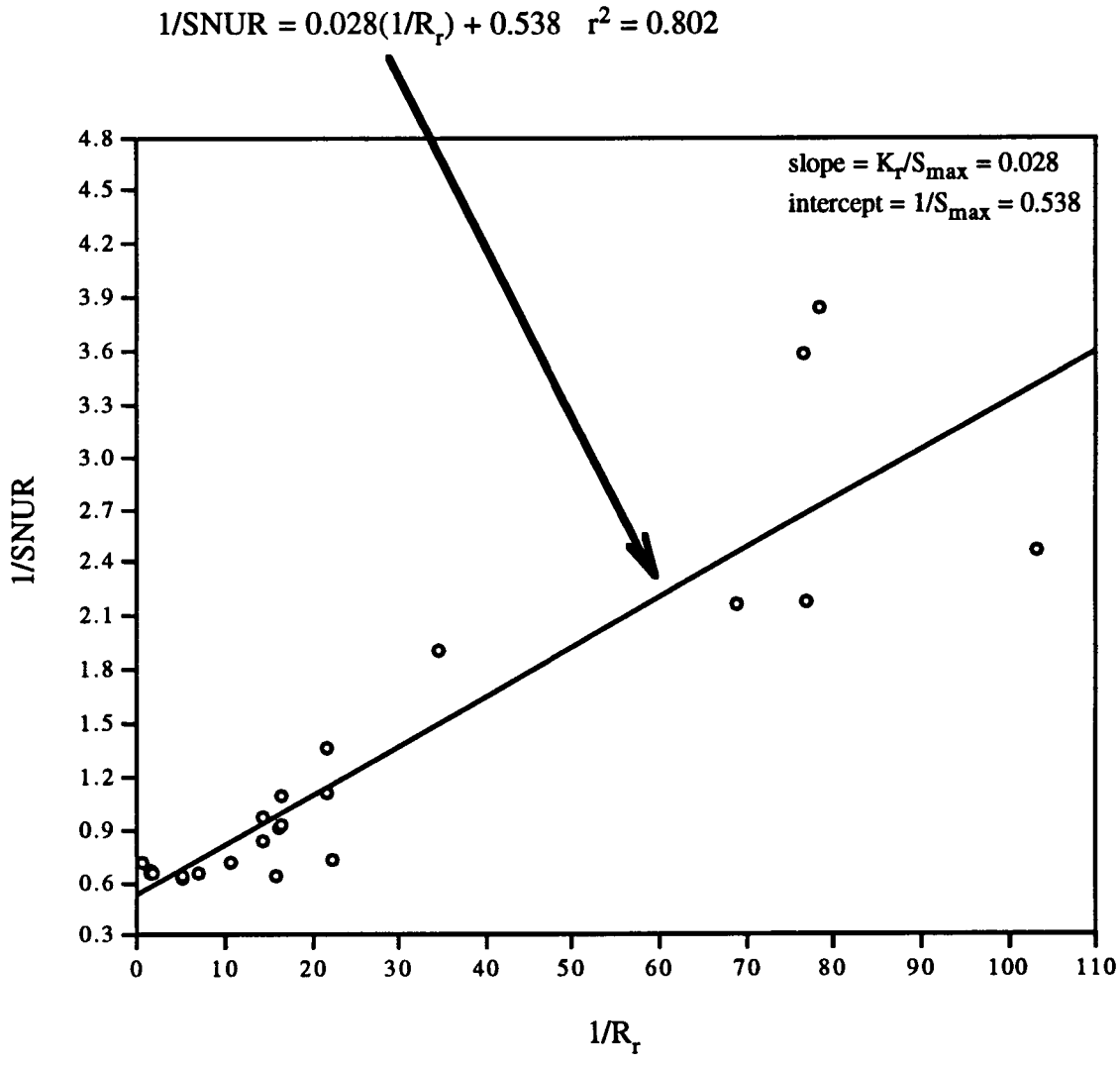


Figure 5.9 The double reciprocal plot for determination of biokinetic constants.

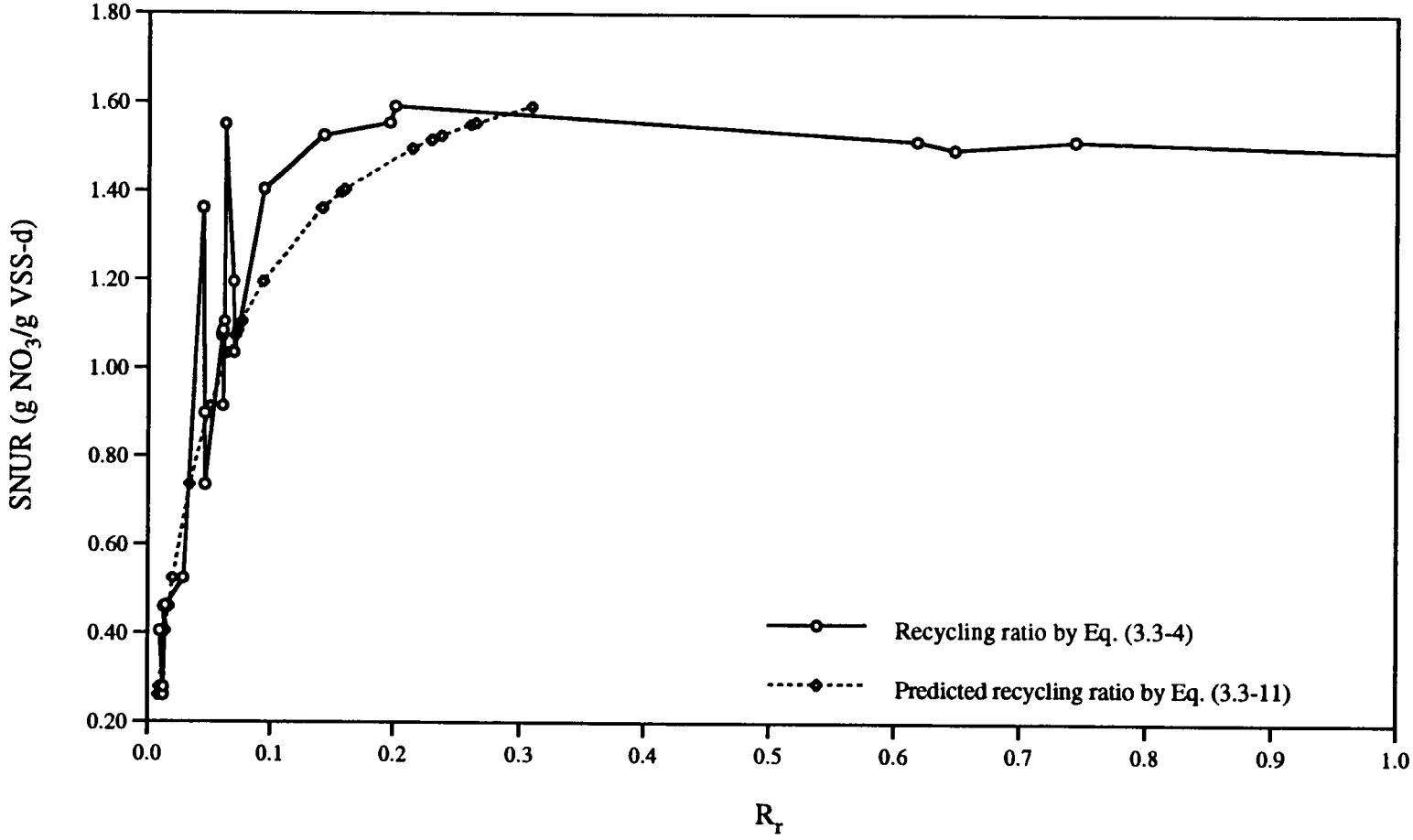


Figure 5.10 Comparison between predicted recycling ratio and experimental recyling ratio.

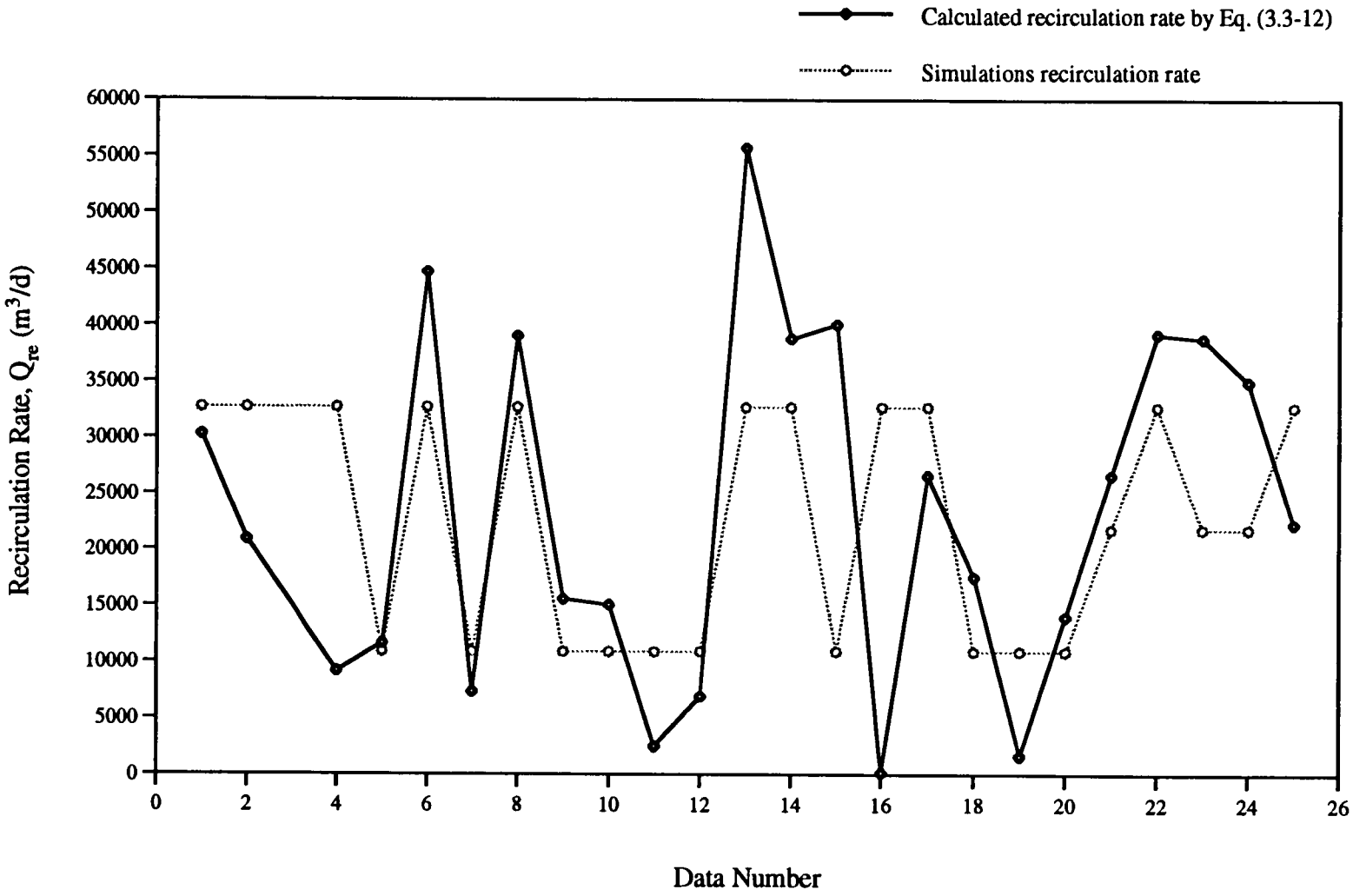


Figure 5.11 Comparison profile of predicted and simulation recirculation rate.

axis intercept of $1/S_{max}$. The biokinetic constants K_r and S_{max} are calculated as 0.052 and 1.859 g NO_3/g VSS-d, respectively. With the known biokinetic constants, the recycling ratio is predicted by Eq. (3.3-11).

A comparison of the R_r predicted by Eq. (3.3-4) and by Eq. (3.3-11) is provided in Table 5.12. The percent difference varies from 5.5% to more than 100%. The large percent differences are caused by the over-simplification of the relationship between SNUR and R_r and from the data for the regression analysis, which is too small for a analysis with five-variables. Usually, for a five-variables analysis, more data are required for better linear regression analyses. The plots of SNUR versus the recycling ratio, R_r, predicted by Eq. (3.3-11) and Eq. (3.3-4) are generated in Figure 5.10 for comparison between the two equations. The percent differences are small at a low recycling ratio, and the difference increases as the recycling ratio increases. The general trend of the plot by Eq. (3.3-11), however, is adequately agreed with the plot by Eq. (3.3-4). The distinction between Eq. (3.3-11) and Eq. (3.3-4), is that Eq. (3.3-11) is based on the Monod assumption applied on the SNUR and R_r, while Eq. (3.3-4) is based on the ratio of the effluent to influent substrate concentrations.

Also provided in Table 5.12 are the predicted recirculation rate represented by Eq. (3.3-12) and the percent differences as compared to the simulation (original) recirculation rate. To further illustrate the differences between the two recirculation rates, the predicted Q_{re} and the original Q_{re} are plotted in Figure 5.11. The predicted Q_{re} increases when the original Q_{re} increases and the predicted Q_{re} decreases when the original Q_{re} decreases. Again, the general agreement between the predicted Q_{re} and the original Q_{re} can be observed in Figure 5.11.

The percent differences in Figure 5.11 are quite large, but, for a better regression analyses more data are needed. For a five-variables analysis (as described in Chapter 4.2)

more than 3000 simulations are required. In the statistical factorial method, however, a total of only 25 simulations are performed; therefore, one can predict large variations in percent differences. In addition, the Monod equation assumption is too simple and ideal for such a large number of variables and the complexity of the treatment model. A more detailed model such as a structured model should be used to establish the relationship between SNUR and R_r.

As shown in Table 5.13, the steady-state denitrification zone empirical model is also tested using the SSSP program. The influent variables such as COD, ammonium, nitrate and inlet flowrate in Eq. (3.3-4) are constant at the values of 7000 g COD/m^3, 550 g N/m^3, 80 g NO_3/m^3, and 3000 m^3/d, respectively. The SNUR is specified at certain value with respect to recycling ratio (R_r) according to Figure 5.8 or using Eq. (3.3-11). The nitrate concentration at the aerobic zone outflow is to be maintained at 40 g/m^3 which corresponds to a specified SNUR value (Eq. (3.3-4) and Eq. (3.3-11)). As shown in Table 5.13, the required recirculation rate, Q_{re}, is estimated by Eq. (3.3-12) at the specified influent conditions and the SNUR, the calculated R_r, and the aerobic zone nitrate concentration. This predicted Q_{re} .along with the influent variables are input to the SSSP program to calculate the steady-state effluent variables.

The first run in Table 5.13 is simulated at a SNUR of 0.755 g NO_3/g VSS·d, which corresponds to R_r of 0.0356. The aerobic zone outlet nitrate concentration is maintained at a concentration of 40.0 g/m^3 and the calculated Q_{re} is 17850 m^3/d for first run. The SSSP program yields an aerobic outlet nitrate concentration of 55.5 g/m^3, which is greater than the desired 40.0 g/m^3 of nitrate concentration. Assuming that the input variables (COD, ammonium, and nitrate inlets concentrations) are fixed, the only manipulated variable is recirculation flow (Q_{re}). In order to manipulate Q_{re}, the SNUR value must be changed: increase in the SNUR will increase the R_r, and result in an

Table 5.13 Analysis of recirculation rate model using SNUR as a process parameter[1].

Run	Influent Organics $[COD]_i$ g COD/m^3	Influent Ammonium $[NH_4]_i$ g N/m^3	Influent Nitrate $[NO_3]_i$ g NO_3/m^3	Inlet Flow rate Q_i m^3/d	Sludge Recycle Q_{rs} m^3/d	Specified[2] Outlet Nitrate $[NO_3]_e$ g NO_3/m^3	Specific Nitrate[3] Uptake Rate SNUR g NO_3/g VSS·d
1	7000	550	80	3000	2500	40	0.755
2	7000	550	80	3000	2500	40	0.855
3	7000	550	80	3000	2500	40	0.900
4	7000	550	80	3000	2500	40	0.915
5	7000	550	80	3000	2500	40	0.920
6	7000	550	80	3000	2500	40	0.925

1. Fixed parameter: $\theta_c = 5$ d; $V_{anoxic} = 1000$ m^3; $V_{aerobic} = 7000$ m^3; and $DO_{aerobic} = 9.0$ g O_2/m^3
2. Set point aerobic zone effluent nitrate concentration to be maintained.
3. SNUR value for prediction of Q_{re}.

Table 5.13 (continued)

Run	Calculated[4] Recycling Ratio R_r	Predicted[5] Recirculation Q_{re} m^3/d	Aerobic[6] Outlet Nitrate $[NO_3]_e$ g NO_3/m^3	Anoxic[6] Outlet Nitrate $[NO_3]_e$ g NO_3/m^3	Effluent[6] Organic $[COD]_e$ g COD/m^3	Effluent[6] Ammonium $[NH_4]_e$ g N/m^3
1	0.0356	17850	55.5	0.2	2.2	1.6
2	0.0443	22841	45.8	0.2	2.2	1.6
3	0.0488	25426	42.0	0.2	2.2	1.6
4	0.0504	26343	40.8	0.2	2.2	1.6
5	0.0509	26655	40.4	0.2	2.2	1.6
6	0.0515	26970	40.0	0.2	2.2	1.6

4. R_r calculated by Eq. (3.3-11).
5. Q_{re} predicted by Eq. (3.3-12).
6. Steady-state solutions from SSSP program.

increase of Q_{re}. The runs 2 through 6 are conducted by increasing SNUR values and the Q_{re} predicted is corresponded to the R_r. Table 5.13 shows the decrease in aerobic zone outlet nitrate concentration (45.8 to 40.0 g/m^3) when the recirculation flow increases from 22841 to 26970 m^3/d. The sixth run indicates that the aerobic nitrate concentration is similar to the desired set-point nitrate concentration. By increasing the recirculation flow, more nitrate is recycled to the anoxic zone for removal, and as a result, the nitrate content at the aerobic zone outlet reduces. Table 5.13 suggests that by manipulating the recirculation flow (manipulated variable) which is corresponded to the SNUR value, one can maintain the desired aerobic zone nitrate concentration (controlled variable).

The overall results generated from Table 5.13 also show that, with the input variations, nitrate concentration set point, and the SNUR, the anoxic zone recirculation model is able to adequately estimate the required Q_{re}. In addition, the results indicate that the anoxic zone nitrate is also in low concentration, which implies that a good denitrification process is in place; from run 1 to run 6, the anoxic zone nitrate concentration is constant at 0.2 g/m^3. Generally, the major objective is accomplished: to demonstrate the application of process measurement parameters such as SNUR for monitoring of a denitrification reactor. More studies are needed to verify the practical applications of SNUR. Controlling the nitrate concentration at the aerobic outflow by manipulating the input variables is beyond the scope of this research activity.

The sensitivity of ORP in the anoxic zone with regards to R_r is depicted in Figure 5.12. ORP values increase when recycling ratios increase and ORP begins to level-off at an R_r of 0.5. It is apparent that, at a high recycling ratio, the effluent aerobic zone nitrate concentration is high. This implies that the nitrate content in the anoxic zone increases as more nitrates are recirculated, resulting in an increase of ORP values in the denitrification

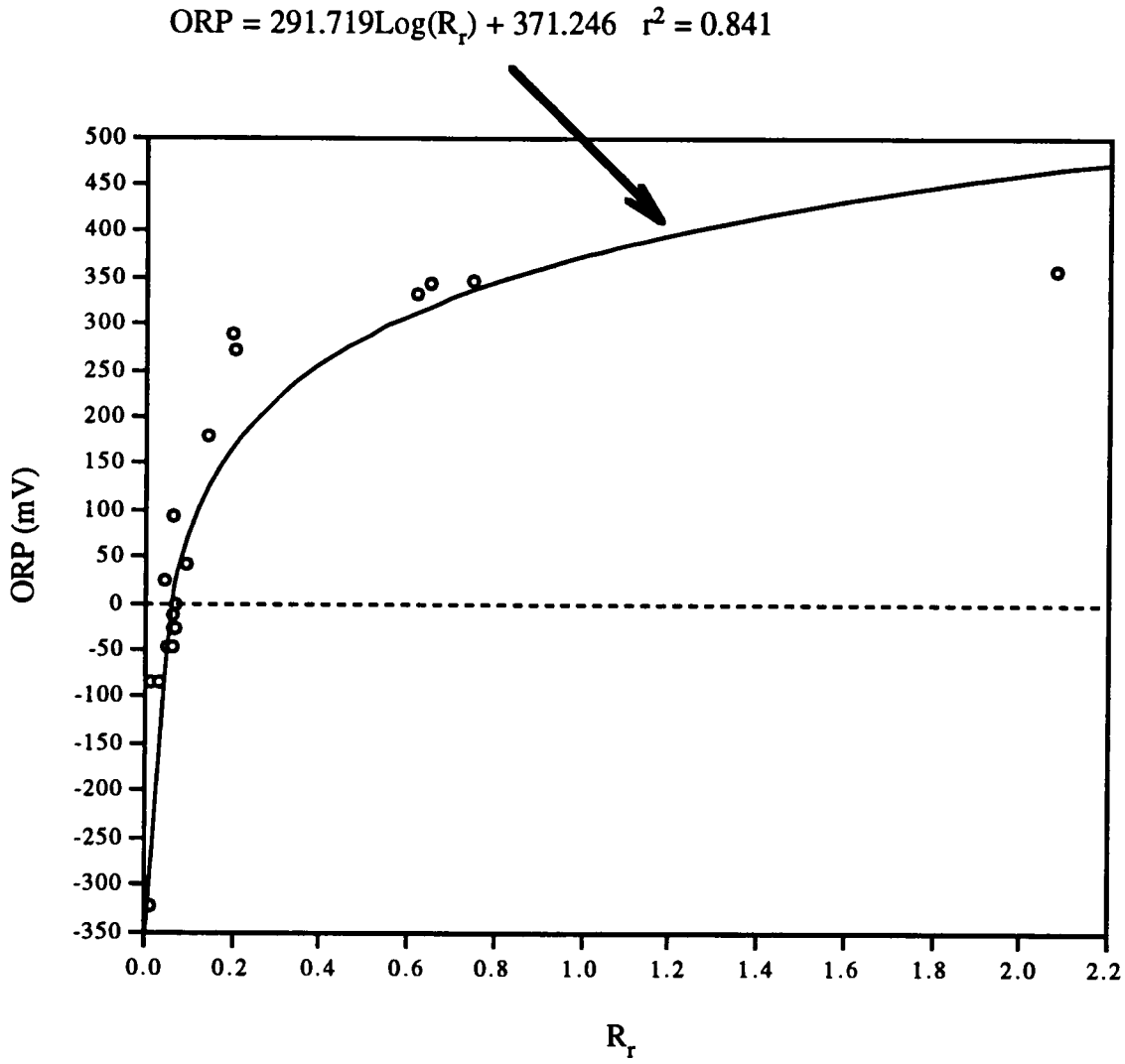


Figure 5.12 **Redox potentials in the anoxic zone as a function of recycling ratio.**

zone. The ORP equation generated by regression analysis is:

$$ORP(mV) = 291.719\ Log(R_r) + 371.246 \qquad (5.2\text{-}1)$$

Using Eq. (5.2-1), an empirical model for the prediction of recirculation flow based on ORP can be derived. Rearranging Eq. (5.2-1) for Q_{re} yields:

$$Q_{re} = \frac{\left(10^{(ORP-371.246/291.719)}\right)Q_i\left([NO_3]_i + [NH_4]_i + [COD]_i\right)}{[NO_3]_e} - Q_{rs} \qquad (5.2\text{-}2)$$

The ORP in Eq. (5.2-2) is computed by Eq. (3.2-18). The comparison between recirculation rates predicted by Eq. (3.3-12) and Eq. (5.2-2) with simulated recirculation rates is depicted in Figure 5.13. The profile in Figure 5.13 indicates that the Q_{re} prediction based on ORP measurement (Eq.(5.2-2)) is similar to the Q_{re} estimation based on SNUR measurement (Eq. (3.3-12)), but is less accurate. The major objective in this typical analysis is to show the potential use of ORP as a controlled variable and that a typical Q_{re} model (Eq. 5.2-2) can be derived through mathematical modeling.

The testing procedure is similar to the SNUR. In this case, the ORP calculated from Eq. (3.2-18) is a function of the anoxic zone nitrate concentration. Thus, by setting the redox potential, the nitrate concentration (0.2 g/m^3) at the anoxic zone is fixed at a particular value. The Q_{re} is predicted by Eq. (5.5-2). This Q_{re} and all the inlet variables are introduced into the SSSP program. Table 5.14 shows the influent variables and the set point for ORP with respect to the anoxic zone nitrate content. All runs are performed at an ORP value of -47.54 mV, which corresponds to 0.2 g/m^3 of nitrate concentration.

Assuming that the input variables are fixed and the only manipulated variable is

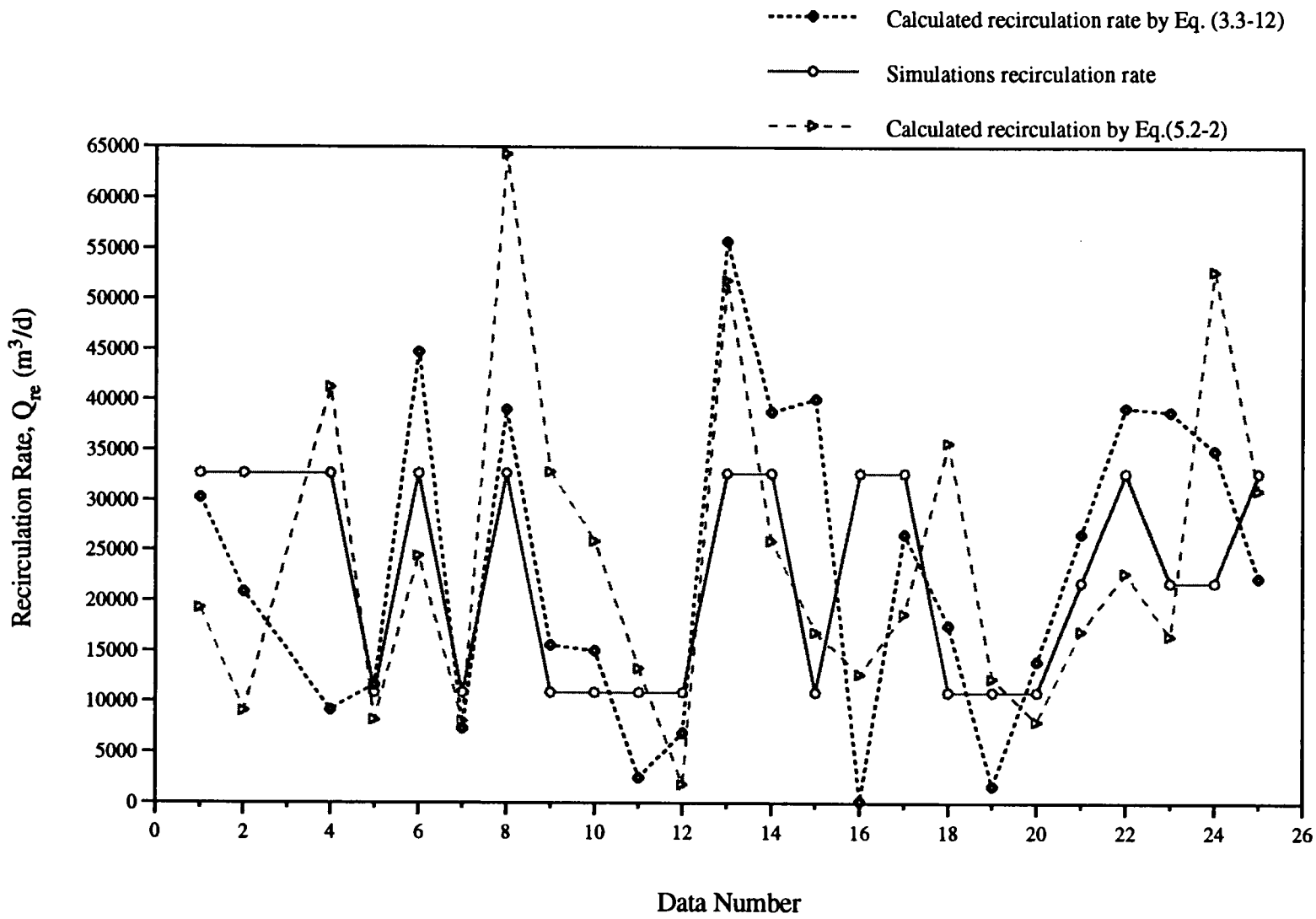


Figure 5.13 Comparison of recirculation rate predictions based on SNUR and ORP parameters.

Table 5.14 Analysis of recirculation rate model using ORP as a controlled variable[1].

Run	Influent Organics $[COD]_i$ g COD/m^3	Influent Ammonium $[NH_4]_i$ g N/m^3	Influent Nitrate $[NO_3]_i$ g NO_3/m^3	Inlet Flow rate Q_i m^3/d	Sludge Recycle Q_{rs} m^3/d	Specified[2] Outlet Nitrate $[NO_3]_e$ g NO_3/m^3	Set Point[3] Anoxic Nitrate $[NO_3]_e$ g NO_3/m^3
1	3000	200	100	5000	2500	15.0	0.2
2	3000	200	100	5000	2500	16.6	0.2
3	3000	200	100	5000	2500	18.2	0.2
4	3000	200	100	5000	2500	19.7	0.2
5	3000	200	100	5000	2500	21.0	0.2
6	3000	200	100	5000	2500	22.2	0.2
7	3000	200	100	5000	2500	23.2	0.2
8	3000	200	100	5000	2500	24.1	0.2
9	3000	200	100	5000	2500	25.0	0.2

1. Fixed parameters: $\theta_c = 5$ d; $V_{anoxic} = 1000$ m^3; $V_{aerobic} = 7000$ m^3; and $DO_{aerobic} = 9.0$ g O_2/m^3
2. Specified aerobic zone effluent nitrate concentration for prediction of Q_{re}
3. Set point anoxic zone outlet nitrate concentration to be maintained.

Table 5.14 (continued)

Run	ORP[4] at Anoxic Zone ORP mV	Predicted[5] Recirculation Q_{re} m^3/d	Aerobic[6] Outlet Nitrate $[NO_3]_e$ g NO_3/m^3	Anoxic[6] Outlet Nitrate $[NO_3]_e$ g NO_3/m^3	Effluent[6] Organic $[COD]_e$ g COD/m^3	Effluent[6] Ammonium $[NH_4]_e$ g N/m^3
1	-47.54	37848	16.6	0.3	2.1	1.6
2	-47.54	33959	18.2	0.3	2.1	1.6
3	-47.54	30754	19.7	0.3	2.1	1.6
4	-47.54	28222	21.0	0.3	2.1	1.6
5	-47.54	26320	22.2	0.3	2.1	1.6
6	-47.54	24762	23.2	0.3	2.1	1.6
7	-47.54	23587	24.1	0.3	2.1	1.6
8	-47.54	22613	24.9	0.3	2.1	1.6
9	-47.54	21709	25.6	0.2	2.1	1.6

4. ORP calculated by Eq. (3.2-18).
5. Q_{re} predicted by Eq. (5.5-2).
6. Steady-state solutions from SSSP program.

Q_{re}, since Eq. (5.5-2) is also a function of aerobic zone nitrate content, the aerobic zone outlet nitrate concentration is used as a feedback value for the Q_{re} predictions. As shown in Table 5.14, the initial aerobic nitrate concentration is set at 15.0 g/m^3; the SSSP program yields an aerobic nitrate concentration of 16.6 g/m^3 and an anoxic zone nitrate concentration of 0.3 g/m^3. The anoxic nitrate content is less than the desired set point of 0.2 g/m^3. One approach is to manipulate the Q_{re} to drive the anoxic zone nitrate content to the desired value. In the second run, the aerobic zone nitrate (16.6 g/m^3) is input to the SSSP program with all the influent variables. The SSSP again yields an anoxic zone nitrate of 0.3 g/m^3, which is still greater than the desired set point. The third run is performed by using the output value of the aerobic zone nitrate concentration (18.2 g/m^3) obtained from SSSP program. Further runs are conducted similarly until the anoxic zone nitrate concentration from the SSSP program is equal to the desired set point of 0.2 g/m^3 (corresponding to -47.54 mV). As shown in run 9, a Q_{re} of 21709 m^3/d results in an anoxic zone value of 0.2 g/m^3, which is similar to the set point value.

If the input variables are not fixed, one can manipulate the Q_{re} by changing the influent concentrations such as inlet COD and ammonium. For example, reducing the ammonium intake to the aerobic zone will decrease the generation of nitrate from ammonium. Also increasing the COD intake to the anoxic zone will provide more carbon for the heterotroph microorganisms to remove nitrate. As discussed in Chapters 2.1.5.6 and 2.1.5.7, nitrification is the conversion of ammonium to nitrate and denitrification is the removal of nitrate (reduced to nitrogen gas) with sufficient supply of organic carbon. As a result, manipulating the influent COD and ammonium maintains the ORP (nitrate concentration) set point in the anoxic zone. This subject, however, is beyond the scope of this research.

The overall results also indicate that the aerobic outlet nitrate concentrations fairly agree with the specified values (Table 5.14), and the effluent COD and ammonium are also at low levels. Thus, monitoring of the anoxic zone by manipulating the recirculation rate is applicable, and the ORP serves as an indicator of the performance of the denitrification process. In other words, in control applications, ORP is the controlled variable.

One of the important factors affecting the applicability of manipulating recirculation for monitoring in the anoxic zone is the measurement of effluent nitrate concentration. The measurement method must be reliable, as the measured value is used to estimate the recirculation rate. As described in Chapter 3.3, the nitrate content at the aerobic outlet is incorporated in the recycling ratio equation (Eq. (3.3-4)) instead of the anoxic nitrate concentration, due to the low concentration of nitrate at the anoxic zone. Low levels of nitrate concentration might affect the accuracy of measurement. Other factors include the dynamic responses of SNUR and ORP to the changes of recirculation rate, because the dynamic behavior of these process parameters is important for process control application.

Some additional information pertaining to the sensitivity of the process parameters are also studied in this analysis. These observations are presented in graphical form in Figure 5.14 through Figure 5.18. According to Figure 5.14, the SOUR increases with respect to overall recycling ratio, R_{all}. R_{all} and R_r are calculated by Eq. (3.3-1) and Eq. (3.3-4), respectively. The increase of SOUR values are caused by an increase in effluent nitrate and effluent COD. Furthermore, when influent COD and/or the inlet flow rate are large, the SOUR is also large (Tables 5.9 and 5.11). This indicates that more oxygen per unit biomass per day is required to oxidize the soluble organics. By regression analysis, the SOUR mathematical model as a function of R_{all} is:

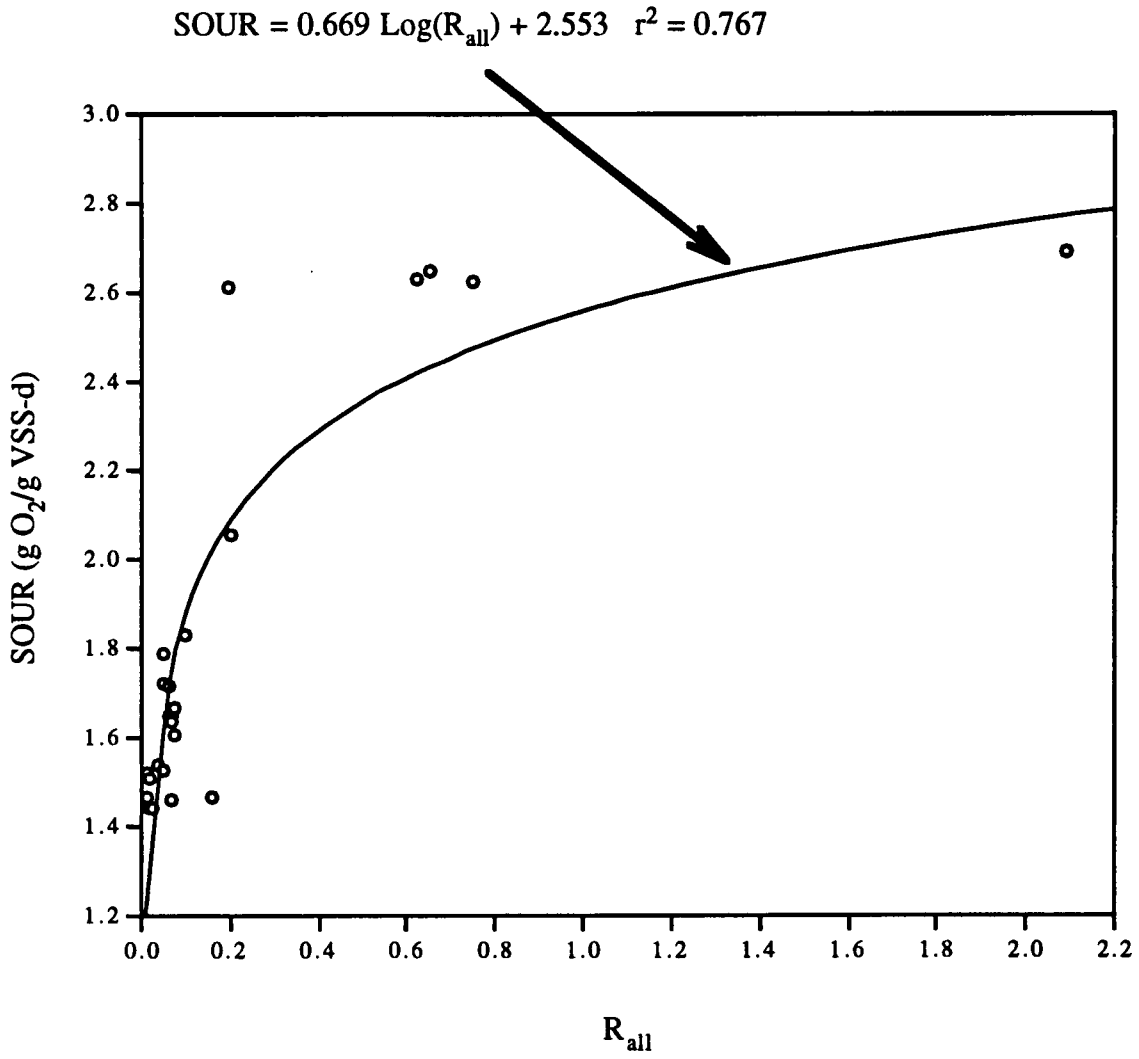


Figure 5.14 Specific oxygen uptake rate variations with overall recycling ratio.

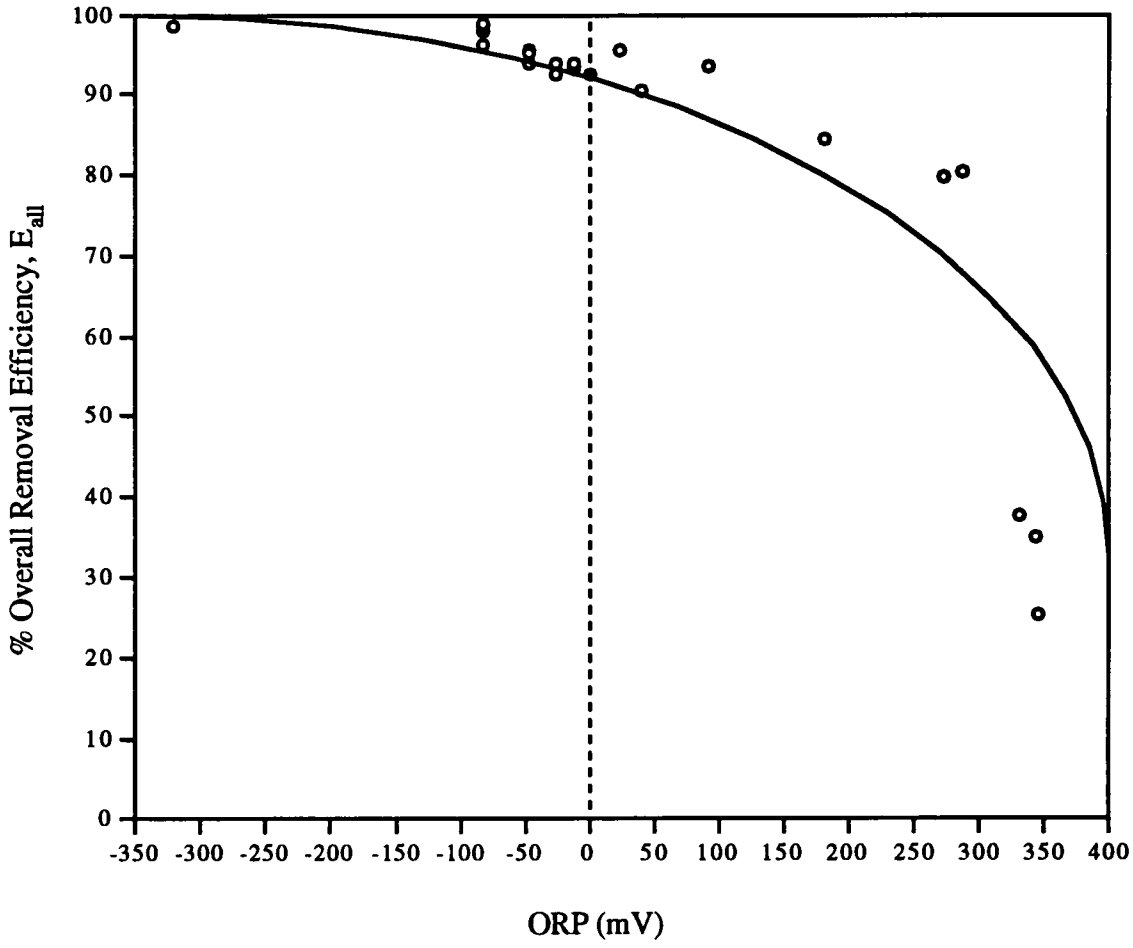


Figure 5.15 **Overall removal efficiency with respect to redox potential in the denitrification zone.**

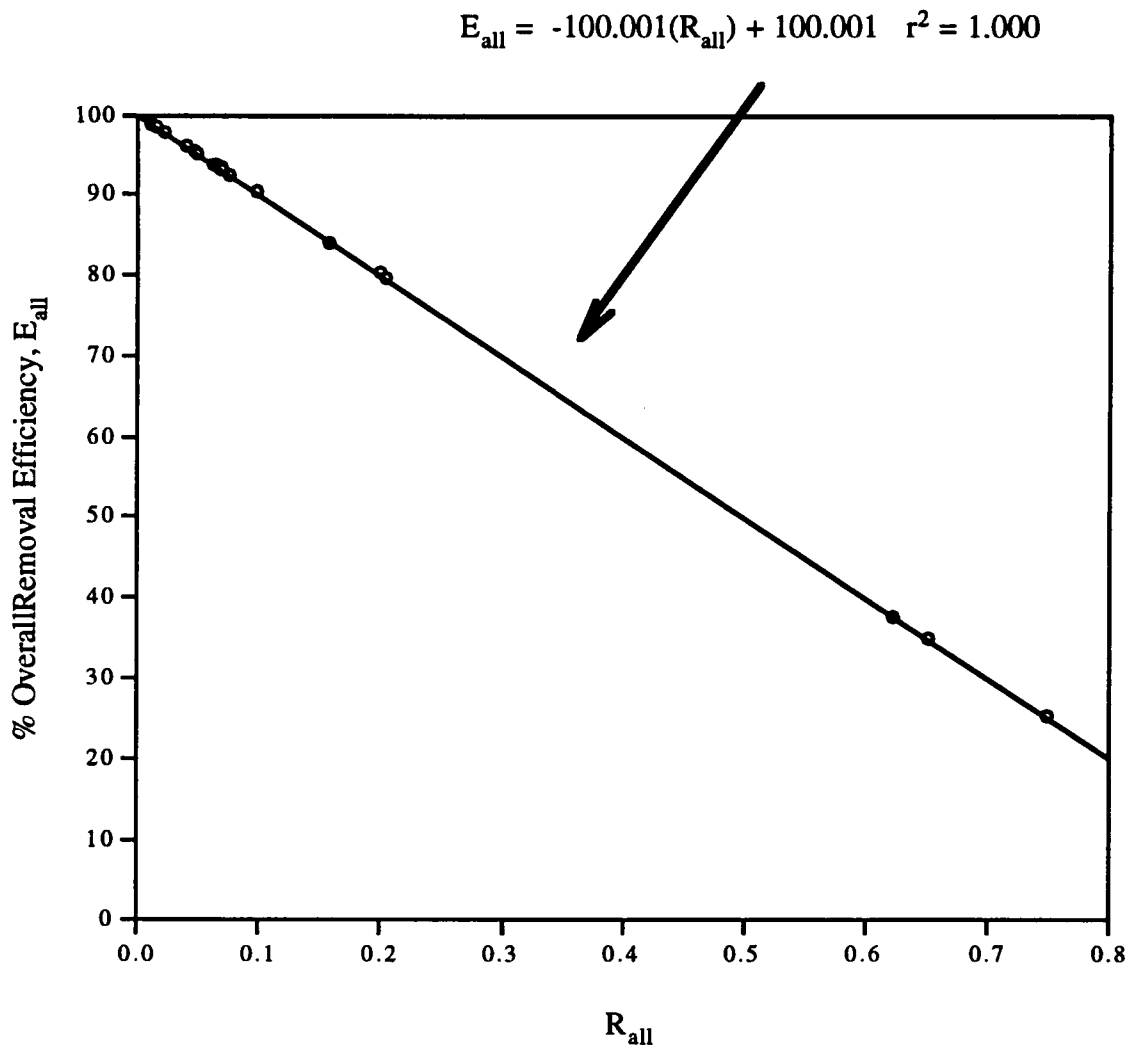


Figure 5.16 **Variations of overall removal efficiency with overall recycling ratio.**

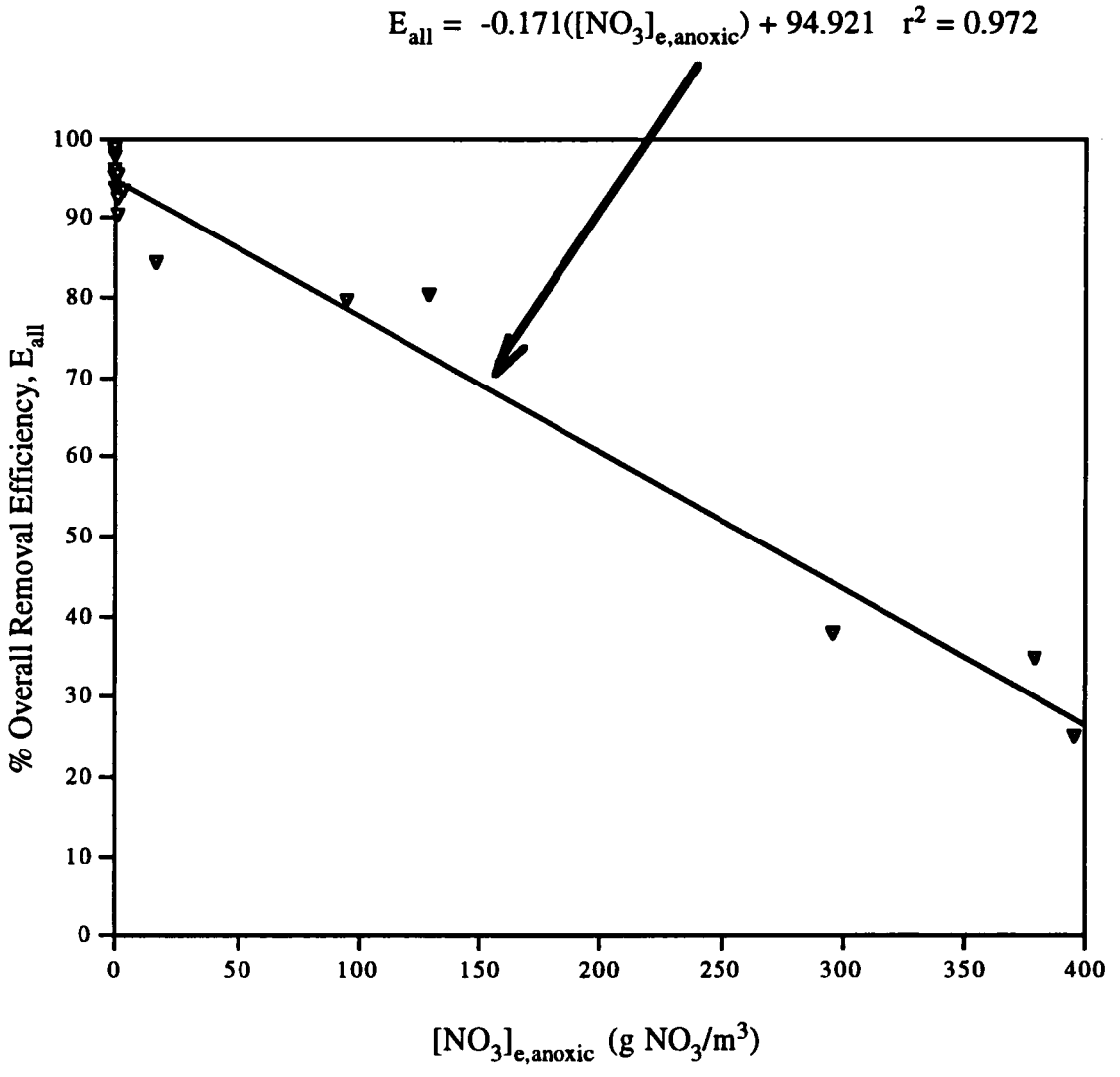


Figure 5.17 **Overall removal efficiency variations with residual nitrate concentration in the anoxic zone.**

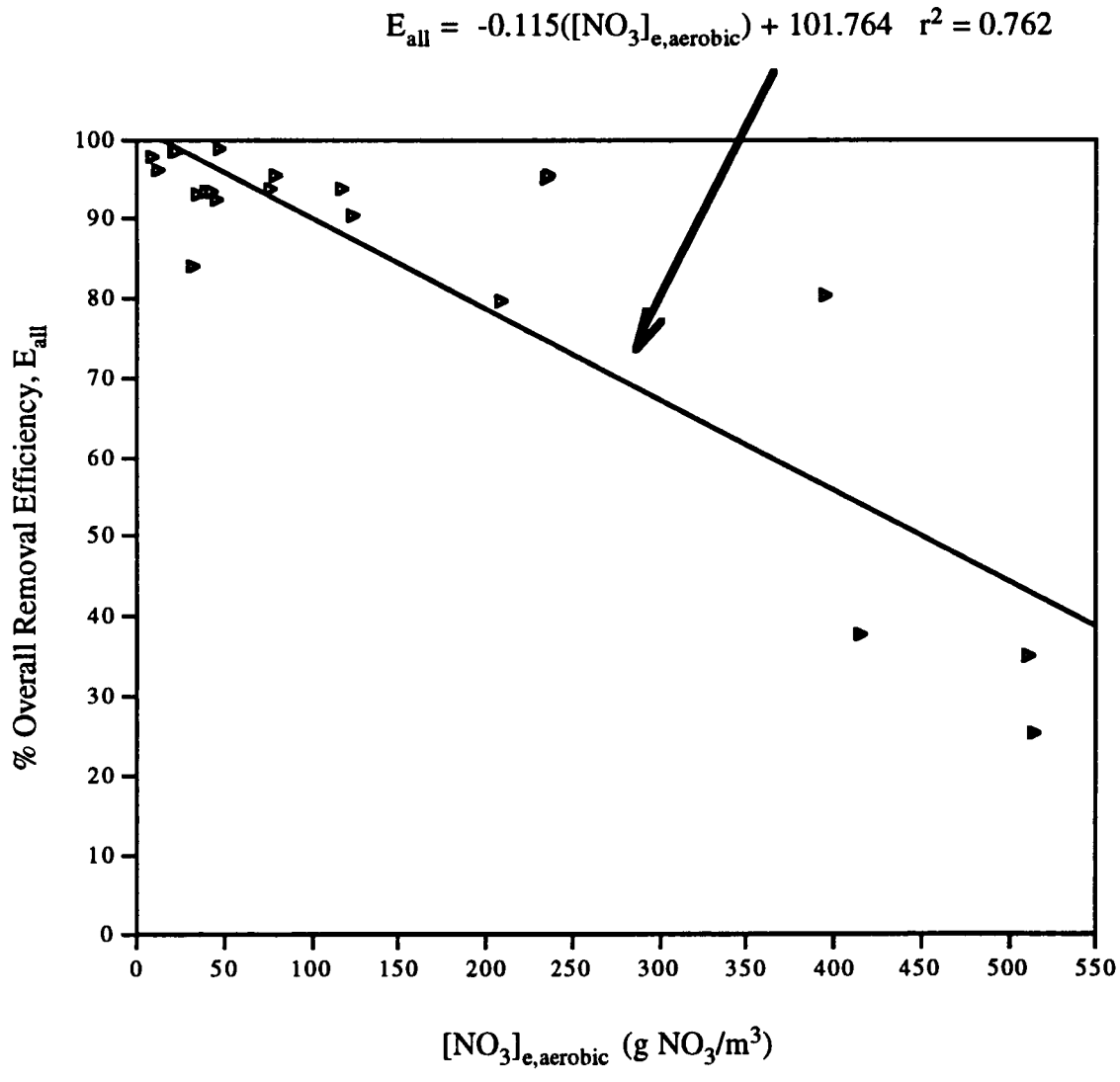


Figure 5.18 **Overall removal efficiency changes with residual nitrate concentration in the aerobic zone.**

$$SOUR(g\ O_2/g\ VSS - d) = 0.669\ R_{all} + 2.553 \qquad (5.2\text{-}3)$$

Through mathematical modeling using Eq. (5.2-3), an empirical model for the anoxic and aerobic zones can be developed. In the case of anoxic reactor monitoring, for example, the influent COD concentration plays a major role in the denitrification efficiency, as COD must be sufficient to accommodate the recirculated nitrate loads. Therefore, a manipulation of the recirculation rate can be developed based on SOUR in the aerobic zone. For monitoring of the aerobic zone (carbon oxidation and nitrification), the dissolved oxygen (DO) content of the aerobic zone can be incorporated in Eq. (3.3-1). This DO concentration is related to the aeration rate. Thus, for monitoring of the carbon oxidation and nitrification process, one can derive an aeration rate control model using SOUR as an indicator of microorganism activities in the aerobic zone. Again, as for SNUR and ORP, this SOUR approach needs more data analyses to confirm its feasibility and validity. Process control using SNUR, ORP, SOUR, or other process measurement parameters investigated in this study can be improved or verified by experimental or real plant data.

Some process parameters are plotted against the overall removal efficiency, E_{all}, (Eq. (3.3-3)) to study their effects. In run number 16 (Table 5.12), an E_{all} of -109.07% is due to the high aerobic zone outlet nitrate concentration (547.4 g/m^3). The combination of influent variables at run 16 shows that the denitrification process has failed totally; hence, run 16 is omitted for all the E_{all} plots. A relationship between overall removal efficiency, E_{all}, (by Eq. (3.3-3)) and ORP in anoxic zone is illustrated in Figure 5.15. The figure illustrates that, at high ORP (positive potential), the removal efficiency decreases. This suggests that ORP can be used as an indicator of process failure.

Figure 5.16 presents a linear relationship between E_{all} and overall recycling ratio, R_{all}. At low R_{all}, effluent substrate concentrations are small; that is, the substrate (waste) removal rates are high. The E_{all} as a function of R_{all} is:

$$E_{all}(\%) = -100\, R_{all} + 100 \qquad (5.2\text{-}4)$$

Figure 5.17 shows the profile of the E_{all} with regards to the nitrate concentration in the denitrification zone. The slope of the graphical representation in this figure implies that the E_{all} decreases when the anoxic zone nitrate content increases; therefore, nitrate content has a major impact on the overall removal efficiency. The correlation between E_{all} and nitrate concentration is:

$$E_{all}(\%) = -0.171\left(\left[NO_{3,anoxic}\right]\right) + 94.921 \qquad (5.2\text{-}5)$$

The aerobic zone nitrate concentration also has a similar effect on overall removal efficiency, which is plotted in Figure 5.18. In this figure, the data are somewhat scattered, but the overall pattern can be seen: when nitrate in the aerobic zone decreases, E_{all} increases. This relationship is formulated as:

$$E_{all}(\%) = -0.115\left(\left[NO_{3,aerobic}\right]\right) + 101.764 \qquad (5.2\text{-}6)$$

Therefore, once the aerobic zone nitrate content begins to increase, one can predict the failure of the treatment process.

The observations discussed so far from the single variable analysis and the anoxic zone recirculation model analysis suggest that the biological treatment model (two-stage

Bardenpho process) is capable of treating the wastewater stream and also allows the analysis of the sensitivity of process measurement parameters (ORP, SOUR, etc.). The results of these investigations also agree with the literature. Chapters 6 and 7 comprise conclusions drawn from the research activity described in the preceding chapters and recommendations for further research.

CHAPTER 6

SUMMARY AND CONCLUSION

Literature reviews showed that promising sensor technologies in the near future include fiber-optic, sensor-promote, non-contact measurement; and microbial- or enzyme-based, biosensor-promote, specific and real-time measurement. The development trend of these sensors or measurement techniques is directed toward on-line application, quick response (within minutes), safety, and longer lifetime. Many of these sensors are available commercially (Chapters 2.2.2, 2.2.3, and 2.2.4), for example, the "BOD-M3" biosensor, which has a three-minute measuring time. Some present and future biological process parameters for control of bio-treatment process were also identified in the literature. These parameters include: adenosine triphosphate, redox potential, oxygen uptake rate, and immediate maximum specific oxygen uptake rate. Sensors for monitoring physical, chemical and biological variables are identified in Tables 2.12 and 2.13.

A general overall development procedure for control strategy was developed. The procedure discussed the critical aspects for control of a bioreactor and the general problems associated with designing control strategy (Chapter 2.3). The major problems causing the failure of bioreactor control were the lack of dynamic models that can represent the complexity of biological systems and the lack of reliable sensors as well as process parameters that can serve as indicator of microbial activity. These studies, however, revealed that with advanced developments in sensor technology and dynamic models, more effective control of bioreactors is likely to be achieved in the future.

The biological treatment model used for the sensitivity analysis of process measurement parameters was a typical two-stage Bardenpho process. The first stage was designed for denitrification and the subsequent stage was designed for carbon oxidation

and nitrification. The volumes of the anoxic zone and aerobic zone were 1000 m^3 and 7000 m^3, respectively. The wastewater stream contained 5000 g COD/m^3, 500 g N/m^3, 100 g NO_3/m^3 with an inlet flow rate of 5451 m^3/d (base case). The input variables were varied from ±50% of the base conditions to study the steady-state responses of the process measurement parameters. These process parameters or control indexes were: redox potential (ORP); oxygen, nitrate, ammonium uptake rates (OUR, NUR, and AUR); and specific oxygen, nitrate, and ammonium uptake rates (SOUR, SNUR, and SAUR).

Two sets of investigations were performed. First was the single variable analysis, in which each input variables (COD, ammonium-nitrogen, nitrate loadings and inlet flow rate) was varied from low to high and others were held constant. This analysis permits the study of the responses of each individual process parameter when subjected to influent variations. The second investigation was the analysis of a proposed anoxic zone recirculation rate model. A total of 25 combinations of the five input variables (the four input variables listed above plus recirculation rate) were generated using the statistical factorial design method which consist of high, low and base cases. The major objective of the second investigation was to show the application of process measurement parameters as control or manipulated variables for denitrification control. In addition to the verification of the proposed recirculation model, the sensitivity of process parameters were also investigated. All the simulations were performed using a single-sludge biological treatment model (SSSP program) developed by Clemson University. The conclusions from both studies are summarized as follow:

Single Variable Analysis:

- The ORP (Eq. (3.3-18)) responded with the changes of nitrate concentration in anoxic zone. The influent nitrate concentration had the greatest effect on ORP, followed by influent ammonium and COD; inlet flow rate had the least effect.

- The OUR, NUR, and AUR (substrates uptake rates) had the greatest sensitivity to influent COD changes; ammonium was second, the inlet flow rate third, and nitrate was the smallest.
- The specific uptakes rates had different responses compared to the substrate uptake rates. Influent COD had the biggest effect on SOUR, SNUR, and SAUR, followed by influent ammonium-nitrogen and nitrate, and inlet flow rate.
- All the process parameters responded to the changes in input variations, thus rendering them applicable to monitoring and control of the bio-treatment process.
- It was concluded that the ORP, SNUR, and NUR can be used as process parameters for monitoring the denitrification reaction in the anoxic reactor. For carbon oxidation and nitrification (aerobic) control, however, SOUR, OUR, SAUR, and AUR can be employed to indicate the activity of microorganisms in the reactor.

Recirculation Model Evaluation:

- The model was based on the assumption of the Monod equation applied to the relationship of SNUR (Eq. (3.3-5)) and the nitrate recycling ratio, R_r, (Eq. (3.3-4)). A double reciprocal plot was used to determine the biokinetic constants, K_r and S_{max}.
- The monitoring of the denitrification zone was implemented via manipulation of the recirculation flow (Q_{re}). The measurements of influent COD, ammonium, and nitrate concentrations; inlet flow rate; and nitrate concentration at the aerobic zone outflow were used to predict Q_{re}.
- The recirculation flow (Q_{re}) predicted by Eq. (3.3-12) did not agree with the original recirculation rate used in the SSSP simulations. However, the general

trend of the predicted recirculation rate agreed with the original recirculation rates (Figures 5.10 and 5.11).

- Large percent differences in the Q_{re} predictions were due to the over-simplification of the relationship between SNUR and R_r. In addition, more data were required for a five-input-variables analysis to yield a better regression analysis.
- The SNUR was used as a manipulated variable to predict Q_{re} for maintaining a set-point nitrate concentration at the aerobic zone outlet (Table 5.13). However, the ORP was employed as a controlled variable in monitoring of the anoxic zone by manipulation of Q_{re} (Table 5.14).The overall results suggested that Eq. (3.3-12) and Eq. (5.2-2) were capable of predicting the required Q_{re} at various loading conditions.
- Using ORP and SNUR for monitoring the anoxic zone showed that these parameters can be used in process control applications.
- The sensitivity analysis indicated that there was a correlation between SOUR and the overall recycling ratio, R_{all} (Eq. (3.3-1)). This suggested that SOUR can be a potential indicator of the activity of aerobic zone.
- The overall removal efficiency, E_{all}, (Eq. (3.3-3)) was also related to the ORP in the anoxic zone. At a positive ORP range, the E_{all} was low and vice-versa.
- Nitrate concentration in the aerobic and anoxic zones had the similar effect on E_{all}; that is, E_{all} was reduced when nitrate concentrations increased.

In general, the results from these investigations suggest that all the parameters studied responded to the influent variables with different sensitivity. The extent of the sensitivity, however, is dependent on the bio-treatment system, wastewater characteristics, and activity of the viable microorganisms. Thus, the conclusions derived

from this research are purely theoretical and specific to the bio-treatment model design as well as the influent wastewater compositions. Nonetheless, the overall findings are within the limits of published results, and the primary objectives of the investigation were accomplished.

On-line methods for measuring the process parameters studied in this investigation are not yet commercially available. Some ion-selective electrodes, for example, are capable of measuring nitrate and ammonium concentrations, but little is known about their on-line application. For an effective wastewater treatment plant control strategy, the reliability and robustness of these sensors are crucial, but the incorporation of these measurements into process control is also important. Therefore, fully-automated measuring systems should be emphasized in future research and development of sensors. The critical needs for sensor technology development are automation, on-line application, less sophistication in the device, and ease of maintenance and use (Chapter 2.2). In other words, development of sensors should not only concentrate on the method of measurement but also should include a completely automated system for process control application. A current example of such an automated measuring system is the "BOD-M3" measuring device. In addition, other critical automated on-line instruments include sensors for monitoring heavy (toxic) metals, suspended solids (biomass), organic matter (such as COD), and inorganic matter (such as nitrate). These on-line monitors play a significant role in the overall process control of a biological wastewater treatment plant. Generally, to maintain optimal conditions and to avoid failure in the bio-treatment process requires reliable on-line measurement methods and an effective process control strategy.

CHAPTER 7

RECOMMENDATIONS

More verification of method is required in order to use the process parameters described in this research as control variables for real-time control of a biological treatment process. Since these sensitivity analyses are performed under the assumption of steady-state conditions, the behavior of these process parameters are unknown under transient influent conditions. In addition, the sensors and measurement methods for these parameters are still underdeveloped, and the reliability of these sensors needs to be improved. Recommendations for future research and development are summarized below:

- Due to the complexity of the biological system, detailed models such as structured, non-segregated models are recommended for modeling the substrate utilization rate.
- More data are required for regression analysis of the denitrification zone control model study.
- A control algorithm is needed for study of the control of process parameters by manipulating the input variables.
- The dissolved oxygen (DO) concentration plays a major role in the efficiency of the denitrification rate. Since the DO concentration is not always zero at the anoxic zone, DO concentration should be incorporated in the recycling ratio model.
- Real plant data are needed to confirm the correlation between influent loading variation and process parameters (ORP, OUR. SOUR, SNUR, etc.).
- Dynamic analysis should be performed to investigate the transient responses of those process measurement parameters when subjected to input variations.

LIST OF REFERENCES

LIST OF REFERENCES

Abeling, U. and Seyfried, C. F., *Anaerobic-aerobic Treatment of High-strength Ammonium Wastewater - Nitrogen Removal via Nitrite.* Wat. Sci. Tech., **26,** 1007-1015 (1992).

Adams, Carl E., Jr., Ford, Davis L., and Eckenfelder, W. W. Jr., *Development of Design and Operational Criteria for Wastewater Treatment.* Enviro Press, Inc., Nashville, TN., (1981).

Alleman, J. E., and Irvine, R. L., *Storage-Induced Denitrification Using Sequencing Batch Reactor Operation.* Water Res., **14,** 1483 (1980).

Anderson, G. K., Donnelly, T., and McKeown, K. The Application of Anaerobic Packed Bed Reactors to Industrial Wastewater Treatment. J. Water Pollut. Control Fed., **83,** 491 (1984).

Andrews, J.F., *Dynamic Models and Control Strategies for Wastewater Treatment Process.* Water Res., **8,** 261 (1974).

Arnold, M. A., *Fluorophore- and Chromophore-Based Fiberoptic Biosensors.*, pp. 195-211. In: Blum, Loic J. and Coulet, Pierre R. (ed.), Biosensor Principles and Applications. Marcel Dekker, Inc., New York (1991).

Arora, M. L., Barth, E. F., and Umphres, M. B., *Technology Evaluation of Sequencing Batch Reactors.* J. Water Pollut. Control Fed., **57,** 867 (1985).

Arthur, R. M., *How to Monitor Biological and Physical Parameters.* In: Arthur, R. M. (ed.), Application of On-Line Analytical Instrumentation to Process Control, Arthur Technology, Ann Arbor Science Publishers, Michigan (1981).

Arthur, R. M., *New Concepts and Practices in Activated Sludge Process Control,* Arthur Technology, Ann Arbor Science Publishers, Michigan (1982).

Arthur, R. M., *Process Control Strategies.* In: Arthur, R. M. (ed.), Procedures and Practices in Activated Sludge Process Control, Arthur Technology, Ann Arbor Science Publishers, Michigan (1983).

Bailey, J. E., and Ollis, D. F., *Biochemical Engineering Fundamentals,* 2nd ed., McGraw-Hill Book Company., New York (1986).

Barnard, J. L. *The Bardenpho Process.* In: Wanielista, M. P. and Eckenfelder, W. W. Jr. (eds.), Advances in Water and Wastewater Treatment - Biological Nutrient Removal. Ann Arbor Science Publishers, Michigan (1978).

Barnard, J. L, Upadhyaya, A. K. and Eckenfelder, W. W. Jr. and Englande A. J., *Design Optimization for Activated Sludge and Extended Aeration Plants,* 6th International Conference of the IAWPRC Jerusalem, Israel (1972).

Barth, E. F., *Sequencing Batch Reactors for Municipal Wastewater Treatment.* Presented at the Eight U.S./Jpn Conf. on Sew. Treat. Technol. (1981).

Beaubien, A., and Jolicoeur, C., *Applications of Flow Microcalorimetry to Process Control in Biological Treatment of Industrial Wastewater.* J. Water Pollut. Control Fed., **57,** 95 (1985).

Beezer, A. E., Bettleheim, K. A., Al-Salihi, S. and Shaw, E. J., *The Enumeration of Bacteria in Culture Media and Clinical Specimens of Urine by Microcalorimetry.* Sci. Tools, **25,** 6-8 (1978).

Benefield, L. D. and Randall C. W., *Biological Process Design for Wastewater Treatment.*, 1st ed., Prentice-Hall, Inc., NJ. (1980).

Berg, L. van den and Lentz, C. P., *Effects of Film Area-to-volume ratio, Film Support, Height and Direction of Flow on Performance of Methanogenic Fixed Film Reactors.* Proceeding of the US Department of the Environment Workshop Seminar on Anaerobic Filters. Howey-in-the-Hill, Florida (1980).

Berg, L. van den and Lentz, C. P., *Comparison between Up- and Down-flow Anaerobic Fixed Film Reactors of Varying Surface-to-volume Ratios for the Treatment of Bean Blanching Waste.* Proceedings of the 34th Purdue Industrial Waste Conference, p319-325 (1979).

Berg, L. van den and Kennedy, K. J. *Support Materials for Stationary Film Reactors for High Rate Methanogenic Fermentations.* Biotechnol. Lett. **3,** 165-170 (1981).

Berthouex, P. M., *Information Management for Wastewater Treatment.* ISA Transactions, **31,** 35-51 (1992).

Bidstrup, S. M. and Grady, C. P.L., Jr. *A User's Manual for SSSP: Simulation of Single-sludge Processes for Carbon oxidation,* Nitrification and Denitrification. Version 1.0. Environmental Systems Engineering, Clemson University, Clemson, South Carolina, February (1987).

Blum, L. J. and Gautier, M. *Bioluminescence- and Chemiluminescence-Based Fiberoptic Sensors.* pp. 213-247. In: Blum, Loic J. and Coulet, Pierre R. (eds.), Biosensor Principles and Applications. Marcel Dekker, Inc., New York (1991).

Boe, O. K., *Data Management for Process Control.* In: Arthur, R. M. (ed.), Procedures and Practices in Activated Sludge Process Control, Arthur Technology, Ann Arbor Science Publishers, Michigan (1983).

Boening, P. H. and Larsen, V. F., *Anaerobic Fluidized Whey Treatment.* Biotechnol. Bioeng., **24,** 2539 (1982).

Briggs, R., *Instrumentation for Waste Treatment Processes.* In: Comprehensive Biotechnology. Pergamon Press, Oxford, England, 4 (1985).

Briggs, R. and Grattan, K.T.V., *Instrumentation and Control in the UK Water Industry: A Review.*, In: R. Briggs (ed), Instrumentation, Control and Automation of Water and Wastewater Treatment and Transport Systems, IAWPRC, Pergamon Press, New York (1990).

Brock, T., Smith, D. W., and Madigan, M. T., *Biology of Microorganisms.* 4th ed., Prentice Hall, Inc., New Jersey (1984).

Bucksteeg, W., and Thiele, H., *Die Beurteilung von Abwasser und Schlamm mittels TTC.* Gass und Wasserfach, (GER) **100,** 916 (1959).

Bucksteeg, W., *Determination of Sludge Activity: a Possibility of Controlling Activated-sludge Plants.* Paper presented at the 4th Int. Conf. on Water Pollution Research, Munich (1966).

Caruana, C. M. (ed.), *Hong Kong Starts Pollution Clean-up in Earnest.* Chemical Engineering Progress, p12-18, February (1994).

Chappell, T. E., *A Computer-based Centralized Control and Supervisory System for an Effluent Treatment plant.* Chem. Eng. (London), **371/2,** 377-380 (1981).

Chappelle, E. W., Piccioli, G. L., and Deming, J. W., *Determination of Bacterial Content in Fluids.* Meth. Enzymol., **57,** 65-72 (1978)

Cheremisinoff, P. N., *Wastewater Treatment.* 3rd., Pudvan Publishing Co. Northbrook, Illinois (1987).

Chen, C. Y., et al., *Response of Dissolved Oxygen to Changes in Influent Organic Loading to Activated Sludge System.* Water Res., **14,** 1449 (1980).

Chen, S. J., et al., *Performance Evaluation of the Anaerobic Fluidized Bed System.* In: Substrate Utilization and Methane Production. J. Chem. Tech. Biotechnol., **35B,** 101 (1985).

Chen, S. J., Li, C. T., and Shieh, W. K., *Anaerobic Fluidized Bed Treatment of an Industrial Wastewater.* J. Water Pollut. Control Fed., **60,** 1826 (1988).

Chiu, S. L. et al., *ATP Pools in Activated Sludge.* J. Water Pollut. Control Fed., **45,** 1746 (1973).

Chung, Y-C and Neethling, J. B., *ATP as a Measure of Anaerobic Sludge Digester Activity.* J. Water Pollut. Control Fed., **60,** 107 (1988).

Chung, Y-C and Neethling, J. B., *Microbial Activity Measurements for Anaerobic Sludge Digestion.* J. Water Pollut. Control Fed., **61,** 343 (1989).

Clarke. D. J., Calder, M. R., Carr, R. J. G., Blakecoleman, B. C., and Moody, S. C., *The Development and Application of Biosensing Devices for Bioreactor Monitoring and Control.* Biosensors (in press), (1985)

Culshaw, B., *Trends in Fibre Optic Sensors.* Int. J. Opt. Sens. **1,** 327-337 (1986).

Davies, L., *The Usefulness of Statistically-Designed Experiments.* Chemistry and Industry, September 7 (1992).

Davis, R. A., *Computerization - Can it Work for You?* In: Arthur, R. M. (ed.), Procedures and Practices in Activated Sludge Process Control, Arthur Technology, Ann Arbor Science Publishers, Michigan (1983).

Dennis, R. W. and Irvine, R. L., *Effect of fill:react ratio on Sequencing Batch Biological Reactors.* J. Water Pollut. Control Fed., **51,** 255 (1979).

DiBiasio, D., *Introduction to the Control of Biological Reactors.* In: Shuler, M. L. (ed), Chemical Engineering Problems in Biotechnology, Vol. 1, New Technology Education Series, AIChE (1989).

Dillon, G. R. and Thomas, V. K., *A Pilot-scale Evaluation of the 'Biocarbone Process' for the Treatment of Settled Sewage and for Tertiary Nitrification of Secondary Effluent.* Wat. Sci. Tech., **22,** 305-316 (1990).

Douglas, J. M., *Process Dynamics and Control.* Englewood Cliffs, New Jersey, Prentice Hall (1972).

Dold, P. L. and Marias, G. v. R., *Evaluation of the General Activated Sludge Model Proposed by the IAWPRC Task Group.* Wat. Sci. Tech., **18,** 63-89 (1986).

Dow, C. S., France, A. D., Khan, M. S., and Johnson, T., *Particle Size Distribution Analysis for the Rapid Detection of Microbial Infection of Urine.* J. Clin. Pathol., **32,** 386-90.

Drake, R. A. R. (ed.), *Instrumentation and Control of Water and Wastewater Treatment and Transport Systems.* Pergamon Press, New York (1985).

Droste, R. L. and Sanchez, W. A., *Microbial Activity in Aerobic Sludge Digestion.* Water Res., **17,** 975 (1983).

Eckenfelder, W. W. Jr., *Industrial Water Pollution Control.* McGraw-Hill, Inc., New York (1989).

Eckenfelder, W. W, Jr., Argaman, Y., and Miller, E., *Process Selection Criteria for the Biological Treatment of Industrial Wastewaters.* Environmental Progress, **8,** 1 (1989).

EPA, Process Control Manual for *AEROBIC BIOLOGICAL WASTEWATER TREATMENT FACILITIES*, Municipal operation Branch, Washington (1977).

EPA, *Technology Assessment of the Biological Aerated Filter.* Water Engrg. Res. Lab., Cincinnati, Ohio, (1988).

Fioroni, E.R. and Frais, W.D., *Good Process Control: Planning and Implementation.* In: Arthur, R. M. (ed.), Procedures and Practices in Activated Sludge Process Control, Arthur Technology, Ann Arbor Science Publishers, Michigan (1983).

Flynn, D. S., *Traditional Sensors.* In: Daniel R. Omstead (ed.), Computer Control of Fermentation Processes. CRC Press, Inc., Florida (1990).

Ford, D.L., Yang, J. T. and Eckenfelder, W. W., *Dehydrogenase Enzyme as a Parameter of Activated-sludge Activities.* Paper presented at the 21st Ind. Waste Conf., Purdue Univ., 534 (1966).

Fortier, J-L., Reboul, B., Philip, P., Simard, M-A., Picker, P., and Jolicoeur, C., *Calorimetric Studies of Biodegradation Processes in Biological wastewater Treatment.* J. Water Pollut. Control Fed., **52,** 89 (1980).

Fox, P., Makram, T. S., and Pfeffer, J. T., Anaerobic Treatment of a Biologically Inhibitory Wastewater. J. Water Pollut. Control Fed., **60,** 86 (1988).

Gaudy, A.L. and Gaudy, E., *Microbiology for Environmental Scientists and Engineers.* McGraw Hill, New York, 1980.

Giona, A.R. and Annesini, M.C., *Oxygen Uptake in the Activated Sludge Process.* J. Water Pollut. Control Fed., **51,** 5, 1009 (1979).

Givens, S. W., Brown, E. V., Gelman, S. R., Grady, C. P. L. Jr., Skedsvold, D. A., *Biological Process Design and Pilot Testing for a Carbon Oxidation, Nitrification, and Denitrification System.* Environmental Progress, **10,** 133-146 (1991).

Goto, M. and Andrews, J. F., *On-line Estimation of Oxygen Uptake Rate in the Activated Sludge Process.* In: Drake, R. A. R. (ed.), Instrumentation and Control of Water and Wastewater Treatment and Transport Systems. IAWPRC, Pergamon Press, New York (1985).

Grady, C. P. Leslie and Lim, H. C., *Biological Wastewater Treatment: Theory and Applications,* Marcel Dekker, Inc., New York (1980).

Grady, C. P. L. Jr., Gujer, W., Henze, M., Marias, G. v. R., and Matsuo, T., *A Model for Single-sludge Wastewater Treatment Systems.* Wat. Sci. Tech., **18,** 47-61 (1986).

Grattan, K. T. V., *Recent Advances in Fibre Optic Sensors Measurement.* J. Int. Meas. Confed. **5,** 122-134 (1987).

Gray, N. F., *Activated Sludge: Theory and Practice,* Oxford University Press, New York (1990).

Gray, N. F., *Biology of Wastewater Treatment,* Oxford University Press, New York (1989).

Gujer, W. and Henze, M., *Activated Sludge Modeling and Simulation.* Wat. Sci. Tech., **23,** 1011-1023 (1991).

Haas, C. N., *Oxygen Uptake Rate as an Activated Sludge Control Parameter.* J. Water Pollut. Control Fed., **51,** 938 (1979).

Hakulinen, R. and Salkinoja-Salonen, M., *Treatment of Pulp and Paper Industrial Wastewater in an Anaerobic Fluidized Bed Reactor.* Proc. Biochem., 18 (1982).

Halász, v. A., *Zusammenhang zwischen Dehydrogenaseaktivitat und Eachstumsrate des Belebtschlammes.* Hydrologie, **34,** 1, 94 (1972).

Halme, A., *The Industrial Application of Modern Measurement and Estimation Techniques in Biotechnology,* In: Johnson, A. (ed.), Modeling and Control of Biotechnological Processes, International Federation of Automatic Control, Pergamon Press, New York (1986).

Harita, K., Otani, Y., Hikuma, M., Yasuda, T. *BOD quick estimating system utilizing a microbial electrode.* p.529-532. In: R.A.R. Drake (ed.), Instrumentation and Control of Water and Wastewater Treatment and Transport Systems, IAWPRC, Pergamon Press, New York (1985).

Hawkes, F. R. and Hawkes, D. L., Anaerobic Digestion. p.337-358. In: Bu'Lock, John and Kristiansen, Bjorn (eds.), Basic Biotechnology, Academic Press, Inc., San Diego (1987).

Hegg, B.A., Rakness, K.L. and Schultz, J.R., Evaluation of Operation and Maintenance Factors Limiting Municipal Wastewater Treatment Plant Performance. J. Water Pollut. Control Fed., **50,** 419 (1978).

Herzbrun, P. A., Irvine, R. L., and Malinowski, K. C., *Biological Treatment of Hazardous waste in Sequencing Batch Reactors.* J. Water Pollut. Control Fed., **57,** 1163 (1985).

Hikuma, M., Matsuoka, H, Kawarai, M, and Karube, I., *Use of Microbial Electrodes for Observation of Microbiological Nitrogen Elimination Process.*, Biotechnol. Bioeng., **40,** 130 (1992).

Hikuma, M., Suzuki, H., Yasuda, T., Karube, I., and Suzuki, S., *Amperometric Estimation of BOD by Using Living Immobilized Yeast.* Eur. J. Appl. Microbiol. Biotechnol., **8,** 289 (1979).

Horan, N. J., *Biological Wastewater Treatment Systems: Theory and Operation,* John Wiley & Sons, New York, 1990.

Howell, J.A., Yust, L.J. and reilly, P., *On-line measurement of Respiration and Mass Transfer Rates in an Activated Sludge Aeration Tank.* J. Water Pollut. Control Fed., **56,** 319 (1984).

Huang, J.Y.C., *Microorganism Viability.* In: Arthur, R. M. (ed.), Application of On-Line Analytical Instrumentation to Process Control, Arthur Technology, Ann Arbor Science Publishers, Michigan (1982).

Iida, Y. and Teranishi, A., *Nitrogen Removal from Municipal Wastewater by a Single Submerged Filter.* J. Water Pollut. Control Fed., **56,** 251 (1984).

Irvine R.L., Miller, G., and Bhamrah, A.S., *Sequencing Batch Treatment of wastewaters in Rural Area.* J. Water Pollut. Control Fed., **51,** 244 (1979).

Irvine Robert L. and Busch, Arthur W., *Sequencing Batch Biological Reactors-An Overview.* J. Water Pollut. Control Fed., **51,** 235 (1979).

Irvine, et al., *Enhanced Biological Treatment of Leachates from Industrial Landfills.* Hazardous Waste, **1,** 123 (1984).

Irvine, R. L., Ketchum, L.H., Arora, M.L., and Barth, E.F., *An Organic loading Study of Full-scale Sequencing Batch Reactors.* J. Water Pollut. Control Fed., **57,** 847 (1985).

Irvine, R.L., et al., *Municipal Application Sequencing Treatment at Culver, Indiana.* J. Water Pollut. Control Fed., **55,** 484 (1983).

Ishimori, Y., Karube, I., and Suzuki, S., *Determination of Microbial Populations with Piezoelectric Membranes.* Appl. Env. Microbiol., **42,** 632-7 (1981)

Jeris, J. S., et al., *Biological Fluidized Bed Treatment for BOD and Nitrogen Removal.* J. Water Pollut. Control Fed., **48,** 816 (1977).

Jones, G. L., *Computer Implementation of Control and Monitoring of Waste Treatment.* In: Murray, M.Y (Ed. in Chief), Comprehensive Biotecnology: The Principles, Applications and Regulations of Biotechnology in Industry, Agriculture and Medicine. Vol. 4, Pergamon Press, New York (1985).

Jones, W.L., Wilderer, P.A., and Schroeder E.D., *Operation of a three-stage SBR System for Nitrogen Removal from Wastewater.* J. Water Pollut. Control Fed., **62,** 268 (1990).

Jorgensen, K.P., *Determination of the Enzyme Activity of Activated Sludge by Methylene Blue Reduction.* J. Water Pollut. Control Fed., **56,** 89 (1984).

Kalte, P., *The Continuous Measurement of Short-Time BOD.* In: R. Briggs (ed), Instrumentation, Control and Automation of Water and Wastewater Treatment and Transport Systems. IAWPRC, Pergamon Press, New York (1990).

Kaneko, M., Kawachi, K. and Matsumoto, A., *Evaluation of Oxygen Uptake Rate Analyzer in Wastewater Treatment Plants.* In: Drake, R. A. R. (ed.), Instrumentation and Control of Water and Wastewater Treatment and Transport Systems. IAWPRC, Pergamon Press, New York (1985).

Karube, I. and Chang, SangMok, *Microbial Biosensors.* p. 267-301. In: Blum, Loic J. and Coulet, Pierre R. (eds.), Biosensor Principles and Applications. Marcel Dekker, Inc., New York (1991).

Karube, I., Matsunaga, T., Mitsuda, S., and Suzuki, S., *Microbial Electrode BOD Sensors.*, Biotechnol. Bioeng., **16,** 1535 (1977).

Kennicutt II, M. C., *ATP as an Indicator of Toxicity.* Water Res., **14,** 325 (1980).

Ketchum, L.H., Irvine, R.L., and Liao, P. C., *First Cost Analysis of Sequencing Batch Biological Reactors.* J. Water Pollut. Control Fed., **51,** 288 (1979).

Klapwijk, A., Drent, J., and Steenvoorden, H. A. M., *A Modified Procedure for the TTC-Dehydrogenase Test in Activated-Sludge.* Water Res., **8,** 121 (1974).

Koch, F. A. and Oldham, W. J., *ORP-A Tool for Monitoring, Control and Optimization of Biological Nutrient Removal System.* Water Sci. and Tech., **17,** Paris, France, 259-281 (1985).

Köhne, M., Siepmann F.W., Dr. te Heesen. *Der BSB5 und der kontinuierliche Kurzzeit-BSB (BSB-M3) im Vergleich.* Korrespondenz Abwasser, **9,** 787-793 (1986).

Kratky, O. and Leopald, H. *Acoustic Resonance Densitometry.* Austrian Patent No. 2704 (1968).

Kucnerowicz, F. and Verstratete, W., *Direct Measurement of Microbial ATP in Activated Sludge Samples.* J. Chem. Tech. Biotechnol., **29,** 707 (1979).

Kulys, J. and Kadziauskiene, K., *Yeast BOD Sensor.*, Biotechnol. Bioeng., **22,** 221 (1980).

Kutcher, T. J. and Ettel, G. E., *Understanding the Application of Analytical Data to Process Control.* In: Arthur, R. M. (ed.), Procedures and Practices in Activated Sludge Process Control, Arthur Technology, Ann Arbor Science Publishers, Michigan (1983).

Lawrence, A. W. and McCarty, P. L., *Unified Basis for Biological Treatment Design and Operation.* Journal of the Sanitary Engineering Division, ASCE, **96,** SA3, 757 (1970).

Lee, K. M. and Stensel, H. D., *Aeration and Substrate Utilization in a Sparged Packed-bed Biofilm Reactor.* J. Water Pollut. Control Fed., **58,** 1066-1072 (1986).

Lenhard, G., Nourse, L. and Schwartz, H. M., *Dehydrogenase Activity as a Parameter of Activated-sludge* Activity. Paper presented at the 3rd Int. Conf. on Water Pollution Research, Tokyo (1964).

Levine, Ira N., *Physical Chemistry.* 3rd ed., McGraw-Hill Book Company, New York, (1988).

Lim, H. C. and Lee, K. S., *Control of Bioreactor Systems.* In: Rehm, H.J., Reed, G., Puhler, A., and Stadler P. (eds.), Biotechnoly. Measuring. Modelling. and Control. Vol 4. 2nd ed., VCH, New York (1991).

Londong, J., *Strategies for Optimized Nitrate Reduction with Primary Denitrification.* Wat. Sci. Tech., **26,** 1087 (1992).

Lubbert, A., *Characterization of Bioreactors.* In: Rehm, H.J., Reed, G., Puhler, A., and Stadler P. (eds.), Biotechnolgy. Measuring. Modelling. and Control. Vol 4. 2nd ed., VCH, New York (1991).

Luong, J.H.T. and Guilbault, G.G. *Analytical Applications of Piezoelectric Crystal Biosensors.* In: Blum, Loic J. and Coulet, Pierre R. (eds.), Biosensor Principles and Applications. Marcel Dekker, Inc., New York (1991).

Mallette, M. F., *Evaluation of Growth by Physical and Chemical Means.* In : J. R. Norris and D. W. Ribbons (Eds), Methods in Microbiology, Vol. 1. Academic Press, London, pp. 531-66 (1969).

Manning F.M. and Irvine, R.L., *The Biological Removal of Phosphorus in a Sequencing Batch Reactor.* J. Water Pollut. Control Fed., **57,** 87 (1985).

Matsunaga, T., Karube, I., and Suzuki, S., *Electrochemical Determinations of Cell Populations.* Eur. J. Appl. Microbiol. Biotechnol., **10,** 125-32 (1980).

Matsunaga, T., Karube, I., and Suzuki, S., *Electrode System for the Determination of Microbial Populations.* Appl. Environ. Microbiol. **37,** 117-121 (1979).

Matsunage, T. and Namba, Y., *Selective Determination of Microbial Cells by a Graphite Electrode Modified with 4,4'-Bipyridine.* Anal. Chim. Acta, **159,** 84-87 (1984).

Matsunage, Y., Karube, I., and Suzuki, S., Eur. J. Appl. Microbiol. Biotechnol., **12,** 97-101 (1981).

McCarty, P. L., *Anaerobic Waste Treatment Fundamentals. Part Three. Toxic Materials and Their Control.* Publ. Wks., **95,** 91 (1964).

Medlock, R.S., A Review of Modulation Schemes for Optical Fibre Sensors. Int. J. Opt. Sens., **1,** 43-68 (1986).

Menardiere, M. de la, Charpentier, J., Vachon, A., and Martin, G., *ORP as a Control Parameter in a Single Sludge Biological Nitrogen and Phosphorus Removal Activated Sludge System.* Water SA., **17,** 2, 123 (1991).

Meredith, W.D., *Recent Innovations in Instrumentation for Sewage Treatment Plant Monitoring and Control.* In: R. Briggs (ed), Instrumentation. Control and Automation of Water and Wastewater Treatment and Transport Systems. IAWPRC, Pergamon Press, New York (1990).

Metcalf & Eddy, Inc., Wastewater *Engineering Treatment, Disposal, Reuse* , 2nd ed., McGraw-Hill Book Co., New York (1979).

Metcalf & Eddy, Inc., Wastewater *Engineering Treatment, Disposal, Reuse* , 3rd ed., McGraw-Hill Book Co., New York (1991).

Mines, R. O. and Sherrard, J. H., Activated Sludge Treatment of a High Strength Nitrogenous Waste,

Mosbach, K. and Danielsson, B., *Thermal Bioanalysis in Flow Streams: Enzyme Thermistor Devices.* Anal. Chem., **5,** 1, 83A (1981).

Mosey, F., *Redox Potentials in Wastewater Treatment.* The Chemical Engineer, May (1985).

Murphy, Thomas D. Jr., *Design and Analysis of Industrial Experiments.* Chemical Engineering, June 6 (1977).

Nestaas, E. and Wang, D. I. C., *A New Sensor, the "Filtration Probe" for Quantitative Characterisation of the Penicillin Fermentation. 111: An Automatically Operating Probe.* Biotechnol. Bioeng., **25,** 1981-7 (1983).

Neufeld, H. A., Zajic, J. E., *A Technique for Monitoring Biomass Levels and Cell Adhesion in Hexadecane Fermentations.* Biotechnol. Lett., **4,** 701-704 (1982).

Nishikawa, S., Sakai, S. Karube, I., Matsunage, T. and Suzuki, S., *Dye-coupled Electrode System for the Rapid Determination of Cell Populations in Polluted Water.* Appl. Env. Microbiol., **43,** 814-18 (1982).

Olsson, G., and Andrews, J. F., *Estimation and Control of Biological Activity in the Activated Sludge Process Using Dissolved Oxygen Measurements.* Presented at the IFAC Symposium on Environmental System Planning, Design and Control, August 1-5, Kyoto, Japan (1977).

Olsson, G., and Andrews, J. F., *The Dissolved Oxygen Profile. A Valuable Tool for Control of the activated Sludge Process.* Water Res., **12,** 985 (1978).

Olsson, G., *Control of Wastewater Treatment Systems.* ISA Transactions, **31,** 1, 87 (1992).

Onken, U., Buchholz, R., and Sitting, W., *Measurement and Instrumentation.*, pp. 763-786. In: Rehm, H.J. and Reed, G. (eds.), Biotechnology, Volume 2, Brauer, H. (Volume ed.) " Fundamentals of Biochemical Engineering ", VCH, (1985)

Paffoni, C., Gousailles, M., Rogalla, F. and Gilles, P., *Aerated Biofilters for Nitrification and Effluent Polishing.* Wat. Sci. Tech., **22,** 181-189 (1990).

Palis, J. C. and Irvine, R.L., *Nitrogen Removal in a Low-loaded Single Tank Sequencing Batch Reactor.* J. Water Pollut. Control Fed., **57,** 82 (1985).

Peddie, C. C., Mavinic, D. S., and Jenkins, C. J., *Use of ORP for Monitoring and Control of Aerobic Sludge Digestion.* J. Environ. Eng., **116,** 461 (1990).

Pettipher, G. L., *The Direct Epifluorescent Filter Technique*, p.55. Research Studies Press: Letchworth, England (1951).

Phillips, Janice A., *"Novel" Sensors for the Monitoring of Fermentation Processes.* p.16-64. In: Daniel R. Omstead (ed.), Computer Control of Fermentation Processes. CRC Press, Inc., Florida (1990).

Pitt, G.D., Estance, P., Neat, R.C., Batchelder, B.A., and Jones R.H., *Fibre Optic Sensors.*, IEE Proc. **132J,** 214-247 (1985).

Postage, J. R., *Viable Counts and Viability.* In: J. R. Norris and D. W. Ribbons (Eds.), Methods in Microbiology, Vol. 1. Academic Press, London, pp. 611-28 (1969).

Prave, P., and Others, *Fundamentals of Biotechnology,* VCH Verlagsgesellschaft, Weinheim, Germany (1987).

Price, V. A., *Strategies in Water/Wastewater Treatment.* INTECH, p36, January (1991).

Princz, P. and Oláh, J., *BOD Measurement of Nontoxic Wastewaters with an Improved Microbial Probe.* In: R. Briggs (ed), Instrumentation, Control and Automation of Water and Wastewater Treatment and Transport Systems. IAWPRC, Pergamon Press, New York (1990).

Ramsay, G., Turner, A. P. F. and Higgins I. J., *The Use of Bioelectrochemical Cells for Biomass and Respiratory Activity Estimations.* Soc. Gen. Microbiol. Quarterly, **10,** 1, M14 (1983).

Ramsay, G., Turner, A.P.F. Franklin, A. and Higgins, I.J. *Rapid Bioelectrochemical Methods for the Detection of Living Microorganism,* In: Johnson, A. (ed.), Modeling and Control of Biotechnological Processes, International Federation of Automatic Control, Pergamon Press, New York (1986)

Randall, E.W., Wilkinson, A. and Ekama, G.A., *An Instrument for the Direct Determination of Oxygen Utilization Rate.* Water SA., 17, 1, 11 (1991).

Rogalla, F., Payraudear, M., Bacquet, G., Bourbigot, M., Sibony, J. and Billes, P., *Nitrification and Phosphorus Precipitation with Biological Aerated Filters.* J. Water Pollut. Control Fed., **62,** 169-176 (1990).

Rogalla, F., Roudon, G., Ravarini, P. and Bourdon, F., *Continuous Follow-up of Aerated Granular Biofilters With On-line Sensors.*, In: R. Briggs (ed), Instrumentation, Control and Automation of Water and Wastewater Treatment and Transport Systems. IAWPRC, Pergamon Press, New York (1990).

Rusten, B., *Wastewater Treatment with Aerated Submerged Biological Filters.* J. Water Pollut. Control Fed., **56,** 424 (1984).

Ryssov-Nielsen, H., *Measurement of the Inhibition of Respiration in Activated Sludge by a Modified Determination of the TTC-Dehydrogenase Activity.* Water Res., **9,** 1179 (1975).

Sato, S., Sekine, T. and Nakano, T., *Advanced Control Strategies for the Activated Sludge Process by the ATU-r_r Meter.* In: R. Briggs (ed), Instrumentation, Control and Automation of Water and Wastewater Treatment and Transport Systems. IAWPRC, Pergamon Press, New York (1990).

Schaffar, B. P. H. and Wolfbeis, O. S., *Chemically Mediated Fiberoptic Biosensors.* pp. 163-194. In: Blum, Loic J. and Coulet, Pierre R. (eds.), Biosensor Principles and Applications. Marcel Dekker, Inc., New York (1991).

Schraa, G. and Jewell, W. J., *High Rate Conversions of Soluble Organics with a Thermophilic Anaerobic Attached Film Expanded Bed.* J. Water Pollut. Control Fed., **56,** 226 (1984).

Schroeder, E. D., Water *and Wastewater Treatment,* McGraw-Hill Book Co., New York (1977).

Schugerl, K., *Common Instruments for Process Analysis and Control.* In: Rehm, H.J., Reed, G., Puhler, A., and Stadler P. (eds.), Biotechnolgy, Measuring, Modelling, and Control. Vol 4. 2nd ed., VCH, New York (1991).

Sekine, T., Iwahori, K., Fujimoto, E., and Inamori, Y., Advanced Control Strategies for the Activated Sludge Process., pp. 269 In: R.A.R. Drake (ed.), Instrumentation and Control of Water and Wastewater Treatment and Transport System. IAWPRC, Pergamon Press, New York (1985).

Shamas, J.Y. and Englande, Jr. A. J., *Use of the Immediate Maximum Specific Oxygen Uptake Rate as an Activated Sludge Process Control Parameter.* Wat. Sci. Tech., **25,** 1, 123-132 (1992).

Sherrard, J. H., Friedman, A. A., and Rand, M. C., *BOD5: Are There Alternatives Available?*, J. Water Pollut. Control Fed., **51,** 1799 (1979).

Shinskey, F. G., *Process Control Systems, Applications, Design, Adjustment*, New York (1979).

Shuler, M. L. and Kargi, Fikret, *Bioprocess Engineering Basic Concepts*, Prentice Hall, New Jersey (1992).

Sibbald A., *A Chemical Sensitive Integrated Circuit: The Operational Transducer, Sensors and Actuators*, **7,** No.1, 23-28 (1985).

Sibbald A., *Recent Advances in Field Effect Chemical Microsensors.* J. Molecular Electron. **2,** 51-83 (1986).

Smith, C. A. and Corripio, A. B., *Principles and Practice of Automatic Process Control.* John Wiley & Sons, New York (1985).

Skrentner R. G., *The Computer as a Tool for Activated Sludge.* In: Arthur, R. M. (ed.), Procedures and Practices in Activated Sludge Process Control, Arthur Technology, Ann Arbor Science Publishers, Michigan (1983).

Stensel, H. D. and Lee, K. M., *Biological Aerated Filter Full-Scale EPA Demonstration Project.* Proc. of the Utah Water Pollution Control Association, Park City, Utah (1983).

Stensel, H. D., Brenner, R. C., Lee, K. M., Melcer, H. and Rakness, K., *Biological Aerated Filter Evaluation.* J. Environ. Eng., **114,** 655-671 (1988).

Stensel, H. D., et al., *Full-Scale Evaluation of the Biological Aerated Filter.* Paper presented at the 57th Annual Conference, Water Pollution Control Federation, New Orleans, La. (1984).

Stephenson, J. P., *Practices in Activated Sludge Process Control.* In: Murray, M.Y (Ed. in Chief), Comprehensive Biotecnology: The Principles, Applications and Regulations of Biotechnology in Industry, Agriculture and Medicine. Vol. 4, Pergamon Press, New York (1985).

Strand, S. E. and Carlson, D. A., *Rapid BOD Measurement for Municipal Wastewater Samples Using a Biofilm Electrode.*, J. Water Pollut. Control Fed., **56,** 464 (1984).

Sundstrom, D. W., and Klei, H. E. Wastewater *Treatment,* Prentice Hall, Englewood Clifts, NJ. (1979).

Switzenbaum, M. S., *Fluidized Bed Anaerobic Reactors.* In: Comprehensive Biotechnology, Pergamon Press, Oxford, England, 4 (1985).

Turner, A. P. F., Ramsay, G. and Higgins, I. J., *Applications of Electron Transfer Between Biological Systems and Electrodes.* Biochem. Soc. Trans., **11,** 445-8 (1982).

Upadhyaya, A. K. and Eckenfelder, W. W. Jr., *Biodegradable Fraction as an Activity Parameter of Activated Sludge.* Water Res. , **9,** 691 (1975).

Van de Werf, H. and Verstraete, W., *ATP Measurement by Bioluminescene: Environmental Applications.* In: Kricka, L. J.(Ed.), International Symposium on Analytical Applications of Bioluminescene and Chemiluminescene, Academic Press, London, 33 (1984).

Viessman, W. Jr. and Hammer, M. J., *Water Supply and Pollution Control.* 5th ed., Harper Collins College Publishers, New York (1993).

Walpole, R. and Myers, R. H., *Probability and Statistics for Engineers and Scientists.* 4th ed., Macmillan Publishing Company, New York (1989).

Wang, Y. T. et al., Anaerobic Treatment by an Expanded-bed Reactor. J. Water Pollut. Control Fed., **58,** 122 (1986).

Waters, J., *Sensitivity of the $^{14}CO_2$ Radiometric Method for Bacterial Detection.* Appl. Microbiol., **23,** 198-9 (1972).

Weddle, C. L. and Jenkins, D., *The Viability and Activity of Activated Sludge.* Water Res., **5,** 621 (1971).

White, S. F., *Requirements and Application of Control and Automation Systems in Wastewater Treatment - A Critical Review.* Wat. Sci. Technol., **13,** 41-48 (1981).

Wild, H. E. Jr., Sawyer, C. N., and McMahon, T. C., *Factors Affecting Nitrification Kinetics.* J Water Pollut. Control Fed. **43,** 1845-1854 (1971).

Wilkie, A., Reynolds, P. J., and Colleran, E. *Media Effects in Anaerobic Filters.* In Proceedings of Anaerobic Treatment Symposium. TNO Corporate Communication Department, The Hague., p242-258 (1983).

Wilkins, J. R., Young, R. and Boykin, E., *Multichannel Electrochemical Microbial Detection Unit.* Appl. Env. Microbiol., **35,** 214-15 (1978).

Wilkins, J.R., *Pressure transducer method for measuring gas production by microorganism.* Appl. Microbiol., **23,** 198-199 (1974).

Wise, D. L., *Bioinstrumentation: Research, Developments and Applications,* Butterworth Publishes, Stoneham (1990).

Wolfbeis, O. S., (ed.), *Handbook of Fiber Optic Chemical Sensors.* CRC Press Boca Raton, Florida USA, (1990)

Young, J. C. and Dahab, M. F. *Effects of Media design on the Performance of Fixed-bed Anaerobic Filters.* Wat. Sci. Tech., **15,** 321 (1983).

Young, J. C. and Steward, M. C., *PBR-A New Addition to the AWT Family.* Water and Wastes Engrg., **20,** (1979).

Zabriskie, D. W. and Humphery, A. E., *Estimation of Fermentation Biomass Concentration by Measuring Culture Fluorescence.* Appl. Env. Microbiol., **35,** 337-43 (1978).

APPENDIX

KINETIC AND STOICHIOMETRIC PARAMETERS

PARAMETERS			HETEROTROPHIC ORGANISMS	AUTOTROPHIC ORGANISMS
mu max	d-1	=	4.000	0.650
ks cod	g cod m-3	=	10.000	
ks NH4-N	g N m-3	=		1.000
ks O2	g O2 m-3	=	0.100	1.000
yield	g g-1	=	0.670	0.240
b decay	d-1	=	0.620	0.120
anoxic growth factor		=	0.800	
ks NO3	g N m-3	=	0.200	
hydrolysis rate	d-1	=	2.200	
hydrol satur ratio	g cod g-1 cod	=	0.150	
anoxic hydrol factor		=	0.400	
ammonification	m3 g-1 cod d-1	=	0.160	
frac. part. product	g cod g-1 cod	=	0.080	
N in biomass	g N g-1 cod	=	0.086	
N in part. prod.	g N g-1 cod	=	0.060	
O2 saturation conc	g o2 m-3	=	9.000	

PROCESS CONFIGURATION AND FLOW DISTRIBUTION

OVERALL PLANT SPECIFICATIONS:		
Number of Reactors (up to 9)	=	2
Solids Retention Time (days)	=	3.5
Average Flow Rate (m3/day)	=	5451

INDIVIDUAL REACTOR SPECIFICATIONS:		1	2
Reactor Volume (m3)	=	1000	7000
Feed Fraction (0 to 1)	=	1.00	0.00
O2 Concentration (g O2/m3)	=	0.00	9.00
Recycle Input (m3/day)	=	2500	0
Recirculation Input (m3/day)	=	21800	0
Recirculation originated from reactor	=	2	*

STEADY-STATE SOLUTION

CONSTITUENTS			FEED	1	2
Heterotrophic Organisms	g cod m-3	=	0.0	6074.8	6405.6
Autotrophic Organisms	g cod m-3	=	0.0	81.5	88.6
Particulate Products	g cod m-3	=	0.0	1042.1	1117.8
Inert Particulates	g cod m-3	=	0.0	0.0	0.0
Particulates Organics	g cod m-3	=	0.0	436.4	374.3
Soluble Organics	g cod m-3	=	3000.0	972.3	2.7
Soluble Ammonia N	g n m-3	=	200.0	72.3	3.6
Soluble Nitrate/Nitrite N	g n m-3	=	100.0	0.2	38.5
Soluble Organic N	g n m-3	=	0.0	0.1	0.3
Biodegrad Part Organic N	g n m-3	=	0.0	38.5	33.0
Oxygen	g o2 m-3	=	0.0	0.0	9.0
Alkalinity	mole m-3	=	80.0	56.6	49.0
MLVSS	g cod m-3	=		7634.7	7986.3
O2 Consumed	g o2 m-3 d-1	=		0.0	3352.8
Nitrate Consumed	g no3-n m-3 d-1	=		1475.7	8.1

A.1. Sample output from SSSP program for final run in Tables 5.1 and 5.2.

KINETIC AND STOICHIOMETRIC PARAMETERS

PARAMETERS			HETEROTROPHIC ORGANISMS	AUTOTROPHIC ORGANISMS
mu max	d-1	=	4.000	0.650
ks cod	g cod m-3	=	10.000	
ks NH4-N	g N m-3	=		1.000
ks O2	g O2 m-3	=	0.100	1.000
yield	g g-1	=	0.400	0.150
b decay	d-1	=	0.620	0.120
anoxic growth factor		=	0.800	
ks NO3	g N m-3	=	0.200	
hydrolysis rate	d-1	=	2.200	
hydrol satur ratio	g cod g-1 cod	=	0.150	
anoxic hydrol factor		=	0.400	
ammonification	m3 g-1 cod d-1	=	0.160	
frac. part. product	g cod g-1 cod	=	0.080	
N in biomass	g N g-1 cod	=	0.086	
N in part. prod.	g N g-1 cod	=	0.060	
O2 saturation conc	g o2 m-3	=	9.000	

PROCESS CONFIGURATION AND FLOW DISTRIBUTION

OVERALL PLANT SPECIFICATIONS:		
Number of Reactors (up to 9)	=	2
Solids Retention Time (days)	=	5
Average Flow Rate (m3/day)	=	8177

INDIVIDUAL REACTOR SPECIFICATIONS:		1	2
Reactor Volume (m3)	=	1000	7000
Feed Fraction (0 to 1)	=	1.00	0.00
O2 Concentration (g O2/m3)	=	0.00	9.00
Recycle Input (m3/day)	=	2500	0
Recirculation Input (m3/day)	=	10900	0
Recirculation originated from reactor	=	2	*

STEADY-STATE SOLUTION

CONSTITUENTS			FEED	1	2
Heterotrophic Organisms	g cod m-3	=	0.0	1732.0	1707.9
Autotrophic Organisms	g cod m-3	=	0.0	93.0	101.0
Particulate Products	g cod m-3	=	0.0	404.5	432.5
Inert Particulates	g cod m-3	=	0.0	0.0	0.0
Particulate Organics	g cod m-3	=	0.0	121.1	100.2
Soluble Organics	g cod m-3	=	2500.0	464.7	1.7
Soluble Ammonia N	g n m-3	=	250.0	80.2	1.6
Soluble Nitrate/Nitrite N	g n m-3	=	150.0	0.8	79.2
Soluble Organic N	g n m-3	=	0.0	0.1	0.3
Biodegrad Part Organic N	g n m-3	=	0.0	10.7	8.8
Oxygen	g o2 m-3	=	0.0	0.0	9.0
Alkalinity	mole m-3	=	80.0	78.5	67.3
MLVSS	g cod m-3	=		2350.5	2341.6
O2 Consumed	g o2 m-3 d-1	=		0.0	2542.8
Nitrate Consumed	g no3-n m-3 d-1	=		2270.6	4.5

A.2. Sample output from SSSP program for Run 15 in Tables 5.9, 5.10 and 5.11.

KINETIC AND STOICHIOMETRIC PARAMETERS

PARAMETERS			HETEROTROPHIC ORGANISMS	AUTOTROPHIC ORGANISMS
mu max	d-1	=	4.000	0.650
ks cod	g cod m-3	=	10.000	
ks NH4-N	g N m-3	=		1.000
ks O2	g O2 m-3	=	0.100	1.000
yield	g g-1	=	0.400	0.150
b decay	d-1	=	0.620	0.120
anoxic growth factor		=	0.800	
ks NO3	g N m-3	=	0.200	
hydrolysis rate	d-1	=	2.200	
hydrol satur ratio	g cod g-1 cod	=	0.150	
anoxic hydrol factor		=	0.400	
ammonification	m3 g-1 cod d-1	=	0.160	
frac. part. product	g cod g-1 cod	=	0.080	
N in biomass	g N g-1 cod	=	0.086	
N in part. prod.	g N g-1 cod	=	0.060	
O2 saturation conc	g o2 m-3	=	9.000	

PROCESS CONFIGURATION AND FLOW DISTRIBUTION

OVERALL PLANT SPECIFICATIONS:			
Number of Reactors (up to 9)	=	2	
Solids Retention Time (days)	=	5	
Average Flow Rate (m3/day)	=	3000	
INDIVIDUAL REACTOR SPECIFICATIONS:		**1**	**2**
Reactor Volume (m3)	=	1000	7000
Feed Fraction (0 to 1)	=	1.00	0.00
O2 Concentration (g O2/m3)	=	0.00	9.00
Recycle Input (m3/day)	=	2500	0
Recirculation Input (m3/day)	=	26970	0
Recirculation originated from reactor	=	2	*

STEADY-STATE SOLUTION

CONSTITUENTS			FEED	1	2
Heterotrophic Organisms	g cod m-3	=	0.0	1723.8	1760.7
Autotrophic Organisms	g cod m-3	=	0.0	74.0	78.1
Particulate Products	g cod m-3	=	0.0	422.6	441.7
Inert Particulates	g cod m-3	=	0.0	0.0	0.0
Particulate Organics	g cod m-3	=	0.0	122.9	105.1
Soluble Organics	g cod m-3	=	7000.0	448.9	2.2
Soluble Ammonia N	g n m-3	=	550.0	46.0	1.6
Soluble Nitrate/Nitrite N	g n m-3	=	80.0	0.2	40.0
Soluble Organic N	g n m-3	=	0.0	0.1	0.3
Biodegrad Part Organic N	g n m-3	=	0.0	10.8	9.3
Oxygen	g o2 m-3	=	0.0	0.0	9.0
Alkalinity	mole m-3	=	80.0	49.8	43.8
MLVSS	g cod m-3	=		2343.3	2385.6
O2 Consumed	g o2 m-3 d-1	=		0.0	2712.6
Nitrate Consumed	g no3-n m-3 d-1	=		1412.4	5.8

A.3. Sample output from SSSP program for Run 6 in Table 5.13.

KINETIC AND STOICHIOMETRIC PARAMETERS

PARAMETERS			HETEROTROPHIC ORGANISMS	AUTOTROPHIC ORGANISMS
mu max	d-1	=	4.000	0.650
ks cod	g cod m-3	=	10.000	
ks NH4-N	g N m-3	=		1.000
ks O2	g O2 m-3	=	0.100	1.000
yield	g g-1	=	0.400	0.150
b decay	d-1	=	0.620	0.120
anoxic growth factor		=	0.800	
ks NO3	g N m-3	=	0.200	
hydrolysis rate	d-1	=	2.200	
hydrol satur ratio	g cod g-1 cod	=	0.150	
anoxic hydrol factor		=	0.400	
ammonification	m3 g-1 cod d-1	=	0.160	
frac. part. product	g cod g-1 cod	=	0.080	
N in biomass	g N g-1 cod	=	0.086	
N in part. prod.	g N g-1 cod	=	0.060	
O2 saturation conc	g o2 m-3	=	9.000	

PROCESS CONFIGURATION AND FLOW DISTRIBUTION

OVERALL PLANT SPECIFICATIONS:			
Number of Reactors (up to 9)	=	2	
Solids Retention Time (days)	=	5	
Average Flow Rate (m3/day)	=	5000	
INDIVIDUAL REACTOR SPECIFICATIONS:		**1**	**2**
Reactor Volume (m3)	=	1000	7000
Feed Fraction (0 to 1)	=	1.00	0.00
O2 Concentration (g O2/m3)	=	0.00	9.00
Recycle Input (m3/day)	=	2500	0
Recirculation Input (m3/day)	=	21709	0
Recirculation originated from reactor	=	2	*

STEADY-STATE SOLUTION

CONSTITUENTS			FEED	1	2
Heterotrophic Organisms	g cod m-3	=	0.0	1233.0	1255.4
Autotrophic Organisms	g cod m-3	=	0.0	42.5	45.1
Particulate Products	g cod m-3	=	0.0	299.7	314.8
Inert Particulates	g cod m-3	=	0.0	0.0	0.0
Particulate Organics	g cod m-3	=	0.0	87.9	74.4
Soluble Organics	g cod m-3	=	3000.0	340 .2	2.1
Soluble Ammonia N	g n m-3	=	200.0	30.1	1.6
Soluble Nitrate/Nitrite N	g n m-3	=	100.0	0.2	25.6
Soluble Organic N	g n m-3	=	0.0	0.1	0.3
Biodegrad Part Organic N	g n m-3	=	0.0	7.8	6.6
Oxygen	g o2 m-3	=	0.0	0.0	9.0
Alkalinity	mole m-3	=	80.0	75.0	71.2
MLVSS	g cod m-3	=		1663.1	1689.7
O2 Consumed	g o2 m-3 d-1	=		0.0	1778.1
Nitrate Consumed	g no3-n m-3 d-1	=		1113.6	4.0

A.4. Sample output from SSSP program for Run 9 in Table 5.14.

VITA

Thomas Tee-Meng Poon was born in Kuala Lumpur, Malaysia, on March 20, 1966. After completing the secondary school in 1985, he joined the Toyota Motor SDN. BHD., Service Division in Malaysia as a Vehicle-paint Coordinator. His job was to recommend the proper paint work for vehicles and advise customers. In June 1987 he went to Singapore to study for the Advanced Level education and then rejoined Toyota company in January 1988. In 1989 he resigned from his work to further his education in United States. He entered the University of Southwestern Louisiana, Lafayette, in August 1989. Then in January 1991, he transferred to The University of Tennessee, Knoxville, and received a Bachelor of Science degree in Chemical Engineering in December 1992. In January 1993 he entered the graduate school, and in December 1994 received a Master of Science degree in Chemical Engineering.

His idea of becoming an engineer has not come to him all of a sudden. The factor that provoked him to become a chemical engineer is his interest in the challenge of solving environmental problems, the challenge to search for new products and new technologies that are beneficial to the environment.