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ABSTRACT

Title of Thesis :

MATHEMATICAL MODELING AND COMPUTER SIMULATIONS OF BIODENITRIFICATION IN BATCH AND SEQUENCING BATCH REACTORS

Sugata Sanyal, Master of Science in Chemical Engineering, 1990

Thesis directed by:

Dr. Basil C. Baltzis, and Dr. Gordon A. Lewandowski LJ

Mathematical models have been derived for describing biodegradation of nitrate and nitrite in an anaerobic environment. Monod model for nitrate and Andrews model for nitrite were used as kinetic models. Experimental data from literature suggest that nitrate is not an inhibitory substance, while nitrite is not only inhibitory but it may also have a toxic effect on the biomass. The models were brought in dimensionless form in order to reduce the number of parameters. Biodegradation was mathematically described for a batch, and a sequencing batch mode of operation. Computer programs were developed for numerically simulating the process. Some of the numerical results (from the batch mode of operation) were compared with experimental data obtained from a pilot plant unit at the Sunflower Army Ammunition Plant in Kansas. It was found that the model could very nicely predict qualitatively the experimental results. Computer simulations were performed for a wide range of parameter values in order to study the effects of these (model and system) parameters on the behavior of the reactors. One of the main objective was to find operating parameter regions which do not lead to high nitrite concentrations, since nitrite is inhibitory and toxic for the biomass. Experiments under controlled conditions are needed in order to find the key kinetic constants, which will then help in optimizing the overall process of biodenitrification, both, from design and operation view point.

MATHEMATICAL MODELING AND COMPUTER SIMULATIONS OF BIODENITRIFICATION IN BATCH AND SEQUENCING BATCH REACTORS

by Sugata Sanyal

Thesis submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering 1990

APPROVAL SHEET

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MATHEMATICAL MODELING AND COMPUTER SIMULATIONS OF BIODENITRIFICATION IN BATCH AND SEQUENCING BATCH REACTORS

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Contents

1	Int	roduct	ion	1
	1.1	Gener	ral Overview	1
2	Dei	nitrific	ation	3
	2.1	Biolog	gy and Biochemistry	3
	2.2	Influe	ncing Environmental Factors	7
		2.2.1	рН	7
		2.2.2	Dissolved Oxygen	8
		2.2.3	Temperature	12
		2.2.4	Other Ions	13
	2.3	Deniti	rification Kinetics	16
		2.3.1	Specific Rate Studies	18
		2.3.2	Inhibition of Denitrification	22
		2.3.3	Nitrite Accumulation	24
	2.4	Carbo	on Source	29
		2.4.1	Methanol	29
		2.4.2	Other C Sources	34
	2.5	Applie	cation of Different Flow Systems	36

3	Ma	thema	tical Modeling	40
U	3.1	Batch	Model	41
		3.1.1	General derivation	41
		3.1.2	Selection of Growth Kinetics	42
		3.1.3	Dimensionless Forms	43
	3.2	SBR 1	Model	47
		3.2.1	General Derivation	48
		3.2.2	Dimensionless forms	49
4	Sim	nulation	n Results & Discussion	54
	4.1	Simula	ation of the Batch Process	55
		4.1.1	1st Cycle Response of the Batch Process	55
		4.1.2	Steady Cycle Response of the Batch Process	59
	4.2	Simula	ation of the SBR Process	60
5	Cor	nclusio	n and Recommendation	62
6	Tab	oles		63
7	Fig	ures		81
8	Pro	gram l	Listing	107
9	Bib	liograp	bhy	151

List of Tables

2.1	Chemosynthetic Bacteria Genera Capable of Denitrification \ldots	4
6.1	Reported Values of Specific Denitrification Rates (SDNR, mg NO_3 -	
	N/g X-day)	64
6.2	Denitrification Rate Data	67
6.3	Denitrification Rates With Various Carbon Sources	67
6.4	BatcH Data From Kansas (10/20/89)	68
6.5	BatcH Data From Kansas (09/03/89)	69
6.6	Batch Data From Kansas (08/31/89)	70
6.7	Batch Data From Kansas (08/28/89)	71
6.8	Batch Data From Kansas (09/08/89)	72
6.9	Batch Data From Kansas (10/10/89)	73
6.10	Batch Data From Kansas $(09/22/89)$	74
6.11	Batch Data From Kansas (09/20/89)	75
6.12	Batch Data From Kansas (09/22/89)	76
6.13	Batch Data From Kansas (09/27/89)	77
6.14	Batch Data From Kansas (10/02/89)	78
6.15	Batch Data From Kansas (09/21/89)	79

6.16 Preselected	Values of Mode	el Parameters	 •	 	••	•		•	80

List of Figures

7.1	Cyclic Operation of A Sequencing Batch Reactor	82
7.2	Comparison of Experimental Data With Simulated Data	83
7.3	Comparison of Experimental Data With Simulated Data	84
7.4	Comparison of Experimental Data With Simulated Data	85
7.5	Comparison of Experimental Data With Simulated Data	86
7.6	Comparison of Experimental Data With Simulated Data	87
7.7	Comparison of Experimental Data With Simulated Data	88
7.8	Comparison of 1st Cycle Batch With Steady Cycle Batch \ldots	89
7.9	Comparison of 1st Cycle Batch With Steady Cycle Batch \ldots	90
7.10	Comparison of 1st Cycle Batch With Steady Cycle Batch \ldots	91
7.11	Comparison of 1st Cycle Batch With Steady Cycle Batch \ldots .	92
7.12	Comparison of 1st Cycle Batch With Steady Cycle Batch \ldots	93
7.13	Comparison of 1st Cycle Batch With Steady Cycle Batch \ldots	94
7.14	Comparison of Batch With SBR	95
7.15	Comparison of Batch With SBR	96
7.16	Comparison of Batch With SBR	97
7.17	Comparison of Batch With SBR	98
7.18	Comparison of Batch With SBR	99

7.19	Comparison of Batch With SBF	ł	•	•	•	•	•	•			•	•	•	•	•	•	•	•	•	100
7.20	Comparison of Batch With SBF	t	•	•	•	•	•	•		•	•		•	•	•		•	•	•	101
7.21	Comparison of Batch With SBR	l	•	•	•	•	•	•			•		•	•	•	•	•	•	•	102
7.22	Comparison of Batch With SBR		•	•	•	•	•	•	• •	•	•	•	•	•	•	•	•	•	•	103
7.23	Comparison of Batch With SBR			•	•	•	•	•		•	•	•	•	•	•	•	•	•	•	104
7.24	Comparison of Batch With SBR		•	•	•	•	•	•		•	•	•	•	•	•	•	•	•	•	105
7.25	Comparison of Batch With SBR	,	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	106

Chapter 1 Introduction

1.1 General Overview

Sunflower Army Ammunition Plant (SFAAP) is owned by the US Army and operated by Hercules, Inc. to produce nitroguanidine (NQ) based explosives and propellant. SFAAP generates a significant quantity of waste waters containing NQ and guanidine nitrate (GN). The wastewaters are pretreated by a lime/steam sparging process and are discharged to evaporative lagoons. The combination of increased waste water volume and less than expected evaporation from the lagoons has led to the investigation of alternative methods of wastewater handling.

The principal pollutants in the wastewater are nitrogen, mostly in the form of nitrates, and sulfur in the form of sulfates. A study conducted by J.M. Montgomery Co. in 1988 identified the Sequencing Batch Reactor (SBR) technology as a viable method for the denitrification of SFAAP pretreated wastewaters.

The wastewaters at SFAAP are very complex and therefore require a thorough understanding before one can proceed to describe the process mathematically. In order to predict the impacts of various wastewater characteristics upon the operation of the denitrifying SBR unit and to avoid duplication of previous efforts, an extensive review of the available literature on denitrification was conducted. The literature review was structured towards identifying the effects of dissolved oxygen, pH, temperature, nutrients, dissolved solids and different carbon sources upon high-rate biological denitrification systems. Specific denitrification rates as they relate to various operating scenarios were also studied in detail to allow comparison of results with previous studies.

Chapter 2 Denitrification

2.1 Biology and Biochemistry

Respiration is an ATP generating process in which chemical compounds are oxidized and the final electron acceptor is almost always an inorganic molecule. In the process called anaerobic respiration, the final electron acceptor is usually an inorganic substance other than oxygen (O_2). Some bacteria, such as *Pseu*domonas and Bacillus, can use a nitrate ion (NO_3^-) , as a final electron acceptor; it is reduced to nitrite ion (NO_2^-), nitrous oxide (N_2O), or nitrogen gas (N_2).

The bacteria carrying out anaerobic respiration generally possess an electron transport system containing cytochromes. In some cases, the anaerobic respiration process competes with an aerobic one. In such cases, if O_2 is present, aerobic respiration is usually favored, and only when O_2 is depleted from the environment an alternate anaerobic electron acceptor (such as nitrate) would be reduced.

Nitrate	Denitrifying	
NO_3^- -	$\rightarrow NO_2^-$	$NO_3^- \rightarrow N_2^-$
Achromobacter	Haemophilus	Achromobacter
Actinobacilus	Halobacterium	Alcaligens
Aeromonas	Leptothrix	Bacillus
Agarbacterium	Micrococus	Chromobacterium
Agrobacterium	Micromonosopora	Corynebacterium
Alginomonas	Mycobacterium	Halobacterium
Arizona	Nocardia	Hyphomicrobium
Aethrobacter	Pasteurella	Micrococus
Bacillus	Propinibacterium	Moraxella
Beneckea	Proteus	Nitrosomonus
Brevibacterium	Providencia	Propinibacterium
Cellulomonas	Pseudomonas	Pseudomonas
Chromobacterium	Rettgerella	Spirillium
CItrobacter	Rhizobium	Thiobacillus
Corynebacterium	Salmonella	Xanthomonas
Cytophaga	Sarcina	
Enterobacter	Selenomonas	
Erwinia	Shigella	
Escherichia	Spirillium	
Eubacterium	Staphylococus	
Flavobacterium	Streptomyces	
	Xanthomonas	

Table 2.1: Chemosynthetic Bacteria Genera Capable of Denitrification

When an inorganic compound such as NO_3^- , SO_4^{2-} , and CO_2 is reduced for use as a nutrient source, it is said to be assimilated, and the reduction process is called assimilative metabolism.

The genera of chemosynthetic bacteria listed in Table 2.1 contain species to reduce nitrate assimilatively and to denitrify. Like green plants, a number of blue-green algae (cyanobacteria), bacteria, and fungi reduce nitrate to ammonia which is assimilated as a source of nitrogen for biosynthesis.

Gas chromatographic procedures are now known to be reliable for identifying components of prepared mixtures of gases likely to result from denitrification. Barbaree and Payne [4] demonstrated that this method can be employed to separate and identify the products of various steps in the denitrification carried out by cells and extracts of *Pseudomonas perfectomarinus*.

Payne et al. [70] reported the anaerobic growth of *Pseudomonas perfectomar*inus at the expense of nitrate, nitrite, or nitrous oxide but not chlorate or nitric oxide. In several repetitive experiments, anaerobic incubation in culture media containing nitrate revealed that an average of 82 % of of the cells in aerobically grown populations could become capable of nitrite respiration. Although they did not form colonies under these conditions, the bacteria synthesised the denitrifying enzymes within 3 hour in the absence of oxygen or another acceptable inorganic oxidant. This was demonstrated by the ability, after anaerobic incubation, of cells and of extracts to reduce nitrite, nitric oxide, and nitrous oxide to nitrogen. From crude extracts of cells grown on nitrate, nitrite, or nitrous oxide, separate complex fractions were obtained that utilized reduced nicotinamide adenine dinucleotide as the source of electrons for the reduction of (i) nitrite to nitric oxide, (ii) nitric oxide to nitrous oxide, and (iii) nitrous oxide to nitrogen. Gas chromatographic analysis revealed that each of these fractions reduced only one of the nitrogenous oxides.

Prakasm and Loehr [73] conducted continuous flow and batch studies to obtain fundamental information on the effect of various parameters on the denitrification process. Higher denitrification rates were observed with NO_2 -N than NO_3 -N, which is contrary to the findings of other researchers. This may be because of the way they analyzed the rates which incorporated the active biomass. They expressed denitratification rates in $mg NO_3-N / (MLSS)(HR)$ and the denitritification rate in $mg NO_2$ -N / (MLSS)(HR). Since MLSS does represent the active denitrifying biomass only, it could easily introduce error into the calculation if there are population shifts among the bacteria from anaerobes to aerobes. Exogenous supplementation of hydrogen donors was not found to be necessary to accomplish denitrification of the nitrified waste. The denitrification of the nitrified waste could be accomplished without controlling pH. Although extreme pH conditions (pH 4 and pH 11) adversely affected the denitrification of the nitrified poultry waste, the pH that resulted generally in the nitrification units (pH 5.0 - 6.5) was found not to be detrimental to denitrification. They also reported that in most of the denitrification runs there was a rapid loss of nitrogen in the first few hours accompanied by a plateau for several hours. This plateau was once more followed by a rapid loss of nitrogen. The biphasic pattern was observed with both $NO_2^- - N$ and $NO_3^- - N$ removal. They hypothesized that the rapid loss of nitrogen in the first few hours was due to the availability of readily assimilable hydrogen donors. When these were exhausted the rate of denitrification decreased causing a plateau. During the period of this plateau a microbial population was presumably adapting to the complex hydrogen donors and, subsequently denitrification proceeded further. This hypothesis was verified

experimentally.

2.2 Influencing Environmental Factors

Biological denitrification is a complex process and takes place in the presence of nitrate and nitrite reductases. Research work is still going on to identify the paths through which nitrate is reduced to nitrogen. Because of the alternate respiration pathways involved, bacterial denitrification is very sensitive to various environmental factors e.g., pH, dissolved oxygen, temperature, presence of other ions. In this section a summary of the previous studies which were carried out to determine the effects of these parameters, is presented.

2.2.1 pH

Denitrification is most rapid in the neutral or slightly alkaline range between pH 7 and 8 [65,23,18,95]. However, it has been observed to occur in wastewater up to a pH 11 [35]. The optimum pH for denitrification of both nitrate and nitrite, with methanol as the carbonaceous substrate, was found to be 7.5 at $25^{\circ}C$, but the reduction of nitrate was less sensitive to pH values below 7.5, while the reduction of nitrite was less sensitive to values above pH 7.5 [6]. Dawson and Murphy [22] have shown that denitrification rates give parabolic curves as function of pH with a peak at 7.0. The rates at pH 6.0 and pH 8.0 were approximately halved. However, Hauck and Melsted [36] have shown that the rate of denitrification increases linearly from pH 4, levels off between pH 7 and 8, and declines, though not ceasing, to pH 9.5. Neutral to slightly alkaline pH ranges lead not only to faster rates of denitrification, but also to the completion of the

reaction sequence to N_2 .

If the wastewater contains large quantities of ammonia, a more suitable pH range may be 6.5 to 7.5 to avoid inhibition due to un-ionized ammonia at the higher pH values (see effects of ions).

At pH values below 6.5, the presence of inhibitory nitrous oxide has been observed.

During denitrification, a pH rise is expected because of the formation of $OH^$ ions. Because biological denitrification raises the pH of the system, excessive alkalinity may influence the rate of denitrification when the wastewater contains NO_3 -N concentrations greater than 1000 mg/l. According to Francis and Callahan [28] it is likely that the pH of mixed liquor in stirred tank reactors will have to be adjusted with acid in the denitrification of nitric acid wastes neutralized with hydroxides of alkali metals. This will also be applicable to batch and semi-batch systems.

2.2.2 Dissolved Oxygen

Since the classical experiments of Gayon and Dupetit [32], it has been known that oxygen inhibits the reduction of nitrate and the formation of nitrogen by denitrifying bacteria.

Wessenberg [94] found that complete denitrification occurred in the anaerobic cultures, whereas aerobically nitrate was reduced only as far as nitrite.

Lloyd and Cranston [54] measured the gas exchange that occurred when denitrifying cultures were grown in air or in a nitrogen atmosphere in a closed system. They observed a large nitrogen evolution under the anaerobic conditions and an almost equally large oxygen uptake in air. They concluded that nitrate was only slightly attacked aerobically, although in one case nitrogen was lost from the medium even under their most aerobic conditions.

Stickland [87] determined the influence of oxygen at various partial pressures in the reduction of nitrate to nitrite by cell suspensions of *Escherichia Coli*. He found that as little as 0.36 % of oxygen caused a 21 % inhibition (i.e., rate of denitrification was decreased by 21 %), and 3.76 %oxygen caused 93 % inhibition. A tenfold increase in nitrate concentration did not modify these results, thus demonstrating that the inhibition was noncompetitive. He found further that carbon monoxide partially relieved oxygen inhibition of nitrate reduction and concluded that different enzymes are involved in the activation of nitrate and oxygen, since they show different affinities for their substrates and carbon monoxide.

Meiklejohn [58] investigated the effect of oxygen on denitrification, maintaining that the notion that oxygen interferes with this process is a neat *teleological explanation* never adequately verified. Her experiments were similar to those of Seiser and Waltz [79]; using an unidentified strain of *Pseudomonas* she observed that denitrification occurred to almost the same extent in aerated and anaerobic cultures. The interpretation of these results is complicated by the fact that the method of aeration was certainly not adequate to keep the culture medium saturated with oxygen at atmospheric pressure. The partial pressure of oxygen in some parts of the aerated medium may have been very low.

Lemoigen et al. [52] found that when Bacillus megatherium was grown in a medium containing nitrate as the sole nitrogen source, a pure oxygen atmosphere greatly increased the lag period. This did not occur if there was a source of organic nitrogen in the medium or if the atmosphere contained less than 64 percent oxygen. They concluded that oxygen arrests the mechanism involved in the assimilation of nitrate, a conclusion that seems to harmonize with the findings of Wessenberg [94] that the reduction of nitrite is especially susceptible to the inhibitory action of oxygen.

Sacks and Barker [78] found that oxygen has twofold action on denitrification: it suppresses the formation of nitrate and nitrite-reducing enzymes systems, and when these systems are present it decreases the rate of the reduction processes. They found that oxygen inhibition of denitrification is almost completely reversible after a 15 minute exposure to oxygen, but is only partially reversible after 1 hour. It is probable that a much more prolonged exposure to oxygen might cause a permanent inhibition, which means that the biomass loses its denitrification capability permenantly. They concluded that the effect of oxygen is largely reversible over short periods of time and the rate of denitrification responds very rapidly to change in experimental conditions. They also reported that the formation of nitrite-reducing enzymes is decreased 29 percent by 1 percent oxygen and is completely prevented by oxygen at a level of 5 percent or higher.

Simpkin and Boyle [80] recently suggested that for an activated-sludge system to have the ability to reduce nitrate, the denitrifying enzymes must be present. These enzymes are generally thought to be inducible. That is, they are only produced in the presence of nitrate and in the absence of oxygen. Coupled to enzyme decay, the inducibility of the enzymes suggests that specific enzyme levels could possibly increase and decrease as the microorganisms of an activated sludge go through the anoxic/ aerobic cycles of the system. An enzyme assay for nitrate reductase and nitrite reductase was used to study the extent of synthesis of the denitrifying enzymes in activates sludge systems. Although it was not possible to say what the exact nature and mechanism of the regulation of the synthesis of denitrifying enzymes was, a general statement can be made regarding the practical aspect of the regulation. The denitrifying enzyme data from their study suggested that in the nitrifying activated sludge systems sampled, repression of synthesis by oxygen was not complete so that the enzymes were synthesized to at least 50 % of their maximum level. If extrapolated to other nitrifying activated-sludge systems, these data further suggested that substantial fluctuations in enzyme activity are not likely to occur through the anoxic/aerobic cycles of activated sludges. This, in turn, implied that inhibition by oxygen of enzyme activity and not repression of enzyme synthesis, must be the most important effect oxygen has on denitrification by an activated sludge. In terms of activated sludge design, the data suggested that anoxic zones for the removal of

nitrate should not have to allow for the synthesis of the enzyme as well as for denitrification.

2.2.3 Temperature

McCarty and St. Amant [55] studied denitrification of agricultural drainage water in packed column. They reported satisfactory results down to 12 deg C with a significant rate decrease below 10 deg C. Mulbarger [63] working with a pilot plant scale activated sludge unit presented a non-linear relationship between specific denitrification rate and temperature on plant data at ranges of 9-12.5 deg C. The data were not sufficient to allow the determination of temperature specific removal rate relationship because they were clustered at two temperature levels (Table 6.2).

Dawson and Murphy [22] found from laboratory batch denitrification tests on a defined medium utilizing a dominant culture of *Pseudomonas denitrificans* that the temperature dependency of the specific denitrification rate can be closely approximated by an Arhenius temperature relationship between 3 and 28 deg C. In all studies nitrate removal was characterized initially by periods of relatively slow nitrate removal during which approximately 25 percent of the nitrate content was removed. They observed this lag or acclimation period to increase with decreasing temperature; from about 5 h for the 27 deg C reactor to about 8 days for the 5 deg C reactor. They pointed out that cultures at the higher temperature were already partially acclimated to the experimental conditions during their growth sequence (27 deg C) while at 5 deg C only a small percentage of the original inoculum was probably adaptable. They reported that the denitrification rate at 5 deg C, although only 1/5 of the rate determined for 20 deg C was still significant. They concluded that with increased organism populations denitrification would certainly be a practical undertaking even at low temperatures in reactors with detention times of 6-8 h.

2.2.4 Other Ions

Anthonisen et al. [1] have shown that the inhibitory effects of ammonia and nitrite are directly related to the concentrations of their un-ionized forms. Because the concentrations of these two forms depend on the solution pH, free ammonia is the main inhibitor at high pH (> 8), whereas free nitrous acid is the main inhibitor at low pH (< 7.5). They also reported that Nitrobacter is inhibited by ammonia concentrations of 0.1 to 1.0 mg/l; only concentrations greater than 10 mg/l are toxic to Nitrosomonas. In both instances, a range of concentrations has been reported, and this was necessary because, though seldom recognized in the literature, microbial toxicity is a function of more than just the concentration of the toxic chemical. Probably the most overlooked principle of microbial toxicity is the very strong relationship between the observable toxic effect(s) and the toxic matter-viable biomass (T/B) ratio. This failure is particularly puzzling in view of the universal acceptance of the food-to- microorganism (F/M) ratio as the fundamental parameter controlling the growth responses of microbes. Furthermore, the importance of food-to-mass ratio was first pointed out more than 20 years ago by the work of Fitzgerald [27], working with copper sulfate and algae, and confirmed shortly thereafter by Randall and Lauderdale [75] for malathon and activated sludge. Since then it has been confirmed numerous times for activated sludge for compounds such as TNT and metals such as nickel. Recognizing this principle for microbial systems, it is obvious that the toxic responses of different systems cannot be adequately compared on the basis of the toxic material concentration alone. The biomass concentration must also be known. When biomass is not used to normalize the concentration information, the toxic threshold concentration is in actuality a range of values.

Randall & Buth [74] reported that nickel is more toxic to nitrate formers than to nitrite formers and its presence at moderate concentrations could result in a build-up of nitrites in activated sludge systems. They found that the inhibitory effects of nickel on nitrification was greater at 14 deg C than at 17 deg C or 30 deg C. Therefore, there is a synergistic inhibitory effect between temperature and nickel toxicity for nitrification. They suggested that the toxic effect of nickel on activated sludge should be evaluated on the basis of the nickel-to-MLVSS ratio rather than the concentration of the nickel alone.

Francis and Mankin [30] used a CSTR to evaluate the maximum denitrification specific removal rates for influent solutions made from NH_4NO_3 , $CaNO_3$, KNO_3 and UO_2 fuel fabrication waste water. They found that excessive methanol was not responsible for the inhibition in denitrification rates at nitrate concentrations > $6Kg NO_3/m^3$. They reported that at approximately the same NH_4^+ concentrations, as the pH of the mixed liquor was decreased, the rate of denitrification increased sharply, implying that the inhibition was not due to NH_4^+ concentrations per se but due to NH_3 concentrations because of the equilibrium reaction

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

where $K_d = \frac{(NH_3)(H)}{(NH_4)} = 5.52 \times 10^{-10}$. Thus, they concluded that the inhibition they had observed was due to NH_3 toxicities rather than excessive nitrate concentrations as the averaged mixed liquor pH value from 25 observations was 8.34 ± 0.16 . They did not detect any significant nitrite concentrations in the CSTR whose influent was prepared from $Ca(NO_3)_2$ until nitrate concentrations exceeded 6 kg/m^3 .

Stewart *et al.* [86] studied the effect of salts on the extended aeration process and the applicability of this process for the treatment of shipboard wastes. They found only temporary reductions in treatment efficiency when abnormally severe changes in salinity were combined with heavy hydraulic and organic loadings. In a study of batch activated sludge, Kincannon and Gaudy [44] found a noticeable decrease in substrate removal rate when sludges developed in fresh water were subjected to slug doses of 30,000 mg/l NaCl. However, the effects of such slugs were temporary and did not appear to cause serious distress to the system.

The two dominant cations in most nitrate waste streams are calcium and ammonium. Calcium nitrate wastes are often associated with operations where limestone or hydrated lime have been used to neutralize excess nitric acid wastes. In designing treatment systems where calcium is the dominant cation in high nitrate wastewater, provision will have to be made for removal of $CaCO_3$ accumulations. Furthermore, it appears that maintaining a sufficient concentration of available phosphorus in the mixed liquor may be a problem. In stirred batch studies Francis and Callahan [28] noted that initial phosphorus concentrations of 10 mg/l rapidly became less than 0.005 mg/l as $CaCO_3$ accumulated. Denitrification rates were observed to decrease accordingly. It was postulated that the decrease in the rate of denitrification was probably due to a phosphorus deficiency created by the precipitation of calcium phosphate. Thus, the quantity of phosphorus available to microorganisms was limited by the solubility if the calcium phosphate species precipitated. As denitrification proceeds, even if phosphorus has been reduced to a very low level, the calcium concentration will be continuously decreased by the precipitation of $CaCO_3$ which is caused by the production of CO_2 during the microbial degradation process. This results in an increase in the total carbonic species concentration and an increase in total suspended solids.

2.3 Denitrification Kinetics

Beccari *et al.* [6] described the denitrification kinetics by the following equation that assumes that two substrates (nitrate or nitrite nitrogen and organic carbon) are growth-limiting.

$$\mu = \bar{\mu} \frac{N}{K_{SN} + N} \cdot \frac{C}{K_{SC} + C} - k_d$$

They concluded the following:

• The inhibitory effect of nitrite is irreversible when biomass comes straight into contact with nitrite concentrations that are above thresholds values. This is revealed by nitrite-nitrogen concentration patterns in two successive tests carried out on the same biomass brought into contact with nitrite. Nitrite concentrations n the first test were higher than inhibition- inducing values and lower in the second test that was performed by first withdrawing supernatant and then by adding plant effluent to restore initial biomass concentrations.

- Repeated experiments show that inhibition by nitrite is probably caused by the presence of free nitrous acid. Drops in nitrite reduction rates for pH values greater than 7.5 are matched by similar decreases in nitrate reduction rates caused by natural metabolism phenomena. Nitrite reduction rates also drop sharply for pH values less than 7.5 in contrast to nitrate reduction rates. This is probably attributable to the inhibitory effects from an increased concentration of free nitrous acid.
- Under non-carbon-limiting conditions, nitrate reduction kinetics were seen to be zero order even at low nitrate concentrations, which contradicts their proposed model.
- The absence of inhibition effects when nitrite concentrations were increased gradually by successive increments, seems to indicate that denitrifying biomass may acclimatize to nitrites. Tests conducted do, however, show that when inhibition occurs, it is irreversible and this makes the biomass, even if acclimatized, particularly vulnerable to fluctuations in the concentrations of nitrites fed into the denitrification reactor.

2.3.1 Specific Rate Studies

In this section denitrification rates found in the literature are summarized. The units reported in the original reference are given. All of the rates are also summarized in Table 6.1 in standardized units of $mg NO_3 - N/gVSS - day$.

One should keep in mind when reviewing the rate data summarized in this section that because the rate at which a substrate will be metabolized is inherently dependent upon a number of environmental parameters, it is difficult to compare in quantitative manner, rates derived from different experimental conditions.

According to Painter [67] values for actual denitrification rates from different sources are in the range of 50 to 150 $g NO_3 - N/gVSS - hr$. These rates were developed from pure cultures (different strains of *Alcaligens*) and were dependent upon the organism, the nitrogenous substrate and temperature. For activated sludge processes, reported denitrification rates are from 1 to 2 g $NO_3 - N/gVSS - hr$. Klapwijk *et al.* [45] observed a nitrate removal rate of 16.7 $gNO_3 - N/gVSS - hr$ in an upflow sludge blanket reactor with fusel oil as the carbon source. Monteith *et al.* [60] found that denitrification rates obtained using various carbonaceous industrial wastewater as a carbon and energy source were as high as 14 $g NO_3 - N/gVSS - hr$ for distillery fusel oil at 20.5°C, compared with an average value for methanol of 4 $g NO_3 - N/kgMLVSS - hr$ at 20.0°C. Bonomo *et al.* [10] reported a denitrification rate of 7.9 $g NO_3 - N/gVSS - hr$ Mulbarger [63] found that the measured rates of aerobic respiration and denitrification were very close when an equivalent mass ratio (O_2/NO_3^-) of 2.86 was used: Respective oxygen and equivalent denitrification rates of $20 \pm 10 \ mg$ and $25 \pm 9 \ mg \ O_2/hr$ per gram of MLVSS were obtained when denitrification rates were adjusted using the equivalent mass ratio.

In stirred tank reactors where the carbon substrate was not limiting but nitrate was limiting, Balakrishnan and Eckenfelder [2] found that the denitrification rate increased as a function of the initial $NO_3 - N$ concentration. At an initial $NO_3 - N$ concentration of 50 mg/l the rate of denitrification was less than 5 mg $NO_3 - N/g$ MLSS-hr while at 250 mg/l $NO_3 - N$ the rate was greater than 10 mg $NO_3 - N/g$ MLSS-hr.

Christianson *et al.* [17] denitrified 1100 mg/l $NO_3 - N$ solutions in a continuous flow stirred tank reactor (CSTR) with methanol as a substrate using a modified activated sludge culture. At a feed rate of 10 mg/min containing 2800 mg/l methanol, a 30-hr residence time was sufficient to reduce the nitrate concentration below the level of detection. Mixed liquor was wasted daily to maintain a suspended solids concentration at approximately 3000 mg/l. The denitrification rate was calculated to be 12 mg/l $NO_3 - N/g$ MLSS-hr. They did not notice any nitrite accumulation, which was probably because of the continuous flow system.

Haltrich [34] reported that the rate and the effectiveness of nitrate depletion are dependent on the supply of hydrogen donors, that is, of organic matter, measured as 5-day BOD, in the wastewater. In the presence of BOD, up to 60 mg of nitrate oxygen was removed per gram of MLVSS per hr. In the absence of BOD, the rate of nitrate oxygen removal was much lower. These observations were confirmed by other researchers also. It was also found that provided adequate BOD was available, i.e., the incoming nitrate oxygen does not exceed 60 % of the available BOD, the removal of nitrate was dependent upon the nitrate oxygen sludge load. In his experiments, values of $1.5 g O_2(NO_3)/g MLVSS$ per day could be achieved with no effect on the efficiency. At nitrate oxygen/BOD ratios greater than 60 %, a reduction of the nitrate oxygen sludge load is necessary. In the denitrification stage the rate of BOD removed is dependent on the nitrate oxygen supply. The BOD is incorporated by the activated sludge despite the very high sludge load, so that only the unconsumed organic matter remains for the aerated stage. He mentioned that a process employing an unaerated denitrification stage preceding the aerated stage not only results in appreciably higher rate of nitrate elimination from the raw waste but also ensures trouble-free operation during sedimentation, because the nitrogen gas formed in the activated sludge is blown out.

Dawson and Murphy [22] have summarized the data for a number of denitrification rate studies (Table 6.2). It should be understood that the rate data presented in this table were derived from incomplete nitrogen balances. In the pure culture work the gas collected was assumed to be nitrogen and the equivalent nitrate removal was then calculated. Rate data from the activated sludge experiments were determined from observations of nitrate disappearance and the assumption was made that reduction to nitrogen gas was occurring. Denitrification rates under non-carbon limiting conditions and under conditions where the endogenous respiration of the biological sludge controls the rate of denitrification, represent the maximum and minimum values, respectively, attainable during denitrification. Eckenfelder and Argaman [24] have summarized the specific denitrification rates for various carbon sources at $20^{\circ}C$ (Table 6.2).

Francis and Callahan [28] presented results (shown here in Table 6.3) of denitrification rates reported in several investigations. In nearly all of the studies, methanol was used as the carbon and energy source, the operating temperature was between 18 and $19^{\circ}C$, and the nitrate nitrogen concentration ranged from 10 to 3600 mg/l. Note, that when denitrification rates are given on a per unit volume basis, the anaerobic column shows rates that are 100 to 500 times higher than those for the modified activated sludge process. However, when the rate is given on a per unit biomass basis, there is little difference between the two processes.

Timmermans and Haute [90] reported *Hyphomicrobrium* sp. as dominant organism in a two-sludge nitrifying-denitrifying wastewater treatment system with methanol as external carbon source. The optimal pH for growth was found to be 8.3 and the organism seemed to be rather temperature sensitive. The denitrification rate was expressed as a function of pH and temperature since it was almost independent on the concentrations of methanol and nitrate- nitrogen. Identical growth rates were found when using either nitrate- or nitrite-nitrogen: the nitrite consumption rate, however, is twice the nitrate reduction rate. Nitrate
to nitrite reduction is the rate limiting step in the denitrification reaction while some inhibition by high concentrations of nitrite on the nitrate reduction was also measured. The methanol/nitrate-N ratio is 2.55 and increasing to 3.5 at extreme pH values. The endogenous denitrification was only 10% of the normal denitrification rate measured. They concluded the following:

- denitrification with methanol led to the enrichment of *Hyphomicrobrium* sp. which was found as the dominant organism in a two-sludge nitrifying-denitrifying system.
- Nitrate to nitrite was the rate-limiting step during denitrification, and no nitrite accumulated; in the presence of only nitrite, the organism grew at the same growth rate but the nitrite reduction rate was twice the normal denitrification rate. An equivalent amount of energy was produced during reduction of nitrate to nitrite as during reduction of nitrite to nitrogen gas.
- A higher denitrification rate (25%) was measured with methanol as carbon source when compared with the rate obtained when internal wastewater carbon is used as carbon source.

2.3.2 Inhibition of Denitrification

Little information is available concerning the functional relationship between a toxic material and the specific growth rate of the organism exposed to such a material. To illustrate the dynamic behavior of microorganisms exposed to a toxicant, a function derived from inhibition of enzyme catalysis is normally used. An inhibitor is a substance which, when it interacts with an enzyme, causes a decrease in enzyme catalytic activity. Enzyme inhibition may be reversible. Reversible inhibition implies that the inhibiting agent may be removed from the enzyme, restoring full activity to it. According to Parkin and Speece [69] many toxicants exhibit some degree of reversibility.

Several pesticides impede but do not suppress reduction of nitrite in soil and in whole cells, but the prospect that the impeding action is exerted at the nitrite reductase rather than at some other structural or functional level has not been determined. Nitrite is known to be toxic to many bacteria, even denitrifiers. The effect is attributable to inhibition of active substrate transport and of several enzymes as reported by Yarbrough *et al.* [99].

The reductases involved in denitrification are susceptible to inhibition by a variety of compounds. The mechanism of action is not clear for any of the inhibitors [71].

Francis and Hancher [29] found that upon initial exposure, very low concentrations (0.5 mg/l) of nickel, significantly inhibited denitrification rates. However, after an eight day acclimation period, concentrations as high as 3.9 mg/l were not inhibitory.

Generally, toxicity is a function of the toxic mass-to-biomass ratio rather than the concentration of toxic materials. This type of toxicity response has been observed by a number of investigators [50,56,74,88]. Nitrite reduction has been shown to be substrate (nitrite) inhibited, with a threshold nitrite concentration of less than 10 mg $NO_2 - N/L$ with low biomass concentrations in suspended growth, but rising with increasing biomass concentration.

Lewandowski [53] investigated the phenomenon of complete substrate conversion within biological reactors in the presence of toxic compounds, called the Reactor Resistance to Inhibition (RRI). It was theoretically demonstrated that the RRI value, which means the highest concentration of inhibitor by which complete substrate conversion is possible, depends on liquid detention time. The influence of detention time in biological denitrification in Packed Bed Reactors in the presence of Cr^{6+} was investigated. The RRI value for 1 h detention time was 1.5 mg/l Cr^{6+} . For 3 h detention time the RRI value was 22 mg/l Cr^{6+} . The relationship between RRI value and detention time was linear. Lewandowski [53] used the following equation to represent the relationship between reaction velocity (V) and inhibitor concentration (i):

$$V = \frac{V_{max} \cdot s \cdot K_i}{(K_m + s)(K_i + i)}$$

2.3.3 Nitrite Accumulation

During the process of denitrification of wastewater nitrite has often been observed to accumulate, most probably because of the nitrite reduction rate falling behind the rate of nitrate reduction.

Results of experiments recently conducted to study denitrification in a SBR activated sludge system by Wilderer and Schroeder [96] indicates that nitrite is often reduced at a much lower rate than anticipated causing nitrite to accumulate in the reactor. Reports in the literature support this observation.

Betlach and Tiedje [7], for instance, studied the denitrification capacity of pure cultures of *Flavobacterium* sp. and *P. fluoescens*. It was observed that nitrite accumulated in the reactor inoculated with *P. fluoescens*. From the results of a mathematical model and from experimental results, it was concluded that accumulation of nitrite was caused by unbalanced concentrations of nitrate and nitrite reductases. Speculation on inhibition of nitrite reductase by dissolved oxygen and by nitrate could not be confirmed.

Kone and Behrens [47] concluded from the results of mixed culture studies that discontinuous operation of denitrification reactors, in particular batch operation, would trigger nitrite to accumulate. Steady state conditions were assumed to be required to maintain high nitrite reduction potentials. From this conclusion, one would expect nitrite accumulation to occur in many denitrification reactors established for wastewater treatment, since none of them can be operated under true steady state conditions. Periodic changes of major environmental conditions are common, even when flow conditions are equalized. In an activated sludge denitrification system, for instance, the bacteria being recirculated in the system experience on going periodic cycles of oxygen availability and oxygen deficiency. Obviously, however, nitrite does not appear in the effluent but only occasionally.

Nitrite accumulation was observed in activated sludge systems as well as in continuous flow fixed film reactors by Requa and Schroeder [77]. Apparently,

comprehensive understanding must include factors, like type of species, nature of substrates etc., other than inhibition and fluctuation of environmental conditions. In this context, results obtained by Blaszczyck *et al.* [8] are of particular interest. Mixed culture studies were conducted to investigate the value of various organic substances as carbon sources and as electron donors for denitrifiers. The rate of nitrate reduction was almost unaffected by the type of substance applied. However, when glucose was applied, nitrite accumulated and extremely high peak concentrations of nitrite were observed. With glucose, the pH value did not increase, in contrast to the results of experiments with ethanol and acetate, but remained below 7.0 for most of the reaction time. Fermentation reactions may have been responsible for the observed low pH level suggesting the presence of microorganisms in the biocommunity capable of performing both fermentation and nitrate reduction. This conclusion was supported by observations made by Ermel [26], Simpkin and Boyle [80] and others. Subsequently, it must be assumed that there are at least two mechanisms responsible for nitrite accumulation:

- Repression of the synthesis of nitrite reductase
- Selection and enrichment in favor of microorganisms capable of reducing nitrate, but only to nitrite.

A third mechanism which might become important under certain conditions was pointed out by Bock *et al.* [9]. It has been discovered that the nitrite oxydase of *Nitrobacter* sp. is actually more efficient in catalyzing the reverse reaction, and may, therefore, be better named nitrate reductase. It might very well be that *Nitrobacter* sp. contributes to the increase of the nitrite concentration under anoxic conditions.

Recently Wilderer et al. [96] have found that the process of nitrite reduction plays a more important role in denitrification of wastewater than previously considered, and that reference only to nitrate reduction can be highly misleading. Use of NO_x as a parameter represents an improvement, but no distinction can be made between factors affecting nitrite reduction alone and factors affecting the entire chain of reactions. The way in which a wastewater treatment plant is designed to operate can have large effects on the phenomena of nitrite accumulation and nitrite reduction rate deterioration. Facultative anaerobes play a critical role in this process. Allowing fermentative conditions to occur with any regularity in the treatment system will enrich the biocommunity for bacteria which reduce nitrate only to nitrite, and no further. In addition, such a population shift must occur at the expense of denitrifiers which can reduce nitrite. Nitrobacter species may grow in significant numbers in combined-sludge systems, further enhancing any nitrite accumulation process. Although fermentation conditions which promote the growth of undesirable facultative anaerobes are uncommon, unless the plant also receives large carbohydrate loadings (i.e., from industrial sources), fecalcoliform bacteria imported to the system can also carry out nitrate reduction under anoxic conditions. Thus, decision on whether primary treatment is required should include consideration of whether denitrification is to be accomplished. Shifts in favor of the denitrifying population are more difficult to carry out directly. Carbon limitations during denitrification should be avoided, and the nature of available carbon sources should be critically examined. Feeding some

nitrite rather than all nitrate to the denitrification system may be beneficial, since the electron acceptor would be of value only for denitrifiers. In practice, this strategy may be difficult to accomplish, though.

Betlach and Tiedje [7] examined the kinetics of denitrification and the causes of nitrite and nitrous oxide accumulation in resting cell suspensions of three denitrifiers. An Alcaligenes species and a Pseudomonas fluorescens isolate characteristically accumulated nitrite when reducing nitrate; a Flavobacterium isolate did not. They found that nitrate did not inhibit nitrite reduction in cultures grown with tungstate to prevent formation of an active nitrate reductase; rather, accumulation of nitrite seemed to depend on the relative rates of nitrate and nitrite reduction. Each isolate rapidly reduced nitrous oxide even when nitrate or nitrite had been included in the incubation mixture. Nitrate also did not inhibit nitrous oxide reduction in Alcaligenes odorans, an organism incapable of nitrate reduction. Thus, added nitrate or nitrite does not always cause nitrous oxide accumulation, as has often been reported for denitrifying soils. All strains produced small amounts of nitric oxide during denitrification in a pattern suggesting that nitric oxide was also under kinetic control similar to that of nitrite and nitrous oxide. Apparent K_m (saturation constant for Monod's model) values for nitrate and nitrite reduction were 15 μM or less for each isolate. The K_m value for nitrate and nitrous oxide reduction by Flavobacterium sp. was $0.5 \ \mu M$. Numerical solutions to a mathematical model of denitrification based on Michaelis-Menten kinetics showed that differences in reduction rates of the nitrogenous compounds were sufficient to account for the observed patterns of

nitrite, nitric oxide, and nitrous oxide accumulation. Addition of oxygen inhibited gas production from NO_3^- by Alcaligenes sp. and Pseudomonas fluorescens, but it did not reduce gas production by Flavobacterium sp.. However, all three isolates produced higher ratios of nitrous oxide to nitrogen as the oxygen tension increased. Inclusion of oxygen in the model as a nonspecific inhibitor of each step in denitrification resulted in decreased gas production but increased ratios of nitrous oxide to nitrogen, as observed experimentally. In the three isolates they used, the concentration of nitrous oxide appeared to be under kinetic control. Such control was especially evident when the nitrous oxide concentration rapidly returned to a steady-state value after addition of more N_20 . The slight accumulation of nitric oxide during denitrification suggested that it, like nitrite and nitrous oxide, was also under kinetic control. The increase in NO after addition of the substrate and its depletion after nitrate and nitrite were consumed, was the pattern expected if NO had been an intermediate or in equilibrium with an enzyme-bound intermediate in the denitrification pathway.

2.4 Carbon Source

2.4.1 Methanol

During the last 35 years considerable research has been conducted for the denitrification of nitrate polluted waters using methanol as sole carbon and energy source.

The first evidence that the biomass in a denitrifying reactor had an unusual population when methanol was used, was in fact reported by Christenson *et al.*

[17]. They commented: So far as the organisms are concerned, they consist of an almost pure culture of as yet unidentified very small ciliated protozoa with large numbers of bacteria.

Sperl *et al.* [83] noted that denitrification with methanol resulted in a selective enrichment for bacteria belonging to the genus *Hyphomicrobium*. This was also confirmed by Nurse [66].

Nurse carried out a kinetic investigation for the denitrification of high level nitrate industrial effluent bearing the above results in mind and proposed equations to describe the stoichiometry of denitrification with methanol, by calculating the amount of methanol and nitrate that has to be oxidized and reduced respectively in order to generate the $NADH_2$ and ATP required for cell biosynthesis of Hyphomicrobium.

Mc Carty *et al* [55] concluded that the denitrifying ability of microorganism differs. With a naturally occurring heterogeneous population, species capable of carrying out denitrification to different degrees will undoubtedly be present and nitrites may or may not appear as an intermediate. However it is convenient to consider denitrification as a two-step process, the first representing reduction of nitrate to nitrite and the second a reduction of nitrate to nitrogen gas as indicated in the following denitrification reaction with methanol:

First step:

$$NO_3^- + \frac{1}{3}CH_3OH = NO_2^- + \frac{1}{3}CO_2 + \frac{2}{3}H_2O$$

Second step:

$$NO_{2}^{-} + \frac{1}{2}CH_{3}OH = \frac{1}{2}N_{2} + \frac{1}{2}CO_{2} + \frac{1}{2}H_{2}O + OH^{-}$$

Overall:

$$NO_{3}^{-} + \frac{5}{6}CH_{3}OH = \frac{1}{2}N_{2} + \frac{5}{6}CO_{2} + \frac{7}{6}H_{2}O + OH^{-}$$

Thus, 5/6 moles of methanol are required for the denitrification reaction alone to reduce one mole of nitrate completely to molecular nitrogen. If only 1/3 mole of methanol were added, it is possible that the nitrate would only be reduced to nitrite so that no effective nitrogen removal would result. Thus, addition of 40 %of the overall required amount of methanol may result in no effective nitrogen removal. This consideration indicates that a treatment process should be designed for nearly complete denitrification of the portion to be treated, rather than for partial treatment as the later would be unpredictable and probably wasteful of chemicals. A Consumptive Ratio was defined as the ratio of the total quantity of an organic chemical consumed during denitrification to the stoichiometric requirement for denitrification and deoxygenation alone. A consumptive ratio of one would indicate that no chemical was required for bacterial synthesis. A ratio greater than one would be expected, and the higher the ratio, the higher the chemical requirement for biological growth. Methanol was selected as the most desirable organic chemical of the five studied for denitrification. It is currently quite inexpensive when compared on an equivalent basis. It yields a consumptive ratio of 1.3 which is in the same range as that for most of the chemicals evaluated except sugar, which has higher value. Methanol is effective for denitrification and

can be obtained as a highly pure liquid which is not bulky for shipment and can be fed easily and accurately. Its aqueous vapor pressure is sufficiently low so that it should not create a hazard by evolution from the treated water. Methanol is not considered toxic chemical to fish life as most can tolerate over 10,000 mg/l. Thus, the small concentrations which would be present in a denitrified effluent should not constitute a public problem.

The stoichiometric amounts can be expressed more conveniently on a weight basis by the formulation:

$$c_m = 2.47N_o + 1.53N_1 + 0.87D_o$$

 c_m = required concentration of methanol, mg/l N_o = initial nitrate nitrogen concentration, mg/l N_1 = initial nitrite nitrogen concentration, mg/l D_o = initial DO concentration, mg/l

If oxygen enters the denitrifying unit during treatment, then the value for D_o should be increased to account for this effect. The quantity of bacteria ((C_b) , in mg/l) produced during denitrification was given by Mc Carty *et al.* [55] as follows:

Biomass Production:

$$C_b = 0.53N_o + 0.32N_1 + 0.19D_o$$

Dahab and Lee [20] examined the potential use of biological denitrification for the removal of nitrates from potential groundwater supplies using static-bed upflow reactors. These reactors were operated for about 10 months using a simulated influent that contained a nitrate concentration of 100 mg/l and was fortified with a carbon source (acetic acid) and the necessary amounts of trace elements and a buffer. Carbon source concentration was varied over time to reduce the effluent residual organics as much as possible. The static-bed reactors were relatively easy to start and fairly trouble free to run and maintain. In general, reactor response to changes in carbon concentrations was immediate and apparent steady-state conditions were reached quickly. The reactors remove nearly 100% of nitrate as long as the influent COD was such that minimal stoichiometric requirements were maintained. COD was used as a measure of the soluble organic carbon. A C:N ratio of 1.5 minimized effluent COD. An attempt to reduce the carbon to nitrogen ratio below 1.5 resulted in the break-through of nitrates. The reactors resulted in the production of suspended solids (SS) and turbidity in the reactor effluent, as expected. This illustrates that biological denitrification can only be considered as a pretreatment process step in a water purification system. A C:N ratio of 1.45 resulted in low soluble and SS in the effluent. It should be possible to minimize effluent residual organics by slight reductions of the C:N ratio below stoichiometric levels. Biological denitrification left residual soluble and SS in the water supply. Although these contaminants can be minimized by proper selection of operating conditions, it is unlikely that this process will result in an organics-free effluent.

2.4.2 Other C Sources

Grabinska-Loniewska [33] reported that glycerol can be used as a hydrogen donator in denitrification. To ensure appropriate efficiency of the process the concentration of glycerol in the feed should give a C:N ratio= 1.9 (as $C_3H_5(OH)_3-C$ and $NO_3 - N$). The requirement for this compound in denitrification is thus lower than for methanol (2.6 mg CH_3OH per mg $N0_3 - N$) as determined by Cheung [13] and Davies *et al.* [21]. The results of the investigation by Grabinska-Loniewska [33] demonstrated that the main factor limiting the efficiency of nitrogen removal was the unit and sludge nitrate load. The highest efficiency of nitrogen removal (97%) was obtained with a load of 220 mg $NO_3 - N l^{-1}day^{-1}$ (0.08 mg $NO_3 - N mg^{-1}day^{-1}$). Similarly high removal of glycerol and COD (97 and 94 % respectively) pointed to full utilization of the carbon source. The rate of nitrogen removal by weight unit of sludge for a range of nitrate loads from 220 to 1330 mg $NO_3 - N l^{-1}day^{-1}$ (0.08-0.26 mg $NO_3 - N mg^{-1}day^{-1}$) increased with load and sludge concentration.

The efficiency of nitrogen removal by weight unit of sludge obtained by Grabinska-Loniewska [33], i.e., 0.12 $mg N mg^{-1}day^{-1}$ with a load of 0.14 $mg NO_3 - N mg^{-1}day^{-1}$ was approximately twice as low as determined by Jewell and Cummings [41] in the presence of methanol but with much higher nitrate load (0.4). Grabinska-Loniewska also reported that although they carried out their process under strict anaerobic conditions the increase in biomass was so great that it was necessary to regulate the sludge concentration in the reactor. A large increase in biomass can be considered desirable since Cheung and Krauth [14] and Jewell and Cummings [41] found that securing an adequate amount of biomass in the technical units, through the use of proper hydraulic residence time and structure design, safeguarded against its washing out but also ensured a high rate of nitrogen removal. Under these conditions the amount of biomass formed, is a function of $NO_3 - N$ and the increase in the rate of nitrogen removal is almost linear with sludge concentration.

Narkis et al. [64] examined whether the residual dissolved organic matter, remaining in chemically treated raw sewage would be able to satisfy the carbon demand for the denitrification process. In the first stage of their research they investigated the effect of type and amount of organic substrate on denitrification efficiency. The critical weight ratios of methanol and sodium acetate to total concentration of nitrite and nitrate which enable the occurrence of complete denitrification were studied. It was found that when the concentration of the organic matter was expressed as BOD, a critical ratio of $(mgBOD/mg \sum NO_x - N) = 2.3$ ensured 100% denitrification. Lower ratios decreased denitrification efficiencies proportionally. The same critical ratio was found when the chemically treated raw sewage was used as an available organic carbon source. The denitrificationnitrification process was also investigated by recirculating the nitrified effluent into the denitrification reactor, to which effluents from chemical treatment of raw sewage were fed to satisfy the carbon demand, and the same critical ratio of $(mgBOD/mg \sum NO_x - N) = 2.3$ was found. By increasing the recycling, nitrate concentration in the effluent was decreased.

2.5 Application of Different Flow Systems

Biological processes for nitrogen removal from wastewater have been extensively studied. System operation to successfully achieve nitrification and denitrification has led to many innovative designs. While two or three sludge systems can offer conceptual appeal, single sludge systems have been shown to produce sufficient removals and also reduce capital costs. In addition, systems designed to denitrify without supplemental carbon addition markedly cut operating costs. Within the past decade, several process configurations that stressed the alternation of aerobic and anoxic conditions have been reported. All these systems are continuous flow, and used organics in raw wastewater as the carbon source for denitrification.

Combined ion exchange/biological denitrification is a process for nitrate removal from ground water in which nitrate is removed by an ion exchanger and the resins are regenerated in a closed circuit through a biological denitrification reactor. Hoek *et al.* [39] conducted ion exchange/biological denitrification experiments on laboratory-scale under three process conditions. Ground water with a relatively low sulfate concentration ($31 \text{ mg } SO_4^{2-}$ /l) was treated with the sulfate selective resin Duolite A 165 and with the nitrate selective resin Amberlite IRA 996. In both cases NaCl was used as regenerant. Although the nitrate concentration in the treated water was hardly influenced by the different resin types, chloride and sulfate concentrations were clearly affected. With the nitrate selective resin sulfate concentrations were high and chloride concentrations were

lower as compared with the sulfate selective resin. Treatment of ground water containing a very high sulfate concentration (181 mg SO_4^{2-}/l) was possible by the combined process with the nitrate selective resin. In all three cases sulfate accumulated in the regeneration circuit without imparing the nitrate removal in the service mode. The regenerant was renewed every two weeks. Compared with conventional ion exchange regeneration this results in reduction of brine production by 95%. For the removal of nitrate from ground water, containing low sulfate concentrations, the use of nitrate selective resins offers no advantages over the use of sulfate selective resins in the combined ion exchange/biological denitrification process with respect to effluent nitrate concentrations. However, with nitrate selective resins chloride concentrations in the treated water are lower as compared with sulfate selective resins, because sulfate is only partly exchanged for chloride concentrations; this can also be a benefit. The experiments showed that water with extremely high sulfate concentrations can also be treated with the combined process when a nitrate selective resin is used. High chloride and bicarbonate concentrations beside high sulfate concentrations caused, no difficulties. Experiments clearly demonstrated that nitrate removal from soil by the combined ion exchange/biological denitrification process is hardly affected by other anions.

Nitrogen and phosphorus have been identified as the nutrients most commonly limiting algal growth in natural waters. The discharge of waste-water high in these inorganic nutrients accelerates eutrophication and often leads to severe water quality problems due to the resulting increase in algal concentrations. Irrigation drainage waters, which commonly contain 5-40 mg/l nitrate nitrogen are of particular interest.

Recent interest in the application of SBR to wastewater treatment is the result of SBR process characteristics, such as: 1) Control of performance in these periodic systems, particularly reaction time and maintenance of sludge solids, is straight forward. 2) Reaction and settling of solids can occur in the same vessel as opposed to the need for seperate clarifiers that are needed when continuous-flow reactors are used. Although research on the SBR process to date has been conducted on activated sludge systems, the basic concept of time-sequenced batch operation could easily be transferred to other process configuration, such as fluidized bed systems. Because experience with the SBR process is limited, questions about operating constraints and appropriate applications of the process still need to be answered. These questions concern the stability of periodic process, the actual economic benefits of an anoxic cycle, other effects of anoxic operation, comparative characteristics of SBRs and continuous flow system, and optimal nitrification and denitrification portions of batch cycles where advanced treatment is required. Silverstein and Schroeder [81] observed the performance of SBR activated sludge processes with nitrification/denitrification and they performed experiments to investigate the effects of organic loading on nitrification and denitrification using endogenous carbon and energy sources. They reported that it appeared that denitrification in the more highly organically loaded system was limited by the concentration of oxidized nitrogen. Because of aeration, reduced nitrogen i.e., ammonia nitrogen became unavailable for the growth of denitrifying bacteria and as a result, after extended aeration, denitrification ceased completely.

Irvine et al. [40] achieved approximately 90% nitrogen removal in a high loaded full-scale SBR. In particular, the results demonstrated that an operation strategy which encouraged some denitrification to occur during fill, that is, when an exogenous electron donor was present, would remove a large percentage of the incoming nitrogen. SBRs provide in this case a viable treatment alternative In their SBR for nitrogen removal without supplemental carbon addition. experiments Irvine et al. reported that although nitrification was insensitive to the aeration policies used in their study, denitrification was affected substantially by the presence or absence of exogenous electron donors. During fill, the rate of oxygen utilization was higher than that during the react phase because of the presence of extracellular soluble substrate. As a result, the time required for DO to be decreased sufficiently for denitrification to occur was reduced, and the rate of denitrification was increased during fill as opposed to the corresponding times and rates during react. They reported denitrification rates from 2.2 to 3.6 mg OX-N/L.h for fill, 1.2 mg OX-N/L.h after fill while the average unit rate of oxidized nitrogen removal was 0.5 mg OX-N/g MLSS.h during fill and 0.4 mg OX-N/g MLSS.h after fill. These unit rates were obtained by dividing the denitrification rates by the appropriate MLSS concentration at the given reactor volume. They mentioned that the denitrification rates will depend on the relative proportion of participating microorganisms, on the distribution between nitrogen and organic substances in raw wastewater, and on the operating strategy selected.

Chapter 3 Mathematical Modeling

Two detailed mathematical models have been developed in order to describe the operation of the batch and sequencing batch reactors respectively. The models have been brought in a dimensionless form, in order to reduce the number of parameters, and thus decrease the amount of numerical work needed to study the sensitivity of the results on the various parameters. The formulation of these models is such that it allows for the comparison of nitrite build up in the batch reactor to that of SBR. The models consist of two different growth principles i.e., Monod Kinetics (non-inhibitory) and Andrews Kinetics (inhibitory). In case of the SBR, the model assumes that the duration of the settling and idle phases is negligible relative to that of the other three phases (fill, react, and draw) and thus can be neglected. Furthermore, the model assumes that biodegradation (reaction) occurs during all three phases (fill, react, and draw). Figure 7.1 shows a qualitative diagram of the change in the working volume of the reactor as a function of time.

3.1 Batch Model

3.1.1 General derivation

The equations describing the batch reactor system at any instant of time are the following:

$$\frac{dV}{dt} = 0 \tag{3.1}$$

Equation 3.1 is written under the (usual and reasonable) assumption of constant density. The symbol in Equation 3.1 is defined as:

• V : Working Volume of the reactor

The nitrate balance:

$$\frac{ds}{dt} = -\frac{b}{Y_1}\mu(s) \tag{3.2}$$

The nitrite balance:

$$\frac{dp}{dt} = \alpha \mu(s)b - \frac{b}{Y_2}\mu(p) \tag{3.3}$$

The biomass balance:

$$\frac{db}{dt} = b[\mu(s) + \mu(p)] - kbp \tag{3.4}$$

The symbols appearing in Equation 3.2, 3.3, 3.4 are defined as :

- b: Concentration of biomass in the reactor.
- s: Concentration of nitrate in the reactor.
- p: Concentration of nitrite in the reactor.
- $\mu(s)$: Specific rate of biomass production which is a function of the concentration of nitrate.

- μ(p): Specific rate of biomass production which is a function of the concentration of nitrite.
- Y_1 : Yield coefficient of the biomass on nitrate
- Y_2 : Yield coefficient of the biomass on nitrite
- α : A proportionality constant which represents the amount of nitrite produced per unit amount of biomass produced due to nitrate consumption.
- k : A constant associated with the death rate of biomass. Death is assumed to be the result of toxic effect of nitrite on the biomass.

3.1.2 Selection of Growth Kinetics

Andrews Kinetics

From previous research it has been established that accumulation of nitrite in the system causes a definite deactivating effect on the denitrifying enzymes of the bacteria. Keeping this in mind and following the principles of inhibitory kinetics one can use Andrews Model for expressing the specific (i.e., per unit of biomass) rate of biomass production based on $N0_2^-$ consumption alone. Therfore, one can write,

$$\mu(p) = \frac{\hat{\mu}p}{K' + p + p^2/K_i}$$
(3.5)

where

- $\hat{\mu}$: A constant having units of inverse time
- $K' \& K_i$: Model constants having units of concentration

Monod Kinetics

Since nitrate itself does not inhibit the growth of the biomass, one can represent the growth rate as:

$$\mu(s) = \frac{\mu_m s}{K+s} \tag{3.6}$$

Where

- μ_m : Maximum specific growth-rate on nitrate only
- K : Saturation constant of the population with nitrate only

It is important to add that all of these parameters are constant at specified environmental conditions (e.g.; pH, temperature). Changes in their values may give deifferent denitrification rates, accumulation of nitrites, deacivation of the dentrifying enzymes etc.

3.1.3 Dimensionless Forms

Using Equations 3.1 through 3.6 we get:

$$\frac{ds}{dt} = -\frac{b}{Y_1} \frac{\mu_m s}{K+s} \tag{3.7}$$

$$\frac{dp}{dt} = \alpha \frac{\mu_m s}{K+s} b - \frac{b}{Y_2} \frac{\hat{\mu} p}{K' + p + p^2/K_i}$$
(3.8)

$$\frac{db}{dt} = b[\frac{\mu_m s}{K+s} + \frac{\hat{\mu}p}{K'+p+p^2/K_i}] - kbp$$
(3.9)

The following dimensionless quantities are now introduced:

- u = s/K = dimensionless concentration of nitrate
- $u_f = s_f/K$ = dimensionless concentration of nitrate in the feed
- $x = b/Y_1K$ = dimensionless concentration of active biomass
- $\theta = t\mu_m = \text{dimensionless time}$
- $\omega = K'/K$ = dimensionless constant associated with Andrews model
- $\phi = \hat{\mu}/\mu_m$ = dimensionless constant
- $\gamma = K/K_i$ = dimensionless inverse inhibition constant
- $\eta = Y_1/Y_2 = \text{dimensionless constant}$
- v = p/K = dimensionless concentration of nitrite
- $v_f = p_f/K$ = dimensionless concentration of nitrite in the feed
- $x_o = b_o/Y_1K$ = dimensionless initial concentration of biomass
- $\rho = \alpha Y_1$ = dimensionless constant indicating the amount of nitrite produced, per unit amount of nitrate consumed
- $\epsilon = kK/\mu_m$ = dimensionless constant associated with death rate of biomass due to toxicity

One can write Equations 3.7, 3.8, 3.9 in dimensionless form, as follows:

$$\frac{du}{d\theta} = -\frac{u}{1+u}x\tag{3.10}$$

$$\frac{dv}{d\theta} = \rho \frac{u}{1+u} x - \phi \eta \frac{v}{\omega + v + \gamma v^2} x$$
(3.11)

$$\frac{dx}{d\theta} = x\left[\frac{u}{1+u} + \phi \frac{v}{\omega + v + \gamma v^2}\right] - \epsilon x v \qquad (3.12)$$

Batch operation is assumed to work in a cyclic mode as follows:

The reaction occurs for a period of time τ (τ is dimensionless), and at the end of it, a fraction δ of the liquid is emptied and immediately replenished by an equal volume of the waste. This mode of operation can be viewed as a special case of the SBR operation (described in the following section) with zero fill and draw-down time. At start-up (that is for the very first cycle) it is assumed that the reactor is filled with the waste, and in it a certain amount of biomass is introduced. Thus, for the first cycle, and at $\theta = 0$, one has $u = u_o = u_f$, $v = v_o = v_f$, $x = x_o$. At $\theta = \tau$ (that is at the end of the first cycle), the concentrations are $u = \tilde{u_1}, v = \tilde{v_1},$ $x = \tilde{x_1}$. At that instant, a fraction δ of the volume of the reactor contents are taken away and immediately substituted by an equal volume of untreated waste. One can then write the following mass balances:

$$u_2 = \delta \tilde{u_1} + (1 - \delta) u_f \tag{3.13}$$

$$v_2 = \delta \tilde{v_1} + (1 - \delta) v_f \tag{3.14}$$

$$\boldsymbol{x}_2 = \delta \tilde{\boldsymbol{x}_1} \tag{3.15}$$

where:

- u_2 =dimensionless concentration of nitrate in the beginning of the second cycle
- v₂ =dimensionless concentration of nitrite in the beginning of the second cycle
- x_2 =dimensionless concentration of biomass in the beginning of the second cycle

In general then, one can write:

$$u_{n+1} = \delta \tilde{u_n} + (1 - \delta) u_f \tag{3.16}$$

$$v_{n+1} = \delta \tilde{v_n} + (1 - \delta) v_f \tag{3.17}$$

$$\boldsymbol{x_{n+1}} = \delta \tilde{\boldsymbol{x_n}} \tag{3.18}$$

where:

- u_{n+1} =dimensionless concentration of nitrate in the beginning of the n + 1 cycle
- u_n =dimensionless concentration of nitrate at the end of the n cycle

- v_{n+1} =dimensionless concentration of nitrite in the beginning of the n + 1 cycle
- v_n =dimensionless concentration of nitrite at the end of the *n* cycle
- x_{n+1} =dimensionless concentration of biomass in the beginning of the n+1 cycle
- x_n =dimensionless concentration of biomass at the end of the *n* cycle

After this type of operation is repeated for enough number of cycles, the following equalities hold for $0 \le \theta \le \tau$:

$$u_{n+1}(\theta) = u_n(\theta) \tag{3.19}$$

$$v_{n+1}(\theta) = v_n(\theta) \tag{3.20}$$

$$x_{n+1}(\theta) = x_n(\theta) \tag{3.21}$$

The equalities above, imply that the system has reached the steady cycle of operation, and each cycle is identically repeated in time. One can say that $\tau/(1-\delta)$ is like a mean hydraulic residence time for the process.

3.2 SBR Model

The SBR model is a mathematical description of the mode of operation known as sequencing batch. It is again a cyclic mode of operating the reactor, and each cycle has five distinct periods: filling, reacting, settling, drawing and idle. Figure 7.1 (a) shows the volume variation during the cycle, under the assumption that filling and drawing occurs at constant flow rates (and, thus the volume changes linearly). In this study, settling and idle phases have been neglected, and Figure 7.1 (b) shows the volume variation considered here. Furthermore, it is assumed that reaction occurs throughout the cycle, and hence the *reacting* phase, in actuality is a phase during which reaction occurs under constant volume in batch mode.

3.2.1 General Derivation

$$\frac{dV}{dt} = Q_f - Q \tag{3.22}$$

where,

- Q_f = Feed flow rate into the reactor
- Q = Effluent flow rate from the reactor

$$\frac{d(Vs)}{dt} = (Q_f s_f - Qs) - \frac{b}{Y_1} \frac{\mu s}{K+s} V$$

or using Equation 3.22 one gets

$$s(Q_f - Q) + V\frac{ds}{dt} = Q_f s_f - Qs - \frac{b}{Y_1} \frac{\mu_m s}{K + s} V$$

or

$$\frac{ds}{dt} = \frac{Q_f}{V}(s_f - s) - \frac{b}{Y_1} \frac{\mu_m s}{K + s}$$
(3.23)

Similarly for the nitrite one can write the following:

$$\frac{d(Vp)}{dt} = (Q_f p_f - Qp) + \alpha \frac{\mu_m s}{K+s} bV - \frac{b}{Y_2} \frac{\hat{\mu}p}{K'+p + p^2/K_i} V$$

Again using Equation 3.22 one gets

$$\frac{dp}{dt} = \frac{Q_f}{V}(p_f - p) + \alpha \frac{\mu_m s}{K + s} b - \frac{b}{Y_2} \frac{\hat{\mu} p}{K' + p + p^2/K_i}$$
(3.24)

For the biomass one can write

$$\frac{d(Vb)}{dt} = -Qb + bV[\frac{\mu_m s}{K+s} + \frac{\hat{\mu}p}{K'+p + p^2/K_i}] - kbpV$$

or using Equation 3.22 one gets

$$\frac{db}{dt} = -\frac{Q_f}{V}b + [b\frac{\mu_m s}{K+s} + b\frac{\hat{\mu}p}{K'+p+p^2/K_i}] - kbp$$
(3.25)

3.2.2 Dimensionless forms

In addition to the dimensionless quantities which were introduced in Section 3.1.3, the following quantities are introduced:

- $Q'_f = (Q_f t_2)/Q_f^* t_1 = Q_f/Q_f^* \sigma_1$ = dimensionless flow rate of the incoming waste and $Q_f^* = Q_f$ during fill phase
- + $Q^{'} = Q/(Q_{f}^{*}\sigma_{1}) =$ dimensionless flowrate of the effluent
- $\sigma_1 = t_1/t_3$ = fraction of the cycle devoted to filling phase
- $\sigma_2 = (t_2 t_1)/t_3 = \text{fraction of the cycle devoted to reacting phase}$
- $\sigma_3 = (t_3 t_2)/t_3 =$ fraction of the cycle devoted to drawing phase

- $V' = V/V_{max}$ = dimensionless volume of the reactor contents
- $\theta = tQ_f^*\sigma_1/V_{max}$ = dimensionless time
- $\beta = \mu_m V_{max}/(Q_f^* \sigma_1)$ = measure of the dimensionless hydraulic residence time
- $\delta = V_o/V_{max}$ = volume fraction of the reactor contents emptied during the draw down phase

Using these quantities one can rewrite Equations 3.22 to 3.25 as following:

$$\frac{dV'}{d\theta} = Q'_f - Q' \tag{3.26}$$

$$\frac{du}{d\theta} = \frac{Q'_f}{V'}(u_f - u) - \beta x \frac{u}{1+u}$$
(3.27)

$$\frac{dv}{d\theta} = \frac{Q'_f}{V'}(v_f - v) + \rho\beta x \frac{u}{1+u} - \eta\phi\beta x \frac{v}{\omega + v + \gamma v^2}$$
(3.28)

$$\frac{dx}{d\theta} = -\frac{Q'_f}{V'}x + \beta x \frac{u}{1+u} + \phi \beta x \frac{v}{\omega + v + \gamma v^2} - \epsilon \beta x v \qquad (3.29)$$

During the filling phase , Q' = 0 and $Q'_f = 1/\sigma_1$. Therefore Equation 3.26 can be written as:

$$V' = \delta + \frac{1}{\sigma_1}\theta \tag{3.30}$$

At the end of the filling phase $(\theta = \theta_1)$, it is V' = 1 and thus Equation 3.30 implies that,

$$1 = \delta + \frac{\theta_1}{\sigma_1} \Rightarrow \theta_1 = (1 - \delta)\sigma_1$$

Hence the filling period is

$$0 \le heta \le (1-\delta)\sigma_1$$

During the reaction phase, $Q'_f = 0 = Q'$. This phase lasts for the following time interval:

$$\theta_1 \leq \theta \leq \theta_2$$

or

$$(1-\delta)\sigma_1 \le \theta \le \theta_2$$

During the draw down period, $Q_f = 0$. Furthermore, if a steady cycle of operation is to be eventually reached, the volume of the waste fed to the reactor during the filling phase must be equal to the volume of the reactor contents emptied during the draw down phase (assuming constant density). Hence,

$$Q_f^* t_1 = Q(t_3 - t_2)$$

or

$$Q = \frac{Q_f^* t_1}{t_3 - t_2} = \frac{Q_f^* \sigma_1}{\sigma_3}$$

hence

$$Q' = \frac{1}{\sigma_3}$$

Now, Equation 3.26 can be written as:

$$\frac{dV'}{d\theta} = -\frac{1}{\sigma_3} \Rightarrow (1 - V') = \frac{1}{\sigma_3}(\theta - \theta_2)$$

or

$$V' = 1 - \frac{1}{\sigma_3}(\theta - \theta_2)$$
 (3.31)

At the end of the cycle $\theta = \theta_3$, $V' = \delta$ and, Equation 3.31 implies that:

$$\delta = 1 - \frac{1}{\sigma_3}(\theta_3 - \theta_2) \Rightarrow \theta_3 - \theta_2 = \sigma_3(1 - \delta)$$
(3.32)

But $(t_3 - t_2)/t_3 = \sigma_3$ i.e.,

$$\sigma_3 = \frac{\theta_3 - \theta_2}{\theta_3} \Rightarrow \theta_3 - \theta_2 = \sigma_3 \theta_3 \tag{3.33}$$

From Equation 3.32 and 3.33 one finds that

$$\theta_3 = 1 - \delta \tag{3.34}$$

Therefore Equations 3.32 and 3.34 imply that

$$(1-\delta)(1-\sigma_3) = \theta_2 \tag{3.35}$$

Hence one can finally conclude the following:

Reaction period : $(1 - \delta)\sigma_1 \le \theta \le (1 - \delta)(1 - \sigma_3)$

Draw-down period: $(1 - \delta)(1 - \sigma_3) \le \theta \le 1 - \delta$

Also during the draw-down period (from Equation 3.31 and Equation 3.35)

$$V' = 1 - \frac{1}{\sigma_3} [\theta - (1 - \delta)(1 - \sigma_3)]$$

In view of the above, the final formulation of the problem is the following:

Filling phase: $0 \le \theta \le \sigma_1(1-\delta)$

$$\frac{du}{d\theta} = \frac{1}{\delta\sigma_1 + \theta} (u_f - u) - \beta x \frac{u}{1 + u}$$
(3.36)

$$\frac{dv}{d\theta} = \frac{1}{\delta\sigma_1 + \theta} (v_f - v) + \rho\beta x \frac{u}{1 + u} - \eta\phi\beta x \frac{v}{\omega + v + \gamma v^2}$$
(3.37)

$$\frac{dx}{d\theta} = -\frac{1}{\delta\sigma_1 + \theta}x + \beta x \frac{u}{1+u} + \phi\beta x \frac{v}{\omega + v + \gamma v^2} - \epsilon\beta x v \qquad (3.38)$$

Reaction and Draw-down phases: $(1 - \delta)\sigma_1 \le \theta \le 1 - \delta$

$$\frac{du}{d\theta} = -\beta x \frac{u}{1+u} \tag{3.39}$$

$$\frac{dv}{d\theta} = \rho\beta x \frac{u}{1+u} - \eta\phi\beta x \frac{v}{\omega+v+\gamma v^2}$$
(3.40)

$$\frac{dx}{d\theta} = \beta x \frac{u}{1+u} + \phi \beta x \frac{v}{\omega + v + \gamma v^2} - \epsilon \beta x v \qquad (3.41)$$

Chapter 4 Simulation Results & Discussion

The mathematical models developed in Chapter 3 have been solved by fourth order Runga-Kutta numerical analysis using FORTRAN based programs on a VAX/VMS system. FORTRAN codings of these programs are listed in Chapter 8.

From Sunflower Army Ammunition Plant, Kansas, batch experimental data were received. The main objective of the simulation was to imitate the experimental data in order to generate a similar qualitative response and thereby confirm the validity of the models.

First, the batch experimental data were analyzed, and they are presented in Tables 6.4 to 6.17. It should be noted that the data did not indicate biomass concentration measurements. Furthermore, environmental factors, such as pH, temperature, and dissolved oxygen were not monitored. Finally, the data were from single cycle batch experiments, that is the operation was never repeated with the same reactor contents. The variation in the data (as can be seen from the tables) is such that it is obvious that many of the parameters that were not monitored, changed from run to run, if not during each run as well. Consequently, the data could not be used but for getting an idea of the response of the system qualitatively and, only during the first batch cycle.

Ranges were selected for the model parameters, which appeared to be reasonable based on past experience. Once successful simulation was achieved, the model parameters were then used to simulate different modes of SBR operation.

4.1 Simulation of the Batch Process

Table 6.16 gives the preselected ranges of the model parameters.

4.1.1 1st Cycle Response of the Batch Process

In Figures 7.2 to 7.7, the comparison between the simulated data and the experimental data is shown. During simulation, it was found that ρ,η and ϕ (see Page 45 for definitions) are the most important parameters. Changes in these parameters give different concentration profiles. If one looks at Equation 3.11, the derivative for nitrite concentration, the rate of change of nitrite concentration will be positive if the first term on the left hand side of the equation is higher than the second term. Physically, this means that the rate of formation of nitrite is more than the rate of biological consumption. Therefore, a high value of ρ and low values of η and ϕ will result in a rapid accumulation of nitrite. On the other hand, for a low value of ρ and high values of ϕ and η , consumption of nitrite is much higher than its formation, and as a result nitrite does not accumulate

at all. Finally, if ρ , ϕ and η are all high then initially (since nitrate is present) nitrite will start to accumulate, but will decrease quite fast when the first term of Equation 3.11 disappears because of zero nitrate concentration. Another way of increasing the second term of Equation 3.11 (i.e., nitrite consumption) would be to decrease its denominator, which means a decrease in ω and γ .

For the simulation dimensionless quantities have been used. Since the main objective of this study is to confirm the correct qualitative response of the models, no effort was made to match the data quantitatively. δ was kept constant at 0.5 in all the runs

In Figures 7.2 (c) and (d) the values of ω , γ and ρ are high while η and ϕ are low. As a result, high nitrite accumulation is observed which can be clearly understood if one looks at Equation 3.11. Only the value of ρ changes for the diagrams of Figures 7.2 (c) and (d). A decrease in ρ (i.e., conversion of nitrate to nitrite), has led to a decrease in nitrite build-up even though the initial nitrate concentration is higher for case of Figure 7.2 (d).

In Figure 7.3 one can see that in (b) because of higher initial nitrate concentration the nitrite accumulation is slightly higher than that of in (a). A similar kind of response was obtained from the simulation (Note, nitrate and nitrite concentration in (d) are higher than those in (c)). Other than this, the time required for nitrate to go to zero is higher in (b) than in (a); (c) and (d) also show similar kinds of behavior. Parameters are changed in (d); this was done to get same derivative $(dv/d\theta)$ in both runs, and as a result the concentration

profile for nitrite does not change significantly from (d) to (c) even though in (d) the initial nitrate concentration is higher.

In Figure 7.4, one can see that high values of ρ , η and ϕ give an initial build-up of nitrite and thus, this concentration goes through a maximum. Physically this means that the production of nitrite is high, but the reaction time is high enough to allow nitrate to be degraded; after that point nitrite is no longer produced while it continues being treated, and thus its concentration drops.

In Figure 7.5, the values of ρ , η and ϕ are decreased from those used in Figure 7.5. As a result, nitrite build-up also decreases.

In Figure 7.6 (a), the initial nitrate concentration is 320 ppm while that in Figure 7.6 (b) is 280 ppm. As a result, there is a higher nitrite accumulation in (a) than in (b). Similar kind of concentration profiles were simulated qualitatively in Figures 7.6 (c) & (d). In (c) the initial nitrate is lower, and therefore there is less nitrite accumulation than in (d). Here also the model is successful in imitating the process dynamics qualitatively.

Finally in Figure 7.7 (a), since the initial nitrite concentration is higher, the accumulation of nitrite is more in (a) than (b). Qualitative simulation of these experimental runs are given in (c) and (d) respectively. In (c) beginning with a higher nitrite concentration, a higher nitrite accumulation is observed. In order to do this γ was increased and η and ϕ were decreased, which means the second term in Equation 3.11 (i.e., consumption rate of nitrite) was decreased, and as a
result nitrite accumulated in the system.

Therefore, from Figures 7.3 through 7.8, one can see that the batch model is capable of reproducing the biodegradation behavior qualitatively.

The cycles of data received from Kansas were unique in nature i.e., there was no continuity from one cycle to another because of several reasons:

- Concentration of biomass was never controlled i.e, it varied form one experiment to another. The total suspended solids may have remained within a certain range, but the activity of the biomass, as well as the concentration of nitrate/nitrite reductases must have varied widely because experiments were never done round the clock and the biomass had enough time to get to exposed to aerobic conditions. As a result of this, the fraction of denitrifiers in the sludge varied, giving different concentration profiles with same inlet nitrate concentration.
- Initial nitrate concentration was not constant in any of the experiments. Previous research as well as simulations, showed that the initial ratio of nitrate to biomass is an important parameter.
- Initial nitrite concentration also varied, thereby introducing another variable parameter in to the system.
- A complex process like denitrification needs meticulous control and constant monitoring of environmental parameters. The pH, dissolved oxygen, and presence of other ions should be controlled, and since this was not

done, different responses were obtained with same inlet concentrations, of nitrate and nitrite.

As a result, it was not possible to reproduce the data quantitatively but the model could simulate the process responses qualitatively with great success.

4.1.2 Steady Cycle Response of the Batch Process

In Figures 7.8 through 7.13, the steady cycle response of the degradation process is shown.

In Figure 7.8, the time allowed for reaction is not sufficient enough for nitrite to be degraded completely, and as a result the steady cycle also shows a high nitrite accumulation.

In Figures 7.9 (a) and (c) in the first cycle there is not only a nitrite build up, but also rection occurs throughout the time allowed while when the steady cycle is reached, complete degradation of both nitrate and nitrite is achieved much before the end of the time allowed. This is because of two reasons:

- I. Because of dilution in case of the steady cycle, one starts with smaller concentration of nitrate and nitrite.
- II. Because of continuous exposure and growth of the biomass, the active biomass concentration in the steady cycle is much higher than in the first cycle.

This indicates that cyclic batch operation is much better than the discontinued batch. One can see the same results in Figures 7.10 to 7.13. The interesting new feature is that while the first cycle there is a nitrite build-up, this does not happen when the steady cycle is reached.

4.2 Simulation of the SBR Process

After successful simulation of the batch data, simulation of a sequencing batch process was carried out to compare the nitrite build up in the first, as well as in the steady cycle. Here the values $\beta = 5.0$ and $\delta = 0.5$ were used on the basis of previous experience [46,11]. The fill time was kept constant at σ_1 at 0.5. In practice σ_1 generally varies from 0.1 to 0.25 but here the fill period was selected to be high in order to eliminate the possibility of nitrite accumulation.

In Figures 7.14 to 7.25 the SBR process is compared with the batch process. For the purpose of comparison, all the model parameters, as well as the initial concentration of biomass, and the feed concentrations of nitrate and nitrite, were kept the same for simulation of both SBR and batch processes.

In Figures 7.14 and 7.15 one can see that for the SBR process, a high fill time could not eliminate nitrite accumulation. In fact, the steady cycle response of the SBR system shows insignificant reduction in nitrite. This may be a result of the suppression of nitrite reductases because of the toxic effect of nitrite. From Figures 7.16 to 7.25, one can see that in the SBR process, accumulation of nitrite is very small in the steady cycle, only 5 to 10 % of that in the batch mode. Therefore, in addition to the operational advantages of the SBR, it greatly reduces the potential for nitrite accumulation.

Chapter 5 Conclusion and Recommendation

The models developed in Chapter 3 are highly realistic and very successful in describing the denitrification process. Selection of the parameters was also consistent with the biology of the process. The batch data received from Kansas have been qualitatively reproduced but because of inconsistency in the experimental data an exact determination of the values of the model parameters could not be obtained. The SBR process shows a definite positive advantage over the batch process as far as accumulation of nitrite is concerned.

Experiments should be conducted in a highly controlled environment in order to obtain the system parameters. One way would be to start carrying out the degradation under nitrite limitation only (i.e., starting with nitrite only). This way, the values for the Andrews model kinetic constants could be calculated. Then, further experiments with both nitrate and nitrite would result in the determination of the Monod kinetic parameters. After the model parameters are obtained the equations describing the degradation process could be used to design reactors and select operating parameters for optimizing the process.

Chapter 6

Tables

Reactor	Substrate	Temperature	SDNR	X	Reference
<u>I ype</u>		deg C		1	
	Fusel Oil	-	400	VSS	19
USB	Fusel Oil	20.5	336	VSS	60
	Methanol	20.0	100	VSS	19
AS	Methanol	21	400-800	VSS	19
Batch	Glucose	25	120-240	VSS	2
CFSTR	Methanol		290	VSS	17
AS	Industrial		620	VSS	34
	Waste				
	Industrial	15	4560	VSS	19
	Waste				
CFSTR	Industrial	20	8640	VSS	19
	Waste				
	Glucose	20	2.2	SS	73
Batch	2 X Glucose	20	7.7	SS	73
	Poultry	20	3.6	SS	73
	Waste				
AS	Methanol	26	92,800	VSS	31
USB	Glycerol	20	50-220	SS	33
UPC &	Methanol	29-31	100-900	VSS	45
CFSTR					
	Methanol	20	40-80	SS	84
AS	Methanol	20	150-180	SS	84
	Pesticide	20	75-100	SS	84
Batch	Methanol	5-27	312-4320	VSS	22
	Industrial	21	82	VSS	51
	Waste				
CFSTR	Industrial	15	71	VSS	51
	Waste				
	Industrial	11	11	VSS	51
	Waste				

Table 6.1: Reported Values of Specific Denitrification Rates (SDNR, mg $NO_{3}\text{-}\mathrm{N/g}$ X-day)

Reactor	Substrate	Temperature	SDNR	X	Reference
Type		deg C			
CFSTR	Methanol	27-31	850	VSS	30
pH=8.0					
CFSTR	Methanol	27-31	2630	VSS	30
pH=8.0					
CFSTR	Methanol	27-31	4680	VSS	30
pH=8.0					
	Methanol	32	1300	VSS	72
	Methanol	32	1400	_	12
	Methanol	9	192	-	63
	Methanol	22.5	593		63
	Methanol	20	852	-	61
	Methanol	25	2900	-	98
	methanol	20	17-264	-	25
	Methanol	20	12-216	-	42
SG	Methanol	20	250	VSS	42
SG	Wastewater	20	70	VSS	42
	Wastewater	25	100-200	VSS	89
AS	or	15	35-90	-	89
	Methanol	7	14-30	-	89
		19	63	VSS	85
		7	30	VSS	85
		20	73	VSS	15
Batch	Raw Waste	15	50	VSS	89
	Water				
Batch	Brewery	-	220-250	VSS	97
	Waste				
Batch	Methanol	_	360-600	VSS	17
Batch	Methanol		150-400	VSS	92
Batch	Volatile	_	360-600	VSS	19
	Acids	-			

Reactor Type	Substrate	Temperature deg C	SDNR	X	Reference
Batch	Glucose	25	60-70	VSS	2
Batch	Sewage	25	34-60	VSS	2
Batch	Sewage	****	50-70	VSS	16
Batch	Sewage		70	VSS	92
AS	Methanol	20	180	SS	61
AS	Raw Sewage	22-25	13	SS	42
AS	Raw Sewage	22-25	46	-	3
AS	Industrial	22-25	324	SS	34
	Waste				
Packed Bed	Raw Sewage	29	12	VSS	57
Packed Bed	Methanol	25	53	SS	77
Anerobic	Methanol	27	214	VSS	82
Column					
CFSTR	10% Ind.	20	624-2400	VSS	51
	Waste				
CFSTR	25% Ind.	20	940-3050	VSS	51
	Waste				

Source	Organisms	Temperature	Specific Rate
		deg C	$(mgNO_3- N/mg-X-day)$
Pichinoty and	Micrococcus	32	0.056
D'Ornano	Denitrificans		
Chang and	Micrococcus	32	0.059
Morvis	Denitrificans		
Mulbarger	Activated	9	0.008
	Sludge	22.5	0.0347
Moore and	Activated	20	0.0355
Schroeder	Sludge		
Meschner and	Mixture of 6	25	0.12
Wuhrmann	Bacterial Sp.		
Eckenfelder	Activated	20	0.0007-0.011
and Balakrishnan	Sludge		
Johnson and	Activated	20	0.0005-0.009
Schroepner	Sludge		

Table 6.2: Denitrification Rate Data

Table 6.3: Denitrification Rates With Various Carbon Sources

Carbon Source	Denitrification Rates	Reference
	$(mgNO_3-N/mg-X-day)$	
Brewary Wastes	0.22-0.25	97
Methanol	0.36-0.60	77
Methanol	0.15-0.40	92
Volatile Acids	0.36	19
Glucose	0.06-0.07	2
	0.34-0.06	2
Sewage	0.05-0.07	16
	0.07	92

NO_3 -N	NO_2 -N
mg/l	mg/l
373.0	19.0
712.0	85.0
321.0	175.0
283.0	250.0
244.0	375.0
227.0	375.0
168.0	400.0
102.0	475.0
67.40	575.0
72.9	650.0
	$\begin{array}{c} NO_3-N\\ mg/l\\ 373.0\\ 712.0\\ 321.0\\ 283.0\\ 244.0\\ 227.0\\ 168.0\\ 102.0\\ 67.40\\ 72.9\\ \end{array}$

Table 6.4: BatcH Data From Kansas (10/20/89)

.

TIME	NO_3 -N	NO_2 -N
hr	mg/l	mg/l
13:30	883.2	31.0
13:50	849.0	59.0
14:10	850.0	65.0
14:33	812.0	74.0
14:50	788.0	72.0
15:10	797.0	79.0
15:30	724.0	86.0
16:30	646.0	142.0
17:30	587.0	275.0
18:30	311.0	295.0
19:30	453.0	280.0
20:30	278.0	350.0

Table 6.5: BatcH Data From Kansas (09/03/89)

TIME	NO_3-N	NO_2 -N
hr	mg/l	mg/l
	740.0	28.0
12:40	707.0	47.0
13:13	707.0	-
13:33	641.0	87.0
14:05	598.0	105.0
14:25	560.0	160.0
15:38	-	172.5
16:38	601.0	295.0
17:30	223.0	92.0
18:30	111.0	262.5
19:30	50.30	137.0
20:30	35.2	125.0

Table 6.6: Batch Data From Kansas (08/31/89)

TIME	NO_3 -N	NO_2 -N
hr	mg/l	mg/l
12:00	669.0	27.40
12:45	644.0	—
14:10	466.0	
15:15	307.0	—
17:15	58.7	128.0
18:15	10.2	40.8

Table 6.7: Batch Data From Kansas (08/28/89)

TIME	NO_3 -N	NO_2-N
hr	mg/l	mg/l
09:15	656.4	74.0
09:35	534.8	113.0
09:55	498.8	140.0
10:15	538.8	150.0
10:35	480.0	200.0
11:15	531.2	250.0
12:15	478.1	350.0
13:15	330.5	475.0
14:15	323.2	550.0
17:15	490.0	850.0
18:45	247.0	850.0
19:15	32.6	600.0
20:15	37.9	425.0

Table 6.8: Batch Data From Kansas (09/08/89)

TIME	NO_3 -N	NO_2 -N
hr	mg/l	mg/l
11:30	666.0	133.0
11:50	679.0	200.0
12:10	589.0	250.0
12:30	570.0	300.0
12:50		325.0
13:10	595.0	400.0
13:30	513.0	450.0
14:30	454.0	500.0
15:30		825.0
17:30	183.0	1000.0
18:30	136.0	1000.0
19:30	40.6	425.0

Table 6.9: Batch Data From Kansas (10/10/89)

TIME	NO_{3} -N	NO_{2} -N
hr	mg/l	mg/l
15:07	336.0	29.0
15:25	345.0	60.0
15:45	271.0	125.0
16:05	224.0	150.0
16:25	176.0	175.0
16:45	126.0	200.0
17:05	78.20	225.0
18:05	0.178	0.0

Table 6.10: Batch Data From Kansas (09/22/89)

.

	NO N	NO N
TIME	IVO_3-IN	NO_2-N
hr	mg/l	mg/l
10:00	222.1	49.0
10:20	181.1	81.0
10:40	148.3	119.0
11:00	130.0	149.0
11:20	110.0	162.0
11:40	77.9	163.0
12:00	44.6	—
13.00	0.45	90
14:00	0.14	0.0

Table 6.11: Batch Data From Kansas (09/20/89)

TIME	NO_3 -N	NO ₂ -N
hr	mg/l	mg/l
	283.1	72.0
10:20	194.5	150.0
10:40	164.3	225.0
11:00	106.7	300.0
11:40	23.2	350.0
12:00	10.6	250.0
13:07	0.24	5.0
14:00	0.19	9.0

Table 6.12: Batch Data From Kansas (09/22/89)

TIME	NO_3 -N	NO_2 -N
hr	mg/l	mg/l
09:40	296.0	70.0
10:00	240.0	150.0
10:20	200.0	250.0
10:40	140.0	350.0
11:00	99.3	400.0
11:20	69.2	425.0
11:40	31.6	500.0
12:40	11.7	200.0
13:40	0.1	9.0

Table 6.13: Batch Data From Kansas (09/27/89)

	-	
TIME	NO_3 -N	NO_2 -N
hr	mg/l	mg/l
10:20	428.6	225.0
10:40	335.8	325.0
11:00	281.6	375.0
11:20	217.0	500.0
11:40	187.0	575.0
12:00	130.6	625.0
13:00	17.10	575.0
14:00	8.0	300.0
15:00	0.10	5.0

Table 6.14: Batch Data From Kansas (10/02/89)

TIME	NO_3 -N	NO_2 -N
hr	mg/l	mg/l
11:20	216.0	68.0
11:40	183.0	160.0
12:00	135.0	156.0
12:20	102.0	196.0
12:40	65.8	228.0
13:00	29.9	256.0
14:00	0.1	0.0

Table 6.15: Batch Data From Kansas (09/21/89)

Parameter	Range
τ	1.0-2.5
ϕ	1.0-8.0
γ	1.0-3.0
η	2.0-16.0
ρ	0.3–2.5
E	0.0–0.001
ω	1.0-10.0

·

Chapter 7 Figures







Figure 7.3: Comparison of Experimental Data With Simulated Data



Figure 7.2: Comparison of Experimental Data With Simulated Data





Figure 7.4: Comparison of Experimental Data With Simulated Data





• NO3-N • NO2-N

TIME, min

200

260

50

MGEI7



PAGE14

Figure 7.5: Comparison of Experimental Data With Simulated Data





(b)

250

Figure 7.6: Comparison of Experimental Data With Simulated Data





Figure 7.7: Comparison of Experimental Data With Simulated Data



Figure 7.8: Comparison of 1st Cycle Batch With Steady Cycle Batch



ASS.CHT

Figure 7.9: Comparison of 1st Cycle Batch With Steady Cycle Batch



BEACHT Figure 7.10: Comparison of 1st Cycle Batch With Steady Cycle Batch



CSI.CHT

Figure 7.11: Comparison of 1st Cycle Batch With Steady Cycle Batch



Figure 7.12: Comparison of 1st Cycle Batch With Steady Cycle Batch


Figure 7.13: Comparison of 1st Cycle Batch With Steady Cycle Batch





SAI.CHT

95

ASI.CHT

SIMULATED BATCH DATA STEADY CYCLE (AFTER 21 CYCLES)





Figure 7.14: Comparison of Batch With SBR





SA2.CHT







Figure 7.15: Comparison of Batch With SBR





AS3.CHT

Figure 7.16: Comparison of Batch With SBR





SIMULATED SBR DATA



SIMULATED SBR DATA

SA4CHT

86

SIMULATED BATCH DATA **STEADY CYCLE (AFTER 19 CYCLES)**







SAS4.CHT Figure 7.17: Comparison of Batch With SBR





Figure 7.18: Comparison of Batch With SBR









Figure 7.19: Comparison of Batch With SBR





SCLCHT

101

SIMULATED BATCH DATA **STEADY CYCLE (AFTER 20 CYCLES)**



SIMULATED SBR DATA **STEADY CYCLE (AFTER 20 CYCLES)**





SCILCRT Figure 7.20: Comparison of Batch With SBR





(b)

0.5

Figure 7.21: Comparison of Batch With SBR

CH1CH?



0.2 0.1

n

0

0.1

0.2

0.3

dimensionless time

---- NO3 ---- NO2

0.4

0.5

0.6



25

2

1.6

1

dimensionless time

---- NO3 ---- NO2

103

0

C\$3.CHT

0

0.5



Figure 7.23: Comparison of Batch With SBR



105

SIMULATED BATCH DATA **STEADY CYCLE (AFTER 20 CYCLES)**



SIMULATED SBR DATA **STEADY CYCLE (AFTER 20 CYCLES)**





40 35 30

25 20 16

10

Figure 7.24: Comparison of Batch With SBR

SCS5.CHT



Figure 7.25: Comparison of Batch With SBR

Chapter 8 Program Listing

С c THIS PROGRAM GIVES THE CONCENTRATION OF SUBSTRATE, BIOMASS, PRODUCT * С IN A SBR С С WITH RESPECT TO TIME. С С HERE RUNGA KUTTA NUMERICAL METHOD IS USED TO SOLVE A SET С OF * С NONLINEAR ORDINARY DIFFERENTIAL EQUATIONS. С * С С C_____ С С INITIALIZATION С implicit double precision (a-h,o-z) C С common tm(100000),um(100000),xm(100000),pm(100000), &tmt(100000),umt(100000),xmt(100000),pmt(100000)

```
open(10,file='[sxs3943.thesis.final]s1in1.dat',status='old')
     open(20,file='[sxs3943.thesis.final]s1out1.dat', status='new')
     open(30,file='[sxs3943.thesis.final]s1out2.dat', status='new')
     open(40,file='[sxs3943.thesis.final]s1out3.dat', status='new')
С
C-----INPUT DATA-----
С
С
     read(10,*) delta,phi,gamma,w
     read(10,*) eta,rho,eps
     read(10,*) beta,uf,xf,pf
     read(10,*) u0,x0,p0
     read(10,*) n_pcycle,n_scycle
     read(10,*) step,last
     read(10,*) sigma1
     read(10,*) dif
     read(10,*) ans
С
С
     time3=(1.0-delta)
     np=time3/step
С
С
```

109

```
u=u0
      x=x0
      p=p0
С
      u_init=u0
      x_init=x0
      p_init=p0
С
С
      if(ans.eq.0.0) then
      n_scycle=1
      endif
с
С
      if (n_pcycle.gt.n_scycle) then
      ncycle=n_pcycle
      else
      ncycle=n_scycle
      endif
С
С
     do 100 icycle=1,ncycle,1
С
С
```

```
tm(1)=0.0
      um(1)=u0
      xm(1)=x0
      pm(1)=p0
С
С
      call process(delta, phi, gamma, w, eta, rho, eps, ncycle,
     & beta,last,u_init,x_init,p_init,np,icycle,step,time3,
     & uf,xf,pf,u,x,p,sigma1,dif,n_pcycle,n_scycle,
     & u_last,x_last,p_last)
С
С
      if (ncycle.eq.1) then
      goto 400
      endif
С
с
      if(icycle.eq.ncycle) then
      goto 100
      endif
С
С
      call new_values(u_last,x_last,p_last,u0,x0,p0)
С
```

c-----here u0,x0,p0 become the initial value for the next cycle---с С С u=u0x=x0p=p0 С c----С if(ans.eq.0.0) then goto 100 endif С С if(icycle.eq.1) then goto 32 endif С С do 31 ii=1,np,1 if(abs(tmt(ii)-tm(ii)).gt.dif) then goto 32 else if(abs(umt(ii)-um(ii)).gt.dif) then

```
goto 32
        else if(abs(xmt(ii)-xm(ii)).gt.dif) then
              goto 32
        else if(abs(pmt(ii)-pm(ii)).gt.dif) then
              goto 32
С
        endif
С
С
      if(ii.eq.np) then
      call print_3(delta,phi,gamma,w,eta,rho,eps,uf,xf,pf,
     & last,tm,um,xm,pm,u_init,x_init,p_init,np,n_pcycle,
     & beta,dif,step,n_scycle,icycle,sigma1)
с
      goto 400
С
      endif
С
c
   31 continue
c
С
   32 do 33 jj=1,np,1
С
```

113

tmt(jj)=tm(jj)

umt(jj)=um(jj)

xmt(jj)=xm(jj)

pmt(jj)=pm(jj)

С 33 continue С С 100 continue С С 400 stop end с С С C-----END OF MAIN PROGRAM------С С c-----SUBROUTINE PROCESS BEGINS HERE------С С С С

subroutine process(delta,phi,gamma,w,eta,rho,eps, æ ncycle,beta,last,u_init,x_init,p_init,np,icycle, \$ step,time3,uf,xf,pf,u,x,p, & sigma1,dif,n_pcycle,n_scycle,unxt,xnxt,pnxt) С С implicit double precision(a-h,o-z) С С common tm(100000),um(100000),xm(100000),pm(100000) С j=1 С С do 30 time=0.000000001,time3,step С С С j=j+1 С С С c----here we check whether the fill period is over------С

```
b=0.0
    if(time.le.(sigma1*(1.0-delta))) then
    b=1.0
    endif
С
С
c----here we determine the values
         of substrate, biomass and product
С
С
       call RungaKutta1(b,delta,phi,gamma,w,eta,rho,
        eps,beta,sigma1,step,time,uf,xf,pf,u,x,p,
   &
   &
        unxt, xnxt, pnxt)
С
С
c-----here we store the instantaneous values-----
С
С
         um(j)=unxt
         xm(j)=xnxt
         pm(j)=pnxt
         tm(j)=time+step
```

```
С
                      c-----
            u=unxt
            x=xnxt
            p=pnxt
С
   30 continue
С
С
     if (icycle.eq.1) then
     call print_1(delta,phi,gamma,w,eta,rho,eps,uf,xf,
    & pf,last,tm,um,xm,pm,u_init,x_init,p_init,np,
    & n_pcycle, beta, dif, step, n_scycle, sigma1)
     endif
С
С
 500 if(icycle.eq.n_pcycle) then
С
     call print_2(delta,phi,gamma,w,eta,rho,eps,uf,
    & xf,pf,last,tm,um,xm,pm,u_init,x_init,p_init,np,
    & n_pcycle, beta, dif, step, n_scycle, sigma1)
С
     endif
С
```

```
С
  600 return
      end
С
С
c-----SUBROUTINE_1 RUNGAKUTTA BEGINS HERE------
с
С
С
     subroutine RungaKutta1(b,delta,phi,gamma,w,eta,rho,
    & eps,beta,sigma1,step,t,uf,xf,pf,u,x,p,unxt,xnxt,pnxt)
С
     implicit double precision (a-h,o-z)
С
С
      fun(t2)=b/(t2+delta*sigma1)
¢
      fun1(t1,u1,x1,p1)=(b/(t1+delta*sigma1))*(uf-u1)-
    & (beta*u1*x1)/(1.0+u1)
      fun2(t1,u1,x1,p1)=(-b/(t1+delta*sigma1))*x1+(beta*x1)*
    & (u1/(1.0+u1))+(beta*phi*x1*p1)/(w+p1+gamma*(p1**2))
    & -eps*beta*x1*p1
      fun3(t1,u1,x1,p1)=(b/(t1+delta*sigma1))*(pf-p1)+(rho*beta*x1)*
    & (u1/(1.0+u1))-(eta*phi*beta*p1*x1)/(w+p1+gamma*(p1**2))
```

```
uk1=step*fun1(t,u,x,p)
xk1=step*fun2(t,u,x,p)
pk1=step*fun3(t,u,x,p)
```

```
uk2=step*fun1((t+step/2.0),(u+uk1/2.0),(x+xk1/2.0),(p+pk1/2.0))
xk2=step*fun2((t+step/2.0),(u+uk1/2.0),(x+xk1/2.0),(p+pk1/2.0))
pk2=step*fun3((t+step/2.0),(u+uk1/2.0),(x+xk1/2.0),(p+pk1/2.0))
```

С

С

С

```
uk3=step*fun1((t+step/2.0),(u+uk2/2.0),(x+xk2/2.0),(p+pk2/2.0))
xk3=step*fun2((t+step/2.0),(u+uk2/2.0),(x+xk2/2.0),(p+pk2/2.0))
pk3=step*fun3((t+step/2.0),(u+uk2/2.0),(x+xk2/2.0),(p+pk2/2.0))
```

С

С

С

С

```
uk4=step*fun1((t+step),(u+uk3),(x+xk3),(p+pk3))
xk4=step*fun2((t+step),(u+uk3),(x+xk3),(p+pk3))
pk4=step*fun3((t+step),(u+uk3),(x+xk3),(p+pk3))
```

```
unxt=u+(1.0/6.0)*(uk1+2.0*uk2+2.0*uk3+uk4)
xnxt=x+(1.0/6.0)*(xk1+2.0*xk2+2.0*xk3+xk4)
pnxt=p+(1.0/6.0)*(pk1+2.0*pk2+2.0*pk3+pk4)
```

```
return
    end
С
c-----END OF RUNGAKUTTA SUBROUTINE-----
С
С
С
c-----SUBROUTINE NEW_VALUUES BEGINS HERE-----
С
с
    subroutine new_values(u_last,x_last,p_last,u0,x0,p0)
С
С
    implicit double precision (a-h,o-z)
С
С
    u0=u_last
    x0=x_last
    p0=p_last
С
С
    return
    end
```

c-----SUBROUTINE NEW_VALUUES ENDS HERE-----С С c----- SUBROUTINE PRINT-1 BEGINS HERE------С С subroutine print_1(delta,phi,gamma,w,eta,rho,eps,uf,xf, & pf,last,tm,um,xm,pm,u_init,x_init,p_init,np,n_pcycle, & beta,dif,step,n_scycle,sigma1) С С implicit double precision (a-h,o-z) С dimension tm(100000),um(100000),xm(100000),pm(100000) С C-----PRINT INPUT DATA ON OUTPUT FILE------С С WRITE(20,140) WRITE(20,160)

- 160 FORMAT(//10X,' SEQUENCING BATCH REACTOR ') WRITE(20,150)
- 150 FORMAT(//10X,'CONCENTRATION OF SUBSTRATE, BIOMASS AND PRODUCT'//) WRITE(20,140)

WRITE(20,151)

151 FORMAT(//10X,' DURING Ist CYCLE'//) WRITE(20,140)

write(20,201)delta, phi, gamma, w

201 format(/1x,'DELTA='F10.5,4X,'PHI=',F10.5,4X,

&'GAMMA=',F12.5,4X,'W=',F10.5)

write(20,202) eta, rho, eps, beta

202 format(/1x,'ETA=',F10.4,4X,'RHO=',F10.5,4X,'EPS=',F10.5,4X,
& 'BETA=',F10.5)

write(20,203)uf,xf,pf

- 203 format(/1x,'UF=',F10.5,4X,'XF=',F10.5,4X,'PF=',F10.5)
 write(20,204)u_init,x_init,p_init
- 204 format(/1x,'U0=',F10.5,4X,'X0=',F10.1,4X,'P0=',F10.5)
 write(20,205) np,step
- 205 format(/1x,'NUMBER OF POINTS IN THE TIME DOMAIN=',I10,10X//

& 1x,'STEP SIZE =',F10.6//)

WRITE(20,140)

write(20,206) sigma1

206 format(//1x,' SIGMA1 = ', F10.5//)

WRITE(20,140)

```
write(20,207)
  207 format(/1x,'TIME',15X,' U ',15X,' X ',15X,' P ')
С
C-----PRINT COMPUTED DATA INTO OUTPUT FILE------
С
С
     do 40 i=1,np+1,last
С
С
          write(20,210) tm(i),um(i),xm(i),pm(i)
  210 format(1X,f10.5,5x,f10.5,5x,f10.5,5x,f10.5)
  40 continue
С
С
     return
С
     end
С
С
c----- SUBROUTINE PRINT-1 ENDS HERE------
С
С
С
С
```

123

c----- SUBROUTINE PRINT-2 BEGINS HERE------С С subroutine print_2(delta,phi,gamma,w,eta,rho,eps, & uf,xf,pf,last,tm,um,xm,pm,u_init,x_init,p_init,np, & n_pcycle,beta,dif,step,n_scycle,sigma1) С С implicit double precision (a-h,o-z) С dimension tm(100000),um(100000),xm(100000),pm(100000) с С C-----PRINT INPUT DATA ON THE SECOND OUTPUT FILE------С С WRITE(30,1400)

WRITE(30,1600)

1600 FORMAT(//10X,' SEQUENCING BATCH REACTOR ') WRITE(30,1500)

1500 FORMAT(//10X, 'CONCENTRATION OF SUBSTRATE, BIOMASS AND PRODUCT'//)

WRITE(30,1400)

write(30,1550)n_pcycle

1550 format(//10x,' DURING ',15,4x,'CYCLES'//) WRITE(30,1400)

write(30,2010)delta,phi,gamma,w

2010 format(/1x,'DELTA='F10.5,4X,'PHI=',F10.5,4X,

&'GAMMA=',F12.5,4X,'W=',F10.5)

write(30,2020) eta, rho, eps, beta

2020 format(/1x,'ETA=',F10.4,4X,'RHO=',F10.5,4X,'EPS=',F10.5,4x,

& 'BETA=',F10.5)

write(30,2030)uf,xf,pf

2030 format(/1x,'UF=',F10.5,4X,'XF=',F10.5,4X,

&'PF=',F10.5)

write(30,2040)u_init,x_init,p_init

- 2040 format(/1x,'U0=',F10.5,4X,'X0=',F10.5,4X,'P0=',F10.5)
 write(30,2050) np,step
- 2050 format(/1x,'NUMBER OF POINTS IN THE TIME DOMAIN=', I5//

```
& 1x,'STEP SIZE =',F10.6//)
```

WRITE(30,1400)

write(30,2055) sigma1

2055 format(//1x,' SIGMA1 = ', F10.5//)

WRITE(30,1400)

write(30,2060)

2060 format(/1x,'TIME',15X,' U ',15X,' X ',15X,' P ')

С C-----PRINT COMPUTED DATA INTO OUTPUT FILE-----С С do 41 i=1,np+1,last С С write(30,2100) tm(i),um(i),xm(i),pm(i) 2100 format(1X,f10.5,5x,f10.5,5x,f10.5,5x,f10.5) 41 continue С С return С end С c-----SUBROUTINE PRINT-2 ENDS HERE------С С С C c----- SUBROUTINE PRINT-3 BEGINS HERE------С С

```
subroutine print_3(delta,phi,gamma,w,eta,rho,eps,uf,
    & xf,pf,last,tm,um,xm,pm,u_init,x_init,p_init,np,n_pcycle,
    & beta,dif,step,n_scycle,icycle,sigma1)
С
     implicit double precision (a-h,o-z)
С
     dimension tm(100000),um(100000),xm(100000),pm(100000)
С
С
C-----PRINT INPUT DATA ON OUTPUT FILE-----
С
С
    WRITE(40,1401)
WRITE(40,1601)
1601 FORMAT(//10X,' SEQUENCING BATCH REACTOR')
    WRITE(40,1501)
1501 FORMAT(//10X,'CONCENTRATION OF SUBSTRATE, BIOMASS AND PRODUCT'//)
    WRITE(40,1401)
    write(40,2052) icycle
2052 format(//1x,'STEADY STATE IS REACHED AFTER', I6, 4X, 'CYCLES'//)
    WRITE(40,1401)
    write(40,2011)delta,phi,gamma,w
```

2011 format(/1x,'DELTA='F10.5,4X,'PHI=',F10.5,4X,

```
&'GAMMA=',F12.5,4X,'W=',F10.5)
```

write(40,2021) eta, rho, eps, beta

write(40,2031)uf,xf,pf

- 2031 format(/1x,'UF=',F10.5,4X,'XF=',F10.5,4X,'PF=',F10.5)
 write(40,2041)u_init,x_init,p_init
- 2041 format(/1x,'U0=',F10.5,4X,'X0=',F10.1,4X,'P0=',F10.5)
 write(40,2051) np,step
- 2051 format(/1x, 'NUMBER OF POINTS IN THE TIME DOMAIN=', I10//

& 1x,'STEP SIZE =',F10.6//)

WRITE(40,1401)

write(40,2053) sigma1,dif

2053 format(//1x,' SIGMA1 = ',F10.5,10x,'DIF='F10.5//) WRITE(40,1401)

write(40,2061)

2061 format(/1x,'TIME',15X,' U ',15X,' X ',15X,' P ')

С

C-----PRINT COMPUTED DATA INTO OUTPUT FILE-----

с с

do 44 i=1,np+1,last

c
С CTHIS PROGRAM GIVES THE CONCENTRATION OF SUBSTRATE, BIOMASS, PRODUCT С IN A BATCH REACTOR WITH RESPECT TO TIME. С С HERE RUNGA KUTTA NUMERICAL METHOD IS USED TO SOLVE A SET OF С С NONLINEAR ORDINARY DIFFERENTIAL EQUATIONS. С С С FINAL VERSION С С **C*** ***** ********** С implicit double precision (a-h,o-z) С С common tm(100000),um(100000),xm(100000),pm(100000), & tmt(100000), umt(100000), xmt(100000), pmt(100000) С С open(10,file='[sxs3943.thesis.final]bin1.dat',status='old')

```
open(20,file='[sxs3943.thesis.final]bout1.dat', status='new')
      open(30,file='[sxs3943.thesis.final]bout2.dat', status='new')
      open(40,file='[sxs3943.thesis.final]bout3.dat', status='new')
С
c-----INPUT DATA-----
С
С
      read(10,*) delta,phi,gamma,w
      read(10,*) eta,rho,eps
     read(10,*) uf,xf,pf
     read(10,*) u0,x0,p0
     read(10,*) n_pcycle,n_scycle
     read(10,*) step,last
     read(10,*) tow
     read(10,*) dif
     read(10,*) range4
     read(10,*) ans
С
С
     np=tow/step
С
С
     res_t=tow/(1.0-delta)
С
```

```
u0=uf
      p0=pf
      u_init=u0
      x_init=x0
      p_init=p0
С
с
      if(ans.eq.0.0) then
      n_scycle=1
      endif
с
с
      if(n_pcycle.gt.n_scycle) then
      ncycle=n_pcycle
      else
      ncycle=n_scycle
      endif
с
с
      do 100 icycle=1,ncycle,1
c
С
с
```

с

```
if (icycle.eq.1) then
      u=uf
      x=x0
      p=pf
      endif
С
С
      tm(1)=0.0
      um(1)=u0
      xm(1)=x0
      pm(1)=p0
С
С
      call process(delta, phi, gamma, w, eta, rho, eps, ncycle, tow, last,
     & u_init,x_init,p_init,np,icycle,step,uf,xf,pf,u,x,p,
     & res_t,dif,n_pcycle,n_scycle,u_last,x_last,p_last)
С
С
      if (ncycle.eq.1) then
      goto 400
      endif
С
С
      if(icycle.eq.ncycle) then
```

```
goto 100
       endif
С
С
      call new_values(uf,xf,pf,delta,u_last,x_last,p_last,
                      u0,x0,p0)
     &
С
¢
      u=u0
      x=x0
      p=p0
С
c
      if(ans.eq.0.0) then
      goto 100
      endif
С
С
      if(icycle.eq.1) then
      goto 32
      endif
С
с
      do 31 ii=1,np,1
```

```
if(abs(tmt(ii)-tm(ii)).gt.dif) then
               goto 32
        else if(abs(umt(ii)-um(ii)).gt.dif) then
               goto 32
        else if(abs(xmt(ii)-xm(ii)).gt.dif) then
              goto 32
        else if(abs(pmt(ii)-pm(ii)).gt.dif) then
              goto 32
С
        endif
С
С
      if(ii.eq.np) then
      call print_3(delta, phi, gamma, w, eta, rho, eps, uf, xf, pf, last,
     & tm,um,xm,pm,u_init,x_init,p_init,np,n_pcycle,tow,dif,step,
     & n_scycle,icycle,res_t)
С
      goto 400
С
      endif
С
С
   31 continue
C
```

135

```
32 do 33 jj=1,np,1
    tmt(jj)=tm(jj)
    umt(jj)=um(jj)
    xmt(jj)=xm(jj)
    pmt(jj)=pm(jj)
```

С

C

С

33 continue

С С С subroutine process(delta,phi,gamma,w,eta,rho,eps,ncycle, tow,last,u_init,x_init,p_init,np,icycle,step,uf,xf,pf, æ & u,x,p,res_t,dif,n_pcycle,n_scycle,unxt,xnxt,pnxt) с С implicit double precision(a-h,o-z) С с common tm(100000),um(100000),xm(100000),pm(100000) С j=1 С do 30 time=0.000000001,tow,step С j=j+1 С write(*,17) С 17 format(1x,'i am here') С c-----here we determine the values of substrate, biomass----and product c-----_____ С

call RungaKutta1(delta, phi, gamma, w, eta, rho, eps,

step,time,u,x,p,unxt,xnxt,pnxt)

С

```
um(j)=unxt
```

xm(j)=xnxt
pm(j)=pnxt
tm(j)=time+step

с

u=unxt x=xnxt

p=pnxt

С

30 continue

```
С
```

С

if (icycle.eq.1) then

call print_1(delta,phi,gamma,w,eta,rho,eps,uf,xf,pf,last,
& tm,um,xm,pm,u_init,x_init,p_init,np,n_pcycle,tow,dif,step,
& n_scycle,res_t)
endif

c c

500 if(icycle.eq.n_pcycle) then

C call print_2(delta,phi,gamma,w,eta,rho,eps,uf,xf,pf,last, & tm,um,xm,pm,u_init,x_init,p_init,np,n_pcycle,tow,dif,step, & n_scycle,res_t) с endif С с 600 return end с С c-----SUBROUTINE_1 RUNGAKUTTA BEGINS HERE------С С С subroutine RungaKutta1(delta,phi,gamma,w,eta,rho,eps, step,t,u,x,p,unxt,xnxt,pnxt) & С С implicit double precision (a-h,o-z) С С fun1(t1,u1,x1,p1)=-(u1*x1)/(1.0+u1)

```
fun2(t1,u1,x1,p1)=x1*(u1/(1.0+u1))+(phi*x1*p1)/
     &
                       (w+p1+gamma*(p1**2))-eps*x1*p1
       fun3(t1,u1,x1,p1)=(rho*x1)*(u1/(1.0+u1))
     & -(eta*phi*p1*x1)/(w+p1+gamma*(p1**2))
С
С
      uk1=step*fun1(t,u,x,p)
      xk1=step*fun2(t,u,x,p)
      pk1=step*fun3(t,u,x,p)
с
С
      uk2=step*fun1((t+step/2.0),(u+uk1/2.0),(x+xk1/2.0),(p+pk1/2.0))
     xk2=step*fun2((t+step/2.0),(u+uk1/2.0),(x+xk1/2.0),(p+pk1/2.0))
     pk2=step*fun3((t+step/2.0),(u+uk1/2.0),(x+xk1/2.0),(p+pk1/2.0))
С
С
     uk3=step*fun1((t+step/2.0),(u+uk2/2.0),(x+xk2/2.0),(p+pk2/2.0))
     xk3=step*fun2((t+step/2.0),(u+uk2/2.0),(x+xk2/2.0),(p+pk2/2.0))
     pk3=step*fun3((t+step/2.0),(u+uk2/2.0),(x+xk2/2.0),(p+pk2/2.0))
С
С
     uk4=step*fun1((t+step),(u+uk3),(x+xk3),(p+pk3))
     xk4=step*fun2((t+step),(u+uk3),(x+xk3),(p+pk3))
     pk4=step*fun3((t+step),(u+uk3),(x+xk3),(p+pk3))
```

С С unxt=u+(1.0/6.0)*(uk1+2.0*uk2+2.0*uk3+uk4)xnxt=x+(1.0/6.0)*(xk1+2.0*xk2+2.0*xk3+xk4)pnxt=p+(1.0/6.0)*(pk1+2.0*pk2+2.0*pk3+pk4) С С return end С c-----END OF RUNGAKUTTA SUBROUTINE-----С С c-----С c-----SUBROUTINE NEW_VALUUES BEGINS HERE------С С subroutine new_values(uf,xf,pf,delta,u_last,x_last,p_last, u0,x0,p0) & С С implicit double precision (a-h,o-z) С

с u0=delta*u_last+(1.0-delta)*uf x0=delta*x_last+(1.0-delta)*xf p0=delta*p_last+(1.0-delta)*pf С ¢ return end С c-----SUBROUTINE NEW_VALUUES ENDS HERE-----С С c----- SUBROUTINE PRINT-1 BEGINS HERE------С С subroutine print_1(delta,phi,gamma,w,eta,rho,eps,uf,xf,pf, & last,tm,um,xm,pm,u_init,x_init,p_init,np,n_pcycle,tow,dif, & step,n_scycle,res_t) С С implicit double precision (a-h,o-z) С dimension tm(100000),um(100000),xm(100000),pm(100000)

C-----PRINT INPUT DATA ON OUTPUT FILE-----

С

С

С

WRITE(20,140)

WRITE(20,160)

160 FORMAT(//25X,' B A T C H M O D E L ')

WRITE(20,150)

150 FORMAT(//10X,'CONCENTRATION OF SUBSTRATE, BIOMASS AND PRODUCT'//) WRITE(20,140)

WRITE(20,151)

151 FORMAT(//10X,' AFTER Ist CYCLE'//) WRITE(20,140)

write(20,201)delta,phi,gamma,w

201 format(/1x,'DELTA='F10.5,4X,'PHI=',F10.5,4X,

&'GAMMA=',F12.5,4X,'W=',F10.5)

write(20,202) eta, rho, eps, tow

202 format(/1x,'ETA=',F10.4,4X,'RHO=',F10.5,4X,'EPS=',F10.5,4X,
& 'TOW=',F10.5)

write(20,203)uf,xf,pf

203 format(/1x,'UF=',F10.5,4X,'XF=',F10.5,4X,'PF=',F10.5)
write(20,204)u_init,x_init,p_init

```
204 format(/1x,'U0=',F10.5,4X,'X0=',F10.1,4X,'P0=',F10.5)
      write(20,205) np,step
  205 format(/1x,'NUMBER OF POINTS IN THE TIME DOMAIN=', I10, 10X//
     £
              1x,'STEP SIZE=',F10.6//)
      WRITE(20,140)
      write(20,206) res_t
  206 format(//1x,' TOW/(1.0-DELTA) = ', F10.5//)
      WRITE(20,140)
      write(20,207)
  207 format(/1x,'TIME',15X,' U ',15X,' X ',15X,' P ')
С
C-----PRINT COMPUTED DATA INTO OUTPUT FILE------
С
С
     do 40 i=1,np+1,last
С
с
          write(20,210) tm(i),um(i),xm(i),pm(i)
  210 format(1X,f10.5,5x,f10.5,5x,f10.5,5x,f10.5)
  40 continue
С
С
     return
С
```

end С С c-----SUBROUTINE PRINT-1 ENDS HERE------С С С С c-----BUBROUTINE PRINT-2 BEGINS HERE-----С С subroutine print_2(delta,phi,gamma,w,eta,rho,eps,uf,xf,pf, & last,tm,um,xm,pm,u_init,x_init,p_init,np,n_pcycle,tow,dif, & step,n_scycle,res_t) С С implicit double precision (a-h,o-z) с dimension tm(100000),um(100000),xm(100000),pm(100000) С С C-----PRINT INPUT DATA ON THE SECOND OUTPUT FILE------С С

WRITE(30,1400)

WRITE(30,1600)

1600 FORMAT(//25X, 'BATCH MODEL')

WRITE(30,1500)

1500 FORMAT(//10X,'CONCENTRATION OF SUBSTRATE, BIOMASS AND PRODUCT'//) WRITE(30,1400)

write(30,1550)n_pcycle

1550 format(//10x,' AFTER ',15,4x,'CYCLES'//) WRITE(30,1400)

write(30,2010)delta,phi,gamma,w

2010 format(/1x, 'DELTA='F10.5,4X, 'PHI=', F10.5,4X,

&'GAMMA=',F12.5,4X,'W=',F10.5)

write(30,2020) eta, rho, eps, tow

2020 format(/1x,'ETA=',F10.4,4X,'RH0=',F10.5,4X,'EPS=',F10.5,4x,

& 'TOW=',F10.5)

write(30,2030)uf,xf,pf

2030 format(/1x,'UF=',F10.5,4X,'XF=',F10.5,4X,

&'PF=',F10.5)

write(30,2040)u_init,x_init,p_init

2040 format(/1x,'U0=',F10.5,4X,'X0=',F10.5,4X,'P0=',F10.5) write(30,2050) np,step

```
2050 format(/1x,'NUMBER OF POINTS IN THE TIME DOMAIN=', I5//
     &
              1X,'STEP SIZE=',F10.6//)
      WRITE(30,1400)
      write(30,2055) res_t
 2055 format(//1x,' TOW/(1.0-DELTA) = ', F10.5//)
      WRITE(30,1400)
      write(30,2060)
 2060 format(/1x,'TIME',15X,' U ',15X,' X ',15X,' P ')
с
C-----PRINT COMPUTED DATA INTO OUTPUT FILE------
С
С
      do 41 i=1,np+1,last
С
С
          write(30,2100) tm(i),um(i),xm(i),pm(i)
 2100 format(1X,f10.5,5x,f10.5,5x,f10.5,5x,f10.5)
  41 continue
С
С
     return
С
     end
С
```

```
c-----SUBROUTINE PRINT-2 ENDS HERE------
С
С
С
С
c-----SUBROUTINE PRINT-3 BEGINS HERE------
С
С
    subroutine print_3(delta,phi,gamma,w,eta,rho,eps,uf,xf,pf,
   & last,tm,um,xm,pm,u_init,x_init,p_init,np,n_pcycle,tow,dif,
   & step,n_scycle,icycle,res_t)
С
    implicit double precision (a-h,o-z)
С
    dimension tm(100000),um(100000),xm(100000),pm(100000)
С
С
C-----PRINT INPUT DATA ON OUTPUT FILE-----
С
С
    WRITE(40,1401)
WRITE(40,1601)
```

1601 FORMAT(//25X, ' B A T C H M O D E L ')

WRITE(40,1501)

1501 FORMAT(//10X,'CONCENTRATION OF SUBSTRATE, BIOMASS AND PRODUCT'//) WRITE(40,1401)

write(40,2052) icycle

2052 format(//1x,'STEADY STATE IS REACHED AFTER', 16,4X, 'CYCLES'//) WRITE(40,1401)

write(40,2011)delta,phi,gamma,w

2011 format(/1x,'DELTA='F10.5,4X,'PHI=',F10.5,4X,

&'GAMMA=',F12.5,4X,'W=',F10.5)

write(40,2021) eta, rho, eps, tow

2021 format(/1x,'ETA=',F10.4,4X,'RHO=',F10.5,4X,'EPS=',F10.5,4X,

& 'TOW=',F10.5)

write(40,2031)uf,xf,pf

- 2031 format(/1x,'UF=',F10.5,4X,'XF=',F10.5,4X,'PF=',F10.5)
 write(40,2041)u_init,x_init,p_init
- 2041 format(/1x,'UO=',F10.5,4X,'XO=',F10.1,4X,'PO=',F10.5)
 write(40,2051) np,step
- 2051 format(/1x,'NUMBER OF POINTS IN THE TIME DOMAIN=', I10//

& 1X,'STEP SIZE=',F10.6//)

WRITE(40,1401)

write(40,2053) res_t,dif

2053 format(//1x,' TOW/(1.0-DELTA) = ',F10.5,10x,'DIF='F10.5//) WRITE(40,1401)

```
write(40,2061)
2061 format(/1x,'TIME',15X,' U ',15X,' X ',15X,' P ')
С
C-----PRINT COMPUTED DATA INTO OUTPUT FILE-----
С
С
    do 44 i=1,np+1,last
С
С
         write(40,2101) tm(i),um(i),xm(i),pm(i)
2101 format(1X,f10.5,5x,f10.5,5x,f10.5,5x,f10.5)
  44 continue
С
С
    return
С
     end
С
c-----END OF SUBROUTINE PRINT-3------}
```

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