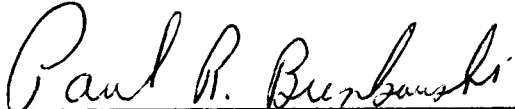


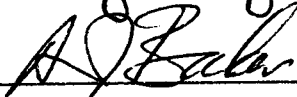
To the Graduate Council:

I am submitting herewith a dissertation written by Nathalie Rouhana-Bhojraj entitled "Development and Modeling of a Vapor Phase Radial-Flow Bioreactor for the Removal of Para-Xylene." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.


Paul R. Bienkowski, Major Professor

We have read this dissertation
and recommend its acceptance:






Accepted for the Council:


Associate Vice Chancellor and
Dean of The Graduate School

**DEVELOPMENT AND MODELING OF A
RADIAL-FLOW VAPOR PHASE BIOREACTOR FOR
THE REMOVAL OF PARA-XYLENE**

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Nathalie Rouhana-Bhojraj

August 1996

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ABSTRACT

The work presented investigated the experimental and theoretical development of a radial-flow, vapor phase bioreactor for the biodegradation of para-xylene. A vapor phase bioreactor which utilizes porous metal membranes in a cylindrical design and employs radial flow as opposed to traditional axial flow for the vapor stream was developed. The system was evaluated for the biodegradation of para-xylene from a water-saturated air stream by *Pseudomonas putida* ATCC 23973 immobilized onto sand. The biocatalyst was placed in the annular space between two cylindrical, porous stainless steel membranes. Details of the reactor system are presented along with biological experimental results verifying reactor performance.

The operating parameters that were examined and allowed to vary were the influent p-xylene concentration and the flow rates of the influent vapor streams. The influent concentrations were in the range of 15 to 200 ppm at flow rates between 60 and 130 cm³/min. Continuous reactor operation was maintained for 80 to 200 hours with fractional removal of p-xylene achieving 80 to 95%. The effluent concentration curves were compared to determine the operating range of the bioreactor.

As the influent para-xylene concentration increased from 50 to 100 to 150 ppm, the fractional removal successively decreased while still remaining as high as 80% for the 50 ppm case and 60% for the 100 ppm case for up to 80 hours. The system did appear to become saturated after 60 hours of operation with an influent para-xylene concentration of 147 ppm.

A mathematical model for reactor operation suitable for design purposes was developed. The Galerkin finite element model was applied to the solution of the developed transport and constitutive equations. The effluent concentration curves of para-xylene for $15 \leq C_0 \leq 50$ ppm could be closely correlated with the predictive model consisting of the

transport and constitutive equations combined with Monod kinetics. For the concentration range $50 < C_0 \leq 150$ ppm, a modified model incorporating a cell death as well as growth with the original Monod kinetics was successful in describing the data.

The biomass radial profiles developed from the computational models indicate two different types of behaviour within the reaction zone: a growth region, termed type I, where $B \geq B_0$ at all radial nodes and biomass continues to increase with time; and a death region, type II, where $B < B_0$ at all radial nodes and biomass decreases as time increases. Profiles representative of type I occurred with the growth kinetics model, whereas the growth/death kinetic model resulted in profiles of type II.

TABLE OF CONTENTS

	Page
CHAPTER I. INTRODUCTION	1
1.1 Para-xylene as a Hazardous Air Pollutant	4
1.2 Objectives	5
1.3 Methodology.....	6
CHAPTER II. BACKGROUND AND LITERATURE SURVEY.....	8
2.1 Treatment of Gaseous Effluents	8
2.1.1 Radial Flow	10
2.2 Vapor Phase Bioreactors in Organic Compound Biodegradation	12
2.3 Microbial Kinetics	14
2.3.1 Stoichiometry and Yield Coefficient	16
2.3.2 Biochemical Pathways	18
2.4 Reactor Designs	22
CHAPTER III. REACTOR CONFIGURATION AND INSTRUMENTATION.....	23
3.1 Reactor Description and Operation	24
3.2 Instrumentation.....	28
CHAPTER IV. EXPERIMENTAL PROCEDURE	29
4.1 Mass Flow Meters.....	29
4.2 Cell Culture Growth.....	30
4.3 Reactor Packing.....	36
4.3.1 Nutrient Delivery.....	37
4.3.2 Transfer of Cell Culture to Reactor.....	37
4.4 Measurement of Cell Mass.....	40
CHAPTER V. THEORY.....	42
5.1 Reactor Model.....	42
5.2 Finite Element Method.....	47
5.2.1 General Procedure.....	49
5.2.2 The Weak Statement and Approximation.....	50
5.2.3 Discretization.....	52
5.3 Nondimensionalization of Equations.....	55
5.4 Development of Galerkin Weak Statements and Jacobians..	59
CHAPTER VI. RESULTS AND DISCUSSION.....	65
6.1 Experimental Parameters.....	65
6.2 Abiotic Experiments.....	67
6.3 Biodegradation Experiments.....	70

6.3.1	Initial Stages of Reactor Operation.....	71
6.3.2	Feed Concentration of 15 ppm p-Xylene.....	76
6.3.3	Feed Concentration of 28-36 ppm p-Xylene.	79
6.3.4	Feed Concentration of 50-52 ppm p-Xylene.	82
6.3.5	Feed Concentration of 100-147 ppm p-Xylene.....	85
6.4	Correlation with Predictive Model.....	90
6.4.1	Modification of Model.....	99
6.4.2	Functional Dependence of k_d on p-Xylene Flow rate.....	105
6.4.3	Radial Concentration Profiles.....	107
6.5	Biomass Growth.....	116
6.6	P-Xylene Removal Rates.....	118
CHAPTER VII.	CONCLUSIONS AND RECOMMENDATIONS.....	122
BIBLIOGRAPHY.....		127
APPENDICES.....		133
APPENDIX I.	NUMERICAL QUANTITIES USED IN SIMULATIONS.....	133
1.1	Diffusion Coefficient.....	133
1.1.1	Sample Calculation.....	135
1.2	Parameters in Template File.....	139
APPENDIX II.	TEMPLATE AND MODEL FILES FOR AKCESS.....	141
2.1	Template File.....	141
2.2	Model File.....	145
VITA.....		148

LIST OF TABLES

Table	Page
1.1 Industrial applications of vapor phase bioreactors in air pollution treatment.....	3
1.2 Health exposure limits for common organic compounds.....	5
2.1 Comparison of biofilters and bioscrubbers.....	11
2.2 Summary of papers investigating p-xylene biodegradation.....	15
4.1 Composition of benzoate medium 1271, 1L solution basis.....	33
4.2 Chemical and physical data of bioremediation nutrient source.....	38
4.3 Operating conditions of gas chromatography system.....	39
6.1 Summary of experimental conditions for biodegradation experiments.....	66
6.2 Experimental conditions and dimensionless model parameters.....	91
6.3 Nondimensional reaction parameters calculated from confidence interval of kinetic parameters.....	99
6.4 Fitted cell deactivation constants, k_d	105
6.5 Experimental and theoretical final cell mass.....	117
6.6 Average p-xylene removal rates.....	119

LIST OF FIGURES

Figure	Page
1.1 Methodology overview.....	7
2.1 Classification of reactor types in the treatment of gaseous effluent streams..	9
2.2 Aerobic biochemical reaction pathway for the degradation of aromatic compounds (Bouwer <i>et al.</i> , 1993).....	19
2.3 Pathway for oxidation of p-xylene by <i>P.putida</i> 23973 (a) structural pathway (adapted from Ribbons <i>et al.</i> , 1982) (b) nomenclature.....	20
3.1 Schematic of reactor configuration showing concentric cylindrical shell arrangement. Height of filled reactor is 40.5 cm (16in).....	25
3.2 Pall sintered, porous stainless steel medium (photomicrograph 15X, Pall Corporation, 1992).....	26
3.3 Schematic line diagram of experimental setup.....	27
4.1 Calibration curve for Brooks 5850 mass flow controller 0-50 SCCM. The y-axis is the digital flow meter reading in cm ³ /min, and the x-axis represents the actual measured flow rate.....	31
4.2 Calibration curve for Brooks 5850 mass flow controller 0-100 SCCM. The y-axis is the digital flow meter reading in cm ³ /min, and the x-axis represents the actual measured flow rate.....	32
4.3 Natural logarithm of absorbance at 600nm vs. time for growth of <i>P. putida</i> 23973 at 25°C in benzoate medium 1271.....	35
4.4. Natural logarithm of absorbance at 600 nm vs. time for exponential growth phase of <i>P.Putida</i> 23973 at 25°C in benzoate medium 1271.....	35
4.5 Correlation of optical density at 600 nm of cell culture grown in a solids-free medium with concentration of cells in solution.....	41
5.1 Differential control volume, $rdrd\phi dz$, for shell balance in cylindrical coordinates (r , ϕ , z).....	43
6.1 Elution curve of 284 ppm feed of p-xylene at a flow rate of 60 cm ³ /min in packed bed experiment performed with immobilized cells which had been autoclaved.....	68

6.2	Elution curves of 105 ppm feed of p-xylene at a flow rates of 60 cm ³ /min (squares) and 121 cm ³ /min (circles) in packed bed experiment performed with immobilized cells which had been autoclaved.....	69
6.3	Elution curve of 32 ppm feed of p-xylene at a flow rate of 120 cm ³ /min in packed bed experiment performed with immobilized cells which had been autoclaved.....	69
6.4	Concentration effluent curves in initial stages of reactor operation at specified conditions. (a) C ₀ = 15 ppm (b) C ₀ = 30 ppm.....	72
6.5	Concentration effluent curves in initial stages of reactor operation at specified conditions. (a) 50, 52 ppm (b) 100, 106 ppm.....	73
6.6	Comparison of initial region of biodegradation reaction (ads. + react., initial p-xylene concentration of 32 ppm at 121 mL/min) with the abiotic adsorption experiment (ads., initial p-xylene concentration of 30 ppm at 120 mL/min).....	74
6.7	Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: C ₀ = 15 ppm, flow rate = 62 cm ³ /min. The exit concentration of p-xylene is normalized with respect to its feed concentration.....	77
6.8	Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: C ₀ = 15 ppm, flow rate = 125 cm ³ /min. The exit concentration of p-xylene is normalized with respect to its feed concentration.....	78
6.9	Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: C ₀ = 28 ppm, flow rate = 63 cm ³ /min. The exit concentration of p-xylene is normalized with respect to its feed concentration.....	80
6.10	Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: C ₀ = 36 ppm, flow rate = 121 cm ³ /min. The exit concentration of p-xylene is normalized with respect to its feed concentration. The inset is an enlargement of the initial region of the effluent curve of p-xylene.....	81
6.11	Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: C ₀ = 52 ppm, flow rate = 63 cm ³ /min. The exit concentration of p-xylene is normalized with respect to its feed concentration.....	83
6.12	Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: C ₀ = 50 ppm, flow rate = 125 cm ³ /min. The exit concentration of p-xylene is normalized with respect to its feed concentration.....	84

6.13	Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 100$ ppm, flow rate = $62 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.....	86
6.14	Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 106$ ppm, flow rate = $129 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.....	87
6.15	Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 147$ ppm, flow rate = $62 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.....	88
6.16	Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at influent p-xylene concentrations of 50 ppm (squares), 100 ppm (circles) and 147 ppm (triangles) at flow rates of 63, 62, and $62 \text{ cm}^3/\text{min}$, respectively. The exit concentration of p-xylene is normalized with respect to its feed concentration.....	89
6.17	Comparison of experiment with model for $C_0 = 15$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designations "mid.," "low," and "high" refer to the confidence interval of the kinetic parameters used.....	93
6.18	Comparison of experiment with model for $C_0 = 15$ ppm at a flow rate of $125 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designations "mid.," "low," and "high" refer to the confidence interval of the kinetic parameters used.....	94
6.19	Comparison of experiment with model for $C_0 = 28$ ppm at a flow rate of $63 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designations "mid.," and "low" refer to the confidence interval of the kinetic parameters used.....	95
6.20	Comparison of experiment with model for $C_0 = 36$ ppm at a flow rate of $121 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designation "mid." refers to the midpoint of the confidence interval of the kinetic parameters used.....	96
6.21	Comparison of experiment with model for $C_0 = 50$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designations "mid.," and "low" refer to the confidence intervals of the kinetic parameters used.....	97

6.22	Comparison of experiment with model for $C_0 = 50$ ppm at a flow rate of $125 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designations "mid.," and "low" refer to the confidence intervals of the kinetic parameters used.....	98
6.23	Comparison of experiment with growth and cell deactivation+growth models for $C_0 = 100$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. The value of k_d used is 0.0225 hr^{-1}	102
6.24	Comparison of experiment with growth and cell deactivation+growth models for $C_0 = 147$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. The value of k_d used is 0.0622 hr^{-1}	103
6.25	Comparison of experiment with growth and cell deactivation+growth models for $C_0 = 106$ ppm at a flow rate of $129 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. The value of k_d used is 0.083 hr^{-1}	104
6.26	Functional dependence of cell deactivation constant, k_d , with mass flow rate of p-xylene. The solid line represents the least-squares regression of the k_d values.....	106
6.27	Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 15$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile.....	108
6.28	Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 15$ ppm at a flow rate of $125 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile.....	109
6.29	Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 28$ ppm at a flow rate of $63 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile.....	110
6.30	Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 36$ ppm at a flow rate of $121 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile.....	111
6.31	Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 50$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile.....	112
6.32	Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 50$ ppm at a flow rate of $125 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile.....	113

6.33	Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 147$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile.....	114
6.34	Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 106$ ppm at a flow rate of $129 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile.....	115
6.35	Average removal rate of p-xylene as a function of mass flow rate of p-xylene.....	121
A.1	Effect of diffusion parameter DIFU for $C_0 = 28$ ppm and a flow rate of 62.3 mL/min as predicted by the model.....	138

LIST OF SYMBOLS

A	surface area [L^2]
ATCC	American <i>type culture</i> collection
ATP	adenosine triphosphate
b	biomass concentration [M biomass/M sand]
B	nondimensional biomass concentration
c	substrate concentration [M/L^3]
ccm	cubic centimeters per minute [L^3/t]
C	nondimensional substrate concentration
CS	control surface
d_i	inner diameter [L]
D	effective diffusion coefficient [L^2/t]
D_{AB}	bulk diffusivity in binary gas mixture of A and B [L^2/t]
e_{AB}	maximum energy of attraction between A and B [ML^2/t^2]
FID	flame ionization detector
He	helium
i	element
I	identity matrix
k	basis degree
k_b	Boltzmann constant (1.380662×10^{-23} Joules/Kelvin)
K	Monod constant [M/L^3]
K_i	inhibition constant [M/L^3]
L	length [L]
L_c	characteristic length [L]
M	mass [M]
MW	molecular weight [M/M-mole]
n	dimension
N	total number of elements
N_k	basis function
N_i	mass flux of component i [M/L^2t]
NADH	nicotinamide adenine dinucleotide
ODE	ordinary differential equation
p	progression ratio
P	pressure (atm)
q	dependent variable
r	radial coordinate [L]
r^*	nondimensional radial coordinate
S_e	element assembly
STEL	short-term exposure limit
t	time [t]
t^*	nondimensional time
T	absolute temperature [degrees Kelvin]
T_c	critical temperature [degrees Kelvin]
TS	Taylor series
TWA	time-weighted average
v	radial velocity [L/t]

V	volumetric flow rate [M/L ³]
V_c	critical volume (L ³ /mol)
WS	weak statement
x_j	independent variable
Y	yield coefficient [M cells/M substrate]
z	axial coordinate [L]

Greek letters

ε	void fraction (of packed bed)
θ	parameter in generalized Taylor series
κ	K/c_0 (dimensionless)
μ_m	maximum specific growth rate [1/t]
Ω	solution or problem domain [L ⁿ]
Ω_D	collision integral
ω	weighting function
ρ	mass of packing (sand) per reactor volume [M/L ³]
ρ_s	crystalline density [M/L ³]
σ_{AB}	bimolecular collision diameter [L]
ϕ	trial function set
ζ	natural coordinate
ν_i	stoichiometric coefficient of component i
τ	L_0/v_1 [t]

CHAPTER I

INTRODUCTION

The National Environmental Policy Act (NEPA), signed into law in 1970, initiated ten years of legislative activity with the aim of environmental protection. Environmental Impact Statements became required of federal departments and agencies under NEPA any time a project that could have significant effects on the environment was proposed. Following the enactment of NEPA, many state and federal laws were enacted to protect the environment from hazardous wastes. These major laws include the Marine-Protection, Research, and Sanctuaries Act of 1972, to prevent or limit dumping of wastes into the ocean; the Federal Insecticide, Fungicide, and Rodenticide Act of 1972 (FIFRA), to regulate the storage and disposal of pesticides and to specify tolerance levels for certain pesticides; the Clean Air Act of 1970, to identify hazardous air pollutants and to set and enforce corresponding National Air Quality Standards; the Federal Water Pollutant Control Act of 1972, to establish limits on the amounts of pollutants that may be discharged into waterways; and the Resource Conservation and Recovery Act (RCRA) of 1976, to establish a comprehensive regulative program to control hazardous waste and improve waste management.

The RCRA Amendments of 1984 required hazardous wastes to be rendered non-hazardous, such as by incineration, before they are released into the environment. In addition, the Clean Air Act Amendments of 1990 specified 190 hazardous air pollutants, of which organic hydrocarbons comprise the majority, whose emissions are regulated by the Environmental Protection Agency (EPA). Although source reduction, recycling, and reuse are the most direct ways to reduce hazardous emissions, this is oftentimes not sufficient to

meet federal regulations. Consequently, chemical and biological methods of hazardous waste reduction must be employed.

Among the chemical methods of destruction of hazardous organic compounds are the widely employed incineration processes and the newly-introduced photocatalytic oxidative processes, in which the U.S. Department of Energy (DOE) supports basic research and field testing.

The complete destruction of hazardous chemicals by incineration is questionable, as dioxins and other organic compounds are formed during combustion. For example, when organic compounds are burned in the presence of chlorine, polychlorinated dioxins are formed, of which 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) is the most toxic (Hanson, 1993). Hazardous waste incinerators need to have destruction efficiencies of dioxins of 99.9999% under RCRA, and many incinerators do not meet this standard. Products of incomplete combustion are formed that constitute a major source of plant emissions.

Solar energy harnessed by flat plate collectors, parabolic troughs and dishes, and solar furnaces are used to initiate chemical reactions that destroy hazardous organic compounds in photocatalytic processes. For example, trichloroethylene (TCE) in ground water is effectively oxidized to carbon dioxide and hydrochloric acid with the use of a titanium dioxide catalyst (Mehos, 1992). TCE in humidified air has been photocatalytically degraded (Raupp and Dibble, 1991), and dioxin has been destroyed to levels which exceed EPA requirements (Glatzmaier 1990). Despite these promising results, photocatalytic oxidation is still in its experimental stages and industrial implementation would have to address its disadvantages and problems, which include the variability of solar radiation with geographical location and weather conditions, the need for space for solar collectors, and the high catalyst activity needed to increase reaction rates.

Biochemical processes utilize microorganisms to decompose organic compounds into products such as carbon dioxide, water, organic acids, and salts, thereby transforming

contaminants into benign products. These biocatalytic processes are especially effective in volatile organic compound removal in the treatment of hazardous air emissions (Ottengraf *et al.*, 1983; Diks *et al.*, 1991; Douglass *et al.*, 1991; Davison *et al.*, 1994). Typically, the reactors used consist of a biocatalyst immobilized onto an inert packing material through which the waste gases flow and are microbially degraded. These types of biofilters are installed in the chemical, food processing, and dye industries to remove odorous compounds and to prevent the emission of toxic organic chemicals. For example, over two hundred biofilters are in operation in Holland to remove organic contaminants from air (Atlas, 1995). (The United States being primarily focused on site-specific remediation, vapor phase bioreactors have not yet gained as widespread use in the U.S. as they have in Europe. (Atlas, 1995). Specific examples of the use of vapor phase bioreactors in industry is summarized in Table 1.1.

Table 1.1: Industrial applications of vapor phase bioreactors in air pollution treatment

Industry	Chemical Treated
ceramics	ethanol, isopropanol
resin production facilities	phenol
plywood production facilities	formaldehyde
paint production facilities	solvents
cattle feed extrusion plant	odorous gases

1.1 PARA-XYLENE AS A HAZARDOUS AIR POLLUTANT

The EPA dictates the emission standards of hazardous air pollutants, of which organic compounds comprise a majority. A chemical is considered a hazardous air pollutant if it is listed under sections 112(b)(1) of the Clean Air Act, as given by the Knox County Department of Air Pollution Control, and para-xylene is among the listed compounds. According to this department, the short-term acceptable ambient guideline concentration for p-xylene is 23.8 ppm. This value is calculated by dividing a health exposure limit by an uncertainty factor, and this result is subsequently used in a dispersion model which evaluates the potential impact of such a release on the air quality. The guideline concentration may further be lowered if either the EPA or the State of Tennessee establishes a more restrictive concentration.

Health exposure limits may be characterized by the time-weighted average exposure limit (TWA), and by the short-term exposure limit (STEL). The TWA concentration represents the average concentration to which one may be exposed on a day-to-day basis in a forty-hour work week without adverse health effects. The STEL concentration represents the concentration to which one may be exposed for up to fifteen minutes without the onset of adverse effects. Representative values of health exposure limits for some volatile organic compounds are listed in Table 1.2, which also includes corresponding odor threshold limits. The odor threshold limit for p-xylene is in the range of 0.73 to 5.4 ppm, which is significantly lower than its TWA and STEL concentrations.

Table 1.2: Health exposure limits for common organic compounds

Compound	TWA (ppm)	STEL(ppm)	Odor threshold (ppm)
methanol	200	250	100
methyl ethyl ketone	200	300	10
naphthalene	10	15	0.027
styrene	50	100	0.047
toluene	100	150	2.8
trichloroethylene	50	100	82
xylene (o-, m-, p-)	100	150	0.73-5.4

1.2 OBJECTIVES

With the environmental and health concerns previously discussed in terms of EPA standards, exposure limits, and odor detection limits, a need exists for effective methods of volatile organic compound removal in air pollution treatment. Para-xylene was chosen for the test system because from both process and microbial kinetic standpoints, the system is relatively simple and its kinetics are known (Lee *et al.*, 1993). The utility of vapor phase bioreactors, or biofilters, having been outlined, expanding bioremediation technology and effectively employing vapor phase bioreactors requires innovation and research to establish the proper conditions under which these types of bioreactors can function. To provide a contribution to this end, the research objectives in this thesis are as follows:

- (1) to build and test a novel packed-bed vapor phase reactor for the biodegradation of para-xylene with an immobilized microbial phase

- (2) to evaluate the performance of the reactor by generating a set of data for the biodegradation of para-xylene by *Pseudomonas putida* ATCC 23973 immobilized onto sand at different process conditions
- (3) to develop a mathematical model for the reactor operation suitable for design purposes
- (4) to apply the Galerkin finite element technique to the solution of the developed constitutive equations to provide a comparison with the experimental data and to validate the model.

1.3 METHODOLOGY

The methodology involved in accomplishing these objectives is systematically organized in Figure 1.1, in which the three major divisions of this work are described. Development of the process involved reactor design, integrating the reactor into a proper flow design, and, finally, using the designed process to perform experiments. Chapter III discusses the reactor configuration and the instrumentation utilized for the process. The microbiology part of this study involved selecting a proper microorganism with known growth kinetics for the biodegradation of p-xylene. Biodegradation and microbial kinetics are described in Chapter II. The mathematical part of this work can be described by the modeling of the reactor system, in which equations were developed and a finite element method of solution was used. Chapter V presents the theory supporting the reactor equations and finite element method. Finally, the process is correlated with the modeling in Chapter VI, in which the experimental results are presented in conjunction with the theoretical predictions.

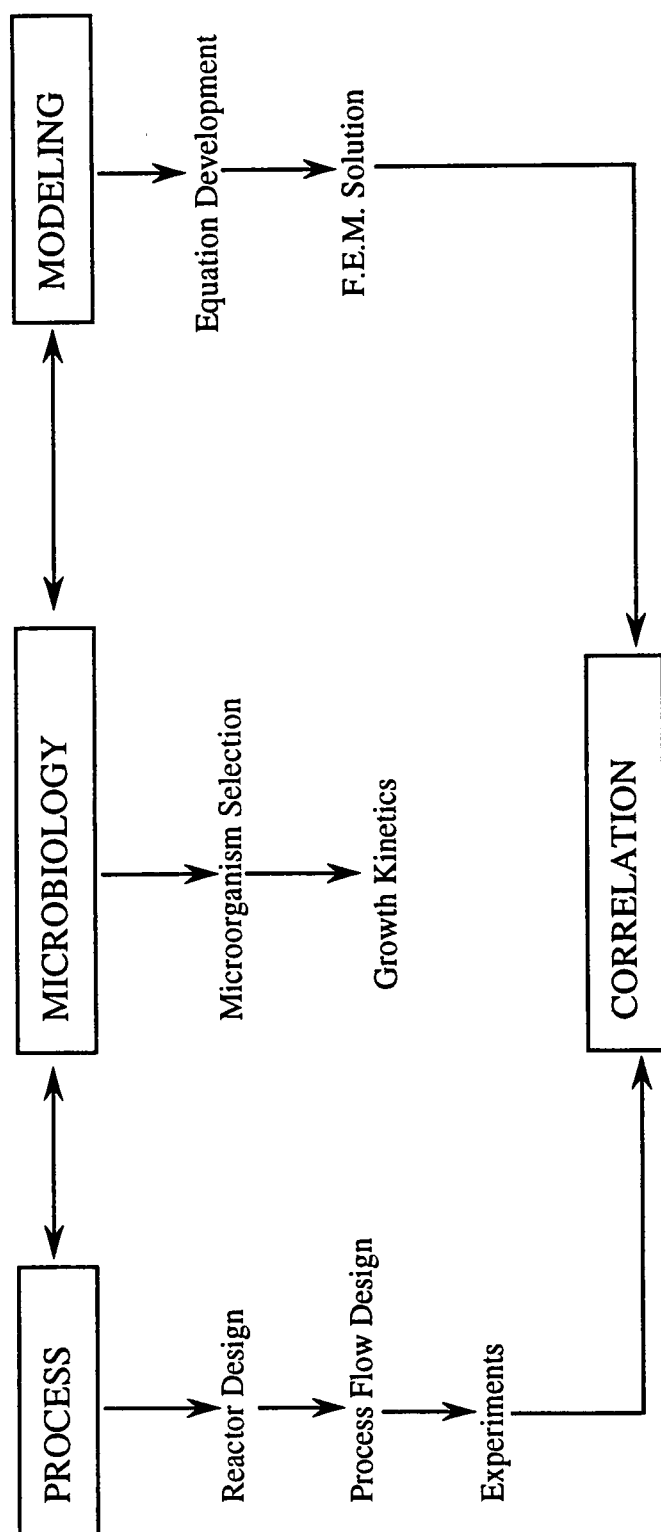


Figure 1.1: Methodology overview

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

A bioremediation process is one in which a biological catalyst is employed to act on a pollutant, usually an organic compound, resulting in biodegradation of the compound. Through cellular enzymatic processes, the organic molecule is decomposed to carbon dioxide, water, organic acids, and salts, with a portion of the carbon in the original organic molecule incorporated into cell mass.

Bioremediation processes may be done in situ, in the original place of occurrence of the waste, by activation of local microbial processes to destroy the pollutant. An example of this process is bioremediation of soil in the field (Fouhy and Shanley, 1991). An alternative to in situ bioremediation is treatment of contaminants in a bioreactor, in which better containment and control provide potentially faster and complete contaminant removal. For treatment of gaseous effluents as such, the types of reactors used are discussed in the following section.

2.1 TREATMENT OF GASEOUS EFFLUENTS

Gaseous streams containing organic pollutants may be purified by reactors of the biofilter, trickling filter, and bioscrubber type. The distinction between these reactor types is made according to the configuration of the microbial and aqueous phases. The distinctions may be visualized according to the diagram shown in Figure 2.1.

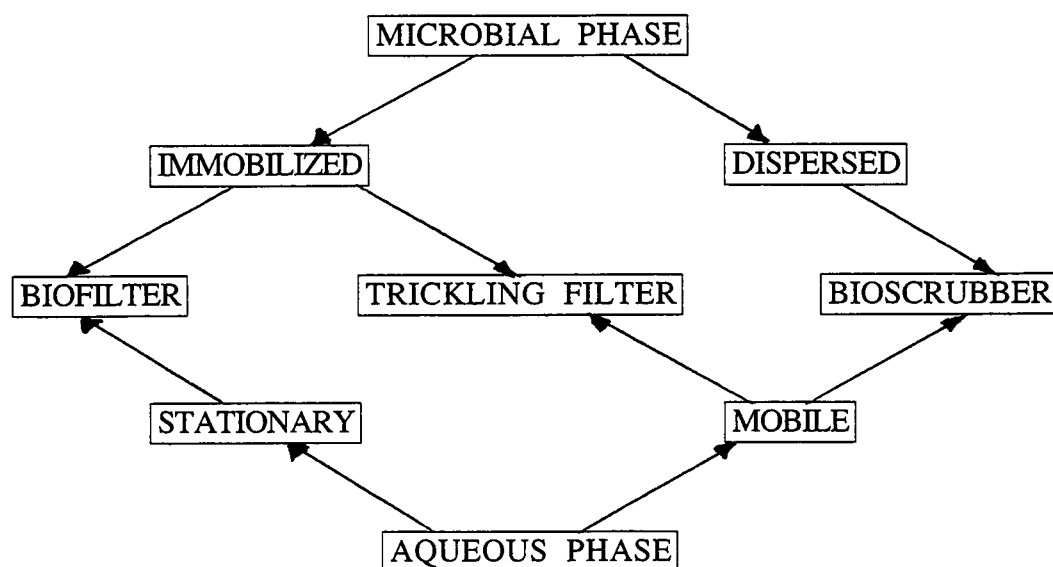


Figure 2.1: Classification of reactor types in the treatment of gaseous effluent streams

In a biofilter, the contaminant-laden gas flows through a packed bed onto which a microbial population is immobilized. The packing may consist of sand, soil, or compost, and is typically about one meter in height (Moo-Young and Chisti, 1994). The cells adhere to the particles of the packing material, and, in combination with the moisture, or aqueous phase necessary for biological activity, form a wet biolayer termed a biofilm. The moisture level is controlled either through saturation of the inlet gas stream with water or through the use of water sprays. As the waste gas flows through the biofilter, the pollutants are degraded through oxidative processes by the immobilized microbes. Typical operating conditions for biofilters are pollutant concentrations up to 1000 mg/m^3 (843 ppm in air at 25°C and 101325 Pa) and temperatures in the range of 10 to 43°C (Moo-Young *et al.*, 1994). Industrial biofilters can attain removal efficiencies of 85 to 100% (Atlas, 1995; Fouhy, 1992).

Bioscrubbers are similar to conventional gas scrubbers in that a gas stream contacts a mobile aqueous phase in an absorption tower. In the case of a bioscrubber, the absorption tower is packed with, for example, activated sludge and silicone oil in an emulsion with water for absorption. The microbial phase is dispersed in the aqueous phase. This system is characterized by three phases in which the contaminants in the gas phase transfer to the sludge water where degradation takes place by the cell phase.

Trickling filter bioreactors are also three-phase systems, but with the microbial phase immobilized onto the packing material. With this configuration, conventional non-biological scrubbing of the gas stream occurs in the aqueous phase. Once absorbed into the water, the contaminants are then degraded by the immobilized microbial phase.

Some of the advantages and disadvantages of biofilters and bioscrubbers are summarized in Table 2.1. As can be seen from this compilation, several of the advantages of biofilters are disadvantages of bioscrubbers, and vice versa. One disadvantage of a biofilter is that because of possible toxicity effects, lower pollutant concentrations can be processed than with a bioscrubber. Bioscrubbers are advantageous over biofilters when levels of contaminants or products of cell metabolism accumulate to an extent which inhibits biological activity. However, in achieving this advantage over biofilters, a waste stream which would need further treatment is generated. With a biofilter, attempts can be made to reduce possible toxicity effects by diluting the waste gas stream prior to its introduction into the biofilter.

2.1.1 Radial Flow

The radial-flow reactor to be discussed in Chapter III was developed with the aim of increasing mass transfer rates of the organic hydrocarbon to the immobilized cells, or biofilm, which is an important factor when treating pollutants whose water solubilities are

Table 2.1: Comparison of biofilters and bioscrubbers^a

Biofilters	Bioscrubbers
<u>Advantages</u>	
simple operation principle (two-phase system)	process control and regulation possible
low investment costs	highly-contaminated waste air treatable
low running costs	
pollutants that are less water soluble able to be treated	high operational stability
<u>Disadvantages</u>	
low pollutant concentrations treatable	expensive operation engineering (three- phase system)
limited service life of filter bed	
regulation of metabolism not readily possible ("black-box" phenomena)	high investment and running costs
	production of excess biomass and waste water (disposal costs)

^a(Wittorf *et al.*, 1993)

low, as is the case with aromatic hydrocarbons. Radial-flow operation provides a high surface area for contacting of the feed stream and maintains a low pressure drop (2 to 4 psi), which in turn ensures a uniform distribution of the feed stream along the entire length of the reactor. Additionally, the occurrence of dry spots within the reactor packing is prevented as the flow is uniformly distributed across the bed. Radial flow enhances the already existing advantages of biofilters over bioscrubbers as outlined in Table 2.1, as lower pressure drops contribute to lower operating costs, and as higher surface areas for contacting of the feed stream enable higher mass transfer of the pollutant to the biocatalyst particles.

2.2 VAPOR PHASE BIOREACTORS IN ORGANIC COMPOUND BIODEGRADATION

There have been a limited number of scientific papers published on vapor phase bioreactors since 1992 (Uchiyama *et al.*, 1992; Apel *et al.*, 1992; Vaughn *et al.*, 1993; Davison *et al.*, 1994). In each of these studies, vapor phase bioreactors were successfully applied in the biodegradation of a gaseous organic compound. A brief description of each of these papers is presented in this chapter to introduce the vapor phase bioreactor as a new and significant method for the bioprocessing of organic vapors. This chapter also provides background on the kinetic rate expression used for cell growth and substrate utilization.

Uchiyama *et al.* (1992) developed a packed bed bioreactor for the degradation of gaseous trichloroethylene (TCE), and this was the first to be published on the biodegradation of gaseous TCE. The biodegradation reaction was performed using immobilized cells of *Methylocystis* strain M in sodium alginate beads, which served as the packing material. The reactor was operated in continuous mode with a 0.3 ppm inlet concentration of TCE at gas flow rates of 0.1 to 5.7 mL/min. During the first twenty-five

days of operation, 100% degradation of TCE was observed, and there was no adsorption of TCE onto the sodium alginate beads. After the seventy fifth day, no appreciable biodegradation was observed. This study concluded that alginate-immobilized cells could be used in the degradation of gaseous TCE.

Hydrocarbon removal has been achieved in a gas phase bioreactor (Davison *et al.*, 1994). A mixture of n-pentane and isobutane, each with an initial concentration of 5000 ppm in air, was degraded to concentration levels of 300 and 2000 ppm, respectively, after 50 hours of operation in a recycle packed bed reactor. The microorganisms consisted of a mixed culture immobilized onto ceramic berl saddles.

Apel *et al.* (1992) used a packed bed bioreactor for p-xylene degradation with *Pseudomonas putida* immobilized onto Pall rings. The reactor configuration consisted of a liquid nutrient feed stream flowing countercurrent to the inlet gas stream. The inlet p-xylene gas feed stream was 140 mg/min with a gas flow rate of 16 mL/min. Although 46% degradation of the entering p-xylene was achieved, significant losses occurred in the liquid stream, as 75 mg/min of the p-xylene was detected in the liquid effluent. A similar type of reactor was also reported by Vaughn *et al.* (1993), but with glass spheres and diatomaceous earth as packing materials. In this study, gas flow rates were varied from 50 to 2000 mL/min, and p-xylene concentrations from 150 to 1500 ppm. For gas flow rates less than 300 mL/min, p-xylene breakthrough into the outlet gas stream did not occur. At higher gas flow rates, p-xylene was detected in the effluent gas stream. However, p-xylene concentrations of 0.76 to 3.6 mg/L were detected in the liquid effluent, which confirmed that not all of the p-xylene removal could be attributed to biodegradation.

2.3 MICROBIAL KINETICS

A summary of published experiments for the biodegradation of p-xylene by various strains of *Pseudomonas putida* in several reactor configurations and conditions is presented in Table 2.2. These studies provided estimates of the biodegradability of p-xylene and the overall effectiveness of the different reactors.

Kinetic parameters for the biodegradation of p-xylene were presented by Lee *et al.* (1993) and Chang *et al.* (1993). Under conditions that the carbon source is growth-limiting, growth kinetics of *P.putida* ATCC 23973 can be represented by the noncompetitive substrate inhibition model (Lee, 1993)

$$\mu = \mu_m \frac{c}{K + c + c^2/K_i} \quad (2.1)$$

where

μ_m = maximum specific growth rate (1/hr)

c = substrate concentration (g/L)

K = Monod constant (g/L)

K_i = inhibition constant (g/L)

Equation 2.1 assumes that the single-substrate enzyme-catalyzed reaction is the rate-limiting step, which is valid when oxygen is present in excess. The estimated parameters by Lee (1993) are: $\mu_m = 0.437 \pm 0.008 \text{ hr}^{-1}$, $K = 0.006 \pm 0.004 \text{ g/L}$, and $K_i = 1.98 \pm 0.090 \text{ g/L}$ at 32°C.

When $c \ll K_i$, equation 2.1 reduces to the Monod equation

$$\mu = \mu_m \frac{c}{K + c} \quad (2.2)$$

Table 2.2: Summary of papers investigating p-xylene biodegradation

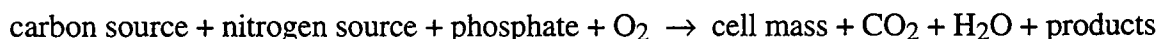
Reference	Bioreactor Type	Organism	Temperature	Initial p-xylene Concentration	Degradation
Jenkins, Michelsen, and Novak (1993)	fixed-bed packing: sand	<i>Pseudomonas putida</i>	38°C	5.5 to 8 ppm. in water, 3mL/min	to below detectable limits (<0.01 ppm) in 10-14 hrs.
Lee, Choi, and Kim (1993)	batch, CSTR	<i>Pseudomonas putida</i> ATCC 23973	32°C	12 to 50 ppm. in liquid phase (estimated from Henry's law)	to 0.24 ppm. in approx. 20 hrs.
Chang, Voice, and Criddle (1993)		<i>Pseudomonas fragi</i>	25°C	10mg/L, in liquid phase, with 10mg/L toluene	to <0.01ppm in 20 hrs
Apel, Dugan Wiebe, Johnson, Wolfram, and Rogers (1993)	fixed-bed packing: Pall Rings	<i>Pseudomonas putida</i>	22°C	139.9 µg/L, in air	46% of feed p-xylene in a single pass (approx. 2 hrs.)
Wolfram, Rogers, Higdem, and Nowers (1990)	batch, CSTR; packed bed (charcoal)	<i>Pseudomonas putida</i>	n.a.	14-25 mg/min, in air	to 0.1-10 ppm, in 1-25 hrs.
Vaughn, Jones and Wolfram (1993)	packed bed (glass spheres, diatomaceous earth)	<i>Pseudomonas Putida</i> Idaho	20-30°C	50-2000mL/min, 150-1500ppm	46% overall conversion for 2 weeks

The kinetic parameters for this case with *P.putida* were determined by Chang (1993) to be $\mu_m = 0.531 \pm 0.07 \text{ hr}^{-1}$, and $K = 0.00455 \pm 0.00037 \text{ g/L}$ at 25°C . The confidence intervals for these two sets of parameters overlap.

In the system under study, the cells are immobilized onto sand, thereby forming a biofilm, which is a microbial population that adheres to a surface through the production of polysaccharides and glycoproteins. The Monod equation previously described will be used in the subsequent reactor equations because microbial kinetics developed for suspended growth systems have been shown to apply equally to fixed-film systems. (San *et al.*, 1993; Gujer *et al.*, 1985, 1990; Harremoes *et al.*, 1990).

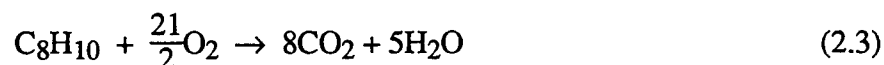
2.3.1 Stoichiometry and Yield Coefficient

The vapor phase bioreactor may be viewed as a catalytic reactor in which the catalyst, or the biomass, evolves through the cycles of birth, growth, reproduction, and death. During the growth process, cell mass is produced through a series of chemical reactions. The general stoichiometric equation for growth and product formation may be expressed by the equation below:



The production of cell mass through the utilization of a carbon source is a bioconversion process. This conversion is characterized by a yield coefficient given by the cell mass produced or product formed per unit mass of substrate consumed, $Y_{X/S}$ and $Y_{P/S}$, respectively. In the particular case under study with p-xylene as the substrate, the yield coefficient represents the mass of cells produced per unit mass of p-xylene consumed.

Theoretical cell yields on the carbon source may be determined by two common methods. One method is based on the observation that the yield of adenosine triphosphate (ATP) by many microorganisms is equal to 10.5 grams of cells per mole of ATP produced (Bauchop *et al.*, 1960). This method, however, requires knowledge of the catabolic pathway for substrate utilization. The other method is based on the number of electrons required for complete oxidization of the carbon source, recognizing that four electrons are required for the reduction of one mole of elemental oxygen. Independent of the substrate or organism, Mayberry *et al.* (1967) found the average yield of cell mass per electron to be 3.14 ± 0.11 when using ammonia as the nitrogen source. As an example, the complete oxidation of p-xylene as the carbon source is considered:



With forty two available electrons, the theoretical cell yield for p-xylene is 0.8 g cells/g p-xylene.

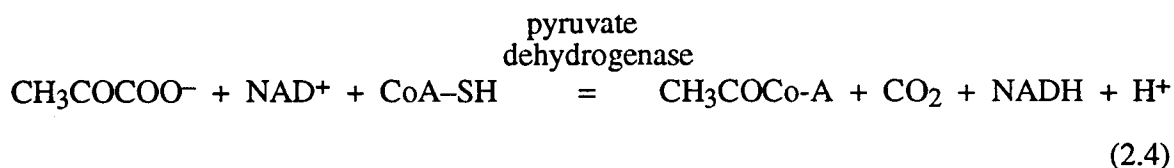
Because the theoretical cell yield is based on the complete oxidation of the carbon source to carbon dioxide and water, this yield does not take into account the carbon source being used for cell mass synthesis or maintenance. Actual cell yields are therefore lower than the calculated theoretical yields. For the degradation of p-xylene by *P.putida* ATCC 23973, a maximum yield coefficient of 0.6 g cells/g p-xylene has been reported by Lee *et al.* (1993).

2.3.2 Biochemical Pathways

The general pathway for the aerobic biodegradation of aromatic compounds is represented in Figure 2.2. The intermediate catechol is produced upon reaction with oxygen through cellular enzymatic processes using a monooxygenase in eukaryotic organisms, and using a dioxygenase in prokaryotic organisms. Ring-cleavage occurs by another dioxygenase reaction, and further metabolism leads to the production of acetyl-coenzyme A and succinate by way of the citric acid, or Krebs, cycle for conversion of pyruvate to CO₂ and formation of NADH (nicotinamide adenine dinucleotide).

The specific biodegradation pathway for the oxidation of p-xylene by *P.putida* 23973 is represented in Figure 2.3 (a) (Ribbons *et al.*, 1982) and Figure 2.3 (b). The bottom half of Fig. 2.3 (a) is referred to as the meta-cleavage pathway, initiated by meta-cleavage enzymes which oxidize catechol, and was initially proposed by Davey and Gibson (1974). *P.putida* 23973 possesses the enzymes benzyl alcohol dehydrogenase and benzaldehyde dehydrogenase necessary to metabolize the intermediates of the meta-pathway (Worsey *et al.*, 1975; Williams *et al.*, 1976). Additionally, Worsey *et al.* demonstrated that the specificities of these enzymes for the p-xylene substrate was independent of the carbon source used for growth.

To illustrate the chemical balance equations involved, the beginning of the Krebs cycle is given by the following reaction which represents the conversion of pyruvate to acetyl-coenzyme A:



The overall reaction in the Krebs cycle is given by the following equation:

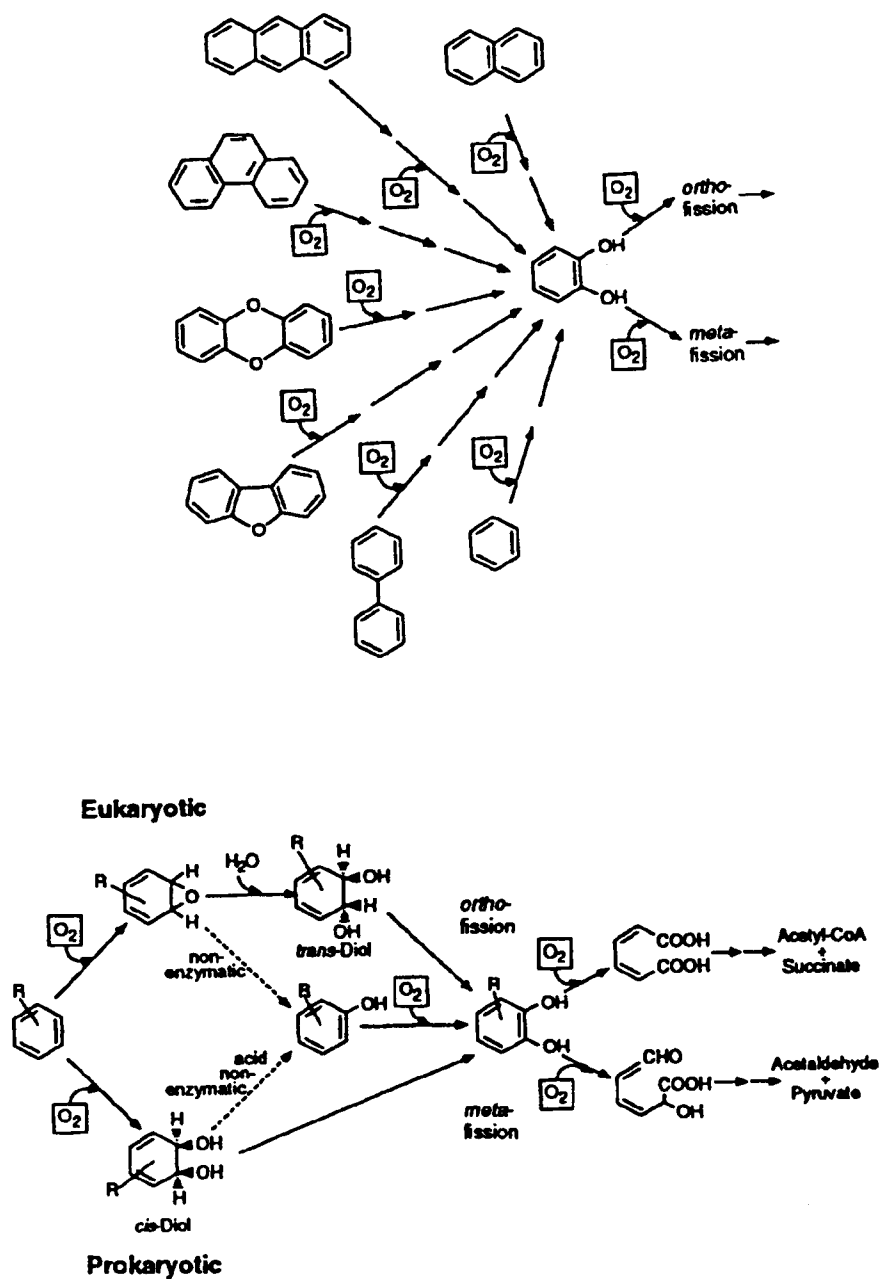
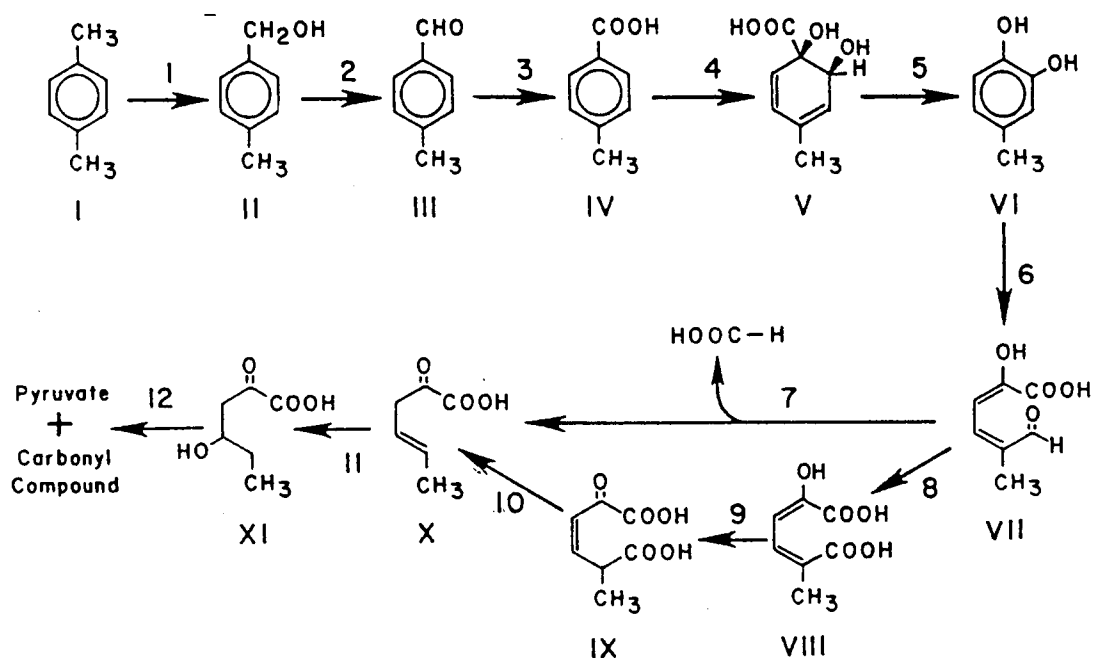


Figure 2.2: Aerobic biochemical reaction pathway for the degradation of aromatic compounds. (Bouwer *et al.*, 1993)

(a)



(b)

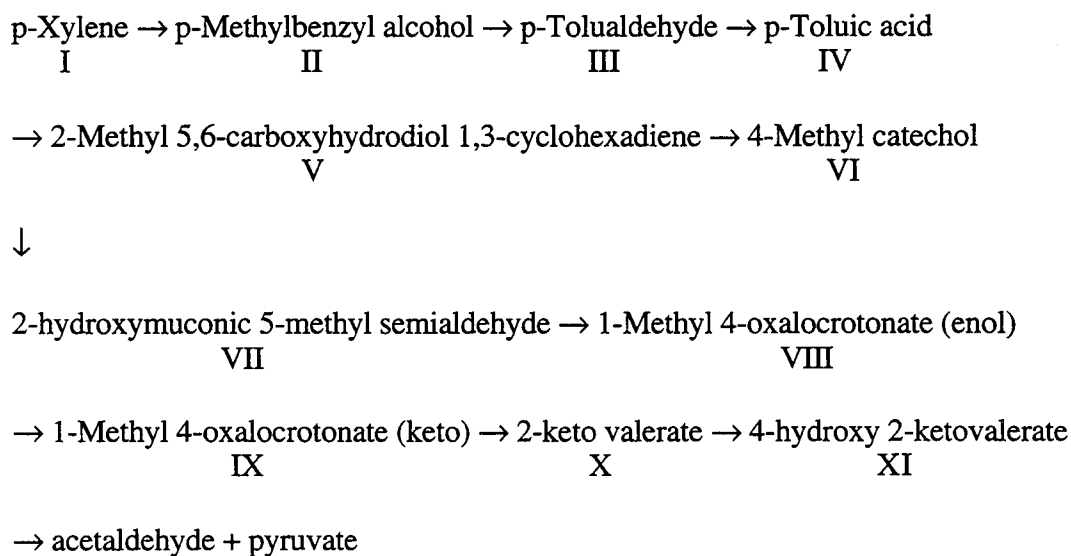
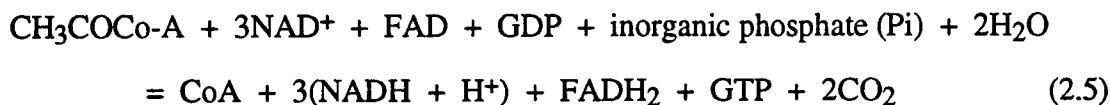
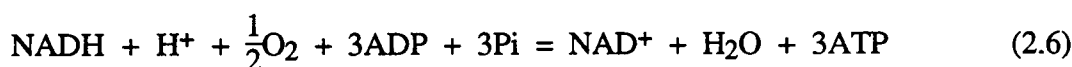


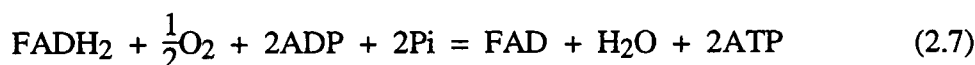
Figure 2.3: Pathway for oxidation of p-xylene by *P. putida* 23973 (a) structural pathway (adapted from Ribbons *et al.*, 1982) (b) nomenclature



The net reactions which describe the respiratory chain in which adenosine triphosphate (ATP) is formed are given by:



and



The overall oxygen, carbon dioxide, and water balances can be determined from a combination of Figure 2.2 and the biochemical equations given above. From equations 2.4 and 2.5, each pyruvate ion yields three CO₂ molecules, three NADH molecules, and one FADH₂ molecule. Two pyruvate ions can be formed from one C-6 compound, resulting in a total of six CO₂ molecules. Because para-xylene has two extra carbon compounds, complete mineralization would give two more carbon dioxide molecules and result in the overall combustion equation of 2.3 previously given. From equations 2.6 and 2.7, four oxygen molecules are required for the oxidation of 6 NADH and 2 FADH₂ molecules, producing seven water molecules. However, a net total of three water molecules are produced when the water requirement of equation 2.5 written for two acetyl-coenzyme A molecules is taken into account. For complete oxidation, the further oxygen requirement of equation 2.3 originates from the reactions of Figure 2.2 with the extra oxygen needed for oxidation of the methyl groups of p-xylene. The water balance of equation 2.3 is then completed as two more water molecules are produced if the two methyl groups are completely oxidized.

2.4 REACTOR DESIGNS

With reference to Table 2.2, the types of reactors used for biodegradation studies have been batch reactors, continuously-stirred tank reactors, and axial-flow fixed-bed reactors. The review of the literature indicates that there has never been a radial-flow vapor phase bioreactor employed in the biodegradation of a hazardous organic compound despite the advantages of the radial flow configuration introduced in section 2.1.1. The following chapter, Chapter III, discusses the details of the radial-flow reactor configuration employed.

In the papers mentioned previously in this chapter, mathematical models of bioreactor kinetics and operation were presented only for the simple batch and continuous stirred tank reactors (Lee *et al.*, 1993; Chang *et al.*, 1993). The equations that resulted were either solved analytically in the case of algebraic equations or by a Runge-Kutta numerical integration procedure in the case of ordinary differential equations. For these cases, the numerical results coincided with the experimental data generated.

In order to evaluate and understand the performance of the reactor under consideration in this thesis, mass balance equations for p-xylene and the biomass will be developed, numerically solved, and compared with the experimental data obtained. The kinetic parameters referenced in Section 2.3 will be used in this modeling procedure, and the observed biodegradation will be compared with the simulated reactor effluent profiles. The equations are presented in Chapter V, along with a generalized description of the finite element procedure to be used in their solution. The following chapter, Chapter III, describes the reactor configuration and the instrumentation employed in its setup and operation.

CHAPTER III

REACTOR CONFIGURATION AND INSTRUMENTATION

Current vapor phase bioreactors are packed bed bioreactors, reactors in which the microorganisms are in the form of a biofilm around a certain type of packing material. Packing materials such as gel beads, glass spheres, and polypropylene Pall rings have been used in vapor phase biodegradation studies of trichloroethylene and p-xylene (Uchiyama *et al.*, 1992; Apel *et al.*, 1993; Vaughn *et al.*, 1993). Sand and soil, however, are more common biofilm supports for industrial-scale air purification operations (Diks *et al.*, 1991; Douglass *et al.*, 1991; Tabak *et al.*, 1991; Ottengraf *et al.*, 1983).

In the studies discussed thus far, the flow of reactants was in the axial direction with negligible convection and dispersion in the radial direction. The bioreactor design presented in this section is unique in that the packing is situated between two concentric cylinders made of stainless steel, microporous metal and the gas flow is in the radial direction. This design is chosen in an attempt to optimize mass transfer of p-xylene to the immobilized microorganisms.

This chapter describes and depicts the details of the bioreactor's construction and configuration. The way in which the reactor is integrated into the experimental setup is also shown, and the different elements of the experimental setup are described. The actual details of the experimental procedures employed are thoroughly presented in the subsequent chapter, Chapter IV.

3.1 REACTOR DESCRIPTION AND OPERATION

Figure 3.1 is a schematic of the reactor showing two different cross-sectional views. The top view represents a cross-section in the longitudinal direction (xy-plane), and the lower view a cross-section in the transverse direction (xz-plane). The core of the reactor consists of two concentric cylinders made of 316 microporous stainless steel (Fig. 3.2, Pall PMM Metal Membrane Filters, NY), each of which was tungsten inert-gas welded to form the cylinders. The outer diameter of the inner cylinder is 1.63 cm, and the inner diameter of the outer cylinder is 2.54 cm, which gives a reactor thickness of 0.91 cm. This entire assembly is fitted and sealed on top and bottom with o-rings into an outer cylindrical casing made of 304 stainless steel. The reactor plumbing is made from 304 stainless steel tubing with a diameter of 0.125 inches. The reactor was tested for operation up to 60 psi, though the experiments did not produce pressures above 20 psi.

The packing material, which also serves as the support medium for the biofilm, consists of white quartz sand particles (Sigma Chemical Company, St. Louis, MO) which are nonporous and have an average diameter of 0.025 cm. The sand is covered with a biofilm and is situated in the cylindrical shell between the first two inner cylinders. The average crystalline density of the sand was measured to be 2.7 g/mL.

The p-xylene contaminant stream is introduced into the reactor through the inner cylinder core (Fig. 3.1). The concentration and humidity of the contaminant stream is regulated using an air tank and a two-stage bubbler, as indicated in the line diagram of Figure 3.3. Because the two inner cylinders are capped, the vapor mixture flows radially outward through the microporous metal to the inner cylindrical shell containing the sand and biofilm where the p-xylene is enzymatically degraded by the microorganism. The gaseous effluent stream then flows to the outer cylindrical shell by convection and leaves the reactor through the exit port located at the top of the reactor.

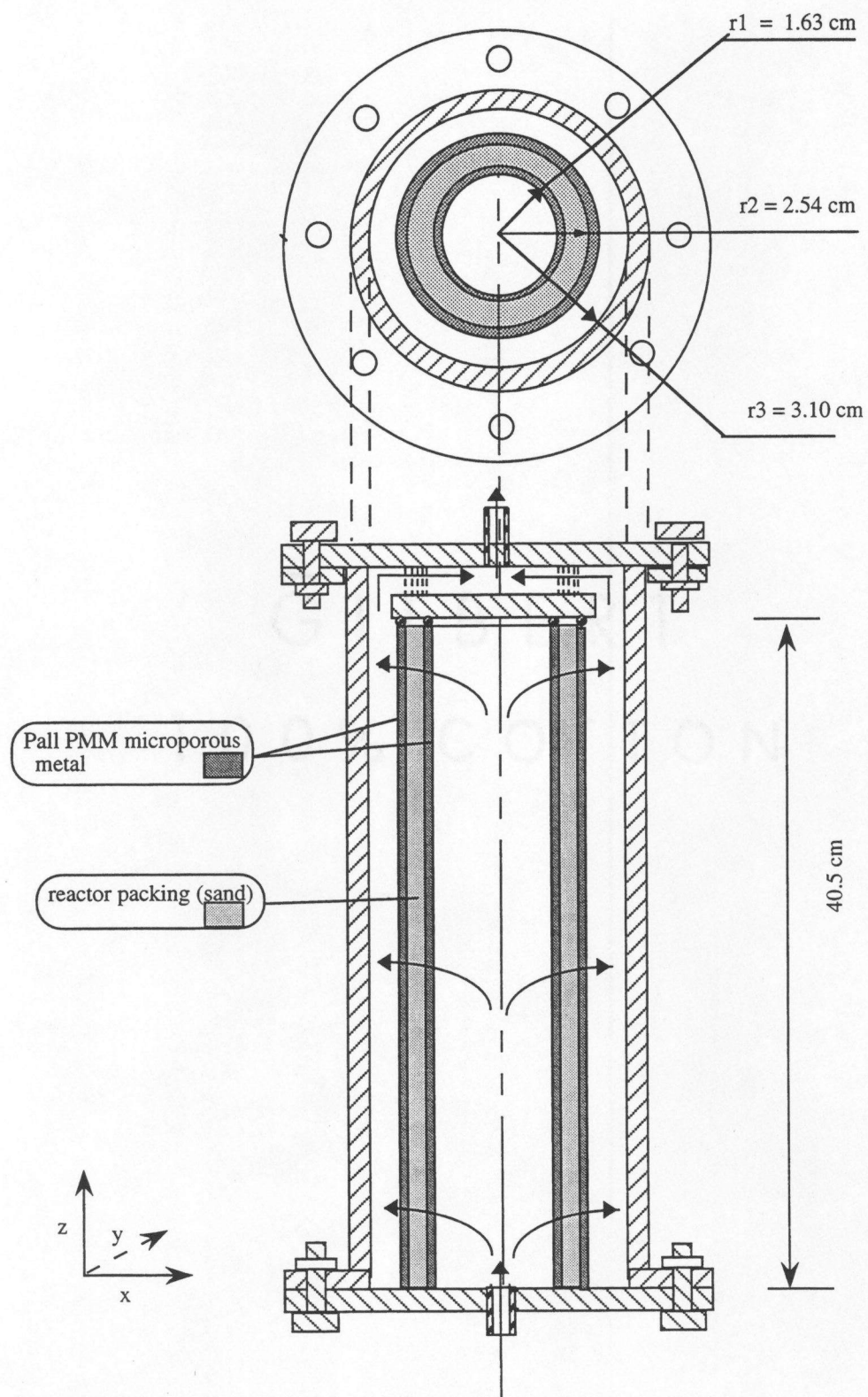


Fig. 3.1: Schematic of reactor configuration showing concentric cylindrical shell arrangement. Height of filled reactor is 40.5 cm. (16 in.)

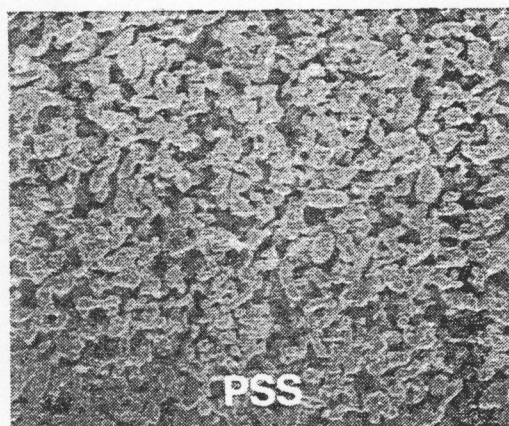


Fig. 3.2: Pall sintered, porous stainless steel medium (photomicrograph 15X, Pall Corporation, 1992).

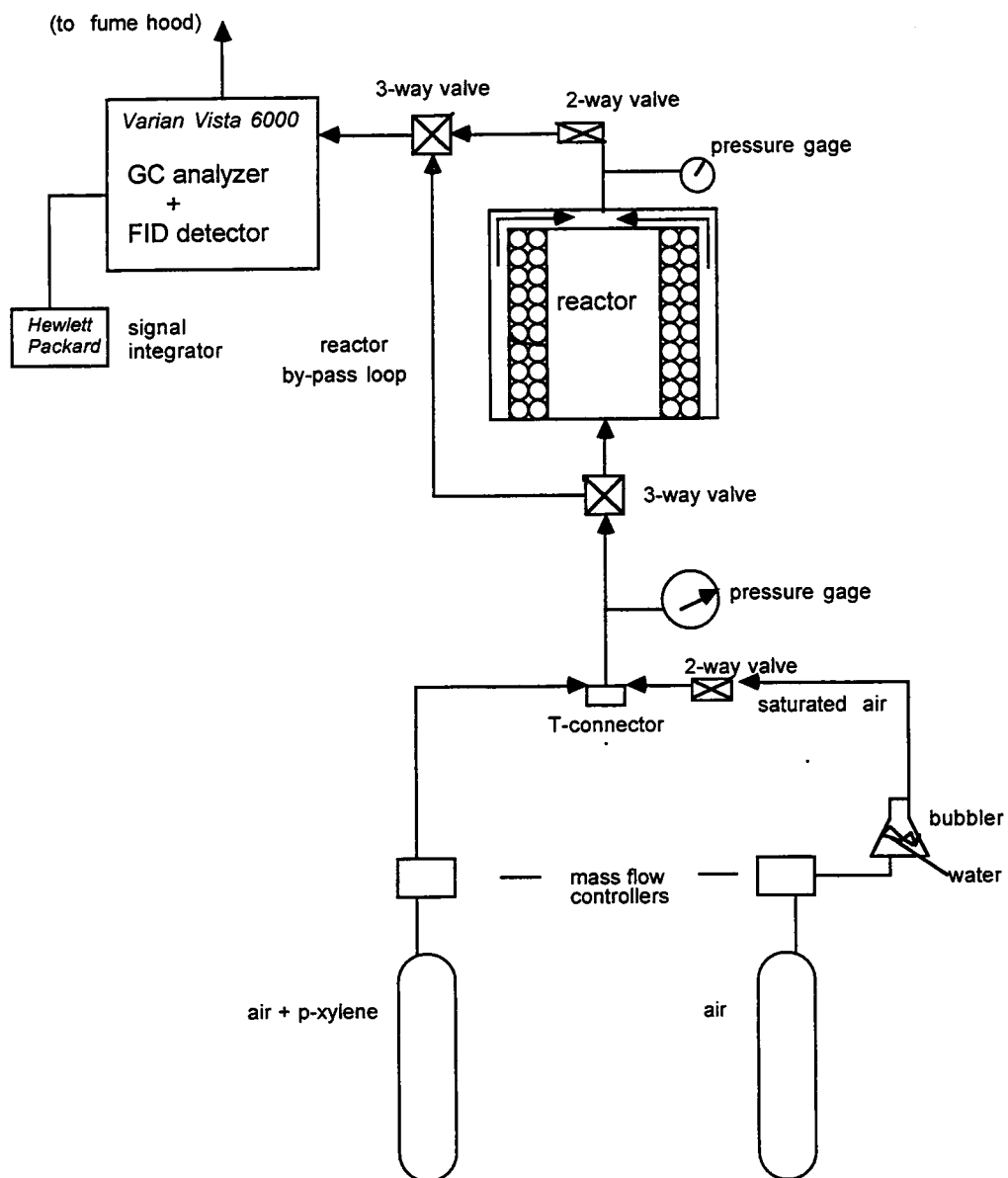


Fig. 3.3 Schematic line diagram of experimental setup.

3.2 INSTRUMENTATION

The essential elements of the experimental setup are depicted in Figure 3.3, in which the reactor is integrated into a flow system for proper control of flow rates and effluent analysis. The 700-800 ppm p-xylene/air mixture comes premixed in a compressed gas tank (Airco, Inc., Port Allen, LA). The air used as the carrying medium is supplied from a second cylinder and is metered through a mass flow controller into a two-stage bubbler, where it becomes saturated. Mass flow controllers from Brooks Instrument Division (models 5850C, Emerson Electric Co., Hatfield, PA) were used to maintain volumetric gas flow rates at specified values up to 200 mL/min. The mass flow meters were calibrated using a bubble flow meter and permitted operational ranges of 0–200 cm³/min and 0–100 cm³/min, respectively, for the p-xylene/air mixture and the air stream.

The effluent from the reactor flows to a Vista 6000 series gas chromatograph (Palo Alto, CA) connected to a Hewlett-Packard integrator (Avondale, PA) where the p-xylene composition of the effluent gas is determined. The GC is equipped with a flame ionization detector for the quantitative analysis of the p-xylene. Two 1-mL sample loops installed in the GC permit direct sampling of both the introduced gas and the effluent gas.

CHAPTER IV

EXPERIMENTAL PROCEDURE

This chapter describes the technique used to grow cell culture solutions, the procedure used to pack the reactor, and the calculation used to determine the initial and final cell mass per gram of sand of the reactor. The manner in which the bed void was determined is detailed. Calibration of the mass flow controllers used in the experimental setup is also presented.

4.1 MASS FLOW METERS

The Brooks Models 5850C mass flow controllers are used to measure and control the flow rates of the gases to the reactor. These mass flow meters measure the mass flow rates of the gas streams and produce stable gas flows. The Brooks Model 5850C is a temperature-rise mass flow meter and is composed of a flow sensor, a control valve, and an electronic control system. At zero flow, a sensor flow tube is heated uniformly as the upstream and downstream sensor coils are heated equally in the absence of flow. As gases begin to flow through the sensor, a temperature differential occurs between the upstream and downstream sensor coils. This temperature difference is directly proportional to the mass flow rate of the gas flowing through the meter. The control valve serves to increase or decrease the mass flow by way of a control circuit until the measured flow rate equals the required, specified flow rate.

The mass flow meters were calibrated by flowing air at various flow rates through each mass flow meter and then calculating the corresponding actual flow rate using a

bubble flow meter. The actual flow rates are related to the digital flow readings of the mass flow controllers through the calibration curves presented in Figures 4.1 and 4.2. Each point on these graphs corresponds to an average flow rate obtained from at least three measurements. The operational ranges of the mass flow meters used for the air stream and for the p-xylene/air mixture are, respectively, 0-200 cm³/min, and 0-100 cm³/min.

4.2 CELL CULTURE GROWTH

The microorganism used in the experiments is *Pseudomonas putida* ATCC 23973, which was ordered freeze-dried from American Type Culture Collection (Rockville, Maryland). Initially, some of the cells are grown on agar plates and the remainder is kept in a freezer at -80°C. The YEPG media for the preparation of the plates is prepared with the following compounds on a one liter solution basis: dextrose (1.0 g), polypeptone (2.0 g), yeast extract (0.2 g), ammonium nitrate (0.2 g), agar (17.87 g), and one liter of distilled, de-ionized water. This solution is autoclaved for forty minutes, poured onto culture plates, and allowed to cool to room temperature. Some of the cells from the stock are then plated and allowed to grow for 24 hours at 25 °C. After this period, the cells are ready to be grown in a culture medium.

The medium that is used for cell growth is a benzoate medium (medium 1271), the suggested choice of medium for *P.putida* 23973 from ATCC . The composition of the medium on a one liter solution basis is given in Table 4.1.

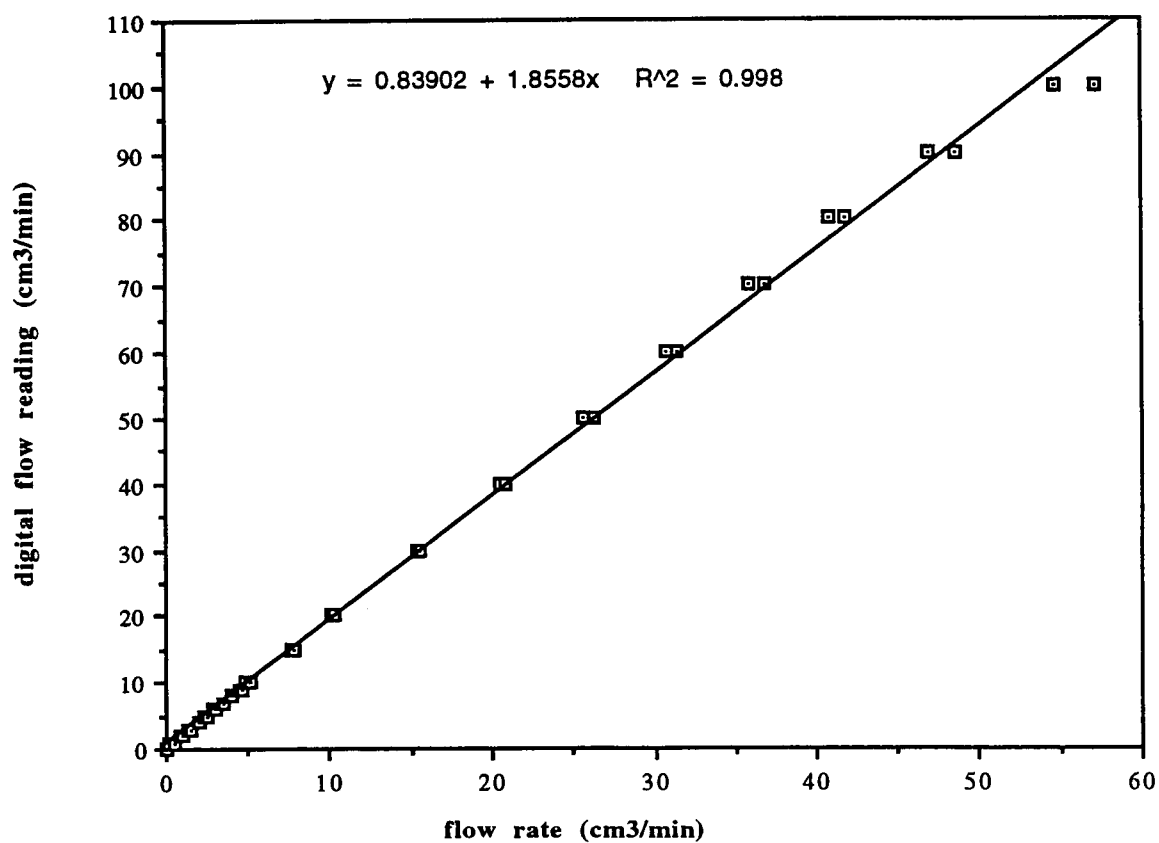


Figure 4.1: Calibration curve for Brooks 5850C mass flow controller 0-50 SCCM. The y-axis is the digital flow meter reading in cm^3/min , and the x-axis represents the actual measured flow rate.

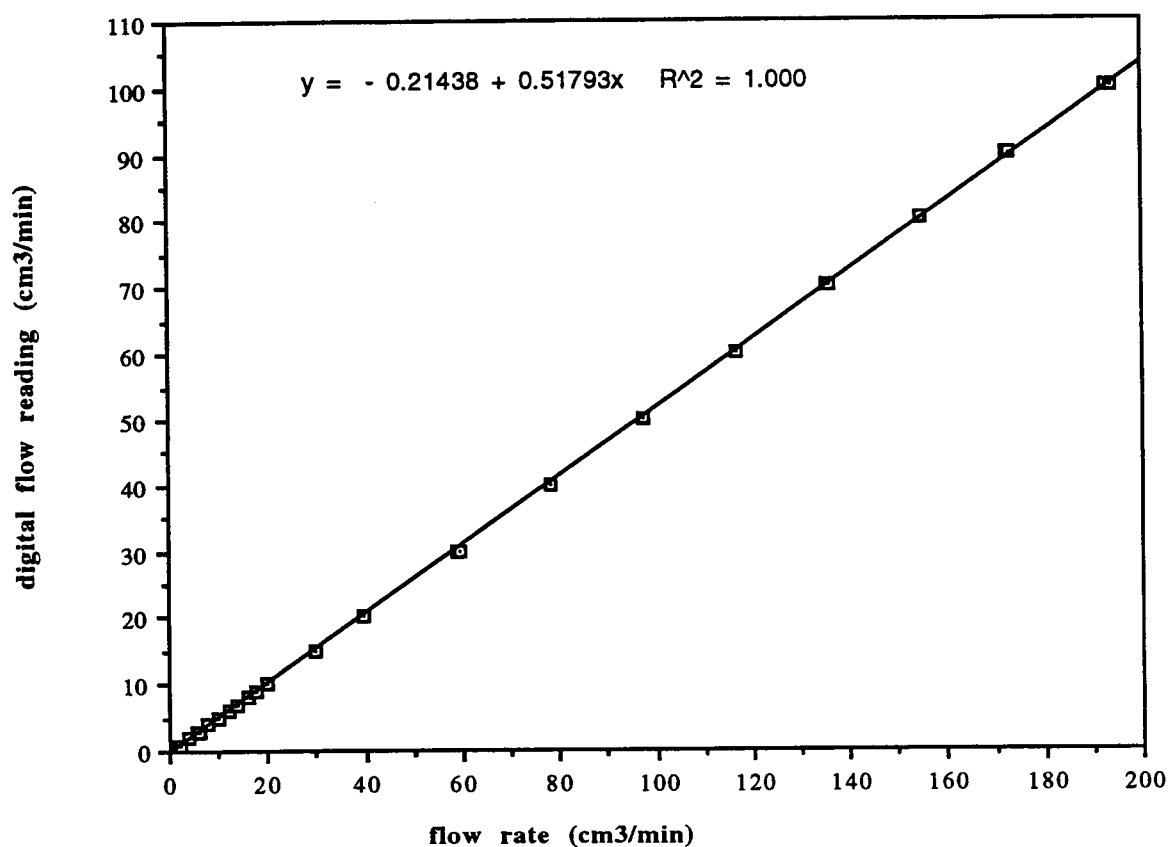


Figure 4.2: Calibration curve for Brooks 5850C mass flow controller 0-100 SCCM. The y-axis is the digital flow meter reading in cm³/min, and the x-axis represents the actual measured flow rate.

Table 4.1 Composition of benzoate medium 1271, 1 L solution basis

compound	origin	amount (grams)
sodium chloride NaCl	Mallinckrodt AR Paris, KY	5.0
ammonium phosphate dibasic (NH ₄) ₂ HPO ₄	Fisher Scientific Fair Lawn, NJ	3.0
sodium benzoate C ₇ H ₅ O ₂ Na	Fisher Scientific Fair Lawn, NJ	3.0
potassium phosphate monobasic KH ₂ PO ₄	Mallinckrodt AR Paris, KY	1.2
yeast extract	Difco Labs Detroit, MI	0.5
magnesium sulfate heptahydrate MgSO ₄ ·7H ₂ O	Mallinckrodt AR Paris, KY	0.2

First, a sodium benzoate solution of known composition, for example, a 12% by weight sodium benzoate solution, is prepared and filter-sterilized. Next, the solution described in Table 4.1 is prepared without the sodium benzoate in 1.0 L of distilled, de-ionized water. Then, in order to grow a biofilm on sand (Dunbar, 1990), the latter solution is divided equally into four 1L flasks with 250 g of white quartz sand (–50 + 70 mesh) per flask. These solutions are then autoclaved for forty minutes and allowed to cool. Finally, the correct amount of the sodium benzoate solution is added to each flask. For example, if a 12% by weight solution of sodium benzoate had been prepared and filter-sterilized, exactly 25 mL of this sodium benzoate solution is needed to satisfy the 3.0 g sodium benzoate requirement for a 1.0 L solution.

The benzoate medium and sand solutions are now ready to be inoculated. These solutions may be inoculated either with cells grown on the agar plates or with a thawed

culture solution from cells kept in a freezer at -80°C . If plated cells are used, cells are transferred directly to the solutions with a transfer loop that is sterilized before and after transferring by flaming with a Bunsen burner. The cells remaining on the agar plates are then kept in a freezer for future inoculations. When a frozen culture solution is used, usually 2.0 mL of cell solution results when thawed. In this case, a digital micropipettor with a sterile tip is used to transfer cell solution to each of the four flasks. Finally, the cell solutions are grown in a shaking flask incubator at 25°C .

The growth state of the cells is monitored by sampling approximately 2 mL of the cell culture solution at various times and measuring the absorbances at a wavelength of 600 nm. Absorbance being directly proportional to the mass of cells in the sample, the growth curve is obtained from a graph of the natural logarithm of absorbance as a function of time, (Fig. 4.3) which was obtained by growing the culture in benzoate medium without sand. During the exponential growth phase of the cells, the composition of the cells is constant. That is, all components of a cell are growing at the same rate. The growth rate is independent of nutrient concentration in this phase because nutrients are present in excess. Because the exponential growth phase is first order with respect to cell mass, a plot of the logarithm of absorbance as a function of time in this region is linear (Fig. 4.4).

To develop an active biofilm on the sand, the cells should be harvested during the stationary phase of growth based on the discussion by Dunbar (1990). At this point, most of the carbon substrate is depleted. The stationary phase begins after the exponential growth phase when the slope of the growth curve decreases and begins to approach zero. As seen from Figure 4.3, cell growth begins to approach steady state at a time of 120 hours, or five days. Therefore, between the fifth and sixth day of growth, the cell cultures are ready to be harvested and transferred to the reactor.

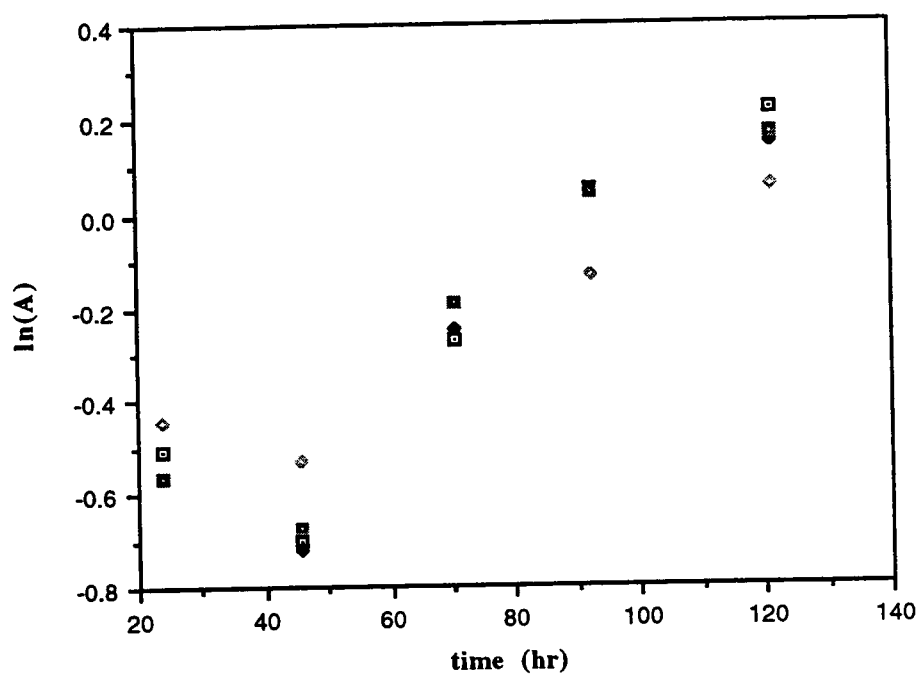


Fig. 4.3: Natural logarithm of absorbance at 600 nm vs. time for growth of *P. putida* 23973 at 25°C in benzoate medium 1271.

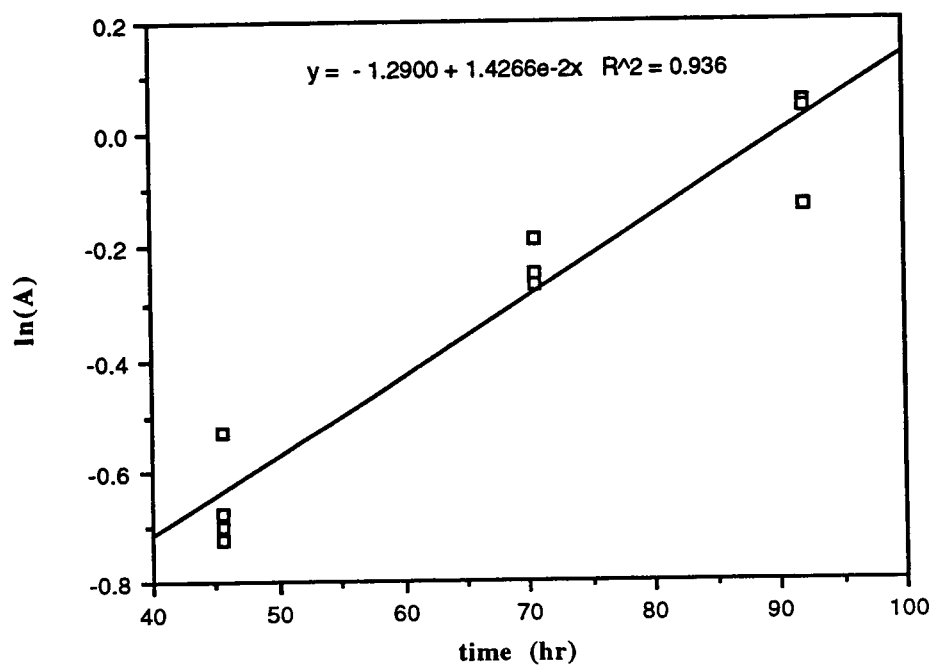


Fig. 4.4: Natural logarithm of absorbance at 600 nm vs. time for exponential growth phase of *P. Putida* 23973 at 25°C in benzoate medium 1271.

4.3 REACTOR PACKING

The support medium for the biofilm is white quartz sand, which also comprises the majority of the reactor packing. The sand has a mesh size of -50 to +70 as specified by the distributor (Sigma Chemical Company, St. Louis, MO.). This mesh size corresponds to an average particle diameter of 0.025 mm. Additionally, the sand is nonporous, restricting cell growth to the surface of the particles.

In order to determine the void fraction of the sand when packed into the reactor, the crystalline density of the sand must first be known. The density of the sand was determined by several repetitions of volume displacement and mass measurements of sand ranging from ten to forty grams of sand. The average crystalline density of the sand was determined to be 2.71 g/mL.

The bed void of the reactor was determined by tightly packing known amounts of sand into the cylindrical shell of the reactor. The corresponding volume of sand transferred to the reactor is then found by dividing the total mass of the sand packed into the reactor by the crystalline density previously determined. The fraction of the reactor volume that is occupied by the sand is the ratio of the volume of the sand to the volume of the cylindrical shell. The void fraction of the bed, denoted by ϵ , is the latter ratio subtracted from unity:

$$\epsilon = 1 - \frac{\frac{\text{mass of sand}}{\rho_s}}{\text{volume of cylindrical shell}}$$

Using this method, the void fraction of the bed was determined to be 0.303.

4.3.1 Nutrient Delivery

A controlled release method of nutrient delivery in the form of nutrient beads is used for the cells when they are transferred to the reactor. The composition and properties of the nutrient beads (provided by Grace-Sierra Horticultural Products Company, Milpitas, CA) are given in Table 4.2. The beads are coated with a resin made from linseed or soybean oil reacted with a cyclic diene. This coating allows for controlled release of nutrients upon exposure to moisture.

When the cells have reached steady-state growth, nutrient beads in an amount approximately equal to the mass of the nutrients in the original growth medium are added to each of the four flasks containing the cell cultures. These cell culture/sand slurries are now ready to be packed into the reactor.

4.3.2 Transfer of Cell Culture to Reactor

Prior to packing the reactor, the two microporous metal cylindrical shells between which the packing is to be situated (Fig. 3.1) are autoclaved for forty minutes. Upon cooling of the metal, the cell culture/sand solutions are carefully poured between the two metal membrane cylinders. After the solution has drained through the base, the assembly is placed within the reactor's metal casing. The top and bottom of the reactor, each of which has three sealing o-rings, are then connected. The biodegradation experiment commences as the flows of the saturated air and p-xylene/air mixture are begun through the reactor.

Gas chromatographic analysis of p-xylene in both the effluent gas stream and the influent stream is performed at various time intervals during reactor operation. The operating conditions of the gas chromatograph used for these samplings are given in Table

Table 4.2: Chemical and physical data of bioremediation nutrient source

Nutrient breakdown	weight %
total nitrogen (N)	24.1
ammonium	10.9
nitrate	9.1
urea	4.0
total phosphorus (P)	5.5
orthophosphate	4.5
total sulfur (S)	0.7
total potash (K)	0.5
micronutrients	3.1
<u>Physical data</u>	
size and appearance:	spherical pellets, 0.15–0.4 cm in diameter
specific gravity:	1.2
water solubility (%):	80–85
pH:	buffered to 6.5–7.0

Table 4.3 Operating conditions of gas chromatography system

Gas chromatograph (GC) conditions	
Oven temperature	130°C
Injector temperature	140°C
FID temperature	150°C
Attenuation	4
Sensitivity	10 ⁻¹² mV
Carrier flow (He)	25 mL/min.
Sample loop size	1 mL
Column	5% Didecyl phthalate plus 5% Bentone 34 on Chromosorb W-HP 80/100
<i>dimensions</i>	$d_i = 2 \text{ mm}$, $L = 2 \text{ m}$
<u>Integrator settings</u>	
Attenuation	2 ⁴
Chart speed	1.0 cm/min.
Peak width	0.04 min.
Threshold	0
Area reject	0

4.3. These settings were selected after having sampled pure p-xylene/air at different conditions.

4.4 MEASUREMENT OF CELL MASS

Quantifying cell mass based on absorbance measurements is done by dry cell weight measurements taken from a culture grown in a solids-free medium. Known volumes of the culture broth are taken at various times, centrifuged, washed with buffer or water, and dried in an oven at 80 °C. The dried cells are then weighed and the corresponding cell concentrations determined. From the absorbance of the cell solution at the time the sample was taken and the concentration of the cells, the linear relation between absorbance and cell concentration is determined (Figure 4.5.).

To determine the amount of cell mass on the biofilm, one gram of sand from the packed reactor is taken before and after each experiment. A known volume of a 10% solution of sodium pyrophosphate (Dunbar, 1990) is added to each sand sample to remove the cells from the sand. The samples are then vortexed, the sand allowed to settle, and the absorbance of the solution at 600 nm measured. From the correlation of optical density with cell mass previously determined (Fig. 4.5), the cell mass removed from the sand is quantified. By drying and weighing the sand, estimates of cell mass per gram of sand can be made.

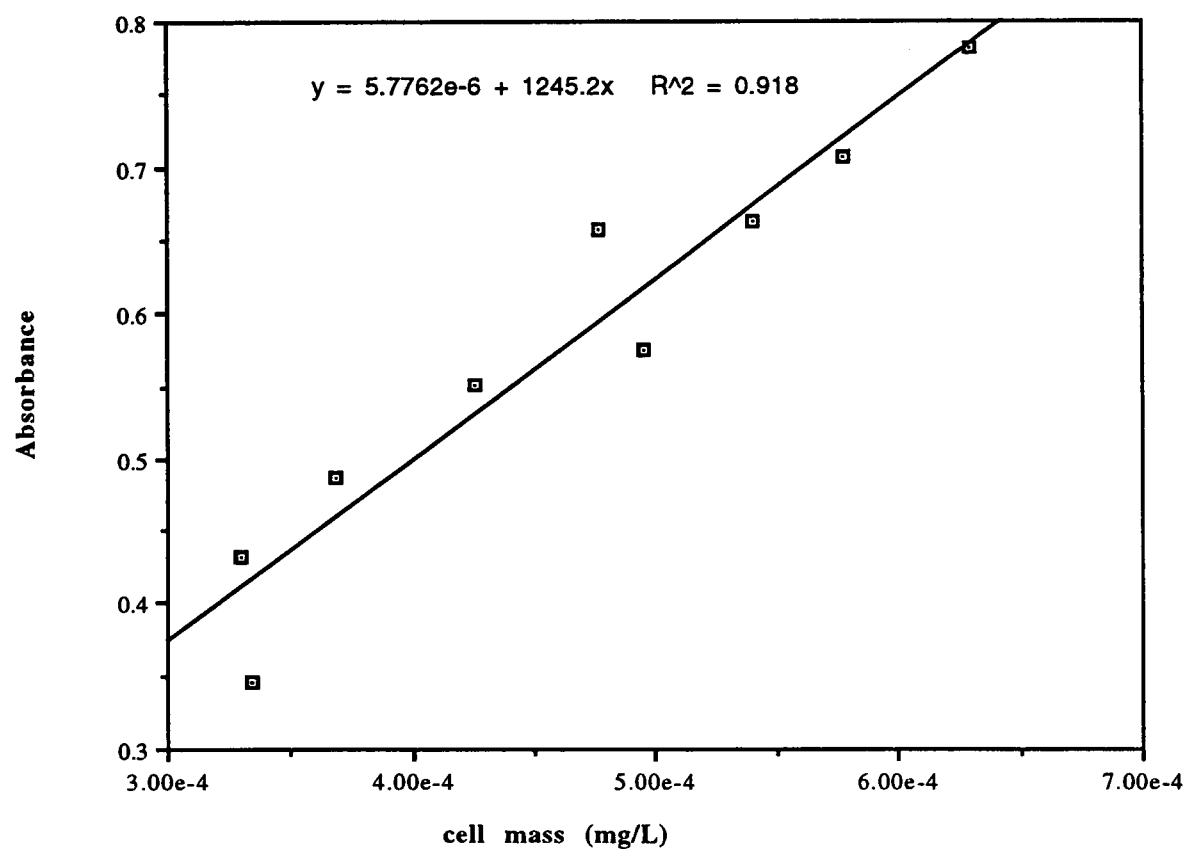


Fig. 4.5: Correlation of optical density at 600 nm of cell culture grown in a solids-free medium with concentration of cells in solution.

CHAPTER V

THEORY

In this chapter, a mathematical model describing reactor operation is presented for the analysis of the experiments treated in Chapter VI. The numerical procedure employed to generate solutions, the finite element technique, is outlined through the presentation of mathematical concepts and methodology, which are then further applied to a general example for illustrative purposes. The basis having been set for the particular case under study, the extensive development for the reactor equations is given in the appendix.

5.1 REACTOR MODEL

The reactor model employed in the analysis of the radial flow reactor is derived through a differential material balance on a cylindrical element (Fig. 5.1). Because the reactor is symmetric in the angular direction, the control volume (CV) is a cylindrical shell of volume $2\pi r\Delta r\Delta z$. A mass balance on this control volume can be stated as:

$$\begin{aligned} &\{\text{mass flux of component } i \text{ into CV}\} - \{\text{mass flux of component } i \text{ out of CV}\} \\ &\quad + \{\text{net generation of component } i \text{ per unit CV}\} \\ &= \{\text{rate of change of mass of component } i \text{ within CV}\} \end{aligned}$$

The mass flux of component i being denoted by N_i , the conservation of mass statement about a cylindrical shell of volume $2\pi r\Delta r\Delta z$ yields:

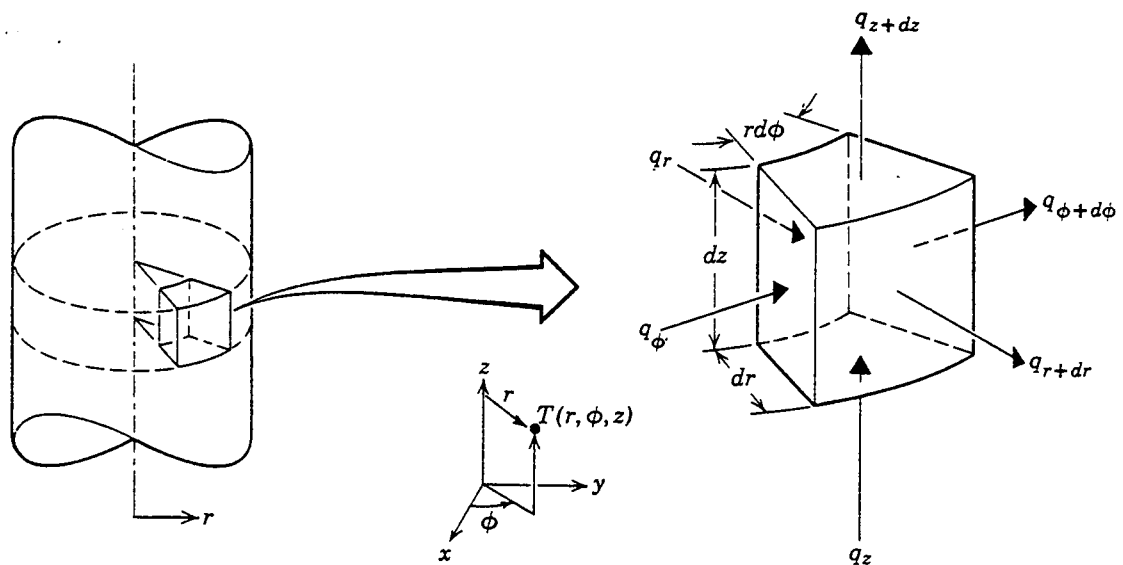


Fig. 5.1: Differential control volume, $rdrd\phi dz$, for shell balance in cylindrical coordinates (r, ϕ, z) .

$$N_i'' 2\pi r|_r \Delta z - N_i'' 2\pi r|_{r+\Delta r} \Delta z + N_i''|_z 2\pi r \Delta r - N_i''|_{z+\Delta z} 2\pi r \Delta r + v_i R 2\pi r \Delta r \Delta z = \frac{\partial c_i}{\partial t} 2\pi r \Delta r \Delta z \quad (5.1)$$

In this equation, v_i is the stoichiometric coefficient of component i . For $v_i < 0$, component i is consumed by reaction, and for $v_i > 0$, component i is generated by the reaction. The rate of reaction per unit control volume is denoted by R .

Equation (5.1) is divided by $2\pi r \Delta r \Delta z$:

$$\frac{N_i''|_r - N_i''|_{r+\Delta r}}{r \Delta r} + \frac{N_i''|_z - N_i''|_{z+\Delta z}}{\Delta z} + v_i R = \frac{\partial c_i}{\partial t} \quad (5.2)$$

In the limit as Δr and Δz approach zero, equation 5.2 becomes

$$-\frac{1}{r} \frac{\partial (r N_i''(r))}{\partial r} - \frac{\partial N_i''(z)}{\partial z} + v_i R = \frac{\partial c_i}{\partial t} \quad (5.3)$$

The symbols $N_i''(r)$ and $N_i''(z)$ represent the net mass fluxes of component i into the control volume in the radial and axial directions, respectively. Each of these fluxes is composed of a convective and a diffusive term given by equations 5.4a and 5.4b

$$\text{flux in r-direction: } N_i''(r) = v_r(r) c_i - D_r \frac{\partial c_i}{\partial r} \quad (5.4a)$$

$$\text{flux in z-direction: } N_i''(z) = v_z c_i - D_l \frac{\partial c_i}{\partial z} \quad (5.4b)$$

where D_r and D_l represent effective dispersion parameters in the radial and axial directions, respectively. These parameters take into account molecular diffusion as well as eddy diffusion which can arise from packing effects and turbulence (Hill, 1977). The radial velocity is denoted by $v_r(r)$ because it is a function of the radial coordinate.

For constant mass density and constant diffusion coefficients, equation 5.3 becomes, with substitution of equations 5.4a and 5.4b:

$$D_r \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_i}{\partial r} \right) + D_l \frac{\partial^2 c_i}{\partial z^2} - v_r(r) \frac{\partial c_i}{\partial r} - v_z \frac{\partial c_i}{\partial z} + v_i R = \frac{\partial c_i}{\partial t} \quad (5.5)$$

Because the reactor under study has only a radial velocity component and is taken to have a uniform distribution in the axial direction, only radial distributions are considered. The equation used to describe reactor operation is then of the form given by equation 5.6 below, where the subscripts r have been dropped for clarity.

$$D_r \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_i}{\partial r} \right) - v(r) \frac{\partial c_i}{\partial r} + v_i R = \frac{\partial c_i}{\partial t} \quad (5.6)$$

The form of the differential material balance having been developed for the radial flow reactor, the assumptions of the particular model to be used are stated:

(1) Kinetics of the reaction are described by the Monod equation. This assumption is reasonable in the system under study because $c \ll K_i$ (section 2.2).

(2) A pseudo-homogeneous model is assumed. This model assumes that the fluid within the volume element is characterized by a given bulk composition, and that this composition varies continuously with position within the reactor. No gradients occur within the biofilm, and the fluid and biofilm have the same composition at any given point in the reactor.

(3) Only radial transport is considered, because the flow is in the radial direction.

(4) Pressure variations are negligible.

(5) The system is isothermal.

(6) Constant physical properties are assumed.

With these assumptions, mass balances for the substrate and the biomass over the cylindrical shell of the reactor core result in the following equations:

$$\frac{\partial c}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) - v(r) \frac{\partial c}{\partial r} - \left(\frac{1}{Y} \right) \rho \frac{\mu_m c b}{K + c} \quad r_1 \leq r \leq r_2 \quad (5.7)$$

$$\frac{\partial b}{\partial t} = \frac{\mu_m c b}{K + c} \quad (5.8)$$

where

c = concentration of substrate [M/L³]

b = concentration of biomass [M biomass/M sand]

$v(r)$ = superficial radial velocity [L/t]

ρ = mass of sand per unit volume of reactor

K = Monod constant [M/L³]

μ_m = specific growth rate [1/t]

D = effective diffusion coefficient [L²/t]

Y = yield coefficient [M cells/M substrate]

In equation 5.7, the radial velocity is a function of the radial coordinate. The functional dependence of radial velocity with radius may be determined by solving the continuity equation in cylindrical coordinates. This derivation is given in Section 5.3, where the model equations are nondimensionalized. The stoichiometric coefficient is given by the factor $-1/Y$, which represents the mass of substrate formed per mass of cell.

Equation 5.8, the biomass balance, represents the accumulation of biomass within the reactor. The biomass is implicitly dependent on the radial coordinate through its functional dependence on substrate concentration.

The boundary and initial conditions for this system are:

$$\text{initial conditions:} \quad c(0,r) = c_0 \quad b(0,r) = b_0 \quad (5.9a)$$

$$\text{boundary conditions:} \quad c(t,r_1) = c_0 \quad (5.9b)$$

$$\left. \frac{\partial c}{\partial r} \right|_{r_2} = 0$$

The initial condition states that at time $t=0$, initial concentrations of substrate and biomass exist for all radial values within the reactor. The boundary condition at the inner radius, r_1 , states that a constant concentration of substrate, c_0 , enters the system. The boundary condition at the outer radius is a no flux boundary condition implying that no dispersion exists at the output of the reactor.

Equations 5.7 and 5.8 constitute a system of coupled, nonlinear, partial differential equations. This system is not amenable to analytic solution techniques because of the nonlinearity. Therefore, a numerical solution procedure is outlined in the following section for the solution of this system of equations.

5.2 FINITE ELEMENT METHOD

While finite element analysis was originally employed by aircraft companies in the late 1950's for structural analysis, it is now also extensively used by auto manufacturers, shipbuilders, and power plant designers. Finite element analysis can be extended beyond its origins in structural mechanics and subsequent applications in heat transfer analysis to

include mass transfer and chemical reactor analysis. For example, a one-dimensional finite element model can be used to simulate toluene diffusion and biodegradation in soil. (L.Sa *et al.*, 1994).

Many partial differential equations arise in engineering for which analytical solutions do not exist because of mathematical nonlinearities, complex and irregular geometry, or discontinuities in physical properties. The finite element method is a formal mathematical theory for determining approximate solutions to such steady-state or transient boundary value problems. In this method, the solution domain, denoted by Ω , is divided into connected subregions, or elements, within which spatial functions multiplied by unknown expansion coefficients are used to approximate the solution. The finite element method then provides approximate solutions at discrete points, or nodes, in the domain.

An important aspect of the finite element method is that it is not limited by geometric complexities. The elements may be one, two, or three dimensional and form a uniform or a non-uniform mesh. One-dimensional elements may be used for uni-directional mass transfer through a film. Two-dimensional elements consist of straight- or curve-sided triangular or quadrilateral regions. The extension to three dimensions produces tetrahedrons and hexahedrons with straight or curved sides. For all of these elements, the domain may be divided into macro-domains as required by physical properties, source terms, or for solution adaptation.

Another important aspect of the finite element method is that there are no restrictions on physical properties or boundary conditions that may be employed. For example, physical properties of many composite materials may change abruptly, or even present discontinuities at certain regions. Different physical properties in each macrodomain, or even at each node, may then be defined. The finite element method also easily incorporates Dirichlet, Neumann, and Robin boundary conditions without employing simplifying assumptions at the boundaries.

5.2.1 General Procedure

The theory for developing finite element approximate solutions for a given partial differential equation with specified boundary conditions involves the steps enumerated below from Baker *et al.*, 1991.

1. State the solution approximation as

$$q(x_j) = q^N(x_j) \quad 1 \leq i \leq N \text{ (elements)}$$

$$= \sum_{i=1}^N a_i \phi_i(x_j) \quad 1 \leq j \leq n \text{ (dimension)}$$

for a steady-state problem, and as

$$q(x_j, t) = q^N(x_j, t) = \sum_{i=1}^N a_i(t) \phi_i(x_j)$$

for a non-steady-state problem. In these equations, the a_i 's are the unknown expansion coefficients, and $\phi_i(x_j)$ are spatial functions known as the trial function set.

2. Select linear, quadratic, or cubic piecewise continuous polynomials which form the basis of Lagrange interpolation for the trial function set, $\phi_i(x_j)$.

3. Define a weak statement to determine the expansion coefficients to ensure that the error in the approximation is a minimum. The weak statement derives its name from the result of using integration by parts which reduces the order of the derivatives by one. The differentiability that the approximation must support is weakened as only the first derivative

of the approximation is required to exist in the examples and problem presented. (For transient problems, employ a Taylor series single-step ordinary differential equation (ODE) algorithm, and define the weak statement and a θ Taylor series, where θ is a parameter that determines the order of the accuracy of the solution.)

4. Discretize the solution domain into finite elements and rearrange the polynomials into basis functions. The basis functions are substituted into the weak statement written on the mesh, WS^h , or $WS^h + \theta TS$, with appropriate linear or quadratic approximations made for variable physical properties in terms of the basis functions.

5. Establish the global matrix statement for solution by element assembly, and evaluate the integrals in the weak statement either in closed form or by a numerical procedure such as Gauss quadrature. The weak statement then takes the form

$$[M]\{Q\}_e - \{b(\text{data})\} = \{0\} \quad (\text{steady state})$$

or

$$[JACOBIAN](\{Q^{n+1}\}_e - \{Q^n\}_e) + \Delta t \{RESIDUAL\}^n = \{0\} \quad (\text{transient})$$

6. Incorporate the boundary and initial conditions and solve the weak statement via a matrix solution process (Gauss elimination, Gauss-Seidel).

7. Estimate the error in the approximation.

5.2.2 The Weak Statement and Approximation

An approximation to the analytical solution may be defined by a Taylor series expansion of known functions of the independent variables, x_j . Any approximation can then be written as

$$q^N(x_j) = \sum_{i=1}^N a_i \phi_i(x_j)$$

where a_i are the unknown constants (to be determined later) and $\phi_i(x_j)$, the trial functions, are the known functions of x_j . For a transient problem, a_i is also a function of time.

The trial function set should consist of piecewise continuous low-order polynomials with defined first derivatives and $\phi_i' \phi_j'$ should be integrable on the solution domain. These polynomials are defined on each element of the problem domain, and may be linear, quadratic, or cubic. For a linear polynomial basis function, the variables ζ_1 and ζ_2 represent the local natural coordinate system spanning an element. The linear basis approximation is

$$Q_e(x) = (\zeta_1, \zeta_2) \{Q\}_e = \{N_1(\zeta_i)\}^T \{Q\}_e$$

Basis functions can also be developed for quadratic and cubic polynomials, and the general representation of the finite element basis set is

$$Q_e(x) = \{N_k(\zeta_i)\}^T \{Q\}_e$$

The measure of the approximation error in the numerical solution is given by $L(q^N)$, where

$$L(q) - L(q^N) = L(e^N)$$

$$-L(q^N) = L(e^N)$$

because $L(q)$ is by definition zero. To require that the measure of the approximation error vanish in an overall integrated sense, the weighted residual of $L(q^N)$ must be zero:

$$\int_{\Omega} \omega_i(x_j) L(q^N) d\tau = 0$$

In this equation, $\omega_i(x_j)$ are the weighting functions. In the Galerkin method, each $\omega_i(x_j)$ is set equal to the trial function, $\phi_i(x_j)$, of the approximation.

$$WS^N = \int_{\Omega} \phi_i(x_j) L(q^N) d\tau = 0$$

The Galerkin weak statement, WS^N , guarantees that the approximation error is a minimum because the error is orthogonal to the trial function set supporting the approximation.

5.2.3. Discretization

The solution domain, Ω , is subdivided into elemental regions by placement of nodes as desired for accuracy. Hence, the domain Ω^h is constructed. The weak statement integrals are then written for each element. The piecewise continuous polynomials, which form the basis of Lagrange interpolation, are rearranged into basis functions to evaluate the weak statement integrals at the nodes of the finite element discretization.

The mathematical statement for the finite element approximation, Q^h , is

$$\begin{aligned} Q^h(x_j, t) &= U_e Q_e(x_j, t) \\ &= \{N_k\}^T \{Q(t)\}_e \end{aligned}$$

where $\{N_k\}^T$ are the basis functions, and k is the basis degree. The symbol U_e represents the union, or non-overlapping sum, of finite element domains. For steady-state problems, Q^b is only a function of the geometrical coordinates.

The finite element discrete approximation to the Galerkin weak statement is done by element assembly to form WS^b . (Element assembly is a type of summation done on rows in the global matrix statement.) Problem data such as physical parameters, source terms, and boundary data must be specified and substituted into the weak statement.

For the steady-state heat conduction problem, the weak statement yields the global matrix statement of the general form

$$S_e([K+H]_e)\{Q\}_e - \{b\}_e = \{0\}$$

This is an algebraic matrix system that can be solved by linear algebra techniques such as Gauss elimination, which involves partitioning $[K]$ into lower, upper and diagonal square matrices.

However, transient problems do not result simply in algebraic matrix systems. For illustrative purposes, the nonsteady-state heat transfer equation is used. An example of a transient problem is the unsteady transport equation with a one-dimensional fluid velocity field (Baker *et al.*, 1991). The conservation of energy equation is

$$L(T) = \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} - \frac{\partial}{\partial x} \frac{k}{\rho C_p} \frac{\partial T}{\partial x} - \frac{s}{\rho C_p} = 0 \quad \text{on } \Omega$$

$$l(T) = k \frac{dT}{dn} + h(T - T_r) = 0 \quad \text{on } \partial\Omega_1$$

$$T(x_b) = T_b \quad \text{on } \partial\Omega_2$$

(Note that this equation is analogous to the mass balance equation for the substrate in the reactor.) Using the finite element approximation for T^h and following the development previously detailed for the steady-state problem, the weak statement written in assembled matrix form yields

$$WS^h = [M] \frac{d\{Q(t)\}}{dt} + [U+K+H]\{Q(t)\} - \{b\} = \{0\}$$

In contrast to the steady-state problem, the above system is not an algebraic matrix system but a system of ordinary differential equations. To solve this equation system, the single-step ODE algorithm is introduced:

$$\{Q\}^{n+1} = \{Q\}^n + \Delta t \left(\theta \frac{d\{Q\}^{n+1}}{dt} + (1-\theta) \frac{d\{Q\}^n}{dt} \right) + O(\Delta t^2, \Delta t^3)$$

The parameter θ defines the type of Taylor series to be used and the order of the truncation error. For $\theta=1$ or 0 , the truncation error is on the order Δt^2 , and for $\theta=0.5$ the truncation error is on the order Δt^3 .

Using this algorithm, the weak statement yields:

$$S_e(([M]_e + \theta \Delta t [U+K+H]_e) \{ \Delta Q \}_e - \Delta t (\{ b \}_e - [U+K+H]_e \{ Q \}_e)) = \{ 0 \}$$

where

$$\{ \Delta Q \}_e = \{ Q \}_e^{n+1} - \{ Q \}_e^n$$

This equation is of the form $[JAC]\{\Delta Q\} = \Delta t\{R\}^{n_e}$. At each time step and for each element, the Jacobian and the residuals are calculated and are then assembled. The matrix statement is solved, from which Q^{n+1} is obtained. The time is updated, and this process is repeated until the final time is reached.

The computer program to be used in the solution of equations (5.7) and (5.8) is AKCESS.*, which is a software platform for general applications (Computational Mechanics Corporation, Knoxville, TN) and is available through the Engineering Science Program at the University of Tennessee. The problem first needs to be written in assembled matrix form, then written as a template from which the main program does the computations. Section 5.3 develops the equations required for the numerical solution of the reactor equations, equations (5.7) and (5.8), with the boundary conditions of (5.9).

5.3 NONDIMENSIONALIZATION OF EQUATIONS

Derivation of weak statements and Jacobians for the partial differential equation system described in Section 5.1 is developed in this section. From Section 5.1, the reactor model equations are

$$\frac{\partial c}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) - v(r) \frac{\partial c}{\partial r} - \left(\frac{1}{Y} \right) \rho \frac{\mu_m c b}{K+c} \quad (5.7)$$

$$\frac{\partial b}{\partial t} = \frac{\mu_m c b}{K+c} \quad (5.8)$$

The dependence of velocity on radius, $v(r)$, is determined using the principle of continuity,

$$\int_{CS} \rho \mathbf{v} \cdot d\mathbf{A} = 0$$

where the symbol CS represents the control surface around which the integral is performed. Given areas A_1 and A_2 , which are the cylindrical shells of radius r_1 and r_2 ($r_1 < r_2$), respectively, the continuity equation is formulated as:

$$\int_{A_1} \rho_1 \mathbf{v}_1 \cdot d\mathbf{A}_1 + \int_{A_2} \rho_2 \mathbf{v}_2 \cdot d\mathbf{A}_2 = 0$$

$$= - \int_{A_1} |\rho_1 \mathbf{v}_1 d\mathbf{A}_1| + \int_{A_2} |\rho_2 \mathbf{v}_2 d\mathbf{A}_2|$$

$$= -\rho_1 v_1 A_1 + \rho_2 v_2 A_2 = 0$$

For constant density, $\rho_1 = \rho_2$ and the equation simplifies to

$$v_1 A_1 = v_2 A_2$$

where

$$A_1 = 2\pi r_1 h \quad \text{and} \quad A_2 = 2\pi r_2 h$$

Substitution of these two equations into the simplified continuity equation gives

$$v_2 = r_1 v_1 / r_2$$

The general dependence of velocity on radius is thus given by

$$v(r) = r_1 v_1 \left(\frac{1}{r} \right) \quad (5.10)$$

With this substitution, the reactor model equations become

$$\frac{\partial c}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) - r_1 v_1 \left(\frac{1}{r} \right) \frac{\partial c}{\partial r} - \left(\frac{1}{Y} \right) \rho \frac{\mu_m c b}{K + c} \quad (5.11)$$

$$\frac{\partial b}{\partial t} = \frac{\mu_m c b}{K + c} \quad (5.12)$$

To proceed with the development of the weak statements, the equations (5.11) and (5.12) are nondimensionalized using the following nondimensional variables for both the dependent and independent variables:

$$C = \frac{c}{c_0} \quad B = \frac{b}{b_0} \quad r^* = \frac{r}{r_2 - r_1} \quad t^* = \frac{t}{\tau}$$

where c_0 and b_0 are the initial substrate and biomass concentrations, respectively, and

$$\tau = \frac{r_2 - r_1}{v_1}$$

The partial derivatives are nondimensionalized as follows:

$$\frac{\partial c}{\partial t} = \frac{c_0}{\tau} \frac{\partial C}{\partial t^*} \quad \frac{\partial c}{\partial r} = \frac{c_0}{(r_2 - r_1)} \frac{\partial C}{\partial r^*} \quad \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) = \frac{c_0}{(r_2 - r_1)^2} \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C}{\partial r^*} \right)$$

$$r_1 v_1 \frac{1}{r} \frac{\partial c}{\partial r} = \frac{r_1 v_1}{(r_2 - r_1)^2} \frac{c_0}{r^*} \frac{\partial c}{\partial r^*}$$

In order to proceed with the development of the weak statement integrals and matrix formulations, it is useful to represent the kinetic growth term by a Taylor series as follows:

$$\begin{aligned} \frac{\mu_{mcb}}{K+c} &= \frac{\mu_{mcb}}{K} \left(\frac{1}{1+c/K} \right) = \frac{\mu_{mcb}}{K} \left(1 - \frac{c}{K} + \frac{c^2}{K^2} - \frac{c^3}{K^3} + \dots \right) \\ &= \frac{\mu_m c_0 b_0 CB}{K} \left(1 - \frac{c_0 C}{K} + \frac{c_0^2 C^2}{K^2} - \frac{c_0^3 C^3}{K^3} + \dots \right) \end{aligned} \quad (5.13)$$

Substitution of the nondimensional partial derivative terms and equation (5.13) into equations (5.11) and (5.12), and multiplying the resulting equations by τ gives:

$$\begin{aligned} \frac{\partial C}{\partial t^*} &= \frac{\tau D}{L_c^2} \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C}{\partial r^*} \right) - \frac{r_1}{v_1 \tau} \frac{1}{r^*} \frac{\partial C}{\partial r^*} \\ &\quad - \frac{\tau \rho \mu_m b_0}{YK} CB \left(1 - \frac{c_0 C}{K} + \frac{c_0^2 C^2}{K^2} - \frac{c_0^3 C^3}{K^3} + \dots \right) \end{aligned} \quad (5.14)$$

$$\frac{\partial B}{\partial t^*} = \frac{\tau \mu_m c_0}{K} CB \left(1 - \frac{c_0 C}{K} + \frac{c_0^2 C^2}{K^2} - \frac{c_0^3 C^3}{K^3} + \dots \right) \quad (5.15)$$

The parameter groupings are nondimensional terms which can be denoted as follows:

$$[DIFU] = \frac{\tau D}{L_c} \quad [CONV] = \frac{r_1}{v_1 \tau} \quad [RCTA] = \frac{\tau \rho \mu_m b_0}{Y} \quad [RCTB] = \tau \mu_m c_0$$

When these nondimensional terms are substituted into equations (5.14) and (5.15), with the reaction term first written in the full form for clarity, the following nondimensional equations result:

$$\frac{\partial C}{\partial t^*} = [\text{DIFU}] \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C}{\partial r^*} \right) - [\text{CONV}] \frac{1}{r^*} \frac{\partial C}{\partial r^*} - [\text{RCTA}] \frac{CB}{K+C} \quad (5.16)$$

$$\frac{\partial B}{\partial t^*} = [\text{RCTB}] \frac{CB}{K+C} \quad (5.17)$$

5.4 DEVELOPMENT OF GALERKIN WEAK STATEMENTS AND JACOBIANS

Equations (5.16) and (5.17) are rewritten with the reaction term written as a Taylor series to proceed with the development of the Galerkin weak statements and Jacobians:

$$\begin{aligned} \frac{\partial C}{\partial t^*} = & [\text{DIFU}] \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C}{\partial r^*} \right) \\ & - [\text{CONV}] \frac{1}{r^*} \frac{\partial C}{\partial r^*} - [\text{RCT1}] CB \left(1 - \frac{c_0 C}{K} + \frac{c_0^2 C^2}{K^2} - \frac{c_0^3 C^3}{K^3} + \dots \right) \end{aligned}$$

$$\frac{\partial B}{\partial t^*} = [\text{RCT2}] CB \left(1 - \frac{c_0 C}{K} + \frac{c_0^2 C^2}{K^2} - \frac{c_0^3 C^3}{K^3} + \dots \right) \quad (5.18) \text{ and } (5.19)$$

where

$$[\text{RCT1}] = \frac{\tau \rho \mu_m b_0}{YK} \quad [\text{RCT2}] = \frac{\tau \mu_m c_0}{K}$$

To begin with the development of the finite element equations, the weak statement is first written and developed for equation (5.18) represented below as:

$$L(C) = \frac{\partial C}{\partial t^*} - [\text{DIFU}] \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C}{\partial r^*} \right) + [\text{CONV}] \frac{1}{r^*} \frac{\partial C}{\partial r^*} + [\text{RCT1}] CB \left(1 - \frac{c_0 C}{K} + \frac{c_0^2 C^2}{K^2} - \frac{c_0^3 C^3}{K^3} + \dots \right) = 0$$

The differential equation for the substrate balance is written in discretized form.

$$(2\pi)WS = \int_{\Omega} \phi_i L(C^N) d\tau = \int_{\Omega} \phi_i L(C^N) r dr d\theta = 0$$

Because the reactor core is symmetrical in the angular direction, the weak statement may be simplified to:

$$WS = \int_{\Omega} \phi_i L(C^N) r dr = 0$$

Substitution of $L(C^N)$ with the Taylor series truncated in this equation leads to:

$$WS = \int_{\Omega} \phi_i \left(r^* \frac{\partial C^N}{\partial t^*} - [\text{DIFU}] \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C^N}{\partial r^*} \right) + [\text{CONV}] \frac{\partial C^N}{\partial r^*} + r^* [\text{RCT1}] C^N B^N \left(1 - \frac{c_0 C^N}{K} \right) \right) dr^*$$

Using integration by parts, the second term is rewritten as

$$- \int_{\Omega} \phi_i \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C^N}{\partial r^*} \right) dr^* = - \phi_i r^* \frac{dC^N}{dr^*} \Big|_{\partial\Omega} + \int_{\Omega} r^* \frac{\partial \phi_i}{\partial r^*} \frac{\partial C^N}{\partial r^*} dr^*$$

$$\begin{aligned}
 WS &= \int_{\Omega} \left(\phi_i r^* \frac{\partial C^N}{\partial t^*} - [\text{DIFF}] r^* \frac{\partial \phi_i}{\partial r^*} \frac{\partial C^N}{\partial r^*} + [\text{CONV}] \phi_i \frac{\partial C^N}{\partial r^*} + r^* [\text{RCT1}] \phi_i C^N B^N \left(1 - \frac{c_0 C^N}{K} \right) \right) dr^* \\
 &= 0
 \end{aligned}$$

The boundary condition term on the endpoints is set to zero in accordance with equation 5.9b.

The discretization on a particular mesh involves elemental values of the dependent variables, for which

$$\phi_i \rightarrow \{N\} \quad C^N \rightarrow C_e \quad B^N \rightarrow B_e$$

The elemental values of the dependent variables, C_e and B_e , are approximated in terms of the basis function N :

$$C_e = \{N\}^T \{C\}_e \quad \text{and} \quad B_e = \{N\}^T \{B\}_e$$

The weak statement written with this approximation is:

$$WS^h(L(C_e)) =$$

$$\begin{aligned}
 &\int_{\Omega_e} \left(\{N\} \{N\}^T \frac{\partial \{C\}_e}{\partial t^*} r^* + [\text{DIFF}] \frac{\partial \{N\}}{\partial r^*} \frac{\partial \{N\}^T}{\partial r^*} \{C\}_e r^* + [\text{CONV}] \{N\} \frac{\partial \{N\}^T}{\partial r^*} \{C\}_e \right) dr^* \\
 &+ [\text{RCT1}] \int_{\Omega_e} \left(\{N\} \{N\}^T \{C\}_e \{N\}^T \{B\}_e - c_0/K \{N\} \{N\}^T \{C\}_e \{N\}^T \{B\}_e \{N\}^T \{C\}_e \right) r^* dr^*
 \end{aligned}$$

For each radial element, the nodal value of the radius on its right and left sides are denoted by RR and RL, respectively. The above integrals may be simplified:

$$\begin{aligned} \int_{\Omega_e} r^* dr^* &= \int_{RL}^{RR} r^* dr^* = \frac{1}{2}(RR^2 - RL^2) = \frac{1}{2}(RR + RL)(RR - RL) \\ &= [RBAR]_e l_e \end{aligned}$$

$$\int_{\Omega_e} dr^* = \int_{RL}^{RR} dr^* = RR - RL = l_e$$

In these equations, which represent integrals taken over an element, $[RBAR]_e$ is the average radius across an element, and l_e is the length of an element.

Using these substitutions and incorporating FORTRAN matrix notation (Baker *et al.*, 1991) to denote the basis functions, the weak statement for the partial differential equation becomes:

$$\begin{aligned} WS_1^h &= [RBAR]_e \{C\}_e^T [A200] \{C\}_e' + [DIFU][RBAR]_e [A211] \{C\}_e \\ &\quad + [CONV]_e [A201] \{C\}_e + [RCT1][RBAR]_e \{C\}_e^T [A3000] \{B\}_e + \\ &\quad - [RCT1](c_0/K)[RBAR]_e \{C, C\}_e^T [A3000] \{B\}_e \\ &= 0 \end{aligned} \tag{5.20}$$

The weak statement with a θ -Taylor series for time discretization yields:

$$WS^h + \theta TS = \{FC\}_e = [RBAR]_e [A200]_e \{\Delta C\}_e + \frac{\Delta t}{2} [\{RC\}_{e,n+1} + \{RC\}_{e,n}]$$

where

$$\begin{aligned}
\{RC\}_e &= [DIFU][RBAR]l_e[A211]\{C\}_e + [CONV]l_e[A201]\{C\}_e \\
&\quad + [RCT1][RBAR]l_e\{C\}_e^T[A3000]\{B\}_e \\
&\quad - [RCT1](c_0/K)[RBAR]l_e\{C,C\}_e^T[A3000]\{B\}_e \\
\{\Delta C\}_e &= \{C_{e,n+1} - C_{e,n}\}
\end{aligned}$$

The Newton–Jacobians are developed as follows:

$$\begin{aligned}
[JCC]_e &= \frac{\partial\{FC\}_e}{\partial\{C\}_e} = [RBAR]l_e[A200][I] + \frac{\Delta t}{2} \frac{\partial\{RC\}_e}{\partial\{C\}_e} \\
\frac{\partial\{RC\}_e}{\partial\{C\}_e} &= [DIFU][RBAR]l_e[A211](I) + [CONV]l_e[A201][I] \\
&\quad - 2[RCT1](c_0/K)[RBAR]l_e\{C,B\}_e^T[A3000][I] \quad (5.21)
\end{aligned}$$

$$\begin{aligned}
[JCB]_e &= \frac{\partial\{FC\}_e}{\partial\{B\}_e} \\
&= \frac{\Delta t}{2} [RCT1][RBAR]l_e\{C\}_e^T[A3000][I] \\
&\quad - \frac{\Delta t}{2} [RCT1](c_0/K)[RBAR]l_e\{C,C\}_e^T[A3000][I] \quad (5.22)
\end{aligned}$$

In these equations, $[I]$ represents the identity matrix.

A similar development is followed for the second equation, equation (5.19):

$$L(B) = \frac{\partial B}{\partial t} - [RCT2]CB(1 - c_0C/K) \quad (5.19)$$

The Galerkin weak statement written on the mesh:

$$WS^h(L(B_e)) = \int_{\Omega_e} \left(\{N\} \left(\frac{\partial B_e}{\partial t^*} - [RCT2]C_e B_e (1 - c_0 C/K) \right) \right) r^* dr^* = 0$$

$$\begin{aligned}
WS^h(L(B_e)) &= (\{N\}\{N\}^T\{B\}_e' - [RCT2]\{N\}\{N\}^T\{C\}_e\{N\}^T\{B\}_e \\
&\quad + [RCT2]c_0/K\{N\}\{N\}^T\{C\}_e\{N\}^T\{B\}_e\{N\}^T\{C\}_e) \int_{\Omega_e} r^* dr^* \\
&= 0
\end{aligned}$$

$$\begin{aligned}
WS_2^h &= [RBAR]l_e[A200]_e\{B\}_e' - [RCT2][RBAR]l_e\{C\}_e^T[A3000]_e\{B\}_e \\
&\quad + [RCT2]c_0/K[RBAR]l_e\{C,C\}_e^T[A3000]_e\{B\}_e \\
&= 0
\end{aligned}$$

$$\begin{aligned}
\{FB\}_e &= WS_2^h + \theta TS \\
&= [RBAR]l_e[A200]_e\{\Delta B\}_e + \frac{\Delta t}{2}(\{RB\}_{e,n+1} + \{RB\}_{e,n})
\end{aligned}$$

where

$$\begin{aligned}
\{RB\}_e &= - [RCT2][RBAR]l_e\{C\}_e^T[A3000]_e\{B\}_e \\
&\quad + [RCT2]c_0/K[RBAR]l_e\{C,C\}_e^T[A3000]_e\{B\}_e
\end{aligned}$$

$$\begin{aligned}
[JBB]_e &= \frac{\partial\{FB\}_e}{\partial\{B\}_e} \\
&= [RBAR]l_e[A3000]_e[I] + \frac{\Delta t}{2} \frac{\partial\{RB\}_e}{\partial\{B\}_e}
\end{aligned}$$

$$\begin{aligned}
\frac{\partial\{RB\}_e}{\partial\{B\}_e} &= - [RCT2][RBAR]l_e\{C\}_e^T[A3000]_e[I] \\
&\quad + [RCT2]c_0/K[RBAR]l_e\{C,C\}_e^T[A3000]_e[I]
\end{aligned}$$

$$\begin{aligned}
[JBC]_e &= \frac{\partial\{FB\}_e}{\partial\{C\}_e} \\
&= -\frac{\Delta t}{2} [RCT2][RBAR]l_e\{B\}_e^T[A3000]_e[I] \\
&\quad + 2[RCT2]c_0/K[RBAR]l_e\{B,C\}_e^T[A3000]_e[I]
\end{aligned}$$

CHAPTER VI

RESULTS AND DISCUSSION

This chapter begins with a summary of the various experimental parameters that were employed in the biodegradation experiments. Next, breakthrough curves obtained in dead-cell, or abiotic, experiments performed within the range of the experimental conditions used in the biotic experiments are presented. Section 6.3 presents the experimental data obtained on the biodegradation of p-xylene and discusses various aspects of the effluent concentration curves obtained. Section 6.4 then integrates both the experimental data and the theoretically-predicted concentration curves based on the model developed in Chapter V. The results are presented in such a way as to facilitate their comparison. Additionally, the model is modified to account for the behavior of some of the effluent curves in Section 6.4. Following these results, the radial profiles generated through the model simulations are discussed.

6.1 EXPERIMENTAL PARAMETERS

The parameters that were investigated and allowed to vary were the influent p-xylene concentration and the flow rates of the influent streams (Table 6.1). The relative values of the p-xylene/air stream and the saturated air stream were chosen such that a range of different p-xylene concentrations would be studied at two different total flow rates.

Table 6.1: Summary of experimental conditions for biodegradation experiments

influent p-xylene concentration (ppm)	flow rates (cm ³ /min):		
	p-xylene/air	saturated air	total
284	22.5	37.5	60.0
147	12.9	49.1	62.0
106	20.5	108.9	129.4
100	8.2	53.8	62.0
50	3.7	58.0	61.7
50	8.6	116.4	125.0
28	2.3	60.0	62.6
36	5.1	116.0	121.1
15	1.4	60.7	62.1
15	2.4	122.6	125

The starting point for choosing the influent substrate concentration was based on the model for the microbial kinetics presented in Chapter II for the biodegradation of p-xylene by *P.putida* ATCC 23973. Influent substrate concentrations were chosen to be much less than the inhibition constant and were limited by the apparent inactivity of the cells above a certain high concentration. The lowest value of concentration presented in Table 6.1 was limited by the accuracy of the mass flow controller for the p-xylene/air stream. The resulting residence times for the total flow rates used are in the range of 3.82–8.25 minutes.

6.2 ABIOTIC EXPERIMENTS

To determine the adsorption breakthrough time of p-xylene on the biofilm/sand support, experiments were performed to determine the effects of any possible adsorption phenomena in the absence of biodegradation reactions. A representative result is shown in Figure 6.1, which shows the elution curve of 284 ppm of p-xylene at a flow rate of 60 cm³/min in an experiment performed with cells that had been autoclaved prior to packing of the reactor. The ordinate in these graphs represents the ratio of p-xylene in the outlet stream to the amount of p-xylene entering the reactor. These ratios were determined from the integrated response areas of the gas chromatographic signals for the p-xylene streams entering and leaving the reactor.

Figure 6.1 shows elution curves at a p-xylene feed concentration of 105 ppm at two flow rates: 60 ccm and 121 ccm. The experiment of Figure 6.1 was done at a reactor pressure of 15 psi with only the saturated air flowing at a flow rate of 60 cm³/min through the system prior to starting the p-xylene/air mixture flow at time $t = 0$. The elution curve for the 121 ccm flow rate shows breakthrough earlier than the breakthrough at 60 ccm. As

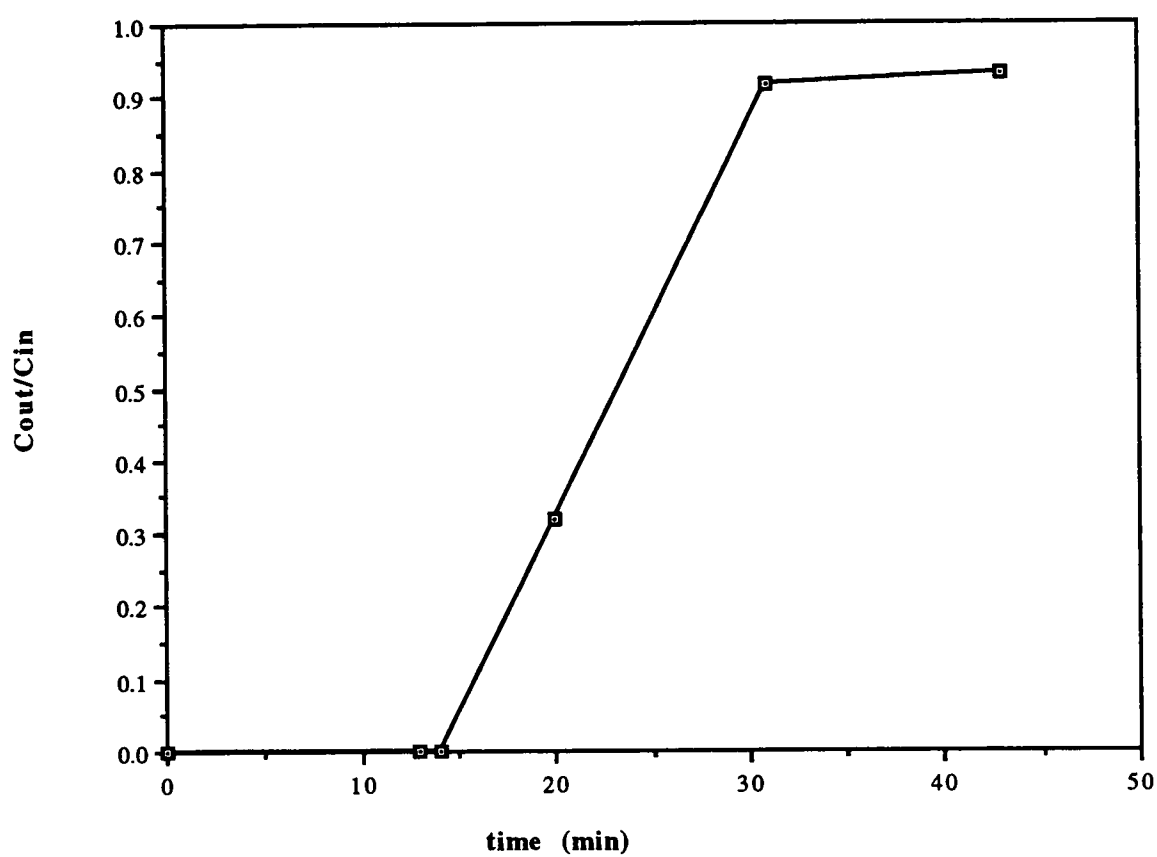


Fig. 6.1: Elution curve of 284 ppm feed of p-xylene at a flow rate of 60 cm³/min in packed bed experiment performed with immobilized cells which had been autoclaved.

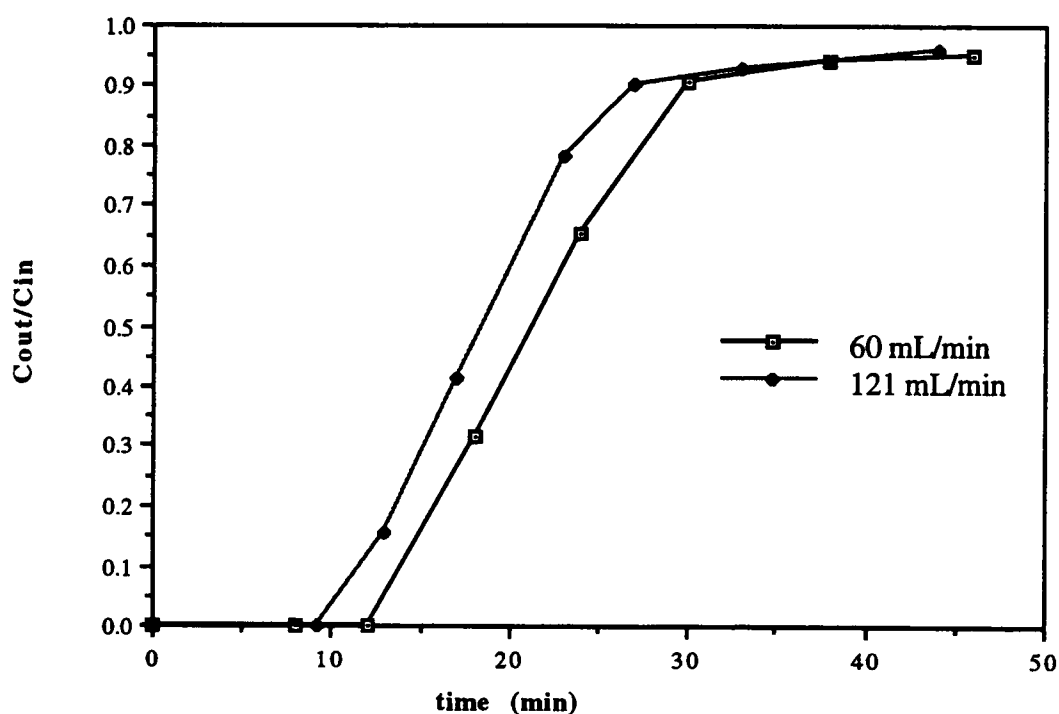


Fig. 6.2: Elution curves of 105 ppm feed of p-xylene at a flow rates of 60 cm³/min (squares) and 121 cm³/min (circles) in packed bed experiment performed with immobilized cells which had been autoclaved.

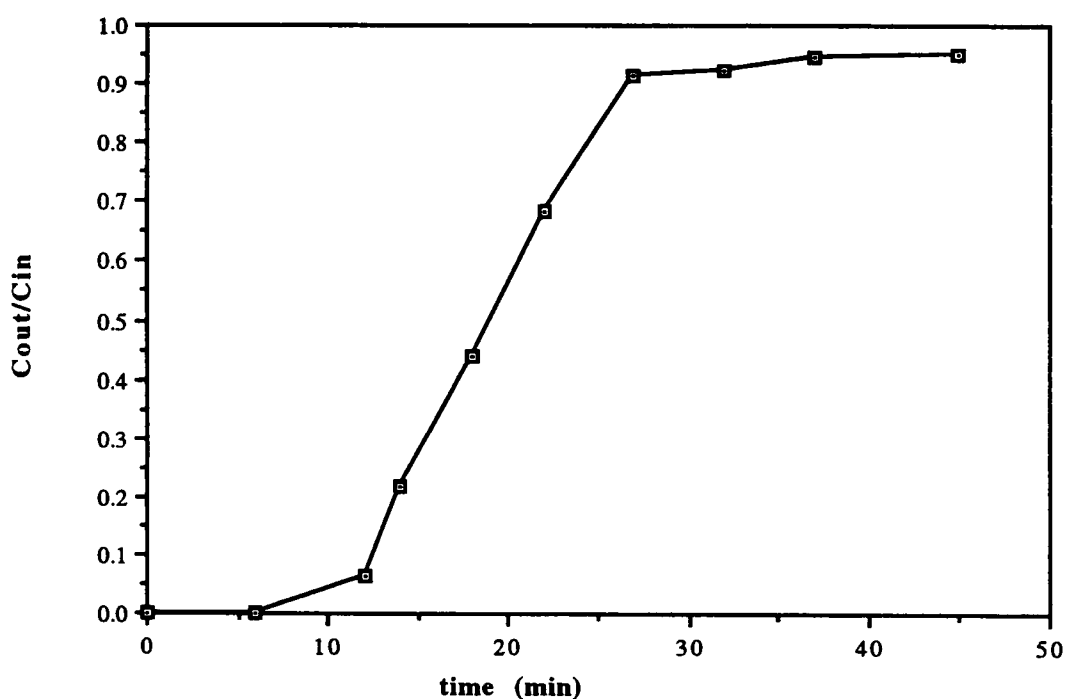


Fig. 6.3: Elution curve of 32 ppm feed of p-xylene at a flow rate of 120 cm³/min in packed bed experiment performed with immobilized cells which had been autoclaved.

expected, with the same feed concentration, breakthrough should occur earlier at the higher flow rate. That the difference is not as great as might be expected (factor of two difference in breakthrough times) is because the experiments were done with different batches of autoclaved cells.

Breakthrough occurs within one hour with an inlet feed of 284 ppm. Thus, any decrease in the outlet concentration of p-xylene at feed concentrations less than or equal to 284 ppm and at flow rates greater than or equal to $60 \text{ cm}^3/\text{min}$ would subsequently be attributed to biodegradation kinetics. That this is indeed the case is shown in Figures 6.2 and 6.3, in which feed concentrations of p-xylene of 105 ppm and 32 ppm are used. The breakthrough times are consistently less than one hour in all of these cases.

The purpose of doing these abiotic adsorption experiments was to determine if adsorption of para-xylene onto cellular matter would be a limiting factor in the biodegradation experiments. Because the breakthrough time of the abiotic experiments is within one hour, then the cell membrane/sand medium is saturated within one hour in the absence of biodegradation. This means that during the first hour of a biodegradation experiment run at p-xylene concentrations lower than 284 ppm and at flow rates higher than 60 ccm (highest concentration and lowest flow rate of adsorption experiment) adsorption would be occurring. With a constant feed, biodegradation would begin to occur no later than after the adsorption would have taken place.

6.3 BIODEGRADATION EXPERIMENTS

The results of the biodegradation experiments performed as per the parameters in Table 6.1 are depicted in Figures 6.4 to 6.15, which show the time evolution of p-xylene in the outlet stream of the reactor. Steep variations in the outlet concentration of p-xylene can

be seen when sampling of the outlet stream is done during the first twenty-five hours of operation, where several factors are simultaneously occurring:

- (a) The pressure inside the reactor is stabilizing as flow to the reactor is begun. Although the pressure drop through the reactor is not greater than 3 psi, the pressure inside the reactor reaches a stable value of 10 to 14 psi during its first hour of operation.
- (b) Adsorption and breakthrough of p-xylene is occurring during the first hour of operation, as discussed in Section 6.2.
- (c) Acclimation of the cells to the new carbon substrate is occurring. During packing of the reactor, cells which have been growing from five to six days in a growth medium with benzoate as their sole carbon source are abruptly immersed into an environment initially containing only nutrient beads (composition given in Table 4.2.). P-xylene as the substrate is introduced to the packed, immobilized cells only after transport to and final assembly of the reactor is completed one to two hours later. During the initial stages of reactor operation, the cells are then becoming accustomed to a new environment.

The initial regions of the output curves is discussed in the next section. The subsequent sections describe in detail the observed output of the bioreactor in the order of increasing value of the feed concentration of p-xylene.

6.3.1 Initial Stages of Reactor Operation

Examples of the reactor output in the initial stages of reactor operation are shown in Figures 6.4 to 6.6, which show the first 30 hours of operation for each of the feed concentrations at the flow rates employed. A general comparison between all of these curves is that, for each feed concentration, C_{out}/C_{in} at the higher flow rates (121-129

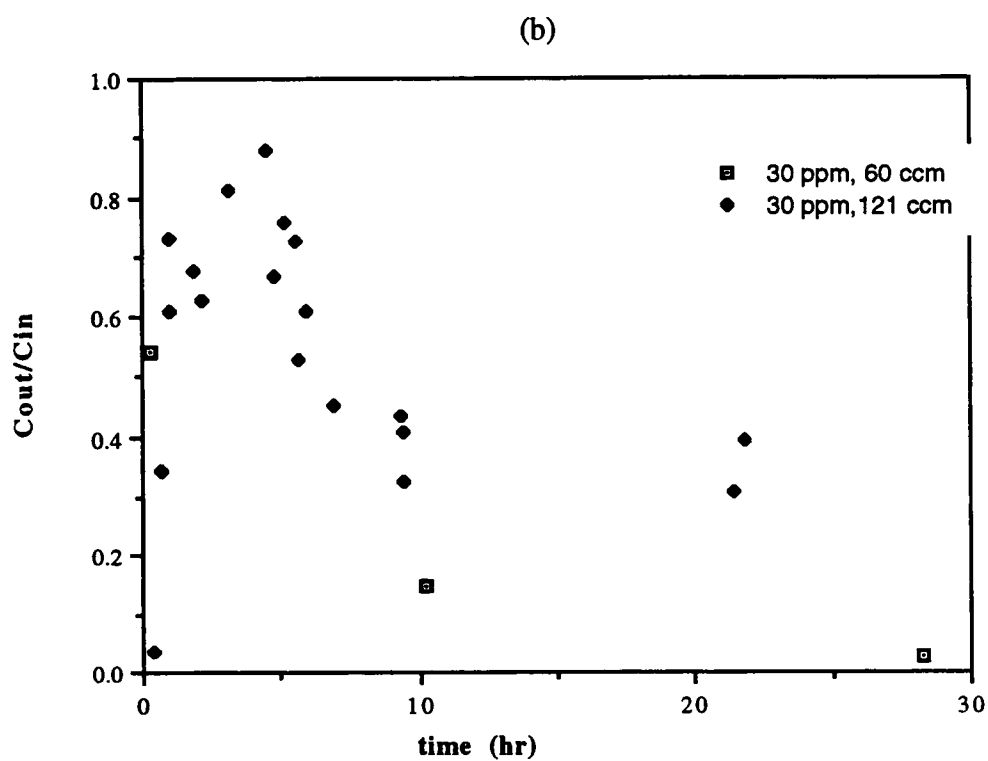
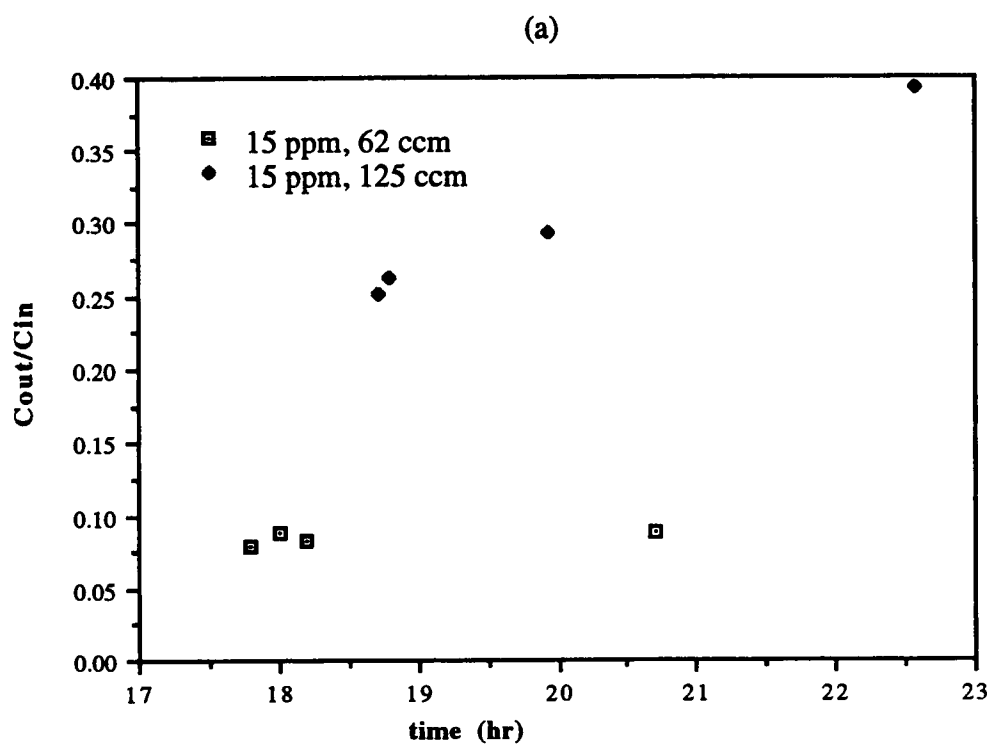


Fig. 6.4: Concentration effluent curves in initial stages of reactor operation at specified conditions. (a) $C_0 = 15$ ppm (b) $C_0 = 30$ ppm

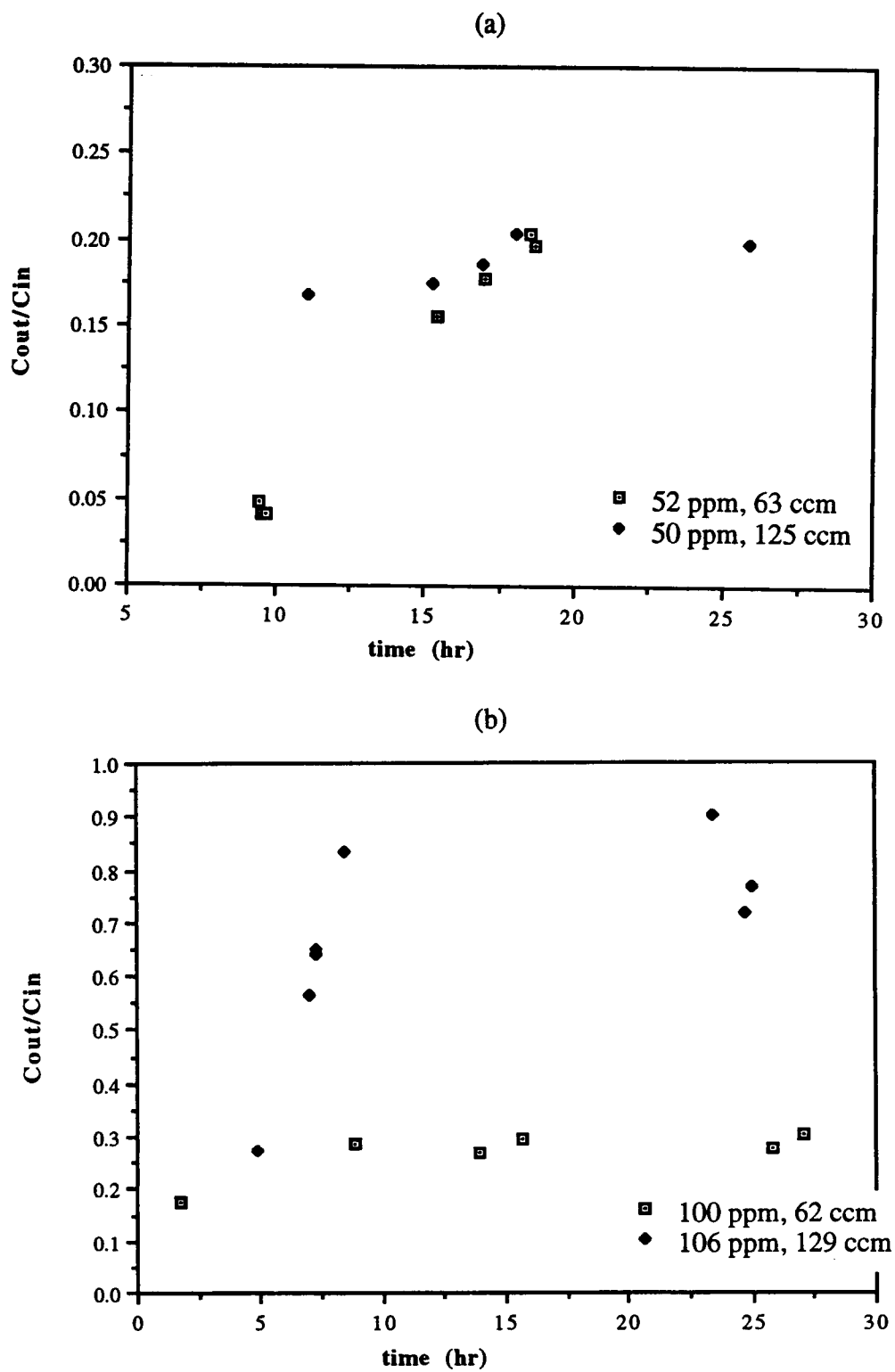


Fig. 6.5: Concentration effluent curves in initial stages of reactor operation at specified conditions. (a) 50, 52 ppm (b) 100, 106 ppm

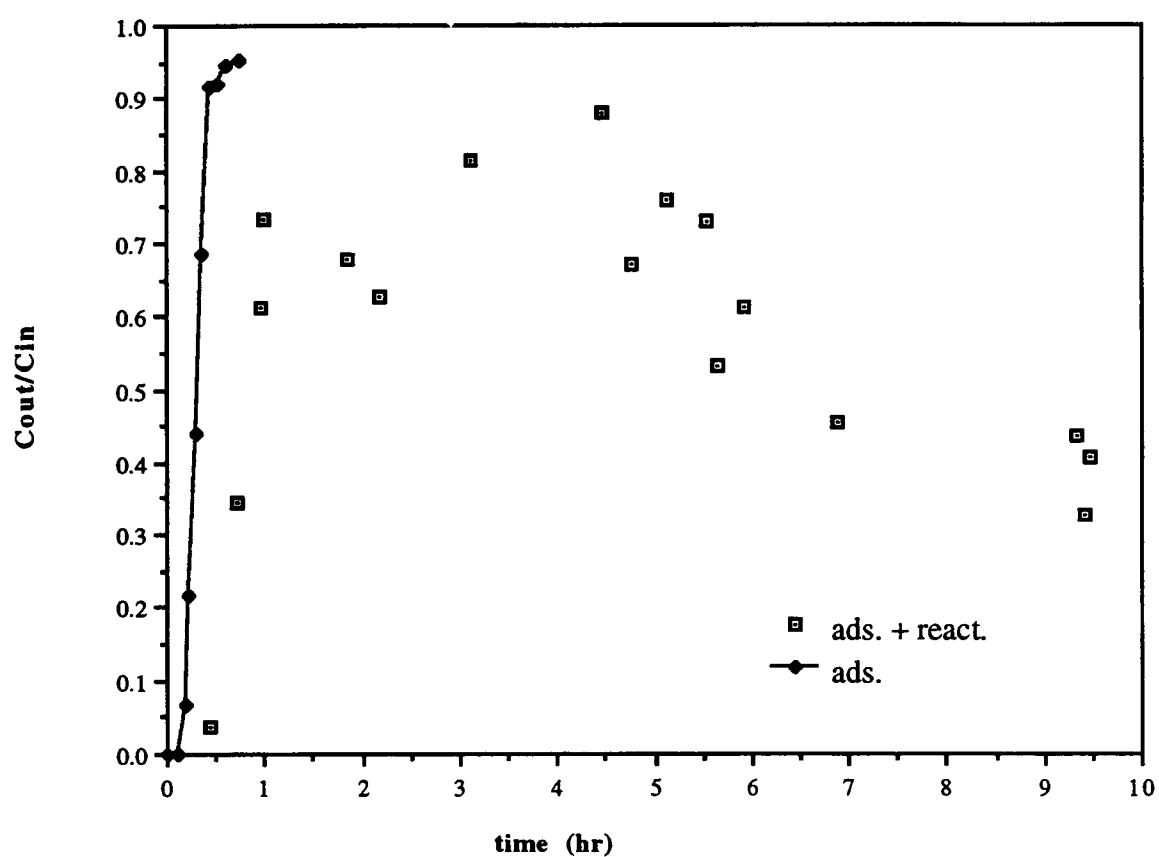


Fig. 6.6: Comparison of initial region of biodegradation reaction (ads. + react., initial p-xylene concentration of 32 ppm at 121 mL/min) with the abiotic adsorption experiment (ads., initial p-xylene concentration of 30 ppm at 120 mL/min).

cm^3/min) at any given time is greater than $C_{\text{out}}/C_{\text{in}}$ at the lower flow rates (60-63 cm^3/min). This means that as the flow rate is doubled for a given input concentration, a greater fraction of the p-xylene of the inlet stream exits the reactor than it does at the lower flow rates at any given time less than 30 hours. From consideration of adsorption phenomena alone, saturation of the bed proceeds at a faster rate as the flow rate of the influent stream increases. This would cause earlier breakthrough of p-xylene. This breakthrough can only be seen when data is available during the first two hours of operation, because that is when breakthrough occurs in the concentration range for this system (Section 6.2).

For the 15 ppm case, the initial region of the effluent curves (Fig. 6.4 (a)) shows a positive slope in the interval of 17.5 to 22.5 hours. (The x-axis runs from 17 to 23 hours because data was not available at earlier times.) The slope of this initial effluent curve is greater at the higher flow rate than it is at the lower flow rate. These initial stages of the effluent curve reflect the subsequent profile, as $C_{\text{out}}/C_{\text{in}}$ continues to take on slightly higher values (0.1 to 0.4) at the higher flow rate than it does at the lower flow rate, where $C_{\text{out}}/C_{\text{in}}$ varies from 0.07-0.13.

The initial profiles of the 30-32 ppm experiments clearly describe the behavior of the reactor in the first hours of operation (Fig. 6.4 (b)). The lower flow rate case (60 cm^3/min) shows a logarithmic decrease in the value of $C_{\text{out}}/C_{\text{in}}$ as a function of time. The higher flow rate case (121 cm^3/min) is also characterized by a steep descent in the value of $C_{\text{out}}/C_{\text{in}}$ vs. time. Because sampling was performed slightly earlier in this case, the actual breakthrough curve of p-xylene is visible, and $C_{\text{out}}/C_{\text{in}}$ reaches values close to 0.9. Simultaneously, growth of the biomass is also occurring, even though this may be during the period of acclimation. Growth kinetics begin to cause a gradual decrease in $C_{\text{out}}/C_{\text{in}}$ at about $t = 7$ hours.

Similar trends are seen in Figure 6.5 (a) and (b), where both the 50-52 ppm cases and the 100-106 ppm cases show a higher fraction of p-xylene in the exit stream at the higher flow rate than at the lower one.

Figure 6.6 compares the initial output for the biodegradation experiment with an initial p-xylene concentration of 30 ppm at 121 mL/min with the comparable abiotic adsorption experiment run at similar conditions. Because of the quantity of data points taken in the initial region for the biodegradation experiment, actual breakthrough of p-xylene is seen in this region. The subsequent decrease in the value of C_{out}/C_{in} reflects the actual biodegradation reaction occurring.

The initial stages of the reactor operation thus represent a region of great variability as three factors, namely, adsorption, acclimation and growth of the biomass, and pressure stabilization are simultaneously occurring. After the first hour of operation, pressure stabilization has occurred, and adsorption breakthrough will have taken place, though simultaneously with the biodegradation reaction. Comparison of each of the complete concentration profiles is done in the next four sections, Sections 6.3.2 to 6.3.5.

6.3.2 Feed Concentration of 15 ppm p-Xylene

Figures 6.7 and 6.8 show the effluent profiles obtained with a feed concentration of 15 ppm at flow rates of 62 cm³/min and 125 cm³/min, respectively. The bioreactor was run for 180 hours (7.5 days) at a flow rate of 62 cm³/min. Only 8% to 16% of the amount of p-xylene fed to the reactor was detected in the reactor output. This corresponds to a removal of 84% to 92% of the p-xylene being fed to the reactor. The effluent curve has a small, positive slope which indicates a gradual increase in C_{out}/C_{in} if extrapolated to longer operating times.

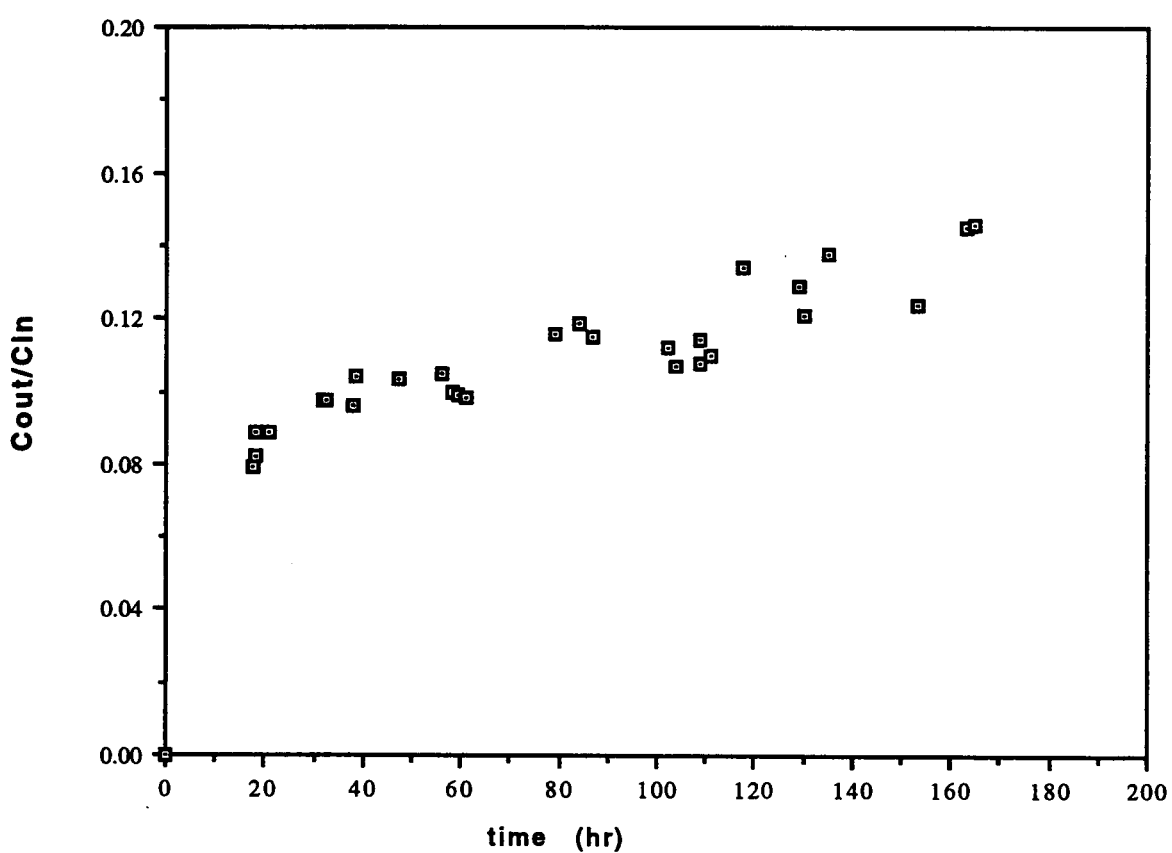


Fig. 6.7: Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 15$ ppm, flow rate = $62 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.

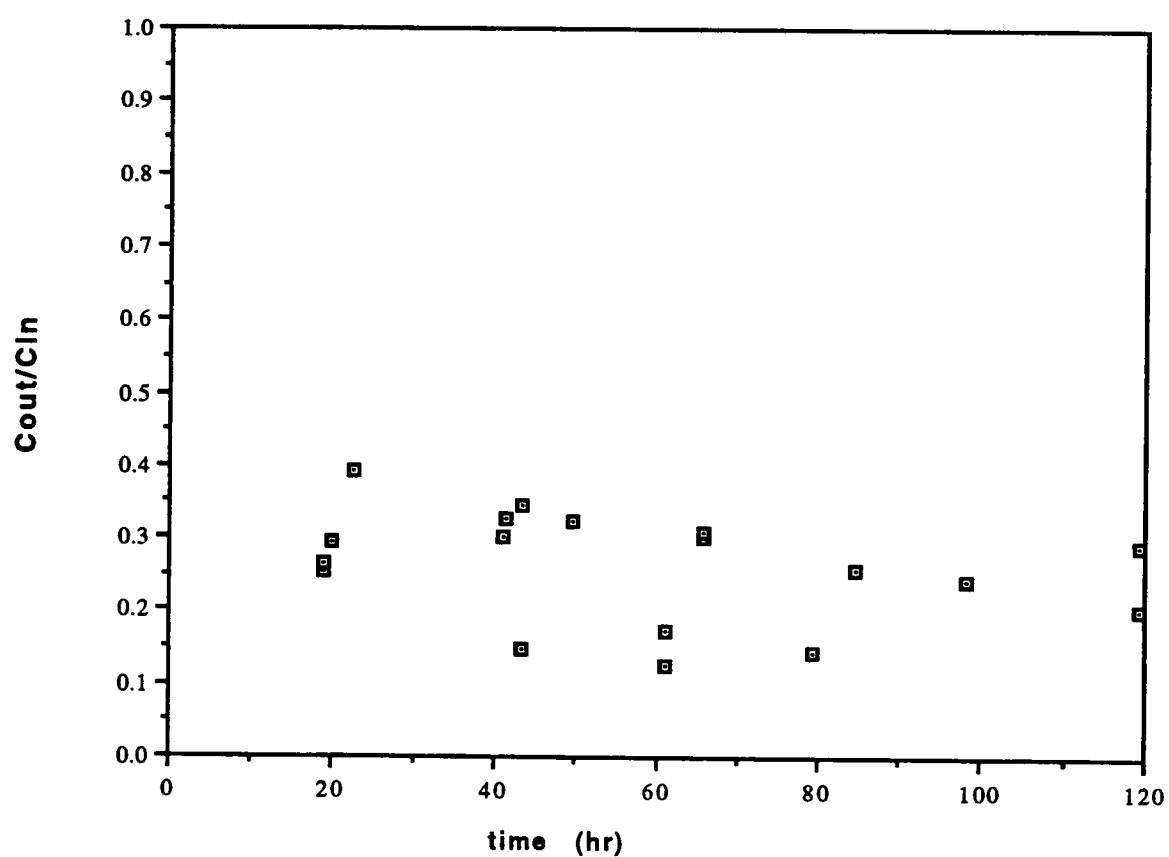


Fig. 6.8: Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 15$ ppm, flow rate = $125 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.

At the higher flow rate of $125 \text{ cm}^3/\text{min}$, the reactor was run for 120 hours (5 days) with 60% to 88% removal of p-xylene. Although there is relatively more scatter (owing to FID fluctuations) in the exit concentrations than in the latter case, the reactor does seem to approach a steady state after 60 hours of operation.

6.3.3 Feed Concentration of 28-36 ppm p-Xylene

The results for this concentration range and flow rates of $60 \text{ cm}^3/\text{min}$ and $121 \text{ cm}^3/\text{min}$ are given in Figures 6.9 and 6.10, respectively. Both of these experiments produced comparable overall results with the bioreactor reaching 80% to 90% removal efficiencies after the first 25 hours of operation. These removal efficiencies were maintained for 128 hours (5.3 days) for the experiment run at $60 \text{ cm}^3/\text{min}$, and for 178 hours (7.4 days) at a flow rate of $121 \text{ cm}^3/\text{min}$.

The experiment run at the lower flow rate seemed to reach a steady-state value with the normalized output concentration of p-xylene varying between 0.06 to 0.15. After 60 hours of operation, less than a 10% change in the effluent concentration of p-xylene was observed.

The experiment run at the higher flow rate produced removal efficiencies above 95% after the 57th hour of operation. This performance continued for the next 48 hours (105 cumulative hours of operation), after which the normalized effluent concentration of p-xylene began a slight increase reaching a relative maximum of 0.2. Approximately 30 hours after this relative peak, the normalized p-xylene effluent concentration decreased to 0.05-0.1. The slight rise in the effluent profile corresponded to an experimental observation of an increase in pressure to 18 psi beyond the 105th hour of reactor operation. This increase in pressure may have been caused by the increase in biomass within the

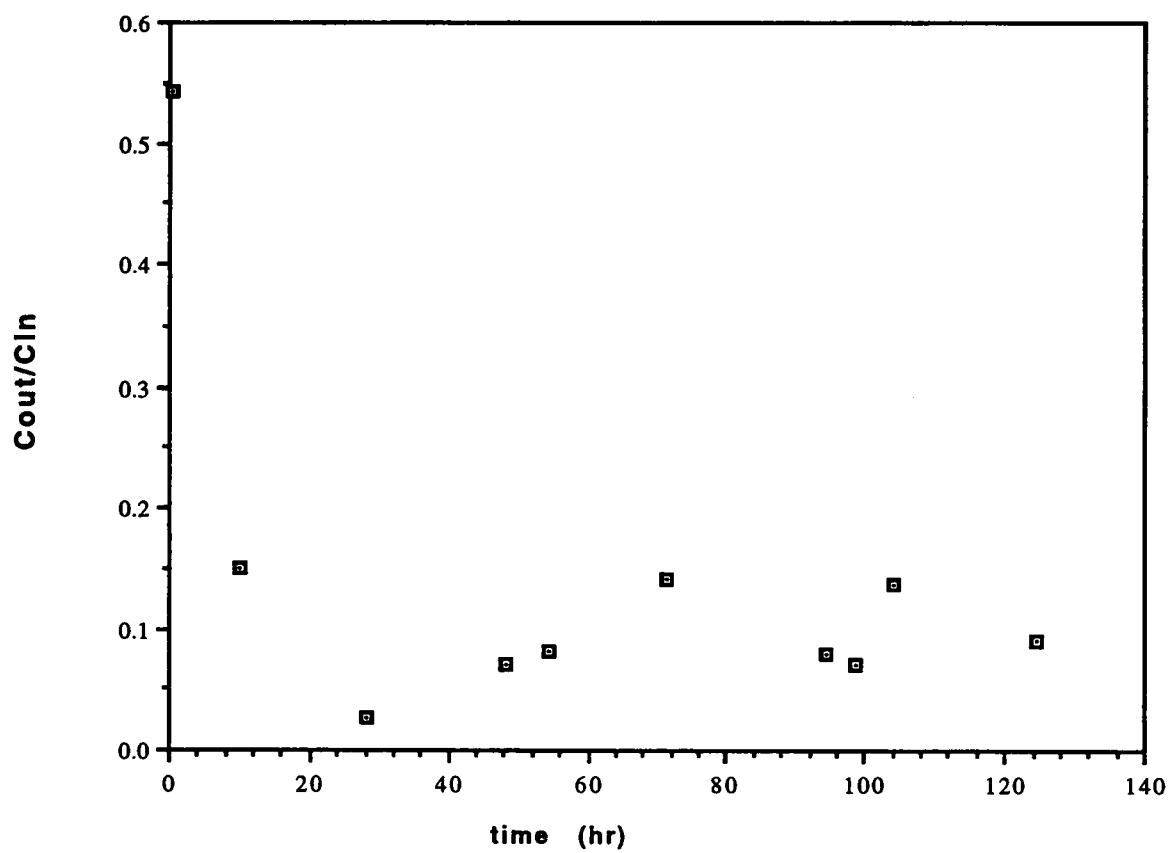


Fig. 6.9: Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 28$ ppm, flow rate = $63 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.

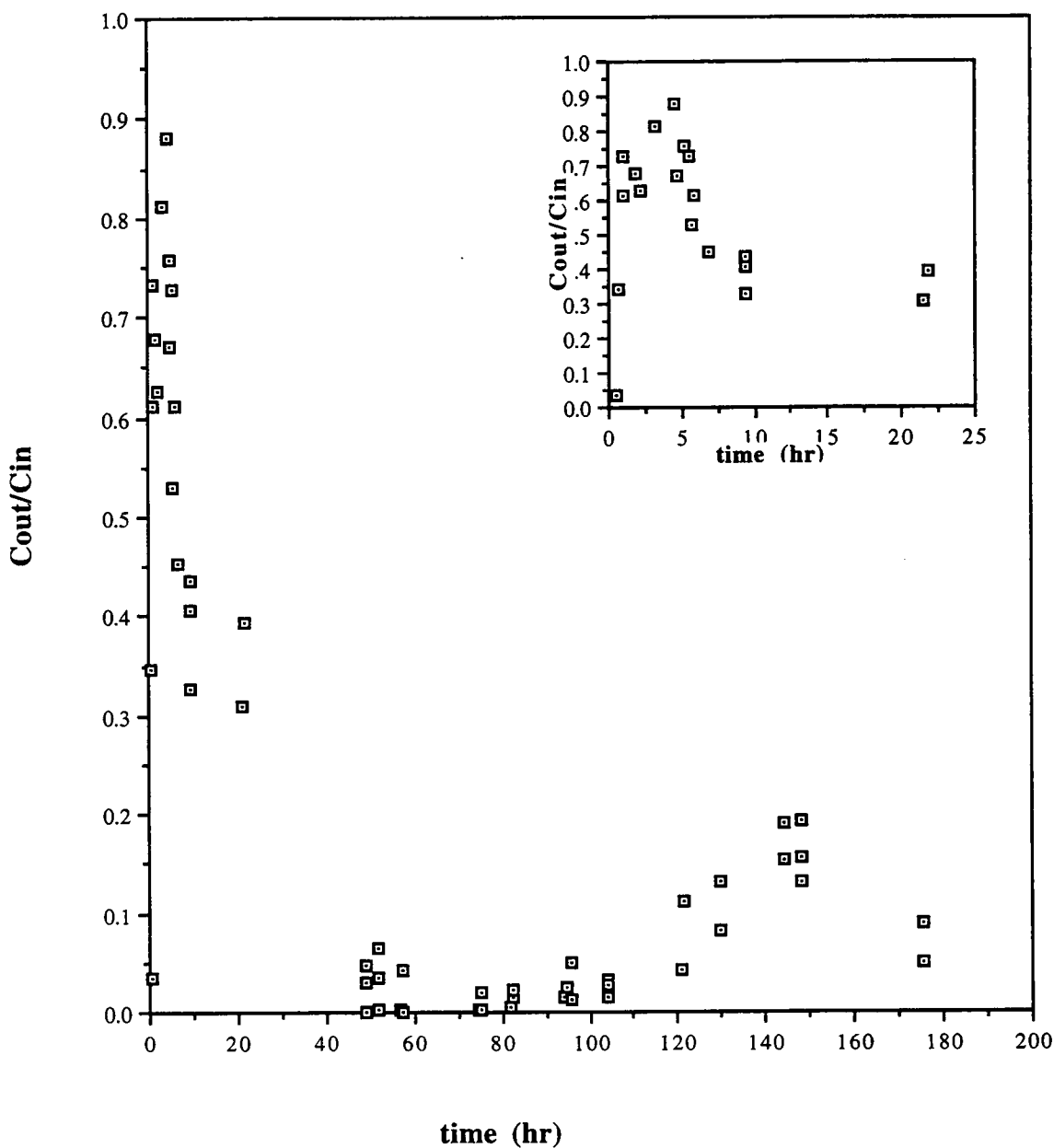


Fig. 6.10: Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 36$ ppm, flow rate = $121 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration. The inset is an enlargement of the initial region of the effluent curve of p-xylene.

packed bed, because removal efficiencies were in the range of 90% to 95% directly preceding this pressure increase.

The inset in Figure 6.10 is an enlargement of the initial region which clearly shows a breakthrough in the p-xylene at approximately 5 hours. Based on the abiotic experiments of Section 6.2 and Figures 6.1 to 6.3, complete adsorption of p-xylene has occurred during this period. In addition to adsorption, biodegradation is occurring to some extent during the first five hours. However, because breakthrough is observed at about $t = 5$ hours following which a steep decrease in the concentration of p-xylene occurs between 5 and 7.5 hours, this indicates an induction period, or lag phase, of up to five hours. Typical growth curves show lag phases with durations between one and two hours (Shuler, 1992; Bailey, 1986) in liquid media. The results indicated by Figure 6.10 are consistent with this to an order of magnitude; the agreement is reasonable given that the cells are immobilized and the substrate is in the vapor phase.

6.3.4 Feed Concentration of 50-52 ppm p-Xylene

The p-xylene effluent profiles for the experiments performed at the flow rates of 63 cm³/min and 125 cm³/min were comparable in character (Figures 6.11 and 6.12). In both cases, steady-state values of the effluent p-xylene concentration were observed. In the case of the lower flow rate, the ratio C_{out}/C_{in} reached a steady-state value of 0.3 ± 0.02 ; for the higher flow rate, the steady-state value of C_{out}/C_{in} was 0.23. Reactor performance at a 70% removal efficiency was maintained for 5 days at a feed flow rate of 63 cm³/min, and at an 80% removal efficiency for 3.2 days at a feed flow rate of 125 cm³/min.

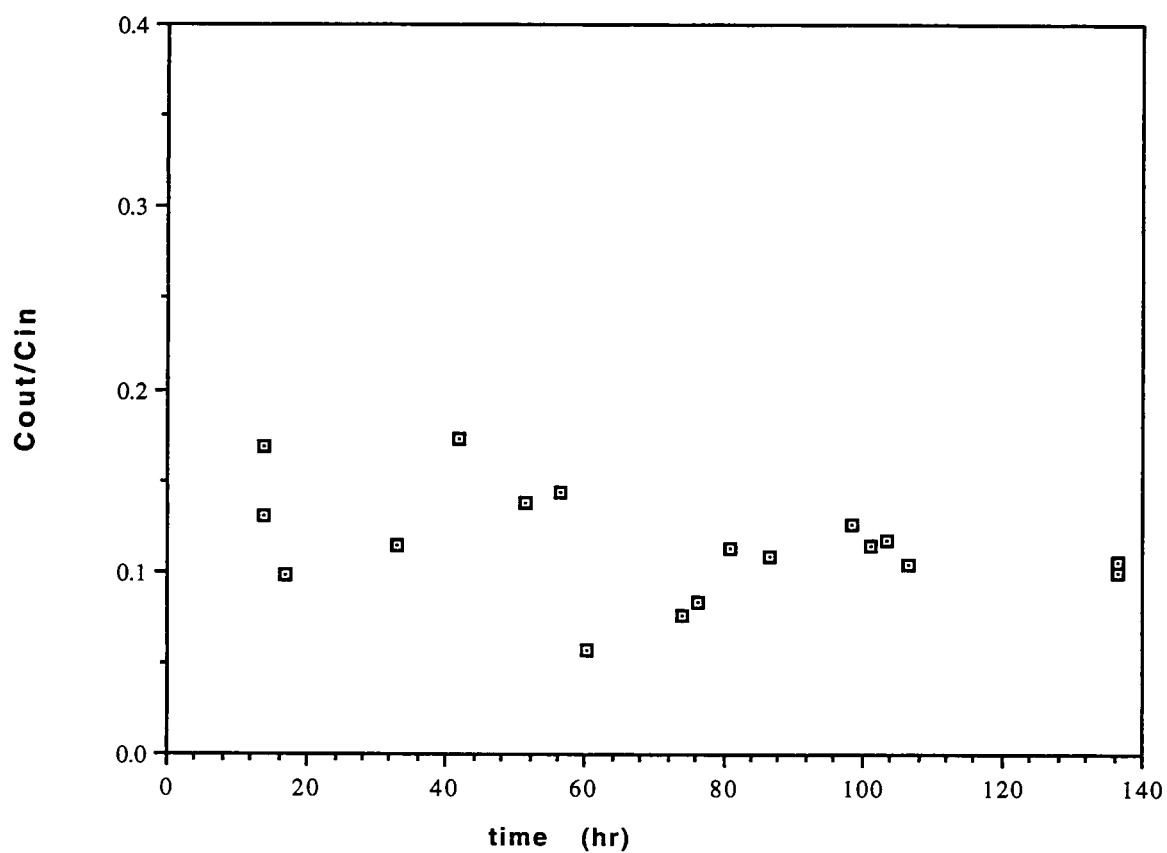


Fig. 6.11: Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 52$ ppm, flow rate = $63 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.

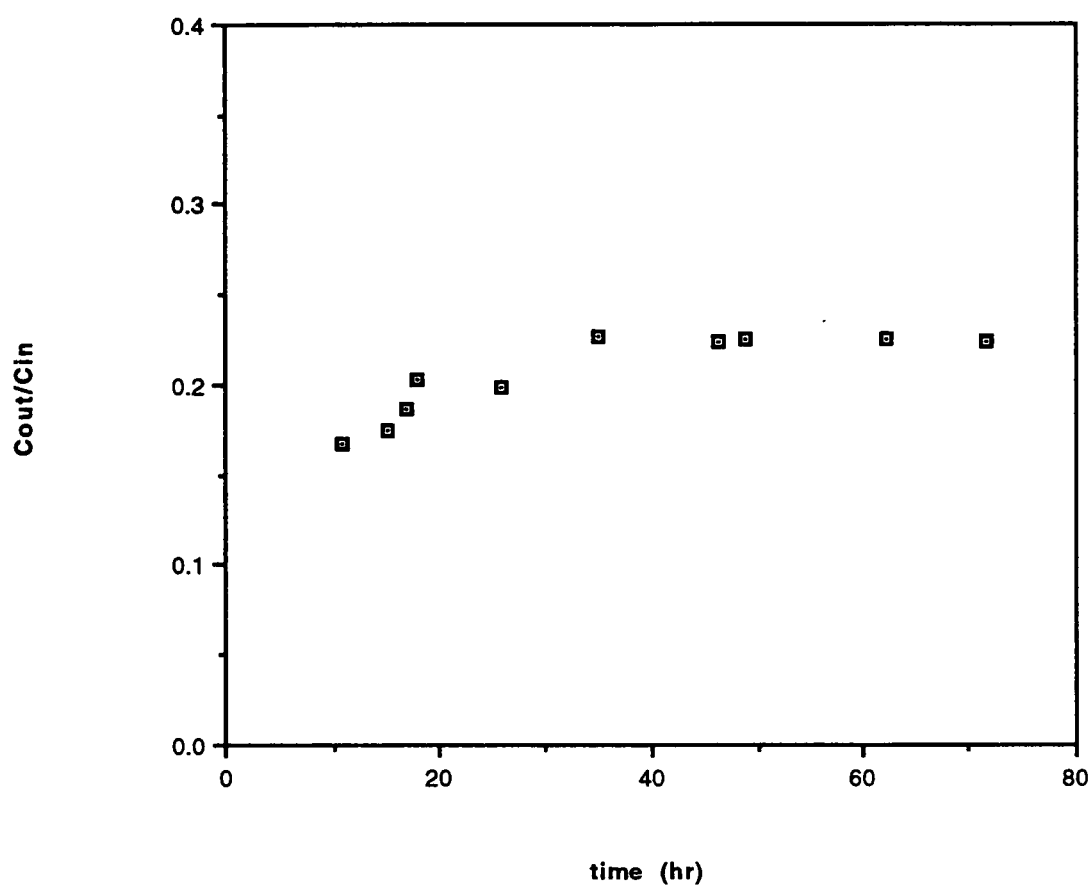


Fig. 6.12: Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 50$ ppm, flow rate = $125 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.

6.3.5 Feed Concentration of 100-147 ppm p-Xylene

The results of the experiments performed within this concentration range are shown in Figures 6.13 to 6.16 for the feed flow rates of $62 \text{ cm}^3/\text{min}$ and $129 \text{ cm}^3/\text{min}$, respectively. The effluent profiles in these two cases are markedly different. At a flow rate of $62 \text{ cm}^3/\text{min}$, the effluent profile does not demonstrate a definitive steady-state value in C_{out}/C_{in} of p-xylene. Although the slope of the C_{out}/C_{in} vs. time curve is gradually increasing, the fraction of p-xylene in the exit stream remains between 0.16 and 0.4 for 63 hours. At twice this flow rate, reactor performance is significantly compromised. The fraction of p-xylene in the exit stream continues to increase from the onset of the experiment, and C_{out}/C_{in} reaches values between 0.70 and 0.95 after only 10 hours of operation. Because C_{out}/C_{in} was maintained between these two limits for 70 hours thereafter, this condition suggests the achievement of steady-state.

Figure 6.15 shows the results of the experiment performed with a feed concentration of p-xylene of 150 ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. The amount of p-xylene in the effluent stream continuously increased with time. After 70 hours of operation, C_{out}/C_{in} reached a value of 0.86.

A graphical compilation of some of the results is shown in Figure 6.16, in which the results of the experiments performed with p-xylene feed concentrations of 52 ppm, 100 ppm, and 150 ppm at comparable flow rates are shown. With increasing levels in p-xylene feed concentrations, the removal efficiencies decrease. The experiment conducted with the 52 ppm feed is seen to reach a steady-state based on the exit concentrations of p-xylene. The other two cases run at feed concentrations of 100 and 150 ppm show a steady increase in the amount of p-xylene in the effluent stream over time. As per Figure 6.16, overall p-xylene removal efficiencies in this range successively decrease as the influent concentration is increased.

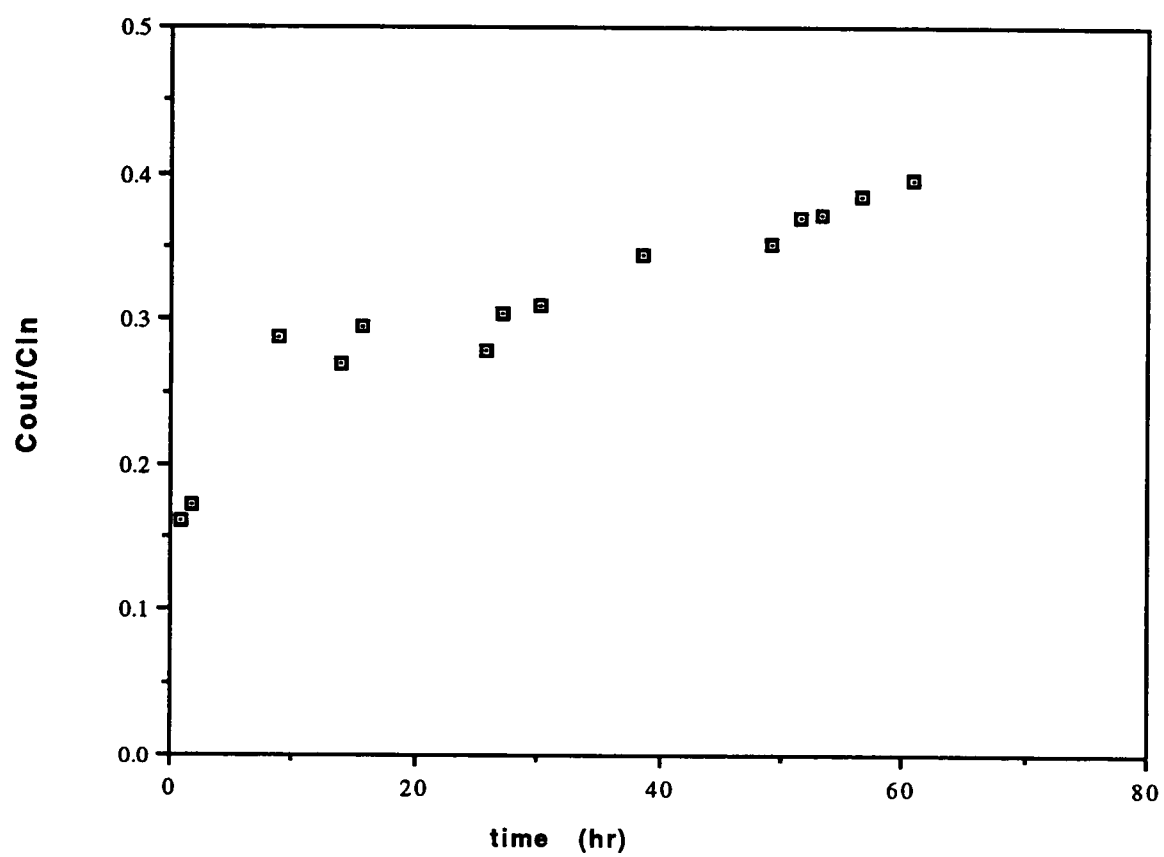


Fig. 6.13: Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 100$ ppm, flow rate = $62 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.

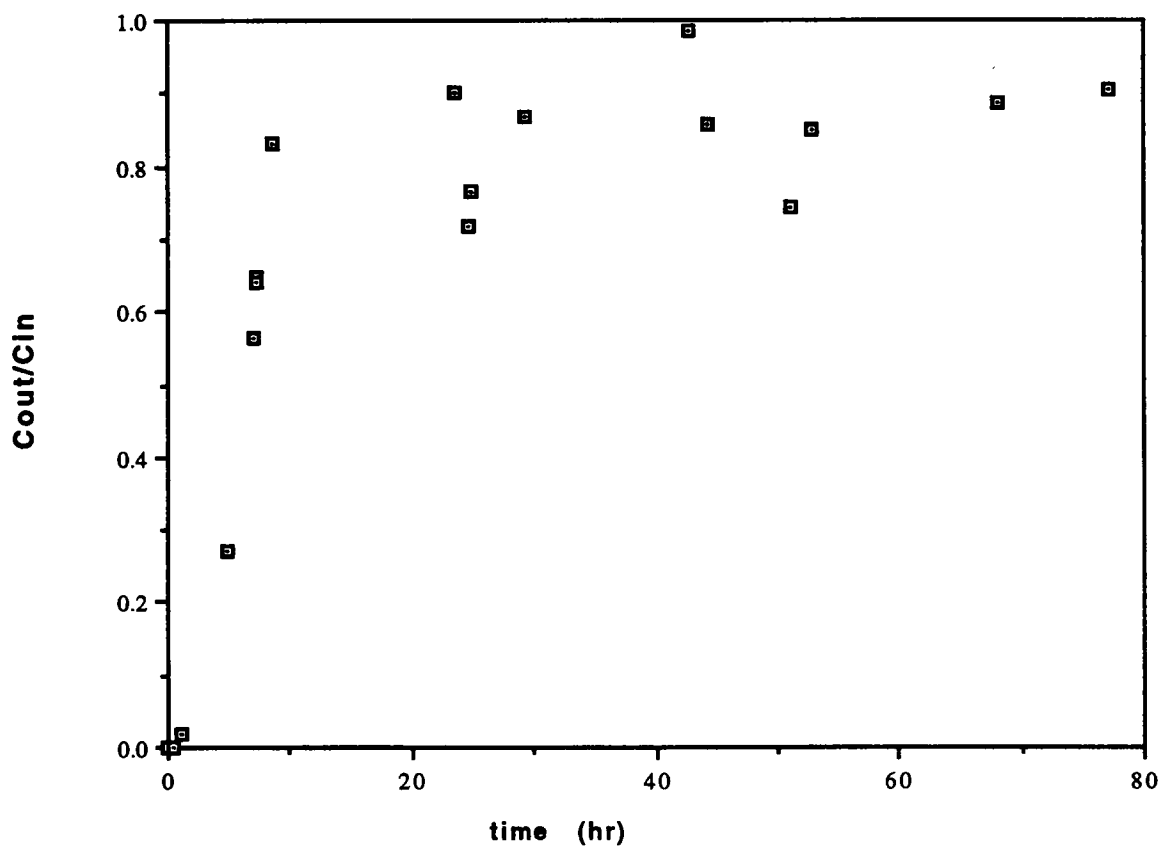


Fig. 6.14: Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 106$ ppm, flow rate = $129 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.

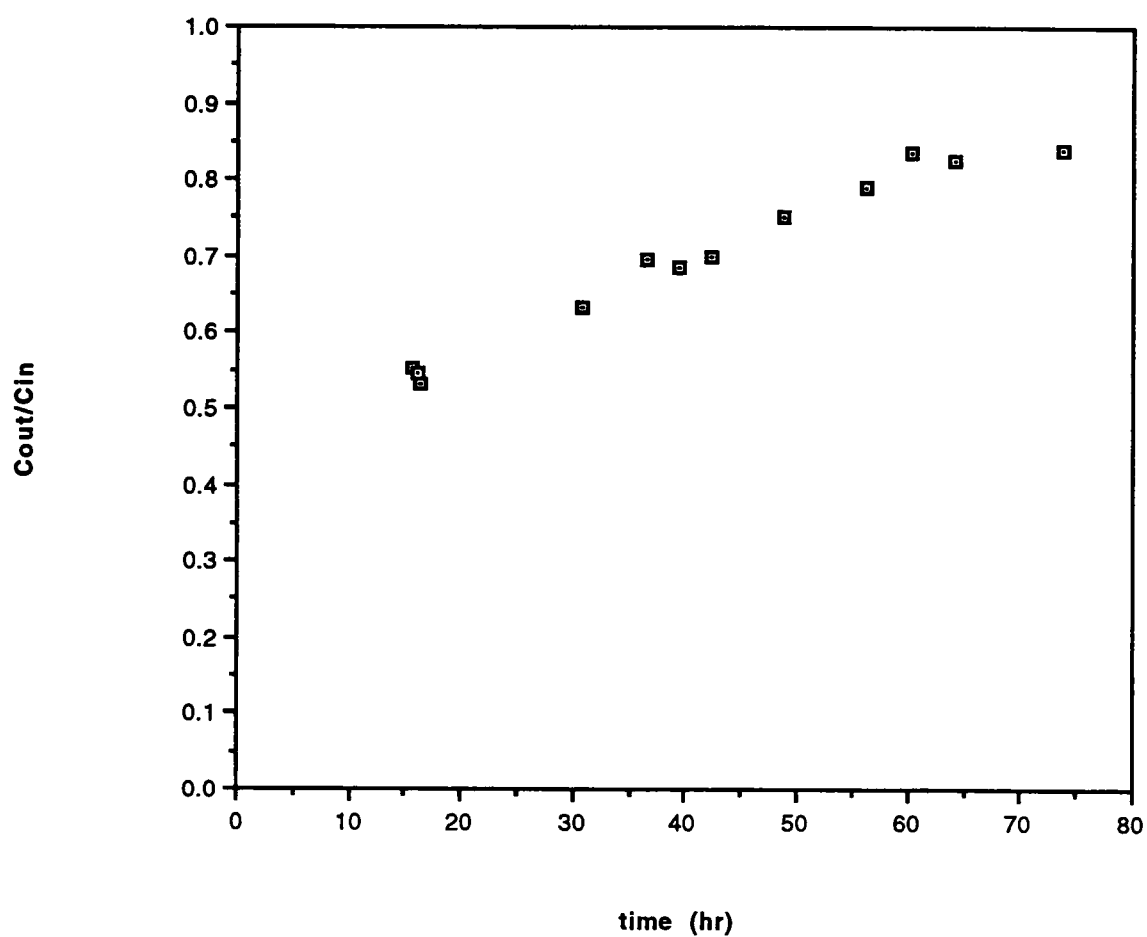


Fig. 6.15: Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at the following conditions: $C_0 = 147$ ppm, flow rate = $62 \text{ cm}^3/\text{min}$. The exit concentration of p-xylene is normalized with respect to its feed concentration.

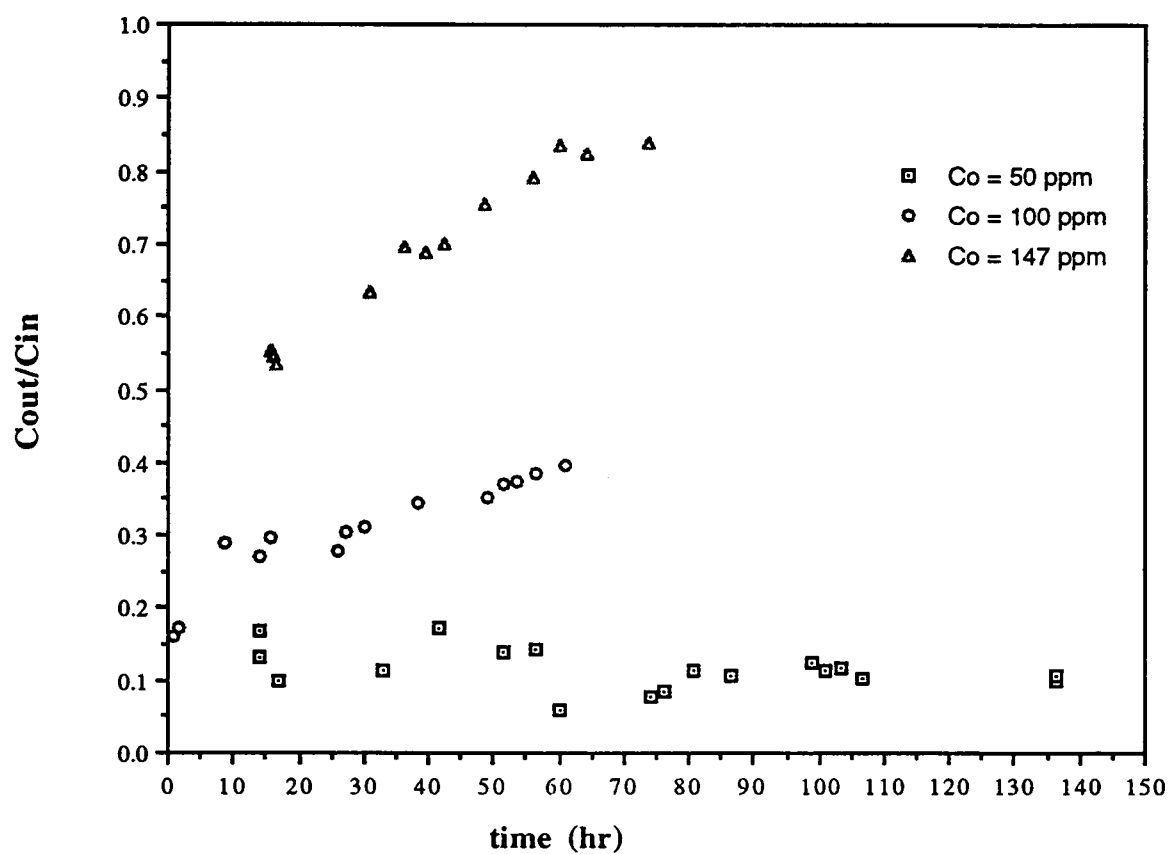


Fig. 6.16: Normalized concentration of p-xylene in the exit stream of the reactor as a function of time at influent p-xylene concentrations of 50 ppm (squares), 100 ppm (circles) and 147 ppm (triangles) at flow rates of 63, 62, and 62 cm^3/min , respectively. The exit concentration of p-xylene is normalized with respect to its feed concentration.

6.4 CORRELATION WITH PREDICTIVE MODEL

This section compares the results of the theoretical model developed in Chapter V with the experiments. The nondimensional model equations rewritten below, equations 5.16 and 5.17, were solved by the finite element technique described in Chapter V.

$$\frac{\partial C}{\partial t^*} = [\text{DIFU}] \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C}{\partial r^*} \right) - [\text{CONV}] \frac{1}{r^*} \frac{\partial C}{\partial r^*} - [\text{RCTA}] \frac{CB}{K+C} \quad (5.16)$$

$$\frac{\partial B}{\partial t^*} = [\text{RCTB}] \frac{CB}{K+C} \quad (5.17)$$

where

$$\begin{aligned} r^* &= \frac{r}{r_2 - r_1} & \tau &= \frac{r_2 - r_1}{v_1} & t^* &= \frac{t}{\tau} \\ [\text{DIFU}] &= \frac{\tau D}{L_c} & [\text{CONV}] &= \frac{r_1}{v_1 \tau} & [\text{RCT1}] &= \frac{\tau \rho \mu_m b_0}{Y} & [\text{RCT2}] &= \tau \mu_m c_0 \end{aligned}$$

The calculated values of each of these nondimensional quantities for the experimental conditions considered (Table 6.1) is presented in Table 6.2. Note that the nondimensional quantities are dependent on the superficial velocity at the inner radial wall, v_1 , through the parameter τ . (Sample calculations are provided in Appendix I.) The values of the kinetic constants, μ_m and K , were taken to be 0.437 hr^{-1} and 0.006 g/L , respectively. These values are at the midpoint of the confidence interval estimated by Lee *et al.* (1993), discussed in Section 2.3:

$$\mu_m = 0.437 \pm 0.008 \text{ hr}^{-1} \quad \text{and} \quad K = 0.006 \pm 0.004 \text{ g/L} \quad (6.1)$$

Table 6.2: Experimental conditions and dimensionless model parameters

C_o (ppm)	V (cm ³ /min)	v_1 (cm/min)	τ (min)	DIFU	CONV	RCT1	RCT2
15	62.0	0.1513	6.013	6.208	1.791	35.30	3.879E-04
15	125	0.3051	2.982	3.079	1.791	18.44	1.924E-04
28	62.6	0.1528	5.955	6.148	1.791	33.29	7.172E-04
36	121	0.2954	3.081	3.181	1.791	25.69	4.507E-04
50	62.0	0.1513	6.013	6.208	1.791	35.49	1.313E-03
50	125	0.3051	2.982	3.079	1.791	17.51	6.415E-04
100	62.0	0.1513	6.013	6.208	1.791	35.30	2.742E-03
106	129	0.3159	2.881	2.974	1.791	24.02	1.314E-03
147	62.0	0.1513	6.013	6.208	1.791	35.30	3.801E-03

The value of the yield coefficient used was 0.3 g biomass/g p-xylene (Lee *et al.*, 1993). The effective diffusion coefficient, D , which represents diffusion and dispersion in the radial direction, was estimated to be $4.750\text{E-}06 \text{ m}^2/\text{s}$, or $2.850 \text{ cm}^2/\text{min}$ from the equation developed by Hirshfelder (1949) for bulk diffusivity in a gas mixture at 298 K. (Details of the calculation are provided in Appendix I). The value of C in the kinetic expression represents substrate concentration.

A 100-element nonuniform mesh was used to solve equations 5.16 and 5.17. The length of the elements was defined as a geometric progression with a progression ratio, p , being given as $p = l_{e+1}/l_e$, where l_e is the length of an element. A progression ratio of 1.04 was chosen in order to have more elements and refine the mesh near the entrance of the reaction zone. An initial time step of $2.5\text{E-}05$ in nondimensional units was used. Representative model and template files are provided in Appendix II.

The predictive model results are shown in Figures 6.17 to 6.22, where the model simulation results are depicted by dashed lines. In some cases, several model solutions are shown in order to illustrate the sensitivity of the model to the values of the reaction parameters. These correspond to the sensitivity of the model to the values of the kinetic constants given in equations 6.1. The high and the low values of the confidence intervals of the kinetic constants can be used to calculate high and low values of the nondimensional reaction parameters, $RCT1$ and $RCT2$, tabulated in Table 6.3. These values were in turn used along with the other parameters of Table 6.2 to generate effluent concentration curves for comparison with the theoretical results.

The predictive model results of Figures 6.17 to 6.22 verify the experimental results with the reaction parameters taken in the middle of the confidence interval. When the low values of $RCT1$ and $RCT2$ are taken within an experimental case, the model predictions are above the experimental results in the values of C_{out}/C_{in} obtained. This represents lower values of the reaction kinetic constants, or slower kinetics which would cause less of the

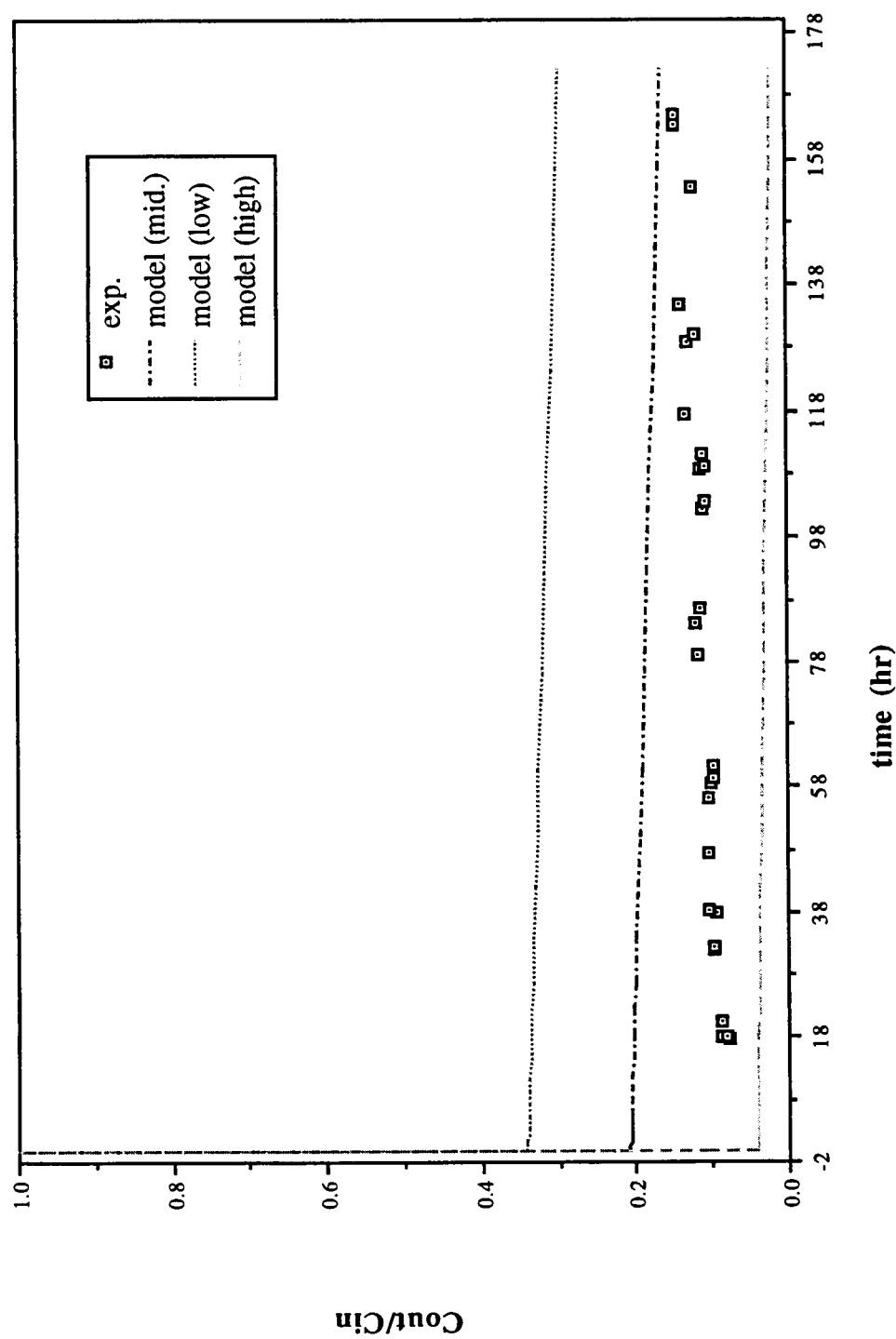


Fig. 6.17: Comparison of experiment with model for $C_0 = 15$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designations "mid.," "low," and "high" refer to the confidence interval of the kinetic parameters used.

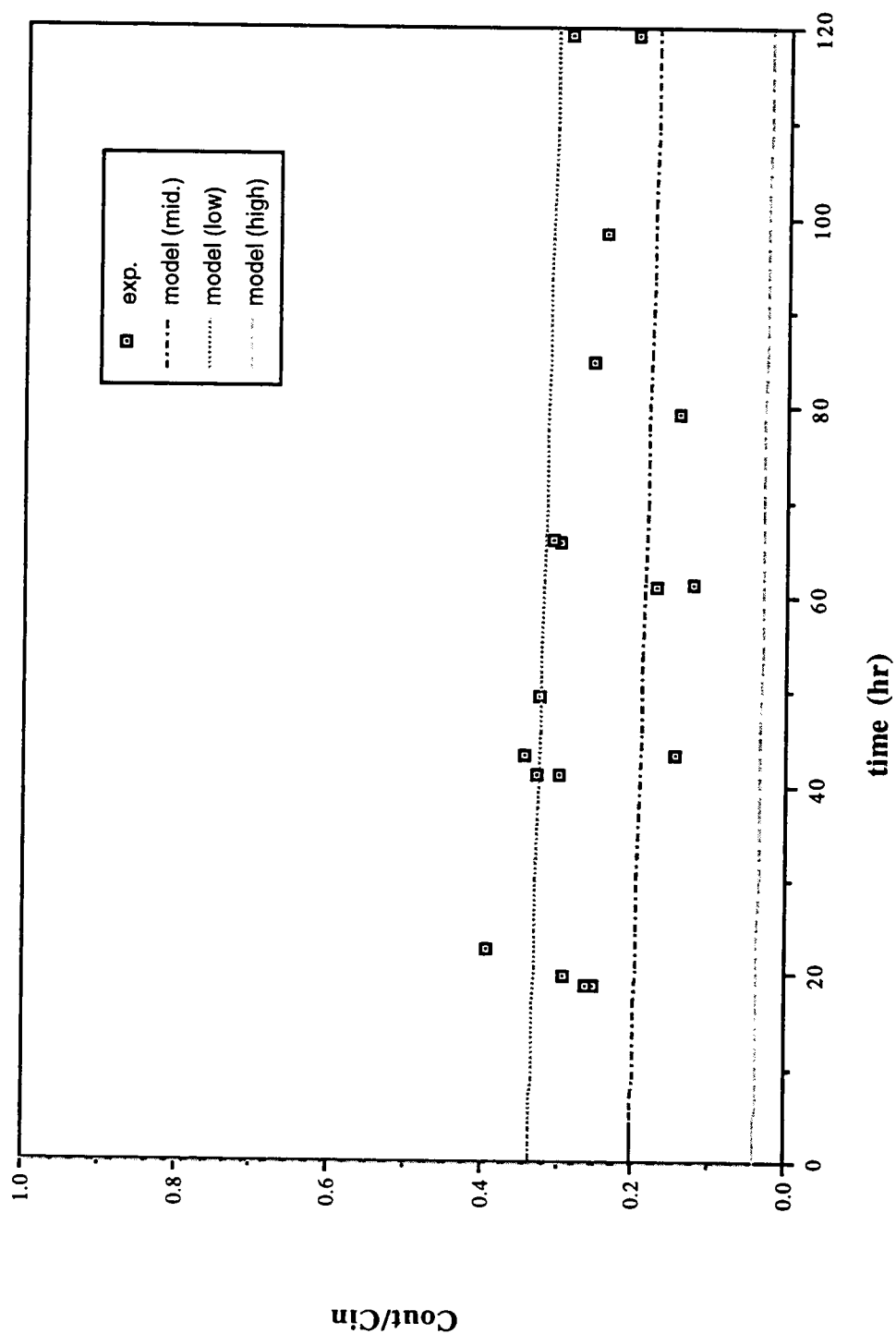


Fig. 6.18: Comparison of experiment with model for $C_0 = 15$ ppm at a flow rate of 125 cm³/min. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designations "mid.," "low," and "high" refer to the confidence interval of the kinetic parameters used.

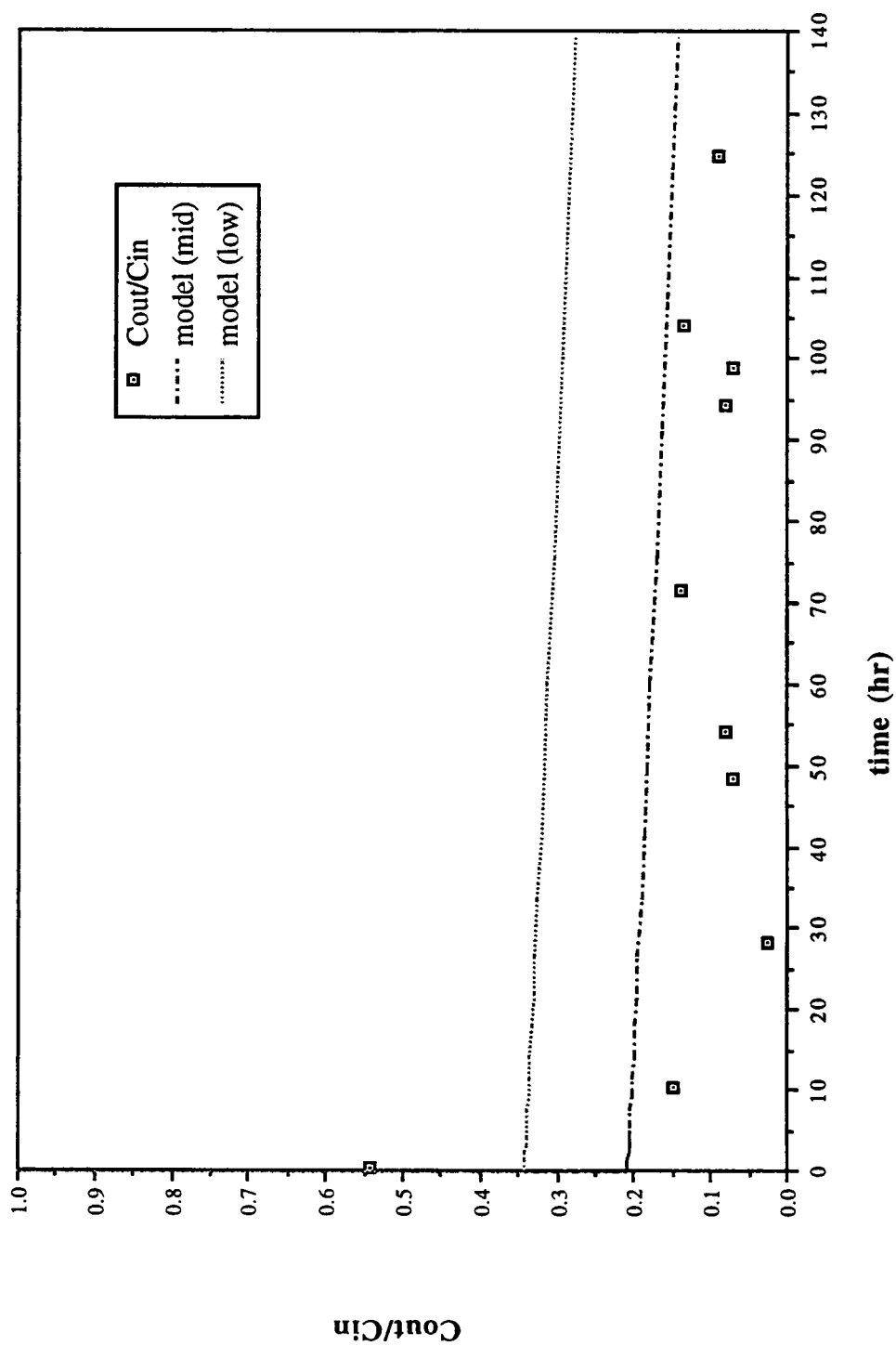


Fig. 6.19: Comparison of experiment with model for $C_0 = 28$ ppm at a flow rate of $63 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designations "mid," and "low" refer to the confidence interval of the kinetic parameters used.

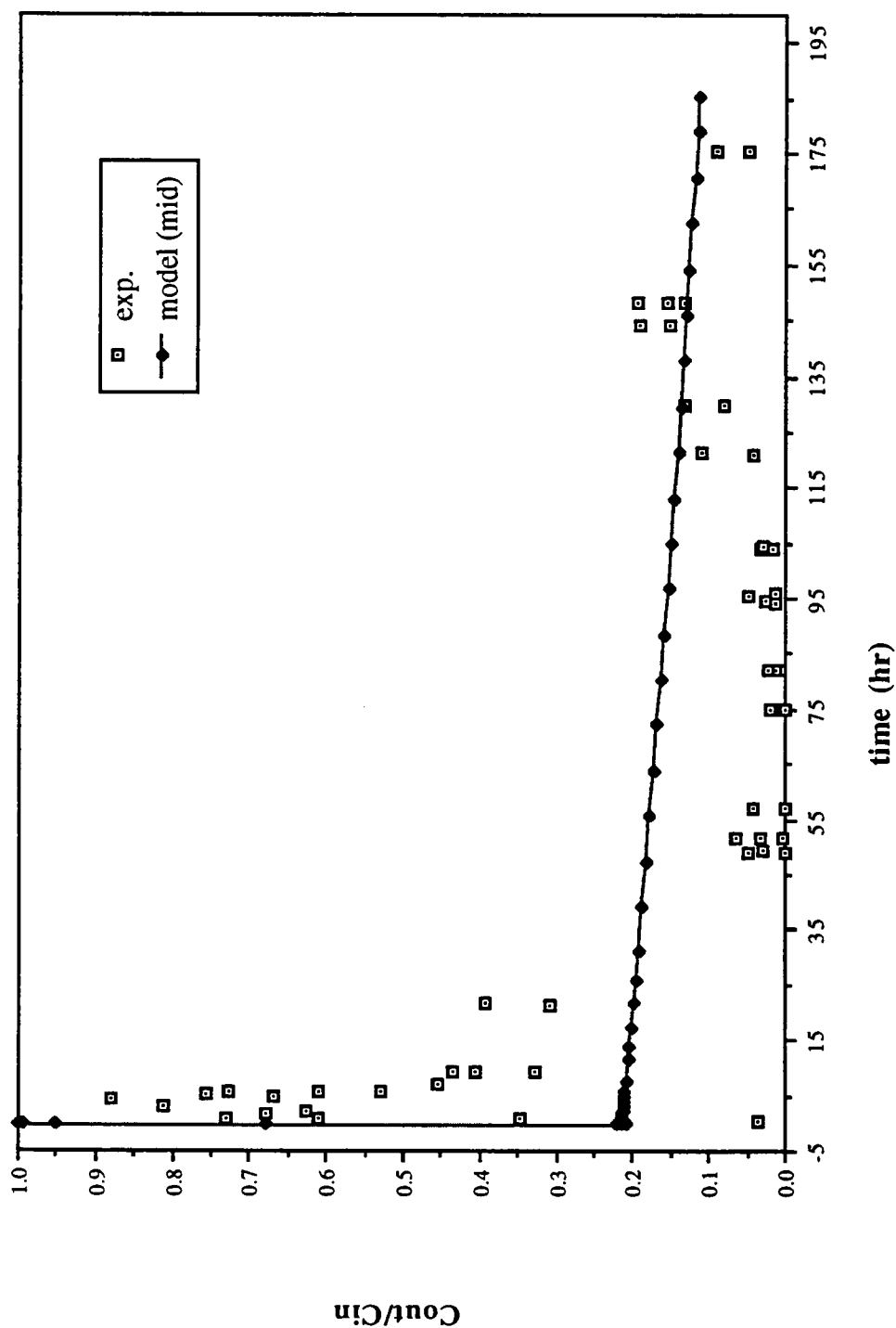


Fig. 6.20: Comparison of experiment with model for $C_0 = 36$ ppm at a flow rate of $121 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designation "mid." refers to the midpoint of the confidence interval of the kinetic parameters used.

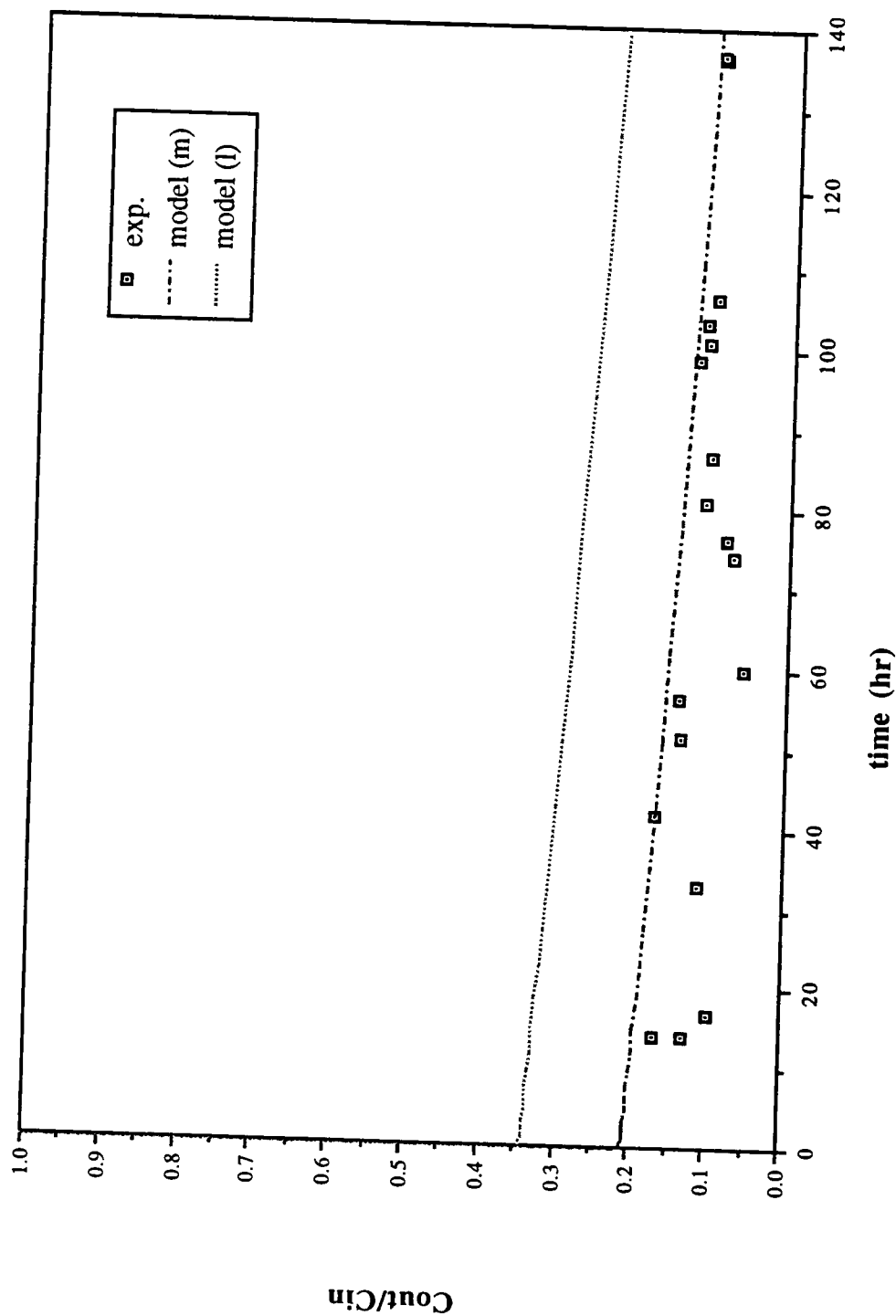


Fig. 6.21: Comparison of experiment with model for $C_0 = 50$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designations "mid." and "low" refer to the confidence intervals of the kinetic parameters used.

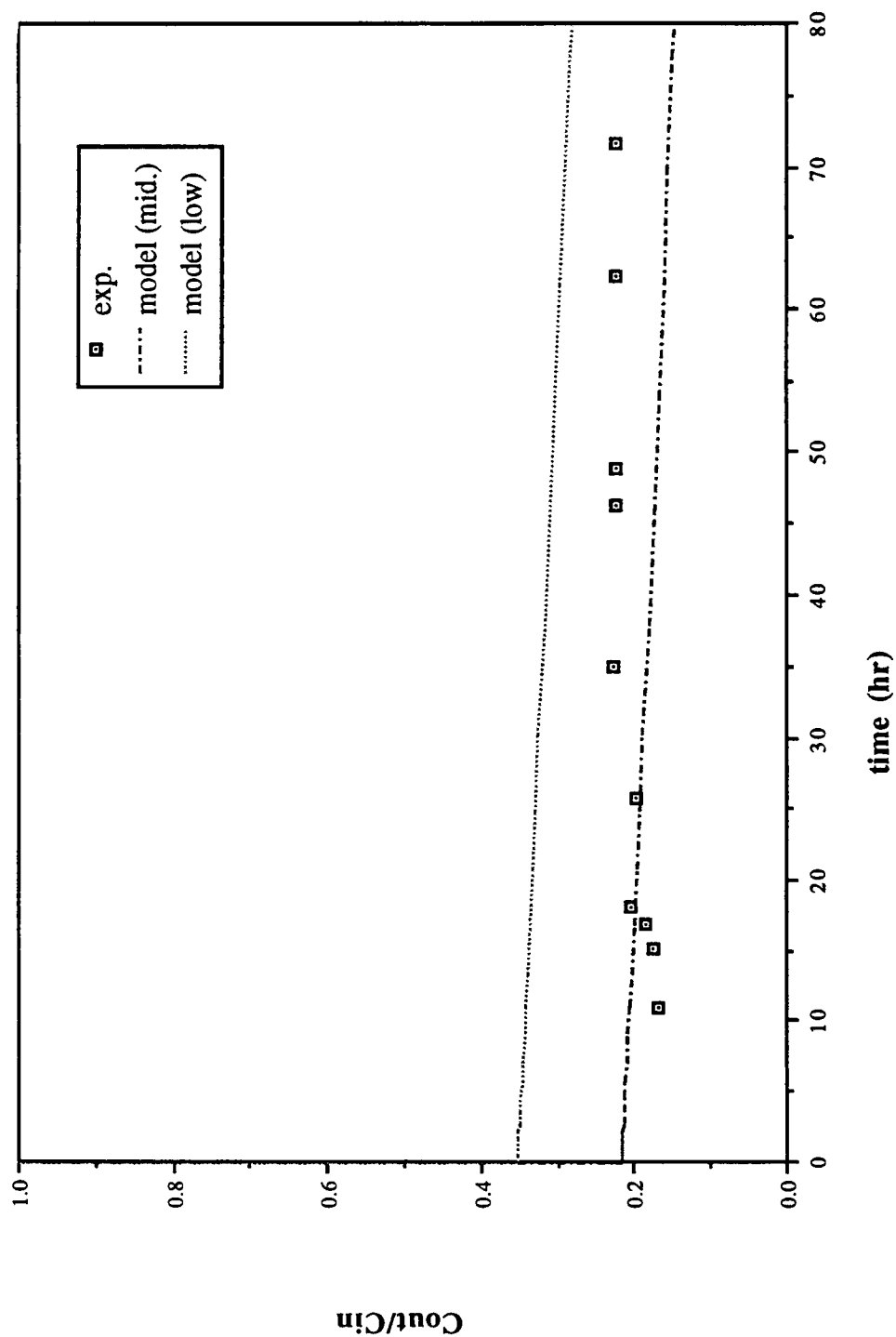


Fig. 6.22: Comparison of experiment with model for $C_0 = 50$ ppm at a flow rate of $125 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. Designations "mid." and "low" refer to the confidence intervals of the kinetic parameters used.

Table 6.3: Nondimensional reaction parameters calculated from confidence interval of kinetic parameters

C_0	V (cm ³ /min)	RCT1			RCT2		
15	62.0	20.79	35.30	107.8	2.285E-04	3.879E-04	1.185E-03
15	125	10.86	18.44	56.32	1.133E-04	1.924E-04	5.877E-04
28	62.6	20.59	34.96	106.8	4.224E-04	7.172E-04	2.191E-02
50	62.0	20.90	35.49	108.4	7.739E-04	1.313E-03	4.014E-03
50	125	10.31	17.51	53.49	3.778E-04	6.415E-04	1.960E-03

substrate to be degraded. With the highest values of RCT1 and RCT2 taken in an experimental case, the model under-predicts the values of C_{out}/C_{in} obtained. High values of RCT1 and RCT2 correspond to fast reaction kinetics, and to higher amounts of substrate being degraded.

6.4.1 Modification of Model

The experimental results at the inlet p-xylene feed concentrations of 100, 106, and 147 ppm at flow rates of 62, 125, and 62 cm³/min, respectively, show increasing amounts of p-xylene in the outlet of the reactor as time increases. Three possible explanations are presented to explain this type of behaviour:

- (1) Cell death or inactivation of the cells is occurring in addition to cell growth.

The amount of p-xylene being fed to the reactor could cause deactivation of the enzymatic

processes responsible for p-xylene degradation or could cause cell death. In this case, a modified model which incorporates a cell death or deactivation constant in the kinetic expression is subsequently presented.

(2) At the higher inlet p-xylene concentrations and flow rates considered, cell deactivation or death could be occurring because the amount of micronutrients may be insufficient to sustain degradation of p-xylene. When p-xylene is present in excess, the limiting nutrients become the micronutrients, and the carbon source is no longer rate-limiting. In this case, one of the primary assumptions for the use of Monod kinetics is no longer maintained. The kinetic model presented is only valid when the carbon source is rate-limiting.

(3) Finally, another possible explanation is that cell growth is still occurring with or without the possible effects of cell inactivation, but that at the high feed conditions considered, the growth of the biomass was not keeping up with the amount of substrate being fed. The amounts of p-xylene being fed in were too great to be processed by the cells, and much of the p-xylene fed to the reactor appeared in the effluent as a result. These three explanations are possible ways of explaining the behavior of some of the data. The experimental data does taken cannot distinguish between these explanations. One of the possible explanations was explored further, which resulted in a modification of the present model incorporating a fitted cell death or inactivation constant to be discussed.

Prior to this point, all of the model results have been predictive in nature. The model represented by equations 5.16 and 5.17 predicts that as time increases, the amount of p-xylene in the outlet stream decreases monotonically. This behaviour, however, is not the case with the high concentration experiments where the influent p-xylene concentration is above 100 ppm, where C_{out}/C_{in} actually increases with time. In this case, a model is needed to predict increasing amounts of substrate as time progresses. This means that progressively less of the substrate is being degraded with increasing time. This could

correspond to biomass actually being depleted as opposed to growing. In order to verify this and attempt to predict the trend of the data observed for $100 \leq C_0 \leq 147$ ppm at the flow rates considered, a cell death rate or inactivation term denoted by k_d was incorporated into the kinetic growth term:

$$\mu = \frac{\mu_m c}{K+c} - k_d \quad (6.1)$$

Including a cell death term to the microbial kinetic equation leads to the following biomass balance equation, which is a modification of equation 5.17:

$$\frac{\partial B}{\partial t^*} = [RCT2] \frac{CB}{K+C} - k_d \tau B \quad (6.2)$$

This new biomass equation was solved with the substrate equation 5.16 with different values of k_d to produce the results of Figures 6.23 to 6.25, which show the substrate concentration profiles for the modified model represented by equations 5.16 and 6.2. These model results do predict increasing values of C_{out}/C_{in} . For comparison, two of these plots also show the results of the original predictive model, from which a great disparity between the experimental data is seen. Upon comparison of Figures 6.23 to 6.25, as the value of the k_d increases, the slope of the C_{out}/C_{in} elution curve that results also increases. The fitted values of the parameter k_d for each of the cases considered are presented in Table 6.4. This model was suitable for reproducing the experimental data in all three cases with the appropriate fitted cell death constants.

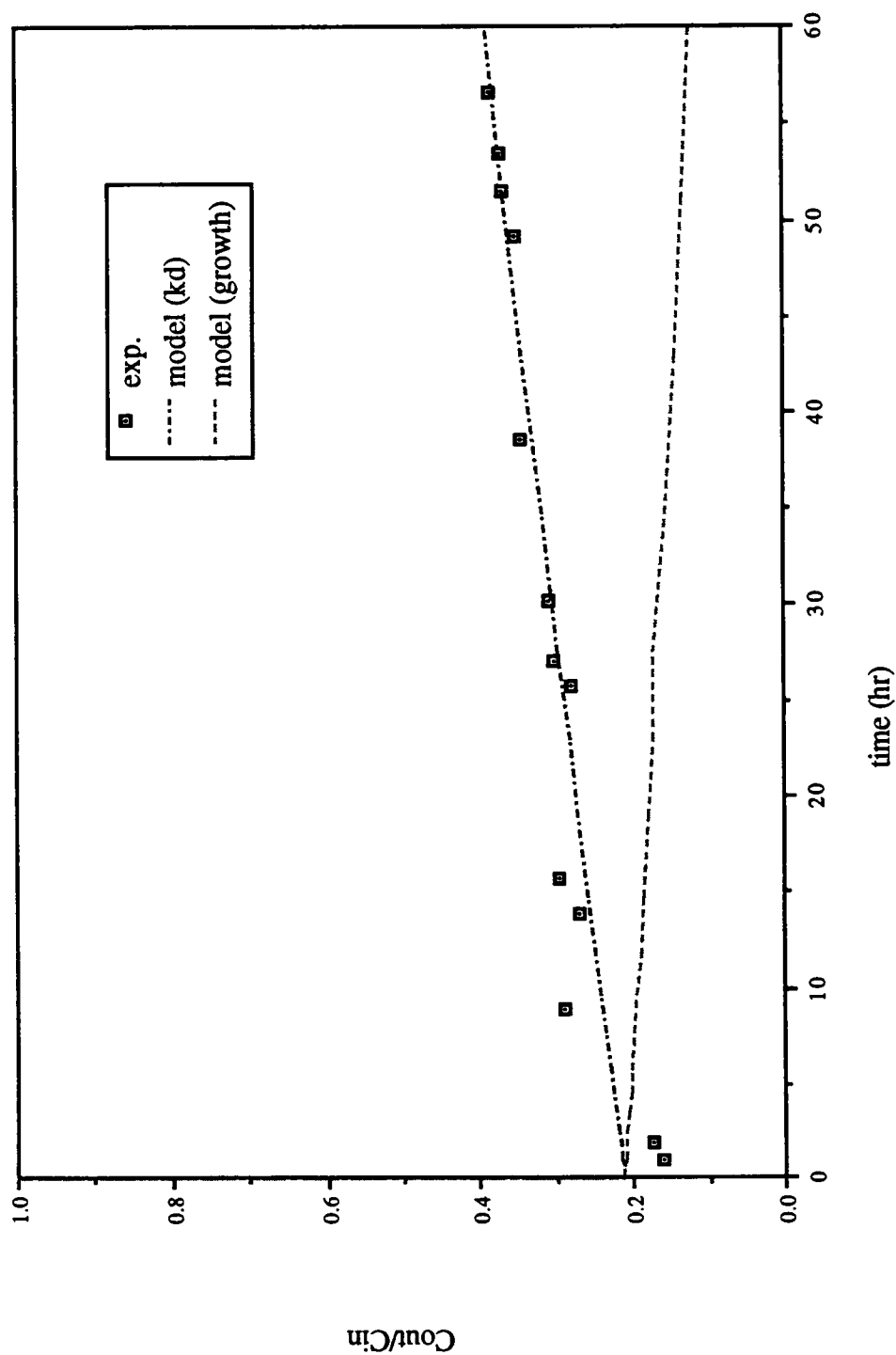


Fig. 6.23: Comparison of experiment with growth and cell deactivation+growth models for $C_0 = 100$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. The value of k_d used is 0.0225 hr^{-1} .

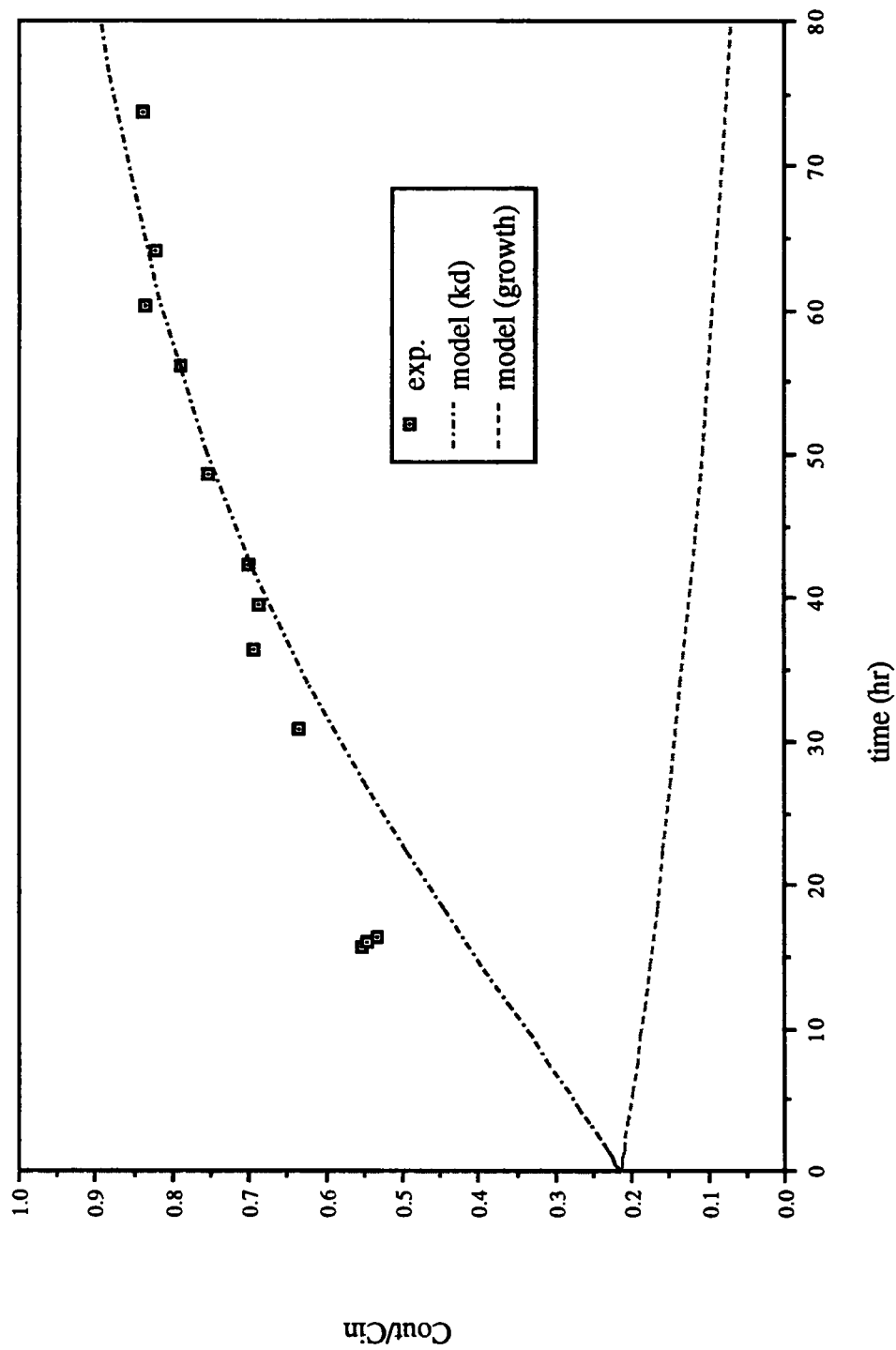


Fig. 6.24: Comparison of experiment with growth and cell deactivation+growth models for $C_0 = 147$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. The value of k_d used is 0.0622 hr^{-1} .

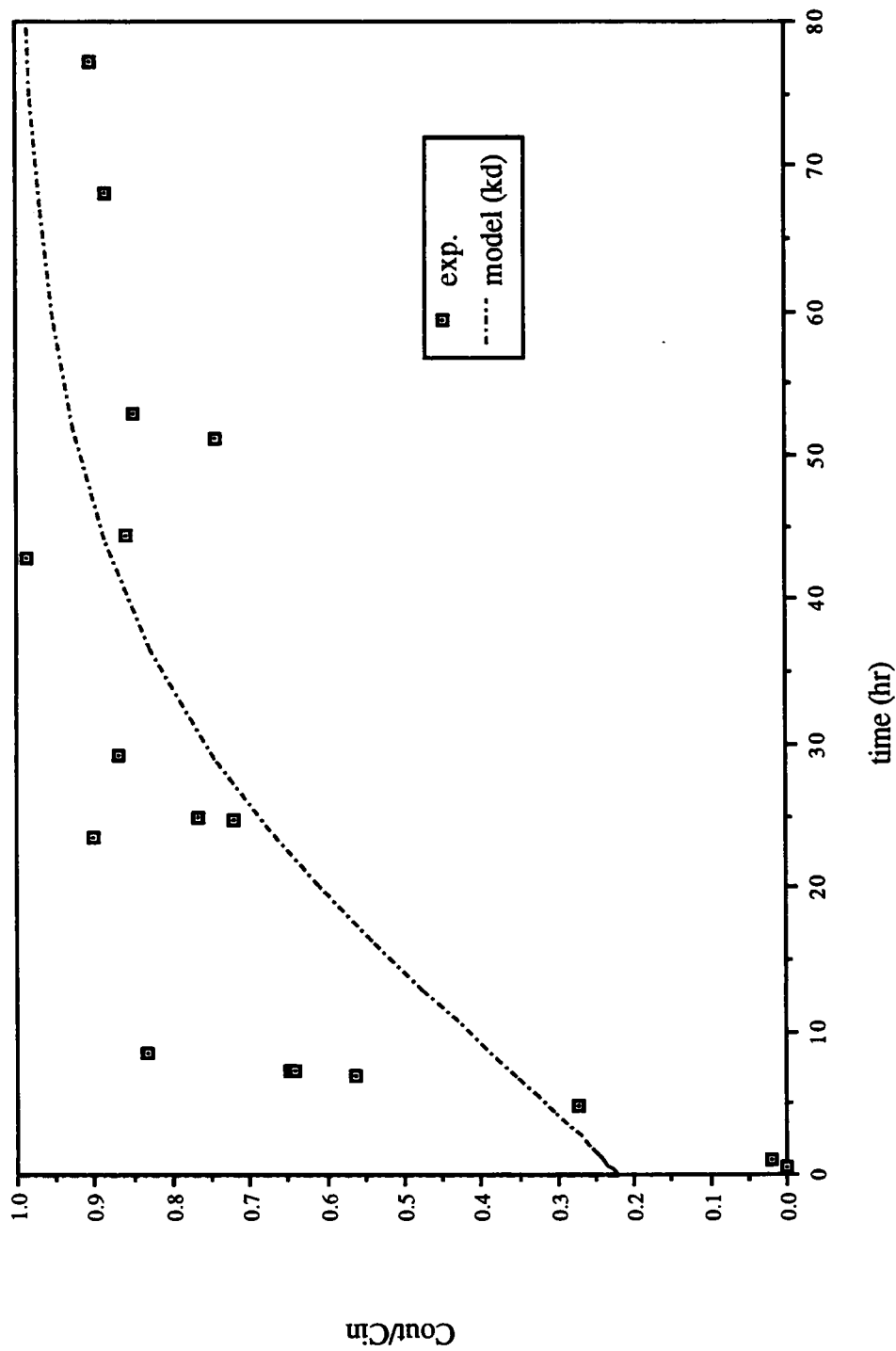


Fig. 6.25: Comparison of experiment with growth and cell deactivation+growth models for $C_0 = 106$ ppm at a flow rate of $129 \text{ cm}^3/\text{min}$. Normalized concentration of p-xylene in outlet stream is plotted as a function of time. The value of k_d used is 0.083 hr^{-1} .

Table 6.4: Fitted cell deactivation constants, k_d

C_o (ppm)	$V(\text{cm}^3/\text{min})$	p-xylene mass flow rate (mg/min)	k_d (hr^{-1})
100	62.0	0.02197	0.0225
147	62.0	0.03229	0.0622
106	129	0.04845	0.0830

6.4.2 Functional Dependence of k_d on p-Xylene Flow Rate

If the fitted deactivation constants of Table 6.4 are plotted as a function of the flow rate of p-xylene being fed to the cells as shown in Figure 6.26, then a functional dependence of k_d with p-xylene feed rate can be estimated (correlation coefficient = 0.981):

$$\begin{aligned} &\text{for} \quad \text{p-xylene flow rate [mg/min]} \geq 0.016 \\ &\quad k_d [\text{hr}^{-1}] = 0.31722 + 0.076274 \ln(\text{p-xylene flow rate [mg/min]}) \quad (6.3) \end{aligned}$$

$$\begin{aligned} &\text{for} \quad 0 \leq \text{p-xylene flow rate [mg/min]} \leq 0.016 \\ &\quad k_d = 0 \end{aligned}$$

Because this model does closely represent the experimental data in the three cases considered with the appropriate fitted cell death constants, the functional dependence of k_d on p-xylene flow rate given in equation 6.3 is presented. Through this functional dependence of k_d with p-xylene flow rate, one model may be written by taking into account

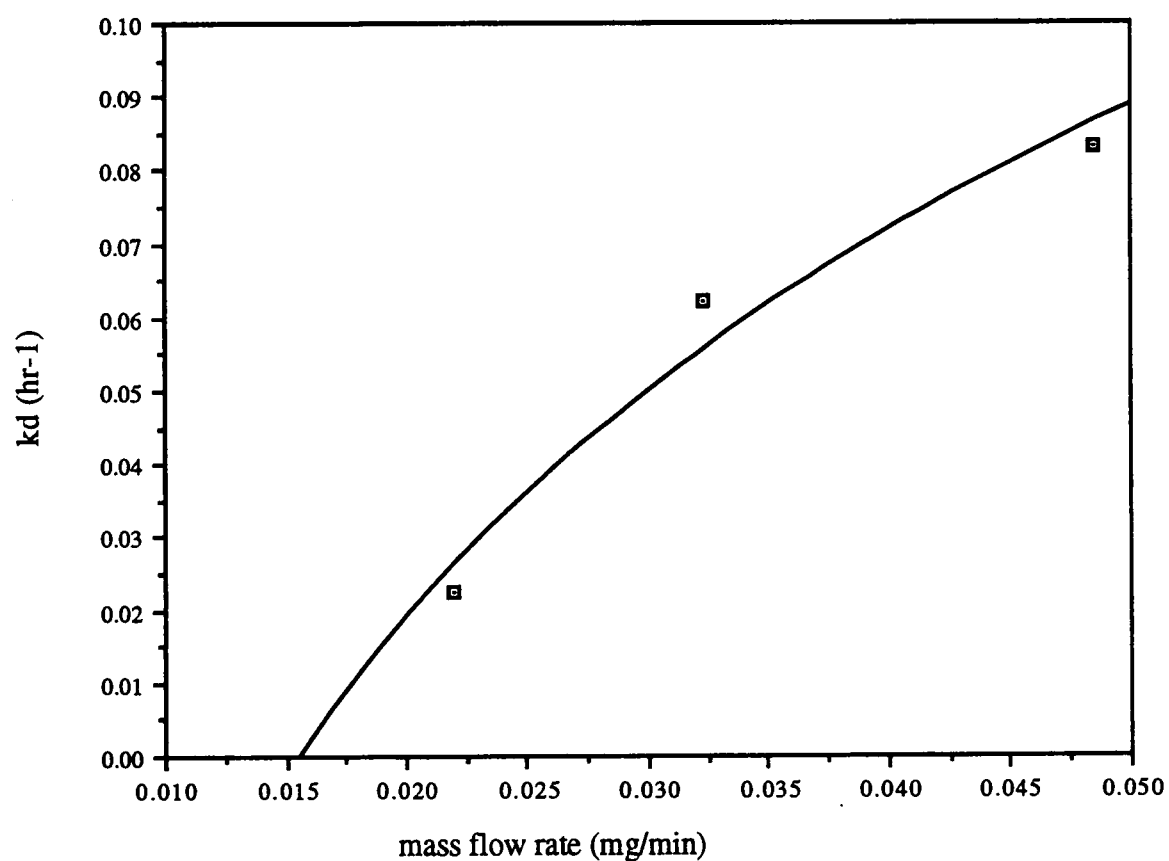


Fig. 6.26: Functional dependence of cell deactivation constant, k_d , with mass flow rate of p-xylene. The solid line represents the least-squares regression of the k_d values.

the region where k_d is defined, where cell deactivation as well as cell growth occurs. Where k_d is equal to zero, the model would reduce to the Monod growth kinetic model. This analysis seems to suggest the existence of a threshold value of p-xylene mass flow rate, below which cell growth occurs in the absence of cell deactivation, and above which a gradual deactivation occurs as a functional dependence of p-xylene flow rate.

6.4.3 Radial Concentration Profiles

The substrate and biomass radial concentration profiles through the reaction zone are depicted in Figures 6.27 to 6.32 for the model of equations 5.16 and 5.17. The substrate profiles show decreasing values of substrate with increasing radial distance, with $C/C_o \leq 1$. The biomass profiles also show decreasing values of substrate with increasing radial distance, but with $B/B_o \geq 1$. At any point within the reaction zone, there is less substrate present than is being fed to the reactor, but more biomass than there was initially. Because the amount of biomass decreases with increasing radial distance, this indicates that there is more biomass growth at the smaller radial distances than at larger radial distances. As time increases, the substrate concentration decreases at any given radial node, whereas the biomass concentration increases at any given radial node.

Figures 6.33 and 6.34 show the substrate and biomass concentration profiles for two cases representative of the modified model represented by equations 5.16 and 6.2, the model incorporating cell deactivation. The substrate concentration profiles are similar to the previous ones in that C/C_o decreases with radial distance. However, as time progresses, C/C_o increases at any given radial node. The biomass profiles show declining values of B/B_o with increasing time and radial distance, demonstrating progressive loss of biomass

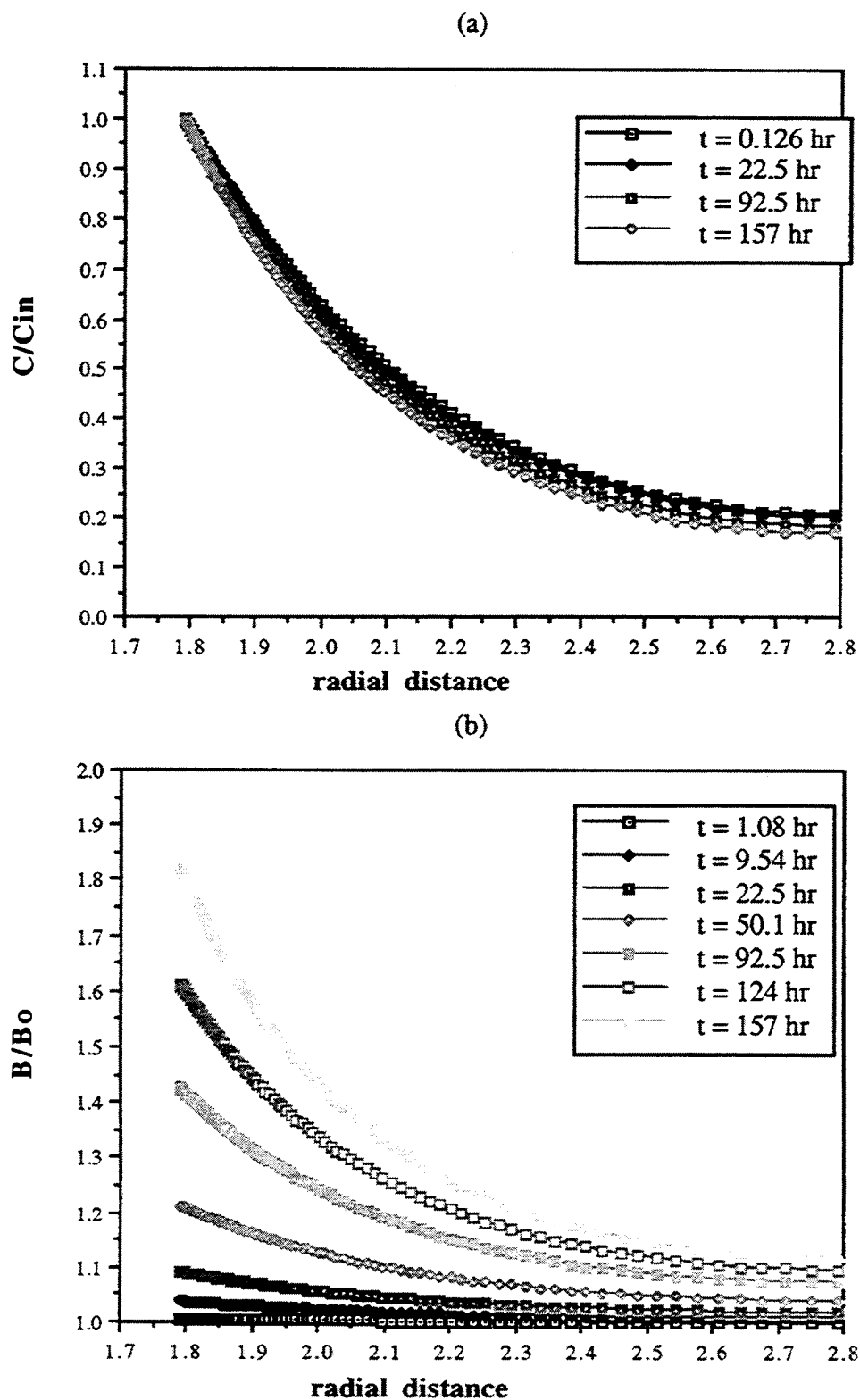


Fig. 6.27: Normalized concentration profiles as a function of radial distance through the reaction zone for $C_o = 15$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile

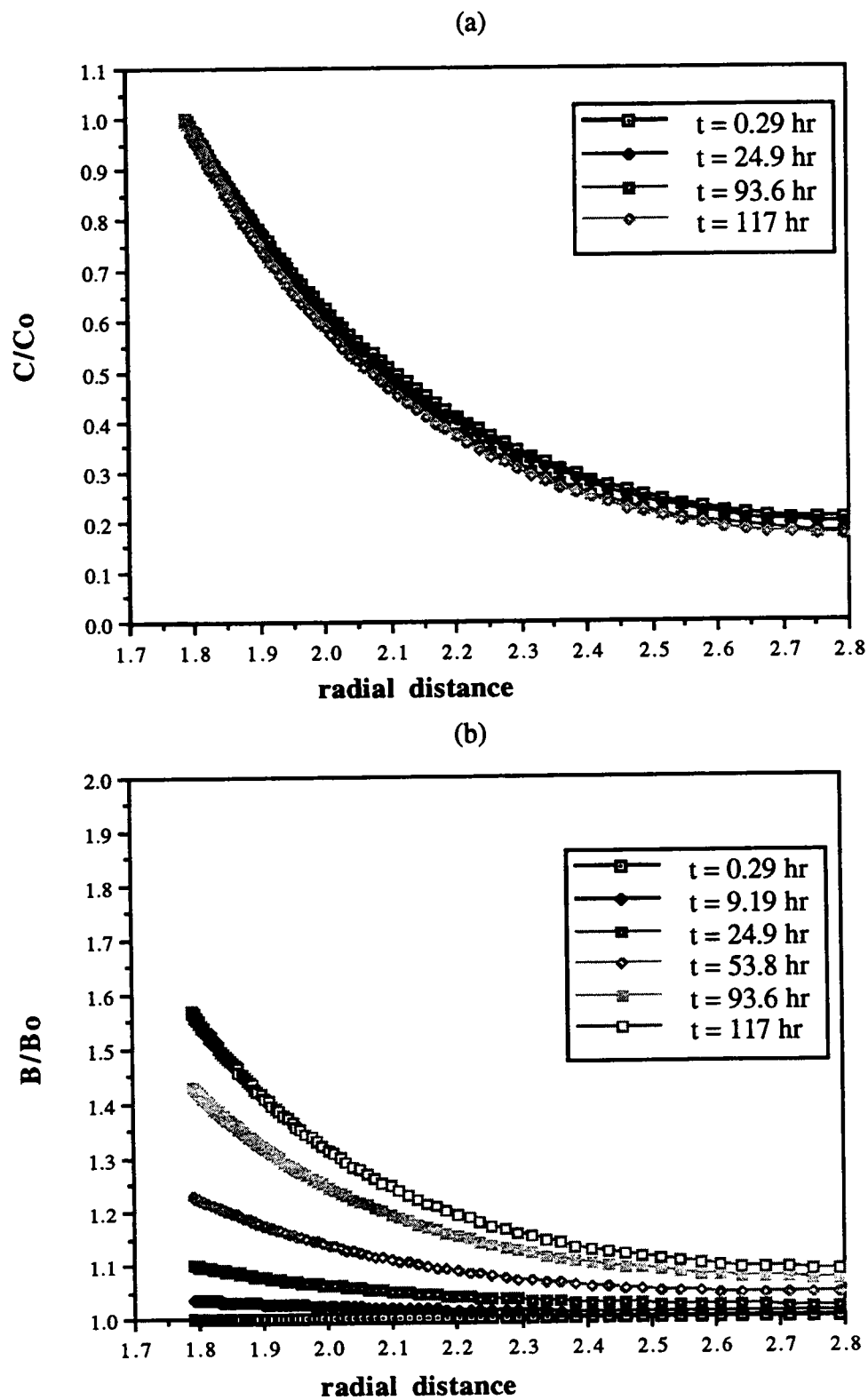


Fig. 6.28: Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 15$ ppm at a flow rate of $125 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile

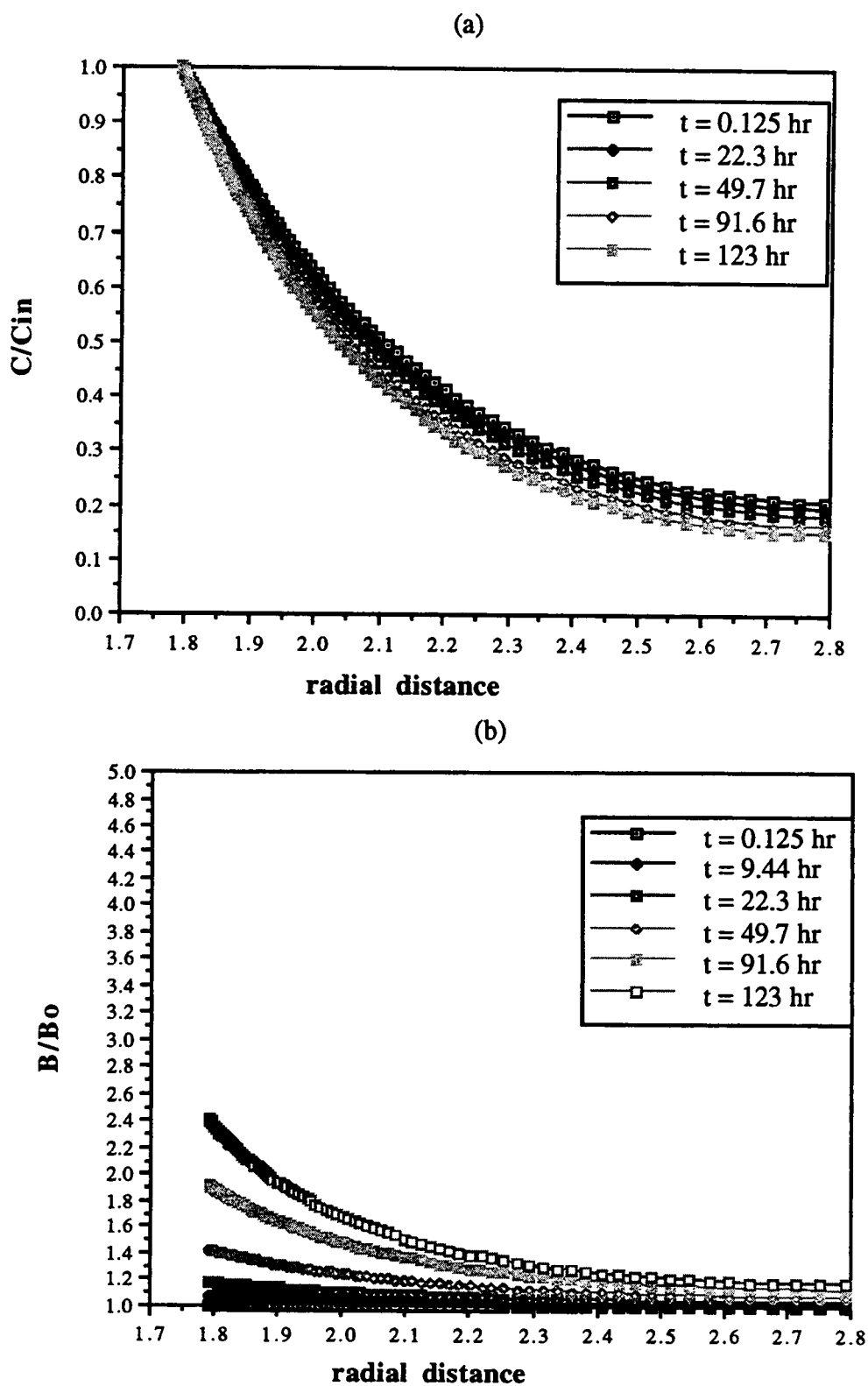


Fig. 6.29: Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 28$ ppm at a flow rate of $63 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile

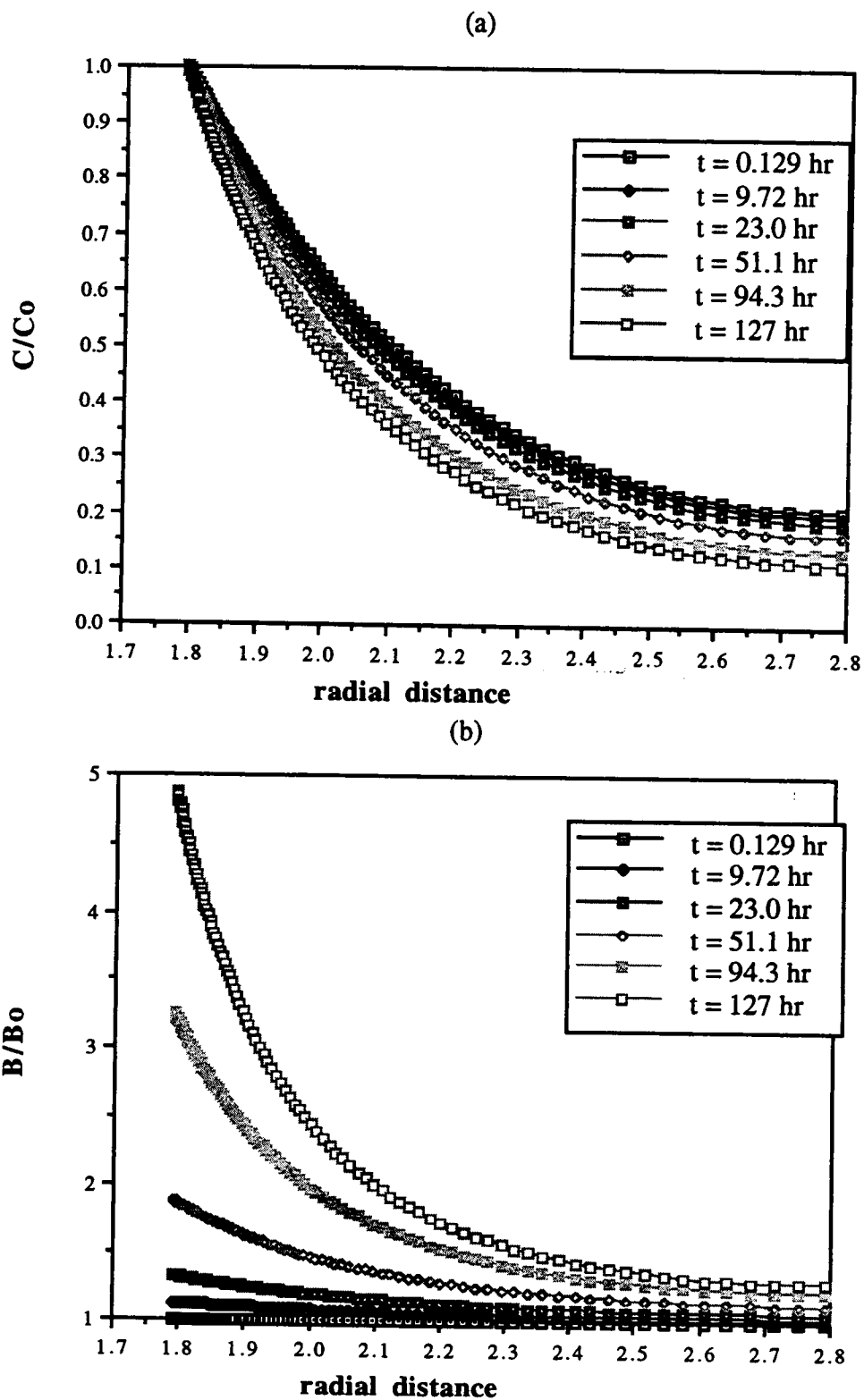


Fig. 6.30: Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 36$ ppm at a flow rate of $121 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile

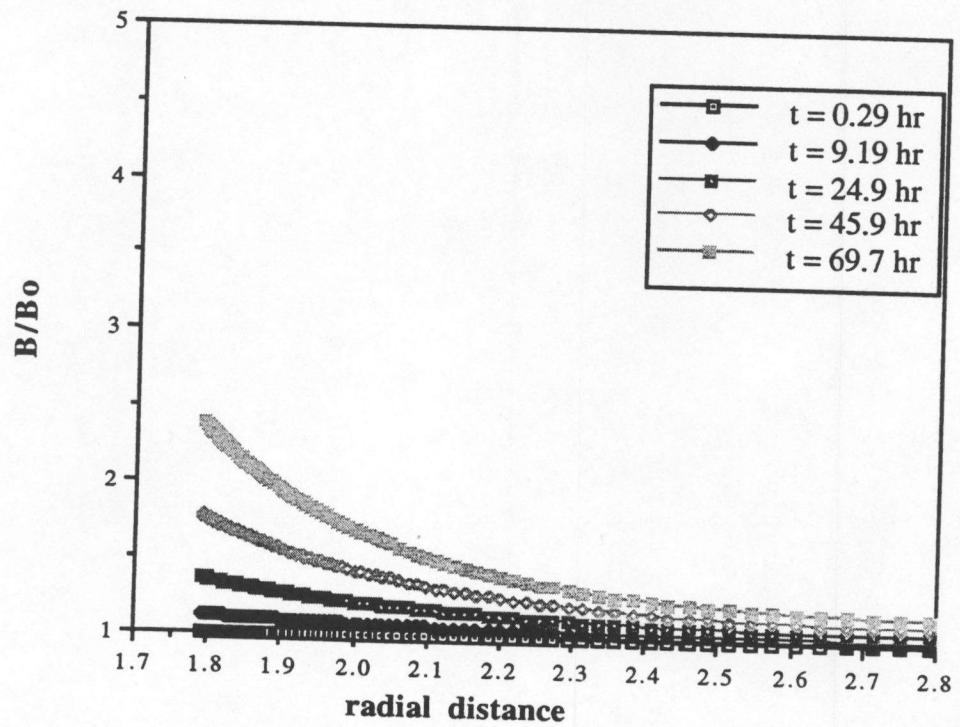
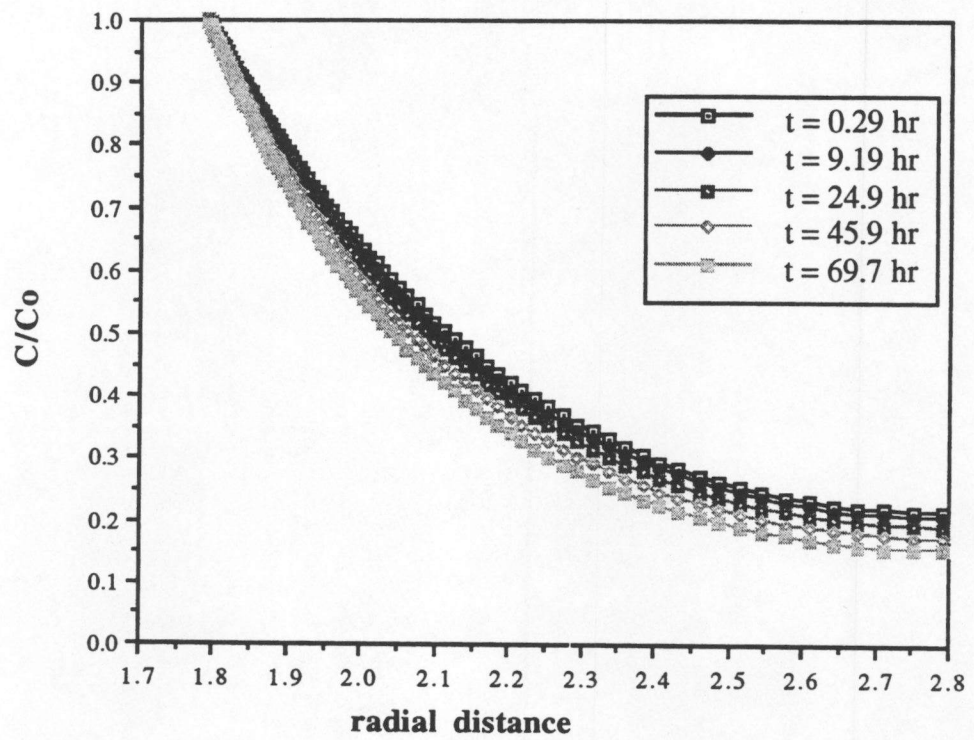


Fig. 6.31: Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 50$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile

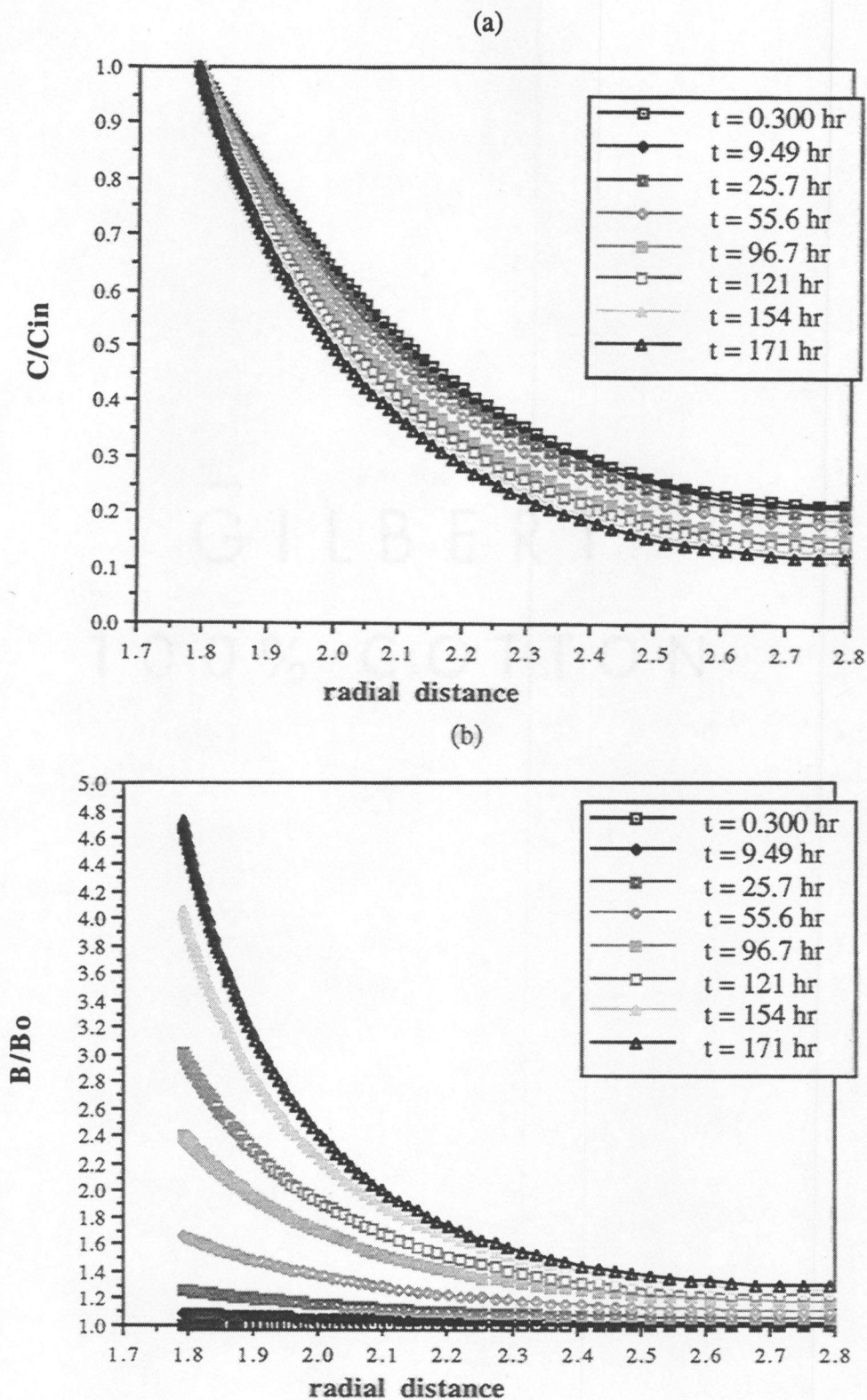


Fig. 6.32: Normalized concentration profiles as a function of radial distance through the reaction zone for $C_o = 50$ ppm at a flow rate of $125 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile

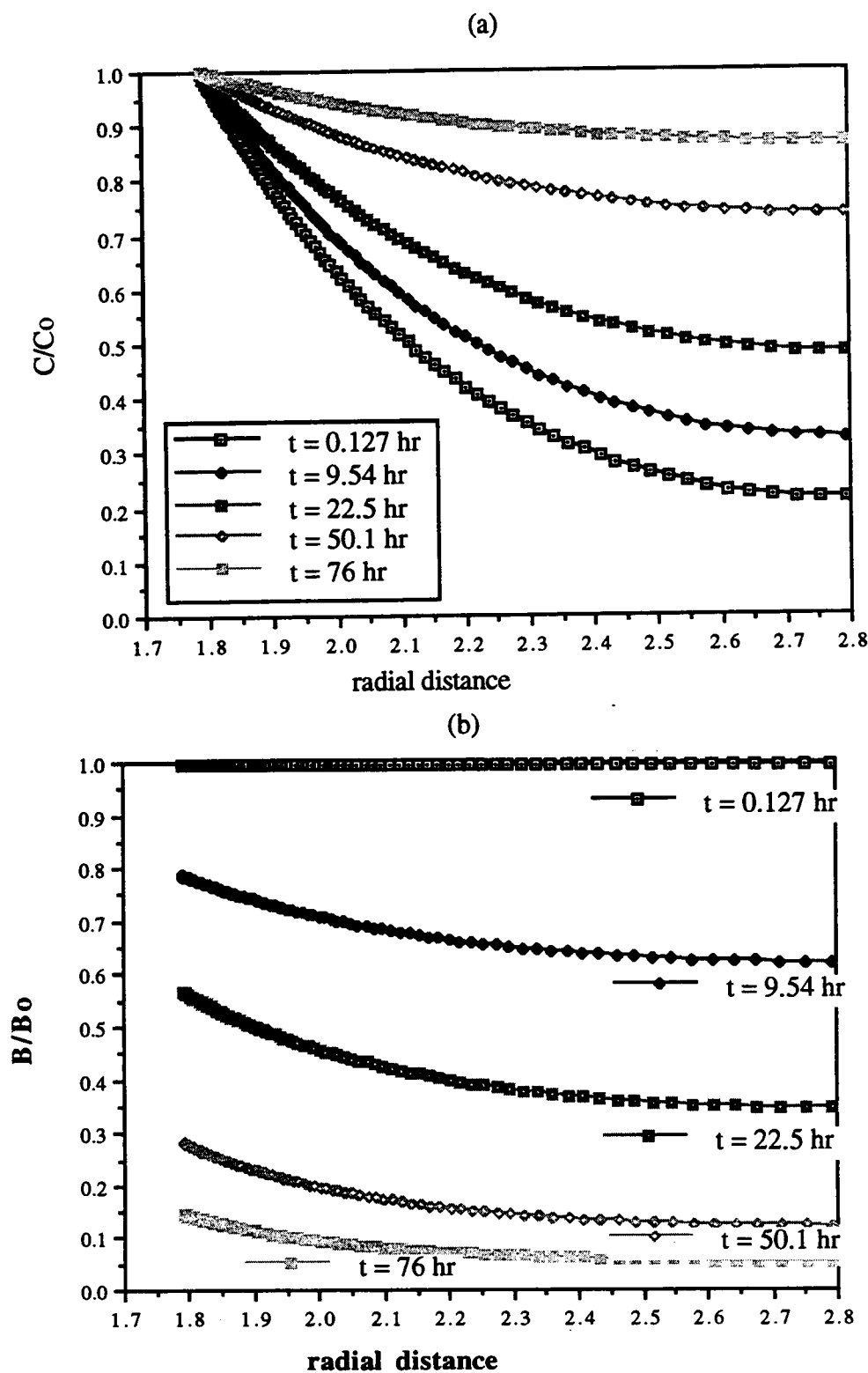


Fig. 6.33: Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 147$ ppm at a flow rate of $62 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile

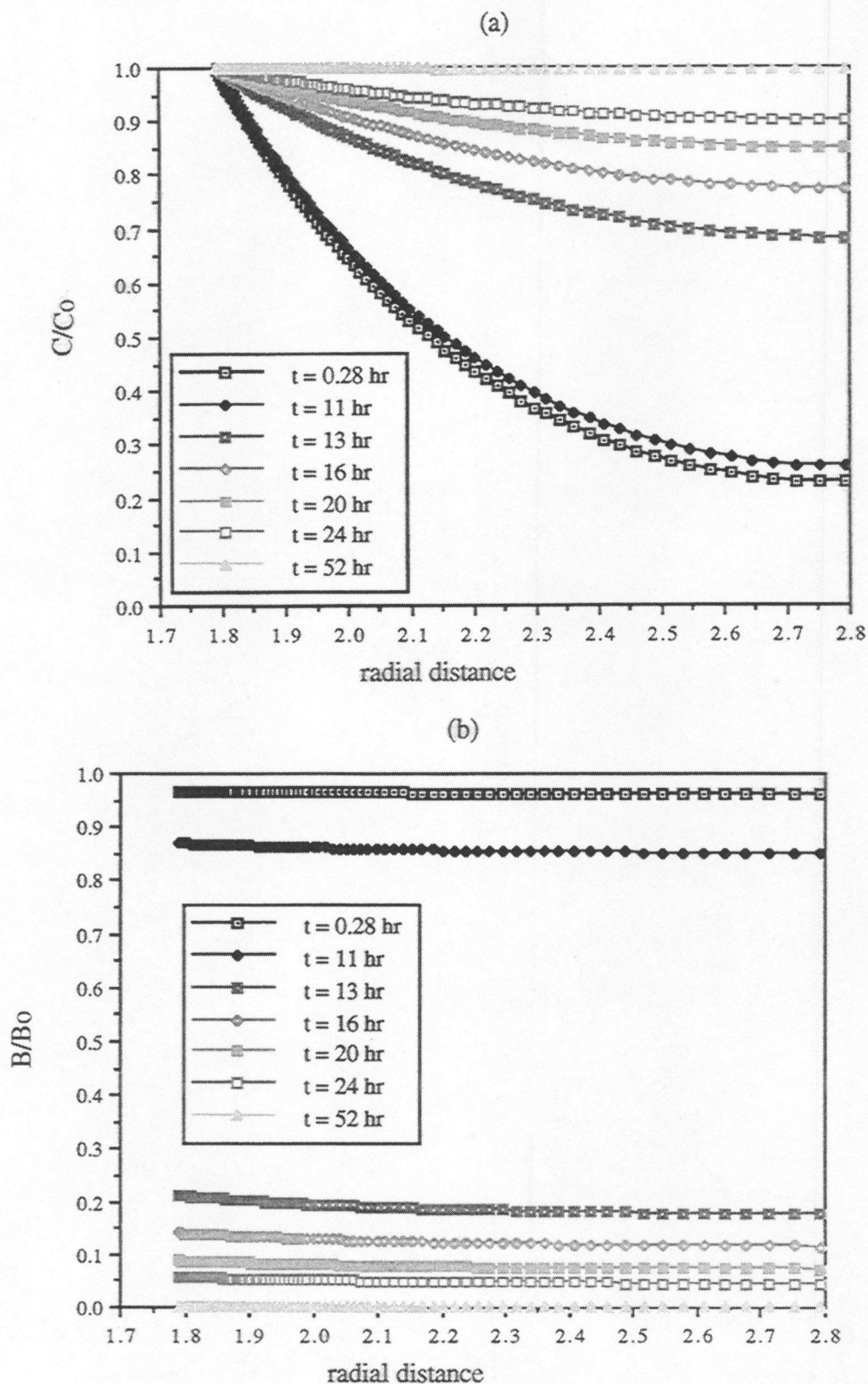


Fig. 6.34: Normalized concentration profiles as a function of radial distance through the reaction zone for $C_0 = 106$ ppm at a flow rate of $129 \text{ cm}^3/\text{min}$. (a) p-xylene profile (b) biomass profile

as time increases. The biomass profiles for the $C_o = 106$ ppm at 129 mL/min case, modeled with $k_d = 0.0830 \text{ hr}^{-1}$, are flatter throughout the reaction zone than the profiles for the $C_o = 147$ ppm at 62.0 mL/min case, modeled with $k_d = 0.0622 \text{ hr}^{-1}$. The former condition corresponds to the highest mass flow rate of p-xylene studied, and these results seem to suggest that higher mass flow rates of substrate lead to flatter biomass profiles through the reactor.

The general behaviour of the biomass profiles can be stated as follows, where type I profiles correspond to solutions of the model incorporating only growth kinetics ($k_d = 0$), and type II profiles correspond to solutions obtained with specified k_d values:

type I:	type II:
$C/C_o \leq 1.0$ for $t > 0$ at every r^*	$C/C_o \leq 1.0$ for $t > 0$ at every r^*
$B/B_o \geq 1.0$ for $t > 0$ at every r^*	$B/B_o \leq 1.0$ for $t > 0$ at every r^*
C/C_o decreases with t at every r^*	C/C_o increases with t at every r^*
B/B_o increases with t at every r^*	B/B_o decreases with t at every r^*

6.5 BIOMASS GROWTH

The procedure described in Section 4.4 for the determination of cell mass was followed to obtain the amount of biomass per gram of sand before and after each experiment. The correlation of optical density at 600 nm with cell mass was used to quantify the mass of cells. Initially, the amount of biomass for the experiments fell within the range of

$$B_o = 8.45\text{E-}04 \pm 3.20\text{E-}04 \quad [\text{grams cells/gram sand}]$$

which represents a 95% confidence interval. Experimentally, the final cell mass was determined by averaging the cell mass obtained from 3 to 5 separate reactor sand samples.

The value of n in Table 6.5 represents the number of final samples taken, and S.D. represents the standard deviation of these measurements.

Comparison of the final cell mass with the model was done by integrating the area under the curve of the B/B_0 profile at the final time and finding the average value of this function in the interval of the reaction zone. This average value of B/B_0 is the closest representation of the final biomass to the experimentally measured values. Table 6.5 presents a summary of the values obtained, and shows agreement between the experimental and theoretical final cell mass to be within 15 to 36%.

Table 6.5: Experimental and theoretical final cell mass

C_0 (ppm)	V (mL/min)	r^*_{av}	% rct.vol.	$\left(\frac{B}{B_0}\right)_{av,th.}$	$\left(\frac{B}{B_0}\right)_{av,ex.}$	$n, S.D.$	% difference
15	62.0	2.24	39.5	1.26	1.67	4, 0.23	32
15	125	2.25	40.4	1.17	1.49	3, 0.31	27
28	62.2	2.23	38.5	1.28	1.53	5, 0.19	20
36	121	2.01	18.6	1.91	2.20	4, 0.26	15
50	62.0	2.05	21.7	2.41	3.24	4, 0.41	34
50	125	2.22	42.9	1.18	1.49	5, 0.35	21
100	62.0	2.19	35.1	0.741	1.01	4, 0.22	36

The average radial values in Table 6.3 represent the radial distance within which 50% of the biomass has grown. At this point, the average value of B/B_0 is found. The percent reactor volume is the percentage of the reactor volume within the reaction zone in

which 50% of the biomass growth has occurred. These values are all below 50%, which means that more than 50% of the biomass growth occurs within the first 50% of the reaction zone, which is also apparent by the radial profiles generated in Figures 6.27 to 6.32. Additionally, the higher the average values of B/B_0 , the lower the r_{av}^* . This would mean that the more the biomass grows, the more this growth becomes concentrated near the inner radial wall.

6.6 P-XYLENE REMOVAL RATES

In order to attempt to provide some understanding and support for the use of a deactivation or cell death constant, k_d , previously discussed in Section 6.4.1, the amount of p-xylene degraded is determined in an approximate manner through the calculation of the area under the effluent curves of Figures 6.12 and 6.16. The amount of p-xylene appearing in the outlet of the reactor corresponds to the area under the concentration/time effluent curves. The amount of p-xylene removed is then determined by subtracting the latter area from the total amount of p-xylene that has passed through the reactor. (Because the y-axis is in non-dimensional units, the calculated areas are multiplied by the p-xylene mass flow rate to obtain mass values of p-xylene.) Average removal rates can then be determined by dividing this amount by the inlet flow rate. The results of such calculations are summarized in Table 6.6.

The overall removal rates range from 0.17 to 1.06 mg p-xylene per hour. The p-xylene removal rates for the first three cases ($C_0 = 15\text{-}28$ ppm) range from 0.17 to 0.3 mg/hr and are relatively smaller than the others. Figures 6.7 to 6.9 represent the effluent curves of these experiments, for which C_{out}/C_{in} is between 0.1 to 0.3 for these experiments and is not seen to increase beyond this range. Because the inlet flow rates of

Table 6.6: Average p-xylene removal rates

C _o (ppm)	V(cm ³ /min)	p-xylene mass flow rate (mg/min)	Area (mg p-xyl. out)	mg p-xyl. removed	av. removal rate (mg/hr)
15	62.0	0.003295	3.96	29.0	0.174
15	125	0.006642	14.3	33.5	0.279
28	62.3	0.006181	6.95	39.4	0.315
36	121	0.01543	33.2	132	0.740
50	61.7	0.01093	12.6	77.2	0.564
50	125	0.02215	19.3	75.0	1.06
100	62.0	0.02197	24.3	56.7	0.945
147	62.0	0.03229	94.2	45.3	0.630
100	129	0.04845	227	34.1	0.437

p-xylene are smaller in comparison to the others, as shown in Table 6.6, and the duration of the experiments is between 120 to 180 hours, the average removal rates of p-xylene are smaller relative to the other experiments. This does not mean that the experiments are not successful in terms of the p-xylene degradation, as Figures 6.7 to 6.9 represent 70 to 95% removal of the influent p-xylene, but that the mass flow rates of p-xylene are small relative to the duration of the experiment.

As mass flow rates are increased, the p-xylene removal rates range from 0.5 to 1 mg/hr. Again, these average p-xylene removal rates are dependent upon the duration of each experiment. The highest of these values, 1.06 mg p-xylene removed/hr, occurred for a p-xylene mass flow rate of 0.02215 mg/min (C_o = 50 ppm at 125 mL/min), and Figure

6.12 shows that the experiment reached steady state after 80 hours. The predictive model was adequate in representing the effluent curve corresponding to this case (Fig.6.22).

Although the duration of the experiments varied from 60 to 180 hours, many of the experiments were either carried out until the variations in C_{out}/C_{in} were very little (± 0.02 to 0.05) or until C_{out}/C_{in} reached a high value beyond which very little removal was observed ($0.75 \leq C_{out}/C_{in} \leq 0.95$). In general, as the mass flow rate of p-xylene increases, the removal rate of p-xylene increases up to a mass flow rate of 0.022 mg/min . Up to this point, removal rate is a linear function of mass flow rate of p-xylene whose intercept nearly approximates 0, as expected, and whose slope is positive (Figure 6.35):

$$(\text{removal rate [mg/hr]}) = 2.96\text{E-}02 + 44.7 (\text{mass flow rate [mg/min]})$$

(correlation = 0.992)

At p-xylene flow rates greater than approximately 0.022 mg/min , there is a sharp decrease in the removal rate of p-xylene.

This analysis supports using a deactivation constant because these results are consistent with the use of k_d in the model: k_d was only used in the cases where C_o was greater than or equal to 100 ppm , which corresponds to the right hand side of Figure 6.35 where p-xylene removal increases with increasing mass flow rate. All the predictive model results done with $k_d = 0$ are situated on the linear, increasing region of the removal rate vs. mass flow rate graph of Figure 6.35. Based on this analysis along with the modeling results, deactivation of the cells appears to be occurring at p-xylene mass flow rates above 0.023 mg/min and inlet p-xylene concentrations greater than or equal to 100 ppm . This analysis thus lends support to the use of the relation of k_d with p-xylene mass flow rate (equation 6.3) developed in Section 6.4.2.

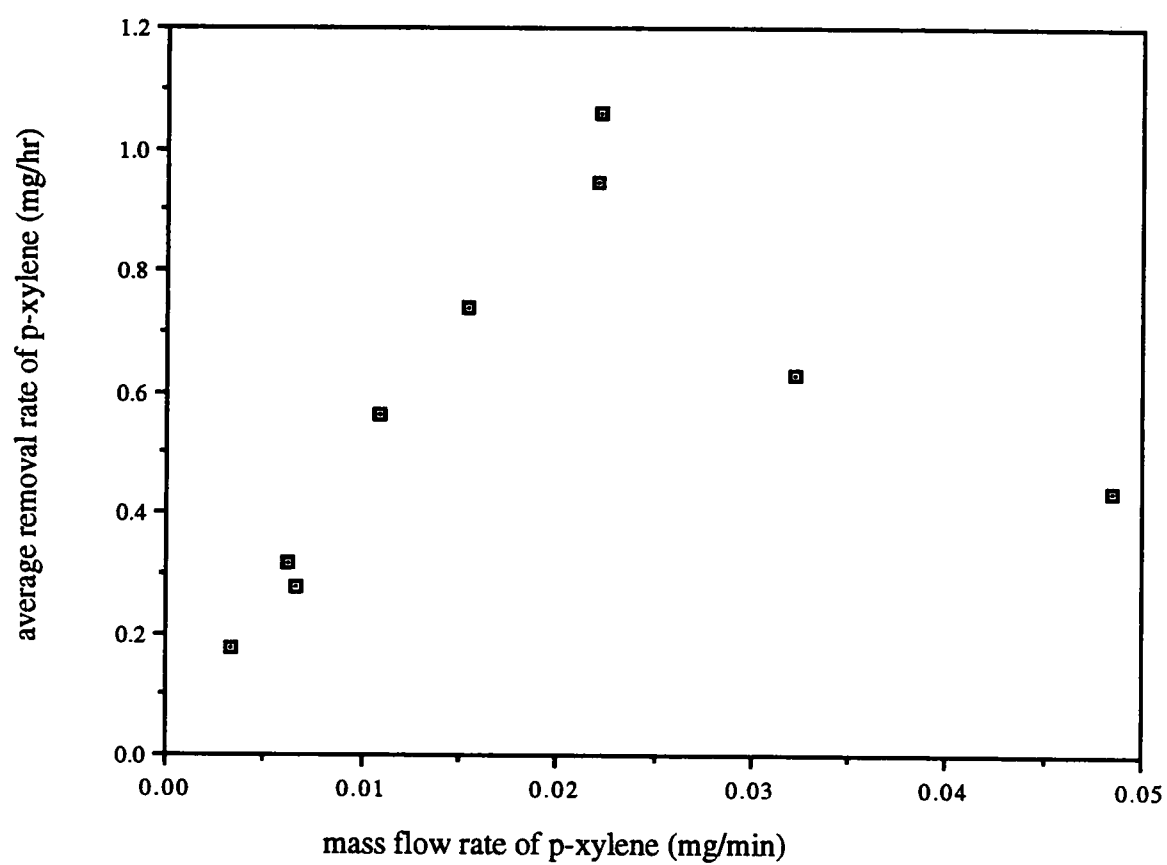


Figure 6.35: Average removal rate of p-xylene as a function of mass flow rate of p-xylene.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

This thesis has evaluated both experimentally and theoretically the vapor phase biodegradation of para-xylene by *Pseudomonas putida* 23973 immobilized onto sand in a radial-flow membrane-based reactor. The operating parameters that were examined and allowed to vary were the influent para-xylene concentration and the total influent flow rate. Influent concentrations studied were in the range of 15 to 150 ppm at flow rates between 60 and 130 cm³/min.

As a result of the experimental data accumulated in this study, the following conclusions are made:

1. The initial stages of reactor operation represent a region of variability as adsorption, acclimation and growth of the biomass, and pressure stabilization are simultaneously occurring. From the abiotic adsorption experiments performed on autoclaved immobilized cells, breakthrough occurs within one hour. After the first hour of operation, pressure stabilization has occurred, and adsorption breakthrough will have taken place, though simultaneously with biodegradation kinetics.
2. The region of operation for the defined reactor system/immobilized *P.putida* microbial phase was found to be within the range of 15 ppm to 150 ppm for the influent para-xylene concentration at flow rates between 60 and 130 cm³/min. Continuous biodegradation was demonstrated within this defined operating region and resulted in removal efficiencies between 70 and 95% for operating times up to 200 hours for influent para-xylene concentrations up to and including 50 ppm.
3. As the influent para-xylene concentration increased from 50 to 100 to 150 ppm, the removal efficiencies successively decreased while still remaining as high as 80% for the 50

ppm case and 60% for the 100 ppm case for up to 80 hours. The system did appear to become saturated after 60 hours of operation with an influent para-xylene concentration of 147 ppm.

4. Mass transfer limitations did not appear to be significant in the reactor system studied as removal efficiencies in the 15 to 36 ppm range were comparable and remained above 60% when the total flow rate was doubled.

5. In general, as the mass flow rate of p-xylene increases, the removal rate of p-xylene increases up to a mass flow rate of 0.022 mg/min. Up to this point, removal rate is a linear function of mass flow rate of p-xylene:

$$(\text{removal rate [mg/hr]}) = 2.96\text{E-}02 + 44.7 (\text{mass flow rate [mg/min]})$$

At p-xylene flow rates greater than 0.023 mg/min, there is a sharp decrease in the removal rate of p-xylene. Deactivation of the cells appears to be occurring at p-xylene mass flow rates above 0.023 mg/min and inlet p-xylene concentrations greater than or equal to 100 ppm.

The following conclusions can be established from the solution of the pseudo-homogeneous reactor model, which consisted of coupled, nonlinear partial differential equations derived from the mass balance of the para-xylene and the biomass through the radial reaction zone:

1. The effluent concentration curves of para-xylene for $15 \leq C_0 \leq 50$ ppm could be closely modeled with the developed predictive model consisting of the constitutive equations incorporating Monod kinetics. The overall slope of the resulting effluent curves was negative and agreed with the majority of the data within this concentration range, indicating that as time increases, the amount of para-xylene leaving the reactor decreases. The experimental data fell within the range of the curves predicted using the high, low, and middle values of the specified confidence interval of the kinetic constants.

2. For $50 < C_0 \leq 150$ ppm, the model as written with only a biomass growth term was not sufficient to describe the general behavior of the effluent curves, which had an overall positive slope indicating that as time increases, the amount of para-xylene in the effluent curve increases. In this concentration range, a modified model incorporating a cell death, or deactivation constant k_d , as well as growth with the original Monod kinetics was successful in describing the data. The fitted cell death constants were between 0.022 and 0.083 hr^{-1} .

3. The functional dependence of k_d with p-xylene feed rate was estimated to be $k_d [\text{hr}^{-1}] = 0.31722 + 0.076274 \ln(\text{p-xylene flow rate} [\text{mg/min}])$. Through this functional dependence of k_d with p-xylene flow rate, one model may be written by taking into account the region where k_d is defined, where cell deactivation as well as cell growth occurs.

Where k_d is equal to zero, the model reduces to the Monod growth kinetic model. This analysis seems to suggest the existence of a threshold value of the mass flow rate of p-xylene, below which cell growth occurs in the absence of cell deactivation, and above which a gradual deactivation occurs as a functional dependence of p-xylene flow rate.

4. The general behaviour of the biomass profiles are as follows, where type I profiles correspond to solutions of the model incorporating only growth kinetics ($k_d = 0$), and type II profiles correspond to solutions obtained with specified k_d values:

type I:

$$C/C_0 \leq 1.0 \text{ for } t > 0 \text{ at every } r^*$$

$$B/B_0 \geq 1.0 \text{ for } t > 0 \text{ at every } r^*$$

$$C/C_0 \text{ decreases with } t \text{ at every } r^*$$

$$B/B_0 \text{ increases with } t \text{ at every } r^*$$

type II:

$$C/C_0 \leq 1.0 \text{ for } t > 0 \text{ at every } r^*$$

$$B/B_0 \leq 1.0 \text{ for } t > 0 \text{ at every } r^*$$

$$C/C_0 \text{ increases with } t \text{ at every } r^*$$

$$B/B_0 \text{ decreases with } t \text{ at every } r^*$$

The radial concentration profiles show that both the substrate and the biomass concentrations decrease with increasing radial distance. As time increases for the model incorporating cell growth (type I), the amount of substrate successively decreases, and the

amount of biomass successively increases at any given radial node. The radial biomass profiles indicate that biofilm growth is occurring predominantly at the inner radial wall adjacent to the feed stream. For the model incorporating growth as well as deactivation (type II), the radial substrate concentration profiles are similar to the ones resulting from the original model except that substrate concentrations increase with time instead of decreasing with time at any given radial node. In this case, the biomass profiles show declining values of B/B_0 with increasing time and radial distance, demonstrating progressive loss of biomass as time increases.

5. The use of a deactivation or cell death constant in the cases where C_0 is greater than or equal to 100 ppm is consistent with the functional dependence of p-xylene removal rate with p-xylene mass flow rate determined. All the predictive model results done with $k_d = 0$ are situated on the linear, increasing region of the graph of removal rate vs. mass flow rate, whereas the results modeled with fitted k_d values are situated on the negative slope region of the removal rate vs. mass flow rate graph.

In summary, the bioreactor developed in this study does support and verify the novel design for the vapor phase biodegradation of para-xylene. The pseudo-homogeneous reactor model along with the proper kinetics adequately describes the reactor behaviour.

Recommendations for future work could include performing additional experiments in the range of 50 to 100 ppm influent p-xylene concentration at various flow rates, and mathematically optimizing this reaction system to determine the optimal flow rates, influent para-xylene concentrations, and, possibly, optimal reactor thickness. The optimal conditions could be tested by conducting additional experiments and comparing with the data generated in this study. Additionally, a mathematical scale-up of this system to industrial-scale could be done. Furthermore, the design of this reactor could be tested with another microbial phase and substrate through bench top experiments.

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APPENDICES

APPENDIX I

NUMERICAL QUANTITIES USED IN SIMULATIONS

The parameters used in the numerical simulations of reactor profiles are presented and evaluated in this appendix. The sources for the equations and properties used are referenced directly after their initial presentations.

1.1 DIFFUSION COEFFICIENT

The effective diffusion coefficient, D , represents diffusion and/or dispersion in the radial direction. It is a parameter that includes the effects of molecular diffusion and eddy diffusion, which arises from turbulence and packing effects. This quantity is determined by knowledge of the bulk diffusivity in a binary gas mixture of A and B, D_{AB} . The equation used to estimate D_{AB} is the equation developed by Hirschfelder *et al.* (1949), in which the Lennard-Jones 6-12 potential is employed to relate attractive and repulsive atomic forces. This equation is used to predict the diffusivity for nonpolar gas pairs and is as follows:

$$D_{AB} = \frac{1.858 \times 10^{-27} T^{1.5}}{P \sigma_{AB}^2 \Omega_D} \left(\frac{1}{MW_A} + \frac{1}{MW_B} \right)^{0.5}$$

where

D_{AB} = diffusivity (m^2/s)

T = absolute temperature (K)

P = pressure (atm)

σ_{AB} = bimolecular collision diameter (m)

Ω_D = collision integral

MW = molecular weight (g/gmol)

The collision integral, Ω_D , is evaluated for the Lennard-Jones potential and is presented in tabular form (Hines and Maddox (1985), Table 2-4, p.23) as a function of $k_b T/e_{AB}$, where e_{AB} is a Lennard-Jones force constant representing the maximum energy of attraction and k_b is the Boltzmann constant. The force constants, e_{AB} and σ_{AB} , are determined by the pure substance collision diameters and force constants using the following relations:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \quad \text{and} \quad \frac{e_{AB}}{k_b} = \left(\frac{e_A}{k_b} \times \frac{e_B}{k_b} \right)^{0.5}$$

The collision diameters and energy parameters for selected pure substances are given in Table 2-3 (p.21-22) of Hines and Maddox (1985); for those substances not listed, the collision diameters and force constants may be calculated from the following equations (Hines and Maddox, 1985):

$$\sigma \times 10^{10} \text{ m} = 8.33 V_c^{1/3} \quad \text{and} \quad \frac{e}{k_b} = 0.75 T_c$$

In these equations, V_c is the critical volume in m^3/kgmol , and T_c is the critical temperature on the Kelvin scale.

1.1.1 Sample calculation

The diffusion coefficient for the para-xylene/air system at 25°C (298.15 K) and 0.68 atm (10 psia) is estimated using the relation by Hirshfelder previously discussed.

From Table 2-3 of Hines and Maddox (1985), the collision diameter and the energy parameter for air are $\sigma_{\text{air}} = 3.771 \times 10^{-10} \text{ m}$ and $(e/k_b)_{\text{air}} = 78.6 \text{ K}$. The corresponding values for p-xylene are calculated using the critical temperature and critical molar volume according to the equations previously presented. From the CRC Handbook of Chemistry and Physics (1983-1984), the critical temperature and molar volume of p-xylene are 618.15K, and 1.4962 m³/kgmol, respectively. The collision diameter and energy parameter are calculated as

$$\sigma_{\text{p-xyl.}} = 8.33 \times 1.4962^{1/3} \times 10^{-10} \text{ m} = 9.527 \times 10^{-10} \text{ m}$$

and

$$e/k_b = 0.75 \times 618.15 \text{ K} = 463.61 \text{ K}$$

The force constants σ_{AB} and e_{AB}/k_b are determined:

$$\sigma_{AB} = 0.5(3.711 \times 10^{-10} \text{ m} + 9.527 \times 10^{-10} \text{ m}) = 6.619 \times 10^{-10} \text{ m}$$

and

$$e_{AB}/k_b = (78.6 \text{ K} \times 463.61 \text{ K})^{0.5} = 190.89 \text{ K}$$

The parameter $k_b T/e_{AB}$ at 298.15 K is 1.5619, and the collision integral Ω_D is found from Table 2-4 of Hines and Maddox (1985) to be 1.182. With the molecular weight of air and p-xylene, 28.86 g/gmol and 106.18 g/gmol, respectively, substitution into the equation for diffusivity at $p = 0.816 \text{ atm}$ (12 psi) yields:

$$D_{AB}(\text{m}^2/\text{s}) = \frac{1.858 \times 10^{-27} \times 298.15^{1.5}}{0.816 \times (6.619 \times 10^{-10})^2 \times 1.182} \left(\frac{1}{28.86} + \frac{1}{106.18} \right)^{0.5}$$

$$= 4.750 \times 10^{-6} \text{ m}^2/\text{s} = 2.850 \text{ cm}^2/\text{min}$$

This binary diffusion coefficient is used in an approximation to the effective dispersion parameter, which lumps together molecular diffusion and eddy diffusion arising from packing effects and turbulence. The relation between the effective diffusivity and the combined diffusivity, which in the present case is the bimolecular diffusion coefficient, is taken from Hill (1977):

$$D_{\text{eff}} = \frac{D_{AB}\epsilon}{\tau'}$$

where τ' is a tortuosity factor which takes into account the length of the diffusion path that molecules must travel. From the correlation of average Peclet number with Reynolds number and the ratio of particle to tube diameter (Hill, 1977), the diffusivity that results is approximately $7\text{E}-05$ for Reynolds numbers below 10. (Reynolds numbers on the order of 10^{-04} as is the case for this system are not shown on the graph.) However, the reference does specifically say that longitudinal dispersion, which in this case would be radial dispersion, is negligible in comparison with mass transport due to bulk flow if the ratio of the reactor length to the size of the particles is 100 or more. In the present case, the reactor length being the reactor thickness, this ratio is $1 \text{ cm}/0.0025 \text{ cm} = 400$. For the diffusion term in the model in which essentially only an order of magnitude accuracy is required, the effective diffusion coefficient is approximated by the above equation given for D_{eff} with a tortuosity factor of one, as the microporous membranes act as diffusers to

equalize flow.

To give an example of the effect of the diffusion coefficient, a sample case, $C_0 = 28$ ppm at 62.3 mL/min, was run with the model (equations 5.16 and 5.17) developed in Chapter V at the midpoint of the kinetic parameters with the value of DIFU as written in Table 6.2 (DIFU = 6.148), and with DIFU/2 and DIFU x 2. The numerical results are shown in Figure A.1 along with the experimental values. The experimental data are bounded between the results obtained for DIFU and DIFU/2. The value of the diffusion coefficient used is therefore adequate for representing the experimental data. (The effluent curve for DIFU/2 lies below the effluent curve obtained for DIFU and shows increased removal of substrate. This is explained by consideration of the mass flux vector, which is

$$N_i'' = v(r)c_i - D \frac{\partial c_i}{\partial z}$$

As the value of D decreases, the mass flux of substrate increases and leads to higher conversions, as shown in Figure A.1. As D increases, the mass flux vector decreases, and lower conversions occur, which is why the effluent curve (C_{out}/C_{in} vs. time) for DIFU x 2 lies above that for DIFU.)

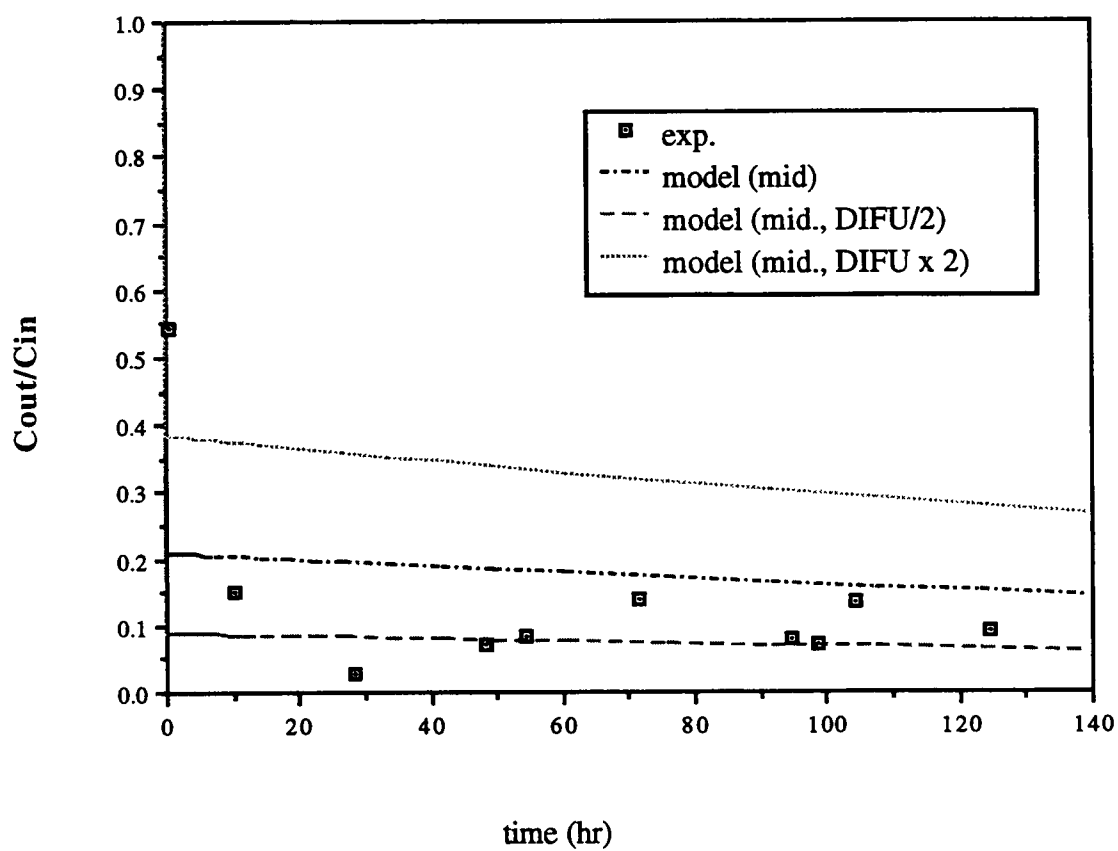


Figure A.1: Effect of diffusion parameter DIFU for $C_o = 28$ ppm and a flow rate of 62.3 mL/min as predicted by the model.

1.2 PARAMETERS IN TEMPLATE FILE

The nondimensional parameters as written in the equations of Chapter V are [DIFU], [CONV], [RCT1], and [RCT2]. The notation in the template file is identical except that [RCT1] is denoted by [RCT], and [RCT2] is denoted by [RCTB].

$$L_c = r_2 - r_1 = 2.54 \text{ cm} - 1.63 \text{ cm} = 0.91 \text{ cm}$$

$$A_c = \text{inner cross sectional area} = 2\pi r_1 L = 2\pi(1.63 \text{ cm})(40.0 \text{ cm}) = 409.664 \text{ cm}^2$$

The following sample calculation is provided for an inlet p-xylene concentration of 50 ppm at a total influent flow rate of 62.0 cm³/min. All of the quantities provided in Table 6.2 are calculated in the same manner.

$$\text{Volumetric flow rate}/A_c = \text{superficial velocity} = v$$

$$\text{At the inner radius, } r_1, v = v_1 = \frac{62 \text{ cm}^3/\text{min}}{409.66 \text{ cm}^2} = 0.15134 \frac{\text{cm}}{\text{min}}$$

$$\tau = \frac{L_c}{v_1} = \frac{0.91 \text{ cm}}{0.15134 \text{ cm/min}} = 6.0128 \text{ min}$$

$$[\text{DIFU}] = \frac{\varepsilon \tau D}{L_c^2} = \frac{(0.3)(6.0128 \text{ min})(2.850 \text{ cm}^2/\text{min})}{0.91^2 \text{ cm}^2} = 6.2081$$

$$[\text{CONV}] = \frac{r_1}{v_1 \tau} = \frac{1.63 \text{ cm}}{(0.15134 \text{ cm/min})(6.0128 \text{ min})} = 1.791$$

$$\begin{aligned}
 [\text{RCT1}] &= \frac{\tau \mu_m b_o}{YK} \\
 &= \frac{(6.0128 \text{ min}) \frac{850 \text{ g sand}}{0.495 \text{ L}} (0.437 \text{ hr}^{-1}) \left(\frac{1 \text{ hr}}{60 \text{ min}} \right) \left(\frac{8.4497 \text{ E-04 g cells}}{\text{g sand}} \right)}{\left(\frac{0.3 \text{ g cells}}{\text{g p-xyl.}} \right) \left(\frac{0.006 \text{ g p-xyl.}}{\text{L}} \right)} \\
 &= 35.301 \\
 &= [\text{RCT}]
 \end{aligned}$$

$$\begin{aligned}
 [\text{RCT2}] &= \frac{\tau \mu_m c_o}{K} = \frac{(6.0128 \text{ min}) \left(\frac{1 \text{ hr}}{60 \text{ min}} \right) (0.437 \text{ hr}^{-1}) (0.18 \text{ mg p-xyl./L})}{6 \text{ mg p-xyl./L}} \\
 &= 1.314 \text{ E-03} \\
 &= [\text{RCTB}]
 \end{aligned}$$

$$[\text{COK}] = \frac{c_o}{K} = \frac{0.18 \text{ mg p-xyl./L}}{6 \text{ mg p-xyl./L}} = .03$$

APPENDIX II

TEMPLATE AND MODEL FILES FOR AKCESS

2.1 TEMPLATE FILES

INTEGRATION FACTORS

INITIAL_TIME
 FINAL_TIME
 PROBLEM_CONVERGENCE_CRITERIA
 MAXIMUM_CHANGE_IN_Q__(DQ)
 INITIAL_TIME_STEP
 TIME_STEP_MULTIPLIER
 MAXIMUM_TIME_STEP
 CRITERIA_TO_RAISE_MAX_TIME_STEP
 MAXIMUM_NUMBER_OF_STEPS
 MAXIMUM_NUMBER_OF_ITERATIONS_PER_STEP
 ITERATION_CONVERGENCE_CRITERIA
 THETA_IMPLICITNESS_FACTOR
 MAXIMUM_VALUE_OF_ANY_DELTA_Q

TRANSFORMATION ARRAYS

ETKJ 1.
 DETJ 1
 # DETE 0.

BOUNDARY CONDITIONS

C B
 DIRI_C D 0
 #DIRI_B 0 D

TITLE ***** TEMPLATE FILE TEMP.MODT *****
 RADIAL-FLOW REACTOR WITH 2 MASS VARIABLES

RESIDUALS

C 1 # INITIAL VALUE TERM IN F(C)
 ()(RAD)()(0;1)(A200)(-C)

C 2 # RESIDUAL TERMS IN F(C)
 (DIFU)(RAD)()(0;-1)(A211)(C)
 +(CONV)()(0;0)(A201)(C)
 +(RCT)(RAD)(B)(0;1)(A3000)(C)
 +(-,RCT,COK)(RAD)(C,C)(0;1)(A3000)(B)

B 1 # INITIAL VALUE TERM IN F(B)
 ()(RAD)()(0;1)(A200)(-B)

B 2 # RESIDUAL TERMS IN F(B)
 (-,RCTB)(RAD)(C)(0;1)(A3000)(B)
 +(RCTB,COK)(RAD)(C,C)(0;1)(A3000)(B)

JACOBIANS

C C 1 1 T INITIAL VALUE TERM IN DF(C)/DC
 ()(RAD)()(0;1)(A200)()

C C 2 1 T RESIDUAL TERMS IN DF(C)/DC
 (DIFU)(RAD)()(0;-1)(A211)()
 +(CONV)()(0;0)(A201)()
 +(RCT)(RAD)(B)(0;1)(A3000)()
 +(-,TWO,RCT,COK)(RAD)(C,B)(0;1)(A3000)()

C B 2 1 T RESIDUAL TERM IN DF(C)/D(B)
 (RCT)(RAD)(C)(0;1)(A3000)()
 +(-,RCT,COK)(RAD)(C,C)(0;1)(A3000)()

B B 1 1 T INITIAL VALUE TERM IN DF(B)/D(B)
 ()(RAD)()(0;1)(A200)()

B B 2 1 T RESIDUAL TERMS IN DF(B)/D(B)
 (-,RCTB)(RAD)(C)(0;1)(A3000)()
 +(RCTB,COK)(RAD)(C,C)(0;1)(A3000)()

B C 2 1 T RESIDUAL TERMS IN DF(B)/D(C)
 (-,RCTB)(RAD)(B)(0;1)(A3000)()
 +(TWO,RCTB,COK)(RAD)(B,C)(0;1)(A3000)()

GROUP FREQUENCY

1
 SOLUTION TYPE
 DELTA_Q
 GAUSS_ELIMINATION
 IMPLICIT_EULER

END

INTEGRATION FACTORS

INITIAL_TIME
 FINAL_TIME
 PROBLEM_CONVERGENCE_CRITERIA
 MAXIMUM_CHANGE_IN_Q_(DQ)
 INITIAL_TIME_STEP
 TIME_STEP_MULTIPLIER
 MAXIMUM_TIME_STEP
 CRITERIA_TO_RAISE_MAX_TIME_STEP
 MAXIMUM_NUMBER_OF_STEPS
 MAXIMUM_NUMBER_OF_ITERATIONS_PER_STEP
 ITERATION_CONVERGENCE_CRITERIA
 THETA_IMPLICITNESS_FACTOR
 MAXIMUM_VALUE_OF_ANY_DELTA_Q

TRANSFORMATION ARRAYS

ETKJ 1.
 DETJ 1
 # DETE 0.

BOUNDARY CONDITIONS

C B
 DIRI_C D 0
 #DIRI_B 0 D

TITLE ***** TEMPLATE FILE TEMP.MODTD *****
 RADIAL-FLOW REACTOR WITH 2 MASS VARIABLES WITH KD

RESIDUALS

C 1 # INITIAL VALUE TERM IN F(C)
 ()(RAD)()(0;1)(A200)(-C)

C 2 # RESIDUAL TERMS IN F(C)
 (DIFU)(RAD)()(0;-1)(A211)(C)
 +(CONV)()(0;0)(A201)(C)
 +(RCT)(RAD)(B)(0;1)(A3000)(C)
 +(-,RCT,COK)(RAD)(C,C)(0;1)(A3000)(B)

B 1 # INITIAL VALUE TERM IN F(B)
 ()(RAD)()(0;1)(A200)(-B)

B 2 # RESIDUAL TERMS IN F(B)
 (-,RCTB)(RAD)(C)(0;1)(A3000)(B)
 +(RCTB,COK)(RAD)(C,C)(0;1)(A3000)(B)
 +(KDT)()(RAD)(0;1)(A3000)(B)

JACOBIANS

C C 1 1 T INITIAL VALUE TERM IN DF(C)/DC
 ()(RAD)()(0;1)(A200)()

C C 2 1 T RESIDUAL TERMS IN DF(C)/DC
 (DIFU)(RAD)()(0;-1)(A211)()
 +(CONV)()(0;0)(A201)()
 +(RCT)(RAD)(B)(0;1)(A3000)()
 +(-,TWO,RCT,COK)(RAD)(C,B)(0;1)(A3000)()

C B 2 1 T RESIDUAL TERM IN DF(C)/D(B)
 (RCT,H)(RAD)(C)(0;1)(A3000)()
 +(-,RCT,COK)(RAD)(C,C)(0;1)(A3000)()

B B 1 1 T INITIAL VALUE TERM IN DF(B)/D(B)
 ()(RAD)()(0;1)(A200)()

B B 2 1 T RESIDUAL TERMS IN DF(B)/D(B)
 (-,RCTB)(RAD)(C)(0;1)(A3000)()
 +(RCTB,COK)(RAD)(C,C)(0;1)(A3000)()
 +(KDT)()(RAD)(0;1)(A3000)()

B C 2 1 T RESIDUAL TERMS IN DF(B)/D(C)
 (-,RCTB)(RAD)(B)(0;1)(A3000)()
 +(TWO,RCTB,COK)(RAD)(B,C)(0;1)(A3000)()

GROUP FREQUENCY

1
 SOLUTION TYPE
 DELTA_Q
 GAUSS_ELIMINATION
 IMPLICIT_EULER

END

2.2 MODEL FILE

TITLE **** MODEL FILE ****

1D RADIAL-FLOW REACTOR, ESM 552 .. 2/96

INTEGRATION FACTORS

0. \$ INITIAL_TIME
 1400. \$ FINAL_TIME
 1.E-60 \$ PROBLEM_CONVERGENCE_CRITERIA
 0.1 \$ MAXIMUM_CHANGE_IN_Q_(DQ)
 -0.000025 \$ INITIAL_TIME_STEP # - SIGN MEANS VARIABLE STEPPING
 1.5 \$ TIME_STEP_MULTIPLIER
 1. \$ MAXIMUM_TIME_STEP
 5 \$ CRITERIA_TO_RAISE_MAX_TIME_STEP
 5000 \$ MAXIMUM_NUMBER_OF_STEPS
 4 \$ MAXIMUM_NUMBER_OF_ITERATIONS_PER_STEP
 E-8 \$ ITERATION_CONVERGENCE_CRITERIA
 0.5 \$ THETA_IMPLICITNESS_FACTOR
 1 \$ MAXIMUM_VALUE_OF_ANY_DELTA_Q

GLOBAL SCALARS

[0.] \$ TDELX

CELL SCALARS

1 1 # ALLOW FOR 1 INPUT CASE; CASE: CO = 50 PPM, V = 62 CCM
 [1., -1., 0., 0., 1.E-05 \$ ONE, -ONE, DIFF, DUM1, REI
 0., 1.E-10, 1.E10, 1.E-5, 0., \$ RAYLE, RE2I, GR, PEI, TREF
 6.20833, 35.49, 1.791, 1.313E-03 \$ DIFU, RCT, CONV, RCTB
 0.0295333, \$ COK

-0.5, 0.5, 2.0 \$ -HALF, HALF, TWO
 1., 0., 1.E5, 0., \$ DELTEM, ARCH, PECLET, ATERM
 -1., 5.] \$ GDOTI, VSET

PRINT

101 1 1 # N1,N2,N3
 5 # PRINT INTERVAL(STEPS)
 1,101 # I WINDOW
 1,1 # J WINDOW
 1,1 # K WINDOW
 C, B, RAD # VARIABLES PRINTED IN COUT
 NONE # VARIABLES PRINTED FIRST STEP ONLY
 (13(1X,5E13.6),1X,E13.6)

DEBUG

NONE # STEP NUMBER TO PRINT ALL ITERATIONS
 0 # TYPE OF DEBUG PRINT
 4 # ITERATION NUMBER
 2,1,1 # I,J,K LOCATION, (K=0, ALL PLANES)
 ALL # VARIABLE OR ALL
 ALL # TERM NUMBER OR (- FOR SET NO.), OR ALL

OTHER

7. T I THERM
 1.1, 1.1, 2*0 1. 2*0 T ALC, REFLN N1 N2 N3 N4 N5
 GRAPHICS T PLOT VARIABLE LIST
 RAD C B
 THREE INTEGER T INTEGER PRINT FIELD
 RAD C B CL BL T

BOUNDARY CONDITIONS

DIRI_C 1 [1] \$ FIXEDSET 1
 #DIRI_B 1 [1] \$ FIXEDSET 1
 #DIRI_T 1 [1] \$ FIXEDSET 1

INITIAL CONDITIONS

[1. 100*1.] \$ C
 [101*1.] \$ B
 # [0. 100*0.] \$ TEM # WALL TEMP IS HELD FIXED AT ZERO
 # [1. 100*0.] \$ TEM # WALL TEMP IS HELD FIXED AT ONE
 [101*1.] \$ CBAR
 [101*0.] \$ UPR
 [101*0.] \$ RET
 [101*0.] \$ MTRL
 [101*0.] \$ DPDX
 # [0. 100*1.] \$ UOL1
 [101*1.] \$ BOLD
 # [101*0.] \$ VOL1
 [1. 100*1.] \$ COLD
 [1(1.7912 100R1.04 2.7912)] \$ RAD # MESHING WITH PROG. RATIO "R"
 # [101*0.] \$ U3
 # [101*0.] \$ X2
 # [0. 100*0.] \$ VNUE 2
 [101*0.] \$ DETJ
 [101*0.] \$ DETC
 [101*0.] \$ ETkj
 [101*0.] \$ EJK2
 [101*0.] \$ EJK3
 [101*0.] \$ EJK4
 [101*0.] \$ EJK5
 [101*0.] \$ EJK6
 [101*0.] \$ EJK7
 [101*0.] \$ EJK8
 [101*0.] \$ EJK9
 [101*1.] \$ CL
 [101*1.] \$ BL

```
# [101*0.] $ TEMPL
[101*0.] $ F1
[101*0.] $ F2
# [101*0.] $ F3
[101*0.] $ G1
[101*0.] $ G2
# [101*0.] $ G3
[1(1.7912 100R1.04 2.7912)] $ X1 # MESHING WITH PROG. RATIO "R"
[101*1.] $ ONES
TTT
END
```

VITA

Nathalie Rouhana was born in Montpellier, a city along the Mediterranean in southern France. She completed her secondary school education in 1985 at Brebeuf Preparatory School, a Jesuit college preparatory school in Indianapolis, Indiana. In May of 1988, she graduated with a Bachelor of Science honors degree in chemistry from Purdue University. She continued on at Purdue in the School of Engineering to obtain her Master of Science degree in Chemical Engineering in 1990. After graduation, she returned to France to work in polymer research in a laboratory associated with the CNRS, the Centre Nationale de Recherche Scientifique (National Center for Scientific Research) in Mulhouse. In January of 1993 she was offered a teaching assistantship in the Department of Chemical Engineering at the University of Tennessee, Knoxville, to pursue a doctoral degree in chemical engineering. This dissertation represents the culmination of that endeavor.