

Biological Treatment of Hazardous Contaminants in Sequencing Batch Reactors

by

Ibrahim Muhammad Al-Harazin

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CIVIL ENGINEERING

January, 1992

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 1354044

**Biological treatment of hazardous contaminants in sequencing
batch reactors**

Al-Harazin, Ibrahim Muhammad, M.S.

King Fahd University of Petroleum and Minerals (Saudi Arabia), 1992

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106



**BIOLOGICAL TREATMENT OF HAZARDOUS
CONTAMINANTS IN SEQUENCING
BATCH REACTORS**

BY

IBRAHIM MUHAMMAD AL-HARAZIN

A Thesis Presented to the
FACULTY OF THE COLLEGE OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CIVIL ENGINEERING

JANUARY, 1992

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

This thesis, written by

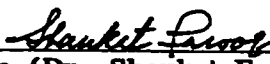
IBRAHIM MUHAMMAD AL-HARAZIN

under the direction of his Thesis Advisor, and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN CIVIL ENGINEERING

Thesis Committee


Chairman (Dr. Girgis F. Nakhla)

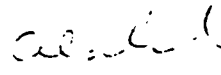

Co-Chairman (Dr. Shaukat Farooq)


Member (Dr. Sakhawat Hussain)


Member (Dr. Emmanuely Y. Osei-Twun)



Dr. Ghazi J. Al-Sulaimani
Department Chairman


Dr. Ala H. Al-Rabeh, Dean,
College of Graduate Studies

Date : 2011/01/01



Dedicated
To
My Beloved Parents

ACKNOWLEDGEMENT

Praise and gratitude be to Allah Almighty, with whose gracious help it was possible to accomplish this work. Acknowledgement is due to King Fahd University of Petroleum and Minerals for extending the facilities to carry out this research.

I would like to express my profound gratitude and appreciation to my advisor Dr. Girgis F. Nakhla for his valuable supervision and helpful suggestions throughout this study. The continuous guidance and constructive discussions provided by Dr. Nakhla on all phases of research and thesis preparation are greatly appreciated. I also wish to thank Dr. Shaukat Farooq, Dr. Emmanuely Y. Osei-twum and Dr. Sakhawat Husain for their cooperation and participation as committee members.

Special thanks to Mr. Essam El-Deeb and Mr. M. K. Abdulappa for their assistance during experimentation. Thanks are also extended to my friends especially Mr. Nabil Abu-Zeid who helped a lot during the different stages of the work.

TABLE OF CONTENTS

| | <i>Page</i> |
|--|-------------|
| Acknowledgement | ii |
| List of Tables | v |
| List of Figures | vi |
| Abstract | xi |
| Symbols | xiii |
| | |
| 1. INTRODUCTION | 1 |
| 2. LITERATURE REVIEW | 4 |
| 2.1 Physico-chemical Treatment of Hazardous Waste..... | 4 |
| 2.2 Biological Treatment of Hazardous Waste | 12 |
| 2.3 Sequencing Batch Reactors | 15 |
| 3. MATERIALS AND METHODS..... | 20 |
| 3.1 Source of Wastewater | 20 |
| 3.2 Experimental Set-up | 21 |
| 3.3 Experimental Procedures..... | 21 |
| 4. RESULTS & DISCUSSIONS | 28 |
| 4.1 (Part-I) Biotreatment of Phenol Bearing Wastewater..... | 28 |
| 4.1.1 Phase I: Start-up the System | 28 |
| 4.1.2 Phase II: Organic Loading Study | 41 |
| 4.1.3 Phase III: Solids Residence Time Study..... | 65 |
| 4.2 (Part-2) Biotreatment of O-cresol Bearing Wastewater..... | 66 |

| | | |
|-------|--|-----|
| 4.2.1 | Phase I: Start-up the System..... | 86 |
| 4.2.2 | Phase II: Organic Loading Study | 99 |
| 4.2.3 | Phase III: Solids Residence Time Study..... | 121 |
| 4.3 | Kinetic Modeling..... | 141 |
| 5. | CONCLUSIONS | 155 |
| | REFERENCES..... | 157 |

LIST OF TABLES

| <i>Table</i> | | <i>Page</i> |
|--------------|---|-------------|
| 3.1 | Waste water characterization | 20 |
| 4.1 | Reactors performance during Phase-I phenol study | 39 |
| 4.2 | Reactors performance during Phase-II phenol study | 42 |
| 4.3 | Reactors performance during Phase-III phenol study | 67 |
| 4.4 | Reactors performance during Phase-I cresol study | 87 |
| 4.5 | Reactors performance during Phase-II cresol study | 100 |
| 4.6 | Reactors performance during Phase-III cresol study | 123 |
| 4.7 | Values of cell concentrations during the kinetic study | 143 |
| 4.8 | Chi-square values | 150 |
| 4.9 | Kinetic coefficients..... | 154 |

LIST OF FIGURES

| <i>Figure</i> | | <i>Page</i> |
|---------------|--|-------------|
| 3.1 | Experimental Set-up | 22 |
| 4.1 | Concentration of MLSS in the SBRs during Phase-I, phenol study | 29 |
| 4.2 | Concentration of MLVSS in the SBRs during Phase-I, phenol study | 30 |
| 4.3 | Influent and effluent phenol concentration during Phase-I, Reactor 1 | 32 |
| 4.4 | Influent and effluent phenol concentration during Phase-I, Reactor 2 | 33 |
| 4.5 | Influent and effluent phenol concentration during Phase-I, Reactor 3 | 34 |
| 4.6 | Influent and effluent phenol concentration during Phase-I, Reactor 4 | 35 |
| 4.7 | Residual phenol concentration | 36 |
| 4.8 | Effluent concentration of TSS in the SBRs during Phase-I, phenol study | 38 |
| 4.9 | Dynamic loading study of phenol | 40 |
| 4.10 | Concentration of MLSS in the SBRs during Phase-II, phenol study | 44 |
| 4.11 | Concentration of MLVSS in the SBRs during Phase-II phenol study | 45 |
| 4.12 | Influent and effluent phenol concentration during Phase-II, Reactor 1 | 48 |
| 4.13 | Influent and effluent phenol concentration during Phase-II, Reactor 2 | 49 |
| 4.14 | Influent and effluent phenol concentration during Phase-II, Reactor 3 | 50 |
| 4.15 | Influent and effluent phenol concentration during Phase-II, Reactor 4 | 51 |

| | | |
|------|--|----|
| 4.16 | Influent and effluent BOD and COD concentrations in Rector 1 during Phase-II, phenol study..... | 53 |
| 4.17 | Influent and effluent BOD and COD concentrations in Rector 2 during Phase-II, phenol study..... | 54 |
| 4.18 | Influent and effluent BOD and COD concentrations in Rector 3 during Phase-II, phenol study..... | 55 |
| 4.19 | Influent and effluent BOD and COD concentrations in Rector 4 during Phase-II, phenol study..... | 56 |
| 4.20 | Effluent concentration of TSS in the SBRs during Phase-II, phenol study | 59 |
| 4.21 | Effluent concentration of VSS in the SBRs during Phase-II, phenol study | 60 |
| 4.22 | Sludge volume index in the SBRs during Phase-II phenol study | 62 |
| 4.23 | Influent and effluent phenol concentration during transient phase..... | 66 |
| 4.24 | Concentration of MLSS in the SBRs during Phase-III, phenol study..... | 69 |
| 4.25 | Concentration of MLVSS in the SBRs during Phase-III, phenol study..... | 70 |
| 4.26 | Influent and effluent phenol concentration during Phase-III , Reactor 1..... | 72 |
| 4.27 | Influent and effluent phenol concentration during Phase-III , Reactor 2..... | 73 |
| 4.28 | Influent and effluent phenol concentration during Phase-III , Reactor 3..... | 74 |
| 4.29 | Influent and effluent BOD and COD concentrations in Rector 1 during Phase-III, phenol study..... | 76 |
| 4.30 | Influent and effluent BOD and COD concentrations in Rector 2 during Phase-III, phenol | |

| | | |
|------|--|-----|
| | study..... | 77 |
| 4.31 | Influent and effluent BOD and COD concentrations in Rector 3 during Phase-III, phenol study..... | 78 |
| 4.32 | Effluent concentration of TSS in the SBRs during Phase-III, phenol study | 81 |
| 4.33 | Effluent concentration of VSS in the SBRs during Phase-III, phenol study | 82 |
| 4.34 | Sludge volume index in the SBRs during Phase-III, phenol study..... | 84 |
| 4.35 | Concentration of MLSS in the SBRs during Phase-I, cresol study..... | 88 |
| 4.36 | Concentration of MLVSS in the SBRs during Phase-I, cresol study..... | 89 |
| 4.37 | Influent and effluent o-cresol concentrations during Phase-I, Reactor 1..... | 91 |
| 4.38 | Influent and effluent o-cresol concentrations during Phase-I, Reactor 2..... | 92 |
| 4.39 | Influent and effluent o-cresol concentrations during Phase-I, Reactor 3..... | 93 |
| 4.40 | Influent and effluent o-cresol concentrations during Phase-I, Reactor 4..... | 94 |
| 4.41 | Residual o-cresol concentration..... | 96 |
| 4.42 | Effluent concentration of TSS in the SBRs during Phase-I, cresol study | 97 |
| 4.43 | Dynamic loading study of cresol..... | 98 |
| 4.44 | Concentration of MLSS in the SBRs during Phase-II, cresol study | 103 |
| 4.45 | Concentration of MLVSS in the SBRs during Phase-II, cresol study | 104 |
| 4.46 | Influent and effluent o-cresol concentration during Phase-II, Reactor 1 | 106 |

| | | |
|------|---|-----|
| 4.47 | Influent and effluent o-cresol concentration during Phase-II, Reactor 2 | 107 |
| 4.48 | Influent and effluent o-cresol concentration during Phase-II, Reactor 3 | 108 |
| 4.49 | Influent and effluent o-cresol concentration during Phase-II, Reactor 4 | 109 |
| 4.50 | Influent and effluent BOD and COD concentrations in Rector 1 during Phase-II, cresol study..... | 111 |
| 4.51 | Influent and effluent BOD and COD concentrations in Rector 2 during Phase-II, cresol study..... | 112 |
| 4.52 | Influent and effluent BOD and COD concentrations in Rector 3 during Phase-II, cresol study..... | 113 |
| 4.53 | Influent and effluent BOD and COD concentrations in Rector 4 during Phase-II, cresol study..... | 114 |
| 4.54 | Effluent concentration of TSS in the SBRs during Phase-II, cresol study..... | 116 |
| 4.55 | Effluent concentration of VSS in the SBRs during Phase-II, cresol study..... | 117 |
| 4.56 | Sludge volume index in the SBRs during Phase-II, cresol study | 119 |
| 4.57 | Influent and effluent o-cresol concentration during transient phase..... | 122 |
| 4.58 | Concentration of MLSS in the SBRs during Phase-III, cresol study | 125 |
| 4.59 | Concentration of MLVSS in the SBRs during Phase-III, cresol study | 126 |
| 4.60 | Influent and effluent o-cresol concentration during Phase-III, Reactor 1..... | 128 |
| 4.61 | Influent and effluent o-cresol concentration during Phase-III, Reactor 2..... | 129 |

| | | |
|------|---|-----|
| 4.62 | Influent and effluent o-cresol concentration during Phase-III, Reactor 3..... | 130 |
| 4.63 | Influent and effluent BOD and COD concentrations in Reactor 1 during Phase-III, cresol study..... | 132 |
| 4.64 | Influent and effluent BOD and COD concentrations in Reactor 2 during Phase-III, cresol study..... | 133 |
| 4.65 | Influent and effluent BOD and COD concentrations in Reactor 3 during Phase-III, cresol study..... | 134 |
| 4.66 | Effluent concentration of TSS in the SBRs during Phase-III, cresol study..... | 136 |
| 4.67 | Effluent concentration of VSS in the SBRs during Phase-III, cresol study..... | 137 |
| 4.68 | Sludge volume index in the SBRs during Phase-III cresol study | 139 |
| 4.69 | Relationship between experimental data and predicted data, Reactor 1 - phenol study | 145 |
| 4.70 | Relationship between experimental data and predicted data, Reactor 2 - phenol study | 146 |
| 4.71 | Relationship between experimental data and predicted data, Reactor 1 - cresol study..... | 147 |
| 4.72 | Relationship between experimental data and predicted data, Reactor 2 - cresol study..... | 148 |
| 4.73 | Determination of y and K_d for phenol..... | 152 |
| 4.74 | Determination of y and K_d for o-cresol..... | 153 |

ABSTRACT

Name: Ibrahim Muhammad Al-Harazin

Title: Biological Treatment of Hazardous Contaminants
in Sequencing Batch Reactor

Major: Civil Engineering

Date: January, 1992.

The effect of organic loading rates and the solids residence time (SRT) on the aerobic treatment of phenol and o-cresol bearing wastewater by sequencing batch reactors (SBRs) was investigated. SBRs were utilized to treat phenol and o-cresol, aerobically at a hydraulic retention time (HRT) of one day and varying SRTs. The reactors achieved over 99.5% removal of phenol and o-cresol at toxicant loading in the ranges of 100-800 kg phenol/m³-day and 100-600 kg cresol/m³-day at SRTs of 10 days and above with the effluent BOD and TSS concentrations consistently about 5 and 12 mg/l, respectively. However, a rapid breakthrough resulting in only 65% removal efficiency of phenolics at loads of 800 kg phenol/m³-day and 600 kg cresol/m³-day occurred at 3 and 5-day for phenol, and o-cresol, respectively, simultaneously with a breakthrough of total suspended solids (TSS). The rapid deterioration in effluent quality ensued toxicant loadings of 0.7 mg phenol/mg MLVSS and 0.8 mg cresol/mg MLVSS. Better than 94% phenol removal efficiency was achievable at the 5-day SRT biotreatment.

ملخص الرسالة

- اسم الطالب : ابراهيم محمد ابراهيم الحرازين .
عنوان الدراسة : المعالجة البيولوجية للمخلفات الخطرة بطريقة الأحواض المتتابعة .
التخصص : هندسة مدنية .
تاريخ الشهادة : يناير ١٩٩٢ م .

لقد تم اجراء دراسة مخبريه لدراسة تأثير الحمولة العضوية وزمن استبقاء الحماء على المعالجة الهوائية للفينول والأرثوكرثول بواسطة الأحواض المتتابعة . هذا وقد استخدمت الأحواض المتتابعة لمعالجة الفينول والأرثوكرثول عند زمن استبقاء يوم واحد وعند زمن استبقاء الحماء متغير . قد ازلت هذه الأحواض ٩٩% من تركيز الفينول والأرثوكرثول حيث كان تركيز الفينول يتراوح بين ١٠٠ إلى ٨٠٠ كغم فينول /م^٣ - يوم وكان تركيز الكرثول يتراوح بين ١٠٠ - ٦٠٠ كغم كرثول /م^٣ - يوم عند زمن استبقاء لحماء مقداره ١٠ أيام وأكثر وكان معدل المتطلبات العضوية للأوكسجين والعوالق الكلية ٥ ر ١٢ ملغم/ل على الترتيب .

أما بالنسبة للأحواض التي شغلت على زمن استبقاء الحماء مقداره ٢ أيام للفينول و ٥ أيام للأرثوكرثول فقد حصل تراجع وظيفي مما أدى إلى هبوط نسبة التنقية إلى ٦٥% من التركيز الأصلي حيث كان تركيز الفينول ٨٠٠ كغم/م^٣ - يوم وتركيز الأرثوكرثول ٦٠٠ كغم/م^٣ - يوم . وجدير بالذكر ان هذا التراجع الوظيفي قد رافقه زيادة في كمية العوالق الكلية . هذا وقد حصل هذا التراجع السريع في نوعية المياه الناتجة عند الأحمال ٧ ملغم فينول / ملغم من العوالق المتطايرة و ٦ ملغم كرثول / ملغم من العوالق المتطايرة .
ولقد كانت نتيجة الحوض الذي استخدم لمعالجة الفينول عند زمن استبقاء الحماء ٥ أيام جيدة . حيث تمكن من ازالة ٩٤% من الفينول .

درجة الماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
الظهران ، المملكة العربية السعودية
التاريخ تموز يوليو ١٩٩١ م

SYMBOLS

| | |
|-----------------|---|
| SRT: | Solids residence time |
| SBR: | Sequencing batch reactor |
| HRT: | Hydraulic retention time |
| MLSS: | Mixed liquor suspended solids |
| MLVSS: | Mixed liquor volatile suspended solids |
| TSS: | Total suspended solids |
| VSS: | Volatile suspended solids |
| COD: | Chemical oxygen demand |
| BOD: | Biochemical oxygen demand |
| TKN: | Total Kjeldahl nitrogen |
| Total-p: | Total phosphorous |

Chapter 1

INTRODUCTION

The generation of hazardous wastes is widespread in today's world and Saudi Arabia is no exception. Oil refineries and petrochemical industries which represent the backbone of the Kingdom's flourishing economy, produce wastes that contain a wide variety of phenolic compounds that are extremely toxic and potentially carcinogenic. The dependence of Saudi Arabia on non-renewable water sources such as ground water aquifers, and the growing industrialization particularly in the areas of petroleum refining and petrochemicals processing mandates the proper treatment, handling and disposal of complex toxic wastes generated by such industries.

Traditionally toxic industrial wastes were not treated but simply stored in landfills or applied to soil. It is only recently that the consequences of such unwise practices have become tangible. The pollution of ground water bodies beneath or in the neighborhood of the dumping sites is a critical problem of disastrous dimensions in countries with dwindling non-replenishable water supplies.

Recently, in response to voiced public concern, the removal of hazardous contaminants from wastewaters has been the

focus of numerous researches world wide. The treatment of toxic compounds has been accomplished by physical/chemical processes, such as ozonation, carbon adsorption, solvent extraction...etc. as well as biological processes such as activated sludge systems, aerated lagoons, and tricking filters.

Biological treatment of hazardous waste offers unique and extremely diverse opportunities for the cleanup of contaminated environments, because the results of treatment are usually innocuous materials such as biological cell mass and carbon dioxide, thus eliminating potential latent liability of the treated waste [1]. The SBR is one of several innovative and alternative biological waste treatment systems that have been evaluated by the U.S. Environmental Protection Agency (U.S.EPA) [1]. The EPA demonstration study showed that the SBR is an excellent alternative for municipal wastewater treatment [2]. The SBR process was selected for investigation as the method of biological treatment because the process has been successfully applied at many locations for hazardous waste treatment [3], and the process in many cases offers the advantages of better stability and greater operational flexibility and control compared with continuous flow process [4].

In the light of the aforementioned discussion, the main objective of this research was to study the continuous degradation of phenol and ortho-cresol bearing wastewater by aerobic organisms

in sequencing batch reactors. These compounds were selected because they are priority pollutants commonly present in industrial wastewaters generated by coal and petroleum distillation process and petrochemical process. Consequently, they are excellent representative of hazardous pollutants generated by the flourishing petrochemical industries in the Kingdom.

The principal objectives of this study were:

- 1) to demonstrate that sequencing batch reactors could be readily and rapidly started without seeding and to determine the highest organic loading which can be treated effectively without inhibition;
- 2) to assess the impact of organic loading rate on the treatment efficiency under constant solids residence time (SRT);
- 3) to determine the effect of biological solids residence time on the removal efficiency.

This research was divided basically into two parts: biotreatment of phenol bearing wastewater and biotreatment of ortho-cresol bearing wastewater. Each part included three phases namely; start-up of the system, an organic loading study, and a biological solids residence time study.

Chapter 2

LITERATURE REVIEW

2.1 PHYSICO-CHEMICAL TREATMENT OF HAZARDOUS WASTE

- Coagulation and Flocculation

Ng et al. [5] evaluated cationic polymers, lime and alum for destabilizing effluent suspensions from palm oil mills. Cationic polymers were judged to be the most effective based on cost, ease of use and settleability. Bershad Koya et al. [6] achieved 99% removal of oil from oil/wastewater emulsions by coagulation with cationic surfactants such as quaternary ammonia salts. Removal of toxic pollutants from industrial laundry wastewater using high dosages of inorganic coagulants was researched by Van Gils and Pirbazari [7] and found to be effective.

VanSon [8] investigated the development and use of synthetic organic flocculants as replacements for inorganic flocculants such as alum in industrial wastewater treatment and found to be very effective.

- Precipitation

The lime softening process is widely employed for the

removal of hardness from water supplies and for treatment of municipal and industrial discharges containing suspended solids, metal ions, phosphate and other contaminants. Although this process has been found to remove certain organic contaminants, the types of organic contaminants amenable to treatment and the factors influencing their removal have not been clearly elucidated. The removal of organic contaminants by lime softening and the molecular characteristics influencing removal were experimentally and theoretically examined by Liao and Randtke [9]. Polyvinyl alcohol (PVA) was effectively removed from wastewaters using precipitation with magnesium carbonate (Mg_2CO_3), optimum removal of PVA was obtained at a Mg_2CO_3 : PVA ratio of 1:1 and at a temperature of 0-5°C [10]. However, such treatment methods are expensive and sometimes not effective.

- Oxidative Processes

Ozone has been proposed as an oxidizing agent for phenols, cyanides and unsaturated organics [11-16]. Neigowski [11] studied the oxidation of phenol with ozone and found that at a pH of 12.0 the oxidation was virtually complete. This value is close to the optimum value of 11.4 given by Anon [12]. Eisenhauer [13] found that the pH of the wastewater decreased as the reaction proceeded. He also concluded that the phenol removal was directly

proportional to the flow rate, the concentration of ozone, the detention time and inversely proportional to the gas bubble size. In another study by Eisenhauer [14] higher temperatures were found to favor the oxidation of phenols. Thiocyanates and cyanides were found to be effectively oxidized in the wastewater containing phenols [15].

Kwie [16] evaluated ozone treatment of three water streams from a synthetic polymer plant containing high concentrations of unsaturated organics. As much as 90% COD removal was observed in the case of a waste containing unsaturated hydrocarbons at an optimal pH of 12.6 [17]. The oxidation of organic matter with ozone, in terms of TOC reduction from a petroleum refinery wastewater was studied by Schwartz et al. [18]. They found a reduction of 5.5, 10.4 and 20.4 percent for ozone dosage of 26, 60, and 159 mg/l respectively. The initial TOC in all cases were 81.5 mg/l. Buys and Reynolds [19] studied oxidation of phenol-bearing wastewaters using H_2O_2 produced by electro reduction of O_2 dissolved in wastewater.

Gurol and Vatistas [20] compared oxidation of phenols by ozone, ultraviolet radiation and ozone/UV combination and found that the removal rate of phenol and TOC was highest for O_3 /UV and lowest for UV alone. Gamma radiation coupled with ozonation performed better than chlorination followed by radiation in

degrading pollutants from dyeing and washing wastewaters [21]. Ozonation was favored over chlorination because chlorinated EPA priority pollutant by-products were not formed [22]. Even though, strong oxidizing agents such as ozone have been proven effective in organic oxidation, oxidation process are energy intensive and highly costly [23].

- Reverse Osmosis

The first practical application of reverse osmosis membrane technology was in the early 1960's with the desalination of sea water [24]. By 1983, commercial membranes had been developed for separation of organics, including carboxylic acids, phenols, and carbohydrates, etc. [25]. It was demonstrated that the effectiveness of separation depended on a variety of factors, the principal one being the molecular size of the rejected compounds. The molecular weight cut-off point for membranes developed until then was about 100-110.

Improvements in materials since 1983 have led to membranes with enhanced ionic rejection properties. Acceptable rejection of organic species with molecular weights of about 50 can now be achieved successfully [24].

With the growing interest in the application of reverse osmosis for industrial wastewater treatment and for water

reclamation and recycling, it is important that data should be available on the rejection of phenol by membranes and on factors affecting rejection. Different studies have shown phenol to be so poorly rejected by cellulose acetate membranes that in some cases it even permeated membranes preferentially to water [26]. Matsuura and Sourirajan [27] found rejections of +1% and -2% respectively for two cellulose acetate membranes at 1700 KPa and 25°C. They also studied the removal of a series of alcohols and concluded that alcohols are separated better than phenol. Matsuura et al [28] studied also the separation of phenols by aromatic polyamide membranes and concluded that the positive separation of polyamide membranes is due to the preferential sorption of solute at the membrane-solution interface caused by both the non-polar character of the membrane and the acidity of the solute. In a study on the rejection of a group of low molecular mass organics by five different membranes, Chian and Fang [29] found different patterns of removal of organics by cellulose acetate and by polyamide membranes. For the group of organics in general and phenol in particular they found very good removal by the polyamide membranes and relatively poor removal by the cellulose acetate membranes. Johnson [30] used different membrane models to determine the intrinsic membrane rejection factors R_{max} for different solutes. Nakagowa et al. [31] reported on the rejection of organics by composite PEC 1000 membrane, in which the active

membrane layer is prepared from cross-linked polyether. This membrane has excellent rejection properties with respect to dissolved organics, e.g. rejection factor for ethanol, acetic acid and phenol were 97%, 86% and 99%, respectively, at 5600 Kpa and 25°C. Schutte and Belfort [26] compared the phenol rejection of two commercially available membranes. They found that phenol were effectively rejected by the FT.30 membrane (>90%) while the SEPA 99 cellulose acetate membrane has virtually achieved no phenol rejection.

- *Ion Exchange*

Himmelstein et al. [32] proposed two methods for phenol treatment, that is, the reactive regeneration with sodium hydroxide and the solvent regeneration. As the concentration of phenols increased, solvent and reactive regeneration systems became more economical than thermal regeneration.

Phenol is a weak acid and can be removed effectively from aqueous solution by anion-exchange resins [33]. Although the regeneration was complete for weak base anion-exchange resins (the adsorption capacity of phenol was incomplete for strong ones the capacity was high). Synthetic resins without ion-exchange functional group such as Amberlite XAD resins [34] and the vinylpyridine-divinylbenzen copolymer have also been used for the

removal of phenols. The regeneration was complete, but the capacity was rather low. Goto et al. [35] compared the adsorption equilibria of phenol on anion-exchange resin in the chloride form. For strong base anion-exchange resins, there was a great difference in the amount of phenol adsorbed between hydroxide and chloride forms. Phenol adsorbed on resins in the hydroxide form could be desorbed by using hydrochloric acid. Goto et al [36] studied the extent of adsorption and desorption of phenolic compounds on anion-exchange resins and activated carbon and investigated two methods of regeneration of adsorbents. They found that the regeneration by sodium hydroxide or hydrochloric acid might be possible for anion-exchange resin. Both methods were effectively performed. In case of activated carbon, the regeneration by sodium hydroxide was possible. However, phenol adsorbed was not desorbed completely.

- Adsorption

The application of carbon adsorption in petrochemical industry can be at two points in the process train. It can be used as a tertiary treatment step to remove refractory compounds before or after conventional biological systems. Ford [37] evaluated the applicability at both points. The results of the study were based on the treatability studies conducted by the author at eight refineries and petrochemical installations. The data tabulated from

the study indicated that the BOD for effluents of activated sludge treatment, total carbon treatment, and combined activated sludge/carbon treatment was found to be in the range of 20-50 mg/l, 40-100 mg/l and 5-30 mg/l, respectively. The influent BOD ranged from 250 to 350 mg/l. These values show that the removal efficiency of activated sludge treatment for biodegradable organics (measured by the BOD test) is better than that of the carbon treatment.

Ford and Buercklim [38] also discussed the applicability of activated carbon at the two points. Based on the extensive experimental work undertaken by them at a pilot-scale system for the treatment of refinery and petrochemical wastewaters, they suggested pilot scale studies for evaluating the application of activated carbon for a particular application.

In order to establish the feasibility of using activated carbon as an advanced treatment process for petrochemical wastewaters, pilot scale experimental work using both Granular Activated Carbon (GAC) and Powdered Activated Carbon (PAC) was undertaken by Guarino et al. [39]. The results showed that GAC system was far superior to the PAC system. The study also found out a considerable reduction in the concentration of heavy metals and priority pollutants was also realized.

Walter and Weber [40] reported that adsorption is neither

perfect technology nor an infallible process. There are mainly two areas of challenge of the adsorption: (1) the adsorption behavior of complex mixtures of organic compounds typically found in waters and wastewaters, (2) the role of biological transformation in adsorption systems.

Although some of the results of the fore-mentioned studies indicated that significant reduction in phenol content is achievable with physiochemical processes, the high cost associated with these process renders them uneconomical for raw wastewater treatment and more appropriate for effluent polishing.

Additionally, physical processes such as carbon adsorption and solvent extraction do not destroy the hazardous pollutants, but merely concentrate them in smaller volumes which in turn have to be dealt with as hazardous matter. Fortunately, this shortcoming is non-existent in biological processes as they destroy the toxic pollutant. Consequently biological processes have attracted a lot of interest as an alternative to physiochemical processes in the field of hazardous waste treatment.

2.2 BIOLOGICAL TREATMENT OF HAZARDOUS WASTE

The treatment of phenol-bearing wastewaters has been accomplished traditionally by aerobic biological processes such as the extended aeration activated sludge process and oxidation

lagoons. Coe [41] reported up to 90% BOD and phenol removal during the treatment of a petrochemical wastewater. Huber [42] achieved effluent phenol concentration as low as 0.1 mg/l for acetylene and ethylene wastes.

Sack and Bokey [43] achieved over 90% removal of BOD in two reactors treating a coal gasification wastewater at hydraulic retention times of 4 and 6 days. Ganczarczyk and Elion [44] used extended aeration in the treatment of a coke plant effluent at detention times of 13.8 and 24 hours, and achieved over 99% phenol removal. Luthy, et al [45] observed over 99% phenol removal efficiencies during the treatment of 33% strength coal distillation wastewater in four reactors operating at hydraulic retention times of 9 to 18 hours.

Despite the excellent removal of phenolics, these processes generally require long aeration times and are energy intensive. Furthermore, some major pollutants have been reported to escape treatment [43].

More recently, Healey and Young [46] demonstrated the anaerobic degradation of phenol and catechol. Further work elucidated the mechanisms and pathways of the anaerobic biodegradation of alkyl phenols [47] and chlorinated phenols [48]. The anaerobic degradation of phenolics to methane was confirmed in continuous flow attached growth [49, 50, 51, 52] systems known as

anaerobic reactors. The amenability of hazardous wastes generated during coal and petroleum distillation to anaerobic treatment was demonstrated by Suidan et al [53], Suidan and Nakhla [54] and Nakhla et al [55]. The reactors used in the continuous processing of such toxic wastes employed activated carbon as an attachment media for bacteria films that degrade some of the constituents of the waste and an adsorbent to control the toxicity of the remaining constituents of the wastes. Partial replacement of the reactor medium with virgin GAC on a regular basis was necessary for continuous operation.

Evidently, the operational cost of such units is not insignificant. Despite the several advantages offered by anaerobic treatment over aerobic treatment such as low sludge production, no oxygen requirements and production of methane, the sensitivity of anaerobic cultures to toxicants and the long adaptation time has limited their applicability in the areas of toxic waste treatment and hazardous waste sites remediation. More recent research has focused on the adaptation and acclimatization of aerobic organisms to degrade the toxic components of the waste that not only resist biodegradation but also inhibit the utilization of readily biodegradable waste constituents by unacclimated microbial populations.

Halogenated aromatic hydrocarbons [56], substituted benzenes [57], halogenated aliphatic compounds [58], polychlorinated

biphenyls [54] have been shown to biodegrade aerobically.

These recent advances in microbiology have found immediate applications in the clean-up of hazardous waste sites, a problem which has challenged engineers and scientists for several decades. Biological detoxification of hazardous wastes, despite being in its infancy, has been established as an efficient, cost-effective approach to resolving one of our most challenging ever-increasing environmental problems.

2.3 SEQUENCING BATCH REACTOR

Biological wastewater treatment can be carried out in continuous flow systems as well as batch semi-batch process. Although, continuous flow systems such as activated sludge and aerated lagoons have dominated the field of wastewater treatment, these processes are prone to occasional upsets due to fluctuations in waste strength and flow rates. In addition to having a kinetic advantage over completely-mixed systems, batch processes never operate under steady state conditions and are thereby more suited to handle fluctuations than continuous systems. These dynamic characteristics of batch process enhance their applicability to industrial waste treatment where waste fluctuations are frequent. Additionally, due to recent technological advances in process control, batch processes can be readily automated resulting in

substantial savings in operating costs.

The sequencing batch reactor (SBR) is the most commonly used batch system in wastewater treatment. The SBR process is a batch biological process characterized by periodic filling and decanting of reaction basin and separation of the biological solids from the treated effluent in the same reaction basins rather than in separate sedimentation basins. The advantage of the SBR process lies in the ability to periodically change the environmental conditions in the reaction basins in a very controlled manner and thereby select and enrich a microbial population with desired specific metabolic capacities and setting characteristics.

The SBR is one of several innovative and alternative biological waste treatment systems that have been evaluated by the U.S. Environmental Protection Agency (EPA) [1]. The EPA demonstration study showed that the SBR is an excellent alternative for municipal wastewater treatment [2]. In addition, results from bench-scale studies indicated that the SBR can provide substantial savings in energy and costs by removing organic compounds found in hazardous wastes biologically rather than with activated carbon [59]. Irvine et al [2] concluded that the SBR is a viable alternative to conventional continuous flow activated sludge treatment of domestic wastewaters for BOD and SS removals, nitrification, denitrification and biological phosphorous removal. Hsu [60] showed that the performance of SBR's during

the treatment of a petrochemical waste is slightly superior to the performance of the conventional activated sludge. In general, SBR systems have been reported by Arora et al. [61] to possess several advantages such as flow equalization, ideal settling, simple operation compact layout, and costs savings, over conventional activated sludge systems.

The ability of the SBR to effectively provide nitrification [62, 63], denitrification [63, 64], and biological phosphorous removal [65, 66], is noteworthy. More recently, the SBR was demonstrated to successfully treat municipal wastewaters, [67, 68], industrial wastes [69]; hazardous wastes [70] and toxic landfill leachate [71]. Herzbrun et al. [3] investigated the treatability phenolic waste using SBR. They reported that TOC degradation ranged from 55 to 81% and phenol degradation ranged from 96.8 to 99.2% during retention times that varied from 10 days down to 1.25 days. Smith and Wilder [4] studied the biodegradability of synthetic leachate in a SBR and reported that over 90% reductions in COD, TOC and TOX and complete nitrification were achievable with two-stage SBR. Oleszkiewicz et al. [72] treated wastewater in laboratory SBR operated in different combination of streams of industrial wastes, anaerobically pretreated wastes and raw sewage. They found that all reactors yielded good BOD, COD removals and the denitrification was inversely proportional to the strength of the influent. Misbahuddin [73] investigated the treatment of

petrochemical wastewater from Jubail using SBR. The value of effluent BOD was 5 mg/l as compared to the influent BOD of 69 mg/l. The wastewater was pretreated in flowmeter/clarifier using lime ferric chloride and polyelectrolyte solutions.

The SBR systems which were used for different purposes were traditionally seeded with activated sludge from other activated sludge system. Hsu [60] seeded his SBR systems with biological waste to study the treatment of petrochemical waste. Oleszkowitz et al. [72] used activated sludge as a seed for a SBR to study the treatment of food industry wastewater. Abu Fayed et al. [74] used activated sludge to study the denitrification in SBR and Jones et al. [75] seeded his SBR systems for nitrogen removal. However, in some areas such as unsewered remote villages, military installations and isolated industries, activated sludge may not be readily procurable. Additionally, seeding SBR's with activated sludge to ultimately treat toxic wastes, may prolong the growth of microbial populations that specifically degrade the toxicants. Moreover, in case of seeding, the reactor microbial activity is not truly reflected by the concentration of volatile suspended solids and consequently the kinetics of the system will not be assessed with reasonable accuracy. The growth of a culture that is specific to the toxicants is not only desirable from the standpoint of treatment efficiency, but also necessary to safeguard against shock loading.

Most researchers have reported the degradation of up to 500 mg/l of phenol. Herzburn et al [59] reported that 570 mg/l of phenol was degraded in SBR with a hydraulic retention (HRT) of 5 to 9 days. Hsu [60] reported the biodegradation of a wastewater containing up to 950 mg/l of phenol in a SBR operated at an HRT of 2 days. It is evident therefore, that dilutions to phenol concentrations of about 500 mg/l at the start of the SBR cycle were often necessary to preclude inhibition and accomplish successful treatment.

Chapter 3

MATERIALS AND METHODS

3.1 SOURCE OF WASTEWATER

The wastewater used for the present study was raw sewage obtained from North Aramco Wastewater Treatment Plant in the Eastern Province of Saudi Arabia. The characterization of wastewater is shown in Table 3.1:

Table 3.1: Wastewater Characterization

| Determination | Average Con- centration | Range |
|-------------------|----------------------------|-----------|
| pH | 6.7 | 6.1-7.1 |
| TSS (mg/l) | 156 | 130- 185 |
| VSS (mg/l) | 118 | 105- 135 |
| COD (mg/l) | 88 | 70- 108 |
| BOD (mg/l) | 65 | 55- 82 |
| Chloride (mg/l) | 1364 | 1294-1412 |
| Alkalinity (mg/l) | 277 | 252- 285 |
| TKN (mg/l) | 31 | 24- 36 |
| Total-P. (mg/l) | 8 | 7- 10 |

The wastewater was collected (twice a week) and was stored in the refrigerator prior to use, to retard biological activity.

3.2 EXPERIMENTAL SET-UP

The experimental set-up for SBR as shown in Fig. 3.1, consists mainly of four reactors (SBR-1, SBR-2, SBR-3 and SBR-4), mounted on a wooden bench. Each of the reactors was constructed of 3/4 inches thick and 3.5 inches internal diameter plexiglass tube. Each reactor was 10 inches high resulting in a total volumetric capacity of 1.5 liters. Air was supplied through medium porosity diffusers fixed at the bottom of each reactor to ensure the dissolved oxygen concentration was maintained above 2 mg/l. Four small motors manufactured by Dayton Elec. Mfg. (Chicago, IL., U.S.A.) and operated on 110V AC supply with a speed of 120 rpm were mounted on the top of each reactor to provide sufficient mixing

3.3 EXPERIMENTAL PROCEDURES

The experimental program was divided into two parts: biotreatment of phenol bearing wastewater, and biotreatment of O-cresol bearing wastewater.

A. PART I: BIOTREATMENT OF PHENOL BEARING WASTEWATER

This part consisted mainly of three phases namely; start-up of culture, organic loading study, and solids residence study.

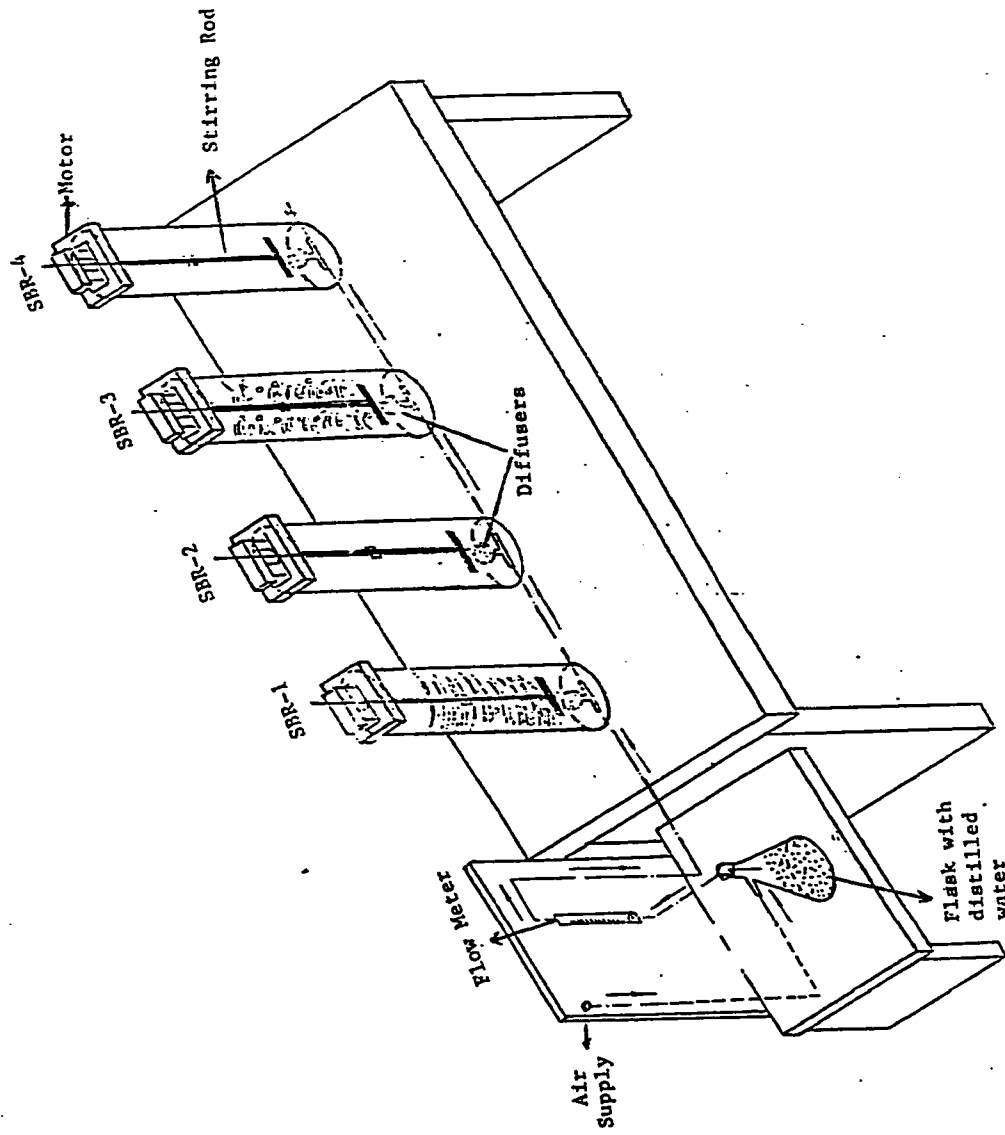


Fig. 3.1: Experimental Set-up

Start-up of the System

In this phase, the reactors were started without seeding for the aforementioned reasons. The four reactors were daily fed with 1.2 liter of phenol augmented raw sewage at pH of 7.0. The operating strategies for the four reactors were the same, i.e. 22 hours react period and 2 hours settle and draw periods. The react period was terminated by shutting off the air supply and the mixers. The microorganisms were then allowed to settle for 2 hours by gravity. Clarified supernatant was removed by suction. The operation normally required 20 minutes. It must be noted that the volume of sludge retained after suction was never in excess of 100 ml, and consequently the effective hydraulic retention time of the waste was 1.1 days. The initial organic loading rates of phenol that were applied during the first 3 weeks of the study were 50 mg/l, 100 mg/l, 200 mg/l and 400 mg/l, respectively. To speed the building up of mixed liquor volatile suspended solids (MLVSS), two cycles per day were employed between days 20 and 32 of this study. However, at the absence of any signs of inhibition, these concentrations were doubled after one month of commissioning the study.

The response of the SBR to a shock load of phenol was determined at the end of this study. The effect of shock loading was carried on SBR-4, since it treated the highest concentration by increasing the influent phenol concentration to a very high

level and subsequently reducing it in a stepwise fashion. This method was preferred to a gradual increase in the influent phenol concentration to insure better simulation of real life conditions where high loads of toxicants are suddenly applied to treatment process and to safeguard against possible adaptation if the load increments were not substantial.

The analysis carried out during this study were daily measurements of the effluent and influent concentrations of phenol using a spectrophotometer (Bausch-Lomb Model UV-D) at a wave length of 270 nm, mixed liquor total and volatile suspended solids (MLSS and MLVSS) and effluent total suspended solids (TSS), three times a week following the procedure described by Standard Methods [76].

Organic Loading Study

This study was initiated about 45 days after the start-up for SBR-1, SBR-2 and SBR-3 and 60 days for SBR-4 to study the effect of constant solids residence time (SRT) on different organic loading for the reactors. The experimental procedures for this study was the same as for the start-up phase except for the sludge wastage. The biological SRT in this study was kept constant at 14 days by wasting by suction 85 ml of mixed liquor from the reactors at the end of the react period. The organic loading rates of phenol employed in this phase were the highest

loadings sustained during the start-up phase, i.e. 100 mg/l, 200 mg/l, 400 mg/l and 800 mg/l, for SBR-1, SBR-2, SBR-3 and SBR-4, respectively. All the reactors were operated for three turnovers of mean SRT.

Measurements for influent and effluent chemical oxygen demand (COD), the 5-day biochemical oxygen demand (BOD) (every three days), concentration of phenol (daily), MLSS, MLVSS, TSS and VSS (every two days) were conducted to check for steadiness of the data. When pseudo-steady state was attained, measurement for the prementioned parameters were continued in addition to weekly measurements of TKN, total phosphorous, chloride, alkalinity and sulfate. All of these tests except the measurement of phenol were conducted according to Standard Methods [76].

Solids Residence Time Study

This study was initiated about 3 months after the start-up for all the reactors. During this study the highest loading rate of the organic pollutants achieved in the previous study was kept constant in all the reactors and the SRT varied. To avoid inhibition the phenol concentration was stepped gradually to 800 mg/l. According to the results of the previous study for SBR-4, which was operated on highest organic loading rate and SRT of 14 days, the SRT chosen for the investigation varied between 3 and

10 days. Every reactor was operated for three turnovers of mean SRT.

The analytical techniques were exactly the same as for the organic loading phase.

B. PART II: BIOTREATMENT OF O-CRESOL BEARING WASTEWATER

This part consisted mainly of three phases namely; start-up of culture, organic loading study, and solids residence study.

Start-up of the System

In this phase, the reactors were started with approximately 500 mg/l of MLSS brought from the reactors treating the phenol waste. The o-cresol concentrations for first week were 25 mg/l, 50 mg/l, 75 mg/l and 100 mg/l for SBR-1, SBR-2, SBR-3 and SBR-4, respectively and then they were doubled depending on the reactors performance. The concentrations of o-cresol at end of this phase were 100 mg/l, 200 mg/l, 300 mg/l and 600 mg/l for SBR-1, SBR-2, SBR-3 and SBR-4, respectively.

The shock loading study of o-cresol was also conducted at the end of this phase on SBR-4 since it treated the highest concentration. In this study the influent o-cresol concentration was increased incrementally by 50 mg/l of o-cresol until the

effluent o-cresol exceeded 2 mg/l of o-cresol.

Organic Loading Study

This study was initiated after one month of phase I. The organic loading rates of o-cresol were same as in phase I. The SRT was kept constant at 14 days. The experimental procedures were exactly the same as for phase II of the phenol study.

Solids Residence Time Study

In this phase the o-cresol concentration was kept constant at 600 mg/l in all the reactors and the SRT was varied between 5 and 20 days. The experimental procedures were identical to those of phase III of the phenol study.

Chapter 4

RESULTS AND DISCUSSION

4.1 Part-I: Biotreatment of Phenol Bearing Wastewater

4.1.1 Phase-1: Startup of the System

The performance of the SBR's during this phase as reflected by the concentration of mixed liquor in the reactor, the effluent phenol and suspended solids concentration was evaluated. Figures 4.1 and 4.2 show the build up of mixed liquor total and volatile suspended solids respectively, during the startup phase in which no sludge was wasted. It is worth noting that all four units were started without seeding and therefore the initial concentration of suspended solids in each of the four reactors was essentially that of raw sewage. All four units exhibited the same tendency of a steady increase in mixed liquor suspended solids until day 22, followed by a steep ascent after the employment of two cycles per day until day 33. After that one cycle was employed and the phenol concentration was doubled until the end of this phase. The concentration of MLVSS in the SBR's behaved as expected, i.e. SBR's with higher concentration of phenol resulted in higher levels of MLVSS. For example, the MLVSS in SBR-4 which treated 800 mg/l of phenol was about three times that in SBR-1 which treated 100 mg/l of phenol. As anticipated, the reactors mixed liquor

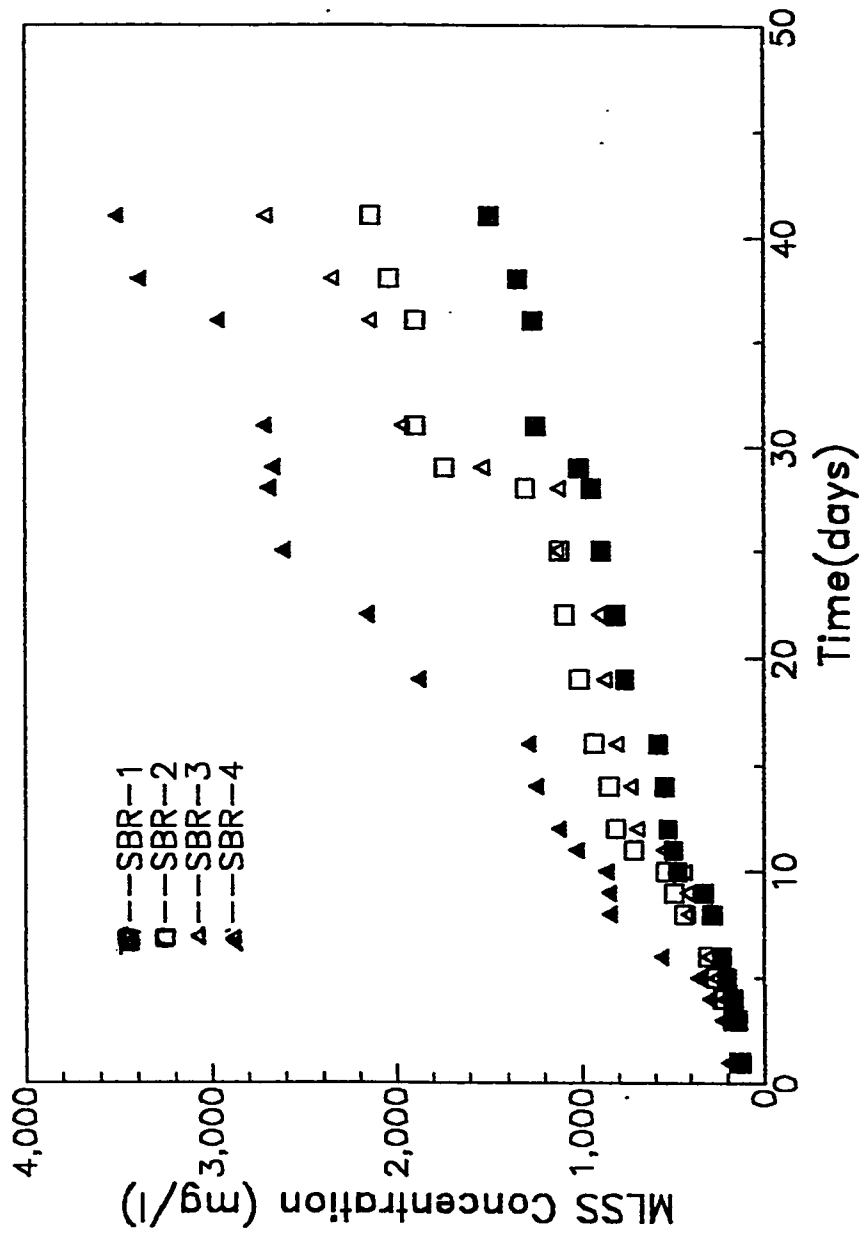


Fig. 4.1 Concentration of MLSS In The SBRs During Phase-I, Phenol Study

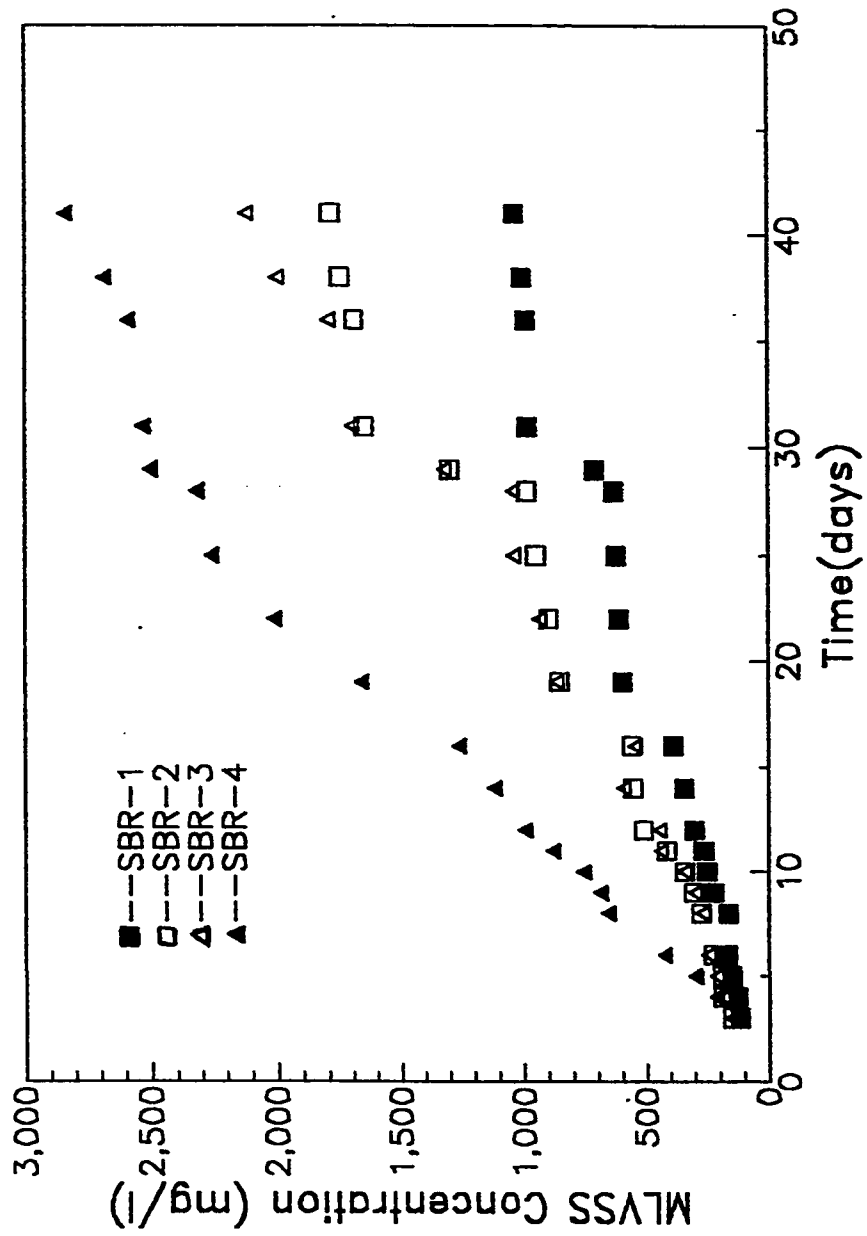


Fig. 4.2 Concentration of MLVSS In The SBRs During Phase-I, Phenol Study

concentration build-up data shown in Figures 4.1 and 4.2 clearly emphasizes the rapid and steady growth of the raw sewage culture on phenol and preclude any inhibitory effects of phenol at concentration as high as 800 mg/l.

Figures 4.3, 4.4, 4.5 and 4.6 show the temporal profile of the concentrations of phenol in the influent wastewater and the effluents from reactors 1, 2, 3 and 4 respectively. Figures 4.3 and 4.4 indicate that the effluent phenol concentrations from SBR-1 and SBR-2 decreased very rapidly from about 7 mg/l to 0.5 mg/l in the first few days of the build up phase. However, as apparent from Figures 4.5 and 4.6, the effluent phenol concentrations from SBR-3 and SBR-4 were consistently higher than 10 mg/l during the first 10 days of operation before subsequently dropping to 0.5 mg/l by the end of the first three weeks. It must be emphasized that the removal of phenol was merely due to biogradation and no evidence of phenol volatility was observed. Figure 4.7 shows the initial and residual concentrations of phenol in an identical SBR to the reactors but treating a phenol solution at neutral pH. It is evident from Figure 4.7 that no significant drop in phenol concentration was observed after 24 hours of aeration. As depicted in Figures 4.5 and 4.6, phenol removal efficiencies as high as >99% that were achieved in the reactors in less than 3 weeks after commissioning of the study, were sustained thereafter.

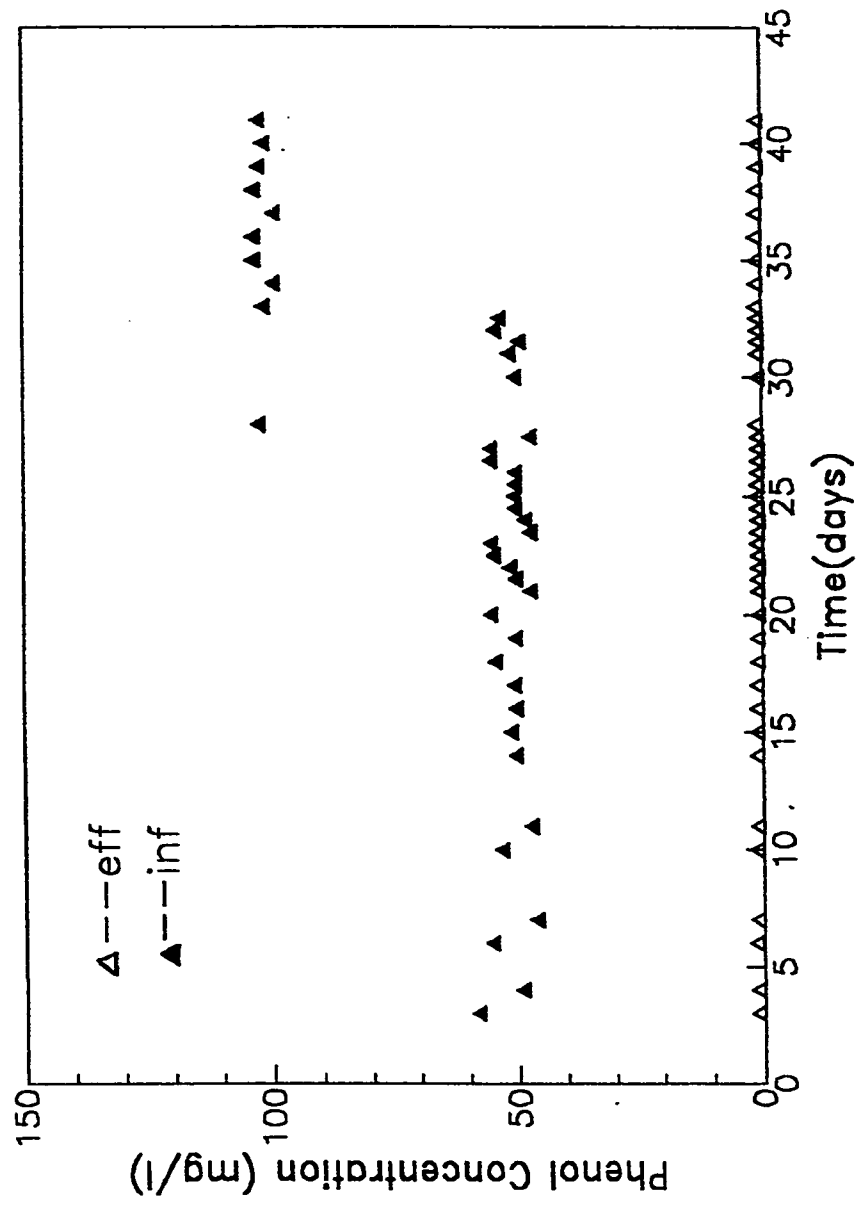


Fig. 4.3 Influent and Effluent Phenol Concentration During Phase-I, Reactor 1

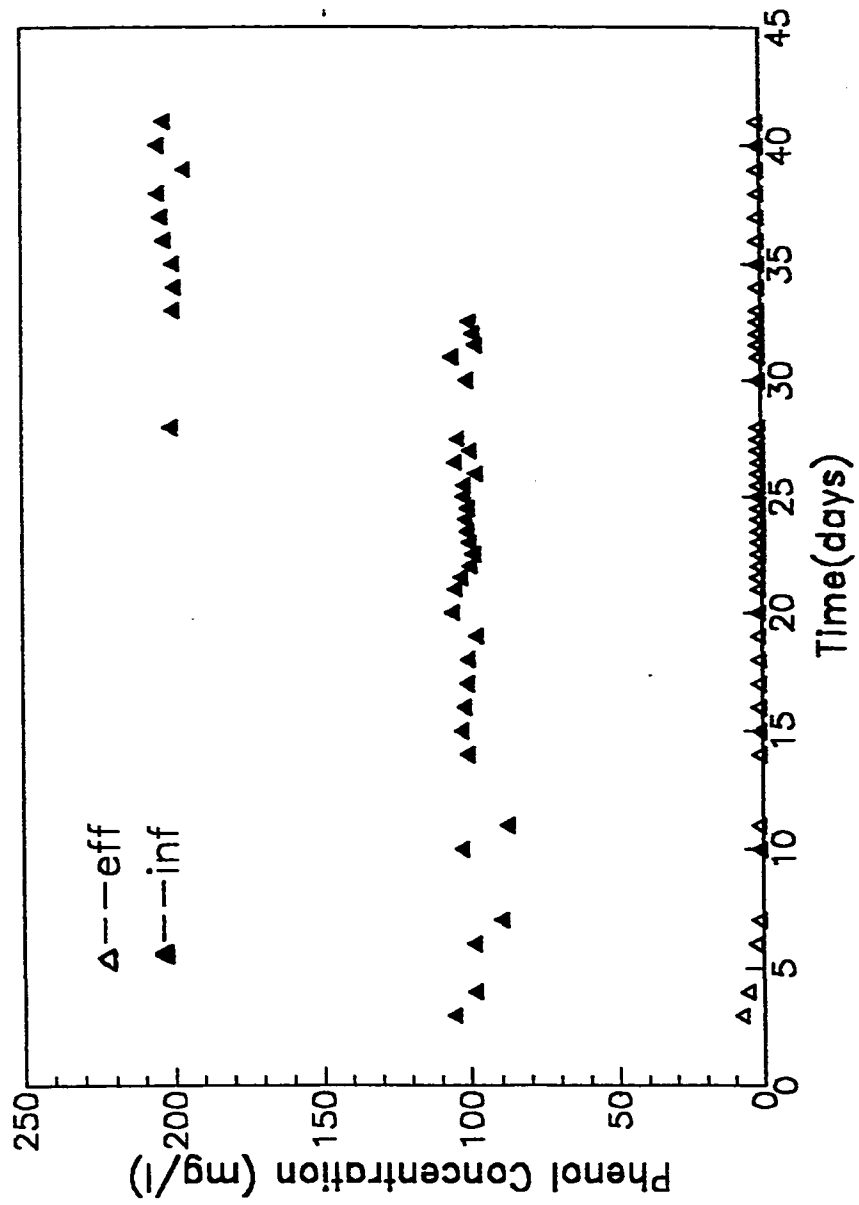


Fig. 4.4 Influent and Effluent Phenol Concentration During Phase-I, Reactor 2

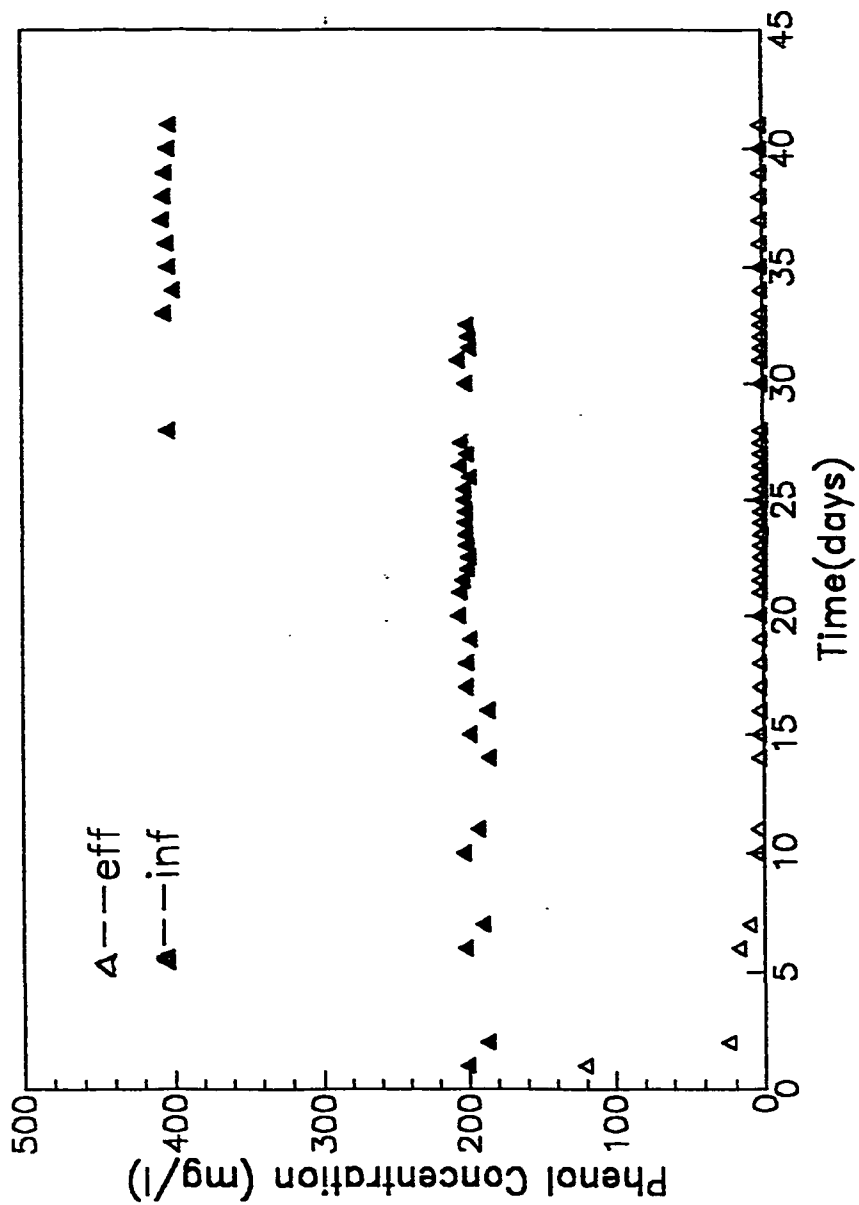


Fig. 4.5 Influent and Effluent Phenol Concentration During Phase-I, Reactor 3

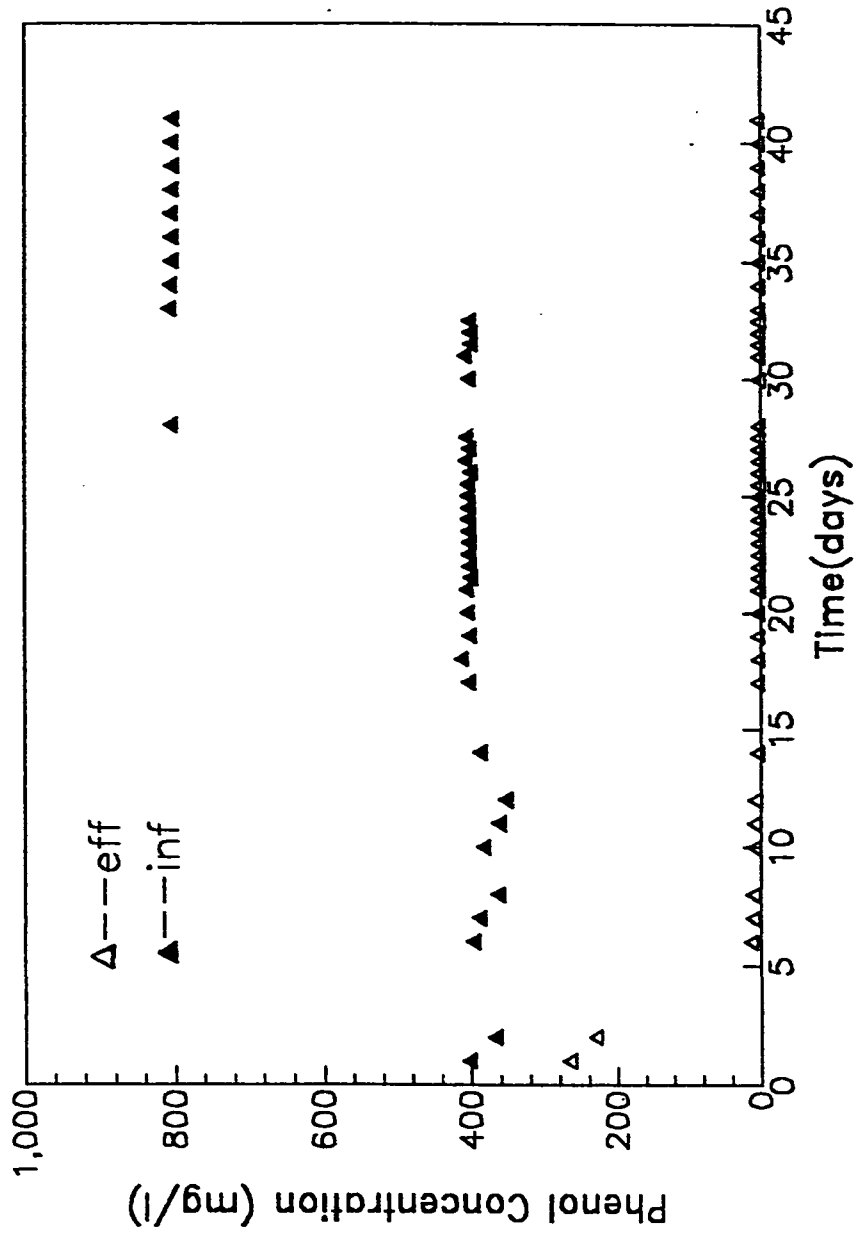


Fig. 4.6 Influent and Effluent Phenol Concentration During Phase-I, Reactor 4

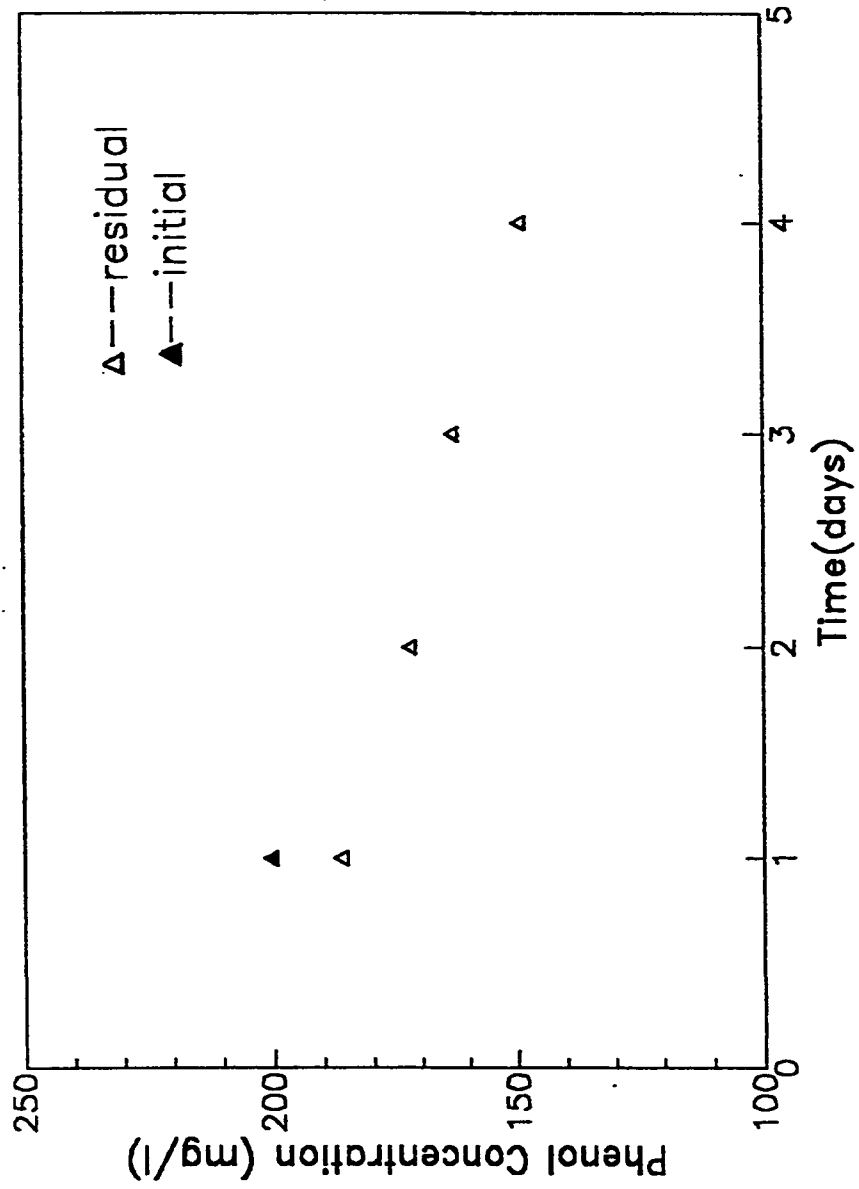


Fig. 4.7 Residual Phenol Concentration

The concentration of effluent suspended solids is a significant water quality parameter that is often stipulated in the disposal criteria set up by regulatory agencies. Consequently, the effect of toxicants such as phenol on the settleability of the sludge is of paramount importance from the application viewpoint. Figure 4.8 shows the diurnal variation in effluent suspended solids exhibited by the four reactors. The concentration of effluent suspended solids from the sequencing batch reactors decreased continuously throughout the acclimatization phase from as high as 130 mg/l at the start of the study to about 14 mg/l on day 33. It is apparent that the feed phenol concentration did not have any adverse impact on the effluent suspended solids and the settleability of the sludge. The results of this phase are summarized in Table 4.1.

The response of SBR-4 to a shock loading is shown in Figure 4.9 when the influent phenol concentration was increased suddenly from 800 to 1600 mg/l, the effluent phenol concentration was about 400 mg/l, which means that 75% removal of phenol was accomplished when a shock loading of 1600 mg/l was applied. The influent concentration was reduced to 400 mg/l to avoid further inhibition and subsequent culture mortality and then stepped up gradually to reach the highest concentration of 800 mg/l that the SBR can successfully treat without exceeding an effluent concentration of 0.5 mg/l.

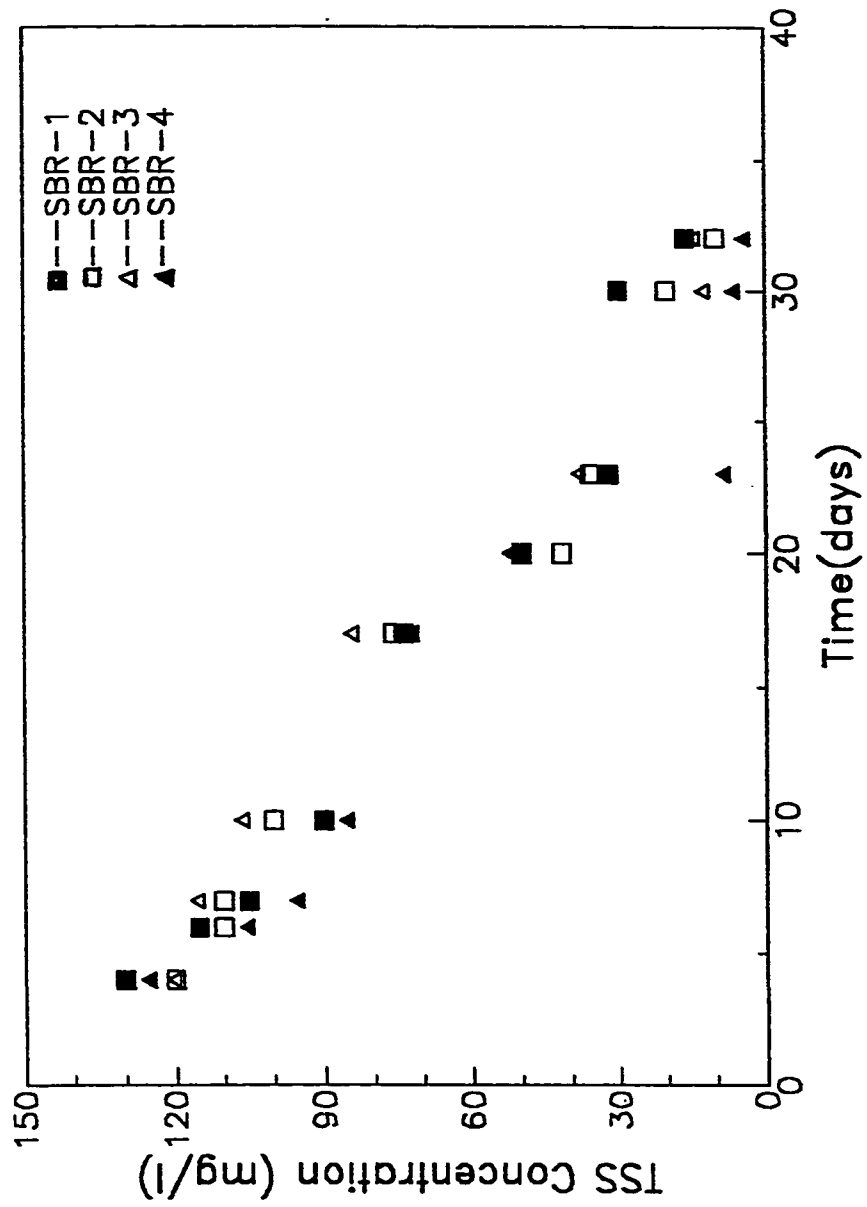


Fig. 4.8 Effluent Concentration of TSS In The SBRs During Phase-I, Phenol Study

Table 4.1: Reactors Performance During Phase I - Phenol Study

| Reactor | SBR-1 | SBR-2 | SBR-3 | SBR-4 |
|---------------------------------|-----------|-----------|-----------|-----------|
| Influent phenol Conc. (mg/l) | 61.9(42)* | 123.8(42) | 247.8(42) | 495.2(42) |
| S.D.** | 21.6 | 43.1 | 86.1 | 169.1 |
| Effluent phenol Conc. (mg/l) | 0.7(42) | 0.8(42) | 4.1(42) | 11.7(42) |
| S.D. | 0.6 | 0.8 | 18.60 | 47 |
| MLSS (mg/l) | 661(21) | 955(21) | 975(21) | 1581(21) |
| S.D. | 431 | 654 | 762 | 1103 |
| MLVSS (mg/l) | 536(20) | 714(20) | 760(20) | 1341(20) |
| S.D. | 349 | 490 | 594 | 937 |
| Influent TSS(mg/l) | 162(4) | 162(4) | 162(4) | 162(4) |
| S.D. | 10 | 10 | 10 | 10 |
| Effluent TSS(mg/l) | 61(9) | 60(9) | 63(9) | 59(9) |
| S.D. | 42 | 43 | 45 | 43 |

*Parenthesis indicate the number of samples

**Standard deviation

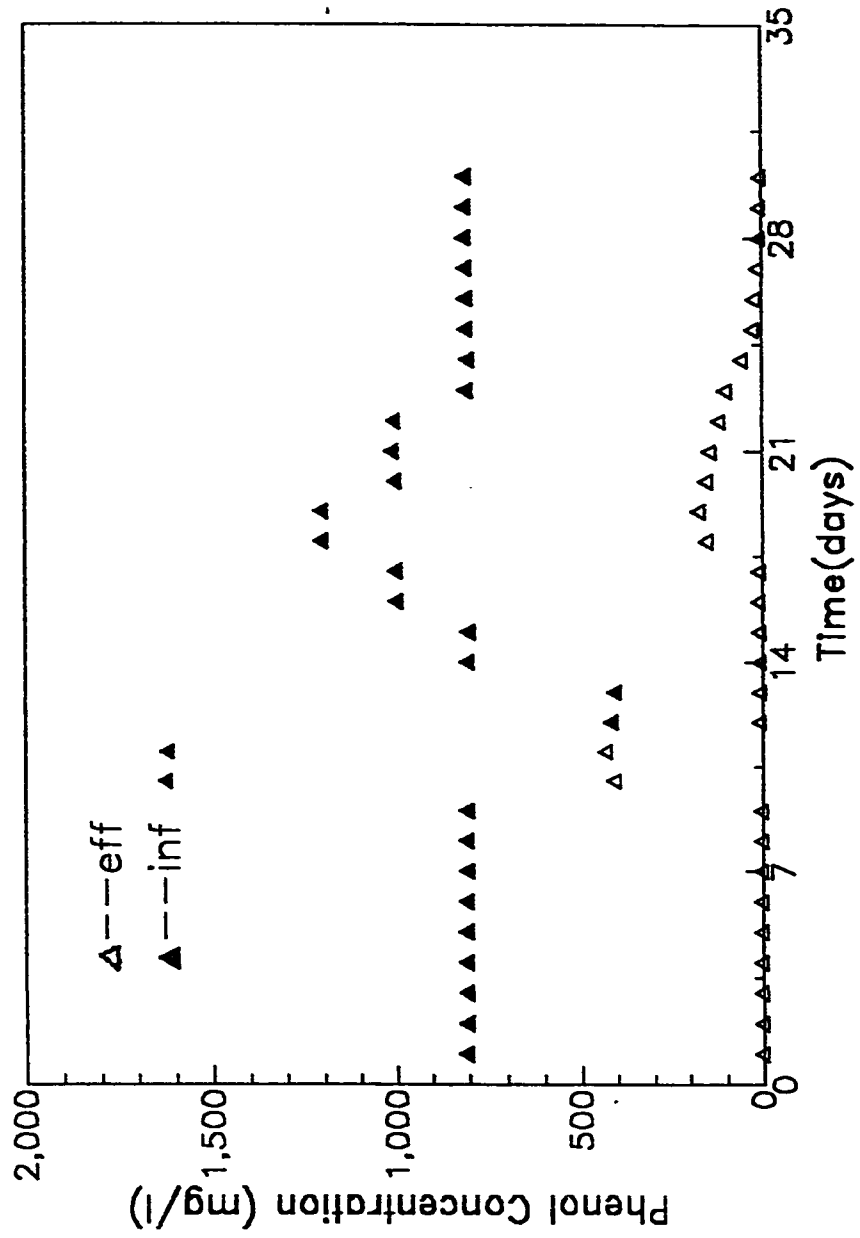


Fig. 4.9 Dynamic Loading Study Of Phenol

4.1.2 Phase II. Organic Loading Study

In this phase, the reactors were operated under a constant SRT of 14 days and different organic loading rates. The organic loading rates selected for the purpose of this study were 100, 200, 400 and 800 mg phenol/L-day for reactors 1, 2, 3 and 4, respectively. This phase was carried out to investigate the effect of different organic loading rates at constant SRT and subsequently to choose the highest concentration of phenol that can be treated successfully. Table 4.2 gives a summary of the results during this phase. The summary includes the average values of the influent and effluent concentrations of phenol, TSS, VSS, BOD, COD, total-phosphorous, TKN, alkalinity and chloride in addition to the MLSS, MLVSS and SVI. The reported values in the table are the averages taken over a period of one and half month except for the MLSS and MLVSS which were averaged over the third turnover of the SRT which was 15 days.

MLSS

The concentration of the MLSS and MLVSS in all the four reactors decreased with time as shown in Figures 4.10 and 4.11 respectively. The MLSS decreased from 1490 to 1054 mg/l in SBR-1, from 2136 to 1276 mg/l in SBR-2, from 2732 to 1708 mg/l in SBR-3 and from 3040 to 2068 in SBR-4. This decrease was merely due to the sludge wastage. Furthermore, due to the batch nature

Table 4.2: Reactors Performance During Phase II - Phenol Study

| Reactor | SBR-1 | SBR-2 | SBR-3 | SBR-4 |
|---------------------------------|------------|----------|----------|----------|
| Influent phenol Conc. (mg/l) | 103.2(44)* | 204(44) | 403(44) | 804(44) |
| S.D.** | 4 | 5 | 6 | 7 |
| Effluent phenol Conc (mg/l) | 0.5(44) | 0.55(44) | 0.5(44) | 0.6(44) |
| S.D. | 0.05 | 0.06 | 0.06 | 0.07 |
| MLSS (mg/l) | 1066(6) | 1288(6) | 1756(6) | 2133(6) |
| S.D. | 9 | 13 | 42 | 46 |
| MLVSS (mg/l) | 850(6) | 1070(6) | 1405(6) | 1760(7) |
| S.D. | 9 | 13 | 34 | 51 |
| Influent TSS(mg/l) | 170(3) | 170(3) | 170(3) | 170(3) |
| S.D. | 7 | 7 | 7 | 7 |
| Effluent TSS(mg/l) | 9.8(19) | 9.4(19) | 9(19) | 12.6(19) |
| S.D. | 3.3 | 3.1 | 345 | 5.4 |
| Influent VSS(mg/l) | 125(3) | 125(3) | 125(3) | 123(3) |
| S.D. | 3 | 3 | 3 | 3 |
| Effluent VSS(mg/l) | 9.1(19) | 8.5(19) | 8.1(19) | 12.1(19) |
| S.D. | 2.8 | 2.5 | 2.3 | 3.3 |
| Influent BOD(mg/l) | 225(19) | 400(19) | 725(19) | 1383(19) |
| S.D. | 18 | 15 | 12 | 14 |
| Effluent BOD(mg/l) | 4.9(19) | 4.7(19) | 4.6(19) | 4.9(19) |
| S.D. | 0.4 | 0.5 | 0.5 | 0.6 |
| Influent COD(mg/l) | 320(15) | 564(15) | 1024(15) | 1990(15) |
| S.D. | 16 | 17 | 13 | 15 |
| Effluent COD(mg/l) | 42(15) | 41(15) | 43(15) | 47(15) |
| S.D. | 8 | 7 | 7 | 10 |
| SVI (ml/g) | 58(11) | 63(11) | 70(11) | 123(10) |
| S.D. | 3 | 8 | 6 | 37 |

| Reactor | SBR-1 | SBR-2 | SBR-3 | SBR-4 |
|---------------------------------------|---------------|----------------|----------------|----------------|
| Influent total-p (mg/l) S.D. | 8(2) 0.5 | 8(2) 0.5 | 8(2) 0.5 | 8(2) 0.5 |
| Effluent total-p(mg/l) S.D. | 6.1(2) 0.3 | 6.5(2) 0.6 | 5.9(2) 0.8 | 5.7(2) 0.7 |
| Influent TKN(mg/l) S.D. | 31(2) 2 | 31(2) 2 | 31(2) 2 | 31(2) 2 |
| Effluent TKN(mg/l) S.D. | 16.1(2) 1 | 16.1(2) 0.8 | 15.8(2) 0.6 | 13.2(2) 0.6 |
| Influent alkalinity (mg/l) S.D. | 265(2) 5 | 265(2) 5 | 265(2) 5 | 265(2) 5 |
| Effluent alkalinity (mg/l) S.D. | 172(2) 4 | 168(2) 5 | 164(2) 3 | 160(2) 3 |
| Influent chloride(mg/l) S.D. | 1364(2) 10 | 1364(2) 10 | 1364(2) 10 | 1364(2) 10 |
| Effluent chloride(mg/l) S.D. | 1364(2) 14 | 1351(2) 8 | 1311(2) 8 | 1285(2) 6 |

*Parenthesis indicate the number of samples

**Standard deviation

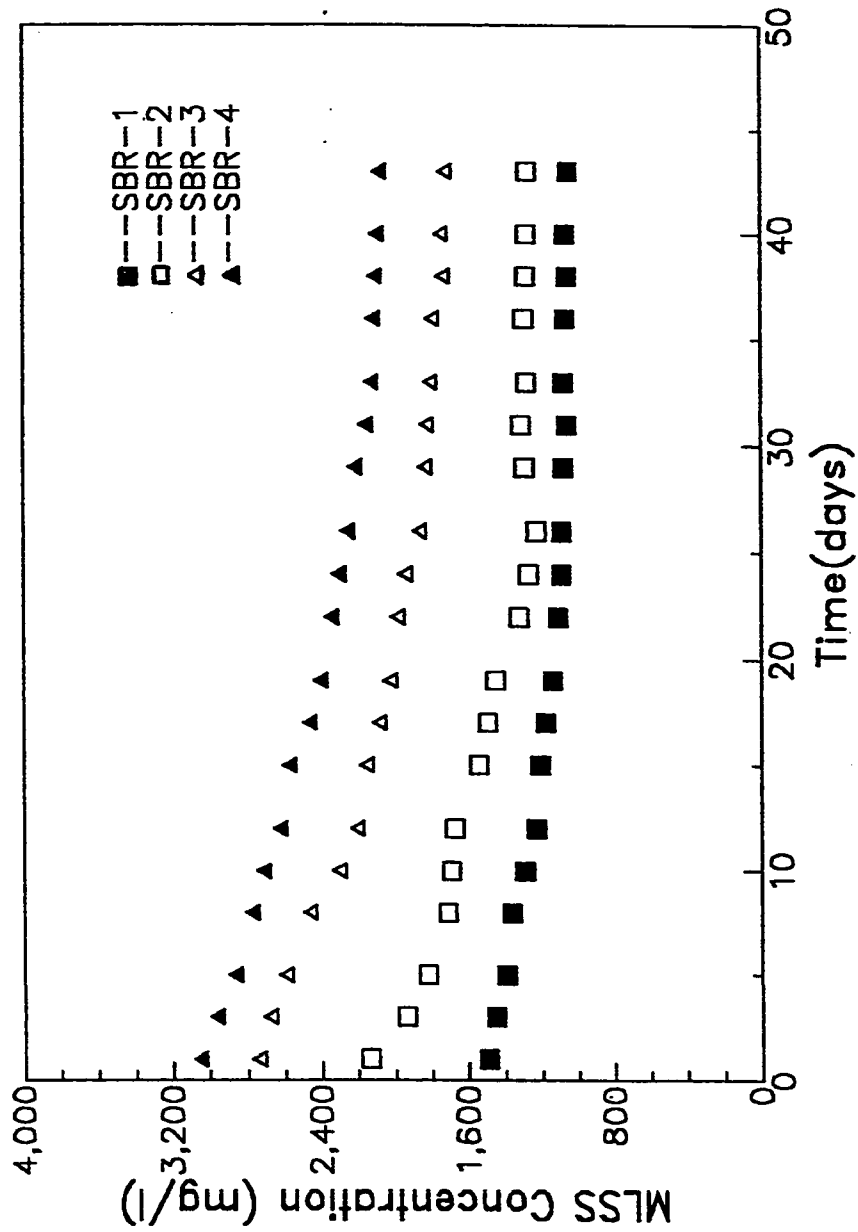


Fig. 4.10 Concentration of MLSS In The SBRs During Phase-II, Phenol Study

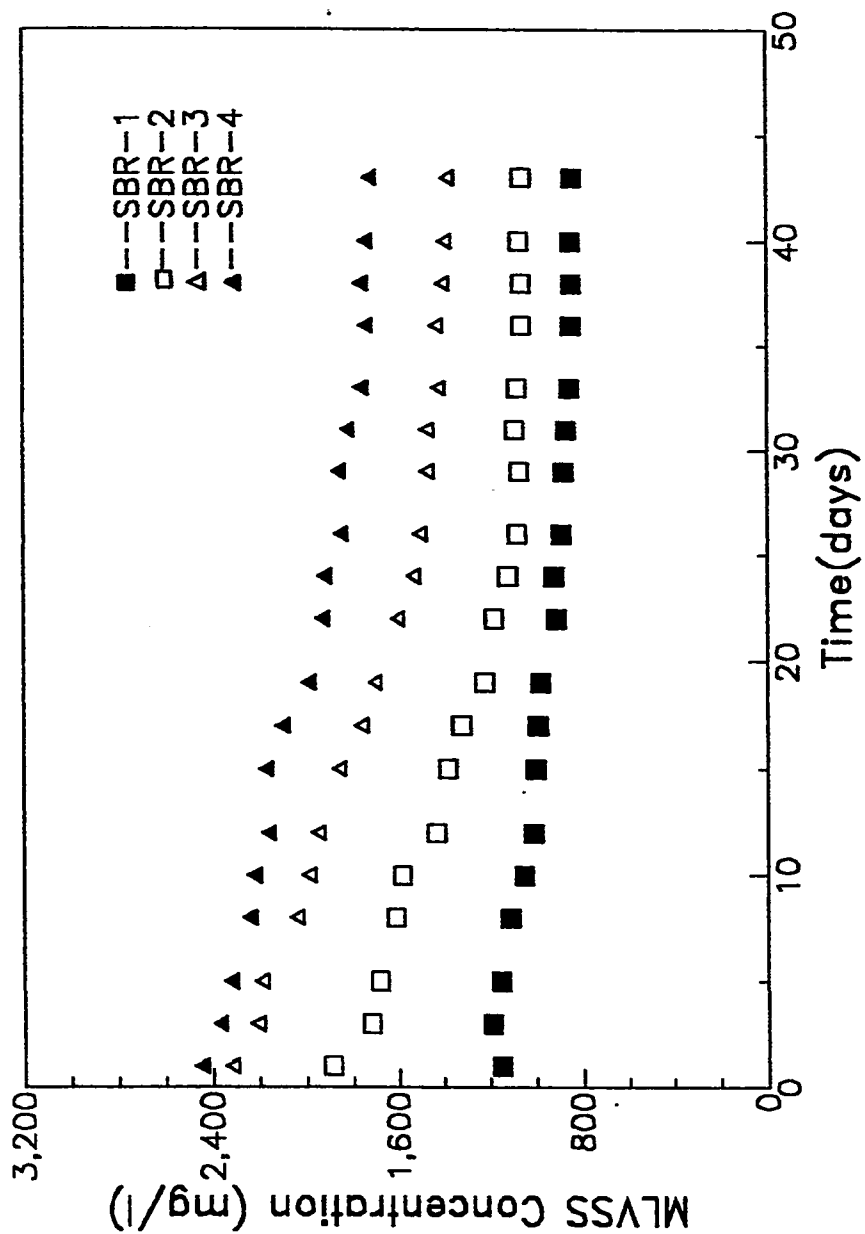


Fig. 4.11 Concentration of MLVSS In The SBRs During Phase-II, Phenol Study

of SBRs, as the MLSS and MLVSS concentrations did not remain constant during the course of an operating cycle [60]. It is apparent from Figures 4.10 and 4.11 that the MLSS and MLVSS of the four reactors depicted the same trend of a rapid decrease in the first turnover followed by a milder drop during the course of the second and third turnover. This could be due to the transient condition in the beginning of this phase, in which the loss of the MLSS and MLVSS wastage was greater than the buildup. With time equilibrium was reached which makes end of the phase. It can be seen from Figures 4.10 and 4.11 that the rate of MLSS and MLVSS decrease was greater in the reactors that treated higher concentration of phenol, i.e. the lowest rate of biomass loss was encountered in SBR-1, which treated 100 mg/l, of phenol, and the highest rate was encountered in SBR-4, which treated 800 mg/l of phenol. Since the desired SRT was achieved by disposing of the necessary volume of the reactor contents at the end of the aeration period, the rate of loss of mixed liquor solids increased with increasing mixed liquor concentrations. Consequently, after the first turnover, the rate of biomass loss continued to subside until it stabilized towards the end of the third turnover. The average values of the food to microorganism (F/M) ratio during the third turnover of SRT were 0.12, 0.19, 0.29 and 0.46 $\frac{\text{mg/l of phenol}}{\text{mg/l of MLVSS}}$ for reactors, 1, 2, 3 and 4, respectively. It must also be emphasized that the high ratios of F/M prevalent during the third

turnover did not impair performance or adversely affect the quality of the effluent.

Effluent phenol

Figures 4.12, 4.13, 4.14, and 4.15 show the temporal profile of the concentrations of phenol in the influent wastewater and the effluents from reactor 1, 2, 3 and 4, respectively. As apparent from these four figures, the influent concentration of the phenol fluctuated for all the reactors. This is due to the manual operation and the presence of some aromatic organic compounds in the raw sewage that contributed absorbance at the wave length at which the phenol was measured. It can be seen from Table 4.2 that the standard deviation of the effluent concentration of the phenol for all the reactors was less than 0.1 mg/l. This indicates that not only were the effluent concentrations of the phenol from all the reactors less 1 mg/l, but they exhibited very little variability. It is also clear from Table 4.2 that the percentage removal of phenol in all the reactors was reactors was > 99%. This indicates that phenol can be treated effectively at mean SRT of 14 days and at concentration as high as 800 mg/l.

The treatment efficiencies of SBRs in this phase were compared to the removal efficiencies of other biological systems dealing with hazardous wastes. Herzburn (70) attained 96.8% removal of phenol using SBRs. The MLSS concentration was 6900

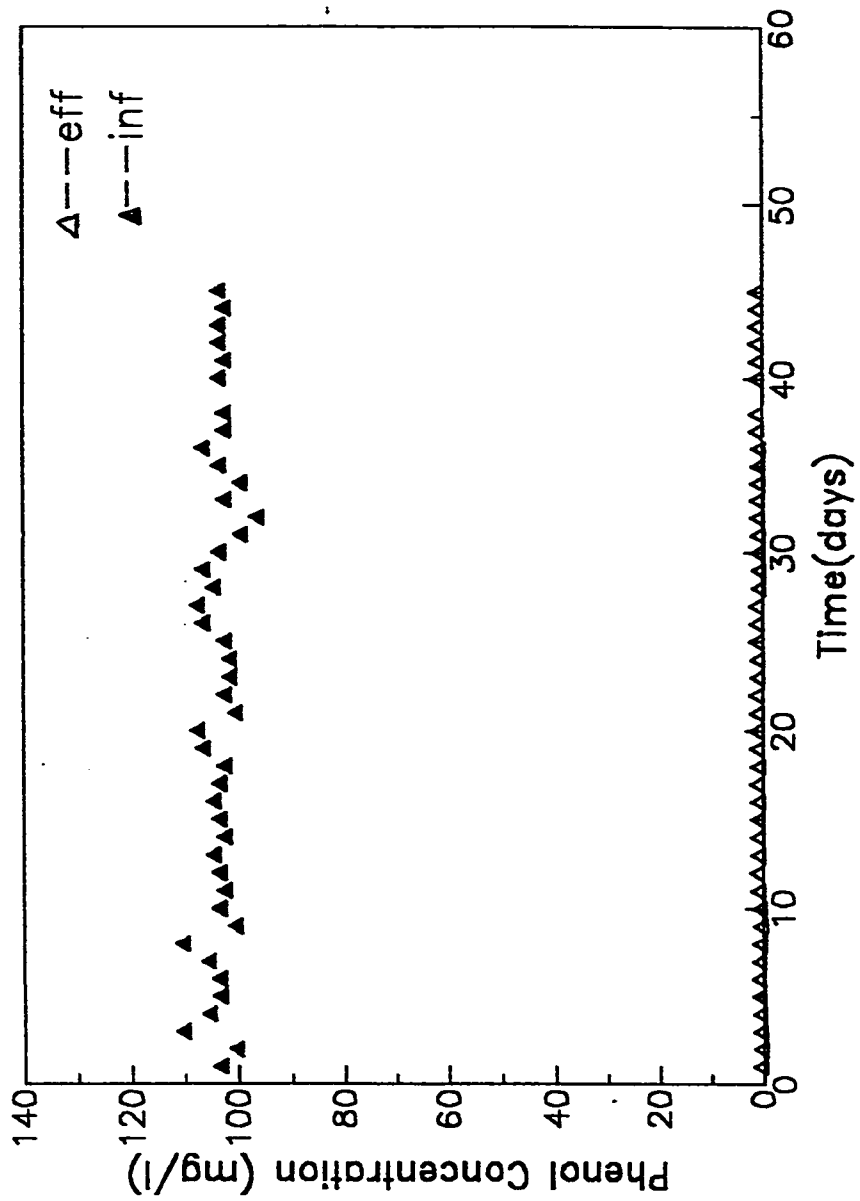


Fig. 4.12 Influent and Effluent Phenol Concentration During Phase-II, Reactor 1

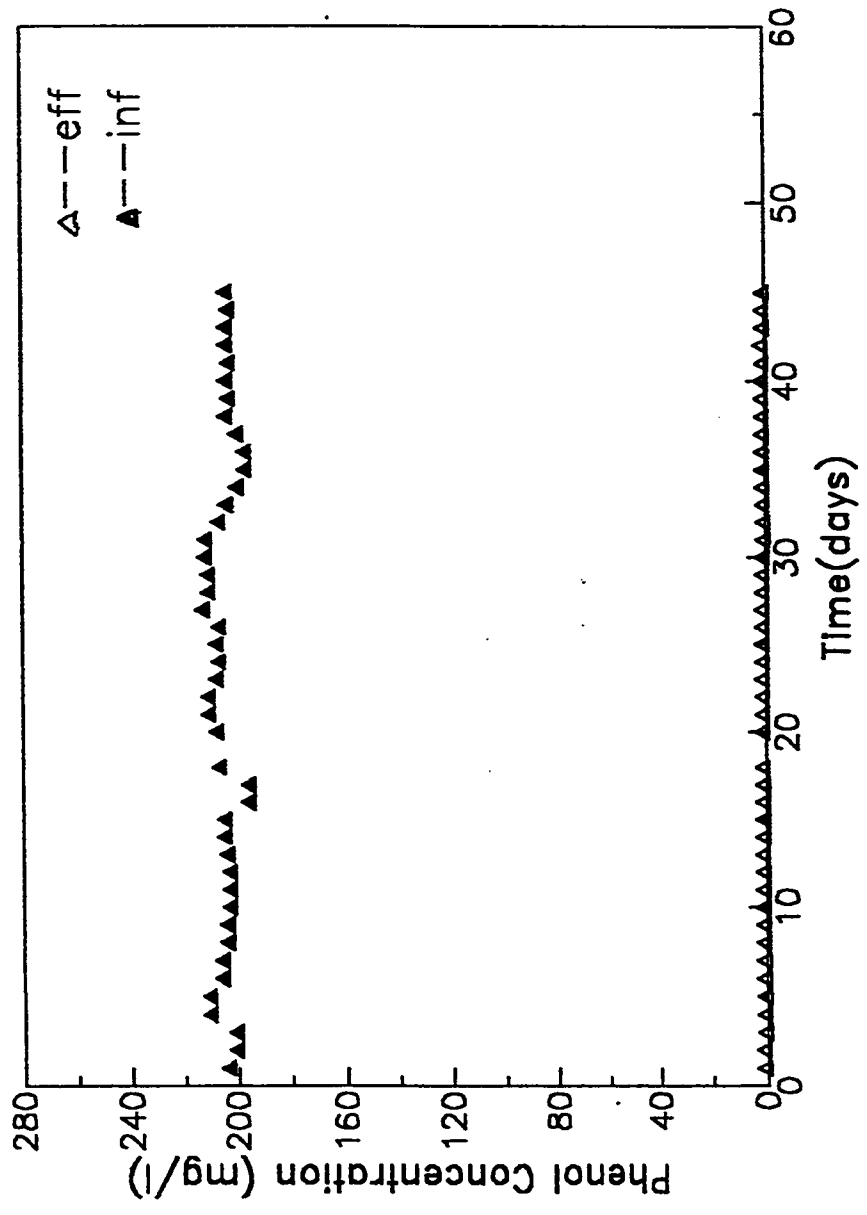


Fig. 4.13 Influent and Effluent Phenol Concentration During Phase-II, Reactor 2

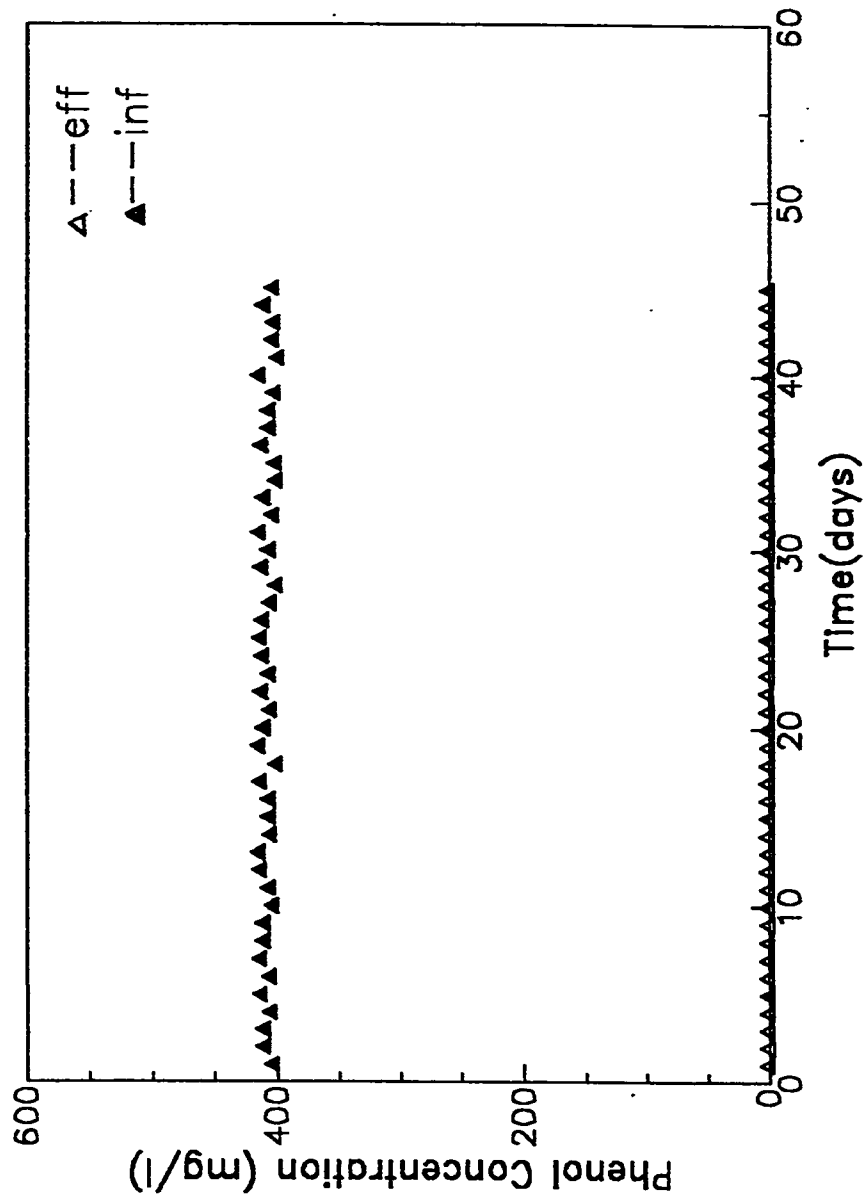


Fig. 4.14 Influent and Effluent Phenol Concentration During Phase-II, Reactor 3

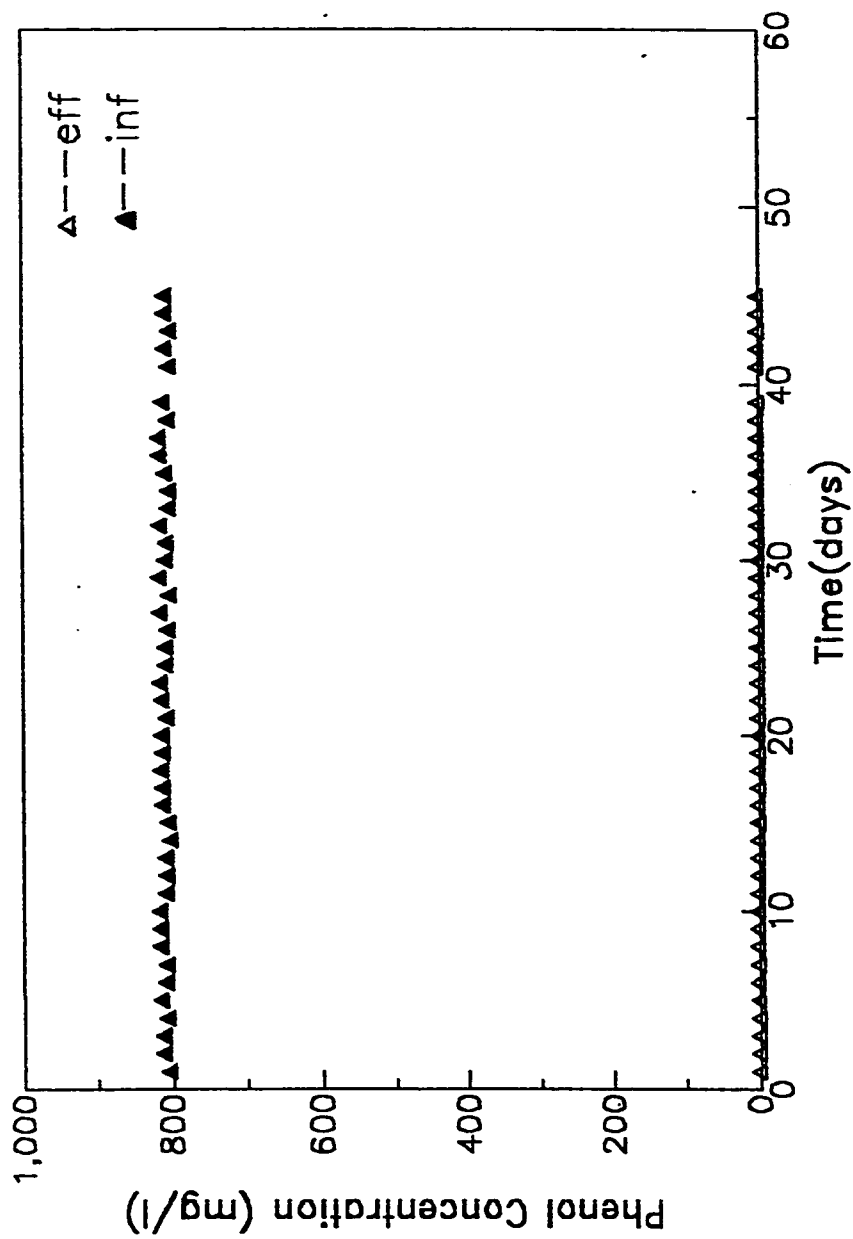


Fig. 4.15 Influent and Effluent Phenol Concentration During Phase-II, Reactor 4

mg/l and there was no sludge wastage. the operating strategies were 10 hours fill and react periods, 1 hour settle period and 1 hour draw period and the HRT was 1.25 day. Drinkwater (77) attained 86.4% removal of phenol using activated sludge system. The MLSS concentration was maintained close to 3790 mg/l by wasting necessary amount of the mixed liquor. The aeration time of the reactor was 20 hours. It is evident from this comparison that our system achieved higher removal efficiencies at lower level of the mixed liquor concentrations. This may be attributed to the startup procedure wherein the reactors were not seeded with any sludge but rather slowly allowed to buildup the mixed liquor using the microbial solids present in the raw sewage, thus enriching the phenolic compounds degrading microbes.

Effluent BOD and COD

The influent and effluent BOD and COD for reactors 1, 2, 3 and 4 are shown in Figures 4.16, 4.17, 4.18 and 4.19, respectively. As apparent from these four figures the influents concentration of COD and BOD fluctuated slightly for all the reactors. This is due to the manual operation and due to the biological activity even though the wastewater was stored in the refrigerator. It can be seen from Table 4.2 that the concentrations of the effluent BOD from all the reactors, which averaged around 5 mg/l, were quite consistent as reflected by the standard deviations which were less than 1 mg/l. Additionally the

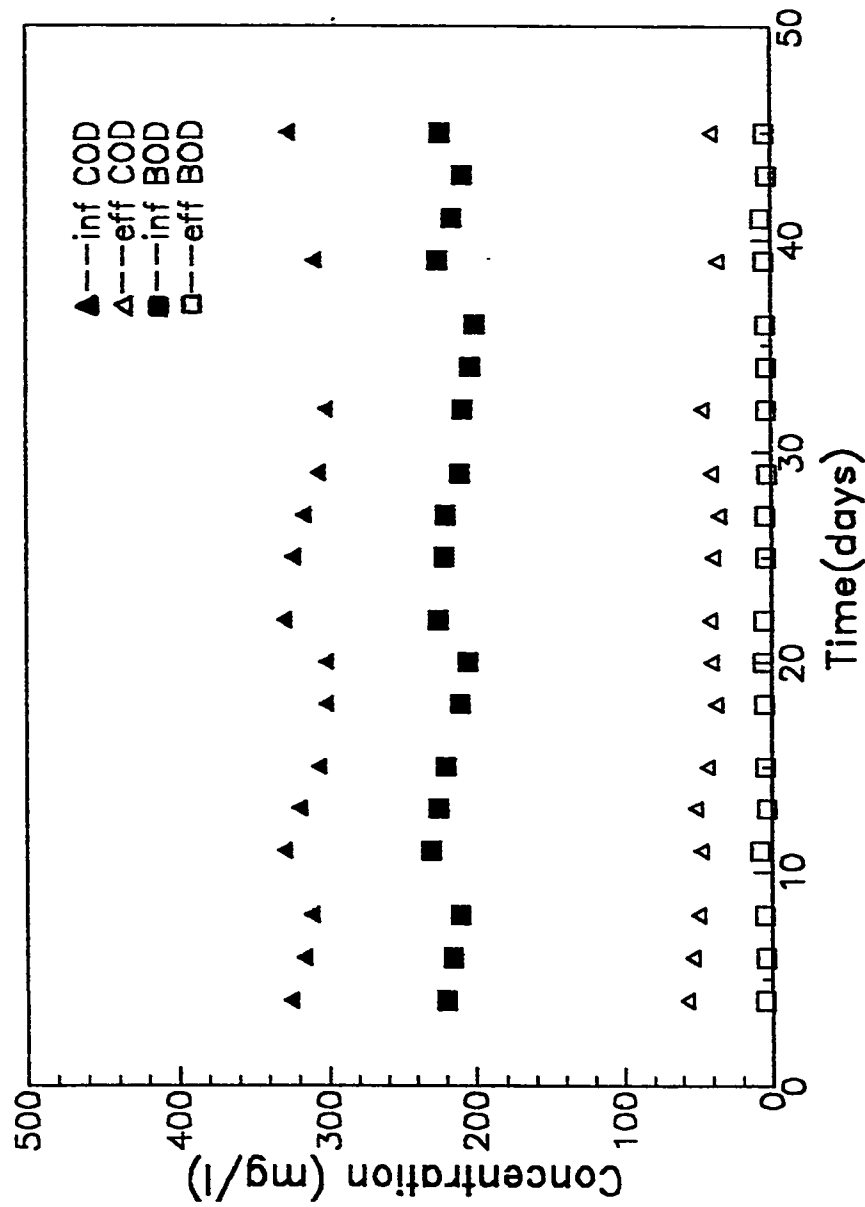


Fig. 4.16 Influent And Effluent BOD And COD Concentration In Reactor 1 During Phase-II, Phenol Study

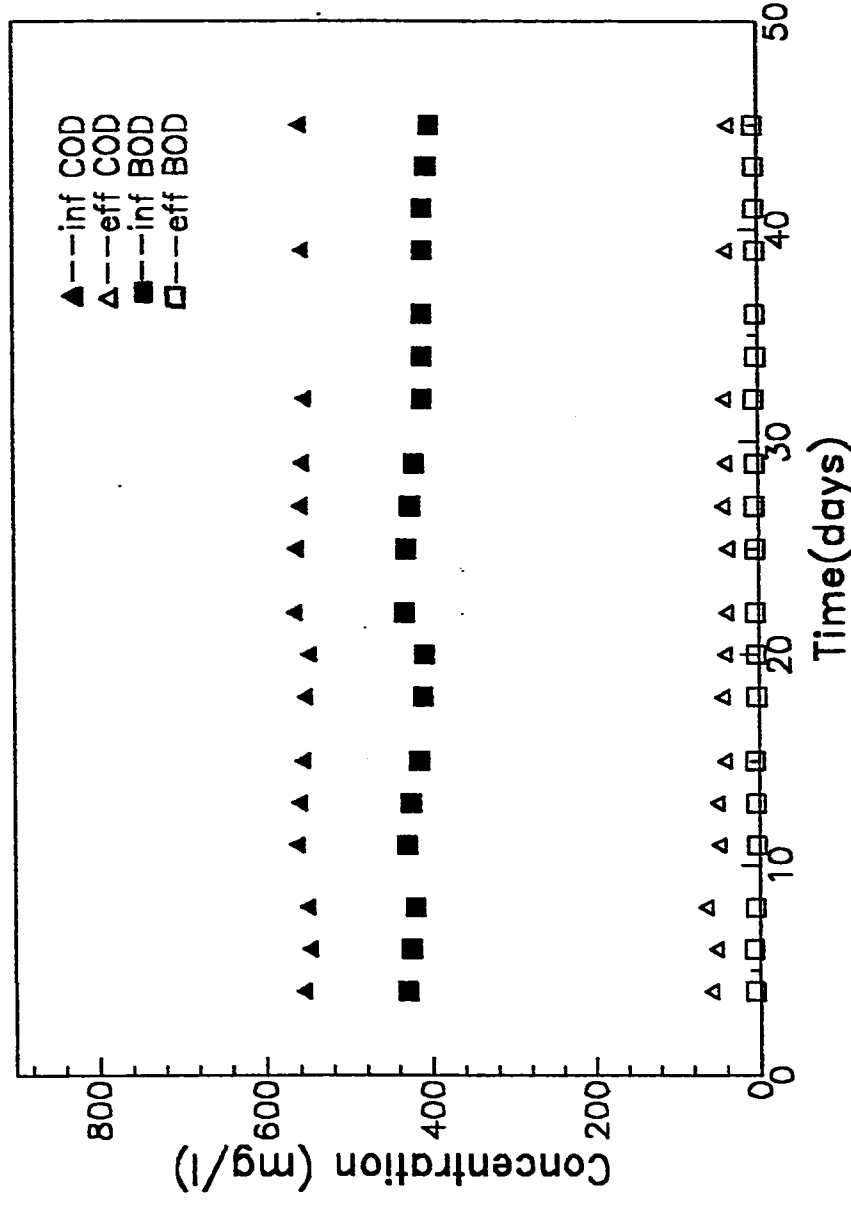


Fig. 4.17 Influent And Effluent BOD and COD Concentration In Reactor 2 During Phase-II, Phenol Study

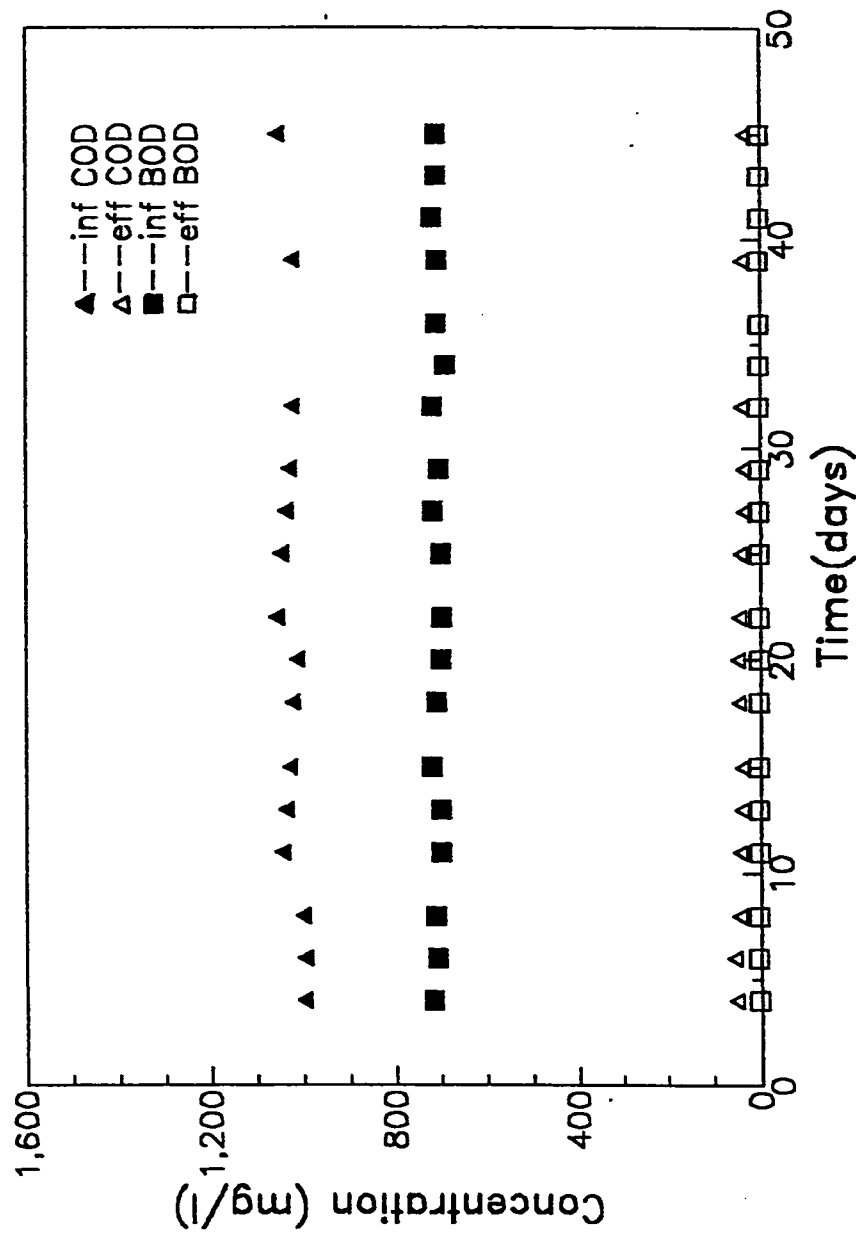


Fig. 4.18 Influent And Effluent BOD And COD Concentration In Reactor 3 During Phase-II, Phenol Study

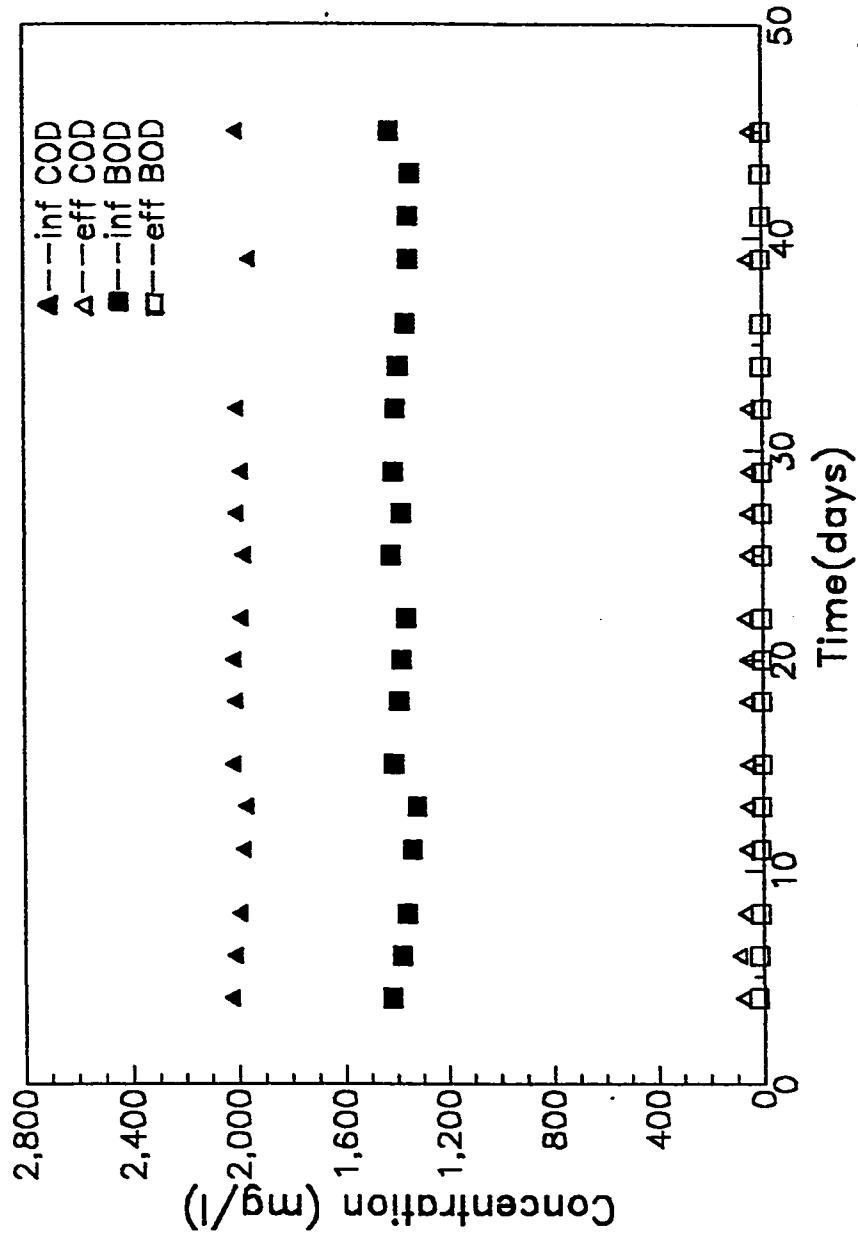


Fig. 4.19 Influent And Effluent BOD And COD Concentration In Reactor 4 During Phase-II, Phenol Study

percentage removals of the BOD during this phase were 97.8%, 98.8%, 99.3% and 99.6% for reactors 1, 2, 3 and 4 respectively. This indicates that all the reactors affected essentially the same BOD removal efficiency.

The average percentage removals of the COD during this were 87%, 93%, 96% and 98% for reactors 1, 2, 3 and 4 respectively. Surprisingly, it was found that the change in the influent concentration had no effect on the effluent concentration which was found to be about 40 mg/l. In an attempt to investigate this finding, a sample from the raw wastewater was analyzed by gas chromatography. The sample was characterized to contain different non-biodegradable chemicals which are not reflected in the BOD test and resulted in high COD values. To emphasize this finding the secondary effluent of the North Aramco Wastewater Treatment Plant (which was activated sludge system) was observed to contain about 45 mg/l as COD. As apparent from Table 4.2, the standard deviation of the effluent COD in all the reactors was about 8 mg/l. This relatively high variability was due to the non-biodegradable organics present in the influent raw sewage and not due to the residual phenol.

Hsu (60) attained 97% removal of BOD using SBRs. The BOD concentration of 242 mg/l was reduced to 8 mg/l. Misbahuddin (73) attained 94% and 87% removal of BOD and COD respectively. In his study petrochemical wastewater was treated in

SBR system. Drinkwater (77) attained 83% removal of BOD using activated sludge for phenolic waste. It can be noted that although the maximum BOD removals are the same for most of the wastewaters, the treatment efficiencies in terms of COD are highly variable. The relatively higher BOD and COD removal efficiencies accomplished in this phase of the study may be attributed to the fact that the system treated relatively simple hazardous contaminants in comparison with the complex hazardous wastes treated in the aforementioned studies.

Effluent TSS and VSS

The concentration of the effluents TSS and VSS are shown in Figures 4.20 and 4.21, respectively. As shown in Table 4.2, the average concentration of effluents TSS and VSS for all the reactors were about 12 mg/l and their standard deviations were about 4 mg/l. This indicates that the effluents TSS and VSS were consistent during this phase. It is apparent that sludge wastage did not have any adverse impact on the effluent suspended solids and the settleability of the sludge. As depicted in Figures 4.20 and 4.21, the differences between the TSS and VSS are insignificant. This indicates that all the suspended solids are biological solids.

Misbahuddin (73) reported effluent TSS of 9 mg/l when the influent TSS was 22.8 mg/l and the settling time was one hour.

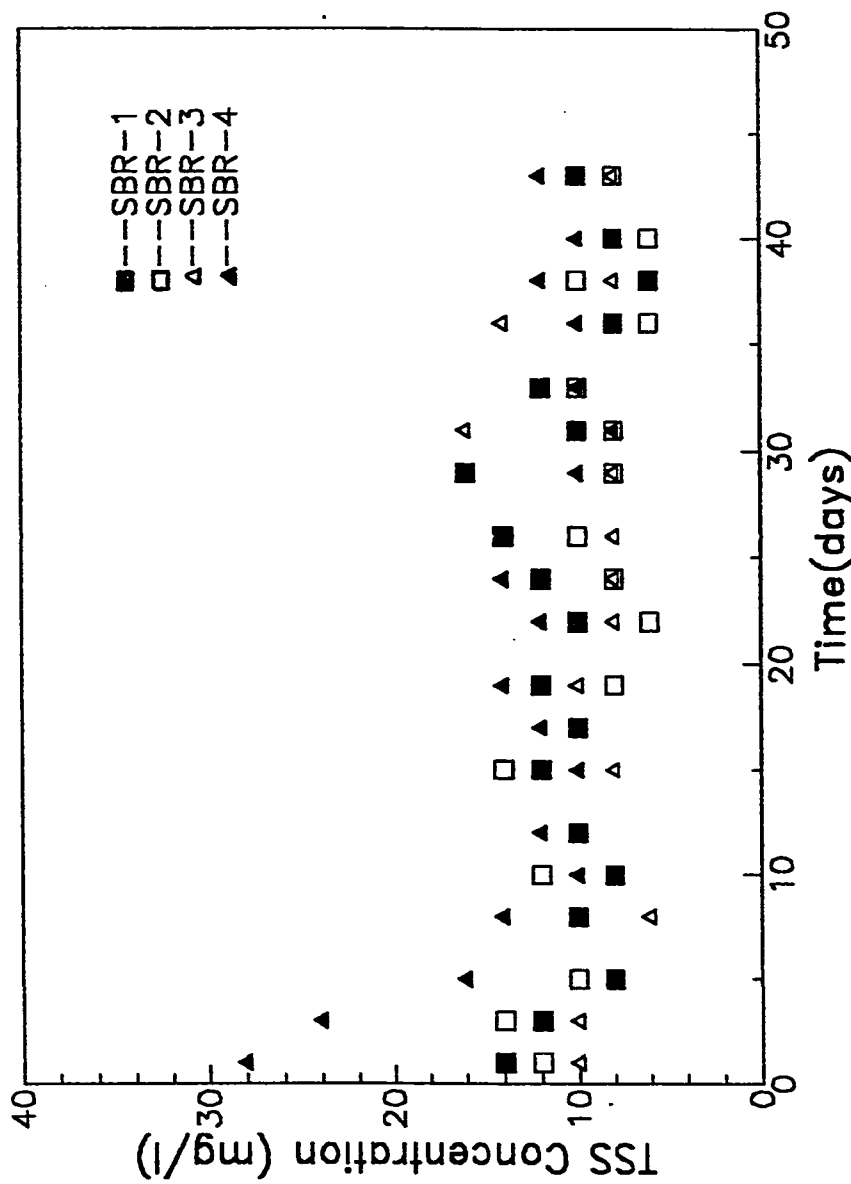


Fig. 4.20 Effluent Concentration of TSS in The SBRs During Phase-II Phenol Study

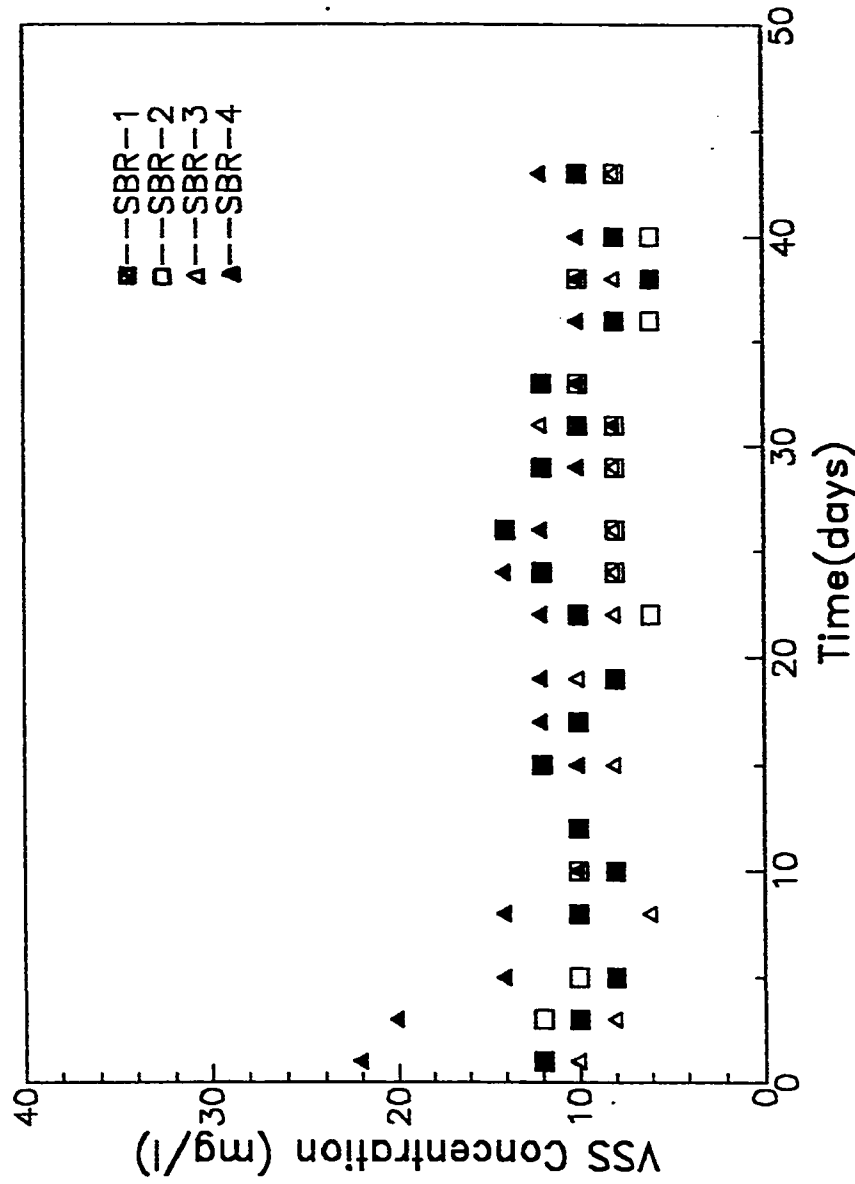


Fig. 4.21 Effluent Concentration of VSS In The SBRs During Phase-II Phenol Study

Hsu (60) produced effluent TSS between 11 and 21 mg/l at settling time of one hour. Thus it is apparent that the effluent quality in terms of TSS concurred with what was reported in the aforementioned studies, and was well above the quality of secondary effluents.

SVI

The sludge-volume index was calculated according to the following equation:

$$SVI = \frac{V}{MLVSS \times V_c} \times 10^6 \quad (4.1)$$

where:

V = the volume in millimeters occupied by sludge after settling for 1 hour.

$MLVSS$ = the concentration of the MLVSS in (mg/l).

V_c = the volume of graduated cylinder, in this case it was a 25 ml cylinder.

Figure 4.22 shows the variation of the SVI values during this phase. As depicted in Figure 4.22, the SVI increased slightly from 53 to 69, from 57 to 64, and from 68 to 76 for reactors 1, 2 and 3, respectively. This increase in the SVI values with

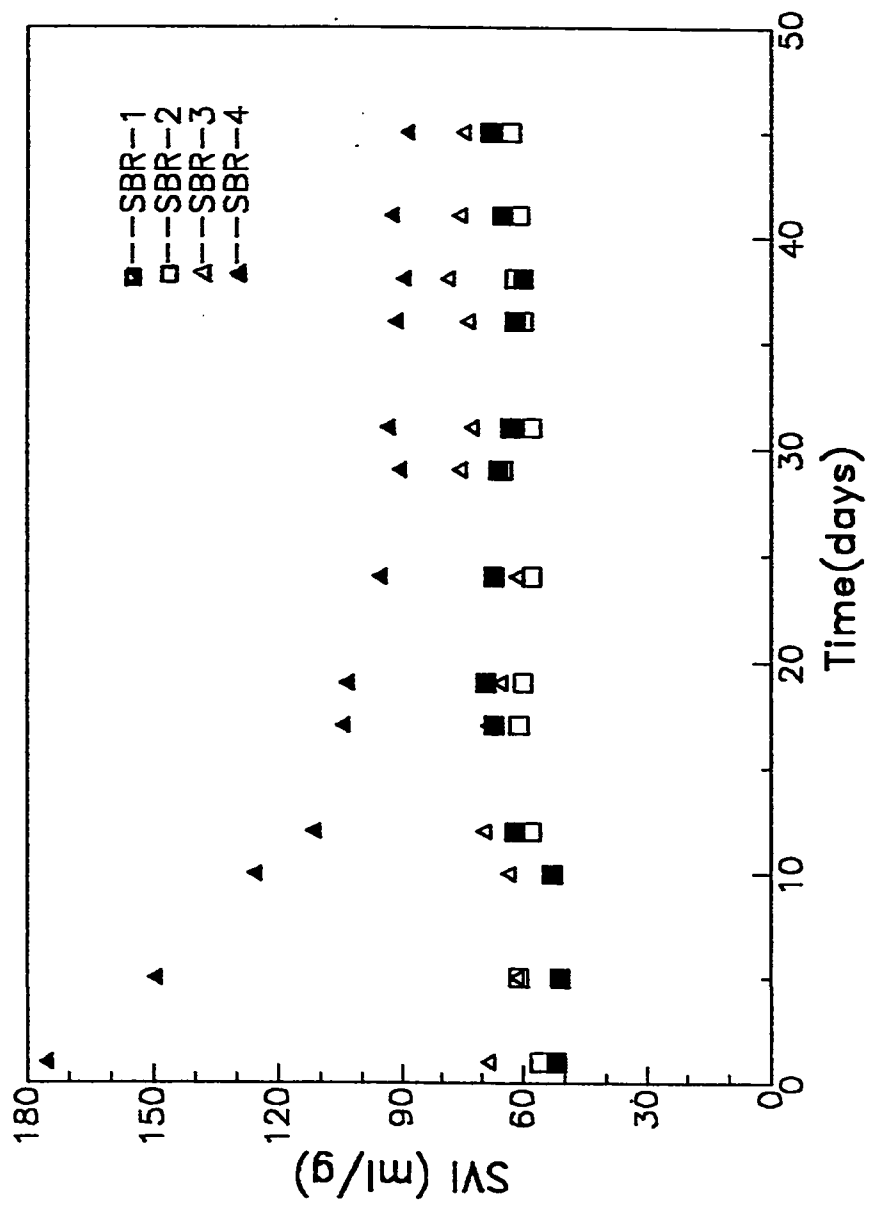


Fig. 4.22 Sludge Volume Index In The SBRs During Phase-II, Phenol Study

operating time must not be attributed to the reduction in the MLVSS concentration, but rather to the change in settling properties of the sludge. As shown in Table 4.2, the average values of the SVI were 58, 63 and 70 ml/g for reactors 1, 2 and 3 respectively. This indicates that reactors 1, 2 and 3 had very compact sludge.

For SBR-4, the SVI decreased with time from 175 ml/g to 85 ml/g. This initial high SVI is owed to the disturbance of the culture of the SBR-4 during the start-up phase (during the shock loading study) which took the microbial culture about 35 days to return back to its normal condition. Additionally, it is clear from Figure 4.22 that the SVI of SBR-4 stabilized around 85 ml/g after 35 days until the end of this phase. This indicates that SBR-4 ultimately accommodated compact sludge and it also indicates that high toxicant concentrations did not hinder sludge settleability.

Smith and Wilderer (4) obtained SVI values between 106 ml/g and 69 ml/g depending on the days of operation using sequencing batch reactors for treating hazardous landfill leachate. Misbahuddin (73) obtained SVI between 69 ml/g and 59 ml/g depending on the reactors strategies of varying the ratio of the anoxic fill to react time periods. Thus, the SVI reported herein, despite the relatively high values of SBR-4 are well within the range of literature values for similar wastes.

Nutrient Removal

The concentrations of the TKN and total-p were analyzed only two times at the end of this phase. As can be seen from Table 4.2, the TKN decreased from 31 mg/l to 16.1, 16.1, 15.8, and 13.2 mg/l, respectively, in SBR-1, SBR-2, SBR-3 and SBR-4. SBR-4 achieved the highest reduction in the TKN, since it synthesized more cells than all the others. The decrease in the influent TKN can be attributed to the utilization of nitrogen for cell synthesis plus the conversion of organic nitrogen to ammonia nitrogen and subsequently to nitrite and nitrate nitrogen.

It is also evident from Table 4.2 that the total-p decreased from 8 mg/l to 6.1, 6.5, 5.9, and 5.7 mg/l, respectively, SBR-1, SBR-2, SBR-3 and SBR-4. The decrease in the influent total-p can be attributed to the utilization of phosphorous for the cell synthesis.

The BOD/N/P ratios for SBR-1, SBR-2, SBR-3 and SBR-4 were 100/6.6/1.3, 100/3.7/0.4, 100/2.1/0.3, and 100/1.3/0.2, respectively. However, it is evident that the BOD/N/P ratios for the reactors did not match with the general ratio of BOD/N/P which is 100/5/1 (78). This might be due to the microorganisms were well acclimatized that they consumed less amount of nitrogen and phosphorous, or due to experimental error during the measurements of TKN and total-p.

4.1.3 Phase III. Solids Residence Time Study

This phase was carried out to investigate the effect of different SRT on the treatability of the wastewater at a constant organic loading rate. In this phase, the influent concentration of the phenol of reactors 1, 2 and 3 was stepped to 800 mg/l gradually to avoid inhibition. The influent and effluent phenol concentration during transient phase are shown in Figure 4.23. The mean SRTs selected for this study were 3, 5 and 10 days for reactors 1, 2 and 3, respectively. SBR-4 was not operated during this phase of the study since it treated phenol concentration of 800 mg/l and SRT of 14 days without any sign of failure. Table 4.3 gives a summary of the results during this phase. The summary includes the average values of the influent and effluent concentrations of phenol, TSS, VSS, BODs, COD, total-p, TKN, alkalinity and chloride in addition to the MLSS, MLVSS and SVI. The reported values in the table are the averages taken over a period of three turnovers of the SRT in each reactor except for the MLSS and MLVSS which were averaged over the third turnover period of the SRT in each reactor.

MLSS

The concentration of the MLSS and MLVSS are shown in Figures 4.24 and 4.25 respectively. It is worth noting that the levels of the MLSS were about 2350 mg/l in all the reactors at the

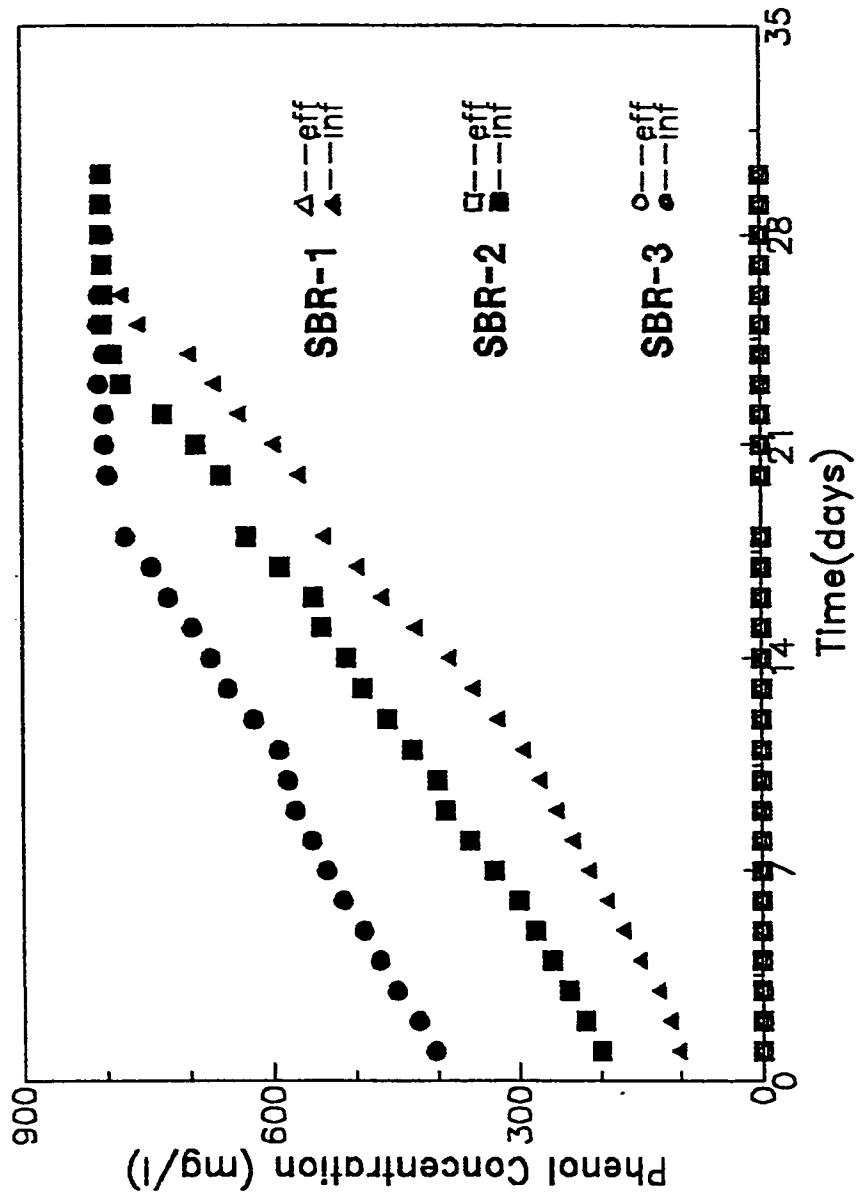


Fig. 4.23 Influent and Effluent Phenol Concentration During Transient Phase

Table 4.3: Reactors Performance During Phase III - Phenol Study

| Reactor | SBR-1 | SBR-2 | SBR-3 |
|---------------------------------------|---------------|-----------------|-----------------|
| Mean SRT (days) | 3 | 5 | 10 |
| Influent phenol Con. (mg/l) S.D.** | 805(9)* 9 | 804(15) 7 | 802(30) 5 |
| Effluent phenol Con. (mg/l) S.D. | 90(9) 89 | 4.6(15) 12.5 | 0.5(30) 0.05 |
| MLSS (mg/l) S.D. | 926(3) 221 | 1231(3) 229 | 1765(5) 57 |
| MLVSS (mg/l) S.D. | 753(3) 160 | 1011(3) 165 | 1412(5) 40 |
| Influent TSS (mg/l) S.D. | 178(2) 6 | 178(2) 6 | 178(2) 6 |
| Effluent TSS (mg/l) S.D. | 78(5) 43 | 15(7) 11 | 10(13) 3 |
| Influent VSS (mg/l) S.D. | 124(2) 4 | 124(2) 4 | 124(2) 4 |
| Effluent VSS (mg/l) S.D. | 66(5) 40 | 14(7) 8 | 9.5(13) 2.5 |
| Influent BOD (mg/l) S.D. | 1392(4) 12 | 1385(7) 12 | 1386(10) 12 |
| Effluent BOD (mg/l) S.D. | 188(4) 155 | 20(7) 37 | 5(10) 0.5 |
| Influent COD (mg/l) S.D. | 1988(4) 22 | 1984(7) 18 | 1988(10) 18 |
| Effluent COD (mg/l) S.D. | 296(4) 224 | 57(7) 43 | 39(10) 4 |

| Reactor | SBR-1 | SBR-2 | SBR-3 |
|------------------------------------|----------------|----------------|----------------|
| SVI (ml/g) S.D. | 135(5) 84 | 80(7) 53 | 52(11) 7 |
| Influent total-p (mg/l) S.D. | 9.4(2) 0.6 | 9.2(2) 0.7 | 9.6(2) 0.6 |
| Effluent total-p (mg/l) S.D. | 7.6(2) 1.2 | 7.4(2) 2 | 6.8(2) 0.6 |
| Influent TKN (mg/l) S.D. | 29.2(2) 2 | 28.4(2) 1 | 29(2) 2 |
| Effluent TKN (mg/l) S.D. | 22.3(2) 5.7 | 20.4(2) 8.5 | 14.5(2) 0.8 |
| Influent Alkalinity (mg/l) S.D. | 266(2) 5 | 260(2) 5 | 286(2) 5 |
| Effluent Alkalinity (mg/l) S.D. | 197(2) 3 | 169(2) 4 | 175(2) 2 |
| Influent Chloride (mg/l) S.D. | 1332(2) 12 | 1330(2) 10 | 1328(2) 12 |
| Effluent Chloride (mg/l) S.D. | 1292(2) 10 | 1284(2) 12 | 1258(2) 6 |

*Parenthesis indicate the number of samples
**Standard deviation

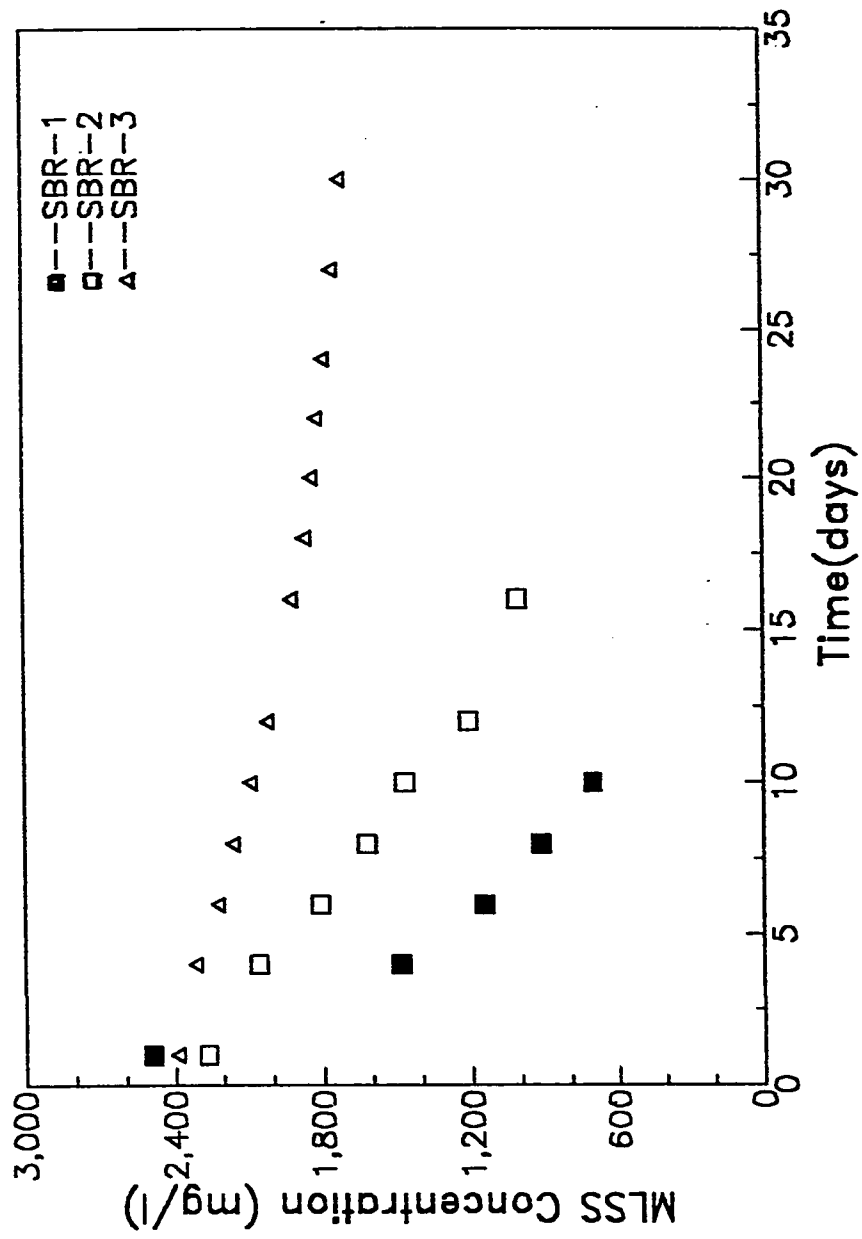


Fig. 4.2.4 Concentration of MLSS In The SBRs During Phase-III, Phenol Study

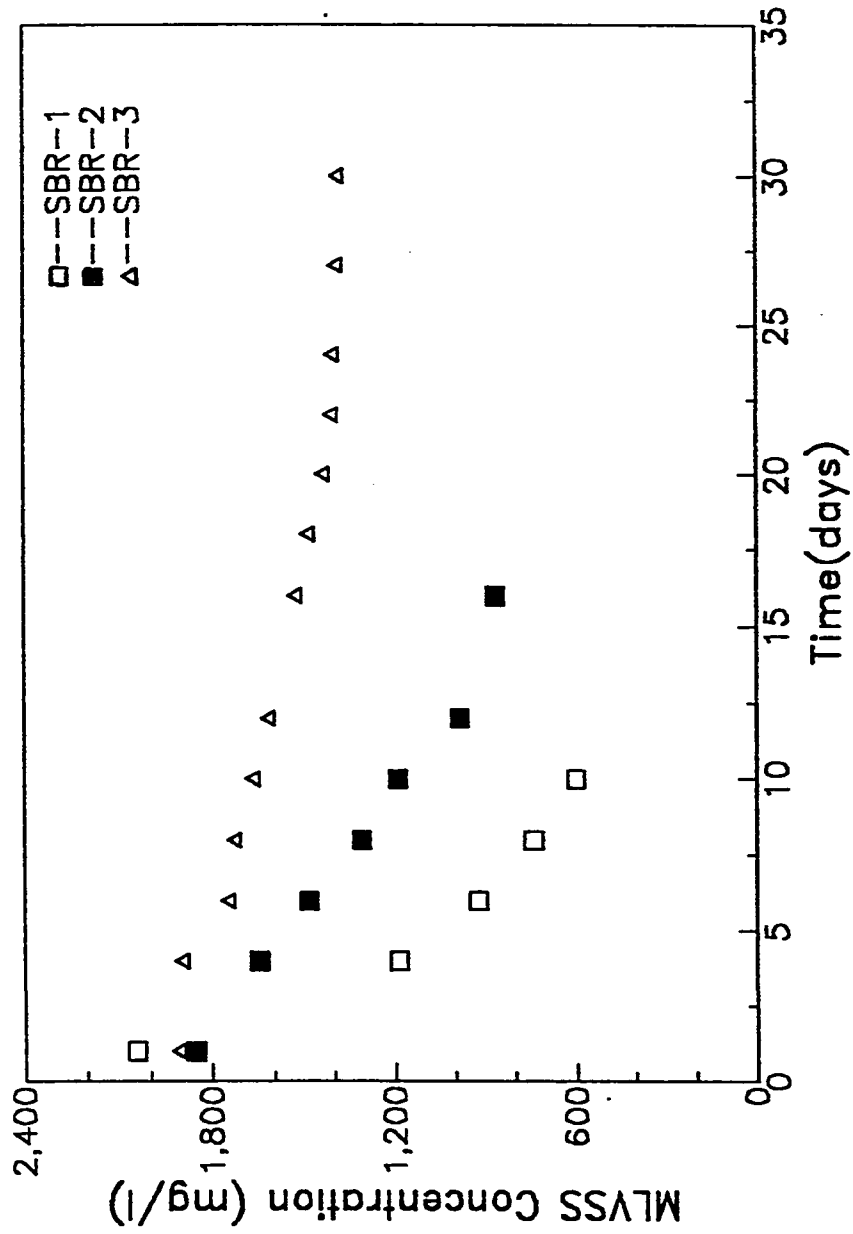


Fig. 4.25 Concentration of MLVSS In The SBRs During Phase-III, Phenol Study

beginning of this phase. As depicted in these figures, the expected decrease in the MLSS and MLVSS with decreasing SRT was observed. The MLSS decreased from 2492 mg/l to 708 mg/l in SBR-1, from 2264 mg/l to 1012 mg/l in SBR-2 and from 2384 to 1712 mg/l in SBR-3. It is clear from these figures that SBR-1 and SBR-2 did not reach the steady state condition, since their standard deviation during the third turnover were very high, (about 225 mg/l). However, it is also clear from Figure 4.24 and Table 4.3 that SBR-3 did reach the steady state condition, since its standard deviation was relatively low (about 55 mg/l). As apparent from Figures 4.24 and 4.25, the rate of MLSS and MLVSS decrease was greater in the reactors that operated at lower mean SRT. However, this is expected, since the feed concentration was same in all the reactors and the sludge wastage was different, i.e. the wastage rate was higher in the reactor operated at the lowest SRT.

Effluent phenol

Figures 4.26, 4.27 and 4.28 show the temporal profile of the concentrations of phenol in the influent wastewater and the effluents from reactors 1, 2 and 3, respectively. As depicted in Figures 4.26 and 4.27, failure occurred in SBR-1 and SBR-2, since their effluent concentration increased to 205 mg/l and 50 mg/l at the end of the third turnover of SRT. The percentage removals of the phenol for both reactors were >99% at beginning of the phase

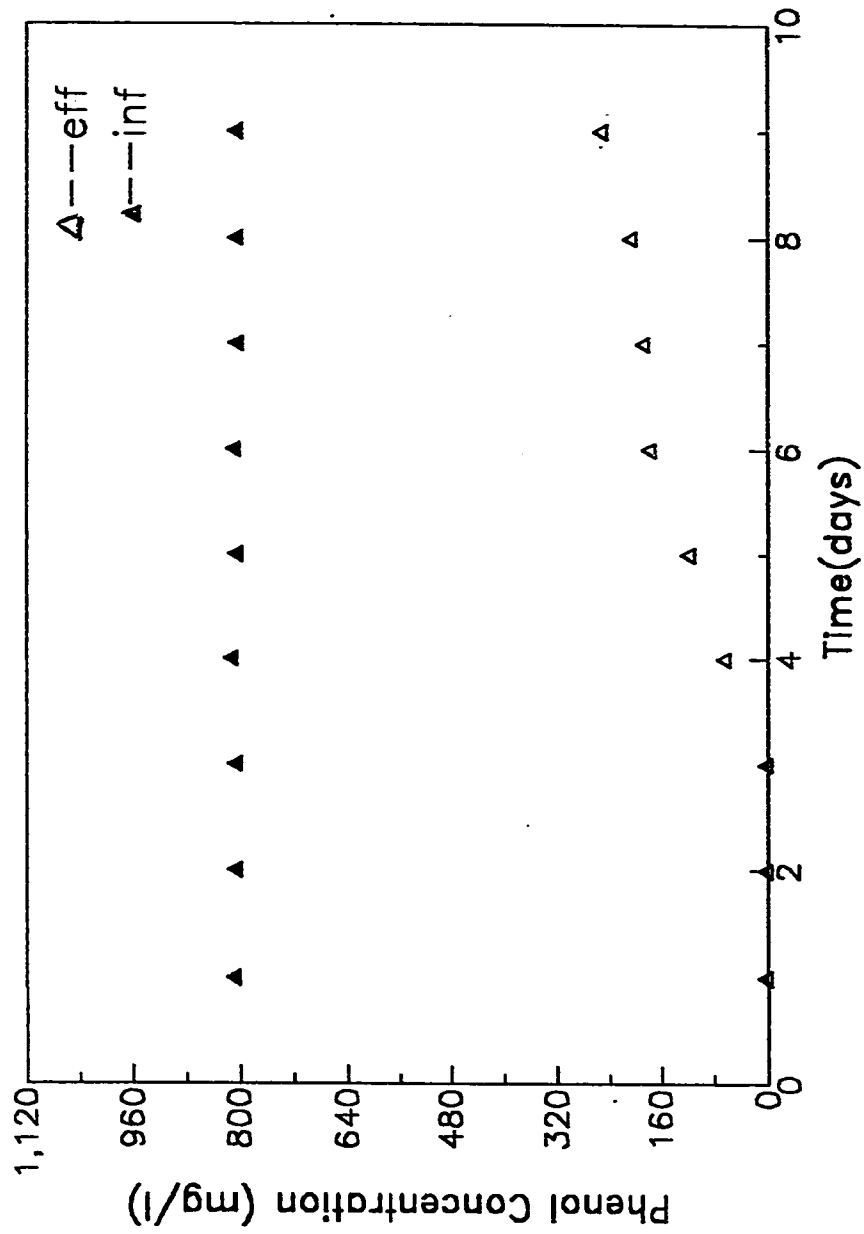


Fig. 4.26 Influent and Effluent Phenol Concentration During Phase-III, Reactor 1

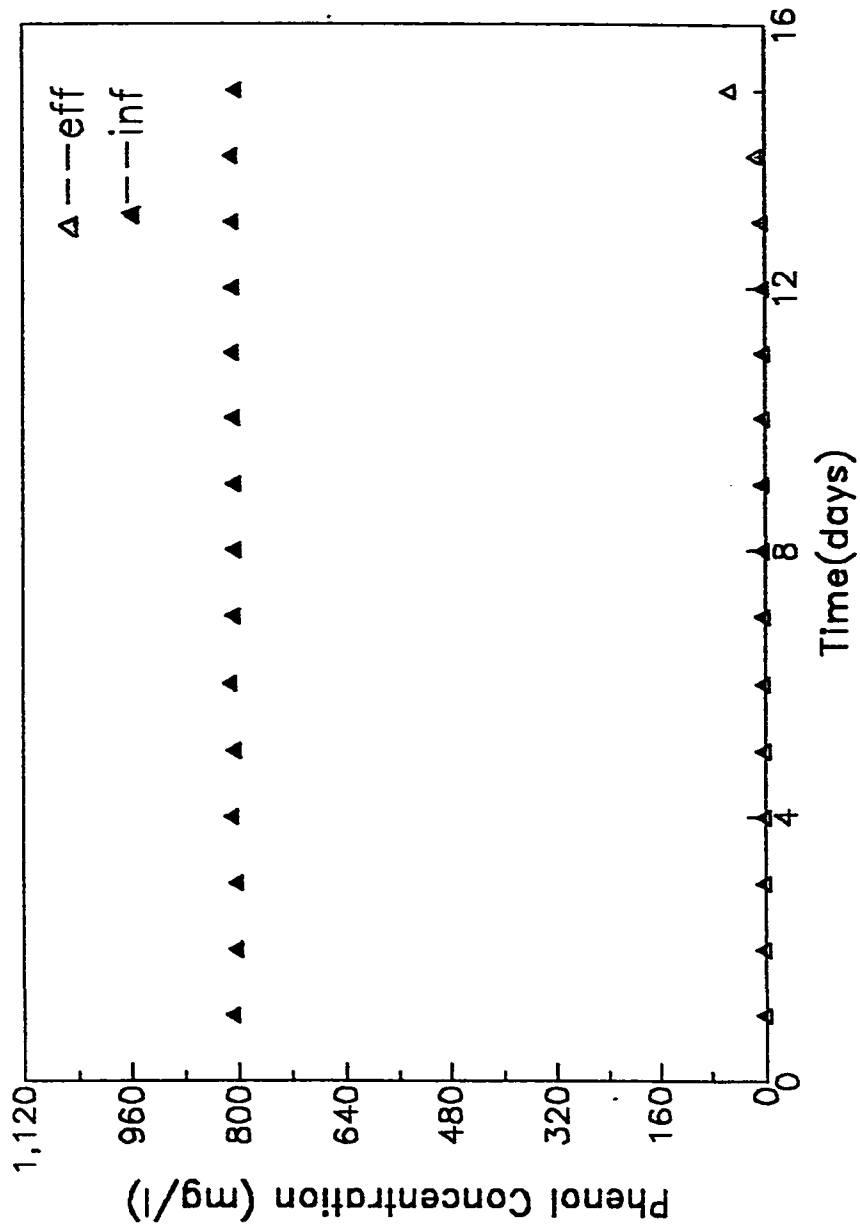


Fig. 4.27 Influent and Effluent Phenol Concentration During Phase-III, Reactor 2

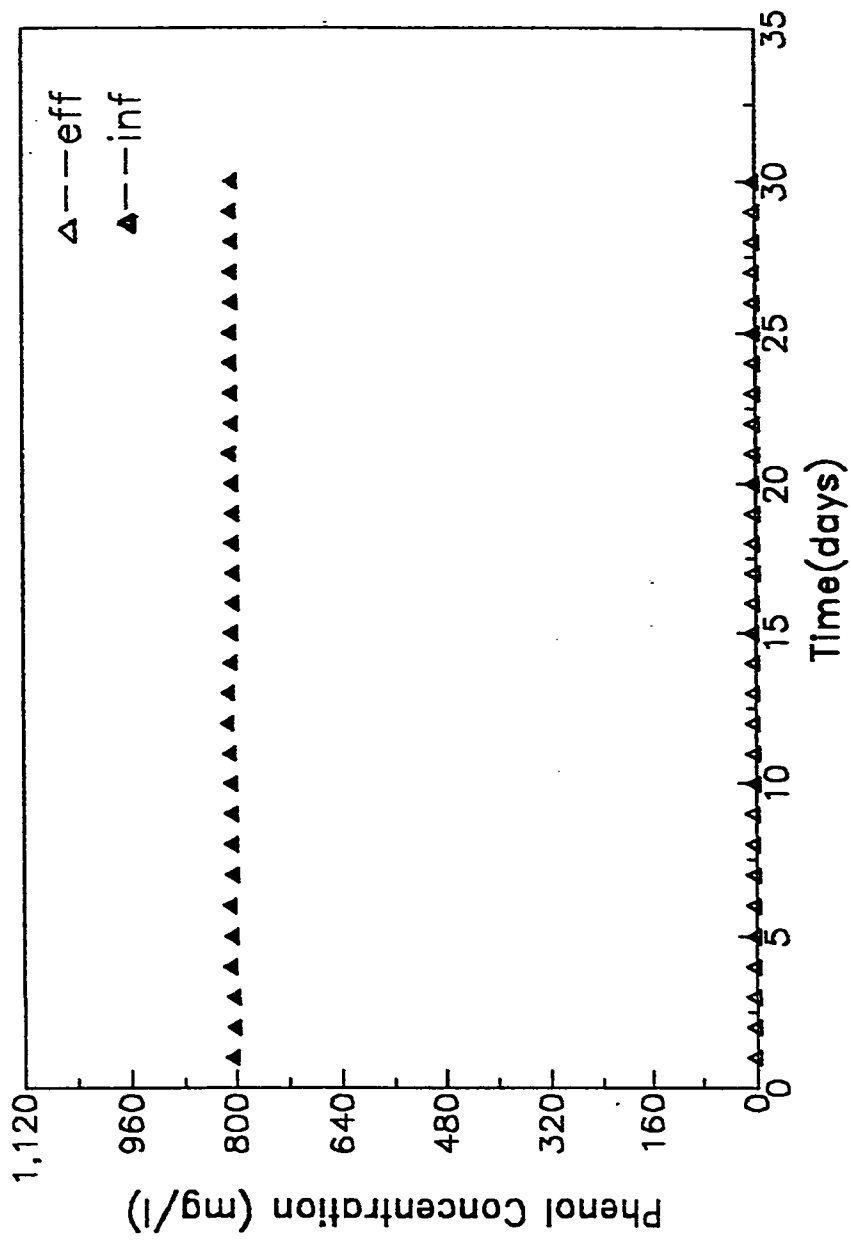


Fig. 4.28 Influent and Effluent Phenol Concentration During Phase-III, Reactor 3

and decreased to 74% and 94% at the end of this phase for reactors 1 and 2, respectively. The F/M ratio at the incipience of failure for reactors 1 and 2 were 0.7 and 0.8 $\frac{\text{mg of phenol}}{\text{mg of MLVSS}}$ respectively. Figures 4.26 and 4.27 indicate that phenol cannot be treated successfully at mean SRT of 5 days and at concentrations as high as 800 mg/l.

As depicted in Figure 4.28 and Table 4.3, the average concentration of the effluent phenol was about 0.5 mg/l with standard deviation less than 0.1 mg/l for SBR-3. This indicates that the percentage removal of the phenol, which was >99%, was consistent during the phase. The noteworthy finding of this study depicted in Figure 4.28 that phenol can be treated effectively at mean SRT of 10 days and at concentration as high as 800 mg/l. The toxicant loading ranged from 0.4 - 0.6 mg of phenol/mg and MLVSS. This treatment efficiency of better than 99% concurs with that reported by Herzburn et al. (1970) who attained efficient phenol concentrations of about 0.4 mg/l during the treatment of a hazardous phenolic waste at a temperature of 23°C to 25°C and hydraulic retention times of 5 and 9 days.

Effluent BOD and COD

Figures 4.29, 4.30 and 4.31 show the influent and effluent BODs and COD concentrations for reactors 1, 2 and 3 respectively.

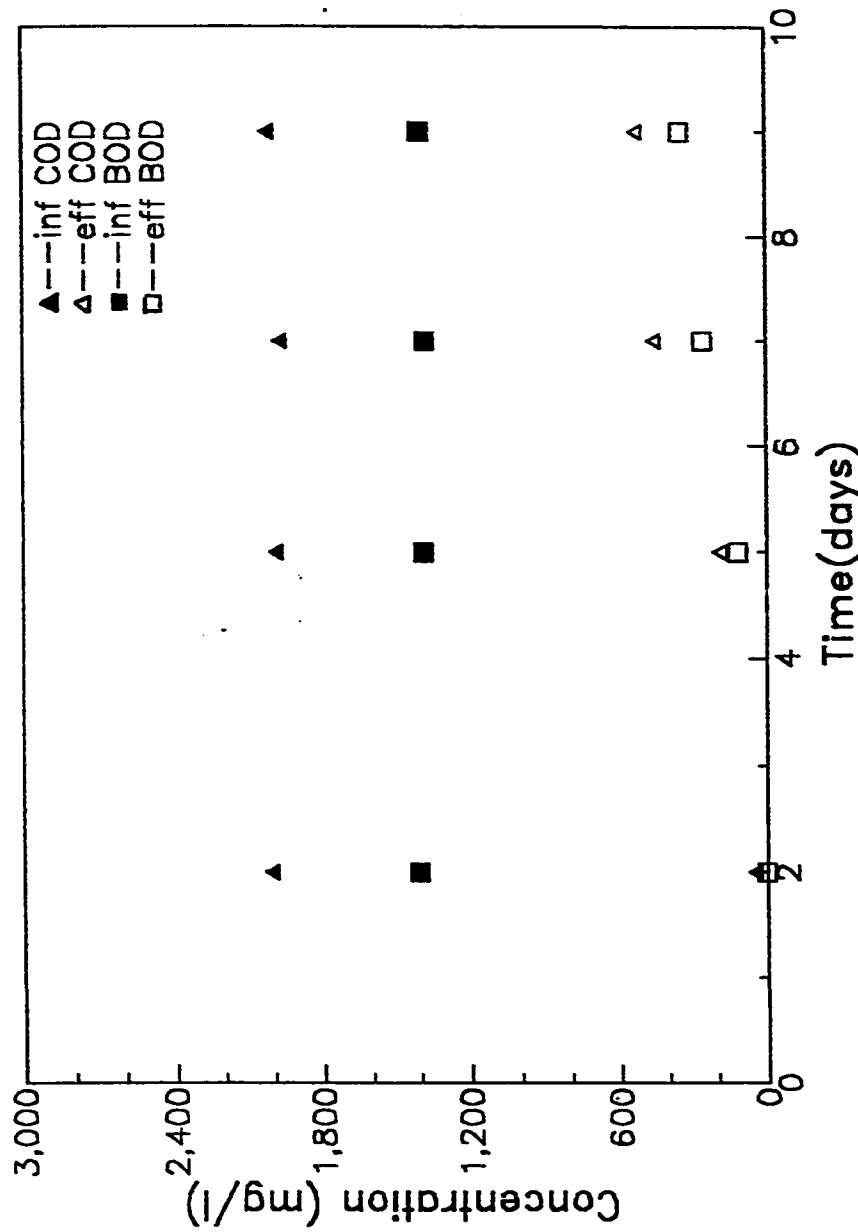


Fig. 4.29 Influent and Effluent BOD and COD Concentration in Reactor 1 During Phase-III, Phenol Study

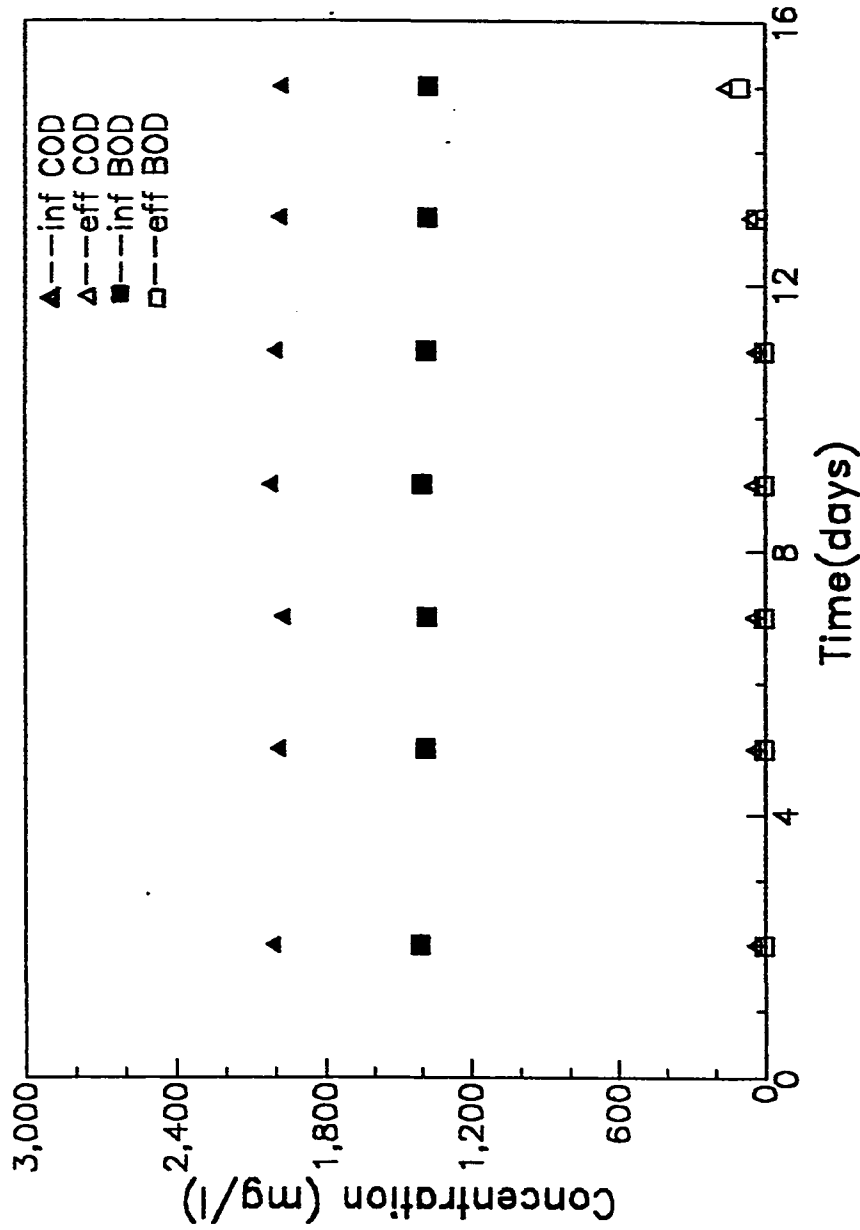


Fig. 4.30 Influent and Effluent BOD and COD Concentration in Reactor 2 During Phase-III, Phenol Study

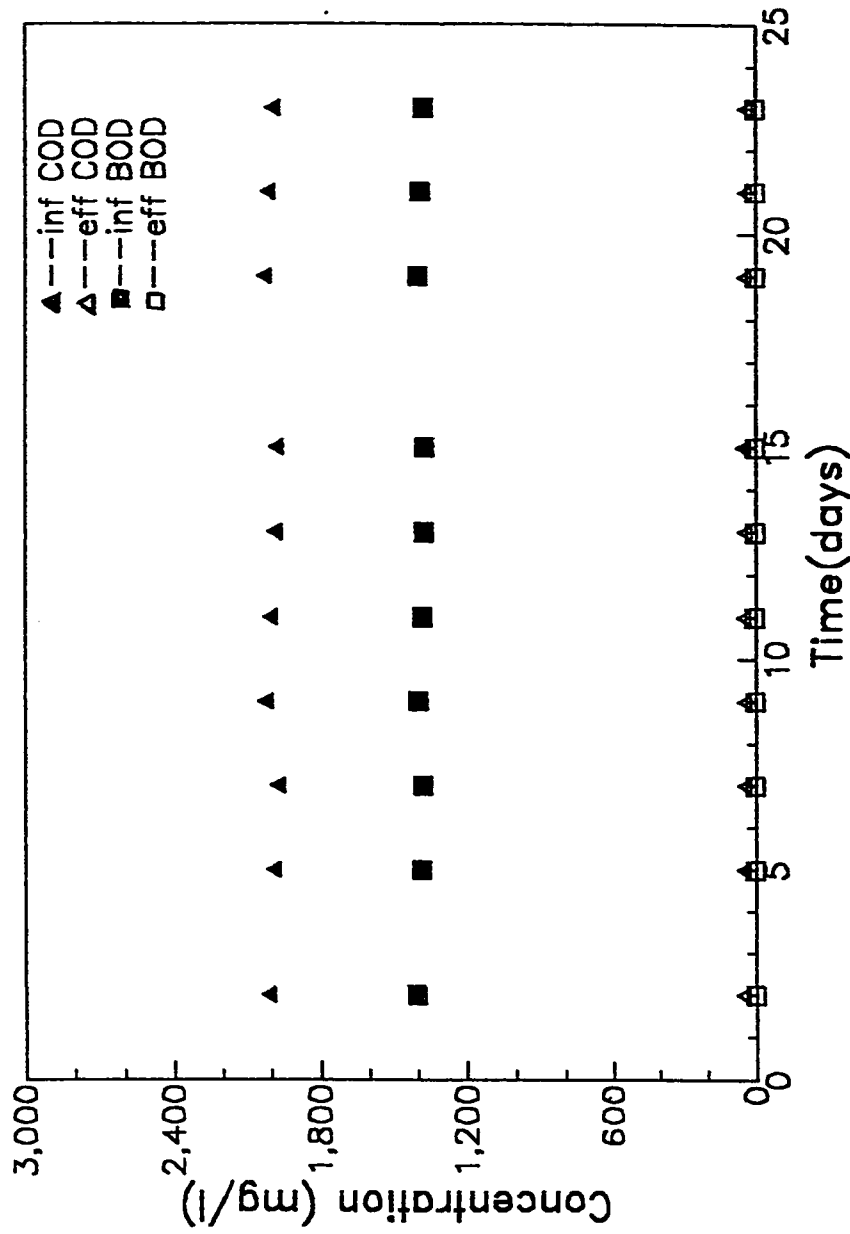


Fig. 4.31 Influent and Effluent BOD and COD Concentration In Reactor 3 During Phase-III, Phenol Study

As can be seen from Table 4.3 the average effluent BOD and COD concentrations from reactor 1 and 2 were 188 mg/l and 296 mg/l, respectively. The corresponding figures for reactor were 20 and 57 mg/l, respectively. Even though, these effluents exceeded the limits of the secondary treatment, the minimum percentage removals for reactors 1 and 2 of the BOD were 86% and 99% and of the COD were 85% and 97% respectively. The removal efficiencies of reactors 1 and 2 compares well with those reported by Hsu (60), Misbahuddin (73) and Drinkwater (77) for phenolic waste.

As can be seen from Table 4.3, the effluent concentration of the BOD was about 5 mg/l for SBR-3. The percentage removal of the BOD was >99% for SBR-3. This removal efficiency of the BOD was sustained with minimal variability throughout the phase as reflected by the low standard deviation which was about 0.5 mg/l. As apparent from Table 4.3, the average percentage removal of the COD for SBR-3 was 98%. It is also clear from Table 4.3 that the average concentration of effluent COD was about 40 mg/l and the standard deviation of the effluent COD was about 4 mg/l for SBR-3. This high effluent COD and the standard deviation were due to the nature of the raw sewage and not due to the residual phenol. As apparent from Figure 4.31 that the effluent COD and subsequently the COD removal efficiency in reactor 3 were consistent during this phase. Misbahuddin (73) obtained 94% and 87% removal efficiency of BOD and COD, respectively during the

SBR treatment of petrochemical waste while Smith and Wilderer (4) reported a 93.5% reduction in the COD of a hazardous landfill leachate using the SBR. The relatively higher BOD and COD reduction efficiencies reported may be attributed to the fact that a relatively simpler hazardous waste was treated in comparison with the complex wastes investigated by the foregoing researchers.

Effluent TSS

Figures 4.32 and 4.33 show the effluent concentration of TSS and VSS respectively. As can be observed from these figures, the TSS and VSS increased with time for reactors 1 and 2 and they were consistent for reactor 3. As shown in Figure 4.31, the TSS values for SBR-1 and SBR-2 increased from about 12 mg/l at the beginning of the phase to 130 mg/l and 32 mg/l, respectively at the end of the phase. These values exceeded the limits of the secondary treatment, which indicate that the culture were disturbed by the high phenol concentrations. It is apparent from Figures 4.26, 4.27 and 4.32 that the breakthrough of phenol and TSS for reactors 1 and 2 happened at the same time, i.e. for SBR-1 the concentration of effluent phenol exceeded the limits at day 4, and the effluent TSS exceeded the limits at day 4. This indicates that the failure of the system can be known by measuring phenol or TSS. The average concentration of the suspended solids for SBR-3 was about 10 mg/l with standard deviation around 3 mg/l. This indicates that a mean SRT of 10 days did not have any

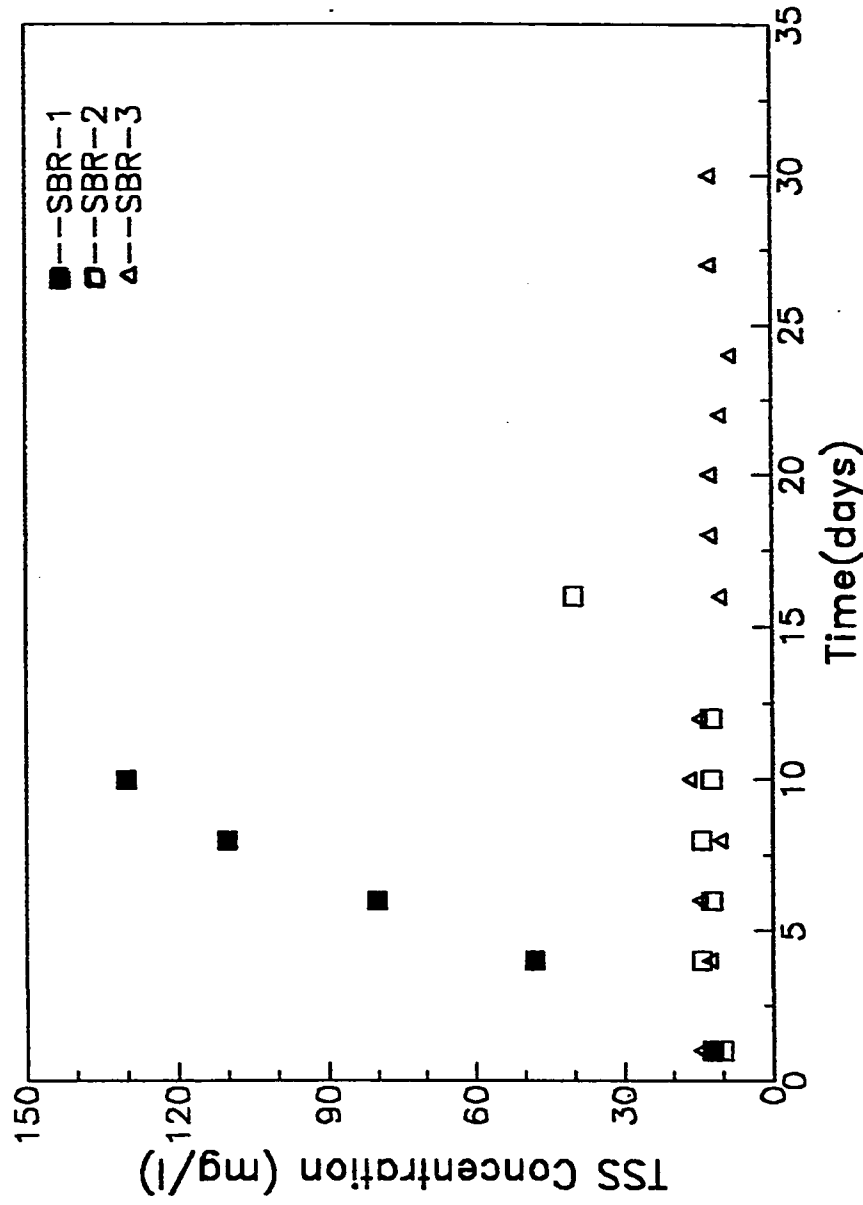


Fig. 4.32 Effluent Concentration of TSS In The SBRs During Phase-III Phenol Study

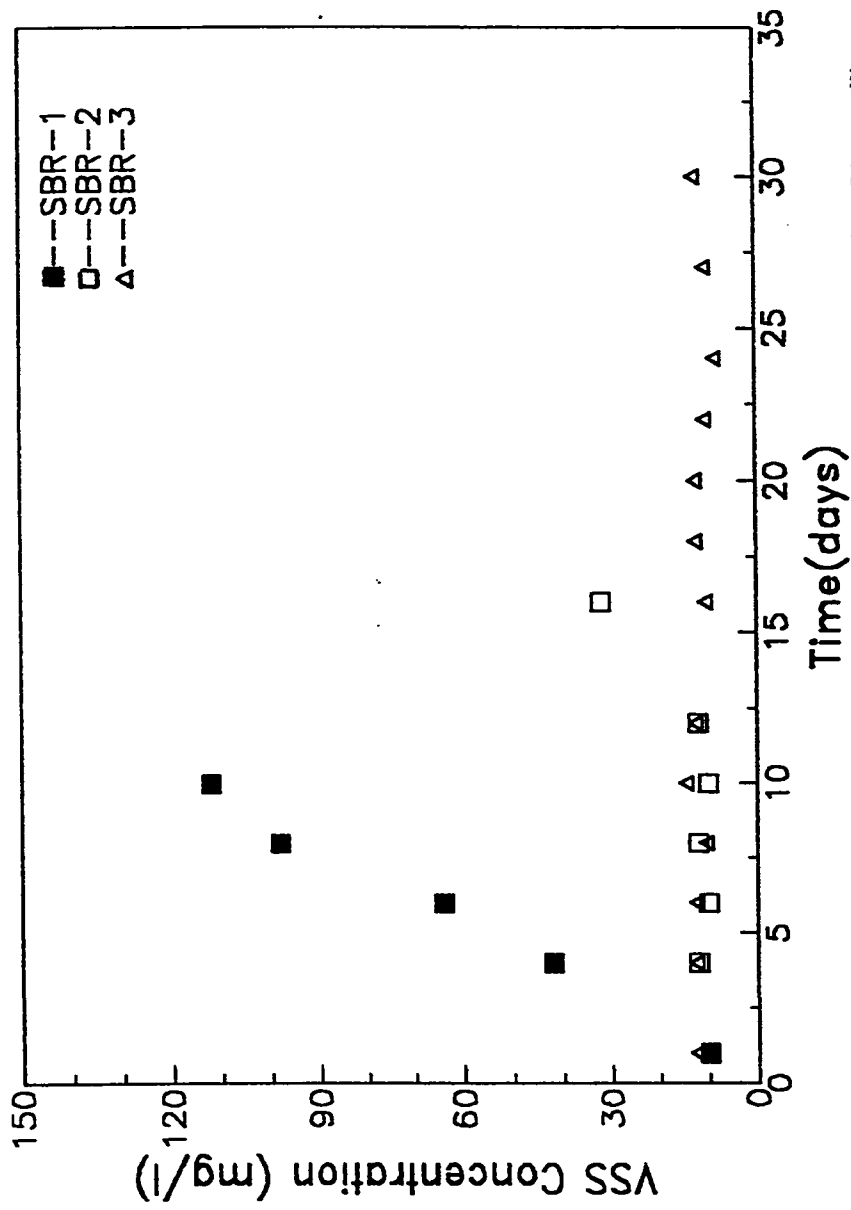


Fig. 4.33 Effluent Concentration of VSS in The SBRs During Phase-III Phenol Study

adverse impact on the effluent suspended solids.

SVI

The SVI was calculated according to Equation 4.1. The SVI values in the reactors increased with time as shown in Figure 4.34. As expected, the highest value of SVI was encountered in SBR-1 which operated at lowest SRT values. As shown in Figure 4.34, the SVI was initially about 40 ml/g in SBRs 1 and 2 but continued increasing to reach 262 ml/g and 197 ml/g for reactors 1 and 2, respectively at the end of the phase. This indicates that reactors 1 and 2 had sludge of poor settleability. As can be seen from Table 4.3 the average value of the SVI for reactor 3 was about 52 ml/g and the standard deviation was about 7 ml/g. This reflects the good settleability of the mixed liquor of reactor 3. Smith and Wilderer (4) obtained SVI values between 106 and 69 ml/g depending on the days of operation using SBRs for treating hazardous landfill leachate. Misbahuddin (73) obtained SVI between 69 and 59 ml/g depending on the reactors strategies of varying ratio of the anoxic fill to react time periods. Thus, the SVI reported herein for reactors that did not fail are well within the range of literature values for similar wastes.

Nutrient Removal

As can be seen from Table 4.3, the TKN decreased from 29.3 mg/l to 22.3 mg/l in SBR-1, from 28.4 mg/l to 20.4 mg/l in

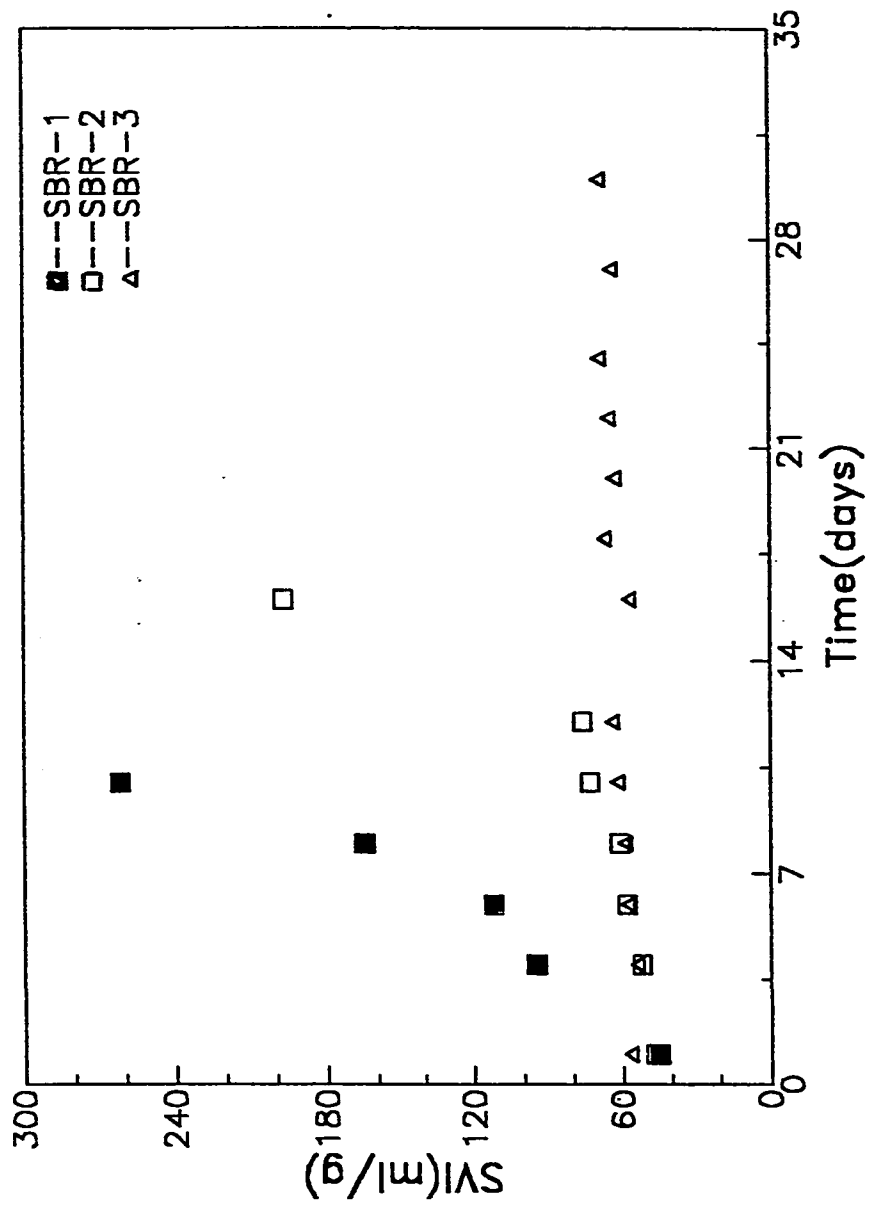


Fig. 4.34 Sludge Volume Index In The SBRs During Phase-II, Phenol Study

SBR-2 and from 29 mg/l to 14.5 mg/l in SBR-3. It is apparent that the highest reduction in TKN occurred in SBR-3, since it synthesized more cells than the others. The decrease in the influent TKN can be attributed to the utilization of nitrogen for the cell synthesis.

The total-p decreased from 9.4 mg/l to 7.6 mg/l in SBR-1, from 9.2 mg/l to 7.4 mg/l in SBR-2 and from 9.6 mg/l to 6.8 mg/l in SBR-3. The decrease in the influent total-p can be attributed to the utilization of phosphorous for the cell synthesis.

The BOD/N/P ratios for SBR-1, SBR-2 and SBR-3 were 100/0.5/0.13, 100/0.58/0.13 and 100/1.04/0.2, respectively. It is evident that these ratios did not match with general BOD/N/P ratio. This could be due to the reasons mentioned in Phase II of this study.

4.2 Part-II: Biotreatment of O-Cresol Bearing Wastewater

4.2.1 Phase-1: Startup of the System

The performance of the sequencing batch reactors during this phase was indicated by the concentration of mixed liquor in the reactor, the effluent phenol and suspended solids concentrations. Table 4.4 gives a summary of the results during this phase. This includes the average of the influent and effluent concentrations of o-cresol and TSS in addition to the MLSS and MLVSS. The reported values in the table are the averages taken over a period of 36 days. The standard deviations for the parameters mentioned are also included.

Figures 4.35 and 4.36 show the build up of mixed liquor total and volatile suspended solids respectively, during the start-up phase in which no sludge was wasted. It is worth noting that all four units were seeded with approximately 500 mg/l of mixed liquor from identical reactors treating 800 mg/l of phenol in raw wastewater. As depicted in Figures 4.35 and 4.36, the concentration of the MLSS and MLVSS in the sequencing batch reactors increased steadily with time. Furthermore, the rate of buildup of MLSS and MLVSS increased with increasing influent concentrations of o-cresol. However, it is also clear from these two figures that upto day 18 the same rate of MLSS increase was observed in all four SBRs. While, after 18 days the rate of MLSS

Table 4.4: Reactors Performance During Phase I - Cresol Study

| Reactor | SBR-1 | SBR-2 | SBR-3 | SBR-4 |
|-----------------------------------|----------|----------|----------|----------|
| Influent o-cresol Conc. (mg/l) | 73(35)* | 147(35) | 220(35) | 294(35) |
| S.D.** | 32 | 35 | 96 | 128 |
| Effluent o-cresol Conc (mg/l) | 0.65(35) | 0.71(35) | 0.75(35) | 1.1(35) |
| S.D. | 0.7 | 0.96 | 0.90 | 1.2 |
| MLSS (mg/l) | 1060(14) | 1208(14) | 1450(14) | 1485(14) |
| S.D. | 320 | 410 | 578 | 905 |
| MLVSS (mg/l) | 835(14) | 970(14) | 1142(14) | 1200(14) |
| S.D. | 245 | 310 | 440 | 690 |
| Influent TSS(mg/l) | 154(2) | 154(2) | 154(2) | 154(2) |
| S.D. | 9 | 9 | 9 | 9 |
| Effluent TSS(mg/l) | 23(10) | 30(10) | 32(10) | 35(10) |
| S.D. | 32 | 34 | 35 | 40 |

*Parenthesis indicate the number of samples

**Standard deviation

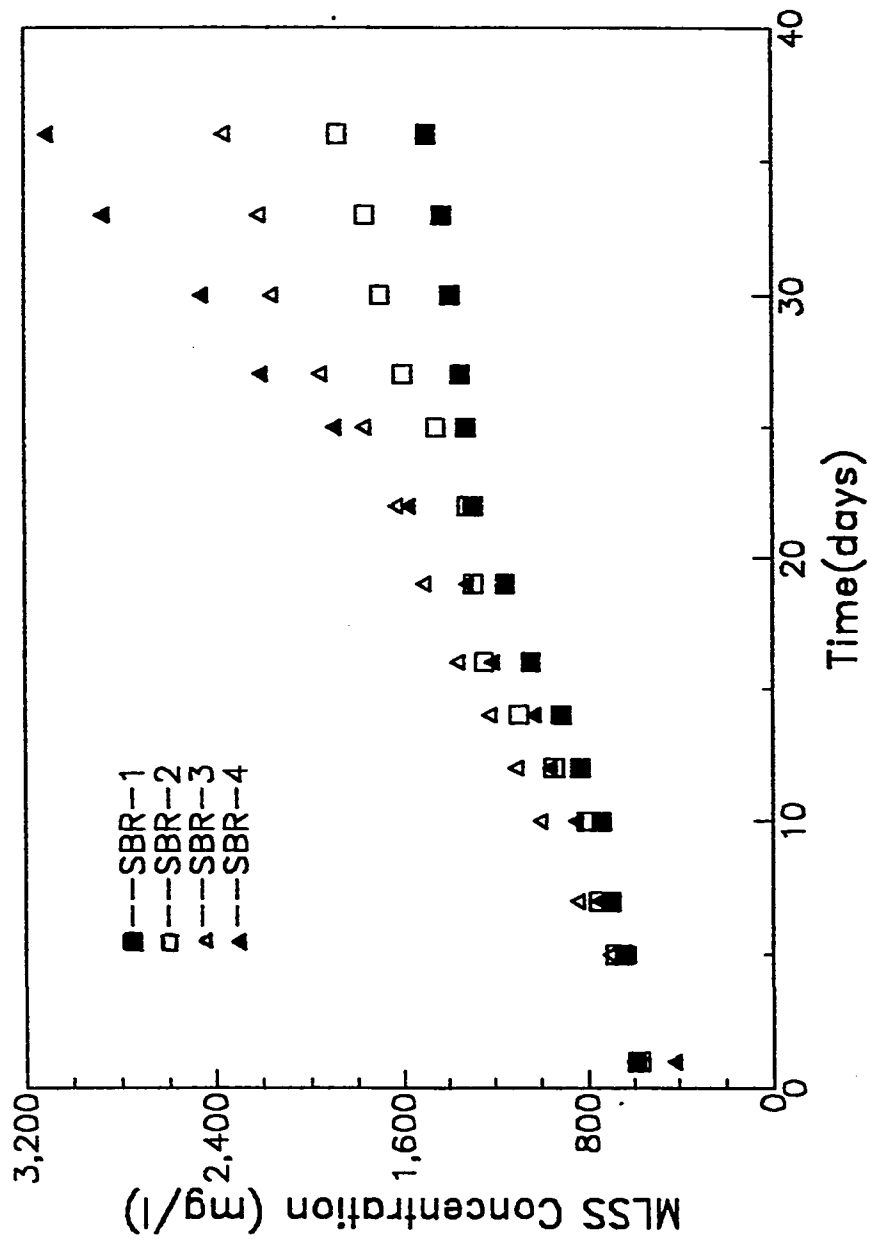


Fig. 4.35 Concentration of MLSS In The SBRs During Phase-I, Cresol Study

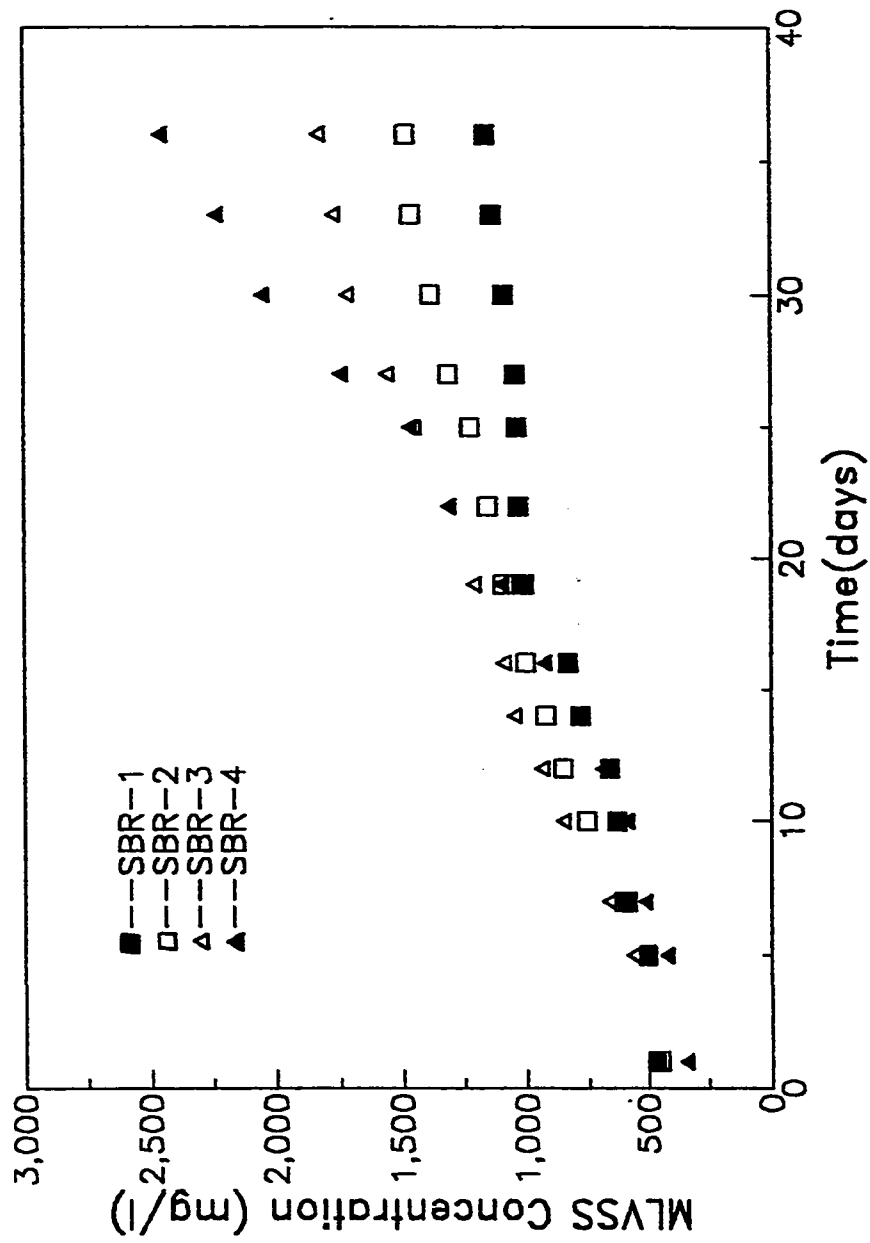


Fig. 4.36 Concentration of MLVSS In The SBRs During Phase-I, Cresol Study

and MLVSS increase was found to be directly proportional to the influent concentration of o-cresol, i.e. the reactor with higher concentration of o-cresol resulted in higher rate of MLSS and MLVSS increase. For example, the curve of the MLSS and MLVSS of the SBR-1, which treated 100 mg/l of o-cresol was flatter than that of the SBR-3 which treated 300 mg/l of o-cresol. This is due to the fact that the reactor which treated a relatively high influent concentration of o-cresol, had higher food to microorganisms ratio (F/M) than the reactor that treated low influent concentration. The average values of the F/M ratio, which were calculated during the period from day 18 until the end of this phase, were 0.077, 0.161, 0.208 and 0.263 $\frac{\text{mg/l of o-cresol}}{\text{mg/l of MLVSS}}$ for reactors 1, 2, 3 and 4 respectively. Thus, the feed concentration was the limiting factor for cell synthesis.

Figures 4.37, 4.38, 4.39 and 4.40 show the influent and effluent concentration of o-cresol for reactors 1, 2, 3 and 4 respectively. These figures indicate that the effluent o-cresol concentrations from all the reactors decreased very rapidly from about 7 mg/l to 0.5 mg/l in the first three days of the build up phase. Additionally, the effluent o-cresol concentrations were not affected by doubling the influent concentration of o-cresol at the beginning of the second week and then again at the beginning of the third week. It must be emphasized that the removal of o-

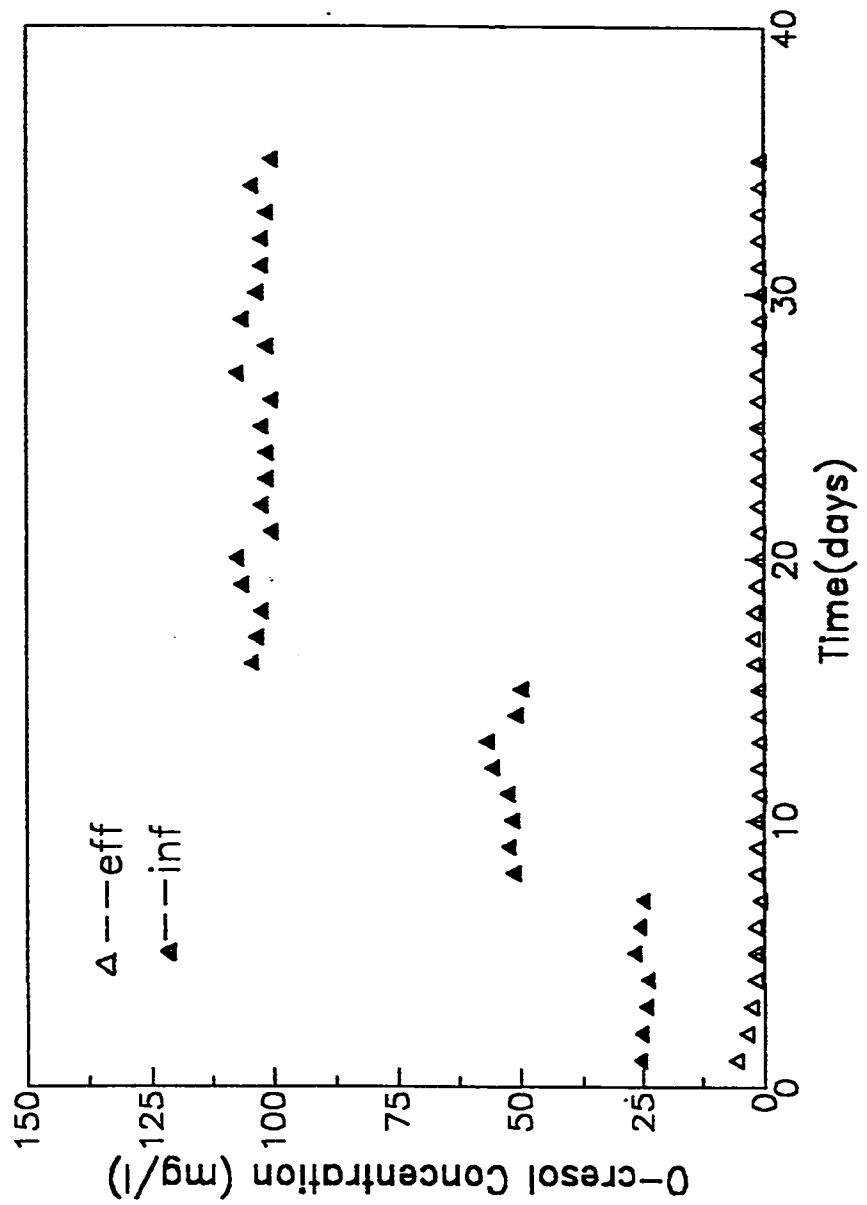


Fig.4.37 Influent and Effluent O-cresol Concentration During Phase-I, Reactor 1

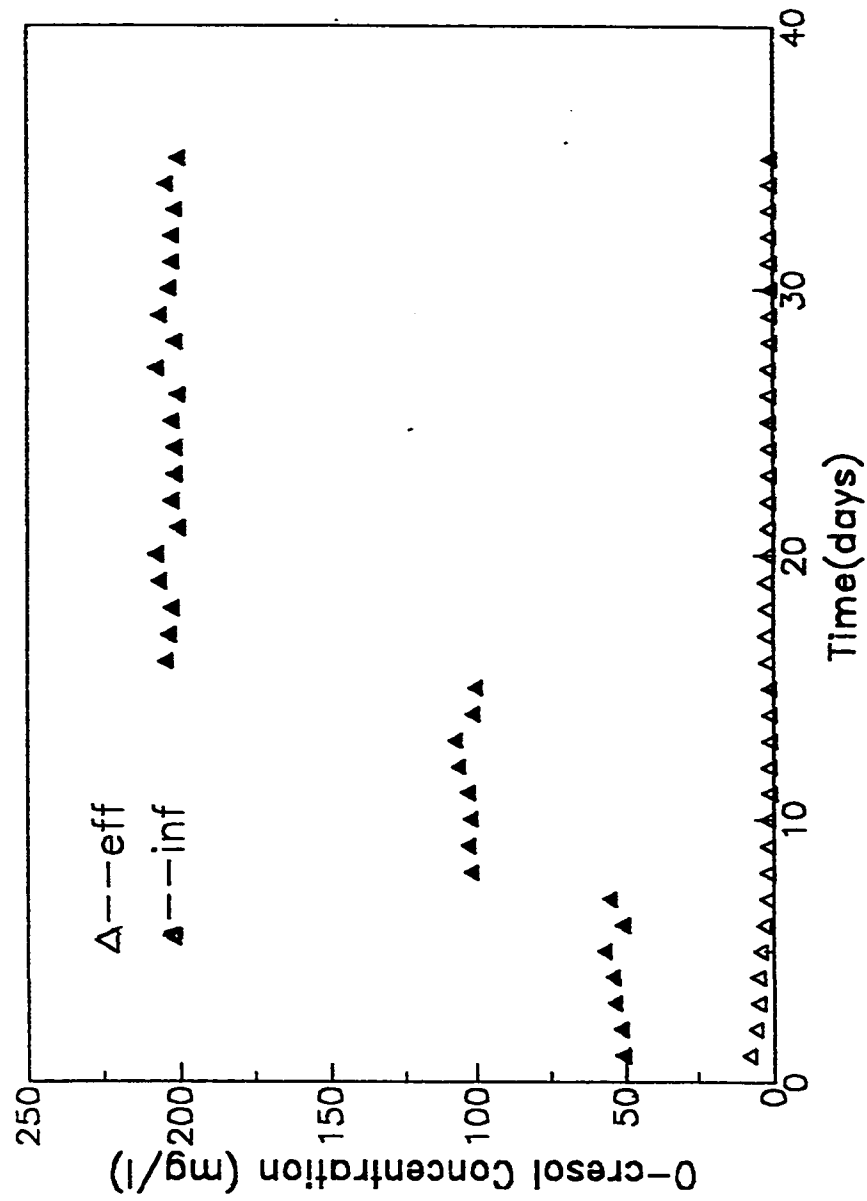


Fig. 4.38 Influent and Effluent O-cresol Concentration During Phase-I, Reactor 2

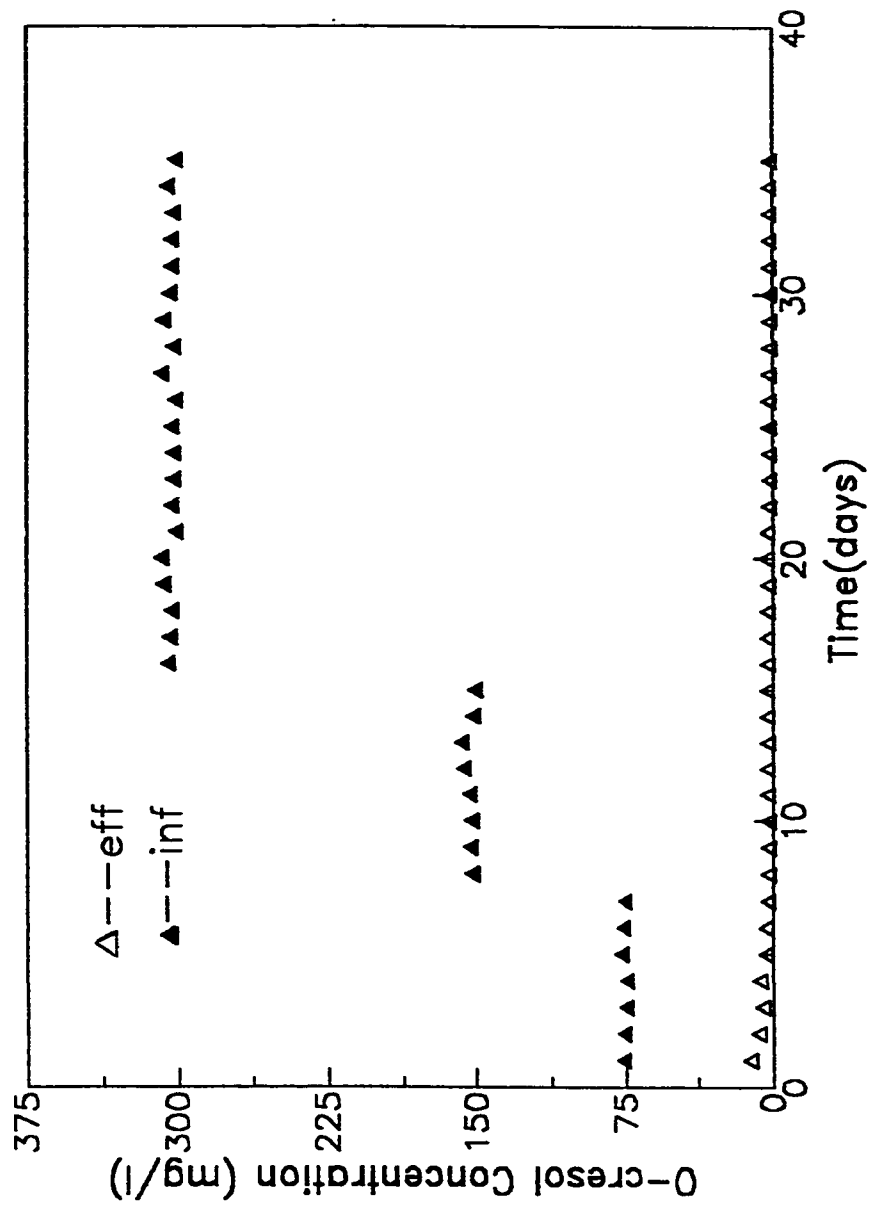


Fig. 4.39 Influent and Effluent O-cresol Concentration During Phase-I, Reactor 3

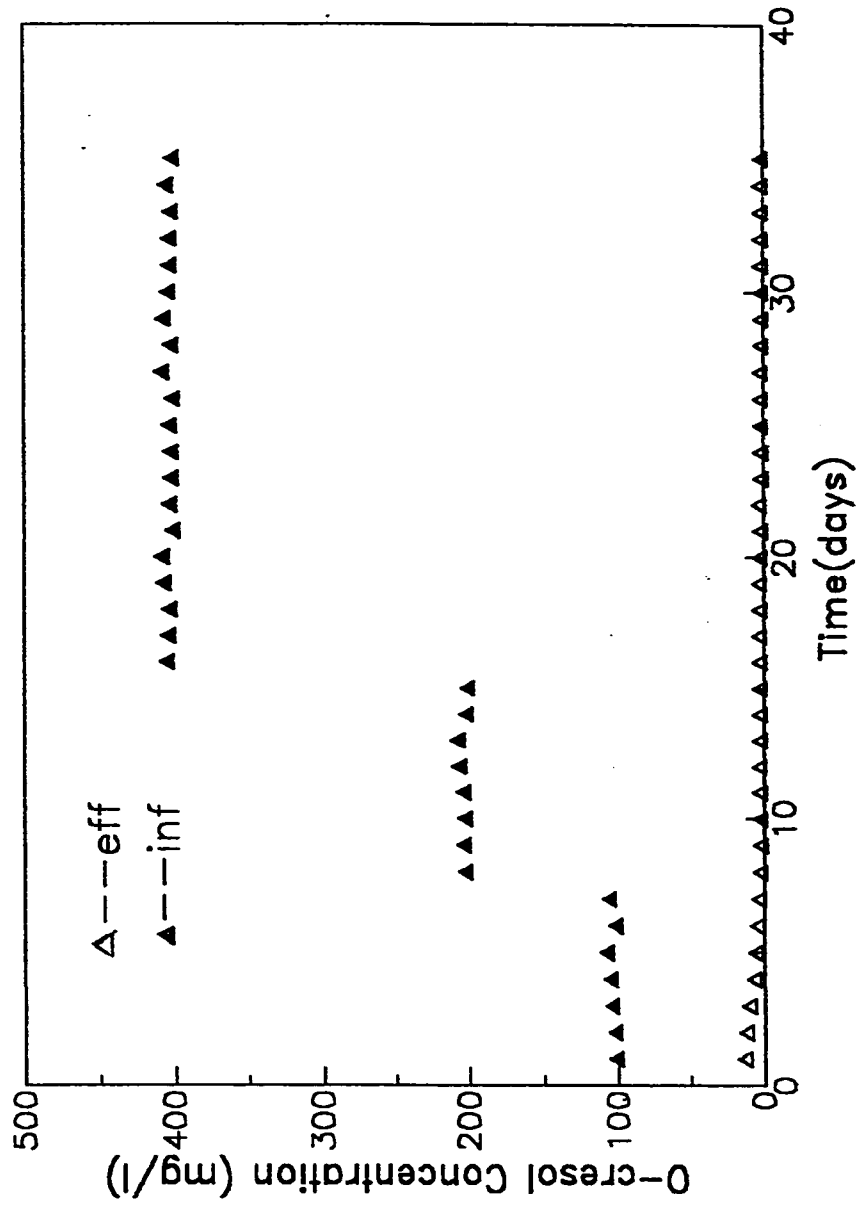


Fig. 4.40 Influent and Effluent O-cresol Concentration During Phase-I, Reactor 4

cresol was merely due to biogradation and no evidence of o-cresol volatility was observed. Figure 4.41 shows the initial and residual concentrations of o-cresol in an identical SBR to the reactors but treating a 200 mg/l solution of o-cresol solution at neutral pH. It is evident from Figure 4.41 that no significant drop in o-cresol concentration was observed after 24 hours of aeration. As depicted in Figures 4.37 to 4.40, the o-cresol removal efficiencies as high as > 99% that were achieved in the reactors in less than one week after commissioning the study, were sustained thereafter. This indicates that microorganisms which degrade phenol from a phenol-bearing wastewater can be adapted to treat effectively other hazardous phenolic compounds such as o-cresol very rapidly.

Figure 4.42 shows the diurnal variation in effluent suspended solids exhibited by the four reactors. The concentration of effluent suspended solids from the sequencing batch reactors decreased continuously throughout the start-up phase. It is clear from Figure 4.42 that the concentration of suspended solids in all the effluents was about 10 mg/l. It is apparent that the feed o-cresol concentration did not have any adverse impact on the effluent suspended solids and the settleability of the sludge.

The dynamic loading study which was carried on SBR-4, is shown in Figure 4.43. As can be seen from this figure, the influent o-cresol concentration was stepped gradually (by 50 mg/l

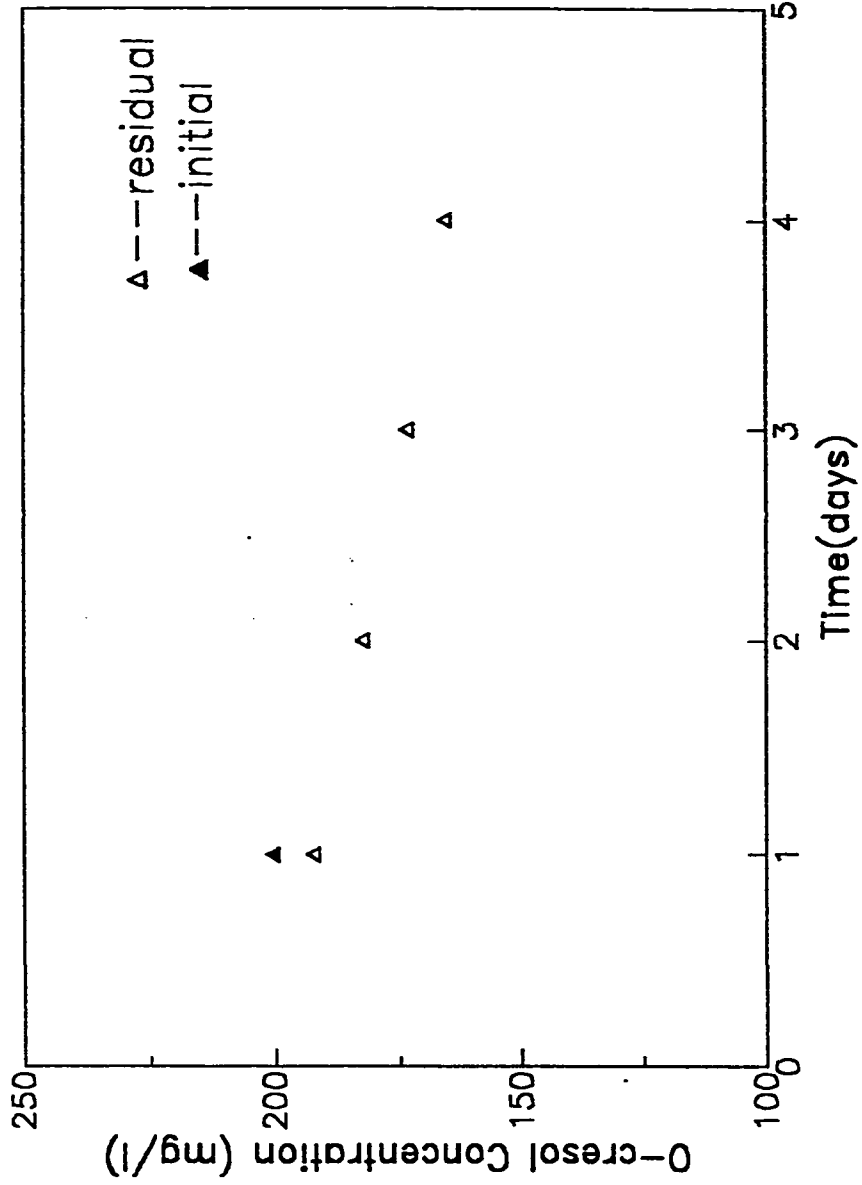


Fig. 4.41 Residual O-cresol Concentration

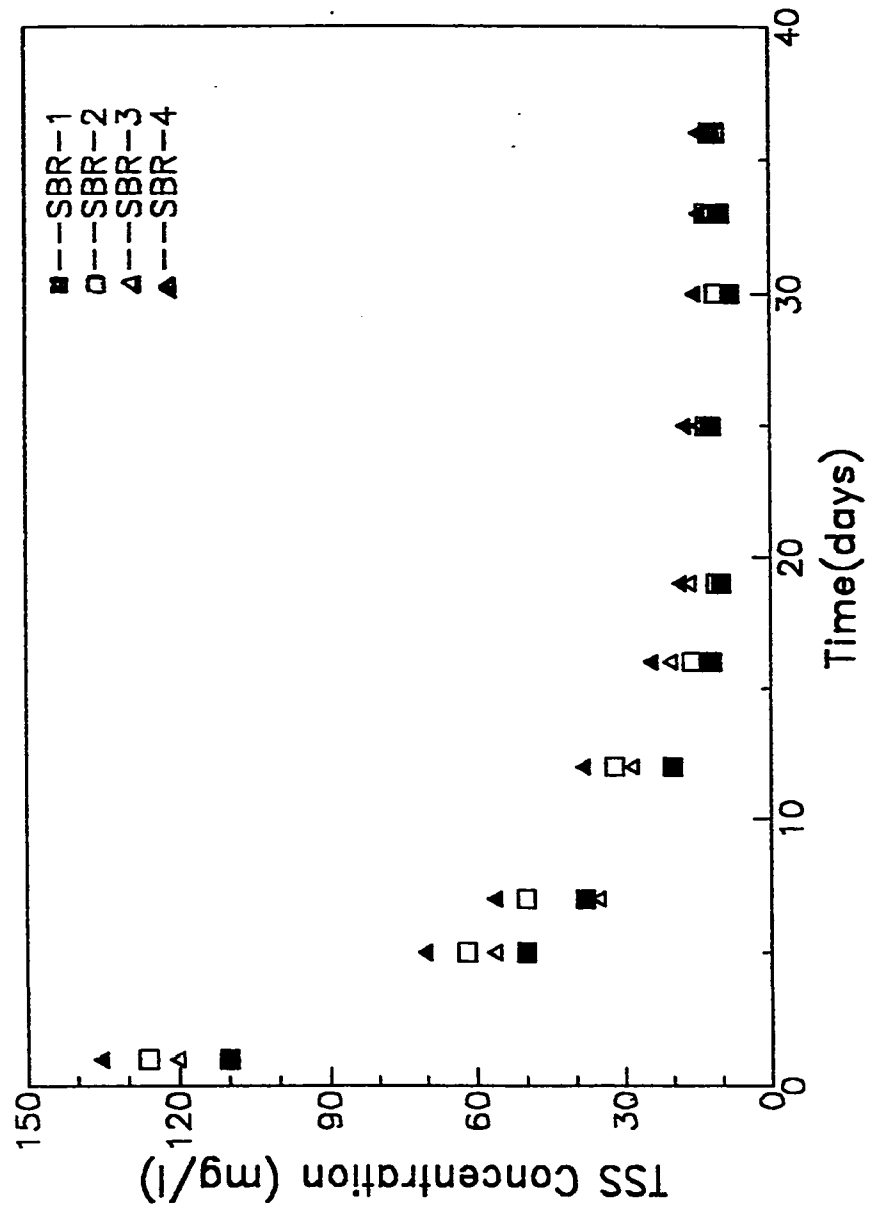


Fig. 4.42 Effluent Concentration of TSS In The SBRs During Phase-I, Cresol Study

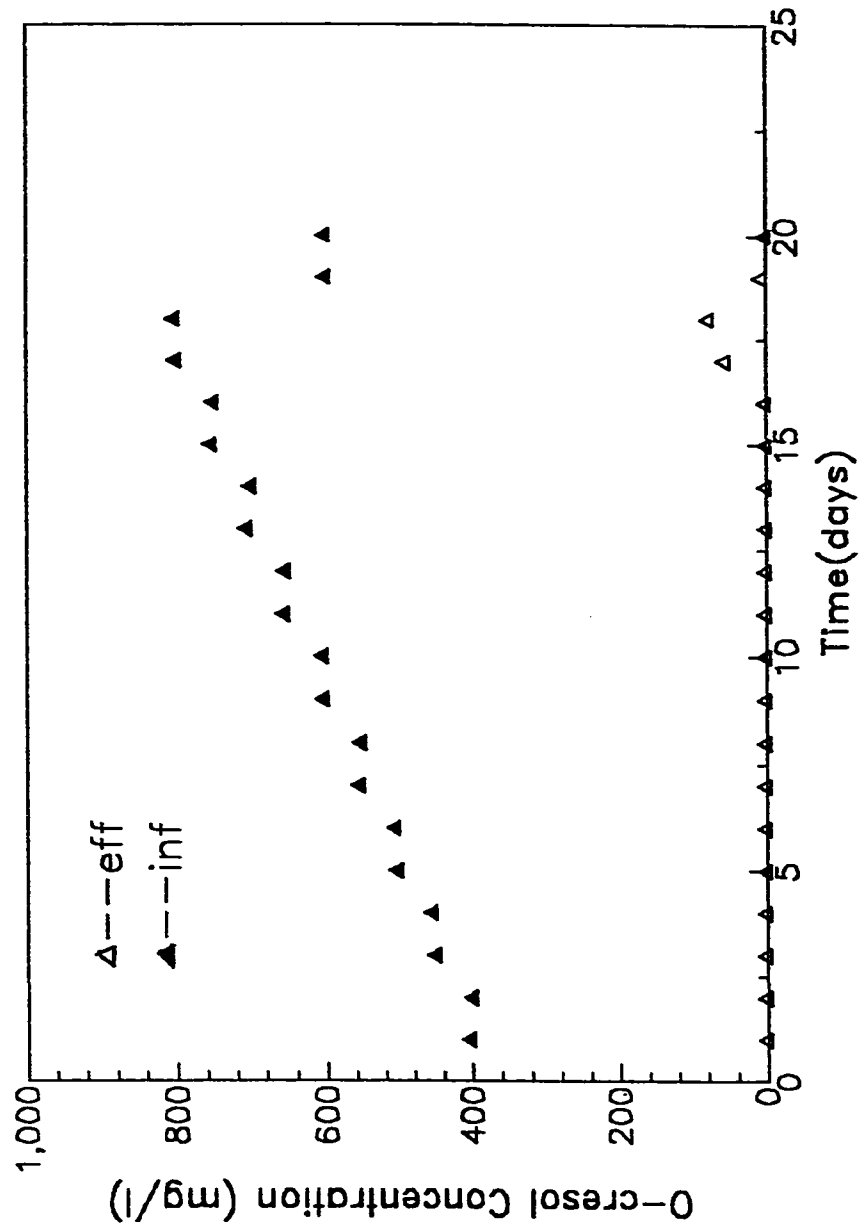


Fig. 4.43 Dynamic Loading Study of O-cresol

of o-cresol every two days) to reach the highest concentration of 750 mg/l that the SBR can successfully treat, without exceeding an effluent concentration of 1 mg/l.

Although it is reported in the literature (79) that concentrations of o-cresols higher than 250 mg/l are toxic and hence non-biodegradable, the outstanding finding of this study clearly demonstrates the biodegradability of o-cresol at concentrations as high as 750 mg/l.

4.2.2 Phase-II: Organic Loading Study

In this phase, the reactors were operated under a constant SRT of 14 days and different organic loading rates. The organic loading rates selected for the purpose of this study, were 100, 200, 300 and 600 mg/l for reactors 1, 2, 3 and 4, respectively. This phase was carried out to investigate the effect of different organic loading rates at constant SRT and subsequently to choose the highest concentration of o-cresol that can be treated successfully. Table 4.5 gives a summary of the results during this phase. The summary includes the average values of the influent and effluent concentrations of o-cresol, TSS, VSS, BOD, COD, Total-p, TKN, alkalinity and chloride, in addition to the MLSS, MLVSS and SVI. It is noteworthy that the reported values in the table are the averages taken over a period

Table 4.5: Reactors Performance During Phase II - Cresol Study

| Reactor | SBR-1 | SBR-2 | SBR-3 | SBR-4 |
|-----------------------------------|----------|----------|----------|----------|
| Influent o-cresol Conc. (mg/l) | 103(44)* | 203(45) | 302(45) | 600(44) |
| S.D.** | 3.5 | 3 | 2 | 3 |
| Effluent o-cresol Conc. (mg/l) | 0.5(44) | 0.45(45) | 0.5(45) | 0.6(44) |
| S.D. | 0.06 | 0.05 | 0.07 | 0.1 |
| MLSS (mg/l) | 1208(8) | 1367(8) | 1593(8) | 2285(8) |
| S.D. | 19 | 48 | 51 | 114 |
| MLVSS (mg/l) | 898(8) | 1038(8) | 1193(8) | 1736(8) |
| S.D. | 14 | 36 | 36 | 86 |
| Influent TSS (mg/l) | 162(2) | 162(2) | 162(2) | 162(2) |
| S.D. | 8 | 8 | 8 | 8 |
| Effluent TSS (mg/l) | 10.6(20) | 11(20) | 11.6(20) | 12(20) |
| S.D. | 2 | 2 | 2 | 7 |
| Influent VSS (mg/l) | 122(2) | 122(2) | 122(2) | 122(2) |
| S.D. | 8 | 6 | 6 | 6 |
| Effluent VSS (mg/l) | 10.4(20) | 10.8(20) | 11.2(20) | 11.5(20) |
| S.D. | 2 | 2 | 2 | 4 |
| Influent BOD (mg/l) | 237(20) | 391(20) | 558(20) | 1043(20) |
| S.D. | 5 | 10 | 8 | 9 |
| Effluent BOD (mg/l) | 4.7(20) | 4.9(20) | 4.9(20) | 5.1(20) |
| S.D. | 0.4 | 0.8 | 0.7 | 0.9 |
| Influent COD (mg/l) | 330(14) | 580(14) | 840(14) | 1590(14) |
| S.D. | 5 | 8 | 6 | 8 |
| Effluent COD (mg/l) | 37(14) | 35(14) | 38(14) | 35(14) |
| S.D. | 5 | 4 | 6 | 5 |

| Reactor | SBR-1 | SBR-2 | SBR-3 | SBR-4 |
|---------------------------------------|----------------|----------------|----------------|----------------|
| SVI (ml/g) S.D. | 58(10) 4 | 59(10) 5 | 61(10) 5 | 95(10) 26 |
| Influent total-p (mg/l) S.D. | 9.5(2) 0.4 | 9.5(2) 0.4 | 9.5(2) 0.4 | 9.5(2) 0.4 |
| Effluent total-p (mg/l) S.D. | 7.1(2) 0.3 | 6.9(2) 0.6 | 7.2(2) 0.6 | 6.7(2) 0.8 |
| Influent TKN (mg/l) S.D. | 29(2) 3 | 29(2) 3 | 29(2) 3 | 29(2) 3 |
| Effluent TKN (mg/l) S.D. | 14.1(2) 0.3 | 13.8(2) 0.3 | 13.6(2) 0.6 | 13.1(2) 0.6 |
| Influent Alkalinity (mg/l) S.D. | 283(2) 6 | 283(2) 6 | 283(2) 6 | 283(2) 6 |
| Effluent Alkalinity (mg/l) S.D. | 165(2) 3 | 171(2) 4 | 162(2) 3 | 159(2) 5 |
| Influent Chloride (mg/l) S.D. | 1350(2) 7 | 1350(2) 7 | 1350(2) 7 | 1350(2) 7 |
| Effluent Chloride (mg/l) S.D. | 1325(2) 3 | 1310(2) 6 | 1300(2) 7 | 1287(2) 10 |

*Parenthesis indicate the number of samples
**Standard deviation

of one and half month except for the MLSS and MLVSS, which were averaged over the third turnover of the SRT.

MLSS

The concentration of the MLSS and MLVSS in all the four reactors decreased with time as shown in Figures 4.44 and 4.45, respectively. The reductions in the MLSS were 13%, 27%, 35% and 45% for reactors 1, 2, 3 and 4, respectively. This decrease was merely due to sludge wastage and due to the batch nature of the SBRs, as the MLSS and MLVSS concentrations did not remain constant during the course of an operating cycle (60). It is apparent from Figures 4.44 and 4.45 that the MLSS and MLVSS of the four reactors depicted the same trend of a rapid decrease in the first turnover followed by a milder drop during the course of the second and third turnovers. This could be due to the transient condition in the beginning of this phase, in which the loss of the MLSS and MLVSS by wastage was greater than the buildup. With time equilibrium which ends this phase was reached. As can be seen from Figures 4.44 and 4.45 and Table 4.5 the rate of MLSS and MLVSS decrease was greater in the reactors that treated higher concentration of o-cresol, i.e. the lowest rate of biomass loss was encountered in SBR-1, which treated 100 mg/l of o-cresol, and the highest rate was encountered in SBR-4, which treated 600 mg/l of o-cresol. This could be due to that, during the first turnover the rate of biomass loss continued to subside

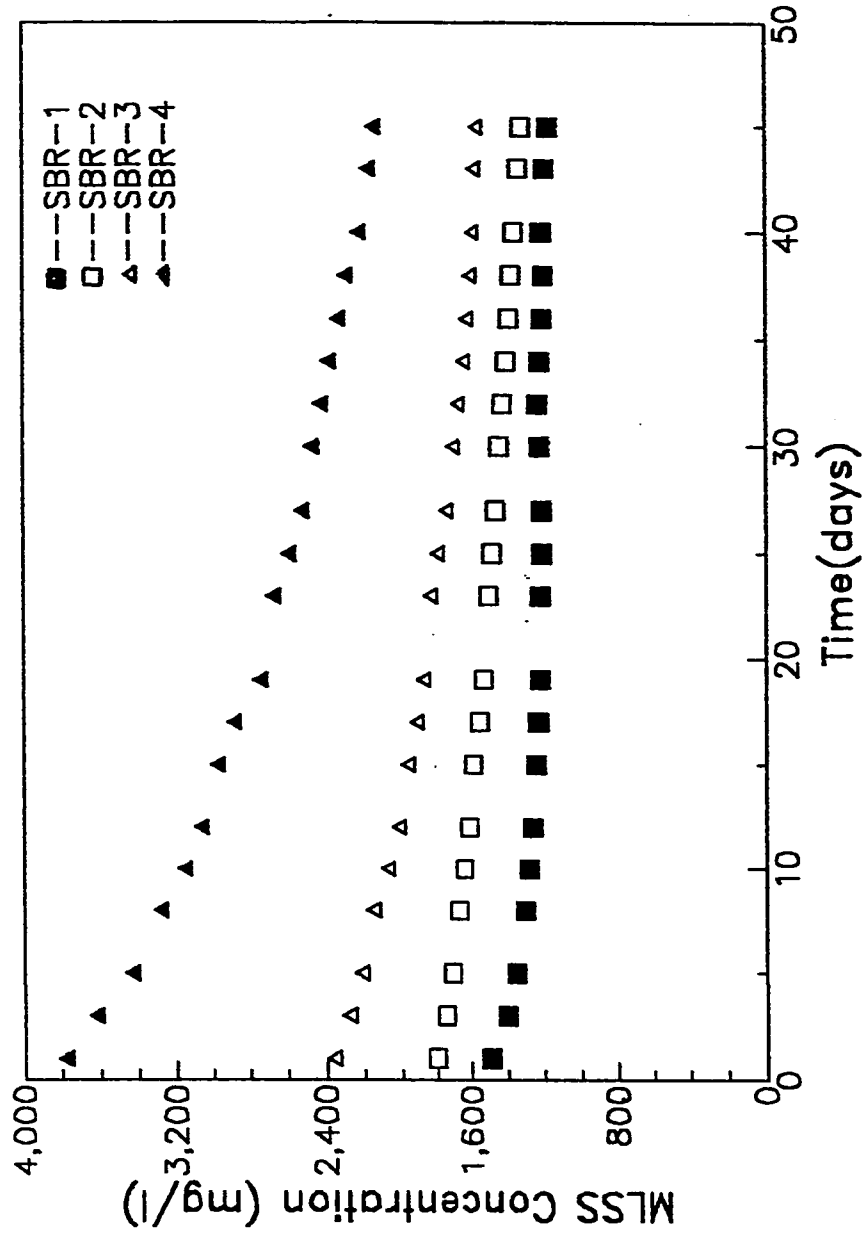


Fig. 4.44 Concentration of MLSS In The SBRs During Phase-II, Cresol Study

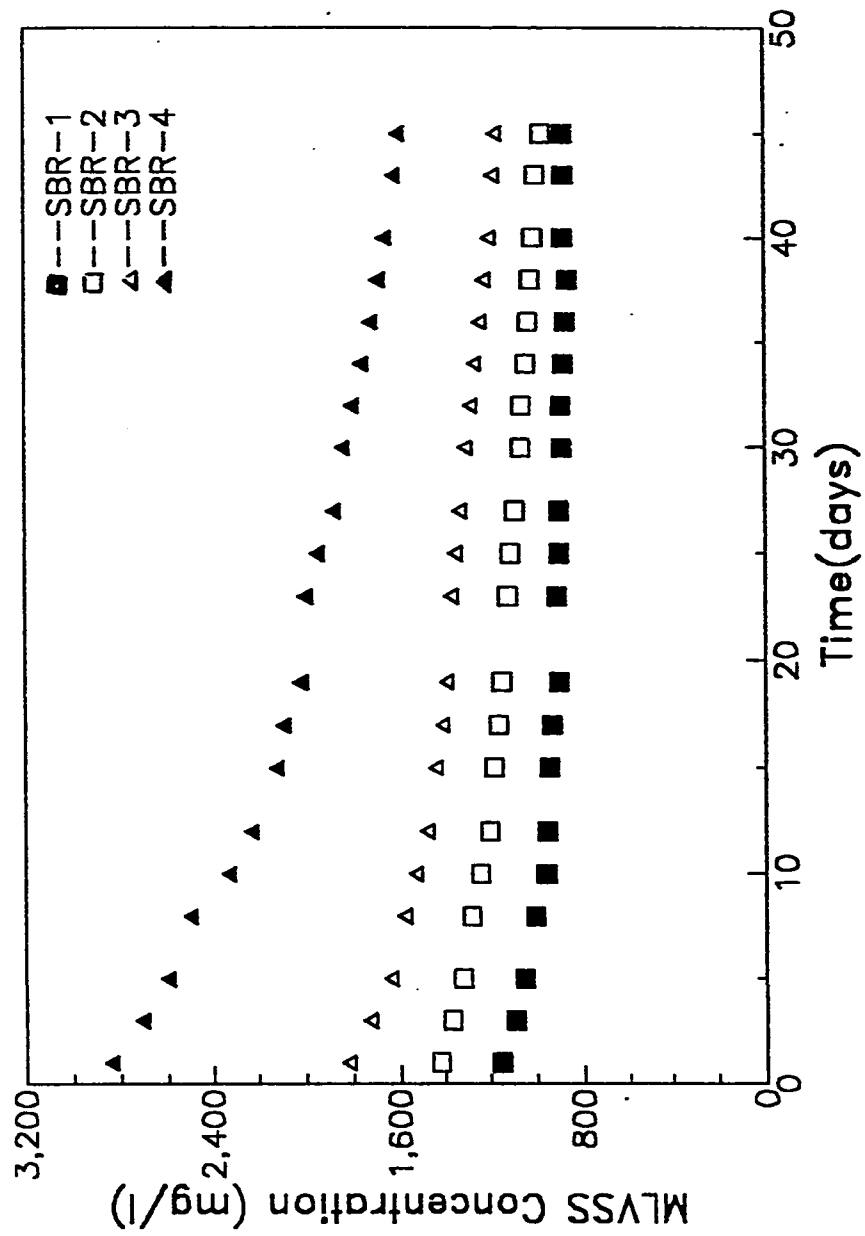


Fig. 4.45 Concentration of MLVSS In The SBRs During Phase-II, Cressol Study

until it stabilized towards the end of the third turnover. The average values of the F/M ratio during the third turnover of SRT were 0.11, 0.2, 0.25 and 0.35 $\frac{\text{mg/l of o-cresol}}{\text{mg/l of MLVSS}}$ for reactors 1, 2, 3 and 4, respectively. It must also be emphasized that the high ratio of F/M prevalent during the third turnover did not impair performance or adversely effect the quality of the effluent.

Effluent o-cresol

Figures 4.46, 4.47, 4.48 and 4.49 show the temporal profile of the concentrations of o-cresol in the influent wastewater and the effluents from reactors 1, 2, 3 and 4 respectively. As apparent from these four figures, the influent concentration of the o-cresol fluctuated for all the reactors. This is due to the manual operation and the presence of some aromatic organic compounds in the raw sewage that contributed absorbance at the wave length at which the o-cresol was measured. As can be seen from Table 4.5 the standard deviation of the effluent concentration of the o-cresol for all the reactors was less than 0.1 mg/l. This indicates that not only were the effluent concentrations of the o-cresol from all the reactors less 1 mg/l but also they exhibited little variability. It is also clear from Table 4.5 that the percentage removal of o-cresol in all the reactors was > 99%. This indicates that o-cresol can be treated effectively at mean SRT of 14 days and at concentrations as high as 600 mg/l.

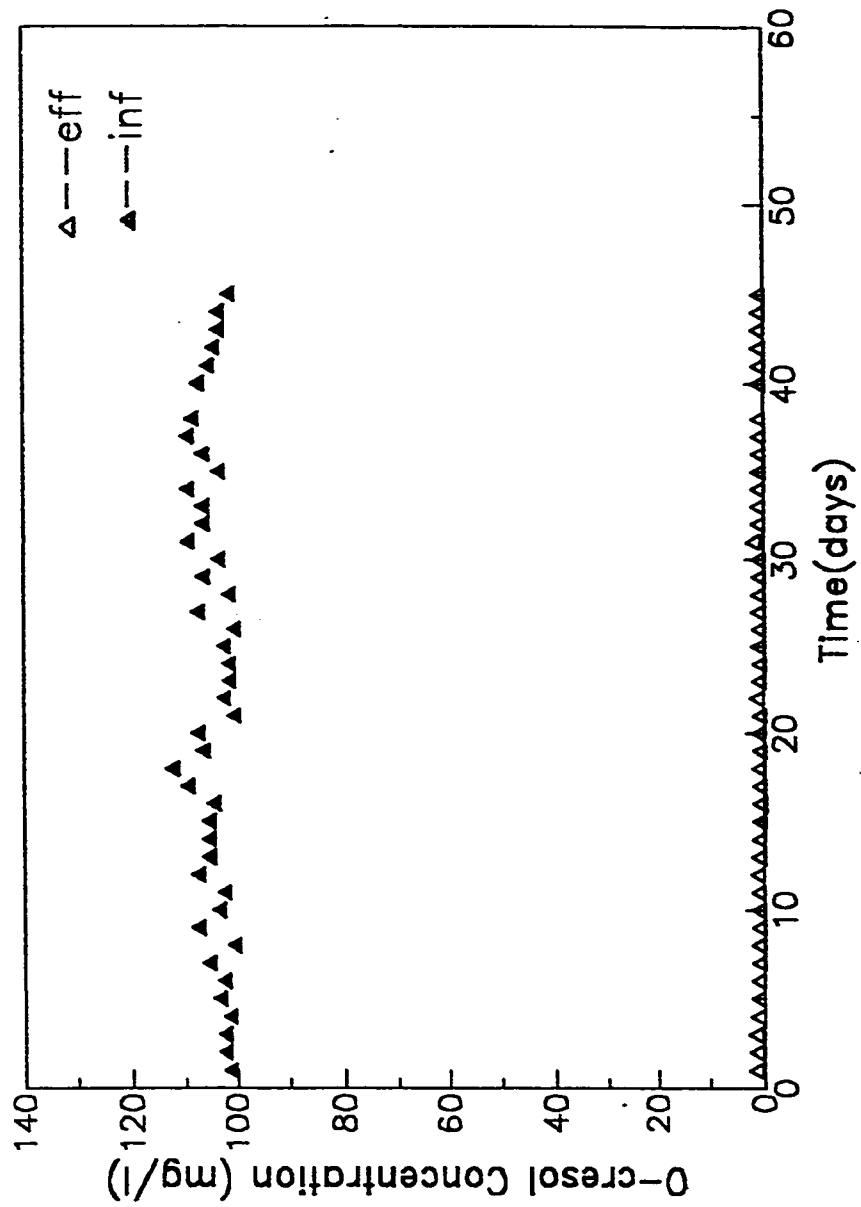


Fig. 4.46 Influent and Effluent O-cresol Concentration During Phase-II, Reactor 1

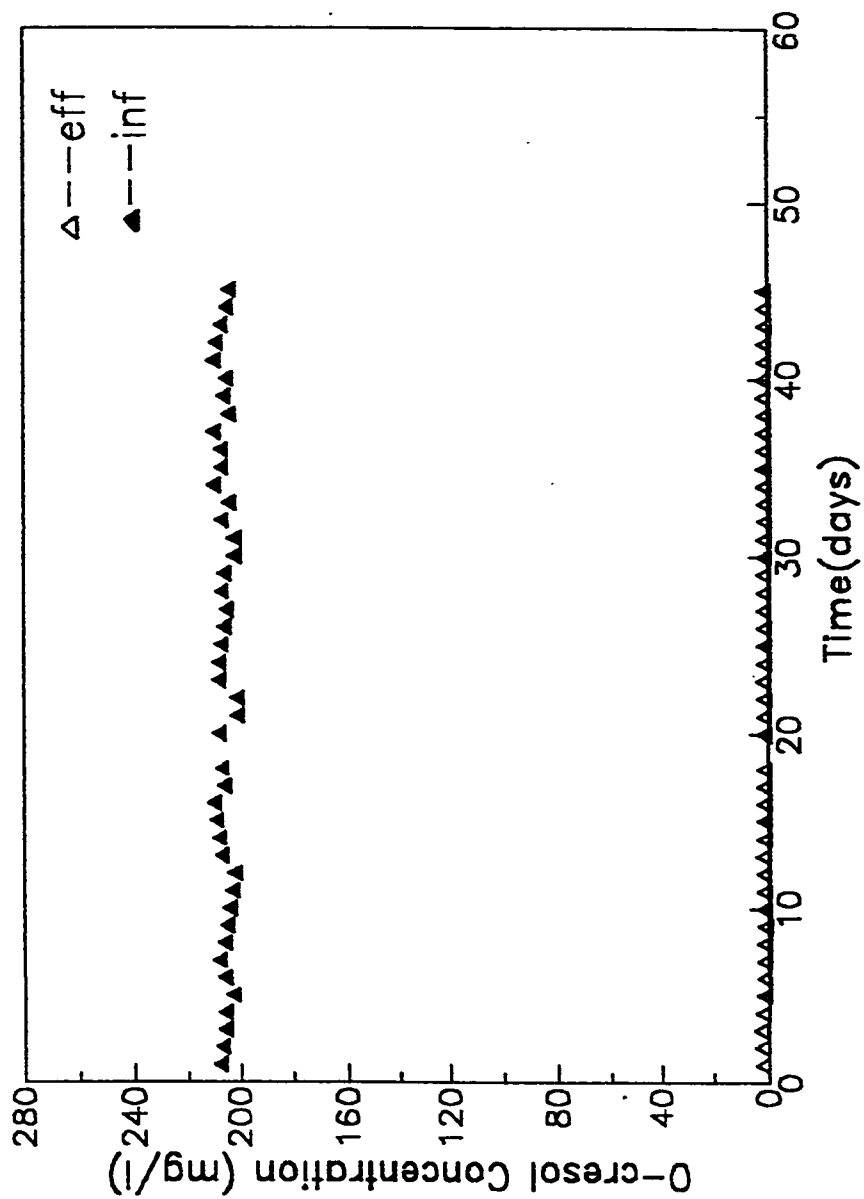


Fig. 4.47 Influent and Effluent O-cresol Concentration During Phase-II, Reactor 2

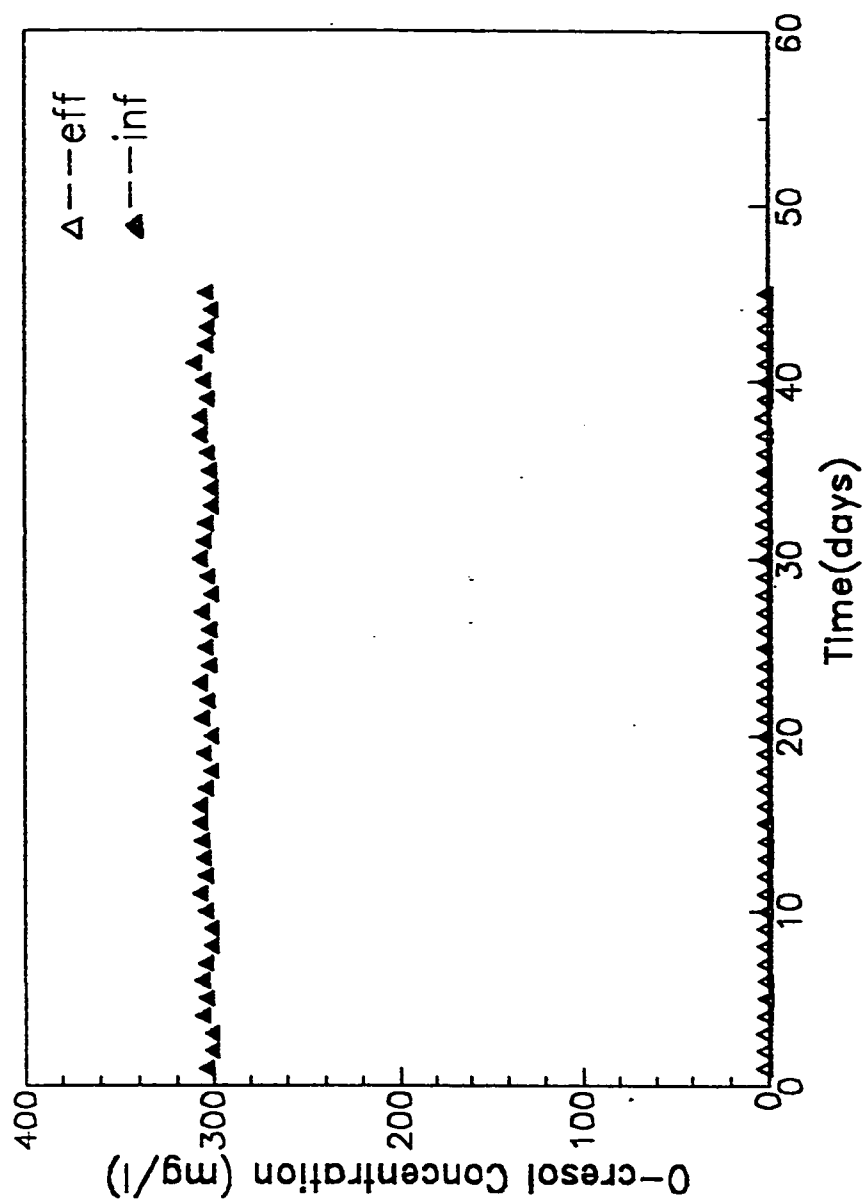


Fig. 4.48 Influent and Effluent O-cresol Concentration During Phase-II, Reactor 3

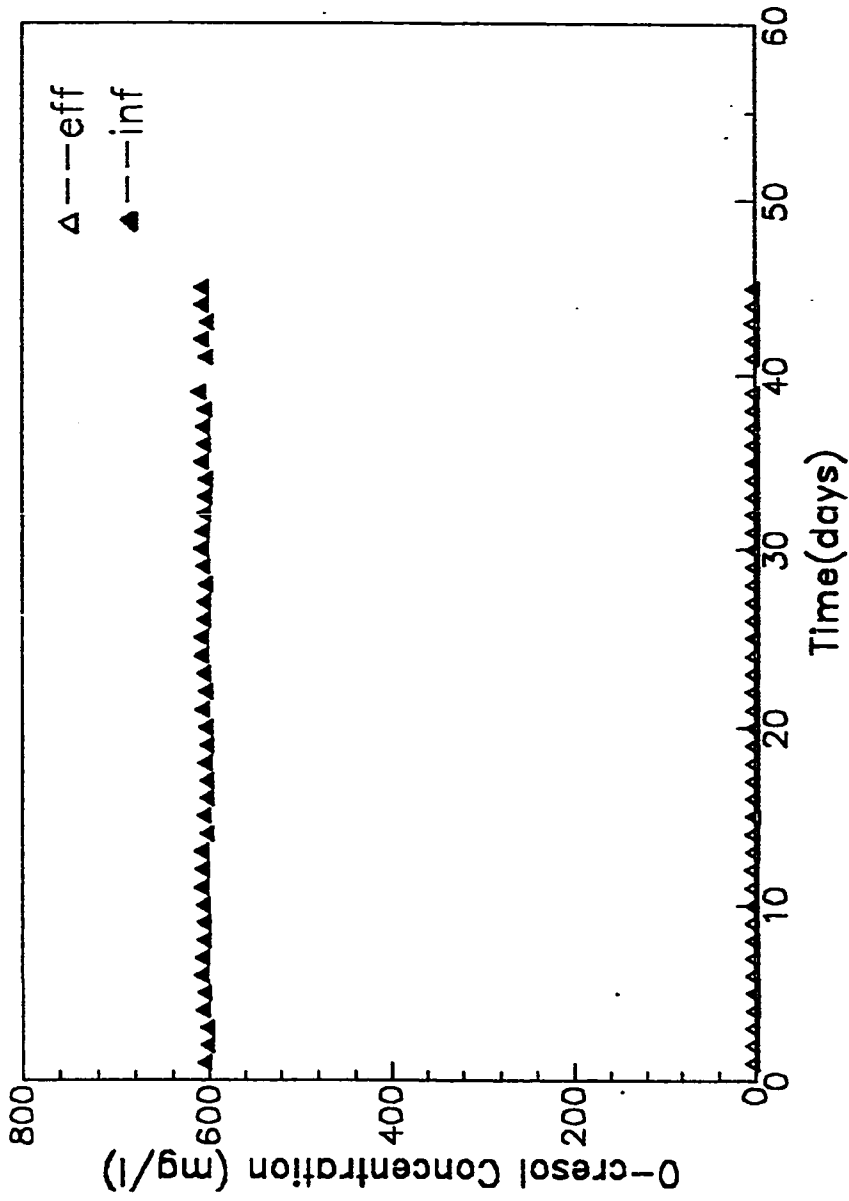


Fig. 4.49 Influent and Effluent O-cresol Concentration During Phase-II, Reactor 4

Drinkwater, et al. (77) attained 99.1% removal of a 3 mg/lo-cresol waste using activated sludge system operated at an HRT of 2 days. The MLSS was maintained close to 3790 mg/l by wasting necessary amount of the mixed liquor. The aeration time of the reactor was 20 hours. It is clear from this comparison that our system achieved the same removal efficiencies at lower levels of the mixed liquor concentrations.

Effluent BOD and COD

The influent and effluent BOD and COD for reactors 1, 2, 3 and 4 are shown in Figures 4.50, 4.51, 4.52 and 4.53, respectively. As apparent from these four figures the influents concentration of COD and BOD fluctuated slightly in all the reactors. This is due to manual operation and due to the biological activity even though the wastewater was stored in the refrigerator. As can be seen from Table 4.5 the concentrations of the effluent BOD from all the reactors, which averaged around 5 mg/l, were rather consistent as reflected by standard deviations which were less than 1 mg/l. Additionally the percentage removals of the BOD during this phase were 98%, 98.8%, 99% and 99.5% for reactors 1, 2, 3 and 4, respectively. This indicates that all the reactors affected essentially the same BOD removal efficiency.

The average percentage removals of the COD during this phase were 88.9%, 94%, 95.5% and 98% for reactors 1, 2, 3 and 4,

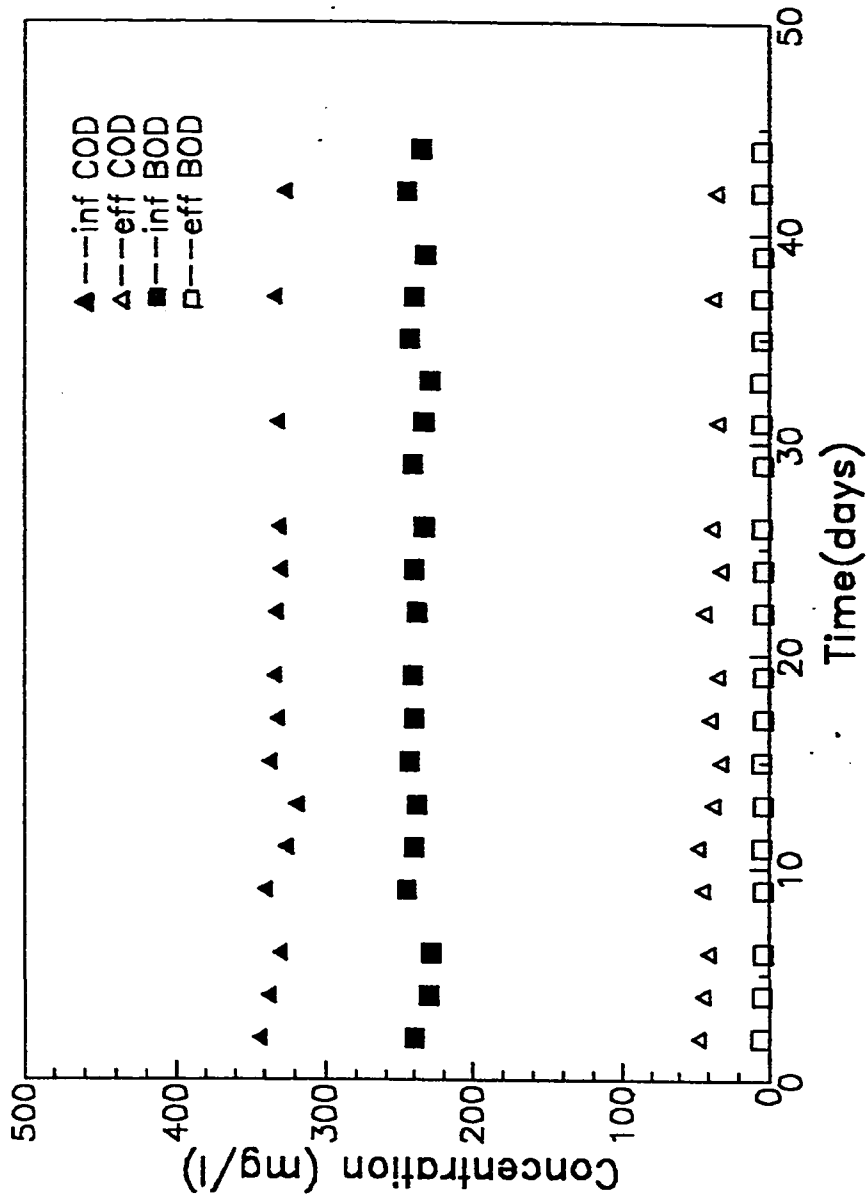


Fig. 4.50 Influent and Effluent BOD and COD Concentration in Reactor 1 During Phase-I, Cresol Study

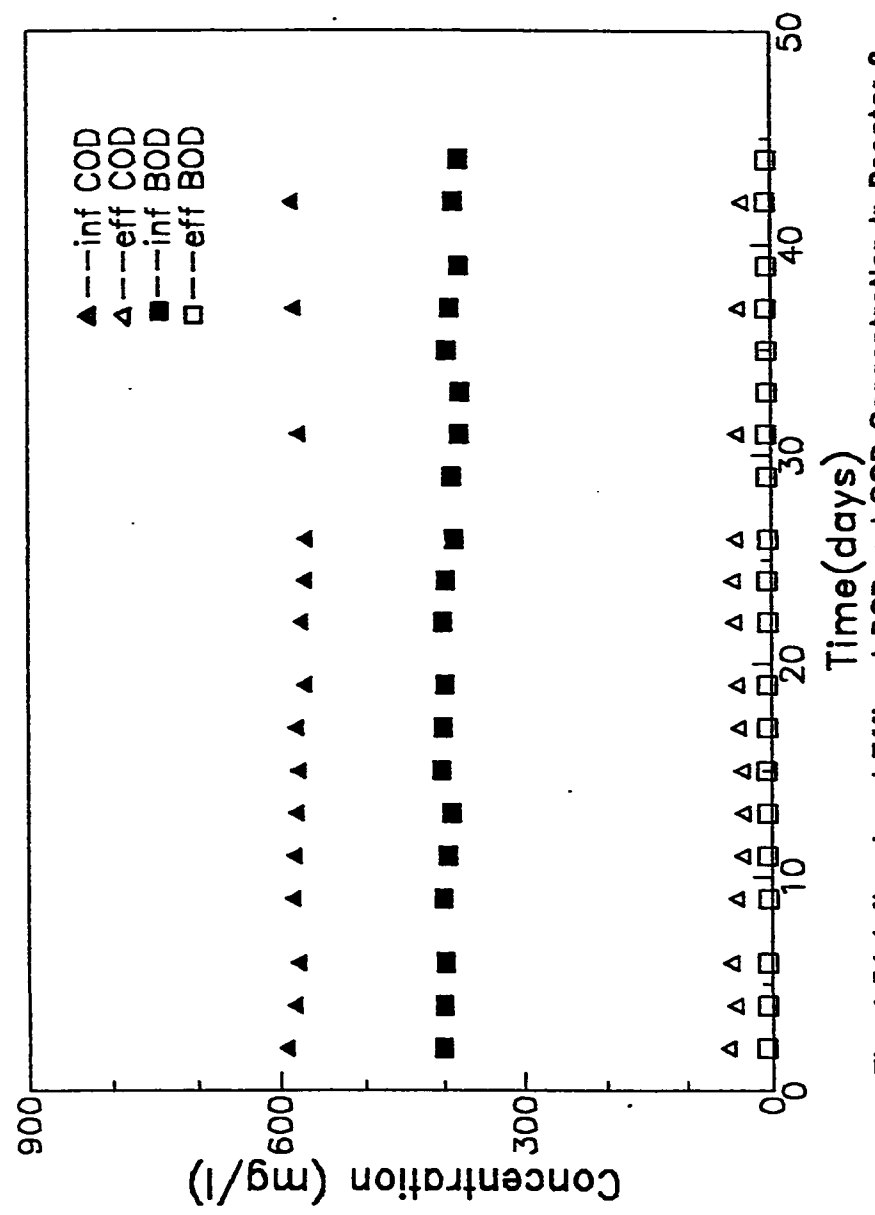


Fig. 4.51 Influent and Effluent BOD and COD Concentration In Reactor 2 During Phase-II, Cresol Study

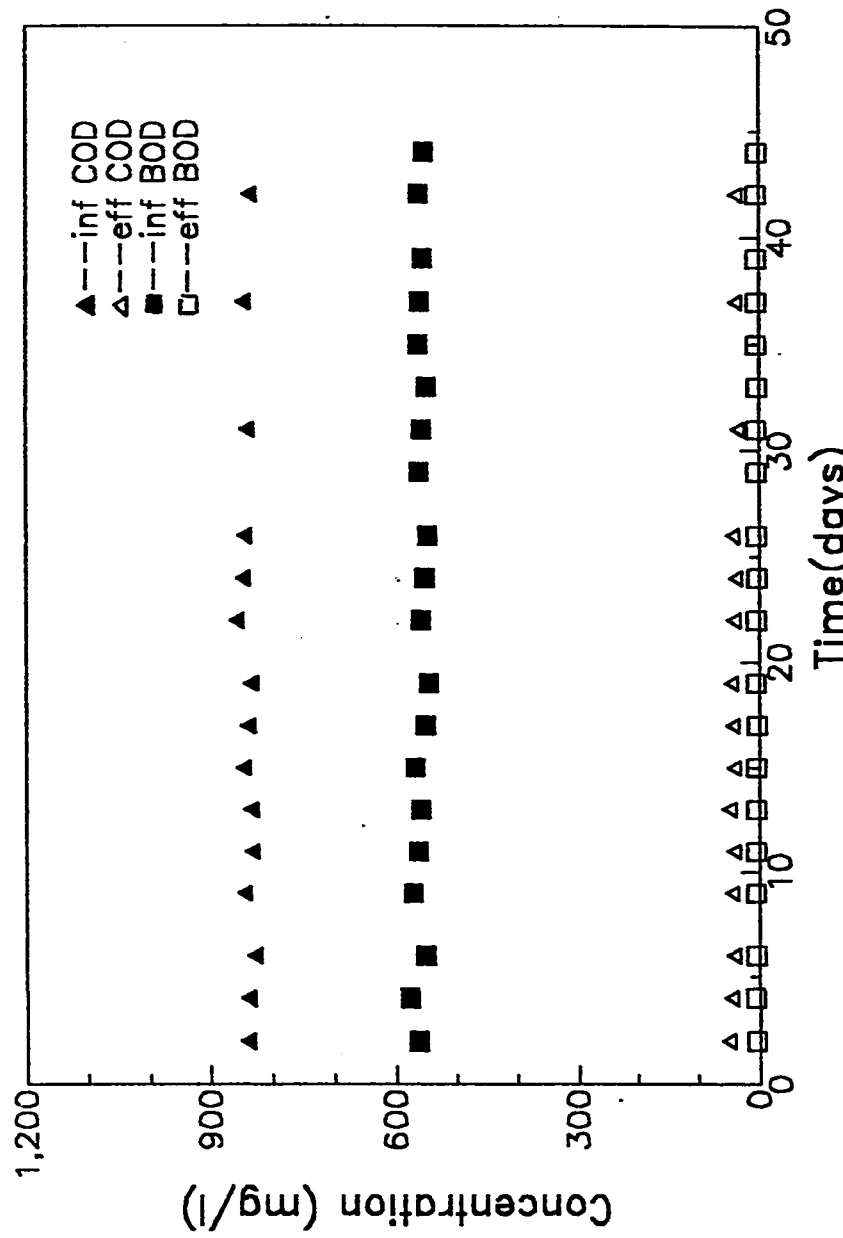


Fig. 4.52 Influent and Effluent BOD and COD Concentration in Reactor 3 During Phase-II, Cresol Study

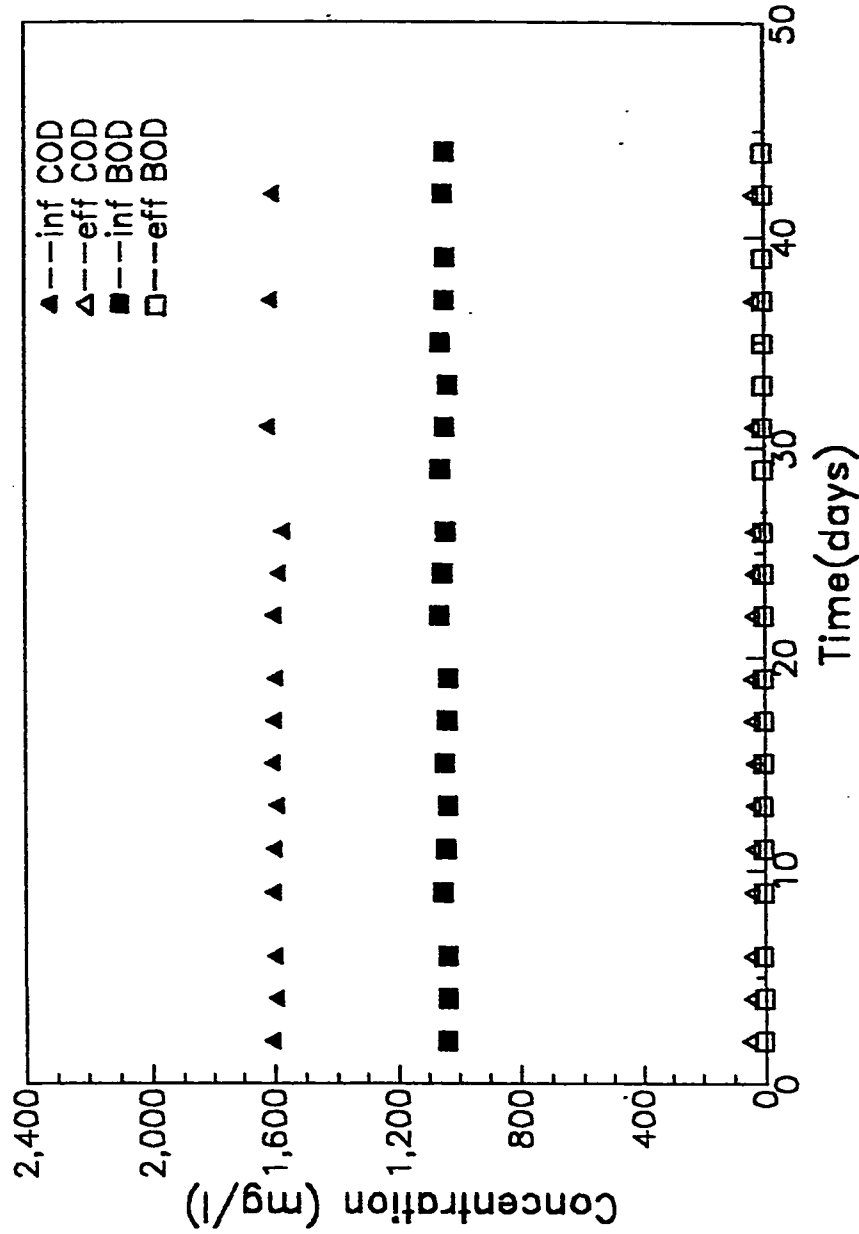


Fig. 4.53 Influent and Effluent BOD and COD Concentration in Reactor 4 During Phase-II, Cresol Study

respectively. Surprisingly, it was found that the change in the influent concentration had no effect on the effluent concentration which was found to be about 35 mg/l. This is due to the nature of the raw sewage which contains non-biodegradable chemicals which are not reflected in the BOD test. As apparent from Table 4.5 the standard deviation of the effluent COD in all the reactors was about 6 mg/l. This relatively high variability was due to that of the influent raw sewage and not due to the residual o-cresol. Comparing these results with the results of the phenol study, it is clear that the removal efficiencies of both systems are similar. However, this is expected since the operating strategies of the reactors and compound treated in the reactors were chemically similar.

Effluent TSS and VSS

The concentration of the effluents TSS and VSS are shown in Figures 4.54 and 4.55 respectively. As shown in Table 4.5 the average concentration of effluents TSS and VSS in the reactors were about 12 mg/l and their standard deviations were about 3 mg/l. This indicates that the effluents TSS and VSS were consistent during this phase. It is apparent that sludge wastage did not have any adverse impact on the effluent suspended solids and the settleability of the sludge. As depicted in Figures 4.54 and 4.55, the differences between the TSS and VSS are insignificant. This indicates that all the suspended solids are

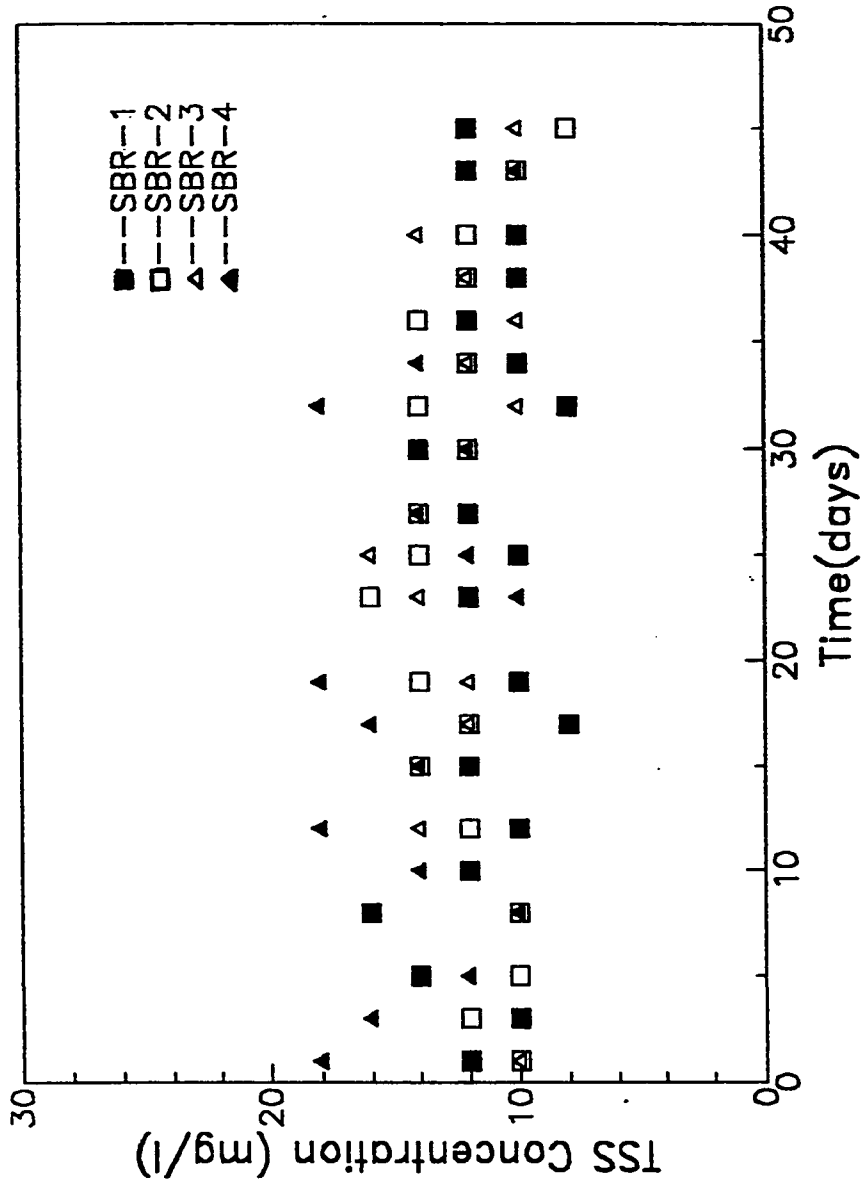


Fig. 4.54 Effluent Concentration of TSS In The SBRs During Phase-II, Cresol Study

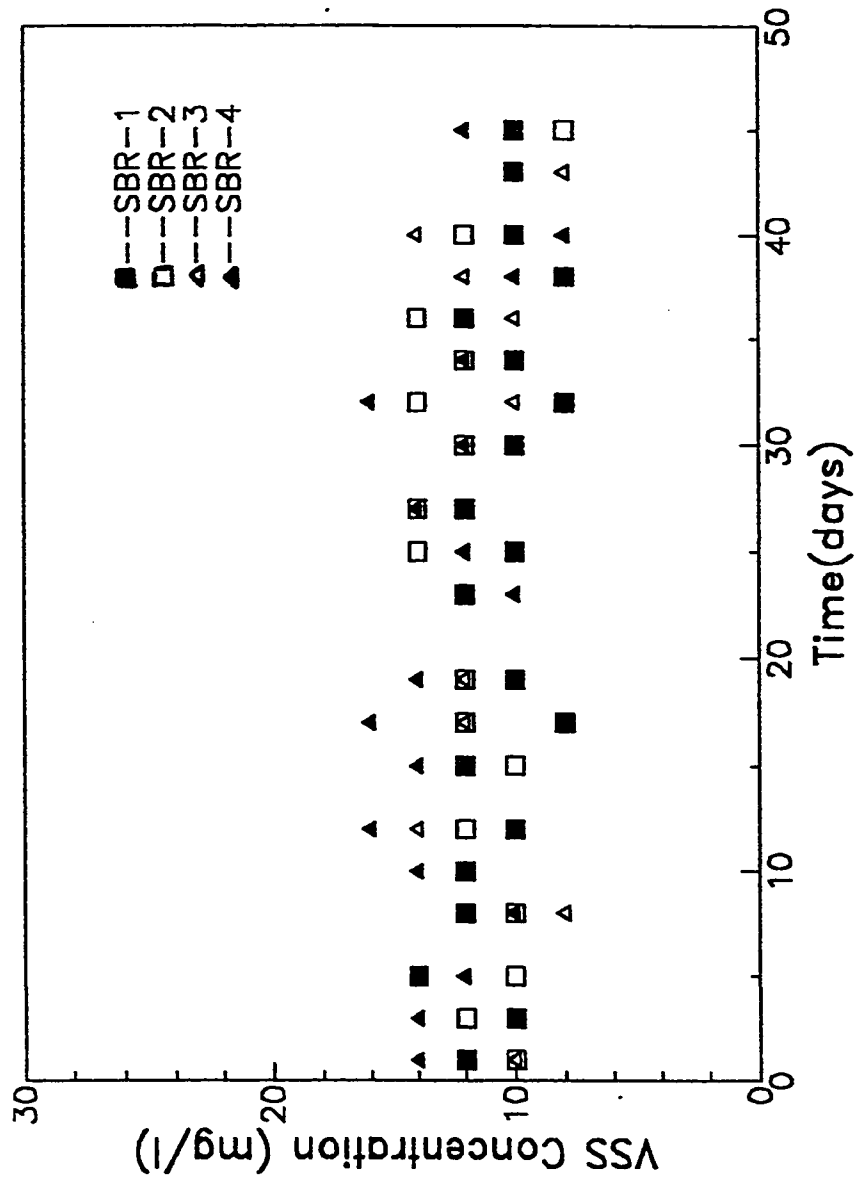


Fig. 4.55 Effluent Concentration of VSS In The SBRs During Phase-II, Cresol Study

biological solids.

The average effluent suspended solids in this phase of the study was about 12 mg/l and in the phenol study was about 12%. It is clear from the results of studies that the two chemicals impacted sludge settleability to the same extent since both systems were operated under identical conditions.

SVI

The SVI was calculated according to equation 4.1. Figure 4.56 shows the variation of the SVI values during this phase. As depicted in Figure 4.56, the SVI increased slightly with time from about 50 to 60 ml/g in reactors 1, 2 and 3. This increase in the SVI values with operating time must not be attributed to the reduction in the MLVSS concentration, but rather to the change in settling properties of the sludge. As shown in Table 4.5, the average values of the SVI were 58, 59, 61 ml/g for reactors 1, 2 and 3 respectively. This indicates that reactors 1, 2 and 3 have very compact sludge.

For SBR-4, the SVI decreased with time from 145 ml/g to 75 ml/g. This initial high SVI is owed to the disturbance of the culture of the SBR-4 during the start-up phase (during dynamic loading study), which took the microbial culture about 20 days to return back to its normal condition. Additionally, it is clear from Figure 4.56 that the SVI of SBR-4 stabilized around 80 ml/g after

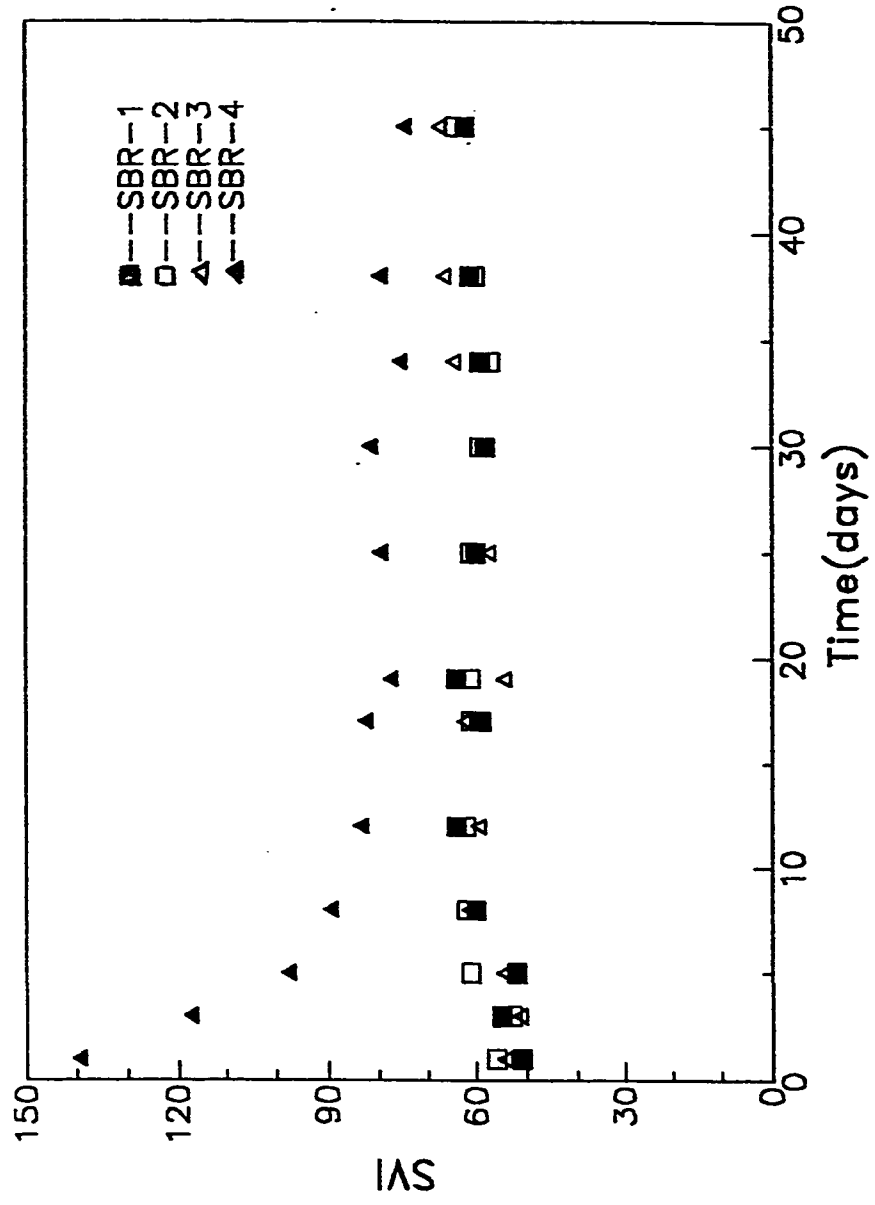


Fig. 4.56 Sludge Volume Index In The SBRs During Phase-II, Cresol Study

day 20 until the end of this phase. This indicates that SBR-4 ultimately accommodated compact sludge, and it also indicates high toxicant concentrations did not hinder sludge settleability. As apparent from Figure 4.56 and Figure 4.22, the trend of the SVI was similar. This is obvious since the operating conditions of the phenol and o-cresol were identical.

Nutrient Removal

The concentrations of TKN and total-p were analyzed only two times at the end of this phase. As can be seen from Table 4.5, the TKN decreased from 29 mg/l to 14.1, 14.6, 13/6 and 13.1 mg/l, respectively in SBR-1, SBR-2, SBR-3 and SBR-4. SBR-4 achieved the highest reduction in the TKN, since it synthesized more cells than all the others. The decrease in the influent TKN can be attributed to the utilization of nitrogen for the cell synthesis plus the conversion of organic nitrogen to ammonia nitrogen and subsequently to nitrite and nitrate nitrogen.

It is also evident from Table 4.5 that the total-p decreased from 9.5 mg/l to 7.2 and 6.9, 7.2 and 6.3 mg/l, respectively in SBR-1, SBR-2, SBR-3 and SBR-4. The decrease in the influent total-p can be attributed to the utilization of phosphorous for the cell synthesis. The BOD/N/P ratios for reactors 1, 2, 3 and 4 were 100/6.3/1, 100/3.7/10.7, 100/2.8/0.4 and 100/1.5/0.3, respectively. It is evident that these ratios did not match the

widely accepted BOD/N/P ratio. This could be due to the reasons mentioned earlier.

4.2.3 Phase III: Solids Residence Time Study

This phase was carried out to investigate the effect of different SRT on constant organic loading rate. In this phase, the influent concentration of the o-cresol of reactors 1, 2 and 3 was stepped to 600 mg/l gradually in about 20 days. The influent and effluent o-cresol concentration during the transient phase are shown in Figure 4.57. The mean SRT was chosen to be 5, 10 and 20 days for reactors 1, 2, 3 respectively. SBR-4 was not operated during this study. Table 4.6 gives a summary of the results during this phase. The summary includes the average values of the influent and effluent concentrations of o-cresol, TSS, VSS, BOD, COD, total-p, TKN, alkalinity and chloride in addition to the MLSS, MLVSS and SVI. The reported values in the table are the averages taken over a period of three turnovers of the SRT in each reactor except for the MLSS and MLVSS which were averaged over the third turnover period of the SRT in each reactor.

MLSS

The diurnal variations of concentrations of the MLSS and MLVSS are shown in Figures 4.58 and 4.59 respectively. It is worth noting that the levels of the MLSS and MLVSS were about

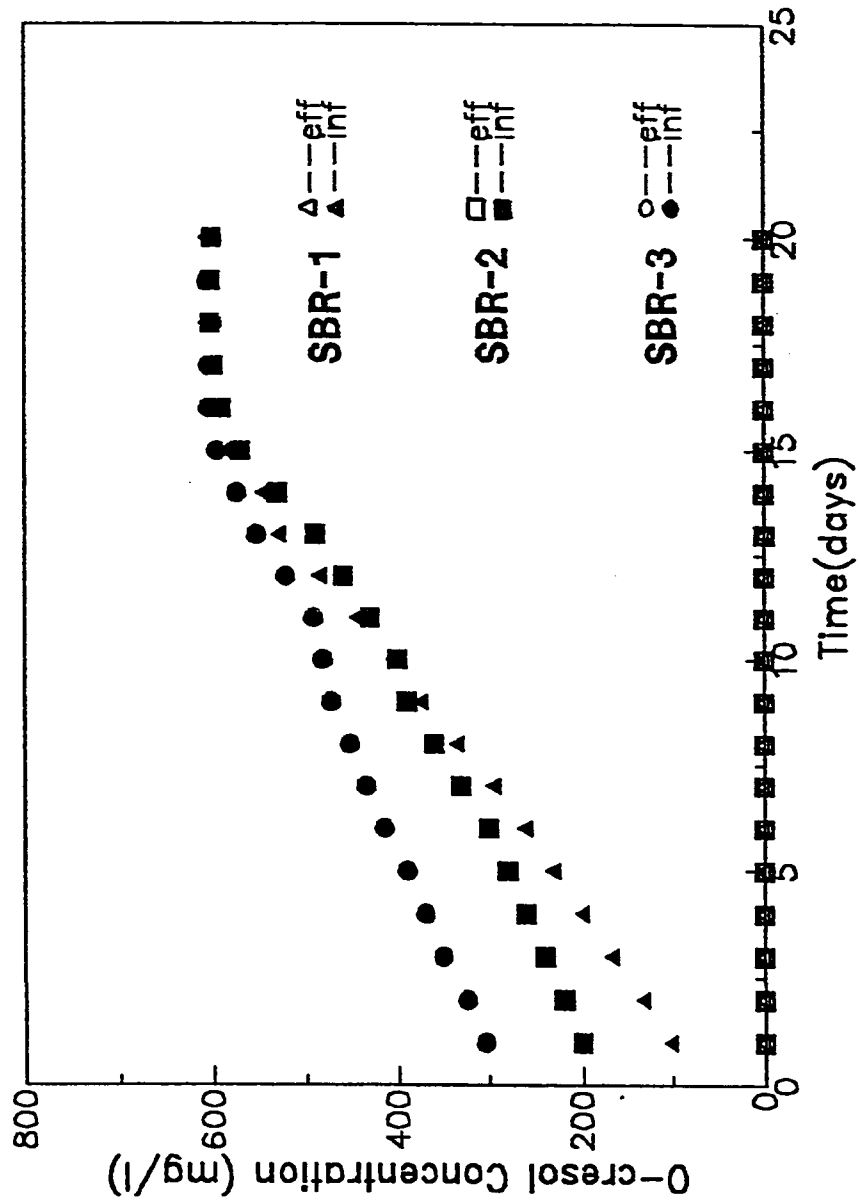


Fig. 4.57 Influent and Effluent O-cresol Concentration During Transient Phase

Table 4.6: Reactors Performance During Phase III - Cresol Study

| Reactor | SBR-1 | SBR-2 | SBR-3 |
|---|----------------|-----------------|-----------------|
| Mean SRT (days) | 5 | 10 | 20 |
| Influent o-cresol conc.(mg/l) S.D.** | 602(15)* 4 | 602(30) 3 | 602(50) 2 |
| Effluent o-cresol conc.(mg/l) S.D. | 38(15) 70 | 0.5(30) 0.05 | 0.5(50) 0.06 |
| MLSS (mg/l) S.D. | 1182(3) 266 | 1582(4) 41 | 2266(5) 13 |
| MLVSS (mg/l) S.D. | 914(3) 184 | 1186(4) 30 | 1768(5) 10 |
| Influent TSS (mg/l) S.D. | 178(2) 11 | 178(2) 11 | 178(2) 11 |
| Effluent TSS (mg/l) S.D. | 27(7) 25 | 12(12) 2.5 | 12(17) 2 |
| Influent VSS (mg/l) S.D. | 126(2) 9 | 126(2) 9 | 126(2) 9 |
| Effluent VSS (mg/l) S.D. | 25(7) 22 | 12(12) 2.5 | 12(17) 2 |
| Influent BOD (mg/l) S.D. | 1020(7) 14 | 1022(13) 13 | 1021(21) 12 |
| Effluent BOD (mg/l) S.D. | 72(7) 122 | 15 0.5 | 4.8 0.4 |
| Influent COD (mg/l) S.D. | 1560(7) 10 | 1556(13) 11 | 1558(21) 10 |
| Effluent COD (mg/l) S.D. | 122(7) 165 | 35(13) 4 | 33(21) 5 |

| Reactor | SBR-1 | SBR-2 | SBR-3 |
|------------------------------------|---------------|---------------|---------------|
| SVI (ml/g) S.D. | 80(6) 31 | 69(13) 9 | 70(18) 8 |
| Influent Total-p (mg/l) S.D. | 9(2) 1.5 | 8.7(2) 1 | 8.5(2) 1 |
| Effluent Total-p (mg/l) S.D. | 7.3(2) 0.4 | 6(2) 0.4 | 5.8(2) 0.6 |
| Influent TKN (mg/l) S.D. | 30(2) 2 | 32(2) 3 | 34(2) 3 |
| Effluent TKN (mg/l) S.D. | 20(2) 6 | 18.2(2) 2 | 17.6(2) 1 |
| Influent Alkalinity (mg/l) S.D. | 283(2) 10 | 275(2) 5 | 270(2) 7 |
| Effluent Alkalinity (mg/l) S.D. | 189(2) 7 | 165(2) 7 | 162(2) 8 |
| Influent Chloride (mg/l) S.D. | 1345(2) 15 | 1330(2) 12 | 1335(2) 13 |
| Effluent Chloride (mg/l) S.D. | 1325(2) 11 | 1310(2) 12 | 1295(2) 10 |

*Parenthesis indicate the number of samples
**Standard deviation

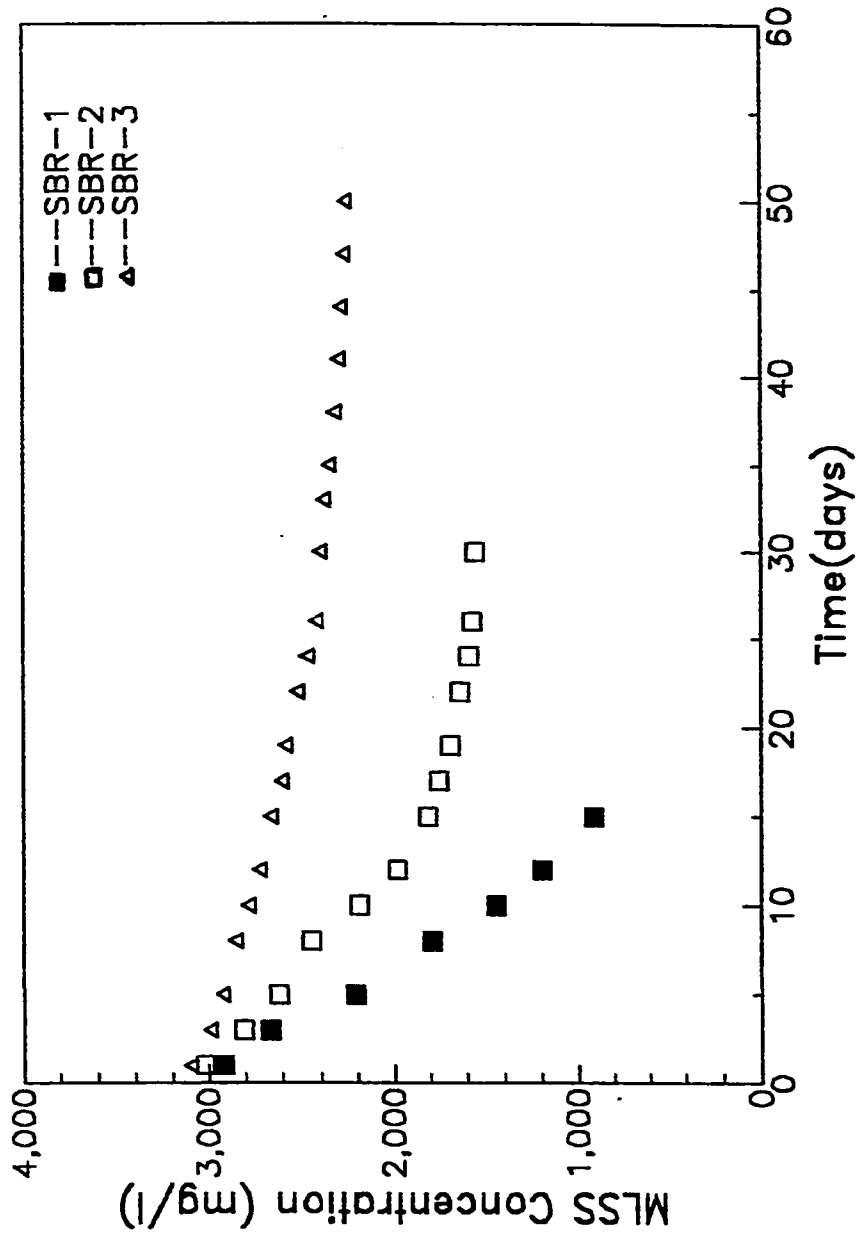


Fig. 4.58 Concentration of MLSS In The SBRs During Phase-III, Cresol Study

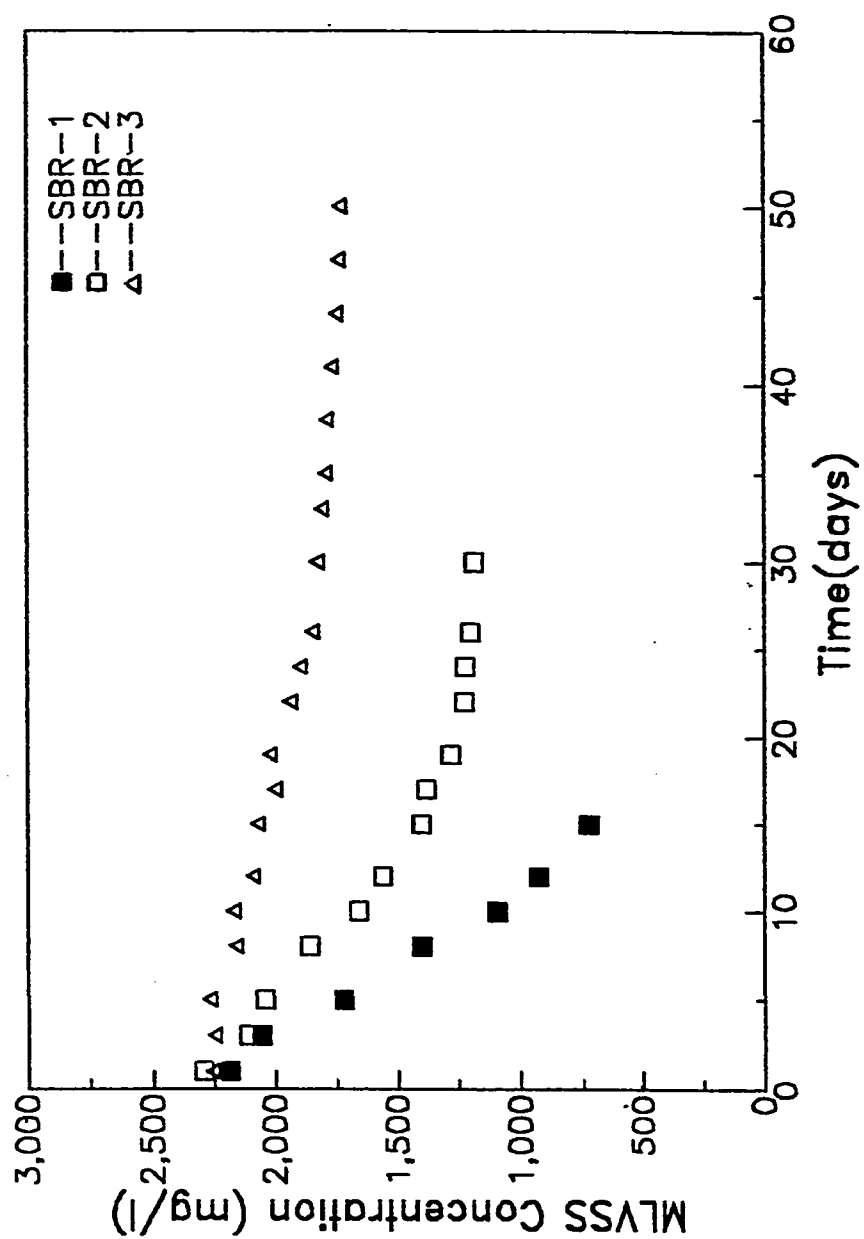


Fig. 4.59 Concentration of MLVSS In The SBRs During Phase-III, Cresol Study

3000 and 2200 mg/l, respectively in all the reactors at the beginning of this phase. As depicted in these figures, the expected decrease in the MLSS and MLVSS with decreasing SRT was observed. The MLSS decreased from 2915 mg/l on day 1 to 910 mg/l on day 15 in SBR-1, from 3024 mg/l on day 1 to 1535 mg/l on day 30 in SBR-2 and from 3090 mg/l on day 1 to 2320 mg/l on day 50 in SBR-3. It is also clear from these figures that SBR-1 did not reach the steady state condition, since its decrease in MLSS during the third turnover of SRT was very rapid (about 37% reduction of the MLSS level). However, it is also clear from Figure 4.58 that SBR-2 and SBR-3 did reach the steady state condition, since the decrease in their MLSS was steady in the third turnover of SRT of each reactor. As apparent from Figures 4.58 and 4.59, the rate of MLSS and MLVSS decrease was greater in the reactors that operated at lower mean SRT. However, this is expected, since the feed concentration was same in all the reactors and the sludge wastage was different, i.e. the wastage rate was higher in the reactor operated at the lowest SRT.

Effluent O-Cresol

Figures 4.60, 4.61 and 4.62 show the temporal profile of the concentrations of o-cresol in the influent wastewater and the effluents from reactors 1, 2 and 3, respectively. As depicted in Figure 4.60, the failure occurred in SBR-1, since its effluent concentration started increasing after the second turnover of SRT

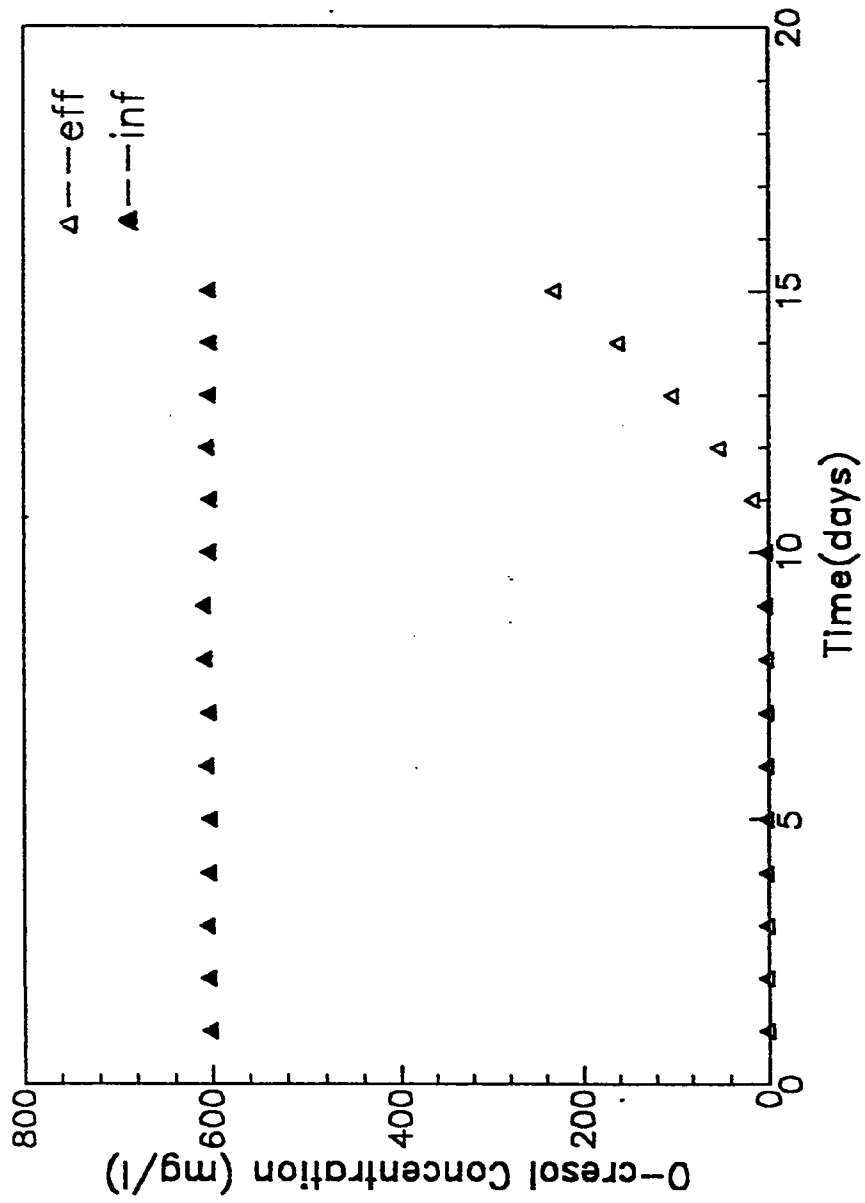


Fig. 4.60 Influent and Effluent O-cresol Concentration During Phase-III, Reactor 1

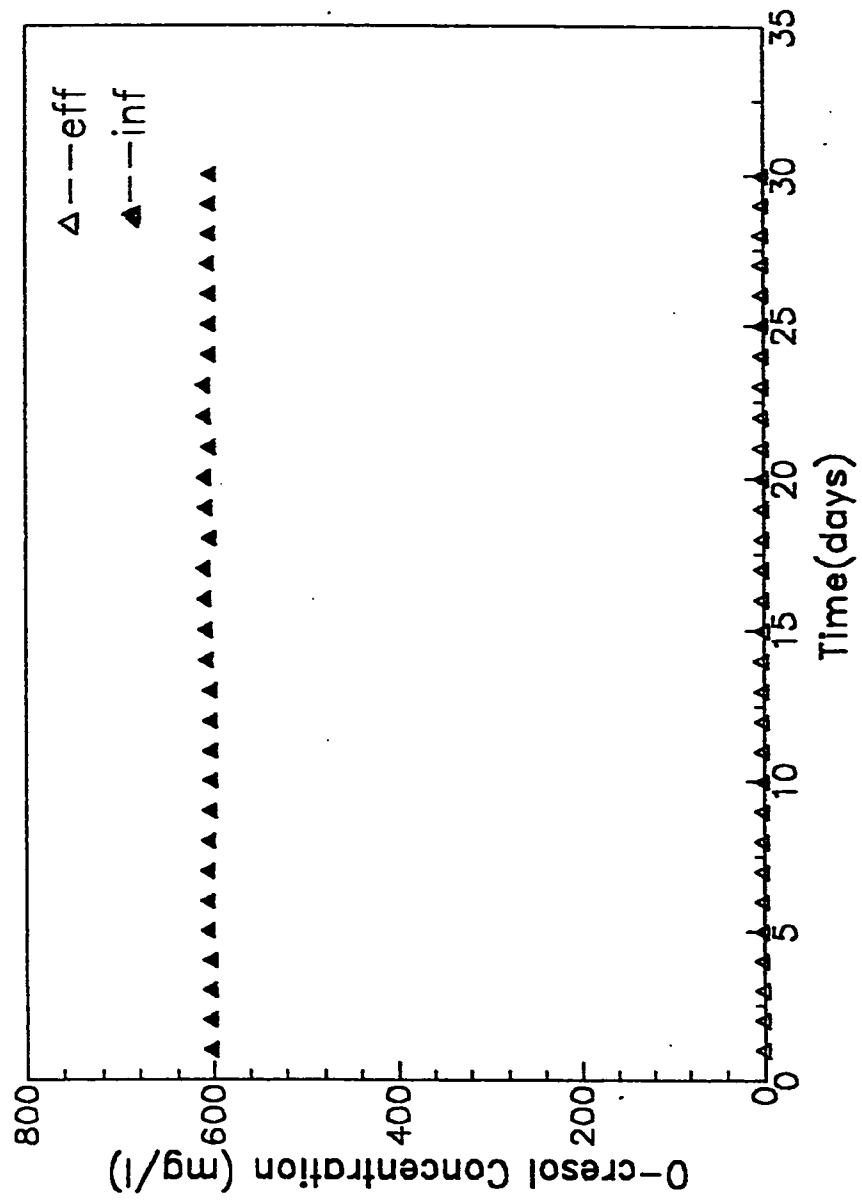


Fig. 4.61 Influent and Effluent O-cresol Concentration During Phase-III, Reactor 2

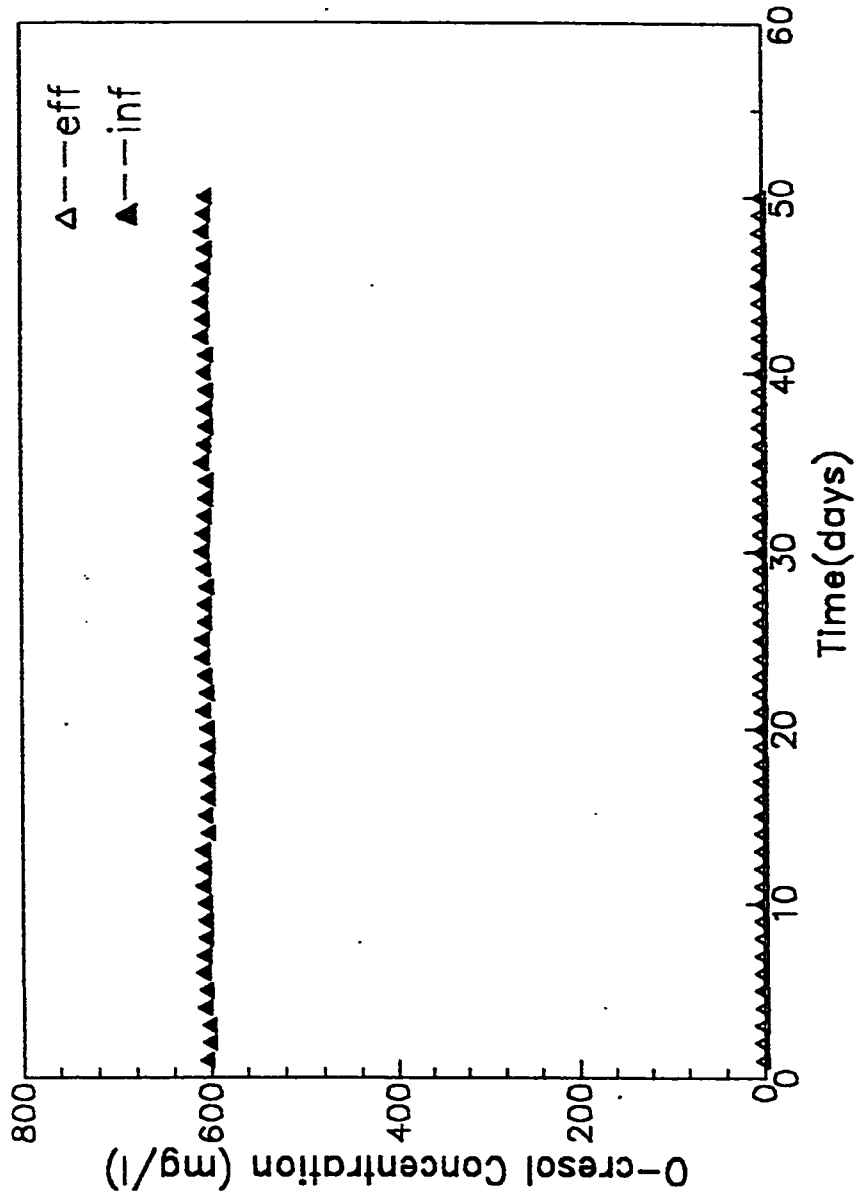


Fig. 4.62 Influent and Effluent O-cresol Concentration During Phase-III, Reactor 3

to reach 210 mg/l at the end of the third turnover of SRT. The percentage removal of the o-cresol was >99% at the beginning of the phase but decreased to 65% at the end of this phase. The F/M ratio of SBR-1 at failure was $0.76 \frac{\text{mg/l of o-cresol}}{\text{mg/l of MLVSS}}$. Figure 4.60 indicates that o-cresol cannot be treated successfully at mean SRT of 5 days and at concentrations as high as 600 mg/l.

As depicted in Figures 4.61 and 4.62 and Table 4.6, the average concentration of the effluent o-cresol was about 0.5 mg/l with standard deviation less than 0.1 mg/l for SBR-2 and SBR-3. This indicates that the percentage removal of the o-cresol, which was >99%, was consistent during the phase. The noteworthy finding of this study depicted in Figure 4.61 that o-cresol can be treated effectively at mean SRT of 10 days and at concentrations as high as 600 mg/l. As shown in Figure 4.28, phenol at higher concentrations than o-cresol can be also treated effectively at mean SRT of 10 days. This might be due to that phenol is less toxic than o-cresol.

Effluent BOD and COD

Figures 4.63, 4.64 and 4.65 show the influent and effluent BOD and COD concentrations for reactors 1, 2 and 3, respectively. As depicted in Figure 4.63 and Table 4.6, the average effluent BOD and COD concentrations from reactor 1 were 72 mg/l and 122

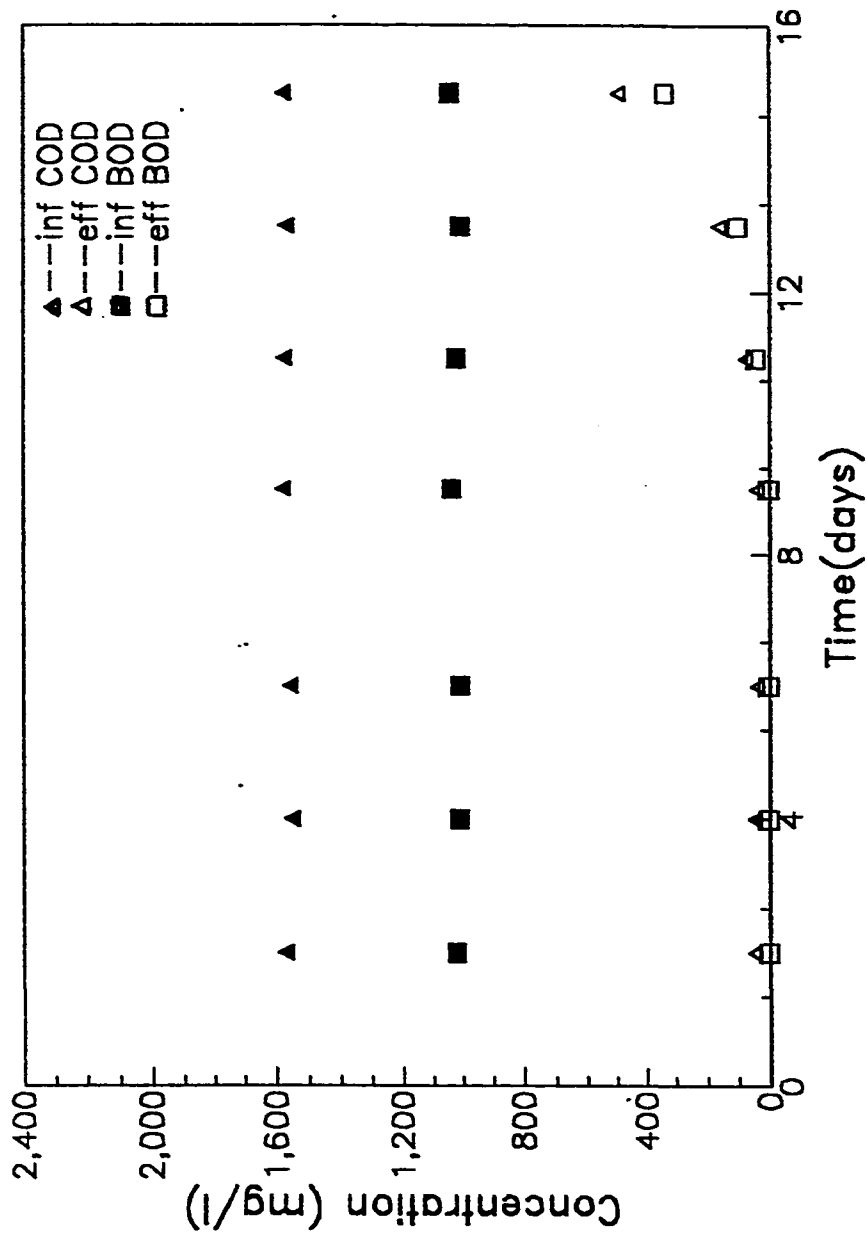


Fig. 4.63 Influent and Effluent BOD and COD Concentration in Reactor 1 During Phase-III, Cresol Study

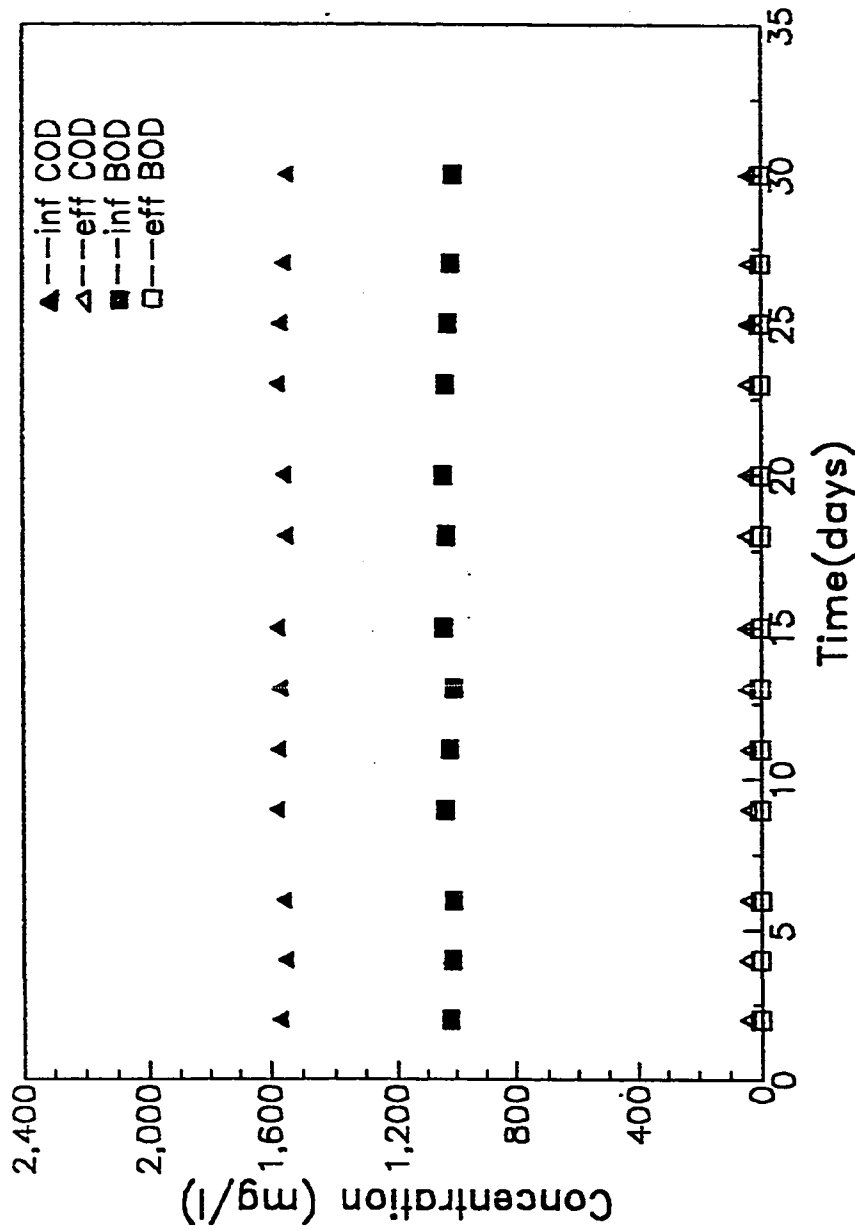


Fig. 4.64 Influent and Effluent BOD and COD Concentration in Reactor 2 During Phase-III, Cresol Study

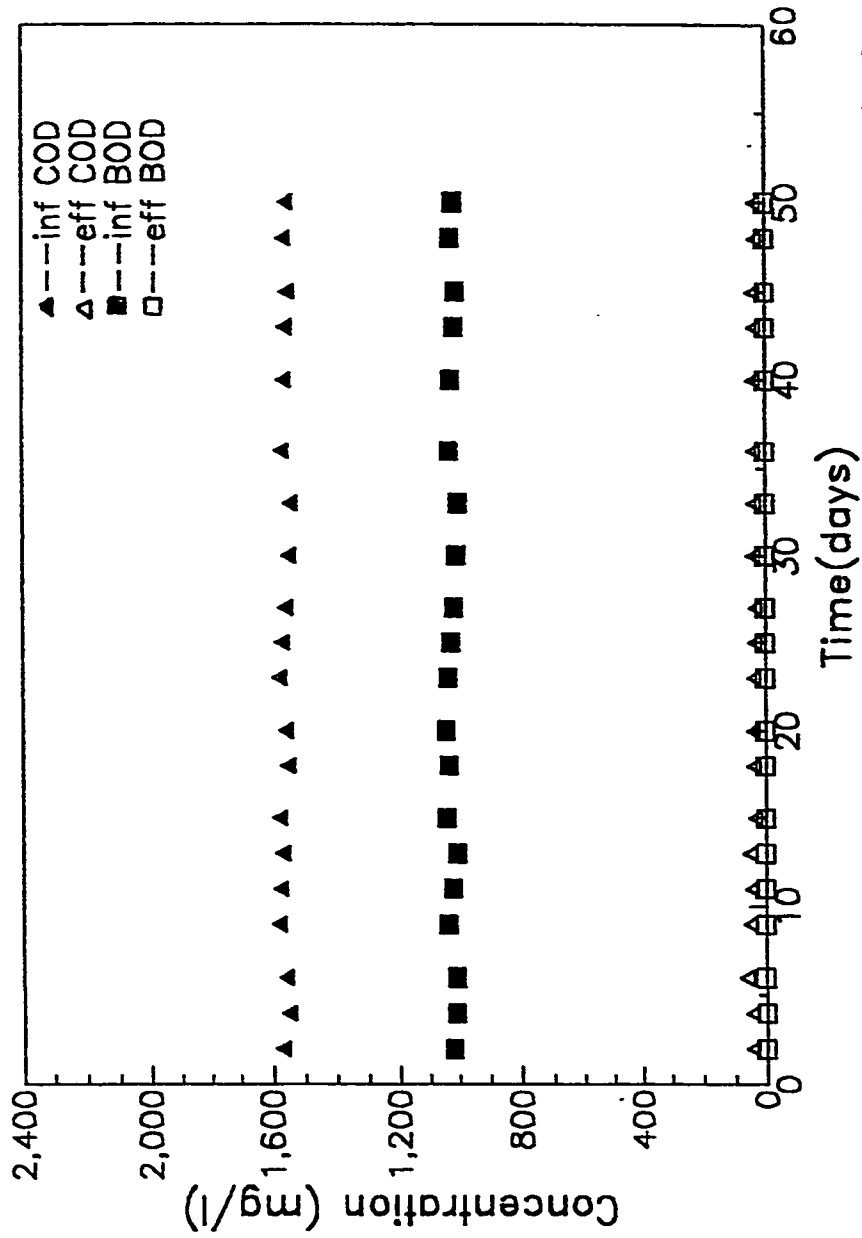


Fig. 4.65 Influent and Effluent BOD and COD Concentration in Reactor 3 During Phase-III-, Cresol Study

mg/l, respectively. Even though, these effluents exceeded the limits of the secondary treatment, the minimum percentage removal efficiencies of the BOD and COD were 68% and 69%, respectively.

As can be seen from Table 4.6, the effluent concentration of the BOD was about 5 mg/l for SBR-2 and SBR-3. The percentage removal of the BOD was 99% for SBR-2 and SBR-3. This removal efficiency of the BOD was sustained with minimum variability throughout the phase, as reflected by the low standard deviation which was about 0.5 mg/l. This indicates that reactors 2 and 3 affected the same BOD removal efficiency. As apparent from Table 4.6, the average percentage removal of the COD for reactors 2 and 3 was 98%. Also this indicates that reactors 2 and 3 affected the same COD removal efficiency. It is also clear from Table 4.6 that the average concentration of effluent COD was about 35 mg/l and the standard deviation of the effluent COD was about 5 mg/l for reactors 2 and 3. This high effluent COD and the standard deviation were due to the nature of raw sewage and not due to the residual o-cresol. As apparent from Figures 4.64 and 4.65 the effluent COD and subsequently the COD removal efficiency in reactors 2 and 3 were consistent during this phase.

Effluent TSS

Figures 4.66 and 4.67 show the effluent concentration of TSS and VSS respectively. As can be observed from these

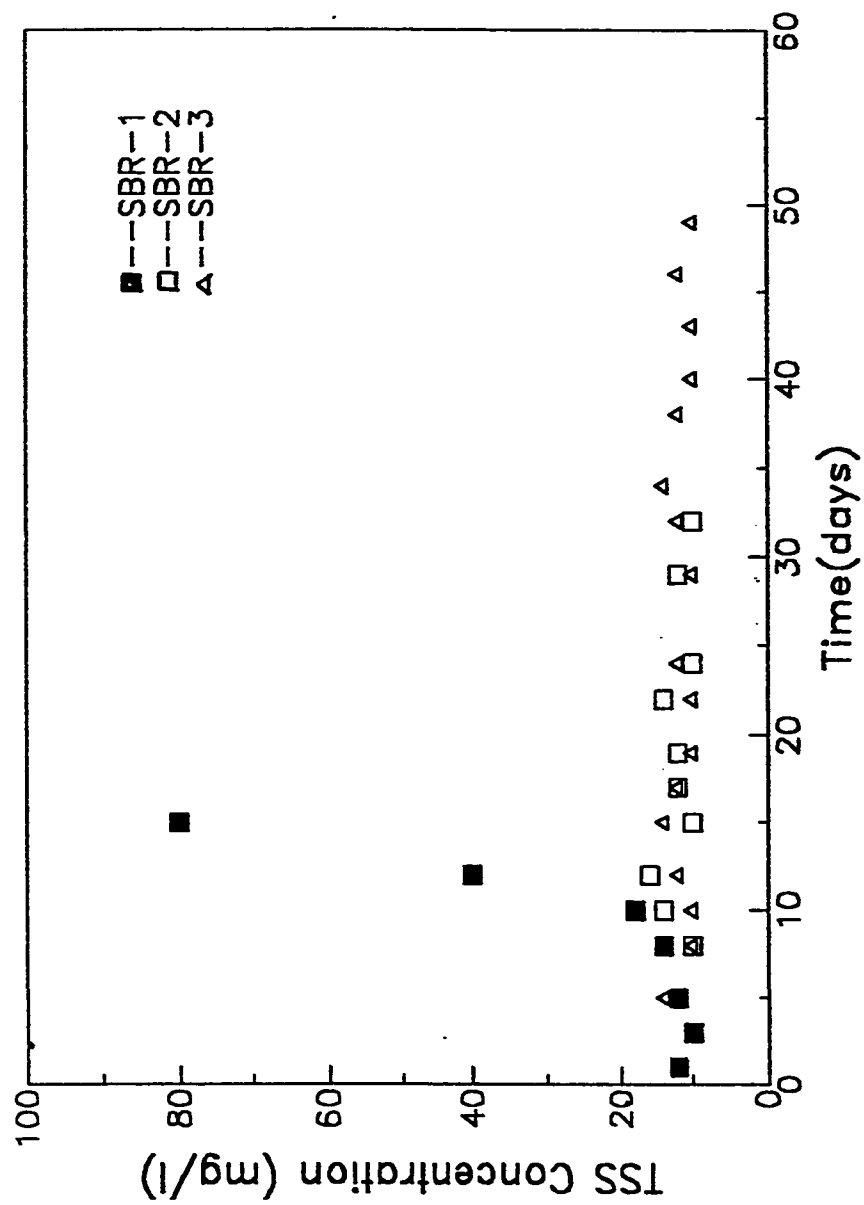


Fig. 4.66 Effluent Concentration of TSS In The SBRs During Phase-III, Cresol Study

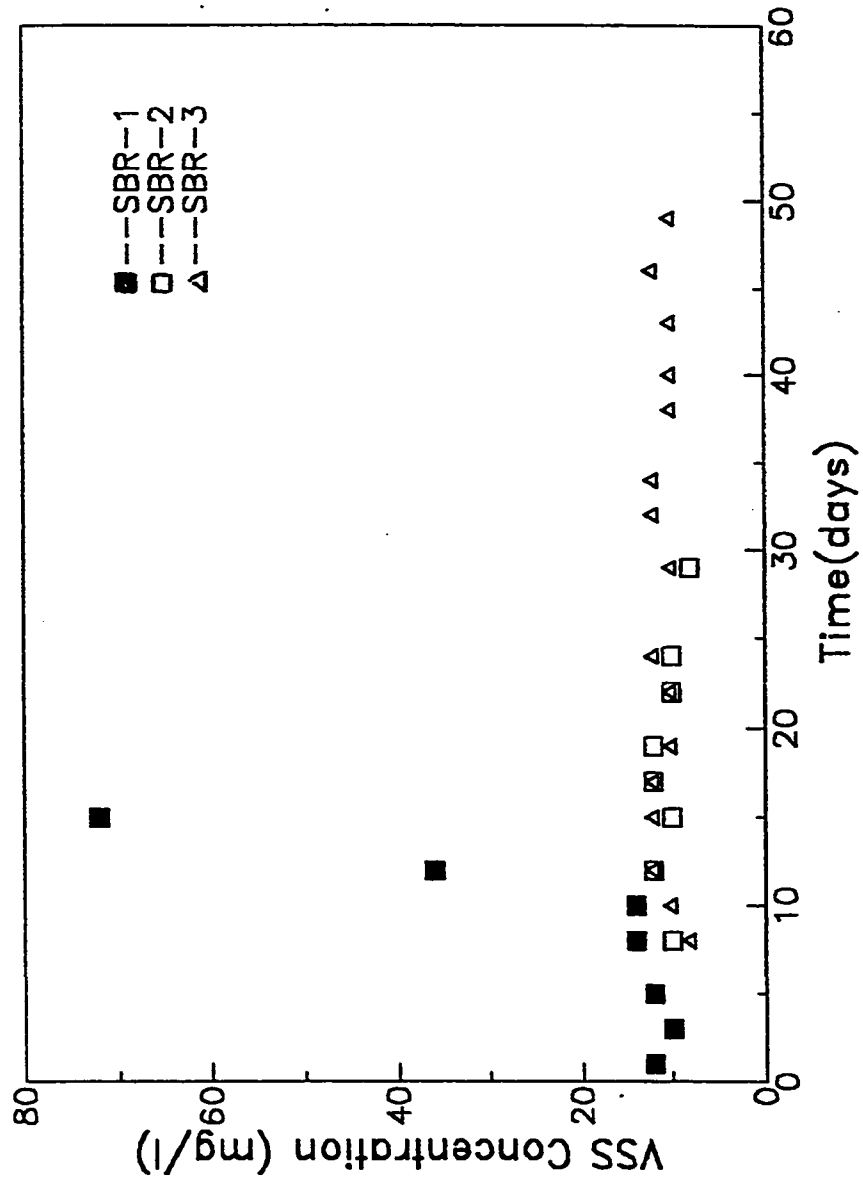


Fig. 4.67 Effluent Concentration of VSS In The SBRs During Phase-III, Cresol Study

figures, the TSS and VSS increased with time for reactor 1 and they were consistent for reactors 2 and 3. As shown in Table 4.6, the average concentration of the TSS for SBR-1 was 27 mg/l which exceeded the limits of the secondary treatment. This indicates that the culture were disturbed by the o-cresol which resulted in high values of TSS. It is clear from Figures 4.66 and 4.60 that the breakthrough of o-cresol and TSS happened at the same time, i.e. the concentration of effluent o-cresol exceeded the limits (2 mg/l) at day 10 and the effluent suspended solids exceeded the limits (30 mg/l) at day 10. This indicates that the failure of the system can be known by measuring organic concentration or suspended solids. The average concentration of the suspended solids for SBR-2 and SBR-3 was about 12 mg/l and the standard deviation was about 2 mg/l. This indicates that a mean SRT of 10 days did not have any adverse impact on the effluent suspended solids.

SVI

The SVI was calculated according to Equation 4.1. The SVI values in the reactors increased with time as shown in Figure 4.68. As expected, the highest value of SVI was encountered in SBR-1, since its culture was greatly disturbed by wastage. It is apparent from Figure 4.66 that the SVI was 67 ml/g at day 2 and continued increasing to reach 140 ml/g at day 12. This indicates that reactor 1 had sludge of poor settleability characteristics. As

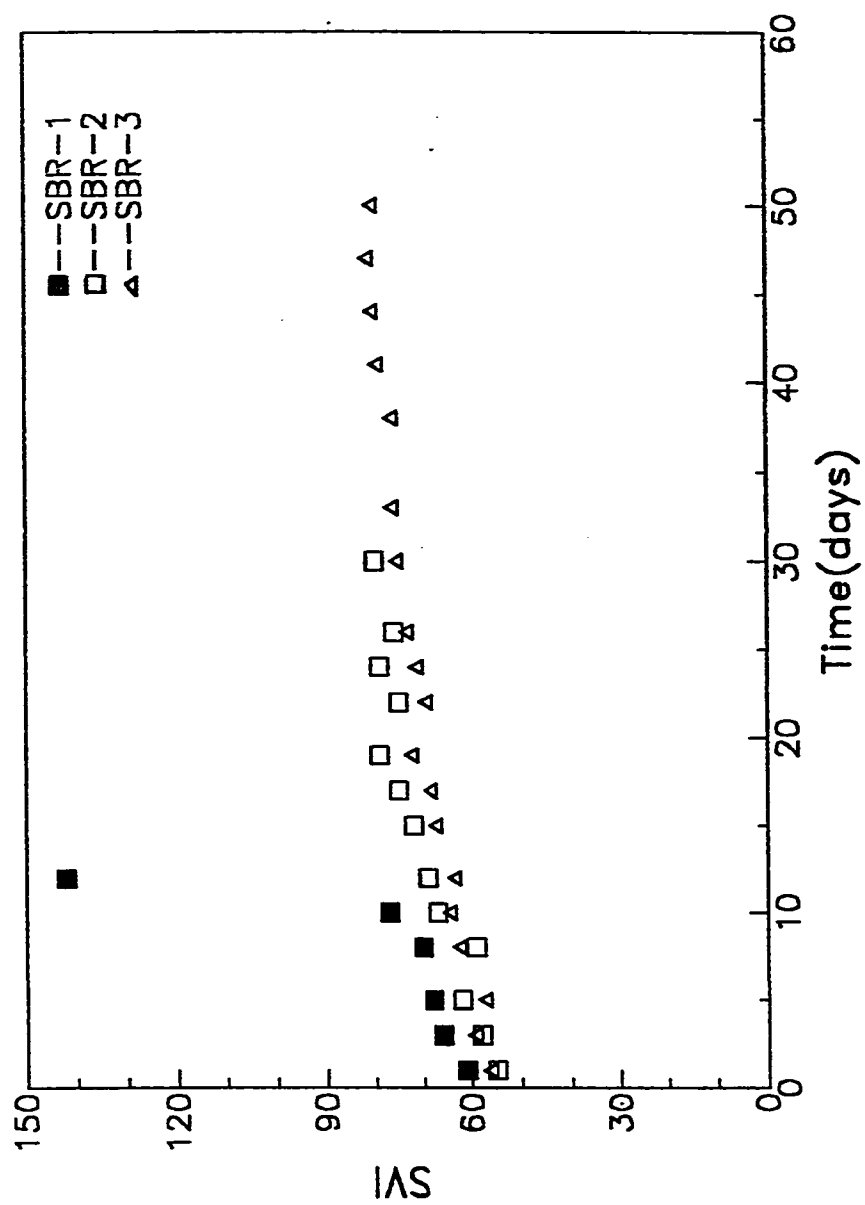


Fig. 4.68 Sludge Volume Index In The SBRs During Phase-III, Cresol Study

can be seen from Table 4.6 the average value of the SVI for reactors 2 and 3 was about 70 ml/g and the standard deviation was about 9 ml/g. This reflects the good settleability of the mixed liquor of reactors 2 and 3.

Nutrient Removal

As can be seen from Table 4.6, the TKN decreased from 30 mg/l to 20 mg/l in SBR-1, from 32 mg/l to 16.2 mg/l in SBR-2, and from 34 mg/l to 12.6 mg/l in SBR-3. It is apparent that the lowest reduction in TKN occurred in SBR-1, since it synthesized less cells than the others (SBR-1 did not consume all the BOD). It is also clear that the reduction in TKN for SBR-2 and SBR-3 was same, since both reactors consumed the same amount of the BOD.

The total-p decreased from 9 mg/l to 7.3 mg/l in SBR-1 from 8.7 mg/l to 6 mg/l in SBR-2 and from 8.5 mg/l to 5.8 mg/l in SBR-3. The decrease in the influent total-p can be attributed to the utilization of phosphorous for the cell synthesis.

The BOD/N/P ratios for reactors 1, 2 and 3 were 1020/10/1.7, 100/0.98/0.17, 100/1.55/0.26 and 100/2.1/0.26, respectively. As can be seen, these ratios did not match with the general BOD/N/P ratio. This might be due to the reasons mentioned earlier.

4.3 Kinetic Study

The relationship commonly used for the description of substrate utilization-bacterial growth is Monod model. The Monod equation can be stated as:

$$\mu = \mu_m \frac{S}{K_s + S} \quad (4.2)$$

where

μ = specific growth rate (time⁻¹)

μ_m = maximum specific growth rate (time⁻¹)

S = substrate concentration (mg/l)

K_s = half-saturated coefficient (mg/l)

During the react period of an SBR cycle, no flow of wastewater into or out of the reactor takes place, as such an SBR can be modeled as a batch reactor. Simple mass balances on the bacterial cell concentration and the substrate concentration yield the following system of ordinary differential equations:

$$\frac{dX}{dt} = (\mu - K_d) X \quad (4.3)$$

and

$$\frac{dS}{dt} = - \frac{KSX}{K_s + S} \quad (4.4)$$

where

X = bacterial cell concentrations (measured in terms of MLVSS, mg/l).

K_d = the cell decay rate (time^{-1})

K = maximum rate of substrate utilization per unit mass of microorganisms.

Assuming that the bacterial cell concentration remains constant during the react period, and indeed this was the case as shown in Table 4.7, Equation 4.3 becomes zero and Equation 4.4 can be integrated for t and S as follows:

$$\frac{dS}{dt} = - \frac{KSX}{K_s + S}$$

$$\frac{dt}{dS} = - \frac{K_s + S}{KSX}$$

$$= \frac{-K_s}{KSX} - \frac{1}{KX}$$

$$dt = \frac{-K_s}{KS} ds - \frac{dS}{KX}$$

Table 4.7: Values of Cell Concentration during the Kinetic Study

| Reactor | Phenol | | O-cresol | |
|------------------|--------|------|----------|------|
| | R1 | R2 | R3 | R4 |
| At the beginning | 2760 | 3010 | 2100 | 3785 |
| At middle | 2792 | 325 | 2130 | 3805 |
| At end | 2810 | 335 | 2140 | 3815 |

$$t = - \frac{K_s}{KS} \ln(S) - \frac{S}{KX} + C \quad (4.5)$$

where

c = integration constant

Equation 4.5 can be solved for K_s and K using non-linear regression analysis, since the variation of S with time can be determined. Phenol and o-cresol were determined every 5 and 10 minutes, respectively. This equation was solved using computer package of the statistical analysis system (SAS). Figures 4.69, 4.70, 4.71, and 4.72 show the relationship between experimental data and predicted data for both compounds. It is apparent from these figures that Monod model was good enough to describe the kinetic data for SBRs. The chi-square test (X^2) which used to determine the goodness of fit of the data was calculated according to Equation 4.6

$$X^2 = \frac{(o_1 - e_1)^2}{e_1} + \frac{(o_2 - e_2)^2}{2} + \dots \quad (4.6)$$

where

o_1 is observed data

e_1 is predicted data

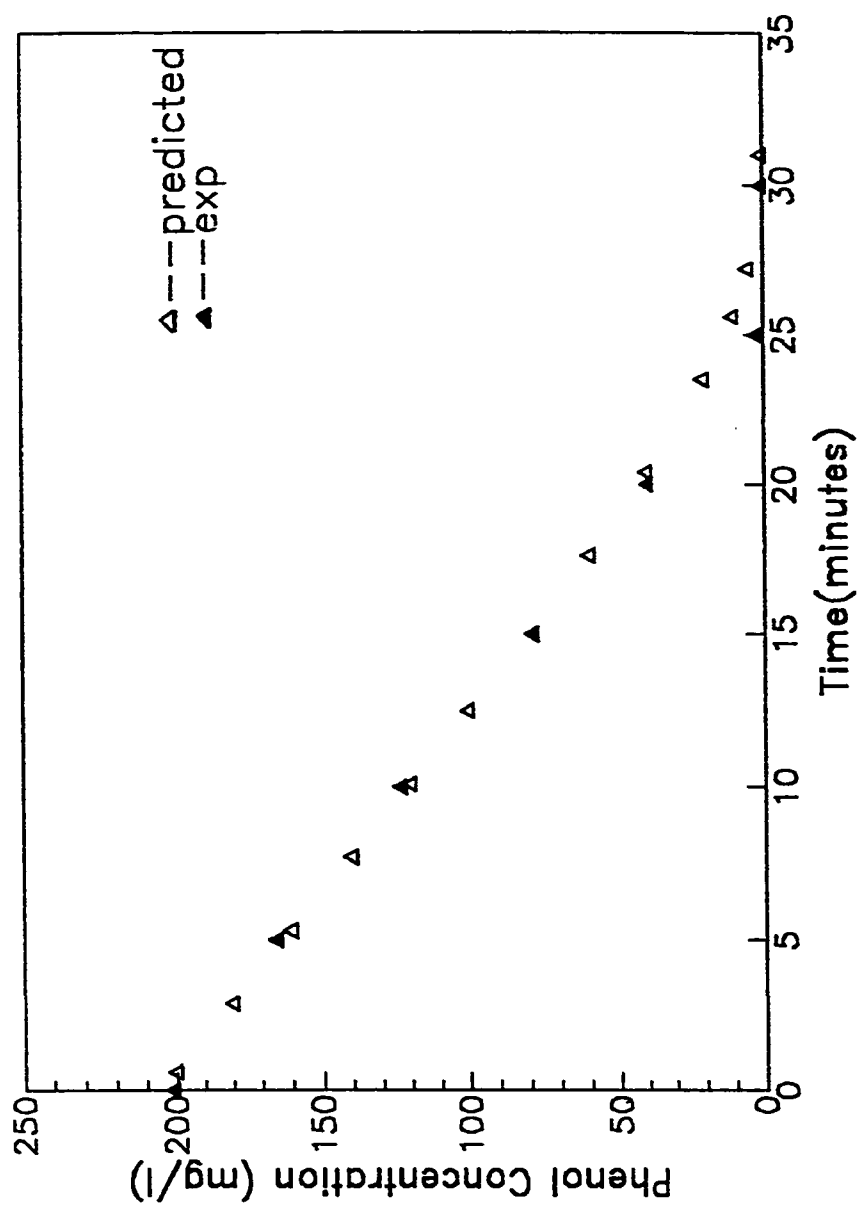


Fig. 4.69 Relationship Between Experimental Data and Predicted Data
Reactor 1-Phenol Study

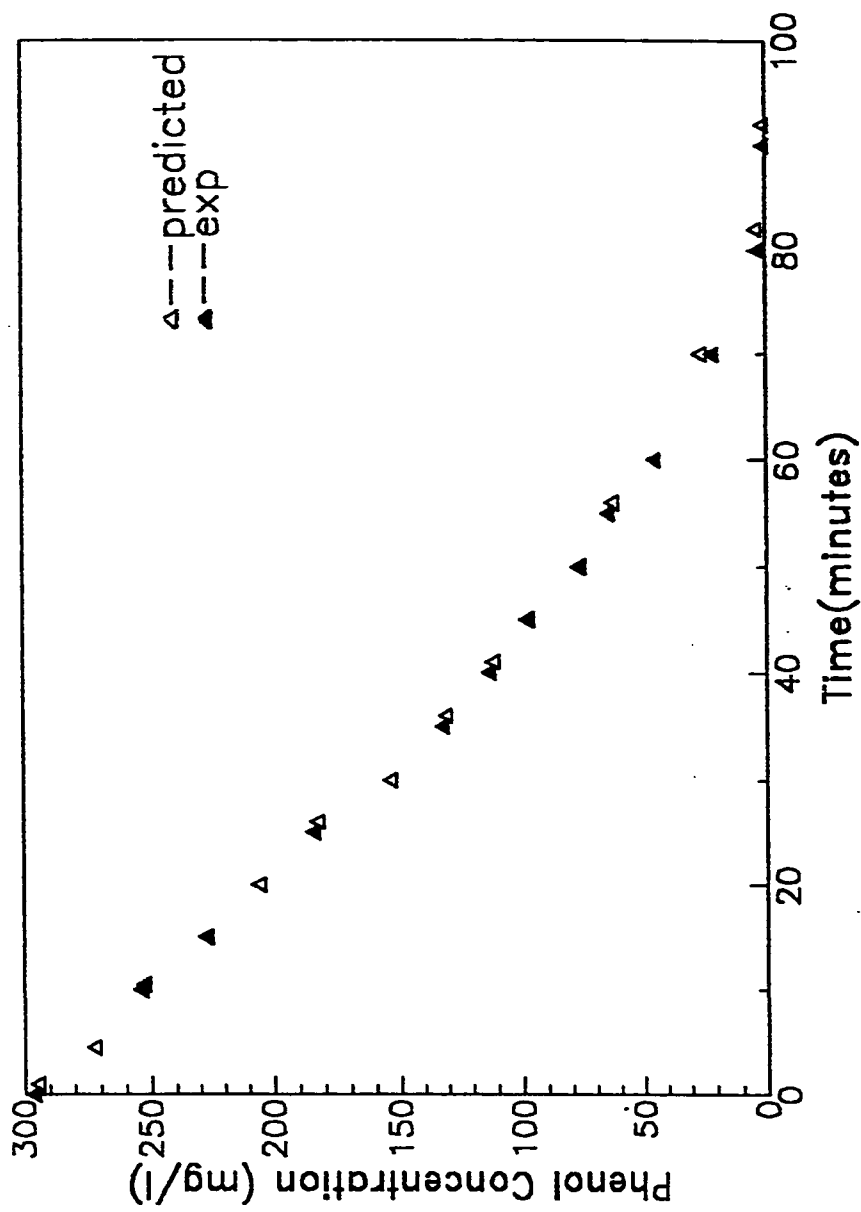


Fig. 4.70 Relationship Between Experimental Data and Predicted Data Reactor 2-Phenol Study

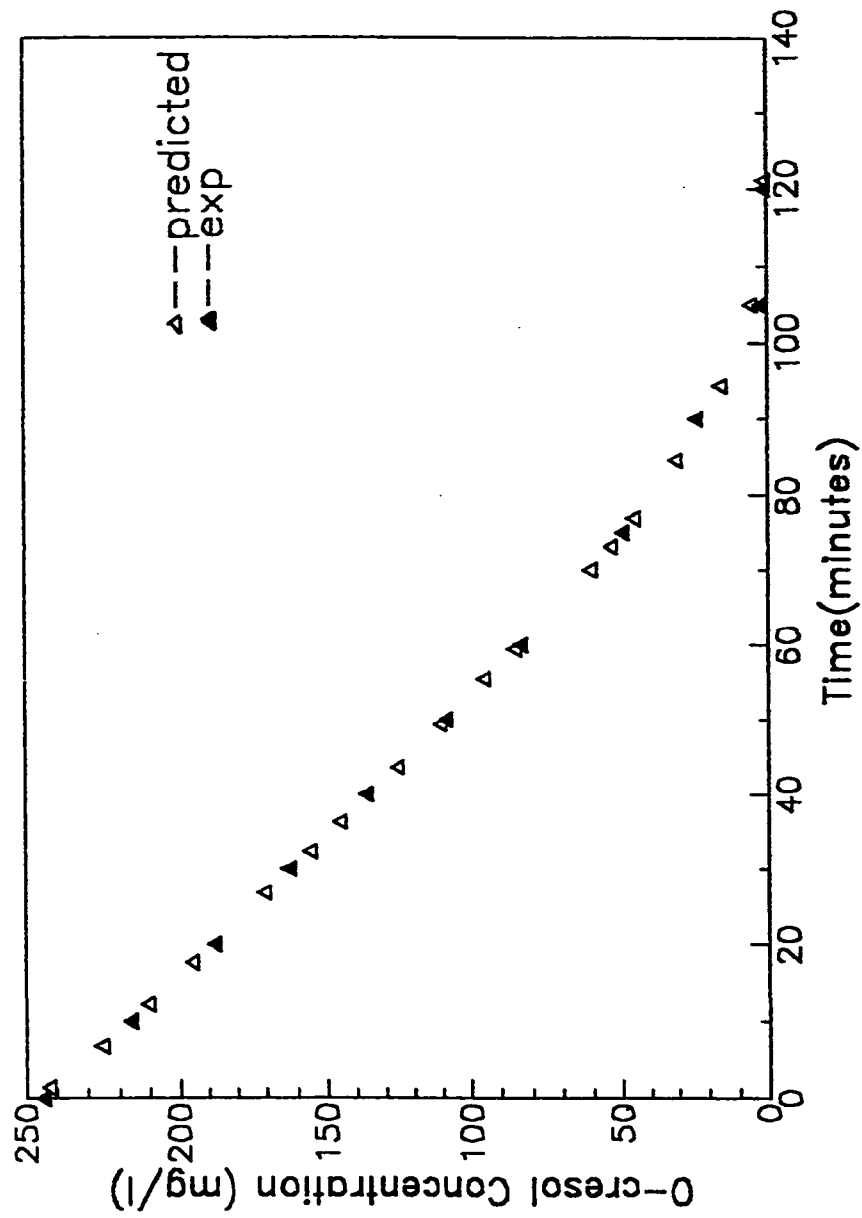


Fig. 4.71 Relationship Between Experimental Data and Predicted Data
Reactor 1-Cresol Study

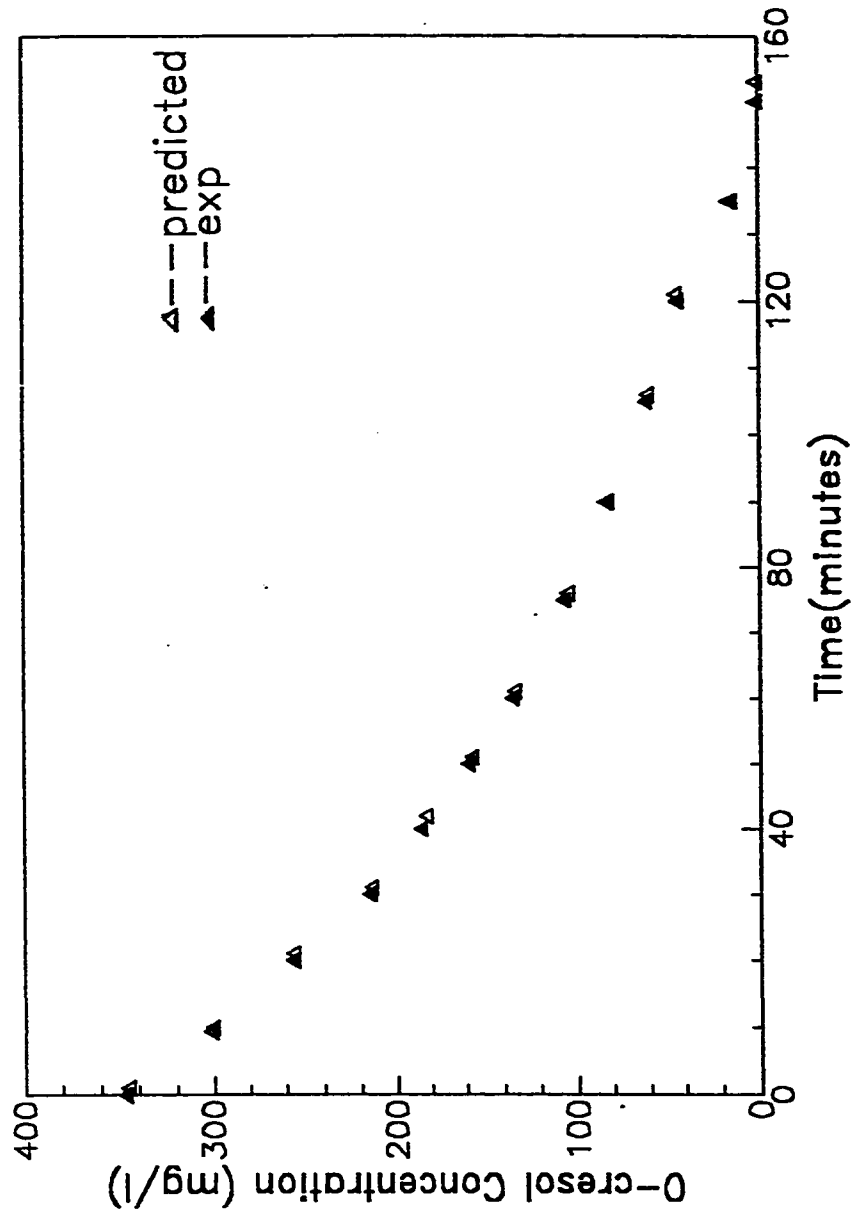


Fig. 4.72 Relationship Between Experimental Data and Predicted Data
Reactor 2-Cresol Study

Table 4.8 shows the values of chi-square calculated from Equation 4.6 and the critical values of chi-square ($X^2_{0.99}$) obtained from standard tables (assuming that the level of significance of 0.01). Since $X^2 > X^2_{0.99}$, the fit of the data is very good.

The Y and K_d coefficients can be obtained from Equation 4.7:

$$\frac{1}{\theta_c} = YU - K_d \quad (4.7)$$

where

θ_c = mean cell residence time

Y = maximum yield coefficient measured during any finite period of logarithmic growth, and defined as the ratio of the mass of cells formed to the mass of substrate consumed, mass/mass.

U = specific substrate utilization rate, and equal to

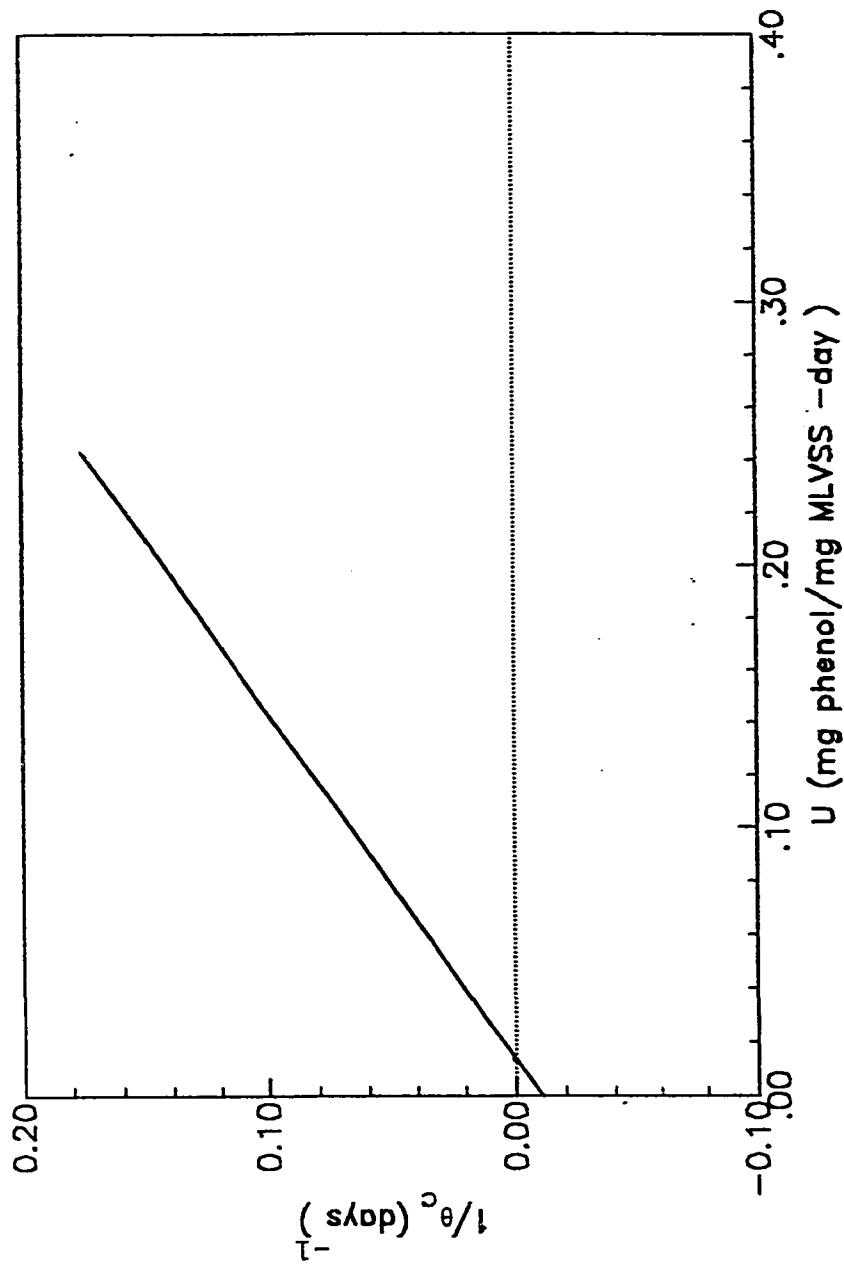
$$\frac{Q}{V} \frac{S_o - S}{X}$$

The coefficient of Y and K_d can be obtained by plotting $\frac{1}{\theta_c}$ versus U , since Y is the slope of the straight line and K_d is the

Table 4.8: Chi-Square Values

| Reactor | | χ^2 | $\chi^2_{0.99}$ |
|---------|----|----------|-----------------|
| Phenol | R1 | 0.21 | 13.3 |
| | R2 | 0.28 | 23.2 |
| Cresol | R1 | 0.29 | 20.1 |
| | R2 | 0.22 | 23.2 |

intercept. It is worth mentioning that the X and S values used for calculating U are the average values of the steady-state data illustrated in Table 4.7. Figures 4.73 and 4.74 show the plot of $\frac{1}{\theta_c}$ versus U for phenol and o-cresol, respectively. The summary of the results of the kinetic coefficients of this study and other studies reported in the literature is listed in Table 4.9. It must be emphasized that conversion factor of 1.67 mg BOD/mg phenolic compounds was used to convert the original data to the units of Table 4.9 to facilitate comparison with literature values. It is evident from Table 4.9 that our system is superior to other systems since the yield value of our system concurred with those values reported in Table 4.9 and our system has a very high maximum substrate utilization rate, K, and it takes small range of substrate concentration to reach this as reflected by a very low half saturation constant K_s . This may be attributed to the startup procedure wherein the reactors were not seeded with any sludge but rather slowly allowed to buildup the mixed liquor using the microbial solids present in the raw sewage, thus enriching the phenolic compounds degrading microbes.

Fig. 4.73 Determination of Y and K_d for Phenol

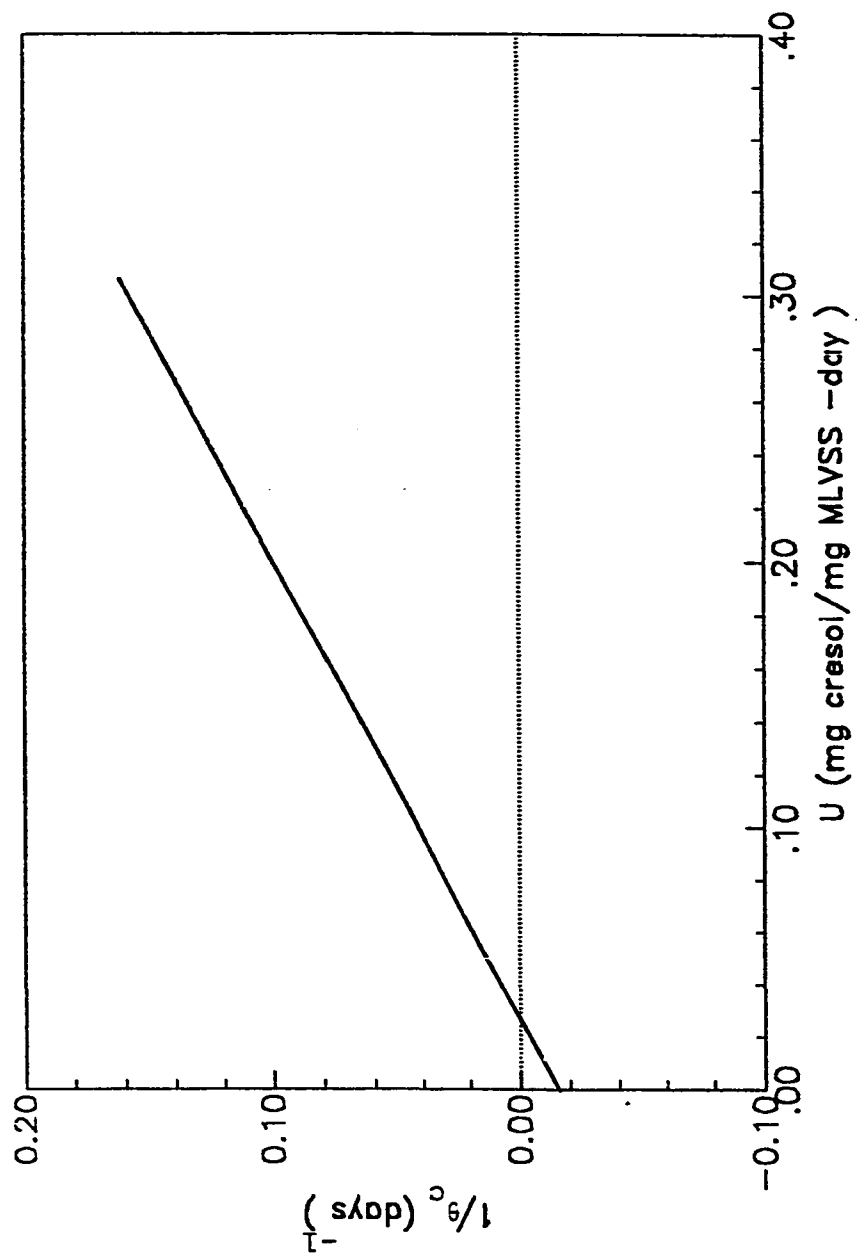
Fig. 4.74 Determination of Y and K_d for Cresol

Table 4.9: Kinetic Coefficients

| Kinetic Coefficients | Method | Waste Type | K (mg/L of BOD) | K(mg BOD/mg MLVSS -day) | y(mg MLVSS /mg BOD) | (K d day ⁻¹) |
|----------------------|--------|---------------------|-----------------|-------------------------|---------------------|--------------------------|
| Phenol R1 | SBR* | Phenolic waste | 20.7 | 4.5 | 0.44 | 0.006 |
| Phenol R2 | SBR* | Phenolic waste | 9.8 | 7.5 | 0.44 | 0.006 |
| Phenol R1 | SBR | Phenolic waste | 26.6 | 3.6 | | |
| Cresol R2 | SBR | Phenolic waste | 15.5 | 2.0 | 0.34 | 0.013 |
| HSU(60) | SBR | Petrochemical waste | 376 | 1.6 | 1.08 | 0.098 |
| Qasim(81) | AS** | Municipal waste | 82 | 3.5 | 0.45 | 0.04 |
| Rehnum(82) | AS | Municipal waste | 18.78 | 1.54 | 0.71 | 0.09 |
| | AS | Municipal waste | 20 | 1.43 | 0.59 | 0.05 |
| Orhon(83) | AS | Fermentation waste | 310 | 4.00 | 0.26 | 0.028 |
| | AS | Fermentation waste | 50 | 0.5 | 0.58 | 0.088 |

SBR: Sequencing Batch Reactor

AS: Activated Sludge

CONCLUSIONS

The following conclusions can be drawn based on the bio-treatment of phenol and o-cresol bearing wastewater.

1. The SBRs can be started very rapidly and effectively without seeding.
2. Microorganisms which degrade phenol can be adapted to treat effectively other hazardous phenolic compounds such as o-cresol very rapidly.
3. With proper acclimation and adaptation, the microorganisms in a SBR can handle a shock loading of phenol as high as 1600 mg/l with over 75% removal at a HRT of 1.1 day.
4. O-cresol can be reduced biologically from 750 mg/l to less than 0.5 mg/l in SBR operating at a HRT of 1.1 day.
5. Both phenol and cresol can be treated with more than 99.9% removal at a SRT of 10 days and a HRT of 1.1 days at loadings of 800 and 600 kg/m³, respectively. The effluent BOD and COD concentrations were about 5 and 35 mg/l, respectively, representing over 99.5% BOD removal efficiency and about 98% COD removal

efficiency.

6. Phenol at a loading of $800 \text{ kg/m}^3\text{-d}$ and an HRT of 1.1 days can be partially removed by 85% at a SRT of 3.0 days and 94% at a SRT of 5 days. Phenol loading of 0.7-0.8 mg phenol/mg MLVSS appear to initiate rapid deterioration in biological activities. Inhibition was more closely associated with toxicant mass to microbial solids ratio than with SRT since the reactors sustained the loading offer the first and sometimes second turnover of SRT.
7. Only 60% cresol at a loading of $600 \text{ kg/m}^3\text{-d}$ and an HRT of 1.1 days was biodegraded at a SRT of 5.0 days with rapid breakthrough of cresol and consequently BOD as well as TSS ensuing from a toxicant loading of 0.6 mg cresol/mg MLVSS. Inhibition again started after the end of the second turnover of SRT.
8. In all inhibited reactors, the breakthrough of TSS concurred with that of organics. The breakthrough of TSS was attributed to loss of sludge settleability due to morphological changes at inhibition.

References

1. Irvine, R. L., "Project Summary Technology Assessment of Sequencing Batch Reactors", EPA/600/S2-85/007, U.S. (1985)
2. Irvine, R. L., Ketchum, L. H., Breyfogle, D., and Barth, E. F., "Municipal Application of Sequencing Batch Treatment", J. Water Pollution Control Federation Vol. 55, pp. 484-489, (1983).
3. Herzbrun, P. A., R. C. Irvine and Hanchak, M. J. "Treatment of Hazardous Wastes in a Sequencing Batch Reactor", Proceeding 39th Annual Purdue Industrial Waste Conference (May 1984).
4. Smith, R. G. and Wilderer, P. A., "Treatment of Hazardous Landfill Leachate Using Sequencing Batch Reactors", Proceeding 41th Annual Purdue Industrial Waste Conference (1986).
5. Ng, W. J. , et al., "Palm Oil Mill Effluent Treatment - An Assessment of Coagulants Used to Aid Liquid Solid Separations", Biol. Wastes, 21, 237, (1987).
6. Bershadskaya, T. M., et al., "Treatment of Oil Emulsion Wastewaters", Stal, (USSR), 1, 107 (1987); (Abstr.) Chem. Abstrs. 107, 832924 (1987).

7. Van Gils, G. J., and Pirbazari, M., "Pilot Plant Investigations for the Removal of Toxic Pollutants from Industrial Laundry Wastewaters", 17th Mid-Atl. Ind. Waste Conf. Proc. (June 23-25, 1985), Lehigh Univ., Bethlehem, Pa., 17, 186 (1985).
8. Van Son, H., "Substitution of Inorganic Chemicals", AES (Ital.), 7, 7, 49 (1985); (Abstr.) Chem, Abstr. 104, 1738284 (1986).
9. Liao, M. Y. and Randteke, S. J. "Predicting the Removal of Soluble Organic Contaminants by Lime Softening", Water Res. Vol. 20, No.1, pp. 27-35, (1986).
10. Arakeiyan, A. S., et al., "Removal of Poly (Vinyl Alcohol) from Wastewaters", Plast. Massy (U.S.S.R.), 19, 46 (1986); (abstr.) Chem. Abstr. 205, 196630; (1986).
11. Niegewski, S. J., "Destruction of Phenols by Oidation with Ozone", Ind. and Engr. Chemistry, Vol. 45, p. 637 (1968).
12. Anon-Manual on Disposal of Refinery Wastes, "Chemical Wastes", American Petrol Inst. New York, N. Y. (1958).
13. Eisenhauer, H. R. "Increased Rate and Efficiency of Phenolic Waste Oidation", JWPCF, 40, 1887 (1968).
14. Eisenhauer, H. R. "Increased Rate and Efficiency of Phenolic

- Waste Oidation", JWPCF, 43, 200 (1971).
15. Niegowski, S. J., "Sewage Ind. Wastes", 28, 1260 (1956).
 16. Kwie, W. W., "Ozone Treats Wastewater from Polymer Plants", Water and Sewage Works, 116, 74 (1964).
 17. "Environmental Control in the Organic Petrochemical Industries", Editor: Jones, H. R. Noyes Data Corp. N.Y., p. 177 (1971).
 18. Schwartz, M., Jones, L. S. Rice, R. G. and Beneddek, A. "Applicability of the Biologically Activated Carbon Process to the Tertiary Treatment of Refinery Wastewater for Reuse Purpose", Proc. 36th Ind. Waste Conf. Purdue Univ. pp. 329-340 (1981).
 19. Buys, R. E. and Reynolds, T. D. "Effect of Mean Cell Residence Time and Ozonation on Carbon Adsorption", Proc. 36th Industr. Wastewater Conf. Purdue Univ. p. 29, Lafayette, Ind. U.S.A. (1981).
 20. Gurol, M. D. and Vatistas, R., "Oxidation of Phenolic Compounds by Ozone and Ozone + U. V. Radiations: A comparative Study", Water Res. (6.B), 21, 895, (1987).
 21. Perkowski, J. et al., "Radiochemical Method for Degradation of Pollutants in Textile Industry Wastewaters", Przegl. Wlok

- (Pol.), 40, 4, 148 (1986), (Abstr.) Chem. Abstr, 105, 1020620 (1986).
22. Hall, R. H. and Rappe, G.G., "An Innovative, Below-Ground Wet Air Oxidation System for the Treatment of Hazardous and Toxic Wastes", Proc. Ind. Waste Conf. (Can.) 32, 209 (1981); (Abstr.) Chem. Abstr., 104, 155187f (1986).
 23. Davis, A. P. and Huong, C. P., "Removal of Phenols from Water by A Photocatalytic Oxidation Process", Wat. Sci. Tech. Vol. 21, pp. 455-464 (1989).
 24. Lyandres, S. and Meardon, J., "Evaluation of Membrane Processes for the Reduction of Trace Organic Contaminants", Environmental Progress, Vol. 8, No. 4 (1989).
 25. Permasep Products, Technical Information Manual, May 1983. Du Pont Company, Wilmington, DE (1988).
 26. Schutte, C. F. and Belfort, G. "Rejection of Alkyl Phenols by Reverse Osmosis Membranes", Wat. Sci. Tech. Vol. 19, pp. 967-979, (1987).
 27. Matsuura, T. and Sourirajan, S., "Physicochemical Criteria for Reverse Osmosis Separation of Alcohols, Phenols and Monocarboxylic Acids in Aqueous Solution Using Porous Cellulose Acetate Membranes, Jour. Appl. Poly. Sci. 15, 2905. (1971).

28. Matsuura, T., Blais, P., Dickson, J. M. and Sourirajan, S., "Reverse Osmosis Separation for Some Alcohols and Phenols in Aqueous Solutions Using Aromatic Polyimide Membranes, Jour. Appl. Sci. 18, 3671 (1974).
29. Chian, E. S. K. and Fang, H. H. P., "Physicochemical Criteria of Removal of Trace Organics by Reverse Osmosis", Water-1976, AIChE Symposium Series, 157.
30. Jonsson, G., "Methods for Determining the Selectivity of Reverse Osmosis Membranes", Desalination, 24, 19 (1978).
31. Nakagawa, Y., Edogawa, K., Kurihava, M. and Tonomura, T., "Solute Separation and Transport Characteristics Theory PEC 1000 Reverse Osmosis Composite Membrane", paper presented at ACS Annual Meeting, Philadelphia, Aug. 26-31, (1984).
32. Himmelstein, K. J., Fox, R. D., and T. H. Winter, Chem. Eng. Prog. 1973, 69, 65-69.
33. Pollio, F. X. and Kunin, R. Environ. Sci. Tech. 1967, 1, 160-163.
34. Farrier, D. S. Hines, A. L. and S. W. Wang, J. Colloid Interface Sci. 1979, 69, 233-237.
35. Goto, S. Goto, M., and S. J. Uchiyama, J. Chem., Eng.

- Jpn. 1984, 17, 204-205.
36. Goto, M., Hayashi, N. and S. Goto, "Adsorption and Desorption of Phenol on Anion-Exchange Resin and Activated Carbon", Environ. Sci. Tech. Vol. 20, No. 5, 1986.
 37. Ford, D. L., "The Application of Carbon Adsorption in the Treatment of Petrochemical Wastewater", Application of New Concepts of Physicochemical Treatment for Wastewater; Sept. 18-22, 1972.
 38. Ford, D. L. and Buerchlin, M.A., "The Interrelationship of Biocil-carbon Adsorption Systems for the Treatment of Refinery and Petrochemical Wastewater", paper presented at Sixth international Conf. held in Jerusalem, June 18-22 (1972).
 39. Guarino, C. F., Da-Rin, B. P., Gazen, A., and Eoettems, E. P., "Activated Carbon as an Advanced Treatment for Petrochemical Wastewater" Wat. Sci. Tech. Vol. 20, No. 10, pp. 115-130, 1980.
 40. Walter J. and Weber, Jr. "Evolution of A Technology", ASCE, pp. 899-917, June 1984.
 41. Coe, R. C., "Bench Scale Method for Treating Waste by Activated Sludge", Petrol. Proc. V. y, pp. 1128, August 1952

42. Huber, L., "Disposal of Effluents from Petroleum Refineries and Petrochemical Plants", Proc. 22nd Ind. Waste Conf., Purdue University. (1967).
43. Sack, W. A. and Bokey, W. R. "Biological Treatment of Coal Gasification Wastewater", Proc. 33rd Ind. Waste Conf., Purdue University, pp. 278-285, (1978).
44. Ganczarczyk, J. and Elion, D., "External Aeration of Coke-Plant Effluents", Proc. 33rd Ind. Waste Conf., Purdue University, pp. 895-902, (1978).
45. Luthy, R. G., Sekel, D. J., and Tallon, J. T., "Biological Treatment of Synthetic Fuel Wastewater", J. Environmental Eng. Div. ASCE, Vol. 106, No. EE5, (1980).
46. Healey, J. and Young, L. Y, "Catechol and Phenol Degradation by a Methanogenic Population of Bacteria", Applied Environ, Microbiology, Vol. 35, pp. 216-222 (1978).
47. Fedorak, F. M. and Hruday, S. E., "The Effects of Phenol and Some Alkyl Phenolics on Batch Anaerobic Methanogenesis", Water Research, Vol. 18, No. 3, pp. 361-367 (1984).
48. Boyd, S. A., Shelton, D. R., Berry, D. and Tiedje, J. M., "Anaerobic Biodegradation of Phenolic Compounds in Digested Sludge", Appl. Environ. Microbiology, Vol. 46, p. 50 (1983).

49. Suidan, M. T., Cross, W. H. and Fong, M., "Continuous Bioregeneration of Granular Activated Carbon During the Anaerobic Degradation of Catechol", *Progress in Water Tech.*, Vol. 12, No. 6, pp. 203-214 (1980).
50. Suidan, M. T., Cross, W. H. and Fong, M. and J. W. Calvert, "Anaerobic Carbon Filter for the Degradation of Phenols", *J. Environmental Eng. Div. ASCE*, Vol. 107, No. EE3, pp. 563-579.
51. Khan, K. A. Suidan, M.T. and Cross, W. H., "Anaerobic Activated Carbon for the Treatment of Phenol-bearing Wastewater", *J. Water Pollution Control Federation*, Vol. 55, pp. 1519-1532 (1981).
52. Wang, Y. T., Suidan, M. T. and Pfeffer, J. T., "Anaerobic Activated Carbon Filter for the Degradation of Polycyclic N-aromatic Compounds", *J. Water Pollution Control Federation*, Vol. 56, pp. 1058-1062 (1984).
53. Suidan, M. T. Strubler, C.E., Kao, S. W. and Pfeffer, J. T., "Treatment of Coal Gasification Wastewater with Anaerobic Filter Technology", *J. Water Pollution Control Federation*, Vol. 55, pp. 1263-1270 (1983).
54. Suidan, M. T. and Nakhla, G. F., "Anaerobic Fluidized-bed Treatment of Hazardous Wastes", Chapter in *Reducing Risks*

- from *Environmental Chemicals Through Biotechnology*, Edited by Gil Omenu, Council for Research Planning in Biological Sciences (1987).
55. Nakhla, G. F., Suidan, M. T. and Pfeffer, J. T., "Operational Control of Anaerobic GAC Reactor Treating Hazardous Wastes", *Water Science and Technology*, Vol.21, pp. 167-173 (1989).
 56. Chapman, P. J. "Constructing Microbial Strains for Degradation of Halogenated Aromatic Hydrocarbons:", Chapter in *Reducing Risks from Environmental Chemicals through Biotechnology*, Edited by G. Oemnu, Council for Research Planning in Biological Sciences, Inc. (1987).
 57. Gibson, D. T., Mahadevan, V. and Dewey, J. F., "Bacterial Metabolism of Para and Meta-Xylene: Oxidation of the Aromatic Ring:", *J. Bacteriology*, V. 19:930-936 (1974).
 58. Vogel, T. M., C. S. Criddle, and McCarty, P. L., "Transformations of Halogenated Aliphatic Compounds", *Environmental Science and Technology*, 21:722-736 (1987).
 59. Irvine, R. L. and Ketchum, L.H., "Sequencing Batch Reactors For Biological Wastewater Treatment", *CRC Critical Reviews in Environmental Control*, 1989, Vol. 18, Issue 4.
 60. Hsu, E. H., "Treatment of a Petrochemical Wastewater in

- Sequencing Batch Reactors", *Environmental Progress*, 1986, 5, 71-81.
61. Arora, M. L., Barth, E.F. and Umphres, M. B., "Technology Evaluation of Sequencing Batch Reactors", *J. Water Pollution Control Federation*, 1985, 57, 867-875.
 62. Alleman, J. E. and Irvine, R. L., "Nitrification in Sequencing Batch Reactor", *J. Water Pollution Control Federation*, Vol. 52, p. 2747 (1980).
 63. Silverstien, J. and Schocoder, E. D., "Performance of SBR Activated Sludge Process with Nitrification/Denitrification", *J. Water Pollution Control Federation*, Vol. 55, No. 1, p. 377 (1983).
 64. Alleman, J. E. and Irvine, R. L., "Storage Induced Denitrification Using Sequencing Batch Reactor Operation", *Water Research*, 14:p.1483 (1980).
 65. Manning, J. F. and Irvine, R. L., "The Biological Removal of Phosphorous in Sequencing Batch Reactors", *J. Water Pollution Control Federation*, Vol. 57, No. 1, p.87 (1985).
 66. Ketchum, L. H., Irvine, R. L., Breyfogle, R. E. and Manning, J. F., "A Comparison of Biological and Chemical Phosphorous Removals in Continuous and Sequencing Batch Reactors", *J. Water Pollution Control Federation*, 57, No. p.487

- (1985).
67. Irvine, R. L., Ketchum, L. H., Breyfogle, R. and Barth, E. F., "Municipal Application of Sequencing Batch Treatment at Culver", J. Water Pollution Control Federation, 55, p.484 (1983).
 68. Irvine, R. L., et. al., "An Organic Loading Study of Full Scale Sequencing Batch Reactors", J. Water Pollution Control Federation, 57, No. 8, pp.847-853 (1985).
 69. Irvine, R. L. and Ritcher, R. O., "A Comparative Evaluation of Sequencing Batch Reactor", J.Environmental Eng. Div. ASCE., p. 503 (1978).
 70. Herzbrun, P. A., et. al., "Biological Treatment of Hazardous Waste in Sequencing Batch Reactors", J. Water Pollution Control Federation, 57, p.1163 (1985).
 71. Irvine, R. L., et. al., "Enhanced Biological Treatment of Leachates from Industrial Landfills", Journal of Hazardous Waste, 1:p.123 (1984).
 72. Oleskiewicz, J. A., Mateja, S. and Hutchinson, J. E., "Treatment of Food Industry Wastewater in Sequencing Batch Reactors", Environmental Technology, 1990, 11, 499-508.
 73. Misbahuddin, M., "Characterization and Treatment of Petro-

- chemical Wastewater for Reuse", M.S. Thesis, KFUPM, June, 1989.
74. Abufayed, A. A. and Edward, D. S., "Performance of SBR/identificatio with a Primary Sludge Carbon Source", J. Water Pollution Control Federation 1986, 58, 387-398.
 75. Jones, W. L., Peter, A. W. and Edward, D. S., "Operation of a Three-Stage SBR System for Nitrogen Removal from Wastewater", Research Journal, Water Pollution Control Federation 1990, 62, 268-274.
 76. Standard Methods for Examination of Water and Wastewater, 15th Edition, APHA-AWINA-WPCF 1980.
 77. Drinkwater, L. A., Zoltek, J., Jr., and Delfino, J. J., "Beach Scale Treatability and Leachate From an Abandoned Phenolic Waste Site", J. WPCF, Vol. 58, No. 11, (1986).
 78. Metcalf and Eddy, Inc., Wastewater Engineering: Treatment, Disposal, Reuse, McGraw-Hill, 1979.
 79. Sawyer, C. N. and McCarty, P. L., "Chemistry for Sanitary Engineers", Second Editin, McGraw-Hill, (1967).
 80. Spiegel, M. R., "Statistics" Theory and Problems", McGraw-Hill, (1961).
 81. Qasim, S. R. and Stinchelfer, M. L., "Effect of Bacterial

- Culture Product on Biological Kinetics", J. WPCF, Vol. 54, No. 3, (1982).
82. Rebhun, M., Galil, M. and Narkis, "Kinetic Studies of Chemical and Biological Treatment for Renovation", J. WPCF, Vol. 57, No. 4, (1985).
83. Orhon, D., Ilhan, R., and Gokeen, S., "Treatment of Strong Fermentation Wastes by Activated Sludge", Wat. Sci. Tech. Vol. 22, No. 9, pp. 65-73, (1990).