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ANAEROBIC TREATMENT OF
GASIFIER EFFLUENT

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ABSTRACT

Studies have been conducted to determine the biological treatability of coal gasification effluent for removal of organic carbon and ammonia. The treatment system consisted of a anaerobic activated carbon filter for organic carbon removal followed by a single stage nitrification system followed by a biological denitrification reactor. Dilute (~10%) wastewater was successfully treated over an extended period of time. However, after extended operation (~one year) inhibition of the biological system was encountered. This inhibition could be overcome by periodic replacement of a portion of the granular activated carbon contact media.

Attempts to utilize the anaerobic system to treat solvent extracted ammonia stripped coal gasification effluent to remove substituted hydantoins was of limited success. Removals of 50% of the influent hydantoins were realized but only very small amounts of gas were produced. Apparently the primary removal mechanism was by adsorption on the granular activated carbon.

Batch inhibition studies showed substituted pyridines as the primary inhibitory compounds in the raw wastewater.

Carbon adsorption-solvent regeneration for hydantoin removal did not appear to be a viable treatment alternative due to low adsorption capacities and incomplete regeneration of the activated carbon.

INTRODUCTION

Coal gasification has been regarded as one of the promising technologies in alleviating the nation's energy problems caused by limited supplies of natural gas and petroleum. However, wastewaters generated from some coal gasification processes contain high concentrations of phenols, cresols and ammonia, and lower amounts of cyanide, thiocyanate, and other trace organic compounds. Pretreatment, i.e., solvent extraction followed by steam stripping, is capable of markedly reducing the concentration of phenolic compounds and ammonia. However, there remains in some wastewaters high concentrations of highly water soluble compounds such as substituted hydantoins.

The aerobic activated sludge process has been used to remove organic contaminants from dilute coal gasification wastewaters¹⁻⁶. Most coal conversion technologies incorporate or project the use of aerobic processes as the principle means for treating the residual organic compounds and other impurities present in such wastewater¹. Such processes are very energy-intensive, with aeration times often exceeding four days. Moreover, instabilities induced by variations in the chemical characteristics of the influent waste stream are often encountered.

In treatability studies conducted on wastewater generated by the Morgantown Energy Research Center fixed-bed coal gasifier, Sack and Bokey³ observed that major constituents of coal gasification wastewater escape treatment in the activated sludge process even at aeration times exceeding six days. Aromatic amines, thiophenes, and polycyclic hydrocarbons were found to be specially resistant to aerobic treatment while the phenolic content of the treated effluent was invariably in excess of desired levels. Ganczarczyk and Elion⁷ obtained similar results from extended aeration treatment of coke plant effluents. Luthy⁴ studied a variety of wastewaters generated by coal coking and coal gasification processes and found, with a number of forms of pretreatment, that biological treatment of coal conversion effluents resulted in good removals of biological oxygen demand (BOD), chemical oxygen demand (COD), phenols, ammonia-nitrogen, and cyanide-nitrogen using hydraulic retention times of 2-20 days. However, microbial yields were relatively low, which was attributed to inhibitory constituents in the wastewater. In a similar study, Stamoudis⁸ obtained comparable results using hydraulic retention times of two to nine days.

Inhibition of aerobic treatment of coal conversion wastewaters is believed to be due to several constituents present in these wastewaters. Thiocyanate, which is poorly degraded in aerobic biological treatment, exhibits an inhibitory effect on the aerobic biodegradation of phenol⁸, while cyanide, thiocyanate, and phenol have been observed to inhibit nitrification of ammonia. Juntgen and Klein⁹ have studied the co-inhibition of phenol, thiocyanate, and ammonia during aerobic treatment.

In cross acclimation studies of the treatment of petrochemical wastes in a conventional anaerobic filter, Chou¹⁰ found that the anaerobic environment provided rather rapid acclimation to shock loadings of phenol, catechol, resorcinol, nitrobenzene, and cyanide. Van Velsen¹¹ demonstrated with treatment of piggery wastes that anaerobic organisms could function efficiently at ammonia concentrations exceeding 6000 mg/L and pH levels of 8.

Lettinga¹² demonstrated that these systems also acclimated rapidly to cyanide.

The feasibility of using anaerobic systems for the treatment of phenol as an alternative to conventional aerobic biological systems has been reported by Hobson et al.¹³. The biokinetics of anaerobic phenol degradation has been studied by Neufeld¹⁴, and Chemielowski¹⁵ has performed specific kinetic research on the anaerobic decomposition of phenol. Healy and Young¹⁶ have demonstrated the process of degradation of phenol and catechol by methanogenic population of bacteria. The anaerobic biodegradability of phenol and catechol has also been confirmed by Khan et al.¹⁷ and Suidan et al.¹⁸. However, most of these anaerobic biological studies on degradation of phenolic substances involved single synthetic substrates of relatively low concentration. The treatment process used in this study combines the advantages of the energy-efficient anaerobic filter process developed by Young and McCarty¹⁹ and later modified by Chian and DeWalle²⁰. Recirculation of the effluent and the adsorptive capacity of activated carbon for the extended detention of less readily biodegradable compounds were originally reported by Khan et al.¹⁷ for the anaerobic degradation of phenols. Recent work by Suidan²¹⁻²² has shown the applicability of anaerobic filters for treating coke wastewaters.

Activated carbon is often used as a contact medium for biological treatment systems since it has the excellent characteristics of being lightweight, having a large surface area, a large void volume, and surface properties that are conducive to the growth of microorganisms. The activated carbon may also adsorb inhibitors to microbe metabolism which would allow the biological treatment process to continue even though inhibitory agents are present in the waste stream. In this regard, it is particularly useful as a medium for anaerobic filters since anaerobic treatment processes are relatively sensitive to inhibition. This report is based on results obtained from anaerobic filters studied as a treatment alternative for the water quench waste stream from a pilot-scale coal gasifier operated by the former Grand Forks Energy Technology Center (GFETC) (currently the University of North Dakota Energy Research Center (UNDERC)).

The UNDERC gasifier is a slagging fixed-bed unit.²³ Coal is gravity fed from hoppers at the top of the gasifier, and is dried, devolatilized and finally combusted and gasified as it descends in the reactor. The non-combustible portion (ash) of the coal is removed from the unit as slag, while the product gas flows upward in the reactor, countercurrent to the coal, and exits at the top of the vessel. An oxygen and steam mixture at about a one to one molar ratio is introduced to the reactor through four tuyeres above the hearth plate. With high moisture lignite, a gas offtake temperature of 325°F is realized. The gasification system can operate at pressures up to 600 psi. The hot product stream enters a water quench spray cooler where soluble gases and devolatilization products are removed. The soluble gases removed include NH₃, CO₂, HCN, and H₂S while the devolatilization products include tars, oils, and water vapor. The product gas then is processed through an overhead gas cooler where additional light oils and water vapor are removed.

The wastewater streams in the gasification process are the gas liquors from the spray cooler and light oils and water vapor from the overhead gas cooler. Both streams are sent to a tar/oil/water separator where oils and tar are gravity separated. Most of the work reported herein was performed on water which had been obtained from the tar/water separator.

UNDERC has the capability to further treat the wastewater from the tar/water separation unit. Sand filtration is used to remove residual tar, followed by solvent extraction and steam stripping. Solvent extraction employs diisopropylether to remove dissolved organic compounds. Steam stripping is utilized to remove ammonia and acid gases. A portion of the study reported here utilized water resulting from the solvent extraction steam stripping operation.

RESEARCH OBJECTIVES

Objectives of the overall research project included:

1. A study of the treatability of raw GFSFBG effluent using a two stage anaerobic activated carbon filter and determination of maximum loading rates and the effect of recycle rate on treatment performance.
2. Identification of compounds inhibitory and/or toxic to the biological treatment system.
3. Determine the applicability of biological treatment for the removal of ammonia from the anaerobically treated effluent (nitrification-denitrification).
4. Determine the treatability of solvent extracted ammonia stripped wastewater for removal of hydantoins using anaerobic activated carbon filters.
5. Determine the adsorption capacity of granular activated carbon for hydantoins.
6. Investigate the solvent regeneration of granular activated carbon saturated with hydantoins.

MATERIALS AND METHODS

Wastewater Sources

All wastewater was produced at the University of North Dakota Energy Research Center (UNDERC) and shipped to the Georgia Institute of Technology (GIT) via refrigerated trucks. Upon receipt at GIT the wastewater was stored frozen in five gallon plastic containers. Individual containers were thawed as needed, composited in fifty gallon batches, diluted and used in the project. Two different batches of gasifier effluent were used in the study. These were designated by UNDERC as RA-52 and RA-87. A separate batch of pretreated (solvent extracted-steam stripped) wastewater was utilized for the feasibility study of the anaerobic treatment of hydantoins and the adsorption-solvent regeneration of granular activated carbon.

Results of the analysis of the raw gasifier wastewater are presented in Tables 1 and 2 and the pretreated wastewater characteristics are presented in Table 3.

Biological Treatment Systems and Carbon Adsorption-Regeneration System

Schematic diagrams, physical dimension, and operating characteristics of all systems used in the study are given in Appendix A.

Analytical Methods

Specific methods of analysis used for the evaluation of all samples are given in Appendix B. In general all samples were filtered through a 0.45 μM membrane filter prior to analysis.

Table 1. Characteristics of Raw UNDERC Coal Gasification Effluent
(Average of Six Samples)

	<u>Concentration^a</u>
pH	8.2
Total organic carbon (TOC)	11,900
Chemical oxygen demand (COD)	26,900
Total alkalinity (as CaCO ₃)	25,000
Total suspended solids (TSS)	3,670
Total volatile solids (TVS)	3,180
Total volatile acids (as CH ₃ COOH)	460
Phenol ^c	5,600
o-Cresol ^c	640
m-Cresol ^c	930
p-Cresol ^c	910
NH ₃ -N	5,300
CN ⁻	140
SCN ⁻	150
S ⁻²	BDL ^b
Metals	
Chromium	BDL
Zinc	BDL
Nickel	BDL
Copper	BDL
Iron	5.5
Manganese	BDL

^amg/L except pH.

^bBelow detection limit.

^cBy gas chromatographic analysis.

Table 2. Minor Constituents of UNDERC Gasification Effluent

Compound	Concentration (mg/L)
Acid Fraction	
2,6-Dimethylphenol	12
2-Ethylphenol	50
2,4-Dimethylphenol+2,5-Dimethylphenol	358
3,5-Dimethylphenol+3-Ethylphenol+4-Ethylphenol	968
2,3-Dimethylphenol	40
Dimethoxybenzene or C ₂ -Benzenediol	46
3,4-Dimethylphenol	158
C ₃ -Phenol	10
C ₃ -Phenol	8
C ₃ -Phenol	20
C ₃ -Phenol	4
C ₃ -Phenol	24
C ₃ -Phenol	20
Naphthol	4
Neutral Fraction	
Benezene	1.1
Toluene	1.4
Cyclopentanone	0.8
Aliphatic hydrocarbon	0.3
C ₁ -Cyclopentanone	0.3
Ethylbenzene	0.1
o-Xylene	0.5
m- and p-Xylene	0.3
Methoxybenzene	0.2
Benzonitrile	0.7
C ₃ -Benzene	0.6
C ₁ -Methoxybenzene	0.5
C ₃ -Benzene	2.0
Naphthalene	0.7
C ₁ -Naphthalene	2.1
Indole	1.0
C ₁ -Naphthalene	0.9
C ₂ -Benzaldehyde	2.2
Acenaphthylene	0.6
1,1'-Biphenyl	0.4
Dihydroacenaphthylene	0.3
Dibenzofuran	0.5
Fluorene	0.5
C ₃ -Naphthalene	0.1
C ₁ -Dibenzofuran	0.2
Phenanthrene	0.6
Anthracene	0.2
Fluoranthene	0.2
Pyrene	0.1
C ₁ -Pyrene	0.04

Compound	Concentration (mg/L)
Base Fraction	
Pyridine	4.62
2-Picoline	3.71
3-Picoline+4-Picoline	2.53
C ₂ -Pyridine	1.4
C ₂ -Pyridine	0.29
C ₂ -Pyridine	1.06
C ₂ -Pyridine	0.32
C ₂ -Pyridine	0.12
C ₂ -Pyridine	0.04
C ₂ -Pyridine	0.07
Aniline	1.10
C ₃ -Pyridine	0.16
C ₂ -Pyridine	0.12
C ₃ -Pyridine	0.20
C ₃ -Pyridine	0.02
C ₃ -Pyridine	0.02
C ₃ -Pyridine	0.01
C ₃ -Pyridine	0.03
C ₁ -Aniline	0.53
C ₁ -Aniline	0.18
C ₂ -Aniline	0.01
C ₃ -Pyridine	0.06
C ₂ -Aniline	0.03
C ₃ -Pyridine	0.01
Quinoline	0.49
Isoquinoline	0.01
C ₁ -Quinoline	0.08
C ₁ -Quinoline	0.03
C ₁ -Quinoline	0.02
C ₁ -Quinoline	0.01
C ₁ -Isoquinoline or C ₁ -Quinoline	0.01
C ₁ -Quinoline	0.01
C ₁ -Isoquinoline	0.01
C ₂ -Quinoline	0.01
C ₂ -Quinoline	0.02

Table 3. Pretreated Wastewater Characteristics^c

<u>Constituent</u>	<u>Concentration^a</u>
pH	8.9
TOC	1,700
COD	5,700
Total alkalinity (as CaCO ₃)	1,500
Methanol	230
Ethanol	BDL ^b
Acetone	10
2-Propanol	BDL
Acetonitrile	2
Diisopropylether	BDL
1-Propanol	BDL
Propionitrile	BDL
Phenol	160
o-Cresol	BDL
m-Cresol	BDL
p-Cresol	BDL
5,5-Dimethylhydantoin	2,140
5-Methyl-5-ethylhydantoin	490
Total volatile acids (as CH ₃ COOH)	BDL
NH ₃	560
Sulfide	8
Cyanide	39
Thiocyanate	210

^amg/L

^bBelow Detection Limit (Detection Limit ~10 mg/L)

^cSolvent Extracted-Ammonia Stripped

ANAEROBIC TREATMENT OF GASIFIER EFFLUENT

Feed Substrate. The feed substrate employed in this study was a dilute solution of coal gasification wastewater having a total organic carbon (TOC) concentration up to approximately 1000 mg/L. This corresponds to approximately 10% wastewater in the feed.

During the initial acclimation phase, glucose was also added to some systems to provide a readily available carbon source for bacterial growth. Unlike the procedure reported by Khan et al.¹⁷, no vitamins or trace metals were added but a mixture of sodium and potassium phosphates were included to supplement the wastewater with phosphorus.

Process Monitoring. Daily checks of pump flow rates, carbon bed expansion, feed reservoir volume, pH, and gas production were made for each system. Weekly determination of total organic carbon, chemical oxygen demand (COD), oxidation reduction potential (ORP), alkalinity, total volatile acids, phenol, and gas composition were performed on influents and effluents from the anaerobic systems. The data were used to assess the performance of each unit in terms of removal efficiency of organic contaminants and the production and conversion of specific compounds, such as organic acids and phenol.

Anaerobic Treatment Systems

During the course of the project four anaerobic treatment systems were utilized. The system configurations were as follows:

- System I - anaerobic upflow Raschig ring packed column followed by an anaerobic fluidized activated carbon filter.
- System II - identical to System I.
- System III - A single anaerobic fluidized activated carbon filter.
- System IV - three anaerobic fluidized activated carbon filter in series.

Details concerning the construction of the individual columns are given in Appendix A.

Systems I and II were started simultaneously, allowed to acclimate (Phase I), operated at pseudo-steady-state (Phase II) until failure occurred. System III was started approximately 90 days after System I and II and was operated with granular activated carbon replacement based on the results obtained with Systems I and II. System IV was started approximately one year after System I and II and was studied as an alternative to granular activated carbon replacement within a single reactor.

RESULTS AND DISCUSSION

Anaerobic Filters

The four pilot-scale two-stage anaerobic Raschig ring and granular activated carbon filter systems used in this study were operated at empty-bed hydraulic retention times of 24 hours in each column. The Raschig ring packed fixed-bed reactor was operated in a plug-flow mode, whereas the granular activated carbon reactor was operated in a fluidized (well mixed) mode. The latter was accomplished by means of effluent recycle at an upflow rate of 5 gpm/ft² (13.3 m³/m²/h). As indicated in Table 4, Systems I and II were started on Day 0 and operated approximately one year; Systems III and IV were started on Days 87 and 380 respectively (Table 5).

Phase I - Acclimation

During the 147 days of phase I, the first-stage Raschig ring packed column was seeded with approximately 4 L of settled digested sludge (ca. 5-6%) solids collected from a local sewage treatment plant (R. M. Clayton Plant, Atlanta, GA). The procedure for seeding the Raschig ring packed column was based on previous experience with difficulty encountered in directly establishing a viable microbial population in the fluidized carbon bed. The procedures for acclimating the system receiving coal gasification wastewater are given in Table 4. As shown, the substrates fed to the system were maintained at 1000 mg/L TOC. During this phase of the study, glucose was added to one reactor system to facilitate rapid accumulation of a bacterial population producing methane gas. An increasing concentration of wastewater with a concomitant decrease of the glucose concentration was added to the feed to enhance acclimation of the microorganisms capable of degrading the coal gasification wastewater. The use of this start-up procedure was found to have little effect on the rate of acclimation of the sludge toward degrading coal gasification wastewaters in either system.

Phase II - Pseudo-Steady-State Operation

During the 47 days of phase II (Day 147-194), both systems were operated under identical conditions with a feed consisting of only diluted coal gasification wastewater (ca. 10% raw wastewater) and phosphates. Feed flow rates were maintained at 10 mL/min (14.4 L/d) to each system and the systems were monitored to assess their performance.

Chemical oxygen demand and TOC removals during this period, indicated in Figures 1-4, exhibit similar performance for both systems, with COD removals increasing with time. The COD removals averaged 77.6 and 87.1% for systems I and II, respectively, while corresponding TOC removals averaged 73.0 and 78.1%. Phenol removals, shown in Figures 5 and 6, were in excess of 90% for both systems. Phenol removals decreased somewhat after day 147, when the overall loading on the system increased, and then began increasing again with final effluent concentrations in the range of 20-40 mg/L. Only 10-20% of the phenol was removed in the first-stage Raschig ring column, with the remainder being removed in the second-stage granular activated carbon column.

Removal of cresols was also monitored during pseudo-steady-state operations. Overall removal efficiencies were 99.9 and 99.4% for systems I and II, respectively, with approximately 58% being removed by the Raschig ring column and 41% by the granular activated carbon columns.

Table 4. Anaerobic Reactor Systems I and II, Feed Composition

PHASE I	DURATION DAYS	FLOW RATE ML/MIN	SYSTEM I		SYSTEM II	
			WASTEWATER MG/L TOC	GLUCOSE MG/L TOC	WASTEWATER MG/L TOC	GLUCOSE MG/L TOC
A ^a	1-50	10	500	500	500	500
B	50-70	10	800	0	800	0
C	70-84	7	800	0	700	300
D	84-112	7	1,000	0	700	300
E	112-147	7	1,000	0	800	200
PHASE II	147-194	10	1,000	0	1,000	0

^aDesignation of incremental substrate changes.

Table 5. Anaerobic Reactor Systems III and IV, Feed Composition

System III - One AFAC ^a with cyclic carbon replacement System IV - Series of three AFAC Filters							
SYSTEM III				SYSTEM IV			
DAYS	FLOWRATE ml/min	GLUCOSE TOC mg/l	WASTE TOC mg/l	DAYS	FLOWRATE ml/min	GLUCOSE TOC mg/l	WASTE TOC mg/l
87-133	10	500	500	380-440	5.0	0	1000
134-147	10	400	600	441-455	6.0	0	1000
148-167	10	300	700	456-466	7.5	0	1000
168-195	10	200	800	467-575	10.0	0	1000
196-216	10	100	900				
217-550	10	0	1000				

^aAnaerobic Fluidized Activated Carbon Filter

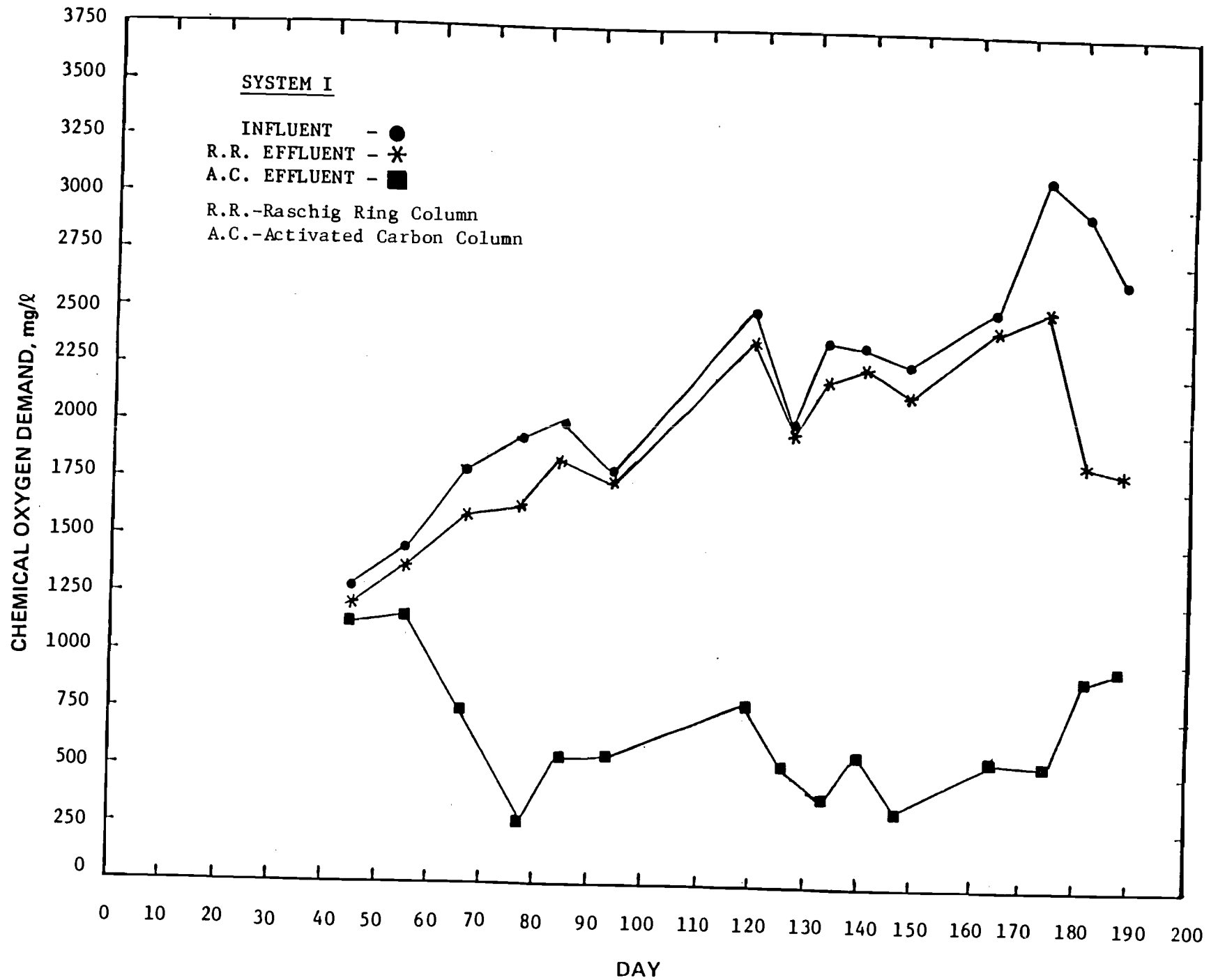


Fig. 1 COD Removal System I.

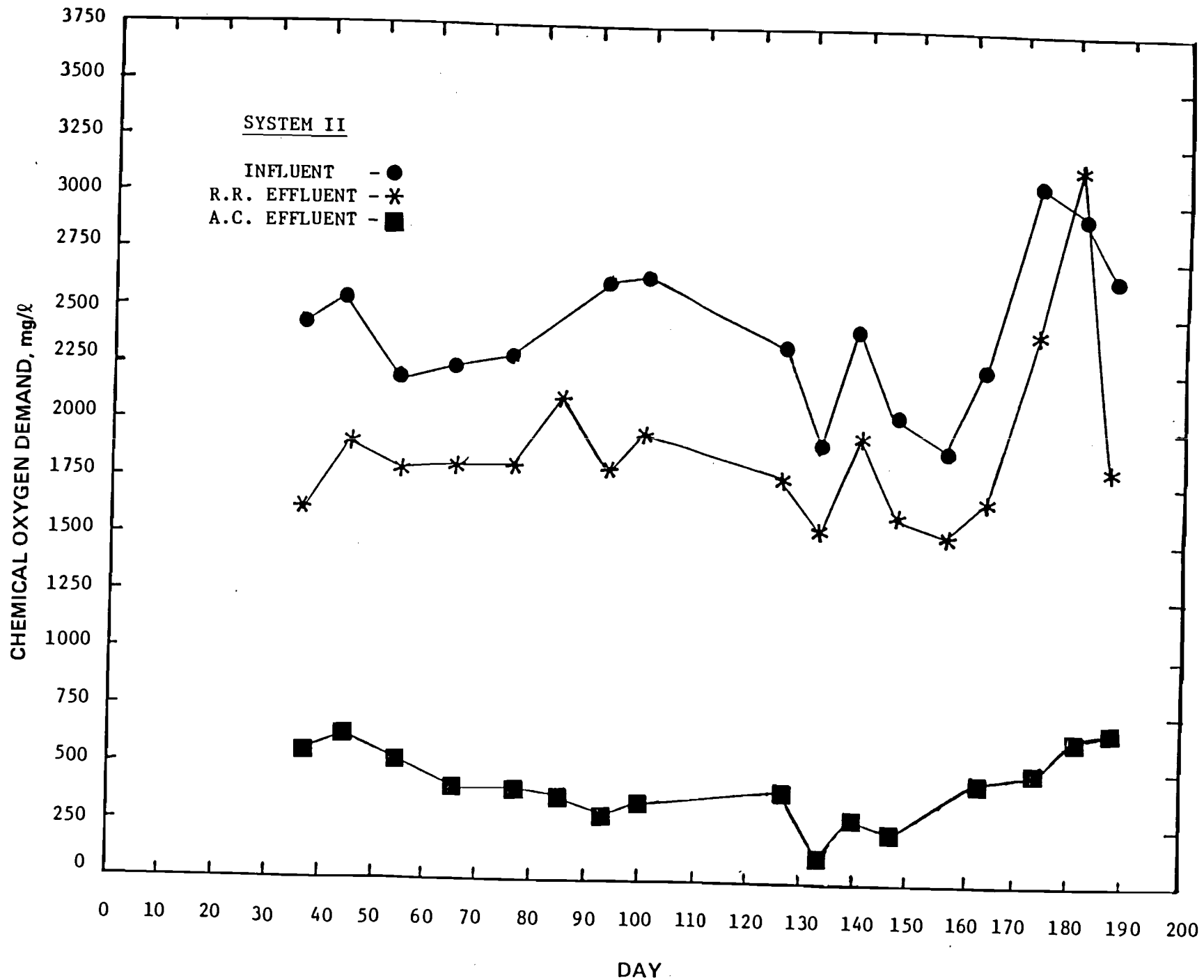


Fig. 2 COD Removal System II.

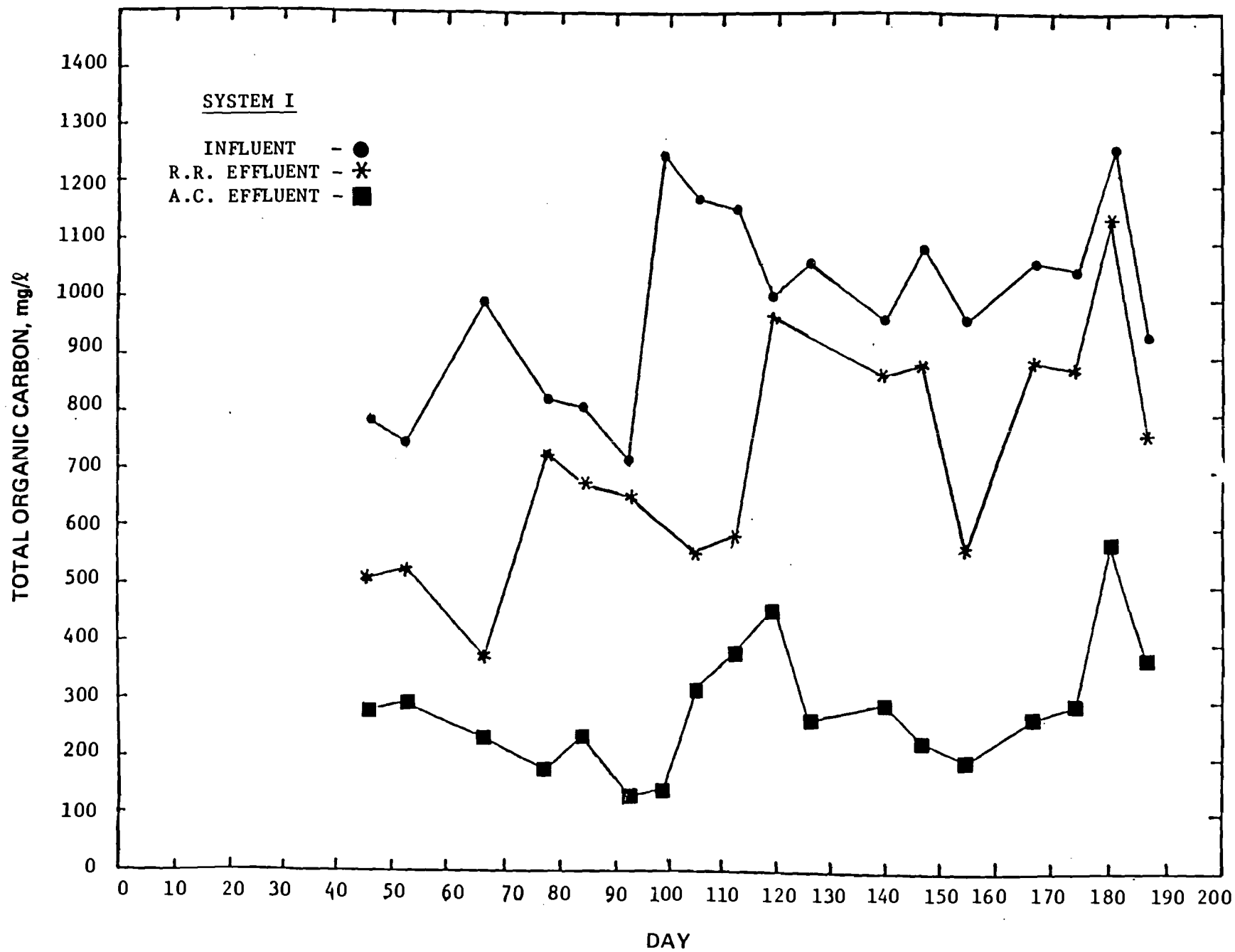


Fig. 3 TOC Removal System I.

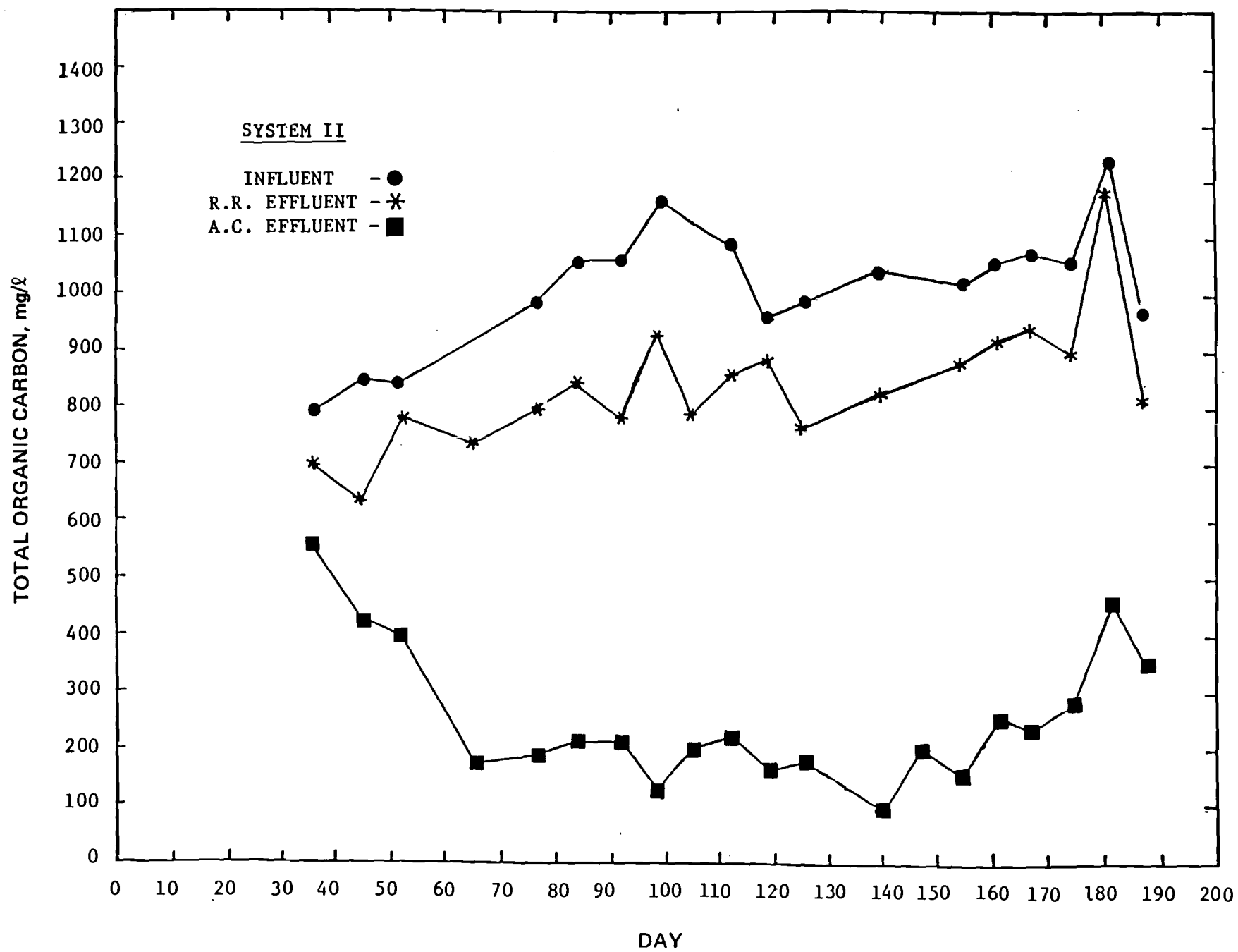


Fig. 4 TOC Removal System II.

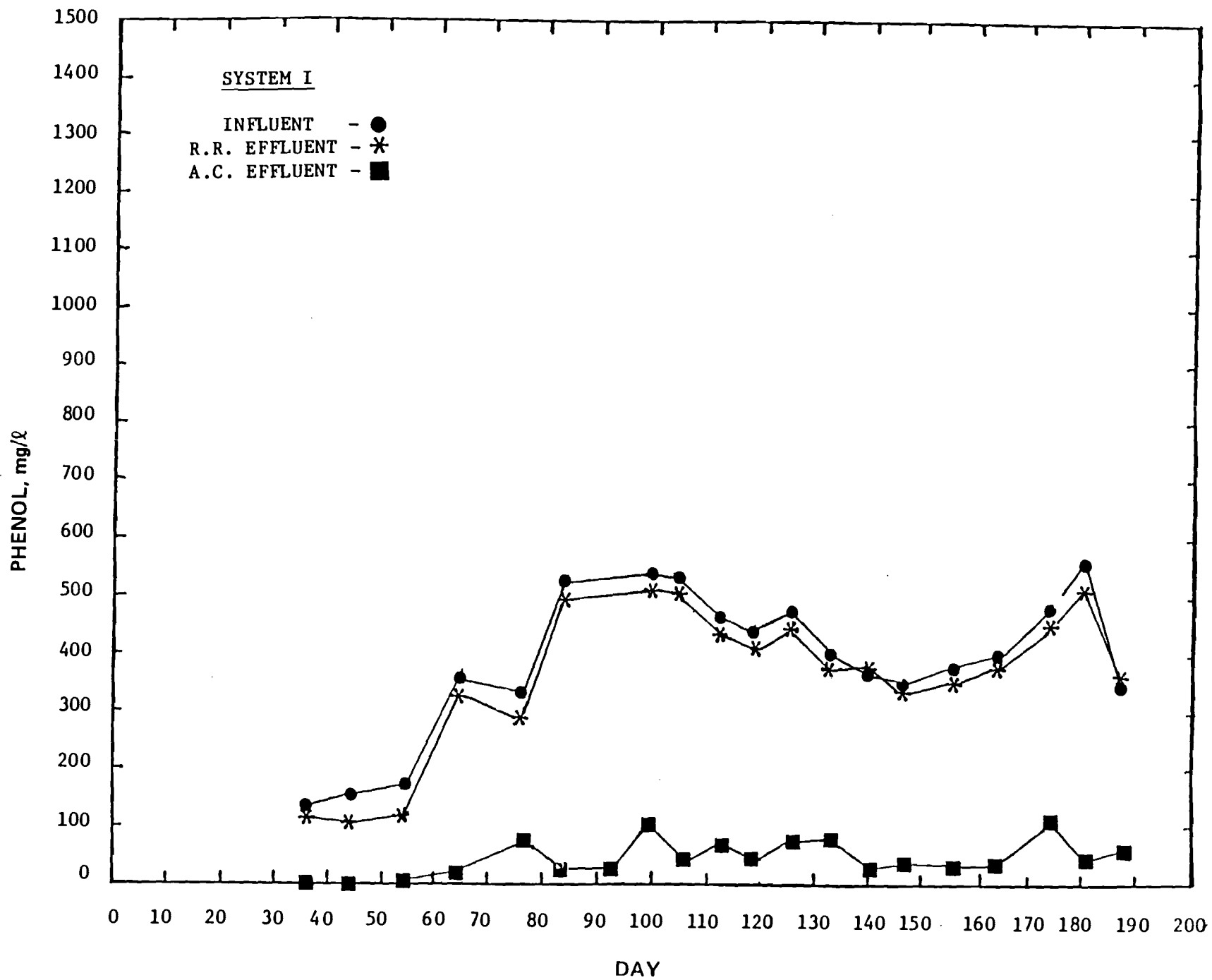


Fig. 5. Phenol Removal System I.

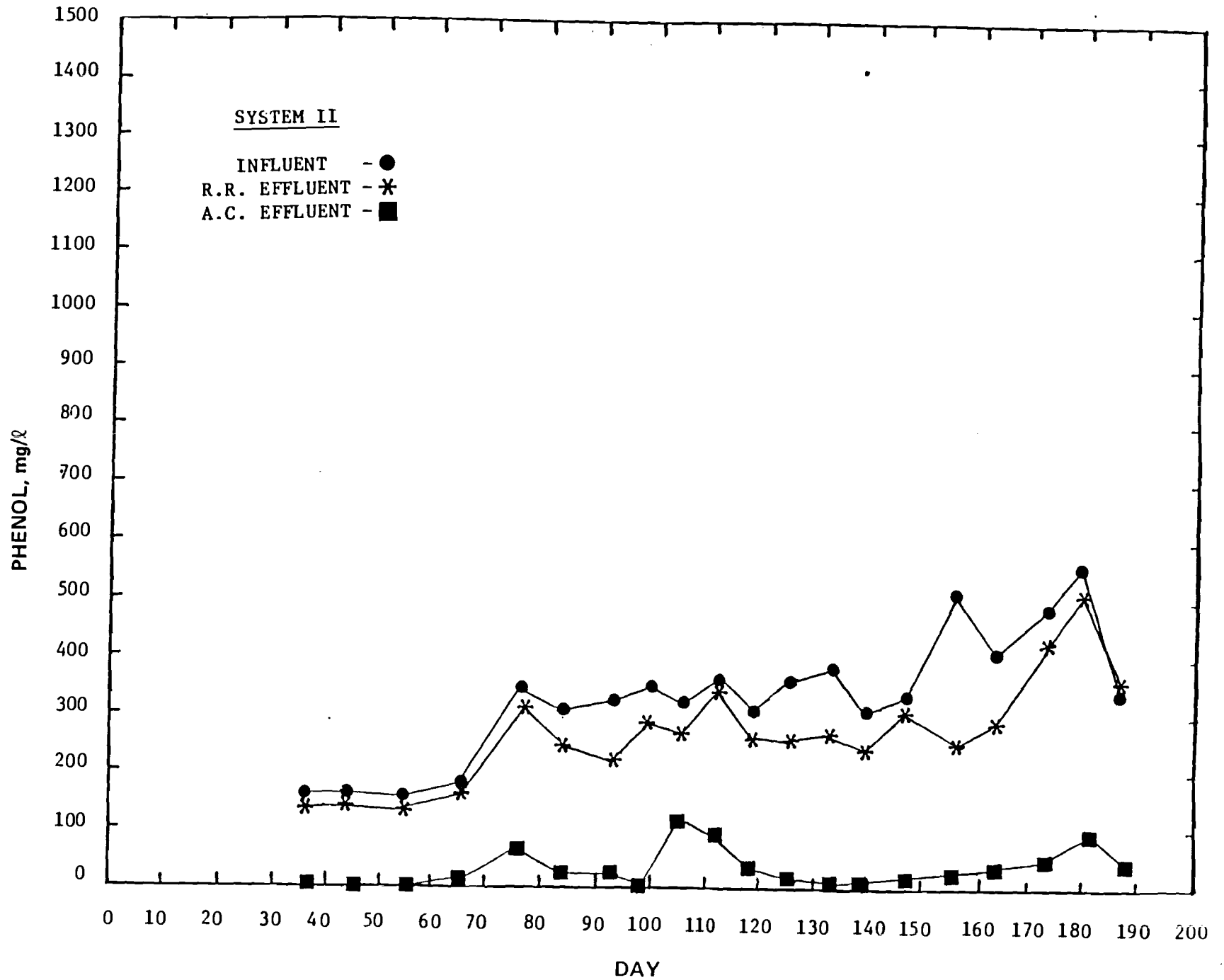


Fig. 6 Phenol Removal System II.

Volatile fatty acids concentrations, shown in Figures 7 and 8, indicate fluctuations in concentration during the acclimation period due to changes in loading and other operational stresses imposed on the systems. However, there was an overall decrease in the acid concentrations as the systems became acclimated and more completely converted the acids to methane and carbon dioxide. Levels of total volatile fatty acids in the final effluent were on the order of 100 mg/L.

Gas production, shown in Figures 9 and 10 continued to increase during the acclimation period until rates of 5.7 L methane/day for system I and 3.6 L methane/day for system II were achieved. The quantity of methane being produced by system I was slightly in excess of that calculated from the anaerobic degradation of the influent phenol, while the amount produced by system II was slightly less. However, no correction has been made for conversion of substrate to biomass or for the solubility of methane in water. Approximately 86% of the methane produced was generated by microbial activity within the granular activated carbon columns.

Suspended solids in the effluent of the granular activated carbon columns were on the order of 20 and 40 mg/L for systems I and II, respectively.

CONCLUSIONS

Wastewater from the UNDERC coal gasification process are amenable to treatment by a two-stage anaerobic filter packed with Raschig rings and granular activated carbon. Results indicate that good removal of the major wastewater constituents were obtainable using a dilute wastewater (ca. 10% raw wastewater) with a total empty-bed retention time of approximately two days. At a loading of 2.5 kg COD/m³d the two-stage system had removal efficiencies of 87% COD, 78% TOC, 93% phenol, and 99% cresols during pseudo-steady-state operation. No apparent inhibition was observed under the stated operating conditions.

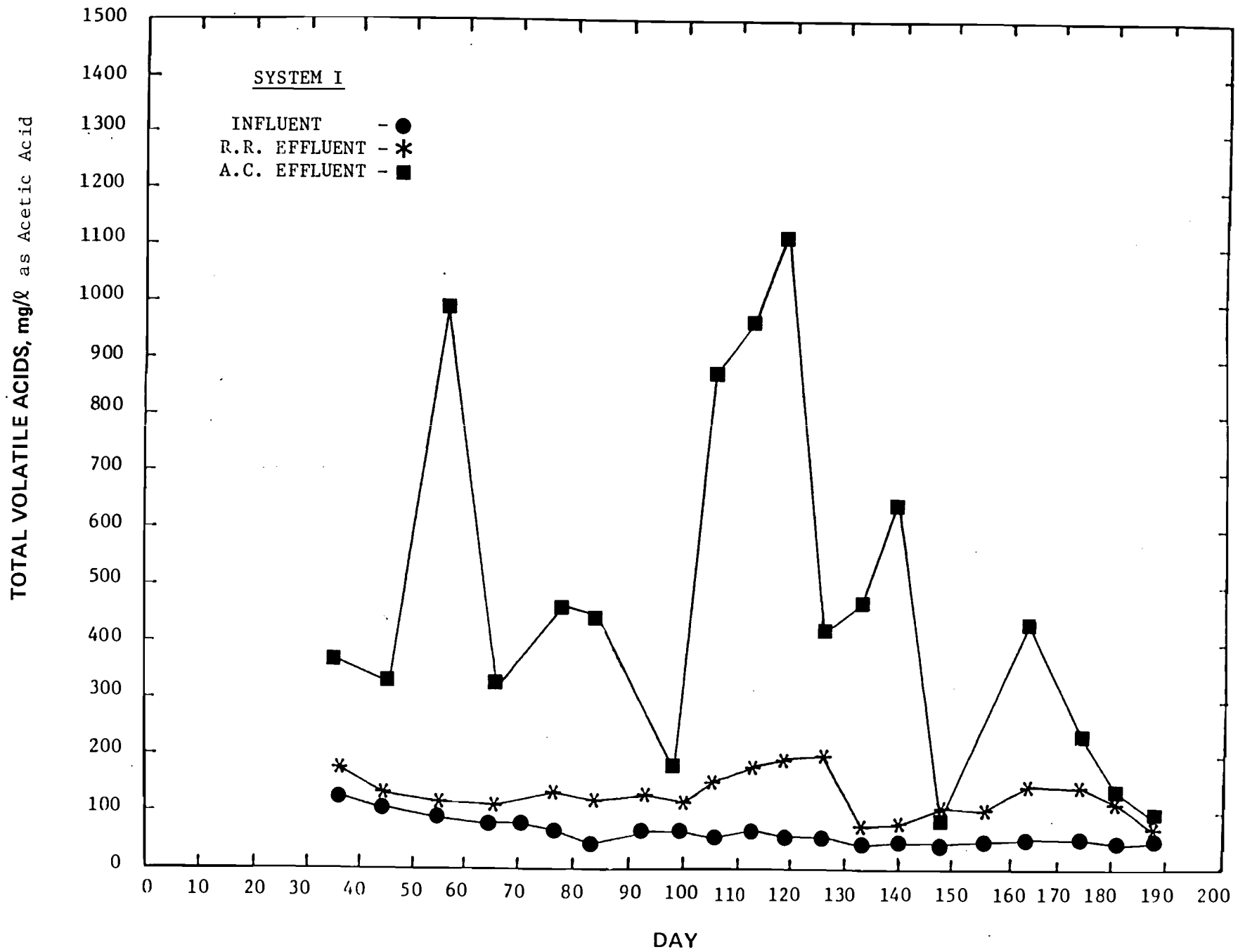


Fig. 7 Total Volatile Acids System I.

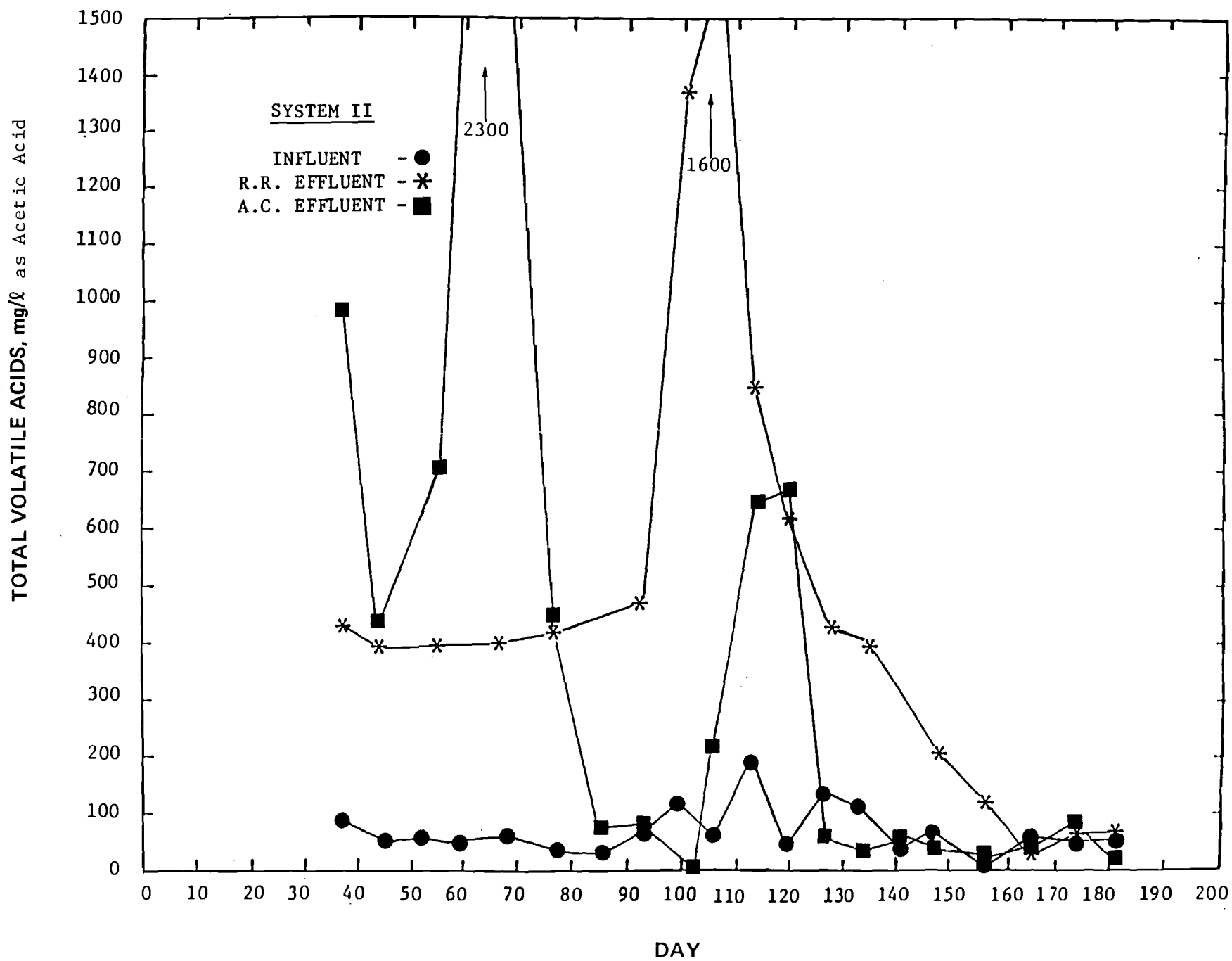


Fig. 8 Total Volatile Acids System II.

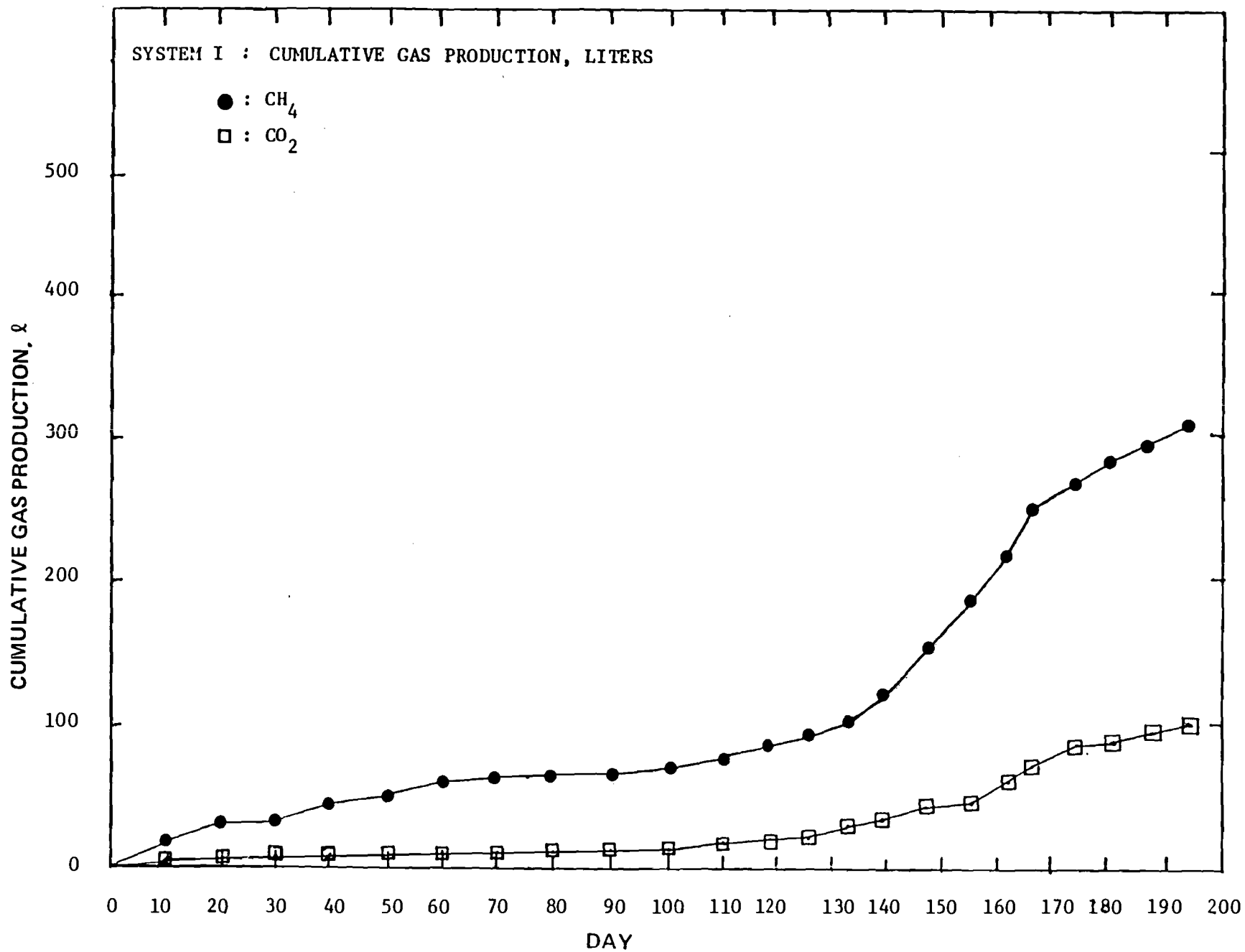


Fig. 9 Gas Production System I.

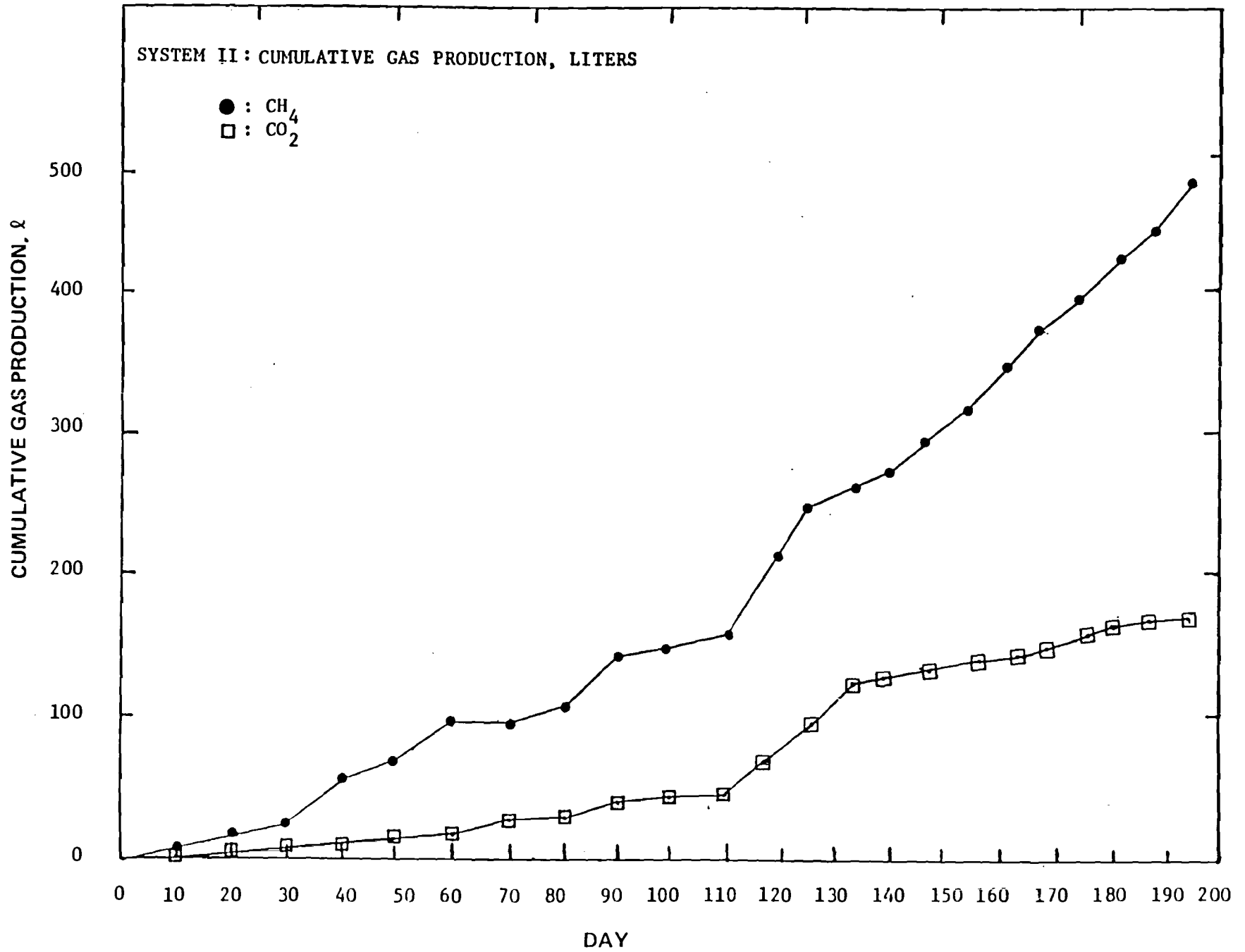


Fig 10 Gas Production System II

CARBON REPLACEMENT DUE TO SYSTEM INHIBITION

The study reported herein establishes the relationship between adsorption provided by the activated carbon and the improvement in biological conversion of coal gasification wastewaters. A mutually beneficial relationship has been observed wherein adsorption serves as an in situ pretreatment which promotes conditions suitable for biological growth; the ensuing biological activity extends the life of the carbon via bioregeneration. An understanding of this relationship was considered central to successful operation of the process and for approaching optimum process performance.

Process Inhibition, System II - Carbon Solvent Extraction

Figure 11 shows the variability in performance as measured by gas production and organic carbon removal of system II during its period of operation. On day 195, the influent TOC to the reactor was increased from 1000 mg/L to around 1500 mg/L by decreasing the wastewater dilution from approximately 10:1 to approximately 8:1. Process performance declined rapidly and failed to recover despite attempts at pH control and an ultimate reduction in the organic load. The ensuing search for the cause of process failure led to solvent extraction of the activated carbon with dioxane and dimethylformamide. Subsequent GC/MS analysis of the solvent extract revealed an accumulation of cresols and C-2 substituted phenols on the carbon as compared to the influent, Table 6 and Table 7.

Examination of Figure 11 reveals that the beginning of process failure appeared to coincide with carbon saturation as indicated by the almost complete breakthrough of cresols at about day 200. This also occurred immediately after the increase in loading, influent TOC increased from 1000 mg/L to 1500 mg/L. Therefore it was not possible to clearly distinguish whether the process failed due to overloading, inhibition due to some component remaining in solution in the absence of adsorptive removal, or a combination of the two.

Process Inhibition, System III - Carbon Cycling for in situ Pretreatment

System III was carefully monitored in terms of gas production and removal efficiencies with speculation that an inhibitory pollutant might appear at around the time of carbon saturation. Figure 12 shows a slow but constant decline in process performance following phenol breakthrough around day 125, and becoming appreciably more notable following the beginning of cresol breakthrough at around day 210. Particularly poor performance was observed in system III around days 330 and 440. Figure 12 shows an accumulation of volatile acids under these conditions, which suggests that the methanogens are inhibited first thus preventing conversion of the volatile acids to methane and carbon dioxide.

Soon after cresol saturation, COD removal efficiencies declined from 70% to around 30%, and gas production ceased. Therefore on day 456 one liter of fresh carbon (10% of the total carbon bed volume) was added to avert reactor failure. Performance of the system in terms of COD, TOC, phenol, and cresol improved immediately, as shown in Figure 13. On day 461 a 10% increase in gas production was noted, but only for a short period of time. Within 10-12 days of carbon addition, the removal efficiencies of the process had declined to their previous unsatisfactory levels. On day 488, a second dose of carbon was added to the reactor by removing 3 L of spent carbon from the reactor and adding 2 L of fresh carbon; returning the carbon bed to its original volume of 10 L.

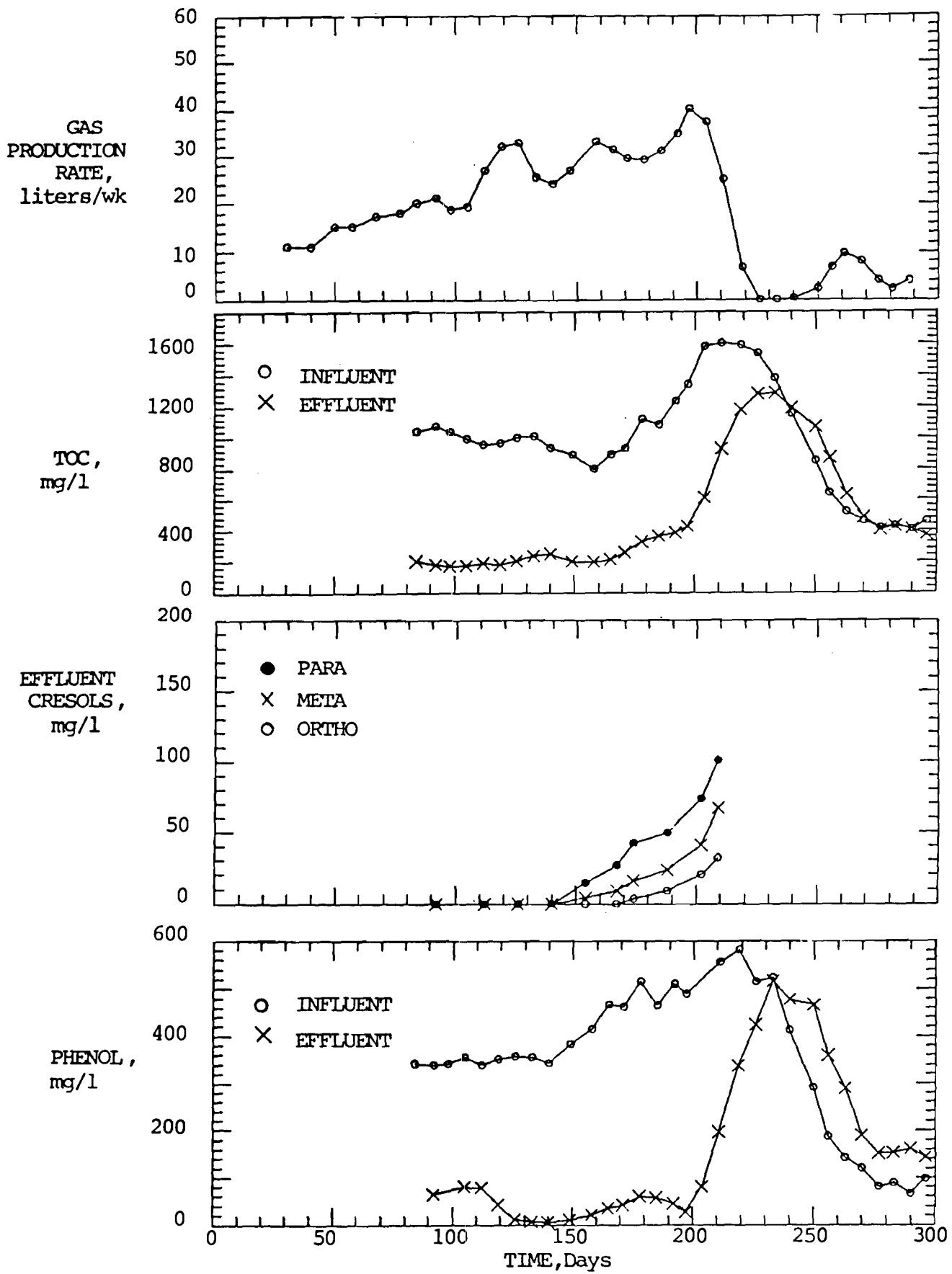


Fig. 11 Gas Production and Constituent Removal, System II.

Table 6. Organic Constituents Extracted from Granular Activated Carbon
Removed from Inhibited Biological Reaction

Compound	Concentration mg/l
Pyridine	4.6
2-Picoline	3.7
4-Picoline	5.8
Aniline	1.9
Benzonitrile	0.7
2-Methoxyphenol	169.0
2,6-Dimethylphenol	6.8
2,4-Dimethylphenol	
2,5-Dimethylphenol	125.0
4-Ethylphenol	
3,5-Dimethylphenol	118.0
3-Ethylphenol	9.2
3,4-Dimethylphenol	28.6
3-Methoxyphenol	1.2
4-Methoxyphenol	1.0
2,3,5-Trimethylphenol	3.4
Indole	2.5

Table 7. Comparison of Ratio of Substituted Phenols to Phenol in Reactor Influent and Granular Activated Carbon Extracted After Reactor Failure

	Influent	Carbon Extract
o-cresol	0.11	2.74
m-cresol	0.17	9.12
p-cresol	0.16	
C ₂ -phenols	0.05	4.90

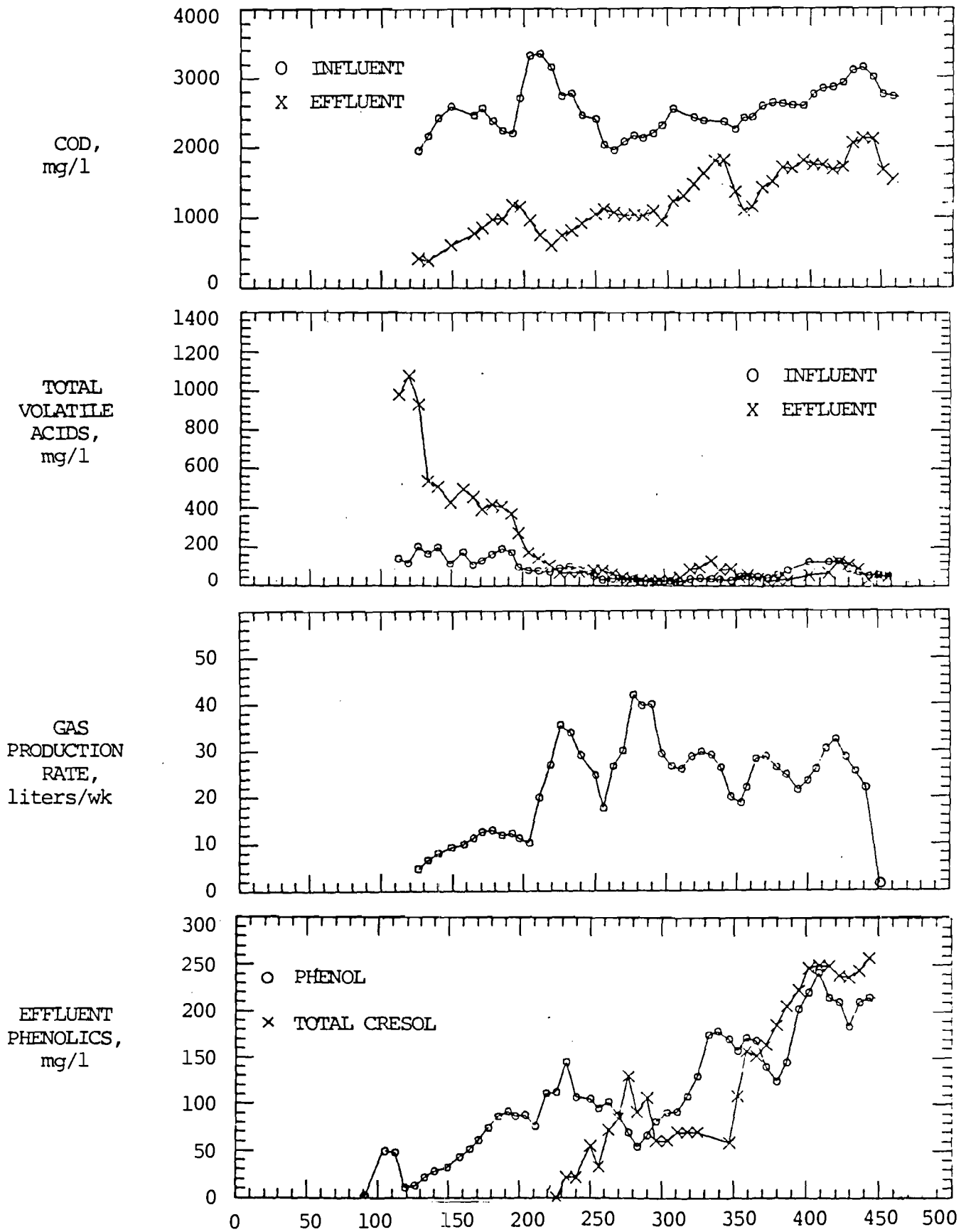


Fig. 12 Gas Production and Constituent Removal of System III Prior to Carbon Cycling.

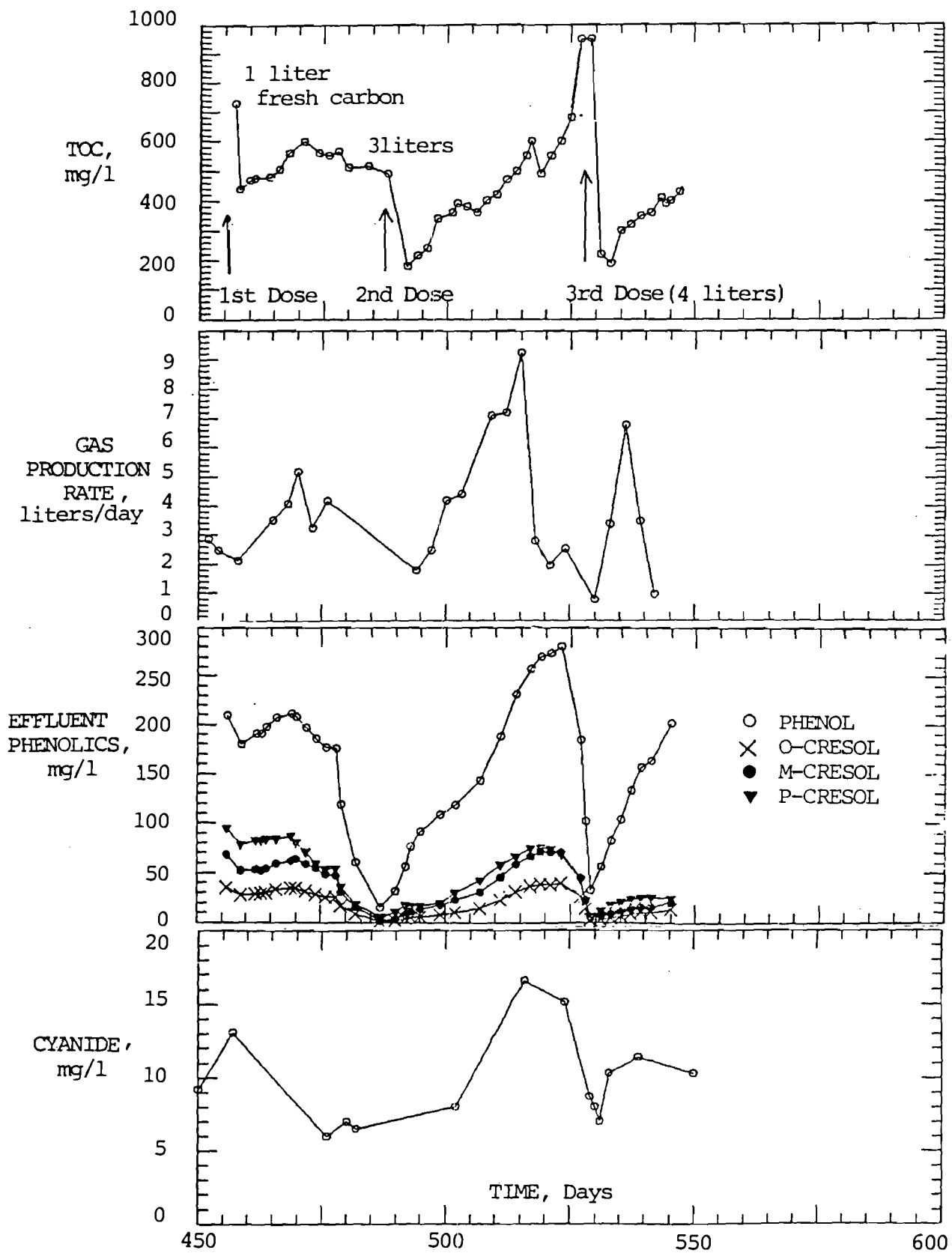


Fig. 13 Gas Production and Constituent Removal of System III During Carbon Cycling.

Removal efficiencies were again improved immediately, and were followed by a large increase in gas production to about 8.4 L per day (70% methane) or approximately the same volume of gas produced during peak performance of both systems II and III. This fact again seemed to point to the existence of an optimum biological growth condition just beyond initial cresol breakthrough but before total saturation (and the possible breakthrough of other organic and inorganic constituents). Additionally, since phenol breakthrough had previously occurred, its availability as a substrate for biological growth was at a maximum under this condition. The pragmatic implications of these observations become clear - if the reactor could be operated at biologically conducive conditions for the long term, maximal substrate use and minimum dilution could possibly be realized. The engineering considerations such as reactor design and operational strategies remain to be optimized. Economic feasibility will ultimately depend on these engineering considerations, and the advantages potentially available from efficient use of anaerobic over aerobic stabilization systems.

Moreover, the AFACF provides a degree of treatment beyond that available from activated sludge, since even at long retention times a number of pollutants which are adsorbed in AFACF escape aerobic conversion. Further, the removal of these same pollutants has been observed as being instrumental in determining the efficiency of nitrification and denitrification systems downstream as discussed later.

Series of AFACF Reactors - Carbon Scheduling

From the observed behavior of the AFACF and nitrification process in response to cyclic additions of fresh activated carbon, the necessity of maintaining active adsorption as an in situ pretreatment was evident. From an operational viewpoint, carbon replacement should occur as infrequently as possible to avoid downtime and minimize loss of biomass. Two immediate needs arise: a simple and effective method for the physical replacement of carbon, and an operating strategy including a carbon replacement schedule and analytical monitoring procedures.

Insofar as the replacement of carbon is concerned, one approach is a series of reactors representing a moving-bed type of system, wherein reactors are operated until carbon saturation and then temporarily removed from service for carbon bed regeneration and/or replacement. This approach was studied and results are illustrated in Figure 14, which shows that virtually no gas production was observed in the second column in the series (B) until phenol breakthrough occurred. At this point the gas production rate began to slowly increase concomitant with the rise in phenol concentration. The third column in the series did not produce any gas nor have any phenol in the effluent. The first reactor in the series would be removed as soon as the second reactor has attained a stable level of performance. Unfortunately, the second reactor's performance declined before substantial biological activity could be established. Perhaps the microorganisms did not have sufficient time to acclimate to the phenolic carbon sources before the onset of inhibition.

The other carbon replacement strategy studied involved the removal of a percentage of the spent carbon and addition of fresh carbon as previously illustrated in Figure 13. This method also works well, although it requires a greater carbon replacement frequency and more operator time than does the series-reactor approach. Additional plumbing is also required to recirculate

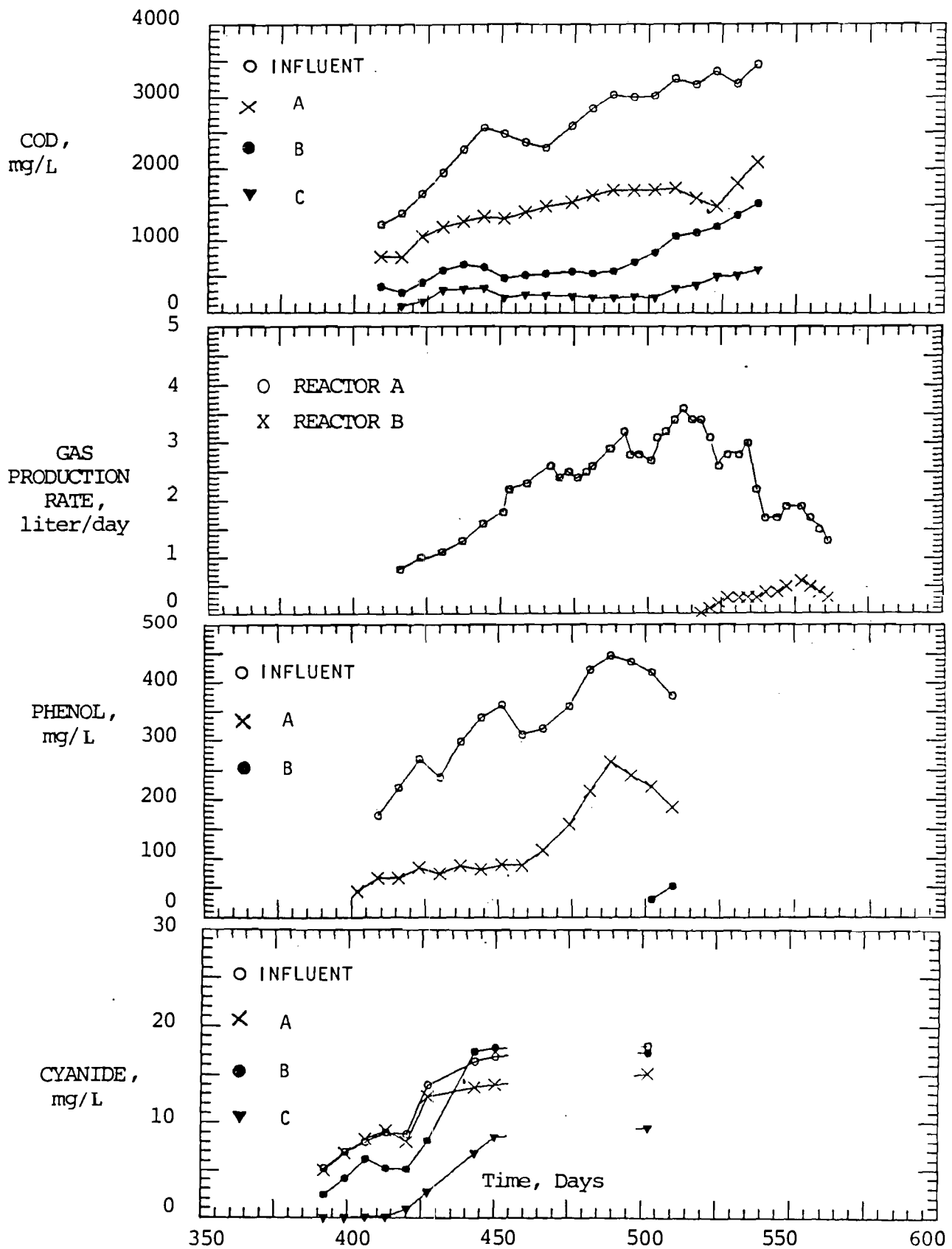


Fig. 14 Gas Production and Constituent Removal of Three Carbon Filters in Series - System IV.

process water through carbon addition and removal appurtenances in order to keep the bed anaerobic during replacement operations. This approach allows for a good deal of flexibility in process control and for rapid generation of operational data from which carbon replacement schedules can be established.

Adsorption Contribution to Wastewater Treatment

The relative contributions of adsorption and biodegradation to the overall TOC removal can be separated through a material balance on carbon as illustrated for system III in Table 8. Table 8 relates the performance of system III for the five months following the last glucose addition. For the period with no glucose in the feed, the table reflects an 80-90% contribution to total carbon (TC) removal by adsorption until biological activity increased around Day 270. During the ensuing two months of peak biological activity (Days 270-340), the adsorption contribution first decreased to 9%, then increased again to 75%, then decreased to zero on Days 334-340 where it appears that bioregeneration (defined as gaseous carbon production in excess of aqueous carbon input) may have occurred.

Biological Contribution to Adsorption

The production of biogas in excess of organic carbon in the influent, as witnessed on Days 334 and 340 (Table 8), possibly indicative of bioregeneration, may have served to increase the service life of the granular activated carbon. A comparison of the breakthrough curve produced for system III to a breakthrough curve generated in the absence of biological activity is shown in Figure 15. The nonbiological breakthrough curve was generated in a 1/2 in. internal diameter I.D. plexiglas column using ten g of 50 x 60 mesh carbon preceded by approximately 5 carbon bed depths of 35 mesh sand. The feed used was effluent which was taken from system III near carbon saturation, then refrigerated and monitored for phenol and cresol stability to assure bioinactivity. Influent phenol and total cresol concentrations were 150 and 190 mg/L, respectively.

The relationship between phenol and cresols for activated carbon (AC) and biological activated carbon (BAC) is illustrated by Figure 15, which shows that total cresol breakthrough for the biological carbon lags behind that of nonbiological carbon by about 200 g of carbon per kg of activated carbon used. This apparent increase in cresol capacity could have been due to bioregeneration and/or desorption of phenol from the carbon to accommodate cresol adsorption. It can be seen from Figure 15 that phenol desorbed from both nonbiological system (AC) as well as the biological activated carbon (BAC) system. The rate of desorption of phenol appeared to be much greater in the BAC system, thus allowing for the better accommodation of cresols and other higher molecular weight organics. It is interesting to note that the area between the phenol curves for AC and BAC roughly corresponds to the area between cresol curves for AC and BAC in Figure 15.

Suggestion for Operation

The effects of adsorption on the cyanide concentration are also particularly interesting. A decrease in cyanide removal efficiency is observable just following cresol breakthrough during both normal operation and carbon cycling studies. At these times, the cyanide concentration reached nearly 20 mg/L, which may well be a principal cause of inhibition. Similar trends can be seen in the data of Suidan et al. in that on Days 40 to 60 and 140 to 210, the cyanide concentration rose to above 20 mg/L and the process

Table 8. Mass Balance^a on Carbon in System III.

DATE	DAY	INFLUENT TOTAL CARBON, (mg/l)	INFLUENT INORGANIC CARBON, (mg/l)	EFFLUENT TOTAL CARBON, (mg/l)	EFFLUENT INORGANIC CARBON, (mg/l)	TOTAL CARBON REMOVED, (mg/l TC)	GASEOUS CARBON PRODUCED, (mg/l)	DISSOLVED GASEOUS CARBON (mg/l TIC)	ESTIMATED BIOMASS CARBON, (mg/l)*	ADSORBED CARBON, (mg/l)	REMOVED AS ADSORPTION, (%)	REMOVED AS BIOGAS, (%)
5/10	219	1370	160	720	190	650	55	30	10	555	85	13
5/17	226	1320	140	540	120	780	30	20	5	725	93	6
5/24	233	1070	150	660	200	410	60	50	10	290	71	27
5/31	240	1040	220	620	240	420	35	20	5	360	86	13
6/10	250	1040	160	580	160	460	80	0	10	370	80	17
6/16	256	940	140	680	190	260	40	50	10	160	62	35
6/24	264	940	160	670	180	270	35	20	5	210	78	20
7/01	271	970	180	620	180	350	245	0	25	80	23	70
7/08	278	920	180	520	140	450	255	-40	20	215	48	48
7/14	284	960	150	620	220	340	205	70	25	40	12	81
7/21	291	1000	125	660	190	340	215	65	30	30	9	82
7/27	297	1080	140	820	160	260	170	20	20	40	15	73
8/04	305	1060	200	660	190	400	180	-10	15	215	54	42
8/11	312	1090	180	550	180	540	135	0	15	390	72	25
8/18	319	1020	180	420	125	600	190	-55	15	450	75	22
8/25	326	1060	150	680	190	380	240	40	30	70	22	74
9/02	334	1100	190	1020	180	80	200	-10	20	-130	0	100
9/08	340	1140	240	1040	240	100	120	0	10	-30	0	100
9/16	348	1160	200	640	190	520	125	-10	10	385	74	22
9/22	354	1040	120	600	180	400	120	60	20	200	50	45
9/28	360	1060	130	600	170	460	70	40	10	340	74	24

*Estimated as approximately 10% of gaseous carbon produced.

^aTotal Carbon Removed = Gaseous Carbon Produced + Dissolved Gaseous Carbon + Estimated Biomass Carbon + Adsorbed Carbon.

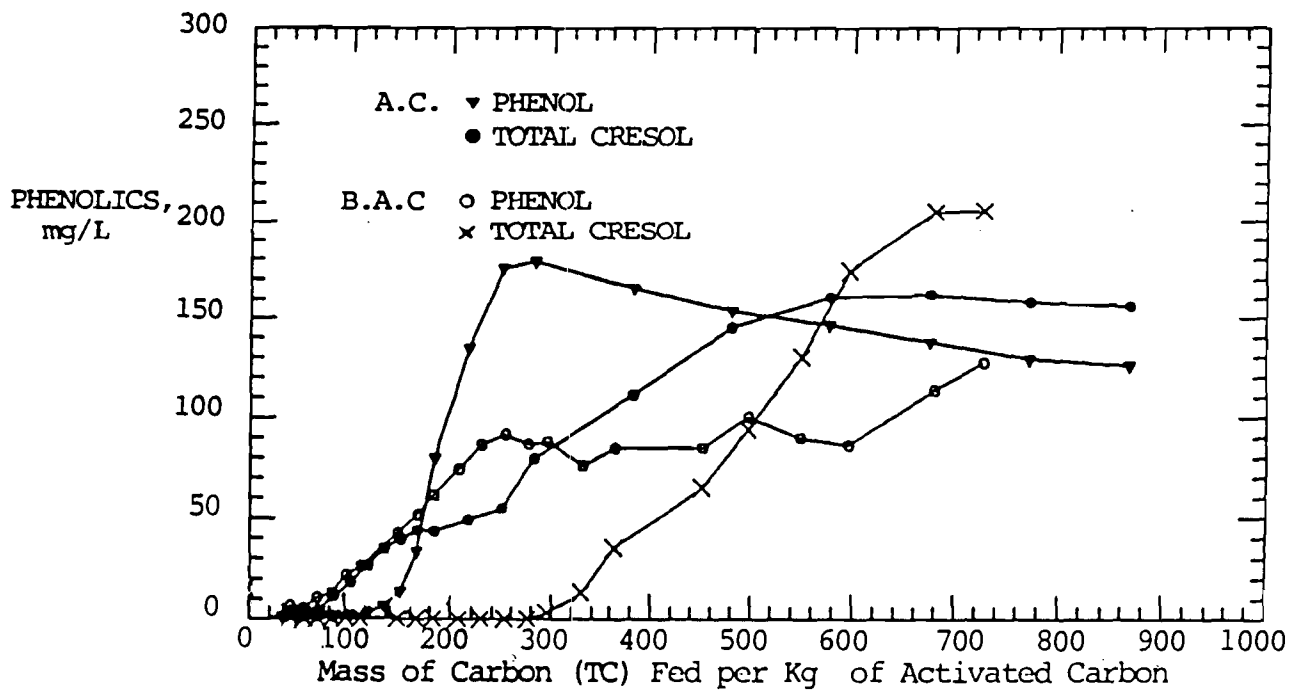


Fig. 15 Comparison of Biological Activated Carbon (BAC) and Non-Biological Activated Carbon (AC) Phenol and Total Cresol Breakthrough Curves

exhibited inhibitory behavior as reflected by decreases in COD and DOC removals²².

Discernment of the true identity of the inhibitory agent(s) would be of great benefit in optimizing biological process performance; however, it is not entirely necessary for process control. Correlations between process efficiency and monitoring parameters such as cresol, cyanide, gas production, and COD can be used as indicators of carbon saturation and biological activity and therefore serve as key control parameters. Recognition of an accumulation of adsorbable and/or inhibitory constituents in the bulk solution could indicate the need for carbon replacement in advance of biological failure and help maintain optimum operating conditions.

From experiences with 10% dilutions of wastewater, approximately 1.2-1.6 kg of activated carbon were required per kg of carbon fed before total inhibition occurred. At loading rates of 15 g of carbon/day this corresponded to around 50 days of operation per kg of activated carbon. Carbon cycling studies indicated a slightly higher frequency of carbon replacement is necessary to assure a high biological conversion rate; around 25 days of operation per kg of activated carbon seem optimum.

For carbon cycling operations, removal of around 25% of the bed volume does not seem to severely affect conversion; however, removal of a larger amount may necessitate a reacclimation period due to excessive biomass removal. For the series reactor approach, reactor size will ultimately be determined by the safety level desired in terms of biological activity overlap between sequential reactors and the degree of effluent polishing desired by adsorption.

Carbon cycling studies and series-reactor data have been combined with initial operational data on three separate reactor systems to suggest carbon replacement frequencies necessary for optimum biological-adsorptive process performances. A carbon replacement frequency of approximately 0.6-0.8 kg AC per kg of carbon fed (25 days/kg AC) seems biologically optimal. For a removal/replacement approach, no more than 25% of the bed volume should be removed at a time in order to avoid excessive loss of biomass.

NITRIFICATION STUDY

In order to remove ammonia nitrogen from the wastewater after TOC removal was accomplished in the anaerobic filter, the anaerobic filter effluent was treated using a single stage activated sludge nitrification system. In this type of biological waste treatment system, microorganisms are encouraged to grow utilizing ammonia-nitrogen as a substrate and converting it to nitrate nitrogen according to the following equation, $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+$. This process occurs when there is a limited amount of TOC available for the microorganisms to use as a substrate. In addition since the processes produces hydrogen ion, sufficient alkalinity must be supplied in order to maintain the pH at a relatively constant value. This was done by the addition of NaHCO_3 to the influent.

The nitrification experiments lasted 367 days and can be divided into five phases as follows:

- Acclimation Phase - when a nitrifying activated sludge was slowly acclimated to feed on the anaerobic effluent.
- Pseudo-Steady-State Phase - operation during which ammonia removal and other operation parameters remained relatively constant.
- Inhibition Phase - period during which poor performance by the anaerobic fluidized activated carbon filters in removing TOC and other constituents resulted in poor performance of the nitrification system.
- Powder Carbon Phase - during which powdered activated carbon (PAC) was added directly to the nitrification system to overcome the inhibition.
- Carbon Cycling Phase - during which a portion of the granular activated carbon was periodically replaced in the anaerobic fluidized activated carbon filters in order to improve their performance and prevent inhibition of the nitrification system.

The performance period for each phase of the nitrification study is shown in Table 9. Note that from Days 132 through 160, the nitrification system was short of feed several times; therefore samples were not routinely obtained and no data were reported.

Acclimation Phase. During Phase 1 of the study (Days 1 to 56), a nitrifying activated sludge obtained from a local pure oxygen wastewater treatment plant (South Cobb Plant, Austell, GA) was gradually acclimated to the anaerobic filter effluent which contained approximately 600 mg Total Kjeldahl Nitrogen (TKN)/L (527 mg $\text{NH}_3\text{-N/L}$). In the acclimation procedure (Table 9), the feed concentration (of the anaerobic filter effluent to the nitrification system) was increased in five steps from 10% to 100% anaerobic effluent. Each step increase in feed concentration during the acclimation phase lasted from 8 to 13 days.

Table 9. Phases of Nitrification Experiments.

PHASES OF NITRIFICATION EXPERIMENTS

Phase 1	Acclimation	Day	0 - 56
Phase 2	Pseudo-steady state operation		57 - 132
Phase 3	Inhibition		160 - 203
Phase 4	Addition of PAC to aeration tank		204 - 249
Phase 5	Replacement of GAC in anaerobic filter		250 - 367

No data available during day 133 - 159

Throughout the acclimation phase, the hydraulic retention time (HRT) was maintained at 18 hours and the solids retention time (SRT) was maintained at 22 days beginning with Period 1c (Table 10). Loadings were gradually increased from 0.06 to 0.23 kg NH₃-N/kg MLVSS·day and from 0.09 to 0.43 kg COD/kg MLVSS·day by increasing the concentration of anaerobic effluent fed to the system. Figure 16a (Days 1 to 56) indicates that effluent NH₃-N level occasionally increased suddenly at the beginning of each step but after 2 to 3 days, it decreased rapidly to its original level again. However, in other cases, there were no changes in final effluent ammonia from one step to another, indicating that the activated sludge could quickly acclimate to the feed change.

Table 10 also shows that during the acclimation phase as much as 99% of the NH₃-N was removed; effluent NH₃-N was less than 2 mg/L and almost all NH₃-N was converted to NO₃⁻-N. During the acclimation phase, COD and TOC removal increased from 40% initially to 80% at the end of the test period. Aeration basin MLSS increased from 1560 mg/L to 3170 mg/L during this same period.

Pseudo-Steady-State Operation. After acclimation, pseudo-steady-state operation of the nitrification system was attained. The system was first operated at the HRT and SRT used in the acclimation phase, (18 hours and 22 days, respectively). Data obtained during Period 2a (Days 57 to 82) showed that, although effluent COD and TOC were relatively constant (206 mg/L and 127 mg/L, respectively, Figure 16b), effluent NH₃-N gradually increased from 2 mg/L to 46 mg/L (Figure 16a) and effluent NO₂⁻-N increased as well (Figure 16c, Days 48 to 76). This indicated some inhibition of the nitrification process under these operating conditions. The SRT was increased from 22 to 31 days and the HRT from 18 to 30 hours; correspondingly, NH₃-N loading decreased from 0.27 to 0.15 kg NH₃-N/kg MLVSS·day and COD loading from 0.52 to 0.35 kg COD/kg MLVSS·day. Figures 16a and 16b (Period 2b, Days 83 to 132), indicate that, under these new operating conditions, the effluent quality from the nitrification system was very stable although influent COD and TOC continuously increased. However, a peak of approximately 125 mg NO₂⁻-N/L occurred in the last several days of Period 2b (Figure 16c, Days 123 to 132). Based on the data in parentheses in Table 10, TKN removal during this period was as high as 97% with effluent TKN of 18 mg/L. The effluent NH₃-N was only 4.4 mg/L, whereas effluent NO₃⁻-N was 485 mg/L. The corresponding COD and TOC removals were 95% and 91%, respectively. These data indicated that nitrification was relatively complete and organic matter reduction was high.

As shown in Table 11, a nitrogen balance was performed for a 30-day span during Period 2b (Days 97 to 127). The average effluent TKN, NO₃⁻-N and NO₂⁻-N accounted for 3%, 83.7% and 3.5% of the influent TKN, respectively. The total effluent nitrogen was 90.2% of the influent TKN or only 9.8% of the influent TKN was unaccounted for (the percentage of unaccounted nitrogen varying from 1.0% to 18.1%). This unaccounted portion of influent TKN was attributed to microbial cell growth, possible denitrification, air stripping, and analytical error.

The production of sludge was estimated during the same period. On the average, the sludge growth rate was 1.2 g/day and COD removed was 9.5 g/day. The computed yield coefficient was 0.13 kg sludge formed/kg COD removed, which

Table 10. Operating conditions and performance of nitrification system

Phase	Duration (days)	Period	Time (day)	Duration (days)	Dilution Ratio	SRT (days)	HRT (hrs)	NH ₃ -N loading	COD loading
1	56	1-a	1-13	13	1:9		18	0.06	0.09
		1-b	14-23	10	1:3		18	0.09	0.14
		1-c	24-31	9	1:1	22	18	0.15	0.14
		1-d	32-44	13	1:0.33	22	18	0.18	0.28
		1-e	45-56	12	1:0	22	18	0.23	0.43
2	76	2-a	57-82	26	1:0	22	18	0.27	0.52
		2-b	83-132	50	1:0	31	30	0.15	0.35
3	44		160-203	44	1:0	26-40	25-33	0.17-0.13	0.43-0.33
4	46	4-a	204-218	15	1:0	31	30	0.20	0.61
		4-b	219-249	31	1:1	31	43	0.08	0.24
5	118	5-a	250-277	28	1:1	30	30	0.08	0.20
		5-b(1)	278-303	26	1:0	30	18	0.18	0.24
		5-b(2)	304-325	22	1:0	30	30	0.15	0.40
		5-c	326-367	42	1:0	30	30	0.15	0.36

Phase: 1. Acclimation; 2. Pseudo-steady state operation; 3. Inhibition; 4. Addition of powdered activated carbon to aeration basin; 5. Periodical replacement of granular activated carbon in anaerobic filter.

Dilution ratio: Ratio of parts of anaerobic effluent to parts of tap water.

Unit of NH₃-N loading: kgNH₃-N/kgMLVSS/day.

Unit of COD loading: kgCOD/kgMLVSS/day.

Period	TOC(mg/l)			COD(mg/l)			NH ₃ -N(mg/l)		Eff NO ₂ ⁻ -N mg/l ²	Eff NO ₃ ⁻ -N mg/l ³	MLSS mg/l	Alkalinity consumption
	Inf	Eff	Rem%	Inf	Eff	Rem%	Inf	Eff				
1-a	48	28	42	99	60	39	65	0.8		56	1563	5.6
1-b	110	30	73	182	48	74	111	0.4	0.3	101	1902	5.7
1-c	227	46	80	256	91	64	263	1.8	2.4	221	2655	6.0
1-d	466	56	88	613	91	85	397	1.6	0.3	369	3294	6.1
1-e	692	131	81	895	196	78	485	2.1	10	419	3167	5.6
2-a	594	125	79	894	210	77	473	23	64	341	2509	5.5
2-b	776	72	91	1286	189	85	527 (TKN601)	4.4 (TKN18.3)	16	485	3238	5.8
3				1364	455	67	543	30-520	85	466-18	3318	
4-a				1711	398	77	568	414	24	16	2715	
4-b				955	204	79	294	208-1.8	12	25-295	2451	
5-a				682	84	88	260	1.9	0.3	194	2911	5.9
5-b(1)				680	92	86	515	3.7	0.5	476	4188	6.7
5-b(2)				1810	369	80	682	142-3.0	384-0.7	346-700	4153	
5-c				1393	184	87	579	7.0	4.2	597	3411	7.2

Unit of alkalinity consumption: mg Alkalinity consumed/mg NH₃-N removed

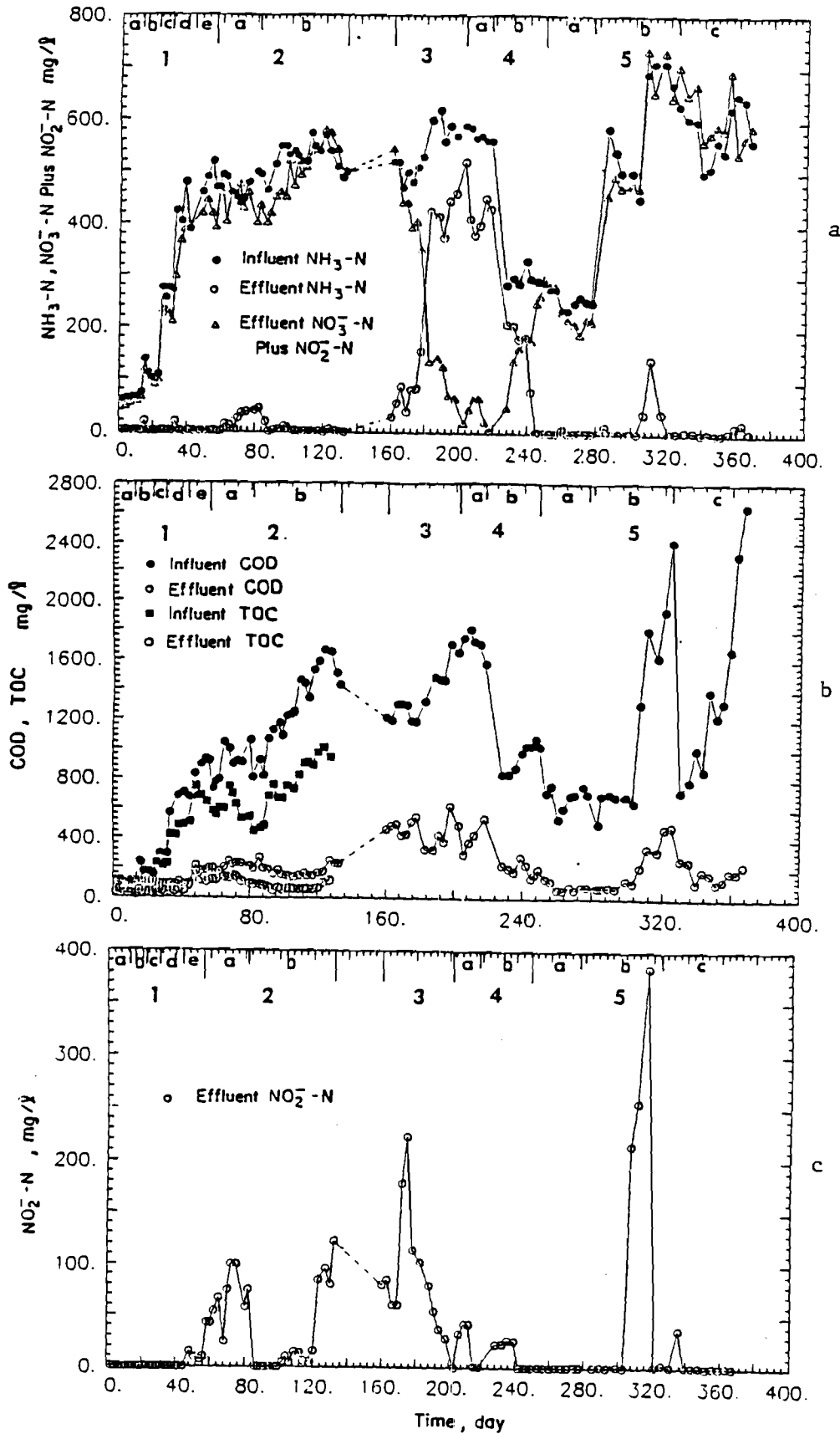


Fig. 16 Nitrification System NH₃-N, NO₃⁻-N, NO₂⁻-N, COD, TOC Concentrations

Table 11. Nitrogen Balance Data (Day 97-127)
For Nitrification System.

Day	Inf.	Eff.				Total N not accounted for	
	$\Sigma N_{inf} = \text{TKN}$	TKN	$\text{NO}_2^- - \text{N}$	$\text{NO}_3^- - \text{N}$	ΣN_{eff}^*	$\Sigma N_{inf} - \Sigma N_{eff}$	%
97	580	24.5	0.7	450	475	105	18.1
99	555	20.9	0.4	520	541	14	2.5
102	580	15.0	5.0	468	488	92	15.9
104	595	15.5	10.2	512	538	57	9.6
106	590	14.0	3.9	490	508	82	13.9
109	595	14.2	14.7	494	523	72	12.1
112	625	19.5	14.1	524	557	68	10.9
114	615	16.2	5.9	536	558	57	9.3
117	635	15.8	4.6	536	556	79	12.4
120	635	13.6	16.0	564	594	41	6.5
123	635	23.5	85.0	490	598	37	5.8
127	575	27.2	96.0	446	569	6	1.0
Ave.	601	18.3	21.4	503	542	59	9.8
% of Inf TKN	100	3.0	3.5	83.7	90.2	9.8	

All values are in mg/L except for percentages.

$$*\Sigma N_{eff} = \text{TKN} + \text{NO}_2^- - \text{N} + \text{NO}_3^- - \text{N}$$

was consistent with data obtained by Olthef¹⁰ for coke oven wastewater treatment. Calculated alkalinity consumption for the same period was 5.8 mg alkalinity consumed/mg NH₃-N removed.

Inhibition of Nitrification. The anaerobic filter effluent quality began to deteriorate from saturation of the activated carbon in the filter with refractory compounds such as cresols after 10 months of operation. The effluent COD eventually increased to 2100 mg/L with only 30% COD removal. Correspondingly, effluent phenol from the anaerobic filter increased to 270 mg/L with only 50% phenol removal and effluent total cresols increased to 230 mg/L without any evidence of cresol removal. That the poorer quality of anaerobic effluent resulted in inhibition of the nitrification process can be seen from Figure 16a where from Day 160 the performance of the nitrification system began to deteriorate. By Day 203 the system was almost completely inhibited and effluent NH₃-N was as high as 520 mg/L and effluent NO₃⁻-N plus NO₂⁻-N as low as 18 mg/L. Although the SRT and HRT were increased to 40 days and 33 hours, respectively, and an automatic pH controller was installed in the aeration basin to maintain pH between 7.0 and 7.5, the system performance did not improve.

As shown in Table 9, the loadings to the nitrification system during the inhibition period (Phase 3) were maintained at 0.17 to 0.13 kg NH₃-N/kg MLVSS·day and 0.43 to 0.33 kg MLVSS·day, comparable to those during pseudo-steady-state operation (Phase 2). Other operating parameters such as pH, alkalinity, and DO were also normal. The inhibition of the nitrification system might, therefore, have been attributable to the presence of some inhibitory compounds in the influent of the nitrification system; the most likely candidates were CN⁻, SCN⁻, S⁻², phenol, cresols, and other trace organic compounds in the coal gasification wastewater. However, analytical determinations indicated that the influent concentrations of CN⁻, SCN⁻ and S⁻² in the nitrification system were within the range of 3 to 17 mg/L, 4 to 20 mg/L, and 2 to 5 mg/L, respectively. Results reported in the literature^{4-6, 22,24-27} indicate no inhibition to nitrifying organisms attributable to these compounds at these concentrations.

Similarly, phenol in the influent to the nitrification system varied from 53 mg/L to 409 mg/L, and in most cases could be removed completely in the system as shown in Figure 17a. As indicated by several investigators^{4,24,26} phenol concentrations much higher than 400 mg/L could be removed entirely in the activated sludge process. Therefore, the inhibition of the nitrification system was not attributed to the presence of phenol.

Tomlinson, et al.²⁸ reported that nitrification (using activated sludge as a source of nitrifying bacteria) was inhibited by 12.8 mg/L o-cresol, 11.4 mg/L m-cresol, and 16.5 mg/L p-cresol. Suidan et al.²² showed that 7.8 mg/L o-cresol and 12.1 mg/L m-cresol and p-cresol could be removed completely without causing any inhibition. This may have been the result of a difference in the acclimated activated sludge. In this study, in all cases influent o-cresol concentrations from 3 to 46 mg/L were readily removed in the nitrification system (Figure 17b). However, only 80% of m-cresol and p-cresol was removed during the inhibition phase (Days 160 to 218); 20 to 35 mg/L remained in the effluent (Figure 17c). This level of m-cresol and p-cresol concentrations were implicated as a cause of nitrification inhibition although they could not be specifically identified as the sole inhibiting compounds.

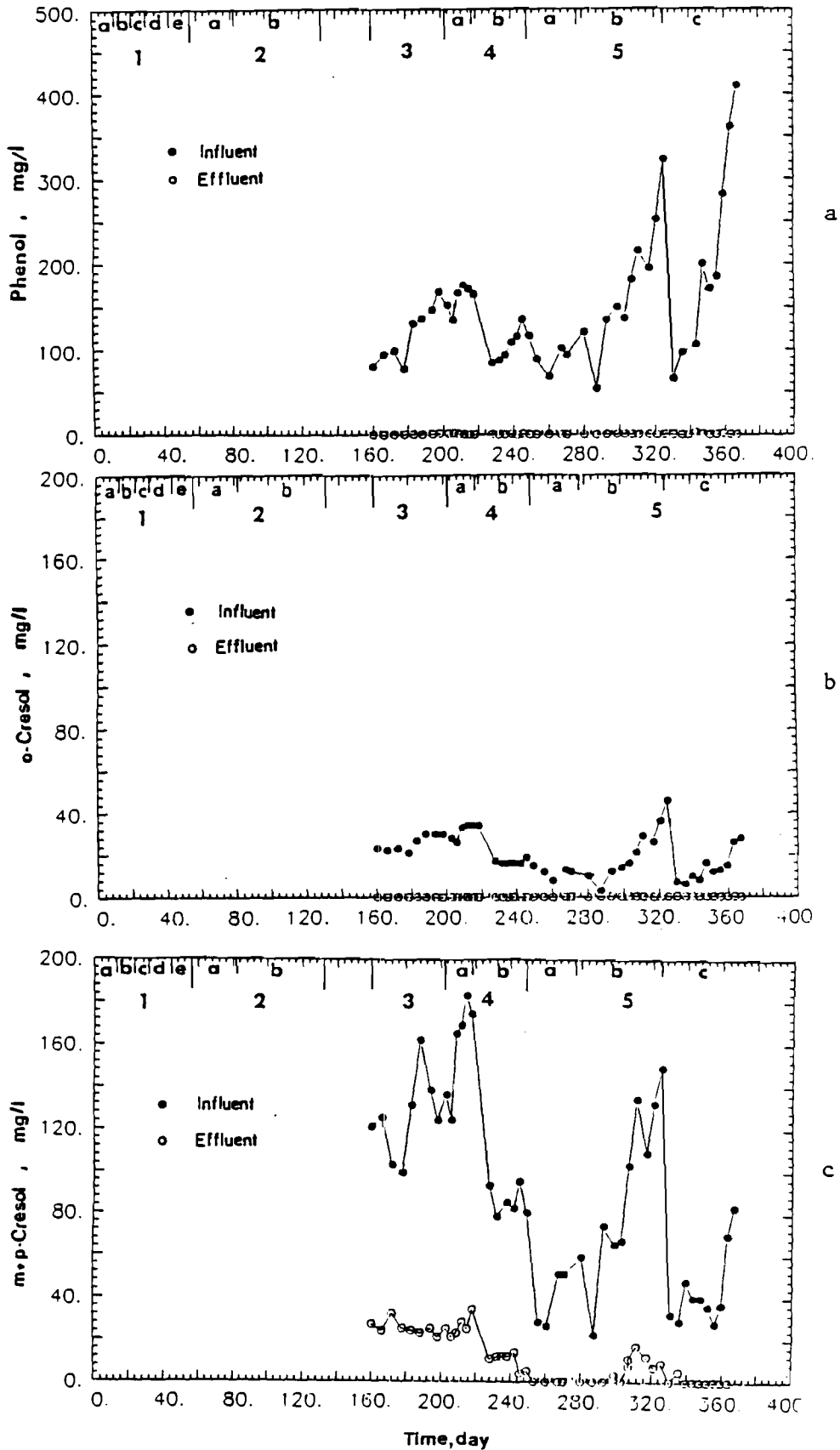


Fig. 17 Nitrification System Phenol, Cresol Concentrations

Because of the complex composition of the coal gasification wastewater, results shown in Figure 16a and Figure 16c (Days 244 to 304, and 321 to 367) indicated that when the total concentration of m-cresol and p-cresol in the nitrification effluent was less than 5 mg/L, the system performed very well with complete $\text{NH}_3\text{-N}$ removal. However, when the effluent concentrations were higher than 15 mg/L (Figure 17c, Days 160 to 220 and 311), the system showed signs of inhibition (Figure 16a) with corresponding increases in effluent $\text{NH}_3\text{-N}$.

In general, there are two types of microorganisms that exist simultaneously in the activated sludge of a single-stage nitrification process. One is the autotrophic nitrifiers that convert $\text{NH}_3\text{-N}$ to $\text{NO}_2^- \text{-N}$ and $\text{NO}_3^- \text{-N}$ and are extremely sensitive to inhibitory compounds. The other is the heterotrophic microorganisms responsible for removal of organic compounds. In this study, the ratios of COD to $\text{NH}_3\text{-N}$ normally ranged from two to four and the heterotrophs accounted for a substantial fraction of microorganisms in the activated sludge²⁹. Therefore, phenol and o-cresol in all cases, and m-cresol and p-cresol in most cases could be completely removed by the heterotrophs; effluent concentrations were below detection limits. The autotrophs were not inhibited and complete nitrification occurred. However, if influent m-cresol and p-cresol were more than, for example, 150 mg/L, although 80% of m-cresol and p-cresol could be removed by the heterotrophs, the remaining 30 mg/L of m-cresol and p-cresol in the aeration basin could inhibit the autotrophs and lead to nitrification inhibition.

Recovery of Nitrification from Inhibition. Addition of powdered activated carbon (PAC) improves the performance of nitrification by partial or complete removal of inhibitory compounds³⁰⁻³³. PAC was added to the nitrification system to restore the system to its original operating efficiency. During Phase 4 of the study, the initial carbon equilibrium concentration was 2500 mg/L in the aeration basin. A daily dose of PAC was added to supplement the loss of PAC from withdrawal of PAC-activated sludge mixed liquor to maintain the SRT. The dose corresponded to 100 mg/L of PAC added to the influent of the nitrification system. At a 31-day SRT and a 30-hour HRT, there was no apparent improvement in the nitrification system. Average effluent $\text{NH}_3\text{-N}$ was 414 mg/L, and $\text{NO}_3^- \text{-N}$ plus $\text{NO}_2^- \text{-N}$ totalled 40 mg/L (Figure 16a, Period 4a, Days 204 to 218). The PAC concentration, with respect to the influent was, therefore, increased to 150 mg/L by decreasing the influent flow rate to two-thirds of its original value. At the same time, the influent was diluted one-to-one with tap water to expedite the recovery of the system from inhibition. As shown in Figure 16a and Figure 16c (Period 4b, Days 129 to 249) under the new SRT of 31 days and HRT of 43 hours, the nitrification system recovered very rapidly. $\text{NH}_3\text{-N}$ in the effluent decreased from 208 mg/L to 3 mg/L, effluent $\text{NO}_3^- \text{-N}$ increased to 250 mg/L (Figure 16a), and effluent $\text{NO}_2^- \text{-N}$ decreased to 0.3 mg/L (Figure 16c).

In the meantime, a portion of the granular activated carbon (GAC) was periodically replaced to improve the performance of the anaerobic filter beginning on Day 250. At that time, PAC addition was discontinued. The system was operated at a one-to-one dilution until Day 278, at which time the system began receiving undiluted anaerobic filter effluent. As can be seen from Figure 16b, 17a, 17b and 17c (Phase 5, Days 250 to 367), each time a portion of the GAC in the anaerobic filter was replaced (Days 250, 278, and 326), the anaerobic effluent quality improved significantly. For instance,

COD, phenol, and cresols were reduced markedly, but over time their concentrations increased rapidly again. Although influent $\text{NH}_3\text{-N}$ was relatively stable throughout each carbon replacement in the anaerobic filter, influent COD, phenol, and cresol varied significantly from the beginning to the end of each replacement period. However, the salient feature appeared during Phase 5 when the influent m-cresol and p-cresol in the nitrification system were much lower than during inhibition Phase 3a (except for Days 307 to 321 during which period a sudden increase in feed concentrations caused temporary nitrification inhibition, when effluent $\text{NH}_3\text{-N}$ increased and effluent m-cresol and p-cresol concentrations exceeded 15 mg/L). Therefore, during Phase 5 the nitrification system performed well and the effluent $\text{NH}_3\text{-N}$ remained very low (Figure 16a, Days 250 to 367).

Table 9 shows that during Periods 5b¹, 5b², and 5c (except Days 307 to 321) with undiluted anaerobic effluent used as feed, the nitrification system was operated at an SRT of 30 days, $\text{NH}_3\text{-N}$ loading of 0.15 to 0.18 kg $\text{NH}_3\text{-N}/\text{kg MLVSS}\cdot\text{day}$, and COD loading of 0.24 to 0.40 kg COD/kg $\text{MLVSS}\cdot\text{day}$, similar to the operating conditions during the pseudo-steady-state operation Period 2b. System performance was excellent during Periods 5b and 5c; $\text{NH}_3\text{-N}$ removal (99%) and COD removal (86%) matched those obtained in Period 2b.

A second nitrification system with the same configuration as the first, and seeded with activated sludge from the first nitrification system obtained during the inhibition period, was started and received effluent from a new anaerobic activated carbon filter system on Day 206. Because most of the organic compounds, including cresols, were removed by the newly installed anaerobic filter, the second nitrification system recovered completely in only 12 days and was continuously operated for 150 days with no sign of inhibition caused by organic compounds as shown in Figure 18. From Figure 18 it can also be seen that there were several peaks in effluent $\text{NH}_3\text{-N}$ concentration, in most cases resulting from pH less than 6.5, and in the last case also from low DO (0.4 mg/L). After adjustment of pH and DO in the aeration basin, the effluent $\text{NH}_3\text{-N}$ was reduced rapidly to its original concentration of less than 5 mg/L.

Solids Retention Time. As is well known, the nitrification process is characterized by the fact that the growth of autotrophic nitrifying organisms is very much slower than that of heterotrophs and the reaction rate of nitrification is correspondingly slower. This means that to maintain a population of nitrifiers, the SRT must be long enough to avoid "wash out" of nitrifying organisms from the system. The published research on nitrification of wastewater containing high concentrations of ammonia, was conducted with an SRT of 20 days or more and an $\text{NH}_3\text{-N}$ loading of 0.01 to 0.5 kg $\text{NH}_3\text{-N}/\text{kg MLVSS}\cdot\text{day}$. In this study the SRT was 22 days and 31 days and the $\text{NH}_3\text{-N}$ loading was 0.27 and 0.15 kg $\text{NH}_3\text{-N}/\text{kg MLVSS}\cdot\text{day}$. This is consistent with the data cited above. In general, the performance of the nitrification system seemed to become better and more stable under the conditions of longer SRT and lower $\text{NH}_3\text{-N}$ loading.

NO_2^- -N Accumulation. Incomplete nitrification occurred in some studies^{27,30,33,34} and ammonia was mainly oxidized to nitrite rather than nitrate, which lead to NO_2^- -N accumulations. In this study NO_2^- -N accumulation occurred in certain cases. Figures 16a, and 16c indicate that NO_2^- -N gradually increased during Period 2b (Days 83 to 132) without an increase in effluent $\text{NH}_3\text{-N}$. Otherwise, NO_2^- -N accumulation always occurred

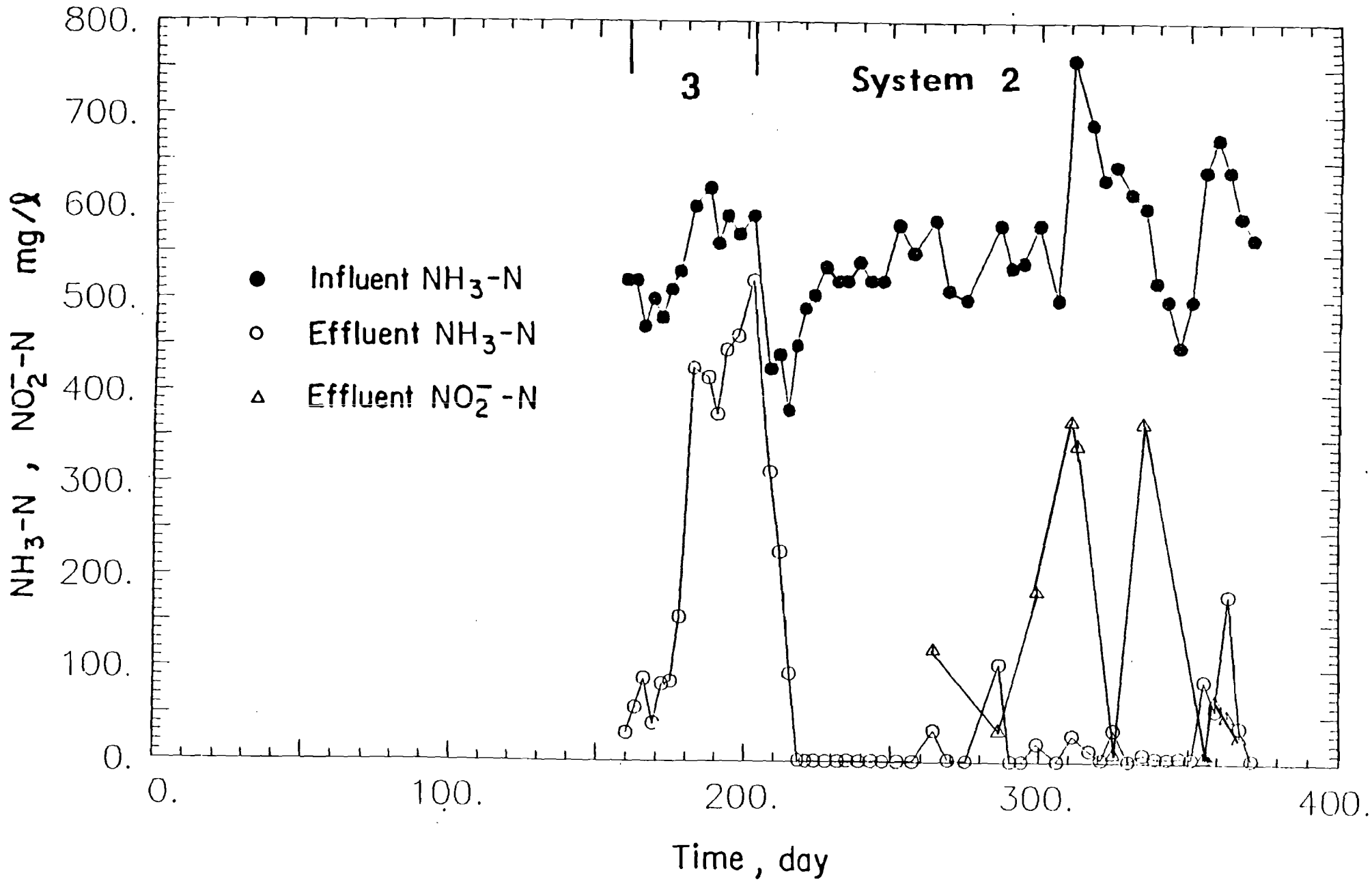


Fig. 18 Ammonia Removal and $\text{NO}_2^- \text{-N}$ Accumulation in the Second Nitrification System

with an increase of effluent $\text{NH}_3\text{-N}$ during partial inhibition of nitrification (Days 57 to 82, 160 to 184, 307 to 321). Furthermore, pH control is a very important operating parameter for nitrification of high strength ammonia wastewaters. The aeration basin pH sometimes dropped to less than 6.5 because of insufficient supplementary alkalinity in the feed and resulted in temporary increases in effluent $\text{NO}_2^- \text{-N}$ as shown in Figure 18. However, as long as the pH in the aeration basin was adjusted to between 7 and 8, the effluent $\text{NO}_2^- \text{-N}$ disappeared immediately.

Sludge Settling Characteristics. A problem encountered in some nitrification studies was that the MLSS maintained in the aeration basin was too low and effluent suspended solids were too high as a result of poor settling in the clarifier. Filamentous organisms grew at high loadings in the absence of trace nutrients^{26,34}. In the present study, the activated sludge had good settling characteristics; the sludge volume index (the volume in mL occupied by 1g of a suspension after 30 minutes settling) (SVI) was around 100 mL/g (from 34 to 195) and no filamentous organisms were observed by microscopic examination. The MLSS in the aeration basin were maintained at 3000 mg/L (from 1560 to 4190). However, occasional sludge accumulations in the bottom of the clarifier because of problems with the sludge scraper and sludge recycle apparatus, resulted in denitrification and production of a large block of floating sludge which, in turn, temporarily led to high suspended solids in the effluent.

CONCLUSIONS

From the results of these investigations the following conclusions can be drawn:

- A single-stage activated sludge nitrification system can successfully remove ammonia-nitrogen from the effluent of an anaerobic filter treating 10% coal gasification wastewater containing as much as 600 mg TKN/L.

- Performance of the nitrification system was significantly dependent on the effluent quality of the anaerobic fluidized-bed activated carbon filter. Under the normal 32-day SRT and loadings of 0.15 kg $\text{NH}_3\text{-N}$ MLVSS·day and 0.35 kg COD/kg MLVSS·day, removals of 97% TKN, 91% TOC and 95% COD were achieved.

- For effective nitrification of the coal gasification wastewater, solids retention time should be more than 22 days.

- Residual phenol and o-cresol could be completely removed in the nitrification system in all cases, but m-cresol and p-cresol removal depended on their influent concentrations. In some instances, the total amount of effluent m-cresol and p-cresol exceeded 15 mg/L and inhibition of the nitrification process occurred.

- Addition of powdered activated carbon to the nitrification system or periodic replacement of a portion of granular activated carbon in the anaerobic filter removed or reduced the concentration of the inhibitory compounds and eliminated inhibition of nitrification.

- Nitrogen balances indicated that the total effluent nitrogen accounted for 90.2% of influent TKN; the unaccounted nitrogen was attributed to microbial cell growth requirements and possible losses from denitrification, air stripping, and analytic error.

- Average alkalinity consumption was 5.8 mg alkalinity consumed/mg $\text{NH}_3\text{-N}$ removed.

DENITRIFICATION STUDY

A 283-day study was conducted to study the denitrification of anaerobically treated and nitrified coal gasification effluent. The study was divided into three phases: 1 - acclimation; 2 - stable operation with a relatively constant mean cell residence time (MCRT) using methanol as an external carbon source; and 3 - stable operation with a relatively constant MCRT substituting phenol for methanol as the carbon source. During phase 2 of the operation, two-substrate limitations were imposed on the system. The first was nitrate limitation, where nitrate was not sufficiently available to bacteria for the oxidation of methanol. The second was methanol limitation, where methanol was not available in sufficient quantity for bacteria to reduce all of the nitrate-nitrogen in the influent. The summary of these phases are presented in Table 12.

Phase 1

During the first 99 days the system was acclimated to the use of nitrate from the nitrification reactor as a substrate. The concentration and total mass of suspended solids in the reactor during this period are presented in Figures 19 and 20. To accelerate this phase, i.e., acclimation, for a period of 19 days, some of the solids in the effluent were settled by gravity and returned manually to the reactor. The initial mass of suspended solids in the reactor was 5 g and concentration of suspended solids was 0.5 g/L, which remained relatively constant until Day 560, as presented in Figures 19 and 20. During this period, Day 541 to 560, the concentration of nitrate-nitrogen in the effluent decreased from 420 mg/L to 100 mg/L (see Figure 21), indicating that the microorganisms responsible for denitrification were acclimating and accumulating in the system. The TOC concentration in the influent ranged between 350 and 950 mg/L, and the TOC concentration in the effluent varied between 100 and 550 mg/L from Day 541 to 560 (see Figure 22). The large variation in TOC concentration in the influent is due to incomplete mixing of the methanol-water mixture, and is discussed in more detail later. The variation in the effluent TOC was a direct result of the varying influent TOC.

From Day 561 to 637, the concentration of solids increased from 0.5 g/L to 5.5 g/L (see Figure 19), and as a result, all the nitrate-nitrogen in the effluent disappeared, indicating that denitrifying microorganisms had accumulated to a sufficient level. The TOC concentration in the influent varied between 50 and 2300 mg/L and in the effluent ranged between 50 and 1250 mg/L during this period (these variations are due to the reason mentioned above). In addition, the contribution of TOC from the coal gasification wastewater is illustrated in Figure 22. As illustrated in Figure 22, the TOC concentration of coal gasification wastewater is much lower than the values of the total influent and effluent TOC concentration.

Phase 2

Phase 2 of the study began on Day 641 and continued for 134 days. During this phase, two-substrate limitations, nitrate-nitrogen and methanol, were imposed to study the performance of the denitrification under these conditions. From Day 641 to 775, a predetermined amount of solids were wasted from the reactor (see Figure 23). Due to this wastage, the concentration of suspended solids was maintained at a relatively constant level (see Figure 19). The total mass of solids lost during daily operation, as a result of solids lost in the effluent as well as those wasted directly from reactor, is presented in

Table 12. Summary of Denitrification Operational Phases

Phases	Type of Operation	Carbon Source	Period* (day)	Duration (day)
1	Acclimation	Methanol	541-640	99
2	Stable operation with a relatively constant MCRT	Methanol	641-774	134
3	Stable operation with a relatively constant MCRT	Methanol and Phenol	776-825	50

*Indicated period is consistent with day designation used on anaerobic filter portion of project, i.e., anaerobic filter operation was started on Day 1.

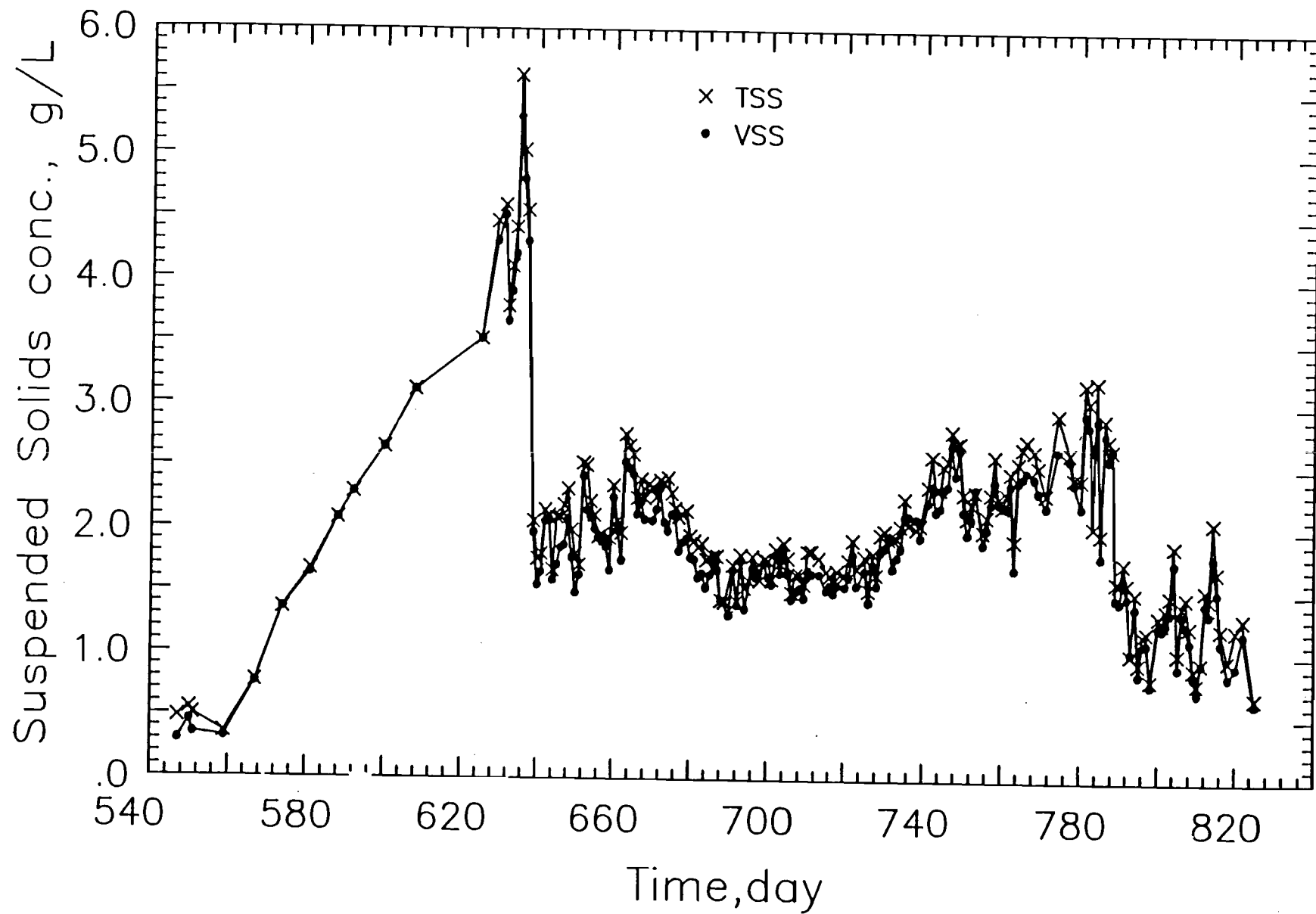


Fig. 19 Suspended Solids Concentration, Denitrification Reactor.

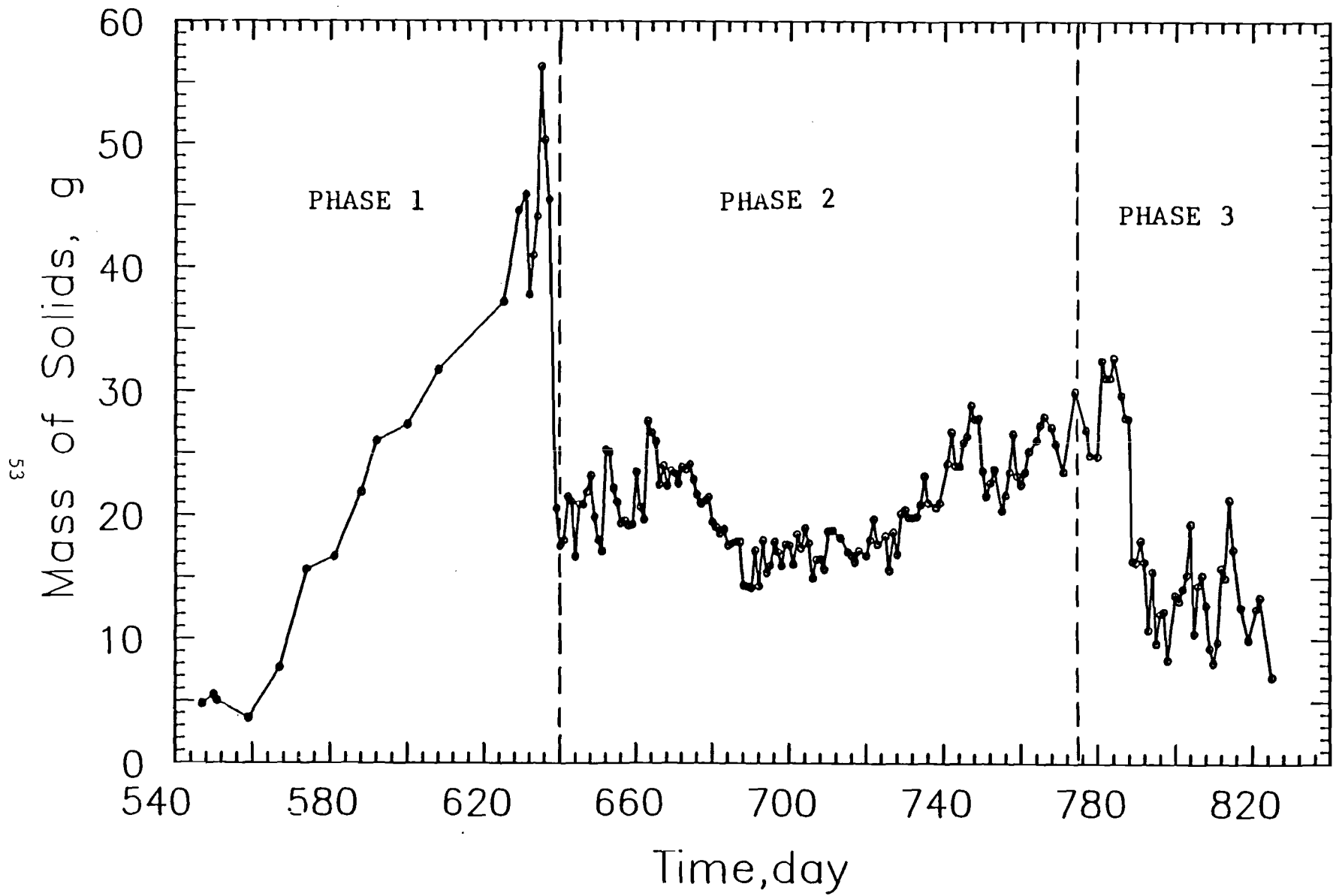


Fig. 20 Total Solids, Denitrification Reactor.

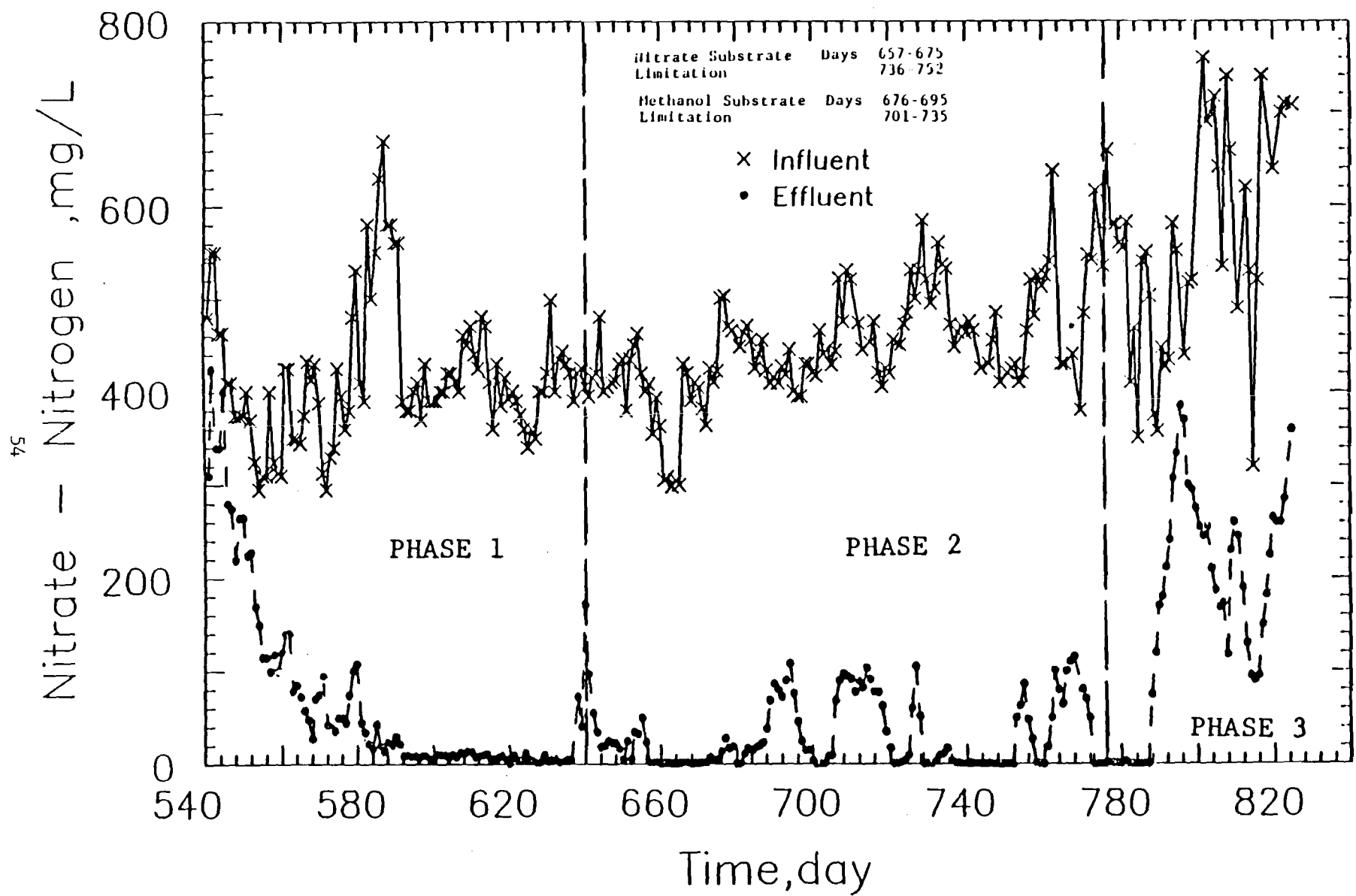


Fig. 21 Nitrate Concentration, Denitrification Reactor.

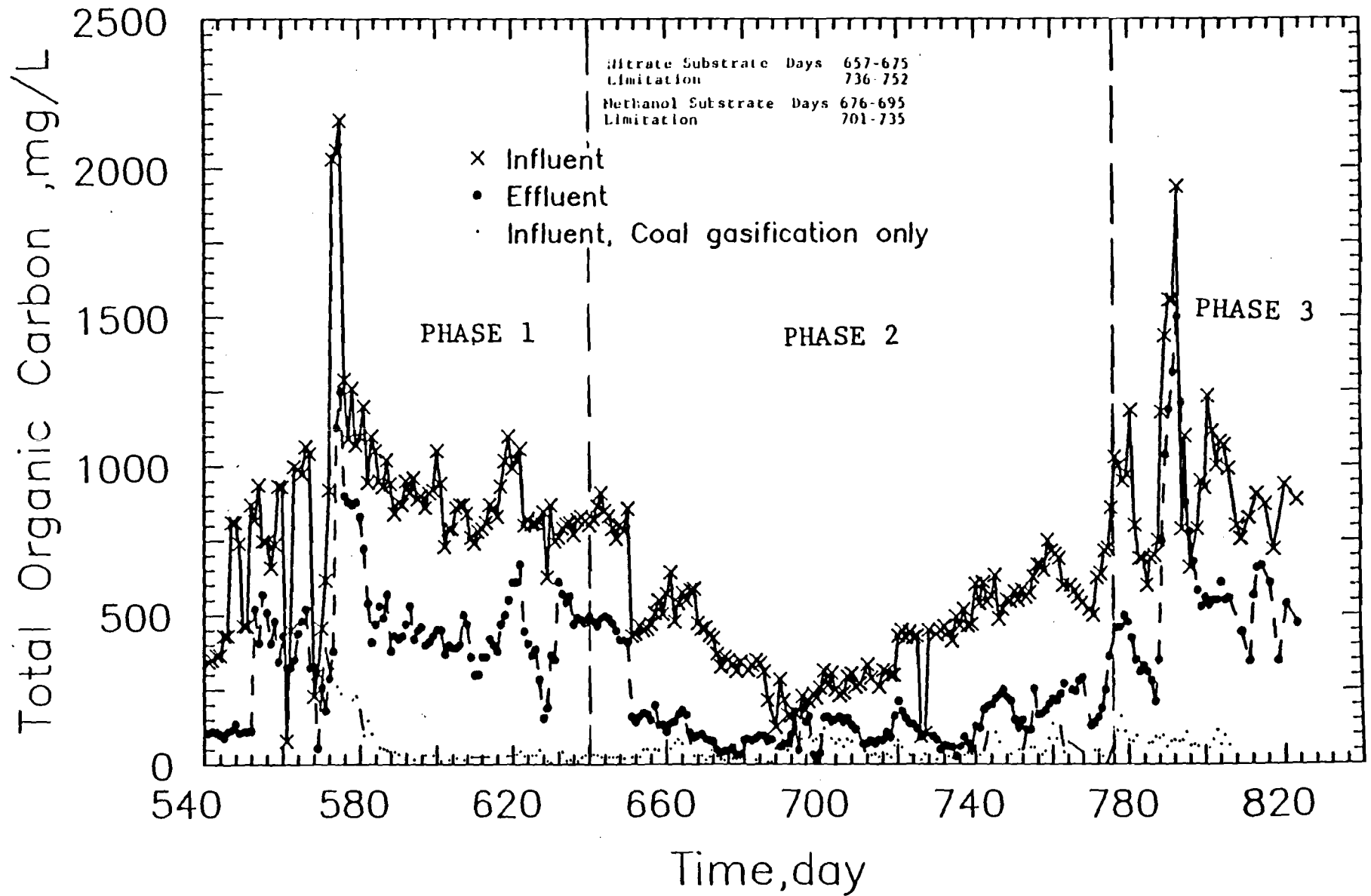


Fig. 22 Total Organic Carbon Concentration, Denitrification Reactor.

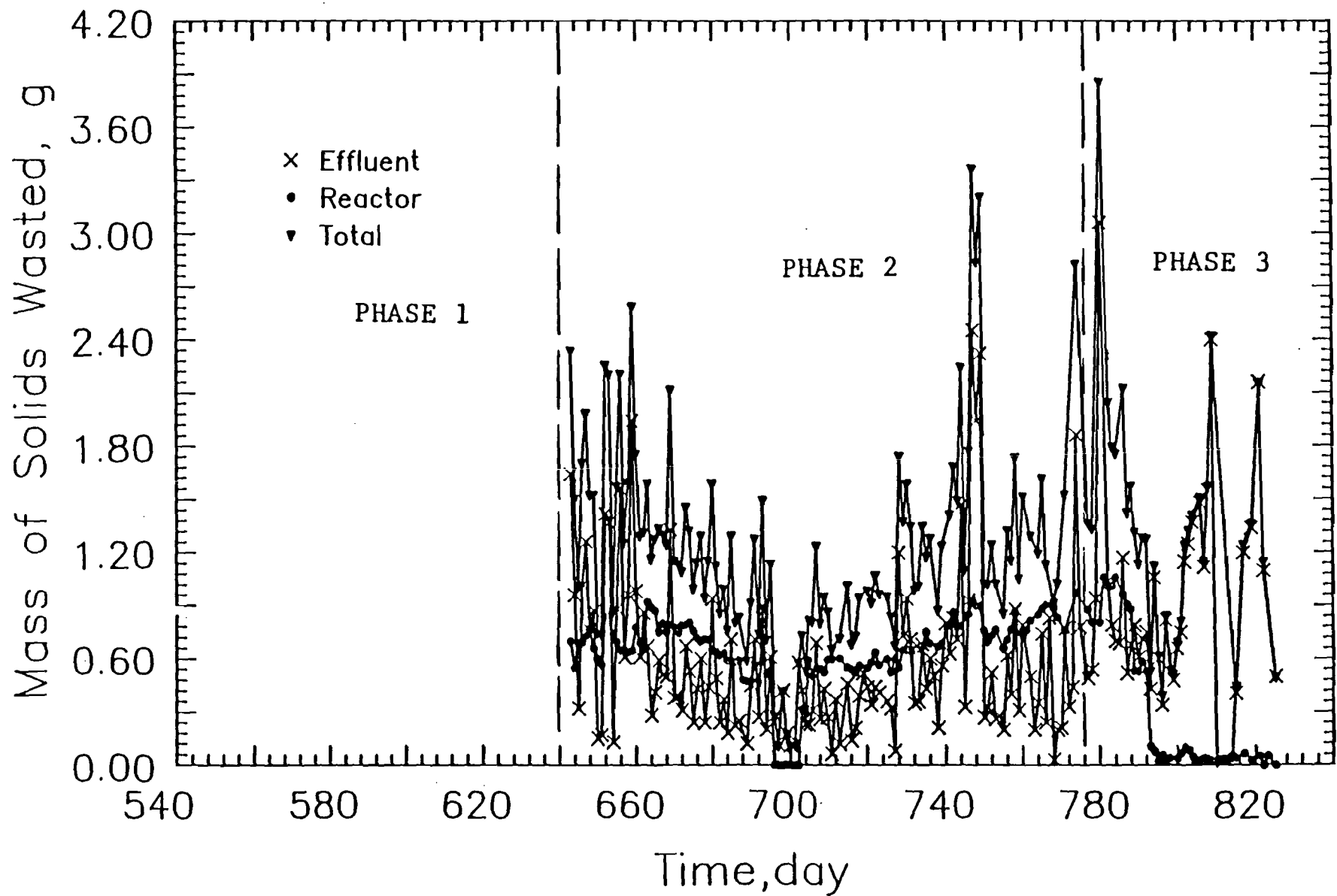


Fig. 23 Solid Wasted, Denitrification Reactor.

Figure 23. The concentration of total suspended solids lost in the effluent ranged between 5 and 380 mg/L (see Figure 24). The MCRT for this phase of operation is presented in Figure 25. During the period of Days 641-775, the MCRT ranged between 8 and 150 days, with an average of approximately 20 days.

During this phase of the operation, nitrate-nitrogen substrate limitation was imposed on the system, i.e., the nitrate flow rate (nitrification effluent) was maintained at a constant level but methanol was supplied at a decreased rate of 17.5 g/d. This rate corresponded to a ratio of 3.5 g methanol per g of nitrate-nitrogen, i.e., this ratio was deliberately chosen because it is in excess of theoretical ratio of 2.47 g methanol per g nitrate-nitrogen (McCarty et al.³⁶). Due to the excess of methanol in the reactor, all the nitrate-nitrogen was removed from the effluent. The periods when nitrate-nitrogen was the limiting substrate, Days 657-675 and Days 736-752, are illustrated in Figures 21 and 22. During this substrate limitation, the concentrations of TOC in the influent and the effluent ranged between 450-750 mg/L and 50-250 mg/L, respectively (see Figure 22).

The second, and last, limitation imposed on the system during phase two of the operation, was a methanol limitation. The methanol feed rate was gradually reduced from 17.5 g/d to 10-12 g/d. This lower feed rate of methanol corresponded to a ratio of 2-2.4 g methanol/g nitrate-nitrogen. Since this ratio was below the theoretical ratio of 2.47 g methanol/g nitrate-nitrogen and there was less methanol available to the microorganisms to reduce the influent nitrate-nitrogen, the concentration of nitrate-nitrogen in the effluent increased. The periods for which methanol was the limiting substrate, i.e., Days 676-695 and 701-735, are illustrated in Figures 21 and 22. During this substrate limitation, nitrate-nitrogen concentration in the effluent increased from 0 to 250 mg/L, the TOC concentration in the influent was gradually reduced from 500 to 150 mg/L and the resulting effluent concentration dropped from 220 to 40 mg/L (see Figures 21 and 22).

Daily pH measurements of the system during phase 2 are presented in Figure 26. The pH of the influent and the reactor during this phase of operation varied between 6.5 to 8.4 and 8.95 to 9.37, respectively. The pH of the effluent was almost the same as the pH of the reactor (i.e., 1-2% variation).

The alkalinity of the influent and the effluent is illustrated in Figure 27. During this phase of operation, the average values for the influent and the effluent alkalinity were 530 and 1510 mg/L as CaCO₃, respectively. The temperature of the reactor was maintained at ambient temperature and varied in extreme from 16 to 30°C with the average temperature of 22 to 25°C (see Figure 28).

Phenol Substitution

During the last phase of the study, beginning on Day 776, methanol was replaced by phenol as the external carbon source and MCRT was maintained at approximately 20-day (see Figure 25). The amount of organic carbon required to reduce the nitrate-nitrogen was determined by performing a mass balance on the system and on a gradual basis, phenol was substituted for methanol. For example, during the initial period, if 4 g of organic carbon was needed to reduce 1 g of nitrate-nitrogen, 60% or 2.4 g of organic carbon was supplied as methanol and the rest, 40% or 1.6 g of organic carbon, was used as phenol.

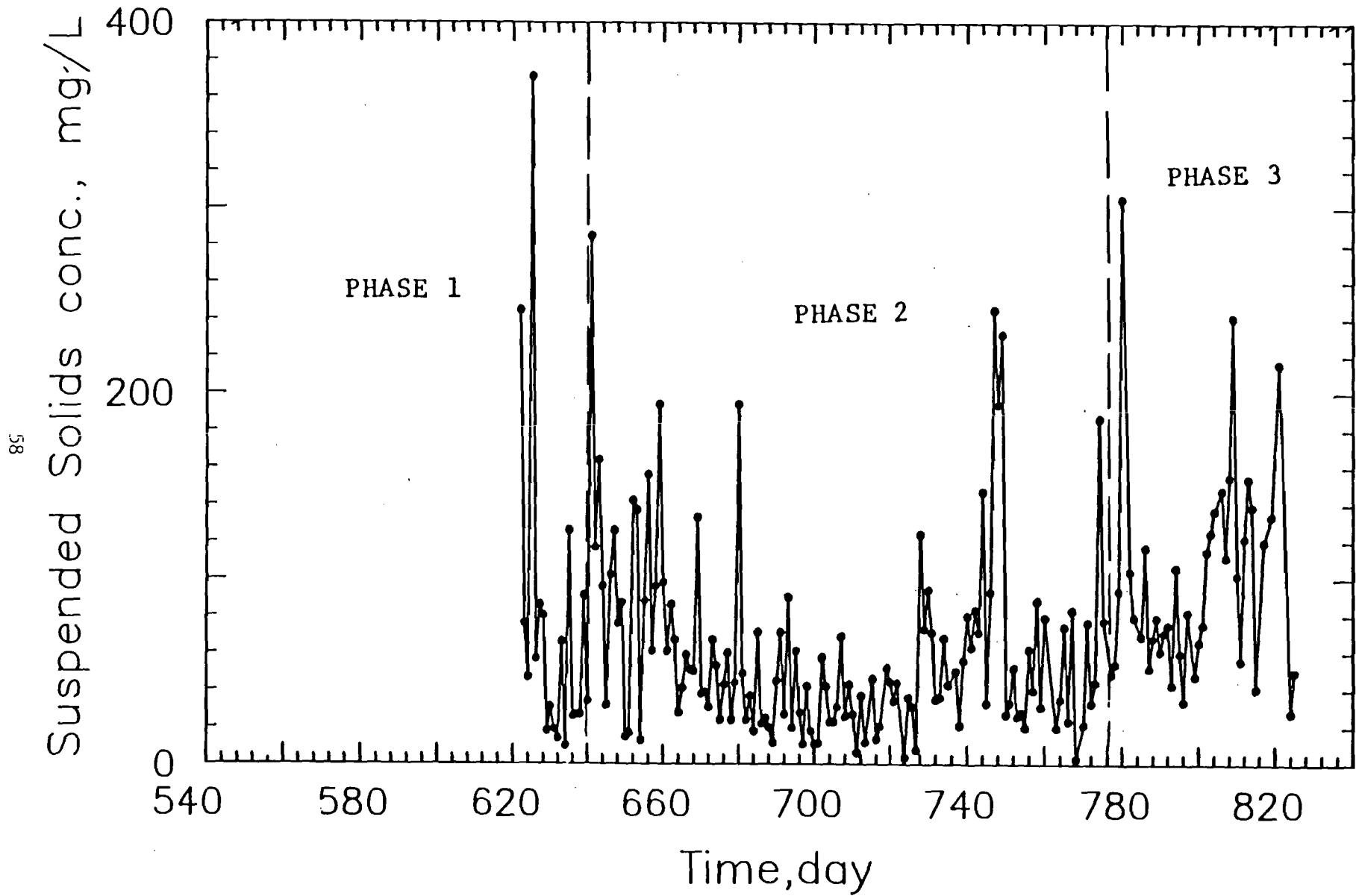


Fig. 24 Effluent Suspended Solids, Denitrification Reactor.

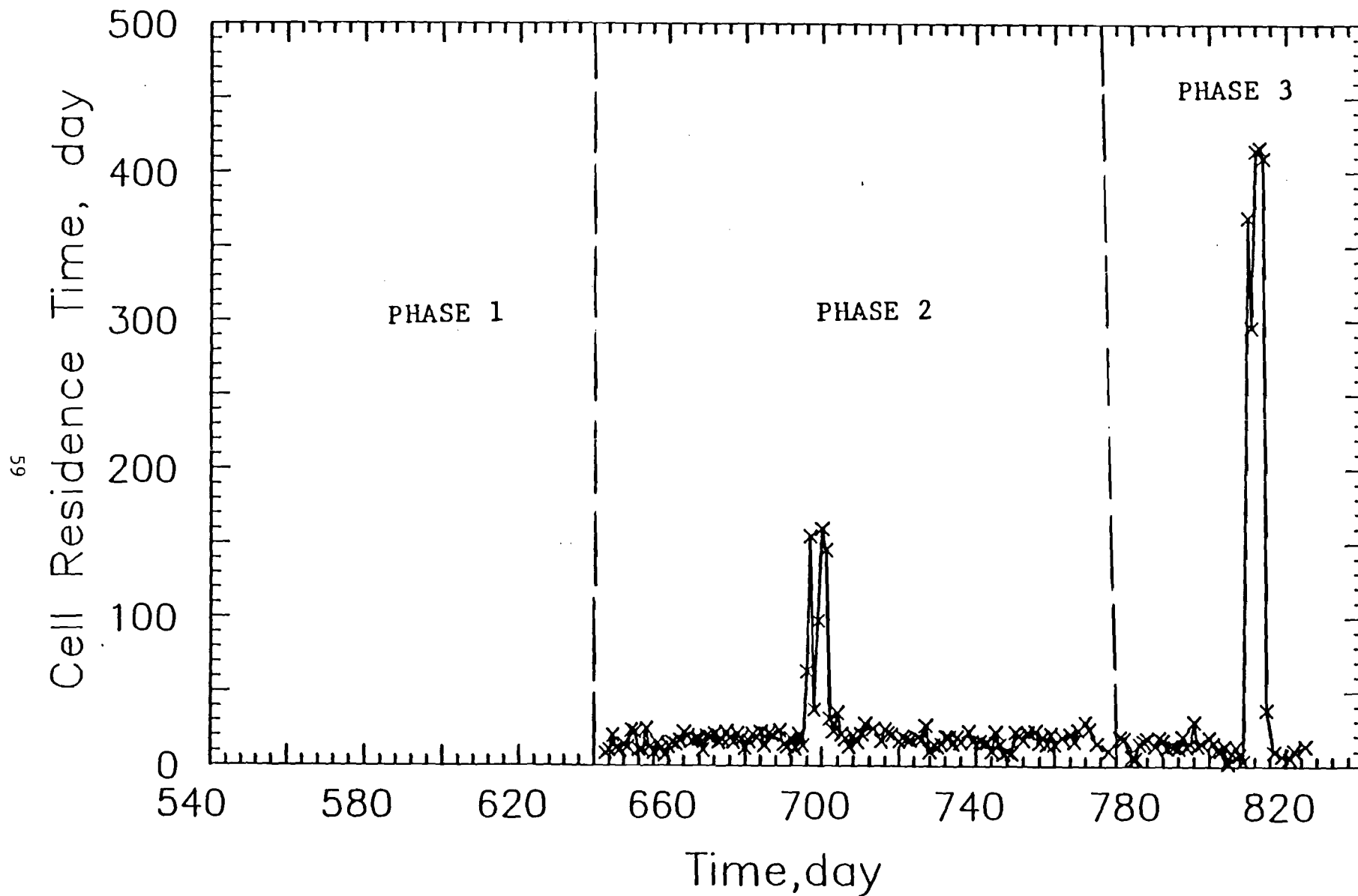


Fig. 25 Cell Residence Time, Denitrification Reactor.

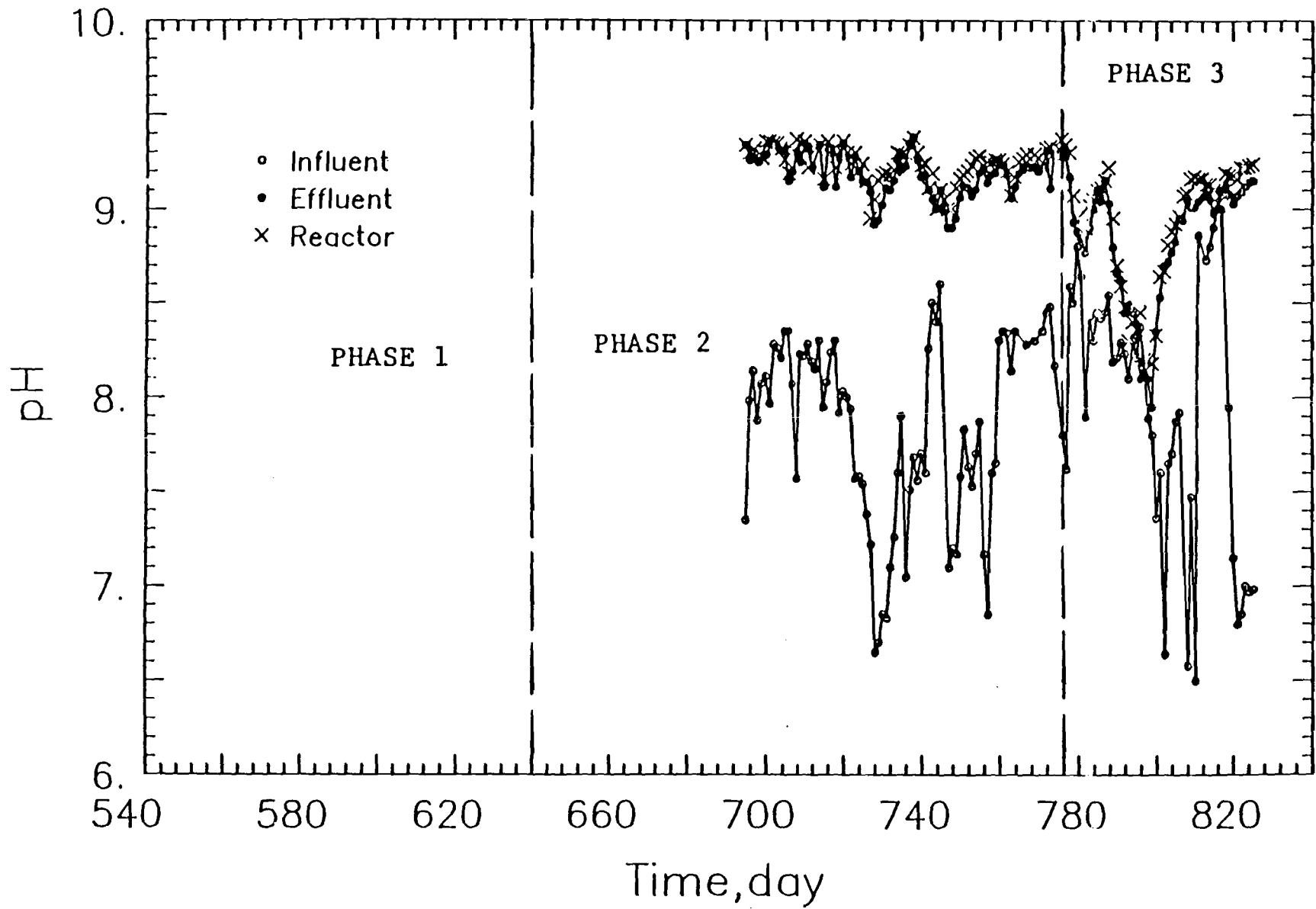


Fig. 26 pH, Denitrification Reactor.

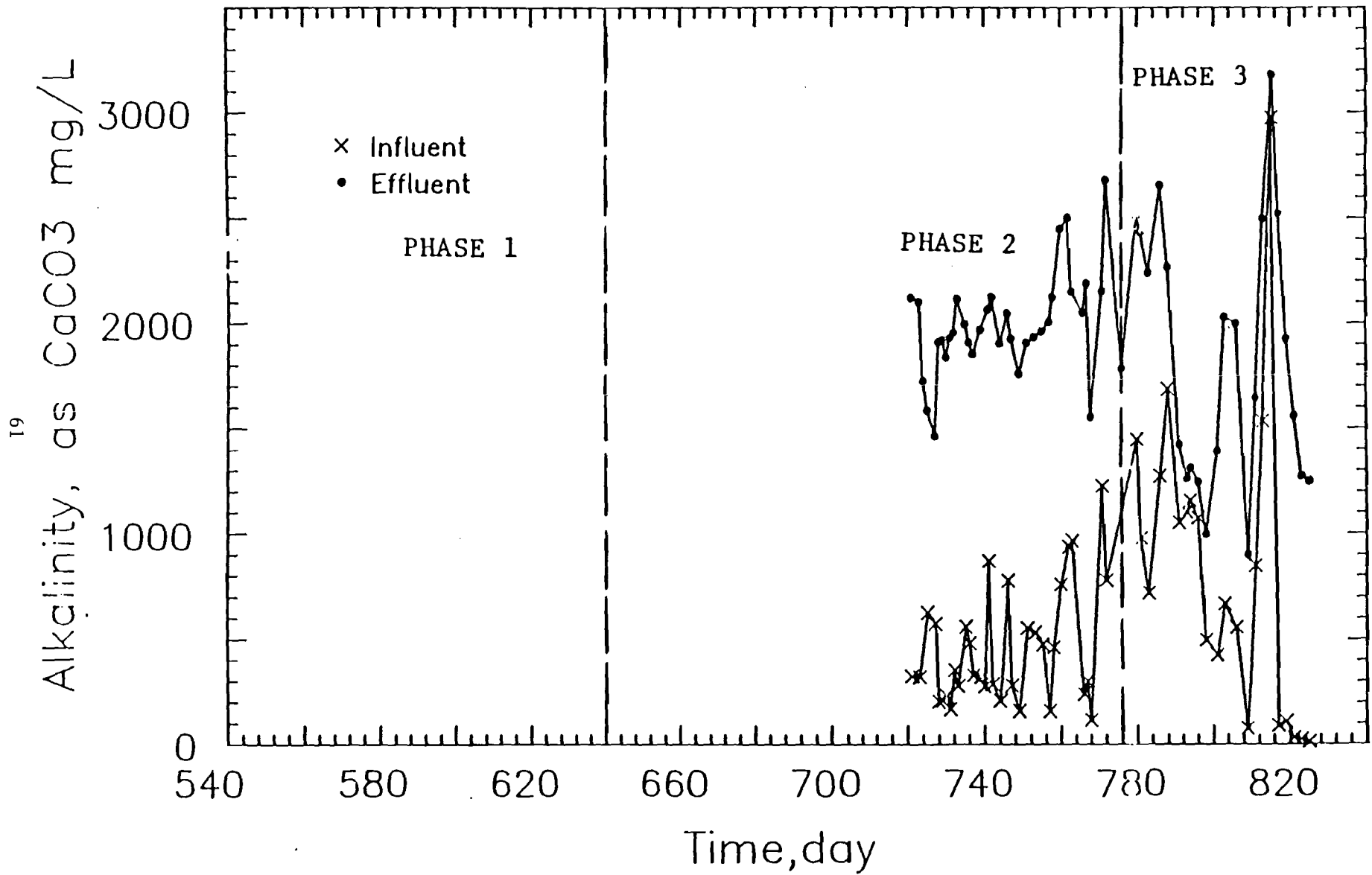


Fig. 27 Alkalinity, Denitrification Reactor.

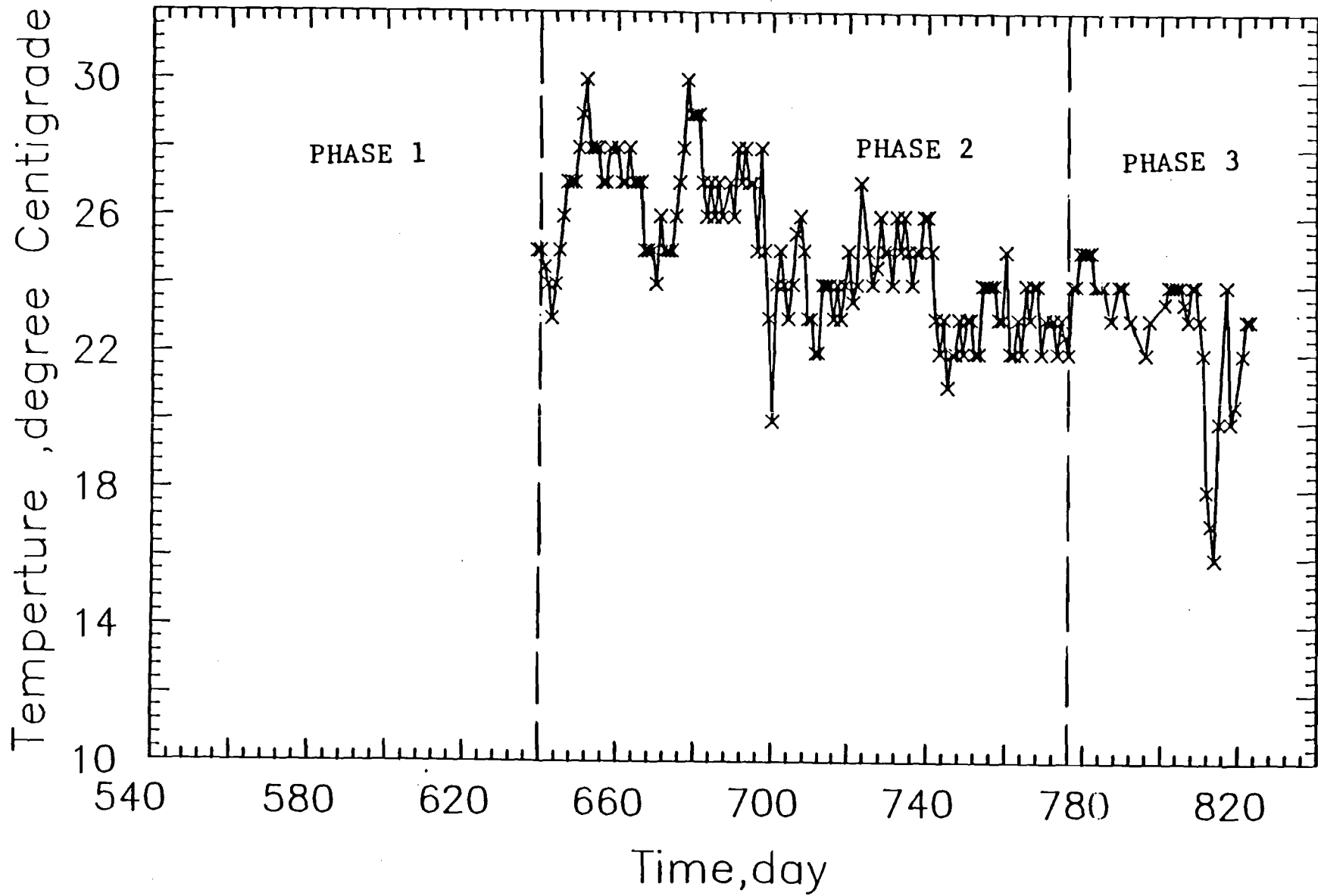


Fig. 28 Temperature, Denitrification Reactor.

The phenol substitution steps for this phase of the operation were as follows: 1) 100% methanol-30% phenol; 2) 60% methanol-40% phenol; 3) 20% methanol-80% phenol; 4) 0% methanol-100% phenol; 5) 269% phenol; 6) 122% phenol; 7) 100% phenol; 8) 90% phenol-10% methanol; 9) 70% phenol-30% methanol; and, 10) 50% phenol-50% methanol. These substitutions of phenol for methanol are illustrated in Figure 29.

100% Methanol - 30% Phenol. In the first substitution step, the mass of organic carbon to reduce all the nitrate in influent was determined and 100% of that was supplied as methanol. Phenol was supplied as a 30% excess of organic carbon. This period lasted 6 days, beginning on Day 776. All influent nitrate-nitrogen was removed and the total mass of solids in the reactor remained relatively stable at 25-35 g (see Figure 20). The pH of the reactor varied between 8.95 and 9.37. The influent and effluent TOC concentrations were 1000 and 1400 mg/L, respectively.

60% Methanol - 40% Phenol. During the next 5 days, phenol was used as the organic carbon, and was supplied as 40% of the TOC required to reduce a unit mass of nitrate-nitrogen. The effluent concentration of nitrate-nitrogen remained unchanged, i.e., the concentration was almost zero. The pH of the reactor ranged between 8.95 and 9.37 and the influent and effluent TOC concentrations were 600-800 mg/L and 300-400 mg/L, respectively (Figures 26 and 22). The concentration of solids in the reactor was approximately 2.5-3.5 g/L.

20% Methanol - 80% Phenol. The mass of phenol was increased from 40% of the TOC to 80% of the TOC during Days 787-788. The performance of the system remained relatively unchanged, i.e., the pH, mass of solids, MCRT, and nitrate-nitrogen in the effluent remained stable.

100% Phenol. For the next three days, 789-791, phenol was used as the sole source of carbon. Due to this increase in phenol mass, the pH decreased to 8.6 and the concentration of solids in the reactor decreased from 2.3 to 1.6 g/L. The concentration of nitrate-nitrogen in the effluent started increasing on Day 789 (Figure 21).

269% Phenol. For one day the mass of organic carbon added to reactor was increased by 269%, i.e., the organic carbon mass was increased from 6.8 to 18.3 g or the phenol mass was increased from 8.9 to 23.9 g.

The resulting pH of the reactor decreased to 8.2 and nitrate-nitrogen concentration increased to 200 mg/L in the effluent.

122% Phenol. For the next period, Days 793-794, the mass of organic carbon was reduced to 122%, i.e., the organic carbon mass was decreased from 18.3 to 8.3 g or phenol mass was decreased from 23.9 to 10.87 g. The resulting pH of the reactor was 8.7 and 8.6 during these two days.

100% Phenol. During the next three days, 795-797, the mass of organic carbon was reduced by 22.0%, i.e., the mass of organic carbon was decreased from 8.3 to 6.8 g or phenol mass was reduced from 10.87 to 8.9 g. The concentration of nitrate-nitrogen in the effluent increased to 380 mg/L and the pH of the reactor was about 8.4.

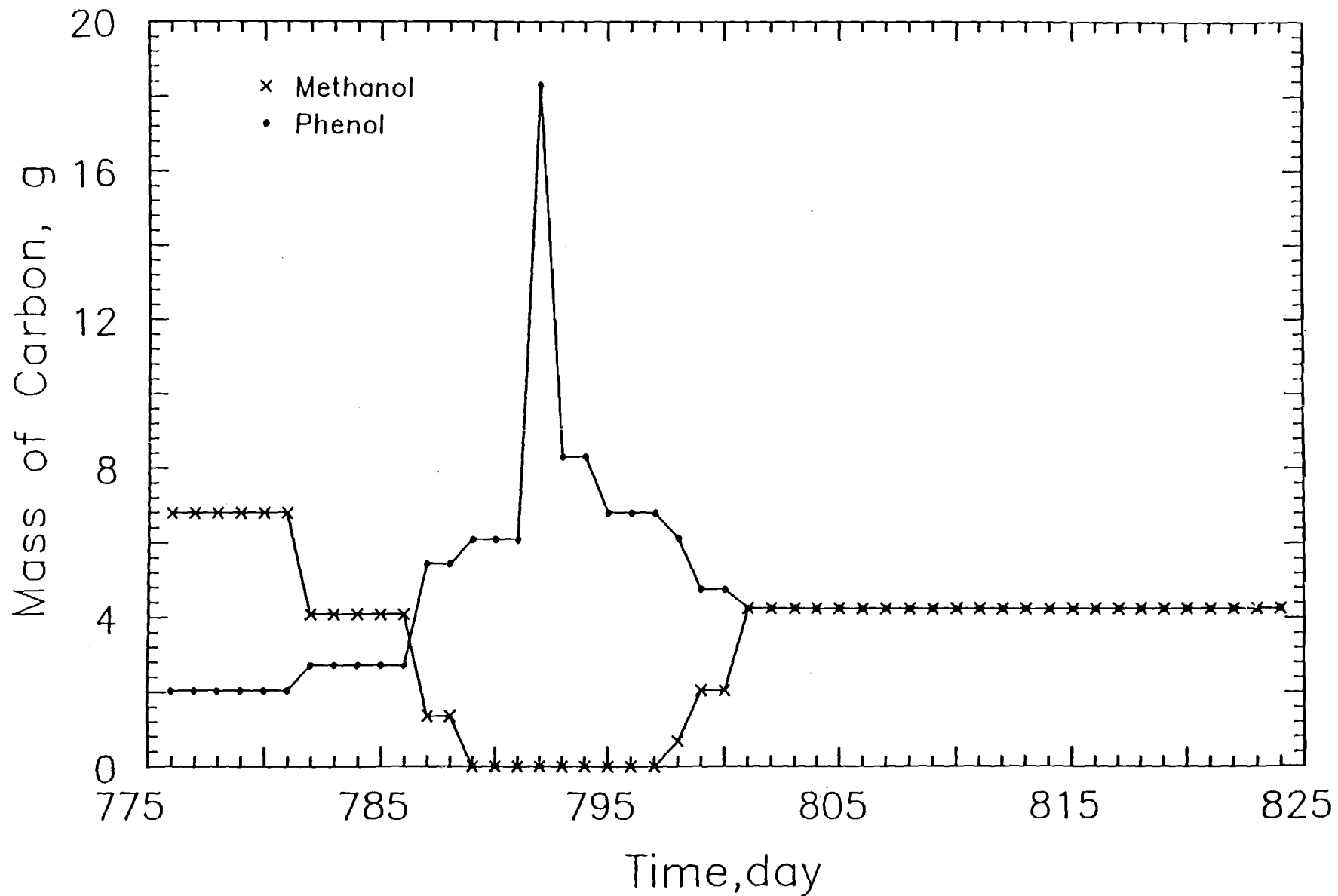


Fig. 29 Carbon Feed Composition - Phase 3 - Denitrification Reactor.

10% Methanol - 90% Phenol. For Day 798, 10% of the TOC was supplied as methanol and the rest as phenol, i.e., 0.68 and 6.12 g of carbon as methanol and phenol, respectively. The nitrate-nitrogen concentration in the effluent remained above 300 mg/L.

30% Methanol - 70% Phenol. During the Days 799-800, 30% of the TOC was supplied as methanol and the rest as phenol, i.e., 2.04 and 4.76 g of carbon as methanol and phenol, respectively. The nitrate-nitrogen concentration in the effluent decreased to 290 mg/L.

50% Methanol - 50% Phenol. During the next twenty-five days, beginning on Day 801, 50% of the TOC was supplied as methanol and the rest as phenol, i.e., 4.25 g of carbon as phenol and methanol. At the beginning of this period the concentration of influent to the anaerobic filter was increased, and as a result the nitrate-nitrogen concentration of the influent increased from 500-550 to 700-750 mg/L and consequently the organic carbon concentration increased to 800-900 mg/L.

The pH of the reactor steadily returned to a range of 9-9.2 and the nitrate-nitrogen concentration in the effluent was reduced to 100 mg/L due to decrease in the influent nitrate-nitrogen concentration. However, as the influent nitrate-nitrogen concentration increased to 700 mg/L the effluent concentration increased to 300-400 mg/L. Daily pH measurements of the system during Phase 3 is presented in Figure 26. The pH of the influent and reactor varied between 6.5 - 9.0 and 8.2 - 9.25, respectively. Daily alkalinity measurements of the system during Phase 3 are presented in Figure 27. The alkalinity of the influent and effluent varied between 300-2900 and 900-3200 mg/L as CaCO_3 , respectively. The temperature of the reactor ranged from 16 to 26°C and is presented in Figure 28.

CONCLUSIONS

Based on the results from the suspended growth denitrification of the anaerobically treated-nitrified coal gasification wastewater, the following conclusions are made.

1. Suspended growth denitrification using methanol with cell recycle can be used to remove virtually 100% of the nitrate-nitrogen from anaerobically treated and nitrified coal-gasification wastewater.

2. The anaerobically treated and nitrified coal gasification wastewater had an insignificant amount of TOC, therefore, it was necessary to use an external carbon source, e.g., methanol, to reduce nitrate in the nitrified coal gasification wastewater.

3. One-hundred percent removal of nitrate-nitrogen was achieved at a ratio of 2.45 g of methanol per g of nitrate-nitrogen, a 20-day cell residence time, a 24-hour hydraulic retention time; the pH of the reactor ranged between 8.95-9.35 during this operation.

4. The pH of the nitrification effluent in the range of 6.0-8.5 had an insignificant effect on the denitrification performance, i.e., the nitrate removal did not change.

5. The pH of the reactor and alkalinity production were directly related to the nitrate-nitrogen and methanol concentration in the influent, i.e., high concentration in the influent resulted in more production of hydroxide ion and alkalinity.

6. Increasing the methanol flow rate resulted in instantaneous reduction in the nitrate concentration in the influent or vice versa.

7. Phenol can be partially substituted for methanol as the external carbon source. However, the inhibitory effect of phenol was observed when 100% phenol was used at a concentration of 600-700 mg/L. As a result the nitrate removal was reduced to 20-30% and the pH decreased to 8.2-8.3.

INHIBITION STUDY

Serum Bottle inhibition studies were carried out utilizing the mixed liquor from an active anaerobic activated carbon reactor and ten compounds found in coal gasification effluent at relatively high concentrations. Table 13 summarizes the results of the study, while Figures 30 and 31 show the results of the addition of phenol and raw wastewater to the mixed liquor.

As can be seen in Figures 30 and 31 the addition of phenol or raw wastewater does not appear to cause any inhibition of gas production.

Figures 32, 33, and 34 show that the addition of hydantoin to the mixed liquor do not inhibit gas production and the sample containing the additional substrate produce more gas than these without the additional substrate.

The addition of the cresol isomers had no effect on the gas production, indicating no inhibition. However, the addition of any of the picolines caused complete cessation of gas production indicating either severe inhibition and/or toxicity. Individual concentration of picolines and pyridines found in the raw wastewater is approximately 5-10 mg/L with a total concentration of approximately 20 to 25 mg/L. Therefore, accumulation of these materials by the granular activated carbon could result in severe inhibition of the microbiological system.

Continuous Flow Anaerobic Activated Carbon Filter Treatment of Pretreated Wastewater

In conjunction with the serum bottle inhibition studies an activated carbon filter was operated with dilute pretreated wastewater as the feed. The system was operated for a period of 200 days with limited success. Figure 35 shows the performance of the filter in terms of TOC removal. Although the feed substrate was primarily hydantoin from the pretreated wastewater, only 40 to 60% of the TOC was removed and gas production during the entire period averaged less than 1 L/d. Although extensive efforts were expended in searching for gas leaks, none were found. The lack of gas production coupled with the 40 to 60% TOC removal indicates the predominant removal mechanism was adsorption of the TOC onto the granular activated carbon. Total hydantoin removal for the period averaged 60%.

Table 13. Gas Production Inhibition by Coal Gasifier Effluent Constituents

Compound	Concentration mg/L	Results
phenol	280	No inhibition
o-cresol	150	No inhibition
m-cresol	150	No inhibition
p-cresol	150	No inhibition
hydantoin	200	No inhibition
5,5-dimethylhydantoin	800	No inhibition
5-methyl-5-ethylhydantoin	260	No inhibition
2-picoline	25 to 75	Complete inhibition
3-picoline	25 to 75	Complete inhibition
4-picoline	25 to 75	Complete inhibition

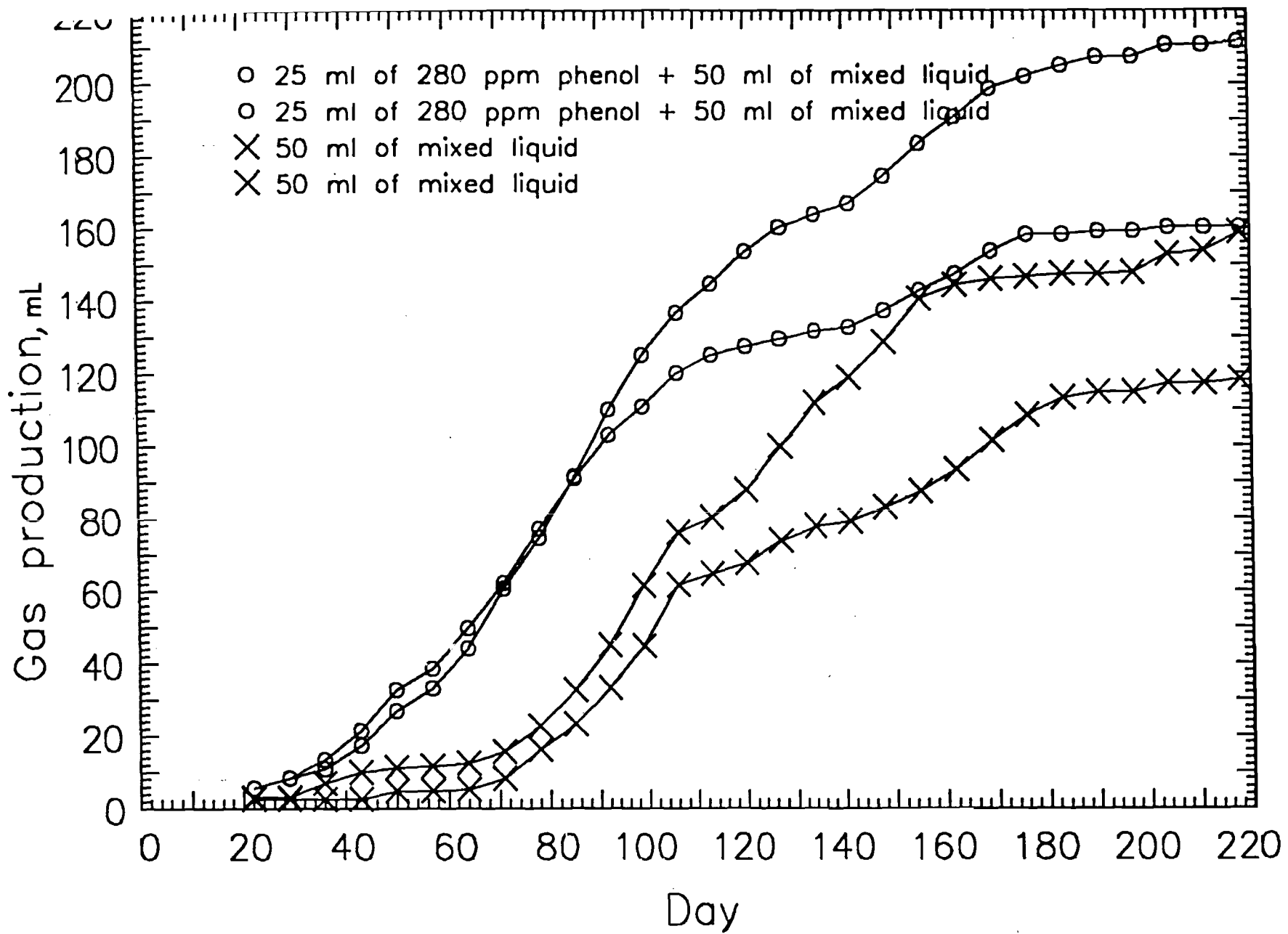


Fig. 30 Effect of Phenol Addition on Gas Production During the Biodegradation of Coal Gasifier Effluent.

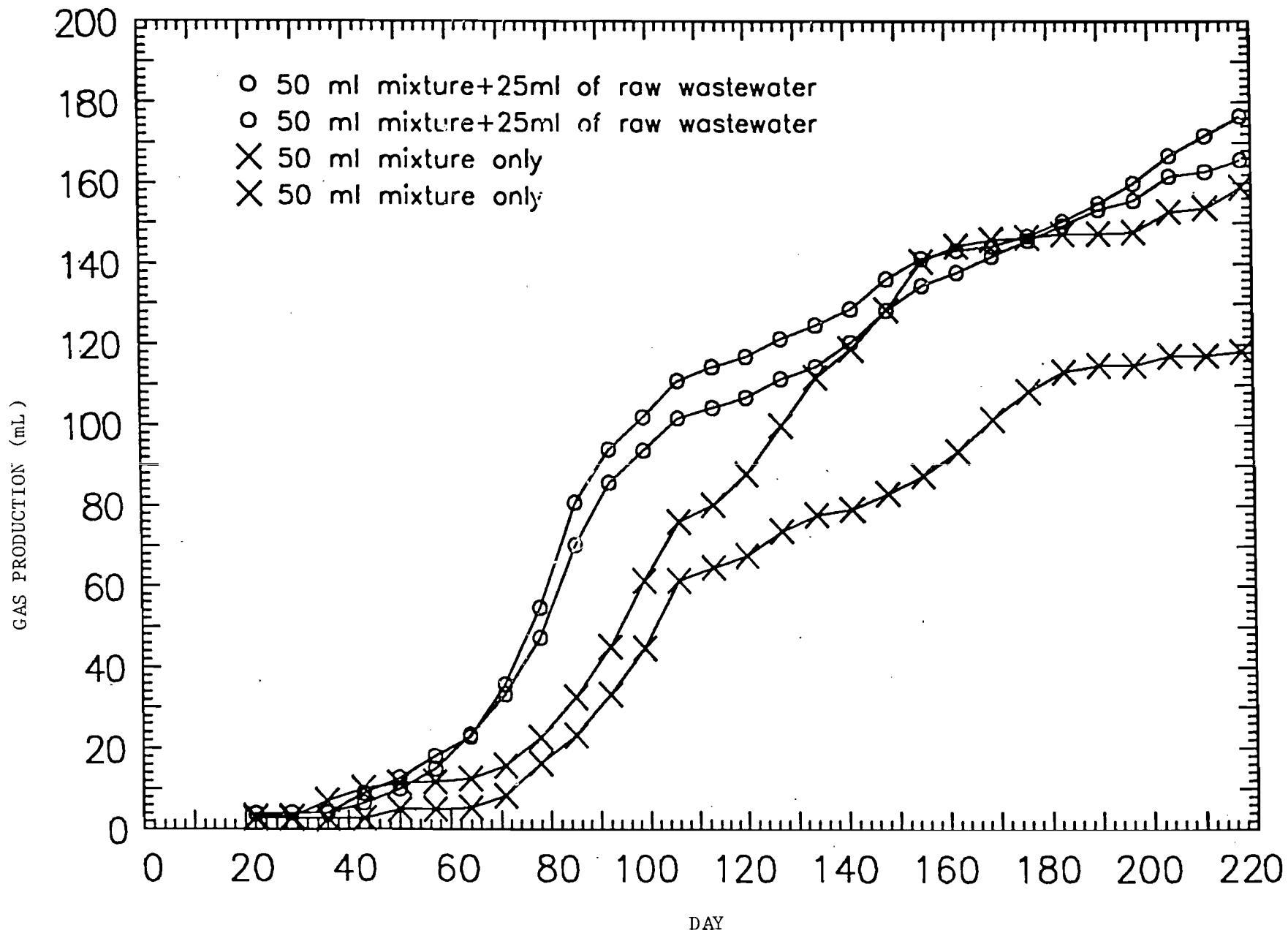


Fig. 31 Effect of Raw Wastewater Addition on Gas Production During the Biodegradation of Coal Gasifier Effluent.

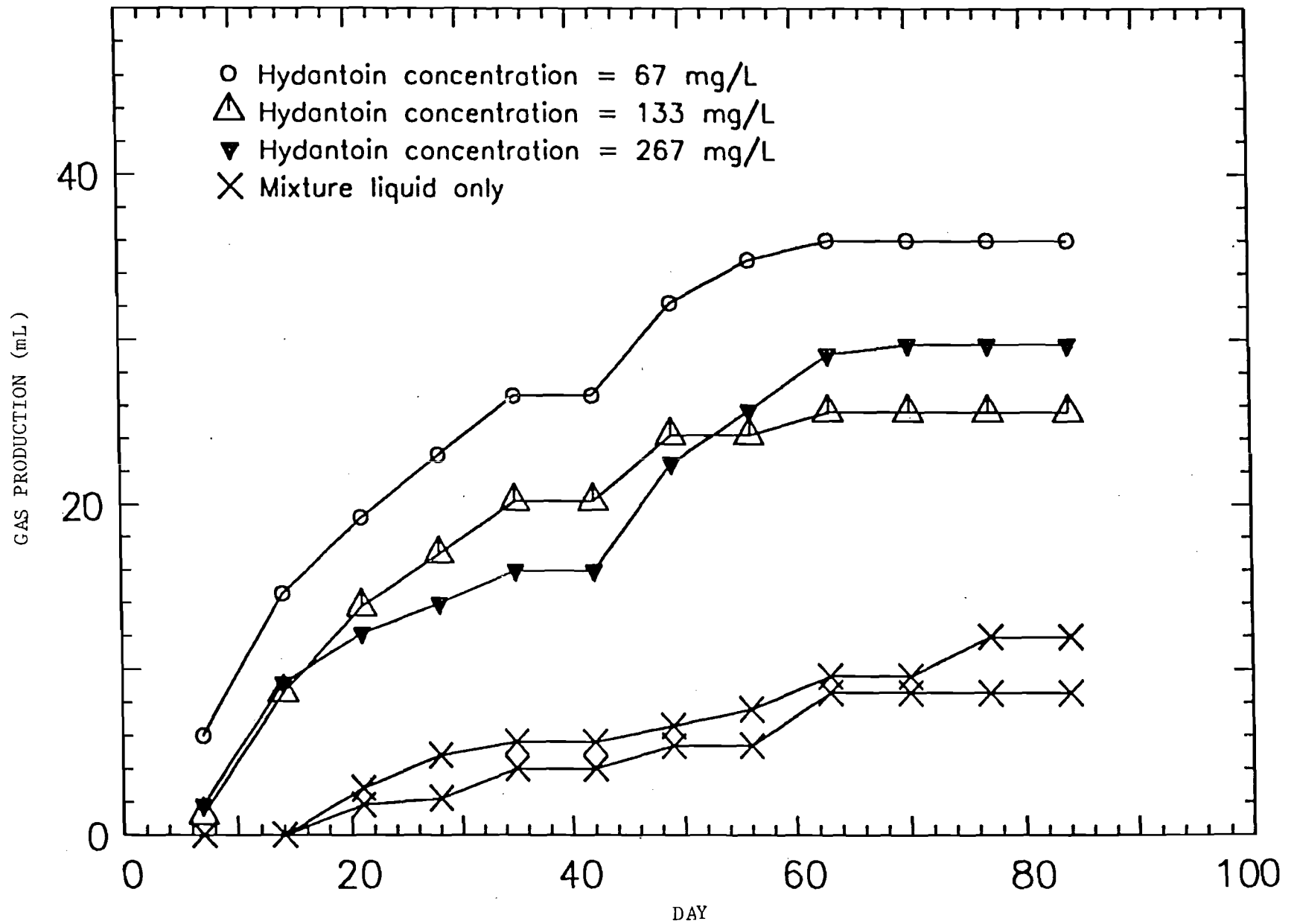


Fig. 32 Effect of Hydantoin Addition on Gas Production During the Biodegradation of Coal Gasifier Effluent.

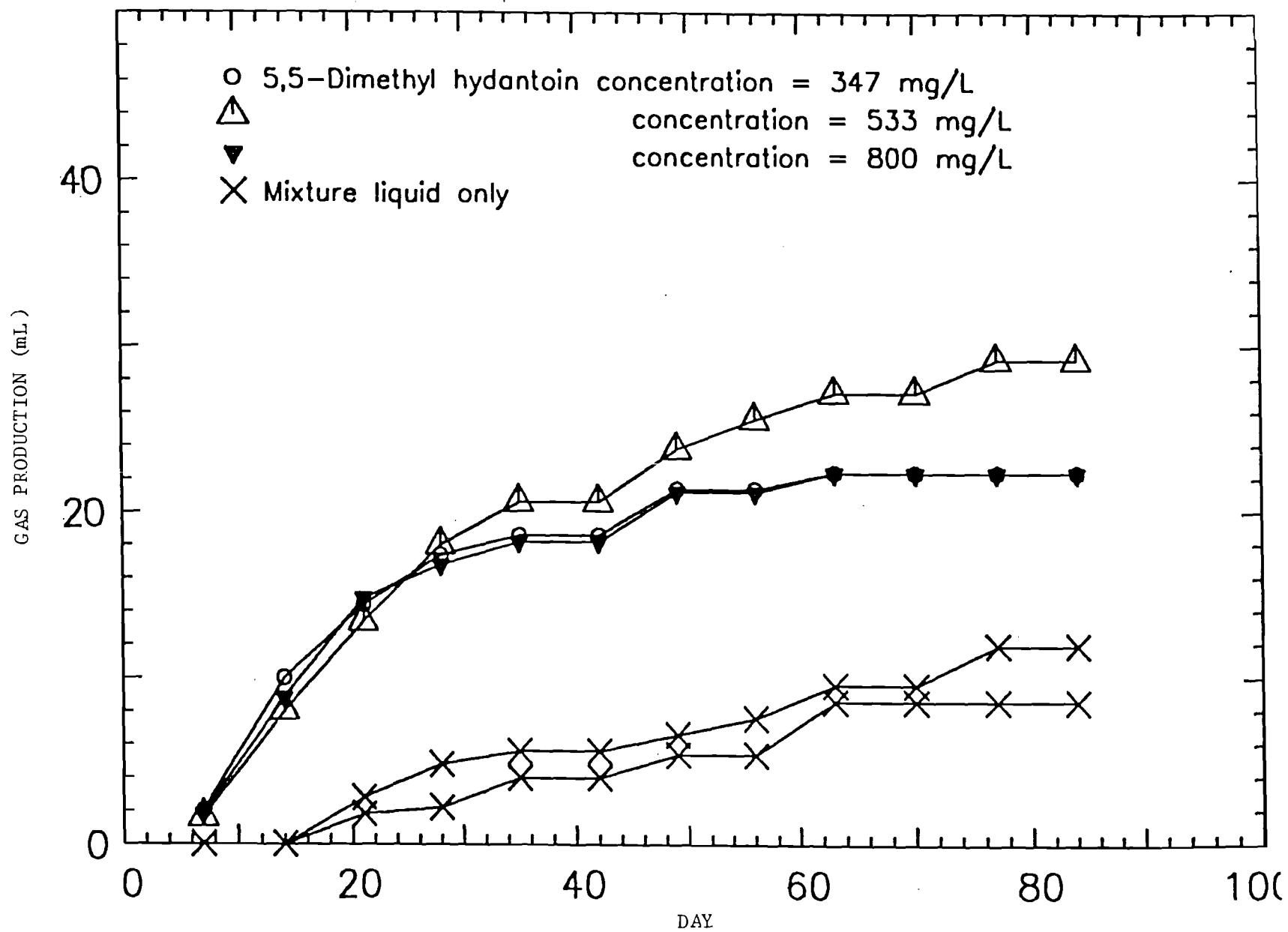


Fig. 33 Effect of 5,5-Dimethylhydantoin Addition on Gas Production During the Biodegradation of Coal Gasifier Effluent.

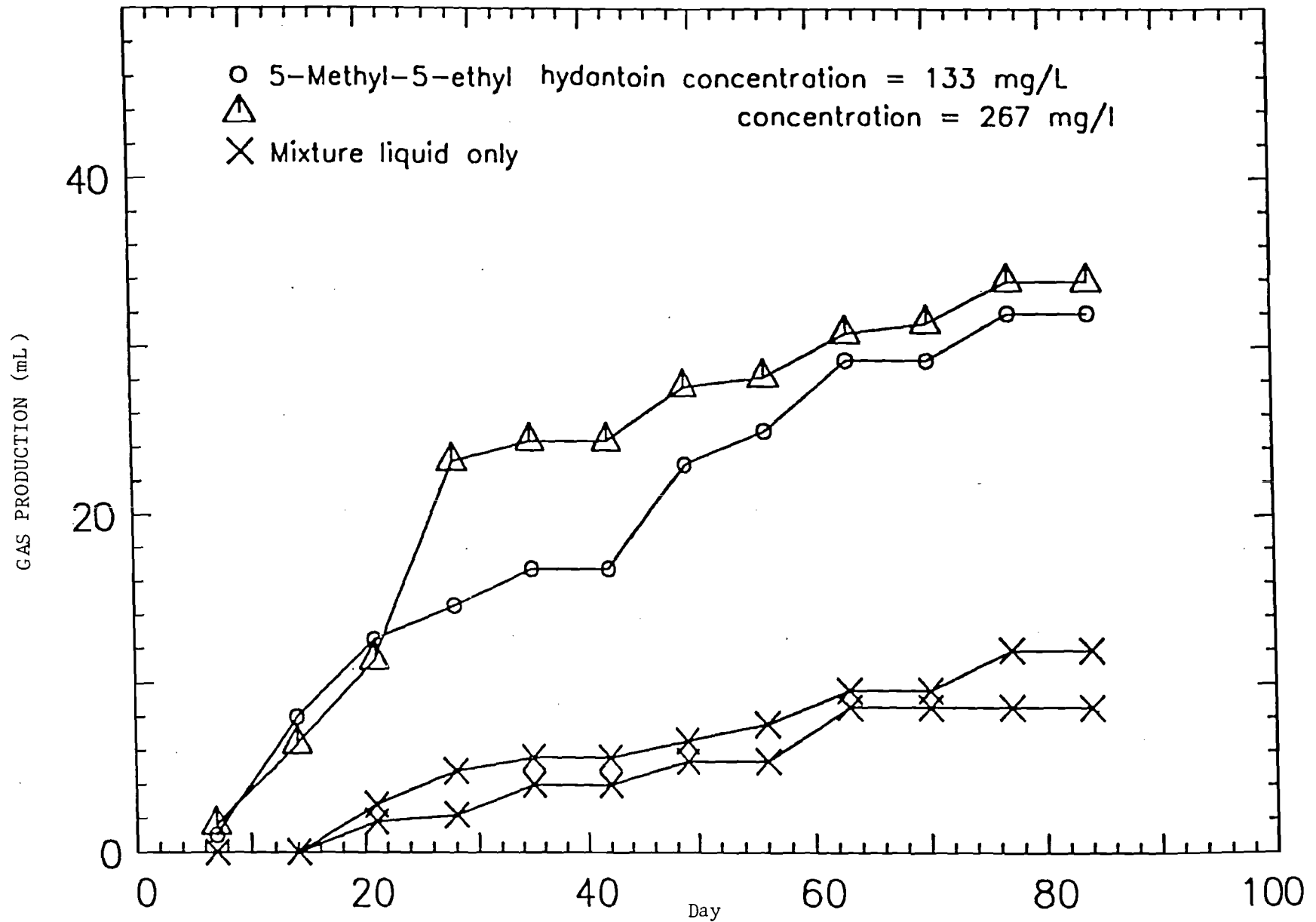


Fig. 34 Effect of 5-Methyl-5-Ethylhydantoin Addition on Gas Production During the Biodegradation of Coal Gasifier Effluent.

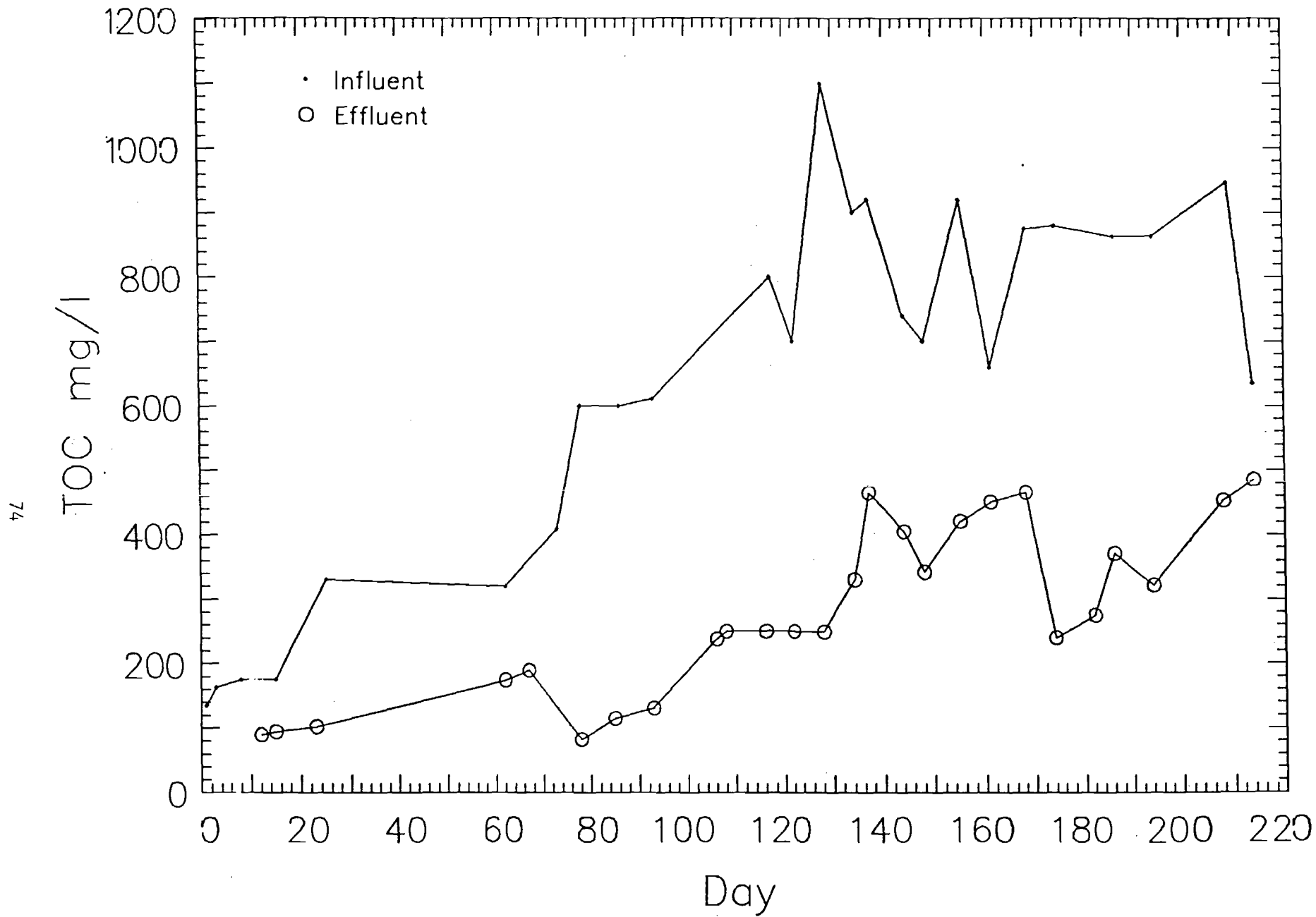


Fig. 35 Total Organic Carbon Removal in an Anaerobic Fluidized Activated Carbon Filter Using Pretreated Wastewater as Feed.

HYDANTOIN ADSORPTION STUDIES

Pretreated Wastewater

A solvent extracted-steam stripped wastewater was furnished by UNDERC for use in a treatability study. This wastewater has most of the TOC and NH_3 removed by the solvent-extraction-steam stripping process. The major constituents remaining are the highly water soluble hydantoins and traces of other organic constituents. Table 3 gives the major constituents found in the pretreated wastewater.

Studies using anaerobic activated carbon filters for the removal of hydantoins did not lead to a successful biological removal system. Therefore, studies were initiated to investigate the feasibility of 1) utilizing physical adsorption of the hydantoins onto the granular activated carbon to remove them from solution and 2) regenerate the exhausted carbon by use of a solvent. Initially, pure compound studies were carried out using the two most predominant hydantoin in the pretreated wastewater, 5-ethyl-5-methyl hydantoin and 5,5-dimethyl hydantoin. In addition, data was obtained on the adsorption of the parent compound, hydantoin.

Batch Kinetic Tests. The results of the single solute batch kinetics tests are shown in Figures 36, 37, and 38. The initial experimental conditions are shown in Table 14.

The batch tests were performed by preparing 4 L of an aqueous solution of one of the compounds, placing the solution in a constant temperature room, stirring the solution at a fixed rpm and then adding a known mass of carbon (Calgon, Filtrasorb 400) to the solution. Periodically, aliquots of the solution were removed from the reactor and filtered or centrifuged to remove the suspended carbon. The resulting filtrate or centrifugate was then quantitatively analyzed for the target compound.

The batch kinetic study for hydantoin had a C_0 value of 450 mg/L which decreased to 395 mg/L, the equilibrium concentration, in a 1.5 hour time period. Eighty-five percent of the adsorption by the activated carbon occurred in the first 20 minutes of the experiment. The same basic sequence occurred for the other two solutes. The batch kinetic tests for 5,5-dimethylhydantoin with a C_0 of 500 mg/L reach equilibrium concentration after 3 hours, as did the 5-ethyl-5-methylhydantoin with the same initial concentration. Most of the adsorption of both solutes also occurred in the first 20 minutes of the test.

From the batch kinetic test results, it can be concluded that the adsorption of the hydantoins was very rapid. Equilibrium was definitely reached after 3 hours for each compound and, therefore, three hours would be the minimum elapsed time required to ensure that equilibrium concentration is reached.

Isotherm Tests. The results of the isotherm tests are shown in Figures 39, 40, and 41. The initial experimental conditions are shown in Table 15.

The isotherms for hydantoin and 5,5-dimethylhydantoin were very similar with the only difference being a slight increase in curvature for the 5,5-dimethylhydantoin isotherm over the hydantoin with equilibrium concentrations in excess of 10 mg/L. The mass of solute adsorbed per mass of carbon (X/m) values for a given equilibrium concentration were also very similar.

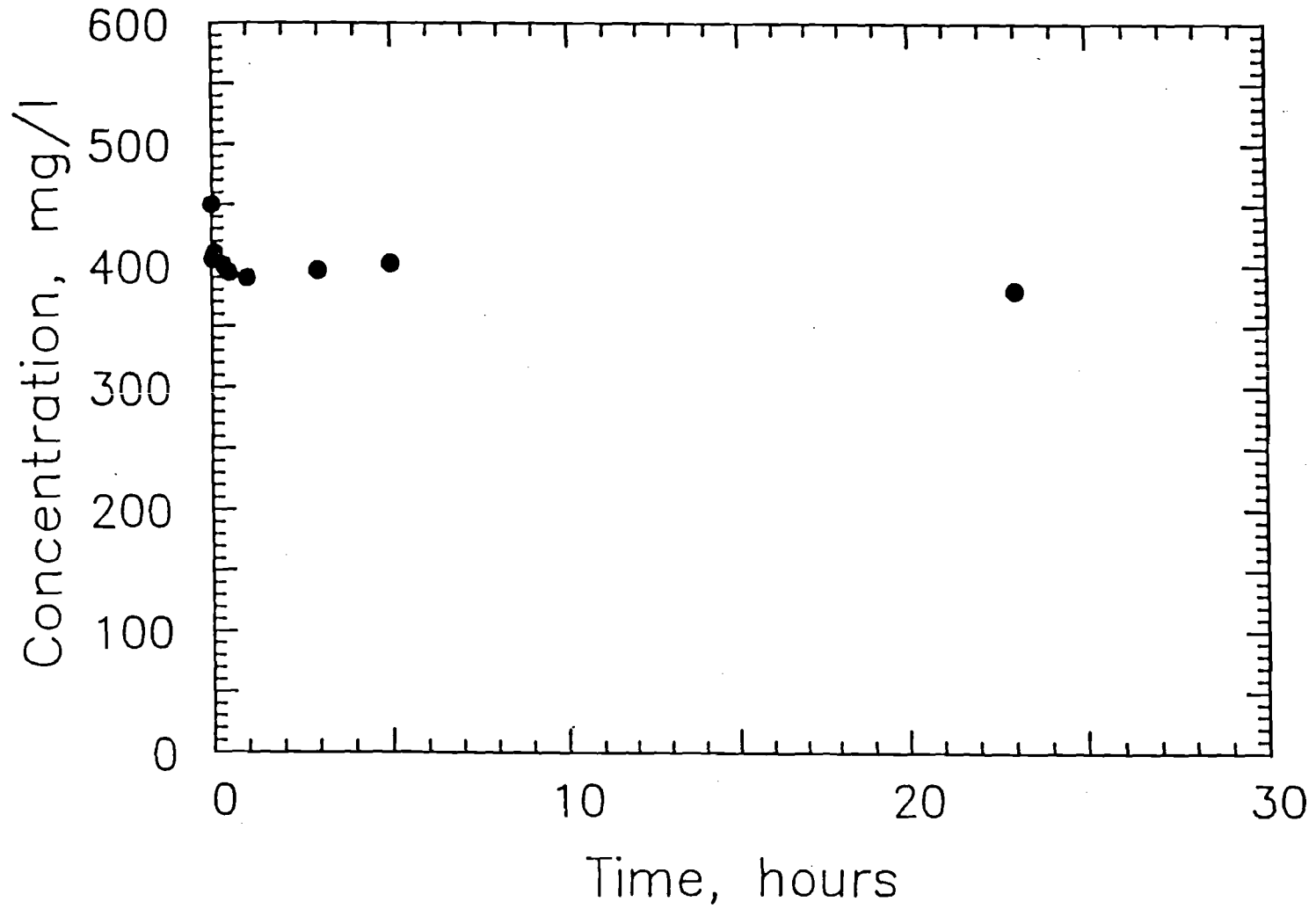


Fig. 36 Batch Kinetic Curve - Hydantoin Adsorbed on Filtrasrob 400.

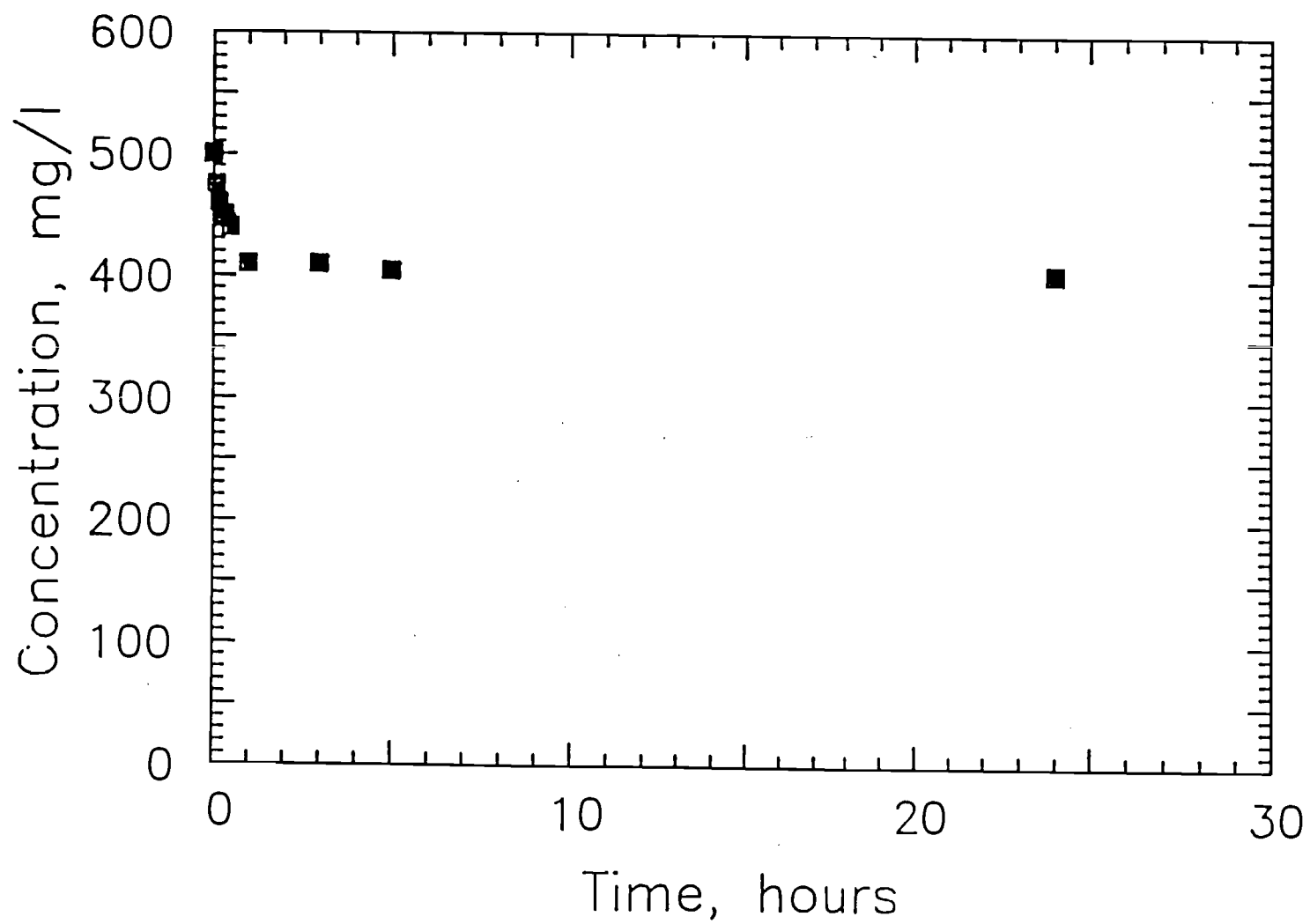


Fig. 37 Batch Kinetic Curve - 5,5-Dimethylhydantoin Adsorbed on Filtrasorb 400.

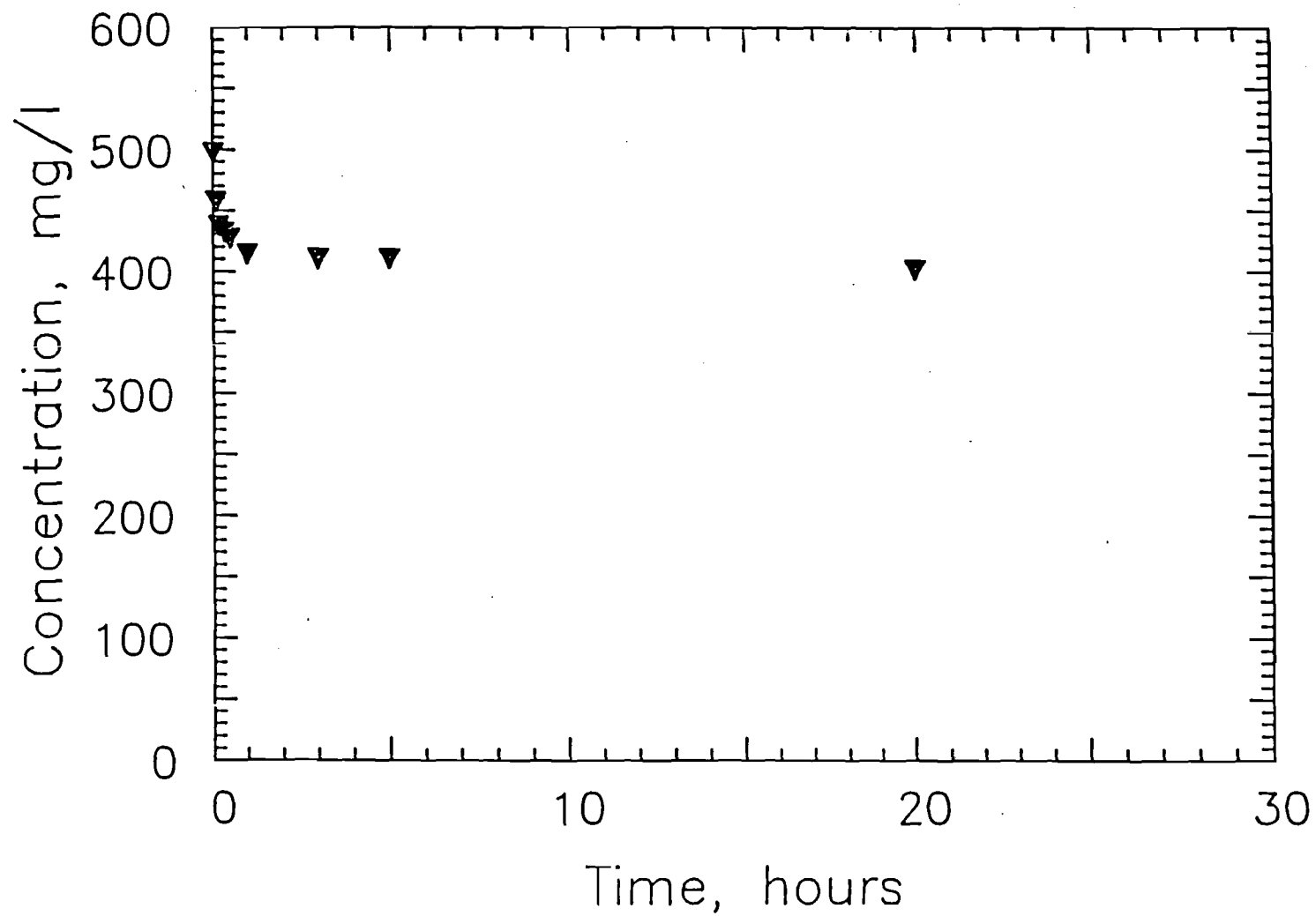


Fig. 38 Batch Kinetic Curve - 5-Methyl-5-Ethylhydantoin Adsorbed on Filtrasorb 400.

Table 14. Initial Experimental Conditions - Adsorption Batch Kinetic Tests

hydantoin

temperature	24°C
C ₀	450 mg/L
carbon, Filtrasorb 400, 60x80 Mesh	0.75 g/L
stirrer speed	800 rpm
adsorbate volume	4.0 L
pH	approx. 5.2

5,5-dimethylhydantoin

temperature	24°C
C ₀	500 mg/L
carbon, Filtrasorb 400, 60x80 Mesh	0.75 g/L
stirrer speed	800 rpm
adsorbate volume	4.0 L
pH	approx. 5.2

5-ethyl-5-methylhydantoin

temperature	25°C
C ₀	500 mg/L
carbon, Filtrasorb 400, 60x80 Mesh	0.75 g/L
stirrer speed	800 rpm
adsorbate volume	4.0 L
pH	approx. 5.2

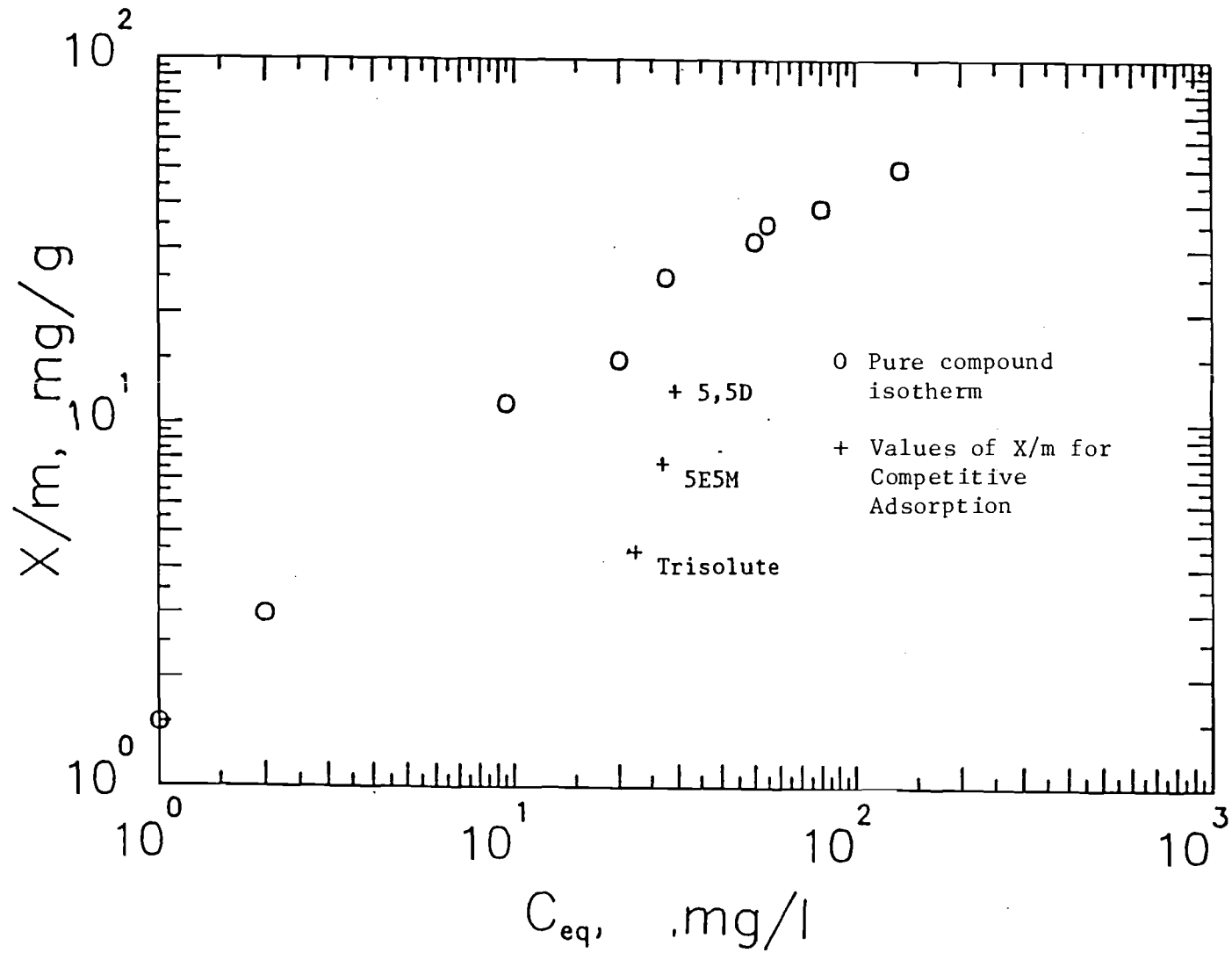


Fig. 39 Adsorption Isotherm - Hydantoin on Filtrasorb 400.

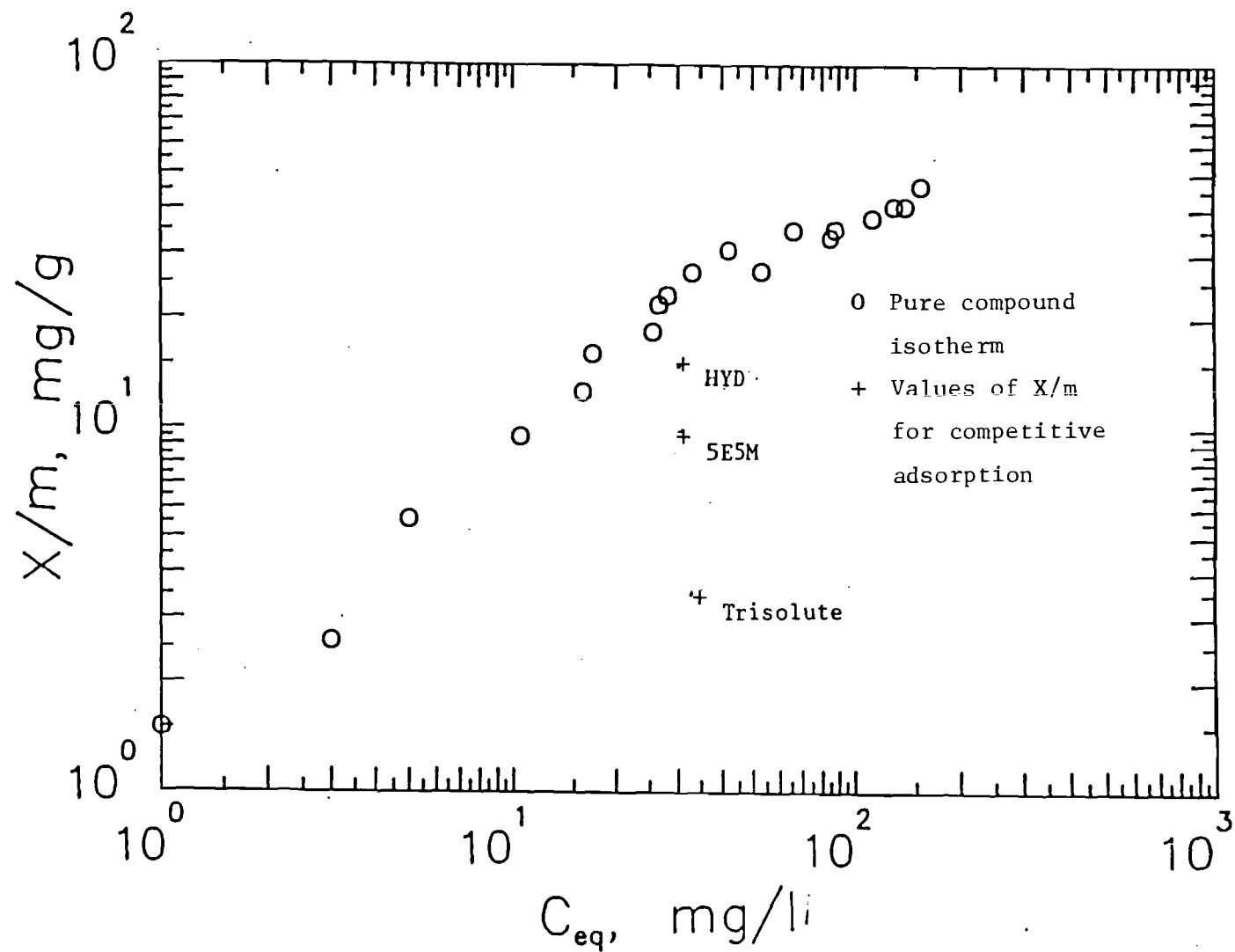


Fig. 40 Adsorption Isotherm. - 5,5-Dimethylhydantoin on Filtrasorb 400.

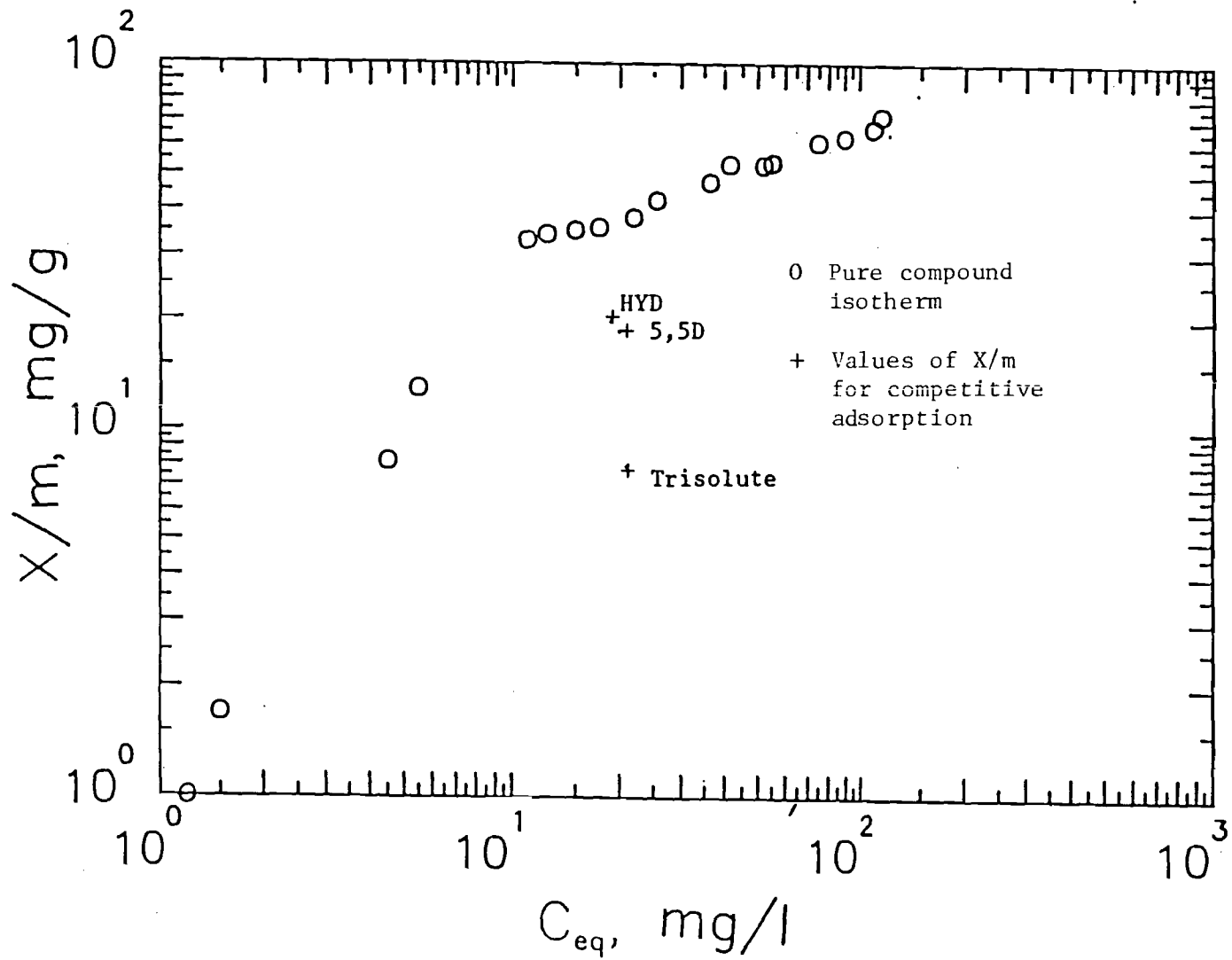


Fig. 41 Adsorption Isotherm - 5-Methyl-5-Ethylhydantoin on Filtrasorb 400.

Table 15. Initial Experimental Conditions for Isotherm Tests

Single solute adsorption

temperature	28°C
C ₀	various
carbon, Filtrasorb 400, 60x80 Mesh	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	approx. 5.2

Bisolute competitive adsorption

temperature	28°C
C ₀	50 mg/L each
carbon, Filtrasorb 400, 60x80 Mesh	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	approx. 5.2

Trisolute competitive adsorption

temperature	28°C
C ₀	50 mg/L each
carbon, Filtrasorb 400, 60x80 Mesh	2.5 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	approx. 5.2

The isotherm for 5-ethyl-5-methylhydantoin was much different from the other two solutes. The isotherm, when plotted in a log-log mode, showed a distinct change in slope with increasing C_{eq} values. The change in slope occurred at a C_{eq} value of 12 mg/L and an X/m value of 35. Overall, there was a higher X/m value for any given equilibrium concentration indicating an adsorption preference for 5-ethyl-5-methylhydantoin over the other solutes. In examining all three curves as a whole, there appears to be a systematic transition in curvature in concentrations in excess of 10 mg/L from hydantoin to 5-ethyl-5-methylhydantoin. Also shown are the results of the bisolute and trisolute isotherm points. Each point represents the X/m and equilibrium concentration found for a given solute in competition with the labelled solute. For instance, in Figure 39, which is the isotherm for hydantoin, the point labelled 5,5 D represents the X/m value found for hydantoin in the bisolute hydantoin/5,5-dimethylhydantoin isotherm point. The point labelled trisolute represents the X/m value for hydantoin in the trisolute isotherm point. As can be expected, competition tends to reduce the amount of adsorbate adsorbed for a given equilibrium concentration. The relative affinity for the various solutes is also indicated by the fact that less hydantoin was adsorbed when in competition with 5-ethyl-5-methylhydantoin than when in competition with 5,5-dimethylhydantoin. When in competition with two different solutes, the amount adsorbed is even less. Since there are only a finite number of adsorption sites available, it was reasonable to assume that the increased competition between solutes in the trisolute isotherm point caused less of the individual solutes to be adsorbed than would be the case for the single or bisolute isotherm point.

In comparing each of the bisolute isotherm points, it appears that the relative affinity of activated carbon is in the order of hydantoin < 5,5-dimethylhydantoin < 5-ethyl-5-methylhydantoin.

The curvature found in the adsorption isotherms represents a departure from the strict Freundlich equation at equilibrium concentrations over approximately 10 mg/L. Therefore, some of the assumptions on which the Freundlich equation are based are invalid for the case in hand. Such assumptions were: 1) exponential distribution of adsorption energies; 2) one adsorbate molecule per adsorption site; 3) no surface transmigration of solute molecules; and, 4) monolayer adsorption. The three assumptions may or may not be valid, but it is probable that monolayer adsorption was still occurring at the highest equilibrium concentration tested.

pH Tests. The results of the high, medium, and low isotherm points with pH adjusted to values of 4, 7, and 9 are shown in Figures 42, 43, and 44. The initial conditions for each of the three solutes are shown in Table 16.

The isotherm points with pH adjusted to 4 and 7 provided equal X/m values for all three solutes at the medium and high concentration points. The variation in X/m values at the low isotherm points were small and probably due to experimental error. Of consequence were the X/m values of the isotherm points with the pH adjusted to 9. These points have X/m values significantly lower than the single solute curve and the X/m values at pH 4 and 7. Therefore, less solute is adsorbed at pH 9 than at a pH of 4 or 7.

Column Studies. The initial conditions for the column studies are shown in Table 17.

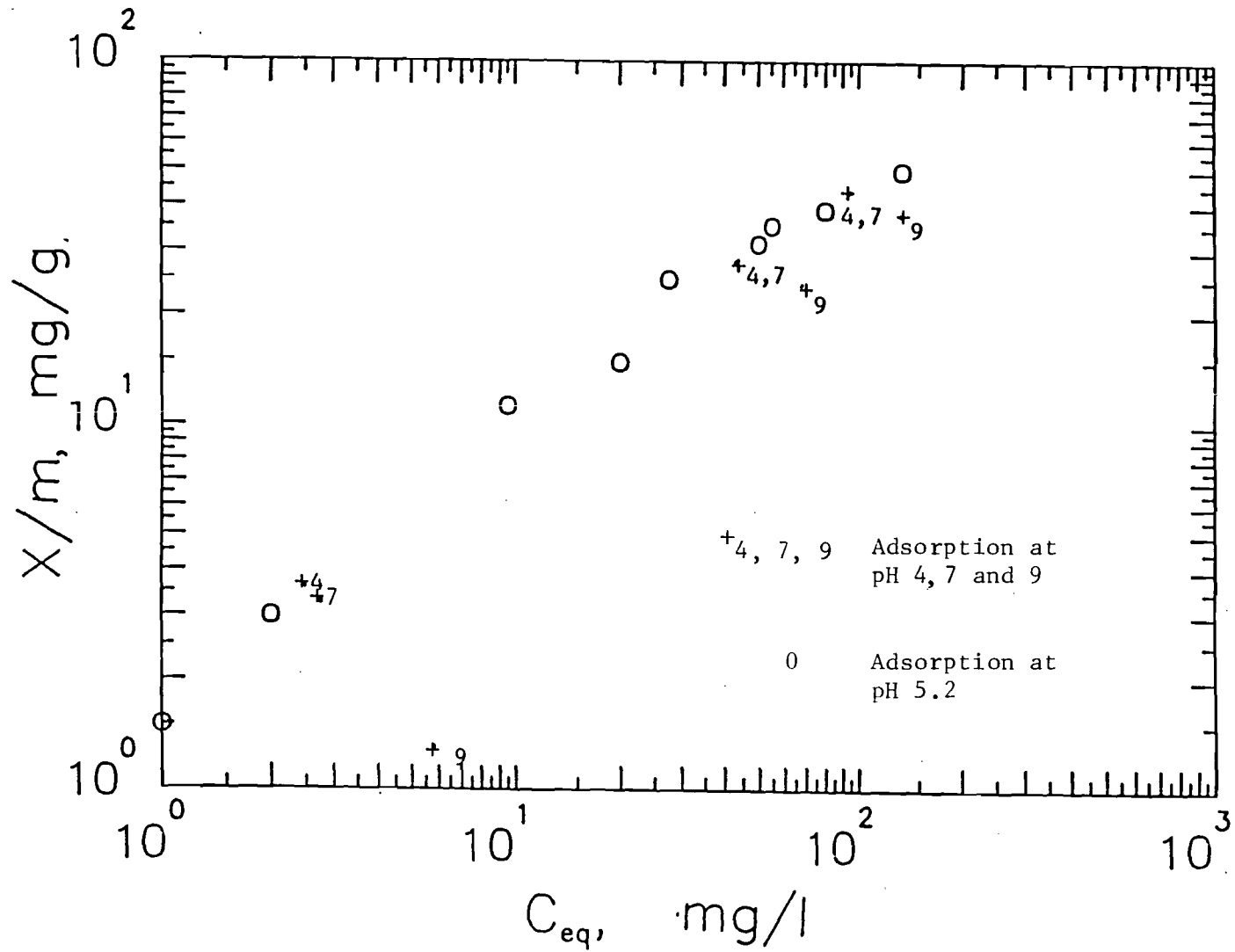


Fig. 42 Isotherm - pH Plot - Hydrantoin Adsorbed on Filtrasorb 400.

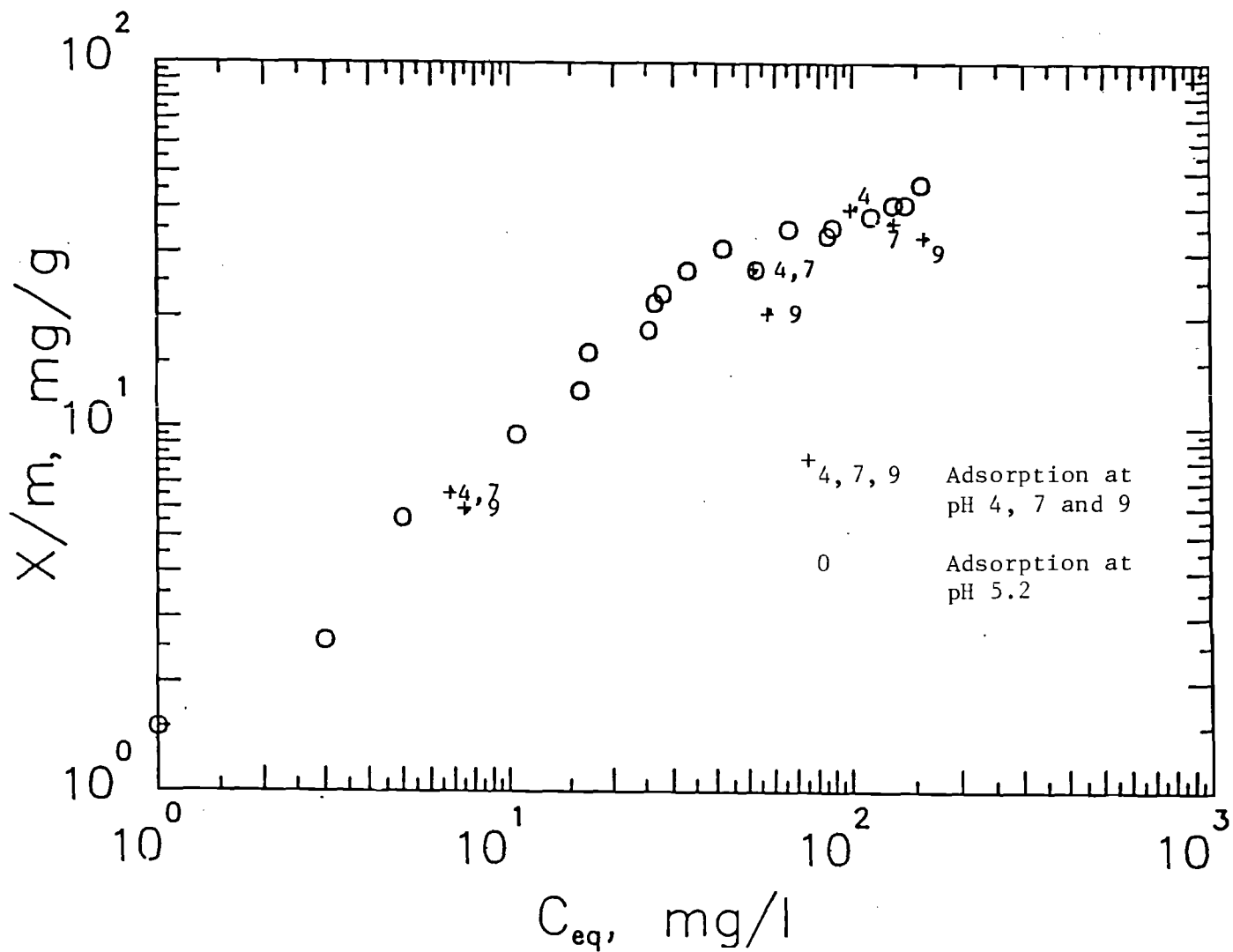


Fig. 43 Isotherm - pH Plot - 5,5-Dimethylhydantoin
Adsorbed on Filtrasorb 400.

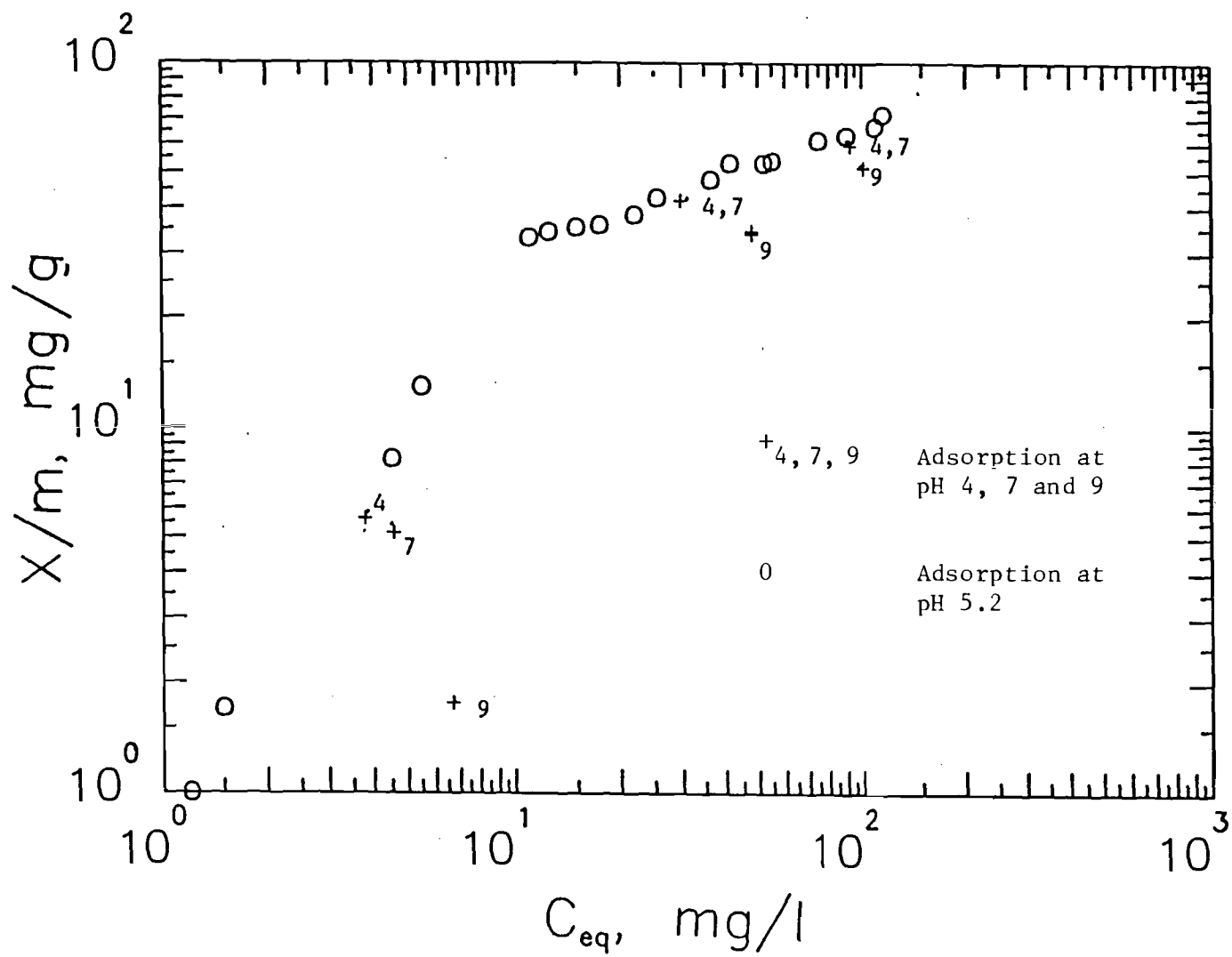


Fig. 44 Isotherm - pH Plot - 5-Methyl-5-Ethylhydantoin
Adsorbed on Filtrasorb 400.

Table 16. Initial Experimental Conditions for Adsorption Tests at Various pH Values

Temperature	28°C
C ₀	50 mg/L
carbon	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 mL
pH	4, 7, 9

Table 17. Initial Experimental Conditions
for Continuous Flow Adsorption Studies

hydantoin		
temperature		28°C
influent concentration		55 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
5,5-dimethylhydantoin		
temperature		28°C
influent concentration		45 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
5-ethyl-5-methylhydantoin		
temperature		28°C
influent concentration		50.5 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
hydantoin/5,5-dimethylhydantoin		
temperature		28°C
influent	hydantoin	40 mg/L
	5,5-dimethylhydantoin	59 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
hydantoin/5-ethyl-5-methylhydantoin		
temperature		28°C
influent	hydantoin	30.9 mg/L
	5-ethyl-5-methylhydantoin	50 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin		
temperature		27°C
influent	5,5-dimethylhydantoin	49.5 mg/L
	5-ethyl-5-methylhydantoin	54 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
trisolute		
temperature		27°C
influent	hydantoin	41.5 mg/L
	5,5-dimethylhydantoin	38 mg/L
	5-ethyl-5-methylhydantoin	33 mg/L
flow rate		20 mL/min
carbon		3.75 g
pH		5.6
coal gasification wastewater		
temperature		28°C
influent		undiluted
flow rate		100 mL/min
carbon		30.0 g
pH		8.76

The results of the single solute column studies are depicted in Figures 45, 46, and 47. To provide a meaningful basis for comparison of the relative adsorption preferences of the three solutes, a calculation of the X/m values, Table 18, (amount of solute adsorbed per unit weight of carbon) reveals the following:

The X/m value for hydantoin is slightly higher than expected. However, if the X/m value of 41 mg/g with a C_{eq} of 55 mg/L is plotted on the single solute isotherm for hydantoin (Figure 39), it will be seen to be within experimental error. The X/m values for the other two solutes plot directly on the single solute curves (Figures 40 and 41). From the single solute column studies, it is readily apparent that 5-ethyl-5-methylhydantoin is more strongly adsorbed than the other two adsorbents.

More vivid evidence for the various affinities of the carbon for the different solutes was provided by the bisolute and trisolute breakthrough curves which are shown in Figure 48, 49, 50 and 51. The calculated X/m values for the bisolute and trisolute breakthrough curves are shown in Table 19.

Although from Figure 41 it appeared that the affinity of the carbon for hydantoin and 5,5-dimethylhydantoin was equal, the X/m values for the hydantoin/5,5-dimethylhydantoin in Table 19 showed that the carbon had a higher capacity for 5,5-dimethylhydantoin over hydantoin. The bisolute curve hydantoin/5-ethyl-5-methyl-hydantoin (Figure 49) showed a stronger adsorption of 5-ethyl-5-methylhydantoin by the fact that hydantoin was displaced from the activated carbon during the column test. This was demonstrated by the effluent concentration of the hydantoin becoming greater than the influent concentration. This was caused by all hydantoin in the influent passing through the column unadsorbed, and additional hydantoin was added to the effluent due to displacement from the carbon through competition with the more strongly adsorbed 5-ethyl-5-methylhydantoin. A comparison of the X/m values in Table 19 also showed that 5-ethyl-5-methylhydantoin was more strongly adsorbed than hydantoin. The bisolute curve 5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin again showed a displacement of the more weakly adsorbed solute, 5,5-dimethylhydantoin, by the more strongly adsorbed 5-ethyl-5-methylhydantoin. The X/m values in Table 19 verify that the carbon has a higher adsorption capacity for the 5-ethyl-5-methylhydantoin over the 5,5-dimethylhydantoin.

A double displacement effect occurred in the trisolute breakthrough curve. The most strongly adsorbed 5-ethyl-5-methylhydantoin displaced both hydantoin and 5,5-dimethylhydantoin from the carbon as can be seen in Figure 51. From Table 19, the X/m values for hydantoin and 5,5-dimethylhydantoin were equal while the carbon exhibited a much higher adsorption capacity for the 5-ethyl-5-methylhydantoin.

Overall, a review of the results in Table 19 show an adsorption preference of 5-ethyl-5-methylhydantoin > 5,5-dimethylhydantoin > hydantoin.

The breakthrough curves for two of the hydantoins and phenol in the actual pretreated coal gasification effluent is shown in Figure 52. Immediately following is the breakthrough curve for total organic carbon for the wastewater, Figure 53. The amount of carbon used in the column was 30 grams with a flow rate of 100 mL/min. From Figure 52, the least strongly

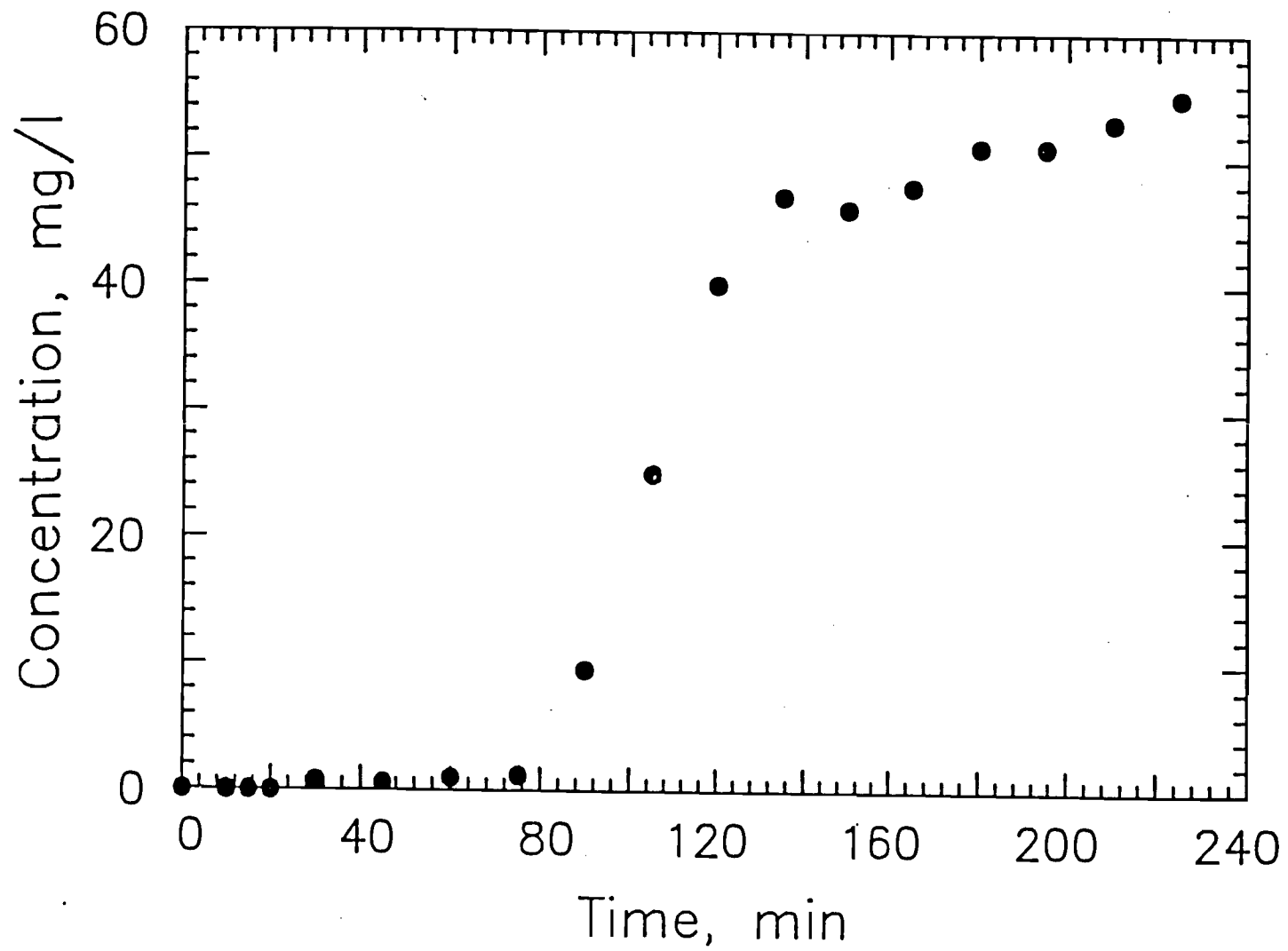


Fig. 45 Column Breakthrough Curve - Hydantoin
Adsorbed on Filtrasorb 400.

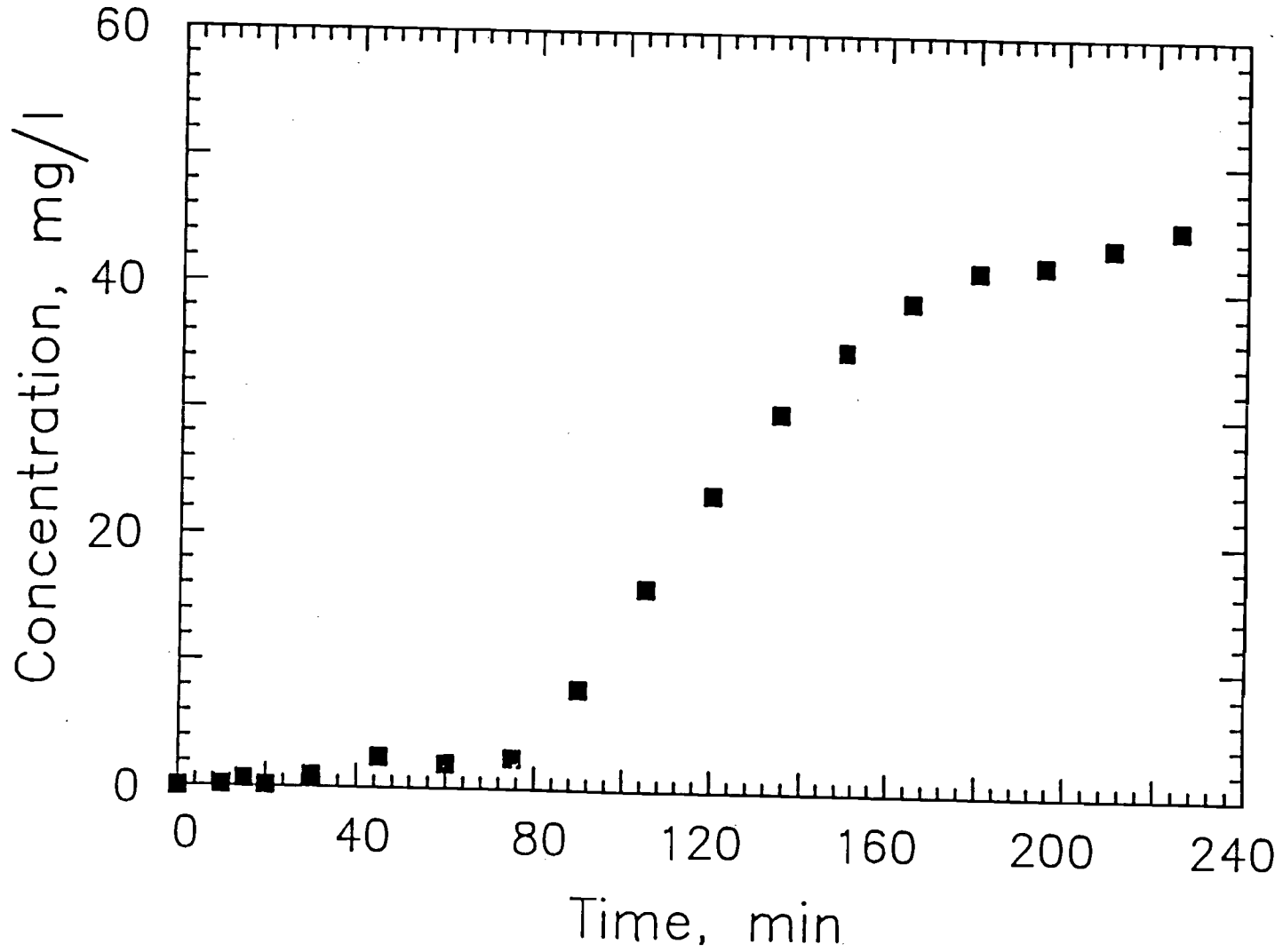


Fig. 46 Column Breakthrough Curve - 5,5-Dimethylhydantoin
Adsorbed on Filtrasorb 400.

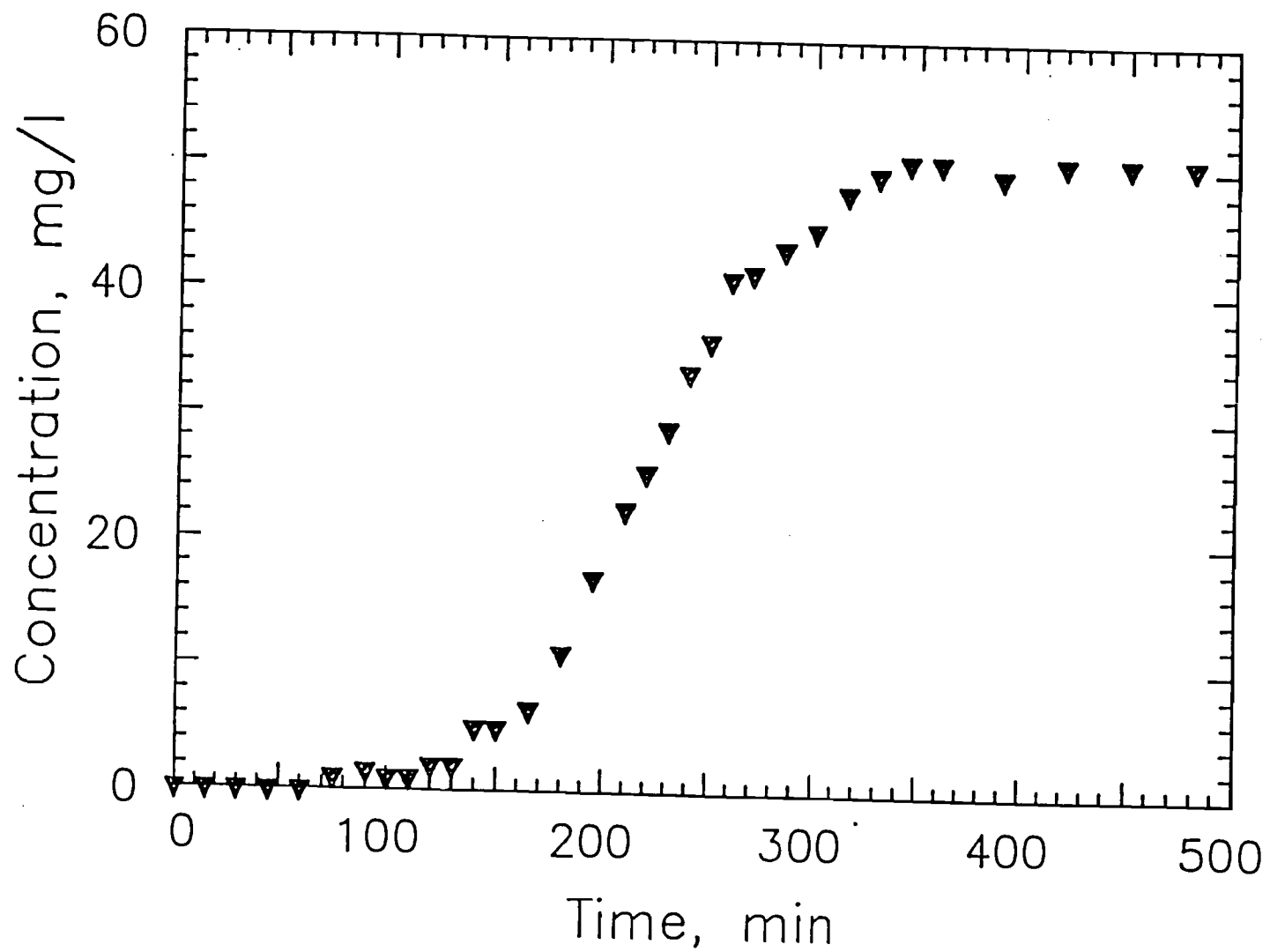


Fig. 47 Column Breakthrough Curve - 5-Methyl-5-Ethylhydantoin
Adsorbed on Filtrasorb 400.

Table 18. Single Solute X/m Values for Continuous Flow Column Adsorption Studies

hydantoin	43 mg/g
5,5-dimethylhydantoin	31 mg/g
5-ethyl-5-methylhydantoin	61 mg/g

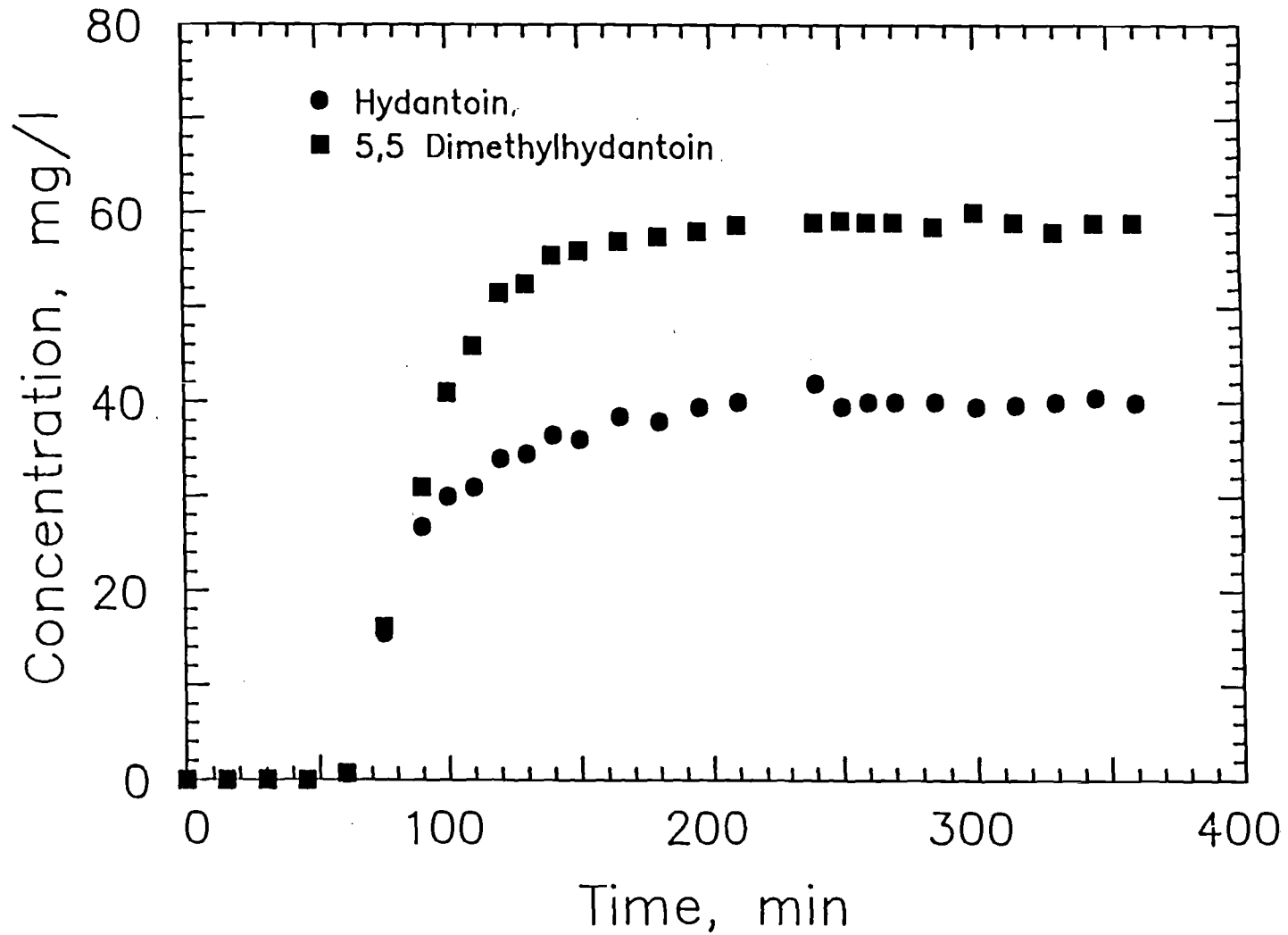


Fig. 48 Bisolute Breakthrough Curve - Hydantoin/5,5-Dimethylhydantoin Adsorbed on Filtrasorb 400.

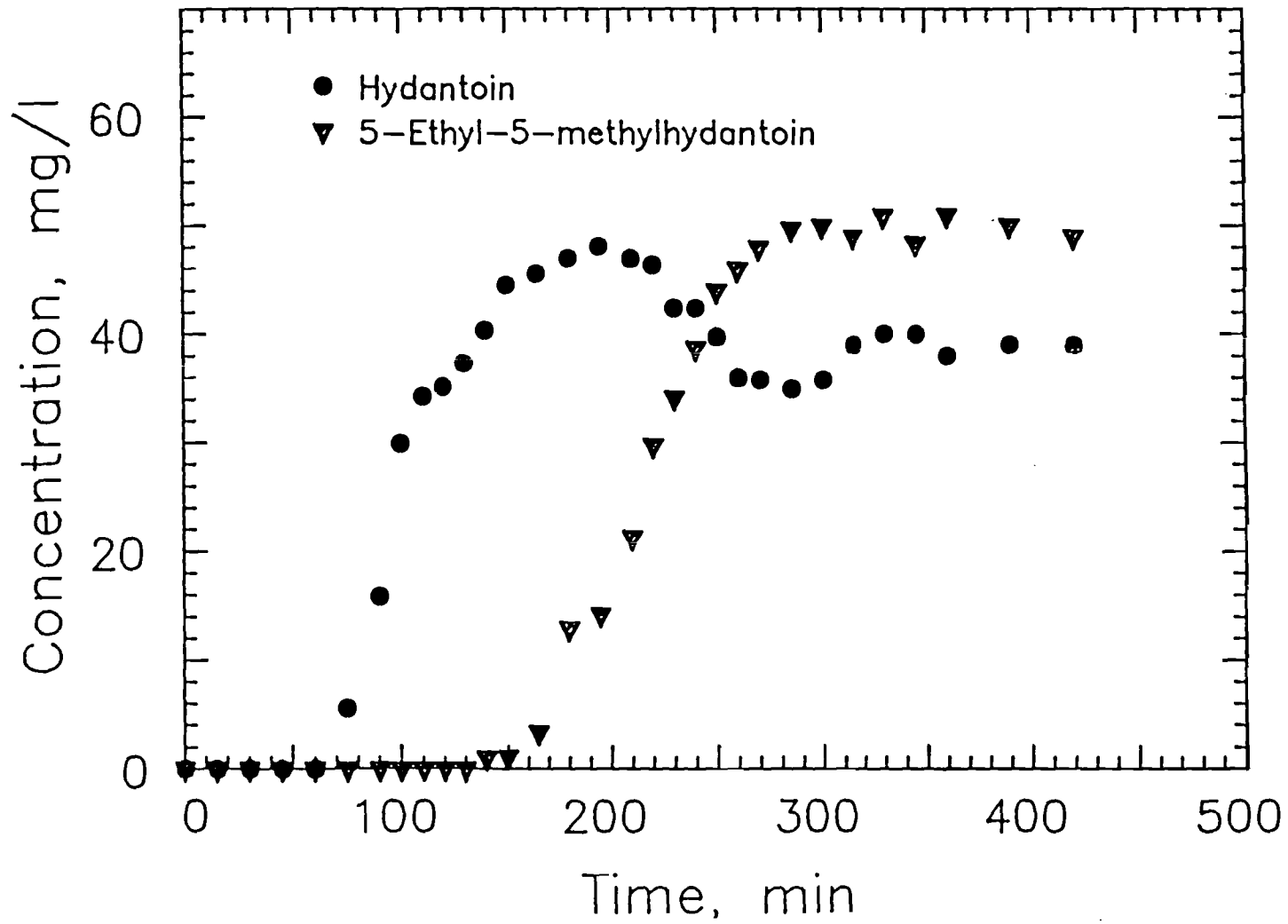


Fig. 49 Bisolute Breakthrough Curve - Hydantoin/5-Methyl-5-Ethylhydantoin Adsorbed on Filtrasorb 400.

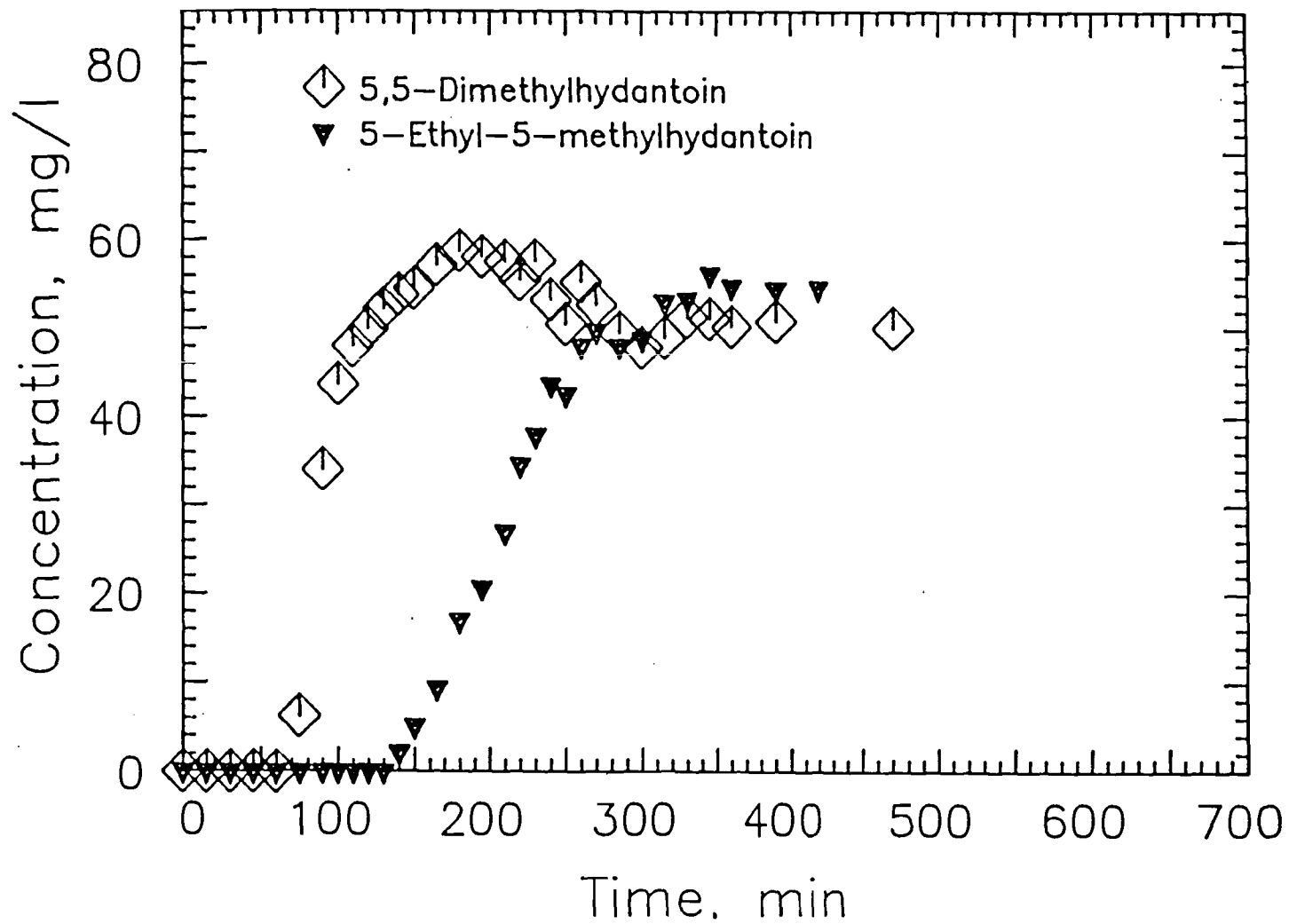


Fig. 50 Bisolute Breakthrough Curve - 5,5-Dimethylhydantoin/5-Methyl-5-Ethylhydantoin Adsorbed on Filtrasorb 400.

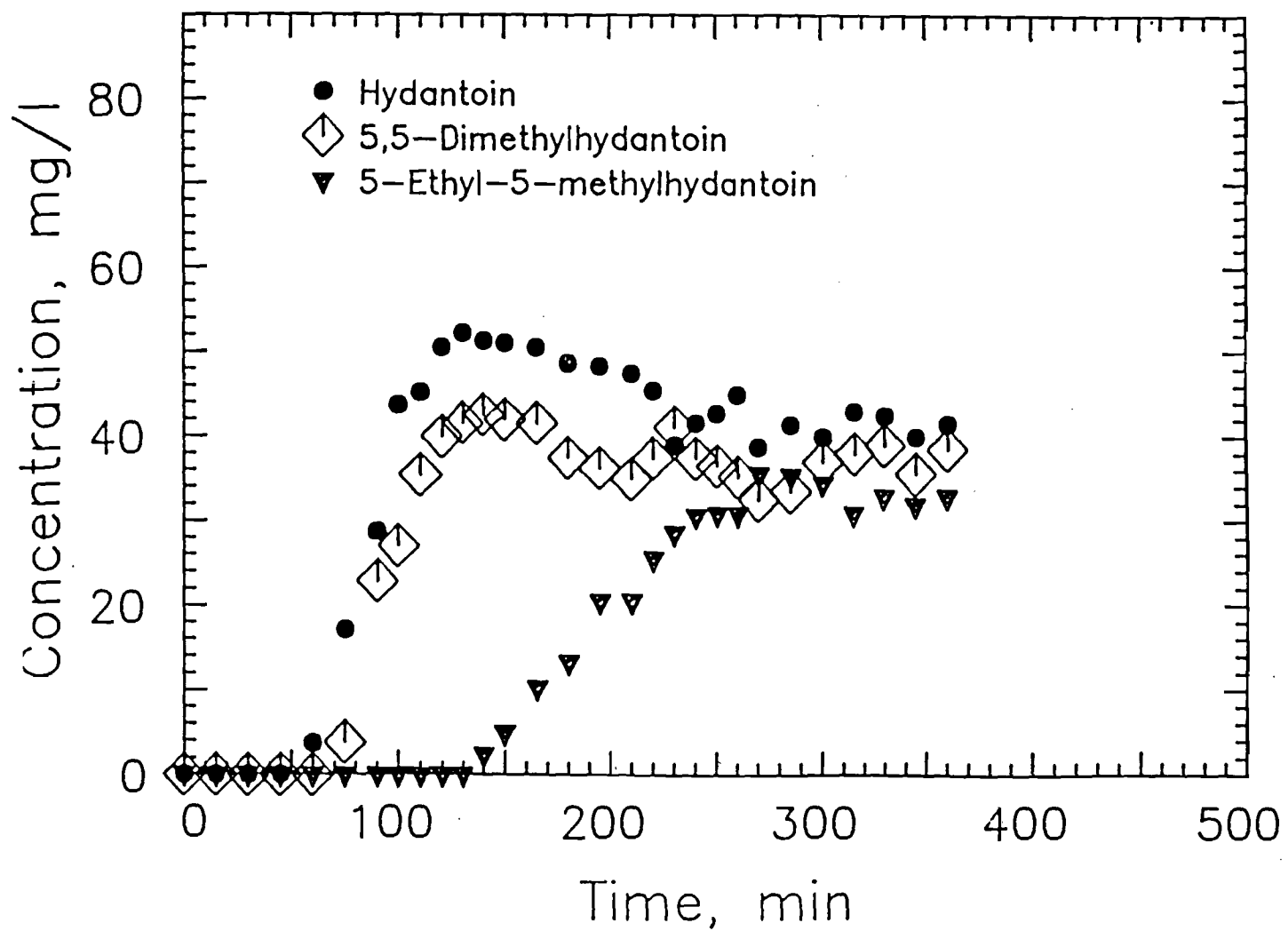


Fig. 51 Trisolute Breakthrough Curve Hydantoin, 5,5-Dimethylhydantoin, 5-Methyl-5-Ethylhydantoin Adsorbed on Filtrasorb 400.

Table 19. Bisolute and Trisolute X/m Values for Continuous Flow Column Adsorption Studies

hydantoin/5,5-dimethylhydantoin	
hydantoin	21 mg/g
5,5-dimethylhydantoin	36 mg/g
hydantoin/5-ethyl-5-methylhydantoin	
hydantoin	19 mg/g
5-ethyl-5-methylhydantoin	57 mg/g
5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin	
5,5-dimethylhydantoin	22 mg/g
5-ethyl-5-methylhydantoin	58 mg/g
trisolute	
hydantoin	17 mg/g
5,5-dimethylhydantoin	17 mg/g
5-ethyl-5-methylhydantoin	33 mg/g

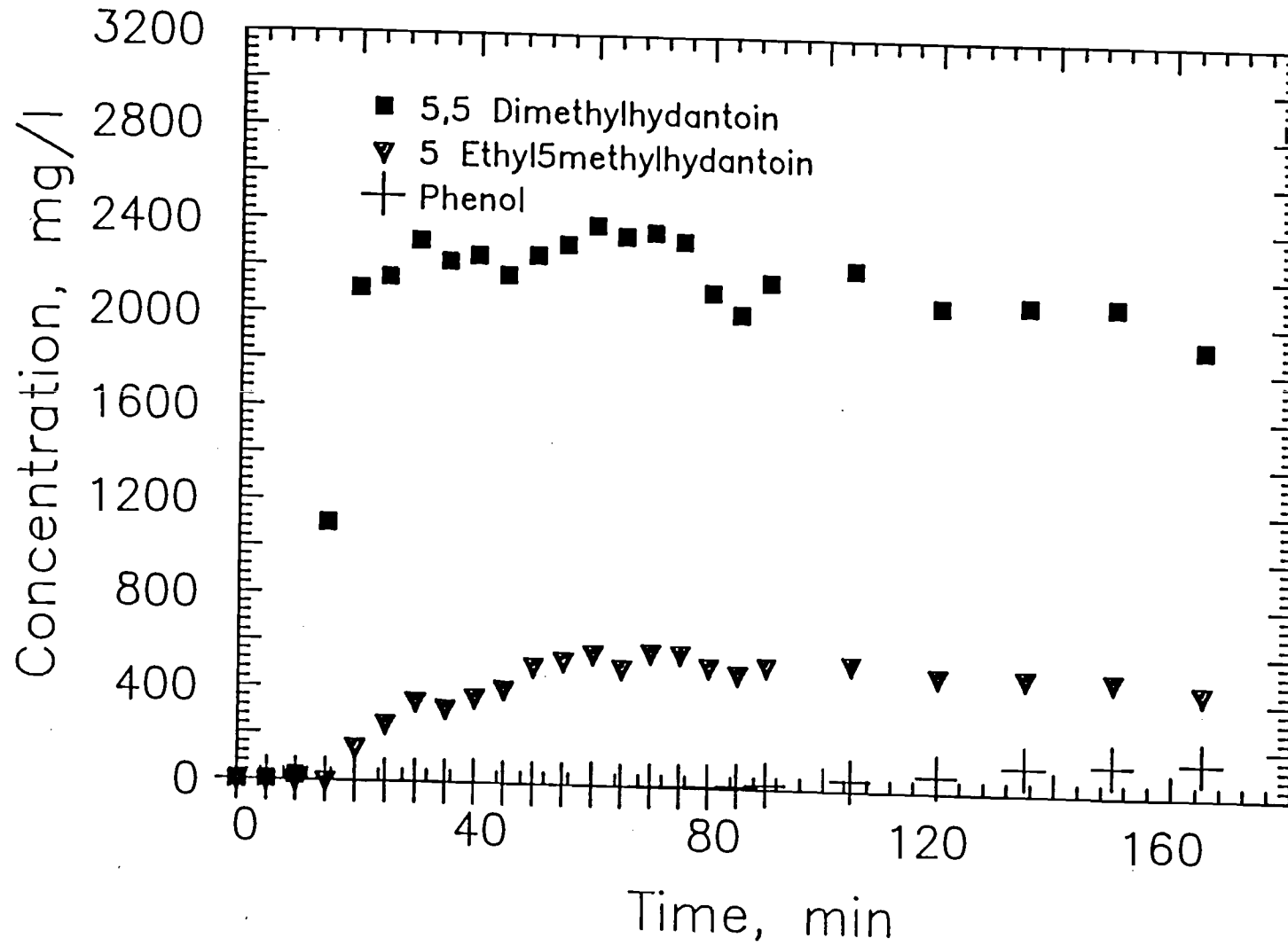


Fig. 52 Breakthrough Curve - Pretreated Coal Gasification Effluent Adsorbed on Filtrasorb 400.

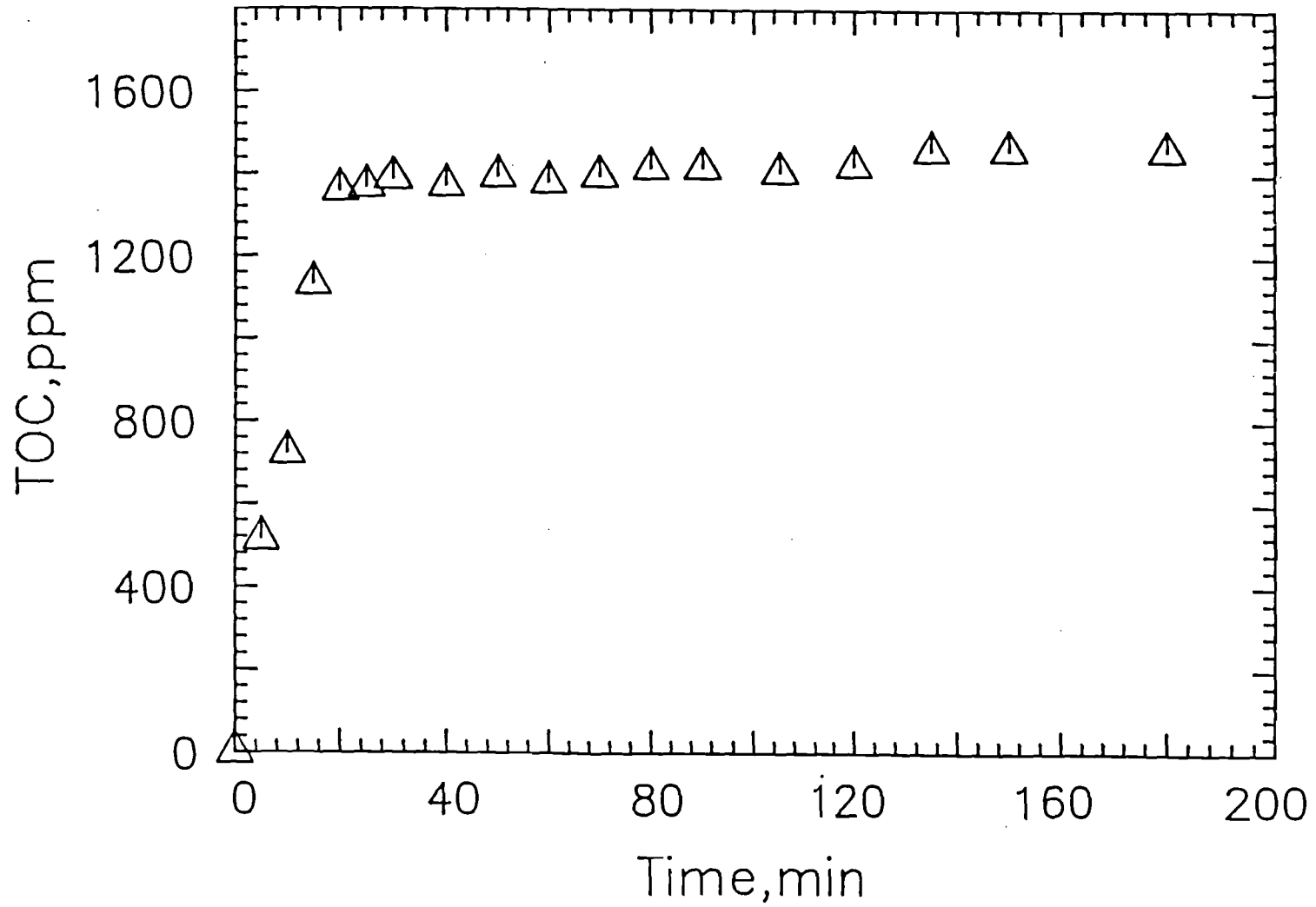


Fig. 53 TOC Breakthrough Curve - Pretreated Coal Gasification Effluent Adsorbed on Filtrasorb 400.

adsorbed 5,5-dimethylhydantoin broke through first between 10 and 15 minutes from the start of the test followed by 5-ethyl-5-methylhydantoin breakthrough between 15 and 20 minutes. 5,5-Dimethylhydantoin reached carbon exhaustion at 1977 mg/L within 10 minutes of initiating breakthrough. 5-Ethyl-5-methylhydantoin reached influent concentration after 55 minutes. Phenol did not appear in the effluent until 85 minutes from the test start and slowly reached exhaustion at 165 minutes. A slight displacement of solute occurred with 5,5-dimethylhydantoin being displaced by the 5-ethyl-5-methylhydantoin. Also, slight displacement of the 5-ethyl-5-methylhydantoin by the phenol occurred.

The X/m values for each of the solutes measured in the pretreated coal gasification effluent are shown in Table 20.

At face value, it appears that 5,5-dimethylhydantoin was more strongly adsorbed than phenol in the coal gasification wastewater due to its higher X/m value in Table 20. However, the higher X/m value is due to the concentration of the 5,5-dimethylhydantoin being an order of magnitude higher than the phenol concentration. A more definitive determination of adsorption preferences can be obtained from the coal gasification wastewater breakthrough curves where phenol was the last compound to be observed in the column effluent, and where phenol displaced both 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin from the carbon. Phenol was apparently the most strongly adsorbed compound.

A comparison of the X/m values found in Table 20 with the single solute isotherm curves for 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin (Figures 40 and 41) reveals that the X/m values found in the column study for coal gasification wastewater were significantly lower than the expected X/m values for the pure single solute system given equivalent solute concentrations. A comparison of X/m values for pure solute and actual wastewater is given in Table 21.

The TOC breakthrough curve is interesting since it shows that the wastewater contains some substances that are apparently not readily adsorbed on activated carbon. This is shown by noting that some TOC broke through the carbon column immediately from the start of the test. It is assumed that the compounds that were not adsorbed were large molecules that could not physically fit inside the carbon pore.

CONCLUSIONS

The batch kinetic tests for single solutes demonstrated that the kinetics of adsorption for hydantoin, 5,5-dimethylhydantoin, and 5-ethyl-5-methylhydantoin were very rapid with most of the adsorption occurring in the first 20 minutes.

The relative strength of adsorption of the three solutes was established by the single solute, bisolute, and trisolute isotherm points as follows: hydantoin < 5,5-dimethylhydantoin < 5-ethyl-5-methylhydantoin. This relationship held true regardless of the relative concentration of each solute with respect to the other as demonstrated by the coal gasification wastewater breakthrough curve. Even though 5,5-dimethylhydantoin was present in concentrations of 1980 mg/L, 5-ethyl-5-methylhydantoin at concentrations of 460 mg/L

Table 20. Pretreated Coal Gasification Effluent X/m Values
from Continuous Flow Column Adsorption Studies

5,5-dimethylhydantoin	96 mg/g
5-ethyl-5-methylhydantoin	42 mg/g
phenol	64 mg/g

Table 21. Comparison of X/m Values for Coal Gasification
Wastewater and Pure Solutes

5,5-dimethylhydantoin	
concentration in wastewater	1980 mg/L
pure single solute X/m	145 mg/g
wastewater X/m	96 mg/g
5-ethyl-5-methylhydantoin	
concentration in wastewater	460 mg/L
pure single solute X/m	120 mg/g
wastewater X/m	42 mg/g

was still able to displace it from the carbon, and was therefore more strongly adsorbed. The bisolute and trisolute isotherm points also demonstrated competitive effects between the solutes relative to their respective strengths of adsorption. The X/m values for each adsorbate was markedly reduced by the presence of a second and third solute. Within a given weight of activated carbon, there was a finite number of adsorption sites that could be utilized by the three adsorbates. Although hydantoin was the least strongly adsorbed solute, it was not totally desorbed by either the 5,5-dimethylhydantoin or the 5-ethyl-5-methylhydantoin, and 5,5-dimethylhydantoin was not totally desorbed by the 5-ethyl-5-methylhydantoin. Since the X/m values for the less strongly adsorbed compounds are lower than the corresponding X/m value for the single solute, it is obvious some displacement of the weaker by the more strongly adsorbed compound occurs. However, since an apparently large percentage of the weaker adsorbate, hydantoin, would still be adsorbed on the carbon after the most strongly adsorbed compound, 5-ethyl-5-methylhydantoin, had reached equilibrium, adsorption sites on the carbon appear to have a site specific affinity for one particular solute over the other.

The characteristics of the various adsorbates could be the leading cause of the adsorption preferences encountered. The difference in molecular structure of the three solutes was the presence of the alkyl groups or hydrogen bonded to the C⁵. Hydantoin had no alkyl groups and was the most weakly adsorbed. 5-Ethyl-5-methylhydantoin had the largest molecular weight function groups and was the most strongly adsorbed. 5,5-Dimethylhydantoin was in an intermediate position of adsorption strength. Examples of adsorption strength based upon functional groups attached to the solute molecules were previously found by Belfort³⁷.

The pH adjusted isotherm points within the high, mid-range, and low-range for each single solute isotherm conclusively showed that at a pH of 4 and 7, the X/m values were within experimental error of the isotherm curve. At pH 9, however, the X/m value was much lower. Therefore, at a pH of 9, the amount of solute adsorbed per unit weight of carbon is significantly reduced.

The X/m values for the single solute breakthrough curves were either directly on or within experimental error of the X/m value for an equivalent solute concentration on the pure solute breakthrough curves. This phenomena enhances the probability that the single solute isotherms are accurate.

For the bisolute and trisolute curves, the X/m values demonstrated the adsorption preference of the activated carbon for the three adsorbates. From Table 19, it is obvious that 5,5-dimethylhydantoin is more strongly adsorbed than hydantoin from the hydantoin/5,5-dimethylhydantoin X/m values, and from the trisolute X/m values, that 5-ethyl-5-methylhydantoin is more strongly adsorbed than both of the other two adsorbates. Also, by observing the solute displacements which occurred on the actual bisolute and trisolute breakthrough curves (Figures 48 through 51), a relative adsorption preference can be observed.

The pretreated coal gasification effluent breakthrough curves (Figure 52) with the associated X/m values (Table 20) yielded interesting results. A comparison of the X/m values for the coal gasification wastewater and pure solutes for equivalent solute concentrations (Table 20) showed significant reductions in the X/m values in the wastewater. The adsorption of

5,5-dimethylhydantoin was reduced by 34% and that of 5-ethyl-5-methylhydantoin was reduced 65% from the adsorption that would be expected in a pure solute system. The probable reasons for the reduction in adsorption capacity are twofold: (1) the increase in pH from 5.2 in pure systems to 8.76 in the actual wastewater, and (2) competition between the various solutes in the wastewater. From Figures 42, 43, and 44, it was shown that at a pH of 9, the amount of pure solute adsorbed on the carbon was reduced. Since the wastewater has a pH of 8.76, it is probable that the pH had an effect in reducing the X/m values for the wastewater. In addition, from the bisolute and trisolute isotherm points (Figures 42, 43, and 44) it was demonstrated that competition between the solutes will reduce the amount of hydantoins that will be adsorbed on activated carbon. In the coal gasification wastewater, the hydantoins were in competition with phenol (which was more strongly adsorbed) which would reduce the X/m values for the hydantoins. It is probable that both conditions contributed to a reduction in the amount of hydantoins adsorbed.

CARBON REGENERATION STUDY

If carbon adsorption were to be used as a method for removal of the hydantoins from the pretreated wastewater, a relatively inexpensive and rapid method of regeneration of the exhausted granular activated carbon would be desirable. Without a rapid and inexpensive regeneration scheme the use of carbon adsorption would not be economically viable due to the relative low capacity of the carbon for hydantoins.

Continuous flow carbon adsorption - solvent regeneration studies were carried out using 30 x 40 mesh Filtrasorb 400, pretreated (solvent extracted - steam stripped) wastewater and a series solvents. Flow rates were 5 mL/min and 2 mL/min for adsorption and regeneration, respectively. The results of the adsorption regeneration cycles are summarized in Table 22. Typical breakthrough and regeneration curves are given in Figures 54, 55, 56, and 57.

Regeneration values were calculated by determining the amount of compound adsorbed from the raw wastewater and the amount desorbed by the solvent.

Regeneration was then defined as: $\frac{\text{amount desorbed}}{\text{amount adsorbed}} \times 100$.

CONCLUSIONS

Based on the quantity of carbon required for adsorption and the limited regeneration by the solvents used, it does not appear that this process is a viable one for the removal of hydantoins from the pretreated wastewater.

Table 22. Solvent Regeneration of Exhausted Activated Carbon

Solvent	% Capacity Regenerated
NaOH, 0.1 M	70
NaOH, 0.2 M	57,72*
HCl, 0.2 M	38
HCl, 1 M	40
Methanol	69,54,51*
Methyl Ethyl Ketone	48*
2-Propanol	15*

*Successive regeneration cycles.

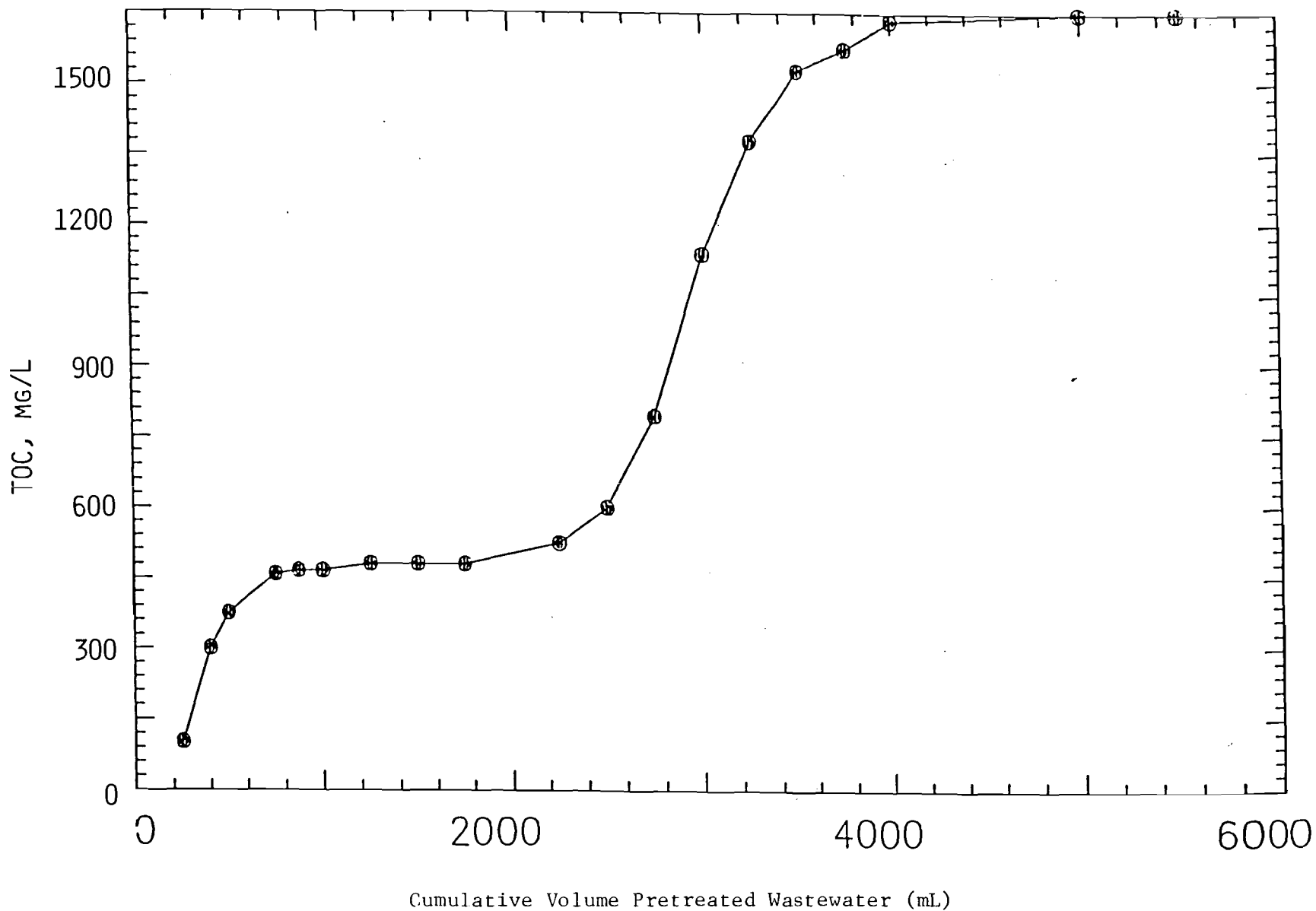


Fig. 54 TOC Breakthrough Curve - Pretreated Coal Gasification Effluent.
Adsorption-Regeneration Study

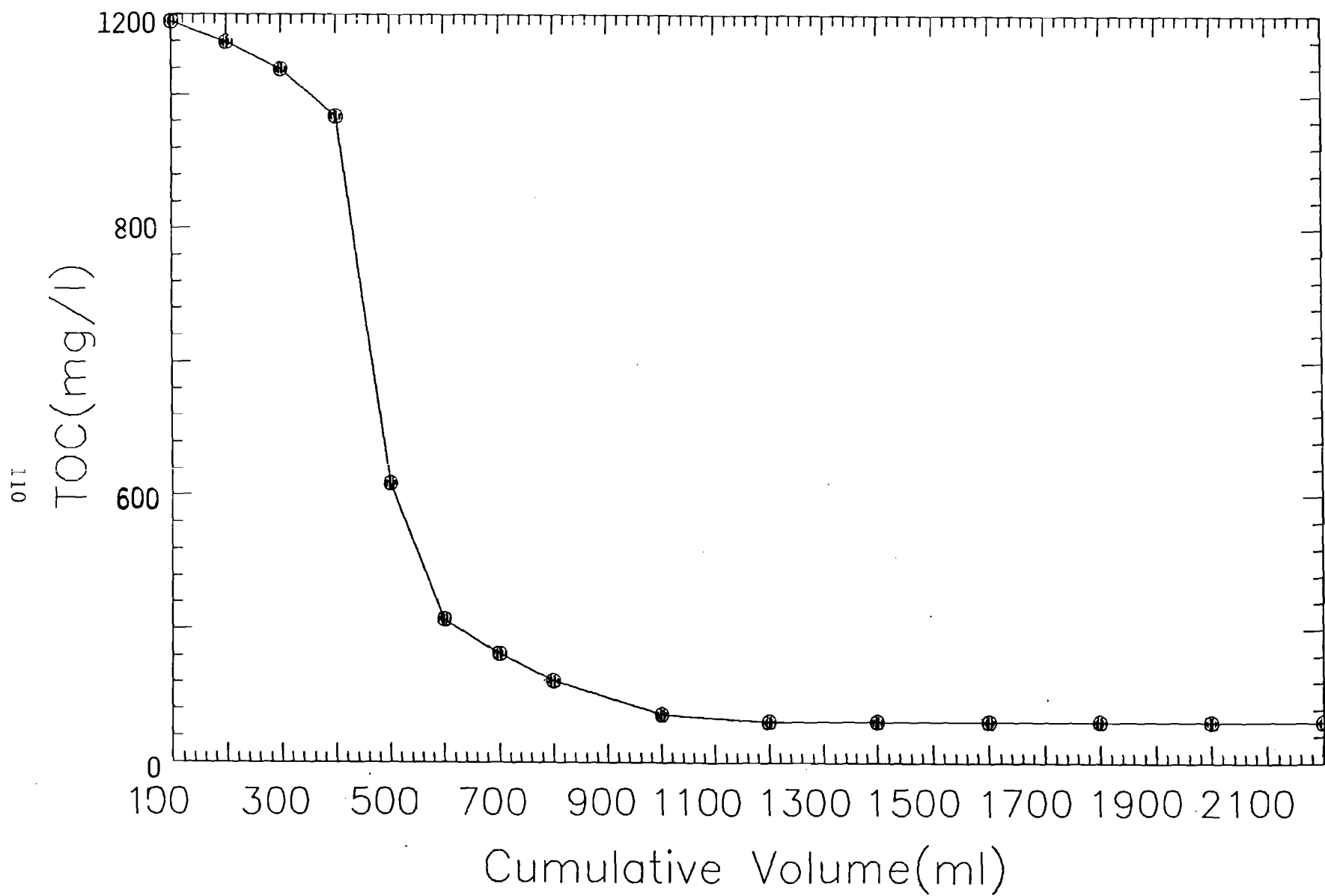


Fig. 55 Solvent Regeneration of Exhausted Activated Carbon Using Sodium Hydroxide (0.1M).

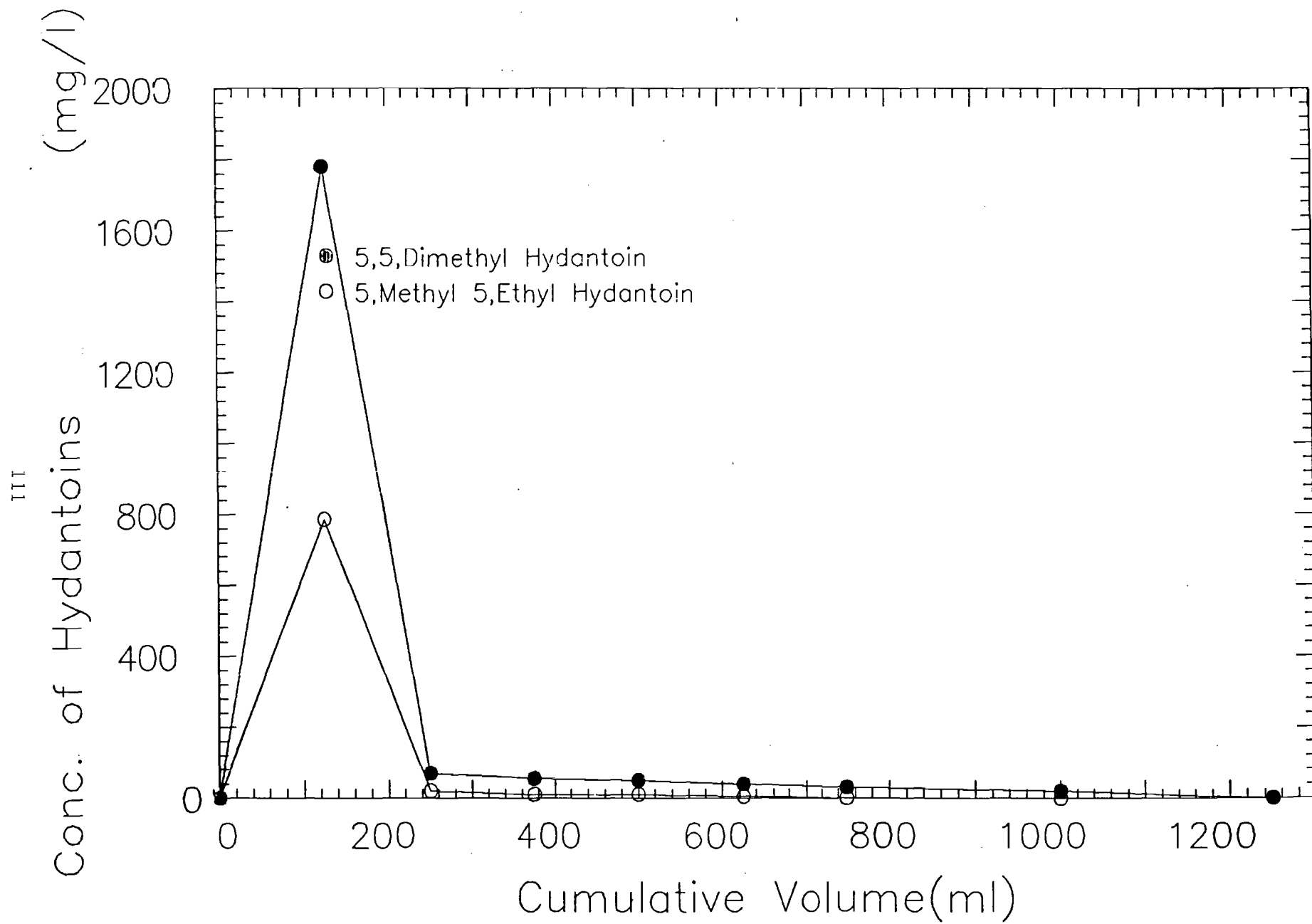


Fig. 56 First Regeneration of Exhausted Activated Carbon Using Methanol.

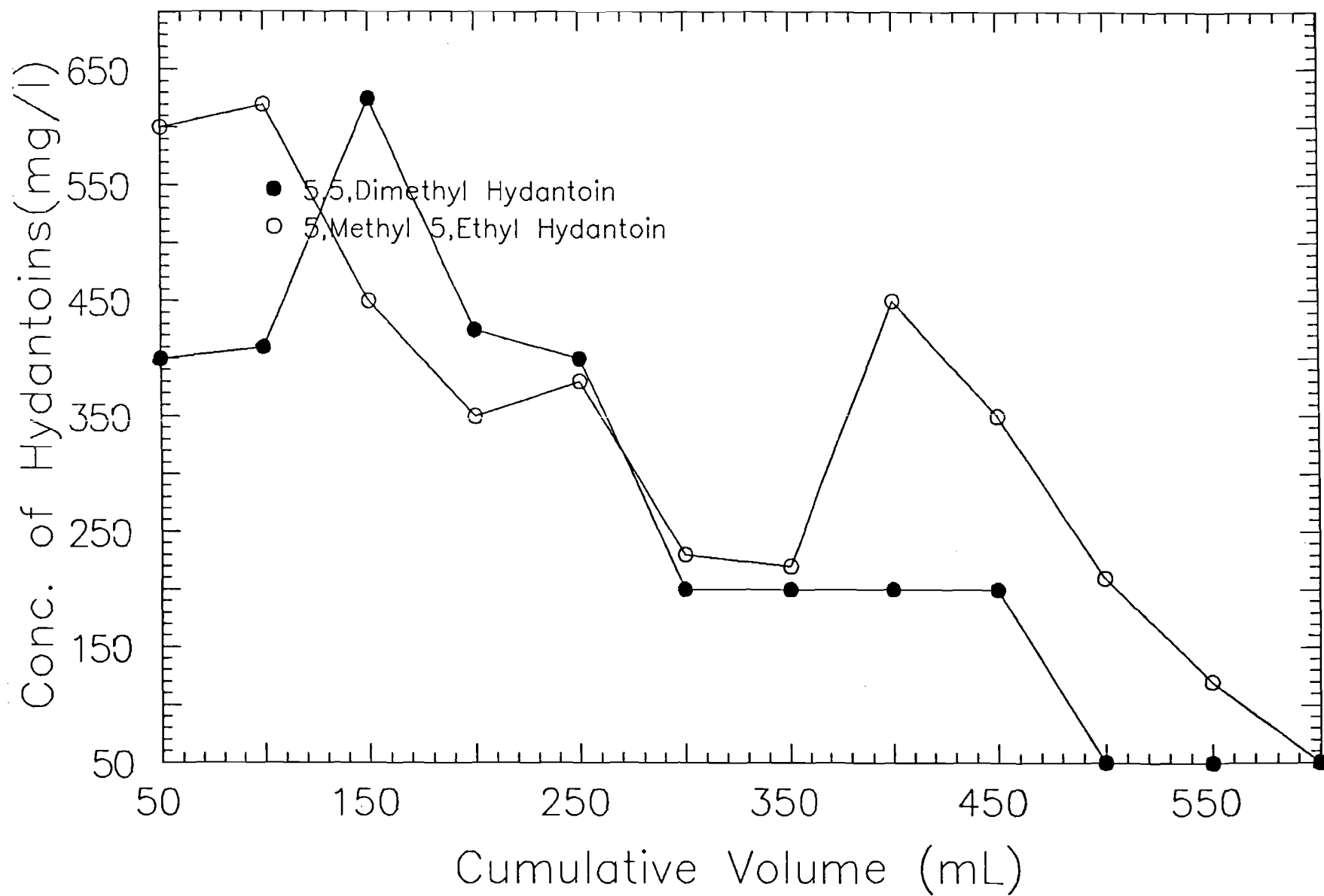


Fig. 57 Second Regeneration of Exhausted Activated Carbon Using Methanol.

SUMMARY

Dilute (~10%) coal gasification effluent was successfully treated biologically for the removal of organic carbon and ammonia. The complete treatment train consisted of a two-stage anaerobic activated carbon filter for organic carbon removal followed by a single sludge nitrification system for conversion of ammonia nitrogen to nitrate-nitrogen and finally conversion of nitrate-nitrogen to nitrogen gas in a biological denitrification system.

After an extended period of operation on ~10% coal-gasification effluent inhibition of both the anaerobic and the nitrification systems occurred. Inhibition of the anaerobic system was partially overcome by replacement of a portion of the granular activated carbon in the filter. Continued periodic replacement of the activated carbon was required to maintain a viably operating anaerobic filter. Nitrification inhibition was eliminated by either addition of powdered activated carbon to the aeration basin or by the periodic replacement of a portion of the granular activated carbon in the anaerobic filter.

Batch inhibition studies indicated that substituted pyridines (picolines) were inhibitory to the anaerobic system. Inhibition of the nitrification system was attributed to the increase in effluent cresol concentrations from the anaerobic filter as the adsorption capacity of the granular activated carbon was exceeded.

Carbon adsorption-solvent regeneration studies on pure compounds (hydantoin and substituted hydantoins), and on solvent extracted-ammonia stripped coal gasifier effluents indicated that the limited adsorption capacity for the hydantoins coupled with incomplete regeneration of the exhausted carbon would limit the utility of this method as a treatment process for the removal of organic carbon from pretreated coal gasification effluent.

APPENDIX A

TREATMENT SYSTEMS

TREATMENT SYSTEMS

The systems used in the treatment of coal gasifier effluent and pretreated coal gasifier effluent are described in the following sections with pertinent data for each system.

Two-Stage Anaerobic Reactor System

The two-stage pilot-scale anaerobic filter columns employed in this study (Figure 58) consist of two identical Plexiglas columns, each having a height of 183 cm and an internal diameter of 10 cm. Each of these columns was connected to a 20-cm-long inverted conical base to accommodate the influent. The upper end of the first-stage column was connected to a similar conical effluent section also equipped to allow gas collection while the second-stage column was connected to a 30-cm-long by 15-cm-i.d. expansion chamber to allow for the settling of gas-bound carbon particles. A 13-cm-diam concentric Plexiglas water jacket was placed around each column to maintain constant temperature conditions ($35 \pm 0.5^\circ\text{C}$). The water jackets were connected, in series, to a constant temperature water bath (Lauda model B, Westbury, NY).

The first-stage filter was packed with Raschig rings (0.5-in. nominal size) to a depth of 173 cm, whereas the second-stage fluidized bed column was packed to a depth of 125 cm with 10 x 20 U.S. mesh Filtrasorb 400 granular activated carbon (Calgon Corp., Pittsburgh, PA). A $\frac{1}{2}$ -hp stainless-steel centrifugal pump (Teel Pump, Dayton, OH) was used for recirculation and to fluidize the granular activated carbon to minimize gas entrainment, to provide dilution, and to furnish buffering capacity by recirculating the system effluent at a high rate compared to flow through the system.

Anaerobic Columns in Series

The anaerobic activated carbon columns in series were of identical size and design of those used in the two-stage anaerobic reactor system and are depicted in Figure 59.

Nitrification Reactor

The biological nitrification system used in this study (Figure 60) was a single-stage, completely mixed activated sludge unit which consisted of an aeration basin (18.5-cm internal diameter, 40-cm height, 10.8-L volume) was fed with a variable flow positive displacement pump. Compressed air was controlled by a pressure regulator, metered with a rotameter, and supplied from a diffuser at the bottom of the basin. The clarifier consisted of a plexiglas column (10-cm internal diameter by 80-cm height, 6.6-L volume) with an inverted conical base and a rotating sludge scraper to minimize sludge adhering to the wall of the clarifier or logging the conical bottom. A tubing pump was used for sludge recycle to the aeration basin. Both the tubing pump and scraper were operated intermittently by a timer. The system was operated indoors at ambient temperature (19 to 23°C) for 1 year.

Denitrification Reactor

Suspended growth denitrification of anaerobically treated and nitrified wastewater with cell recycle was performed in a 10-L covered reactor. The reactor was coupled to a small aeration basin which was used to remove nitrogen gas prior to clarification, as presented in Figure 61. Settled solids were recycled to maintain the proper solids retention time. Influent (nitrification effluent and methanol solution) was applied to the

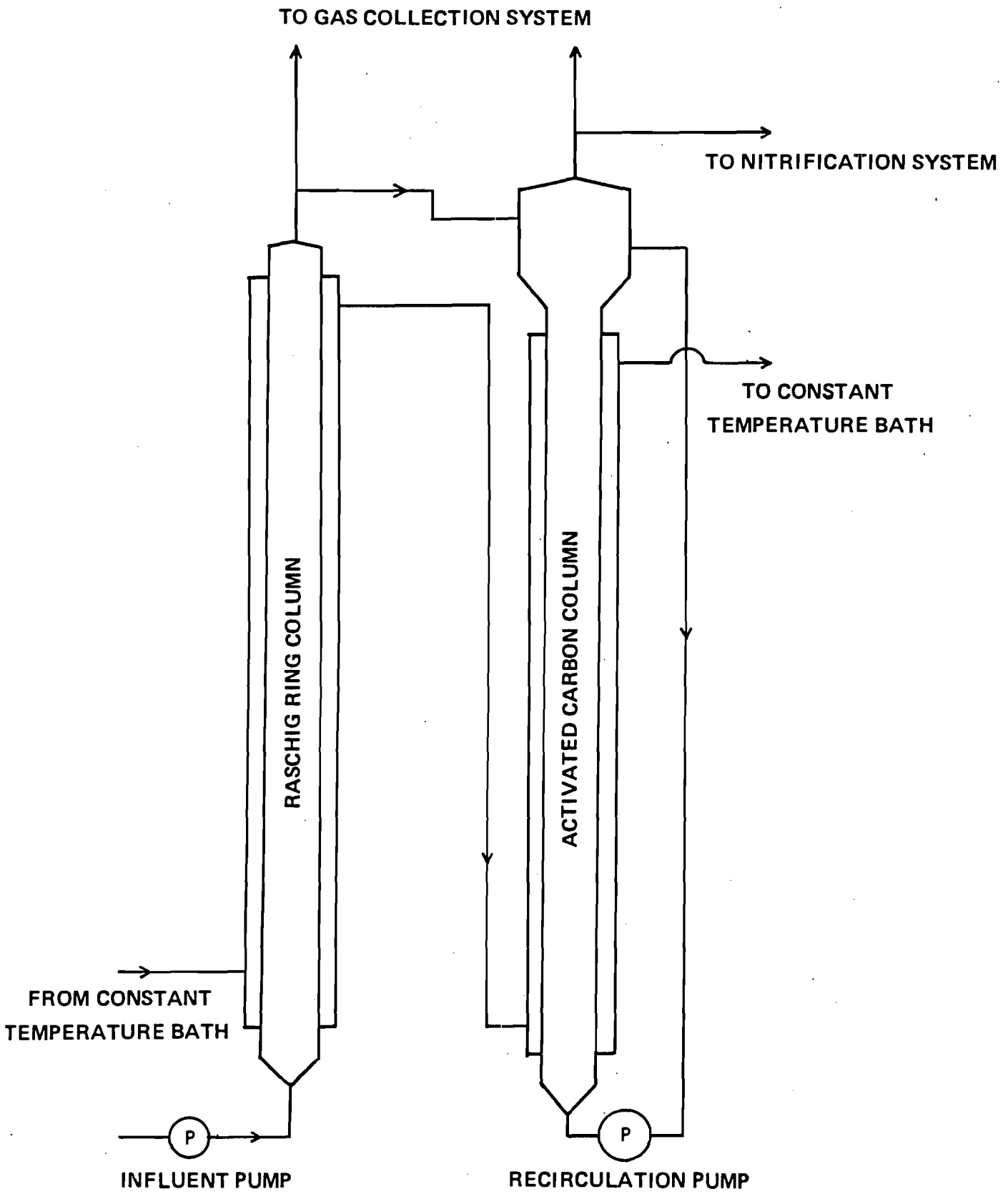


Fig. 58 Two Stage Anaerobic Activated Carbon Filter.

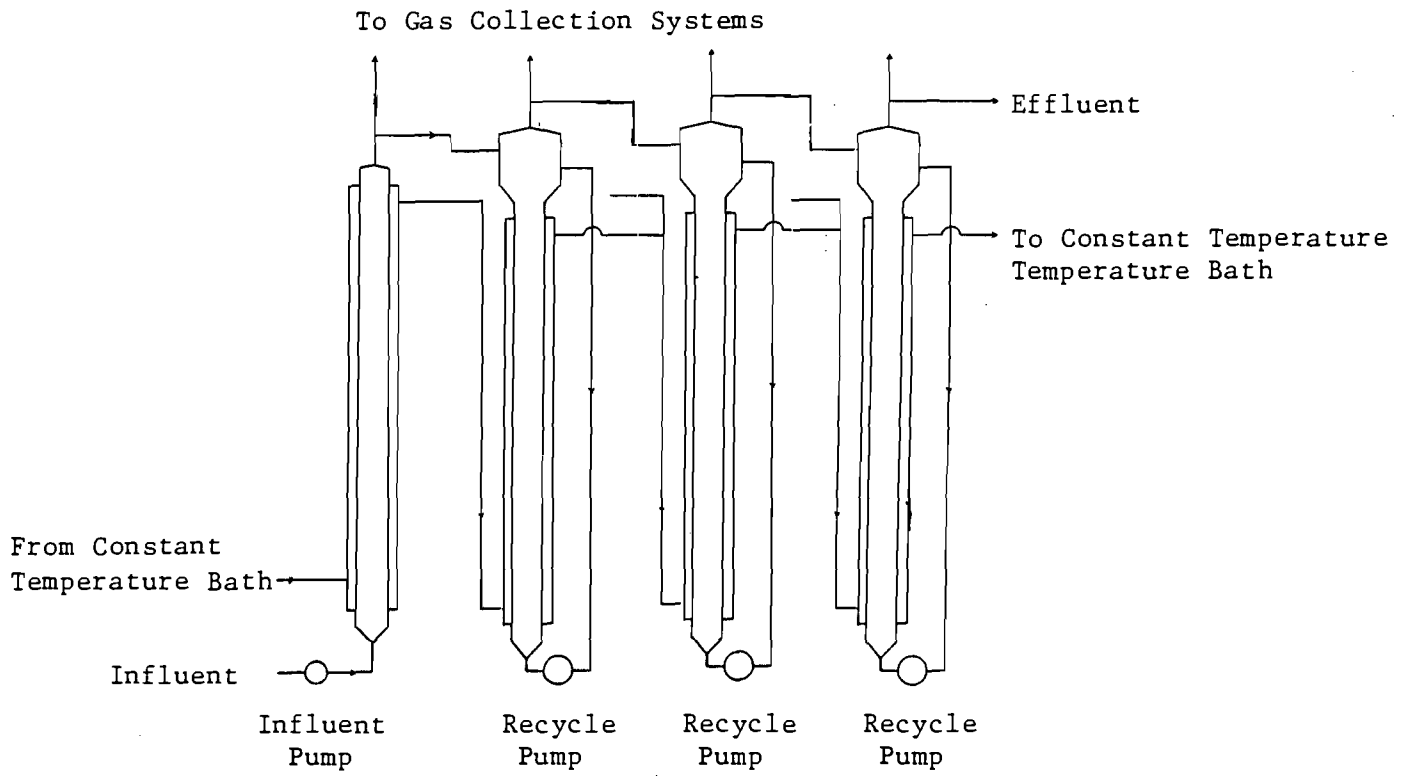


Fig. 59 Anaerobic Activated Carbon Filter in Series.

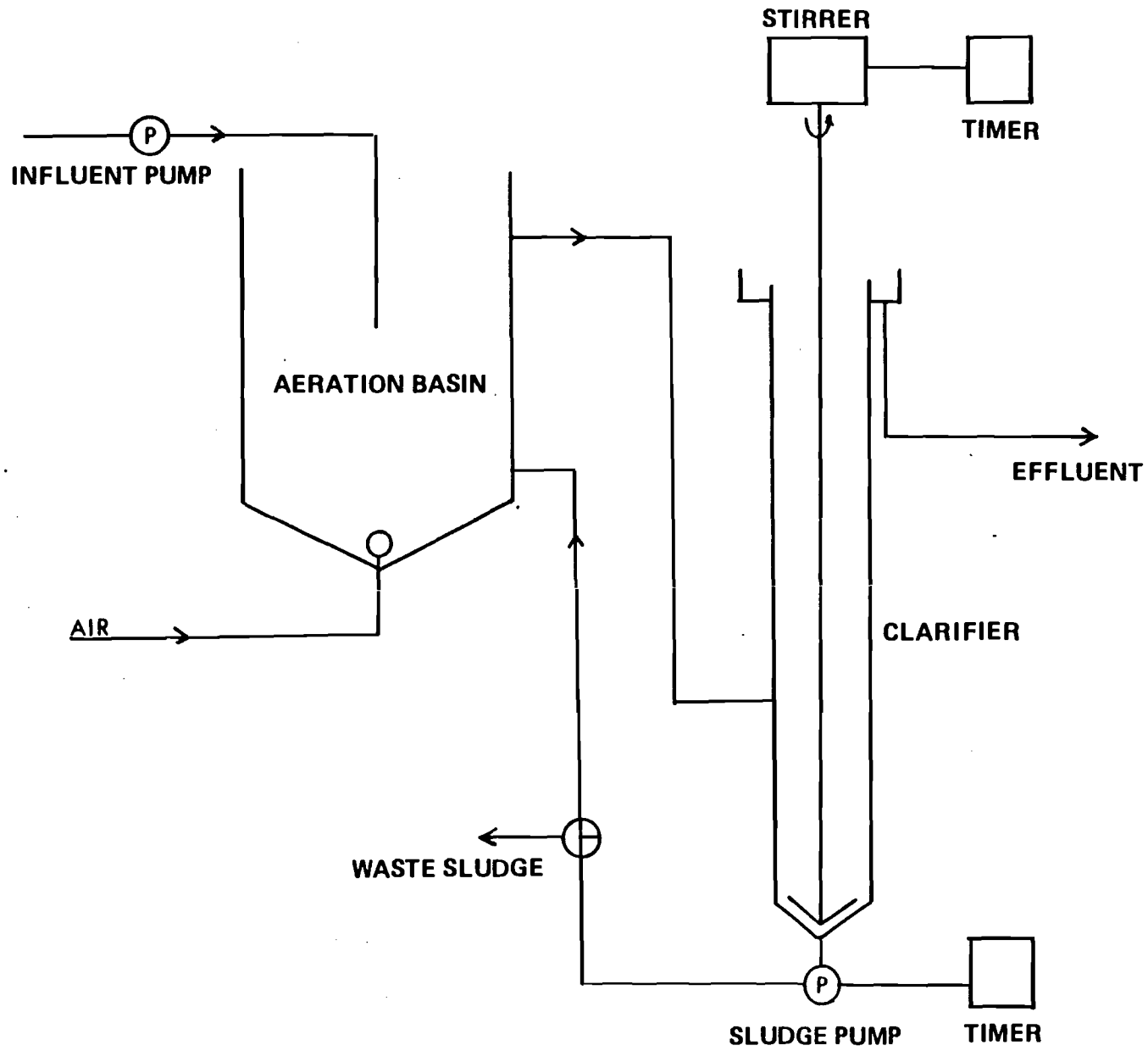


Fig. 60 Biological Nitrification System

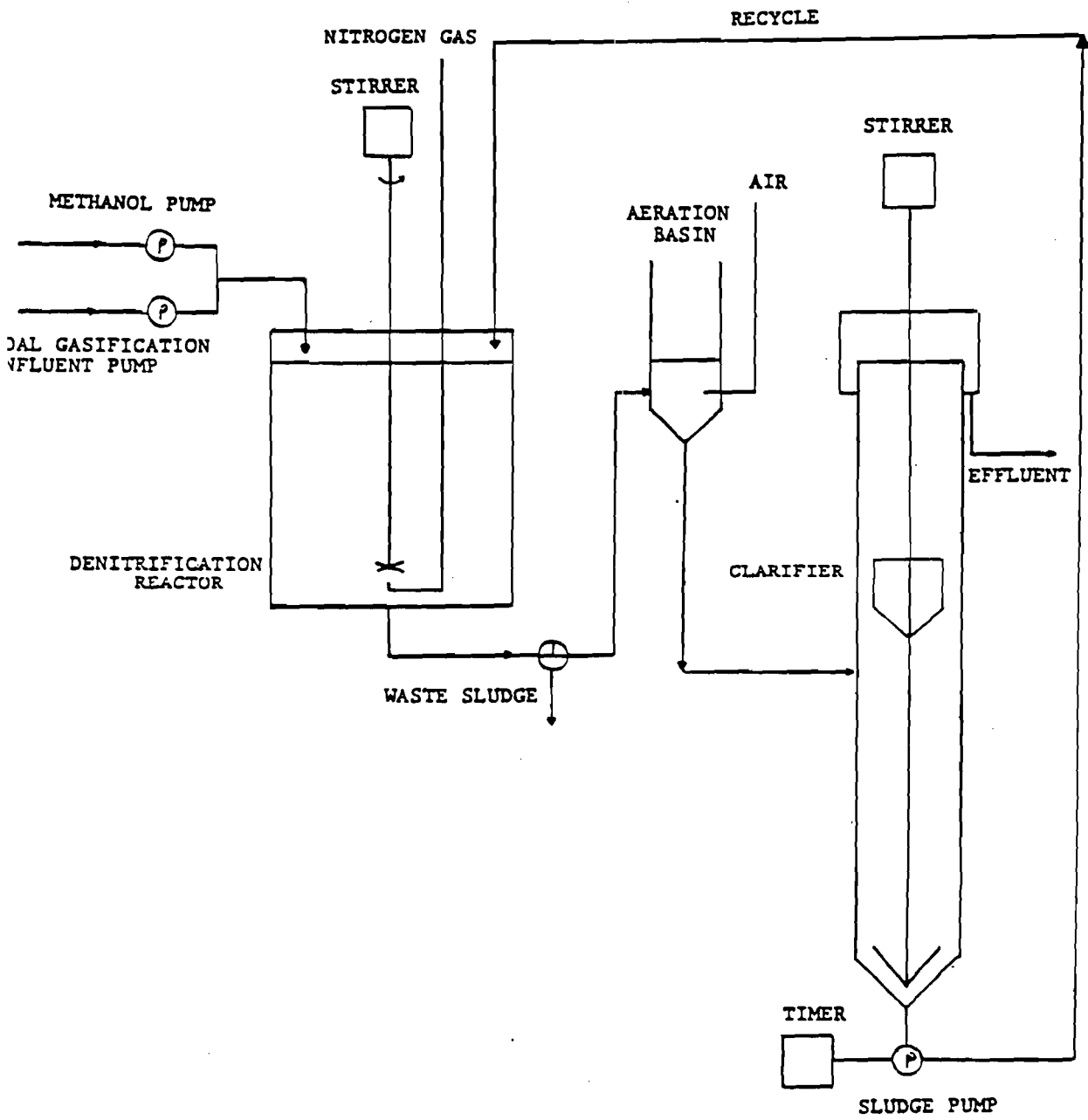


Fig. 61 Biological Denitrification System.

denitrification reactor from two reservoirs equipped with variable-speed, positive-displacement pumps (Fluid Metering, Inc., Oyster Bay, NY). An airtight cylindrical acrylic reactor served as the denitrification chamber (dimensions are given in Table 23). The reactor was equipped with a variable speed stirrer, which was continuously operated at 2500-3000 rpm. Nitrogen gas was supplied at a rate of 80-109 mL/min to strip oxygen from the influent and to exclude air from the reactor. The effluent from the denitrification reactor was fed into an aeration basin (see dimensions in Table 23). Pressurized air was introduced into the aeration basin through an air diffuser at a rate of 120-160 mL/min. The effluent from this unit then flowed to the clarifier (see dimensions in Table 23). The clarifier had an inverted conical base and settled solids were recycled using a peristaltic tubing pump (Cole Parmer, Chicago, IL). The pump was controlled to recycle solids at a rate of approximately 100 mL/min for three minutes at fifteen-minute intervals resulting in a recycle ratio of 2.9. The clarifier was equipped with two wall scrapers. One was located 37 cm from the top of the clarifier and the second one was at the bottom of the clarifier. In addition, the stirrer was connected to a motor speed controller (Bodine Electric Co., Chicago, IL) and was rotated at a rate of 1 rpm to minimize the quantity of sludge adhering to the walls of the clarifiers or bridging in the conical bottom.

Overall Treatment System

Figure 62 is a schematic diagram for the overall biological treatment system utilized in the study for treating UNDERC effluent.

Inhibition Studies

Batch inhibition studies were carried out in 125 mL serum bottles using a modified Hungate technique. The bottles were flushed with a carbon dioxide-nitrogen mixture (30% CO₂, 70% N₂) prior to and during filling and inoculation.

Adsorption-Regeneration Studies

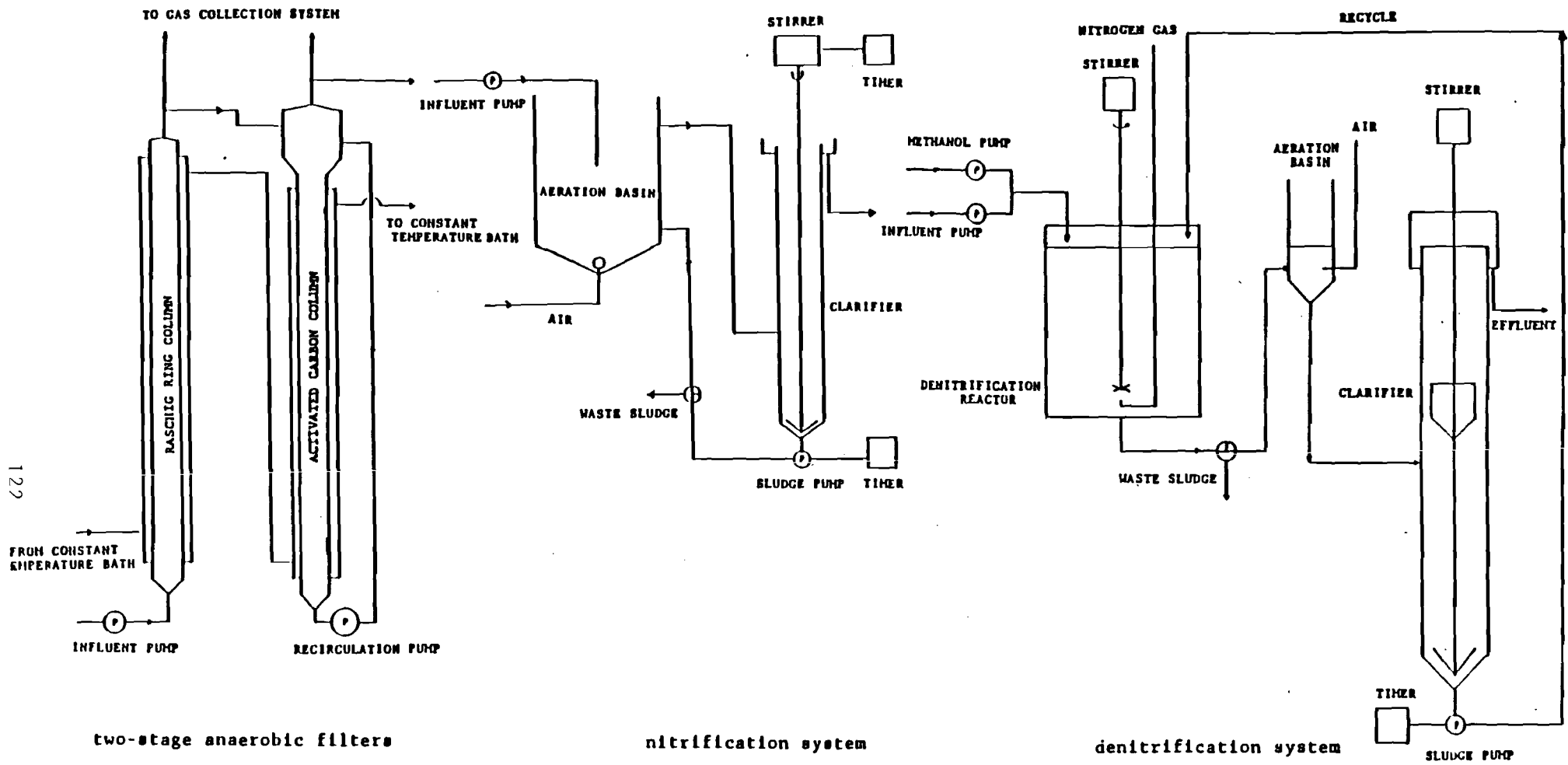
Glass columns (Figure 63) (2.5-cm i.d. x 30-cm long) equipped with a positive displacement pump and operated in a upflow mode were used for the adsorption-regeneration cycle studies. Two reservoirs were coupled to the pump via a 3-way stopcock in order to switch from wastewater to regenerant and vice versa without having to shut down the system or interrupt flow through the column.

An automatic time-operated fraction collector was used to obtain samples for analysis.

Table 23. Dimensions of the Denitrification Reactor System

Reactor System	Internal Diameter cm	Height cm	Total Volume L	Liquid Volume L	HRT* Hours
Denitrification Reactor	20	38	11.9	10	24
Aeration Basin	6.2	30.5	1.0	0.25	0.5
Clarifier	11.0	100	10.2	10.2	24

*At flow of 10 L/d



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Fig. 62 Overall Processes Used to Treat Coal Gasification Effluent.

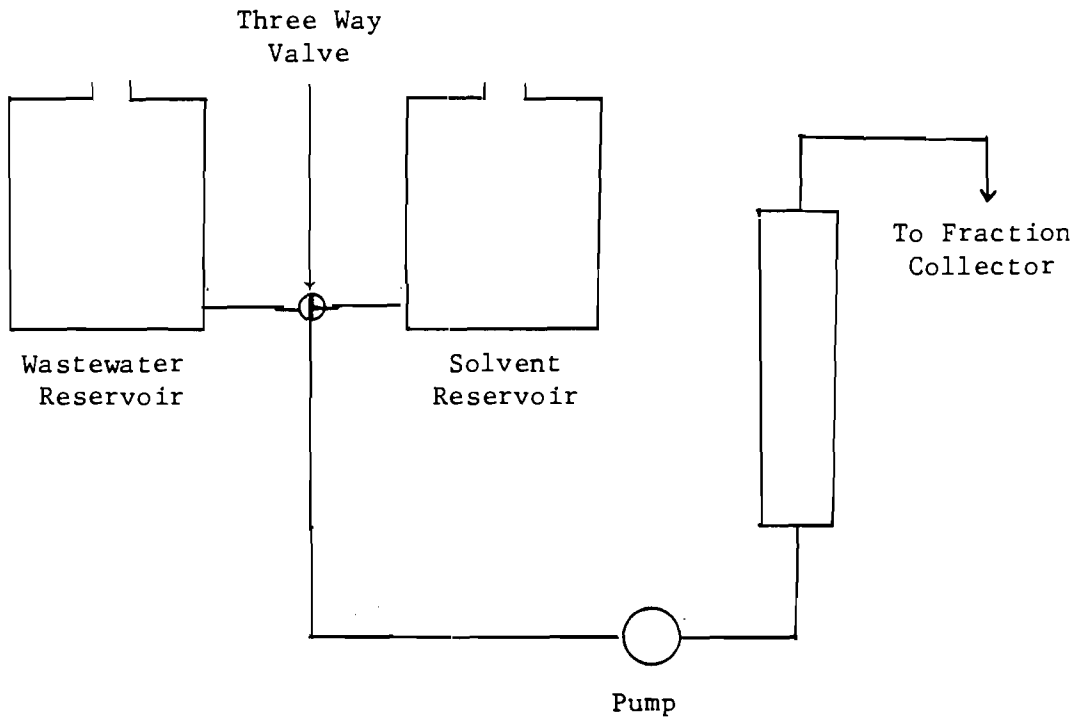


Fig. 63 Carbon Adsorption - Solvent Regeneration System.

APPENDIX B
ANALYTICAL METHODS

PARAMETER	METHOD
pH	potentiometric, Standard Methods ³⁵ 423
Alkalinity	Standard Methods 403, endpoint pH = 3.5
ORP	potentiometric, platinum electrode
CN ⁻	Standard Methods 412E
NH ₃ -N	Standard Methods 417G
TKN-N	acid digestion (H ₂ SO ₄ -HClO ₄) followed by Standard Methods 417G
PO ₄ ⁻³ -P	Standard Methods 424G
Suspended solids	Standard Methods 209C
Volatile solids	Standard Methods 209D
Total organic carbon	Standard Methods 505A
Chemical oxygen demand	Standard Methods 508A
NO ₂ ⁻ -N	Standard Methods 419
NO ₃ ⁻ -N	Standard Methods 414D
Metals	HNO ₃ , H ₂ O ₂ oxidation followed by atomic absorption analysis
Phenol, cresols	gas chromatography, 1.8-m long glass column, 2-mm i.d., packed with 0.1% SP-10000 on 80/100 mesh Carbopack C (Supelco, Inc.). 195°C, nitrogen carrier at 20 mL/min, direct aqueous injection, internal standard benzyl alcohol, FID
Volatile acids	gas chromatography, 1.2-m long glass column, 2-mm i.d., packed with 3.0% Carbowax 20 M, 0.5% H ₃ PO ₄ on 60/80 mesh Carbopack B (Supelco, Inc.). Temperature program 100°C for 2 min to 150°C at 4°C/min and hold for 15 min. Nitrogen carrier 20 mL/min, direct aqueous injection, internal standard 1-butanol or 2-propanol, FID.
Gas composition	gas chromatography, 75-cm long aluminum column, 0.64-cm i.d., packed with 30% DEHS on 60/80 mesh ColumnPak (Fisher Scientific Co.) followed by a 1.8-m long aluminum column 0.48-cm i.d. packed with 60/80 mesh 5A Molecular Sieve (Fisher Scientific Co.) 25°C, Helium carrier 80 mL/min, TCD.

Hydantoins, individual pure solutions	UV/VIS spectroscopy and/or TOC hydantoin, λ_{\max} 193 nm; 5-ethyl-5-methyl hydantoin, λ_{\max} 193 nm; 5,5-dimethylhydantoin, λ_{\max} 198 nm.
Mixtures of hydantoins	gas chromatography, 1.8-m long glass column, 2-mm i.d., packed with 3% AT-1000 on 100/120 mesh Chromosorb W-HP (Alltech Assoc.) 225°C, nitrogen carrier 40 mL/min, FID; calibration curve.
Other organic constituents	solvent extraction and concentration followed by gas chromatographic separation using mass spectrometry for identification.

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