OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT INITIATION

Date: 8/8/77

Project Title: "Treatment of Phenolic Waste Water with Anaerobic-Activated Carbon Filters."

Project No: E-20-618

Project Director: M. T. Suidan

Sponsor: U. S. Energy Research and Development Administration

Agreement Period: From 9/1/77 Until 8/31/79

Type Agreement: Grant No. EF-77-G-01-2756

Amount: $37,800 ERDA Funds
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Sponsor Contact Person (s):

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Defense Priority Rating: N/A

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CA-3 (3/76)

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

Date: December 21, 1979

Project Title: Treatment of Phenolic Waste Water with Anaerobic-Activated Carbon Filters

Project No: E-20-618

Project Director: Dr. M. T. Suidan

Sponsor: U. S. Department of Energy

Effective Termination Date: 8/31/79

Clearance of Accounting Charges: 8/31/79

Grant/Contract Closeout Actions Remaining:

- X Final Invoice and Closing Documents
- X Final Fiscal Report
- X Final Report of Inventions
- X Govt. Property Inventory & Related Certificate
- _ Classified Material Certificate
- _ Other _____

Assigned to: Civil Engineering (School/Laboratory)

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CA–4 (1/79)

School of Civil Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

TREATMENT OF PHENOLIC WASTEWATER WITH ANAEROBIC ACTIVATED CARBON FILTER

First Annual Progress Report
for the Period

Sept. 1, 1977-Aug. 31, 1978

M. T. SUIDAN, W. H. CROSS, and K. A. KHAN

Prepared for
University Programs

U.S. Energy Research and Development Administration
Washington, D.C. 20545

INTRODUCTION

Phenolic compounds account for a major fraction of the organic compounds that are typically present in the liquid wastewaters emanating from the power generation industry[1,2]. Such wastewaters have conventionally been treated by aerobic biological treatment processes, particularly the extended aeration activated sludge process. Such treatment systems are very energy intensive as they have been typically operated at hydraulic detention times in the aeration chamber in excess of four days[2].

The present study involves the development of the technology for a new process designed for the treatment of phenolic wastewaters. This treatment system combines the energy producing anaerobic contact process with granular activated carbon acting as a contact medium. The presence of the granular activated carbon serves as a concentration surface for the adsorbable organic matter as well as an attachment surface for the biological slime layer. This concentration polarization tends to accelerate the biodegradation of the adsorbable organic matter. The activated carbon will also provide a buffer to accommodate shock loads of adsorbable refractory organic matter as well as providing food for the biological population, through the desorbtion of the adsorbed organic matter, during low flow or shut down conditions. The stability of the process is also increased in such a treatment system because the activated carbon tends to even out the composition and strength of the incoming wastewater through a combination of adsorbtion and desorbtion of organic matter.

Because of the anaerobic environment within the filter, the capacity of the activated carbon for adsorbing organic matter will not be reduced with time because the final products (methane and carbon dioxide) as well as the intermediates (low molecular weight volatile fatty acids and alcohols) of the anaerobic degradation process will not adsorb on the carbon surface under the conditions within the reactor. Because of this, the process in study will provide a very stable system for the treatment of such wastewaters.

A number of investigators have studied the anaerobic degradation of some aromatic compounds in small batch cultures. Tarvin and Buswell[3] were the first to report on the anaerobic degradation of aromatic compounds by methanogenic bacteria. They observed the complete breakdown and gasification of benzoic, phenylacetic, hydrocinnamic and cinnamic acids. The intermediates were analysed as the lower fatty acids while the final products were carbon

dioxide, methane, and protoplasm. Some decomposition of o-phthalic, salicyclic acid and phenol were noted. Benzyl alcohol was also slightly attacked whereas benzaldehyde, benzene, bromobenzene, toluene and aniline were not. Clark and Fina[4] and Stadtman and Baker[4] conducted further studies on the anaerobic degradation of benzoic acid in batch cultures and the conclusion of their work could be summarized as a demonstration of the ability of methanogenic bacteria to degrade some aromatic compounds and utilize them for both a carbon source as well as an energy source. They concluded that long acclimation periods were required prior to the production of carbon dioxide and methane. Fina and Fiskin[5], Clark and Fina[4] and Roberts[6] studied the intermediates of the breakdown of some aromatic compounds and postulated, on the basis of some tracer studies, mechanistic pathways for the anaerobic breakdown of benzoic acid.

Healy and Young[7] found support for a reductive pathway during batch anaerobic degradation studies conducted on phenol and catechol. Acclimation periods of 16 and 27 days were required for the degradation of phenol and catechol, respectively.

Recent toxicity investigations by Chou et al.[8] resulted in high levels of degradation for many compounds after prolonged acclimation periods of several months in continuous flow anaerobic filters. Among the large number of petrochemicals acclimated were catechol, resorcinol and nitrobenzene.

SCOPE OF WORK

The scope of work of the present research is to study the degradation of phenol and glucose in a continuous flow anaerobic filter containing activated carbon as a contact medium. The treatability of each substrate is to be studied separately in the first stage of the study while in the second stage of the experimental work, the biodegradability of the two organic compounds will be studied simultaneously in the same reactor. The objectives behind the selection of the two compounds is to study the response of the system to two very different types of organic substrates; phenol being adsorbable and somewhat refractory in nature while glucose is readily biodegradable and non-adsorbable.

EXPERIMENTAL MATERIALS AND METHODS

Experimental Apparatus

The experimental apparatus consists of two sets of anaerobic filter

columns and one completely mixed closed batch reactor. Figure 1 gives an overview of the three experimental units. Each unit of the anaerobic filters contains four columns and three clarifiers (see Figures 2 and 3). The clarifiers are located after each of the first three columns and the four columns and three clarifiers are connected in series. Each column is 24" long and 2" in internal diameter. Each column has a 3½" internal diameter water jacket. In order to maintain a constant and uniform temperature throughout the experimental apparatus, water from a constant temperature bath (see Figure 1) is circulated at a high flow rate through the water jackets of the columns. Each set of columns is equipped with a multiple head tubing pump (Cole-Palmer Model 7567) (see Figure 3). The function of this pump is to recirculate the liquid contents around each column individually. The top of every column is connected to a gas buret in order to monitor the gas production from each column.

The internal weir structure of the clarifiers is 4½" long and 2" in internal diameter. The clarifiers serve to remove the excess biomass and provide a separation between liquid and gas phases of each individual column (see Figure 4).

The closed batch reactor (Figure 5) is constructed of a 7¼" internal diameter Plexiglas column and is 17¼" in height. This reactor is filled to a liquid volume of 10 liters and is well mixed with a Gerald Kheller mixer (Gerald Kheller Co., Las Vegas, Neveda). The mixing rod is introduced through the top cover of the reactor through an oil seal. The batch reactor is air tight and is connected to a gas buret to provide a means for monitoring gas production. The temperature of the liquid contents of the batch reactor is controlled by wrapping a heating tape around the reactor. This heating tape is connected to a temperature controller (Thermistemp Model 63). The Plexiglas and the heating tape are separated by a layer of asbestos cloth which serves to protect the wall of the reactor from excessive temperature gradients.

Granular Activated Carbon Substrates

The activated carbon used in this study is bituminous base Filtrasorb 400 (Calgon Corporation, Pittsburgh, PA). The activated carbon was prepared by sieving into a number of particle size fractions. The individual fractions were then washed with distilled water to eliminate fines. These fractions were subsequently dried at 105°-110°C. The specific characteristics of the

FIGURE 1

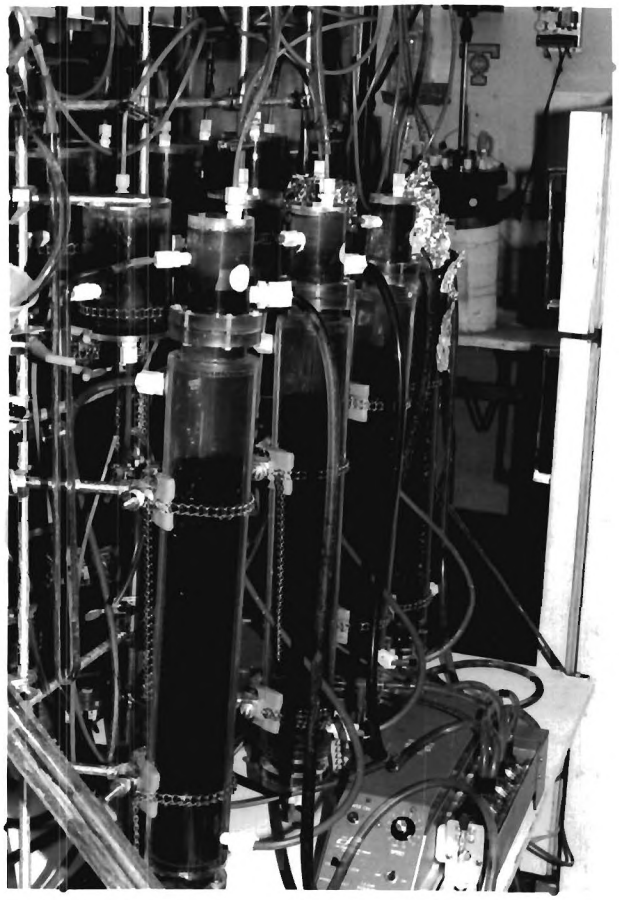


FIGURE 2

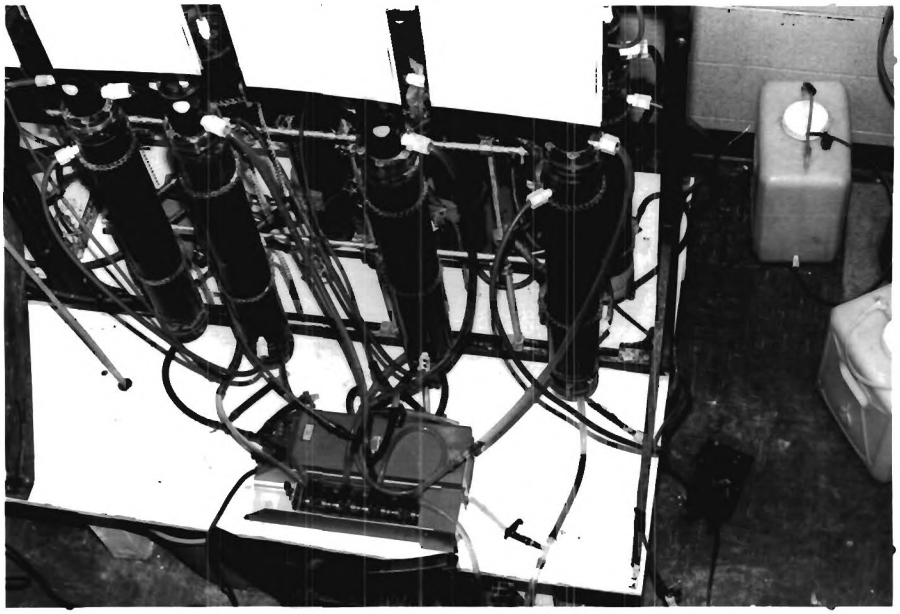


FIGURE 3

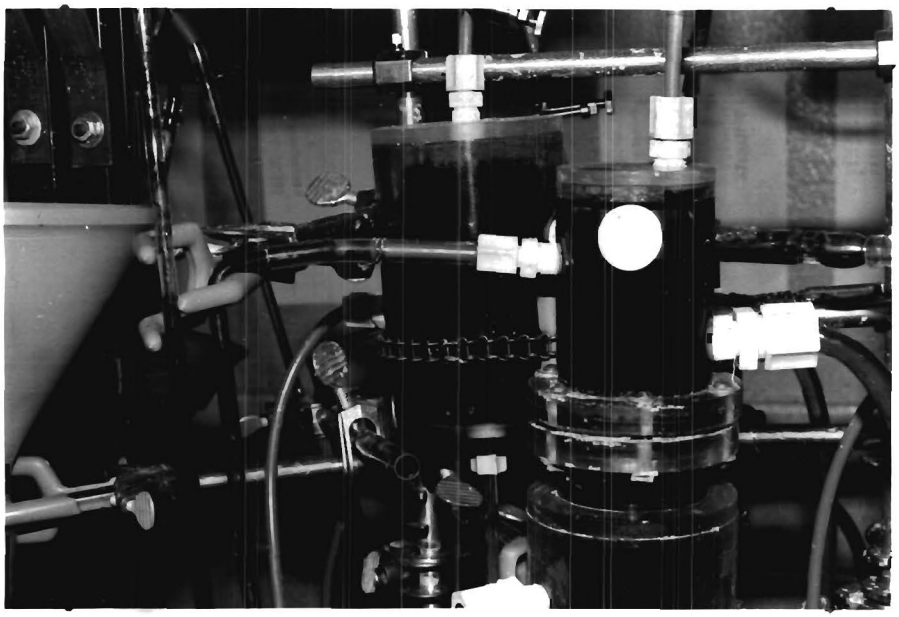


FIGURE 4

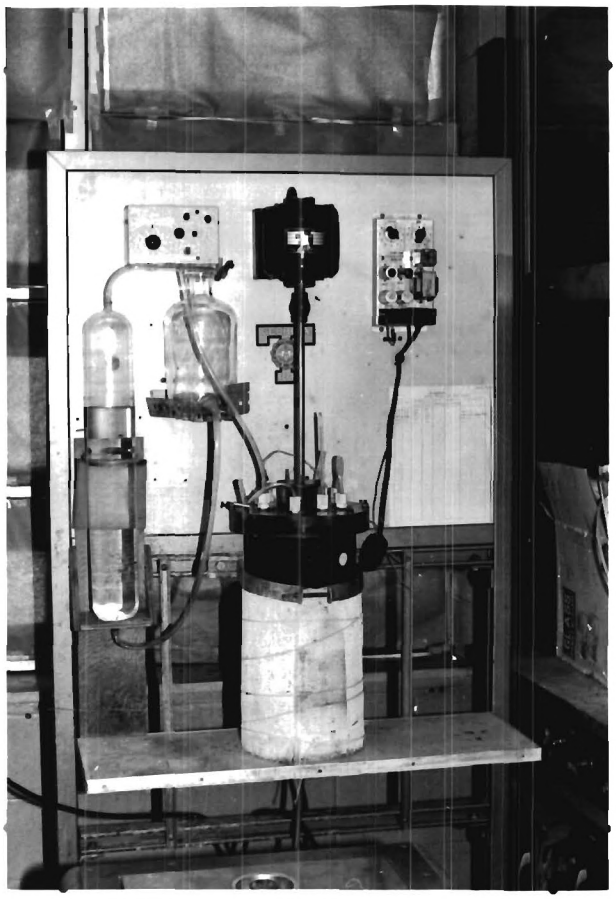


FIGURE 5

carbon are given in the manufacturer's bulletin (Calgon Corporation, 1969).

The anaerobic filters were charged with 446.6 grams of carbon per column. Only the size fraction falling within the 10 x 20 U.S. Standard Mesh size were used in this study. The selection of this particular size range was based primarily on the fact that this range is large enough in particle size to avoid serious clogging problems with the perforated plates used to retain the carbon within an individual column. This size range constitutes the major fraction by weight, 74%, of the commercial carbon Filtrasorb 400. The make up of the carbon used in the study is:

18 x 20 U.S. Mesh	16%
16 x 18 U.S. Mesh	27%
10 x 16 U.S. Mesh	57%

The synthetic substrates are prepared by the following procedure.

Trace Salt Solution

The trace salts and the complexing agent, sodium citrate, are prepared in a solution 240 times their strength in the diluted substrate. The salts are added to distilled water in the quantities given in Table I and made to two liters with distilled water.

Salt Solution

One liter of a stock salt solution is prepared by adding salts to distilled water in the quantities given in Table II.

Phosphate Buffer

A 1.5 molar stock phosphate buffer solution is prepared by adding a mixture of monobasic and dibasic sodium and potassium phosphate to distilled water.

Glucose Substrate

The glucose substrate is prepared in 4 liter batches. Each batch is prepared by adding 80 ml of the salt solution, 140 ml of the phosphate buffer solution and 8 grams of glucose; and sufficient distilled water to make the final volume 4 liters. Each batch is purged with nitrogen gas and placed in a refrigerator maintained at 2°C.

Phenol Substrate

The phenol substrate is prepared in 4 liter batches. Each batch is prepared by adding 20 ml of the salt solution, 60 ml of the phosphate buffer solution and 0.80 grams of phenol; and sufficient distilled water to make

Table I

Trace Salt Solution[9]

Compound	Mass, grams
$FeCl_3$	38.88
$MnCl_2 \cdot 4H_2O$	9.48
$ZnCl_2$	6.54
$CuCl_2 \cdot 2H_2O$	4.10
$CuCl_2 \cdot 6H_2O$	5.71
$Na_2B_4O_7 \cdot 10H_2O$	2.29
Na_3 Citrate	353.00
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	4.15

Table II

Salt Solution

Compound	Quantity
KH_2PO_4	13.61 grams
$NaH_2PO_4 \cdot H_2O$	8.28 grams
$(NH_4)_2SO_4$	5.28 grams
NH_4Cl	25.00 grams
$CaCl_2$	4.44 grams
$MgCl_2 \cdot 6H_2O$	8.13 grams
Vitamin Mixture	35.00 ml
Cystein Hydrochloride	5.00 ml
Trace Salt Solution	33.30 ml

the final volume 4 liters. Each batch is purged with nitrogen gas and placed in a refrigerator maintained at 2°C.

Temperature

The temperature of the two anaerobic filter units and the closed batch reactor is maintained at 35°C.

Analysis

The liquid effluent from each of the four columns of each anaerobic filter unit is analysed twice a week. The analyses include:

a. pH
b. Total Inorganic Carbon
c. Total Organic Carbon
d. Chemical Oxygen Demand
e. Volatile Acids
f. Phenol where appropriate

Once steady state is reached additional analysis for a period of two weeks will include:

a. Total Suspended Solids
b. Volatile Suspended Solids
c. Alkalinity
d. Ammonia Nitrogen
e. Total Nitrogen
f. Phosphorus
g. Oxidation Reduction Potential

The volume of the gaseous products from each column are measured daily and corrected for moisture content and converted to standard conditions of temperature and pressure. The gas is also analysed for methane, carbon dioxide, hydrogen, nitrogen and oxygen.

Flow Rate and Detention Time

The flow rate of substrate into each of the two filter units is maintained at 2.88 liters per day by using two Fluid Metering Pumps that are placed in the refrigerator along with the substrate reservoirs. At the stated flow rate, the actual detention time in the columns is 20 hours.

EXPERIMENTAL RESULTS AND DISCUSSION

Closed Batch Reactor for the Degradation of Phenol

The closed batch reactor was started using anaerobically digested sludge obtained from a local sewage treatment plant. Glucose was initially used as a substrate in order to test the viability of the sludge. When the anaerobic activity of the sludge was established as determined by the production of appreciable quantities of methane gas over a number of glucose feed cycles, the system was subjected to a phenol dose of 200 mg/l. Upon the introduction of the phenol, the rate of gas production decreased drastically for an extended period of time. The concentration of phenol was monitored and when it was observed to decrease significantly, more phenol was added in an effort to maintain a solution phenol concentration of between 200-500 mg/l. Between days 71 and 88 of the operation of the batch reactor on phenol as a substrate, (see Figure 6) gas production was decreased to a minimum while the concentration of phenol in the liquid phase decreased to about 100 mg/l. At this point, 200 mg/l of phenol were added to the reactor. This phenol addition resulted in an almost immediate response from the system as manifested in an increase in the gas production rate. Data collected after the period presented in Figure 6 indicates that the batch culture is now fully acclimated to phenol as the only organic carbon substrate and from this time on, the batch reactor will be operated on a phenol cycle that varies between 500 mg/l of phenol as a maximum down to 5 mg/l minimum. Other organic compounds produced as intermediates during this degradation process will also be monitored.

Phenol Fed Anaerobic Activated Carbon Filter

The phenol fed anaerobic filter columns were charged with granular activated carbon and then reducing conditions were established by passing oxygen free water through the columns and purging the column head spaces and the gas burets with nitrogen gas. Each column was later charged with 500 ml of settled anaerobic sludge. The columns were then operated in a down flow batch mode, i.e. no influent flow rate, and were fed a small anount of phenol on a daily basis. This mode of operation continued for sixteen days, at which time the system was set into a continuous flow mode at a flow rate of 5 ml/min with upflow recycle. This mode of operation continued for sixty one days and no consistent gas production was obtained. After that period, the flow rate was reduced to 2 ml/min.

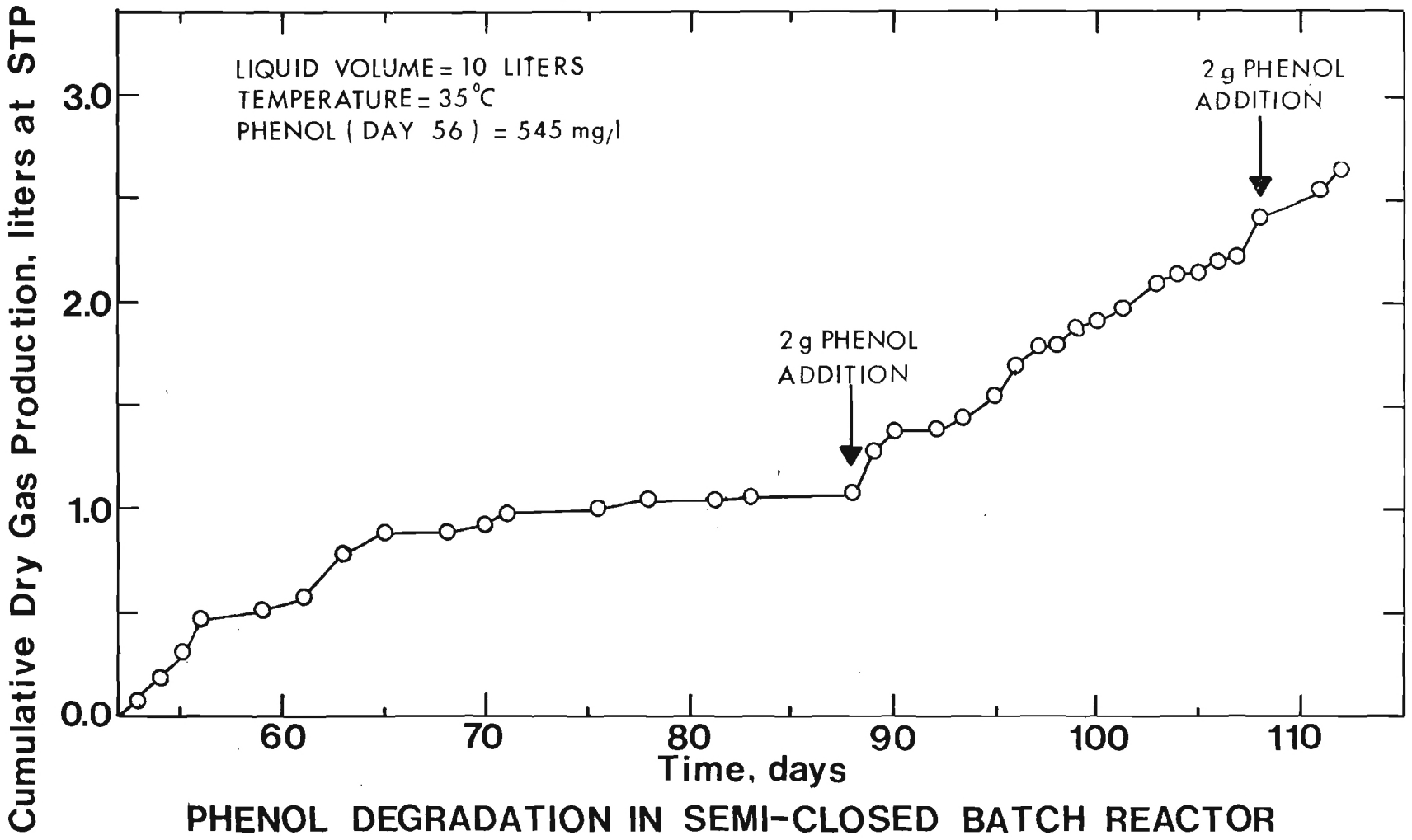

LIQUID VOLUME = 10 LITERS
TEMPERATURE = 35 °C
PHENOL (DAY 56) = 545 mg/l
2 g PHENOL ADDITION
2 g PHENOL ADDITION
Cumulative Dry Gas Production, liters at STP
3.0
2.0
1.0
0.0
60
70
80
90
100
110
Time, days
PHENOL DEGRADATION IN SEMI-CLOSED BATCH REACTOR

FIGURE 6

At present the phenol fed anaerobic filter is operated at 2 ml/min feed flow rate which is equivalent to a detention time of twenty hours. This mode of operation has proven to be very stable and the anaerobic degradation of phenol is occurring at a very rapid rate and is steadily moving towards steady state conditions.

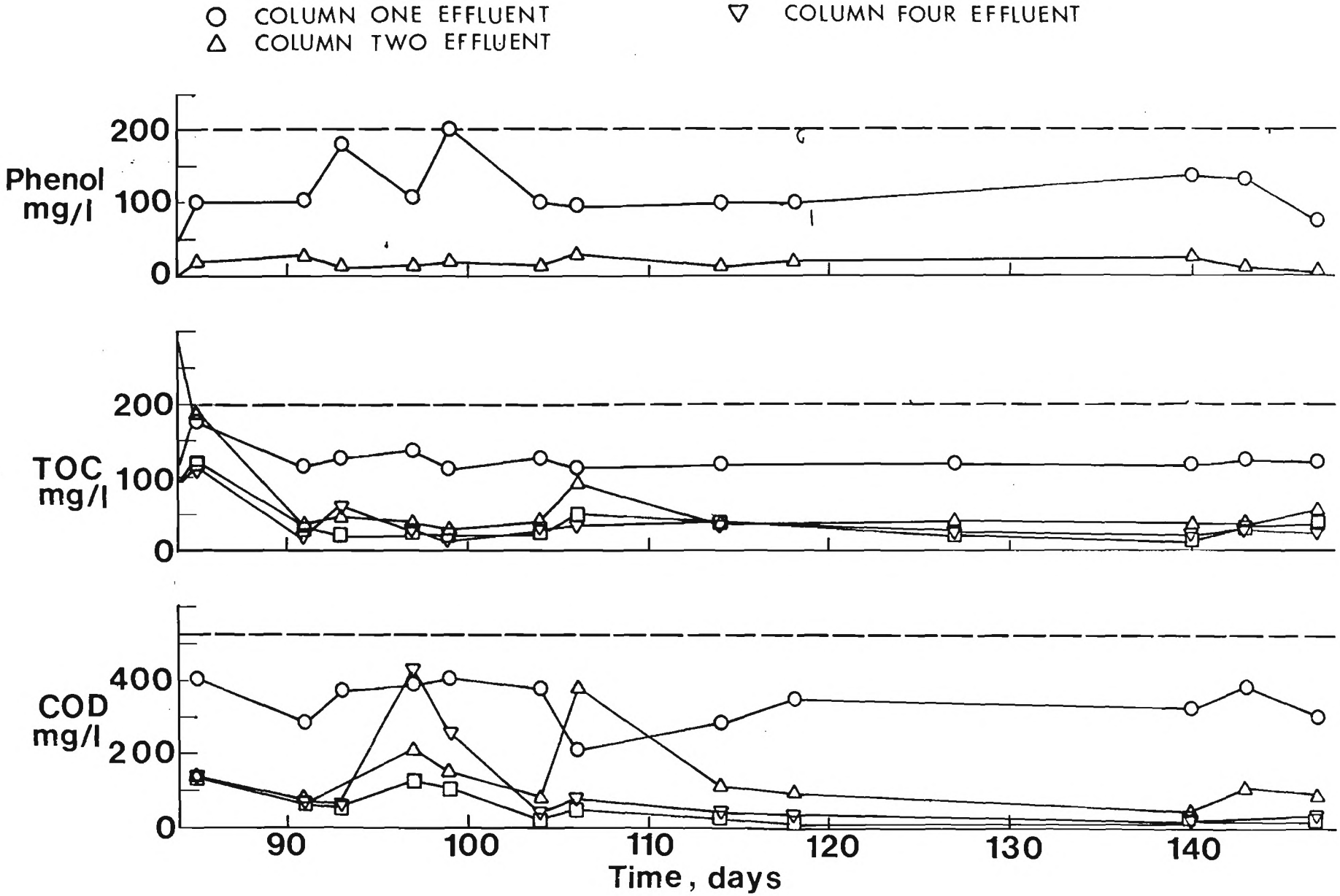
The concentration of phenol in the influent feed has been maintained at 200 mg/l. No measurable phenol concentration has been detected in the effluents from the third and fourth carbon columns while the effluent concentrations from columns one and two have been decreasing steadily, (see Figure 7). The anaerobic filter has also been producing a consistently low effluent TOC and COD.

The cumulative total gas production from the phenol fed anaerobic filter is given in Figure 8. The volume of gas produced has been corrected for moisture content and reduced to standard conditions of temperature and pressure. The total gas daily production rate is averaging around 1094 ml/day, 90.88% of which is methane while the remaining 9.12% is carbon dioxide. If the increase in the total inorganic carbon in the effluent over the level in the influent is included in the gas phase material balance across the filter, then that total daily gas production will increase to 1293 ml/day of which 77% is methane. This high percentage of methane gas is appreciably greater than the 62.4% observed by Healy et al.[11]

The theoretical gas production rate based on the total organic carbon content in the influent minus the organic carbon in the effluent was computed to be only 781 ml/day which is appreciably less than the actually measured amount. However, a detailed analysis of Figure 9 indicates that the additional gas produced could be attributed to the phenol that has already been adsorbed onto the carbon during the period when biological activity was negligible. The data in Figure 9 represent a material balance on the carbon across the anaerobic filter. As is apparent, the filter is doing an excellent job in treating the phenolic wastewater as well as producing large quantities of methane rich gas.

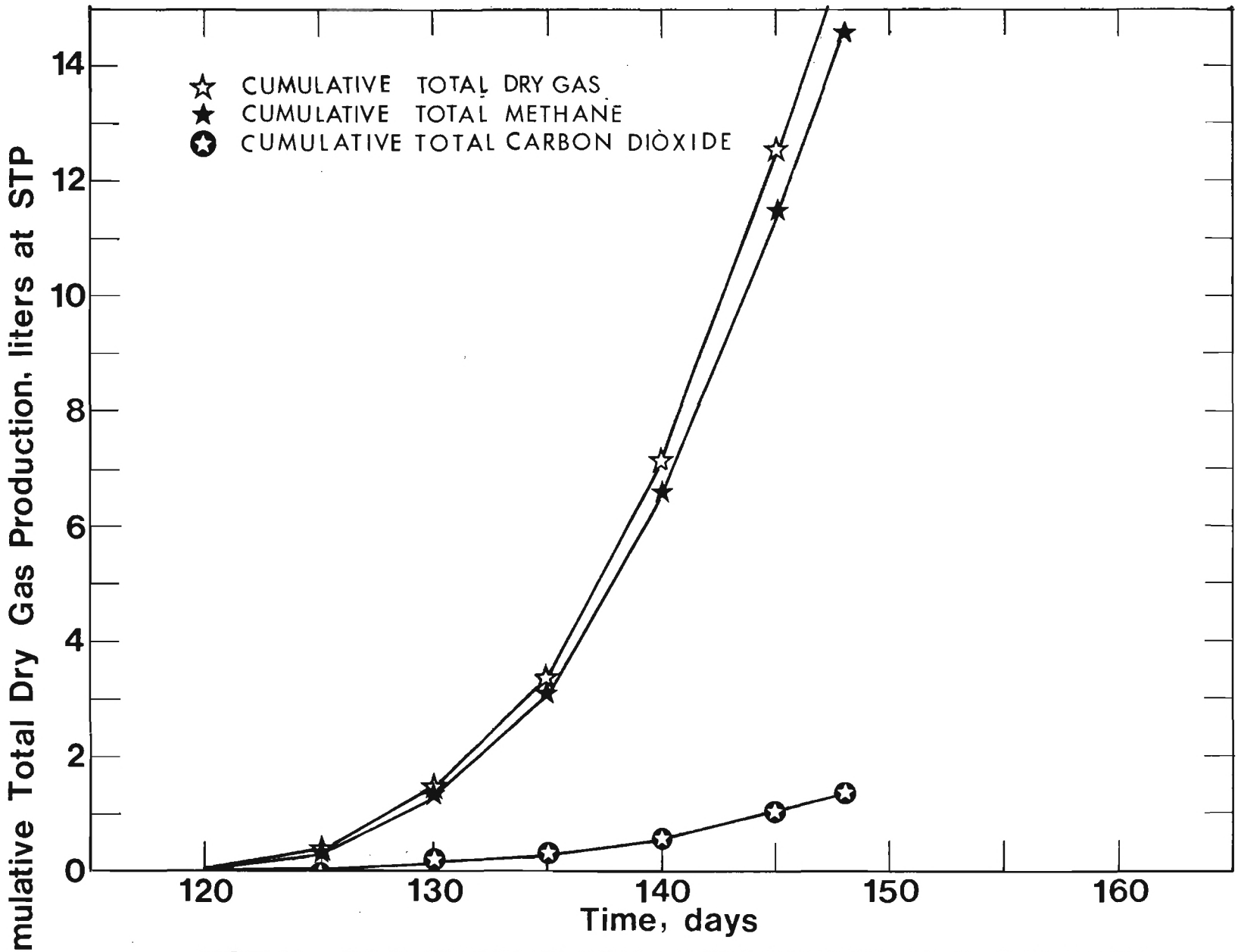
Glucose Fed Anaerobic Activated Carbon Filter

The glucose fed anaerobic filter columns were charged with activated carbon, deoxygenated and seeded in a manner similar to that used for the phenol fed columns. The system was operated at an influent flow rate and glucose concentration of 5 ml/min and 2000 mg/l, respectively, for a period



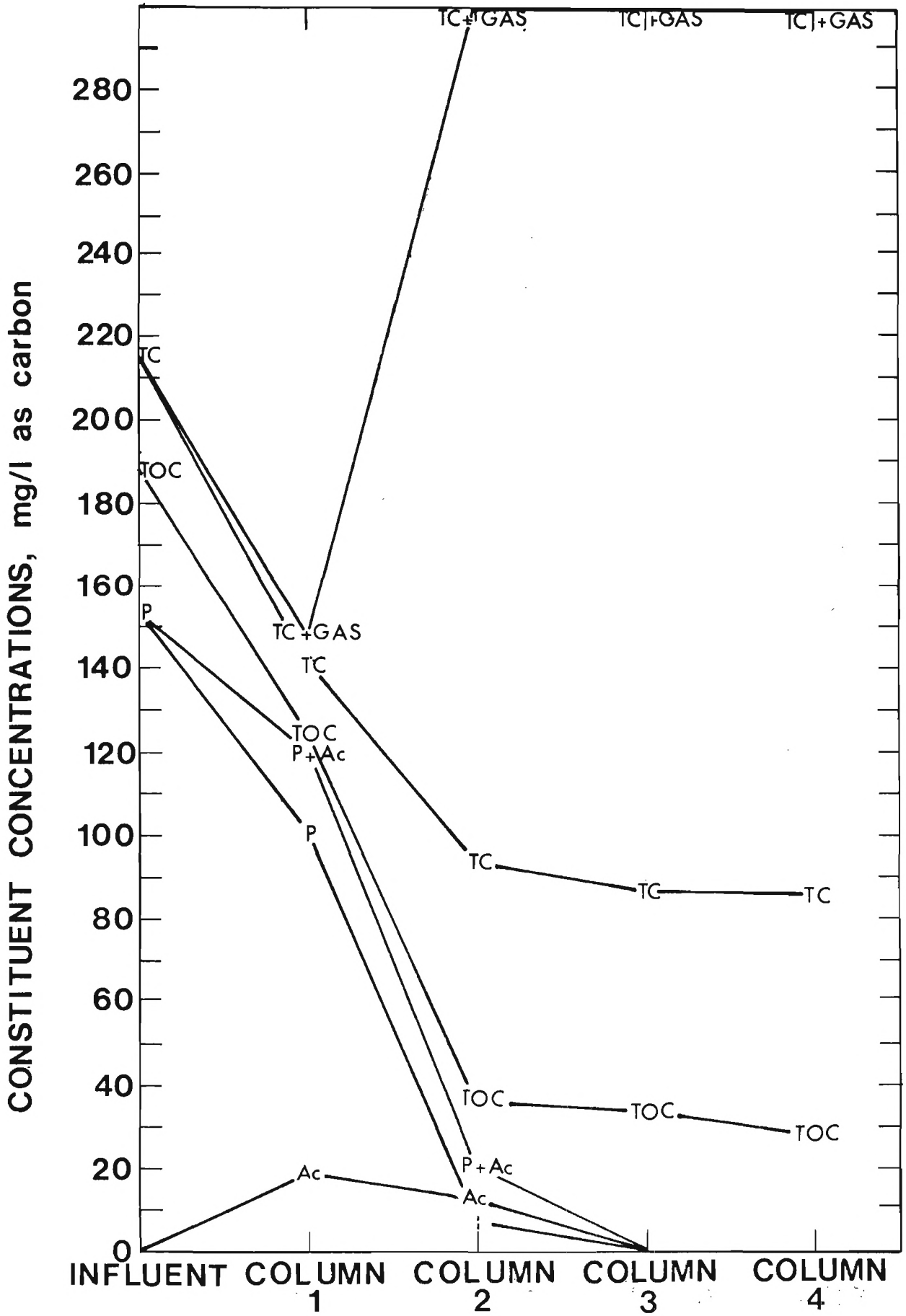
CONSTITUENT CONCENTRATIONS IN INDIVIDUAL COLUMN EFFLUENTS FROM PHENOL FED REACTOR

FIGURE 7



TOTAL GAS PRODUCTION FROM PHENOL FED REACTOR

FIGURE 8

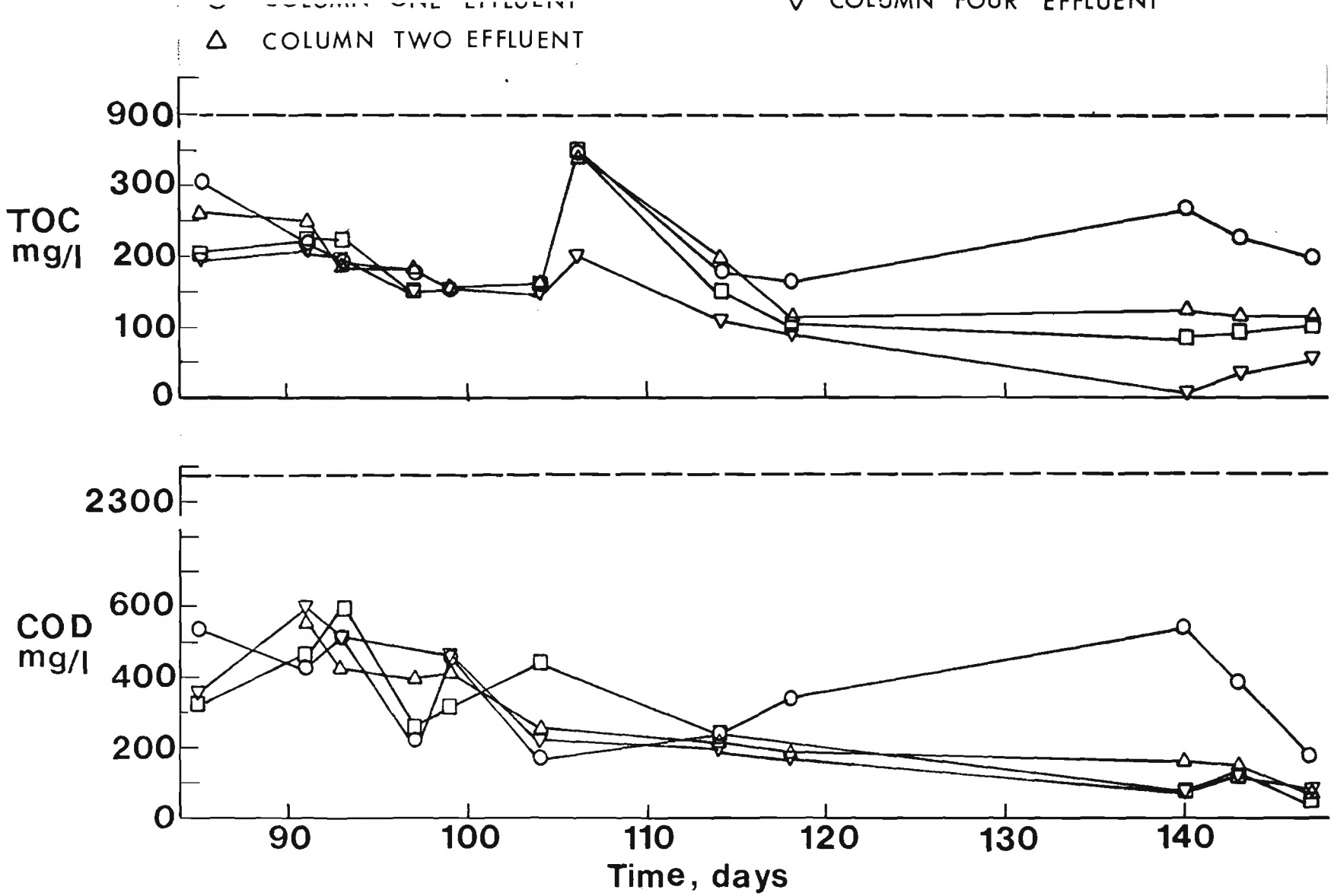


CARBON BALANCE ACROSS PHENOL FED REACTOR

FIGURE 9

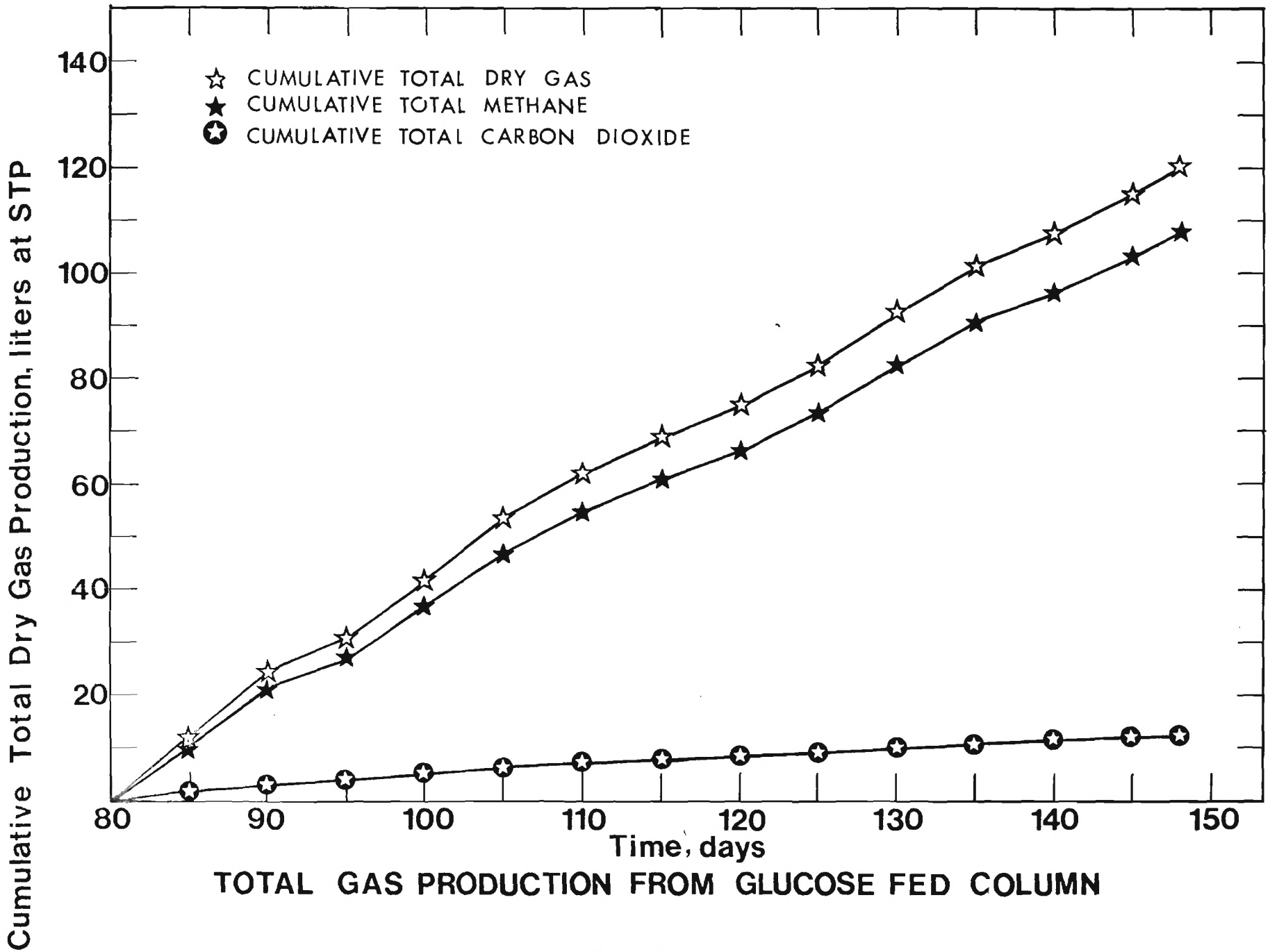
of 66 days at which time the influent flow rate was reduced to 2 ml/min in order to maintain uniformity with the phenol fed columns.

The unit is currently approaching steady state operating conditions as defined by the effluent TOC and COD, and the gas production rate. At present, the organic carbon reduction efficiency is approximately 94% (see Figure 10) while the chemical oxygen demand reduction is averaging around 96%. Both of these removal efficiencies are in excess of what was obtained by Young and McCarty[12] using crushed stone as the contact media in an anaerobic filter. The data in Figure 11 represent the cumulative total dry gas production, total methane and carbon dioxide. The total gas daily production is averaging about 1534 ml/day, 90% of which is methane. If the increase in the total inorganic carbon in the effluent over the influent level is included in the gas phase material balance across the filter, then the total daily gas production will increase to 2640 ml/day of which 53% is methane and 47% is carbon dioxide. This is very close to the even distribution between methane and carbon dioxide that may be predicted based upon the stoichiometry in the Buswell Equation.



CONSTITUENT CONCENTRATION IN INDIVIDUAL COLUMN EFFLUENTS FROM GLUCOSE FED REACTOR

FIGURE 10



TOTAL GAS PRODUCTION FROM GLUCOSE FED COLUMN

FIGURE 11

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ATLANTA, GEORGIA 30332

SCHOOL OF
VIL ENGINEERING

TELEPHONE:
(404) 894-2265

February 21, 1978

Ms. Amy L. Antoine, Grants Officer
Operations, Division of Procurement
U.S. Energy Research and Development Admin.
400 First Street, N. W.
Washington, D. C. 20545

Dear Ms. Antoine:

Enclosed are three copies of a semi-annual progress report on the project entitled "Treatment of Phenolic Wastewater with Anaerobic-Activated Carbon Filters", Grant No. EF-77-G-01-2756. Currently we are almost through with the acclimation phase and are about to initiate continuous flow experimentation. Once some experimental results are available, I would appreciate the opportunity to discuss some of them with your personnel.

Sincerely,

Makram T. Suidan
Assistant Professor of Civil Engineering

Enclosures
MTS:jp

PROGRESS REPORT

Treatment of Phenolic Wastewater with Anaerobic-Activated Carbon Filters

Principal Investigator: Makram T. Suidan
Granting Agency: U.S. Energy Research and Development Administration
Grant Number: EF-77-G-01-2756
Grant Period: From 9/1/77 to 8/31/79

The construction of the experimental apparatus for the project has been completed. The apparatus consists of two sets of units, each unit containing four columns (Figure 1) and three clarifiers (Figure 2). The clarifiers are located after each of the first 3 columns and the four columns and three clarifiers are connected in series (see Figure 3). Each column is 24" long and 2" in internal diameter. Each column has a 3-1/2" internal diameter water jacket (see Figure 1). In order to maintain a constant and uniform temperature throughout the experimental apparatus, water from a constant temperature bath is circulated at a high flow rate through the water jackets of the columns. Each set of columns is equipped with a multiple head tubing pump (Cole-Parmer Model 7567). The function of this pump is to recirculate the reactor liquid contents around each column individually. As such recirculation serves two purposes:

i. To provide a buffering and stabilizing effect on the influent of each column.

ii. To expand the carbon in each unit thus reducing the entrainment of the gaseous products on the carbon.

The feed substrate is introduced into the first column of each set with a low flow precision FMI pump (Fluid Metering, Inc., Oyster Bay, NJ). Flow to the subsequent columns is assured because the whole unit is sealed and was tested to be gas tight.

The head space of every column is connected to a gas buret in order to allow gas collection. The gas produced is monitored for production rate and composition.

The columns were charged with 10 x 20 U.S. Mesh size Fitrasorb 400 activated carbon. Each column was filled to a depth of 19" of carbon. Once the columns were charged with carbon, three tracer studies were conducted using Lithium chloride. The three tracer studies were designed to provide insight into the hydraulic regimes within the reactors and to detect shortcircuiting if any. These studies were conducted as follows:

i. A step input to one column with recirculation around the column.

ii. A step input to one column followed by one clarifier with recirculation around the column.

iii. A step input to a complete unit with recirculation about each column.

The results from the study indicated that each column was very close to being completely mixed.

At present one set of columns is being acclimated to phenol. The columns were initially seeded with an active anaerobic culture from a local treatment plant and phenol is added to each column on a batch basis. Upon acclimation, the unit will be operated in a continuous manner.

The second unit was acclimated to glucose. In this case, however, the acclimation period was much shorter and at present the unit is operating continuously with a feed of 2000 mg/l of glucose and a hydraulic flow rate of 5 ml/minute.

A 10 liter completely mixed anaerobic batch reactor has also been constructed. This reactor is maintained at a constant temperature by wrapping it with a heating tape connected to a temperature controller. At present, this reactor is used to sustain a viable anaerobic culture in order to provide a seed for the reactors in case of system failure.

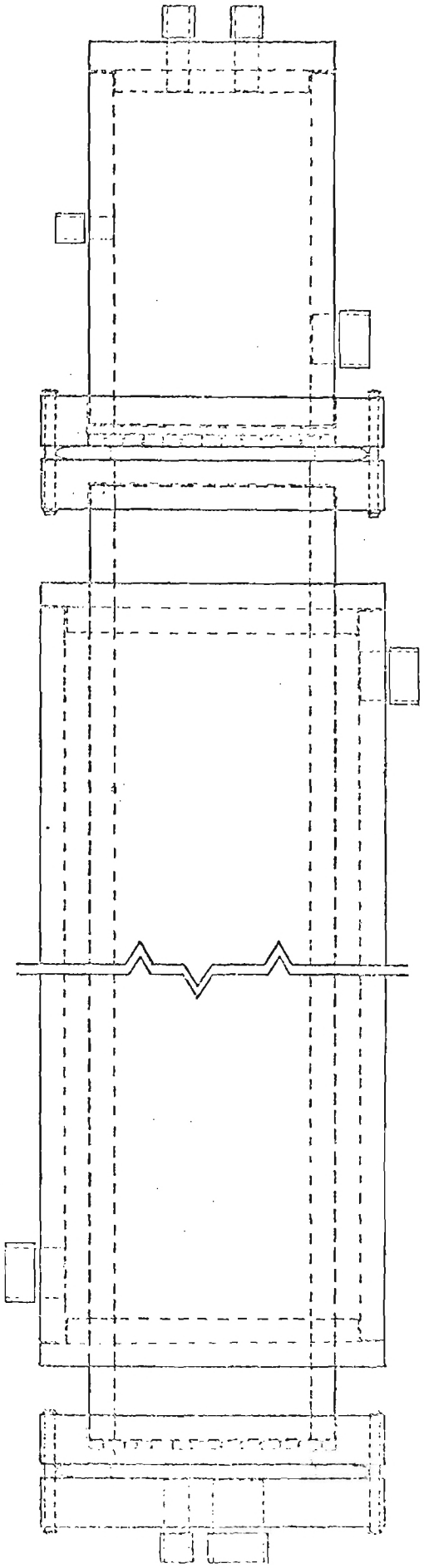

FIGURE 1. COLUMN SCHEMATIC

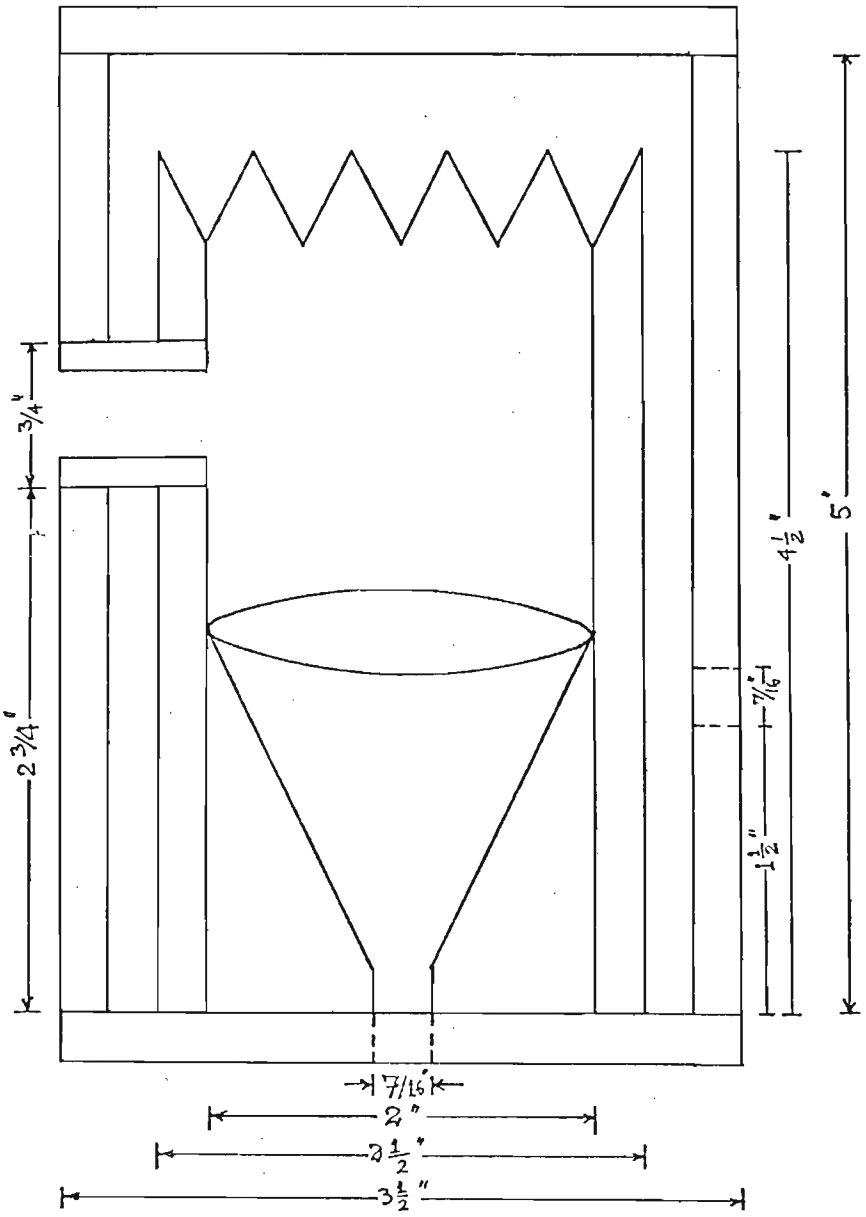

FIGURE 2. SCHEMATIC OF CLARIFIER

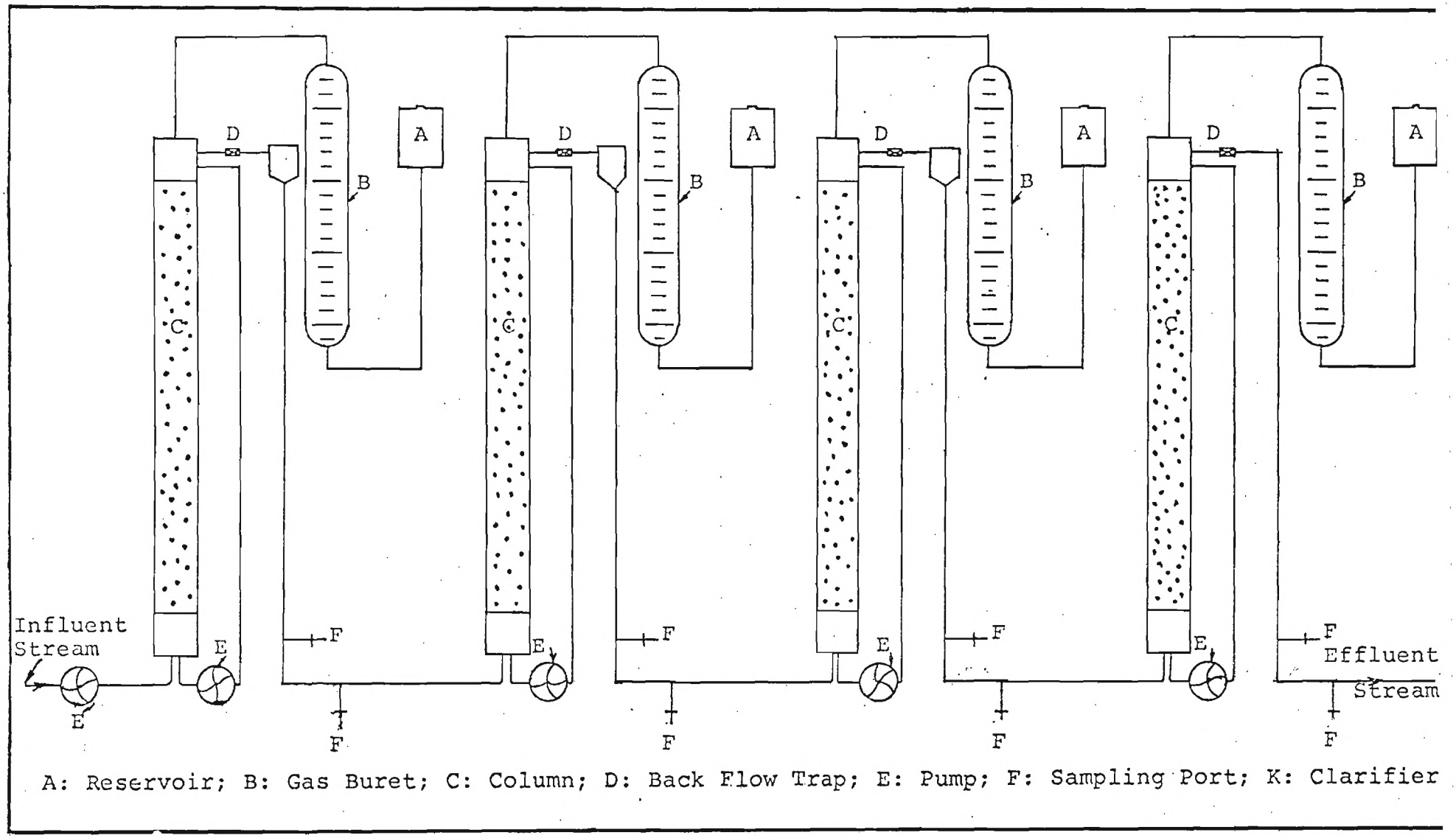

FIGURE 3. SCHEMATIC OF THE EXPERIMENTAL APPARATUS

PROGRESS REPORT

Treatment of Phenolic Wastewater with Anaerobic-Activated Carbon Filter

Principal Investigators: Makram T. Suidan and Wendall H. Cross
Granting Agency: U.S. Department of Energy
Grant Number: EF-77-G-01-2756
Grant Period: From 9/1/77 to 8/31/79

The objectives of the present research effort involve the conception and development of an advanced wastewater treatment system capable of handling high strength phenol bearing wastewaters. The treatment process consists of a series of anaerobic biological filters utilizing granular activated carbon for a contact medium. This process is potentially applicable to the treatment of wastewaters produced in coal gasification processes as well as the wastes generated from other coal conversion operations. The anaerobic activated carbon filter has the potential of providing a stable and economically attractive treatment process because of the production of a methane rich gas.

Research Progress

Two anaerobic activated carbon filter systems, each consisting of four columns in series, have been constructed, tested and in continuous operation for approximately one year. Initial microbial acclimation of these units was accomplished utilizing single organic carbon sources in the respective synthetic substrates. One unit has been acclimated and operated using a synthetic feed containing 2000 mg/l of glucose as the only organic carbon source while the other unit has been operated with 200 mg/l of phenol as the feed organic carbon. Extensive chemical and microbial analyses have been performed on the system during their startup and when steady state operating conditions had been reached. These analyses indicate that at steady state over 95% of the organic carbon in the feed has been converted to methane, carbon dioxide and biomass. In

addition, the inorganic carbon content of the effluent was enriched resulting in a headspace gas having an excess of 85% methane. The effluent concentration of phenol was consistantly below detectable limits.

Since achieving steady state operation of the single carbon feed source experiments, the feed substrates have been altered to examine (1) the cometabolism of 2000 mg/l of glucose and 200 mg/l of phenol, and (2) the degradation of higher feed concentrations of phenol.

Plans for the Coming Year

The system operation will be continued under a varying number of loading conditions and system performance parameters will be evaluated until the termination date of the current project which is August 31, 1979. Final performance data for this system will be included in the final report. Additional work on the treatment of actual coal gasification wastewaters should be done.

SCEGIT-79-104
DOE OCTOBER, 1979

TREATMENT OF PHENOLIC WASTEWATER WITH ANAEROBIC-ACTIVATED CARBON FILTERS

Makram T. Suidan, W. H. Cross, Khalique Khan

Technical Completion Report
DOE Project No. EF-77-G-01-2756
Initiated September 1977, completed September 1979

The work on which the report is based was supported by the School of Civil Engineering, Georgia Institute of Technology and by the University Projects in Coal Research Branch, U.S. Department of Energy.

SCHOOL OF CIVIL ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

Abstract

The research reported herein involved the development of an effective and energy efficient process for the treatment of phenol bearing wastewaters. This process consists of an anaerobic filter containing granular activated carbon as a contact medium which serves the purpose of microbial attachment and substrate concentration and polarization.

The anaerobic activated carbon filter was found to be very effective in treating synthetic wastewaters containing only phenol or glucose as the carbon source or a synthetic wastewater containing both glucose and phenol. In all instances, steady state operation was achieved and removal efficiencies exceeding 96, 98, and 100percent were obtained for total organic carbon, chemical oxygen demand and phenol where applicable, respectively. In addition the system proved to be stable to varying feed concentrations of phenol.

Granular activated carbon proved to be a superior contact medium than anequivalent sized anthracite medium. The granular carbon system resulted in greater organic carbon removal and greater methane gas production.

Suidan, Makram T., Wendall H. Cross and Khalique A. Khan.

TREATMENT OF PHENOLIC WASTEWATER WITH ANAEROBIC-ACTIVATED CARBON FILTERS

Final Report to Department of Energy on Grant Number EF-77-G-01-2756, September 1979.

KEYWORDS: Phenol/Glucose/Anaerobic Filter/Activated Carbon

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INTRODUCTION

The growth of industry and advancement in technology over the last two decades have resulted in the formation of increasingly complex wastewaters. Chemical, biological and physical treatment processes have been applied and are continuously being investigated in an effort to obtain treated wastewater characteristics that are "environmentally acceptable" for discharge. Phenolic compounds, monohydroxy derivatives of benzene, have been and are presently prioritized as a major environmental concern.

The presence of phenols in water has special adverse effects. Phenol and some of its derivatives are either toxic (reduce enzymatic activity) or lethal to fish at concentrations of 5 to 25 mg/l, depending on temperature (Brown, 1967; Reichenback, 1969). The presence of phenols at concentrations of only 0.002 mg/l imparts an objectionable taste to drinking water supplies when combined with chlorine. For this reason, drinking water standards have established 0.001 mg/l as the maximum recommended limit for the concentration of phenols in drinking water. As technology advances and the long term effects of consuming such organic compounds are determined, however, even present limitations may prove to be insufficient.

Sources of phenol discharge to the environment are both natural and industrial in origin. Natural sources of phenol include the urine of some animals and vegetation decay (Rosfjord, 1975). Industrial sources of phenolic wastes include petroleum refineries, pharmaceutrical plants, fertilizer manufacturers, solvent and explosive industries, coking and coal gasification plants, dye manufacturing, steel mills, paint stripping and degreasing operations, and wood and paper production (Patterson, 1975; Rosfjord, 1975; Nebel et al., 1976; Nemerow, 1978). Table 1 summarizes

Table 1. Industrial Sources of Phenol Bearing Wastewaters (Patterson, 1975)

Industrial Source	Phenol Concentration, mg/l
Coke Ovens	
Weak ammonia liquor,	3350-3900
without dephenolization	1400-2500
	2500-3600
	3000-10000
	580-2100
	700-12000
	600-800
Weak ammonia liquor,	28-332
after dephenolization	10
	10-30
	45-100
Wash oil still wastes	30-150
Oil Refineries	
Sour water	80-185 (140 ave)
General waste stream	40-80
Post-stripping	80
General (catalytic cracker)	40-50
Mineral oil wastewater	100
API separator effluent	0.35-6.8 (2.7 ave)
General wastewater	30
General wastewater	10-70
General wastewater	10-100
Petrochemical	
General petrochemical	50-600
Benzene refineries	210
Nitrogen works	250
Tar distilling plants	300
Aircraft maintenance	200-400
Herbicide manufacturing	210
(includes chloroderivatives and phenoxy acids)	239-524
Other	
Rubber reclamation	3-10
Orlon manufacturing	100-150
Plastics factory	600-2000
Fiberboard factory	150
Wood carbonizing	1000
Phenolic resin production	1600
Stocking factory	6000
Synthetic phenol,	12-18
plastics, resins	360 (after cooling water separation)
Fiberglass manufacturing	40-400

some of the industrial dischargers of phenol and the corresponding phenol levels in the wastewaters. The major contributors of phenols to the environment at present are coking plants and oil refineries, however, the single major potential contributor of these compounds is coal gasification in particular and coal conversion plants in general. These plants are net consumers of water and depending upon the extent of utilization of coal as a source of gaseous or liquid fuels, the potential for generating large volumes of strongly polluted wastes containing among other compounds mono and dihydric phenols, cyanide, thiocyanate and ammonia is imminent.

A number of studies have been conducted to determine the nature of the organic constituents of the aqueous by-products of coal conversion processes (Fornet et. al., 1974; Schmidt, 1974; Ho et al., 1976; Klemetson, 1977). The chemical composition of these wastes was found to vary considerably depending on the type of coal used, the conversion process employed, and the operating conditions which include the degree of water recycle (Sack and Bokey, 1978). In a recent survey aimed at determining the chemical characteristics of coal conversion wastewaters, Singer et al. (1972) concluded that these constituents may be classified into six distinct groups; these were the (a) monohydric phenols, (b) dihydric phenols, (c) polycyclic hydroxy compounds, (d) monocyclic N-aromatics, (e) polycyclic N-aromatics, and (f) aliphatic acids. Table 2 presents a summary of the organic constituents of coal conversion wastewaters and the concentration ranges within which these compounds have been detected.

The treatment of phenol bearing wastewaters has traditionally been accomplished through the use of conventional aerobic biological processes, such as the activated sludge process or oxidation lagoons, or through the use of chemical oxidants or activated carbon adsorption. In the case of

Table 2. Summary: Organic Constituents in Coal Conversion Wastewaters
(All Concentrations in mg/l)
(Singer, Pfaender, Chinchilli, Lamb III, 1977)

	Synthane TPR-86 (1)	Oil Shale (2)	Syn-thane (3)	COED (4)	SRC (5)	Lurgi-Westfield (6)	Syn-thane (7)	Lurgi-Sasol (8)	Hydro-carboniz. (9)	COED (10)
Monohydric Phenols										
Phenol	1000-4480	10	2100	2100		1250-3100		1250		
o-cresol		30	670	650		153-343	2209	340		
m-cresol	530-3580					170-422		360		
p-cresol		20	1800	1800		160-302		290		
2,6-Xylenol			40	30						
3,5-Xylenol			230	240				50		
2,3-Xylenol			30	40						
2,5-Xylenol	140-1170		250	220		100-393				
3,4-Xylenol			100	900			2185			
2,4-Xylenol			-	-				120		
o-Ethylphenol			30	30						
m-ethylphenol										
p-Ethylphenol										
3-Methyl, 6-Ethylphenol										
2-Methyl, 4-Ethylphenol										
4-Methyl, 2-Ethylphenol	20-150									
5-Methyl, 3-Ethylphenol							66			
2,3,5-Trimethylphenol										
o-Isopropylphenol							40			
Dihydric Phenols										
Catechol						190-555			1700	
3-Methylcatechol						30-394			11	
4-Methylcatechol						110-385				
3,5-Dimethylcatechol										
3,6-Dimethylcatechol						0-45				
Methylpyrocatechol										
Resorcinol						176-272			2000	

Table 2. (continued) Summary: Organic Constitutents in Coal Conversion Wastewaters
(All concentrations in mg/l) (Singer, Pfaender, Chinchilli, Lamb III, 1977)

	Synthane TPR-86 (1)	Oil Shale (2)	Syn-thane (3)	COED (4)	SRC (5)	Lurgi-Westfield (6)	Syn-thane (7)	Lurgi-Sasol (8)	Hydro-carboniz. (9)	COED (10)
5-Methylresorcinol						40-64			2000	
4-Methylresorcinol						0-36			2000	
2-Methylresorcinol										
2,4-Dimethylresorcinol										
Hydroquinone									4-7	
Polycyclic Hydroxy Compounds										
γ-Naphthol			10							
β-Naphthol	30-290		30							
Methylnaphthol										
Indenol	20-110									
C_1-Indenol										
4-Indanol	40-150						66			
C_i-Indanol										
Biphenol	0-110									
Monocyclic N-Aromatics										
Pyridine								117		
Hydroxypyridine									10	
Methylhydroxypyridine									10	
Methylpyridine								104		
Dimethylpyridine	30-580						5	<1		
Ethylpyridine									20	
C_3-Pyridine										
C_4-Pyridine										
Analine							21	12		
Methylaniline							9			
Dimethylaniline							11			

Table 2 (continued) Summary: Organic Constituents in Coal Conversion Wastewaters (All concentrations in mg/l)(Singer, Pfaender, Chinchilli, Lamb III, 1977)

	Synthane TPR-86 (1)	Oil Shale (2)	Syn-thane (3)	COED (4)	SRC (5)	Lurgi-Westfield (6)	Syn-thane (7)	Lurgi-Sasol (8)	Hydro-Carboniz. (9)	COED (10)
Polycyclic N-Armonatics										
Quinoline							7			
Methylquinoline							27			
Dimethylquinoline										
Ethylquinoline	0-100									
Benzoquinoline										
Methylbenzoquinoline										
Tetrahydroquinoline										
Methyltetrahydroquinoline										
Isoquinoline										
Indole										
Methylindole							63			
Dimethylindole	0-110									
Benzoindole										
Methylbenzoindole										
Carbazole										
Methylcarbazole									4	
Acridine										
Methylacridine										
Aliphatic Acids										
Acetic Acid		600	620	600				171		
Propanoic Acid		210	60	90				26		
n-Butanoic		130	20	40				13		
2-Methylpropanoic Acid		-	-	-				2		
n-Pentanoic Acid		200	10	30				12		
3-Methylbutanoic Acid		-	-	-				1		

Table 2 (continued). Summary: Organic Constituents in Coal Conversion Wastewaters. (all concentrations in mg/1) (Singer, Pfaender, Chinchilli, Lamb III, 1977)

	Synthane TPR-86 (1)	Oil Shale (2)	Syn-thane (3)	COED (4)	SRC (5)	Lurgi-Westfield (6)	Syn-thane (7)	Lurgi-Sasol (8)	Hydro-carboniz. (9)	COED (10)
n-Hexanoic Acid		250	20	30						
n-Heptanoic Acid		260	-	-						
n-Octanoic Acid		250	-	-						
n-Nonanoic Acid		100	-	-						
n-Decanoic Acid		50	-	-						
Others										
Benzofurans	10-110									
Benzofuranols	50-100									
Benzothiophenols	10-110									
Acetophenones	90-150									
Hydroxybenzaldehyde or Benzoic Acid	50-110									

aerobic biological treatment, process instability problems have been frequently encountered either due to vast changes in the phenol content of the wastewater or due to the presence of other compounds in the waste which exhibit coinhibition with phenol (Juntgen and Klein, 1977). Chemical oxidation and carbon adsorption have been shown in a number of instances to be very effective in treating phenol bearing wastewaters, however, due to the high organic content typically associated with such wastewaters, such processes have been shown to be economically unfeasible for industrial applications.

In the research reported herein, a new wastewater treatment process is developed for the purification of phenol bearing wastewaters. This process combines the energy producing anaerobic fermentation process with granular activated carbon serving as a microbial attachment as well as a substrate concentration and polarization surface. When the environmental conditions for proper microbial growth are provided, this process is shown to undergo carbon bioregeneration which not only renders steady state operation feasible but produces methane gas and, consequently, the whole process very economical for the treatment of such wastewaters.

LITERATURE REVIEW

The objective of the present study was to develop and test a new process for the effective treatment of phenol bearing wastewaters. This process combines the anaerobic environment with biologically active granular activated carbon adsorption. At the time the research was initiated, very little information was available in the literature on the anaerobic degradation of phenol and the present research serves to demonstrate that the anaerobic process when combined with granular activated carbon serving as a microbial attachment surface as well as for substrate concentration provides a very effective and energy efficient process for the treatment of phenol bearing wastewaters. Because of the number of diverse areas that the process engulfs, this literature review will focus on each of these areas in general with the overall intent of familiarizing the reader with the various aspects of: (a) the state of the art in the treatment of phenol bearing wastewaters, (b) a thorough review of the limited data available on the anaerobic degradation of aromatic compounds, (c) typical performance characteristics of activated carbons in adsorbing phenolics, and (d) the state of the art in the development of the anaerobic filter.

State-of-the-Art in the Treatment of Phenol Bearing Wastewaters

Phenol bearing wastewaters have been treated using a number of different unit processes and unit operations, however the methods that have most commonly been used to date include the use of chemical oxidants, physical separation either through extraction or adsorption, incineration, and aerobic as well as anaerobic biological treatment processes.

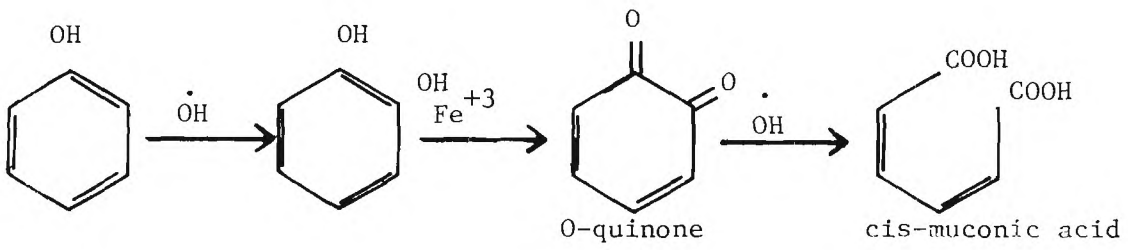
Chemical Oxidation of Phenols

The chemical oxidation of phenolic compounds involves the addition of an oxidizing agent that promotes the cleavage of the parent benzene ring. Further degradation of the byproducts may be accomplished through oxidation or some other form of treatment such as biological degradation.

Oxidation with Hydrogen Peroxide. Hydrogen peroxide in combination with a ferrous salt has been used for the oxidation of phenols. This mixture of reagents, generally referred to as Fenton's reagent, functions as an oxidizing agent through the formation of a free hydroxyl radical as shown in Equation 1.

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + \dot{O}H \qquad (1)$$

This reagent has been shown to be a powerful oxidant for a number of compounds including alcohols and ketones (Merz and Waters, 1949a; Kolthoff and Medalin, 1949), benzene (Merz and Waters, 1949b), nitrobenzene (Lobel, et al., 1949), and phenols (Chawla and Pailer, 1939; Stein and Weiss, 1951; Cosgrove and Waters, 1951). It has been demonstrated that the oxidation of phenol results in the formation of catechol and hydroquinone which are then oxidized by the ferric ion formed in Equation 1 to the corresponding quinones (Weiland and Franke; 1928; Merz and Waters, 1949b; Stein and Weiss, 1951). Catechol can be oxidized very effectively to muconic acid using hydrogen peroxide and a ferrous salt (Pospisil and Ettel, 1957). These results suggest that phenol oxidation proceeds according to the equation:



(2)

The rate of oxidation of phenol increases with increasing concentrations of hydrogen peroxide and ferous ion (Eisenhauer, 1964), however, a ratio of three moles of hydrogen peroxide to one mole of phenol was observed to yield optimum results (see Table 3).

Table 3. Reaction of Phenol with Fenton's Reagent* (Eisenhauer, 1964)

$Fe(NH_4)_2(SO_4)_2$ (moles/mole of phenol)	H_2O_2 (moles per mole of phenol)	Phenol Concentration (mg/ℓ)		
		2 min.	5 min.	15 min.
0.1	9	33.6	27.8	8.5
0.25	9	21.2	11.6	0.0
0.5	9	3.0	0.0	0.0
1.0	9	0.0	0.0	0.0
1.0	3	2.0	0.0	0.0
1.0	2	13.2	8.8	8.0
1.0	1	16.0	14.2	13.6
1.0	0.5	22.4	19.0	16.0

* Solutions containing 50 mg/ℓ of phenol were reacted with Fenton's reagent at pH 3.0 and 10°C utilizing air agitation.

The oxidation of phenols with Fenton's reagent involves the formation of a free radical and as such, the position of the substituent groups on the benzene ring has a strong influence on the effectiveness of this reagent. Mono substituted phenols are oxidized almost as readily as simple phenol. For more highly substituted phenols, however, an increase in the degree of substitution results in a decrease in the rate of reaction of the phenol with hydrogen peroxide. This is particularly true when the substituents are in the ortho and para positions. Work done by Keating et al. (1978) on the oxidation of eighteen different phenolics with hydrogen peroxide (see Table 4) demonstrates the effect of the degree and position of substitution on the rate of reaction of phenols with hydrogen peroxide. Dichlorophenols are more readily oxidized than phenols bearing electron donating substituents such as the dimethyl phenols. Dinitrophenols which have a strong

electron withdrawing group should be readily oxidized, however, since nitrophenols have dissociation constants in the pH range of 3 to 4, and since at normal pH operating conditions they would be present in the dissociated form, they were observed to be resistant to oxidation by hydrogen peroxide. The data presented in Table 4 was obtained using a ratio of three moles of hydrogen peroxide per mole of phenol in the absence of iron salts, whereas the added

Table 4. Oxidation of Substituted Phenols with Hydrogen Peroxide in the Absence of Iron Salts* (Keating et al, 1978)

Phenolic Compound	% Oxidized 1-hour	Phenolic Compound	% Oxidized 1-hour
Phenol	0	P-cresol	6
2-Chlorophenol	9	2,4-Dimethyl phenol	10
3-Chlorophenol	50	2,5-Dimethyl phenol	6
4-Chlorophenol	20	2-Nitrophenol	34
2,4-Dichlorophenol	0	4-Nitrophenol	0
2,5-Dichlorophenol	2	2,4-Dinitrophenol	2
Pentachlorophenol	6	2,5-Dinitrophenol	10
O-cresol	0	α-Napthol	8.5
M-cresol	0	β-Napthol	9.5

the added advantage of the presence of the ferrous salt is demonstrated by the data shown in Table 5. Theoretically, no reaction should occur between hydrogen peroxide and pentachlorophenol since all available positions on pentachlorophenol are occupied. However, Keaton et al. (1978) observed reductions in pentachlorophenol due to its oxidation with hydrogen peroxide both in the presence as well as in the absence of a ferrous salt.

The concentration of iron salt also has a noticeable effect on the rate of oxidation of phenol with hydrogen peroxide. The data in Table 6 (after Keating et al, 1978) shows the effect of phenol to iron concentration on the rate of oxidation of phenol by hydrogen peroxide for initial phenol and hydrogen peroxide

Table 5. Oxidation of Substituted Phenols with Hydrogen Peroxide in the Presence of Iron Salts*
(Keating et al, 1978)

Phenolic Compound	% Oxidized 1-hour	Phenolic Compound	% Oxidized 1-hour
Phenol	100	P-cresol	100
2-Chlorophenol	100	2,4-Dimethyl phenol	72
3-Chlorophenol	100	2,5-Dimethyl phenol	0
4-Chlorophenol	100	2-Nitrophenol	100
2,4-Dichlorophenol	100	4-Nitrophenol	100
2,5-Dichlorophenol	74	2,4-Dinitrophenol	30
Pentachlorophenol	100	2,5-Dinitrophenol	73
O-cresol	100	α-Napthol	100
P-cresol	100	β-Napthol	100

*Same conditions as in Table 4.

concentrations of 50 mg/ℓ and 150 mg/ℓ, respectively. An initial pH of 5-6 was selected although the optimum reaction pH is between 3 and 4. This pH was selected to compensate for the decrease in pH during the course of the reaction. The reaction temperature was maintained at 25°C. As can be seen from examining the data in Table 6, the oxidation of phenol is essentially complete in thirty minutes for iron concentrations of 5 mg/ℓ and a hydrogen peroxide to phenol weight ratio of 3:1 or a mole ratio of 8:1. At this concentration of iron, both the ferrous form as well as the ferric form appear to function equally well. Further work done by Keating et al. (1978) at phenol to iron ratios higher than 10:1 indicated that both the rate and the extent of reaction were severely affected by the decreased iron levels. They observed that severe competition occurred between phenol and other water constituents for the hydrogen peroxide and, more importantly, phenols were not generally the first compounds to undergo oxidation.

In a pure solution, the optimum molar ratio of hydrogen peroxide to phenol has been shown to be 3:1 (Keating et al, 1978). However, field data shows that in the presence of competing species, this ratio will be much higher. Eisenhauer

Table 6. Effect of Iron Concentration on the Oxidation of Phenol by Hydrogen Peroxide (Keating et al., 1978)

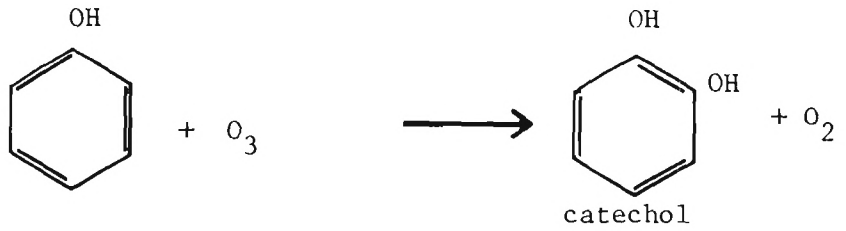
Iron	Phenol:Iron	H_2O_2:Iron	% Reduction 15 min.	30 min.	60 min.
50 mg/ℓ Fe^{+2}	1:1	3:1		100	100
50 mg/ℓ Fe^{+3}			96	100	100
25 mg/ℓ Fe^{+2}	2:1	6:1	97	100	100
25 mg/ℓ Fe^{+3}			92	98	100
5 mg/ℓ Fe^{+2}	10:1	30:1	91	99^{+}	99^{+}
5 mg/ℓ Fe^{+3}			94	97	99^{+}

(1964) showed from studies on wastewaters emanating from refineries, steel plants, and insulation plants that a hydrogen peroxide to phenol molar ratio much higher than 3 is required (see Table 7).

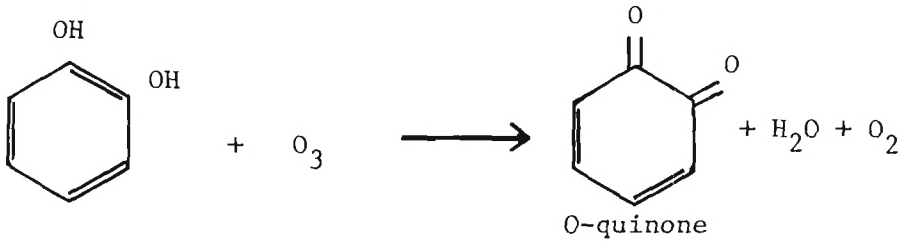
Table 7. Treatment of Industrial Effluents with Fenton's Reagent

Effluent	H_2O_2 (moles per mole of phenol)	Phenols (mg/ℓ)	COD mg/ℓ Due to Phenol	Total
Refinery	0	83	198	408
(Stripped)	3	28	67	-
	4.5	9.1	22	-
	6	3.2	8	-
	9	1.6	4	-
Refinery	0	119	280	970
(Stripped)	3	35	83	338
	4.5	16.4	39	-
	6	4.0	10	242
	9	0.9	2	246
	12	1.8	4	176
Steel Plant	0	64	152	1250
	4	54	128	492
	8	36	86	437
	12	38	90	454
	16	41	97	466
Insulation Plant	0	10.9	26	285
	3	3.6	9	112
	6	0.2	0.5	57
	9	0.5	1	16
	12	0.0	0	48
Insulation Plant	0	16.5	39	394
	3	11.1	26	-
	6	8.6	20	-
	9	4.8	11	-
	12	1.7	4	-

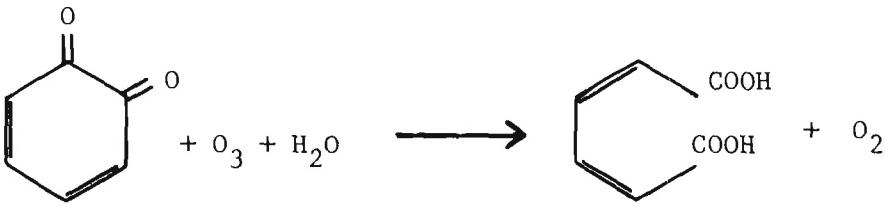
Oxidation with Ozone. A number of researchers have reported on the oxidation of phenolic compounds with ozone (Eisenhauer, 1968; Kroup, 1973; Throop, 1975; Gould and Weber, 1976; Nebel et al., 1976). Eisenhauer (1968) proposed a reaction mechanism for the oxidation of phenol with ozone, whereby the phenol is degraded to catechol, o-quinone and other degradtion products as shown in Equations 3 - 7.



(3)

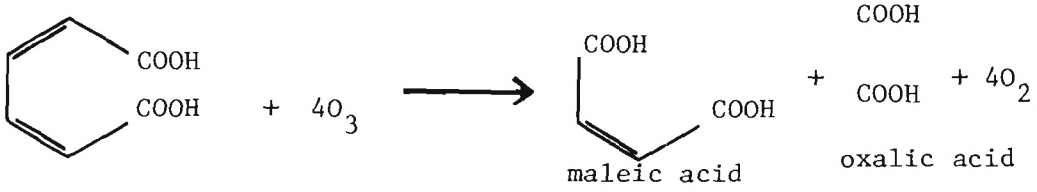


(4)

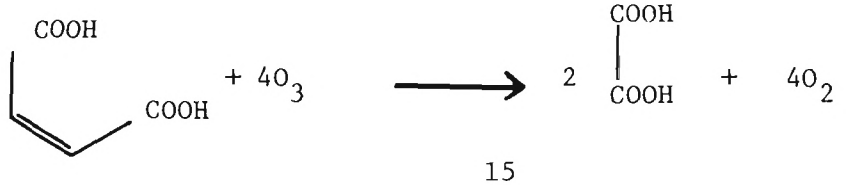


(5)

cis,cis-muconic acid



(6)



(7)

The formation of oxalic and fumaric acids as oxidative intermediates of the reaction between catechol and per acids has also been shown by Pospisil and Ettel (1958). Carbonyl compounds other than glyoxal and glyoxalic acid were not detected (Gould and Weber, 1976). Formic acid, oxalic acid, and carbon dioxide have been identified as intermediates and end products of the ozonalysis of shale tar waters (Sharanova and Kuzmina, 1968).

The dose of ozone needed for the oxidation of phenol depends upon the amount of phenol present and the degree of phenol degradation desired. Using a pure solution of phenol, Eisenhauer (1968) and Gould and Weber (1976) determined that 4 to 6 moles of ozone are needed per mole of phenol to achieve substantial degradation of the parent molecule. For the complete oxidation of phenol to carbon dioxide and water, 14 moles of ozone are needed per mole of phenol provided no other ozone demanding materials are present in the water (Equation 8). In wastewaters containing phenols, a higher molar ratio would

$$C_6H_5OH + 14O_3 \rightarrow 6CO_2 + 3H_2O + 14O_2 \qquad (8)$$

be required based on the amount of phenol and the origin of the waste discharge.

Nebel et al. (1976) evaluated the effectiveness of ozone in degrading phenols present in a number of industrial discharges. In treating the effluent from a resin manufacturing plant producing a waste flow of 0.25 mgd, a total of 625 pounds of ozone were needed daily. Concurrent with phenol removal, 17 percent of the chemical oxygen demand (COD), 30 percent of the color, and 29 percent of the turbidity were removed. In the case of a papermill effluent, 600 pounds of ozone were needed daily to treat an equivalent volume of wastewater. This ozone demand far exceeded the phenol demand of the wastewater, which implies the presence of other ozone demanding components in the wastewater. In the treatment of a coking plant effluent, it was observed that cyanide and thiocyanate

competed very strongly with the phenol for the ozone applied. Consequently, the ozone dose needed depends on the relative concentrations of these three components in the coking wastewater. The data in Table 8 represents a summary of ozone demand for the treatment of various coking plant wastewaters.

Table 8. Ozonation of Coking Plant Wastewaters (Nebel et al., 1976)

Source	Initial Phenols (mg/ℓ)	Ozone Demand (mg/ℓ)	Ozone/Phenol Ratio	Residual Phenol (mg/ℓ)
Coke Plant A	1,240	2,500	2.0	1.2
Coke Plant B	800	1,200	1.5	0.6
Coke Plant C	330	1,700	5.2	1.0
Coke Plant D	140	950	6.8	0.1
Coke Plant E	127	550	4.3	0.2
Coke Plant F	102	900	8.8	0.0
Coke Plant G	51	1,000	20.0	0.4
Coke Plant H	38	700	18.0	0.1
Refinery A	605	750	1.3	0.3
Refinery B	11,600	11,000	1.0	2.5

Kroop (1973) investigated the feasibility of treating air craft stripping wastewater with ozone. Employing no pH adjustment or control and using batch processes, he determined that 10.4 moles of ozone were required per mole of phenol in order to achieve a 99 percent reduction in phenol. However, the adjustment of the solution pH to 11.0 reduced the ozone demand to 3.46 moles per mole of phenol. In a continuous flow system, however, 5.2 moles of ozone were needed per mole of phenol to achieve a 99 percent reduction in the feed phenol concentration even when the feed pH was maintained at 11.5. Nebel (1976) reported that for pure solutions of phenol, the optimum pH for ozonalysis was 11.8. This is also true for phenol bearing wastewaters since ozone becomes more selective to phenol over other oxidizable constituents present in the wastewater (Kroop, 1973). The drawback to the use of such a pH, however, is the fact that

the rate of ozone autodecomposition is faster at higher pH values than it is in the low pH range (Stum, 1954).

In an extensive treatability study on coking plant wastewaters, Cleary and Kinney (1951) demonstrated that substantial reductions in phenol concentration may be achieved with ozone. Hall and Nellist (1951) achieved a reduction in the phenolic content of a coking wastewater from 2000 mg/ℓ to less than 1 mg/ℓ using an average ozone dose of 1.7 grams per gram of phenol. Niegowski (1953) suggested that an economical treatment process would result when ozone-consuming constituents such as sulfides, cyanide, and thiocyanite were removed from coking wastewaters prior to ozonation. Hall and Nellist (1966) concluded that the ozonation of such wastewaters was economical only as a final polishing step after biological treatment.

Oxidation with Potassium Permanganate. Potassium permanganate has also been used for the oxidation of phenols and their degradation to smaller fragments. Based on the stoichiometry given in Equation 9, a theoretical weight ratio of 15.7 pounds of potassium permanganate is needed per pound of phenol to achieve complete oxidation of the parent phenol. However, weight ratios of 6 to 7 pounds of potassium permanganate per pound of phenol have been found to be sufficient for the partial oxidation of the molecule to simpler compounds (Kroop, 1973). This oxidative reaction has been reported to proceed favorably in the

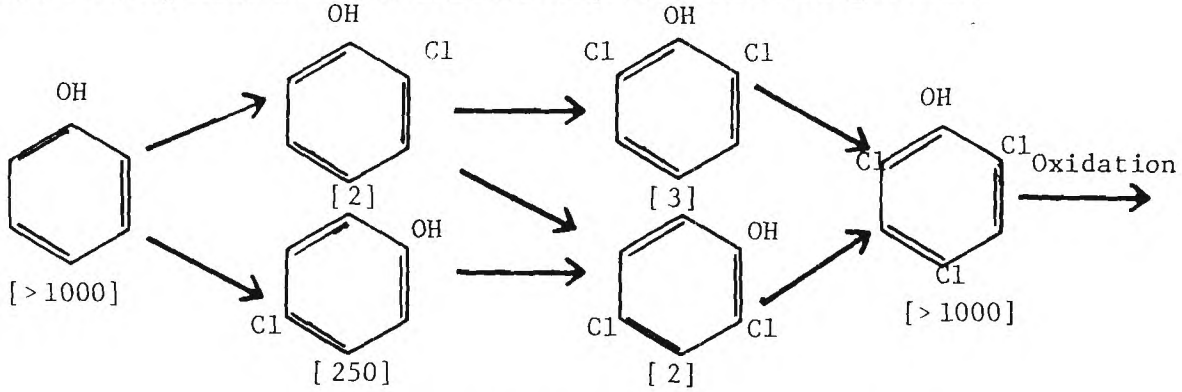
$$3C_6H_5OH + 28KMnO_4 + 5H_2O \rightarrow 18CO_2 + 28KOH + 28MnO_2 \quad (9)$$

pH range of 7 to 10 (Lanouette, 1977).

Oxidation with Chlorine Compounds. Chlorination as a means of phenol removal has been evaluated by several investigators (Eisenhauer, 1964; Throop, 1975; Lanouette,1977) but has generally been found to be ineffective as an oxidant because of the tendency of the chlorine to combine with phenol to form chlorophenols

which are generally more toxic and have a stronger taste and odor effect than the original phenolic compound. Chlorine has also been shown to react with phenolic acids such as p-hydroxybenzoic acid to form chlorophenols. In addition, the expected addition products such as 3-chloro-4-hydroxybenzoic acid, 3-, and 3,5-dichloro-4-hydroxybenzoic acid react further with chlorine to form 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. The compounds found in water that are most notorious in leading to taste and odor problems upon chlorination are phenol and some of its substitution products (Lee, 1962).

According to Burtschell et al. (1959), the reaction of chlorine with phenol results initially in the formation of either 2- or 4-chlorophenol. Upon further substitution, 2-chlorophenol is converted to either 2,4 or 2,6-dichlorophenol, while 4-chlorophenol is further chlorinated to form 2,4-dichlorophenol. Both 2,4- and 2,6-dichlorophenol react further with chlorine to form 2,4,6-trichlorophenol (see Figure 1.). Two-chlorophenol, 2,4- and 2,6-dichlorophenol are the compounds that have been reportedly responsible for the chlorophenolic tastes and oders arising from the chlorination of phenol containing waters.



[ ] Odor threshold concentration microgram/liter
(After Burtschell)

Figure 1. Reaction Scheme for the Chlorination of Phenol

Eisenhauer (1964) reported that when 800 mg/ℓ of available chlorine was added to a refinery effluent containing 78 mg/ℓ of phenol at a temperature of

50°C, trichlorophenol was formed very rapidly achieving a maximum concentration after 15 minutes at which point 65 percent of the hypochlorite was consumed. At the end of 1 hour of contact, the trichlorophenol concentration had dropped to one half its maximum value at which point 97 percent of the hypochlorite was consumed. A similar phenomenon was observed at lower temperatures, however, the rates of formation and disappearance of the trichlorophenol were appreciably slower in the latter case. When phenol solutions are reacted with relatively low doses of hypochlorite, stable chlorophenols are formed (Chamberlin and Griffin, 1952; Burtschell et al., 1959), whereas when larger does of hypochlorite are used the phenols undergo destructive oxidation (Inglos and Ribenoua, 1948; Chamberlin and Griffin, 1952). Throop (1975) also noted the removal of phenols to levels below detectable concentrations when high chlorine to phenol ratios are applied (see Table 9). For the complete elimination of chlorophenols, a chlorine residual should be maintained and the operating pH should be held in the range of 7 to 8.3. Maintaining a good chlorine residual and controlling the pH to within such a narrow range might not always be practical in field installations, however.

Table 9. Phenol Removal by Chlorination
(Throop, 1975)

Chlorine Dosage (mg/ℓ)	Cl:Phenol Ratio	Residual Chlorine (mg/ℓ)	Phenol Concentration (ppb)	
			Initial	Final
1.2	98:1	0.27	123	97
12.0	98:1	1.60	123	n.d.*
24.0	196:1	5.10	123	n.d.
36.0	392:1	7.50	123	3

* non detectable

Incineration of Phenol. Waste liquid incinerators have been used in industry for the disposal of wastewaters that contain high concentrations of organic matter (on the order of 50,000 mg/ℓ) and for which recovery methods are not practical (Rosjford et al., 1976). Upon incineration, the phenolic content of the wastewater is converted to carbon dioxide and water according to the chemical reaction given in Equation 10.

$$C_2H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O \qquad (10)$$

Theoretically a heat of combustion of 13,300 British Thermal Units (BTU) should be liberated for every pound of phenol that is completely oxidized. Consequently, the combustion of a mixture of about 18 percent by weight of phenol and 82 percent by weight of water should be self sustaining when burned in 10 percent excess air at 760°C (1400°F) (Lanouette, 1977). The high heat capacity of water renders this process very sensitive to the water content of the waste and more dependent on fuel costs. Winter (1973) proposed an equation (Equation 11) for computing the annual operating cost of the process.

$$O = \frac{(330)QB}{8340C} + 0.20 \frac{Q}{\left[\frac{[8.34 \times 1440\ C]}{3}\right] 0.6} Tc \qquad (11)$$

Where:
- O = annual operating cost, dollars
- Q = daily phenol production rate, pounds
- C = phenol concentration, pound phenol/pound water
- B = burning cost of fuel per 1000 gallons of water feed, dollars
- Tc = capital cost, dollars

Reductions in COD of 98 percent have been reported when a phenolic waste containing 29,000 mg/ℓ COD was passed through the pores of a carbon electrode (Nagamori, et al., 1973). In another case, a flow of 250 gallons per hour of a 13.5 percent aqueous phenol solution has been effectively incinerated at

871°C (1600°F) (Lanouette, 1977). An experimental oxidative method, employing copper coated aluminum as a catalyst, is claimed to provide an economic alternative for the treatment of wastewaters containing up to 4000 mg/ℓ of phenol (Ficke, 1973).

Physical Separation Through Extraction and Adsorption

Phenols may be extracted from aqueous solutions either by extraction into an organic solvent phase or by adsorption onto activated carbon or similar adsorbents. Extraction is usually practiced when both purification and phenol recovery are the objectives, while activated carbon is often used for the sole purpose of purification.

Extraction of Phenols. Extraction is, by design, a method intended for the recovery of one material through the use of another. Proper selection of the extracting agent is very critical for the proper performance of the process. Witt et al. (1972) emphasized the desirable properties of an extracting solvent as being: the extractant must be readily available; relatively inexpensive; essentially insoluble in water; and most importantly, separable from the extracted material at a reasonable cost.

Solvent extraction has generally been reported to achieve 90 to 95 percent reduction in the phenolic content of wastewaters (Kao, 1972). Coking wastewaters have been dephenolized using anthracene oil (Smetanina, 1972), or fluorene oil (Benecke, 1972). Di-isopropyl ether (Malz, 1972) and mixtures of butyl acetate and isopropyl alcohol have also been used (Sharonova, 1970).

Phenol has been extracted from the liquid wastes generated from a cumene processing plant using acetophenone or mesityl oxide as the extracting media. This process resulted in a reduction of the phenolic content of the wastes from 180 mg/ℓ down to less than 1 mg/ℓ (Cyrus W. Rice and Company, 1969; Sittig,

1974; Hauschulz et al., 1974). The use of additives, such as sodium sulfate (Maratova et al., 1973) and organosilicon compounds (Aleksandrova et al., 1973), to control or enhance the extraction process has also been reported.

The information presented in Table 10 represents an overview of the performance characteristics of some of the more commonly used solvent-extraction processes for the recovery of phenol (Wurm, 1968; Lanouette, 1977). These systems have generally been reported to account for phenol recoveries of up to 99.7 percent. However, the significant residual phenol concentration in the extracted waste streams necessitates additional treatment prior to discharge (Wurm, 1968).

Table 10. Extraction Processes for Phenol Recovery

Process	Extractor Type	Influent Concentration, mg/ℓ	Removal Efficiency %
Benzne-caustic	Packed column	3000	92-93
	Podbielniak centrifuge	2000	95
	Pulsed packed column	2200-2600	98.6-98.8
Phenolsolvan (low boiling point solvent)	Multistage	1570-2465	99.6-99.7
Ifawol (high-boiling point solvent)	Packed column	4000	99

Adsorption onto Activated Carbon

Activated carbon, in its various forms (both granular and powdered), is characterized by a high surface area to weight ratio. Because of its excessive surface area, activated carbon has been found to be a good adsorbent for many organic compounds in general, and phenols in particular (Stoneburner, 1966; Asonov, 1972; Apostolov, 1972; Eckenfelder et al., 1972; Hager, 1974; Grail and

Zanitsch, 1974; Zogorski and Faust, 1977). The use of activated carbon adsorption for the treatment of phenol bearing wastewaters presents several advantages, the most important of which are: carbon adsorption systems are physical chemical in nature and, as such, are not subject to toxic effects of phenolics of higher feed concentrations (2000 to 5000 mg/ℓ phenol). At the same time, these systems are capable of providing excellent reductions in the feed phenol concentration (Gould and Taylor, 1969, Baker et al., 1973).

Zogorski and Faust (1977) evaluated the effect of particle size, temperature, pH and the initial adsorbate concentration on the adsorption capacity and kinetics of several phenols onto activated carbon. In general, Zogorski and Faust (1977) observed that particle size had no effect on the adsorption capacity of activated carbon for 2,4-dinitrophenol and 2,4-dichlorophenol, while a decrease in particl size resulted in an increase in the rate of uptake of such molecule, indicating pure and/or film diffusional resistance. The hydrogen ion concentration was found to have a very pronounced effect on the adsorption capacity onto activated carbon of 2,4-dichlorphenol and 2,4-dinitrophenol. In both instances maximum adsorption capacity was noted at a pH value very near the pK_2 of the weak acids with a slight decrease in capacity at lower pH values and a marked decrease in capacity at higher pH values when the fraction of the phenols in the ionized form increases with increasing pH (Ward and Getzen, 1970; Zogorski and Faust, 1977; Snoeyink et al., 1977).

An increase in the extent of substitution onto the benze ring of phenol has been observed to result in a decrease in the water solubility of the substituted product and an increase in the adsorbivity of the compound onto activated carbon. Garnetlett and Packham (1973) observed that as the substitution of chlorine onto phenol progresses, the resulting compounds become less soluble in water and more adsorbable onto carbon. Once again, they also observed that the

dissociated species adsorbed much more poorly than the neutral forms. In another study, Zogorski and Faust (1974) demonstrated using seven phenols that a decrease in the solubility of a phenol results in increasing adsorptive capacity. The carbon adsorption equilibrium and solubility data on phenol, 2,4-dinitrophenol, 2,4-dichlorophenol, 4-methoxyphenol, 4-chlorophenol, 4-nitrophenol, and 4-hydroxyphenol, shown in Table 11, demonstrate this phenomenon rather well (Zogorski and Faust, 1974).

Table 11. Summary of Adsorbate Removal onto Activated Carbon from Solutions of Several Phenolic Compounds (Zogorski and Faust, 1974)

Compound	Solubility, a mole/ℓ	Amount Adsorbed at the Following Equilibrium Concentrations, mM/g					
		0.1	0.2	0.4	0.6	1.0	4.0
2,4-Dinitrophenol	0.011	2.68	3.00	3.28	3.36	-	-
2,4-Dichlorophenol	0.030	2.76	2.90	3.13	3.30	3.40	3.53
4-Nitrophenol	0.101	2.21	2.40	2.64	2.77	3.03	3.33
4-Chlorophenol	0.198	2.06	2.32	2.55	2.66	2.72	3.50
4-Methoxyphenol	0.298	2.32	2.53	2.77	2.90	3.03	3.33
4-Hydroxyphenol	0.619	1.13	1.37	1.49	1.56	1.69	2.10
phenol	0.831	1.13	1.40	1.74	1.92	2.14	2.78

a At 20°C, pH = 6.3 and 0.05M buffer

Huang and Steffens (1976) showed that the adsorptive capacity of phenol, o-aminophenol, pyrocatechol and resorcinol onto activated carbon decreased with an increase in the solubility of these compounds. Phenol exhibited the highest adsorption capacity followed by o-aminophenol, pyrocatechol and resorcinol, while the respective solubilities were 9.3, 1.7, 45 and 123 g/100 g of water.

Phenols are usually present in industrial wastewaters with a large number of other organic compounds that may compete with the phenols for the activated carbon surface. When the phenol of interest is present in a predominant form when compared to other adsorbing species in a particular wastewater, it may be

safe then to utilize single solute adsorption data of that compound in the design of activated carbon contactors for the treatment of the industrial wastewater. However, when other competing species are present in appreciable quantities, detailed information as to the nature and magnitude of that competition is needed. Several investigators have reported on this competition and factors affecting it (Jain, 1972; Jain and Snoeyink, 1973; Murin, 1975; Snoeyink et al., 1977; Zogorski and Faust, 1977).

Zogorski and Faust (1977) investigated the competition between phenol and 4-methoxyphenol. They observed that 4-methoxyphenol had a more pronounced effect on the extent of removal of phenol than did phenol on the adsorptive capacity of 4-methoxyphenol. Increasing the concentration of phenol from 0 to 300 μmole/ℓ resulted in only an 11 percent decrease in the adsorbivity of 4-methoxyphenol, while a similar increase in the 4-methoxyphenol concentration resulted in a 29 percent decrease in phenol capacity (Zogorski and Faust, 1977). In a similar study, Jain (1972) observed that there was only weak competition in the adsorption of p-nitrophenol in the presence of phenol, whereas the uptake of phenol is strongly reduced in the presence of p-nitrophenol. The neutral forms of p-nitrophenol and p-bromophenol, on the other hand, competed for the same adsorptive sites on the carbon surface, while neutral benzene sulfonate and anionic p-nitrophenol were attracted to different sites on the carbon surface, thus implying no competition between the two adsorbates (Jain, 1972).

Murin (1975) and Snoeyink et al. (1977) studied the adsorptive competition between 2,4-dichlorophenol and 2,4,6-trichlorophenol at pH values of 5.2, 7.0 and 9.1. Sizable reductions in adsorptive capacities were sited when both chlorophenols were present, thus indicating strong competition. When both species were present in the neutral form (pH 5.2) at an equilibrium concentration of each of 1.0×10^{-8}M, the carbon capacity for 2,4-dichlorophenol was reduced

by 40 percent, while the capacity for 2,4,6-trichlorophenol decreased by 25 percent. When present in the anionic form, at a pH of 9.1, and at the same equilibrium concentration of 1.0×10^{-8}, the carbon capacity for 2,4-dichlorophenol was reduced by 51 percent, while the capacity for 2,4,6-trichlorophenol decreased by only 20 percent. In general, 2,4,6-trichlorophenol competed more strongly for the carbon surface than 2,4-dichlorophenol (Snoeyink et al., 1977).

The competitive adsorptive effects of four phenolic compounds, phenol, pyrocatechol, o-aminophenol, and resorcinol, on the activated carbon sorptive capacity for formic, acetic, propionic, butyric, hexanoic and octanoic acids were investigated by Huang and Steffens (1976). However, their data is questionable since the concentration of the acids were monitored using the COD test while the phenols were measured using the aminoantipyrene test. In addition, a contact period of only 12 hours was used which is generally insufficient for the attainment of equilibrium. Taking the inadequacies of the analytical and experimental procedures utilized by Huang and Steffens (1976) into consideration, nevertheless they observed that the phenolic compound were capable of displacing some of the already adsorbed volatile fatty acids.

Other researchers have investigated the treatment of phenols present in several industrial discharges. McCrodden (1974) utilized activated carbon adsorption in the treatment of a refinery wastewater bearing and average of 21 mg/ℓ of phenol and reported a 99.9 percent reduction of the phenol in the effluent. In the treatment of a 3000 mg/ℓ phenol bearing "aircraft paint stripping wastewater", Kroop (1973) reported a phenol removal efficiencies of 99.88 and 99.997 percent from a continuous flow system utilizing wastewater carbon contact periods of 75 and 100 minutes respectively. Based on a survey of the available literature data on the removal of phenol from industrial wastewater, Lanonette (1977) reported a carbon adsorption capacity for phenol ranging from 0.09 to 0.4 g phenol/g

activated carbon. Hager (1974) surveyed the carbon adsorption data reported for the removal of phenol from industrial wastewaters and in all cases but two, phenol removal efficiencies exceeding 99 percent were observed (see Table 12).

Table 12. Adsorption of Phenol from Industrial Wastewaters (Hager, 1974)

Source	Phenol Concentration Following Filtration mg/ℓ	Following Adsorption mg/ℓ	Percentage Reduction
Alkalies & Chlorine	36.0	0.001	99.997
Dyes, Dye (cyclic) Intermediates & Organic Pigments	5.0	0.01	99.800
Industrial Organic Chemicals	0.52	0.05	90.380
	0.12	0.003	97.500
	0.313	0.001	99.681
	11.30	0.001	100.000
Industrial Inorganic Chemicals	4800.0	0.25	99.995
Plastics Materials, Synthetic	3.7	0.013	99.65
Resins & Non-Vulcanizable	26.5	0.005	99.981
Elastomere	1.2	0.001	99.917
Explosives	16.6	0.023	99.861
Petroleum Refining	40.0	0.001	99.998
Paving Mixtures & Blocks	6.68	0.001	99.985

Aerobic Biological Treatment of Phenol Bearing Wastewaters

Phenols have been known to degrade in biological treatment systems for some time. As early as 1959, Graves reported on the reduction in the phenolic content of an industrial waste in the unit operations and processes utilized in the treatment of domestic sewage. One hundred pounds of phenol were introduced daily to a domestic sewage treatment plant at a flow of 70 gpm. A material balance on the phenol across the treatment processes revealed that two thirds of the phenol was removed between the point of phenol introduction into the sewer and the point of entry into the sewage treatment plant. Of the remaining phenol, 5 - 10 percent were removed in the Imhoff tank, 80 - 90 percent was absent from

the trickling filter effluent, and an additional 5 percent was removed in the final settling tank. Overall an 85 - 90 percent phenol reduction was reported for the system (Graves, 1959). It was not clear from this work, however, whether the mechanisms responsible for phenol reduction were more adsorptive in nature or whether actual biooxidation was occurring.

Bio-Oxidation of Phenols. Bayly and Wigmore (1973) utilized mutant strains of Pseudomonas putida to determine the metabolic pathways of phenol and cresol biooxidation. These researchers concluded that the selected strain of bacteria was able to metabolize phenol through the following stages: (a) phenol was converted to catechol (a reaction intermediate in the bacterial metabolism of phenol). (b) Through the meta fission of the benzene nucleus, catechol was converted to 2-hydroxy-6-keto-2, 4-heptadienoate and 2-hydroxy-5-methylmuconic semialdehyde. Two pathways for the metabolism of 2-hydroxymuconic semialdehyde have been postulated and are detailed in Figure 2.

Further investigations, with particular emphasis on the metabolism of the products of ring fission, revealed that the mutant strain of interest was capable of metabolizing phenol in three different ways: (a) catechol undergoes meta fission which results in 2-hydroxymuconic semialdehyde which is then metabolized to 4-oxalocrotonate; (b) 2-hydroxymuconic semialdehyde is converted to 2-keto-4-pentenoate; (c) phenol is converted to catechol through ortho rather than meta fission. This metabolistic phenomenon may persist if the other two pathways are blocked (Bayly and Wigmore, 1973).

Using two strains of pseudomonas grown with phenol, Dagley and Gibson (1964) prepared cell extracts capable of metabolizing catechol. Based on their results, they postulated a metabolic pathway (Equation 12) whereby catechol was metabolized to 4-hydroxy-2-oxavalerate, which was further metabolized to acetaldehyde and

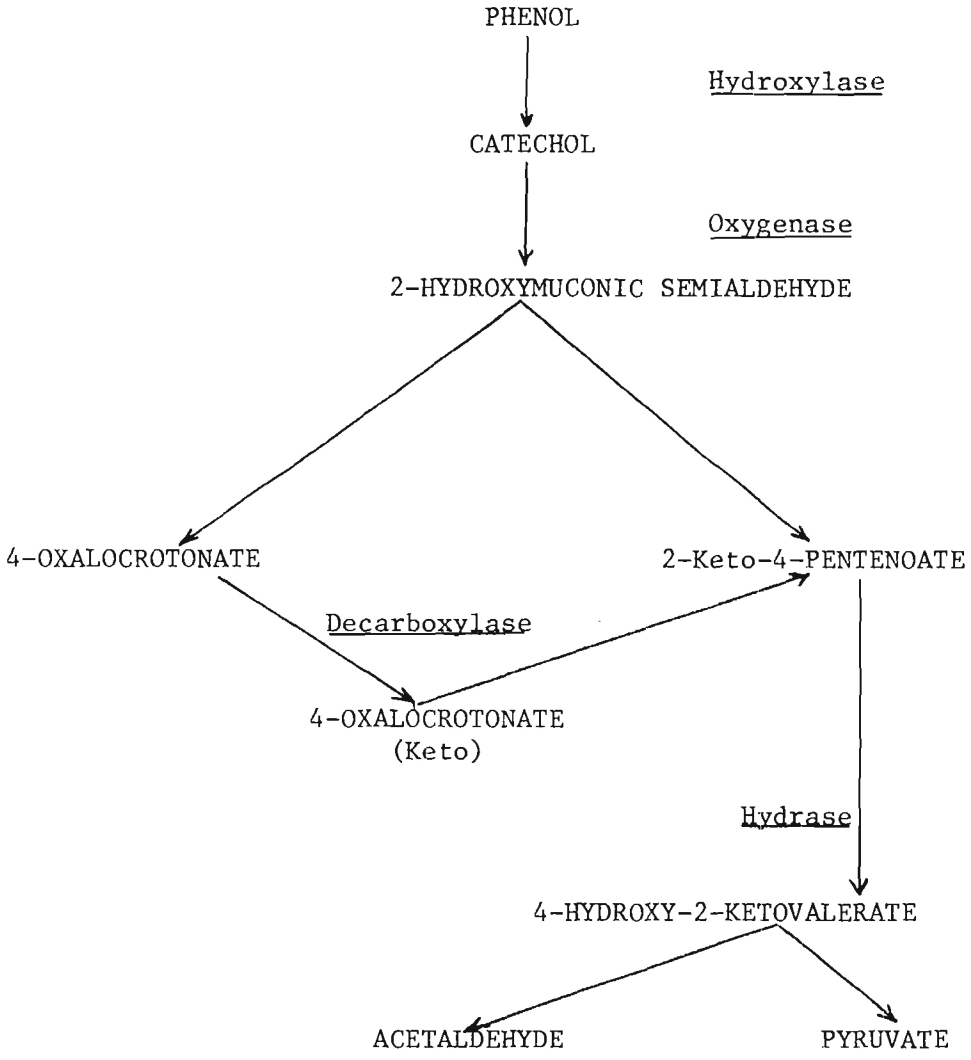
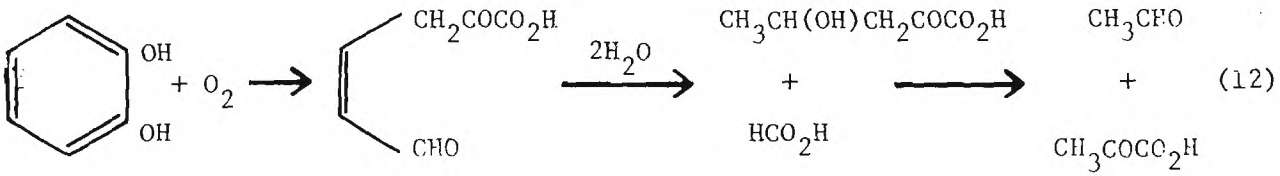


Figure 2. Aerobic Metabolism of Phenol
(Bailey and Wigmore, 1973)

pyruvate. For each micromole of enzymatically formed 4-hydroxy-2-oxovalerate, one micromole of each of acetaldehyde and pyruvate was produced.



(12)

Phenol has been reported to exhibit substrate inhibition characteristics when present at higher concentrations (Hill and Robinson, 1975). Where substrate inhibition is evident, the growth rate will increase with increasing substrate concentrations until the substrate concentration becomes inhibitory, at which time the growth rate will decline to a stage where the substrate concentration becomes toxic to the organism. Haldane (1965) propsed a kinetic model for substrate inhibited reactions which, generally describes the case of competetive inhibition by the substrate itself. At sufficiently high concentrations of the substrate, the enzyme functional groups are weakly bound to a particular substrate molecule, with the other available groups attached to other substrate molecules, giving rise to an EEJ complex. This mechanism is illustrated by Equation 13:

$$\mu = \mu_{max} \; S/(Ks + S + S^2/Ki) \qquad (13)$$

where μ is the specific growth rate; μmax is the maximum specific growth rate for the organism and medium; S is the concentration of the limiting nutrient; and Ks and Ki are constants.

Edwards (1970) further classified inhibition kinetic functions into five categories (Equations 13-15), with the model given by Equation 13 being the first and simplest.

$$\mu = \mu_{max} \; S[1+(S/K]/[S+K_s+(S^2/K_i)] \qquad (14)$$

$$\mu \quad \mu_{max}\, S/[S+K_s+(S^2/K_i)[1+(S/K)] \qquad (15)$$

$$\mu = \mu_{max}\, S\exp(-S/K_i) / (S+K_s) \qquad (16)$$

$$\mu = \mu_{max}\, [\exp(-S/K_i) - \exp(-S/K_s)] \qquad (17)$$

These equations predict an increase in growth rate, μ, until a maximum value is achieved. The maximum growth rate at which inhibition occurs, μmi, has been defined by Andrews (1971) as occurring when $S = Smi = (K_i K_s)^{0.5}$; where Smi is the substrate concentration resulting in inhibition.

These kinetic inhibition models have been applied to the experimental data obtained from pure and mixed cultures in continuous and batch reactors using phenol as the limiting substrate. Hill and Robinson (1975) utilized a pure culture of Pseudomonas patida in batch and continuous operations to describe the previously discussed kinetic equations. Phenol concentrations in the range of 185 to 700 mg/ℓ were used.

As expected, the growth lag times increased with increasing phenol concentration in the batch culture. A lag time of approximately 10 hours was observed at a phenol concentration of 200 mg/ℓ while the lag time significantly increased at higher phenol concentrations (seven days at a phenol concentration of 703 mg/ℓ). Andrews (1971) demonstrated, using the Haldane functions, that the lag time was a function of innoculum size. Following the lag period, growth followed typical logarithmic patterns. Utilizing the Haldane (1965) and Edwards (1970) models, Hill and Robinson (1975) determined the kinetic constants μ_{max}, K_s, K_i and Y that best fit their experimental data (see Table 13).

Howell and Pawlowsky (1973) also studied the kinetics of microbial growth using phenol as a substrate and a mixed bacterial culture derived from soil and activated sludge sources. However, because of the controversy concerning wall

Table 13. Kinetic and Rate Constants for the Bio-Oxidation of Phenol (Hill and Robinson, 1975)

Microbial System		K_s mg/ℓ	K_i mg/ℓ	μ_{max} (hr^{-1})	Y
P. putida IATCC17484)	(a)	1	470	.534	0.52 ± 0.08
	(b)		840	.481	
Spherical Coccoids in	(a)	41.2	383	.29	.545 ± 0.07
Activated Sludge	(b)	10.7	546.6	.185	
Bacterium NCIB(8250)	(a)	1	110	.29	0.59

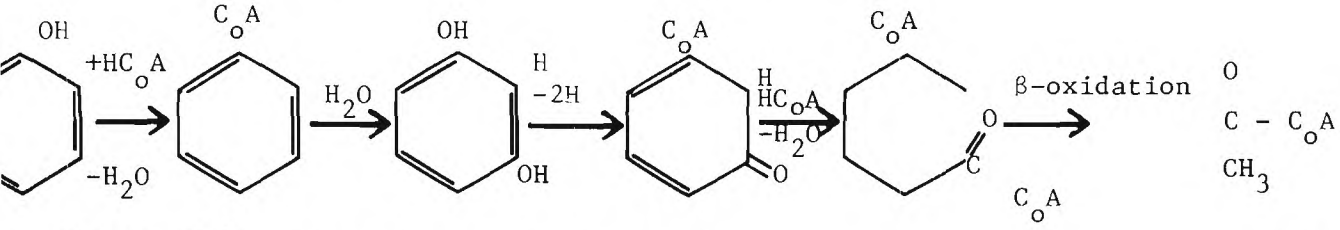
(a) Values obtained using the Haldane Model
(b) Values obtained using the Edward's Model

growth in continuous cultures, only batch studies were conducted. These researchers utilized non-filamentous and filamentous cultures with detention times of six and four hours, respectively. The range of phenol concentrations used was as high as 1000 mg/ℓ. The experimental results yielded growth yield coefficients of 0.545 and 0.616 0.070 for the non-filamentous and filamentous cultures, respectively. The data in Table 14 represent the kinetic parameters obtained from fitting the batch experimental data to the five kinetic models given by Equations 13 through 17.

Table 14. Kinetic Parameters for the Bio-Oxidation of Phenol by Non-Filamentous and Filamentous Cultures (Howell and Pawlowsky, 1973)

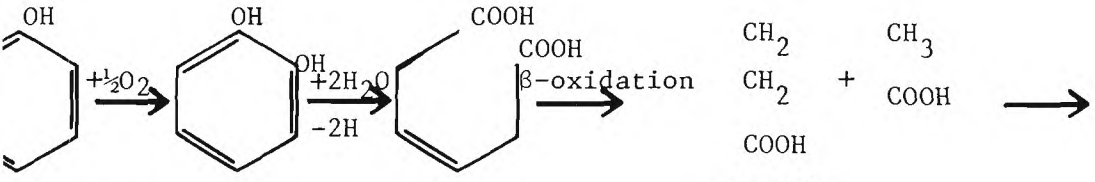
Function Fitted Equation No	μ_{max} (hr^{-1})	K_s (mg/ℓ)	K_i (mg/ℓ)	K (mg/ℓ)
		Non-filamentous Culture		
13	0.260	25.4	173.0	371.0
14	1.01	160.0	14.7	10,756.0
15	0.251	23.7	190.5	
16	0.185	10.7	546.3	
17	0.164	16.85	611.6	
		Filamentous Culture		
13	0.223	5.86	934.5	255.0
14	0.660	86.70	34.2	15,220.0
15	0.220	5.20	1020.0	
16	0.205	2.00	1564.0	
17	0.205	16.07	1550.0	

Aerobic Treatment of Phenolic Wastewaters. McKinney et al. (1956) used continuous flow activated sludge units to study the efficiency of bio-oxidation of phenol and various other aromatic compounds. Phenol removal efficiencies of 39 and 32 percent were obtained for synthetic feed solutions containing 250 and 500 mg/ℓ of phenol, respectively. The aeration time utilized in their studies was 12 hours. The phenol acclimated activated sludge unit also rapidly metabolized resorcinol, pyrogallol, benzoic acid and benzyl alcohol to approximately the same extent of conversion as was observed for phenol. Catechol, on the other hand, showed more resistance to metabolism yielding only a 13 percent conversion. Based on the experimental data, McKinney et al. (1956) concluded that phenol oxidation by activated sludge was related to fatty acid metabolism through β-oxidation (Equation 18) rather than by direct oxidation of the ring structure to catechol as was propsed by Stanier (1950) (Equation 19), Sala-Trepot et al. (1972) (Equation 20), and others.



citric acid cycle

protoplasm + CO_2 + H_2O (18)



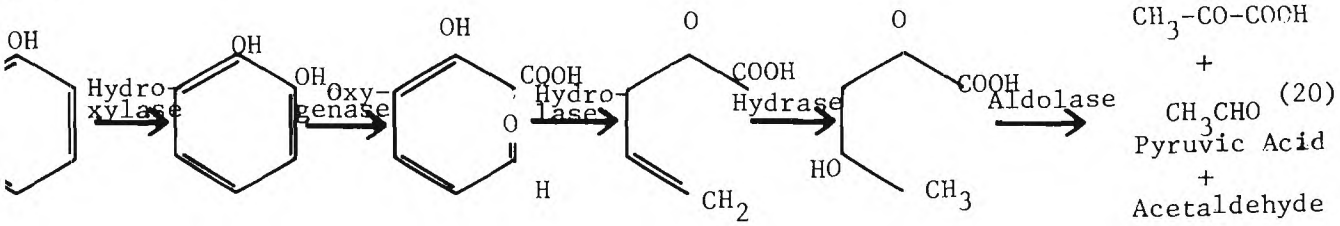
(19)

tric acid

ycle

protoplasm + CO_2 + H_2O

succinic acid



(20)

Adams (1973) reported on the use of single and multistage activated sludge processes in the treatment of a high strength phenolic wastwater. The influent concentration of total phenol averaged 3270 mg/ℓ while even under the best controlled conditions, effluent concentrations of phenol are expected to be less than 0.1 mg/ℓ only 40 percent of the time for a normally loaded activated sludge system (0.1 to 0.3 F/M ratio). Capastany et al. (1977) reported similar results in the treatment of a high strength phenol bearing wastewater eminating from a chemical plant. The phenol in the raw wastewater accounted for 40 percent of the BOD_5 of the sewage and averaged around 1000 mg/ℓ in strength. Phenol removal efficiencies of 99.6 percent were reported.

The treatability of phenol bearing refinery wastewaters with batch and continuous flow bench scale activated sludge units was investigated by Mahmud and Thanh (1978). In the batch study, 90.8 percent phenol removal was attained after 10 hours of aeration and at a chemical oxygen demand (COD) to mixed liquor suspended solids (MLSS) ratic of 0.98 g/g. A similar phenol removal of 90.7 percent was achieved in the continuous flow unit utilizing an aeration time of 7 hours while the COD to MLSS ratio was 1.15 g/g. The same authors investigated the treatability of refinery wastewaters utilizing aerated lagoons. Their conclusions in general were that this mode of treatment could serve effectively for the pretreatment or post-treatment of such wastewaters, however, lagoons should not be used as the sole process for the purification of refinery wastewaters (Mahmud and Thanh, 1978). The data in Table 15 represent a summary of the performance characteristics of aerated lagoons in the treatment of refinery wastewaters.

Table 15. Biological Treatment of Petroleum Refinery Wastewaters Using Aerated Lagoons (Mahmud and Thanh, 1978)

Run	Aeration Period (day)	Phenol (mg/ℓ) Inf.	Eff.	% Effy.
1	3	21.2	1.9	90.7
2	5	20.4	1.3	93.5
3	7	19.7	1.2	93.7
4	10	21.0	1.2	94.1
5	12	18.5	1.0	94.6
6[b]	1	6.5	0.6	90.6
7[b]	3	8.2	0.6	92.8
8[b]	5	7.4	0.4	94.3
9[b]	7	7.3	0.3	94.6
10[b]	10	7.5	0.4	94.7

[b]Settled effluent of activated sludge unit

The activated sludge process and modifications thereof have been used in the treatment of the wastewaters emanating from coal conversion operations. The extended aeration activated sludge treatment of a coking plant effluent at Dominion Founderies and Steel Limited in Hamilton, Ontario yielded 99 percent removal of phenol for a feed phenol concentration ranging between 2.9 and 288 mg/ℓ utilizing an aeration time of 13.8 hours and a solids retention time of 41.4 days (Ganczarcyzk and Elion, 1978). Doubling the aeration time, however, resulted in an increase in the phenol removal efficency to 99.3 percent while the sludge age remained at 41.3 days. The treatment process, however, did not accomplish much removal of thiocyanate where the average removal was 52.5 percent, and no nitrification was achieved inspite of the fact that the high sludge age and elevated aeration temperatures maintained in the system should encourage nitrification (Ganczarcyzk and Elion, 1978).

Sack and Bokey (1978) reported on the treatment of coal gasification wastewaters using bench scale extended aeration activated sludge units. Overall 95 percent phenol removal was achieved when the feed phenol concentration was 1088 mg/ℓ for aeration times of 4 and 6 days. However, the process failed completely when the detention time in the aeration tank was reduced to 1.5 days. For the two aeration detention times of 4 and 6 days, the corresponding solids retention times were 18 and 15 days while the food to mass ratio was maintained at 0.18 and 0.13, respectively.

Lee et al. (1979) have reported on the use of a bench scale, tapered, fluidized bed bioreactor for the degradation of solutions of dissolved phenolic compounds. Their experimental data indicate that this process resulted in a reduction of the phenolic content of a synthetic waste from a feed level of 9 to 260 mg/ℓ down to an effluent concentration of about 0.025 mg/ℓ. In this study, anthracite coal was used as the contact medium.

The aerobic treatment of phenol bearing wastewaters has been demonstrated to be an effective means of phenol removal. In most cases, however, the residual phenol concentration in the treated effluents is in excess of receiving water standards and additional effluent polishing may be required. A troublesome and complicating feature of the aerobic treatment of these wastewaters, however, has been the process instability to variations in the composition and strength of these wastewaters (Sack and Bokey, 1978).

Of special interest in this study is the presence in coal conversion wastewaters of certain organic and inorganic constituents that exhibit toxic inhibition effects on the biological stability of the degradation of other constituents. Of principal interest, in this respect, is the thiocyanate, cyanide, phenol and ammonia antagonistic interaction. Thiocyanate which is poorly degraded in aerobic biological treatment exhibits a noticeable

inhibitory effect on the aerobic biodegradation of phenol (Valiknac and Neufeld, 1978), while cyanide, thiocyanate and phenol have been observed to inhibit the nitrification of ammonia even at hydraulic detention times exceeding 3 days and sludge ages on the order of 41 days (Ganczarczyk and Elion, 1978).

In a study on the purification of wastewaters emanating from coking and coal gasification plants, Juntgen and Klein (1977) presented data on the coinhibition of phenol, thiocyanate and ammonia during aerobic treatment. Phenol degradation was inhibited by concentrations of ammonia, thiocyanate and sulfide exceeding 1700, 250 and 25 mg/ℓ, respectively, while thiocyanate degradation was completely halted at levels of ammonia, thiosulfate and phenol of 1000, 100 and 25 mg/ℓ, respectively. Nitrification, on the other hand, was completely inhibited at levels of phenol, thiocyanate and cyanide as low as 50, 10 and 10 mg/ℓ, respectively.

Another issue of relevance in the evaluation of the effectiveness of aerobic treatment processes in the purification of phenol bearing wastewaters is the fact that in most studies the aminoantipyrene test has been utilized in the analysis for "Phenols". This test has been consistently used inspite of the fact that catechol, which has been reported to be an intermediate of the aerobic degradation of phenol, is not detected with this procedure.

Activated Carbon in Aerobic Biological Treatment. Pure cultures, may, in some instances, possess the potential of purifying wastewaters containing inhibitory compounds such as phenols at a faster rate than mixed cultures. However, the feasibility of such a treatment mode is unlikely. When faced with fluctuating concentrations of toxic and inhibitory substances, physical processes, such as activated carbon adsorption, may be assimilated into the

biological system in order to stabilize the process and reduce the large volume of the aeration tank otherwise needed to dilute the fluctuations.

In wastewater treatment, the adsorption stage has generally been regarded as a separate columnar phase of treatment designed to polish the effluent from the secondary biological processes. It was only recently that researchers have started appreciating the benefits realized from the combination of the two processes in one single reactor configuration. This has been accomplished through the addition of powdered activated carbon (PAC) to the activated sludge process (Robertaccio et al., 1972). Zobell (1937) and Heukelekian and Heller (1940) noted that the presence of solid surfaces enhanced the physiological activity of bacteria, while King and Verma (1968) also reported on the increased rate of degradation of organic matter in the presence of solid surfaces.

The addition of powdered activated carbon to activated sludge has been practiced for several years (Adams, 1973; Scaramelli and DiGiano, 1973). Researchers have cited a number of benefits gained by the addition of PAC to the activated sludge system when the performance data is compared to that obtained from the activated sludge system alone. These benefits include an increase in the removal of soluble organics as well as an enhancement of process stability. DeWalle and Chian (1977) summarized the benefits achieved by adding powdered activated carbon to the activated sludge process as being:

a. Increased stability against toxic organic shock loads;

b. Removal of color and odor;

c. Reduction of oxygen demand in receiving water;

d. Lowered residual effluent toxicity to fish;

e. Reduction of foaming in aerator;

f. Increased stability against heavy metal shock loads;

g. Increased capacity of sludge dewatering units;

h. Increased capacity of secondary clarifiers;

i. Reduction in effluent suspended solids

As detailed above, the presence of PAC in activated sludge results in a number of distinct advantages. Generally, however, improving the effluent water quality beyond the capabilities of conventional biological treatment and enhancing the treatability of wastewaters that inhibit or toxify biological treatment systems are the primary objectives of the utilization of PAC in secondary biological treatment.

Nayor and Sylvester (1979) subjected a continuous culture of E. coli to phenol pulse concentrations of 1 to 1000 mg/ℓ and monitored the transient behavior. No significant change in total organic carbon (TOC) or MLSS was noted for an impulse of 100 mg/ℓ phenol, however, a noticeable decrease in MLSS and increase in TOC was observed for impulse concentrations of 500 and 1000 mg/ℓ. The same procedures were again repeated, however, in this instance, powdered activated carbon was added with the phenol. No enhancement of biological growth was observed, however, although a definite increase in the efficiency of the reactor in removing TOC was noted.

Adams (1973) monitored the performance of a municipal wastewater plant that received 70% of its flow from an industrial textile dyeing and finishing mill. Powdered activated carbon was added at a concentration of 900 mg/ℓ while the average influent BOD was 150 mg/ℓ. The addition of PAC significantly stabilized the effluent quality and increased average BOD removals from 72% to 89%.

Ferguson, Keay, Merrill and Benedict (1976) utilized the PAC-biological contact stabilization process to determine the benefits of PAC on the biological

process in terms of effluent quality and overall hydraulic retention time. A PAC concentration of 150 mg/ℓ was sufficient to stabilize the biological process during toxic shock loadings of trichlorophenol. Heavy metal uptake was also noted in the presence of PAC. The enhancement in sludge settling properties and the allowance of reduced contact detention time and low recycle ratios were also evident because of the addition of powdered activated carbon.

Grieves (1977) reported on the results of a pilot plant study at the Amoco refinery in Texas City, Texas. The existing activated sludge plant was treating a waste having a phenol concentration of 3.95 mg/ℓ and achieving an effluent of 0.019 mg/ℓ, 99.5% removal efficiency. The addition of only 25 and 50 mg/ℓ powdered activated carbon resulted in a reduction of the effluent phenolics to 0.006 and 0.002 mg/ℓ, respectively.

While the benefits realized from the addition of PAC to a biological process have been clearly demonstrated, the process theory of the physico-biological phenomenon remains somewhat controversial. It is apparent that there is much more involved than simply biological oxidation and physical adsorption. The activated carbon and biomass simultaneously physically and biologically remove degradable and adsorbable compounds. The two operations have been described as being synergistic (Frohlick and Vollstedt, 1976).

Scaramelli and DiGiano (1973) conducted a treatability study on a primary effluent from the municipal treatment plant at Amherst, Massachusetts using the PAC activated sludge process. The following conclusions were made: a. Biological growth was not enhanced by the addition of powdered activated carbon and improved substrate removal was totally due to adsorption. b. There was no significant increase in oxygen uptake rates when powdered activated carbon was added to the activated sludge system.

Hals and Benedek (1973) exploited the same topic, and arrived at a similar conclusion to that of Scaramelli and DiGiano (1973). They postulated that the additional decrease in TOC was a result of physical adsorption onto the activated carbon surface. On the other hand, Kalinske (1972) indicated that an increase in COD removal was a result of enhanced biological uptake in the presence of powdered activated carbon. These conclusions were based on higher oxygen uptake rates and some increase in MLSS.

Robertaccio (1976) investigated the treatment of three substrates; phenol, isopropyl alcohol and acetic acid with the PAC activated sludge process. The selected substrates varied quite significantly with respect to adsorbability and biodegradability. It was found that the presence of PAC only slightly enhanced the removal of the relatively non-adsorbable acetic acid, whereas quite significant incremental reductions in phenol and isopropyl alcohol were observed. Again, using phenol as the substrate, Robertaccio (1976) also concluded that the degree of enhancement in substrate removal is related to the carbon concentration in the system.

Koppe et al. (1974) studied the fate of a slowly degradable substrate, pentaerythrital in the activated sludge process. Increased removal and a more rapid acclimation was observed when a single and initial dose of powdered activated carbon was added to the system at a concentration of 30,000 mg/ℓ.

These observations certainly reveal the complexity of this synergistic biological-physical process. Perhaps it is even more complex than it appears. Perotti et al. (1978) postulate that there are four distinct processes occurring in the PAC-activated sludge system that must be considered.

1. adsorption on the surface of the activated carbon;
2. biological adsorption and degradation - the spent carbon settles with the spent sludge with the adsorbed pollutants;
3. activation of the carbon by biological action. The microorganisms present around the carbon desorb, degrade and digest the pollutants, thereby reactivating the surface sites for further adsorption;
4. improved solids settling in the final clarifier gives lower BOD and suspended solids in the effluent.

A review of the pertinent literature revealed that the activation of the carbon surface by biological action; otherwise known as biological regeneration, is still a somewhat controversial topic. Initial studies in this direction revealed that the presence of PAC in activated sludge enhanced the bio-oxidation activity. Further research was promulgated towards the investigation of the purification of the difficult to treat dye wastewater in a PAC-activated sludge process. Enhanced activity, based on color reduction, was also evident.

Parkhurst et al. (1967) utilized columns packed with granular activated carbon and noted the effects from an induced microbial population. It was concluded that the reduction of organic matter was increased by the presence of a biological mass. Burns and Shell (1973) investigated the adsorptive characteristics of a two-stage contactor treating coagulated sewage. The adsorptive capacity of the first stage was found to be approximately five times higher than the capacity resulting from adsorption alone.

DeWalle and Chian (1977) used batch PAC-activated sludge units and columns of activated carbon to investigate the biological regeneration of the carbon surface. The batch units resulted in an increase in the apparent maximum adsorptive capacity as the cell residence time was increased. They

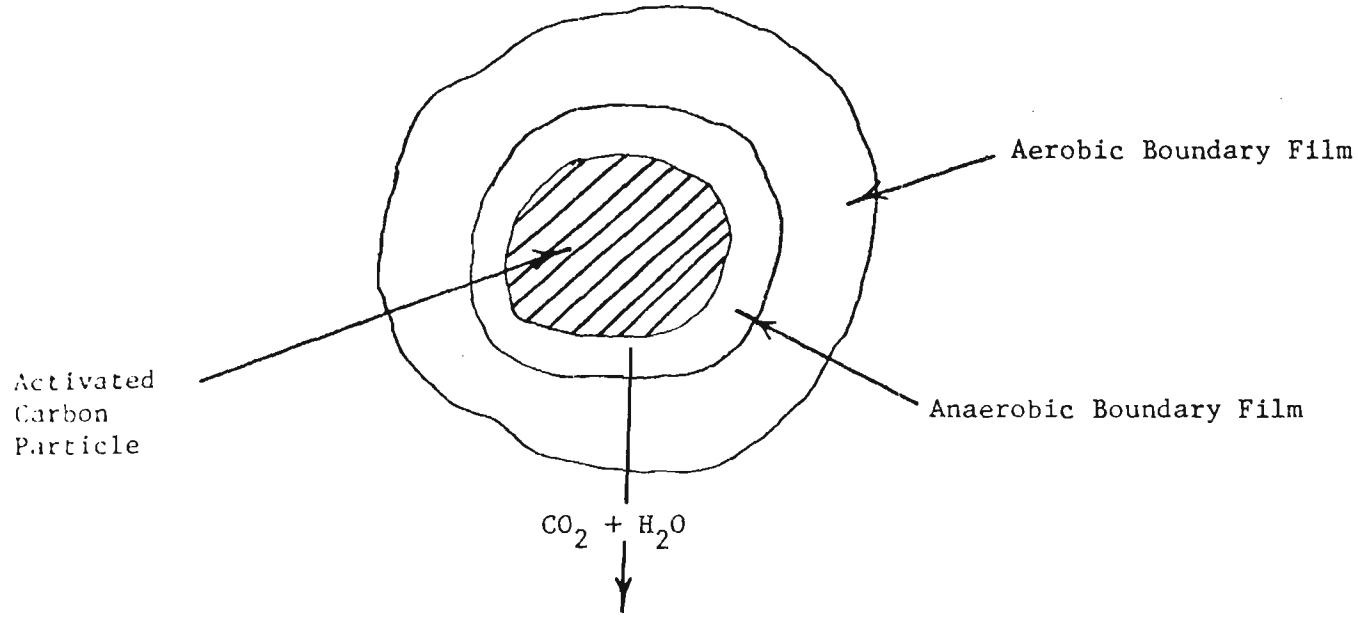
postulated that since the biomass concentration to PAC concentration ratio increases with increasing cell residence time, a more effective regeneration of the carbon surface can occur. The columns of activated carbon, on the other hand, showed a decrease in the maximum adsorptive capacity. It was concluded that biological processes are responsible for this phenomenon.

Although the mechanism of biological regeneration is still unknown, two theories are suggested: 1. regeneration from the removal of adsorbable organics that are slowly biodegradable. 2. regeneration caused by the exchange of adsorbed refractory organics with biodegradable organics directly after batch feeding.

Their hypotheses are explained using a two-layer biological growth theory (Figure 3). The carbon particle is encompassed by an inner anaerobic layer which is surrrounded by an aerobic biological surface. A large organic molecule is adsorbed onto the carbon surface which is then biodegraded to produce CO_2 and H_2O. Intermediates and other degradation products are further absorbed onto the carbon interstices for subsequent biooxidation.

Perotti and Rodman (1974) studied the catalytic effect of activated carbon on an aerobic biooxidation treatment process using phenol and glucose as substrates. As previous research had shown, the presence of activated carbon enhanced the aerobic activity and sustained a high biooxidation level. The following hypothesis was presented: The surface area of activated carbon, as much as 1000 m^2/g, is composed of micropores with diameters on the order of 10-1000 anstrom units. Bacterial cells characteristically have diameters larger than 1000 anstrom units. Biological desorption, as a result of bacteria migration, is therefore, probably limited due to the size relationship. The microbes do, however, have the capability of producing digestive enzymes, approximately 10 angstrom units in diameter, which could diffuse

Figure 3. Two Layer Biological Growth



through the porous carbon structure. By way of an enzyme-substrate complex, the substrate or organic material is desorbed and degraded biologically.

Anaerobic Biological Degradation of Aromatics

Anaerobic treatment has commonly been utilized in waste treatment for the degradation of complex organic solids such as the cellular matter wasted from activated sludge plants and the cellulossic and hemicellulossic materials present in solid waste. A simplistic description of the degradation pattern of these materials in an anaerobic environment may be regarded as consisting of a four stage process where: (a) in the first stage of the process, the enzymatic hydrolysis of these solids to simpler and soluble organic compounds occurs; this stage is followed by (b) the conversion of the soluble organic matter to organic acids by acetogenic bacteria; (c) the organic acids are then converted to soluble gaseous products (d) which are later released from the aqueous phase to the gaseous phase (Jeris and McCarty, 1965; McCarty, 1966; Toerin and Hattingh, 1969).

The anaerobic activated carbon filter process developed in this study was conceived of for the treatment of wastewaters bearing soluble organics and as such no emphasis is placed in this report on the hydrolysis of complex organic solids.

Anaerobic Fermentation of Soluble Organic Matter

The soluble organic matter originally present in the wastewater or produced as a result of the enzymatic hydrolysis of complex organic solids provide the substrate for the acetogenic bacteria. Toerin et al. (1971) suggested that conversion of carbohydrate substrates to the organic acids may be accomplished through one or more metabolic pathways, as shown in Figure 4. The proposition of these pathways was based on a quantitative ecological study of the bacteria present in the acetogenic phase of anaerobic

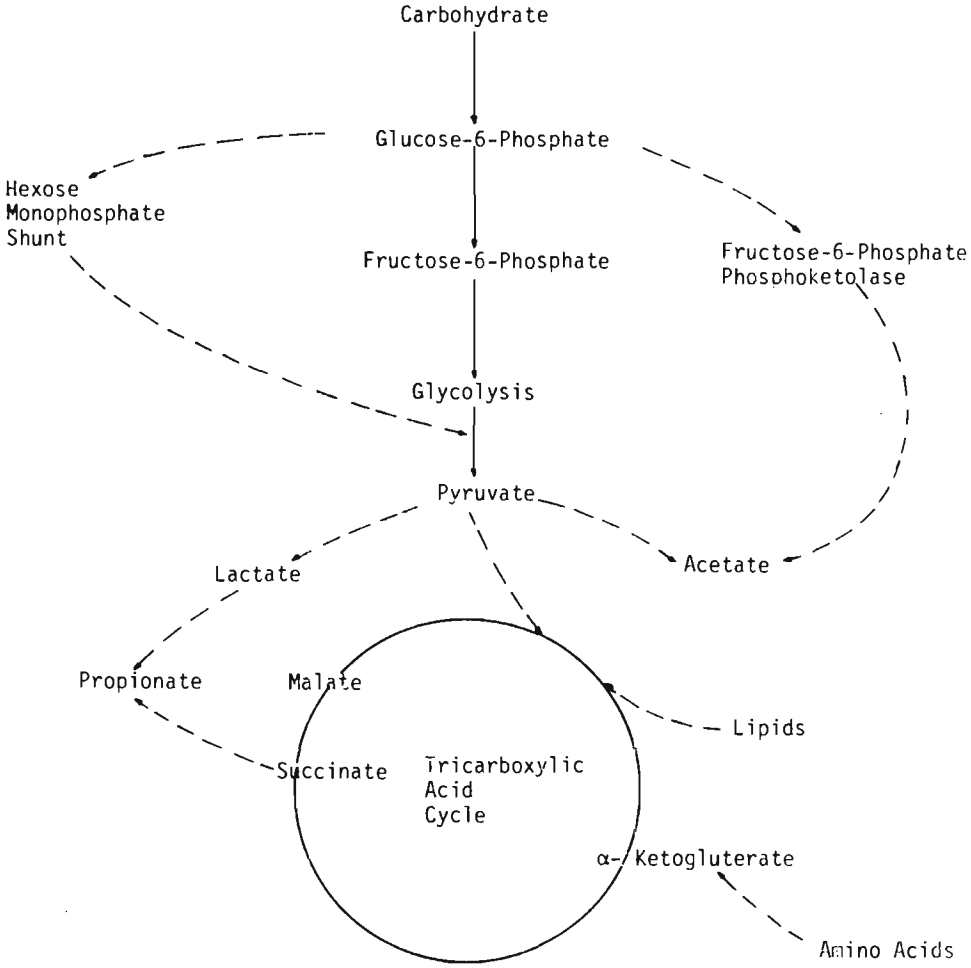


Figure 4. Intracellular Substrate Flow in Acetogenic Bacteria

digestion. The presence of several different groups of non-methanogenic bacteria was demonstrated and their characteristic end product patterns were determined. The organic acids that were produced were generally acetic, propionic, and lactic acid. Studies conducted on enrichment cultures selected from these bacteria indicated that glycolysis of the hexose monophosphate shunt, the fructose-6-phosphate phosphoketolase pathway, amino acid metabolism and the tricarboxylic acid cycle were either totally or partially active in these bacteria.

Earlier work with pure or nearly pure cultures of methanogenic bacteria indicated that these organisms are greatly restricted in their substrate specificity. Only the lower normal fatty acids containing from one to six carbons and the normal and isoalcohols containing from one to five carbons and the three gases H_2, CO and CO_2 were utilized as substrate by the methanogens (Bryant et al., 1967). Essentially all of this information on normal and isoalcohols serving as substrates to methanogens, with the exception of methanol, was based on the studies of M. Omelianski (Bryant et al., 1967). In view of their findings, Bryant et al. (1967) suggested that it is doubtful that methanogenic bacteria are able to attack alcohols other than methanol. They also speculate that fatty acids are anaerobically decomposed with the production of H_2 by non-methanogenic rather than methanogenic microorganisms.

In conclusion, it appears that the end products of the acetogenic stage of anaerobic processes that serve as substrate for the methanogenic organism consist primarily of acetate, H_2, CO_2 and methyl alcohol.

The major source of methane gas resulting from the fermentation of organic substances has been attributed to the cleavage of acetic acid (McCarty, 1965) as illustrated in Figure 5. The only other organic acid

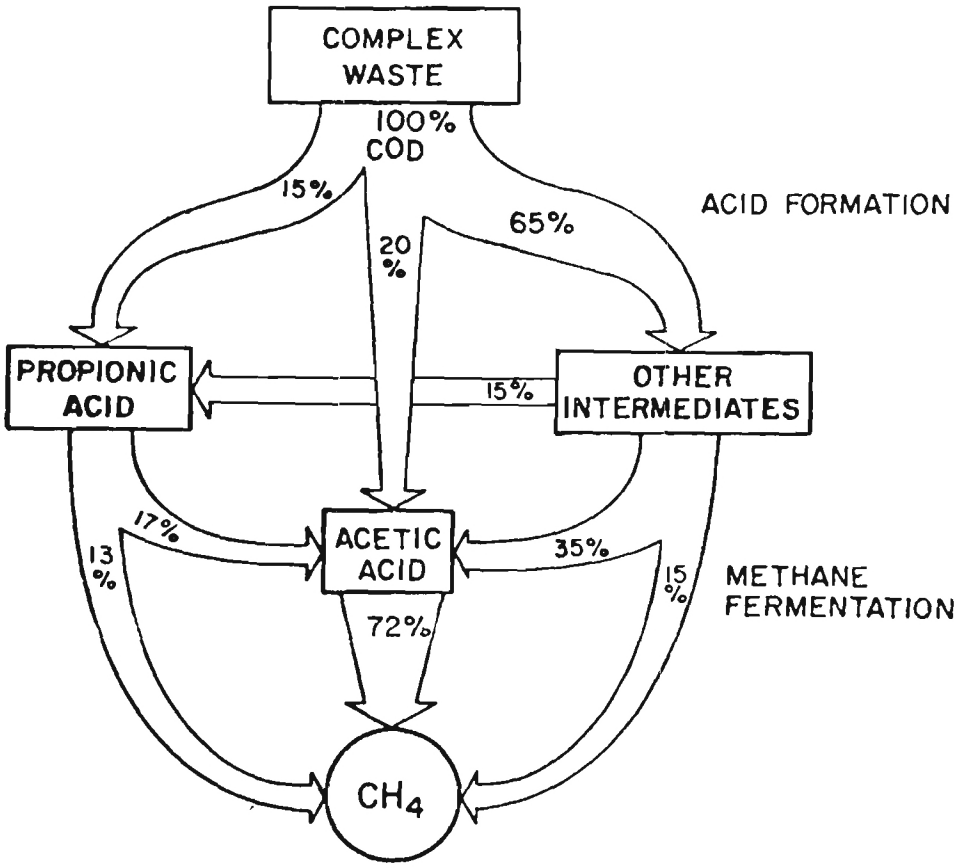


Figure 5. Pathways in methane fermentation of complex wastes such as municipal waste sludges. Percentages represent conversion of waste COD by various routes (McCarty, 1965).

that methanogenic bacteria appear to utilize is formic acid (Bryant et al., 1967). However, the importance of this reaction on methane production does not appear to be great since formic acid is not usually present in the anaerobic digestion system. Methanol is another source of methane. Stadtman and Baker (1951) reported that methane was formed directly from the reduction of methanol.

Buswell and Solo (1978) reported on three possible mechanisms for the fermentation of acetic acid: (a) decomposition to hydrogen and carbon dioxide with the subsequent reduction of carbon dioxide to methane by hydrogen; (b) direct reduction of the carbon dioxide to methane by hydrogen and (c) simple decarboxylation. The first mechanism was suggested by the earlier work of Omelianski and Sohngen as cited by Buswell and Mueller (1952). According to Levine (1938), Sohngen studied the utilization of simple fatty acids in mixed cultures and observed that these acids could be converted to methane and carbon dioxide. It was also reported that Sohngen observed the same culture could utilize hydrogen and carbon dioxide to form methane (Equation 21):

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (21)$$

The second mechanism was proposed by Barker (1956) which involves the direct reduction of CO_2 without the necessity for the presence of free hydrogen as exemplified by the fermentation of ethyl alcohol by Methanobacterium Omelianskii where the ethyl alcohol serves as the hydrogen donor and carbon dioxide serves as the hydrogen acceptor (Equation 22):

$$2CH_3CH_2OH + CO_2 \rightarrow 2CH_3COOH + CH_4 \qquad (22)$$

Equation 22 indicates that acetate may be derived from alcohol while the methane carbon originates from carbon dioxide. This reaction mechanism was confirmed by Stadtman and Barker (1949) using C^{14}-labeled CO_2.

As for the third mechanism, similar experiments by Stadtman and Barker (1949, 1951) using C^{14} labeled CO_2 and acetic acid, confirmed that the resulting methane, which was only slightly labeled, was primarily derived from the methyl group of acetic (86-94 percent) acid and that the CO_2 resulted primarily (96-98 percent) from the carboxyl group.

The anaerobic fermentation of the three volatile acids: formic, acetic and propionic has been studied by a number of researchers separately for each of the three organic acids since each acid apparently required a different species of methane forming bacteria. For example, it was observed that the complete fermentation of propionic acid to methane required two different species of organisms. The first species accomplished the conversion of propionic acid to acetic acid while the other specialized in the conversion of acetic acid (McCarty, 1965).

Equations 23-27 for the methane fermentation of each acid are give below:

Formic Acid: $4HCOOH \rightarrow CH_4 + 3CO_2 + 2H_2O$ (23)

Acetic Acid: $CH_3COOH \rightarrow CH_4 + CO_2$ (24)

Propionic Acid: $4\ CH_3CH_2\ COOH + 2H_2O \rightarrow 3CH_4 + CO_2 + 4CH_3COOH$ (25)

$4\ CH_3COOH \rightarrow 4\ CH_4 + 4CO_2$ (26)

$4CH_3CH_2COOH + 2H_2O \quad 7CH_4 + 5CO_2$ (27)

In addition, the anaerobic fermentation of methanol which, as Barker (1956) indicated, may be used by some of the acetate fermenting species results in the formation of methane according to the Equation 28:

$$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O \quad (28)$$

whereas the metabolism of ethanol by Methanobacillus Omelanskii involves the interspecies hydrogen transfer in which two organisms are mutually dependent (Mah et al., 1977), M. Omelianskii which is an ethanol oxidizing hydrogen producing bacterium (S organism) and Methanobacterium MPH which is a hydrogen-utilizing methanogenic bacterium (Bryant et al., 1967). The reactions proceed as follows (Equations 29-31):

$$2CH_3CH_2OH + 2H_2O \xrightarrow{\text{s Organism}} 2CH_3COOH + 4H_2 \quad (29)$$

$$4H_2 + CO_2 \xrightarrow[\text{MOH}]{\text{Methanobacterium}} CH_4 + 2H_2O \quad (30)$$

$$\text{net: } 2CH_3CH_2OH + CO_2 \rightarrow 2\ CH_3COOH + CH_4 \quad (31)$$

The S organism is inhibited by the hydrogen it produces, while Methanobacterium utilizes the hydrogen as a substrate and thus it displaces the equilibrium by oxidizing the hydrogen through the reduction of carbon dioxide to methane. This synergistic interaction allows the two organisms to survive in an ethanol-carbonate medium (McBride and Wolfe, 1971).

Methane producing organisms have been detected as sarcinae, rods, and cocci and were initially regarded as non-motle, non-spore forming and gram negative (Buswell, 1954). However, a most unusual representative, Methanococcus vaniellii is highly motile (Stadtman and Barker, 1951). These organisms are obligate anaerobes with great sensitivity to oxygen. The substrates of all these organisms appear to be extremely limited (see Table 16).

Anaerobic Degradation of Aromatics

Few literature references are presently available on the anaerobic degradation of aromatic compounds. The fate of benzoate under strict anaerobic conditions has been studied by several investigators (Clark and Fina, 1951; Fina and Fiskin, 1960; Ferry and Wolfe, 1976).

Table 16. Substrate Requirements of Methanogenic Organisms in Pure Cultures (Zeikus, 1977)

Species Name	Substrate serving as sole electron donor for both Methanogenesis and Growth
Methanobacterium arbophilicum	Hydrogen
Methanobacterium formicium	Hydrogen or formate
Methanobacterium ruminantium	Hydrogen or formate
Methanobacterium mobile	Hydrogen or formate
Methanobacterium thermoantotrophicum	Hydrogen
Methanococcus vannieli	Hydrogen or formate
Methanosarcina barkeri	Hydrogen or methanol
Methanospirillum hungatti	Hydrogen or formate

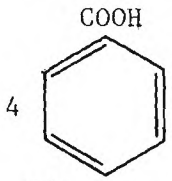
Clark and Fina (1951) demonstrated that the biodegradation of benzoic acid is possible under strict anaerobic conditions. It was observed that only 25 percent of the methane produced originated from carbon dioxide while the remaining 75 percent of the methane resulted from the degradation of benzoic acid through some unknown mechanism. Based on this study, it was concluded that the aerobic and anaerobic pathways that result in the cleavage of the benzene ring in benzoic acid may be different since an anaerobic culture adapted to benzoate did not result in the decomposition of catechol and protocatechuic acid. During the aerobic cleavage of the benzene ring in benzoate, benzoic acid is transformed to catechol prior to ring fission.

Ferry and Wolfe (1976) demonstrated that a methanogenic population of bacteria did not cleave the parent benzene ring in benzoate for this function. The metabolic intermediates that were identified were acetate, formate, hydrogen and carbon dioxide. From degradation studies on a uniformly ^{14}C ring labeled benzoate, it was noted that the resulting radioactivity was equally divided between methane and carbon dioxide. Experimentally it was determined that approximately 25 percent of the methane produced during the degradation of benzoate was derived from the reduction of carbon dioxide.

The addition of o-chlorobenzoic acid inhibited the degradation of benzoate but not the conversion of acetate to methane (Ferry and Wolfe, 1976). Two methanogenic organisms were later isolated from this culture; neither organism was able to degrade benzoate thus confirming that the methanogenic bacteria served as terminal organisms of a metabolic food chain composed of several organisms. The two methanogens that were isolated were methanobacterium formicium and methanospirillum hungattii. Methanosarcina barkiri, a known acetate utilizer, was never observed in benzoate degrading cultures.

Its absence led the investigators to the conclusion that the conversion of acetate to methane was carried out by an unidentified organism (Ferry and Wolfe, 1976). The following reactions were proposed by the same investigators to describe the overall conversion of benzoate to methane:

(a) Degradation of benzoate to acetate, formate and hydrogen



$$+ 24H_2O \rightarrow 12\ CH_3COOH + 4HCHOOH + 8\ H_2 \quad (32)$$

(b) Conversion of acetate to methane and carbon dioxide

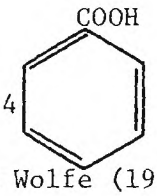
$$12CH_3COOH \rightarrow 12\ CH_4 + 12\ CO_2 \quad (33)$$

(c) Conversion of formate to carbon dioxide and hydrogen

$$4HCOOH \rightarrow 4CO_2 + 4CO_2 \quad (34)$$

(d) Reduction of carbon dioxide with hydrogen

$$12H_2 + 3CO_2 \rightarrow 3CH_4 + 6H_2O \quad (35)$$

net: 

$$+ 18H_2O \rightarrow 15\ CH_4 + 13\ CO_2 \quad (36)$$

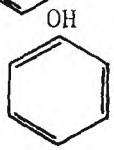
Ferry and Wolfe (1976) concluded from experimentation with methyl labeled acetate that the reaction given by Equation 33 was probably occurring in one organism.

Fina and Fiskin (1960) conducted experiments to determine the fate of the first and seventh carbon during the anaerobic degradation of benzoic acid. Their conclusions were that the carboxyl carbon (C^7) was partly reduced to methane, whereas carbon one was almost totally converted to methane.

Recently published data by Healey and Young (1978) provided evidence on the anaerobic biodegradation of phenol and catechol. Acclimation periods of 32 and 18 days were needed prior to any methane production from the catechol and phenol fed reactors, respectively. After the initiation of gas

production from the 300 mg/l phenol fed unit, 14 days were required for the complete conversion of phenol while a subsequent spike of an equivalent concentration of phenol required only 10 days for complete degradation to occur. These data indicate rapid decomposition after enrichment. The phenol carbon was totally converted to gaseous end products with more than half of the product gas being in the form of methane. Based on their experimental data, Healey and Young (1978) proposed the following stoichiometric relationships for the anaerobic degradation of phenol and catechol:

Phenol:  $+ \quad 4H_2O \longrightarrow 2.5\ CO_2 + 3.5\ CH_4$ (37)

Catechol:  $+ \quad 3.5\ H_2O \longrightarrow 2.75CO_2 + 3.25\ CH_4$ (38)

Further investigations by Healey et al. (1977) revealed that the percent methane in the gaseous products from the anaerobic degradation of phenol and catechol was 62.4 and 42 percent, respectively, rather than the theoretical stoichiometric values of 58.3 and 54.2 percent.

Chou et al. (1977) assessed the treatability of fifty three petrochemical compounds with an anaerobic filter. The selection criteria for these compounds was based on their structural characteristics. These characteristics were the position of double bonds, position of functional groups, odd or even numbered carbons, length of carbon chain, branching, oxidative state, type of functional groups, and number of identical functional groups and configuration. The results from their study revealed that the aromatic compounds utilized required less acclimation time for degradation in an anaerobic filter when this filter has been acclimated to benzoate as compared to an acetate

acclimated culture. With acetic acid being the major precursor to methane formation, it was logical to determine whether bacteria grown on an acetate substrate can readily utilize higher organic compounds. The results of a toxicity study conducted by the same authors (Chou et al., 1977) revealed that all the test compounds containing a benzene ring were toxic to an acetate acclimated sludge with the exception of phthalic acid. An acetate enrichment culture required 30 days to acclimate to phenol while only 23 days were needed by a benzoate acclimated culture.

The intermediate compounds produced during the anaerobic degradation of phenol have not been isolated and identified to date. In a review paper, Evans (1977) proposed a metabolic pathway (Figure 6) but the validity of his hypothesis has yet to be established

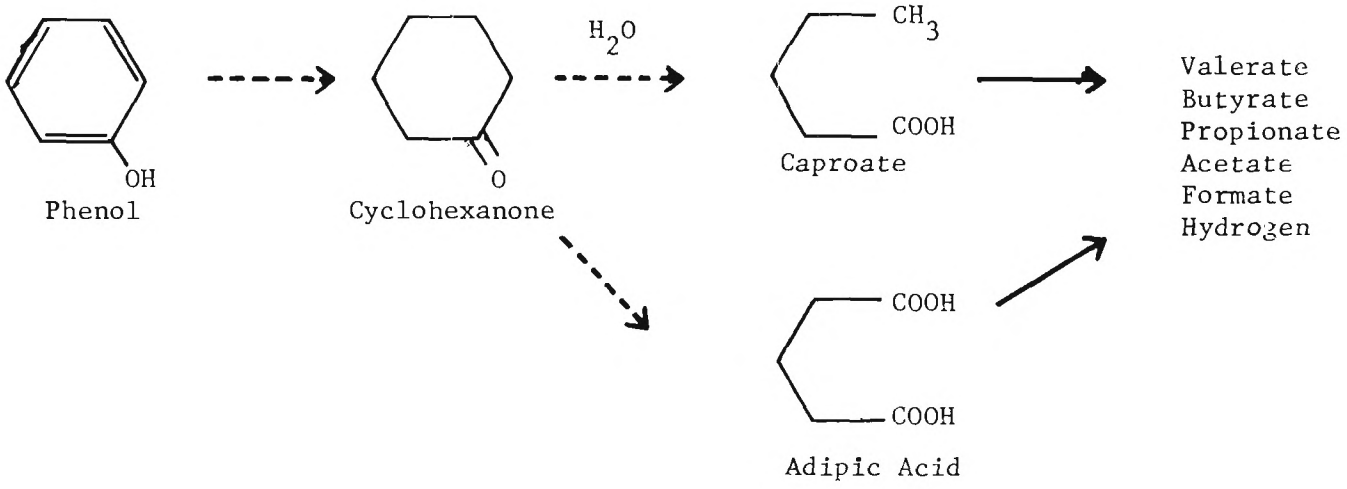


Figure 6. Probable Pathway in the Fermentation of Phenol by Adapted Bacterial Consortia from a Variety of Ecosystems

Anaerobic Treatment Processes

The application of anaerobic processes in wastewater treatment has traditionally been limited to the anaerobic digestion and stabilization of primary, waste activated and trickling filter sludges. These systems have traditionally been of the flow through type with no mass of microorganism recycle (Figure 7a) because of the difficulty of separation between the feed solids and the active anaerobic biomass. Several innovations to the conventional anaerobic digestion system have been proposed and implemented. Most of these innovations, however, are designed for an increase in the retention of the active biomass within the treatment process without a similar increase in the holding time of the aqueous phase.

Anaerobic Activated Sludge Process. The main deficiency in the design of conventional anaerobic sludge digesters has been the need for long hydraulic detention times in these units in order to allow for efficient reductions in the volatile solids content of the feed sludge. The need for long hydraulic detention is due to the low replication rate of methanogens and the difficulty of concentrating and separating the active anaerobes for the purpose of biomass recycle (McCarty, 1967). Several attempts have been cited in the literature where the raw wastes were contacted with a large mass of anaerobic sludge. The anaerobic biomass along with other residual solids were later separated from the treated wastewater and recycled back to the digester for reuse. Such a biomass concentration technique would result in increased active cell concentration in the digestion phase and consequently will allow for a reduction in digester volume (McCarty, 1967).

Schroepfer et al. (1955) as well as Coulter et al. (1956) referred to such a system as the "anaerobic contact process." Schroepfer et al. (1955) also stated, in reference to their particular adaptation of the process,

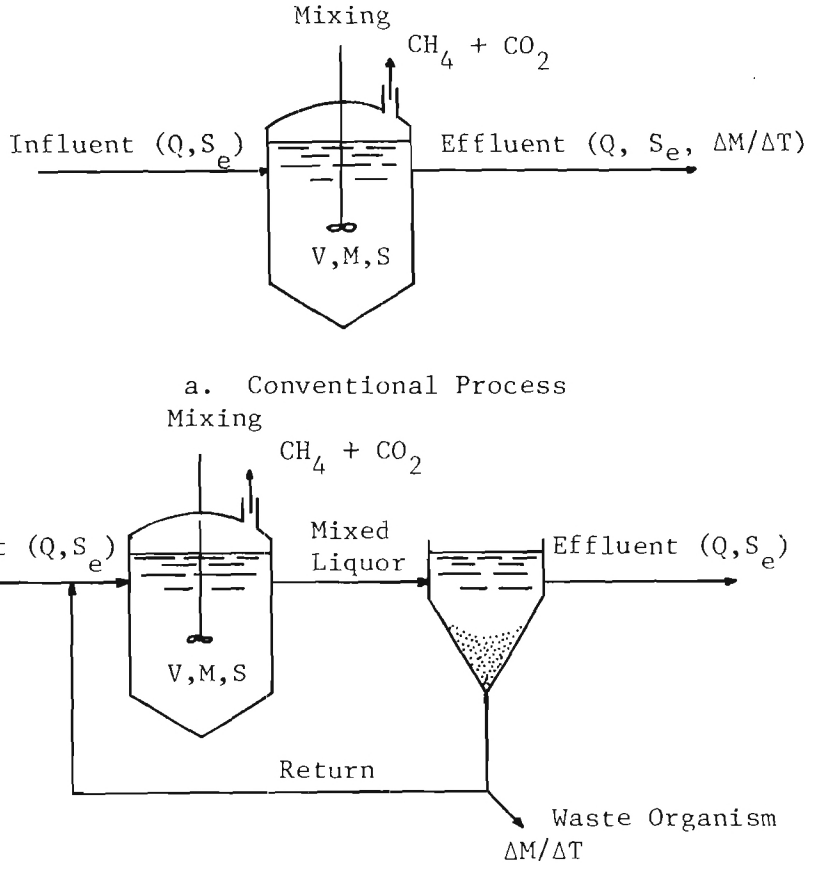


Figure 7. Schematic Diagram of Three Anaerobic Waste Treatment Process. After McCarty

that the "anaerobic activated sludge process appears to be descriptive of the action involved." This is shown in Figure 7b.

The conventional and contact anaerobic processes have been described as effective in the treatment of wastewaters containing high concentrations of suspended solids (Young and McCarty, 1968). The same authors stated that in such systems the bacterial population becomes attached to the solid surfaces and consequently become readily separable from the effluent stream.

In the treatment of soluble wastes, the microbial population tends to remain dispersed and, consequently, a significant portion of it may be lost in the effluent (Steffen and Bedker, 1962). In order to attain high efficiencies of organic removal, these systems have been operated at a recycle ratio from the solids separation unit as high as four times the average feed flow (Schroepfer and Ziemke, 1959; Steffen and Bedker,, 1961).

The maintenance of elevated temperatures during active anaerobic biodegradation has generally been reported to improve the rate of waste stabilization in the anaerobic contact process. However, in most instances, an external heat source will be required since a minimum waste strength of 6000 mg/1 BOD_5 is needed to produce sufficient quantities of methane to raise the feed wastewater temperature by as little as 10°C (McCarty, 1964). Consequently, anaerobic contact processes are better suited for the treatment of concentrated or already warm wastewaters. The anaerobic contact process has generally not proven staisfactory for the treatment of wastewaters containing less than about 2000 mg/1 BOD_5 at operating temperatures below 35°C (McCarty, 1964).

The efficiency of treatment attained from conventional and contact anaerobic processes is dependent on the success of contacting the organic substrate in the feed with an active anaerobic culture for a sufficient

period of time. This objective is realized through the use of excessively long contact periods in the conventional process, and solids concentration and recycle in the anaerobic contact process.

Anaerobic Filter. Young and McCarty (1968) describe this process as a columnar reactor with rocks or aggregates serving as a contact medium (see Figure 7c). Biological solids provide long retention times within this process through either attachment onto the medium surfaces or entrapment within the interparticle void spaces (Young and McCarty, 1967). This process, which is usually operated in an upflow mode, is particularly suited for the treatment of low strength wastewaters at nominal temperatures; which is possible due to the long solids retention offered by the system and the resulting high density of anaerobic biomass within the system (Young and McCarty, 1968).

Young and McCarty (1967) summarized the advantages of the anaerobic filter as follows:

a. The anaerobic filter is ideally suited for the treatment of soluble wastes.

b. No effluent or solids recycle is required since the biological solids are effectively retained within the filter and are not lost in the effluent.

c. The accumulation of high concentrations of active solids permits the treatment of dilute wastes even at nominal temperatures. Heating is not required as in most other anaerobic processes where it is needed to accelerate the conversion kinetics.

Various investigators have utilized a number of different packing media in anaerobic filters. The ideal medium has been described as one that maximizes both surface area and porosity. A large surface area is needed to enhance the attachment of the biomass, while an increased porosity results

in a decrease in the required overall filter volume. A high porosity is also essential in order to minimize filter clogging, short circuiting and associated hydraulic problems. Chian and DeWalle (1976, 1977) utilized "Surpac" slabs for a contact medium in an anaerobic filter designed for the treatment of landfill leachate. The use of this packing material resulted in a bed porosity of 0.94. Smooth quartzite 1-1.5 inches in size and resulting in bed porosities ranging from 0.42-0.47 has also been used (Young and McCarty, 1967; Dennis and Jennett, 1974; Jennett and Dennis, 1975). Anderson and Ibrahim (1978) employed 38 mm polystyrene spheres and Biopac 50E for filter packing which resulted in porosities of 0.51 and 0.97, respectively. Seeler and Jennett (1978) and Sachs et al. (1978) used 1-1.5 inch gravel and stone for filter packing. These researchers reported a bed porosity of 0.43. A similar bed porosity was reported by Lovan and Foree (1971) when 1-1.5 inch crushed stone was used. Mueller and Mancini (1975) employed 5/8 inch size polypropylene pall rings which gave rise to a bed porosity of 0.85, while Plummer et al. (1968) used raschig ring and berl saddle packings in the treatment of a soluble carbohydrate waste; bed porosity of 0.67 and 0.70 were reported.

The anaerobic filter, inspite of being a relatively new process, has been employed in the treatment of wastewaters emanating from a number of different sources.

Young and McCarty (1967) evaluated the performance of an anaerobic filter over an organic loading rate range of 26.5 to 212 lbs COD/day/1000 cu. ft. of total filter volume. Two synthetic organic carbon substrates were used, one a mixture of proteins and carbohydrates while the other was composed of various volatile fatty acids. Employing an influent substrate COD of 3000 mg/l and a 36 hour liquid detention time, 180 days of continuous operation

were needed to achieve a 90 percent reduction in COD for both the protein-carbohydrate and volatile fatty acid fed systems. With a hydraulic detention time of 72 hours, a 93 percent COD removal efficiency was obtained from the protein-carbohydrate fed system. A COD-methane balance on the protein-carbohydrate fed system revealed that 85 percent of the COD removed could be accounted for in the gaseous products while the remaining 15 percent was converted to biomass. A similar analysis on the volatile fatty acids fed unit revealed that almost all of the COD removed could be accounted for in the gaseous products from the process. Very little biomass production was observed.

Chian and DeWalle (1977) utilized a high porosity anaerobic filter for the treatment of a high strength acidic wastewater, originating from a solid waste lysimeter. The aqueous contents of the filter were recycled around the unit in order to achieve complete mixing conditions and to provide sufficient buffer for the feed solution. The methane contant of the gas produced accounted for 93 percent of the COD removal. A material balance on the system revealed that only 0.012 g of volatile suspended solids (VSS) were produced per gram of COD removed. This low solids yield resulted in a treatment system having very low nutrient requirements in addition to low sludge production.

Mueller and Mancini (1975) concluded from treatability studies on a readily biodegradable protein carbohydrate waste at 35°C that for the 5/8 inch polypropylene pall ring packing utilized that the maximum attainable removal rate was 1100 lb COD/day/1000 cu.ft. of total filter volume. At organic loading rates of 200 to 1700 lb COD/day/1000 cu. ft. and the corresponding detention times of 24 to 3 hours, COD removal efficiencies of 90 and 50 percent were obtained, respectively.

Lovan and Forsee (1971) treated a brewery press liquor waste using an anaerobic filter. They reported a 90 percent COD removal efficiency for a raw wastewater COD ranging from 6000 to 24000 mg/1. Throughout the study the organic loading rate was equal to or less than 100 lb COD/day/1000 ft^3 of total filter volume. Sachs et al. (1978) studied the treatability of a synthesized pharmaceutical wastewater with an aanerobic filter. For an organic loading rate of 34.9 lb COD/per day/1000 cu.ft. and at a waste strength of 2000 mg/1 COD, a steady state COD removal ranging from 70 to 80 percent and a BOD_5 removal rate of 94 percent were obtained. When the organic loading rate of the filter increased to 104.6 lb COD/day/1000 cu. ft. at a feed waste strength of 6000 mg/1, only 18 percent COD removal was attained. This reduction in removal efficiency may be due to short acclimation period used or possibly to the increased feed concentration of some inhibitory compounds. Seeler and Jennett (1978) observed similar results from the treatment of synthesized pharmaceutical wastes and concluded that the anaerobic filter was not efficient in treating similar wastewaters bearing more than 1000 mg/1 of COD. At this reduced loading rate, however, these investigators reported improved color removal across the filter as compared to data reported for other operating anaerobic filters.

Jennett and Dennis (1974, 1975) conducted a similar study on the treatment of a synthesized pharmaceutical wastewater using an anaerobic filter operated at a constant temperature of 35°C. COD removal efficiencies of 93.7 and 97.8 percent were reported for feed concentrations ranging from 1000 to 16000 mg/1. High treatment efficiencies were consistently obtained without any solids recycle and over an organic loading rate ranging from 13.8 to 220 lb COD/day/1000 cu.ft. of total filter volume.

Plummer et al. (1968) studied the stabilization of a low solids carbohydrate wastewater in four anaerobic filters loaded at 101, 237, 438 and 638 lb COD/day/1000 cu.ft. Corresponding to these organic loading rates, COD removal efficiencies of 86, 68, 45 and 35 percent were reported, while the BOD_5 removal efficiencies were 94, 72, 43 and 41 percent. Contrary to these observations, Wilt et al. (1979) reported that COD removal efficiencies obtained from anaerobic filters were independent of organic loading.

Anaerobic filters have also been utilized for denitrification. Tamblyn and Sword (1969) employed an anaerobic filter for the denitrification of agricultural drainage and concluded that efficient nitrate removal may be obtained at hydraulic detention times ranging from 0.5 to 2 hours. Factors that influenced the filter performance included temperature and filter media. Anderson and Ibrahim (1978) also showed that wastewaters bearing nitrates exceeding 700 mg/l, as nitrogen, may be efficiently purified using an anaerobic filter.

Control Parameters in Anaerobic Biological Treatment. There are a number of nutritional and environmental parameters that have been shown to strongly influence and control the performance of the anaerobic biological process.

Anaerobic organisms responsible for waste conversion and stabilization require, in addition to a carbon source, nitrogen, phosphorus and trace quantities of other nutrients and growth factors (McCarty, 1964). Consequently, these nutrients should be present in sufficient quantities for efficient conversion of the organic constituents of wastewater to occur. Speece and McCarty (1964) calculated the nitrogen and phosphorus requirement for biological growth to occur based on an average chemical formulation of biological cells of $C_5H_9O_3N$. This formulation yields a nitrogen require-

ment of about 11 percent by weight of the cell volatile solids and a phosphorus requirement equal to one-fifth by weight of the nitrogen requirement.

Electrode potential and pH are two intensive parameters indicative of the respective electron and proton activities associated with the biochemical transformations occurring within the system (Pohland and Ghosh, 1971). Because methanogenic bacteria are obligate anaerobes and since small amounts of oxygen are inhibitory to these organisms, it is essential that a highly reduced environment be maintained around these organisms in order to promote their active growth. Dirasian et al. (1963) stated that optimum digestion, as measured by methane production occurred when the oxidation reduction potential (ORP) of the medium was maintained in the -520 to -530 mv range (E_c - Calomel reference electrode). Blanc and Molof (1973), on the other hand, claimed that optimum digestion in the mesophyllic temperature range occurred at an ORP value in the range from -450 to -550 mv. In addition to oxygen, other highly oxidized materials such as nitrites and nitrates can inhibit the normal function of methanogenic organisms.

The methanogens are also sensitive to the prevailing pH of the digester liquor. McCarty (1964) reported that methane production proceeds very well if the pH is maintained in the range between 6.6 and 7.6, while the optimum pH range appears to be between 7.0 and 7.2 (Pfeffer, 1974). Pohland and Suidan (1978) proposed a predictive mathematical model for pH control that incorporates the various acid and base equilibria and gaseous carbon dioxide partial pressure that control the alkalinity and the pH of a biological anaerobic environment.

Another very important parameter that has been used to determine the stability and state of "health" of an anaerobic system is the quantity and quality of gas production. A sudden or gradual decrease in gas production

or the methane content of the gas produced may be taken as a warning that conditions have been altered within the system environment that may result in a certain degree of inhibition to the methanogens. Examples of such inhibition may be a change in pH, oxygen contamination or chemical toxicity (both organic and inorganic) (Finney and Evans, 1975).

The fermentation of organic matter within a biological anaerobic environment is directly related to methane production and vice versa. Buswell and Mueller (1952) developed a chemical equation (Equation 39) that may be used to predict the quantity of methane to be anticipated from an anaerobic system based on a knowledge of the chemical composition of the waste:

$$C_nH_aO_b + (n - \frac{a}{4} - \frac{b}{2})\ H_2O \rightarrow (\frac{n}{2} - \frac{a}{8} + \frac{b}{4})\ CO_2 + (\frac{n}{2} + \frac{a}{8} - \frac{b}{4})\ CH_4 \qquad (39)$$

or as applied to the conversion of glucose and phenol to carbon dioxide and methane, the reactions will be:

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 \text{ for glucose and} \qquad (40)$$

$$C_6H_6O + 4H_2O \rightarrow 2.5CO_2 + 3.5CH_4 \text{ for phenol,} \qquad (41)$$

Equations 40 and 41 reveal that for every mole of glucose and phenol destroyed 3 and 3.5 moles of methane are produced, respectively. Or in other words, if all the carbon dioxide produced is released to the gas space, glucose will yield a gaseous product containing 50 percent methane while the gas produced from the degradation of phenol will contain 58.3 percent methane.

The carbon dioxide produced through the anaerobic action is not all released as a gas, however. A major fraction of the carbon dioxide remains in solution and enters into reactions with water and the hydroxide ion to form aqueous carbon dioxide, $[H_2CO_3^*]$, and bicarbonate, $[HCO_3^-]$, and carbonate,

$[CO_3^{=}]$,ions. Microorganisms are capable of deaminating biodegradable protein and release ammonia into solution which will react with water (Equation 42)

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (42)$$

The hydroxide ion thus released reacts with the aqueous carbon dioxide to form bicarbonate and carbonate ions as shown in Equations 43 and 44

$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O \quad (43)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{=} + H_2O \quad (44)$$

The carbon dioxide incorporated in the bicarbonate ion is removed from the reactor in the liquid phase and to a lesser extent in the gaseous phase. There are two factors that determine the liquid wash out rate of carbon dioxide and the concentration of the methane in the gaseous phase; there are the hydraulic retention time within a reactor and operating pH of the treatment system. An increase in waste flow rate, which in turn results in a decrease in the hydraulic detention time within the anaerobic system will result in an increase in the wash out rate of CO_2 in the aqueous phase and, consequently, an increase in the methane content of the gaseous phase. On the other hand, an increase in the pH of the aqueous phase of the reactor results in an increased solubility of the total inorganic carbon in that phase and, consequently, an increase in the methane content of the gaseous phase.

MATERIALS AND METHODS

Experimental Apparatus

Two identical experimental reactors were used in this study. Each experimental reactor consisted of four jacketed columns and three clarifiers connected in series with one clarifier located after each of the first three columns. Figure 8 represents a schematic of one jacketed column. Each column was constructed of 0.64 cm (0.25 inch) wall plexiglass tubes having a 5.08 cm (2 inch) internal diameter and 60.96 cm (24 inch) in length. A 0.32 cm (0.125 inch) thick and 5.715 cm (2.25 inch) in diameter perforated plate was placed at the top and bottom of each column in order to retain all particles larger than 0.32 cm (0.125 inch) within the column. The lower plate was glued to the bottom of the column and held in place between the column and a 1.27 cm (0.5 inch) base plate. Two fittings were placed in the base plate in order to allow for entry into the column of the feed solution and the recirculated flow (see Figure 8). The upper perforated plate is situated between the top of a column and a 10.16 cm (4 inch) long capped cylinder constructed of the same plexiglass tube that was used to build the main body of the column. Three fittings were placed in the top section of each column. These fittings were for: (a) effluent withdrawal situated 3.18 cm (1.25 inch) from the top, (b) recycle flow withdrawal situated 5.72 cm (2.25 inch) from the top and (c) gaseous products exit situated on the very top of the 10.16 cm extention to the column.

A thermal water jacket was constructed around the main body of each column using 0.64 cm (0.25) inch wall cylindrical plexiglass tube 57.79 cm (22.75 inch) long and 7.62 cm (3 inch) in internal diameter. Each water jacket had two fittings situated 1.27 cm (0.5 inch) from each end of the

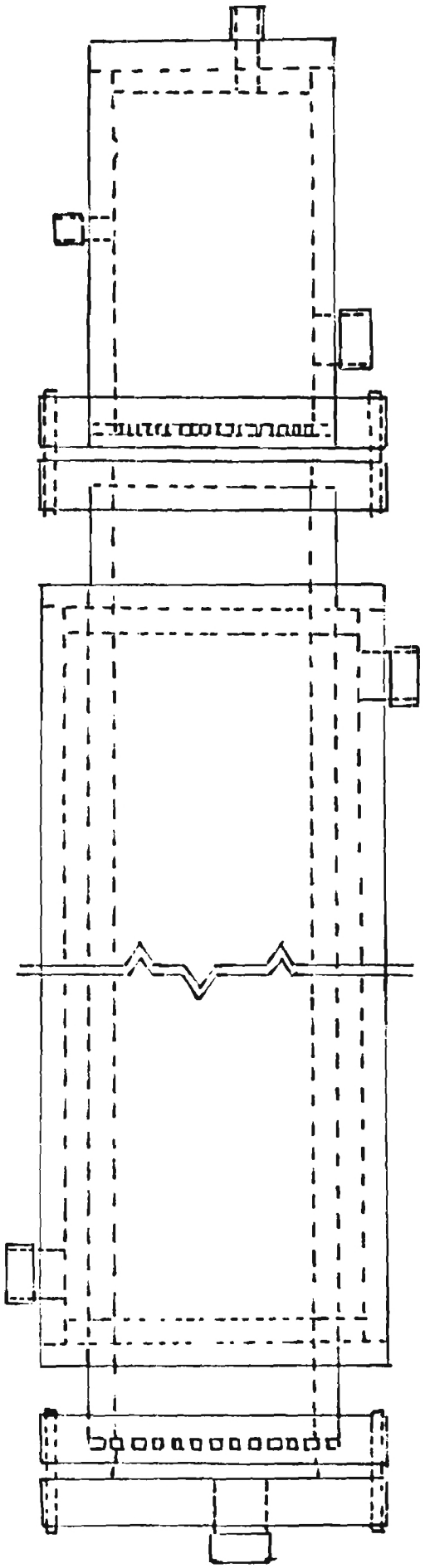


Figure 8. Column Schematic

jacket. The water jackets of all eight columns were connected in series using Imperial Eastman Poly-flo tubing 66-p-3/8 to the inlet of the recirculating pump of a constant temperature bath (American Instrument Model No. 4-8600) while the flow from the jacket of the last column was returned to the same temperature bath. Water was recirculated at a high flow rate through the water jackets in order to maintain a constant and uniform temperature of 35 ± 0.5°C throughout the experimental apparatus.

The aqueous contents of every reactor were continuously recirculated around that reactor using a multiple head tubing pump (Cole-Parmer Model 7567 with Cole-Parmer Masterflex Pumpheads # 7018-20). A combination of 1.27 cm (0.5 inch) outer diameter Tygon Flexible Plastic tubing and Cole-Parmer 6408-09 Tygon tubing having an outer diameter of 1.11 cm (0.44 inch) were used for recirculation. The feed substrate, the effluent from every column and the final effluent were all conducted through 0.66 cm (0.25 inch) outer diameter Imperial-Eastman Poly-flo tubing 44-p-1/4. Similar tubing was used to connect each gas release fitting to the corresponding gas collection system. Each gas collection system consisted of a 1 ℓ buret, 1 ℓ balancing bottle, and one gas release and sampling T-connection and 1 ℓ of acid solution containing methyl orange indicator. The function of the acidic solution was to minimize the dissolution of the carbon dioxide present in the gas buret.

An inline check valve was placed between each column and its corresponding clarifier in order to prevent any accidental backflow through the system. The clarifiers were employed in order to provide a means for the removal of excess biomass from the columns and to provide a separation between the gaseous phases of the different columns. These clarifiers (see Figure 9) were constructed of 0.66 cm (0.25 inch) wall plexiglass tubes having a 7.62 cm (3 inch)

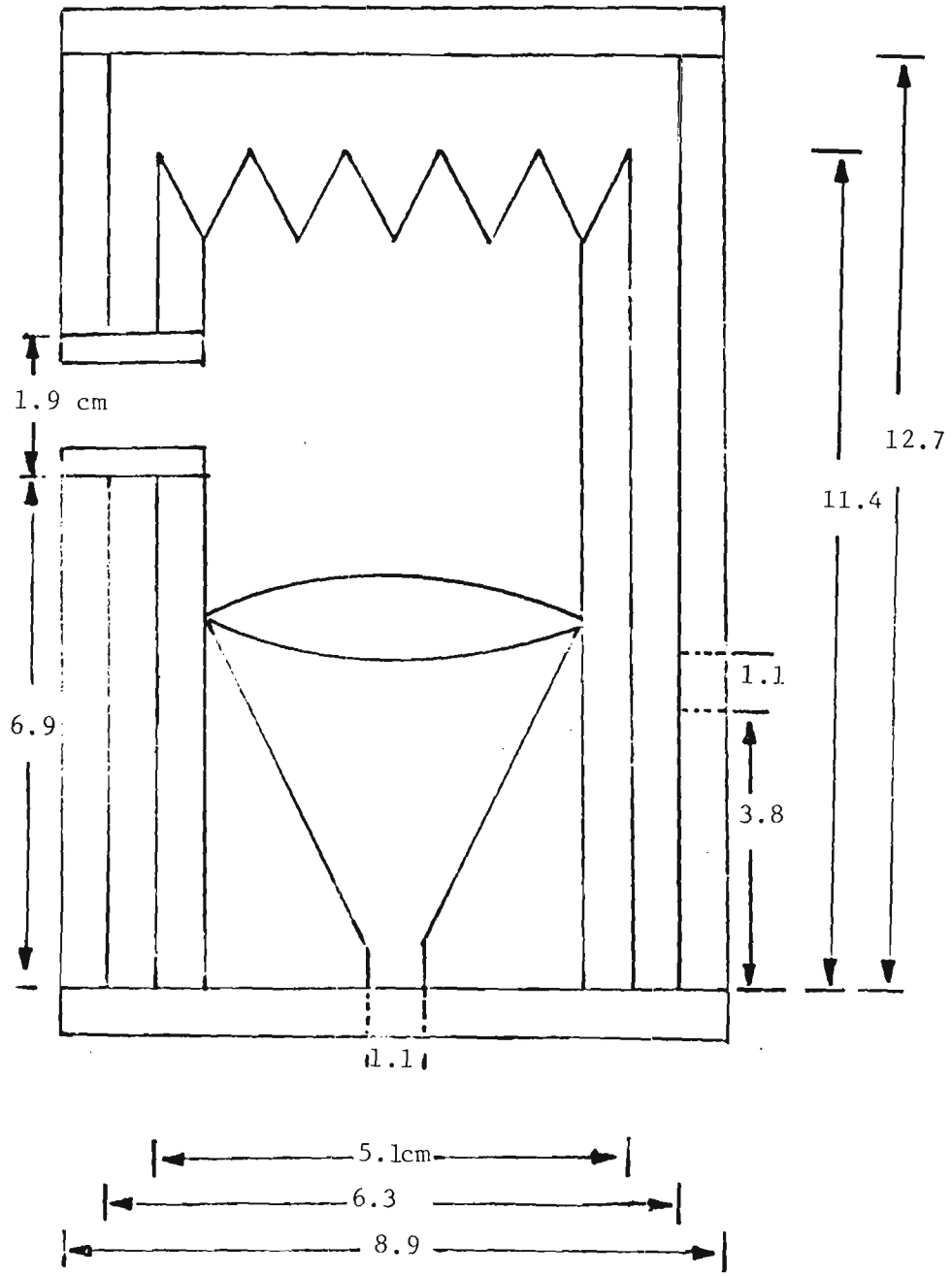


Figure 9. Clarifier Schematic

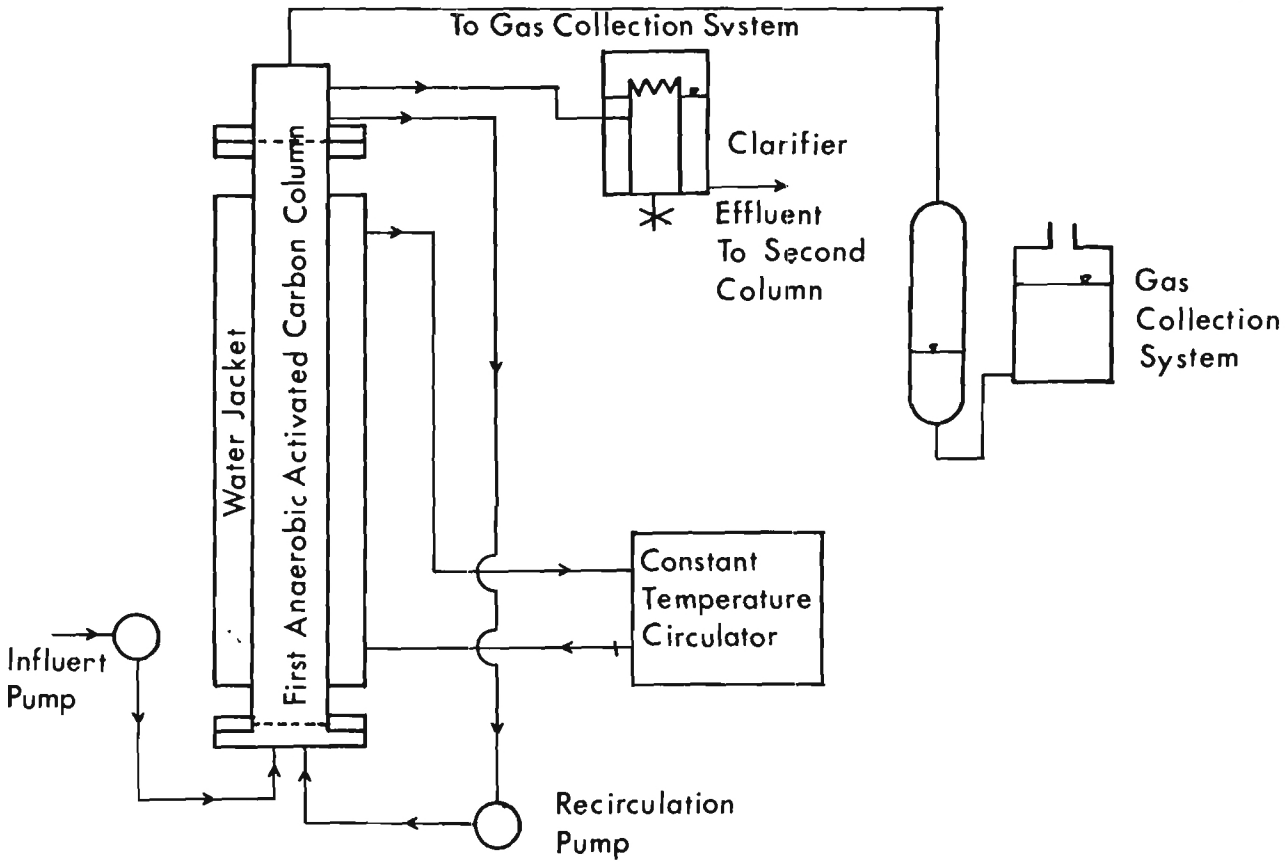


Figure 10. Schematic of a Single Anaerobic Filter Column

internal diameter and 12.7 cm (5 inch) long. The internal weir structure of the clarifier was constructed of a 0.66 cm (0.25 inch) wall plexiglass tube 5.08 cm (2 inch) in internal diameter and 11.43 cm (4.5 inch) long. The weir was provided with a V-shaped notch and an inner cone was situated within the inner tube structure to provide for more efficient removal of settled biomass through a 1.11 cm (7/16 inch) sampling port located at the bottom of the clarifier. A schematic of the first anaerobic activated carbon filter and the associated clarifier and gas collection system is shown in Figure 10.

Granular Activated Carbon Contact Medium

Granular activated carbon was used as a packing medium for the anaerobic filters utilized in this study. The specific commercial activated carbon employed in this research was bituminous base Filtrasorb 400 (Calgon Corporation, Pittsburg, PA). This activated carbon was first sieved into a number of particle size fractions (see Table 17). The individual fractions were then washed with distilled water to eliminate fines and subsequently dried at 105-110°C for forty-eight hours. The specific characteristics of the carbon as given in the manufacturer's bulletin (Calgon Corporation, 1976) are reproduced in Table 18, while the pore volume-pore radius distribution is presented in Figure 11.

Each anaerobic filter column was charged with 446.6 grams of activated carbon. Only the granular size fractions of the sieved, washed and dried Filtrasorb 400 falling within the 10 x 20 U.S. Standard Mesh size was used in this study. The selection of this particular size range was made primarily because this size range represents sufficiently large particles which will minimize clogging problems due to the carbon retaining perforated plates at the end of the reactors. In addition, this size range constituted the major fraction be weight,

Table 17. Sieve Analysis Data on Filtrasorb 400 Activated Carbon

Sieve # U.S.S.M.	Sieve Size (mm)	Weight Retained (g)	Cumulative Weight Retained (g)	Percent Weight Retained
6	3.36	0	0	0
8	2.38	0	0	0
10	2.00	0.11	0.11	0.022
16	1.18	208.03	208.14	41.94
18	1.00	99.53	307.67	62.00
20	0.85	57.20	364.87	73.52
30	0.59	98.66	463.53	93.41
40	0.42	24.10	487.63	98.26
50	0.297	6.51	494.14	99.57
80	0.179	1.53	495.67	99.88
100	0.149	0.33	496.00	99.95
170	0.088	0.18	496.18	99.98
Pan	<0.088	0.06	496.24	100.00

Table 18. Physical Properties of Filtrasorb 400 (Calgon Corporation, 1976)

Total Surface Area (N_2 BET Method) m^2/g	1050 - 1200
Bulk Density, lb/ft^3	25
Particle Density Wetted in Water, g/cc	1.3 - 1.4
Pure Volume, cc/g	0.94
Effective Size, mm	0.55 - 0.65
Uniformity Coefficient	1.6 - 2.1

74 percent, of the commercial carbon Filtrasorb 400. The specific make up of the carbon employed was: (a) 16 percent by weight 18 x 20 U.S. Mesh, (b) 27 percent by weight 16 x 18 U.S. Mesh, and (c) 57 percent by weight 10 x 16 U.S. Mesh.

Synthetic Feed Substrate

Synthetic phenol and glucose bearing substrates were used in this investigation in order to determine the performance of the process in degrading the strongly adsorbing aromatic phenol, the readily metabolized and poorly adsorbing

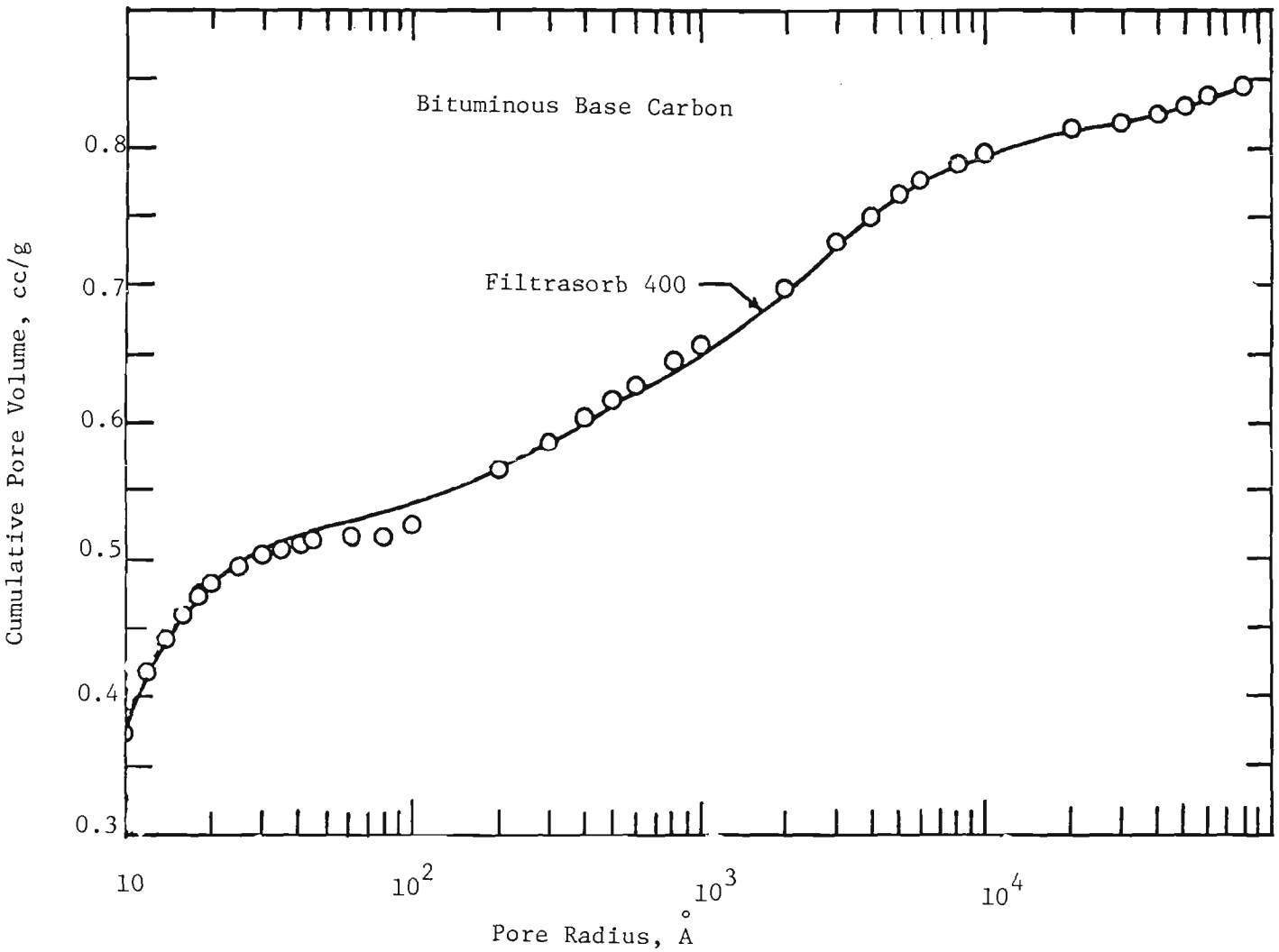


Figure 11. Pore Size Distribution

glucose, and to observe any interaction that occurs during the cometabolism of both substrates. All substrates were prepared daily in 4 ℓ glass reservoirs and were introduced into the first column of every set of reactors using positive displacement FMI Pumps, Model RPG-20 (Fluid Metering Incorporated, Oyster Bay, NY). Each pump was rated at a maximum flow rate of 5.4 mℓ/min and a maximum operating pressure of 50 psi. The synthetic substrates were fed into the respective systems at a flow rate of 2 mℓ/min. At this flow rate, an empty bed contact time of 11.62 hours was provided per reactor resulting in a total empty bed contact time of 46.67 hours for each system.

Trace Salt Solution. A concentrated stock solution of various trace salts and the complexing agent, sodium citrate, was prepared in 2 liter batches in distilled water according to the formulation given in Table 19.

Salt Solution. Each liter of the stock salt solution was prepared by adding the components indicated in Table 20 to distilled water.

The vitamin extract was prepared by the addition of 10 g of Alacer A to Zinc Multimineral ^{R} to a mixture of 250 mℓ of ethanol and 250 mℓ of distilled water. This solution was heated to a temperature of 50°C, stirred for 24 hours and then allowed to settle. The decanted supernatent was utilized as the extract.

Table 19. Composition of Trace Salt Solution

Compound	Quantity (grams)
$FeCl_3$	38.88
$MnCl_2 \cdot 4H_2O$	9.48
$ZnCl_2$	6.54
$CaCl_2 \cdot 2H_2O$	4.10
$CoCl_2 \cdot 6H_2O$	5.71
$Na_2B_4O_7 \cdot 10H_2O$	2.29
Na_3 Citrate	353.00
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	4.15

Dilute to a total volume of 2 liters

Table 20. Composition of Salt Solution

Compound	Quantity
Trace Salt Solution	33.3 mℓ
KH_2PO_4	13.61 grams
$NaH_2PO_4 \cdot H_2O$	8.28 grams
$(NH_4)_2SO_4$	5.28 grams
NH_4Cl	25.00 grams
$CaCl_2$	4.44 grams
$MgCl_2 \cdot 6H_2O$	8.13 grams
Vitamin Mixture	35.00 mℓ
Cysteine Hydrochloride Solution	5.00 mℓ
Dilute to a total volume of 1 liter	

The cysteine hydrochloride solution was prepared by dissolving 10 g of sodium thiosulfate and 0.1 g of cysteine hydrochloride in distilled water to make 1 ℓ of solution.

Phosphate Buffer. A three molar phosphate buffer solution was prepared by adding 261.29 g of K_2HPO_4 and 179.96 g of NaH_2PO_4 or 212.96 g of Na_2HPO_4 and 202.60 g of KH_2PO_4 to distilled water in order to make up one liter of buffer solution.

Phenol Substrates. The phenol fed anaerobic activated carbon filter system was operated in two phases. During the first phase a feed phenol concentration of 200 mg/ℓ was used while in the second phase, the phenol concentration in the feed was increased to 400 mg/ℓ.

The phenol substrate was prepared daily in 4 ℓ batches. Each batch was prepared by adding specific volumes of the salt and buffer solutions along with

a weighed quantity of phenol to distilled water resulting in a final volume of 4 liters of substrate. Prior to introduction into the system, the pH of the feed substrate was adjusted using a 10 N solution of sodium hydroxide and the reservoir and contents were purged with nitrogen gas in order to displace any dissolved oxygen. The substrate reservoir was then placed in a refrigerator from where it was pumped into the treatment system. The composition of the feed substrate for both phases is given in Table 21.

Table 21. Composition of Synthetic Phenol Bearing Substrate*

Compound	Phase 1 Concentration 200 mg/ℓ Phenol	Phase 2 Concentration 400 mg/ℓ Phenol
1. $FeCl_3$	3.24	6.47
2. $MnCl_2 \cdot 4H_2O$	0.79	1.58
3. $ZnCl_2$	0.54	1.09
4. $CaCl_2 \cdot 2H_2O$	0.34	0.68
5. $CoCl_2 \cdot 6H_2O$	0.48	0.95
6. $Na_2B_4O_7 \cdot 10H_2O$	0.19	0.38
7. Na_3 Citrate	29.39	58.77
8. $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.35	0.69
9. KH_2PO_4	68.05	136.10
10. $NaH_2PO_4 \cdot H_2O$	41.40	82.80
11. $(NH_4)_2SO_4$	26.40	52.80
12. NH_4Cl	125.00	250.00
13. $CaCl_2$	22.20	44.40
14. $MgCl_2 \cdot 6H_2O$	40.65	81.30
15. Vitamin Mixture Ethanol Extract	0.175	0.350
16. Cysteine Hydrochloride Solution	0.0250	0.0500
17. K_2HPO_4	3919.35	3919.35
18. NaH_2PO_4	2699.40	2699.40
19. Phenol	200.00	400.00

* All concentrations in mg/ℓ except 15 and 16 in mℓ/ℓ

Glucose Substrate. The glucose fed anaerobic activated carbon filter system was operated with a feed glucose concentration of 2000 mg/ℓ. The feed

substrate was prepared daily in 4 ℓ batches. Each batch was prepared by adding specific volumes of the salt and buffer solutions along with 8 grams of glucose. Distilled water was used to bring the final feed volume to 4 liters. Prior to use, the pH of the feed substrate was adjusted using a 10 N solution of sodium hydroxide and the reservoir was then purged with nitrogen gas. The reservoir was then placed in a refrigerator from which it was pumped to the first column of the glucose fed anaerobic system. The composition of the feed substrate is given in Table 22.

Table 22. Composition of Synthetic Glucose Bearing Substrate*

	Compound	Concentration 2000 mg/ℓ Glucose
1.	$FeCl_3$	12.96
2.	$MnCl_2 \cdot 4H_2O$	3.16
3.	$ZnCl_2$	2.16
4.	$CaCl_2 \cdot 2H_2O$	1.48
5.	$CoCl_2 \cdot 6H_2O$	1.92
6.	$Na_2B_4O_7 \cdot 10H_2O$	0.76
7.	Na_3 Citrate	117.56
8.	$(NH_3)_6Mo_7O_{24} \cdot 4H_2O$	1.40
9.	KH_2PO_4	272.20
10.	$NaH_2PO_4 \cdot H_2O$	165.60
11.	$(NH_4)_2SO_4$	105.60
12.	NH_4Cl	500.00
13.	$CaCl_2$	88.80
14.	$MgCl_2 \cdot 6H_2O$	102.60
15.	Vitamin Mixture Ethanol Extract	0.700
16.	Cysteine Hydrochloride Solution	0.100
17.	K_2HPO_4	9145.15
18.	NaH_2PO_4	6298.60
19.	Glucose	2000.00

* All concentrations in mg/ℓ except 15 and 16 are in mℓ/ℓ

Phenol-Glucose Substrate. The phenol and glucose substrate fed reactor system was operated at feed concentrations of the two substrates of 200 and 2000 mg/ℓ, respectively. The feed substrate was prepared daily in 4 ℓ batches.

Each batch was prepared using specific volumes of the salt and buffer solutions along with 8 g of glucose and 0.8 g of phenol. Distilled water was used to bring the final feed volume to 4 liters. Prior to introduction into the system, the pH of the feed substrate was adjusted using a 10 N solution of sodium hydroxide and the reservoir was then purged with nitrogen gas. The reservoir was then placed in a refrigerator from which it was pumped to the first column of the glucose and phenol fed anaerobic system (previously glucose fed only). The composition of the feed substrate is given in Table 23.

Table 23. Composition of Synthetic Phenol-Glucose Bearing Substrate *

	Compound	Concentration 2000 mg/ℓ Glucose 200 mg/ℓ Phenol
1.	$FeCl_3$	16.20
2.	$MnCl_2 \cdot 4H_2O$	2.50
3.	$ZnCl_2$	2.70
4.	$CaCl_2 \cdot 2H_2O$	1.82
5.	$CoCl_2 \cdot 6H_2O$	2.40
6.	$Na_2B_4O_7 \cdot 10H_2O$	0.95
7.	Na_3 Citrate	146.95
8.	$(NH_3)_6Mo_7O_{24} \cdot 4H_2O$	1.75
9.	KH_2PO_4	340.25
10.	$NaH_2PO_4 \cdot H_2O$	207.00
11.	$(NH_4)_2SO_4$	132.00
12.	NH_4Cl	625.00
13.	$CaCl_2$	111.00
14.	$MgCl_2 \cdot 6H_2O$	203.25
15.	Vitamin Mixture Ethanol Extract	0.875
16.	Cysteine Hydrochloride Solution	0.1250
17.	K_2HPO_4	3919.35
18.	NaH_2PO_4	2699.40
19.	Glucose	2000.00
20.	Phenol	200.00

* All concentrations in mg/ℓ except 15 and 16 are in mℓ/ℓ

Reactor Operation

The schematic diagram of the first column and clarifier of a reactor

system is illustrated in Figure 10. The substrate was fed to the bottom of the first column from the substrate reservoir using a variable speed positive displacement FMI pump, Model RPG-20 (Fluid Metering Incorporated, Oyster Bay, NY). Both pump and reservoir were placed in a refrigerator maintained at 6°C. The substrate was forced upflow through the column. Continuous recirculation of the contents of the first column back to the column inlet was exercised while the effluent was transmitted onwards to the clarifier through a check valve. Any gas produced was collected and measured in the gas buret. The effluent from the first clarifier provided the feed to the second column clarifier configuration and the same was repeated in the third and fourth column clarifier arrangements.

Microbial growth in the feed lines and feed reservoirs was minimized through the daily cleaning of the lines and feed reservoirs.

Reactor Startup

All the anaerobic filters were initially seeded with the supernatant obtained from an anaerobic sludge digester operated by the City of Atlanta at The Clayton Wastewater Treatment Plant. All columns were batch fed with the appropriate phenol or glucose bearing substrates for a period of 10 days. During this period, recirculation of the aqueous contents of each individual filter was exercised in a downflow manner in order to allow the microorganisms to spread throughout the activated carbon medium. After this initial period, the synthetic substrates were continuously fed into the two reactor systems at a flow rate of 5 mℓ/min and feed phenol and glucose concentrations of 200 and 2000 mg/ℓ, respectively.

No biological activity was observed from the phenol fed experimental unit for a continuous operating period of 78 days. This lack of gas production may

be attributed to the combined effect of adsorption of the phenol onto the carbon surface and a consequent starvation of the organisms, as well as to the washout of the anaerobic culture at the initial operating conditions.

This situation was remedied on the seventy-eighth day of continuous operation when the reactor system was reseeded with a mixture of an acetate acclimated methanogenic culture and a phenol acclimated anaerobic sludge provided by Dr. Richard Speece. The feed flow rate was reduced for the remaining period of study down to 2 mℓ/min.

Sampling Procedure and Data Collection

Two T-connections were installed in the recirculation line of each anaerobic filter. Samples were withdrawn from the feed reservoir and the recirculation line of every column and analyzed twice a week. These analyses included:

(a) pH
(b) Total Inorganic Carbon (TIC)
(c) Total Organic Carbon (TOC)
(d) Chemical Oxygen Demand (COD)
(e) Phenol
(f) Volatile Fatty Acids

In addition, the gaseous products from each individual column were measured daily, corrected for moisture content, and converted to standard temperature and pressure using the following equation:

$$V_{D,STP} = V \left(\frac{273.16}{273.16 + T} \right) \left(1 - \frac{V_p}{760} \right) \qquad (45)$$

Where:

T = the room temperature taken in the vicinity of the gas buret, °C;
V = the measured volume of gas produced at 1 atmosphere, mℓ;

V_P = water vapor pressure at temperature T, mm of mercury; and

$V_{D, STP}$ = dry gas produced at standard temperature and pressure, mℓ.

The gas produced was analyzed twice a week for methane, carbon dioxide, hydrogen, nitrogen, and oxygen.

Once study state was reached, additional analyses were conducted for a period of three weeks. These analyses included:

(a) Total Suspended Solids
(b) Volatile Suspended Solids
(c) Alkalinity
(d) Ammonia Nitrogen
(e) Total Kjeldahl Nitrogen (TKN)
(f) Total Inorganic Phosphate
(g) Oxidation Reduction Potential (ORP)
(h) Glucose

In addition, analyses were made to determine the ability of the microorganisms within the system to utilize hydrogen and aqueous carbon dioxide to form methane.

Analytical Methods

pH. The pH of the liquid effluent was measured immediately after sample withdrawal using a Fisher Accumet pH Meter, Model 144. Immediate readings were found to be necessary in order to insure against any shift in pH due to the loss of dissolved CO_2 to the atmosphere.

Total Inorganic and Organic Carbon. The total inorganic carbon (TIC) and total carbon (TC) content of the influent substrate and effluents from all columns was monitored using a Beckman Model 915 Total Organic Carbon Analyser. All samples were filtered through 0.45 μm Gelman Metricel membrane filters prior to analysis. The total organic carbon (TOC) content of the samples was subsequently determined as the difference between the TC and TIC.

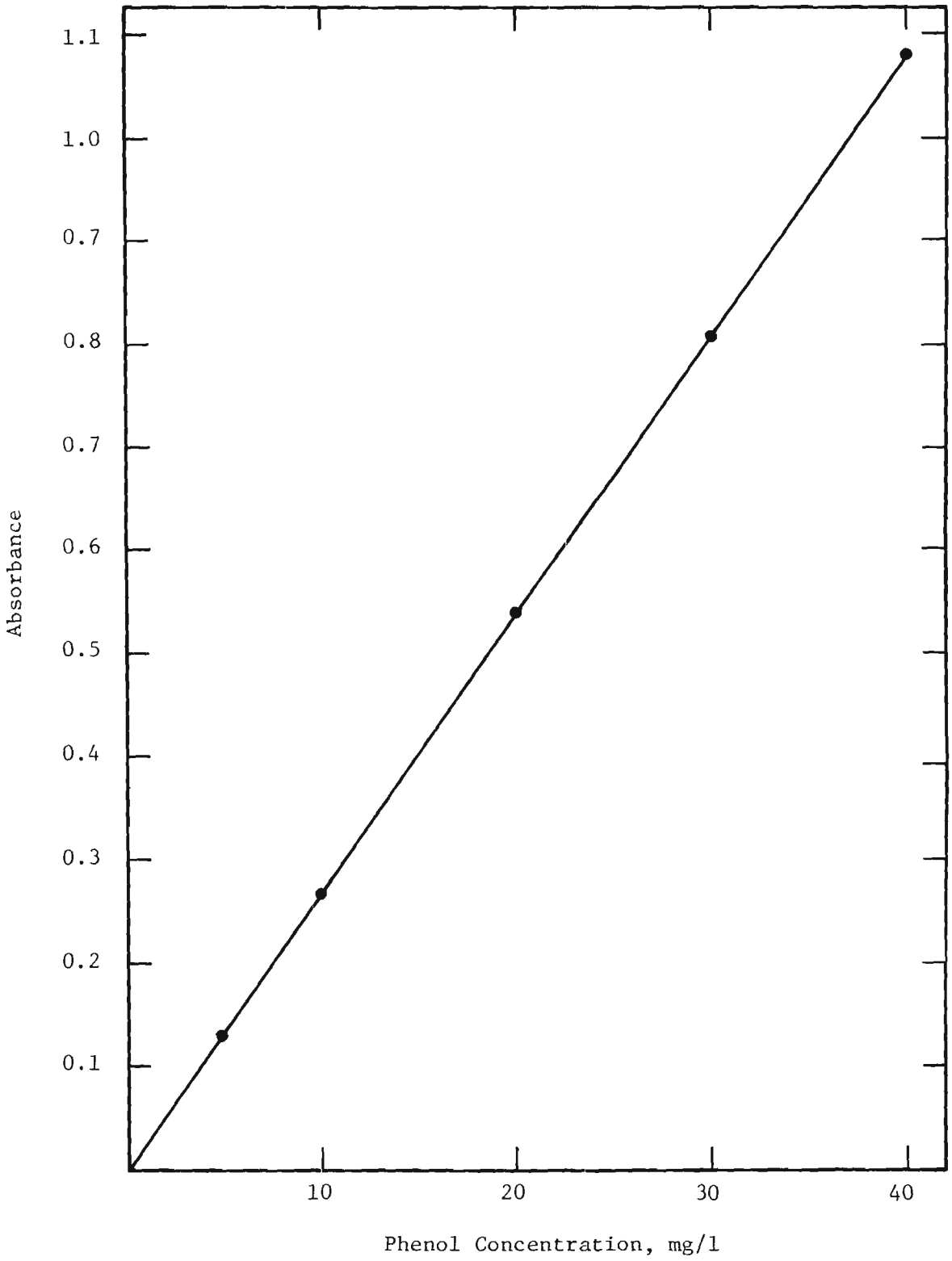


Figure 12. Calibration Curve for Phenol, λ = 286 nm, 1 cm Cell

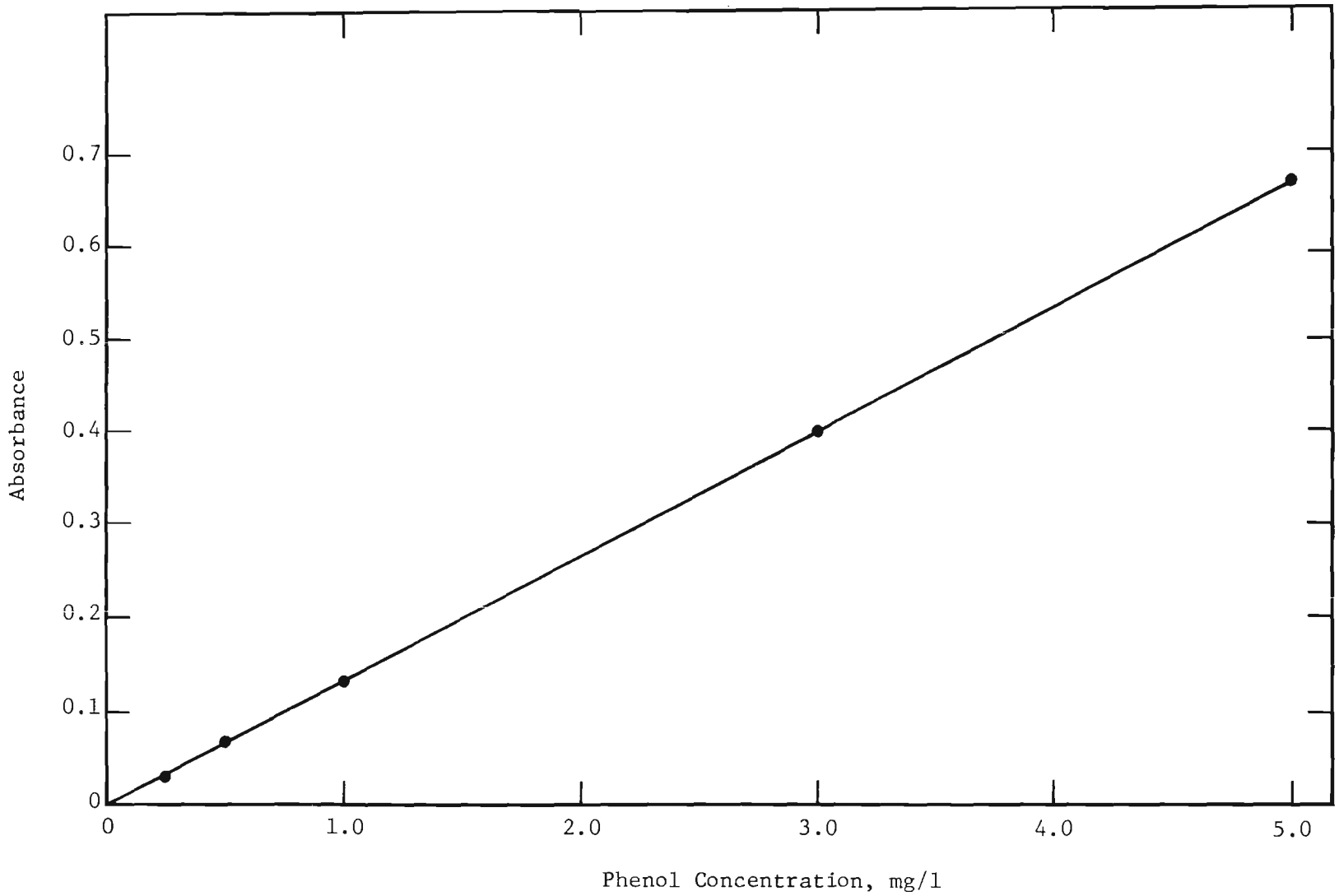


Figure 13. Calibration Curve for Phenol, λ = 286 nm, 5 cm cell

Chemical Oxygen Demand. The chemical oxygen demand (COD) of the organic matter present in the feed and effluents from all columns was determined by the Chemical Oxygen Demand Test as described in section 508 of Standard Methods for the Examination of Water and Wastewater, Fourteenth Edition (1975). All samples were filtered through a 0.45 μm Gelman Metricel membrane filter prior to the analysis.

Phenol Determination. Phenol concentrations were determined using a Beckman Model 26 Spectrophotometer. All samples were filtered through a 0.45 μm Gelman Metricel membrane filter prior to analysis. The pH of each sample was adjusted to 12.0 prior to the absorbance determination. This pH value was found to give the highest sensitivity to absorbance at a wavelength of 286 nm. Standard absorbance versus phenol concentration curves using either 1 cm or 5 cm path length cells are given in Figures 12 and 13. All values are reported in mg/ℓ of phenol.

A Hewlett Packard Model 5830 Gas Chromatograph, Keyboard Control system was utilized in confirming the spectrophotometric results. The Gas Chromatographic column used in the analysis was 183 cm (6 feet) long glass coil with an inner diameter of 2 mm and packed with Carbopak C 60/80 mesh modified with 0.5 percent SP1000. Helium was used as the carrier gas, at an average velocity of 30 cm/sec. The temperature used was 70°C, held for one minute up to 125°C at a rate of 10°C/minute. The injector temperature was 225°C while the FID temperature was 300°C.

Standards and samples were prepared for gas chromatographic analysis according to the following procedure:

(a.) Use a standard or sample of volume equal to 50 mℓ.

(b.) Raise the pH of the sample to 12 in order to insure the complete ionization of the phenols. This high pH was

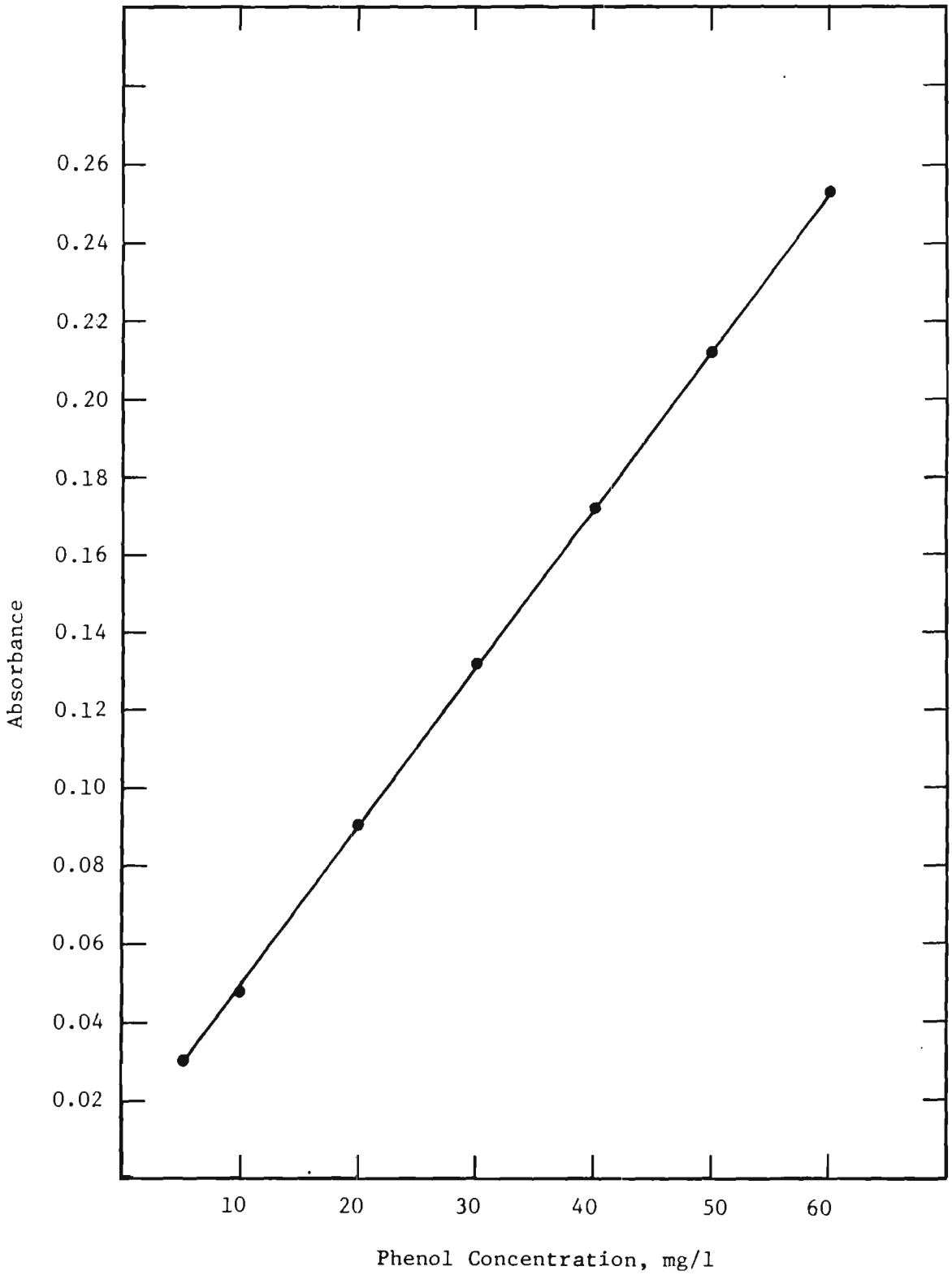


Figure 14. Calibration Curve for Phenol, λ = 460, 1 cm Cell

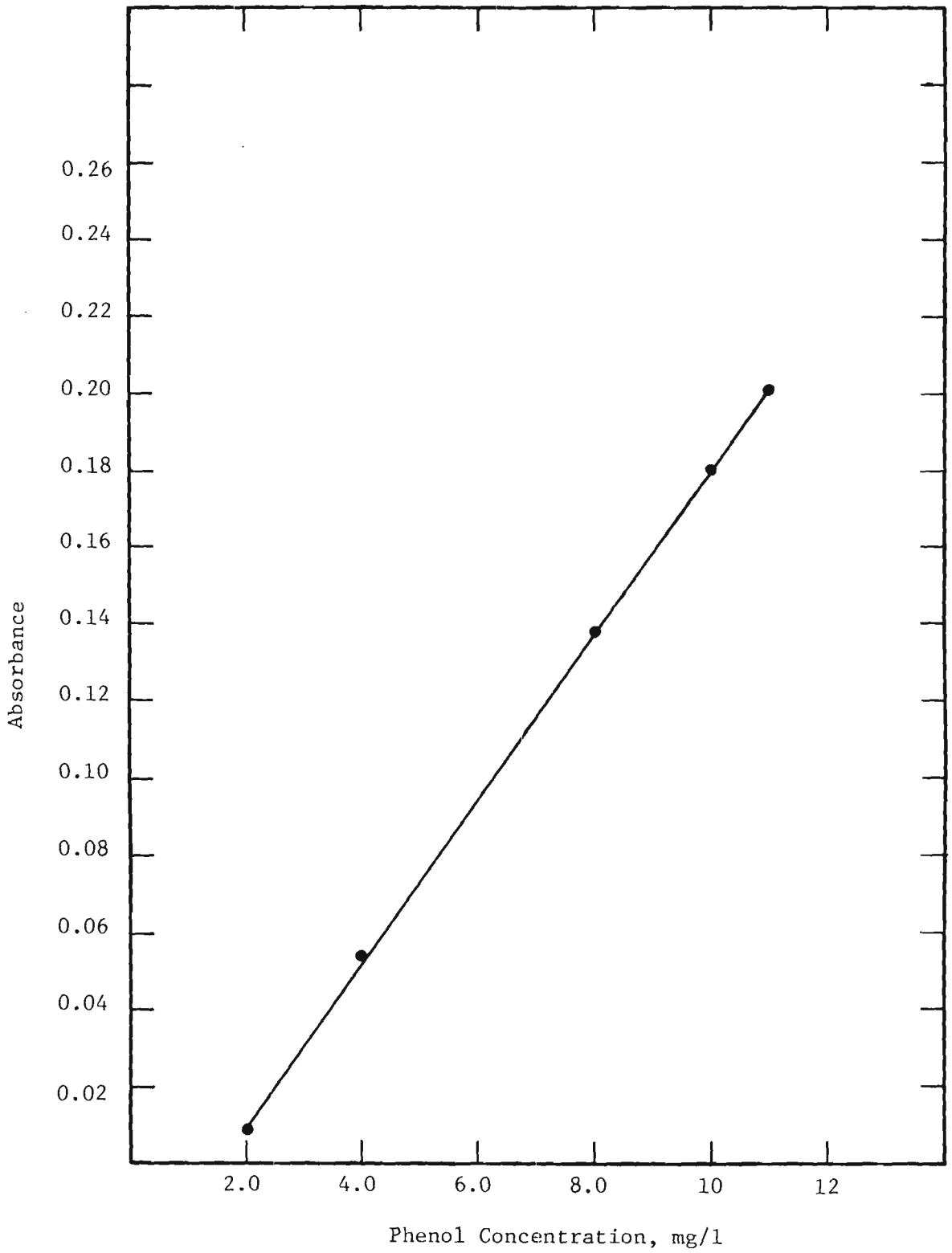


Figure 15. Caliberation Curve for Phenol, λ = 460 nm, 5 cm Cell

achieved by dropping small pellets of sodium hydroxide in the sample.

(c.) Place the sample in a 1 ℓ separatory funnel and add 20 mℓ of methylene chloride (CH_2Cl_2) to the separatory funnel and shake vigorously for one minute. Allow time for phase separation and discard the lower CH_2Cl_2 fraction while retaining the upper water portion.

(d.) Adjust the pH of the resulting water fraction in the separatory funnel to pH 2 using concentrated hydrochloric acid.

(e.) Add 20 mℓ of CH_2Cl_2 to sample in separatory funnel and shake vigorously for one minute. Allow time for phase separation and retain the lower CH_2Cl_2 fraction.

(f.) Concentrate the resulting 20 mℓ of methylene chloride to 1 mℓ by removing the solvent in a Kuderna-Danish Concentrator system.

(g.) One microliter of the extracted and concentrated sample is injected in the injector of the gas chromatographic system.

The chloroform extraction method 510 B of Standard Methods for the Examination of Water and Wastewater, Fourteenth Edition (1975) was also used for the measurement of phenol. The recommended procedure was followed closely with the exception of the distillation step since it was felt that no distillation would be needed due to the nature of the substrate used.

Standard calibration curves for phenol using the chloroform extraction method were developed for both 1 cm and 5 cm light path cells. These curves are given in Figures 14 and 15.

Of the three methods used in this study to monitor the concentration of phenol, the gas chromatographic procedure resulted in more precise measurements. This is due to the excellent resolution and separation obtained with this procedure. Spectrophotometric analysis for phenol using absorbence at 286 nm resulted in a consistent overestimation of the actual phenol residual

concentration. This is due to the interference and additive effects of other organic compounds at the specified absorption wavelength. The results obtained from the chloroform extraction method were, in most cases, intermediate to the concentration values generated using the other two procedures.

Volatile Fatty Acids. The volatile fatty acids (acetic, propionic and butyric acids) were analyzed in the filtered samples using a Hewlett Packard F&M Scientific Model 700 Laboratory Chromatographic system. All values are reported in mg/ℓ as acetic acid.

The Gas Chromatographic Column used in the analysis was a 183 cm (6 feet) long aluminum coil with an internal diameter of 0.32 cm (0.125 inch) and packed with 15 percent SP-1220,1 percent H_3PO_4, 100/120 Mesh Chromosorb wAw. Nitrogen was used as the carrier gas at an average flow rate of 30 mℓ/min. An air to hydrogen ratio of 10 to 1 was maintained. The detector temperature was maintained at 185°C while the injector and column temperatures were held at 180 and 140°C, respectively. Filtered undiluted samples were injected directly into the chromatographic system. Standard solutions of acetic, propionic and butyric acids were used for calibration.

Total and Volatile Suspended Solids. The suspended solids content of the samples was determined using Gooch crucibles and glass fiber filters as described in section 208 D of Standard Methods for the Examination of Water and Wastewater, Fourteenth Edition (1975). In this analysis, the required volumes of samples were added to preweighed crucibles and filtered under vacuum. The crucibles were then placed in a 103°C oven for a period of one hour. After this period, the crucibles were removed and cooled in individual dessicators for over 2 hours and weighed again for the determination of total suspended solids. The total volatile solids were determined by placing the cooled crucibles in a muffle furnace at 550°C for a period of 30 minutes, cooling them in individual

dessicators for a minimum of 2 hours and reweighing.

Alkalinity. Alkalinity determinations were made on all influent and column effluents according to the procedure described in section 403 of Standard Methods for the Examination of Water and Wastewater, Fourteenth Edition (1975). Instead of using methyl orange as an end point indicator, however, the titration was assumed to be complete at pH 4.0. The sulfuric acid titrant was standardized and averaged around a normality of 0.02. The volume of the titrated sample was 50 mℓ. Samples were titrated immediately after withdrawl in order to avoid the loss of CO_2 upon exposure to the atmosphere. All alkalinity values are reported in mg/ℓ as $CaCO_3$.

Ammonia Nitrogen. Ammonia nitrogen determinations were made on the filtered samples using the Technicon Corporation Industrial Method 19-69W. The automated procedure for the determination of ammonia in water using the Technicon AutoAnalyzer Proportioning Pump in conjunction with a Technicon AutoAnalyzer Sampler and Recorder utilizes the Berthelot reaction in which the formation of a blue-indophenol complex occurs when the ammonium bearing solution is added to sodium phenoxide followed by the addition of sodium hypochlorite (Ferrari, 1960). A solution of potassium sodium tartarate (Rochelle Salts) is added to the sample stream to eliminate the precipitation of the hydroxides of any heavy metals which may be present.

An aqueous solution of ammonium chloride was used to obtain standard calibration curves for this analysis. These standards were prepared on the day of analysis using serial dilutions to obtain concentrations ranging from 0.03 mg/ℓ to 3 mg/ℓ.

Total Kjeldahl Nitrogen. The Technicon Corporation Industrial Method 30-69A was utilized in monitoring the total Kjeldahl nitrogen (TKN) content of the samples. This procedure involved the digestion of the organic material using the Technicon Continuous Digester. The ammonia thus released was quantitatively measured using the Berthelot reaction described previously.

Total Inorganic Phosphate. The determination of the total inorganic phosphate in the liquid samples was done using the Technicon Corporation Industrial Method 4-68W. The total inorganic phosphorus is first converted to the orthophosphate form by hydrolysis with sulfuric acid. The addition of aminonaphthol sulfonic acid reduces the phosphomolybdic acid produced in order for the phosphate concentration to be measured (Lundgren, 1960).

Aqueous solutions of anhydrous potassium dihydrogen phosphate were used to generate standard calibration curves in the concentration range of 0 - 40 mg/ℓ - P.

Oxidation Reduction Potential. A 70 cc continuous flow through cell having three parts was designed for the measurement of the insitu oxidation reduction potential (ORP). A platinum combination electrode connected to a Fisher Accumet pH Meter, Model 144, was inserted tightly in the continuous flow cell. The other two parts of the cell were connected to the two T-connections on the recirculation line of the column under consideration using Tygon tubing. The flow through cell was filled slowly in an upright manner to avoid any oxygen contamination and once filled and sealed, the recirculated flow was completely diverted through the cell and the ORP was recorded when the reading was stabilized. All ORP values are reported versus a saturated calomel reference electrode.

Glucose Analysis. The feed substrate and all column effluents were analyzed for glucose in cases where the latter was used in the feed substrate. Glucose analysis was conducted on samples filtered through 0.45 μm Gelman Metricel membrane filters. A 4 mℓ volume of the sample was then well mixed with 5 mℓ of a potassium ferricyanide stock solution containing 0.25 g/ℓ of potassium ferricyanide. The mixture was then heated in a water bath to 95°C. After heating, the sample is brought down to room temperature and analyzed spectrophotometrically for absorbance or percent transmittance at 420 nm. The glucose content of the sample is then computed from the standard calibration curve shown in Figure 16. In case the glucose content of the sample was above 40 mg/ℓ, then the sample was diluted with a solution containing 10 g/ℓ of $NaCO_3$ and 1 mℓ/ℓ of the compound Brij - 35 prior to potassium ferricyanide addition.

Gas Analysis. Gas samples were analyzed for methane, carbon dioxide, nitrogen and oxygen using a Fisher Gas Partitioner Model 25V in conjunction with a Fisher Thermal Stabilizer Model 27 and a Coleman Recorder, Hitachi 165. Helium was used as the carrier gas. Analysis for hydrogen was accomplished using a Fisher Gas Partitioner Model 25V with argon as the carrier gas. Certified Calibration Standards (Matheson, East Rutherford, NJ) were used to calibrate the gas analyzer.

The helium carrier column was a 76.20 cm (30 inch) long aluminum column with a 0.64 cm (0.25 inch) outer diameter. This column was packed with 30 percent diethylhexylsebacate on 60 x 80 mesh Columnpak followed by a 183 cm (6 feet) long by 0.476 cm (0.1875 inch) outer diameter aluminum column packed with 5A Molecular Sieve 60 x 80 mesh. The helium gas flow rate was set at 80 mℓ/minute.

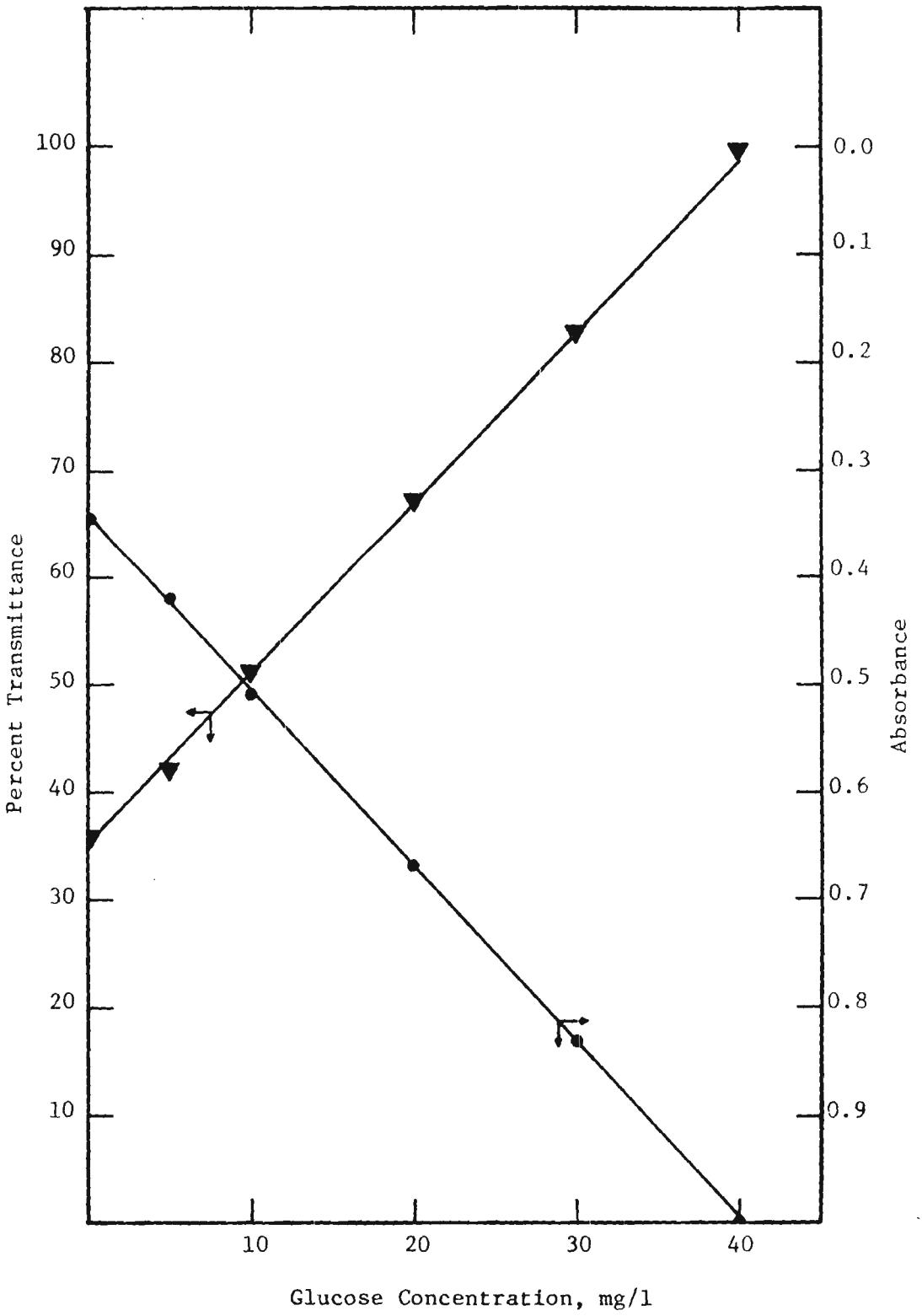


Figure 16. Calibration Curve for Glucose, λ = 420 nm

The argon carrier column had identical dimensions and the same molecular sieve packing as the helium carrier column. However, the first section was packed with 30 percent hexamethylphosphoramide on 60 x 80 mesh Columnpak. The argon gas flow rate was set at 80 mℓ/minute.

Hydrogen Utilization and Methane Formation. Anaerobic pure culture investigations have demonstrated that hydrogen appears to be the only universal substrate for all methanogens. Based on this fact, Hudson (1979) developed a test whereby a biomass bearing sample (either in solution or attached to medium granules) is placed in an environment of hydrogen gas and a carbonate bearing substrate for a period of 84 hours. The quantity of methane gas produced in the vial by the end of the incubation period is then taken as a relative measure of the methanogenic activity within the sample.

The experimental protocol employed involved the maintenance of strict anaerobic conditionsin the innoculation of a series of 22 mℓ vials with the following:

(a.) 7 mℓ of a prereduced nutrient-bicarbonate medium (see Table 23). This medium is essential as the micro-organisms effecting hydrogen metabolism must be restricted only by that substrate. The bicarbonate salt provides the source of electron acceptors for the production of methane.

(b.) 7 mℓ of an anaerobic culture or a specific number of granules of activated carbon were then added to the vials while maintaining a nitrogen atmosphere within the tubes.

(c.) The vials were then sealed with serum stoppers designed for syringe applications.

(d.) The head space and aqueous phase within the vials was then purged with hydrogen gas for a period of 2 minutes in order to completely displace the original head space gas.

(e.) After flushing with hydrogen gas, the vials were mounted on a slowly revolving rack to insure mixing,

and the rack, along with the vials, was incubated for a period of 84 hours at 37°C.

(f.) After incubation, the vials were allowed to stand for 1 hour at room temperature prior to gas analysis.

(g.) The head space of each vial was then brought to a pressure of 1 atmosphere using degassed distilled water. The distilled water was introduced into the vial using a syringe and the volume of distilled water added was measured and recorded.

(h.) Once the head space pressure was equilibriated with the atmospheric pressure, the head space gas was analyzed for methane, carbon dioxide, hydrogen, and nitrogen.

Table 23. Composition of Vial Test Medium

Compound	Quantity
NH_4Cl, g	0.6
KH_2PO_4, g	1.0
K_2HPO_4, g	2.0
$MgCl_2 \cdot 6H_2O$	20.00
$CoCl_2 \cdot 6H_2O$	10.0
$CaCO_3$, g	1.0
$NaHCO_3$, g	5.3
Vitamin-mineral (dry), g	0.5
Cysteine Hydrochloride Solution, mℓ	5.0

Make up to 1 ℓ with distilled water, mix, settle and then decant the supernatant. Add 1 mℓ of 0.01 g/ℓ Resarazin to supernatant.

Electron Micrography. Electron microscopic observations were made on the virgin and biologically coated carbon granules, using a Cambridge Instrument Stereoscan Mark II A Electronmicroscope. The granules were first washed and freeze dried. Individual carbon granules were then placed onto glass slides which were subsequently placed on a brass block in liquid nitrogen for freezing the granules on the glass slides. The slides were then placed in a vacuum chamber to complete the drying process. The granules were then placed on slides which were previously painted with a silver conducting paste. The slides were then placed in the vacuum chamber and a thin layer of gold-palladium was plated on the granule surface.

RESULTS AND DISCUSSION

Two anaerobic-activated carbon filter systems were constructed for use in this study. Each reactor consisted of four columns connected in series with a clarification unit following each of the first three columns. These units were operated separately using a 200 mg/l phenol bearing synthetic substrate to feed one while the other was operated on a 2000 mg/l glucose bearing substrate. The results obtained during this stage of the work revealed that the fourth column of each reactor was essentially redundant with no biological activity occurring in either of the two columns. Consequently, the fourth column of every set of reactors was taken out of service and the remaining three columns of every reactor were operated using a 400 ml/l phenol bearing substrate in one and a mixture of 200 mg/l phenol and 2000 mg/l glucose bearing substrate in the other. The remaining two columns were then equipped with separate feed and recirculation pumps and filled with equal volumes of anthracite in one and granular activated carbon in the other. Both the anthracite and granular activated carbon had the same particle size distribution and the two reactors were fed a 2000 mg/l glucose bearing substrate in order to determine whether there was indeed an advantage to the use of granular activated carbon over the cheaper anthracite coal as a packing medium in the anaerobic filter process.

All anaerobic filters were operated using synthetic substrates where phenol and/or glucose represented the major sources of organic carbon in the feed solutions. An additional source of organic carbon in the feed substrate was due to the ethanol, sodium citrate and vitamin extract content of the salt solution. The COD of the stock salt solution averaged around 25,668 mg/l while the TOC was 6,643 mg/l giving rise to a COD to TOC ratio of 3.86. The data in Table 24 give the contribution to COD and TOC of one gram of glucose or phenol.

Table 24. COD and TOC Contribution of Phenol and Glucose

Compound	Molecular Weight (g)	Contribution of 1g of Organic Compound COD (g)	TOC (g)
Phenol	94	2.3830	0.7660
Glucose	180	1.0667	0.4000

Treatment of Glucose Bearing Substrate

One four stage anaerobic-activated carbon filter system was operated using glucose as the primary organic carbon source for a continuous feeding period of 265 days. Throughout this experiment, the feed substrate was prepared daily in 4 ℓ batches using 80 ml of the salt solution, 140 ml of the phosphate buffer solution, 8.0 g of glucose and distilled water. The theoretical values of the feed COD and TOC, computed using the measured values for the salt solution and the theoretical value for glucose given in Table 24, were 2647 and 933 mg/l, respectively. The measured and theoretical values of the COD and TOC in the feed substrate are presented in Figure 17. The chemical oxygen demand of the feed substrate averaged around 2420 mg/l while the average total organic carbon content of the feed was 898 mg/l. The feed substrate had a computed COD to TOC ratio of 2.84 while the measured ratio was 2.69.

The pH of the feed substrate was maintained at 7.5 throughout the study. At this pH, the feed had an alkalinity of 3360 mg/l as $CaCO_3$ (end point of alkalinity titration was 4.0) which was sufficient to maintain a pH within the reactor system ranging between 6.9 and 7.1.

The experimental reactor was operated at an influent flow rate and glucose concentration of 5 ml/min and 2000 mg/l, respectively, for a period of 66 days at which time the feed flow rate was reduced to 2 ml/min resulting in

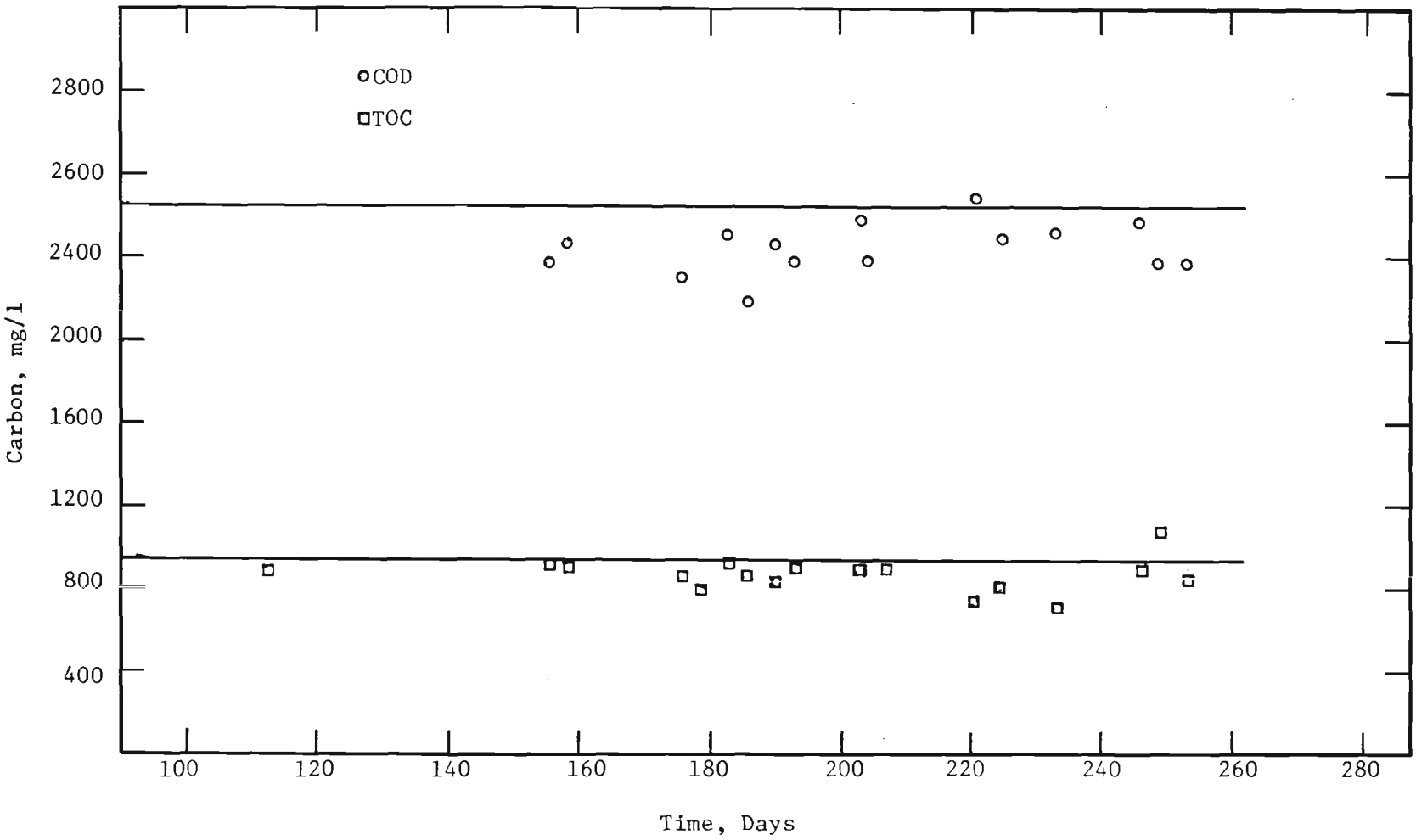


Figure 17. Influent COD, TOC for Glucose Fed Reactor

an empty bed hydraulic retention time of 11.62 h in every reactor column. Recirculation of the aqueous contents around every individual reactor was exercised continuously at a flow rate of 50 ml/min. This recirculation served to help maintain the system pH close to neutral by providing an additional bicarbonate buffer capacity (Chian and DeWalle, 1976).

During the first 90 days of continuous operation, the treatment system went through a transitional period during which methane and hydrogen gas were produced on an intermittant basis. After about 80 days of continuous operation, a more steady gas production rate was observed; while, at the same time, no hydrogen gas was detected in the gas phase after day 80.

Organic and Inorganic Carbon. The organic and inorganic carbon content of the filtered effluents from all four anaerobic columns is presented in Figures 18, 19, 20 and 21 for the continuous operating period extending between day 90 and day 200. The carbon content in the feed substrate was presented in Figure 17 for the same period of operation. The TOC in the feed substrate averaged around 898 mg/l. The organic carbon content in the effluent from the first column ranged from a high of 260 mg/l on day 100 to a low of 92 mg/l on day 255. During the latter 70 days of this experiment, the TOC content of the effluent from the first column averaged around 120 mg/l resulting in a TOC conversion efficiency in the first column of 86.6 percent.

The total organic carbon content of the effluent from the second column varied from a high of 190 mg/l on day 110 to a low of 30 mg/l during the period between days 185 and 190. The TOC in the second column effluent, however, stabilized at an average value of 66 mg/l during the final period extending from day 185 to day 255. During this period, the second column was achieving an average reduction in the TOC of its influent exceeding 45 percent which resulted in an overall organic carbon removal efficiency across the first two columns of 92.6 percent.

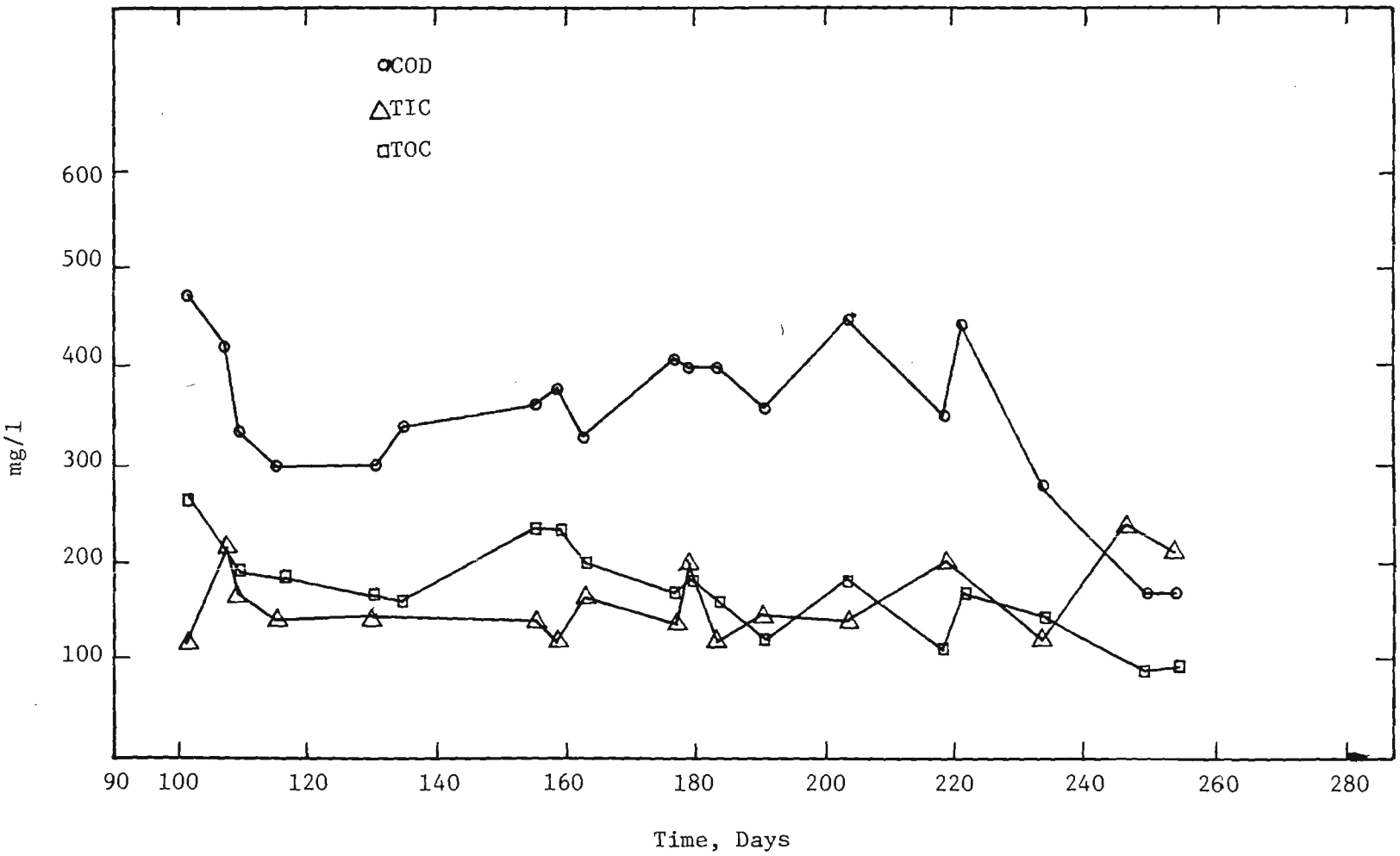


Figure 18. Effluent COD, TOC, TIC from Column Number One Glucose Fed Reactor

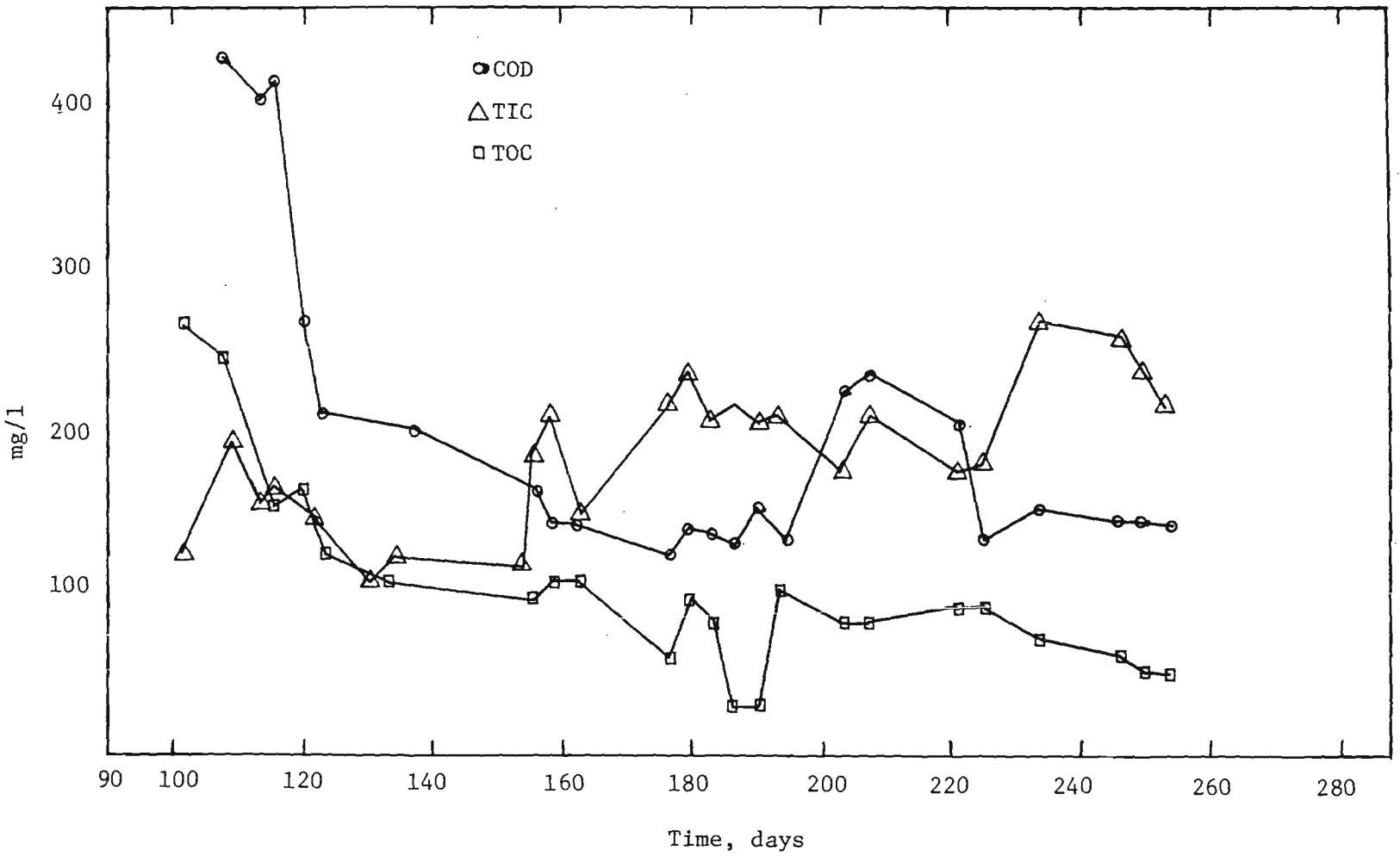


Figure 19. Effluent COD, TOC, TIC from Column Number Two Glucose Fed Reactor

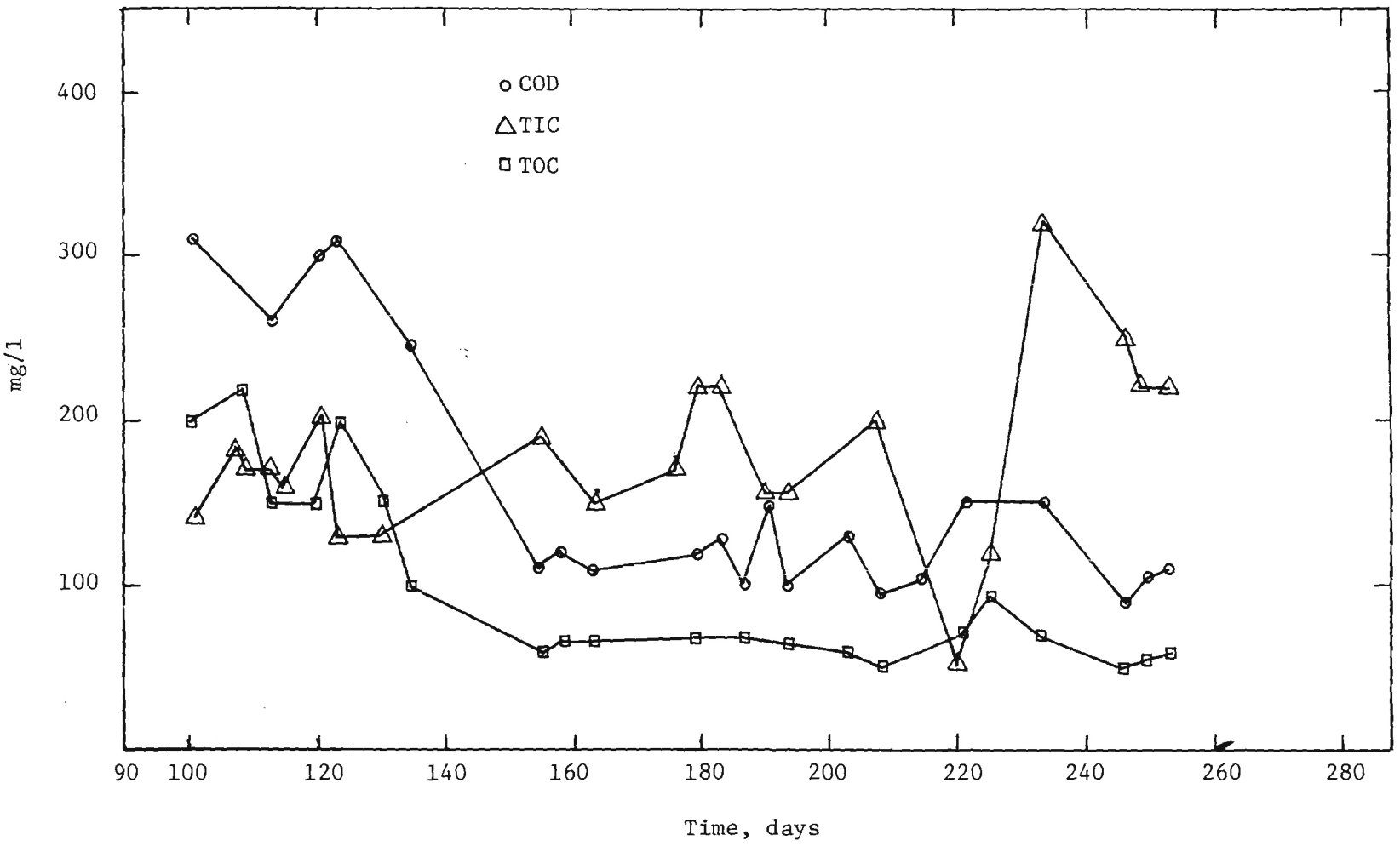


Figure 20. Effluent COD, TOC, TIC from Column Number Three Glucose Fed Reactor

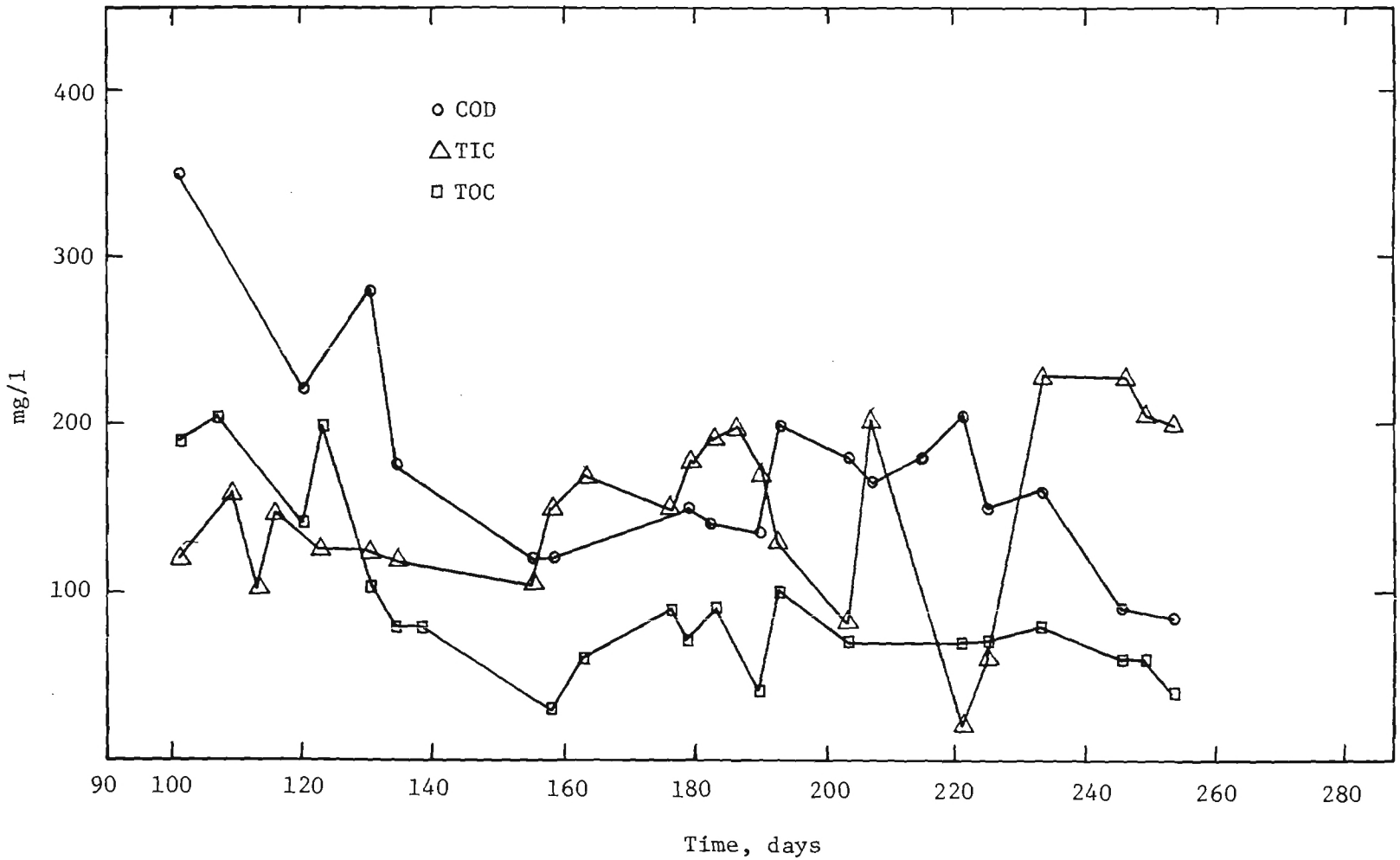


Figure 21. Effluent COD, TOC, TIC from Column Number Four Glucose Fed Reactor

The total organic carbon content in the effluent from the third column fluctuated from a high of 220 mg/l on day 109 to a low averaging 64 mg/l between day 185 and the termination of the experiment on day 255. During this period, the third column resulted in a decrease in the TOC of its influent of only 3 percent which results in an overall organic removal efficiency across the first three columns of 92.9 percent.

The average TOC in the final effluent from the fourth column averaged at 66 mg/l for the period extending between days 185 and 255. This resulted in no TOC removal across this column. Consequently, the fourth column of the reactor system was accomplishing very little as far as TOC removal and, as a result, it was eliminated from the treatment scheme during subsequent experiments.

The inorganic carbon content of the column effluents (see Figures 18, 19, 20 and 21) increased as the organic carbon content in these flows decreased. Carbon dioxide and methane gas represent the major end products of the anaerobic degradation of glucose. According to Equation 20, glucose is converted anaerobically to equal molar quantities of methane and carbon dioxide. However, the high solubility of inorganic carbon (CO_2, HCO_3^- and $CO_3^=$) at the neutral pH of anaerobic digestion and the relatively low carbon content of the feed waste render the gas phase very rich in methane. Monitoring of the inorganic carbon content of the aqueous phase is very essential in that it provides means for establishing a material balance on the fate of the carbon content of the feed wastewater.

Chemical Oxygen Demand. The chemical oxygen demand of the filtered effluents from all four anaerobic-activated carbon columns was presented in Figures 18, 19, 20 and 21 for the continuous operating period extending between day 90 and day 260. The chemical oxygen demand of the feed substrate was presented in Figure 17

for the same period of operation. The COD of the feed substrate averaged at 2420 mg/l. The COD of the effluent from the first column varied from a high of 475 mg/l on day 100 to a low of 170 mg/l on the last day of operation. During the latter 70 days of this experiment, the average COD of the effluent from the first column was 302 mg/l while the average TOC for the same period was 120 mg/l resulting in a COD to TOC ratio of 2.52 as compared to a ratio of these parameters in the feed substrate of 2.69 indicating an increase in the oxidative level of the organic content of the first column effluent over their oxidative level in the feed substrate. A COD reduction of 87.5 percent was achieved across this column during this latter period of operation.

The COD of the effluent from the second column varied from a high of 420 mg/l on day 100 to a low of 120 on day 175. The COD of the effluent from the second column, however, stabilized at an average value of 160 mg/l during the final period of operation which extended from day 185 to day 255. This corresponds to a COD removal across the second column of 47 percent, and a cumulative COD removal across the first two columns of 93.4 percent.

The COD in the effluent from the third column varied from a high of 310 mg/l on day 100 to a low of 90 mg/l on day 245. The average COD in the effluent from the third column during the last 70 days of operation was 116 mg/l which corresponded to a COD removal efficiency across the third column of 27.5 percent and a total COD removal of 95.2 percent in the first three columns.

Once again, the fourth column resulted in no removal of COD. In fact, the average COD in the effluent from the last column exceeded the influent value during the last 70 days of operation indicating that desorption of previously adsorbed organic compounds may be occurring. Overall the COD to TOC ratio decreased from a high of 2.69 in the feed down to 2.52 in the

effluent from the first column, 2.42 in the effluent from the second column and 1.81 in the third column effluent. This continuous reduction in this parameter is due to the removal from the aqueous phase of the system of the highly reduced methane which has a COD to TOC ratio of 5.33.

Gas Production. The anaerobic gas produced from every column reactor was collected separately and monitored for volume and composition. Very little gas production was observed from the reactor system prior to day 90 of continuous operation. After that day, continuous gas production was observed from the first two columns. The gas production rate from the first column (see Figure 22) increased steadily until day 210 after which time it reached a steady production rate of 1,897 ml/day of methane and carbon dioxide measured at standard temperature and pressure (STP). At that time methane constituted 86.1 percent of the gaseous product while carbon dioxide accounted for the remaining 13.9 percent.

Steady gas production from the second column was also observed after day 90 of continuous operation (see Figure 23). Contrary to gas production from the first column, however, the gas production rate from the second column decreased steadily from a high of 651 ml/day of methane and carbon dioxide at STP during the period extending from day 100 to day 120 to a production rate of only 194 ml/day of methane and carbon dioxide at STP during steady state operation. This decrease in the gas production rate from the second column corresponded to an increasing gas production rate from the first column implying that at steady state gas production from the second column was limited by the available substrate in the feed solution to this column.

The cumulative methane and carbon dioxide gas production from the first two columns is presented in Figure 24. During steady state operating conditions,

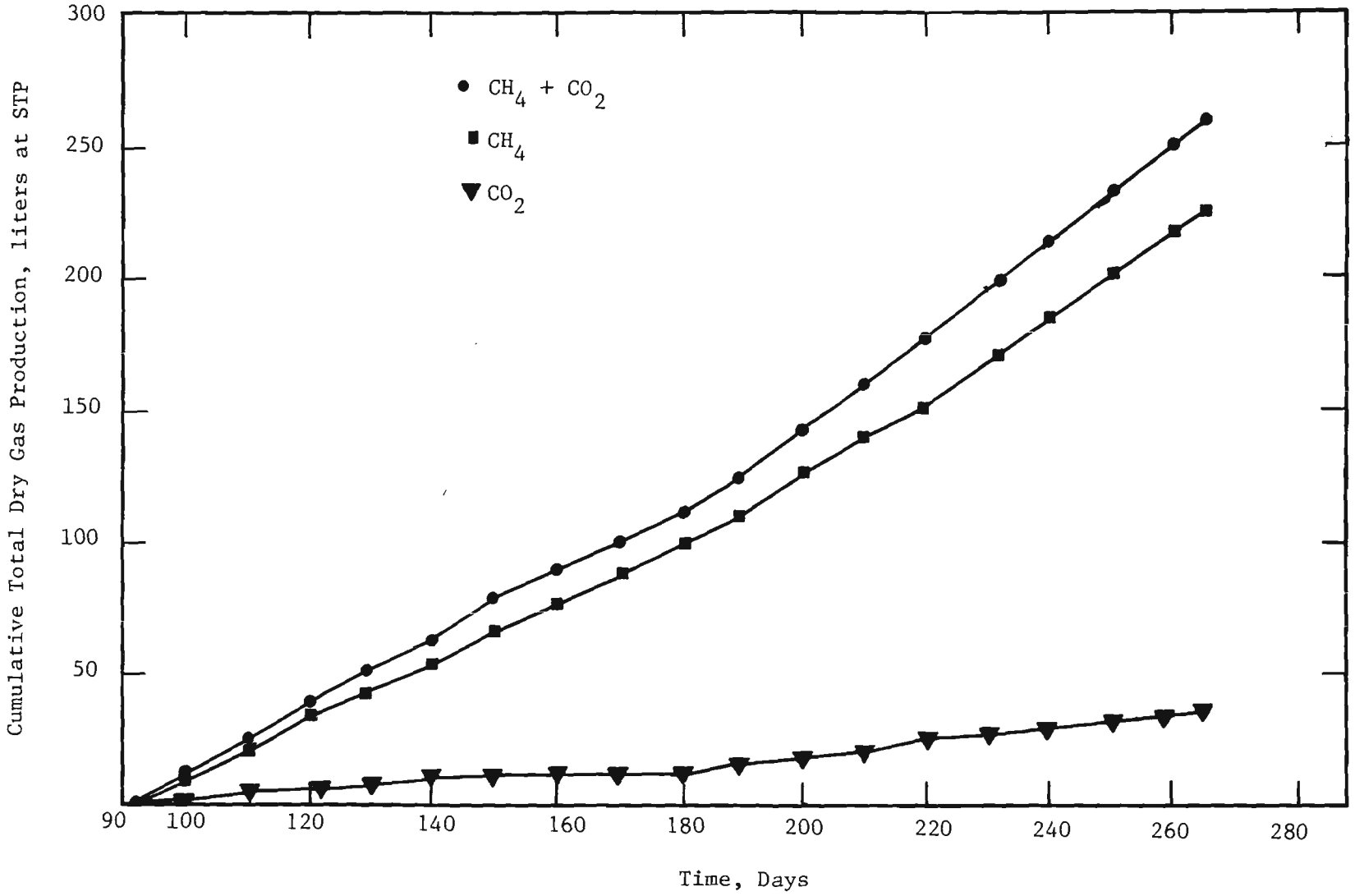


Figure 22. Gas Production from Column One Glucose Fed Reactor

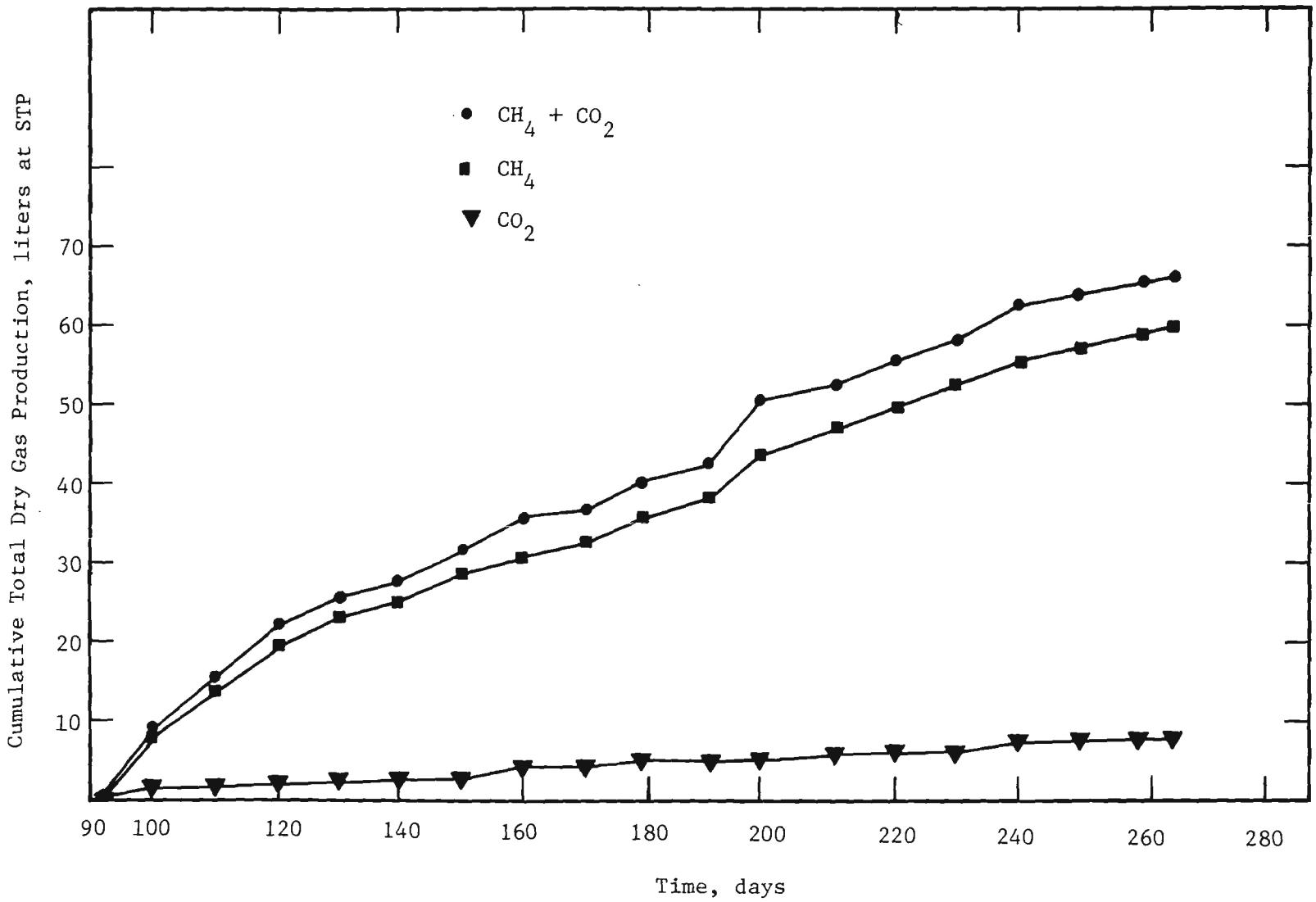


Figure 23. Gas Production from Column Number Two Glucose Fed Reactor

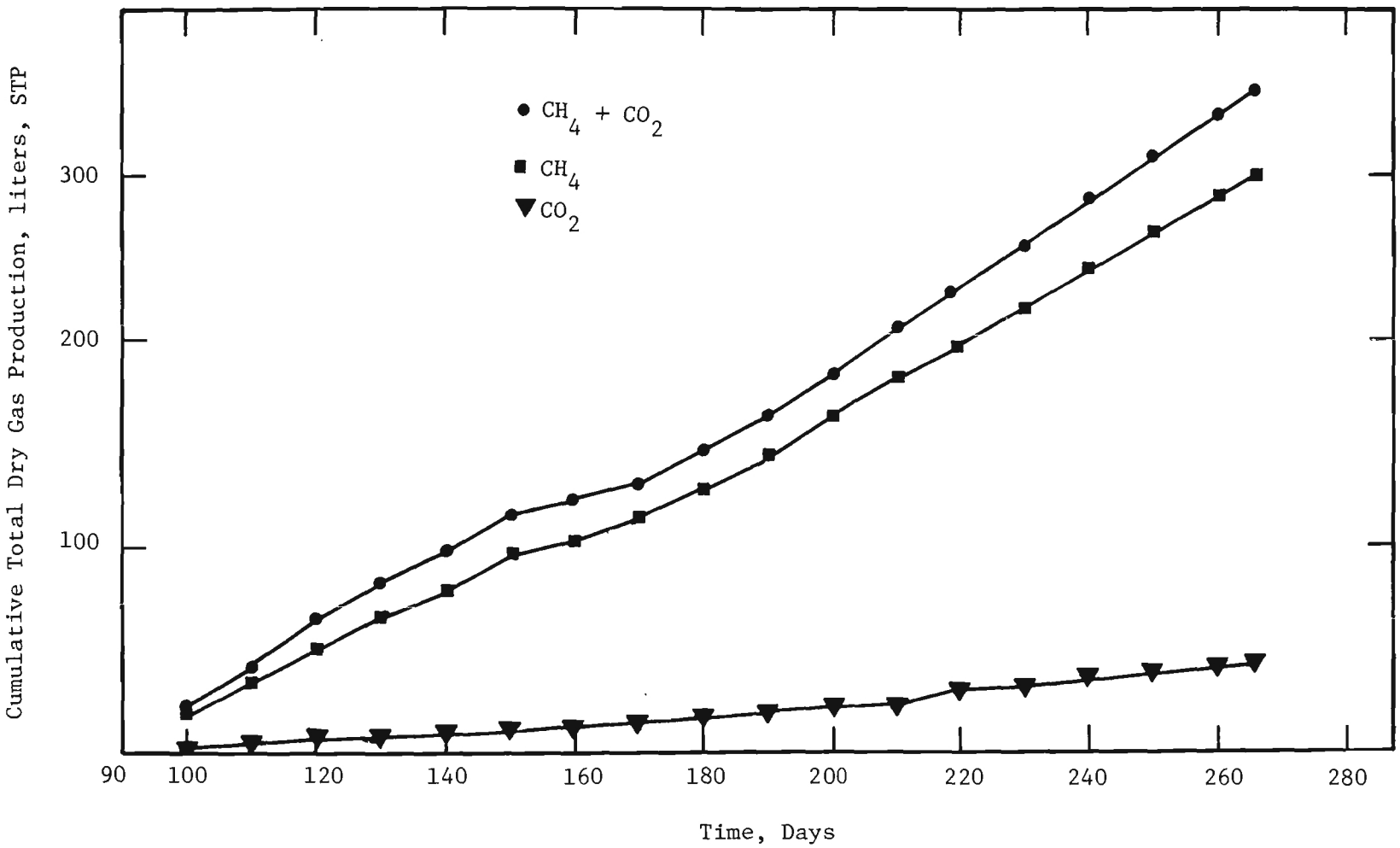


Figure 24. Total Gas Production from Columns One and Two Glucose Fed Reactor

the gas production rate from the first two columns amounted to 2,091 ml/day at STP out of which 86.2 percent was methane. According to Equation 40, a total of approximately 2413 ml of methane at STP should be produced from the treatment system if all the organic carbon in the feed is converted to equal molar quantities of methane and carbon dioxide. At steady state operating conditions, 1802 ml of methane at STP were actually produced leading to the conclusion that 74.7 percent of the organic in the feed had been converted to the anaerobic gaseous products. The total organic carbon concentration data presented earlier revealed that 92.6 percent of the feed organic carbon was removed in the first two columns of the treatment system. This results in an unaccounted for carbon of 17.9 percent of the feed. If the missing carbon is assumed to be converted to biomass, this would result in a TOC growth yield coefficient of 19.33 percent. The COD equivalent of the methane gas produced from the first two columns is 1788 mg/l, while the average COD removal during steady-state operating conditions across the first two columns was 2260 mg/l. If the missing COD is attributed to biomass production, this would result in a COD yield coefficient of 21 percent which is reasonably close to the COD yield coefficient of 15 percent reported by Young and McCarty (1967) on the treatment of a protein carbohydrate waste with the anaerobic activated carbon filter.

In order to illustrate the different stages that the treatment system exhibited during the progress of this experiment, carbon material balances were constructed across the feed substrate and the effluents from all four columns. These material balances are extremely helpful as a tool to better understand the performance of an anaerobic treatment process and help assess its full treatment potential.

The underlying concept behind the construction of such material balances lies in the fact that in an anaerobic environment, the organic carbon content of the feed substrate could be converted to either (a) methane and carbon dioxide gas; (b) dissolved inorganic carbon in the form of aqueous carbon dioxide or bicarbonate and carbonate ions; (c) remain in the aqueous phase either as the parent feed compound or in the form of some intermediate biological product; (d) result in the production of biomass which may remain within the system or escape in the effluent stream; and (e) adsorb onto the activated carbon surface which is a unique and special feature of this treatment process. Mathematically this material balance could be restated as:

$$TOC_{in} + TIC_{in} = TOC_{out} + TIC_{out} + CH_{4_g} + CO_{2_g} \mp \text{Biomass Produced} \mp \text{TOC Adsorbed} \quad (46)$$

The ($\mp$) sign prior to the Biomass Produced and TOC Adsorbed is justified because negative biomass production and adsorption may occur due to organism decay and bioregeneration of the carbon surface. Equation 46 may be rewritten as:

$$\text{Biomass Produced} + \text{TOC Adsorbed} = TOC_{in} + TIC_{in} - TOC_{out} - TIC_{out} - CH_{4_g} - CO_{2_g} \quad (47)$$

All the parameters on the right side of Equation 47 are measurable and may readily be incorporated into the expression. The left hand side of Equation 47, however, is not easy to evaluate directly and consequently the value of the two lumped parameters may be arrived at only though the substitution of the values of the parameters on the right side of the equation. If the value of the quantity to the left of Equation 47 comes out to be positive, it implies that adsorption onto activated carbon and/or biomass production are occurring, if the value of these two terms is negative then biomass decay and bioregeneration of the carbon are proceeding at a rate exceeding adsorption and biomass production.

If Equation 47 is to be evaluated using concentration units in the aqueous phase, then the carbon equivalent of the carbon dioxide and methane gas produced

should be normalized to aqueous phase concentration units. This is accomplished as follows:

(a) The volume of methane and carbon dioxide, expressed in liters at STP per day is divided by the flow rate into the reactor system expressed in liters per day.

(b) The resulting quotient is then divided by the standard gaseous molar volume and multiplied by the atomic weight of the carbon, 12,000 mg/1 to yield the carbon equivalent of the gaseous products.

(c) The carbon equivalents of the gaseous products from the first and second column are added to the total aqueous carbon in the effluent from the second column. This accumulation procedure is repeated for columns 3 and 4 in order to maintain the integrity of the carbon balance throughout the treatment system.

A chemical oxygen demand material balance across the treatment system could also be performed because of the strict anaerobic nature of this treatment process. In this case, the chemical oxygen demand of the methane gas produced is evaluated using the relationship:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{48}$$

which yields a COD equivalent of 2.857 grams per liter of methane gas produced when expressed at standard temperature and pressure. Carbon dioxide is not included in this analysis because its carbon content is already in its highest oxidative state. Mathematically a chemical oxygen demand material balance may be expressed as:

$$COD_{in} = COD_{out} + COD_{methane} \mp COD_{adsorbed} \mp COD_{biomass} \tag{49}$$

The rationale behind the use of ($\bar{+}$) prior to the last two parameters in Equation 49 is due to the same reasoning given the equivalent terms in Equation 46. Equation 49 may be rewritten as:

$$COD_{biomass} + COD_{adsorbed} = COD_{in} - COD_{out} - COD_{methane} \quad (50)$$

Once again, the left hand side of Equation 50 could be evaluated only through the substitution of the appropriate values of the parameters appearing on the right hand side of this equation. If the value of the left hand side turns out to be positive it signifies that biomass production and/or adsorption are occurring, while, on the other hand, if the value of these two terms turn out to be negative then biomass decay and bioregeneration of the carbon are proceeding at a rate exceeding biomass production and adsorption onto activated carbon.

Carbon material balances across the treatment system were constructed for days 155, 190, 194 and 153 of continuous operation. The carbon material balance for day 155 (see Figure 25) represents the treatment system during a period when adsorption of organic matter was occurring in columns 1, 2 and 4. A close examination of Figure 24 reveals that only 56 percent of the total carbon in the feed is accounted for in the final effluent. Such a loss of carbon is too high to attribute to biomass production and it is most probably due to the adsorption onto the activated carbon of some of the higher volatile acids intermediates of the anaerobic degradation of glucose. No loss of carbon was observed across the third column since both the TC and the TC and carbon equivalent of the gas produced were similar in the influent and effluent from that column.

The carbon material balance across the treatment system for day 190 of continuous operation (see Figure 26) represents the state of the treatment system during a period where 44 percent of the total carbon in the feed substrate was

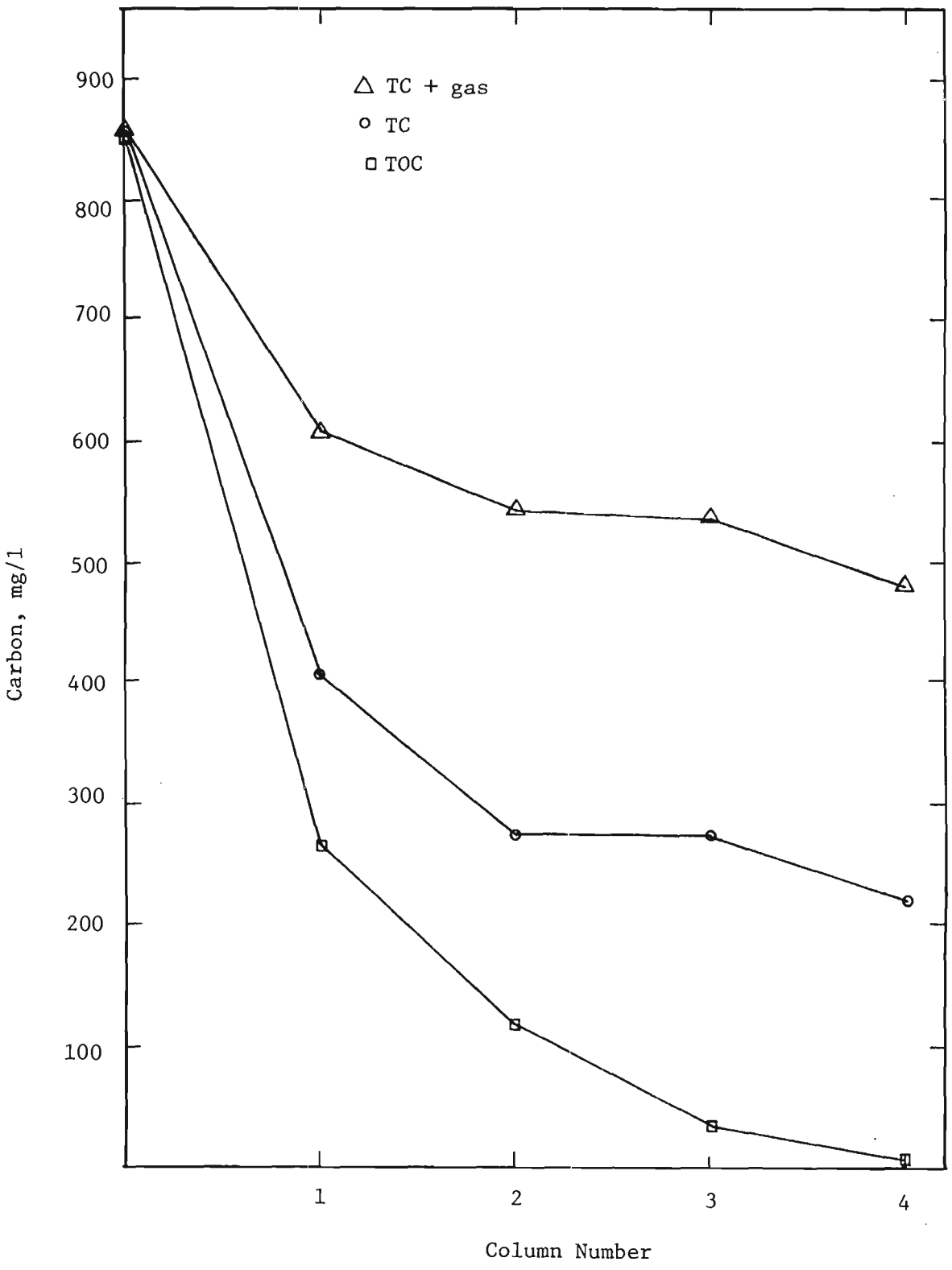


Figure 25. Carbon Profile, Day 155 Glucose Fed Reactor

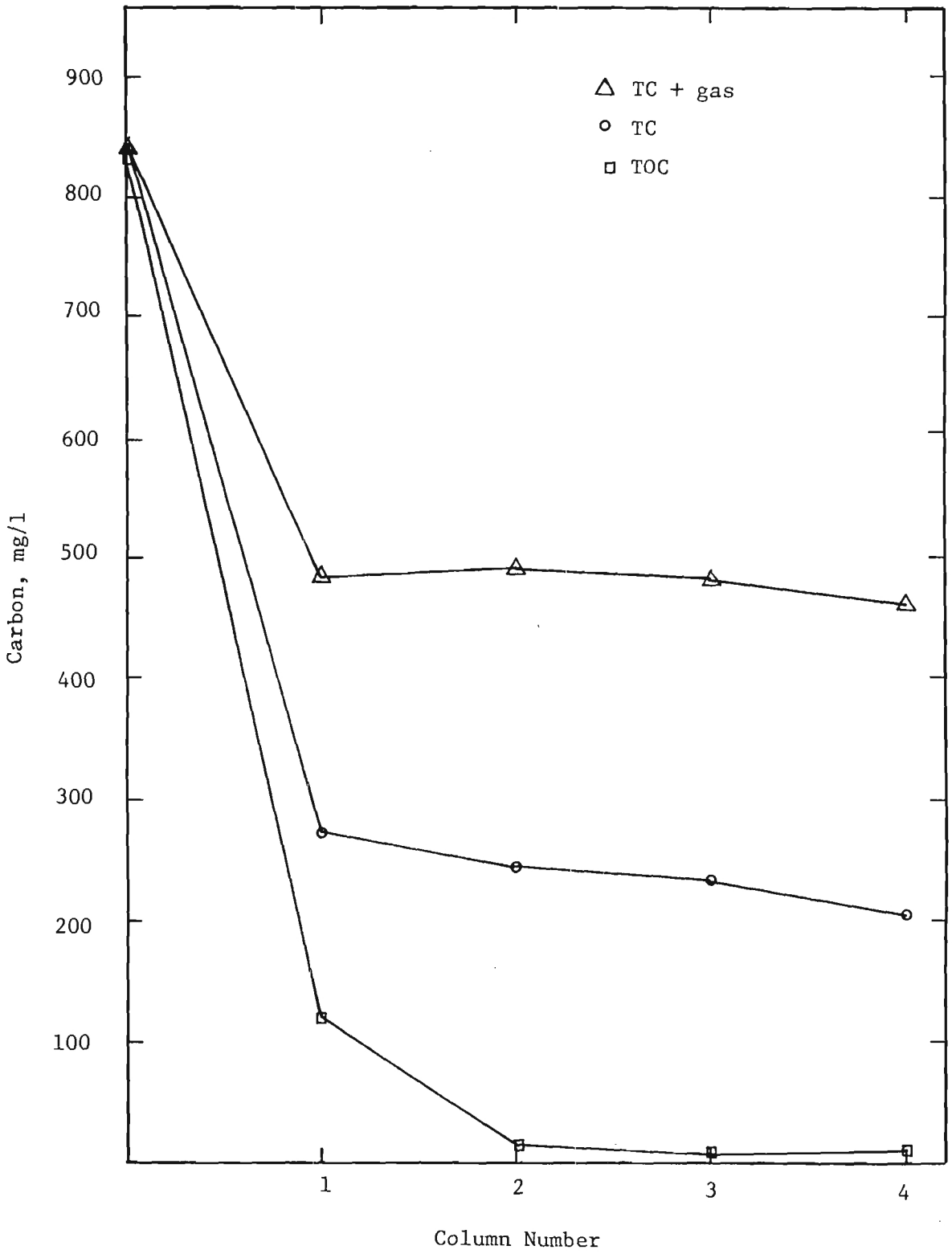


Figure 26. Carbon Profile, Day 190, Glucose Fed Reactor

not accounted for in the effluent from the first column reactor. The carbon profile across the remaining three columns indicates no carbon loss in these columns. On this day, the second column was responsible for a reduction in its influent level of TOC from 110 mg/l down to an effluent level of 15 mg/l. This reduction in organic carbon, however, was accompanied by an equivalent increase in the total aqueous and gaseous carbon thus indicating a stable operation in the second column.

The cumulative gas production data in Figure 23 indicate that the second column exhibited a maximum rate of gas production during the period extending between days 190 and 200 of continuous operation. A carbon material balance across the treatment system on day 194 (see Figure 27) reveals that during this period the second column is going through a period of bioregeneration of the activated carbon thus resulting in an increase of total aqueous and gaseous carbon across this column. Another point of interest is the fact that the level of total aqueous and gaseous carbon in the effluent from the first column has increased from a low of 480 mg/l on day 190 to a high of 730 mg/l indicating that bioregeneration may also be occurring in the first column reactor.

The cumulative mass of carbon fed into the reactor system, the mass of carbon present in the effluent from the fourth column reactor and the total carbon present in both the aqueous and gaseous phase effluents are presented versus time in Figure 28. The data in Figure 27 indicate that at steady state 34 percent of the total carbon present in the feed left the reactor in the aqueous phase of the effluent from the fourth column in the form of total organic and inorganic carbon. Thirty six percent of the carbon present in the feed was converted to an 86 percent methane rich gas; while 30 percent of the feed organic carbon was not accounted for in the soluble aqueous or gaseous phase and may be attributed to biomass production, adsorption onto activated

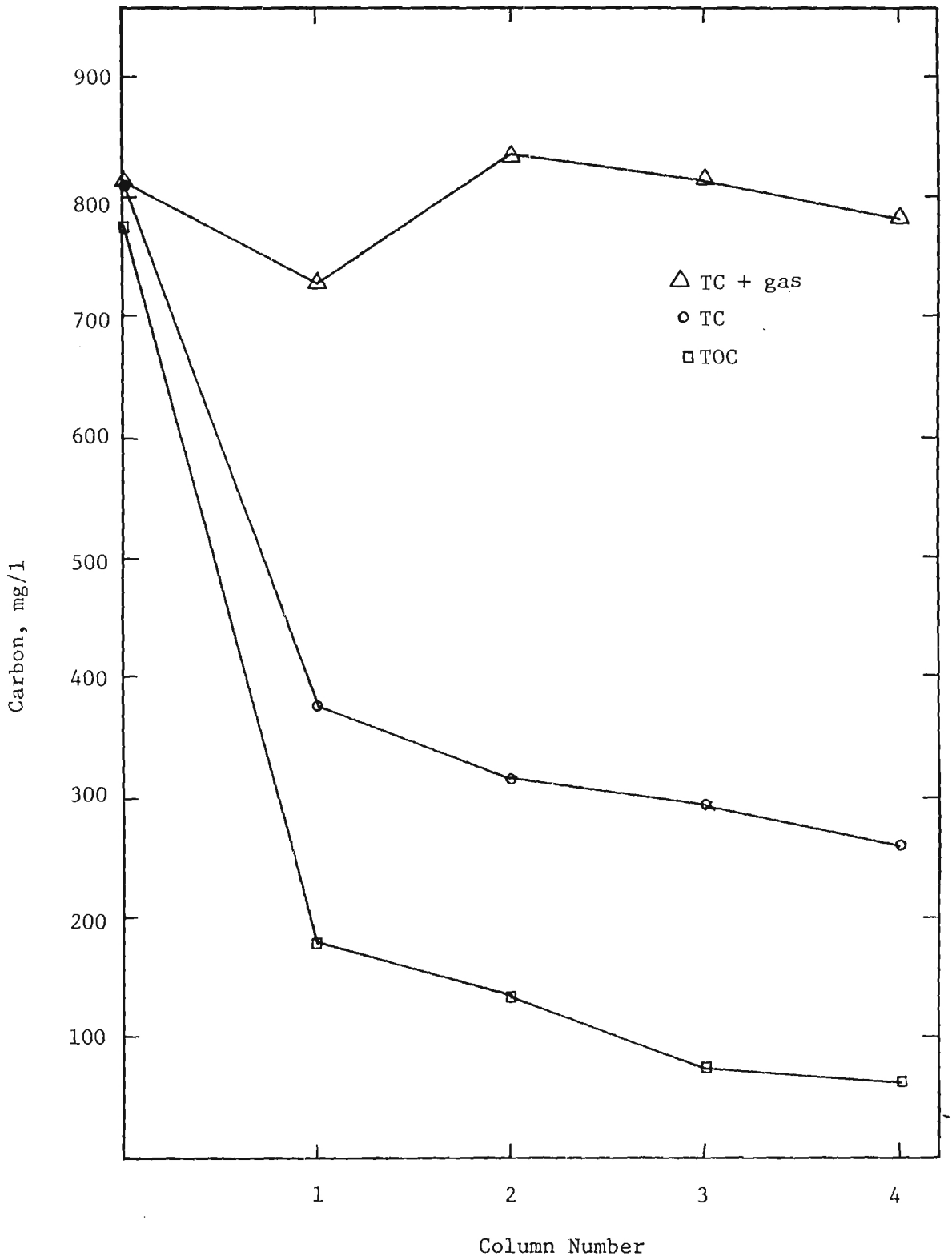


Figure 27. Carbon Profile, Day 194, Glucose Fed Reactor

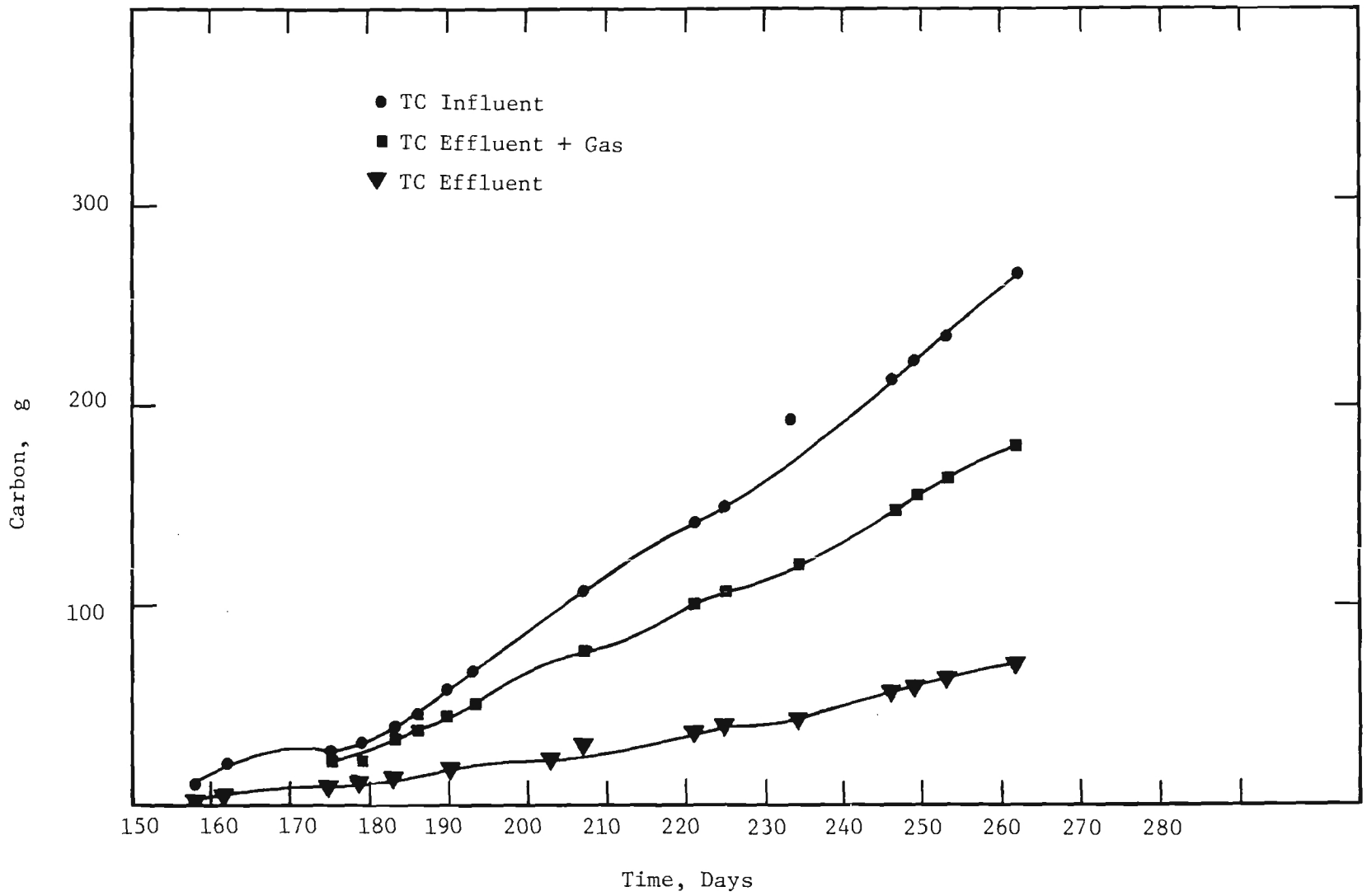


Figure 28. Cumulative Carbon Balance for Glucose Fed Reactor

carbon as well as TIC losses from the experimental reactor and during filtration prior to analysis.

Steady-State Performance

Steady-state intensive analysis was conducted on the feed substrate and all column effluents for the period extending from day 233 to day 265 of continuous operation. A summary of the steady-state operating data for this experiment is presented in Table 25. These data indicate that a process consisting of one single column having an empty bed detention time of 11.62 hours is sufficient to reduce the glucose bearing synthetic wastewater and achieve effective reductions in: (a) TOC of 92 percent, (b) COD of 95 percent, and (c) result in an 86 percent methane rich gas. Steady-state carbon and COD material balances across the treatment system are presented in Figures 29 and 30, respectively. The carbon material balance indicates a loss of carbon in the first column of 158 mg/l which corresponds to 18 percent of the feed total organic carbon or 19.6 percent of the organic carbon removed in the first column. If all the organic carbon removed in the first column reactor was converted to biomass, this results in a carbon biomass yield coefficient of 19.6 percent which is reasonable for a glucose type substrate (Young and McCarty, 1967). Very little additional carbon was lost in the latter three columns. This apparent low biomass production rate in the second column may be attributed to the fact that most of the organic carbon present in the effluent from the first column exists in the form of volatile acids and alcohols and, because of the low growth rate of methanogenic organisms, very little biomass production is anticipated. Young and McCarty (1967) reported a yield coefficient of almost zero from an acetate fed anaerobic filter.

The steady-state COD material balance across the treatment system (see Figure 30) reveals that the chemical oxygen demand of the effluent from the first column is 747 mg/l lower than the feed COD resulting in a COD biomass yield coefficient in the first column of 31 percent which is approximately

Table 25. Average Steady State Performance Data for 2000 mg/l Glucose Fed Reactor

Parameter	Influent Value	Parameter Value in Column Effluents 1	2	3	4
pH	7.53	6.90	6.91	6.93	7.00
TOC, mg/l	876.5	68.7	54.0	52.5	51.7
TIC, mg/l	12.5	295.0	305.0	290.0	275.0
COD, mg/l	2521.4	144.0	125.0	100.8	87.5
Glucose, mg/l	2000.0	25.0	25.0	17.5	10.0
Gas Production, ml/day		1987	194	0	0
Methane	-	1633	169	0	0
Carbon Dioxide	-	264	25	0	0
Alkalinity, mg/l as $CaCO_3$	3360	3954	3885	3886	3865
Total Suspended Solids, mg/l	-	397.1	215.5	169.6	468.3
Total Volatile Suspended Solids, mg/l		137.0	142.2	91.6	283.3
NH_3-N, mg/l		196.0	203.3	176.6	185.8
ORP	-	-331.2	-341.8	-304.6	-274.8

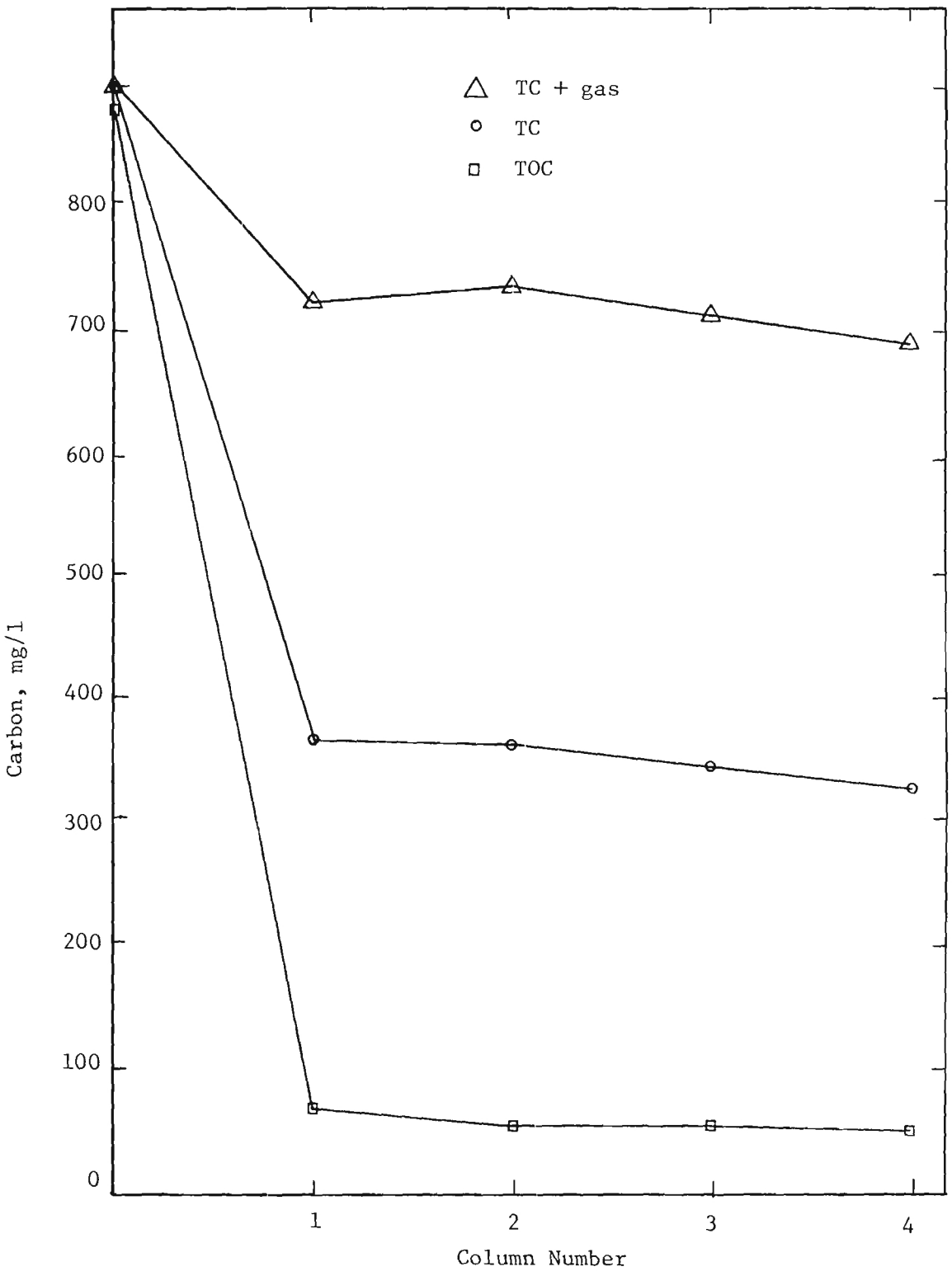


Figure 29. Carbon Profile, Steady State Glucose Fed Reactor

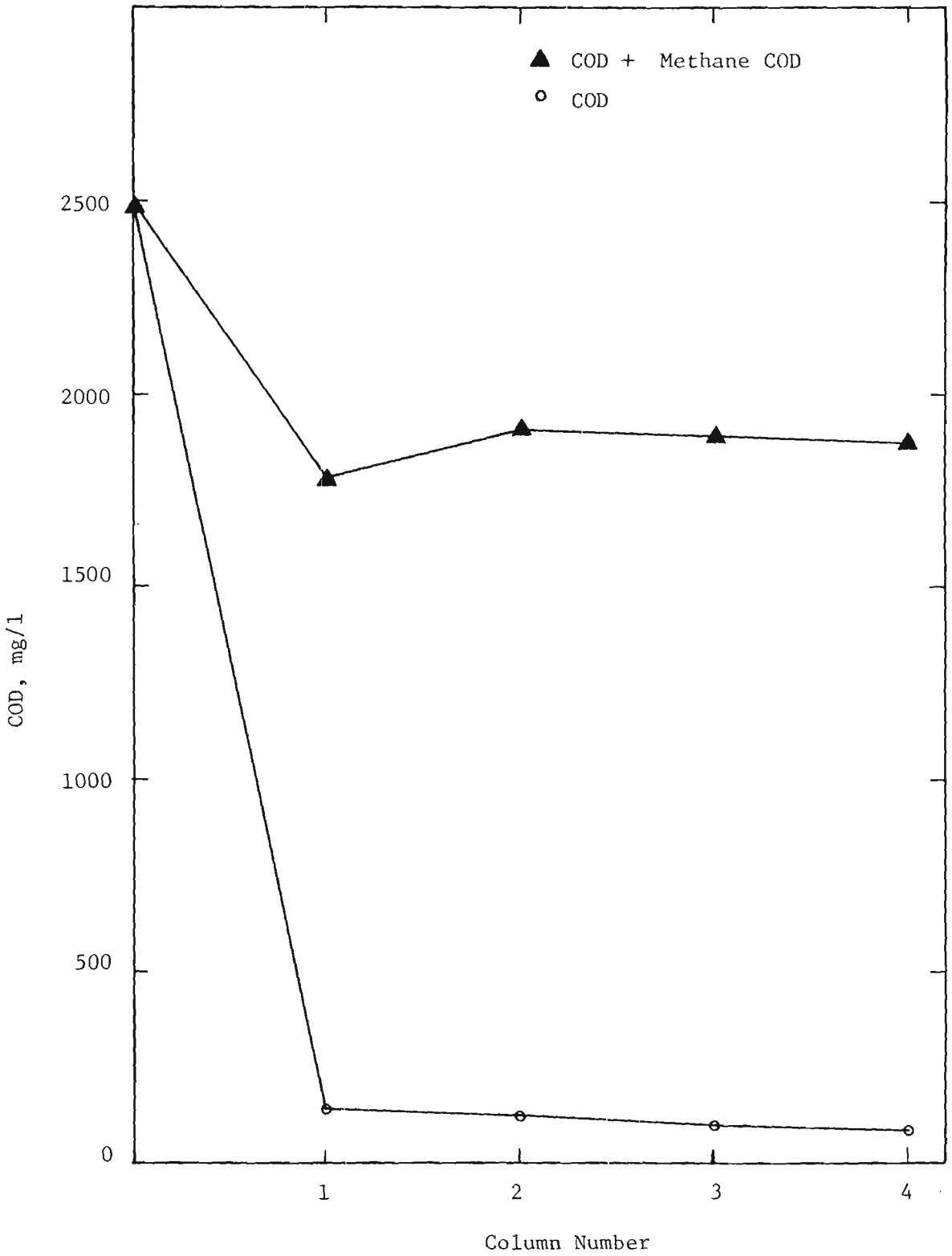


Figure 30. COD Profile, Steady State Glucose Fed Reactor

twice the value reported by Young and McCarty (1967) for carbohydrate protein waste. However, as was discussed earlier, if the average COD in the effluent from the first column during the last 70 days of continuous operation is selected over the effluent COD value shown in Figure 28, a COD yield coefficient of only 20 percent will then result.

The concentration of total and volatile suspended solids in the individual column effluents was measured during the period of intensive analysis (see Table 25). If the volatile suspended solids concentration in the effluent from the first column is accepted as an average value for the concentration of this parameter, this would result in a volatile solids biomass yield coefficient from the first column of only 4 percent which is lower than what should be anticipated from a glucose fed anaerobic filter thus indicating that some of the biomass produced was still retained with the first filter column.

The average alkalinity in the effluents from the four column reactors was 3870 mg/l as $CaCO_3$ while the alkalinity in the feed substrate was only 3360 mg/l as $CaCO_3$. This increase in alkalinity across the treatment system is due to the dissolution of the product gas carbon dioxide into the aqueous phase which results in a bicarbonate buffer. The fact that the pH in the four column effluents rose across the treatment system is indicative of the completeness of the degradation process and the absence of the volatile fatty acids from the effluents.

Hydrogen utilization and methane formation experiments were conducted in triplicates on all effluent samples as well as on samples of granular activated carbon withdrawn from all four column reactors. The average gas composition in the head space of every set of vials, after an incubation period of 84 hours at 37°C, is given in Tables 26 and 27, respectively. The

Table 26. Hydrogen Utilization and Methanogenesis Tests on Effluents from 2000 mg/1 Glucose Fed Reactor

Effluent from Column	Percent Gas Composition		
	Methane	Carbon Dioxide	Hydrogen
1	62.6	9.56	0
2	59.2	10.15	0
3	53.6	8.25	0
4	56.6	7.5	0

Table 27. Hydrogen Utilization and Methanogenesis Tests on the Activated Carbon Medium

Activated Carbon from Column	Percent Gas Composition		
	Methane	Carbon Dioxide	Hydrogen
1	40.3	0.25	25.5
2	17.9	0.6	3.9
3	22.4	0.5	65.0
4	7.1	0.4	68.4

data on the effluent samples, presented in Table 26, revealed that in all cases the hydrogen substrate was completely utilized indicating the presence of methanogens in the aqueous phase but failing to distinguish the relative strength of these organisms in the different column effluents. This was not the case, however, when carbon granules from the different columns were incubated. In this case, the first column was far superior to the latter three columns in its content of attached methanogenic bacteria.

Treatment of Phenol Bearing Substrate

The phenol fed anaerobic-activated carbon filter system was operated continuously for a period of 550 days. During the first phase of this experiment, which extended over a period of 267 days, the phenol concentration in the feed substrate was maintained at 200 mg/l while in the second and last phase of the experiment which lasted for 283 days, the phenol concentration in the feed substrate was increased to 400 mg/l.

Phase I, 200 mg/l Phenol

During this phase of the phenol degradation experiment, the feed substrate was prepared daily in 4 ℓ batches using 20 ml of the salt solution, 60 ml of the phosphate buffer solution, 0.8 g of phenol and distilled water. The theoretical feed COD and TOC computed using the measured values for the salt solution and theoretical values for phenol given in Table 24 were 605 and 186 mg/l, respectively. The measured and theoretical values of the feed substrate COD and TOC are presented in Figure 31. The measured chemical oxygen demand of the feed substrate averaged around 570 mg/l while the average total organic carbon content of the feed was 189 mg/l. The feed substrate had computed COD to TOC ratio of 3.25 while the average measured ratio was 3.02.

During the initial period of this phase of the experiment, the pH of the feed substrate was varied in an attempt to establish an operating pH within the four columns ranging from 6.9 to 7.2. Once the acclimation period was over, the pH of the feed substrate was fixed at 7.4. This resulted in a steady state pH distribution across the treatment system ranging from 7.15 to 7.06. Throughout the course of this phase of the experiment, the pH in the effluents from the column ranged from a low of 6.75 to a high of 7.21 for the first column; 6.95 to 7.23 for the second column; 6.95 to 7.19 for the third column; and 7.01 to 7.21 for the fourth and last column. At a pH of

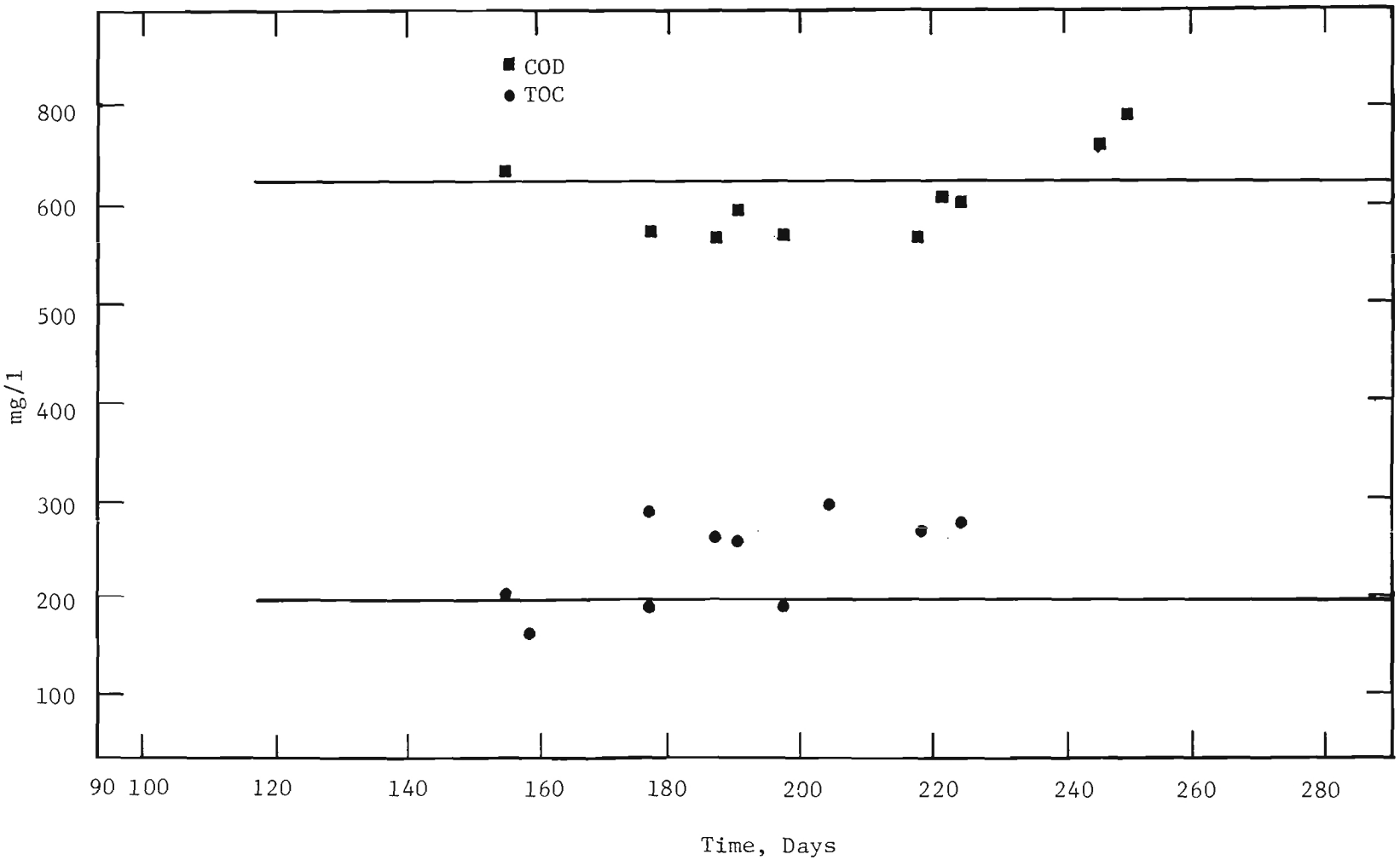


Figure 31. Influent COD and TOC for Phenol Fed Reactor, 200 mg/l

7.4, the alkalinity of the feed substrated was 1440 mg/l as $CaCO_3$ (end point of alkalinity titration was 4.0). This strong buffer capacity coupled with the buffer intensity of the recirculated flow was sufficient to maintain the system pH close to the neutral pH of 7 throughout the experiment.

The experimental reactor was operated at an influent flow rate of 5 ml/min for a period of 66 days at which time the feed flow rate was reduced to 2 ml/min resulting in an empty bed hydraulic retention time of 11.62 hours in every reactor column. Recirculation of the aqueous contents around every individual reactor was exercised continuously at a flow rate of 50 ml/min. This recirculated flow helps in maintaining a neutral pH in the system by providing an additional bicarbonate buffer capacity (Chian and DeWalle, 1976).

During the first phase of this experiment, the first column was observed to go through four distinct stages of activity. During the first stage, which lasted for 135 days of continuous feeding, no appreciable gas production was observed from this system. This was due to the adsorption of the phenol onto the activated carbon surface thus rendering the substrate unavailable for bioregeneration by the microbial culture. The second stage of this phase of the experiment, which lasted for 45 days, was characterized by acclimation and the initiation of gas production. Data collected during this stage of the experiment show a definite decrease in the organic content of the column effluents. The next distinct experimental stage was characterized by an accelerated biological activity and the bioregeneration of the activated carbon. During this stage of the experiment, which lasted for 60 days, the carbon equivalent of the gaseous products (methane and aqueous as well as gaseous carbon dioxide) exceeded the organic carbon removed (influent carbon-effluent carbon) by the process thus indicating the utilization of some of the previously adsorbed organic carbon, or bioregeneration. After this transient period had

elapsed, gas production decreased to a steady state level where the carbon equivalent of the methane and aqueous and gaseous carbon dioxide produced corresponded very closely to the organic carbon removed across the treatment process.

Phenol Reduction. The concentration of phenol (measured spectrophotometrically at 286 nm) in the effluents from the series of four aanaerobic-activated carbon filters is shown in Figures 32, 33, 34 and 35 for the period extending between days 100 and 265 of continuous operation. During the first 50 days of operation, very little phenol was detected in the effluent from the first column. This was primarily due to the removal of this organic compound from solution by adsorption onto the activated carbon surface. After this initial period, the concentration of phenol in the effluents from the first two columns started increasing reaching a high of 112 mg/l in the effluent from the first column and 30 mg/l in the effluent from the second column on day 115 of continuous operation. Shortly after that day gas production was observed from the first two columns and the concentration of phenol in the effluents from the first two columns started decreasing. Steady state operating conditions, as defined by gas production, were reached in the first column at day 240 of continuous operation. After day 240, the phenol content in the effluent from the first column reached a stable value which averaged below 19 mg/l. This corresponds to a phenol removal efficiency in the first column of greater than 90.5 percent.

The concentration of phenol in the effluent from the second column reactor decreased steadily from a level of 24 mg/l on day 155 of continuous operation to a level of less than 4 mg/l on day 193, when it stabilized at this level throughout the remainder of this phase of the experiment (see Figure 33), resulting in a phenol removal efficiency of greater than 98 percent across the first two columns.

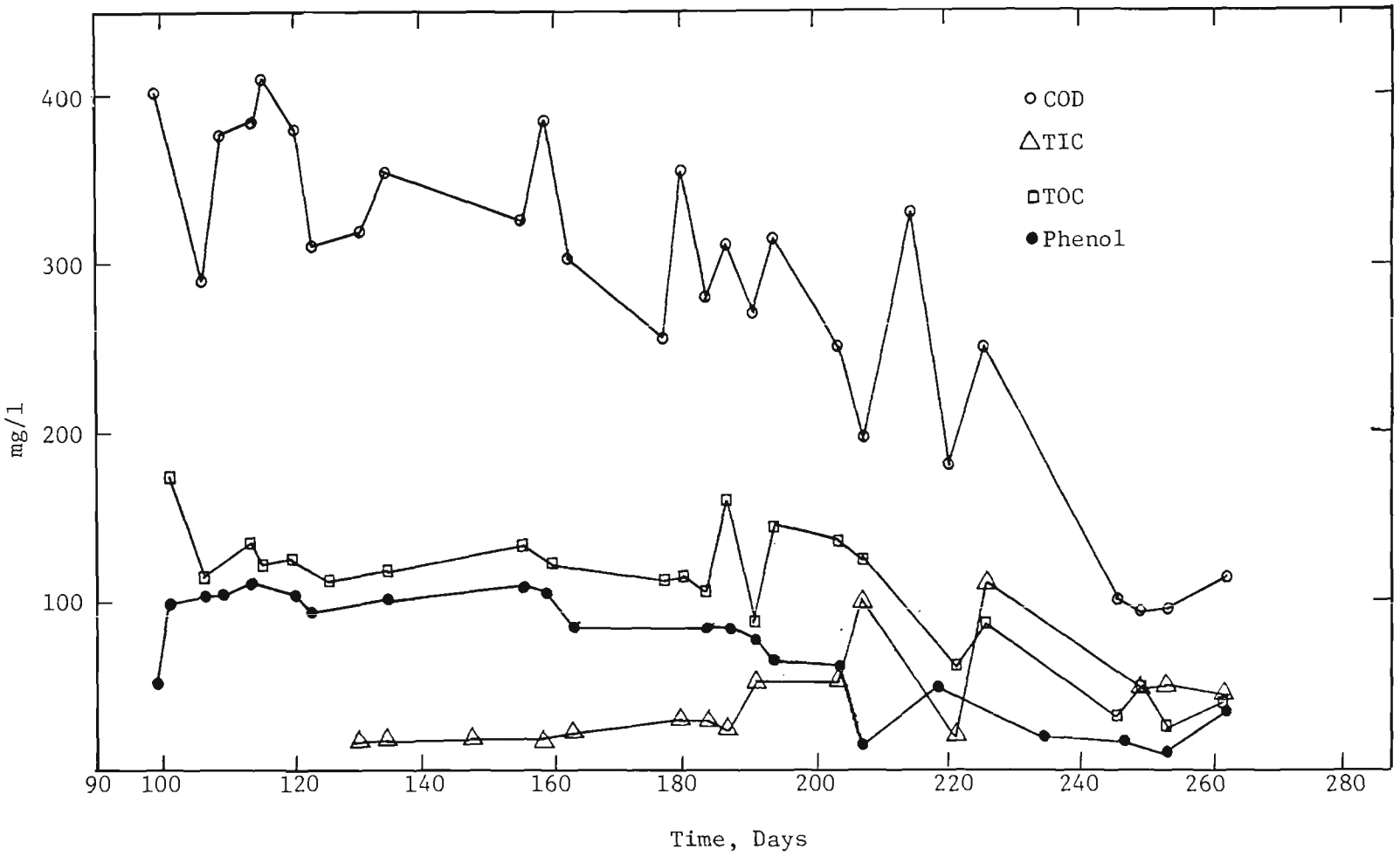


Figure 32. Effluent COD, TOC, TIC, Phenol from Column Number One, Phenol Fed Reactor, 200 mg/l

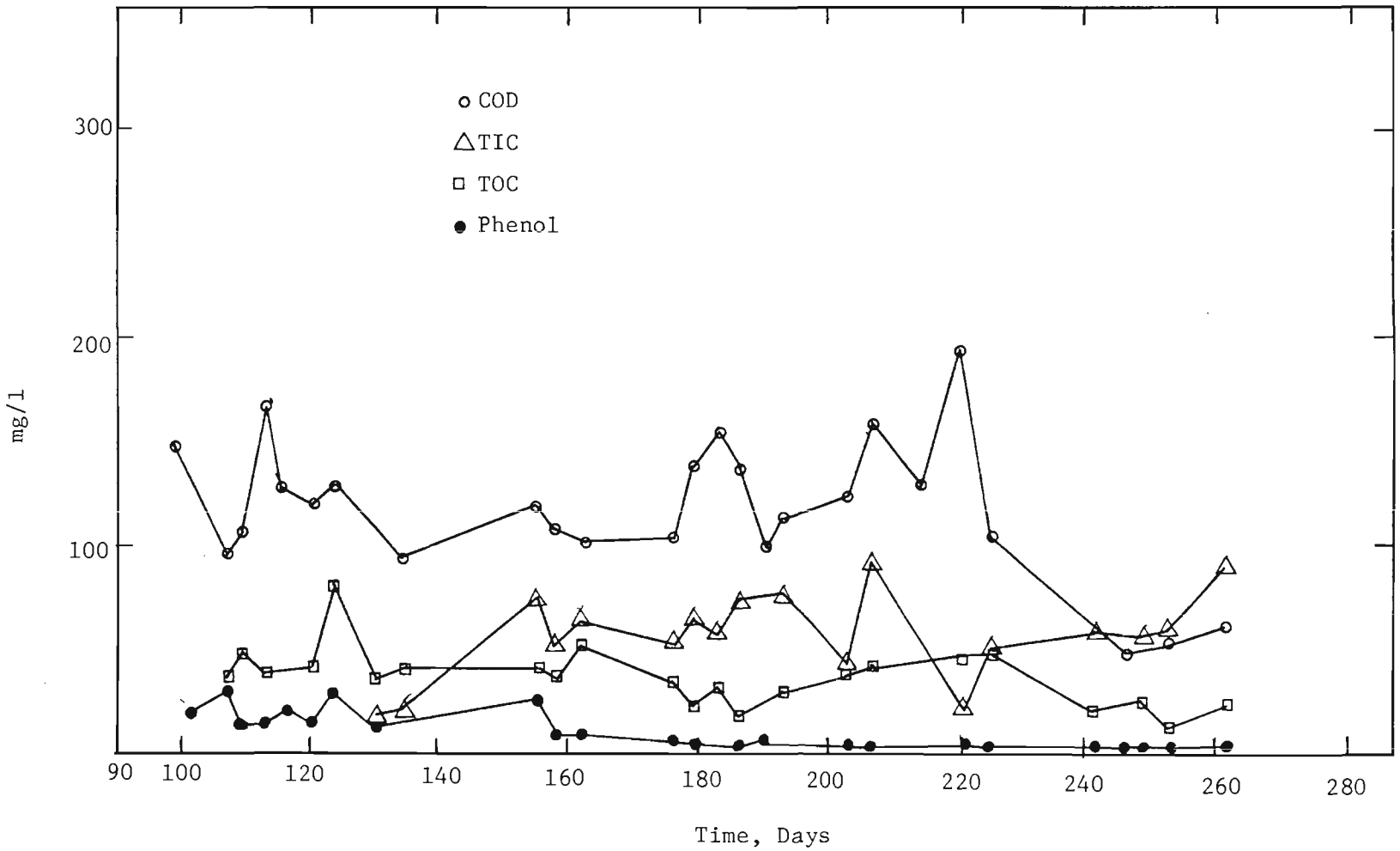


Figure 33. Effluent COD, TOC, TIC, Phenol from Column Number Two Phenol Fed Reactor, 200 mg/l

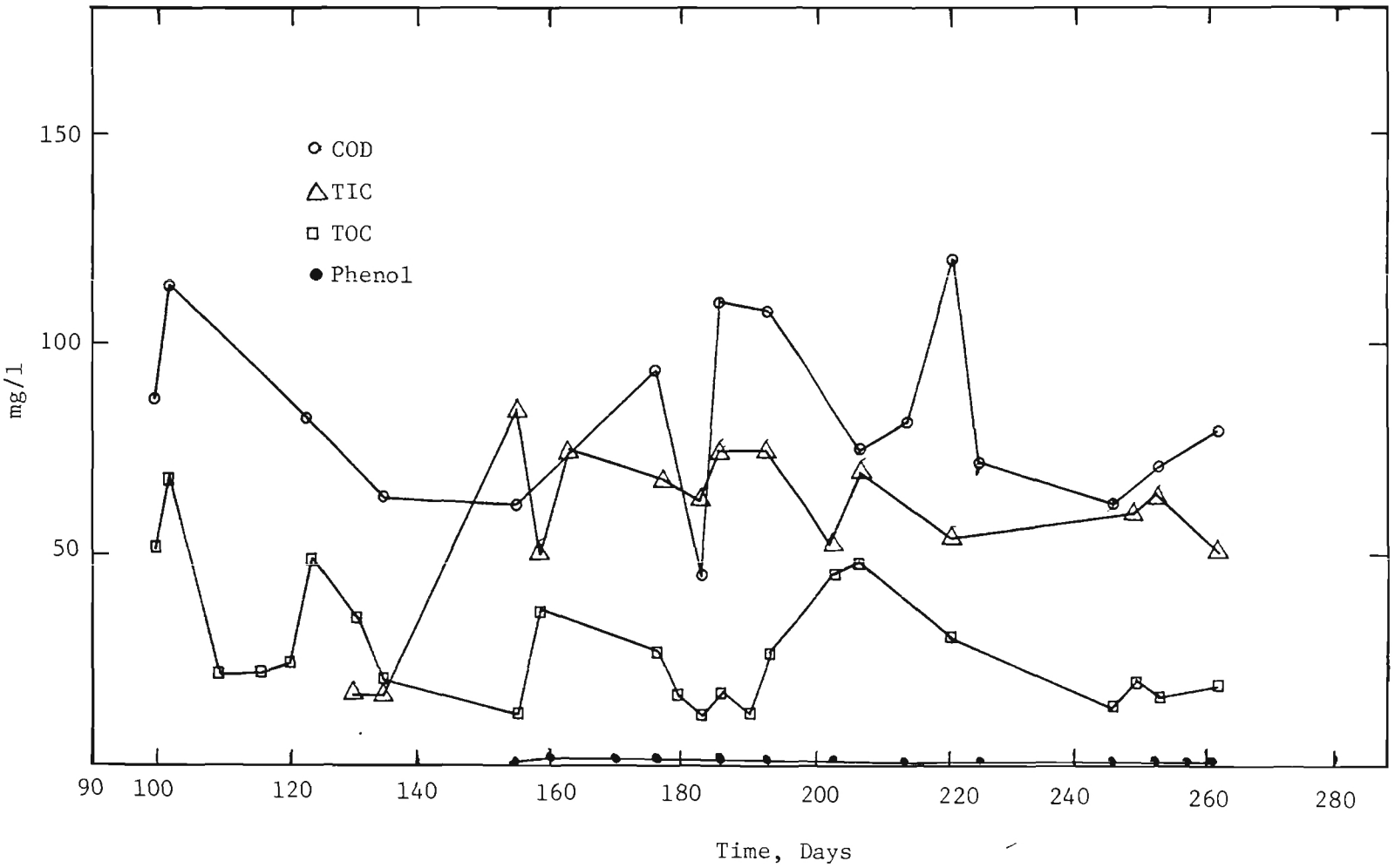


Figure 34. Effluent COD, TOC, TIC, Phenol from Column Number Three, Phenol Fed Reactor, 200 mg/l

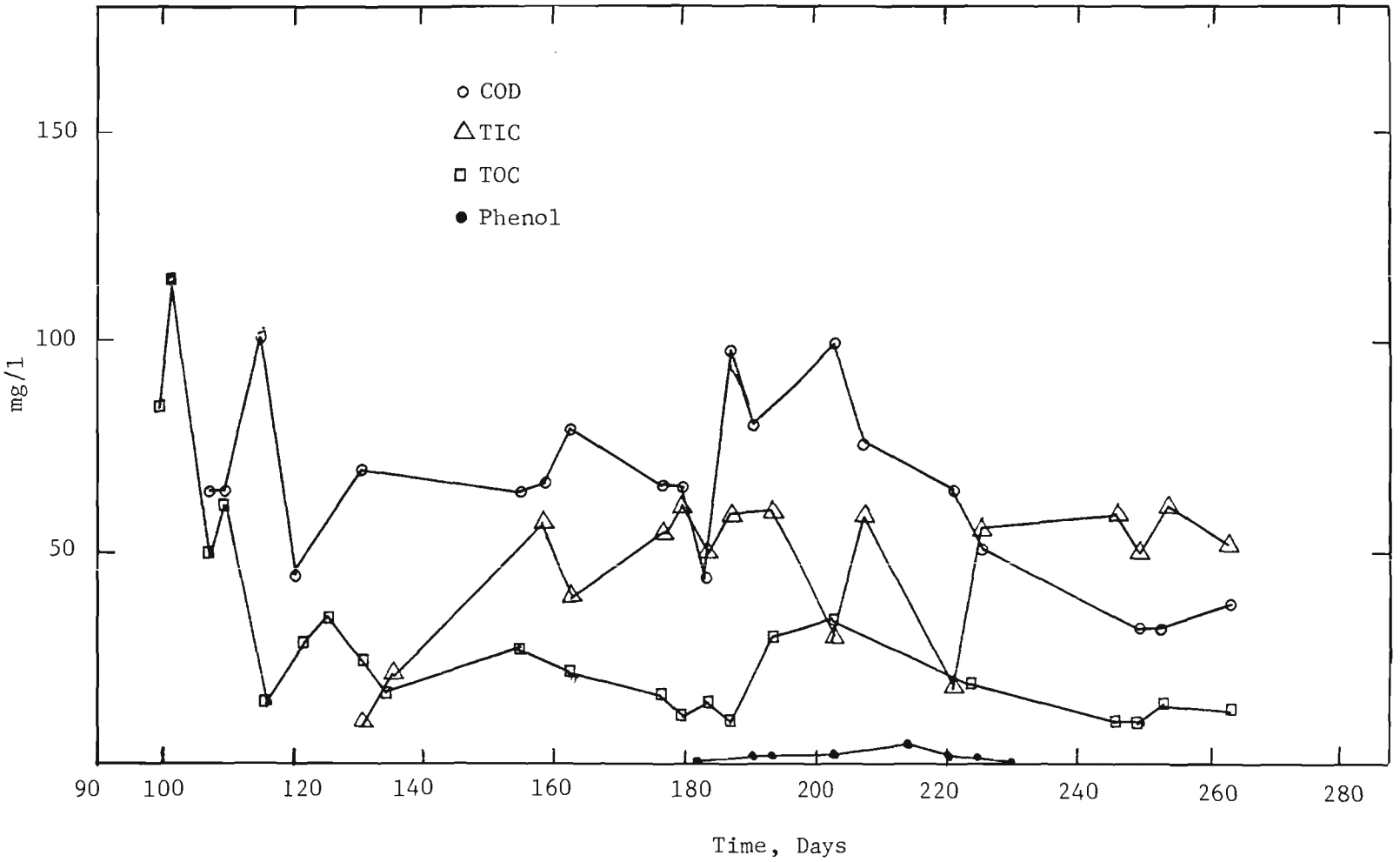


Figure 35. Effluent COD, TOC, TIC, Phenol from Column Number 4, Phenol Fed Reactor, 200 mg/1

Phenol was first detected in the effluent from the third column on day 150 of continuous operation. Shortly after that day, the effluent phenol level from this column stabilized at less than 0.8 mg/l. Phenol was detected in the final effluent from the fourth and last column only during the period extending between days 180 and 230 (see Figure 34). The phenol content of this effluent was consistently below detection limits throughout the remainder of this experiment (see Figure 35). Thus the overall phenol removal efficiency across the four columns was approximately 100 percent.

The phenol concentration values reported in Figure 32-35 were all greater than the actual concentration of phenol in the individual effluents. This discrepancy in the concentration values of phenol as measured in the column effluents is due to the spectrophotometric analytical method utilized to monitor this compound and the contribution to the absorbance reading of the organic degradative intermediates of phenol at 286 nm. To illustrate the interference of other organic matter with the absorbance readings, the absorbance scan of a 10 mg/l phenol-distilled water solution at pH 12 was plotted against a similar scan conducted on a pH 12 adjusted filtered effluent from the second column reactor (see Figure 36). Close examination of the absorbance scans for the two solutions reveals that the phenol-distilled water solution exhibits no absorbance in the U.V. wavelength range

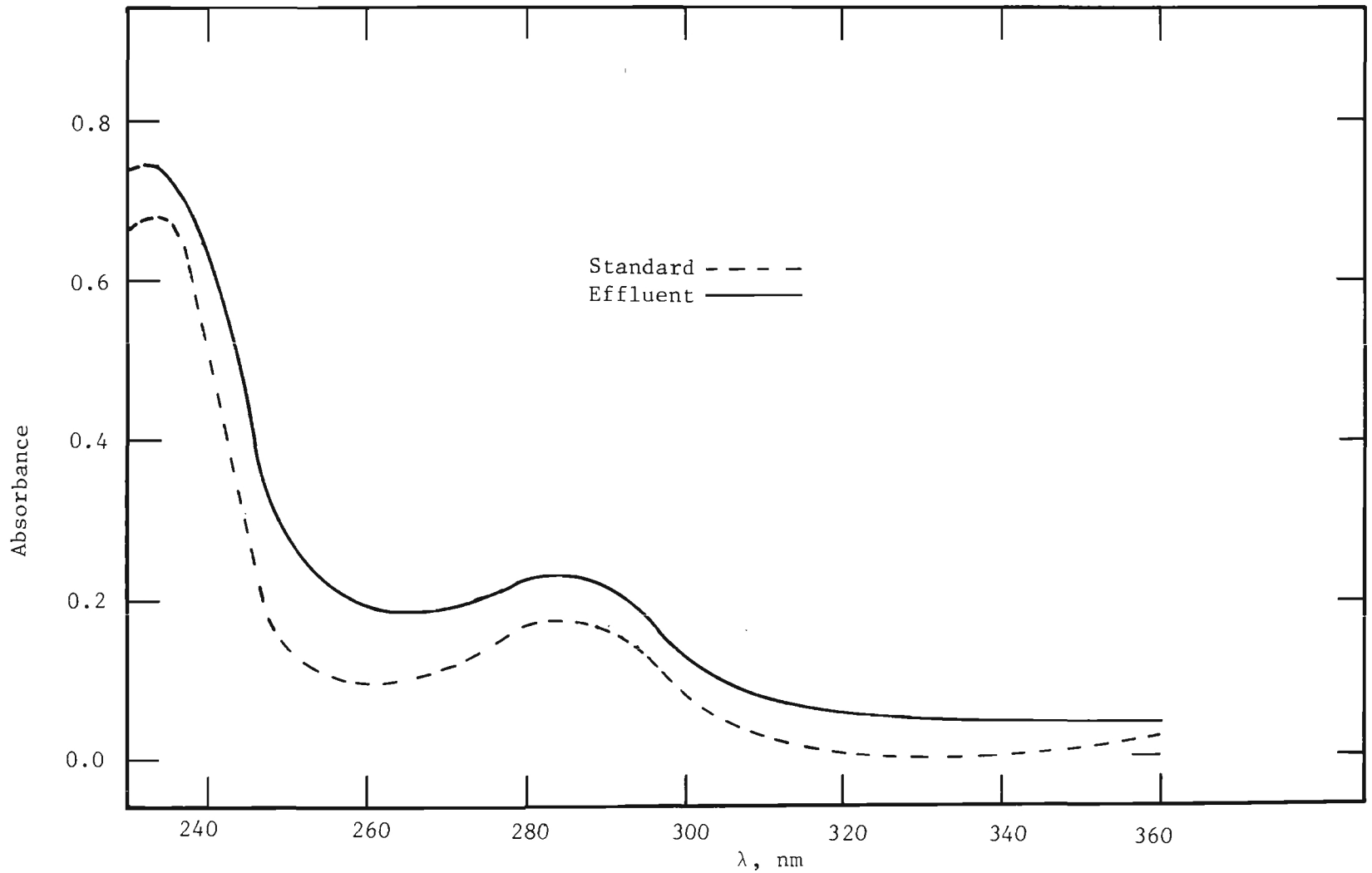


Figure 36. Absorbance Spectra, Phenol Standard and Effluent from Column Two Phenol Fed Reactor, 200 mg/l

between 360 and 320 while the effluent sample exhibits an absorbance ranging from 0.04 at 360 nm to 0.06 at 320 nm. Gas chromatographic analysis of both samples confirmed that the standard solution contained 10 mg/l of phenol while the sample from the effluent from the first column had a phenolic content of only 8.5 mg/l while its absorbance at 286 nm yields a concentration of 12.5 mg/l. Thus in this case, interferences from organic matter other than phenol resulted in an apparent increase in the concentration of phenol as determined by absorbance at 286 nm of 47 percent. The error induced by the interference of organic matter, other than phenol, was observed to be severe when the phenol is present at low concentrations in the sample while this error was negligible at higher concentrations of phenol.

Organic and Inorganic Carbon. The organic and inorganic carbon content of the filtered effluents from all four anaerobic columns was presented in Figures 32, 33, 34 and 35 for the continuous operating period extending between day 110 and day 265. The organic carbon content in the feed substrate was presented in Figure 31 for the same period of operation. The TOC in the feed substrate averaged 189 mg/l, while the TOC in the effluent from the first column ranged from a high of 175 mg/l on day 110 to a low of 25 mg/l on day 255. The average TOC in the effluent from the first column during the last 25 days of steady-state operation was 36 mg/l resulting in a TOC conversion efficiency in the first column of 80.8 percent.

The total organic carbon content in the effluent from the second column varied from a high of 92 mg/l on day 206 to a low of 12 mg/l on day 254. The average TOC in the effluent from the second column during the last 25 days of steady state operation was 19 mg/l resulting in a TOC conversion in this column of 47.2 percent or a cumulative conversion of organic carbon in the first two columns of 90 percent.

The TOC in the effluent from the third column ranged from a high of 68 on day 102 to a low of 12 on day 190. The average TOC in the effluent from this column during the period of steady-state operation was 17 mg/l resulting in an organic carbon removal in this column of 10.5 percent or a cumulative removal across the first three columns of 91 percent. This column as well as the fourth column resulted in very little TOC removal and, consequently, the fourth column was taken out of operation during the second phase of this experiment.

Chemical Oxygen Demand. The performance of the treatment system as far as the reduction of chemical oxygen demand was presented in Figures 31, 32, 33, 34 and 35 for the continuous operating period extending from day 100 to day 265. The chemical oxygen demand in the various column effluents fluctuated appreciably until steady-state operating conditions were attained at which time the average COD values in the four column effluents were 103, 52, 71 and 34 mg/l amounting to cumulative reductions in this parameter of 82, 91, 88 and 94 percent from the respective effluents of the four columns.

The COD to TOC ratio in the feed substrate was 3.02, while this ratio decreased to 2.88 and 2.24 in the effluents from the first and second columns, respectively. This decrease in the COD to TOC ratio is due to the release from the aqueous phase of highly reduced carbon in the form of methane gas (COD to TOC ratio = 4.0) which results in the reduction of this ratio for the organic matter remaining in the aqueous phase.

Gas Production. The anaerobic gas produced from every column reactor was collected separately and monitored for volume and composition. Cumulative dry methane and gaseous carbon dioxide production data that were obtained from the first and second columns are presented in Figures 37 and 38. While

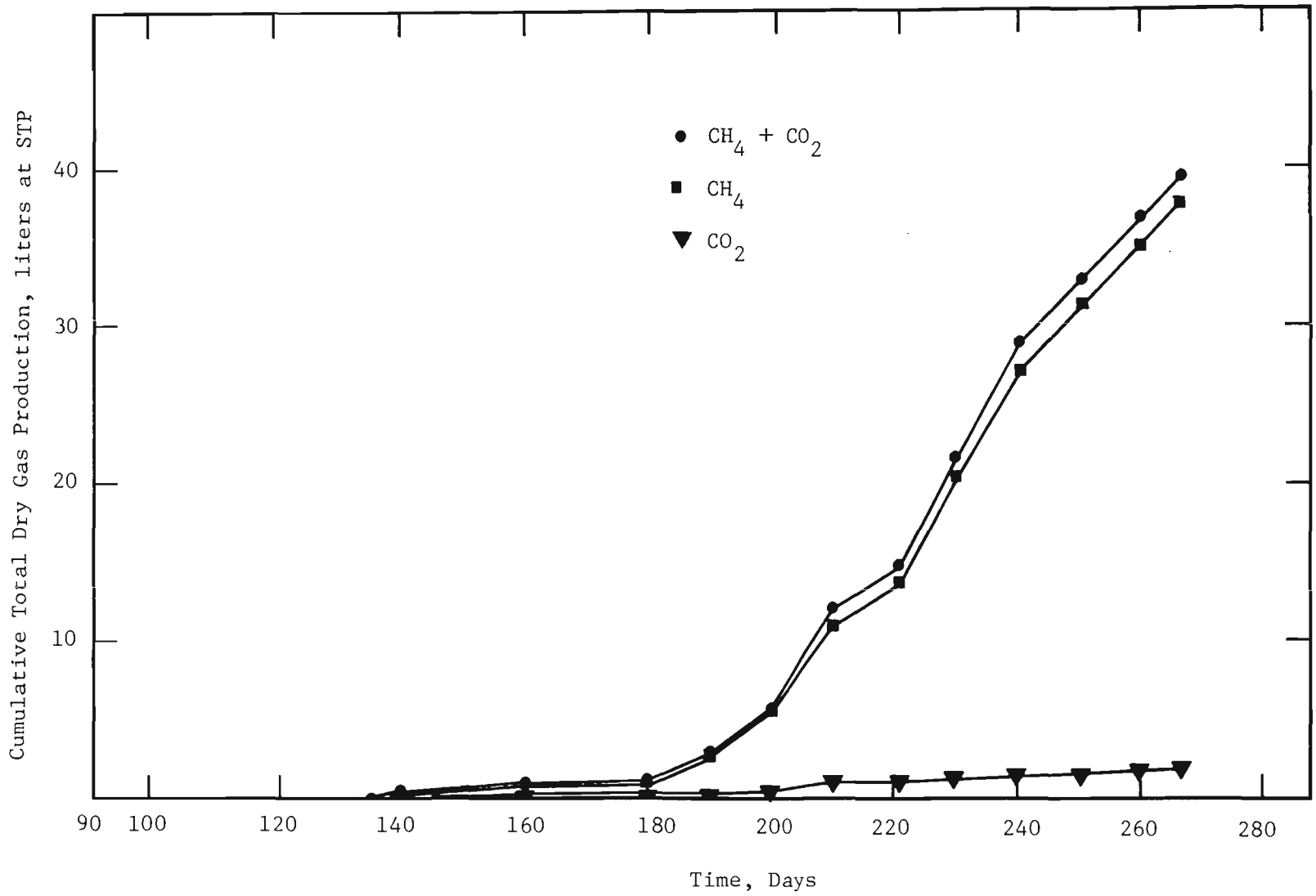


Figure 37. Gas Production from Column One, Phenol Fed Reactor, 200 mg/l

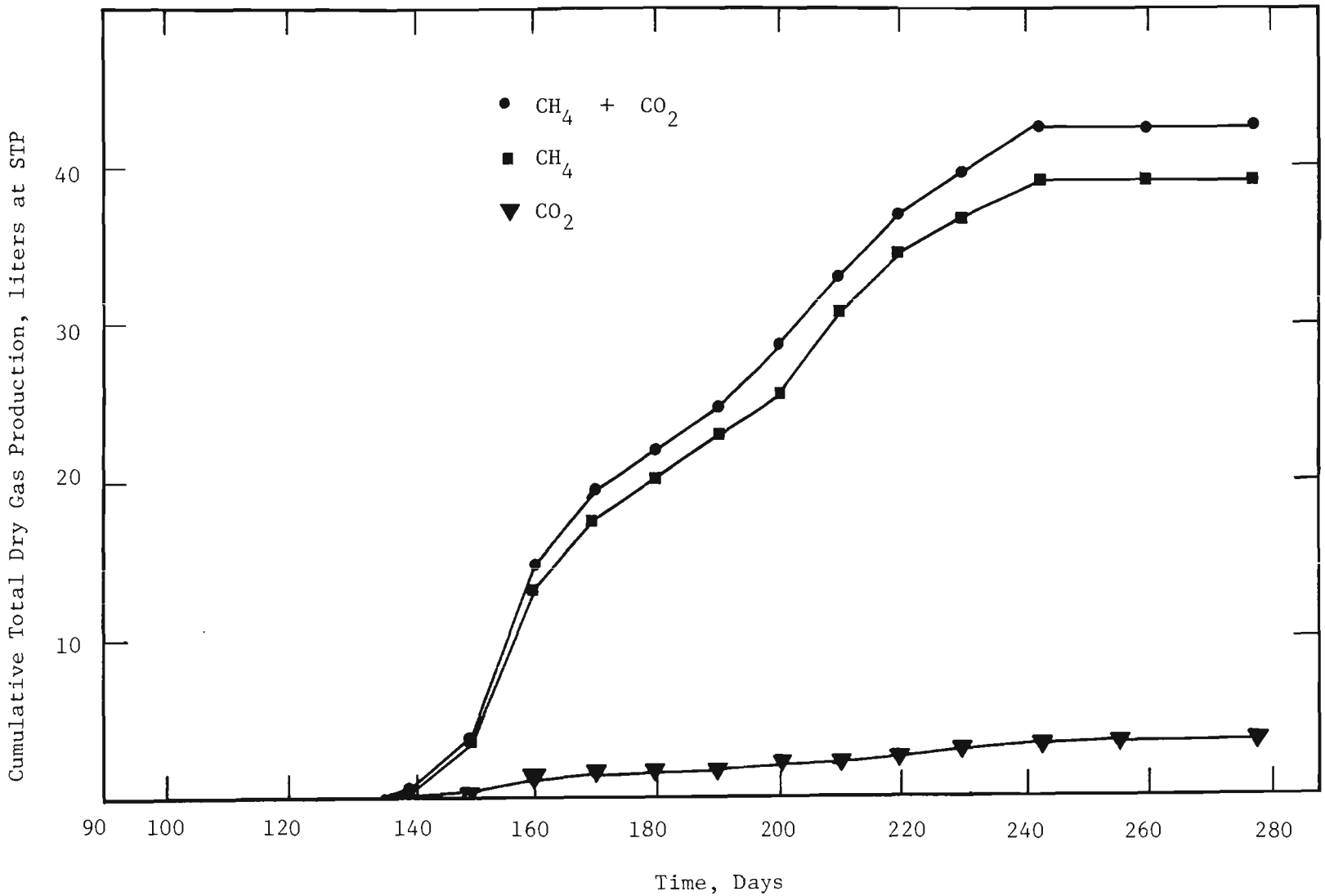


Figure 38. Gas Production from Column Two, Phenol Fed Reactor, 200 mg/l

the cumulative production of these gases from the total reactor system is shown in Figure 39.

Very little gas production was observed from the reactor system prior to day 135 of continuous operation. During the period of operation extending up to day 135, phenol was removed from the aqueous phase primarily by adsorption onto the activated carbon surface. Therefore, during this stage of the experiment, the organic substrate was unavailable for biodegradation by the microorganisms. A carbon material balance across the reactor system constructed to represent the state of the treatment process on day 134 of continuous operation reveals that indeed a major fraction of the organic carbon present in the feed substrate is removed from the aqueous phase through adsorption (see Figure 40). The carbon material balance on day 134 also reveals that the adsorptive capacity of the carbon in the first column for phenol had almost been completely exhausted by that day since the first column appeared to be responsible for removing only 29 percent of the total organic carbon in the feed substrate.

After day 135 of continuous operation, gas production was observed from all columns, however, this activity diminished very rapidly in all columns except for the second unit which, effectively, represented the only methane producing column during the period extending from day 135 to day 180. During this period, gas production from the second column averaged 489 ml/day of methane and gaseous carbon dioxide, while a peak production rate of these gases of 1031 ml/day was observed during the 10 day period extending between day 150 and day 160. The carbon equivalent of the methane and gaseous carbon dioxide produced during the peak period was equal to 192 mg/l of carbon which exceeds the carbon content in the feed substrate which was 190 mg/l. A carbon

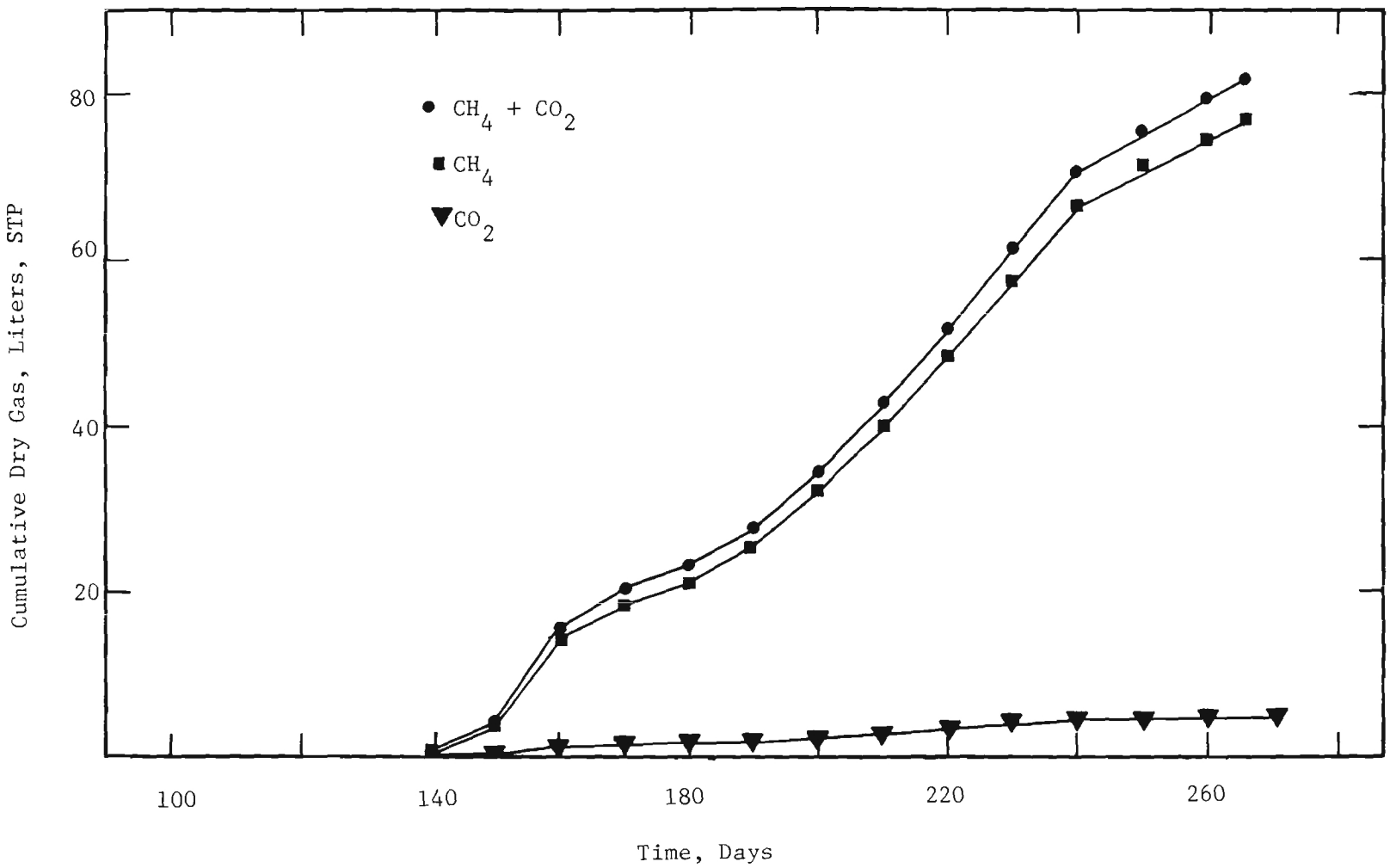


Figure 39. Total Gas Production from Columns One & Two Phenol Fed Reactor, 200 mg/l

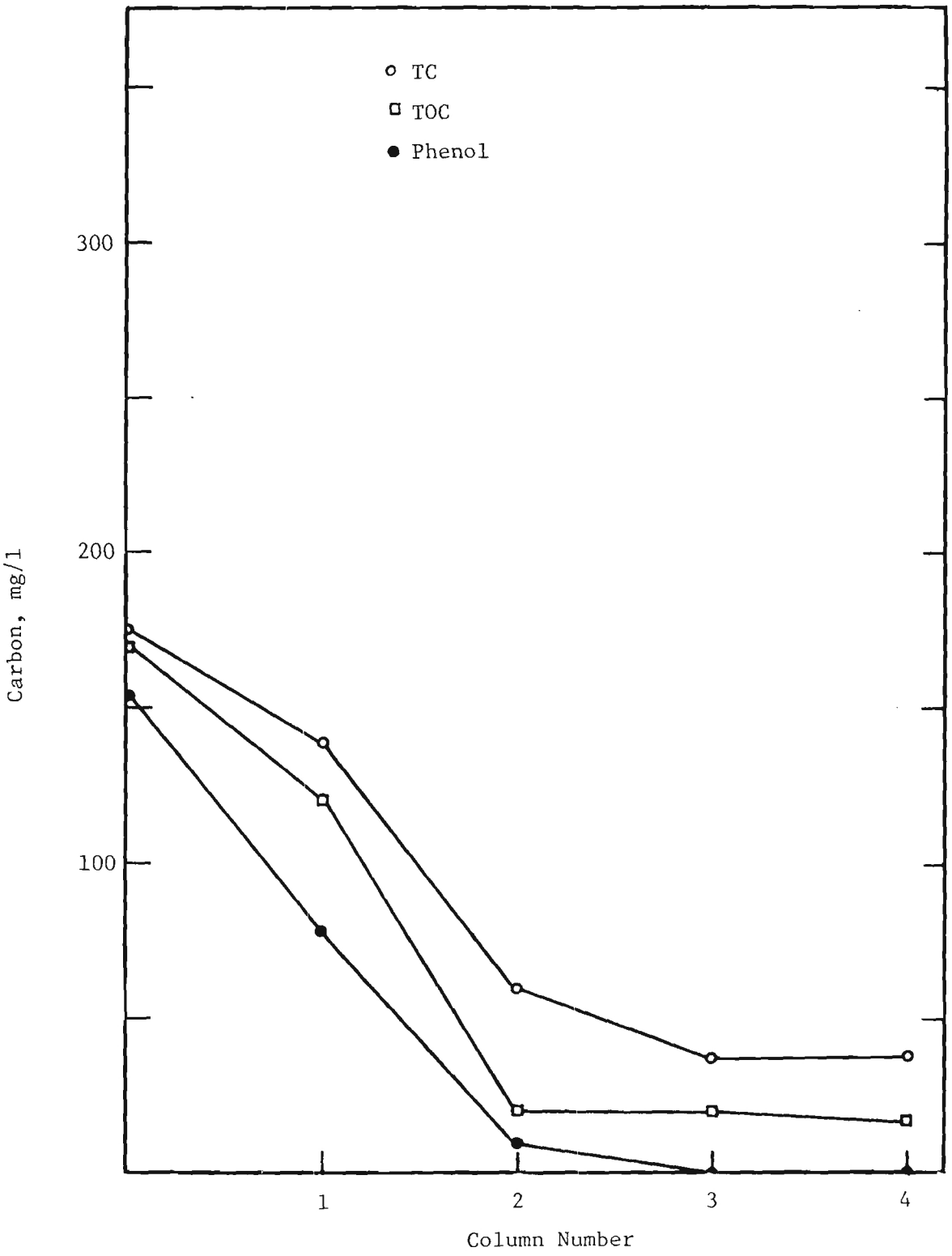


Figure 40. Carbon Profile, Day 134, Phenol Fed Reactor, 200 mg/1

material balance across the treatment system constructed on day 158 which falls within the peak gas production period for the second column is presented in Figure 41. This material balance indicates that, on day 158, the first column was responsible for removing 37.5 mg/l of the organic carbon present in the feed substrate. This removal was accomplished primarily by adsorption, however, since relatively very little gas was produced from the first column on that day. The carbon equivalent of the total aqueous and gaseous carbon leaving the second column exceeded the carbon concentration present in the effluent from the first column by 137.5 mg/l thus providing evidence to the occurrence of intense bioregeneration in the second column during this period of operation.

Healy and Young (1971) demonstrated experimentally that the anaerobic degradation of phenol proceeds according to Equation 37

$$C_6H_6O + 4H_2O \rightarrow 2.5CO_2 + 3.5CH_4 \qquad (43)$$

thus resulting in converting 58.33 percent of the organic carbon in phenol to methane while the remaining 41.67 percent is converted to aqueous and gaseous carbon dioxide. Close examination of the data in Figure 39 reveals that methane constituted 93.42 percent of the gaseous carbon with carbon dioxide providing the balance. The TIC content of the aqueous phase should also be considered in this material balance because of the high solubility of inorganic carbon at a neutral pH. Analysis of the carbon material balance in Figure 41 reveals that methane accounts for 78.62 percent of the carbon present in the gaseous phase and the inorganic carbon content of the final effluent. This observation was followed by an intensive analysis of the inorganic carbon content of filtered and unfiltered column samples revealed that the filtration of samples prior to analysis resulted in a major decrease in the inorganic

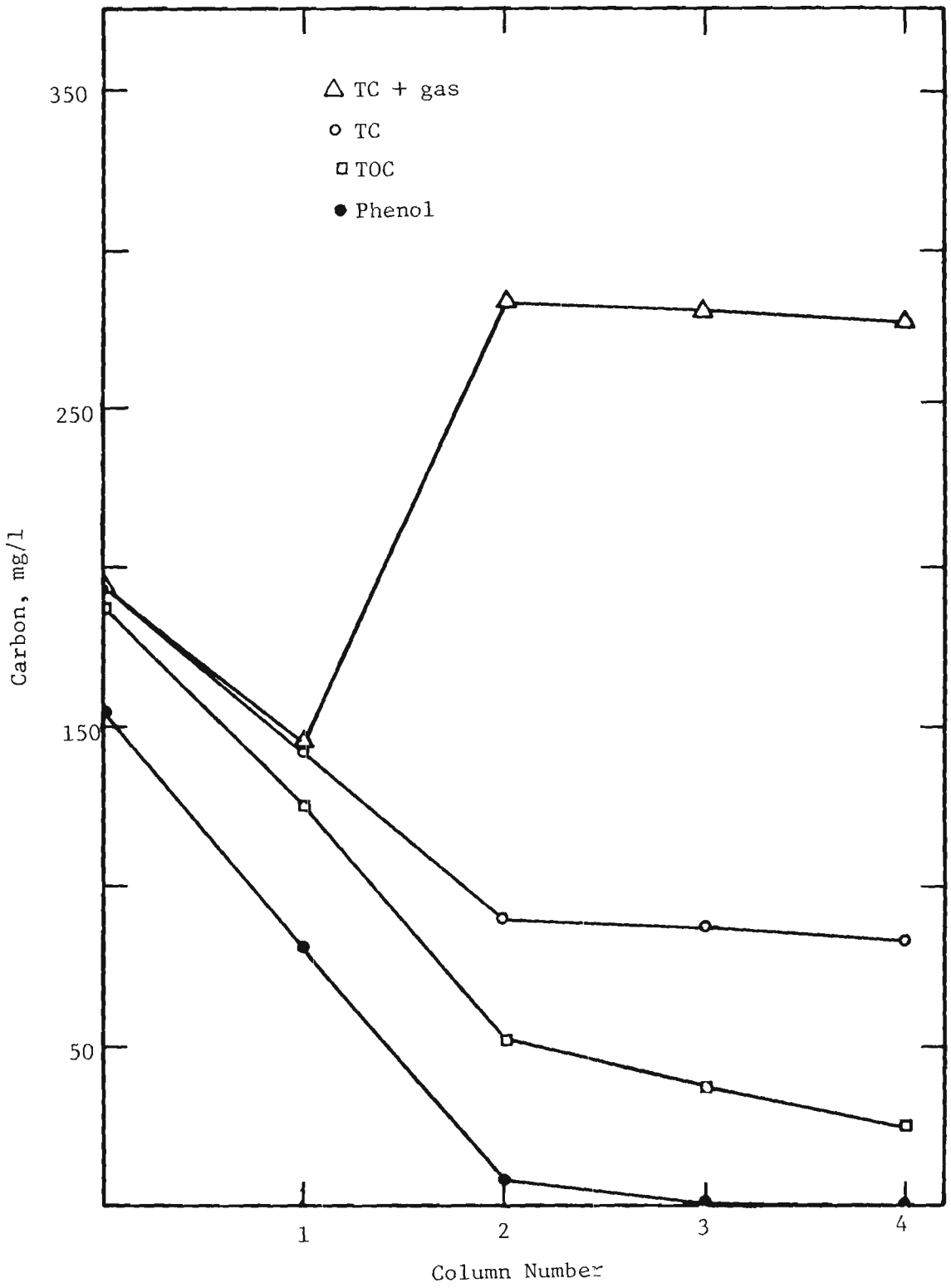


Figure 41. Carbon Profile, Day 158, Phenol Fed Reactor, 200 mg/1

carbon content of these samples. Based on these findings, the actual rate of bioregeneration observed in the second column on day 158 should be 34.8 percent higher than what is shown in Figure 41. A similar conclusion is applicable to most of the remaining carbon material balances reported on in this study.

The gas production rate from the first column exhibited a constant and steady increase during the period extending between days 180 and 240 of continuous operation. Gas production during this period increased from a low production rate of 11.9 ml/day on day 180 to a peak rate of 735 ml/day during the 20 day period extending from day 220 to day 240. During the same period the gas production rate from the second column decreased from a peak rate of 1031 ml/day at the beginning of this period to a rate of 250 ml/day on day 240. The total cumulative gas production from both the first two columns (see Figure 39) show that the combined gas production rate from the first two columns remained somewhat constant during that period averaging 860 ml/day of 93.42 percent methane gas. If all the organic carbon in the feed substrate is converted to methane and aqueous and gaseous carbon dioxide according to the stoichiometry in Equation 43, then a maximum volume production rate of methane equal to 593 ml per day is anticipated. The maximum rate of methane production falls short of the 803 ml/day of methane gas observed during the period between days 180 and 290 of continuous operation indicating that the first two columns were in a state of continuous bioregeneration during that period.

The carbon material balances constructed for the two days 193 and 225 (see Figure 42 and 43) which fall within the carbon bioregeneration period illustrate this phenomenon rather well. Once again the data in Figure 41 do not show bioregeneration in the second column due to the loss of TIC upon

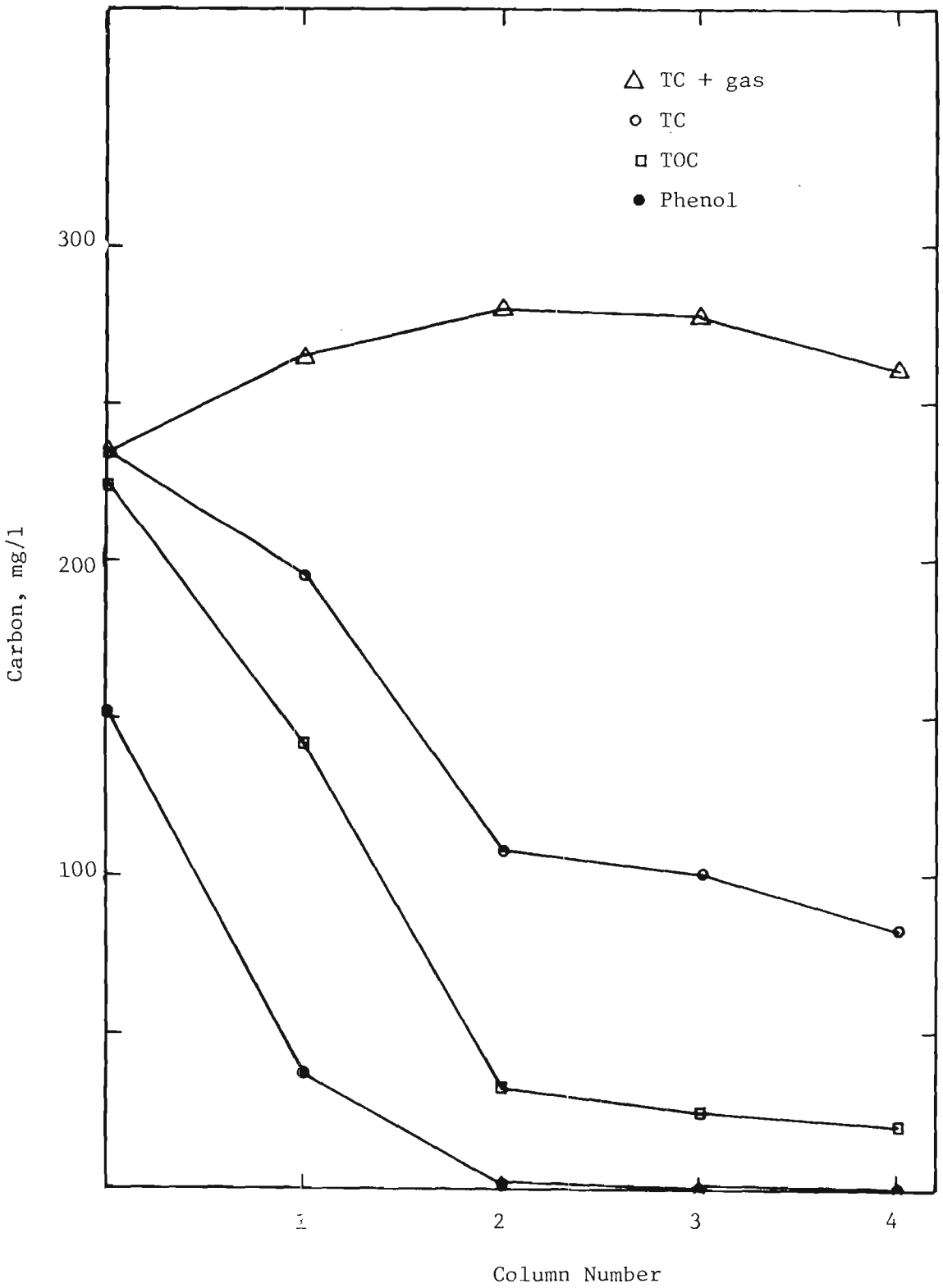


Figure 42. Carbon Profile, Day 193, Phenol Fed Reactor, 200 mg/l

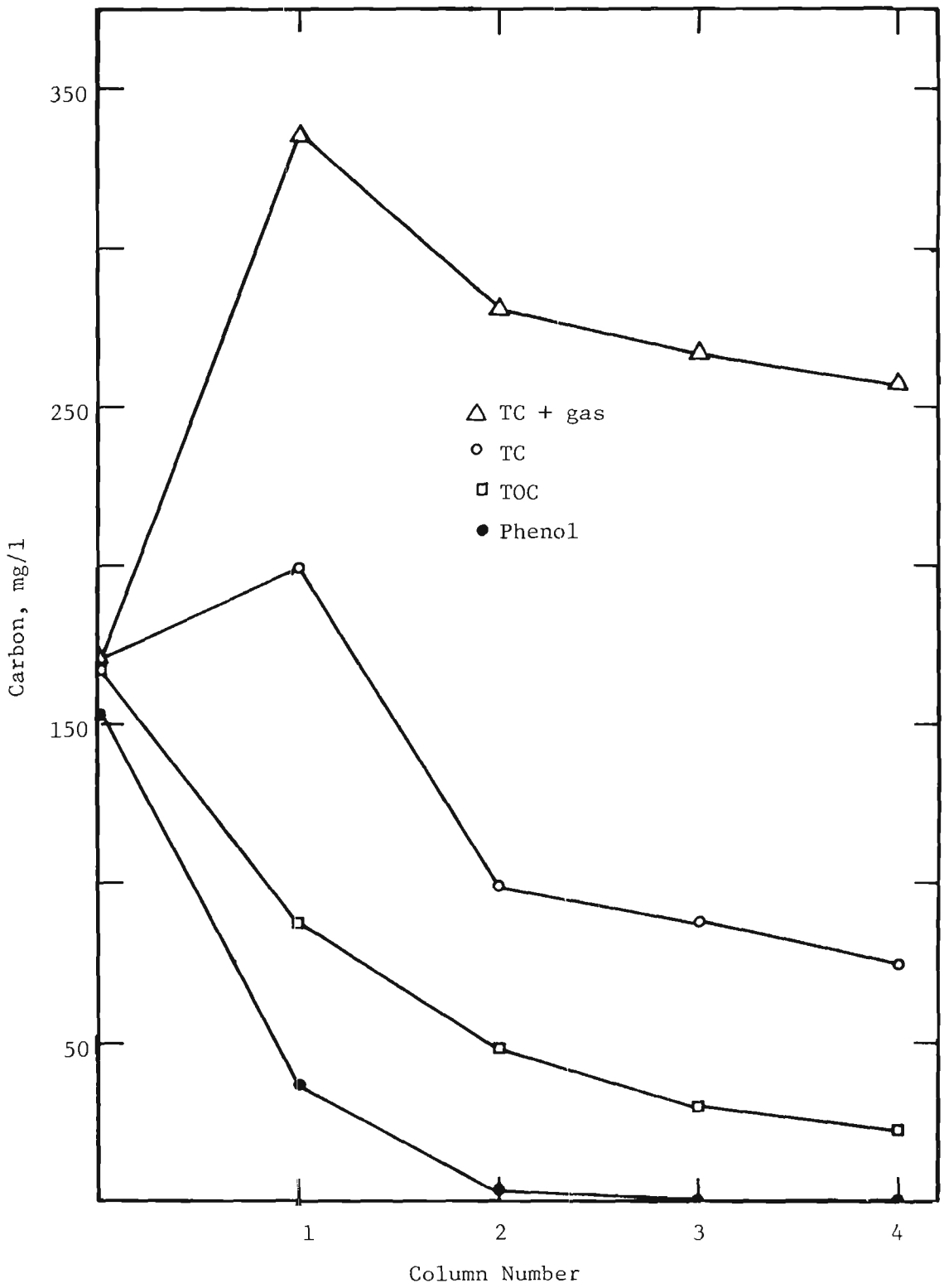


Figure 43. Carbon Profile, Day 225, Phenol Fed Reactor, 200 mg/l

analysis. However, a COD material balance across the treatment system for day 225 shows clearly that the second column is still undergoing bioregeneration on that day (see Figure 44).

The cumulative mass of carbon fed into reactor system, the mass of carbon present in the effluent from the fourth column reactor and the total carbon leaving the system in both the aqueous and gaseous phases are presented versus time in Figure 45. The data in Figure 45 is for the period extending between days 150 and 265 of continuous operation. These data illustrate, once again, that throughout most of this period the system is undergoing regeneration with the total output mass of carbon from the system exceeding the mass of feed carbon. In reality, however, the total mass of carbon and the mass of aqueous carbon leaving the system should be higher than what is indicated in the figure because of the appreciable loss of TIC experienced during the sample preparation prior to analysis.

Steady-State Performance

Steady-state intensive analysis was conducted on the feed substrate and all column effluents for the period extending from day 240 to day 265 of continuous operation. A summary of the steady state data for this experiment is presented in Table 28. These data indicate that reductions in phenol, TOC and COD corresponding to 92.5, 70 and 80 percent, respectively were achieved in the first column of the treatment system using an empty bed detention time of 11.62 hours. Overall the system resulted in reductions in phenol, TOC and COD of 99.95, 93.7 and 93.4 percent, respectively. Steady-state carbon and COD material balances across the treatment system are presented in Figures 46 and 47, respectively.

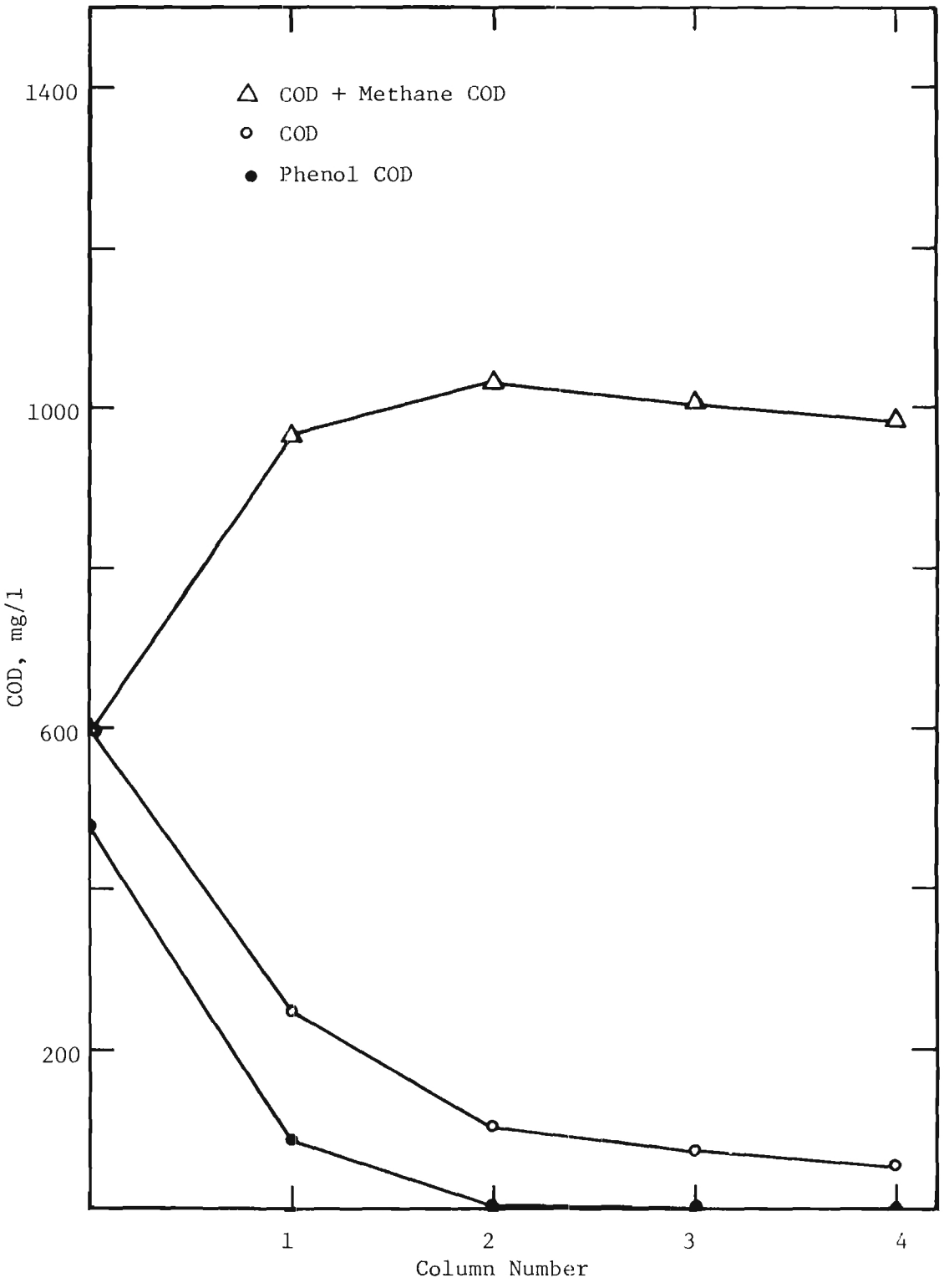


Figure 44. COD Profile, Day 225, Phenol Fed Reactor, 200 mg/l

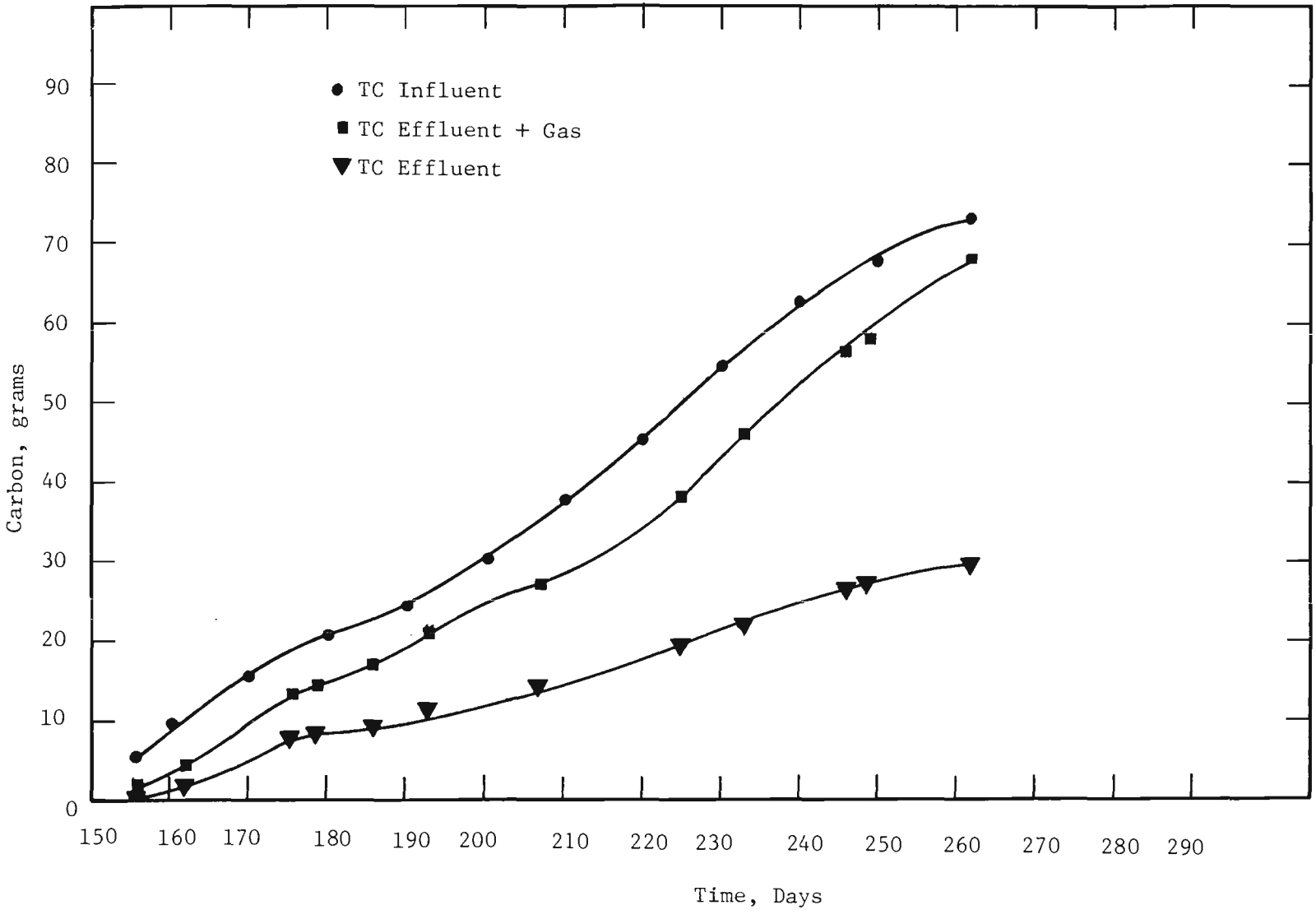


Figure 45. Cumulative Carbon Balance, Phenol Fed Reactor, 200 mg/l

Table 28. Average Steady-State Performance Data for 200 mg/l Phenol Fed Reactor

Parameter	Influent Value	Parameter Value in Column Effluents 1	2	3	4
pH	7.4	7.15	7.08	7.06	7.07
TOC, mg/l	185.0	55.0	25.0	17.3	11.7
TIC, mg/l	7.15	48.8	83.1	74.0	78.0
COD, mg/l	511.7	100.9	66.25	71.6	34.0
Phenol, mg/l					
U.V.-286 nm	200.0	20.3	4.0	3.1	2.1
Chloroform Extraction	-	35.0	1.75	0.0	0.0
Gas Chromatography	200.0	15.0	0.18	0.3	0.1
Gas Production, ml/day	-	409	0	0	0
Methane	-	298	0	0	0
Carbon Dioxide	-	11	0	0	0
Alkalinity, mg/l as $CaCO_3$	1440	1587	1591	1582	1566
Total Suspended Solids, mg/l	-	823	590	162	-
Volatile Suspended Solids, mg/l	-	678	375	96	-
NH_3-N, mg/l	-	72.5	99.9	38.6	29.5
ORP	-	-308	-293	-294	-255

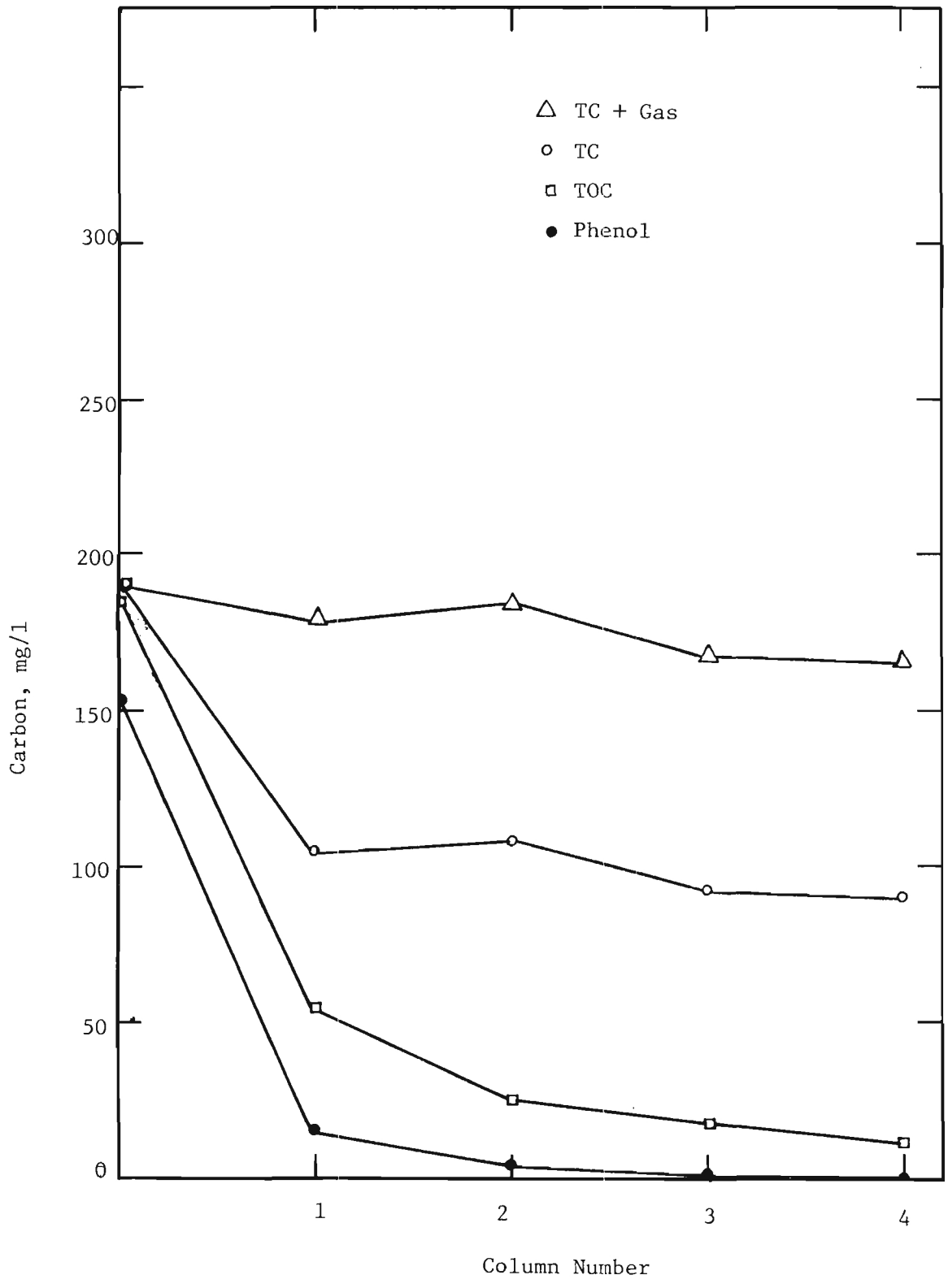


Figure 46. Carbon Profile, Steady State, Phenol Fed Reactor, 200 mg/l

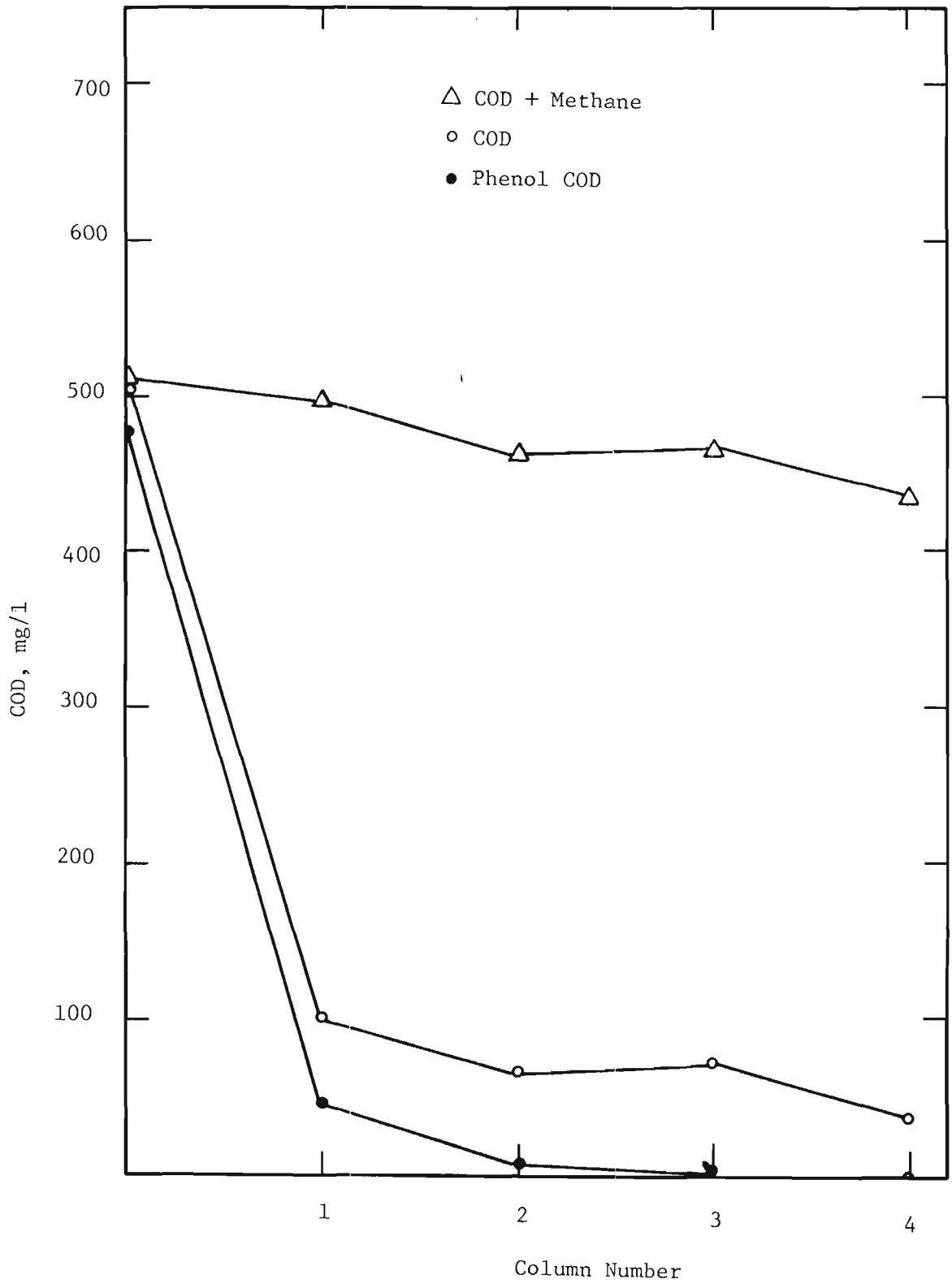


Figure 47. COD Profile, Steady State, Phenol Fed Reactor, 200 mg/l

The carbon material balance indicates a loss of only 6.2 percent of the carbon across the first column, while the COD material balance shows that only 2.7 percent of the COD was unaccounted for in the effluent from the first column. Both material balances seem to indicate minor losses of carbon during the anaerobic degradation of phenol thus leading to the conclusion that the organisms responsible for the anaerobic degradation of this compound have very low growth rates. A similar conclusion was arrived at by Young and McCarty (1967) for the case of the anaerobic degradation of volatile fatty acids. The COD material balance in Figure 45 seems to indicate that at the time steady-state data was collected on the system carbon adsorption was still occurring in the second and third columns.

The average alkalinity in the effluents from the four columns was 10 percent greater than the alkalinity in the feed substrate once again leading to the conclusion that the absence of volatile acids from the column effluents along with the dissolution of carbon dioxide in the aqueous phase serve to improve the resistance or buffer capacity of the system to the production of acids.

Hydrogen utilization in triplicates on all effluent samples as well as samples of granular activated carbon withdrawn from all four column reactors. The results obtained from the tests conducted on the effluent samples revealed that all samples had methanogens within them, however, as was observed in Table 26 in the case when glucose was employed as a substrate, all vials showed the absence of hydrogen gas at the end of the 84 hour incubation period and therefore no conclusions could be drawn as to the relative distribution of the methanogens in the different effluents.

The results from the tests conducted using carbon granules, however, showed definite differences between the methanogenic activity of the various carbon samples. Granules withdrawn from the first column caused the complete

depletion of the hydrogen from the headspace of the three triplicate vials while only 12.8 percent of the hydrogen gas remained in the head space of the vials innoculated with carbon granules from the second column. The third and fourth columns showed lower levels of methanogenic activity (see Table 29).

Table 29. Hydrogen Utilization and Methanogenic Tests on the Activated Carbon Medium

Activated Carbon from Column	Percent Gas Composition		
	Methane	Carbon Dioxide	Hydrogen
1	79.0	0	0
2	76.3	0	12.8
3	9.7	0.2	27.7
4	9.3	0	52.5

Phase II, 400 mg/l Phenol

During this phase of the phenol degradation experiment, the phenol concentration in the synthetic feed substrate was increased to 400 mg/l while keeping the feed flow rate and the recirculation flow rate at the same levels used in the first phase of the experiment, namely 2 ml/min and 50 ml/min, respectively. The feed substrate was prepared daily in four liter batches using 40 ml of the salt solution, 60 ml of the phosphate buffer solution, 1.6 g of phenol and distilled water. The theoretical COD and TOC concentration of the feed substrate computed using the measured values for the salt solution and the theoretical values for phenol given in Table 24 were 1210 and 373 mg/l respectively. The measured and theoretical values of the COD and TOC in the feed substrate are presented in Figure 48. The chemical oxygen demand of the feed substrate averaged around 1133 mg/l while the average total organic carbon content of the feed was 351 mg/l. The feed substrate has a computed COD to TOC ration of 3.24 while the measured ratio was 3.23.

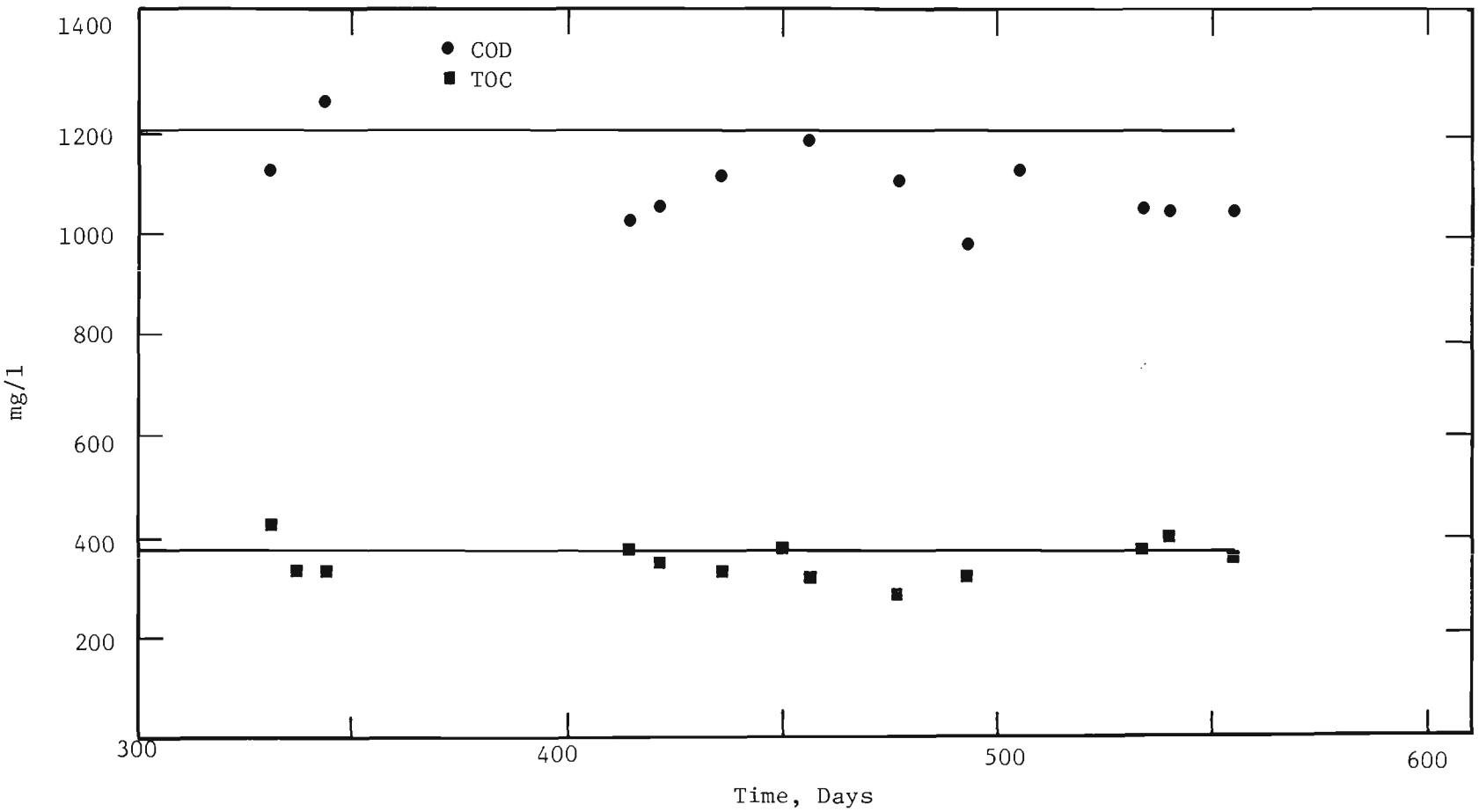


Figure 48. Influent COD and TOC for Phenol Fed Reactor, 400 mg/l

The pH of the feed substrate was maintained at 7.4 throughout this phase of the experiment. The alkalinity of the feed substrate at this pH was 1440 mg/l as $CaCO_3$. This alkalinity was sufficient to maintain the system pH between 6.9 and 7.2 throughout the experiment.

The general response of the first column to an increase in the feed concentration of phenol was an immediate increase in the rate of gas production signifying that no additional acclimation period was needed and that no shock effects were encountered. Steady-state conditions, as defined by a uniform gas production rate, were attained after 170 days of operation as compared to the 240 days required to achieve stable operating conditions during the first phase of the experiment.

Phenol Reduction. The concentration of phenol (measured spectrophotometrically at 286 nm) in the effluents from the series of three anaerobic-activated carbon filters is shown in Figures 49, 50 and 51 for the period of operation extending between day 330 and day 540 of continuous operation.

The phenol content in the effluent from the first column increased steadily after the feed phenol concentration was increased to 400 mg/l. This increase in the phenol concentration present in the first column effluent continued until day 330 of continuous operation where it reached a peak value of 97 mg/l. After that day, the phenol content of the effluent from the first column showed a regular decrease where it eventually reached a steady-state value of 5 mg/l; thus resulting in a phenol removal efficiency in the first column reactor of 98.75.

The phenol concentration present in the effluents from the second and third columns remained consistently below 5 mg/l resulting in very little additional removal of this species. Care must be exercised in evaluating

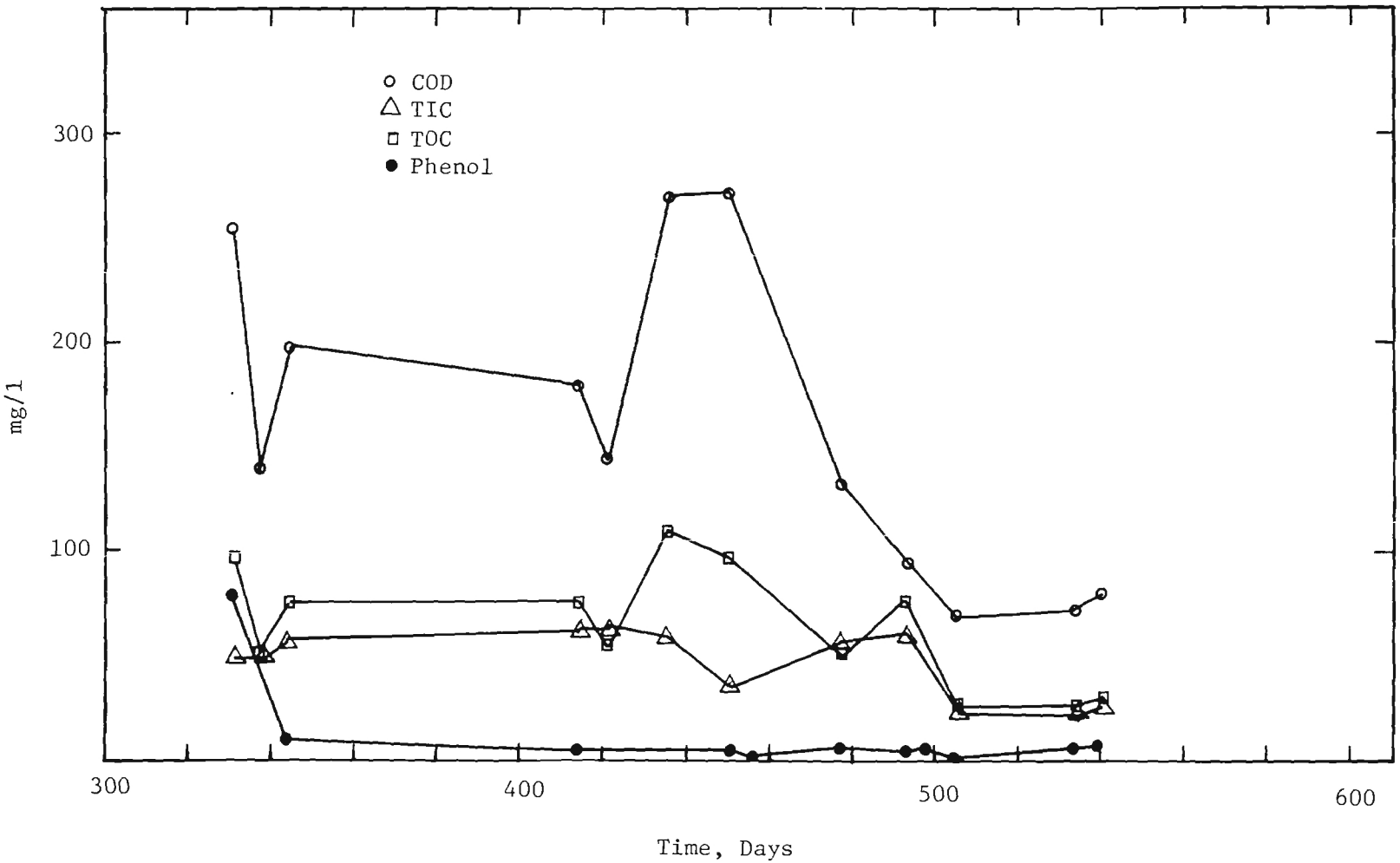


Figure 49. Effluent COD, TOC, TIC from Column One, Phenol Fed Reactor, 400 mg/l

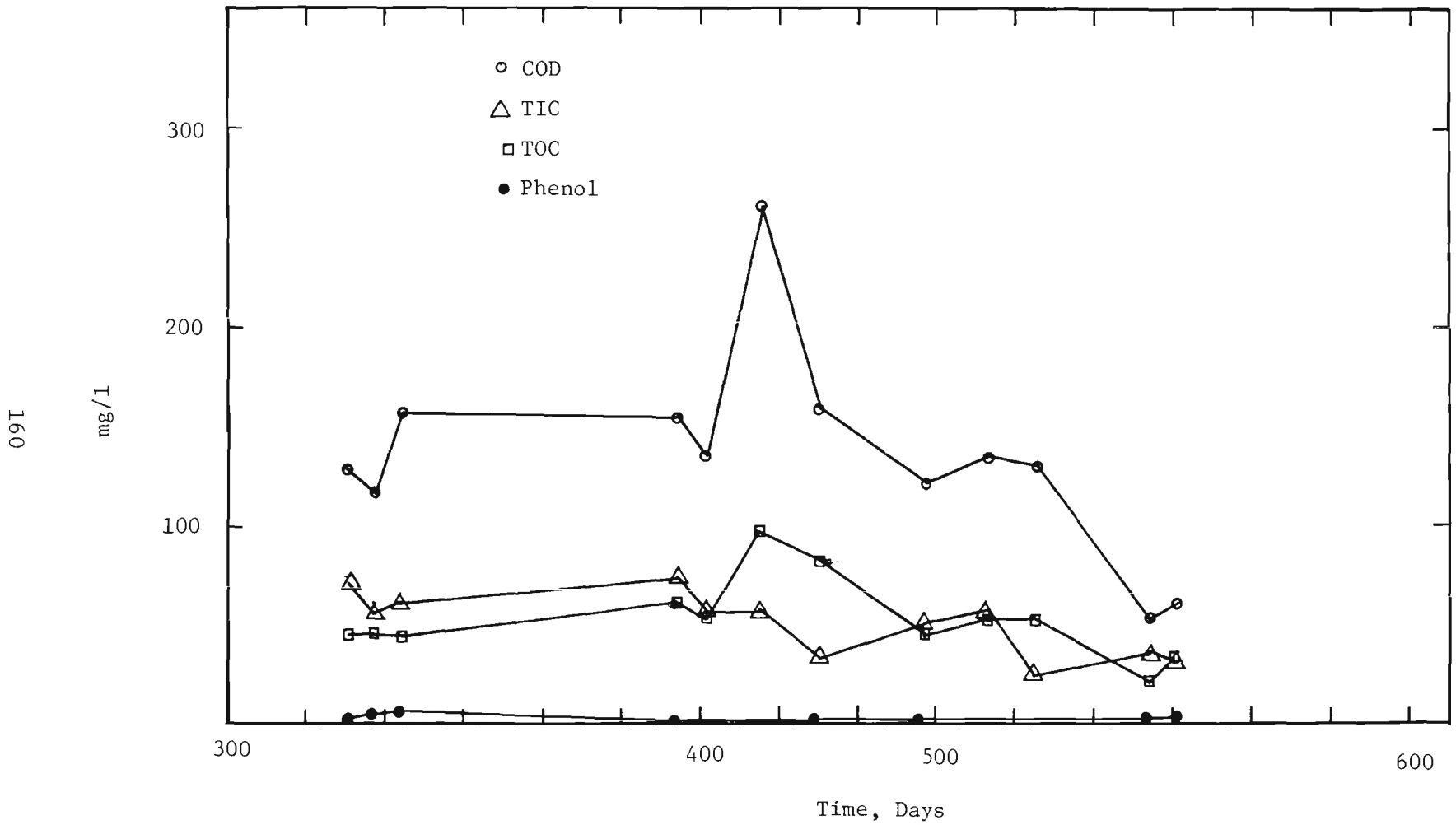


Figure 50. Effluent COD, TOC, TIC from Column Two, Phenol Fed Reactor, 400 mg/l

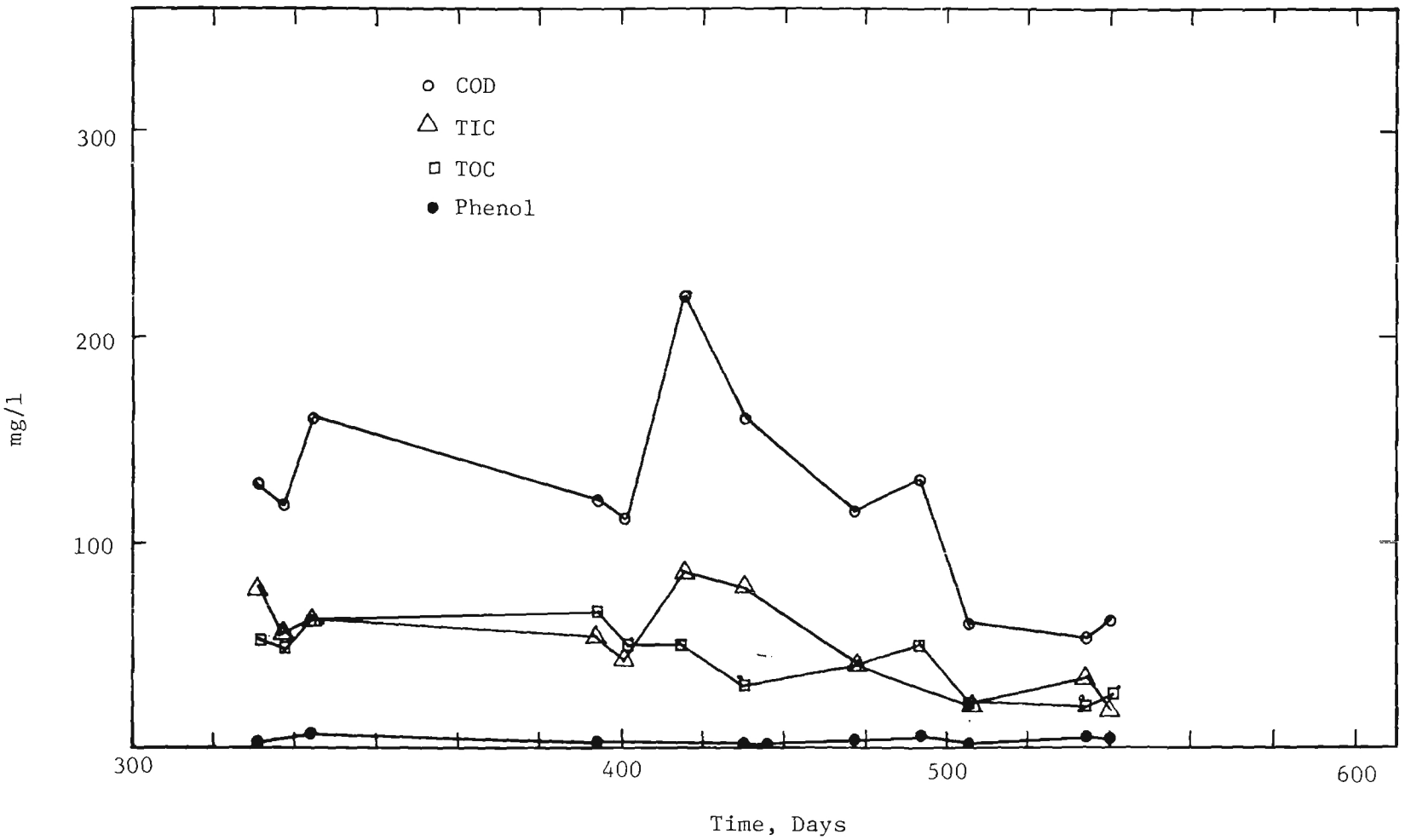


Figure 51. Effluent COD, TOC, TIC from Column Three, Phenol Fed Reactor, 400 mg/l

this data, however, due to the interference of the residual organic matter in these effluents with the absorbance readings at 286 nm. The analysis for phenol using the chloroform extraction 4-aminoantipyrene method revealed that total removal of the phenol was accomplished in this treatment system.

Organic and Inorganic Carbon. The organic and inorganic carbon content of the filtered effluents from all three anaerobic columns was presented in Figures 49, 50 and 51 for the continuous operating period between days 330 and 540. The organic carbon content in the feed substrate was presented in Figure 48. The TOC of the feed substrate averaged 351 mg/l while the TOC in the effluent from the first column ranged from a high of 110 mg/l on day 435 to a low of 28 mg/l near the termination of this experiment. The average TOC in the effluent from the first column during the period of steady gas production (day 470 to day 550) was 42 mg/l resulting in an average carbon removal in this column of 88 percent.

The total organic carbon content in the effluent from the second column varied from a high of 98 mg/l on day 435 to a low of 20 mg/l on day 535. The average TOC in the effluent from the second column during the last 80 days of operation was 40 mg/l thus resulting in an average additional organic carbon removal in this column of 2 mg/l. The organic carbon content in the effluent from the third and last column ranged from a high of 84 mg/l on day 435 to a low of 20 mg/l on day 535 with an average TOC of 29 mg/l in the final effluent during the last 80 days of operation. No gas production was observed from the last column indicating that any carbon removal occurring in this column was due, most probably to adsorption.

Overall it is evident from the TOC removal data presented thus far that the first column was responsible for most of the treatment in this process with very little additional removal occurring in the second and third column.

Chemical Oxygen Demand. The performance of the treatment system as far as the reduction of chemical oxygen demand is presented in Figures 49, 50 and 51 for the period extending between days 330 and 540 of continuous operation. The COD of the various column effluents varied appreciably during the course of this phase of the experiment. However at steady-state operating conditions the average COD values in the three column effluents were 90, 101 and 83.6 mg/l amounting to cumulative reductions in this parameter of 92, 91 and 93 percent from the respective effluents of the three columns. The COD to TOC ratio in the feed substrate was 3.23 while this ratio decreased to 2.14 in the effluent from the first column signifying a very efficient reduction of the COD in the first column.

Gas Production. Gas production in this phase of the experiment was virtually limited to the first column reactor with gas production from the second column averaging 15 ml/day of methane and gaseous carbon dioxide. During the first phase of the experiment, gas production ceased from the second column when steady-state operating conditions were achieved and apparently the reduction or biodegradation capacity of the first column is sufficient to utilize an increased phenol concentration without allowing for sufficient carbon to reach the second column and stimulate active growth within it.

The cumulative total dry gas produced from the first column reactor is presented in Figure 52. The gas production rate from the first column was characterized by two periods of performance. During the first period which extended from the day of initiation of the new feed concentration through day 470, the gas production rate from the first column averaged 882 ml/day of 95.4 percent rich methane gas. A carbon material balance across the treatment system constructed for days 344 and 435 reveal no loss of carbon in the first column (Figures 53 and 54). A closer examination of the data in Figures 53

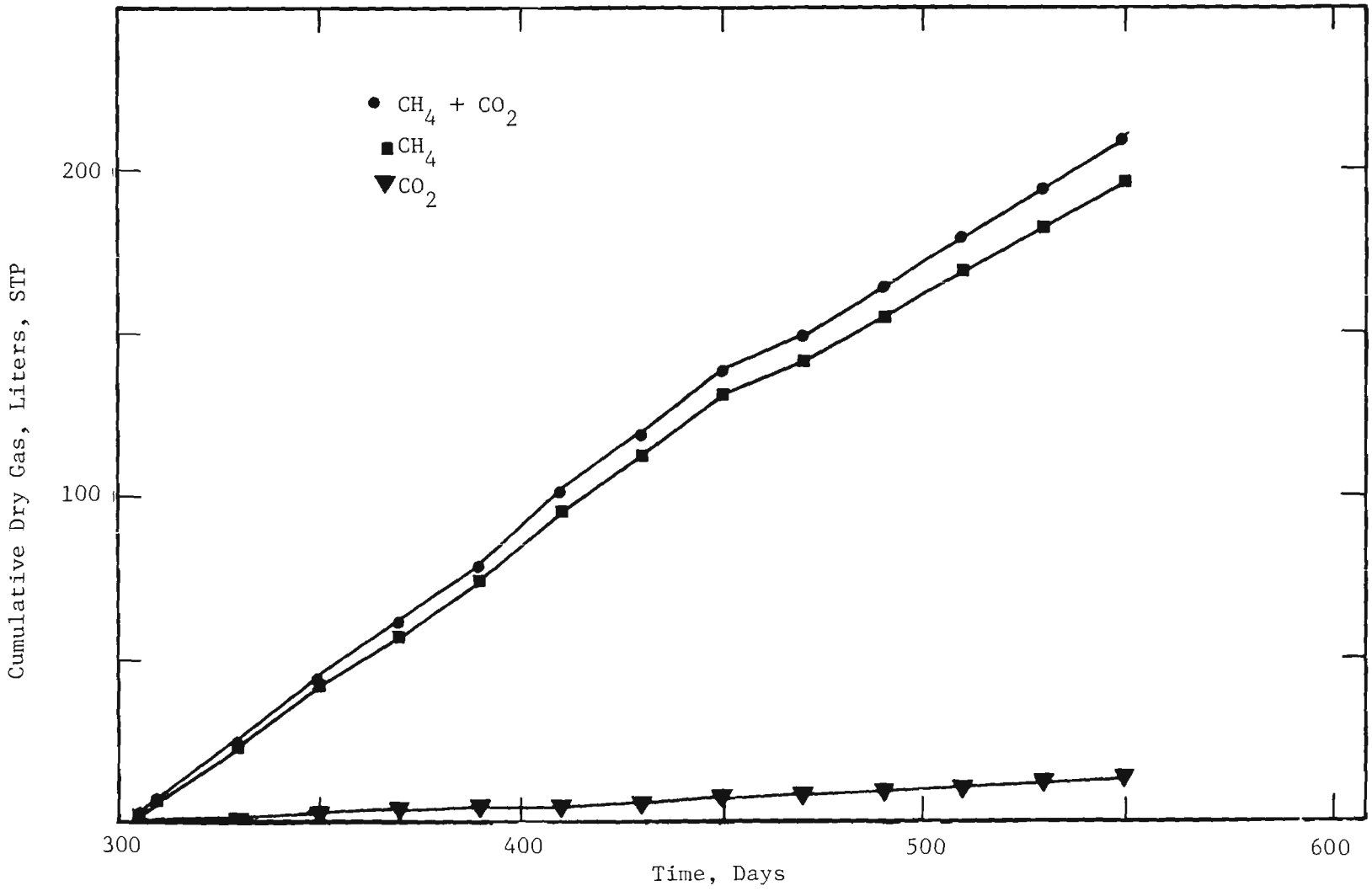


Figure 52. Total Gas Production from Phenol Fed Reactor, 400 mg/l

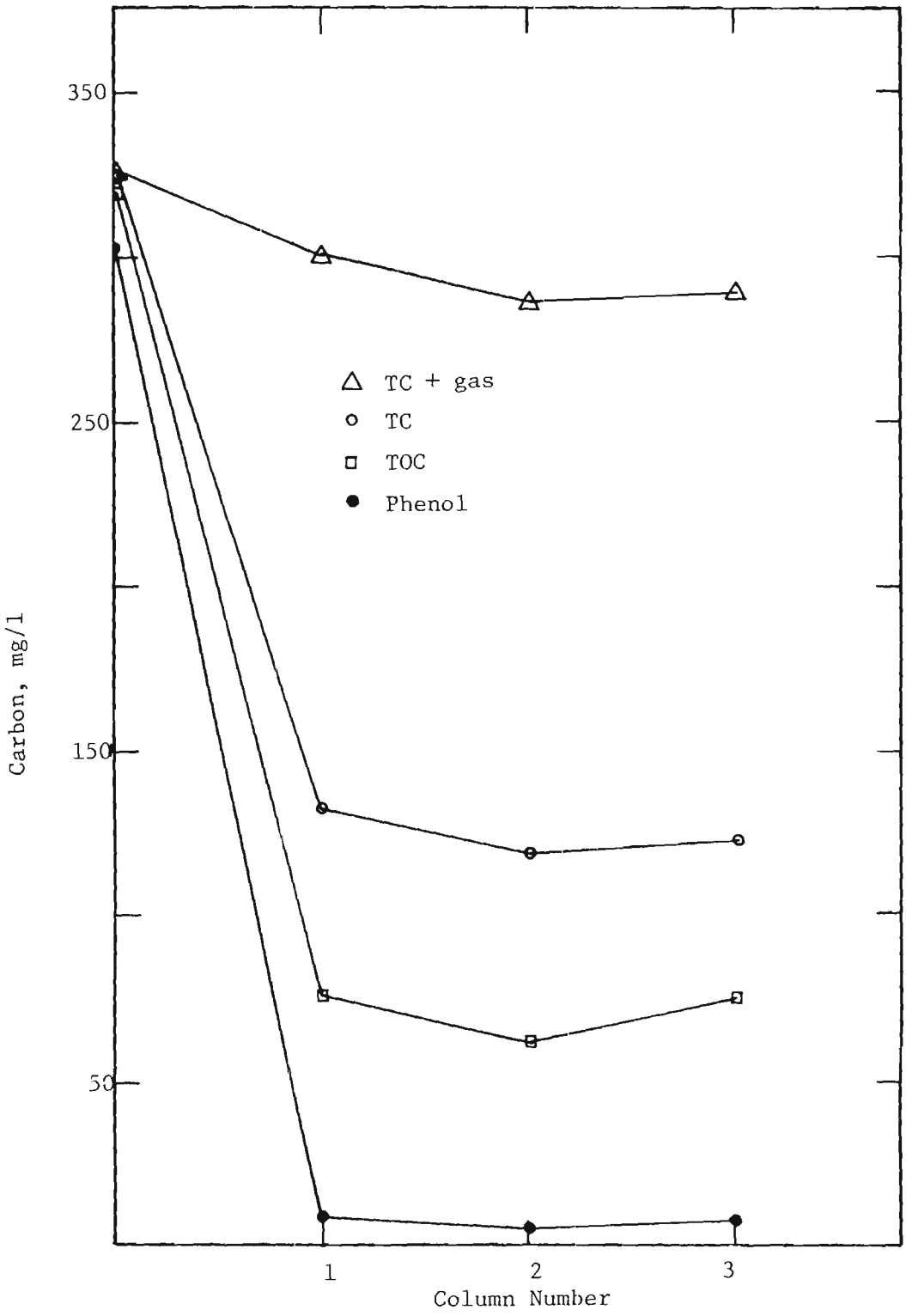


Figure 53. Carbon Profile, Day 344, Phenol Fed Reactor, 400 mg/l

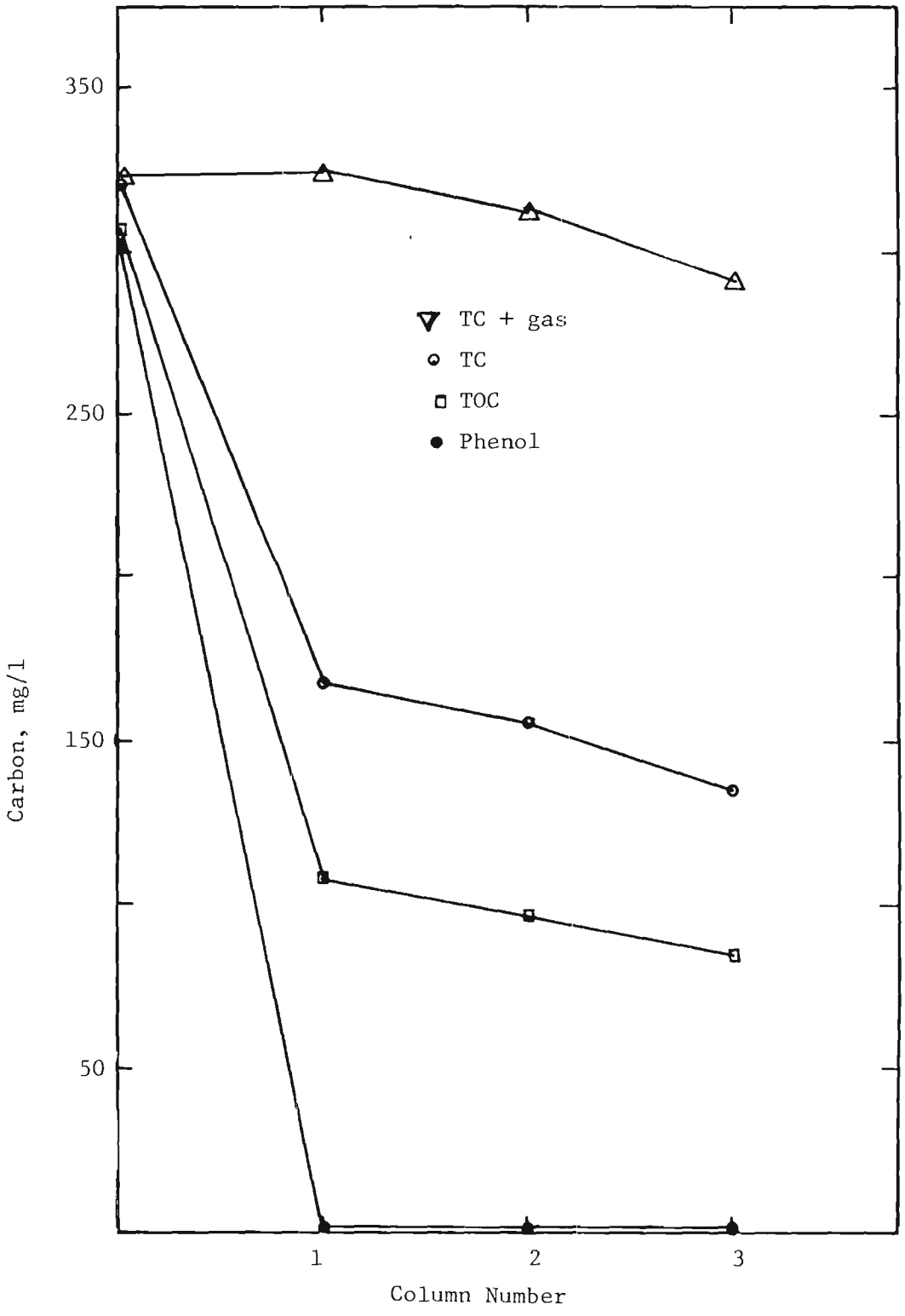


Figure 54. Carbon Profile, Day 435, Phenol Fed Reactor, 400 mg/1

and 54, however, reveals that methane accounts for 69 percent of the gaseous and aqueous organic carbon which exceeds the 58.33 percent occurrence reported by Healy and Young (1977). Using this information and the fact that it was experimentally determined that the reported values for TIC were always smaller than actual concentrations due to the filtration of the samples, it may then be concluded that the first column of the treatment system was undergoing active bioregeneration during this period of the experiment. In order to confirm this hypothesis, a COD material balance was constructed across the system for the same day of operation (Figures 55 and 56). The COD balances in Figure 56 clearly shows that the first column was undergoing bioregeneration to the level of 330 mg/1 of COD per ℓ of solution on day 435 of continuous operation. No COD bioregeneration was observed on day 344 of continuous operation,

After day 470 of continuous operation, gas production from the first column reached a steady production level of 719 ml/day of methane and gaseous carbon dioxide. Steady-state carbon and COD material balanced across the treatment system on day 493 of continuous operation (see Figures 57 and 58) reveal that 30 mg/1 of TOC and 150 mg/1 of COD were not accounted for in the effluent from the first column. If all this carbon is utilized in the production of biomass, then a TOC biomass yield ratio of 12 percent and a COD biomass yield ratio of 16 percent would prevail.

The data in Figure 59 represent a plot of the cumulative carbon mass input into the system along with curves for the carbon output in the aqueous phase and the total output in the aqueous and gaseous phases. The cumulative carbon output curve illustrates the active bioregeneration occurring between days 335 and 450 where on day 450 the cumulative carbon input was exactly equal to the cumulative carbon output from the treatment system. After

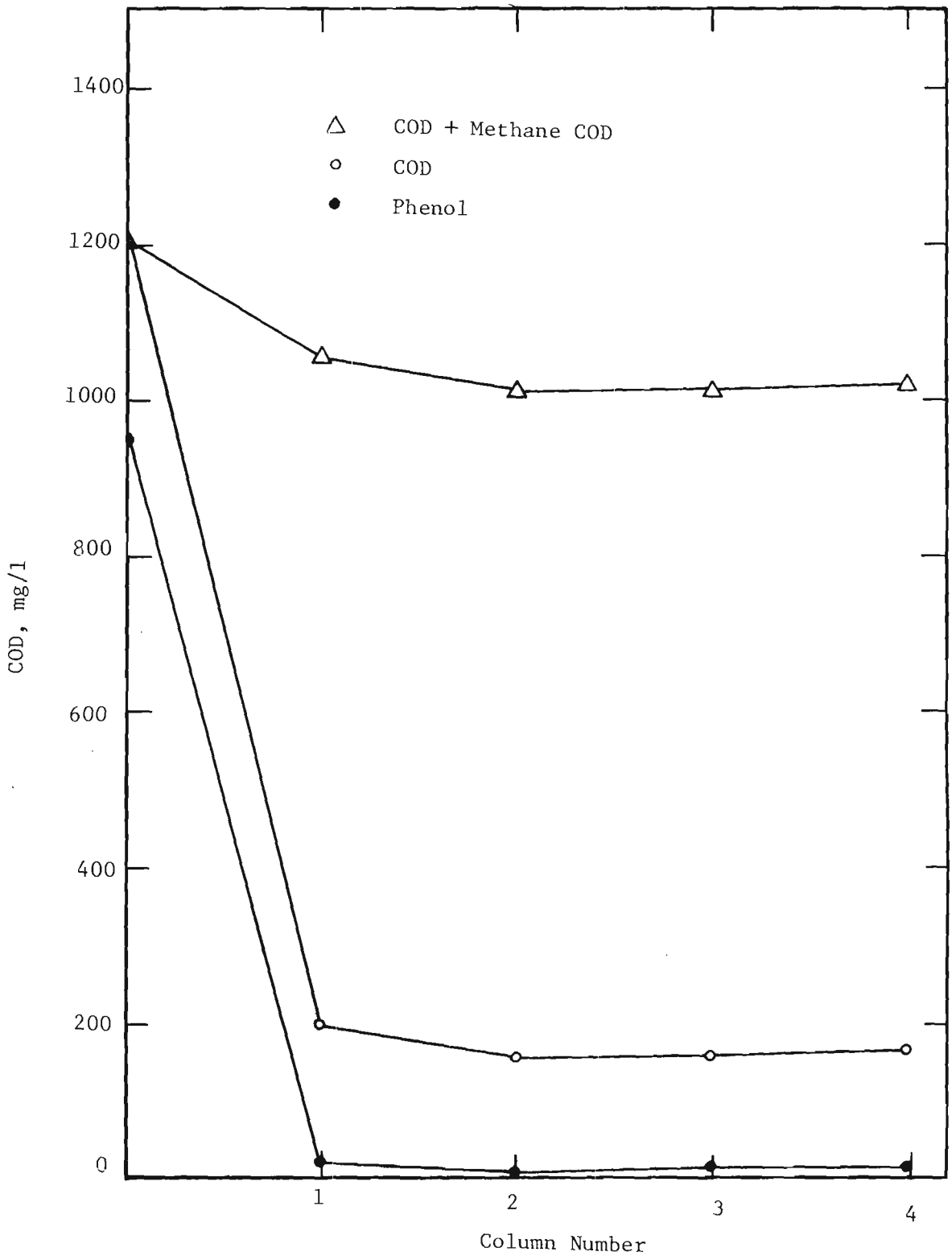


Figure 55. COD Profile, Day 344, Phenol Fed Reactor, 400 mg/l

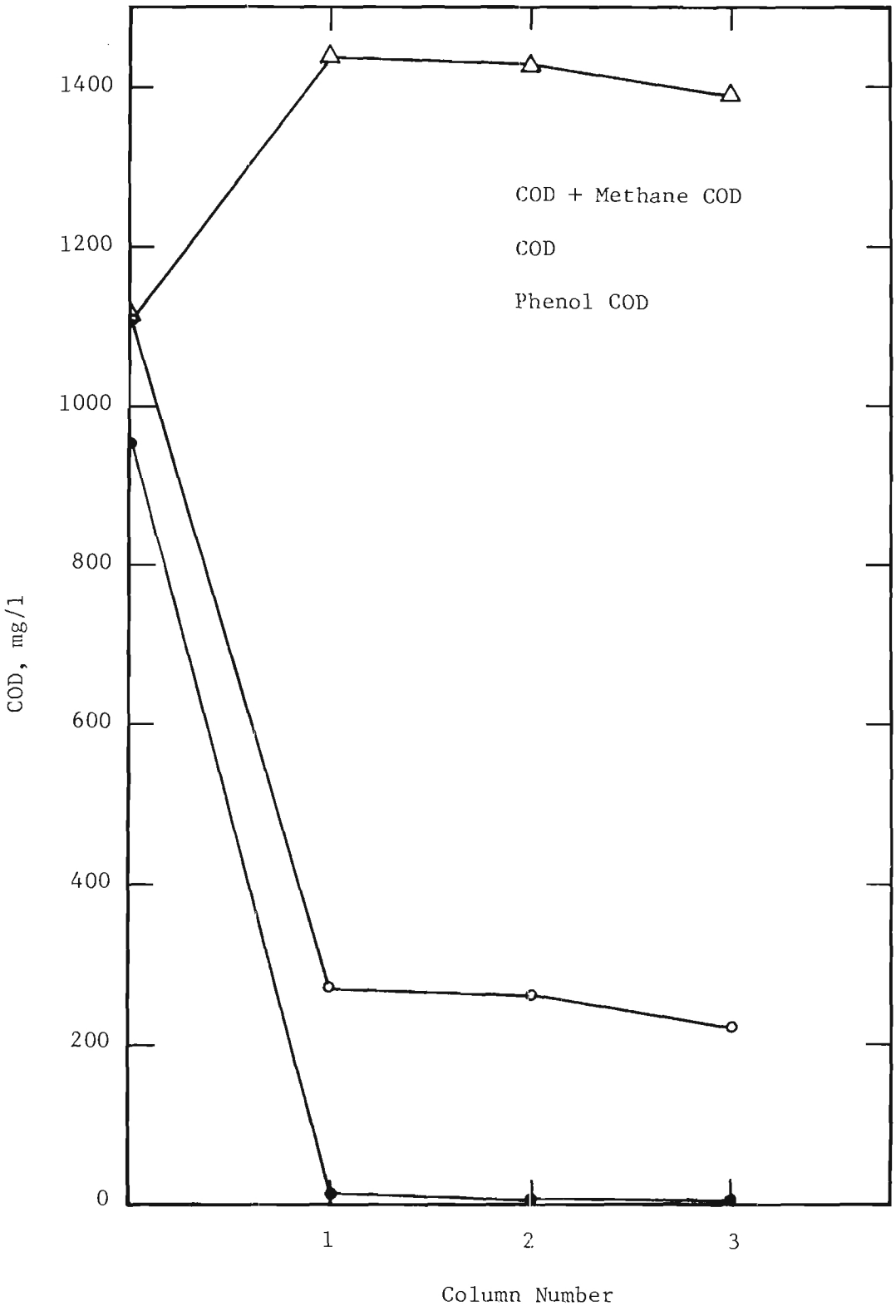


Figure 56. COD Profile, Day 435, Phenol Fed Reactor, 400 mg/l

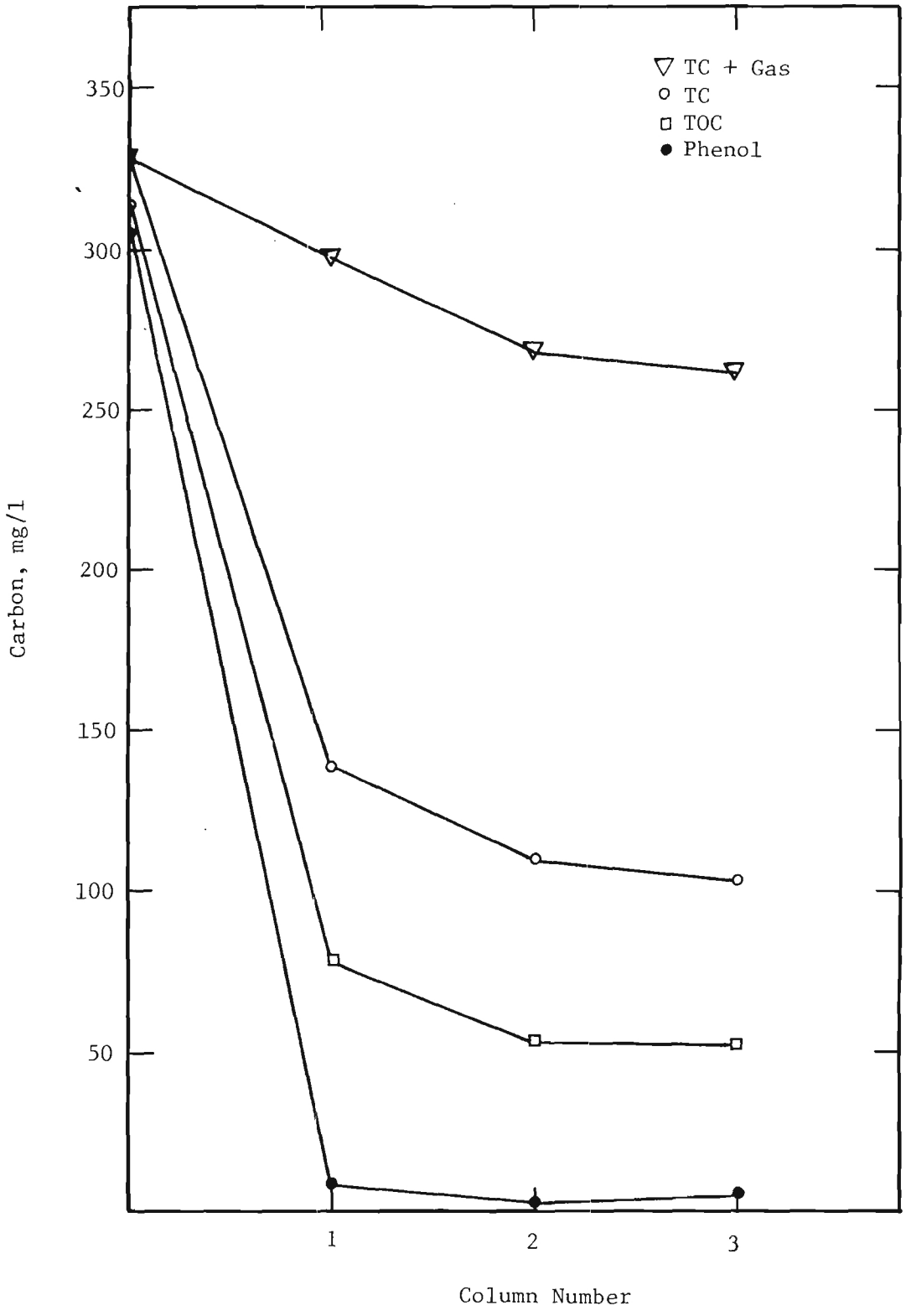


Figure 57. Carbon Profile, Day 493, Phenol Fed Reactor, 400 mg/1

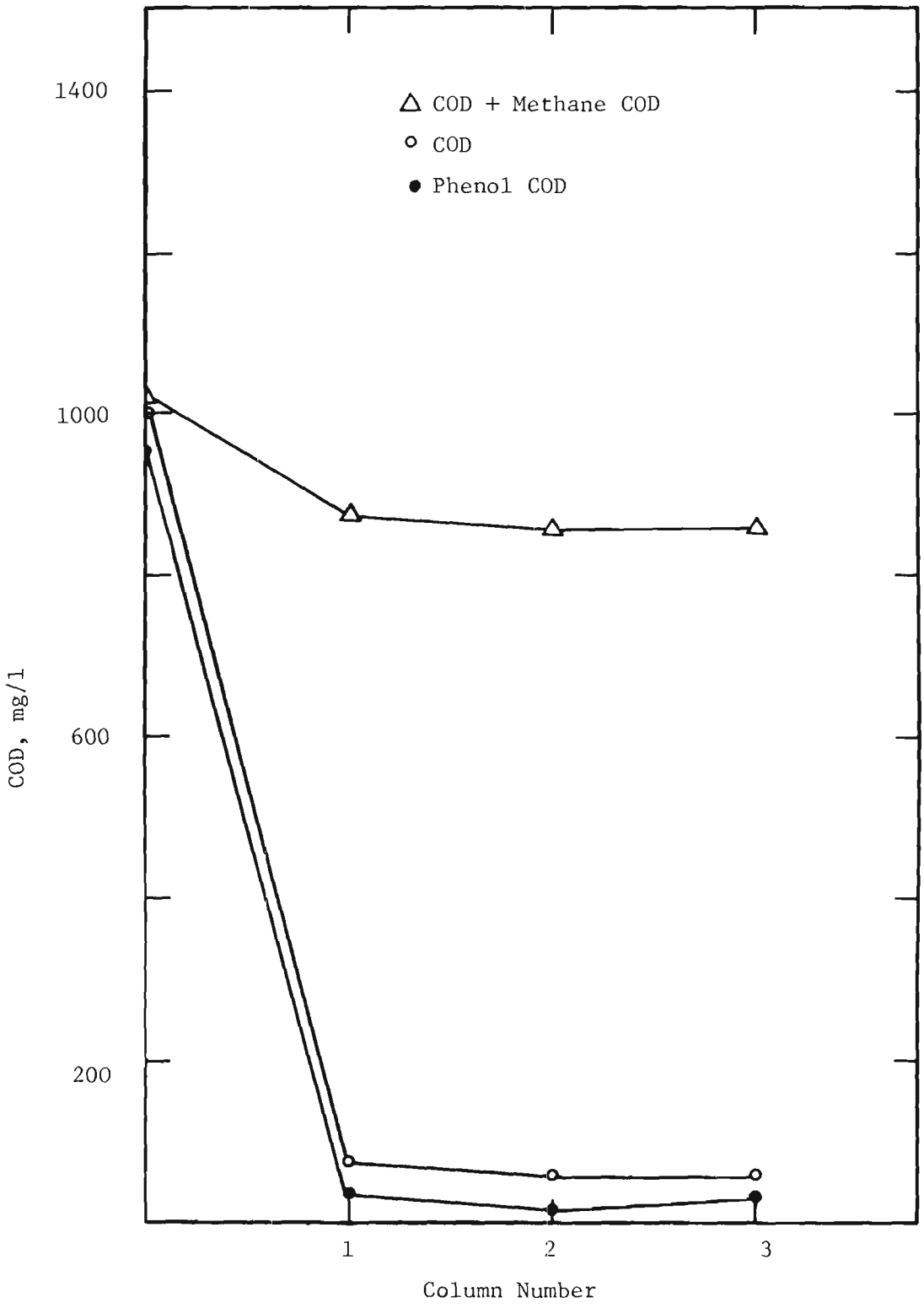


Figure 58. COD Profile, Day 493, Phenol Fed Reactor, 400 mg/l

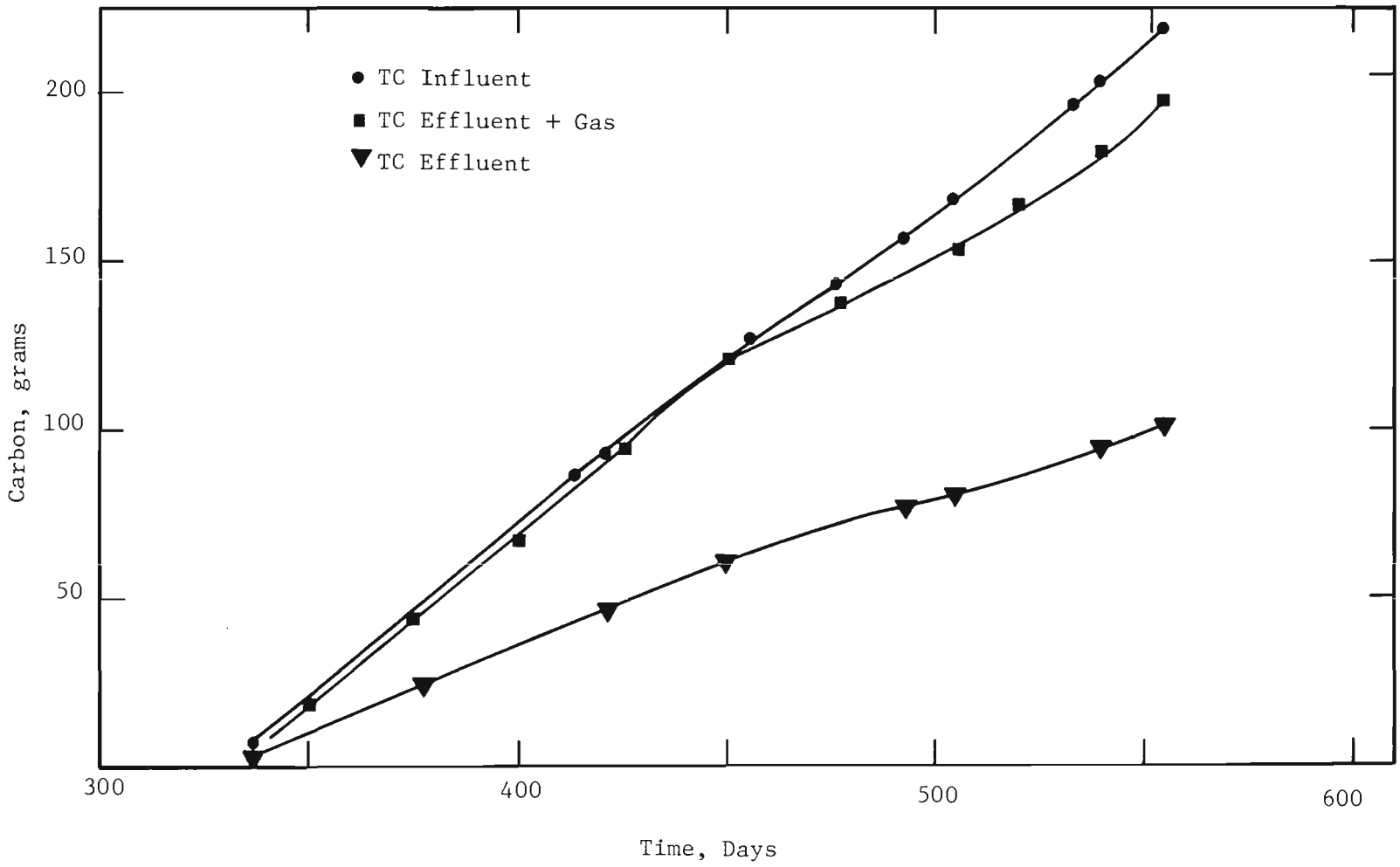


Figure 59. Cumulative Carbon Balance, Phenol Fed Reactor, 400 mg/1

day 450 the carbon leaving the system in the aqueous phase was considerably less than the mass of carbon entering the system. This difference is due to biomass production as well as the loss in TIC upon measurement.

Steady-State Performance

Steady-state analysis was conducted on the feed substrate and all column effluents for the period extending from day 540 to day 560 of continuous operation. A summary of the steady-state data for this experiment is presented in Table 30. These data indicate that reductions in TOC and COD corresponding to 92.4 and 92.7 percent, respectively and reductions in phenol exceeding 98 percent were attained in the first column of the treatment system using an empty bed contact time of 11.62 hours. Overall, the system resulted in reductions in phenol, TOC and COD of 100, 94 and 95 percent, respectively.

A uniform increase in alkalinity was observed across the feed and the respective column effluents indicating, once again, the importance of the role played by the carbonate system in buffering the aqueous phase of the reactor. This increase in alkalinity was realized inspite of the fact that an appreciable drop in pH of 0.42 units was observed between the feed substrate and the effluent from the first column.

Treatment of a Phenol-Glucose Bearing Substrate

After the termination of the experiment where a 2000 mg/l glucose bearing substrate was treated in a series of four anaerobic activated carbon filter columns for a continuous period of 265 days, the fourth column was taken out of operation and the remaining three columns were fed a synthetic substrate containing 2000 mg/l glucose and 200 mg/l phenol for an additional period of 285 days. The objective behind this experiment was to investigate the following:

a. Whether the use of a readily biodegradable and nonadsorbable substrate, such as glucose, to establish a strong growth with the treatment system

Table 30. Average Steady-State Performance Data for 400 mg/l Phenol Fed Reactor

Parameter	Influent Value	Parameter, Volume in Column Effluents 1	2	3
pH	7.33	6.91	6.95	6.97
TOC, mg/l	377.2	28.85	21.6	22.3
TIC, mg/l	12.10	25.85	35.7	26.7
COD, mg/l	1043.7	76.4	55.9	56.0
Phenol, mg/l				
U.V.-286 nm	400	7.5	3.80	3.75
Chloroform Extraction	400	5.0	0	0
Gas Production, ml/day	-	719	15	0
Methane	-	672	14	0
Carbon Dioxide	-	47	1	0
Alkalinity, mg/l as $CaCO_3$	1440	1588	1836	1836
Total Suspended Solids, mg/l	-	323.1	65.5	50.4
Volatile Suspended Solids, mg/l	-	186.1	38.1	19.0
ORP	-	-310.5	-245.9	-240

will result in accelerated acclimation for the degradation of phenol over the long acclimation period that was experienced in the 200 mg/l fed anaerobic filter system.

b. The co-metabolism characteristics of the readily degradable but nonadsorbable substrate glucose in the presence of the very adsorbable and somewhat biologically resistant phenol.

Throughout this experiment, the feed substrate was prepared daily in 4 ℓ batches using 100 ml of the salt solution, 140 ml of the phosphate buffer solution, 8 g of glucose, 0.8 g of phenol and distilled water. The theoretical values of the feed COD and TOC, computed using the measured values for the salt solution and the theoretical values for glucose and phenol given in Table 24, were 3252 and 1119 mg/l, respectively. The measured and theoretical values of the COD and TOC in the feed substrate are presented in Figure 60. The chemical oxygen demand of the feed substrate averaged 2989 mg/l while the average total organic carbon content of the feed was 1013 mg/l. The feed substrate had a computed COD to TOC ratio of 2.91 while the measured ratio was 2.95.

The pH of the feed substrate was maintained at 7.55 throughout the study. At this pH, the feed had an alkalinity of 3360 mg/l as $CaCO_3$ which was sufficient to maintain a pH within the reactor system ranging from 6.8 to 7.1.

The experimental system was operated at a feed substrate flow rate of 2 ml/min thus resulting in an empty bed contact time of $11^{o}62$ h in every column. Recirculation of the aqueous contents around every individual reactor was exercised continuously at a flow rate of 50 ml/min. This recirculation served to assist in maintaining the pH of the aqueous contents close to neutral by providing an additional bicarbonate buffer capacity.

The response of the first column to the addition of 200 mg/l of phenol to the feed substrate was in the form of an immediate increase in the gas

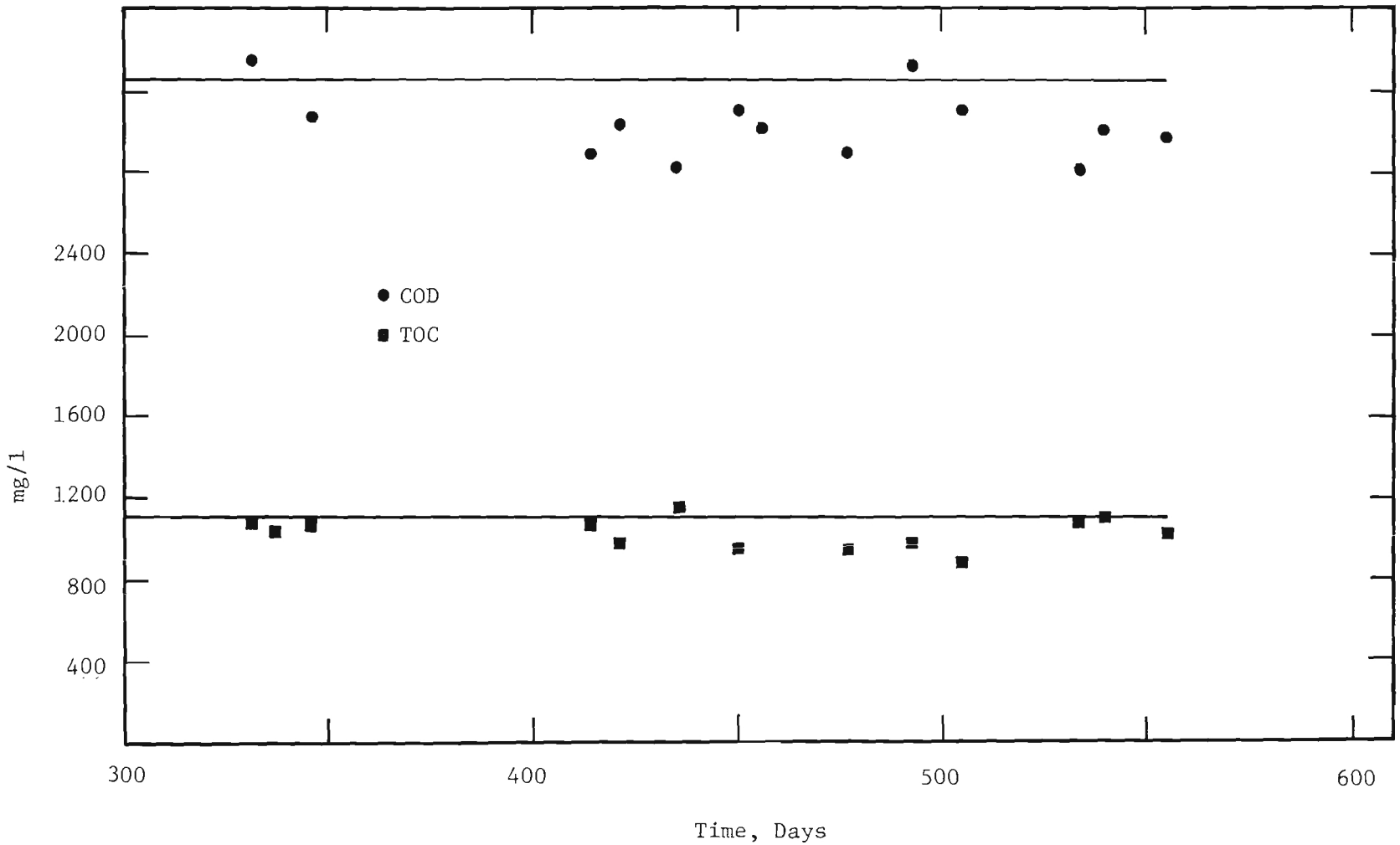


Figure 60. Influent COD and TOC for Phenol + Glucose Fed Reactor

production rate from this column. This indicates that the cometabolism of the two substrates, glucose and phenol, was symbiotic in nature and that the presence of phenol on an intermittant basis in the feed to an anaerobic-activated carbon filter does not lead to the reduction in activity within the filter. The addition of phenol to the feed substrate caused an apparent surge in gas production from the second and third columns. This activity, however, eventually ceased after day 400 of continuous operation and when steady state operating conditions were established in the first column. One possible explanation for the resurgence of anaerobic activity in the last two columns may be that the phenol which is strongly adsorbed onto activated carbon caused the displacement of some of the already adsorbed organic matter (volatile acids) from the carbon surface. These desorbed organic nutrients may have escaped to the subsequent columns where their degradation resulted in the formation of methane gas.

Phenol Reduction. The concentration of phenol (measured spectrophotometrically at 286 nm) in the effluents from the series of three anaerobic-activated carbon filters is shown in Figures 61, 62 and 63 for the period extending between days 330 and 540 of continuous operation. During the first 45 days of operation no phenol was detected in the effluent from the first column. After that period the concentration of phenol present in the first column effluent started increasing until day 414 when it reached a peak value of 102 mg/l. After day 414 the concentration of phenol in the effluent from the first column continued to decrease until a steady state value of 23 mg/l was attained.

The concentration of phenol in the effluent from the second column fluctuated between a high of 28 and a low of 3 mg/l. The steady-state con-

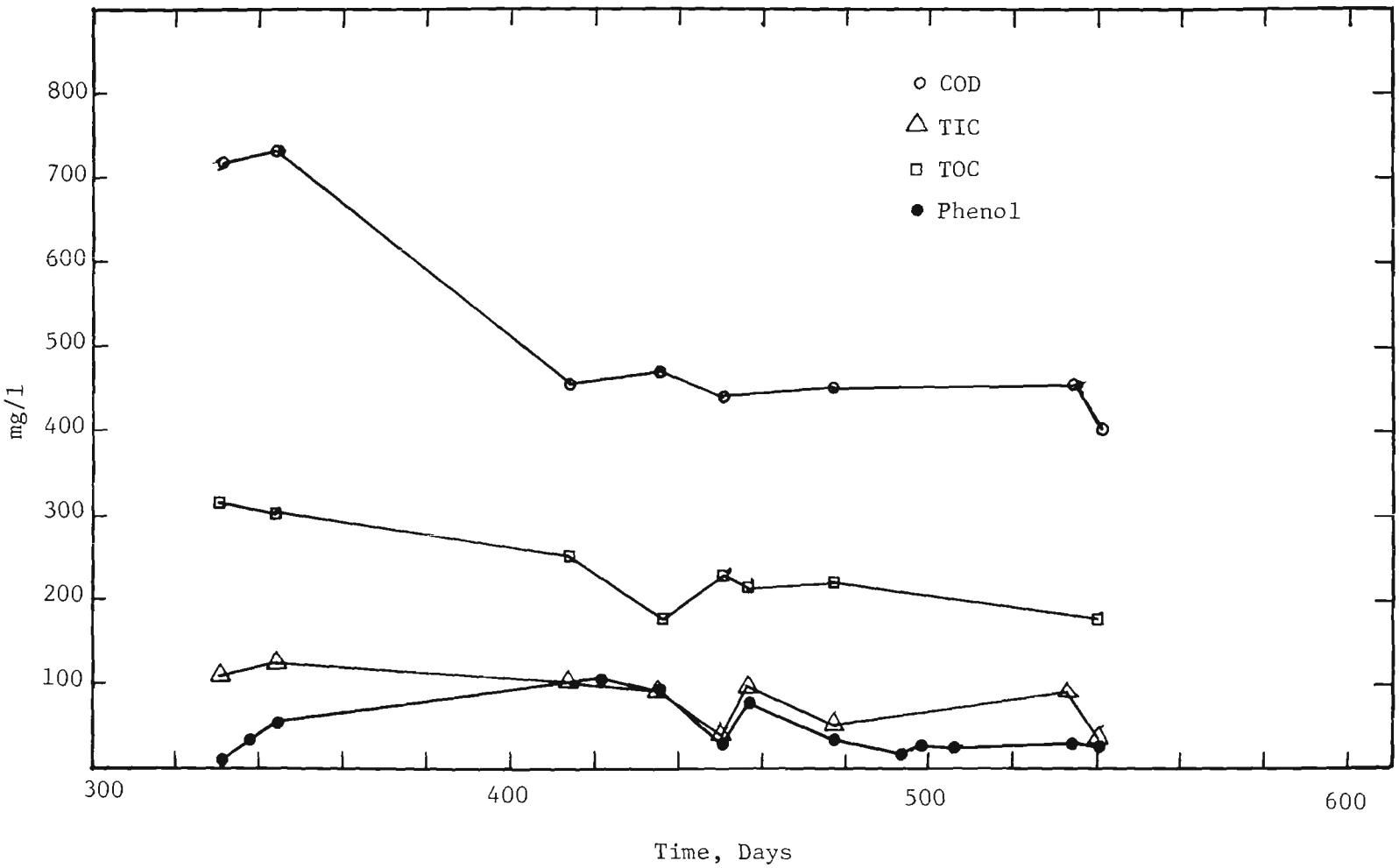


Figure 61. Effluent COD, TOC, TIC from Column One, Glucose + Phenol Fed Reactor

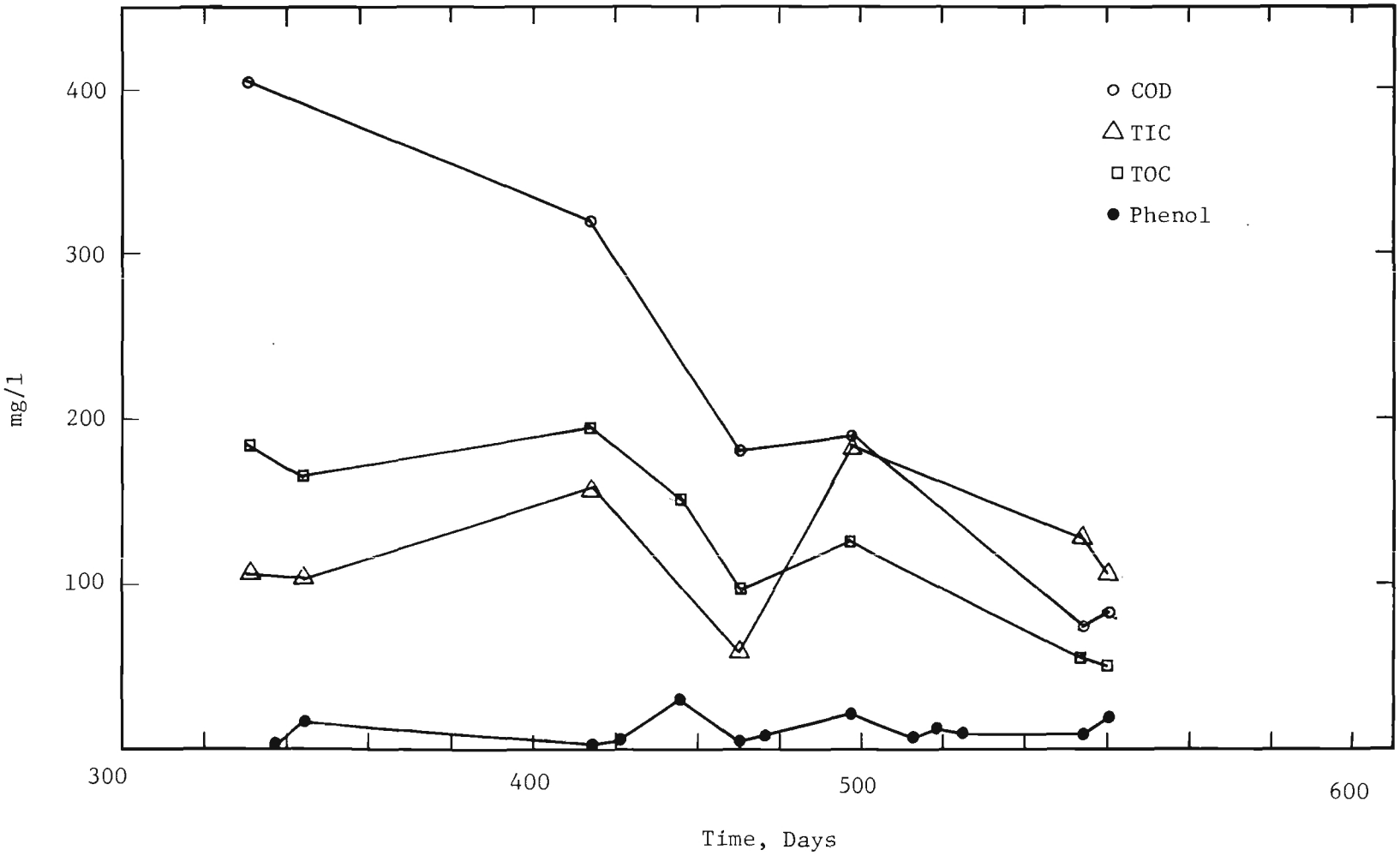


Figure 62. Effluent COD, TOC, TIC from Column Two, Glucose + Phenol Fed Reactor

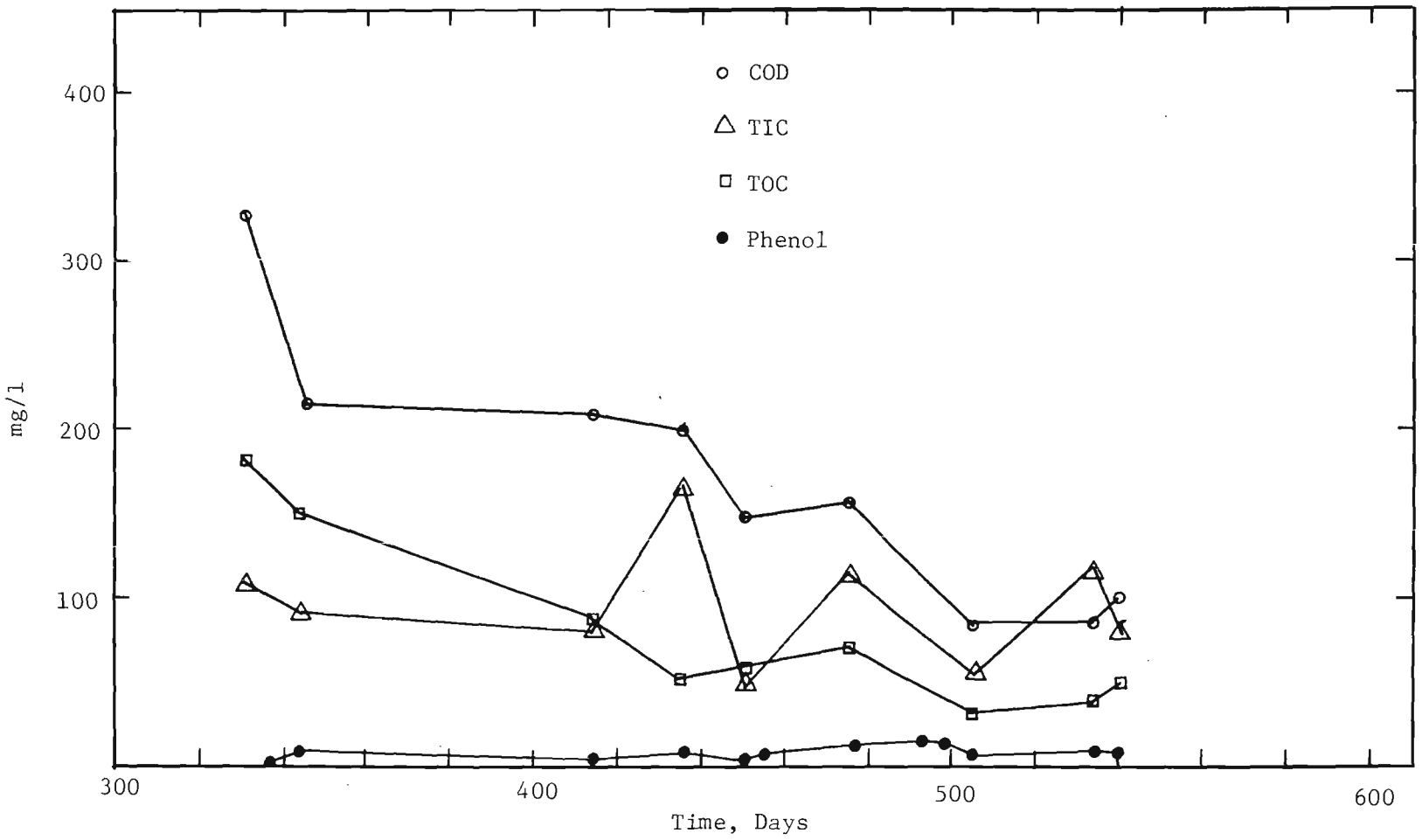


Figure 63. Effluent COD, TOC, TIC From Column Three Glucose + Phenol-Fed Reactor

centration of phenol in the effluent from this column averaged 9.7 mg/l. A similar behavior was observed in the final effluent from the system with the steady-state phenol concentration averaging 7 mg/l.

All the phenol concentration data reported in Figures 61, 62 and 63 were obtained from absorbance readings at 286 nm. These values were all much higher than the actual concentrations of phenol present in the effluents because of the very strong interference of the residual organics produced during the degradation of the co-substrate glucose. A U.V. scan of the filtered effluent from the second column conducted during steady state operating conditions is given in Figure 64.

This scan reveals that the background organics are responsible for almost all the absorbance observed at 286 nm. Using the absorbance reading from the scan at 286 nm and the phenol calibration curve given in Figure 12 would yield a phenol concentration of 13.7 mg/l while the chloroform extraction procedure yielded a phenol concentration in the same sample of only 1.25 mg/l.

Organic and Inorganic Carbon

The organic and inorganic carbon content of the filtered effluents from all three anaerobic columns was presented in Figures 61, 62 and 63 for the continuous operating period extending between day 330 and day 540. The organic carbon content in the feed substrate was presented in Figure 60 for the same period of operation. The TOC in the feed substrate average 1013 mg/l, while the TOC in the effluent from the first column ranged from a high of 315 mg/l on day 330 to a low of 180 mg/l at the termination of the experiment. The average TOC in the effluent from the first column during the period of steady state operation was 183 mg/l resulting in a TOC conversion efficiency in the first column of 86 percent.

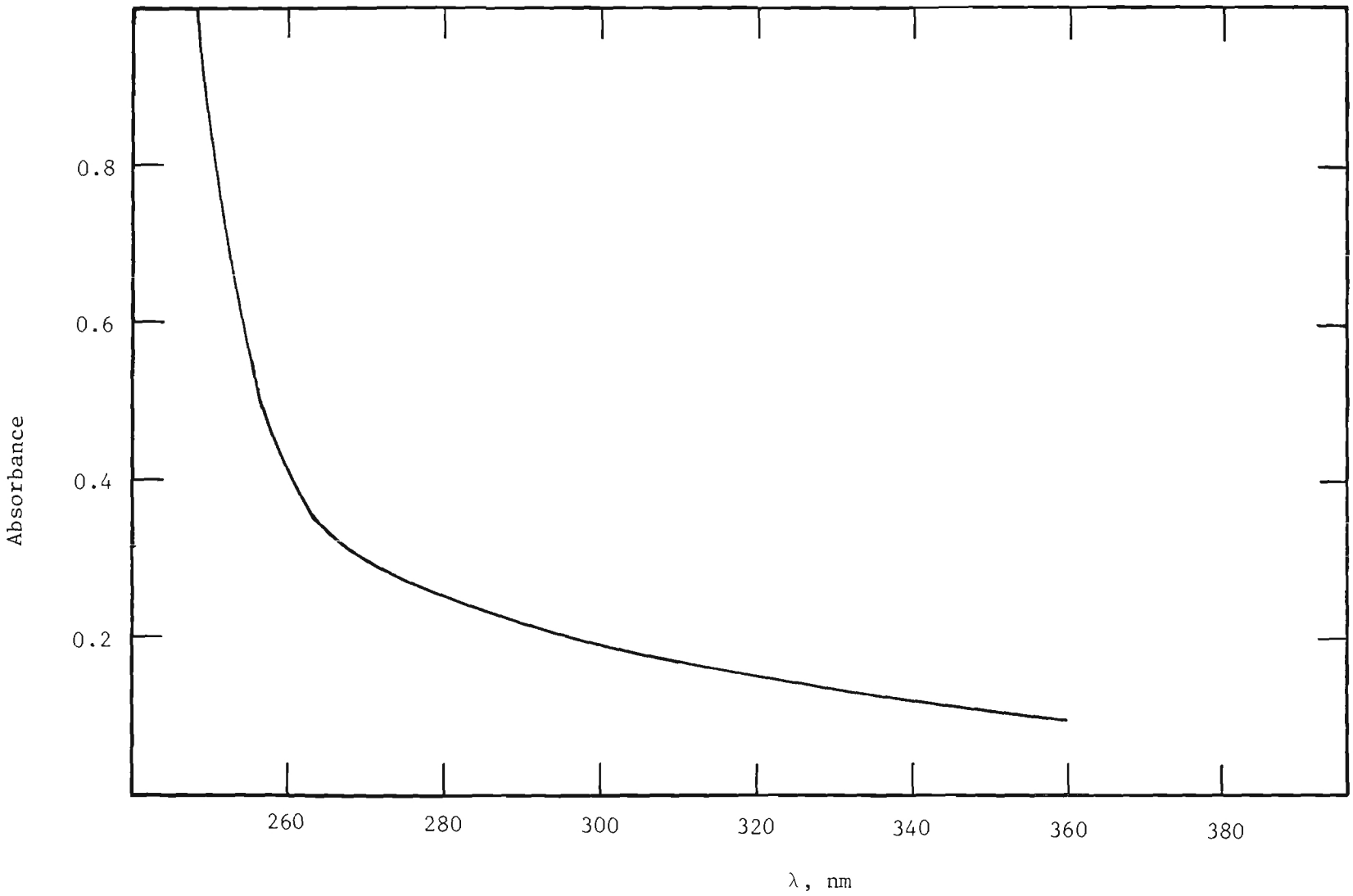


Figure 64. Absorbance Spectrum, Effluent from Glucose + Phenol Fed Reactor, 1 cm cell

The total organic carbon content in the effluent from the second column varied from a high of 195 mg/l on day 414 to a low of 40 mg/l at the termination of the experiment. The average steady-state TOC concentration present in the effluent from the second column was 54 mg/l resulting in a TOC removal efficiency across the first two columns of 94.7 percent. The TOC in the final effluent from the third column steadily declined from a high of 182.5 mg/l on day 330 to an average steady-state effluent concentration of 44 mg/l. This resulted in a total TOC reduction of 95.7 percent across the three columns.

Chemical Oxygen Demand

The performance of the treatment system as far as the reduction of chemical oxygen demand was presented in Figures 61, 62 and 63 for the continuous operating period extending from day 330 to day 540 of continuous operation. The chemical oxygen demand in the effluent from the first column averaged 450 mg/l during the last 130 days of continuous operation. This represented a COD removal efficiency in the first column of 85 percent.

The COD of the effluent from the second column fluctuated between a high of 185 and a low of 57 mg/l while the average steady state concentration averaged 80 mg/l thus resulting in a cumulative reduction effiicency of COD of 97 percent in the first two columns. No additional reduction in COD was observed in the effluent from the third column.

The COD to TOC ratio in the feed substrate was 2.95, while this ratio decreased to 2.46 and 1.48 in the effluents from the first and second columns, respectively.

Gas Production. The anaerobic gas produced from every column reactor was collected separately and monitored for volume and composition. Cumulative dry methane and gaseous carbon dioxide production data that were obtained

from all three column reactors are presented individually in Figures 65, 66 and 67 and collectively in Figure 68.

Gas production from the first column reactor averaged at a daily rate of 2,308 ml over the duration of the experiment, while at steady state operating conditions the rate of gas production was 3000 ml/day of 73 percent methane gas. This methane production rate of 2190 ml/day is equivalent to the combined steady state methane gas production rate from the first column of the 2000 mg/l glucose fed experiment (1897 ml/day) and the first column of the 200 mg/l phenol fed experiment (398 ml/day) which amounts to 2295 ml/day. Consequently, the addition of phenol to the feed substrate of the glucose fed experiment did not result in a retardation of methane production but on the contrary the two substrates were utilized in a manner similar to the utilization of the two substrates when they were fed separately to two reactor systems.

Gas production was observed from the second and third columns of the glucose-phenol fed reactor system. This gas production, however, ceased from the second column after a period of 275 days while gas production from the third and last column ceased after 265 days of continuous glucose and phenol feeding. It was postulated that the rejuvenation of biological activity in the last two columns was due to the competitive adsorption effect of the phenol which because of its strong adsorption energy could readily displace the already adsorbed volatile acids and release them back into solution for their eventual utilization in the last two columns.

Carbon and chemical oxygen demand material balances across the treatment system were constructed for the operating days 331 and 420 and during steady-state operation on day 534. The carbon and COD material balances

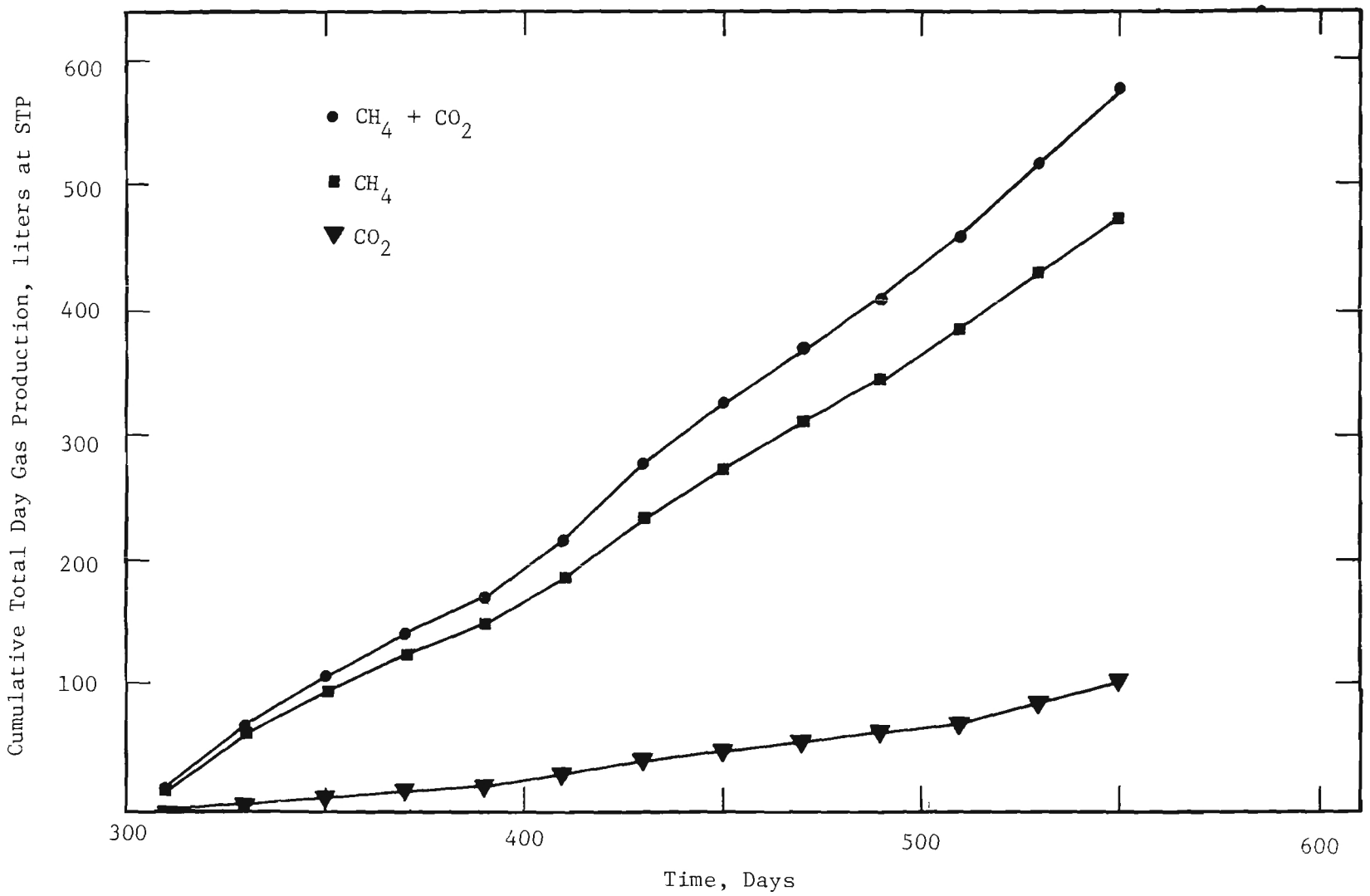


Figure 65. Gas Production from Column One Glucose + Phenol Fed Reactor

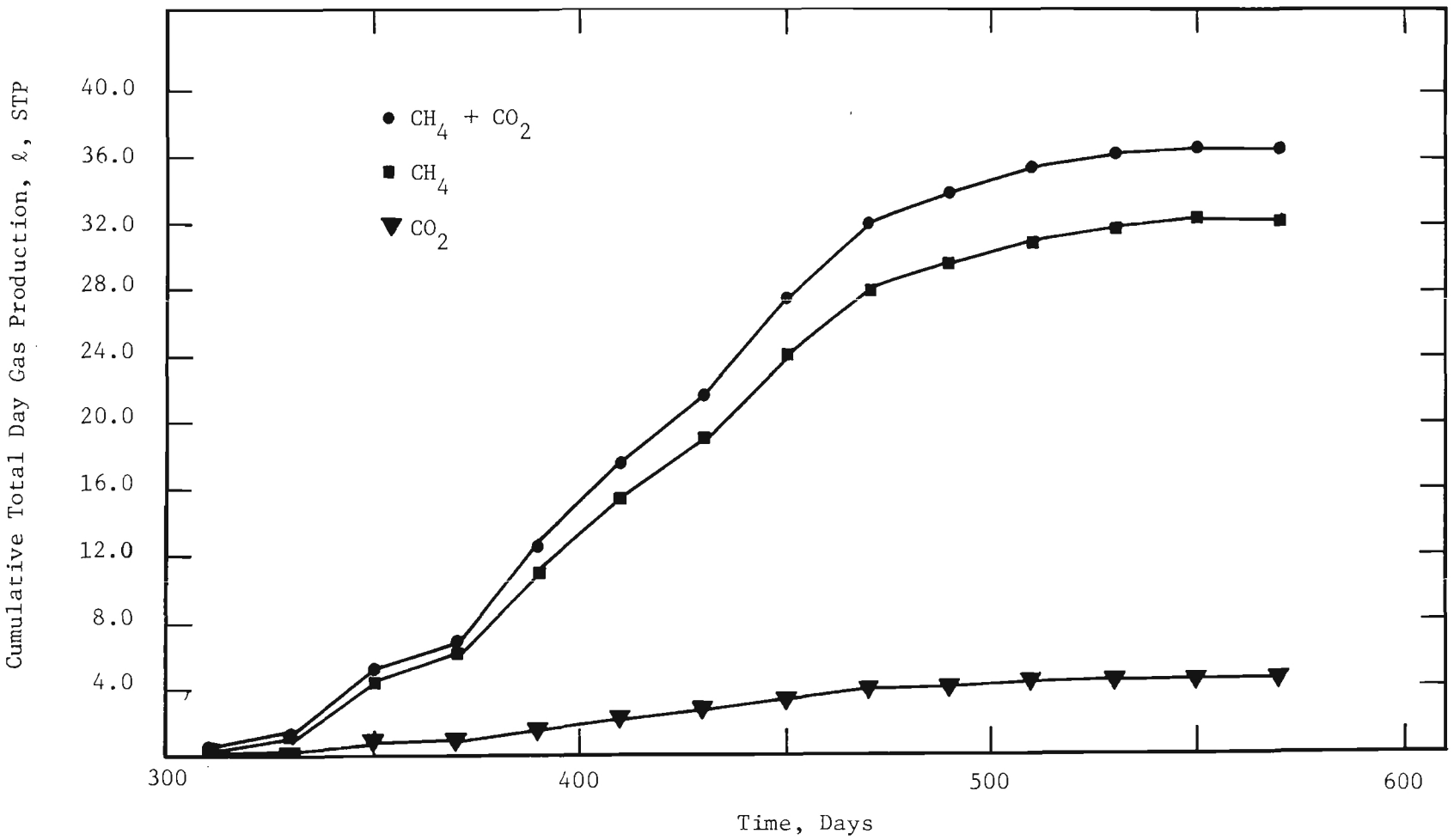


Figure 66. Gas Production from Column Number Two, Glucose + Phenol Fed Reactor

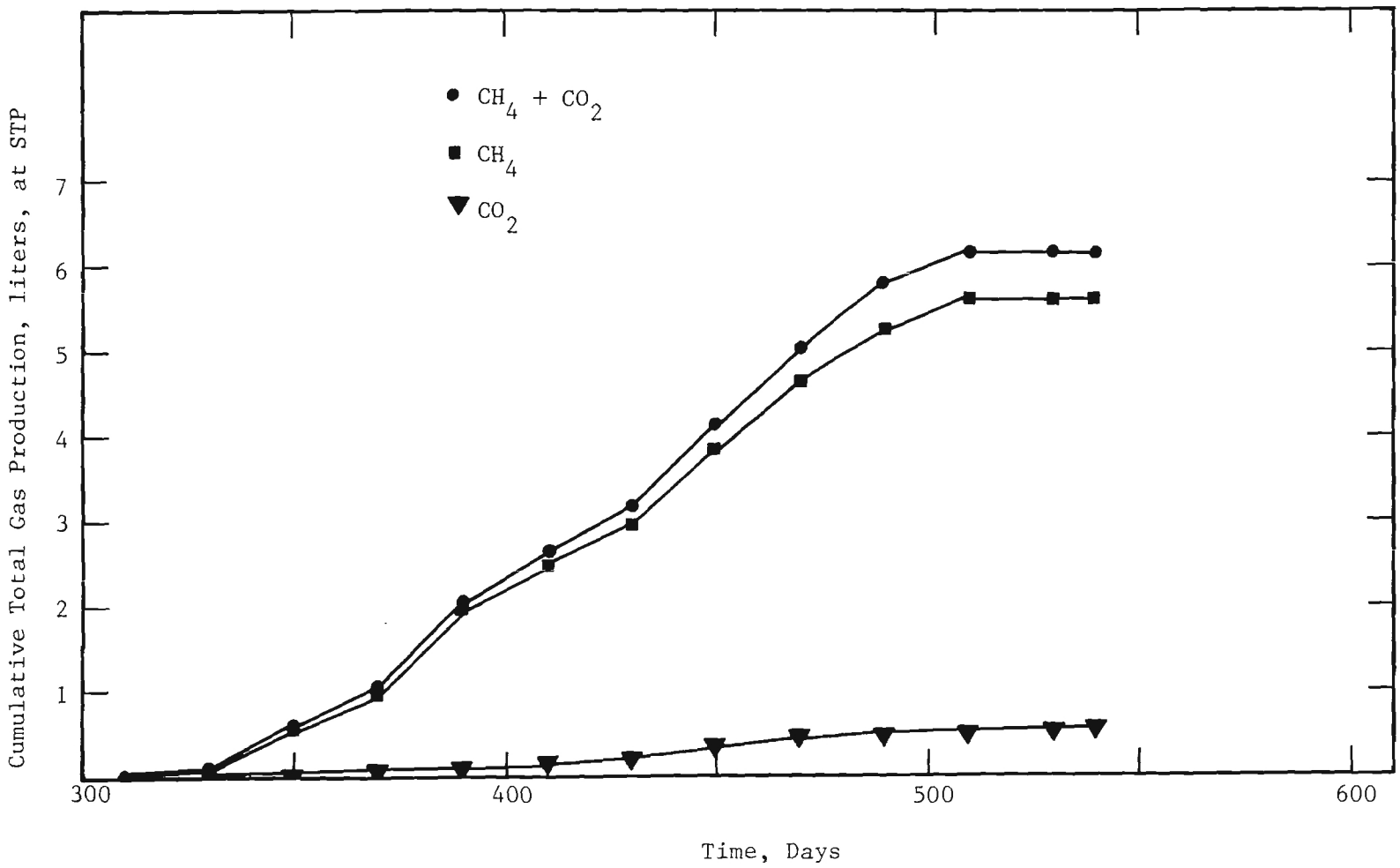


Figure 67. Gas Production from Column Number Three, Glucose + Phenol Fed Reactor

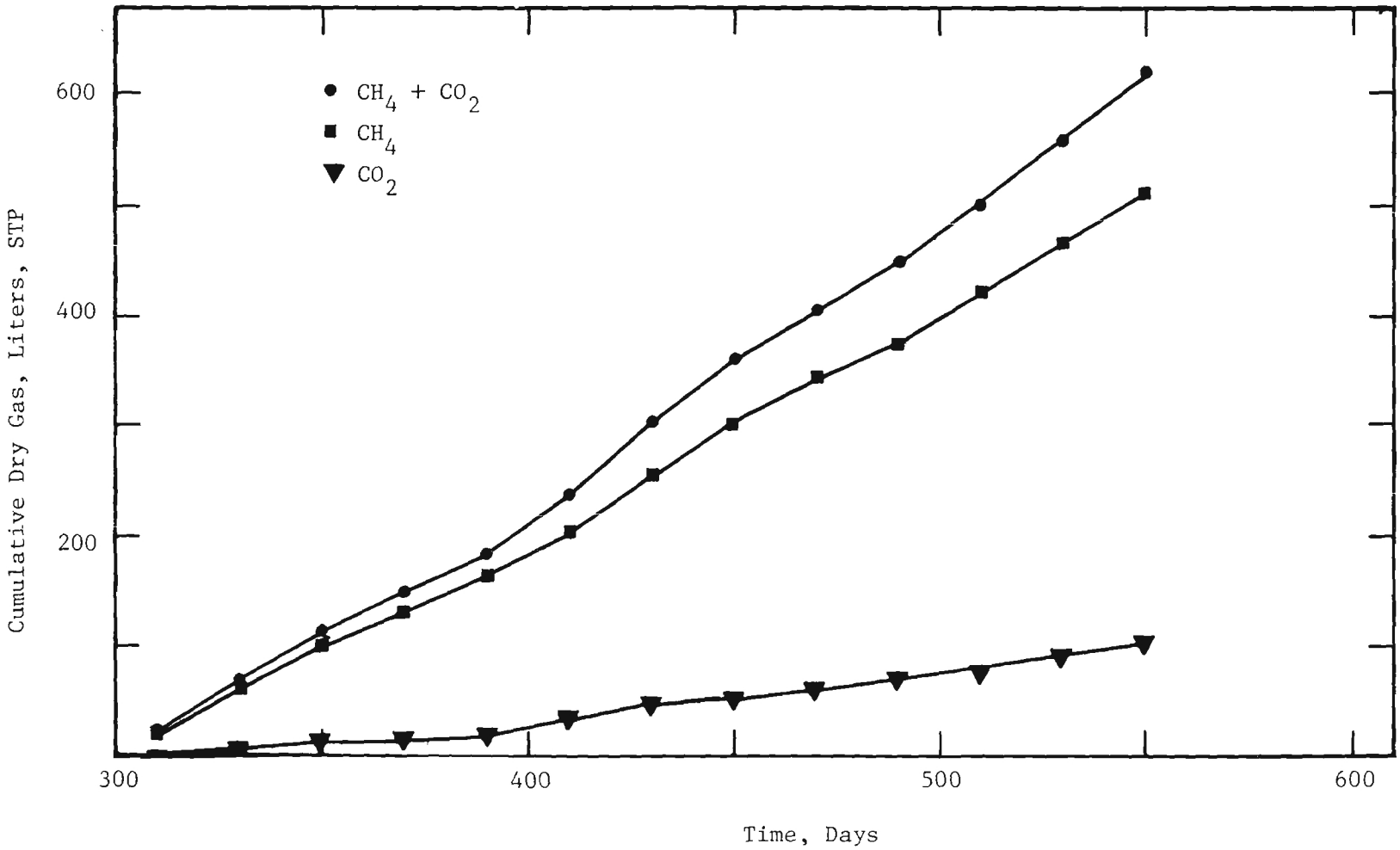


Figure 68. Total Gas Production from the Glucose, 2000 mg/l, and Phenol, 200 mg/l, Fed System

constructed for day 331 (see Figures 69 and 70) reveal that during that period the treatment system was undergoing appreciable adsorption of the phenol resulting in a loss of carbon and COD across the first two reactors. This period was characterized by high values of TOC and COD in the effluent from the first column; a condition which is conducive to adsorption.

The carbon and COD material balances constructed for day 420 (see Figures 71 and 72) represent the period of accelerated gas production which extended between days 400 and 440 reveal that very little carbon and COD were lost across the reactors. This period of operation was characterized by low TOC and COD levels in the effluent from the first column giving credance to the possibility that bioregeneration of the carbon was occurring during this phase of the experiment. The carbon loss across the third column which is indicated in Figure 71 is due to a drop in TOC across that column leading to the possibility of the occurrence of adsorption in that column; however, the COD data in Figure 72 negates that assumption leading to an unresolved conclusion as to the function of the third column during this period.

Steady-state carbon and COD material balances across the treatment system are shown in Figures 73 and 74 for day 534 of continuous operation. The COD material balance reveals that 7.5 percent of the converted COD and 21 percent of the converted TOC were not accounted for in the effluent from the first column. However, as was discussed previously, the integrity of the carbon balance is in question because of the apparent loss of TIC upon filtration prior to analysis. Based on this discussion, it may be surmised that a COD biomass yield ratio of 7.5 percent was observed for the combined treatment of glucose and phenol in the first column reactor.

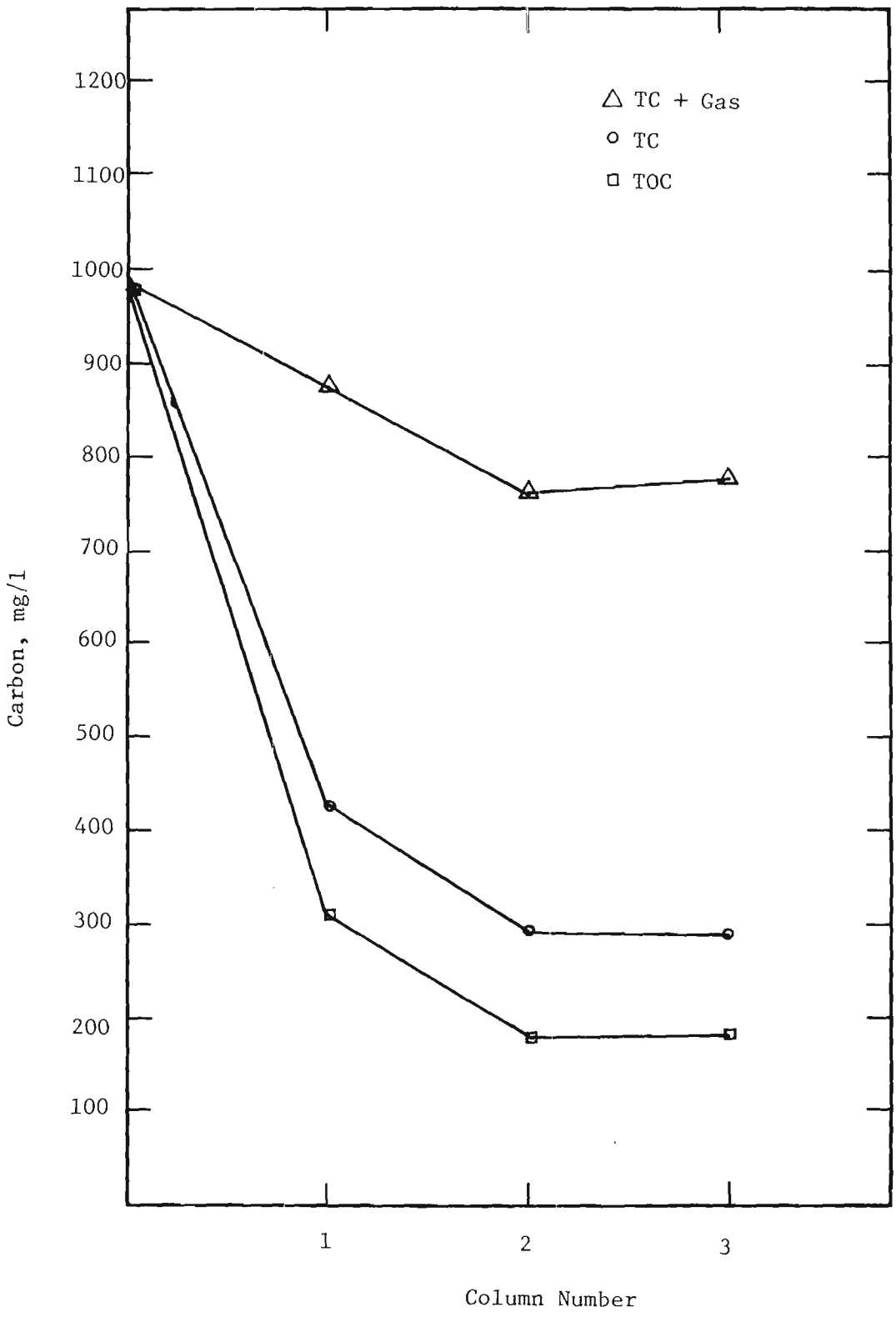


Figure 69. Carbon Profile, Day 331, Glucose + Phenol Fed Reactor

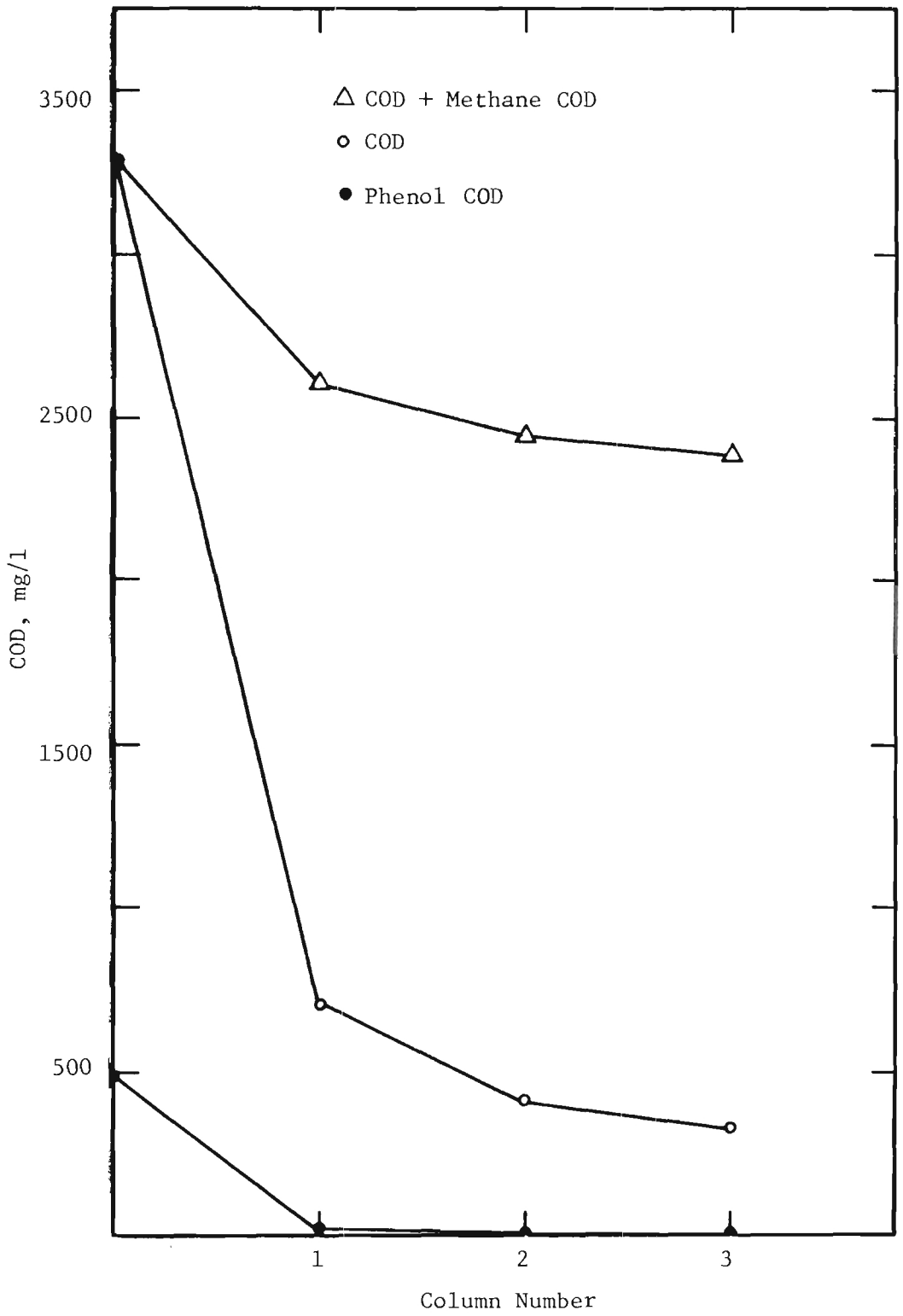


Figure 70. COD Profile, Day 331, Glucose, 2000 mg/1, and Phenol, 200 mg/1, Fed Reactor

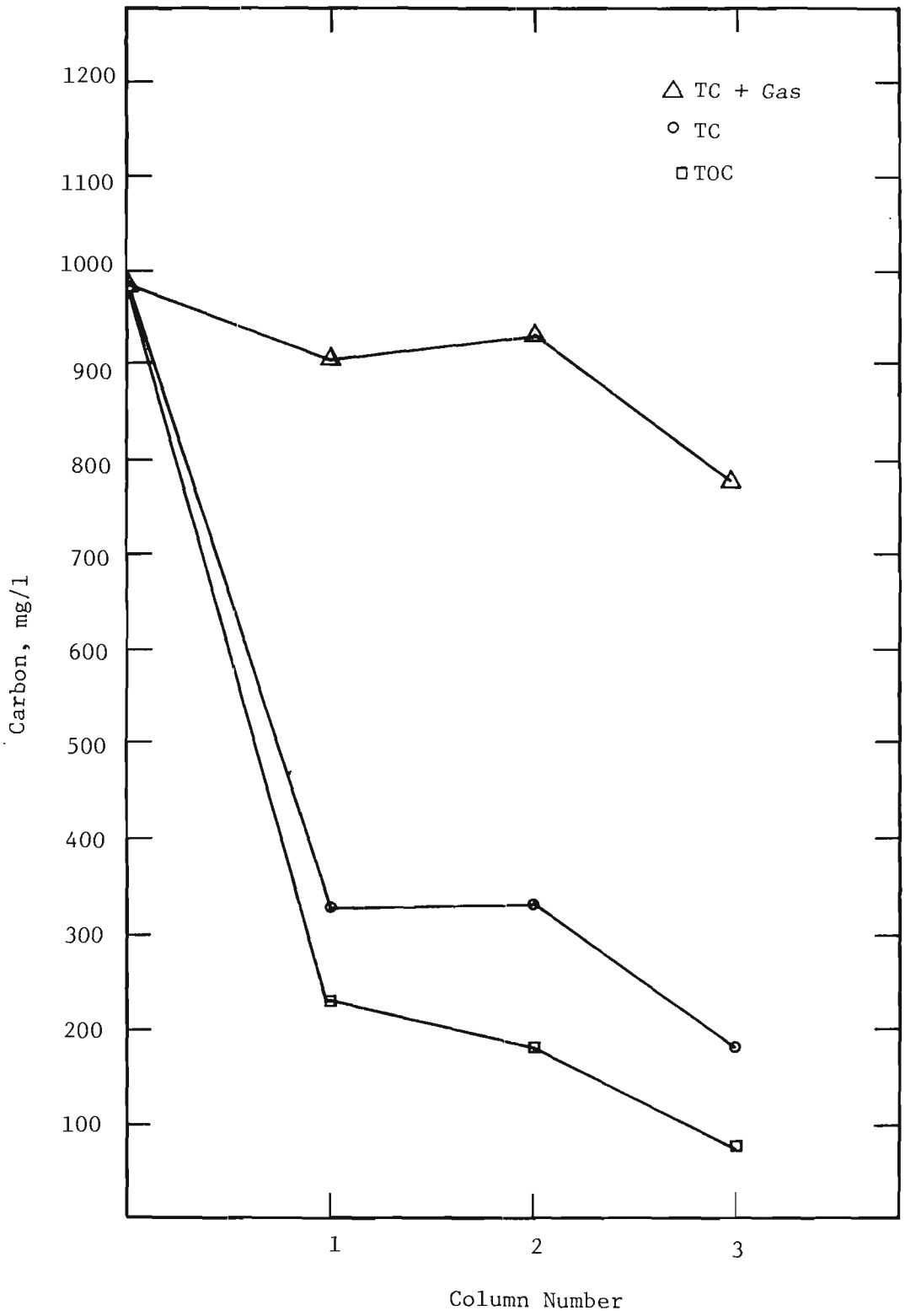


Figure 71. Carbon Profile, Day 420, Glucose + Phenol Fed Reactor

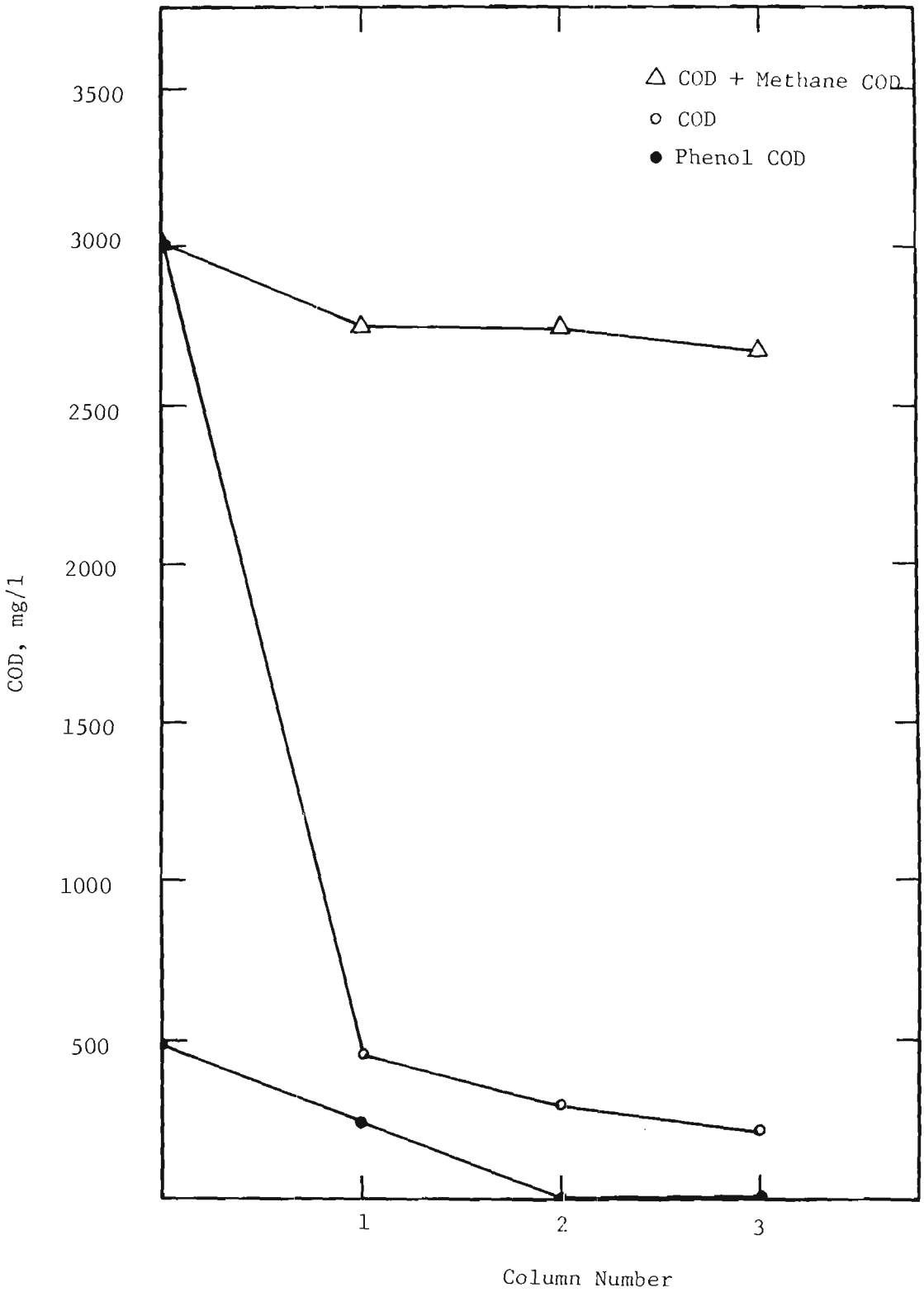


Figure 72. COD Profile, Day 420, Glucose + Phenol Fed Reactor

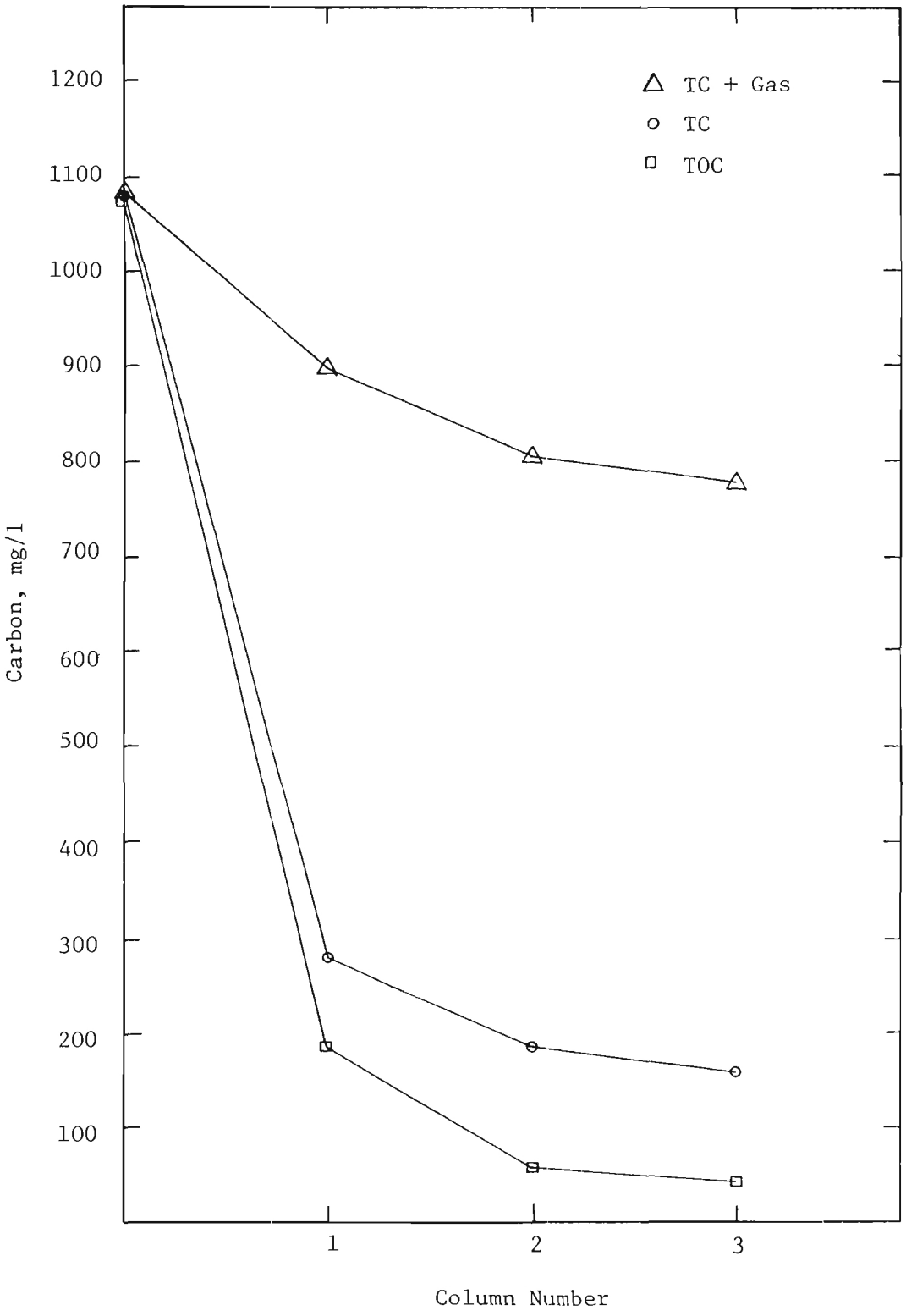


Figure 73. Carbon Profile, Day 534
Glucose + Phenol Fed Reactor

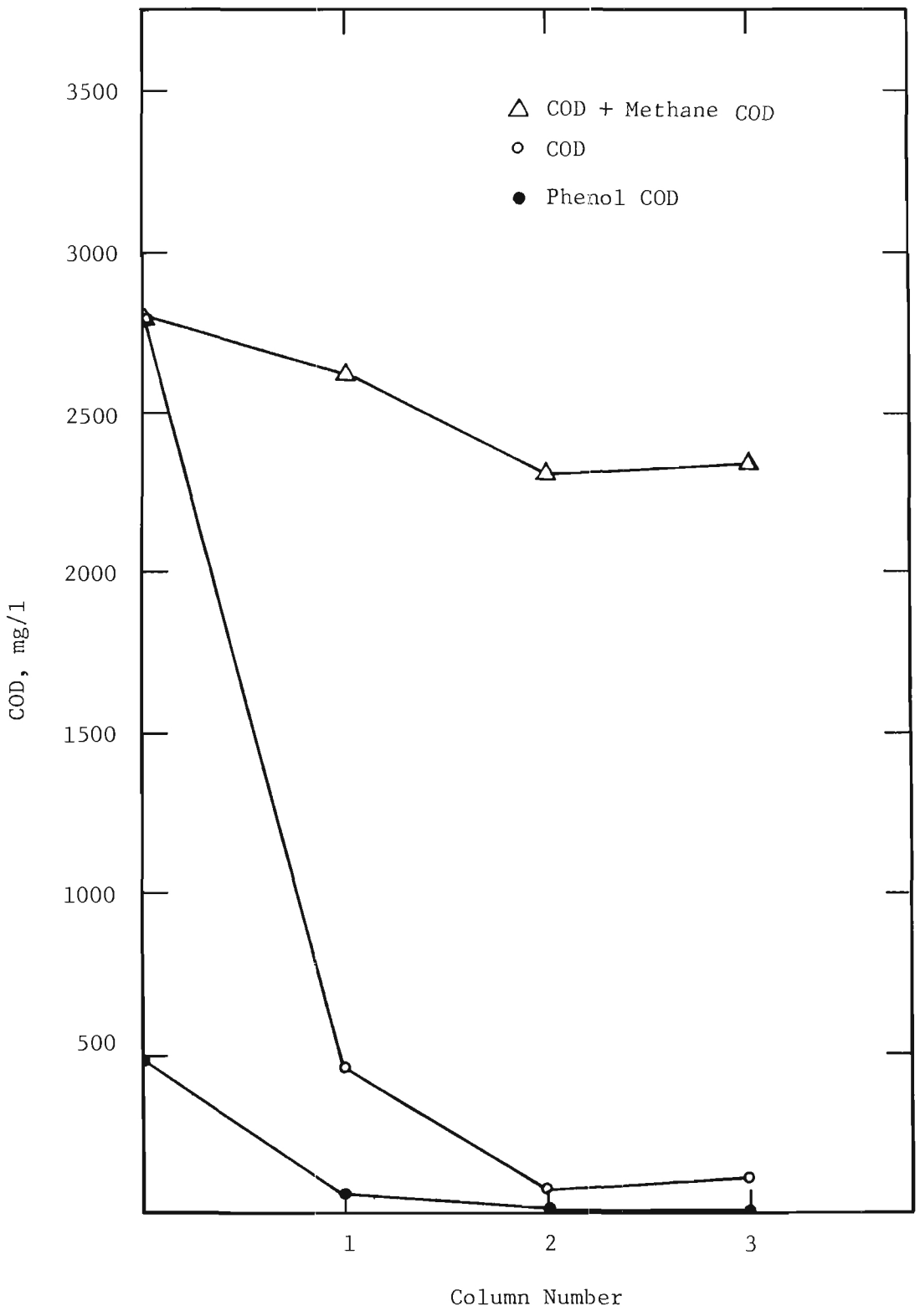


Figure 74. COD Profile, Day 534, Glucose + Phenol Fed Reactor

The data in Figure 75 represent a plot of the cumulative carbon mass input into the system along with curves representing the carbon mass output in the aqueous phase and the total output in the aqueous and gaseous phases. The cumulative carbon output curve indicates that very little carbon was lost thoughout the period of the experiment.

Steady-State Performance

Steady-state analysis was conducted on the feed substrate and all column effluents for the period of operation extending from day 510 to day 550. A summary of the steady-state data for this experiment is presented in Table 31. These data indicate that reductions in TOC and COD corresponding to 82.7 and 84.4 percent, respectively and a reduction in phenol exceeding 95 percent were realized from the first column of the treatment system using an empty bed contact time of 11.62 hours. Overall, the treatment system resulted in reductions in phenol, TOC and COD of 100, 95.5 and 97.6 percent, respectively.

Comparative Study of Activated Carbon and Anthracite Coal as Filter Media

Granular activated carbon was used as a packing medium within the anaerobic filter columns for all the experimental phases that have been discussed thus far in the report. Activated carbon constitutes an expensive capital application with the present price of the Filtrasorb 400 granular activated carbon employed in the experiments averaging 80 cents per pound. Since steady-state operating conditions were achieved in all the experimental phases of this study, it was deemed necessary to determine whether activated carbon was indeed superior to other nonactivated granules in serving as a medium for this process.

In order to answer this very important question, two identical reactor systems, each consisting of one jacketed column (identical to the

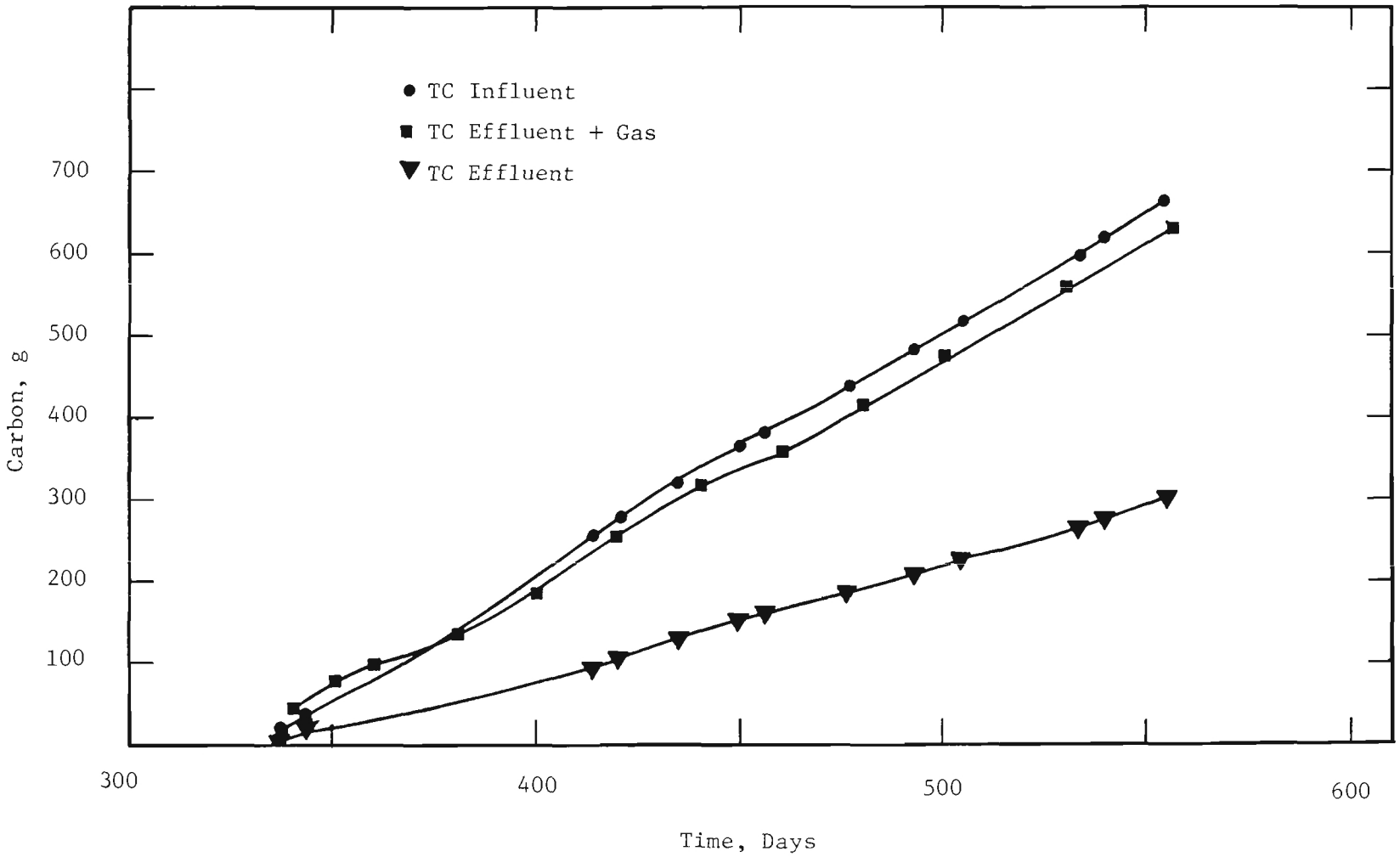


Figure 75. Cumulative Carbon Balance, Glucose + Phenol Fed Reactor

Table 31. Average Steady-State Performance Data for 2000 mg/l Glucose and 200 mg/l Phenol Fed Reactor

Parameter	Influent Value	Parameter Volume in Column Effluent 1	2	3
pH	7.5	6.88	6.99	7.01
TOC, mg/l	1013	183	54	44
TIC, mg/l	12.1	64.8	110.9	110.5
COD, mg/l	2927.4	455.4	74.1	70.0
Phenol, mg/l				
U.V.-286 nm	200.0	57.7	10.6	5.25
Chloroform Extraction	200.0	8.6	1.25	0.0
Gas Production, ml/day	-	3000	0	0
Methane	-	1858	0	0
Carbon Dioxide	-	1142	0	0
Alkalinity, mg/l as $CaCO_3$	-	2284	2518	2644
Total Suspended Solids, mg/l	-	2041.0	158.7	72.0
Volatile Suspended Solids, mg/l	-	972.7	98.0	34.0
ORP	-	-313	-304.7	-289.0

columns utilized in other experiments) and equipped with feed and recirculation pumps were constructed. A glucose bearing substrate was chosen for this test in order to select the conditions that were least favorable to the use of activated carbon (glucose being very poorly adsorbed on carbon).

One reactor column was packed with 200 g of 10 x 16 Filtrasorb 400 activated carbon while the other column was packed with 231g of 10 x 16 anthracite coal (provided by the Taulman Company, Atlanta, GA). Each column was packed to a depth of 24 cm (9.45 inch) with the different media.

One 8 ℓ substrate reservoir was used to simultaneously feed both reactor systems. This was done in order to minimize any variations in the operating parameters that the two columns were exposed to. The feed/substrate was prepared daily in 8 ℓ batches using 160 ml of the salt solution, 200 ml of the phosphate buffer solution, 16 g of glucose and distilled water. The feed substrate was introduced into each column reactor at a flow rate of 2 ml/min while the recirculation flow was maintained at 50 ml/min. The theoretical values of the feed COD and TOC were identical to those used in the 2000 mg/l glucose fed experiment, namely 2647 and 933 mg/l, respectively. The measured and theoretical values of the COD and TOC in the feed substrate are presented in Figure 76. The chemical oxygen demand of the feed substrate averaged 2500 mg/l while the average TOC content of the feed was 852 mg/l. The feed substrate had a computed COD to TOC ratio of 2.84 while the measured ratio was 2.93.

The pH of the feed substrate was maintained at 8. At the stated pH, the feed substrate had an alkalinity of 2050 mg/l as $CaCO_3$. This alkalinity in the feed along with the added bicarbonate alkalinity due to the recycled flow were sufficient to maintain the pH within both reactors between 6.8 and 6.9.

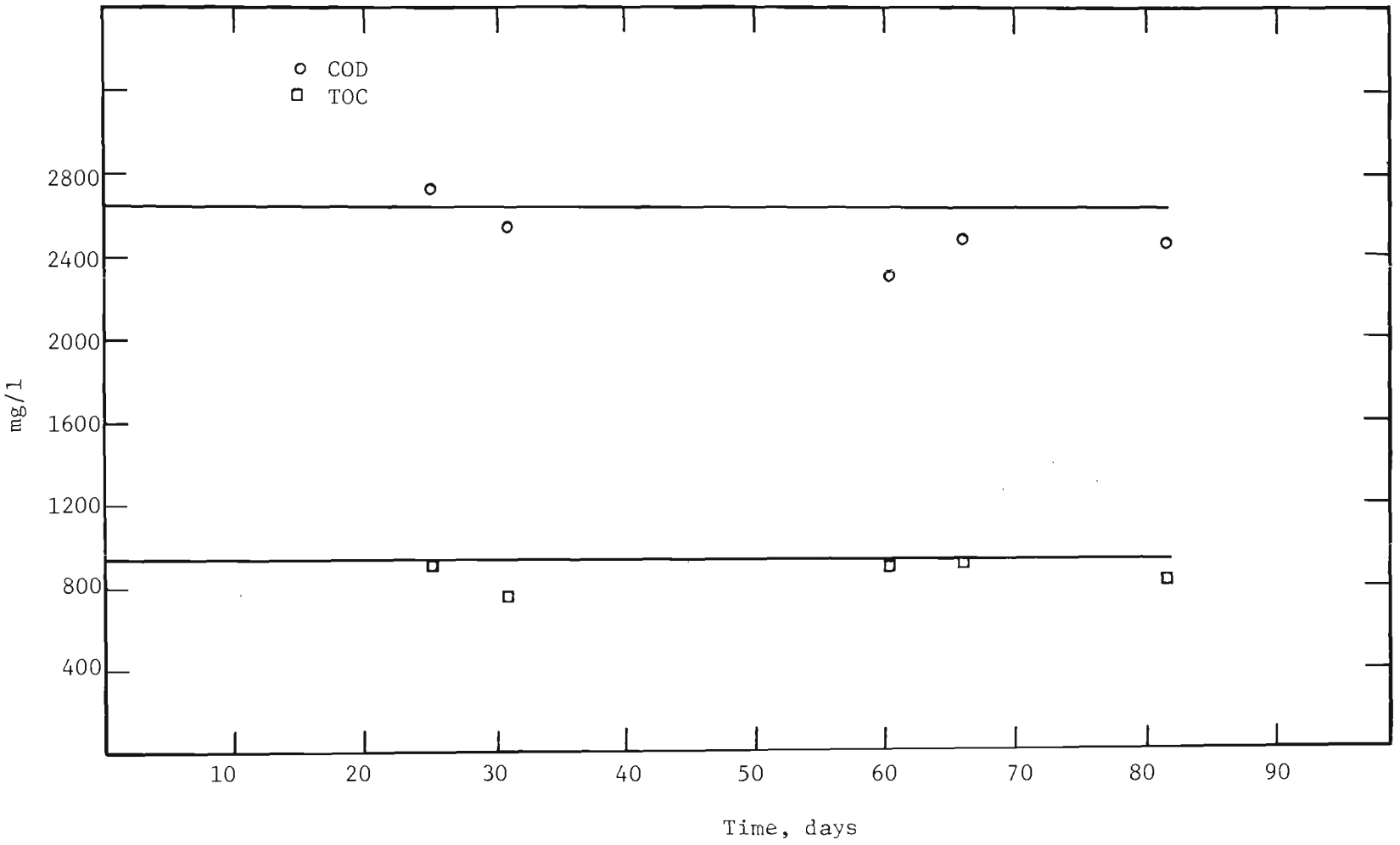


Figure 76. Influent COD and TOC for Anthracite versus Activated Carbon Study

The two column reactors were seeded with equal volumes of sludge obtained from a glucose fed laboratory batch fermenter. After seeding the two columns were operated in parallel for a period of 82 days.

TOC and COD Reduction. The effluents from the two reactor columns were monitored for TOC, COD and TIC and the measured values of these parameters are presented in Figure 77 for the activated carbon packed column and in Figure 78 for the anthracite coal packed column. Examination of the experimental data reveals that the activated carbon packed column outperformed the anthracite packed column in both COD and TOC removal. During the latter 20 days of operation the activated carbon packed column was responsible for average COD and TOC reductions of 73 percent and 71 percent, respectively, while the COD and TOC removal efficiencies in the effluent from the anthracite packed column were only 69.7 and 61 percent, respectively.

Gas Production. Cumulative gas production data (methane and gaseous carbon dioxide) from the two systems are shown in Figure 79. These data indicated that the activated carbon packed column was superior in gas production to the anthracite packed column. Steady state gas production rate indicate that the former column was producing 1442 ml of methane and carbon dioxide per day while the anthracite packed column was responsible for a production rate of 741 ml/day which amounts to only 51.4 percent of the gas production from the carbon packed column. This definite superiority of activated carbon packed column in gas production indicates clearly that aiding in degradation rather than adsorption is the predominant service function of the carbon when treating poorly adsorbable organic waste.

The composition of the cumulative gas produced from each reactor system is given in Figures 80 and 81. Methane constituted 84.6 percent of the gas produced from the activated carbon packed reactor and 84.0 percent of the gas production from the anthracite column.

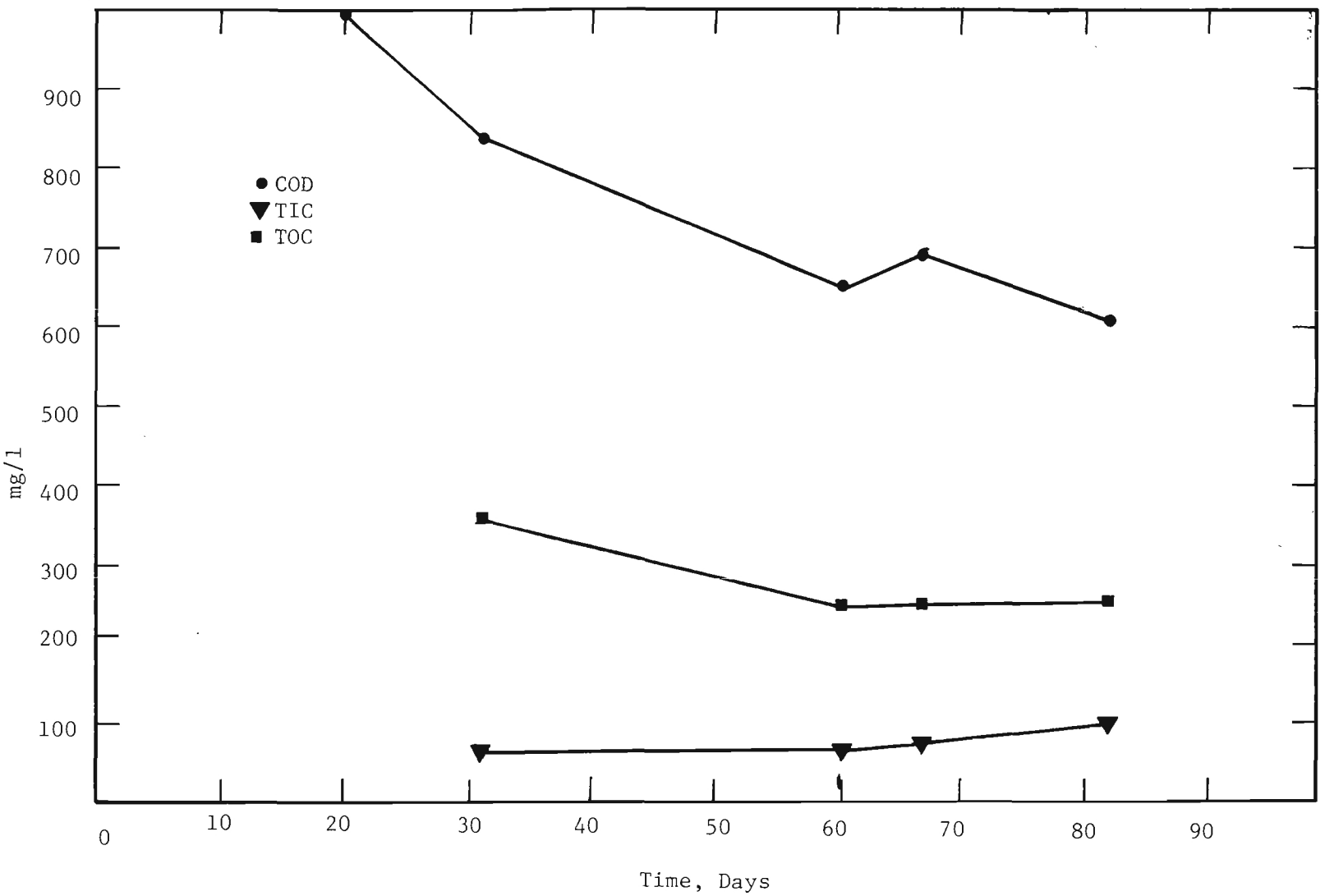


Figure 77. Effluent COD, TOC and TIC from the Activated Carbon Column

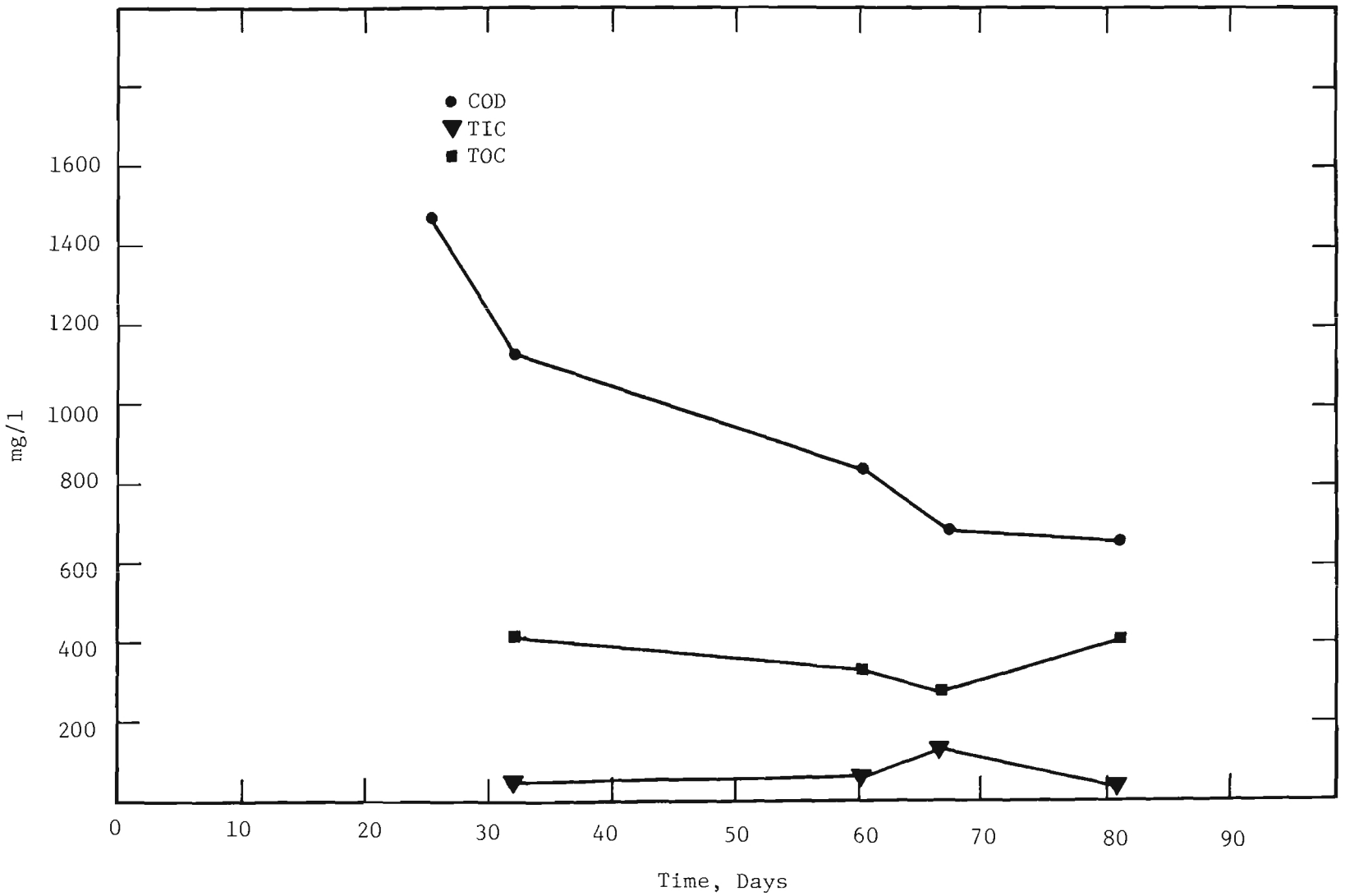


Figure 78. Effluent COD, TOC and TIC from the Anthracite Column

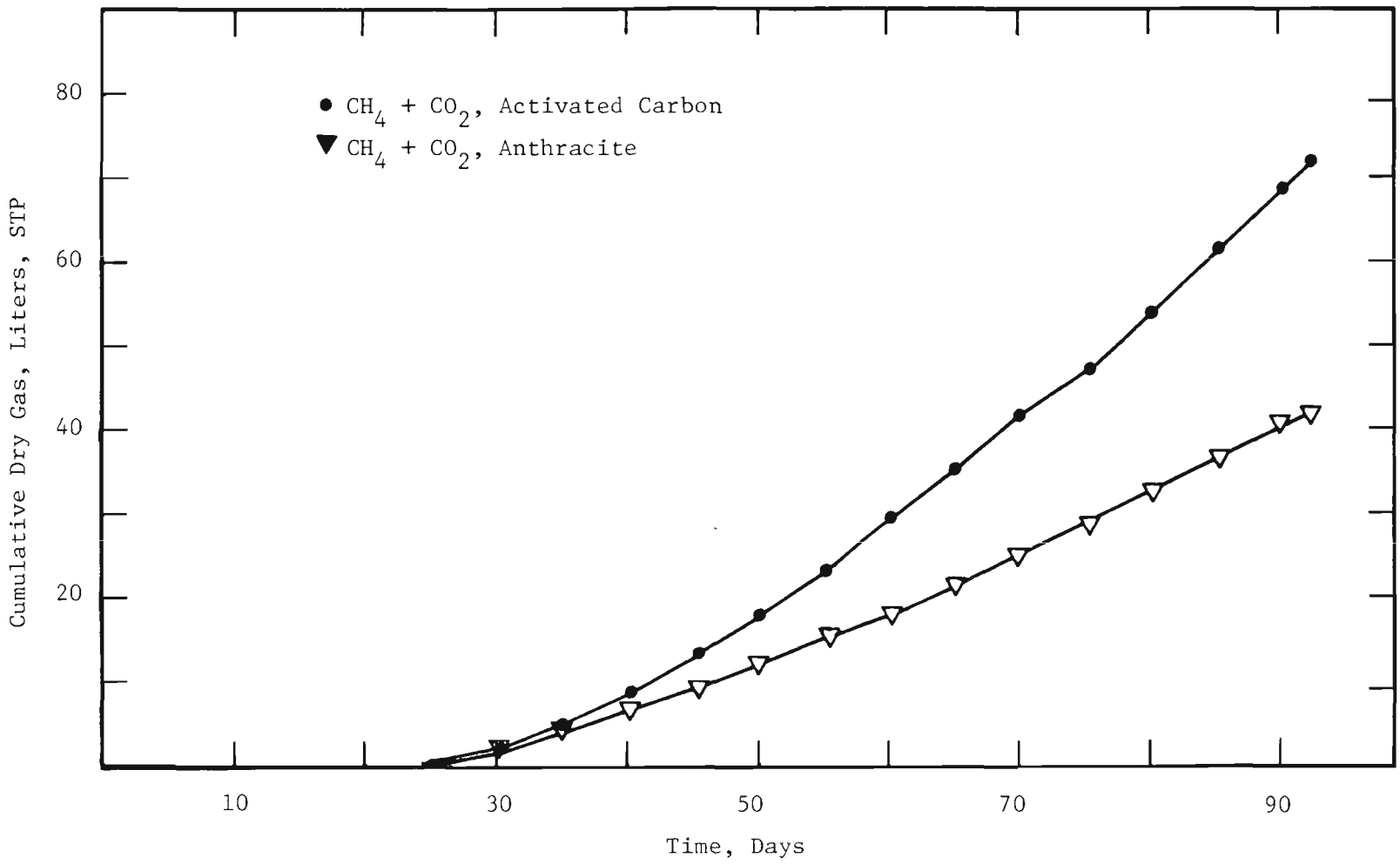


Figure 79. Total Gas Production in Activated Carbon and Anthracite Packed Columns

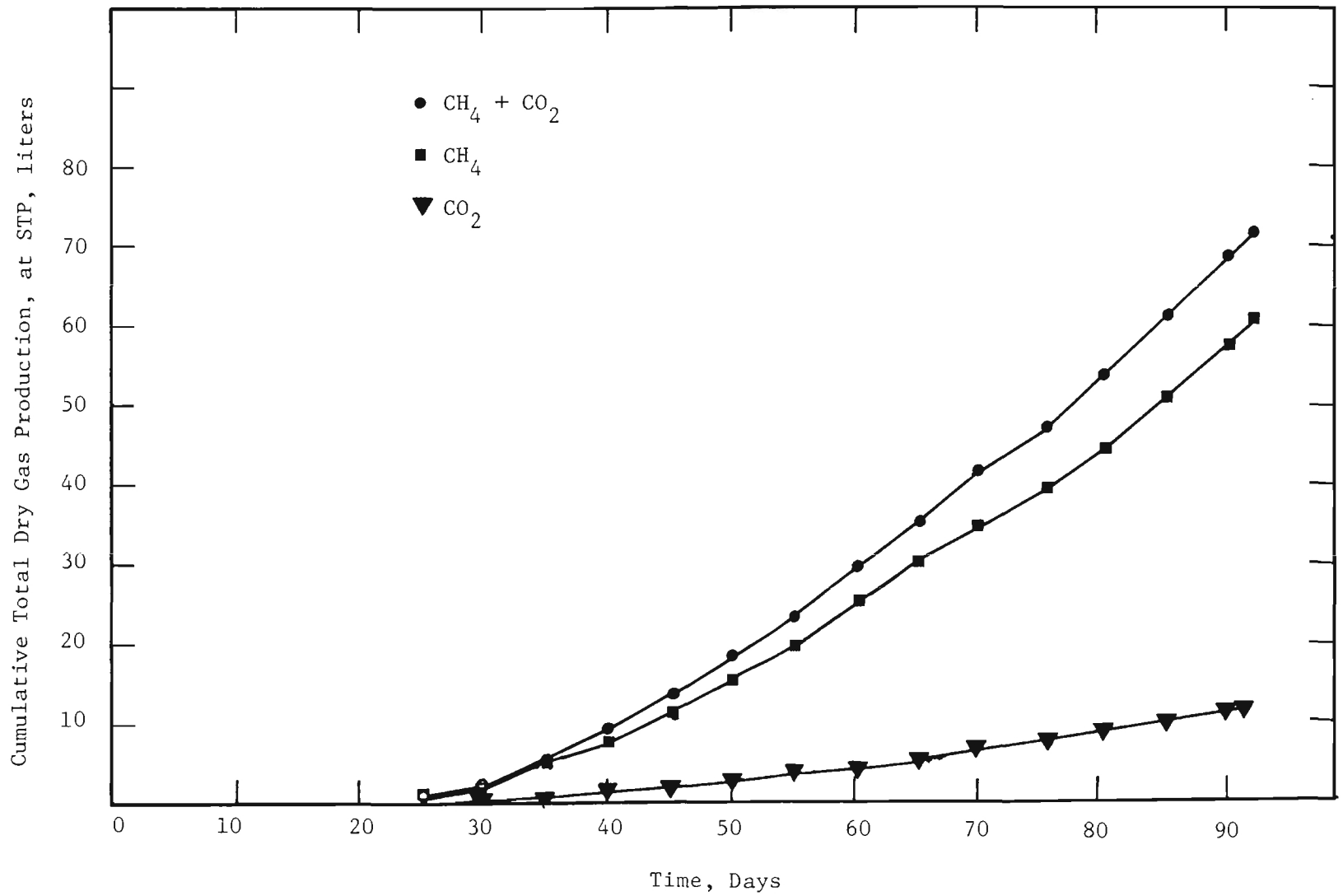


Figure 80. Gas Production from Activated Carbon Column

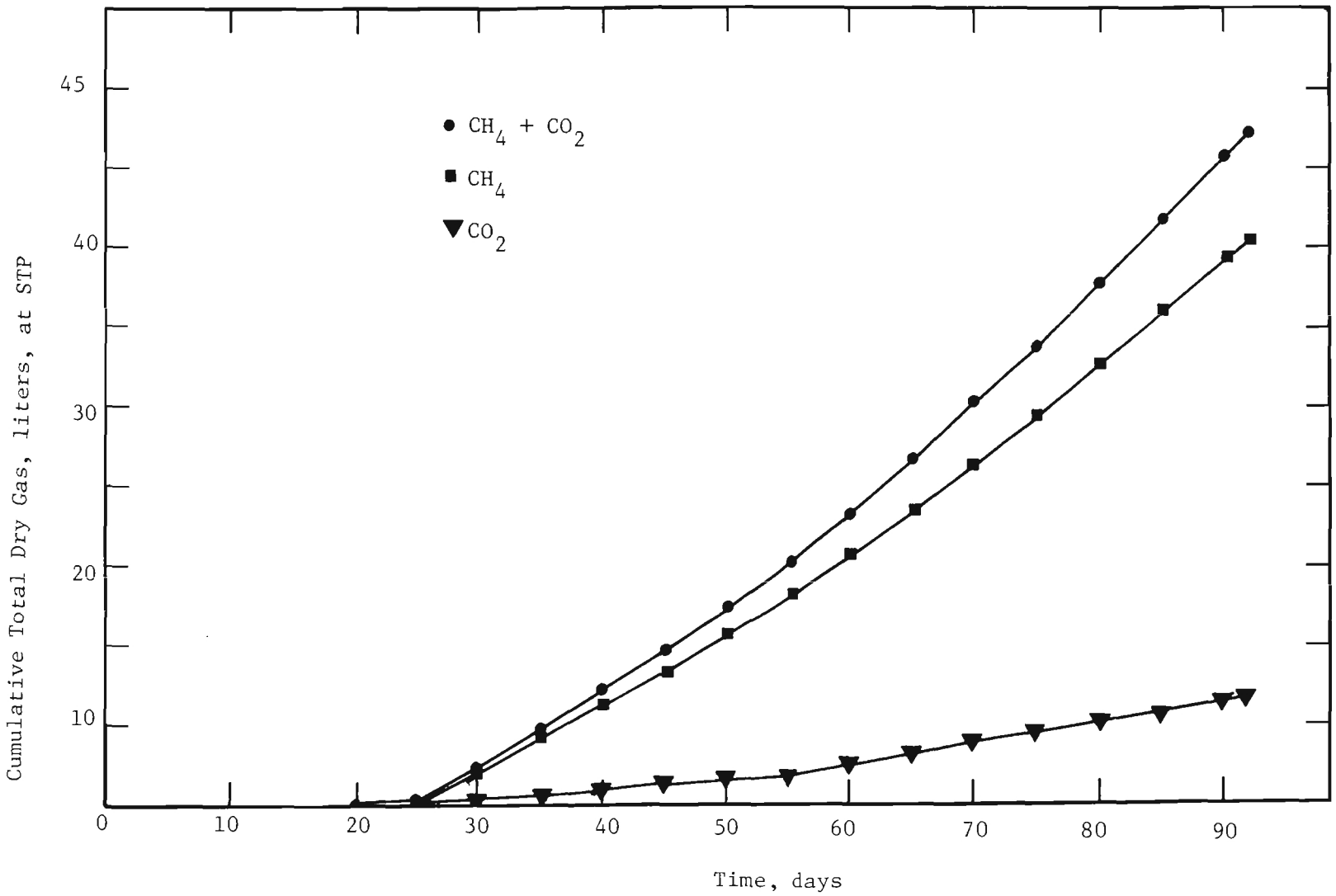


Figure 81. Gas Production from Anthracite Column

Electron Micrographic Scans of Granular Activated Carbon

Electron micrographic scans were conducted on the virgin granular activated carbon used in this study (Filtrasorb 400) (see Figure 82) as well as on activated carbon granules that were withdrawn from the first column of the 2000 mg/l glucose fed reactor (see Figure 83) and the 200 mg/l of the phenol fed reactor (see Figures 84 and 85).

Figure 82 represents a 10K enlargement of the activated carbon surface. Examination of that scan reveals the aggregated structure of that carbon as well as some of the macropores within the carbon.

Figure 83 illustrates the surface structure of the carbon (magnified by 22K) that was withdrawn from the glucose fed reactor. Spherical type organisms were apparent on that surface (appear as doughnuts because of the preparation procedure) in the lower right corner of the photo. In addition, the mouth of one macropore is apparent in the middle of the scan.

Figures 84 and 85 illustrate the type of organisms observed on the carbon granules that were withdrawn from the phenol fed reactor. The organisms in Figure 84 (magnified by 21K) appear to be spherical in shape and clustered while the organisms in Figure 85 (magnified by 11K) were a mixture of spherical and rod shaped organisms. Close examination of Figure 85 reveals, once more, the availability and accessibility of the macropore structure of the carbon.

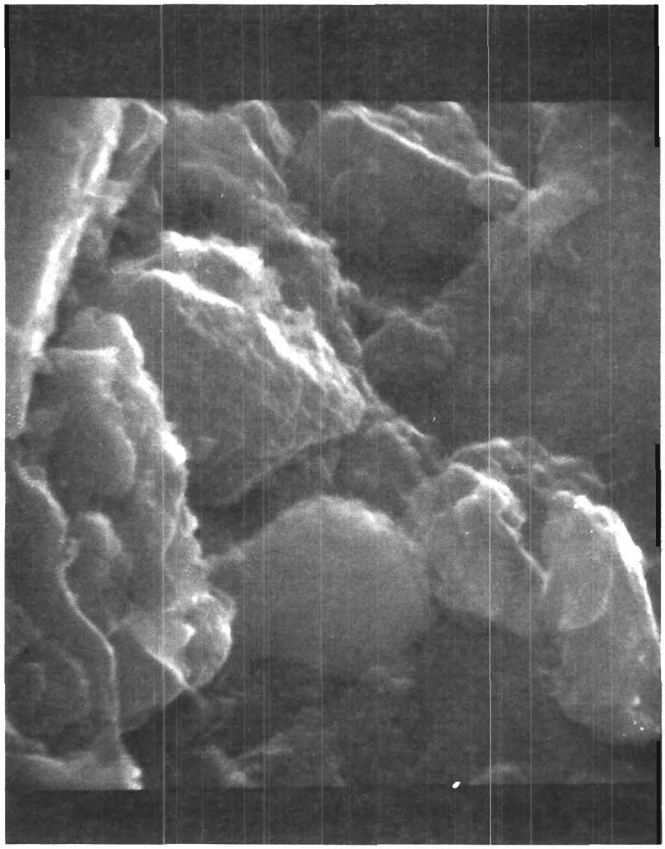


Figure 82
Electron Micrograph, Granulat Activated Carbon, Virgin

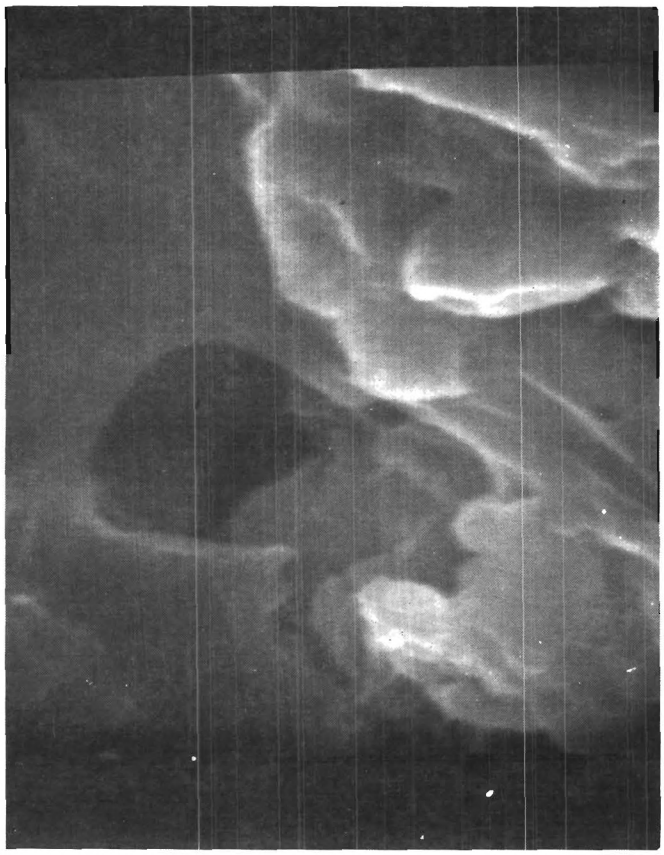


Figure 83
Electron Micrograph, Granular Activated Carbon,
from Glucose Fed Reactor

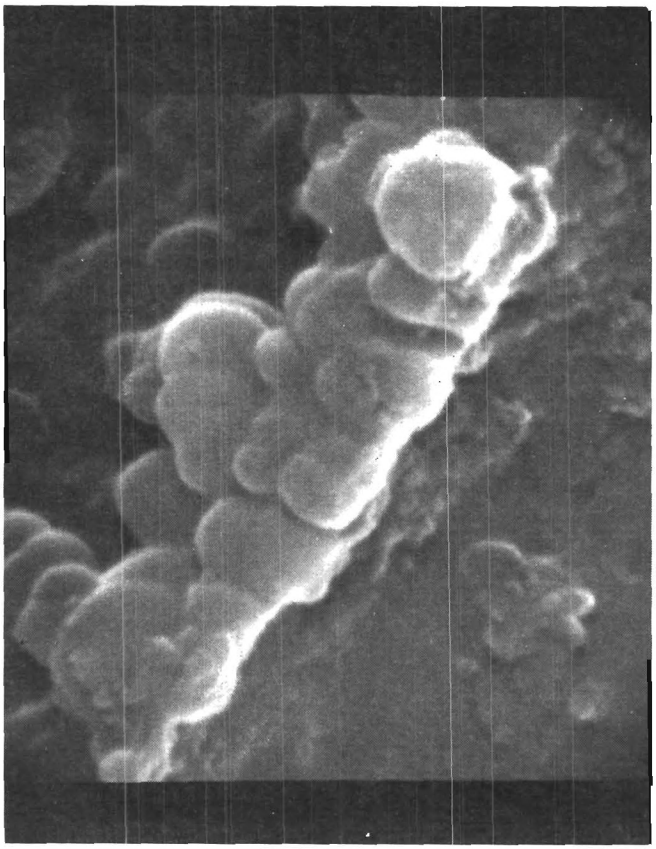


Figure 84
Electron Micrograph, Granular Activated Carbon,
from Phenol Fed Reactor

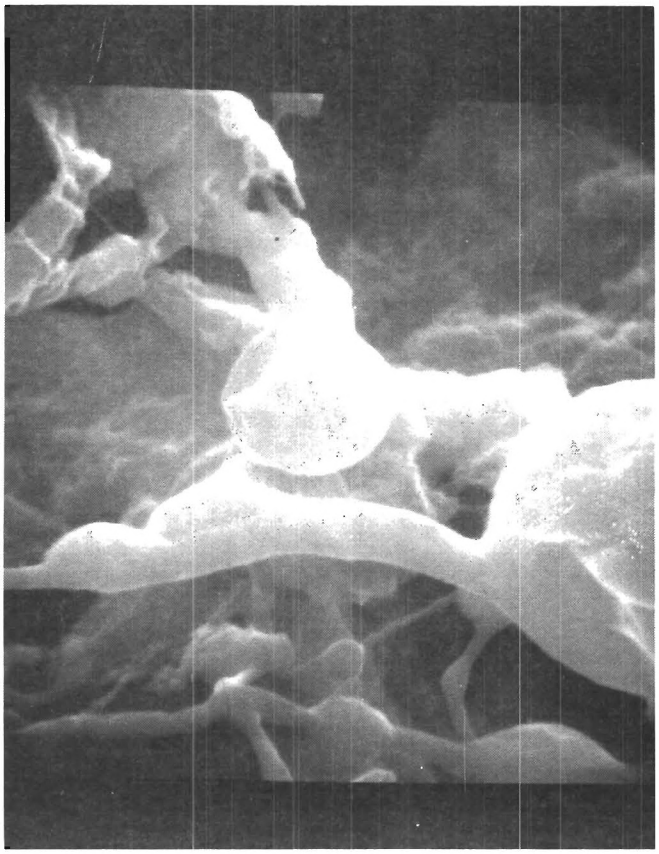


Figure 85
Electron Micrograph, Granular Activated Carbon,
from Phenol Fed Reactor

During the last phase of this study, two column reactors were operated in parallel on a 2000 mg/l glucose substrate. One reactor was packed with granular activated carbon while the other reactor was packed with an equal volume of crushed anthracite coal. The activated carbon packed reactor proved superior in performance to the anthracite packed reactor in both TOC and COD reduction as well as in the rate of gas production.

In conclusion, the anaerobic activated carbon filter was demonstrated to provide an excellent process in the treatment of the readily degradable and poorly adsorbable glucose as well as in the degradation of the strongly adsorbable but somewhat refractory phenol.

Steady-state operating conditions were achieved for all the experimental conditions evaluated. Because of the ability of the process to operate at steady-state without the need for carbon regeneration, the initial capital expense in curred in utilizing granular activated carbon for a filter medium over the more conventional non-activated media is more than compensated for in the improved performance of the process as well as the increased gas production that resulted when activated carbon was used.

It is recommended that the anaerobic-activated carbon filter process be evaluated for the treatment of other classes of compounds commonly found in the liquid wastes emanating from coal conversion processes. If the process results in the successful treatment of all or most of these groups of compounds, it is recommended that the process performance be tested against a real coking or coal gassification wastewater.

SUMMARY AND CONCLUSIONS

Two anaerobic-activated carbon filter systems were constructed for use in this study. Each reactor consisted of four columns in series with a clarifier following each of the first three columns. The feed flow rate into each of the treatment systems was maintained at 2 ml/min thus giving rise to an empty bed hydraulic detention time of 11.62 hours per column. Recirculation of the aqueous contents was exercised around each individual column in an upflow manner at a flow rate of 50 ml/min; this recirculated flow served to buffer the feed substrate and provide for the dilution of the organic carbon concentration as seen by the microbial culture.

Glucose and phenol were used as the major source of organic carbon in the synthetic feed substrates. One column reactor system was tested in treating a 2000 mg/l glucose bearing substrate while the other treatment reactor was fed a synthetic substrate bearing 200 and 400 mg/l of phenol. The first reactor was later subjected to a feed substrate containing 2000 mg/l of glucose and 200 mg/l of phenol in order to assess the cometabolism of the two compounds.

The glucose fed reactor was very effective in reducing the organic content of the feed substrate. An empty bed contact time of 11.62 hours was sufficient in achieving reductions in total organic carbon and chemical oxygen demand of 92 and 95 percent, respectively. Gas was produced at a rate of 1897 ml/day from the first column. This gas was very rich in methane with a steady-state methane content of 87 percent.

The 200 mg/l phenol bearing substrate was fed to another set of four anaerobic-activated carbon filter columns. During the initial 135 days

of the experiment, very little anaerobic biological activity in the form of methane production was noted. During this phase of the experiment, phenol was removed from the feed substrate by adsorption onto the activated carbon medium. After 135 days of operation, however, gas production was observed from the first three columns and at various stages during the experiment, the COD and carbon equivalent of the gaseous products exceeded the rate at which carbon was introduced into the reactor system indicating that bio-regeneration of the activated carbon surface was in progress. Steady-state operating conditions were eventually reached after 240 days of operation. At steady-state the first anaerobic column was responsible for reductions in TOC, COD and phenol of 70, 80 and greater than 93 percent, respectively while the first two columns resulted in a combined removal of TOC, COD and phenol of 86, 87 and 99.9 percent, respectively.

The feed substrate to the phenol fed reactor was increased to 400 mg/l phenol on day 268. Corresponding to this increase in the phenol content of the feed, an immediate increase in gas production was observed leading to the conclusion that no additional acclimation period was needed and no shock effects were encountered. During steady-state operation, the first anaerobic activated carbon column resulted in TOC, COD and phenol removal efficiencies of 92, 93 and 98.75 percent, respectively.

The 2000 mg/l glucose fed anaerobic filter system was then subjected to an addition of 200 mg/l of phenol to the glucose substrate. The response of the treatment system was exhibited by an immediate increase in gas production then confirming that the degradation of the readily biodegradable and poorly adsorbable glucose and the strongly adsorbable but more refractory phenol could occur simultaneously with no antagonistic effects.

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