THE REMOVAL PERFORMANCE OF POWDERED ACTIVATED CARBON (PAC) IN REMOVING SELECTED ORGANIC PRIORITY POLLUTANTS IN AN ACTIVATED SLUDGE PROCESS

By

ALI FAZEL

Licentiate
Arak College of Sciences
Arak, Iran
1974

Master of Environmental Science
University of Oklahoma
Norman, Oklahoma
1978

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
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DOCTOR OF PHILOSOPHY
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Thesis Approved:

Don F Kincannon
Thesis Adviser

Enos L. Stover

Richard C. Essenberg

John N Veenstra

Marcia H Bates

Norman N Durham
Dean of the Graduate College

Dedicated to my wonderful wife

Jeni Fazel (Taheria)

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CHAPTER I

INTRODUCTION

The past decade has witnessed developing convern over the potential public health and ecological implications of trace organic compounds in wastes and receiving waters, specifically those 129 individual compounds identified by the Environmental Protection Agency as priority pollutants. Those compounds were divided into three categories. The first consisted of proven mutagens, carcinogens, and tetrogens. The second group included those compounds that were chemically analogous to the first group although not directly proven harmful. The last group included those compounds shown to be acutely toxic to biological organisms (5, 6).

Activated sludge is a well-known and flexible process employed in municipal and industrial wastewater treatment for removal of organic matter. Unfortunately, many organic compounds in raw wastewater are resistant to complete biodegradation and, thus, a significant quantity of refractory organics are present in the secondary effluent. Therefore, more efficient treatment means have to be employed either as a supplement or as a substitute for the conventional treatment method. One of the most promising methods for improving the removal of organic pollutants is the use of powdered activated carbon to adsorb and remove the residual quantity of organic matter from the wastewater (7, 8, 9, 10).

Powdered Activated Carbon (fresh or regenerated) is fed to the aeration basin of a completely mixed activated sludge reactor. The carbon is used to adsorb some materials while the bacteria biochemically degrades others. The carbon and bacteria form a dark, well-flocculated sludge which settles well in the final clarifier where overflow effluent or tertiary quality is obtained (11). The system is capable of being run on the conventional sludge concept by wasting sludge either from the aerator or clarifier underflow. The wasted sludge can be regenerated to recover a reusable powdered activated carbon (12).

Powdered activated carbon (PAC) addition to the aeration basins of activated sludge has been practiced for several years (13, 14). This combined powdered activated carbon/activated sludge process has been patented by DuPont Company and has become known as the PACT process (15). Plant scale tests of the PACT process were reported by DuPont, Sun Oil and many others, beginning as early as 1982. Adding PAC to activated sludge units resulted in several improvements in both operation and effluent quality as indicated in Table 1 (16, 17, 18, 19). These advantages follow from the following basic concepts (20, 21):

1. Adsorption of non-biodegradable materials
2. Adsorption of normally biodegradable materials
3. The weighting effect of the powdered carbon with the sludge matrix
4. The bridging of carbon particles by biomass to form larger floc

The principal advantages are efficiency of pollutant removal and improved process stability. The process is particularly well suited

TABLE 1

EFFECT OF POWDERED ADDITION TO ACTIVATED SLUDGE UNIT

Beneficial effects of PAC	Results of PAC addition
Removal of adsorbable organics	Removal of color and odor
	Increased stability against toxic organics shockloads
	Reduction of foaming in aeration
	Lowers residual effluent toxicity to fish
Removal of adsorbable biodegradable organics	Reduction of oxygen demand in receiving water
Removal of inorganics	Increased stability against heavy metal shockloads
Improved floc forming	Reduction in effluent suspended solids
Improved sludge settling	Increased capacity of secondary clarifier
Improved sludge dewatering	Increasing capacity of sludge dewatering unit

Adapted from Reference 20

to wastewater containing adsorbable, and poorly biodegradable organics (22, 23, 24).

The principal objective of this research was to investigate the difference in effluent quality attributable to use of powdered activated carbon for removal of selective individual priority pollutants and a combination of these pollutants.

For accomplishing these goals, two complete mix bench-scale continuous flow activated sludge systems were operated at various sludge ages with a hydraulic detention time of eight hours. The priority pollutant or combination of pollutants under investigation were added to a synthetic wastewater composed of biodegradable organic compounds and appropriate inorganic nutrients. Powdered activated carbon was added at various concentrations. The effects of the PAC were assessed.

CHAPTER II

LITERATURE REVIEW

Carbon Adsorption

The use of activated carbon in wastewater treatment has only recently been considered as a viable process although the purifying and adsorptive properties of activated carbon have long been recognized (25). The use of activated carbon dates back to ancient Egypt about 1500 B.C. where it was used for medicinal purposes (26). In the time of Hippocrates wood chars were used to treat various ailments (27). In the 18th Century, an application was found for removing foul odors from gangrene. In subsequent years, the application of charcoal was used mainly as a deodorizing agent for sugar. Other than laboratory work very little utilization of activated carbon was made (28).

The real thrust and rapid development of activated carbon was stimulated by World War I when the Allies sought protection against chlorine gas. Gas masks employing activated carbon were used (5, 6). Activated carbon was used in water treatment dating from approximately 1919 with several isolated applications in the U.S.A. and Great Britain during the nineteenth century (29, 30).

Powdered activated carbon was first used by Swift and Company in 1928 in Chicago during a period of bad taste in their water supply (31). They utilized a pressure filter apparatus and were successful in removing the bad taste. After this success water treatment plants began using powdered activated carbon to remove taste and odor.

In 1935 Rudolf and Trubrik (32) reported that powdered activated carbon is very helpful in sewage treatment for overloaded activated sludge plants. Carbon was observed to improve sludge compaction and filtration. Berg and his co-workers (33) reported that adsorption in powdered activated carbon has been proven to be a feasible method for removing the bulk of dissolved organic materials from municipal secondary effluent. However, the cost of carbon is such that it must be regenerated and reused.

Application of Activated Carbon in Wastewater Treatment

The use of activated carbon for removing dissolved organics from drinking water and wastewater has long been known to be feasible. The increasing need for highly polished effluents, necessary to accommodate stringent requirements for both surface water and water reuse, has stimulated great interest in carbon treatment systems. Adsorption makes it possible to remove compounds that are not readily degradable by biological methods and gives excellent removal of taste, color and odors (34, 35).

Operating under all typical quantity and quality variations encountered in a full-scale sewage treatment situation, Berant and Vollstedt (36) demonstrated that powdered activated carbon used in an activated sludge type process is capable of producing an unusually high quality effluent. Extensive, full-scale field tests involving a variety of industrial and municipal wastewaters have demonstrated that PAC improves organics removal, solids settling, and foam reduction when added to activated sludge treatment processes (37, 38).

Cooper and Hager (39, 40, 41) stated that activated carbon is effective in removing refractory compounds. Furthermore, carbon is effective in adsorbing organics below the concentration where biological treatment systems are efficient. Adsorption process can produce a considerably higher removal of organic contaminants than could be expected from the activated sludge process alone and activated carbon exhibits a strong adsorptive affinity and an appreciable adsorptive capacity for a wide variety of organic compounds.

Combined Industrial-Municipal Wastes

The addition of powdered activated carbon to activated sludge process is particularly advantageous for improving the treatment of industrial or mixed industrial-municipal wastes (42, 43).

Adams (44) treated waste from a manufacturing facility which contained very high average BOD_5 of 1700 mg/ℓ, COD of 3200 mg/ℓ and mixed liquor volatile suspended solids (MLVSS) of 1000 mg/ℓ in the system.

Full-scale field tests indicated that PAC improves organic removal solids settling. For plants that have either hydraulically overloaded or are subject to wide variations in waste loadings, powdered carbon will level treatment efficiency providing higher quality effluent with less operator attention.

He concluded that the higher the density of the carbon, the more effective it becomes. First, the higher density aids solids settling and sludge compaction. Second, less carbon will escape in the secondary effluent when using high density carbon. Third, less makeup carbon is required to maintain an equilibrium level in the system if carbon is lost only during sludge wasting. Fourth, carbon storage requirements are reduced.

Dewalle et al. (45) presented data for bench scale activated sludge systems operated at θ_c values of 5 and 10 days treating a domestic wastewater supplemented with glucose. Analysis of soluble effluent organics indicated high levels of carbohydrates, amino acids and carbony functional groups at a θ_c of 5 days. The unit operated at a θ_c of 10 days contained high levels of aromatic hydroxyls in the effluent. The increased removal of organic matter due to powdered activated carbon addition was considered to be of a physical nature in both units while some enhanced biological activity was induced in the unit operated at a θ_c of 5 days.

Shukrow et al. (46, 47) developed the pilot-tested PACT system for raw and combined sewage. Shukrow and his co-workers successfully demonstrated this physical-chemical process utilizing PAC on a 100,000 GPD unit at Albany, New York. This project established the technical and economic feasibility of this process for sewage treatment while removals in excess of 90% COD, 94% BOD_5 and 99% suspended solids were consistently achieved. The workers noted that the carbon dosage could be adjusted to affect the degree of organics removal required. Additionally, a residual, non-sorbable fraction ranging from 10-20 mg/ℓ BOD_5 and 20-50 mg/ℓ COD existed at times which could not be removed at carbon dosages as high as 1000 mg/liter.

Powdered activated carbon was added to the aerator of the activated sludge process of the Norfolk, Nebraska Water Pollution Control Plant. To help solve operational problems the plant had a 2.1 MGD average flow containing 35-50% meat packing waste. Despite the fact that flows were less than 60% of design capacity (48). The plant effluent was characterized by high and variable solids. After the PAC concentration reached 200 mg/liter, average effluent solids concentration decreased 67%, sludge volume index decreased 33%. Secondary sludge solids decreased 28% and sludge bulking was essentially eliminated. Furthermore, despite a 10% higher organic load, effluent BOD_5 concentrations were maintained at about 4 mg/ℓ. Other noticeable improvements were reduction in effluent color, plant odors, and aerator foam.

Scaramell and Digiano (7) reported that PAC had a significant effect on effluent quality when added to activated sludge systems. They investigated three carbon dosages, (100, 200 and 800 mg/ℓ. The 100 and 200 mg/ℓ dosages offered the most significant enhancement of effluent quality. At these dosages, the effluent TOC was reduced to 7 mg/ℓ at the termination of each dosage period which was significantly less than the effluent TOC concentration of a secondary biological treatment system (15-20 mg/ℓ).

They indicated that adsorption was the primary mechanism responsible for the increased process efficiency with the addition of PAC. Investigation of oxygen uptake and MLSS indicated that no enhancement of biological growth was attributable to PAC addition.

They also showed that, due to the dissimilar nature of the settleable solids in a PAC-biomass mixture, SVI is not a valid indicator of sludge settling characteristics. Settled sludge volume should be considered when determining sludge settleability. PAC addition did not enhance the settled sludge volume in the activated sludge system.

Industrial Wastewater Treatment

Several case histories are presented which show that PAC addition to activated sludge plants has improved removal of organic pollutant and protects biological systems from shock or toxic loadings. The carbon has also been found to level effluent quality and plants subject to periodic organic or hydraulic overloads (49).

For many poultry processing plants, the proposed effluents would necessitate 98% removal of BOD, suspended solids, and oil and grease. Intermittent flow often makes treatment with activated sludge difficult because of problems in maintaining an adequate biomass (50). The addition of powdered activated carbon to activated sludge systems can alleviate this condition by providing a growth site for the microorganisms. In addition, many of the pollutants can be adsorbed on the carbon.

A full-scale evaluation of powdered activated carbon treatment is reported by Black and Anderson (51). In this plant, two activated sludge units treat an average of 400,000 gallons during a 10 hour working day. The variable flow in this system caused frequent sludge bulking, high effluent solids, and variable effluent quality.

Powdered carbon was maintained in the aerator at an equilibrium level of 1000-1200 ppm. This required a daily addition of 10-15 ppm based on influent to make up the carbon lost during sludge wasting. After carbon addition, variability diminished and overall quality improved. Average effluent solids decreased 66%, BOD decreased 57% oil decreased 70% and nitrogen decreased 83%.

Refinery and Petrochemical Wastes

Refinery and petrochemical wastes can be treated biologically by the activated sludge process, however, conventional systems often experience many effluent quality and operating problems.

1. oil that is not removed in the API separators can pass through the aerator and will be measured as TOC or COD
2. oil can also entrap solids, prevent them from settling, and lead to high effluent suspended solids
3. surface active agents often cause foaming in the aerator or the receiving stream
4. toxic shock loads can kill the active biomass
5. oil characteristics of waste sludges can make them difficult to dewater and handle

DeJohn and Adams (37) noted that addition of PAC to activated sludge systems has proven to be a satisfactory method for solving such problems. In addition to improved operation of the activated sludge system, the use of PAC also may result in real operating cost savings. It was reported that four refinery and chemical plants have evaluated the use of powdered activated carbons in full-scale activated sludge systems. In all systems, addition of powdered carbon improved organic removals, aided solids settling and sludge handling, provided protection from toxic or shock loadings, and monitored nearly color loss effluents with a more consistent effluent quality.

In an effort to expand the performance of the existing biological treatment facilities, full-scale studies utilizing powdered activated carbon were conducted at Sun Oil Company's Texas refinery (52). The main objective of adding the powdered carbon was to reduce the effluent suspended solids loading for compliance with 1977 NPDES and state permit conditions. An improvement in performance of the existing system was significant for BOD and COD removal as well as for suspended solids. Compiled data showed reduction in final effluent loadings of up to 56% for suspended solids, 76% for BOD_5 and 36% for COD. Other improvements noted were more uniform effluent quality, a clearer effluent, elimination of foam in the aeration system, more consistent sludge wasting at two-thirds the volume, and reduced biological upsets. The system was maintained at the carbon operating level by batch addition of about 100 pounds per day of carbon. The carbon used in these trials had a bulk density of 44 pounds per cubic feet which is an important factor when improved settleability is the primary objective of carbon addition to the system.

Stenstrom and Grieves (53) and Grieves et al. (54) reported on the evaluation of an alternate process to granular activated carbon treatment of refinery activated sludge effluent. The proposed process would be used by refineries to meet their BAT effluent quality goals in 1983. The new treatment alternative involves using powdered activated carbon to enhance the performance of the activated sludge section of the BPT treatment sequence. The degree of enhancement was found to be considerably affected by the physical characteristics, in particular surface area, of the activated carbon used. The advantage of the high surface area carbon was more pronounced at high sludge ages or high mixed-liquor suspended solids (MLSS) concentrations.

These workers concluded that the powdered activated carbon-activated sludge process is a promising technique for meeting BAT effluent requirements for oil refineries. Data collected during this study generally met or exceeded the target effluent quality.

The process was reported to offer significant cost incentives over add-on granular activated carbon columns while being much easier to operate. It was also found that the use of high sludge age is a viable method of maintaining process performance while lowering carbon addition requirements. The increased sludge age, resulting in higher MLSS concentrations, reduces carbon make-up requirements and size of regeneration facilities.

DeJohn and Black (55) have reported on the results from fourteen refineries that have used powdered activated carbon addition to full-scale activated sludge systems. They found that, in general, refinery wastes can be successfully treated with the PAC process. They also concluded that powdered carbon can improve inorganics removal, aid solids settling, and provide protection from toxic or shock loadings. High density carbons were found to be preferred to minimize carryover from secondary clarifiers and to increase sludge compactions. Nitrogen and phosphorous removals were also improved by the addition of powdered carbon to the activated sludge system. The reasons given for this are that the carbon adsorbs compounds toxic to nitrifiers and allows them to operate normally and phosphorous was probably precipitated with the carbon bio-solids floc.

Carbon treatment has been proposed by Hale and Myers (56) as a relatively efficient method for removing organics from refinery wastewater. Data are presented illustrating that an activated sludge treatment system reduced saturated and aromatic organic materials to low levels in the final clarifier effluent but was relatively ineffective in removing some of the polar type compounds. Carbon treatment removed polar type compounds as well as saturates and aromatics. The authors note that none of the wastewater treatment systems now in use at petroleum refineries will remove all of the organics from the water.

Three bench scale tests, covering different ranges of carbon concentration were conducted by Thibault et al. (57). During both bench-scale and field studies PAC had no impact on activated sludge efficiency at levels up to and including 400 mg/ℓ; however, improved TOC, COD, and BOD_5 removals were observed at 1000 and 2000 mg/ℓ levels during normal operations. They also found that PAC has no effect on ammonia removal regardless of carbon concentration, but PAC treatment substantially improved the shock resistance of the field activated sludge unit. However, the shock-handling characteristics of the bench-scale PAC units were inferior to the control due to the unexpected desorption of previously adsorbed materials which resulted in a decrease in biological activity and removal efficiency.

They showed that PACT can be effective in standby applications during organics shock loadings. This was demonstrated in the field testing program when an upset was controlled by carbon addition. Complete recovery was obtained in four days compared to several weeks for similar previous upsets.

Their bench-scale data showed some improvement in effluent suspended solids concentrations at carbon levels less than 400 mg/ℓ; however, no improvement was observed at 1000-2000 mg/ℓ. Conversely, the sludge volume index (SVI) was not improved at the lower carbon levels but was somewhat reduced at 1000-2000 mg/ℓ.

Organic Chemical Wastewaters

Pilot-plant studies conducted at the DuPont Chambers Works Multi-product organic chemical plant revealed that the addition of powdered activated carbon to the aerator of an activated sludge system would result in a significant increase in performance over an activated sludge system alone (58-65). Some additional improvement in performance also was obtained by combined systems consisting of carbon columns either preceding or following biological treatment. All three combined systems achieved desired effluent quality for this particular waste system during the 15-month test period, while the other two systems, biological treatment alone, or carbon column treatment alone, were found to be inadequate. The DuPont workers determined the PACT system to be the least expensive system meeting Chambers Works effluent criteria for BOD_5, COD, TOC, color, and fish toxicity (66-67).

Hutton and Temple (68) updated the results of the PACT process at the Chambers Works facility. They found that activated carbon addition significantly increased priority pollutant removals as compared to conventional activated sludge units. Feed and effluent data were presented on 12 metals and more than 30 organics.

Hutton (69) also conducted an extensive laboratory treatability study on a variable, multicomponent wastewater. The results achieved are shown in Table II. In general, the activated sludge process produced > 85% removal for 23 of the 36 compounds found in the feed. Adding powdered activated carbon at 100 ppm dosage to the activated sludge process increased performance, so that > 85% removal was achieved for 30 of the 36 compounds.

TABLE II

REMOVAL OF PRIORITY POLLUTANTS BY THE PACT PROCESS AND ACTIVATED SLUDGE

Compound	PACT % Removal	AS % Removal
4-nitrophenol	100	99.0
nitrobenzene	99.9 +	99.2
toluene	99.9	99.7
ethylbenzene	99.9	99.8
chlorobenzene	99.8	99.3
2-4-dinitrotoluene	99.6	99.0
benzene	99.6	99.5
phenol	99.2	98.4
carbon tetrachloride	99.0	99.5
trichloroethylene	98.8	99.5
2-nitrophenol	98.4	86.0
1,1,1-trichloroethane	98.0	98.0
1,2-dichloroethane	98.0	97.0
1,2-dichlorobenzene	97.9	97.0
trichlorofluoromethane	97.0	97.0
chloroform	97.0	97.0
2,4-dinitrophenol	96.6	0
1,4-dichlorobenzene	96.4	95.4
2-chlorophenol	96.0	92.0
methylene chloride	95.0	94.0
bromoform	94.0	95.0
4,6-dinitro-o-cresol	93.0	0
tetrachloroethylene	93.0	97.0
p-chloro-m-cresol	92.0	83.0
2-6-dinitrotoluene	91.4	81.0
1,3-dichlorobenzene	91.3	71.0
pentachlorophenol	89.0	35.0
2,4-dichlorophenol	89.0	73.0
2-4-dimethylphenol	88.0	94.0
1,2,4-trichlorobenzene	88.0	100
dibromochloromethane	83.0	63.0
bromodichloromethane	< 0	< 0
diethylphthalate	< 0	< 0
bis(2-ethylhexyl) phyhalate	< 0	< 0
hexachloroethane	< 0	< 0
2,4,6-trichlorophenol	< 0	< 0
naphthalene	-	-

Flynn and Stadnik (70) reported on an activated sludge-powdered activated carbon facility receiving an organic chemical manufacturing waste. Satisfactory steady state performance was maintained at a θ_c of 45 days, 85 mg/ℓ carbon dosage and with underflow solids concentrations up to 74000 mg/ℓ. The study also showed that the PACT system responded very satisfactorily to toxic or shock loads.

There is little direct information regarding factors which control the effectiveness of PAC for adsorbing trace toxic compounds from wastewater containing high concentrations and complex mixtures of organic priority pollutants. Weber et al. (71) conducted a study to evaluate the performance of such systems under a variety of operating conditions with respect to different commercial carbons and several classes of organics.

The effectiveness of the PACT process was evaluated in a number of completely mixed flow (CMF) bioreactors operated in parallel under steady state conditions. These investigators tried to identify and quantify parameters which critically affect removal of toxic organic compounds in PACT systems. Parameters were evaluated including carbon concentration, toxic organic concentration, sludge age (SRT), hydraulic retention time (HRT), and organic composition and concentration of the wastewater. The adsorbants chosen for study include three different activated carbons, two of which are commercially available to PAC's commonly recommended for use in the PACT process, Nuchor and Hydrodarco C, and third, an experimental powdered carbon. Amoco PX-21, several priority pollutants, different volatility, solubility, biodegradability, etc.

Results of these studies indicate that, in general, all three PAC's tested were able to provide roughly equivalent removals of priority pollutants which are similar in physiochemical properties of 96% or better. Increases in sludge age or SRT between 0.25 and 15 days did not enhance either COD or priority pollutants removed in the system. Increases in fluid detention time, 1.3, HRT, between 5.5 and 11 hours did not impact priority pollutant removal.

Pharmaceutical Wastewaters

The pilot plant studies were conducted by Kincannon and Esfandi (72) to evaluate the effectiveness of PACT on animal pharmaceutical wastewater. It was found that the PACT system provided better treatment than the activated sludge system for both conventional parameters and priority pollutants.

Two identical activated sludge pilot plant systems were operated, one with PAC and one without PAC. They both received the same wastewater. The wastewater was found to be deficient in phosphorus, thus phosphorus acid was added. In addition, the pH of the wastewater was adjusted to 8.0 with NaOH. The PAC dosage was maintained at 347 mg/ℓ.

The comparison of the two pilot plants in regards to TOC, color, reactor solids, return sludge and sludge settleability is shown in Table III. Activated sludge achieved average removal efficiencies for TOC, and color of 72.4 and 46.3 percent respectively. Whereas, the PACT pilot plant achieved removal efficiency for TOC and color of 89.7 percent and 74.9 respectively. The solid level in the PACT system was almost four times higher than in the activated sludge system.

Comparisons of the two pilot plants (Table IV) in removing organics shows the PACT system gives better removal of organics than the activated sludge system.

TABLE III

COMPARISON OF TYPICAL PARAMETERS

Parameter	Activated Sludge	PACT
Influent TOC, mg/ℓ	387.0	387.0
Effluent TOC, mg/ℓ	107.0	40.0
TOC removal efficiency	72.4	89.7
Influent color	4648	4648
Effluent color	2494	238
Color removal efficiency	46.3	94.9
Reactor solids, mg/ℓ	1403	8285
Return solids, mg/ℓ	4540	24975
Concentration, X_R/X	3.24	3.01
Zone settling velocity, ft/hr	5.2	6.8
SVI	44.0	18.0

TABLE IV

COMPARISON OF ACTIVATED SLUDGE AND PACT PILOT PLANTS IN REMOVING ORGANICS FROM PHARMACEUTICAL WASTEWATER

	Activated Sludge				PACT		
	Inf. µg/ℓ	Eff. µg/ℓ	Removal efficiency	Return sludge µg/ℓ	Eff. µg/ℓ	Removal efficiency	Return Sludge µg/ℓ
ONA	12427	5148	58.6	4085	739	94.1	33288
Phenol	1034	43	95.8	138	<10	>99.0	900
2NP	1271	75	93.8	27	<10	>99.2	383
4NP	635	67	89.4	348	22	96.5	53
TCE	4080	236	94.2	--	148	96.4	--
DCE	291	16	94.5	--	<10	>96.6	--

Frohlich et al. (73) reported on results of a side-by-side pilot scale comparison of a conventional activated sludge system and a biophysical system (activated sludge and powdered activated carbon) on a high-strength industrial wastewater from a pharmaceutical organics chemical producer. Both systems appeared to have acceptable stability. However, performance of the biophysical system was superior in terms of removing BOD, COD, color, and nitrogen. Frohlich and his investigators claimed the following advantages for the biophysical system.

1. The weighting effect of the carbon makes possible the ability to carry the active biomass at levels two to three times higher than activated sludge and thus reduce the aeration basin size and hydraulic detention time.
2. Oxygen transfer is improved-probably as a result of adsorption from the activated carbon.
3. A larger portion of marginally degradable organics can be biologically assimilated to the long sludge residence time, enabling the carbon to carry a higher load of truly refractory material.

CHAPTER III

MATERIALS AND METHODS

General Research Approach

The effectiveness of the PACT process to remove toxic organic compounds was evaluated in a number of completely mixed continuous flow bioreactors operated in parallel under steady-state conditions.

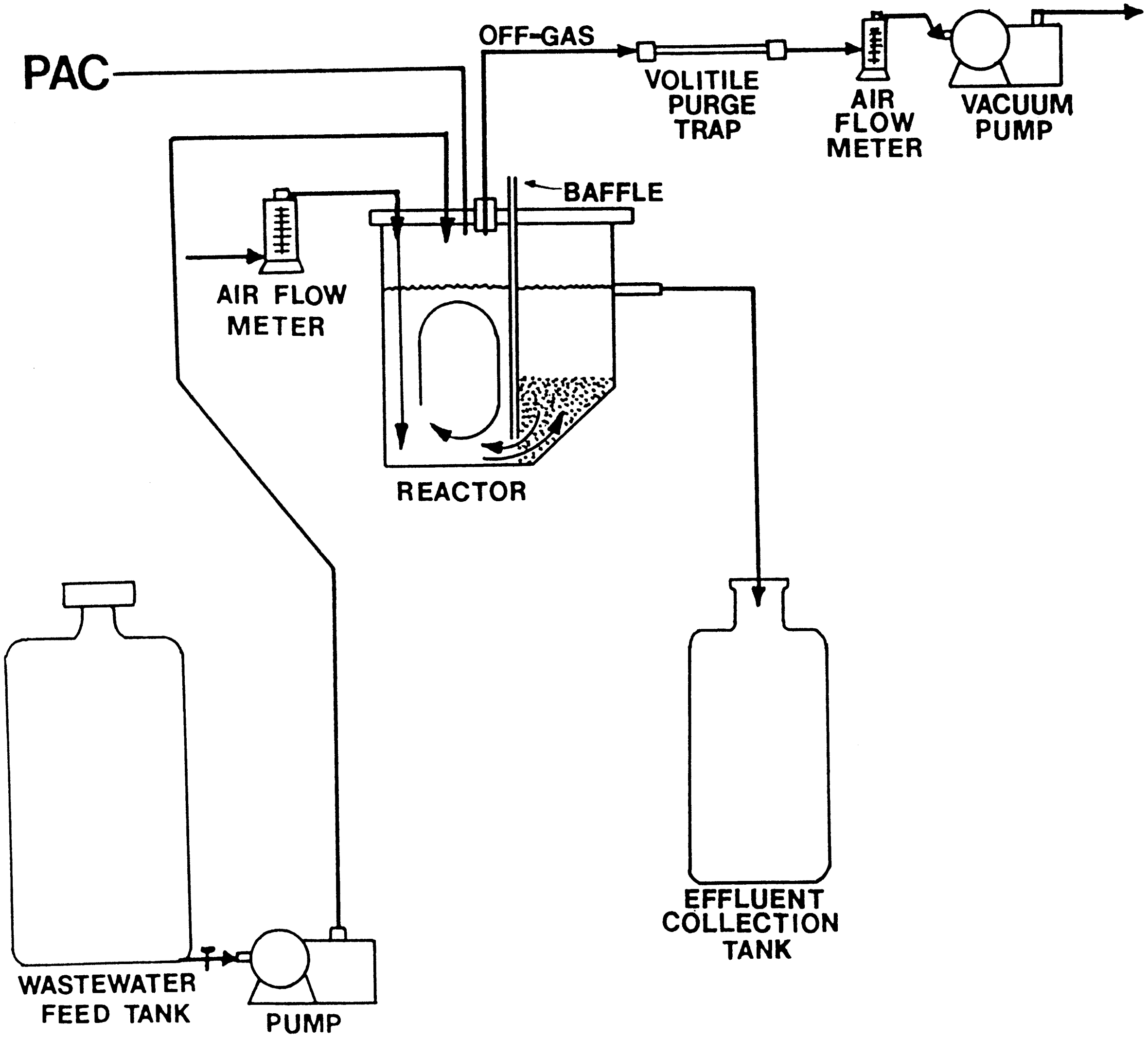
Several organic priority pollutants representing different classes of chemical substances of different volatility, solubility, biodegradability, etc. were studied in this investigation. The activated sludge systems were operated at mean cell residence times (SRT) of 2, 3, 5, and 12 days.

Activated sludge for initial seeding was obtained from a local municipal activated sludge wastewater treatment plant. Two individual systems were acclimated to the synthetic wastewater and priority pollutant(s) for each sludge age.

Description of Pilot Plants

A diagram of the bench-scale activated sludge plants used in this investigation is presented in Figure 1. The reactors, constructed of clear plexiglass, each contained both an aeration section and internal clarifier. The aeration and settling compartments were separated by an adjustable plexiglass baffle. The reactors were tightly covered with plexiglass to facilitate off-gas sampling and analysis. The total

Figure 1. Experimental Reactor


PAC
OFF-GAS
VOLITILE PURGE TRAP
AIR FLOW METER
VACUUM PUMP
BAFFLE
AIR FLOW METER
REACTOR
EFFLUENT COLLECTION TANK
WASTEWATER FEED TANK
PUMP

volume of the identical reactors was 4.5 liters. The volume of the clarifier and aeration chamber of each of the reactors was 1.7 and 2.8 liters.

Operations of Pilot Plant

The synthetic wastewater contained "base mix" plus the organic priority pollutant(s). The wastewater was pumped from sealed feed tanks to reactors and the effluent flowed by gravity from the settling chambers to collection tanks. Slurries of PAC were transferred separately to the reactors from appropriate storage reservoirs. For each different operational condition a biological control reactor that received no carbon was maintained. The SRT within each reactor was controlled by controlling the rate of wastage of mixed liquor from the reactors.

The sludge age (SRT) is defined as the total activated microbial mass in the treatment system (XT) divided by the total active microbial mass wasted daily $(\frac{\Delta x}{\Delta t})_t$. For the PACT process it is assumed the ratio of powdered carbon to biomass is the same in the mixed liquor, clarifier overflow, and clarifier underflow sludges. The equation for calculation of SRT becomes identical to one usually used for activated sludge without carbon (equation 1).

$$\mathrm{SRT} = \frac{VX}{F_W X_R} + (F - F_W)_{xe} \qquad (1)$$

The sludge waste flow rate was calculated by rearranging equation 1 as follows:

$$F_w = \frac{\frac{VX}{\mathrm{SRT}} - F_{xe}}{X_R - x_e} \qquad (2)$$

where SRT = sludge age (days)

V = aerator volume (liter)

X = mixed liquor suspended solids (mg/ℓ)

F_w = wastage rate (ℓ/day)

F = influent flow rate wastewater (ℓ/day)

X_e = clarifier overflow total suspended

X_R = return sludge (mg/ℓ)

Synthetic Wastewater

The synthetic wastewater included the base mix, which is six organic compounds, as a primary carbon source and inorganic compounds, which are necessary for proper bacteria growth (76), plus selected organic priority pollutants. The composition of the synthetic waste chosen to simulate domestic wastewater in character and also to not interfere with the organic priority pollutant analyses is detailed in Table V. Table VI shows the mean value of influent BOD_5, COD, and TOC concentrations of various wastewater as well as pH. The chemical and physical properties of four individual organic priority pollutants which were selected for this study are listed in Table VII.

Powdered Activated Carbon

Nucharc C-190 N, a commercially available PAC of high activity with a surface area >1500 m^2/gm, was used for this investigation.

Experimental Design

This research was conducted in two phases. The first phase investigated the effect of priority pollutant shock loads upon activated sludge systems with and without the addition of powdered activated carbon. Two mean cell residence times (θ_c were studied (2 and 5 days)

TABLE V

BASE MIX

Substrate Name	Formula	Concentration in B.M.	COD mg/ℓ	TOC mg/ℓ
Organic Compounds:				
Ethylene Glycol	$CHCH_2 - CH_2CH$	1.0 volume	105	31.5
Ethanol	CH_3CH_2OH	1.0 volume	121	30.5
Glucose	$C_6H_{12}O_6$	1.0 weight	79	29.2
Glutamic Acid	$C_5H_9O_4N$	1.0 weight	72	30.0
Acetic Acid	$C_2H_4O_2$	1.0 volume	82	30.8
Phenol	C_6H_5OH	1.0 weight	35	11.3
		TOTAL	494 mg/ℓ	163 mg/ℓ
Inorganic Compounds:				
Ammonium Sulfate	$(NH_4)_2SO_4$	1.8 weight		
Phosphoric Acid	PO_4H_3	0.14 volume		
Salts:				
Magnesium sulfate	$Mg\ SO_4,\ 7H_2O$	0.07 weight		
Manganese sulfate	$Mn\ SO_4,\ H_2O$	0.07 weight		
Calcium chloride	$Cacl_2$	0.07 weight		
Ferric chloride	$Fecl_3,\ 6H_2O$	0.04 weight		

1 gram of weight equivalent to 1 mℓ of volume

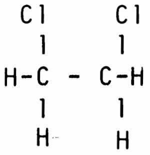
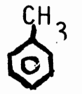
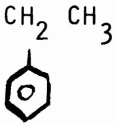
TABLE VI

INFLUENT WASTEWATER CHARACTERIZATION

Parameter	Base Mix	B.M. + Ben.	B.M + 1,2 DCE	B.M. + Toluene	B.M + E.B.	B.M. + Combinant of P.P
BOD mg/ ℓ	265	320	300	195	244	265
COD mg/ ℓ	450	550	620	430	410	450
TOC mg/ ℓ	160	170	250	165	179	145
pH	6.50-7.50	7.70	6.95	7.20	7.0	7.0

TABLE VII

CHEMICAL PHYSICAL PROPERTIES

Compound Name & Formula	Molecular Weight	Melting Point °C	Boiling Point °C	Vapor Pressure (25°)	Solubility mg/ℓ	Henry's Law Constant	mg/mg/ BOD$_5$	Priority Pollutant TOC	COD
Benzene (Benzol) 	78.12	5.5	80.1	95.2	1.780-1.800	555×10^{-3} atmos.m^3 mole^{-1}	0.55	0.92	3.08
1,2-Dichloroethane (Ethylene dichloride)  $\begin{array}{ccc}Cl & & Cl\\ \vert & & \vert\\ H-C & - & C-H\\ \vert & & \vert\\ H & & H\end{array}$	98.98	-35.4	83.5	61	8.300	1.10×10^{-3} atmos.m^3 mole^{-1}	0	0.24	0.97
Toluene (Toluol,methacide) 	92.13	-95	111	28.7	535	5.93×10^{-3} atmos.m^3 mole^{-1}	1.00	0.69	2.5
Ethylbenzene (Phenylethane) 	106.2	-94.9	136	7	206	6.44 atmos.m^3 mole^{-1}	0.73	0.50	1.60

and the priority pollutant utilized was benzene.

In the second phase of this investigation optimization of powdered activated carbon dosage was studied for activated sludge units which received wastewater containing individual and combinations of priority pollutants (Benzene, Toluene, Ethyl Benzene, 1,2 Dichloroethane). Two mean cell residence times (3 and 12 days) were employed.

Table VIII summarizes the experimental design of this research. All of the biological units were continuous flow, internal recycle reactors and were operated at a hydraulic detention time of 8 hours.

Analytical Technique

The analyses employed for determining the experimental data consisted of biochemical oxygen demands (BOD_5), chemical oxygen demands (COD), total organic carbon (TOC), gas chromatography (GC), suspended solids (SS), volatile solids (VSS), pH, and temperature are summarized in Table IX. Table X shows operational conditions used for all four volatile organics priority pollutants and combinations of them.

TABLE VIII

EXPERIMENTAL DESIGN CONDITION

Phase	Unit	Influent	SRT mean cell residence times	Priority Pollutant mg/ℓ	Carbon dosage
I	Control	BM + B (1) (2)	2.5	5,20,50,150	
	PACT	BM + B + PAC (3)	2.5	5,20,50,150	
II	Control	BM + 1,2 DCE (4)	3.12	200	
		BM + T (5)	3.12	100	
		BM + EB (6)	3.12	80	
		BM + COM (7)	3.12	50 (of each P.P.)	
	PACT	BM + 1,2 DCE + PAC	3.12	200	5, 10, 25, 50, 100, 300 600, 1200 +1500
		BM + T + PAC	3.12	100	25, 50, 75, 100
		BM + EB + PAC	3.12	80	5, 10, 20, 30, 35, 50
		BM + COM + PAC	3.12	50	5, 10, 25

1. Base mix 2. Benzene 3. Powdered Activated Carbon 4. 1,2 Dichloroethane 5. Toluene
6. Ethylbenzene 7. Combination of all four priority pollutants 8. Priority Pollutants

TABLE IX

ANALYTICAL TECHNIQUES

Parameter	Technique
Suspended solids (S.S.)	Standard Methods (77) or EPA (80) used glass fiber 934-AH
Volatile solids (VSS)	Standard Methods (77) or EPA (80)
Chemical oxygen demand (COD)	Chromic acid oxidation, Standard Methods (77) or EPA (80).
Total organic carbon (TOC)	Beckman Model 915 - TOC Analyzer
Biological oxygen demand (BOD_5)	Probe method for measuring dissolved oxygen, Biodesign Manual (79), Standard Methods (77).
Specific organic compound	F & M Model 810 Gas Chromatograph with Tekmar LC Purge and Trap and HP 3380 Integrator - U.S. EPA Procedure (80).
Suspended protein	Buiret technique O.S.U. M-2 Manual (78)

TABLE X

GAS CHROMATOGRAPHY OPERATIONAL CONDITIONS

Column	Carbopack C/0 . 2% carbowax 1500 80/100 mesh
Trap	12" x 1.8" metal tubing containing 6" Tenax and 4" silica gel
Detector	FID
Carrier	N_2 gas at 30 mℓ/min
Detector temp.	200°C
Injector temp.	180°C
Oven temp.	2 min. 70°C, 8°/min to 160°C hold 5 min.
Detection limit	1 µg/ℓ

CHAPTER IV

RESULTS

Phase 1 Shock Loads - θ_c = 2 day

General

Two activated sludge reactors were operated at a θ_c of two days, and received a wastewater containing only base mix. One unit was supplemented with 50 mg/ℓ PAC (based on the influent flow rate) while the other, the control, received no carbon. After reaching steady state, influent and effluent substrate analysis were performed periodically during a period of one month. Influent and effluent substrate data are presented for BOD, COD and TOC in Figures 2, 3 and 4 respectively. Operational parameters (θ_c and MLVSS) are also presented. It should be noted that both the control unit and the PAC unit received exactly the same wastewater as feed, and it should be emphasized mean cell residence time was considered as the primary operational control parameter - that the θ_c for both reactors was accurately maintained at 2 day.

Base Mix Feed

As can be seen in Figures 2, 3, and 4, the effluent BOD, COD, and TOC of the PAC unit were approximately 40 to 50% lower than that of the control. The PAC unit effluent BOD also exhibited less variability than

Figure 2. Benzene Shock Load Studies; Influent and Effluent BOD_5 Concentrations and Operational Parameters for θ_c Activated Sludge Systems with and without Powdered Activated Carbon (PAC).

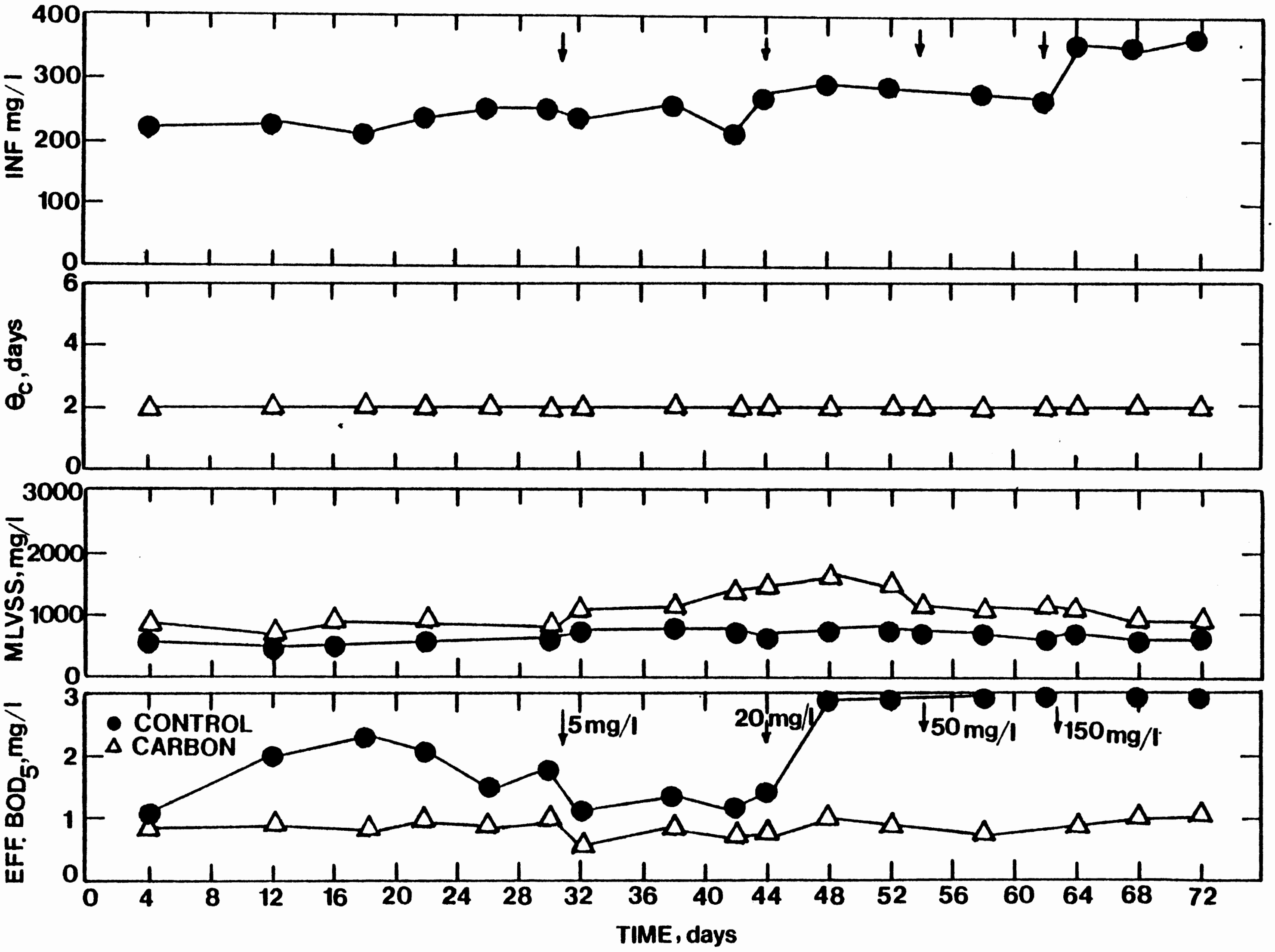

400
300
200
100
0
INF mg/l
6
4
2
0
θc, days
3000
2000
1000
0
MLVSS, mg/l
3
2
1
0
EFF. BOD5, mg/l
● CONTROL
△ CARBON
5mg/l
20mg/l
50mg/l
150mg/l
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
TIME, days

Figure 3. Benzene Shock Load Studies; Influent and Effluent COD Concentrations and Operational Parameters for Activated Sludge Systems ($\theta_c = 2$) with and without Powdered Activated Carbon (PAC).

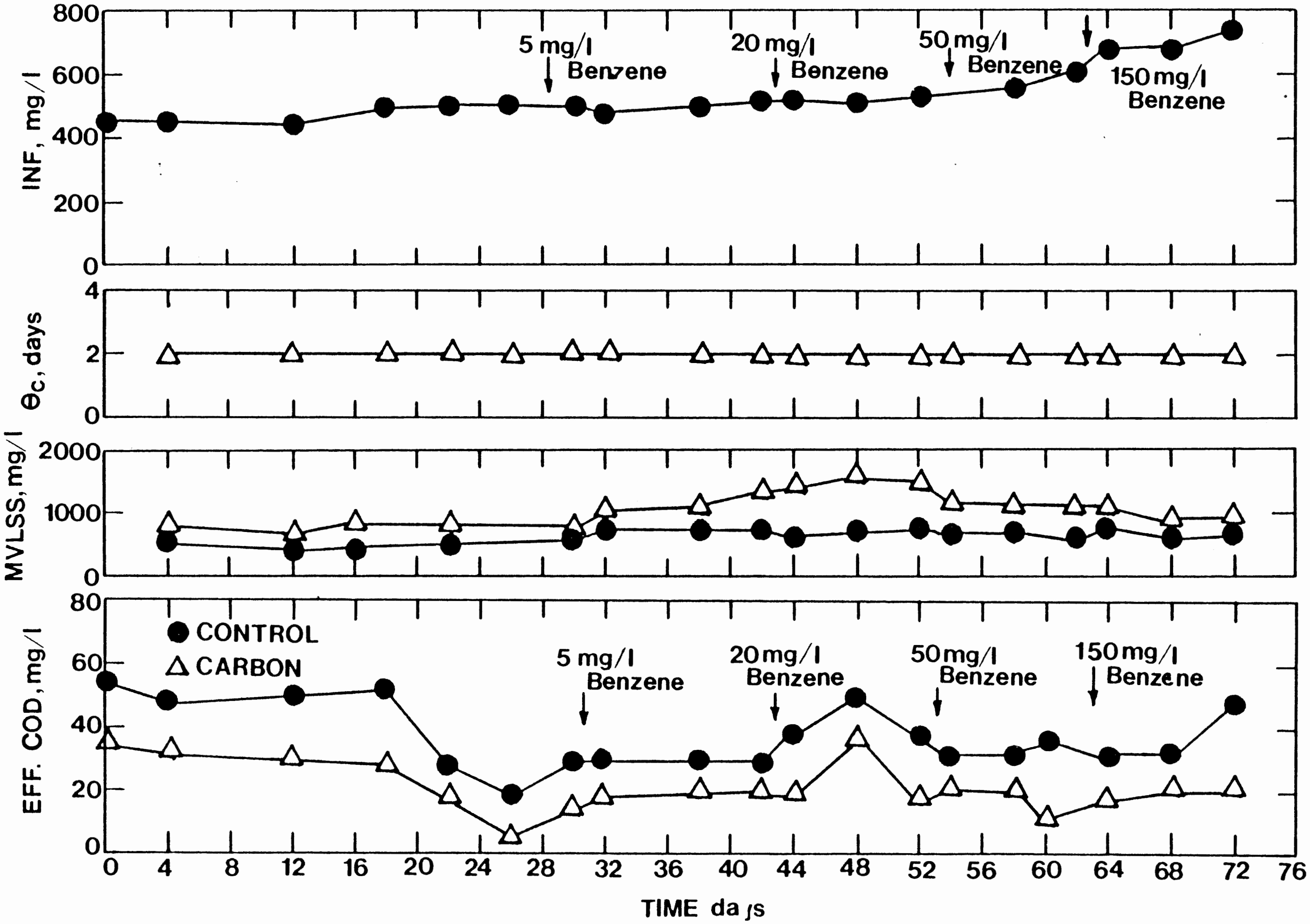
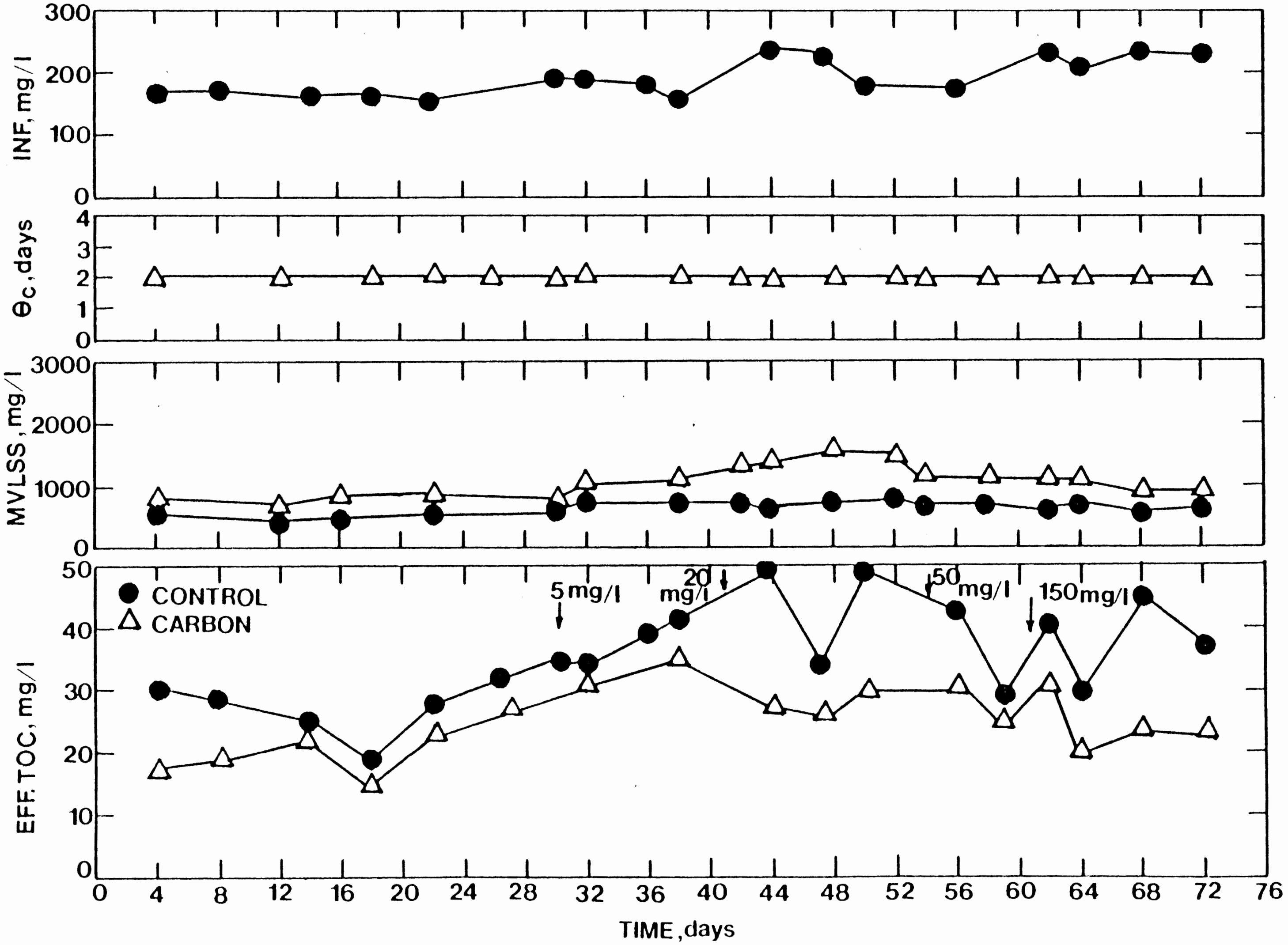

INF, mg/l
800
600
400
200
0
5 mg/l Benzene
20 mg/l Benzene
50 mg/l Benzene
150 mg/l Benzene
θc, days
4
2
0
MVLSS, mg/l
2000
1000
0
EFF. COD, mg/l
80
60
40
20
0
● CONTROL
△ CARBON
5 mg/l Benzene
20 mg/l Benzene
50 mg/l Benzene
150 mg/l Benzene
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
TIME days

Figure 4. Benzene Shock Load Studies; Influent and Effluent TOC Concentrations and Operational Parameters for Activated Sludge Systems ($\theta_c = 2$).

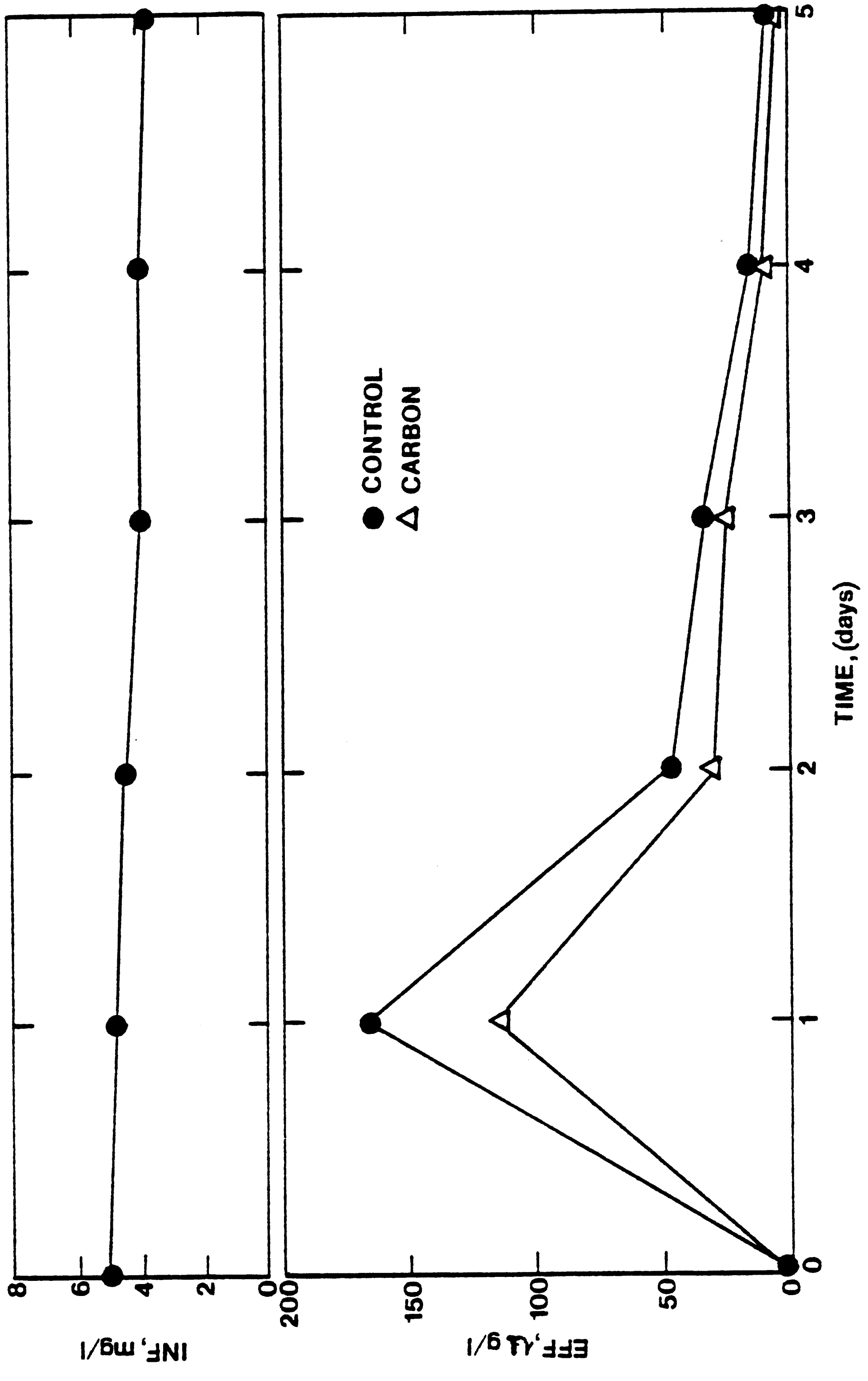

INF, mg/l
300
200
100
0
θc, days
4
3
2
1
0
MVLSS, mg/l
3000
2000
1000
0
EFF. TOC, mg/l
50
40
30
20
10
0
● CONTROL
△ CARBON
5 mg/l
20 mg/l
50 mg/l
150 mg/l
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
TIME, days

the control. The mixed liquor volatile suspended solids (MLVSS) of the PAC unit were generally 265 mg/ℓ higher than the control due to the carbon addition. The mean value for 2 day θ_c substrate and solids analysis can be found in Table XI. It can be seen from Table XI that PAC unit effluent BOD concentration showed only minor increases when benzene dosage was increased from 0 to 150 mg/ℓ. The control unit effluent BOD concentration increased substantially through the same benzene dosage period. For all benzene dosages administered, the PAC unit BOD, COD, and TOC effluent concentrations were lower than those for the conventional activated sludge unit.

5 mg/ℓ Benzene

On day 31, 5 mg/ℓ benzene was added to the base mix feed. Contribution of 5 mg/ℓ benzene addition caused little change in overall influent BOD, COD, and TOC. This shock load caused little effect upon effluent BOD concentrations in both the control and PAC units with actual concentrations remaining at or slightly below the levels achieved during the latter part of the period when only base mix was administered. The PAC unit BOD values were only slightly improved, approximately 2% lower than those of the control. The same trends were also observed for COD and TOC. Benzene analyses for the 5 mg/ℓ shock load are illustrated in Figure 5. After one day, the control unit effluent was found to have a benzene concentration of 165 µg/ℓ; however, this dropped to less than 50 µg/ℓ and continued to decrease to negligible levels after five days. The PAC unit attenuated the benzene shock load so that the maximum level measured was 110 µg/ℓ after one day. The concentrations

Figure 5. 5 mg/ℓ Benzene Shock Load; Influent and Effluent Concentration for Activated Sludge Systems (θ_c = 2) with and without Powdered Activated Carbon (PAC).


INF, mg/l
8
6
4
2
0
EFF, µg/l
200
150
100
50
0
● CONTROL
△ CARBON
0
1
2
3
4
5
TIME, (days)

of benzene measured in the PAC unit effluent were always lower than those found in the control effluent, for corresponding periods of time, the PAC unit only slightly improved the effluent. Again, PAC mixed liquor volatile suspendings were higher than those in the control.

20 mg/ℓ Benzene

On day 43, the benzene concentration was increased from 5 to 20 mg/ℓ. Influent COD and TOC concentrations increased over control conditions by an amount closely paralelling theoretical values for 20 mg/ℓ benzene concentration (theoretical value for COD is 3.07 and for TOC is .93). Influent BOD level was approximately 2.0 mg/ℓ greater than the control condition. The effect upon the effluent concentration in the control unit was more profound with increases in BOD, COD and TOC effluent concentrations increasing 100%, 57% and 36% respectively over those concentrations observed during the 5 mg/ℓ shock load period. On the other hand, BOD, COD and TOC effluent concentrations for the PAC unit showed little change from the 5 mg/ℓ benzene shock load period. The PAC BOD, COD, and TOC values were generally 30% lower than corresponding control values and exhibited less variability (Table XI). PAC mixed liquor volatile suspended solids values were higher than the control solids to a greater extent than would be expected by just the carbon addition. Control unit benzene effluent analyses (Figure 6) showed that 50 μg/ℓ was present the day after administering the shock load while 35 μg/ℓ was found after two days. The 3, 4 and 5 day effluent concentrations were 15 μg/ℓ or less. After 10 days the effluent benzene concentration fell below the detection limit. The PAC unit

TABLE XI

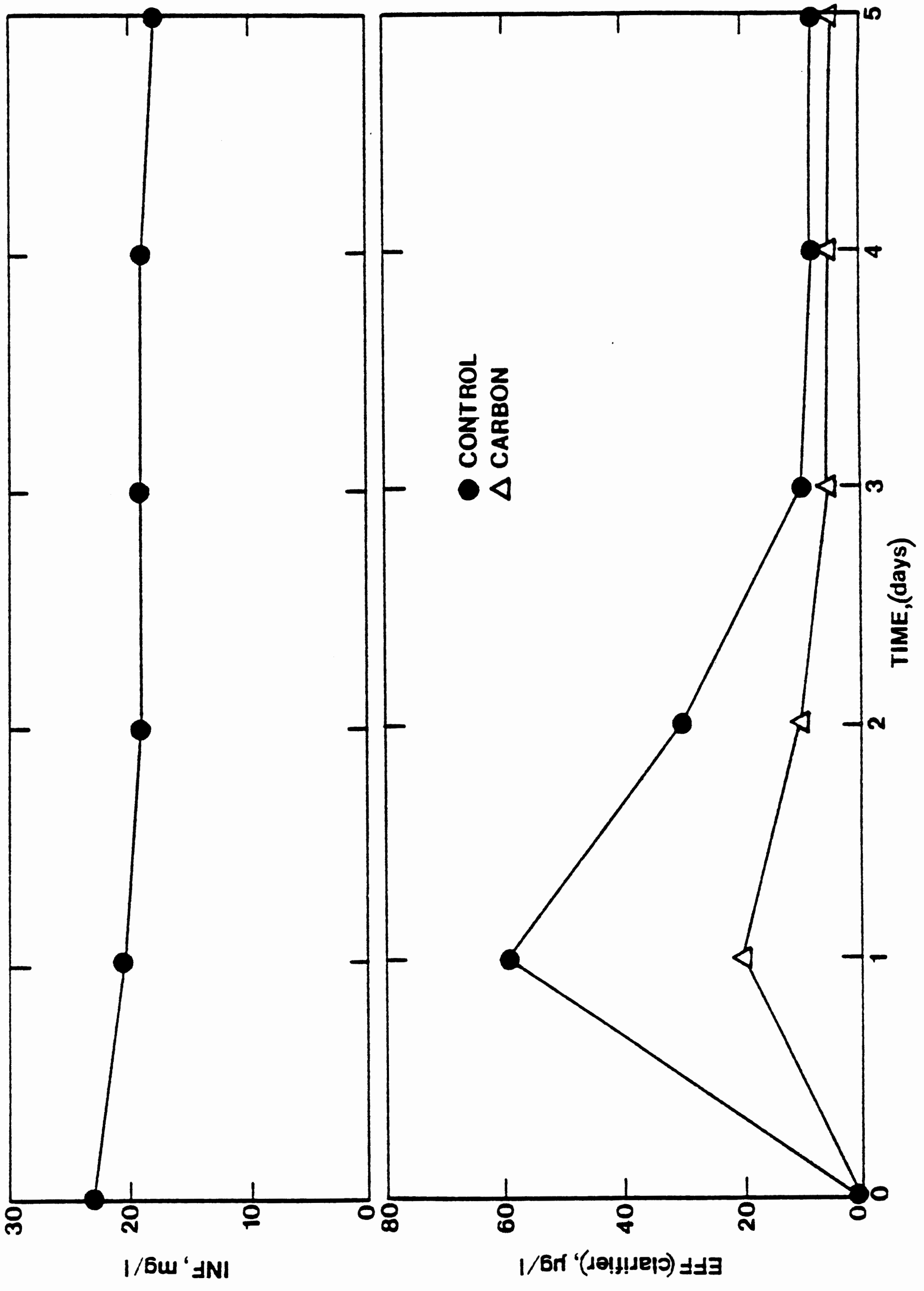
EFFLUENT CONCENTRATION AND BIOLOGICAL SOLIDS FOR PHASE I SHOCK LOAD

θ_c = 2 Benzene Conc. mg/ℓ	BOD		COD		TOC		MLVSS	
	I	II	I	II	I	II	I	II
0	1.95	0.94	41.8	26	27.7	20.3	592	856
5	1.21	0.80	30.7	19.6	22.5	18.75	806	1122
20	2.48	0.94	43	25.3	41.5	33.4	721	1527
50	3.38	1.35	34	19	37.75	28.5	675	1088
150	3.92	1.05	37.3	20.7	38.0	24.7	655	9875

I = Control Unit

II = PAC Unit

Figure 6. 20 mg/ℓ Benzene Shock Load: Influent and Effluent Concentration for Activated Sludge Systems ($\theta_c = 2$) with and without Powdered Activated Carbon (PAC).


INF, mg/l
30
20
10
0
EFF(clarifier), μg/l
80
60
40
20
0
0
1
2
3
4
5
TIME,(days)
● CONTROL
Δ CARBON

attenuated the leakage of benzene so that only 20 µg/ℓ was found on the first day preceding the shock while negligible benzene concentrations were observed after 3 days.

50 mg/ℓ Benzene

On day 53, the influent benzene concentration was increased from 20 to 50 mg/ℓ. Influent BOD, BOD and TOC concentrations increased over control conditions. Additional increases in control unit, after the shock load, BOD increased approximately 30%. Control COD and TOC levels did not exhibit any significant change during the 50 mg/ℓ shock load.

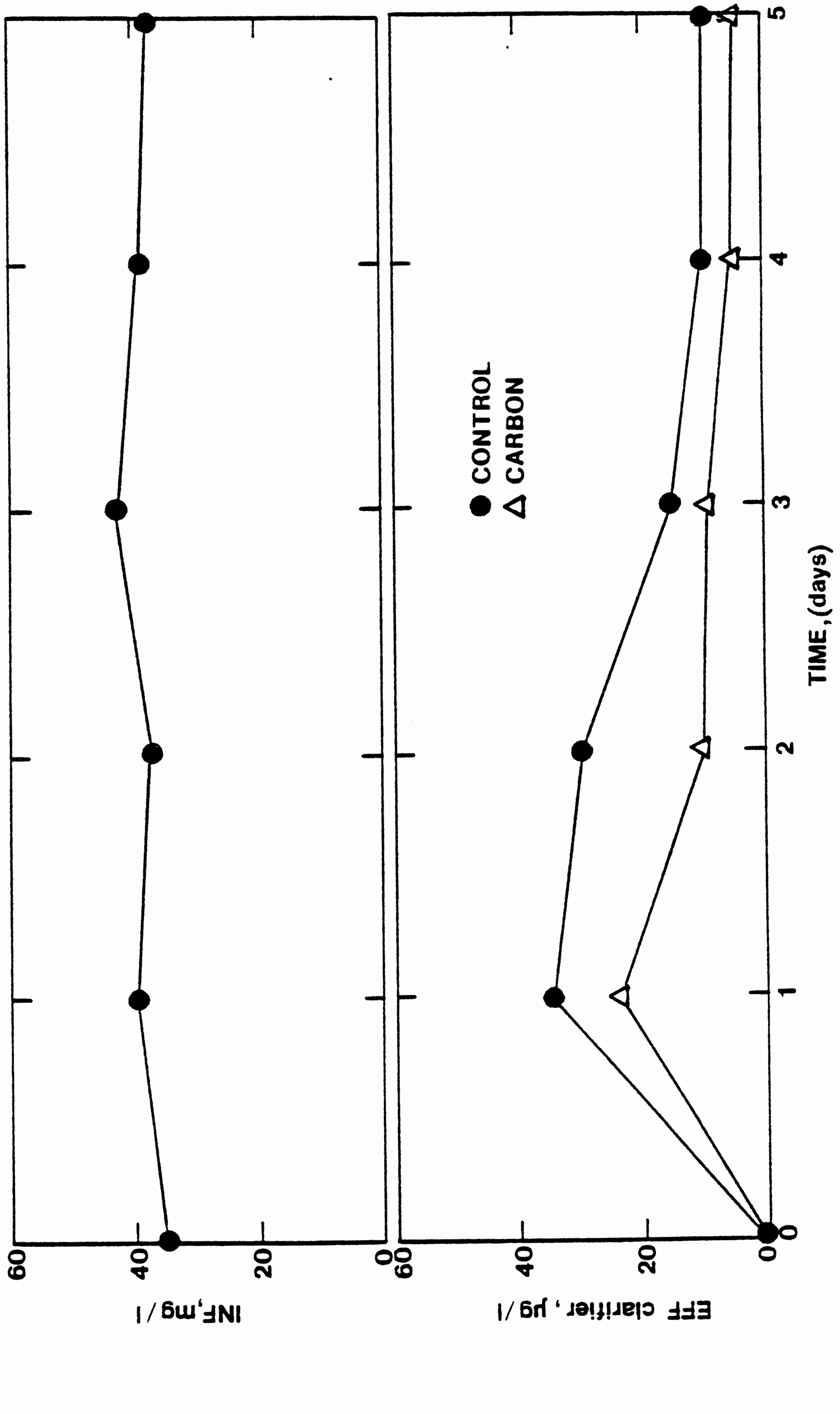
The PAC unit effluent BOD, COD and TOC levels after the 50 mg/ℓ benzene shock load differed very little from the 20 mg/ℓ benzene feed conditions. The PAC unit effluent concentrations for BOD, COD and TOC were 60%, 45% and 25% respectively lower when compared to corresponding control values. Effluent benzene concentrations in the control unit (Figure 7) increased to 35 µg/ℓ after one day and dropped to 10 µg/ℓ by day four. Again, after 10 days the effluent benzene concentration was less than the detection limit. The PAC unit again attenuated the benzene leakage with only 25 µg/ℓ being found after one day and 5 µg/ℓ four days after the shock load.

Mixed liquor volatile suspended solids were higher for the PAC unit by an amount corresponding to the carbon added.

150 mg/ℓ Benzene

On day 63, the benzene concentration was increased from 50 to 150 mg/ℓ. Influent COD and TOC concentrations increased over control by an

Figure 7. 50 mg/ℓ Benzene Shock Load; Influent and Effluent Concentration for Activated Sludge Systems (θ_c = 2) with and without Powdered Activated Carbon (PAC).


INF,mg/l
60
40
20
0
EFF clarifier, µg/l
60
40
20
0
0
1
2
3
4
5
TIME,(days)
● CONTROL
△ CARBON

amount closely paralelling theoretical values for 150 mg/ℓ benzene concentration. Influent BOD level was approximately 150 mg/ℓ greater than control conditions. This shock load caused little effect upon effluent substrate concentrations in the control unit. BOD, COD, and TOC effluent concentration increased by 15%, 10% and 1% respectively over those concentrations observed during the 50 mg/ℓ shock load period.

The PAC unit effluent showed little change from the 50 mg/ℓ benzene shock load period. On the other hand, the PAC BOD, COD and TOC values were 75%, 45% and 35% respectively lower than corresponding control values and again exhibited less variability.

Control unit benzene effluent analysis (Figure 8) increased to 35 μg/ℓ after one day and dropped to 5 μg/ℓ by day four. The PAC unit attenuated the benzene leakage so that only 15 μg/ℓ of benzene after one day and less than 5 μg/ℓ after four days following the shock load. The mean value for 150 mg/ℓ benzene effluent concentration can be seen in Table XI.

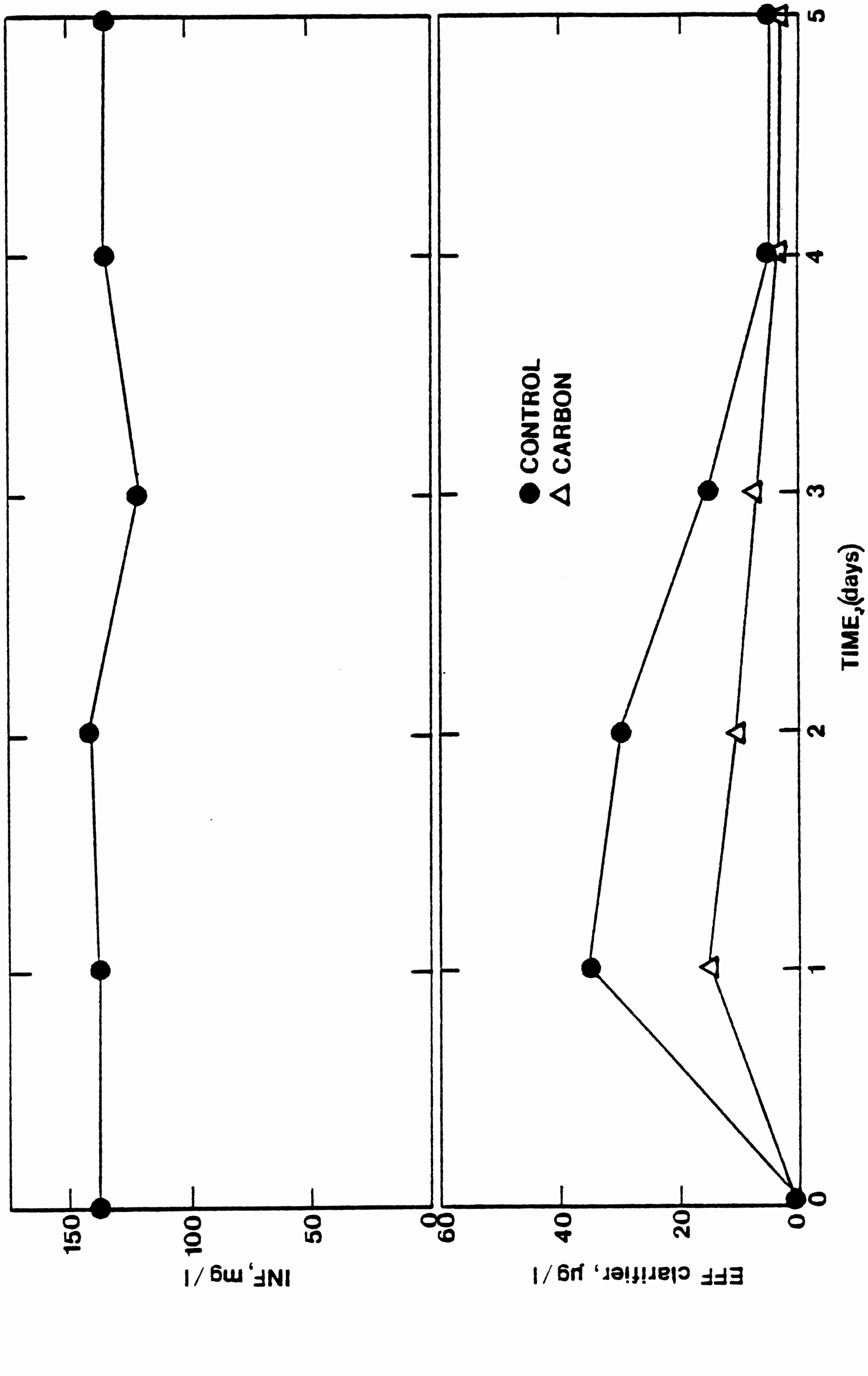
PAC mixed liquor volatile suspended solids were higher than MLVSS of the control unit.

Phase 1 Shock loads - θ_c = 5 day

General

In this part of the study, two bench scale activated sludge reactors were operated at mean cell residence times of 5 days. One of these reactors was supplemented with 50 mg/ℓ PAC (based upon the influent flow rate). The units received exactly the same influent which consisted first of only base mix but were later shock loaded with progressively increasing

Figure 8. 150 mg/ℓ Benzene Shock Loads; Influent and Effluent Concentration for Activated Sludge Systems (θ_c = 2) with and without Powdered Activated Carbon (PAC).


INF, mg/l
150
100
50
0
EFF clarifier, µg/l
60
40
20
0
0
1
2
3
4
5
TIME, (days)
● CONTROL
△ CARBON

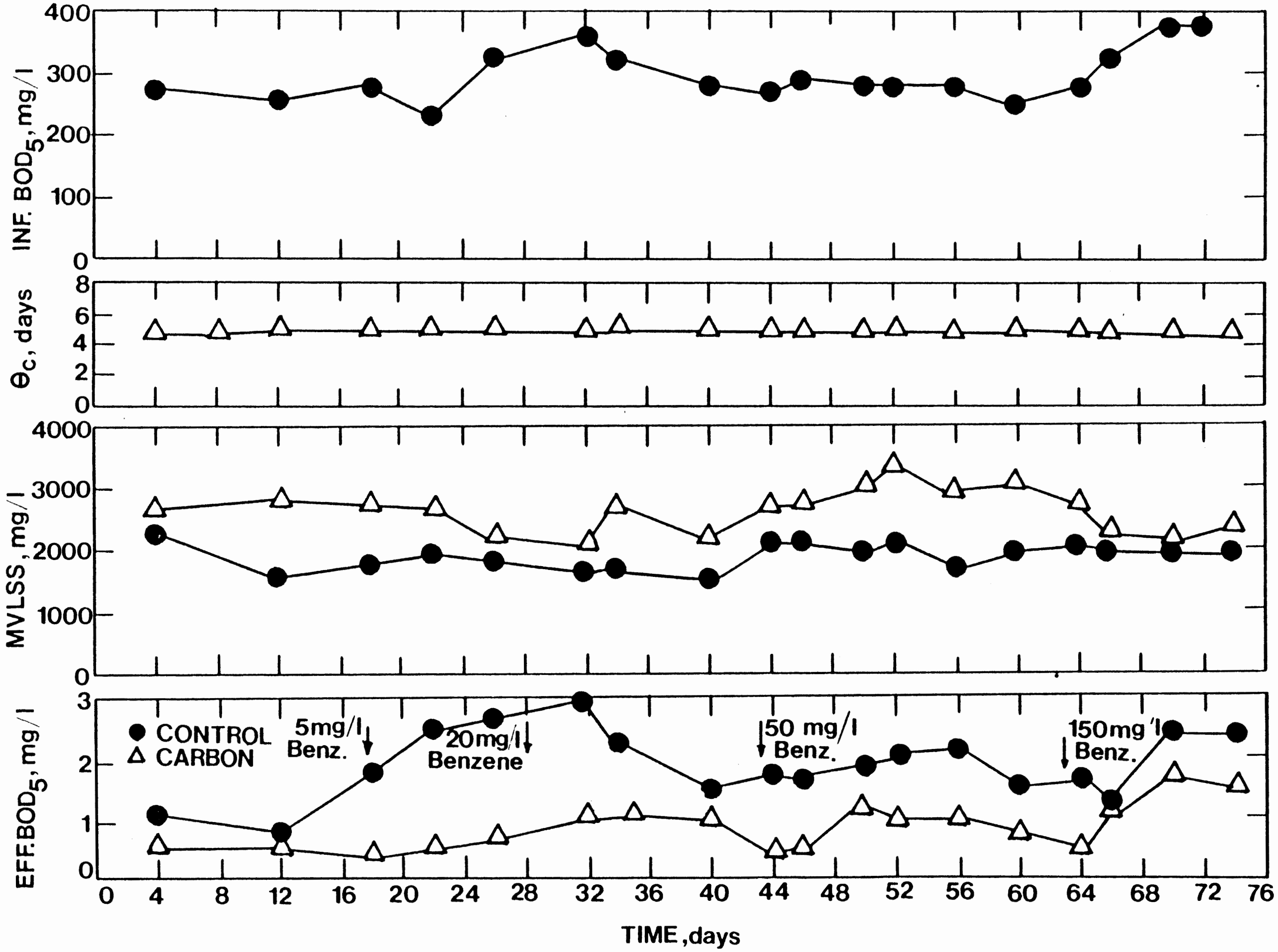
doses of benzene. Mean cell residence time was considered as the primary operational control parameter and it should be emphasized that the θ_cs for both units were accurately maintained at 5 days for the duration of the study. Influent and effluent substrate data are presented for BOD, COD and TOC in Figures 9, 10 and 11 respectively. Operational parameter (θ_c and MLVSS) are also presented. Mean values for the base mix feed period as well as for each of the shock load periods can be found in Table XII. As can be seen from the table, effluent BOD concentrations for conventional activated sludge units showed greater increases as the benzene concentration was increased than did the PAC unit. However, the magnitude of the increase was less than that observed for the 2 day unit (Table XI).

Unlike θ_c = 2 day, the θ_c = 5 day effluent COD concentration for conventional activated sludge showed a definite increase with increased benzene dosage. For θ_c = 5 day effluent COD concentration for PAC showed little variation between benzene dosages. For effluent TOC both PAC and conventional activated sludge showed increases with increasing benzene feed concentrations.

<u>5 mg/ℓ Benzene</u>

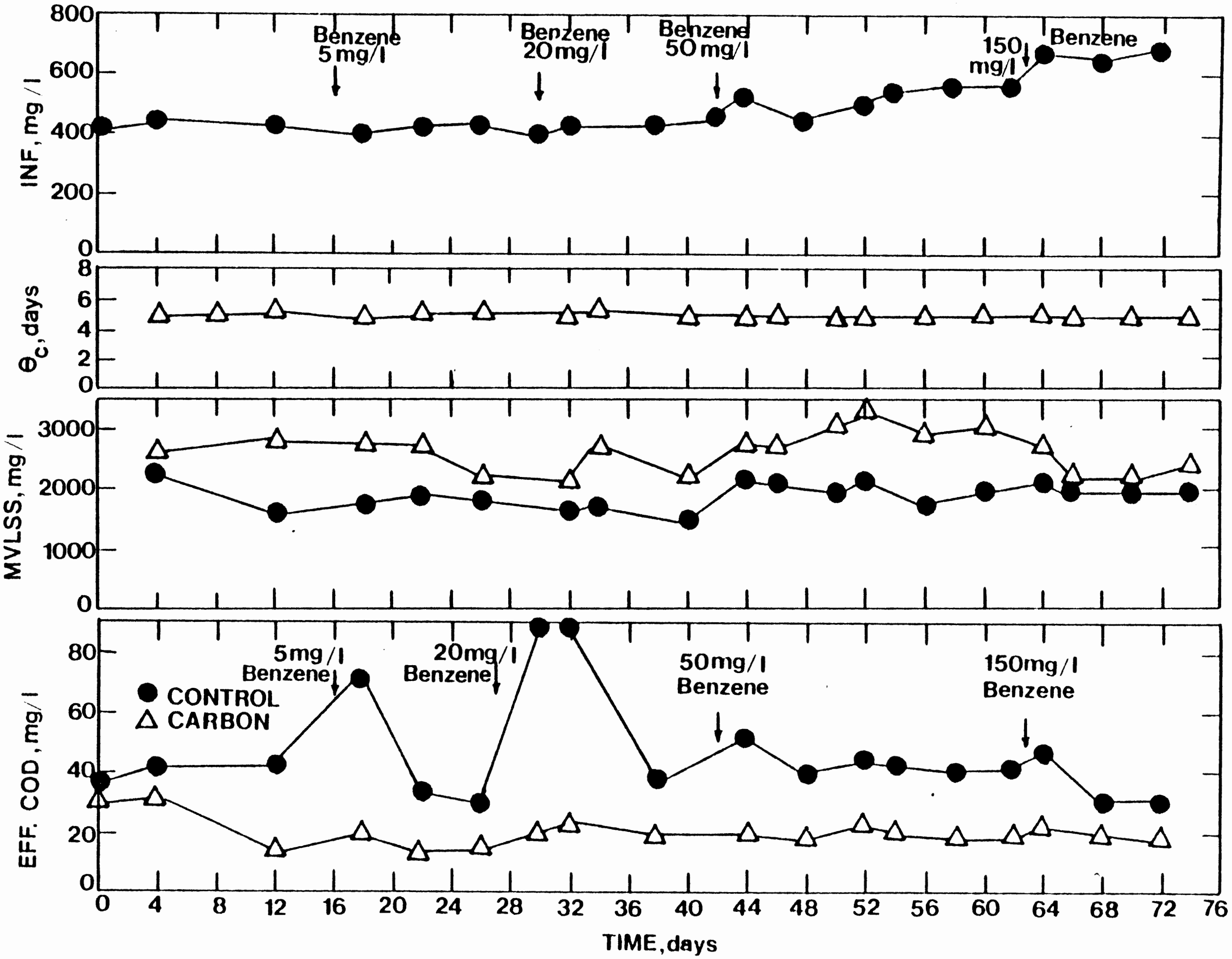
On day 17, the two units were subjected to a five mg/ℓ benzene shock load. Influent BOD analysis showed inconsistencies throughout various benzene dosages. This may be due to inherent variability of BOD test procedures. Influent BOD values range was between 236 and 330. Control unit BOD, COD and TOC increased 60, 13, and 30% during the period following the shock. PAC unit BOD and TOC increased 10 and 44% respectively over levels achieved during the period when only the base mix

Figure 9. Benzene Shock Load Studies; Influent and Effluent BOD Concentrations and Operational Parameters for Activated Sludge Systems ($\theta_c = 5$) with and without Powdered Activated Carbon (PAC).



INF. BOD$_5$, mg/l
400
300
200
100
0
θ$_c$, days
8
6
4
2
0
MVLSS, mg/l
4000
3000
2000
1000
0
EFF. BOD$_5$, mg/l
3
2
1
0
● CONTROL
△ CARBON
5mg/l Benz.
20mg/l Benzene
50 mg/l Benz.
150mg/l Benz.
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
TIME, days

Figure 10. Benzene Shock Load Studies; Influent and Effluent COD Concentrations and Operational Parameters for Activated Sludge Systems ($\theta_c = 5$) with and without Powdered Activated Carbon (PAC).



800
600
400
200
0
INF, mg/l
Benzene 5 mg/l
Benzene 20 mg/l
Benzene 50 mg/l
150 mg/l
Benzene
8
6
4
2
0
θ_c, days
3000
2000
1000
0
MVLSS, mg/l
80
60
40
20
0
EFF. COD, mg/l
5mg/l Benzene
20mg/l Benzene
50mg/l Benzene
150mg/l Benzene
● CONTROL
△ CARBON
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
TIME, days

Figure 11. Benzene Shock Load Studies; Influent and Effluent TOC Concentrations and Operational Parameters for Activated Sludge Systems ($\theta_c = 5$) with and without Powdered Activated Carbon (PAC).

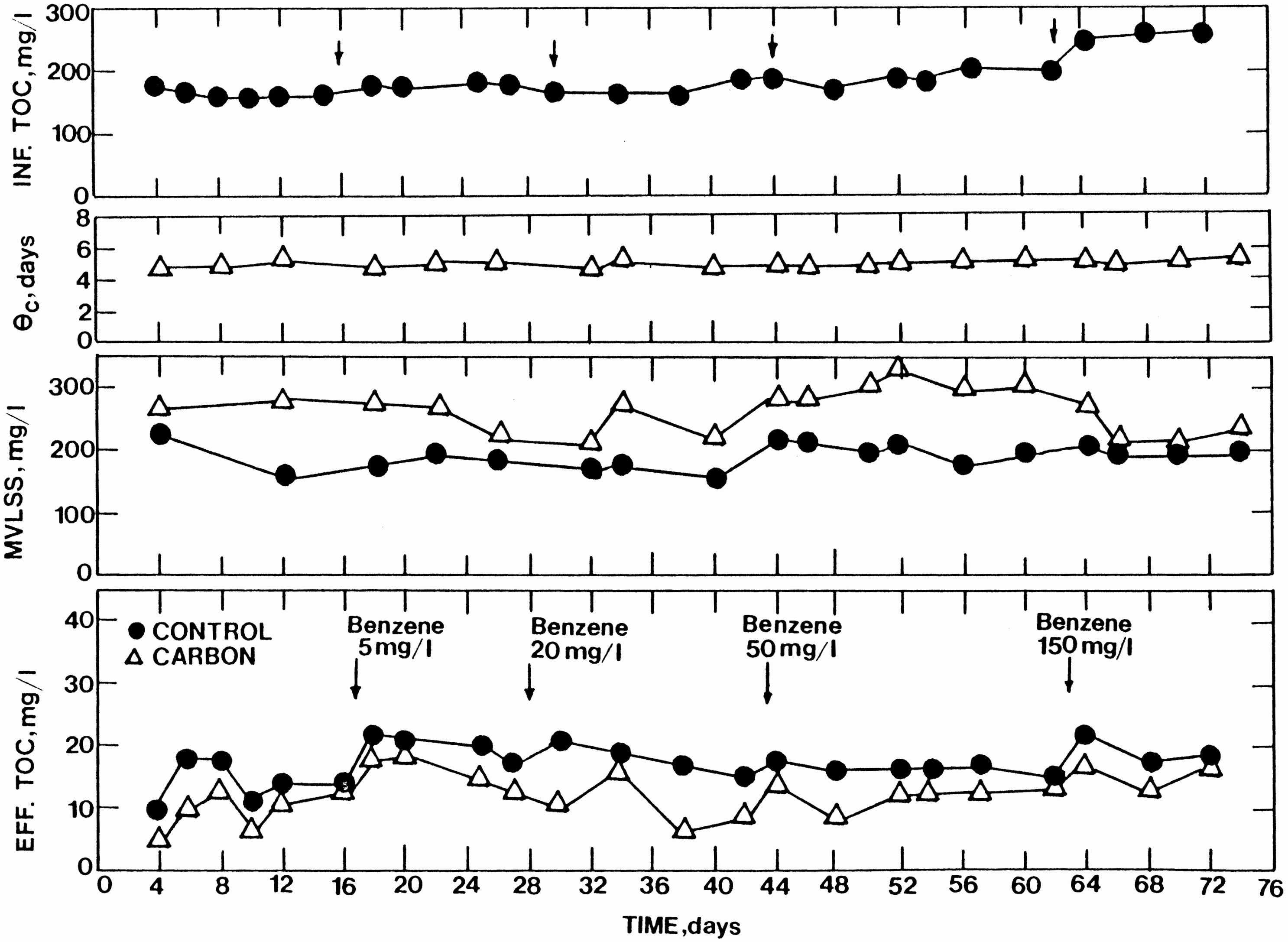

INF. TOC, mg/l
300
200
100
0
θc, days
8
6
4
2
0
MVLSS, mg/l
300
200
100
0
EFF. TOC, mg/l
40
30
20
10
0
● CONTROL
△ CARBON
Benzene 5 mg/l
Benzene 20 mg/l
Benzene 50 mg/l
Benzene 150 mg/l
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
TIME, days

TABLE XII

MEAN VALUE FOR EFFLUENT CONCENTRATION AND BIOLOGICAL SOLID FOR PHASE I SHOCK LOAD

$\theta_c = 5$ Benzene Conc. mg/ℓ	BOD_5		COD		TOC		MLVSS	
	I	II	I	II	I	II	I	II
0	0.95	0.60	39.2	26.1	13.8	10.2	1905	2782
5	2.33	0.67	45.2	15.8	9.75	18.25	1833	2329
20	2.1	0.87	74.1	21.3	17.75	10.75	1802	2550
50	1.78	0.94	44.0	19.80	15.1	12.6	2056.6	3054.5
150	1.94	1.33	36.7	20	19.30	17.0	1952	2238

I = Control Unit

II = PAC Unit

influent was administered. PAC unit CODs for the 5 mg/ℓ benzene shock load actually showed a slight decrease compared with the previous period. PAC unit BOD. COD and TOC were 70, 65 and 8% respectively lower than the control values recorded during the same period. PAC MLVSS averages 500 mg/ℓ higher than the control values.

Effluent benzene analyses for the control unit indicated a 225 μg/ℓ leakage the first day after the shock and 170 μg/ℓ on the second day but these concentrations dropped to 15 μg/ℓ after the fourth day. The PAC unit effluent benzene concentration was 160 μg/ℓ, the first day after shock but decreased to 10 μg/ℓ after three days, (Figure 12).

20 mg/ℓ Benzene

On day 28, the influent benzene concentration was increased to 20 mg/ℓ. The control unit BOD increased slightly (10%) for the first four days following the shock but later decreased to concentrations that were lower than the 5 mg/ℓ shock load period. Similar trends were noted for COD and TOC where initial increases were 150 and 25% respectively but, at the end of the 20 mg/ℓ dosage, COD and TOC values fell to or below the concentrations observed during the 5 mg/ℓ shock loads.

The PAC unit BOD and COD concentrations increased approximately 25% over levels observed during the 5 mg/ℓ shock load while TOC concentrations showed no increase. PAC BOD, COD and TOC were 60, 70 and 40% respectively lower than the control unit during this same period. PAC mixed liquor volatile suspended solids concentrations averaged 750 mg/ℓ higher than the control unit.

Figure 12. 5 mg/ℓ Benzene Shock Load; Influent and Effluent Concentration for Activated Sludge Systems ($\theta_c = 5$) with and without Powdered Activated Carbon (PAC).

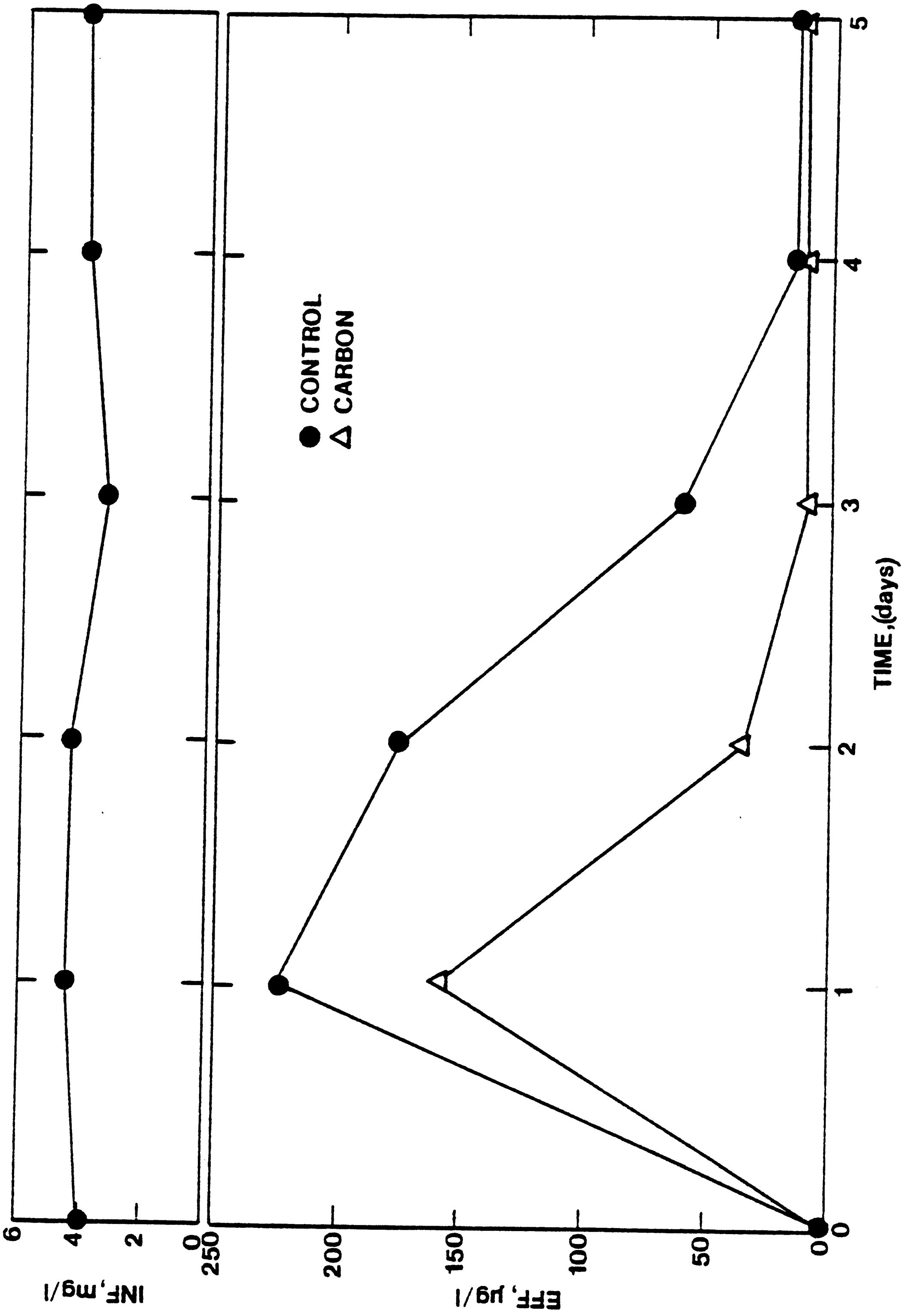
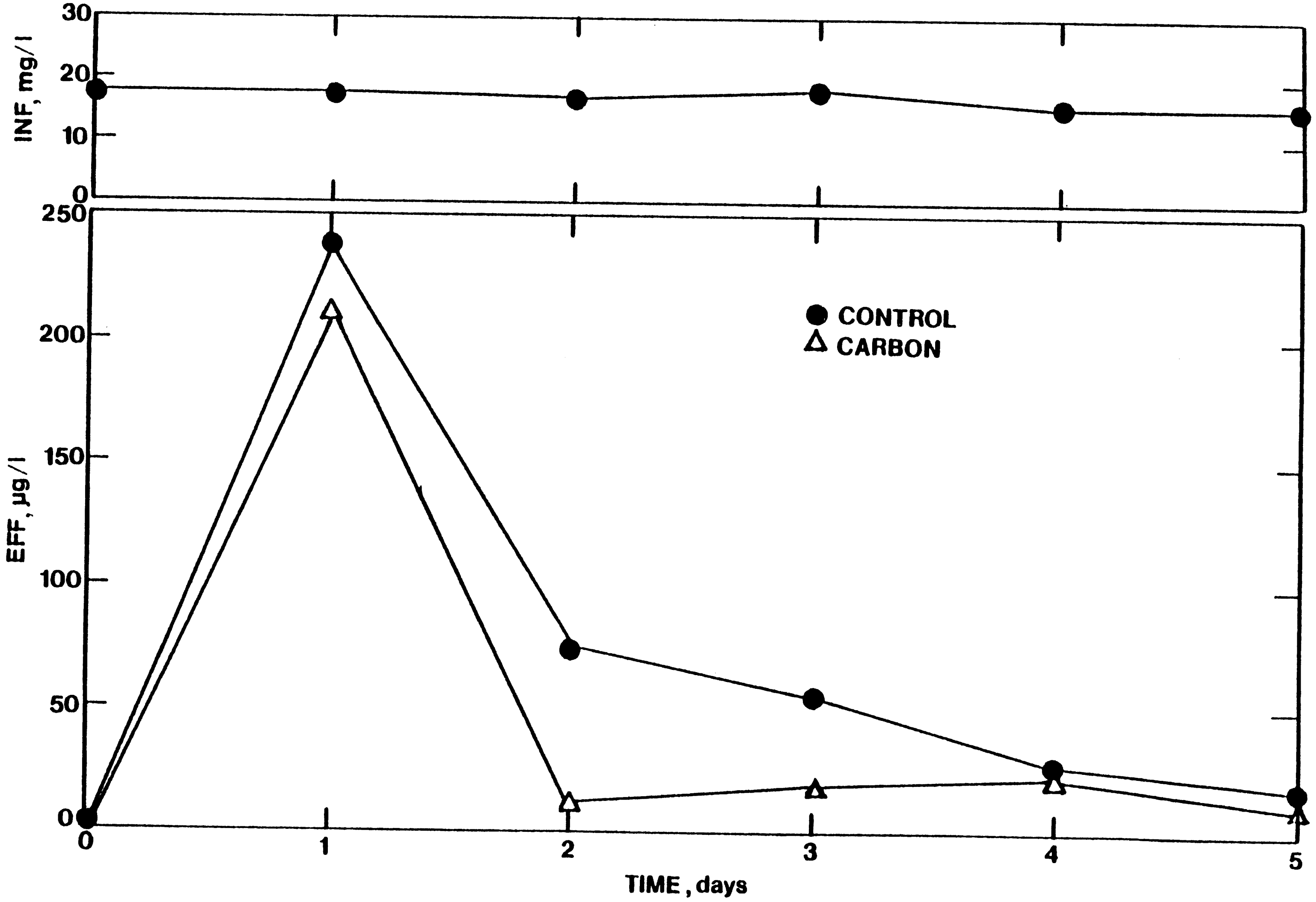

INF, mg/l
6
4
2
0
EFF, µg/l
250
200
150
100
50
0
0
1
2
3
4
5
TIME,(days)
● CONTROL
Δ CARBON

Figure 13. 20 mg/ℓ Benzene Shock Load; Influent and Effluent Concentration for Activated Sludge Systems (θ_c = 5) with and without Powdered Activated Carbon (PAC).


INF, mg/l
30
20
10
0
EFF, µg/l
250
200
150
100
50
0
0
1
2
3
4
5
TIME, days
● CONTROL
Δ CARBON

Benzene analyses for the 20 mg/ℓ shock load are presented in Figure 13. The control unit exhibited a 340 μg/ℓ benzene leakage during the first day, 75 μg/ℓ on day 2, 5 μg/ℓ on day 3 and 55 μg/ℓ on day 3, and 15 μg/ℓ on day 5. For the PAC unit the first day benzene leakage was only slightly attenuated (210 μg/ℓ) but the effluent benzene concentrations observed from day 2 to 5 were all less than 20 μg/ℓ.

50 mg/ℓ Benzene

On day 43, the influent benzene concentration was increased from 20 to 50 mg/ℓ. No significant increases in control BOD, COD, or TOC were observed. The same was true for the PAC unit. The PAC unit effluent BOD, COD, and TOC concentrations were respectively, 50, 55, and 16% lower than the control. PAC unit MLVSS values averaged 1000 mg/ℓ higher than those of the control unit.

Effluent benzene analyses for the control and PAC unit during this 50 mg/ℓ shock load are presented in Figure 14. The control unit effluent benzene concentration was 45 μg/ℓ after one day but dropped to 10 μg/ℓ by the third day. The PAC unit greatly attenuated the benzene leakage and on the first day allowed only 15 μg/ℓ to pass into the effluent. On the third day following the shock only 5 μg/ℓ benzene remained in the effluent.

150 mg/ℓ Benzene

On day 63 the benzene concentration was increased from 50 to 150 mg/ℓ. The control unit BOD and TOC increased slightly (10 and 20%) during the period following the shock. No significant increase was observed in control COD.

Figure 14. 50 mg/ℓ Benzene Shock Load; Influent and Effluent Concentration for Activated Sludge Systems (θ_c = 5) with and without Powdered Activated Carbon (PAC).

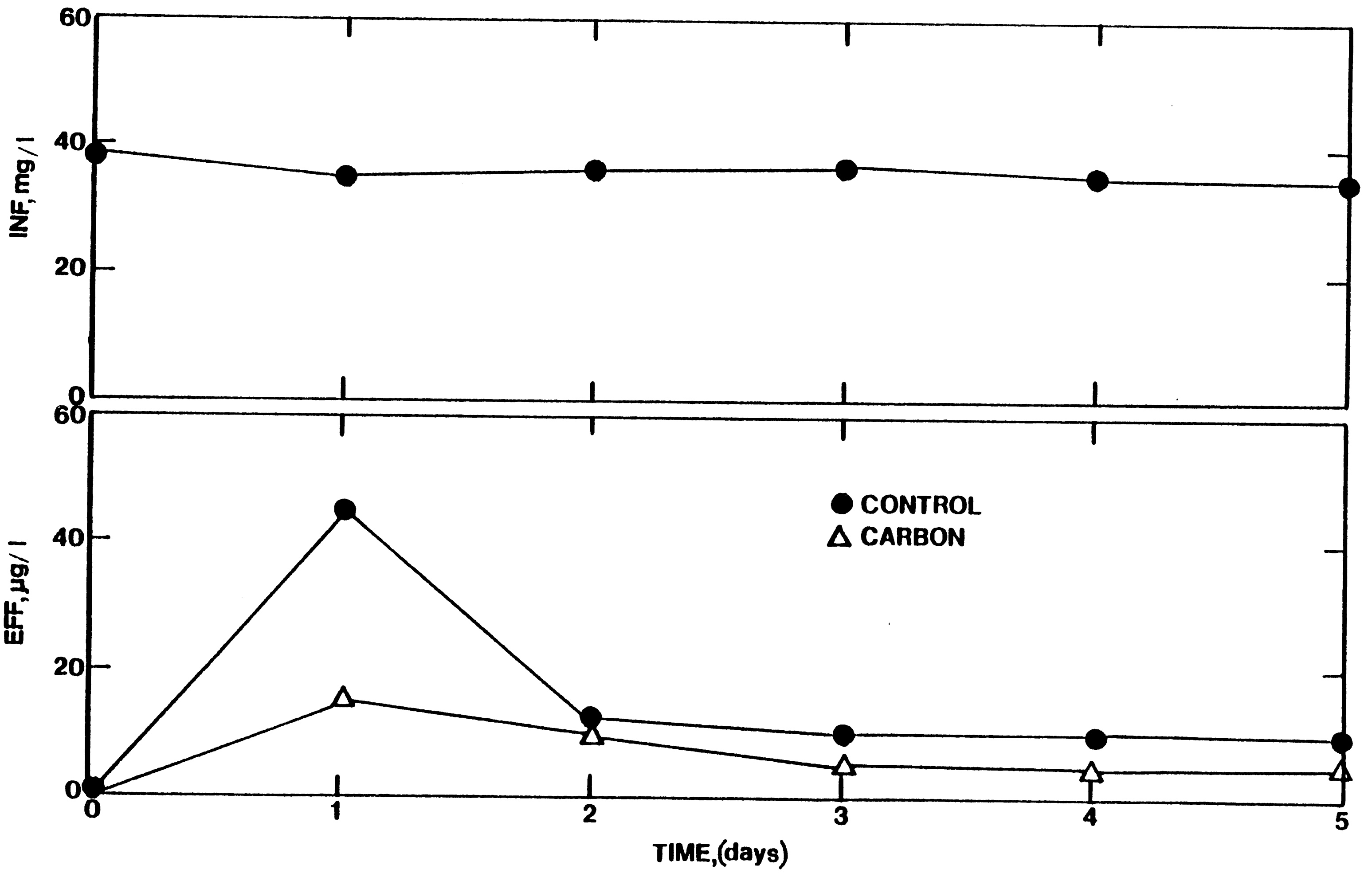
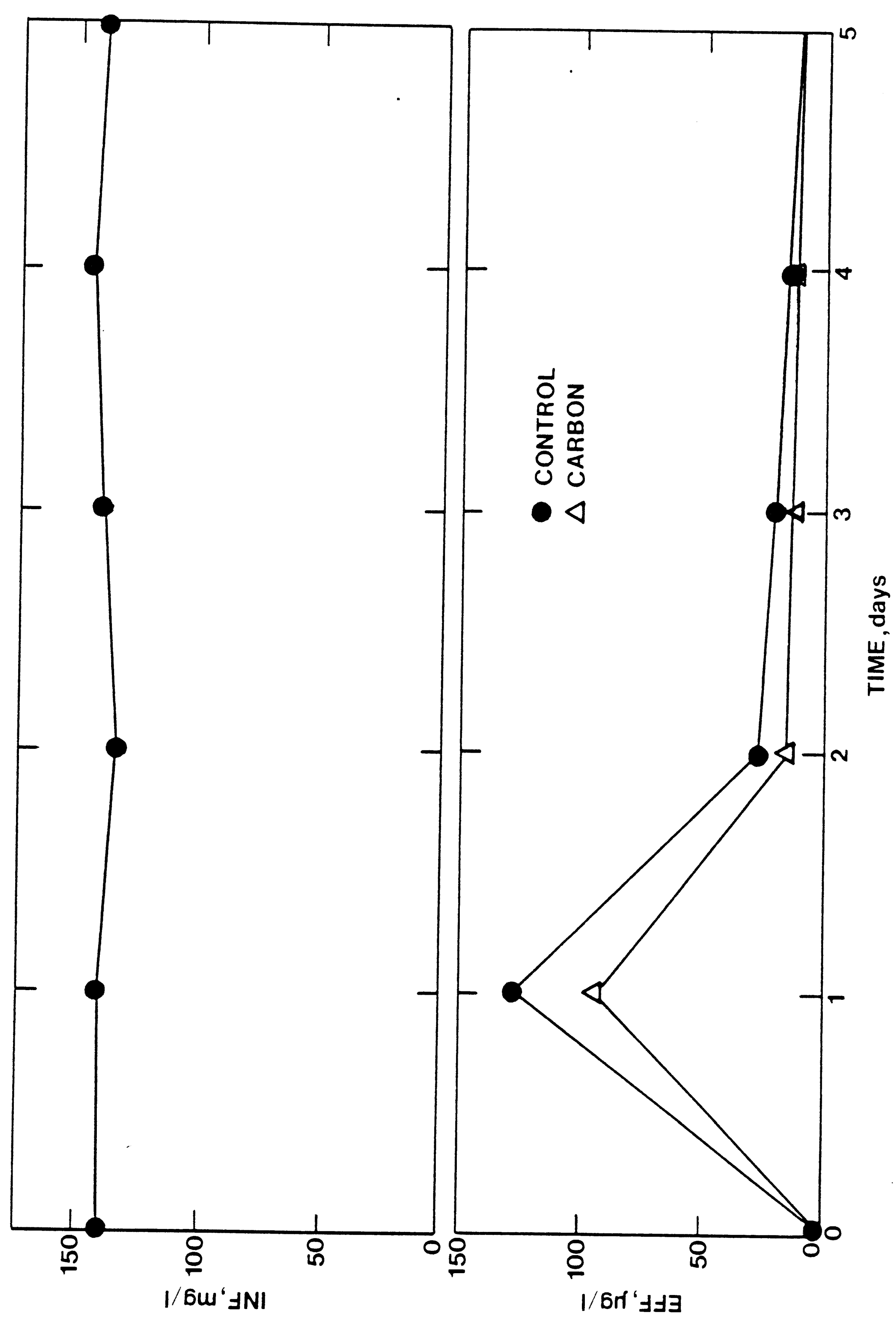

60
40
20
0
INF, mg/l
60
40
20
0
EFF, µg/l
● CONTROL
△ CARBON
0
1
2
3
4
5
TIME,(days)

Figure 15. 150 mg/ℓ Benzene Shock Load; Influent and Effluent Concentrations for Activated Sludge Systems ($\theta_c = 5$) with and without Powdered Activated Carbon (PAC).


INF, mg/l
150
100
50
0
EFF, μg/l
150
100
50
0
0
1
2
3
4
5
TIME, days
● CONTROL
△ CARBON

The PAC unit effluent substrate concentration showed only a slight decrease from the 50 mg/ℓ benzene shock load period. PAC BOD, COD, and TOC were 30, 34, and 12%, respectively, lower than the control unit during this same period. PAC unit MLVSS concentrations averaged 300 mg/ℓ higher than the control unit (Table XII).

Control unit benzene analysis (Figure 15) showed 130 μg/ℓ leakage of benzene one day after the shock, 35 μg/ℓ on the second day and 10 μg/ℓ after the fifth day. The PAC unit effluent was 95 μg/ℓ after the first day but dropped to 15 μg/ℓ after the second day.

Protein

One problem area in the PAC process has been how to differentiate between active cell mass and activated carbon. An attempt was made to solve this problem by analyzing protein content of sludge. Figures 16 and 17 illustrate the plot of sludge protein concentration versus mixed liquor suspended solids concentration for the PACT and conventional activated sludge units which were subjected to various influent benzene dosages. The slopes of best fit were drawn for each figure. For the conventional unit a slope of 0.5 indicated that 50% of the mixed liquor suspended solids was protein while the PAC unit slope indicated that 40% of the mixed liquor suspended solids was protein, so a difference of 10% is due to PAC. However, much scatter was observed and the carbon seemed to interfere with analytical protein determination (biomass technique).

Figure 16. Protein Content of Biomass in Powdered Activated Carbon (PAC) Unit.

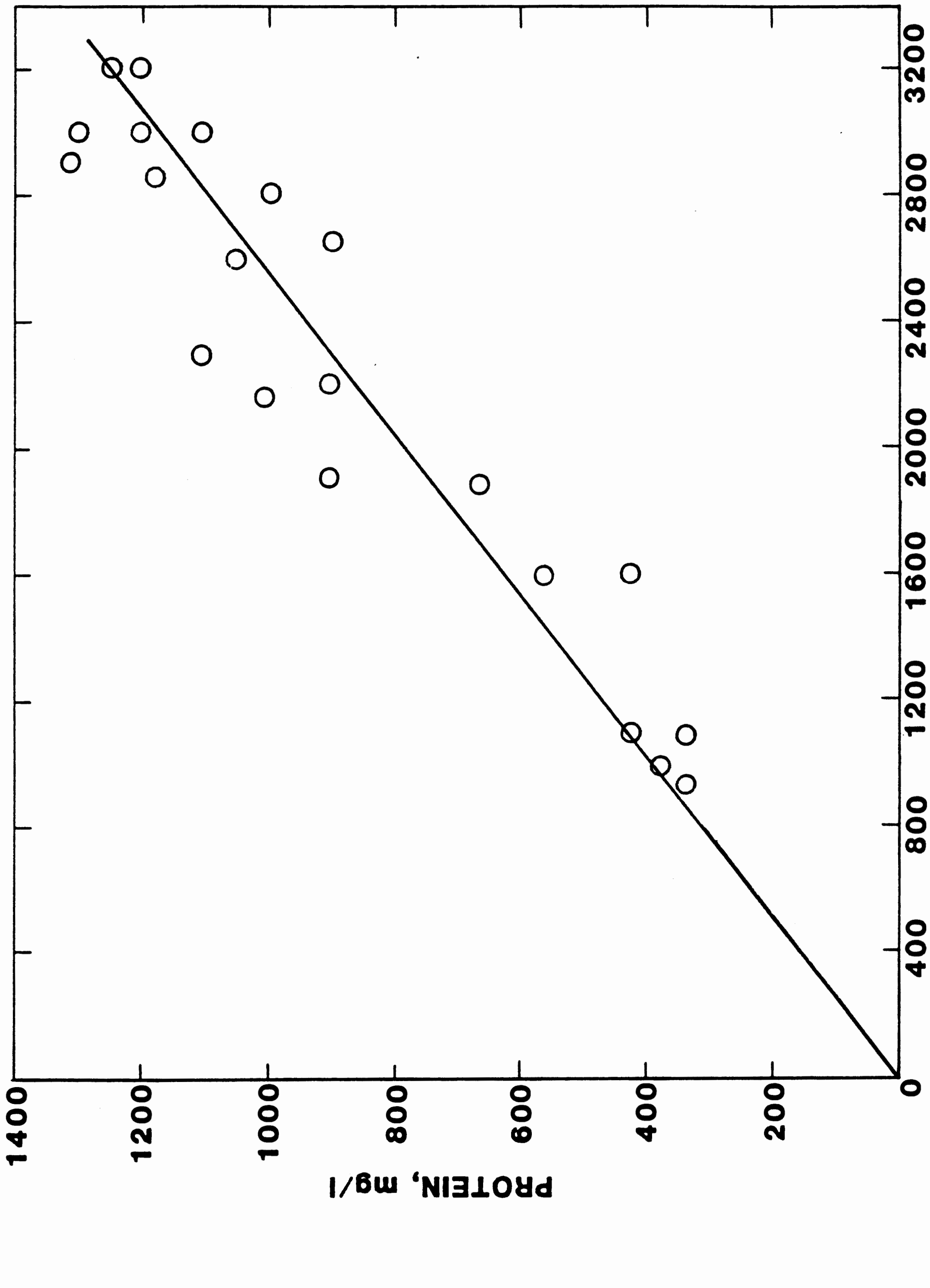
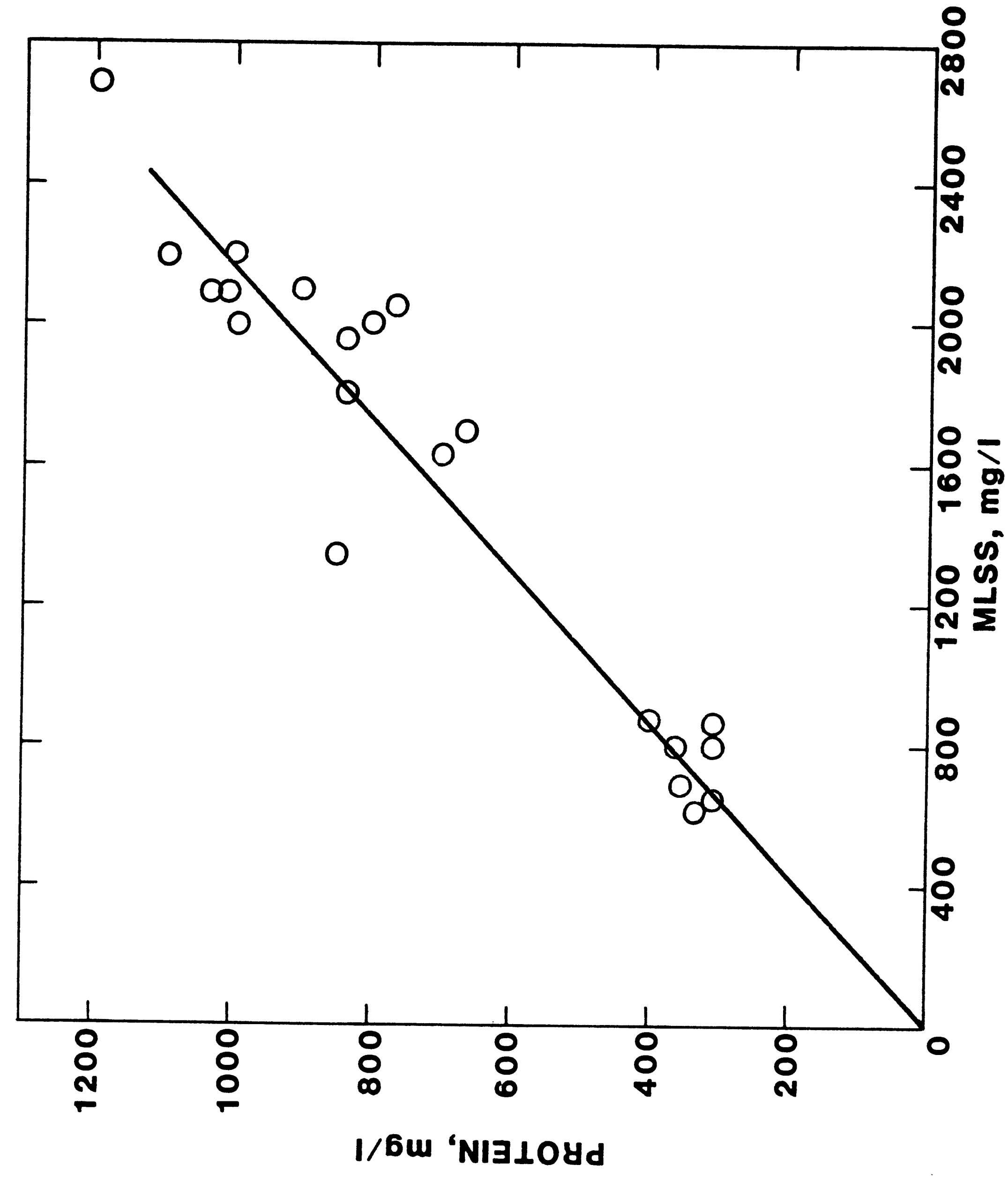

PROTEIN, mg/l
1400
1200
1000
800
600
400
200
0
400
800
1200
1600
2000
2400
2800
3200
MLSS, mg/l

Figure 17. Protein Content of Biomass in Control Unit.


PROTEIN, mg/l
1200
1000
800
600
400
200
0
400
800
1200
1600
2000
2400
2800
MLSS, mg/l

Phase II

General

During the second phase of this study, four wastewaters were subjected to activated sludge/PAC treatment and the resultant effect upon effluent substrate concentrations (in terms of BOD, COD, TOC, and specific compounds) was determined. Wastewaters contained base mix and selected priority pollutants (toluene, ethylbenzene, and 1,2 dichloroethane. Two mean cell residence times (3 and 12 days) and several carbon dosages (including a control period where no carbon was added) were investigated.

Toluene

Two bench-scale internal recycle activated sludge units were subjected to a synthetic wastewater composed of base mix and 100 mg/ℓ toluene. One of these units was operated at θ_c = 3 days while the other was controlled at θ_c = 12 days. Both units were subjected to carbon dosages of 0,25, 50, 75, and 100 mg/ℓ (based upon influent flow rate). At each condition, the biological units were operated until steady state with respect to MLVSS and substrate analyses was achieved. Figures 18, 19, 20, and 21 present mean steady state influent and effluent substrate concentrations obtained for the various carbon dosages for BOD, COD, TOC, and Toluene, respectively. These results are also summarized in Table XIII. MLVSS concentrations are also presented for both units. From these figures can be seen that additional reduction in effluent substrate concentration was minimal beyond the 50 mg/ℓ PAC concentration. The 50 mg/ℓ PAC dosage reduced effluent BOD to 1.62 mg/ℓ

Figure 18. The Effect of Powdered Activated Carbon (PAC) Dosage and θ_c upon the Performance of Activated Sludge Systems (BOD_5) Receiving a Wastewater Containing Toluene.

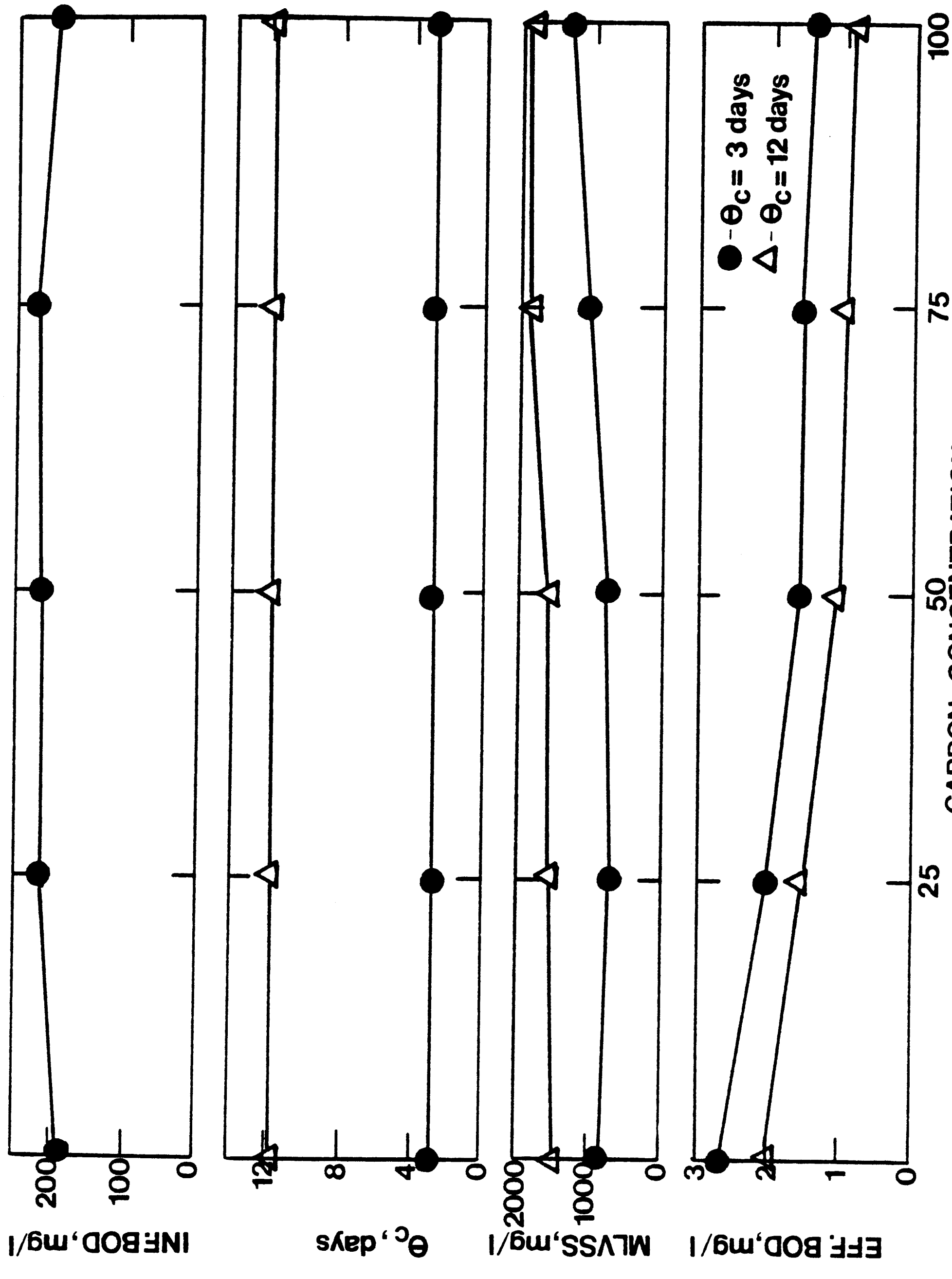

INF BOD, mg/l
200
100
0
θc, days
12
8
4
0
MLVSS, mg/l
2000
1000
0
EFF. BOD, mg/l
3
2
1
0
● - θc = 3 days
Δ - θc = 12 days
25
50
75
100
CARBON CONCENTRATION, mg/l

Figure 19. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of Activated Sludge Systems (COD) Receiving a Wastewater Containing Toluene.

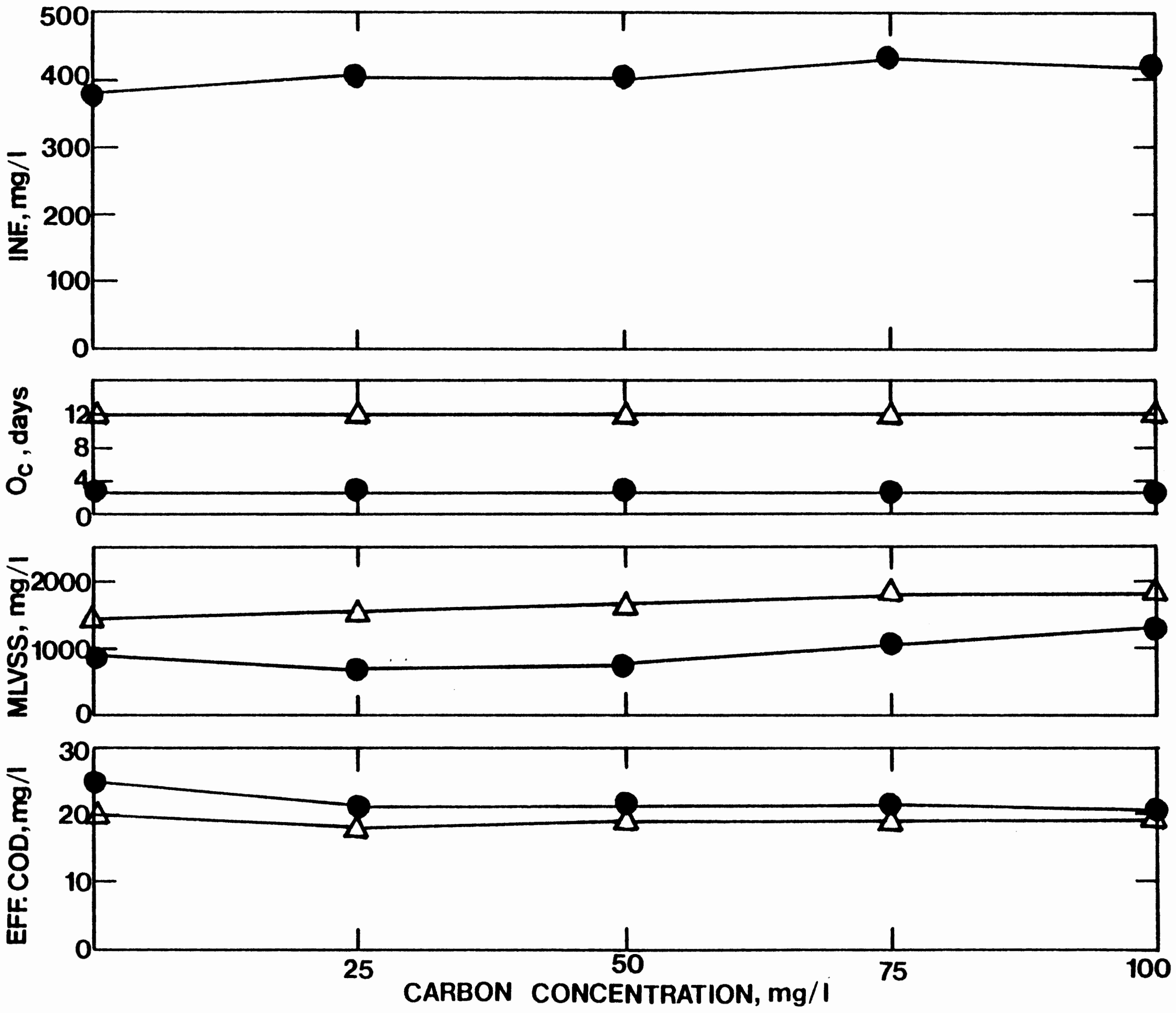

500
400
300
200
100
0
INF., mg/l
12
8
4
0
O_c , days
2000
1000
0
MLVSS, mg/l
30
20
10
0
EFF. COD, mg/l
25
50
75
100
CARBON CONCENTRATION, mg/l

Figure 20. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of an Activated Sludge System (TOC) Receiving a Wastewater Containing Toluene.

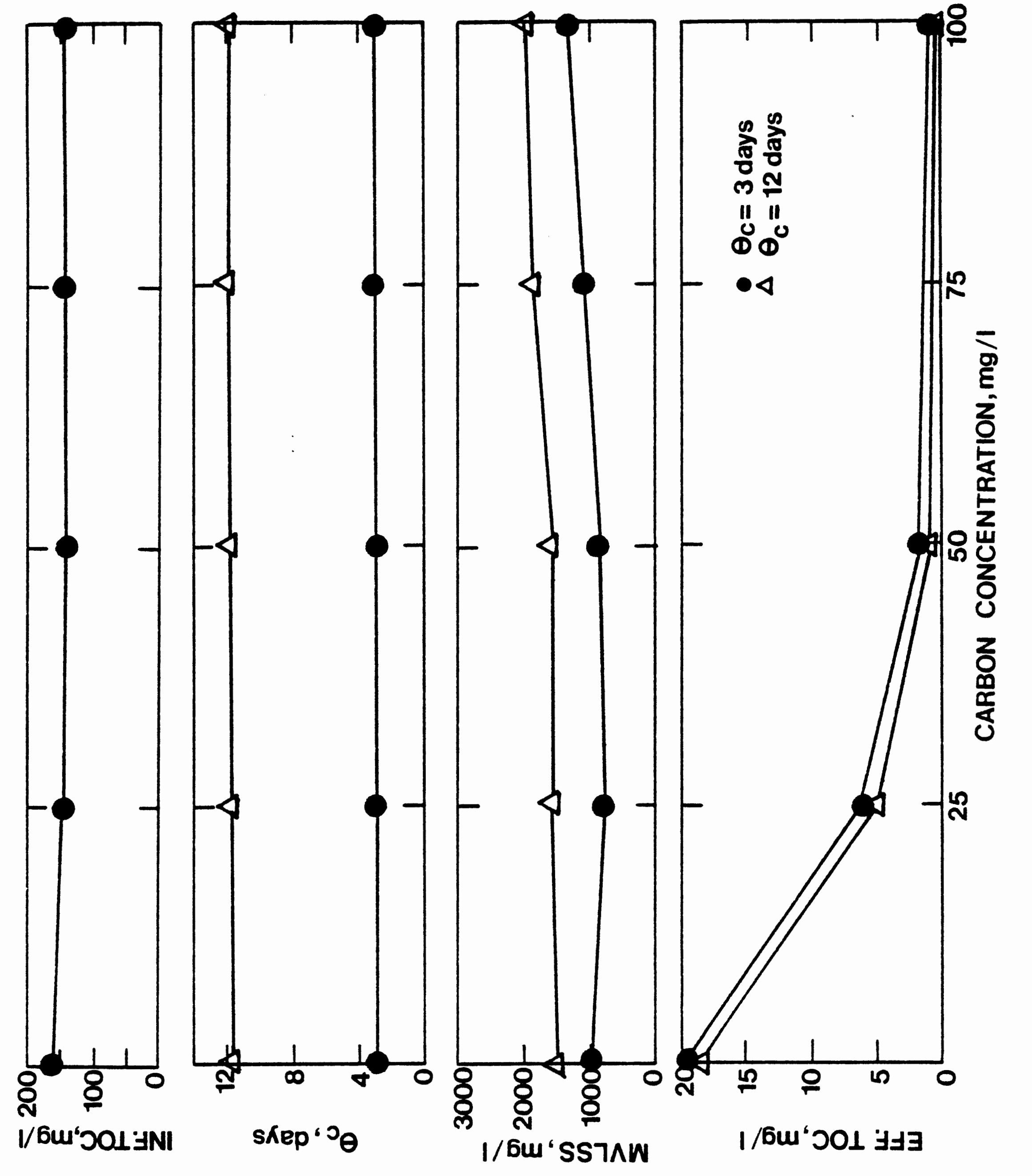

INF TOC, mg/l
200
100
0
θc, days
12
8
4
0
MVLSS, mg/l
3000
2000
1000
0
EFF TOC, mg/l
20
15
10
5
0
CARBON CONCENTRATION, mg/l
25
50
75
100
● θc = 3 days
Δ θc = 12 days

Figure 21. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon Effluent Toluene Concentration of Activated Sludge Systems Receiving a Wastewater Containing Toluene.

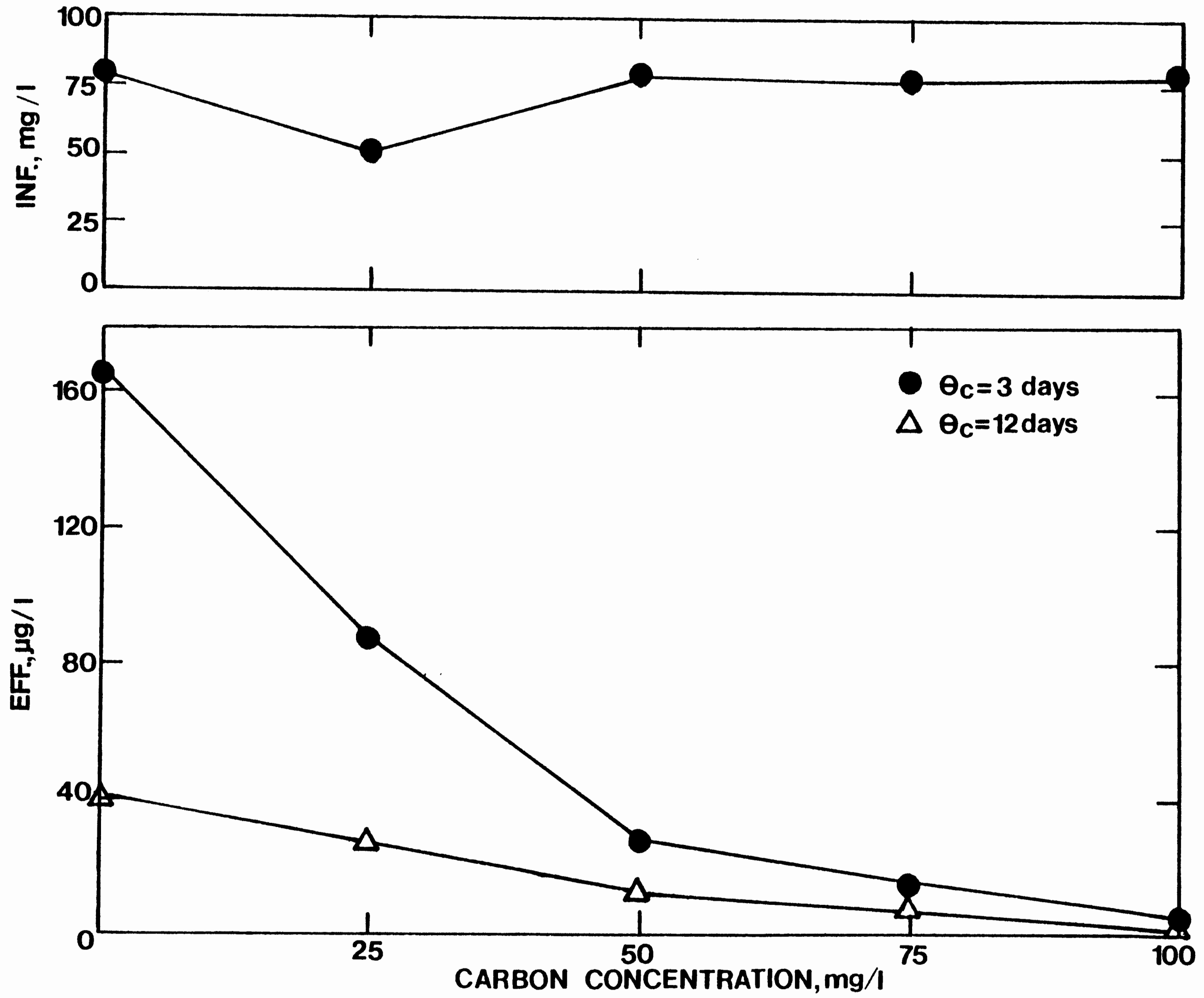

INF., mg / l
100
75
50
25
0
EFF., µg / l
160
120
80
40
0
25
50
75
100
CARBON CONCENTRATION, mg/l
● θc = 3 days
△ θc = 12 days

TABLE XIII

MEAN VALUE FOR EFFLUENT CONCENTRATION AND BIOLOGICAL SOLIDS FOR TOLUENE

Carbon dosage mg/ℓ	Mean Value									
	BOD mg/ℓ		COD mg/ℓ		TOC mg/ℓ		MLVSS mg/ℓ		GC µg/ℓ	
	I	II	I	II	I	II	I	II	I	II
0	27.0	21.0	25	20	19.0	17.0	778	1548	165	40
25	2.06	165	21	18	7.0	5	880	1540	87.5	27
50	1.62	1.10	21	19	3.5	25	916	1568	27	13.5
75	1.60	1.0	21	19	3.5	2.5	1148	1968	16	7
100	1.45	0.90	20	19	3.0	2.0	1258	1992	4	2

(additional 40% reduction when compared to the carbon dosage of 0. mg/ℓ) in the 3 day unit, while the 12 day unit BOD fell to 1.1 mg/ℓ (additional 50% reduction). The effluent COD concentration in the three day unit after addition of 50 mg/ℓ PAC was 21 mg/ℓ (additional 16% reduction), and in the 12 day unit the effluent COD concentration was 19 mg/ℓ (additional 5% reduction. As for effluent TOC, 2.5 mg/ℓ (additional 75% reduction) was observed for θ_c - 3 days after the 50 mg/ℓ PAC additions, while the 12 day effluent had 2.5 mg/ℓ (additional 85% reduction). With respect to toluene analyses, the effluent for the 3 day unit decreased from 165 μg/ℓ when no carbon was added to 27 μg/ℓ after 50 mg/ℓ PAC addition (additional reduction of 84%. The 12 day θ_c unit decreased from a 0 mg/ℓ carbon dosage toluene concentration of 40 μg/ℓ to 13.5 μg/ℓ after addition of 50 mg/ℓ PAC (additional reduction of 60%). After addition of 100 mg/ℓ PAC, both the 3 day and 12 day effluent toluene concentration decreased to less than 4 μg/ℓ .

For corresponding carbon dosages the unit operated at the 12 day θ_c had lower effluent substrate concentrations than the 3 day unit. For BOD, the 12 day effluent was 0.5 to 0.6 mg/ℓ lower than the 3 day unit for all carbon dosages. The 12 day unit had an effluent COD concentration 3 to 5 mg/ℓ lower than the 3 day unit at all corresponding carbon doses while the TOC was 1 to 2 mg/ℓ lower for the 12 day unit. For effluent toluene analyses, the 12 day unit was 2 to 125 g/ℓ lower than the 3 day unit. It should be pointed out that, in general, differences between the 3 and 12 day unit effluent substrate concentration became less obvious as carbon dosage was increased.

MLVSS for the 3 day unit when no carbon was added were 778 mg/ℓ and increased to 1258 mg/ℓ when 100 mg/ℓ carbon was added. For the 12 day unit, the MLVSS was 1548 mg/ℓ when the carbon dosage was 0 but increased to 1992 mg/ℓ when the carbon dosage was increased to 100 mg/ℓ.

An effort was made to ascertain the fate of the toluene administered in the feed through the biological treatment process. Influent, effluent, off-gas, and sludge toluene analyses were performed for each θ_c during each of the carbon dosing periods. A suitable technique for analyzing the sludge samples was not found. Therefore, the results obtained by the method utilized are not considered reliable. Table XIV and Figure 22 present the results of the analyses incorporated to determine the fate of the toluene. The heading "percent" is used to denote the percentage of the toluene fed during the test period that was found in a particular area (effluent, off-gas, or adsorbtion/biological removal). Due to the unreliable sludge results, it was not possible to distinguish between biological oxidation, biological adsorption, and carbon adsorption.

For the 3 day θ_c unit, as carbon dosage was increased from zero to 100 mg/ℓ the percent of administered toluene found in the effluent decreased from 0.2 to 0.02. The percent of administered toluene found in the off-gas decreased from 16.7 to 2.7 during the same carbon dosing periods. By difference, the percent found to be degraded or adsorbed increased from 84 to 97 percent.

For the 12 day θ_c system, as the carbon dosage was increased from zero to 100 mg/ℓ, the percent of the toluene administered which was found in the effluent decreased from .05 to .005. For the off-gas, the toluene recovered decreased from 12.6 to 0.8 percent as the carbon dosage was increased from 0 to 100 mg/ℓ. By difference, the amount of the

TABLE XIV

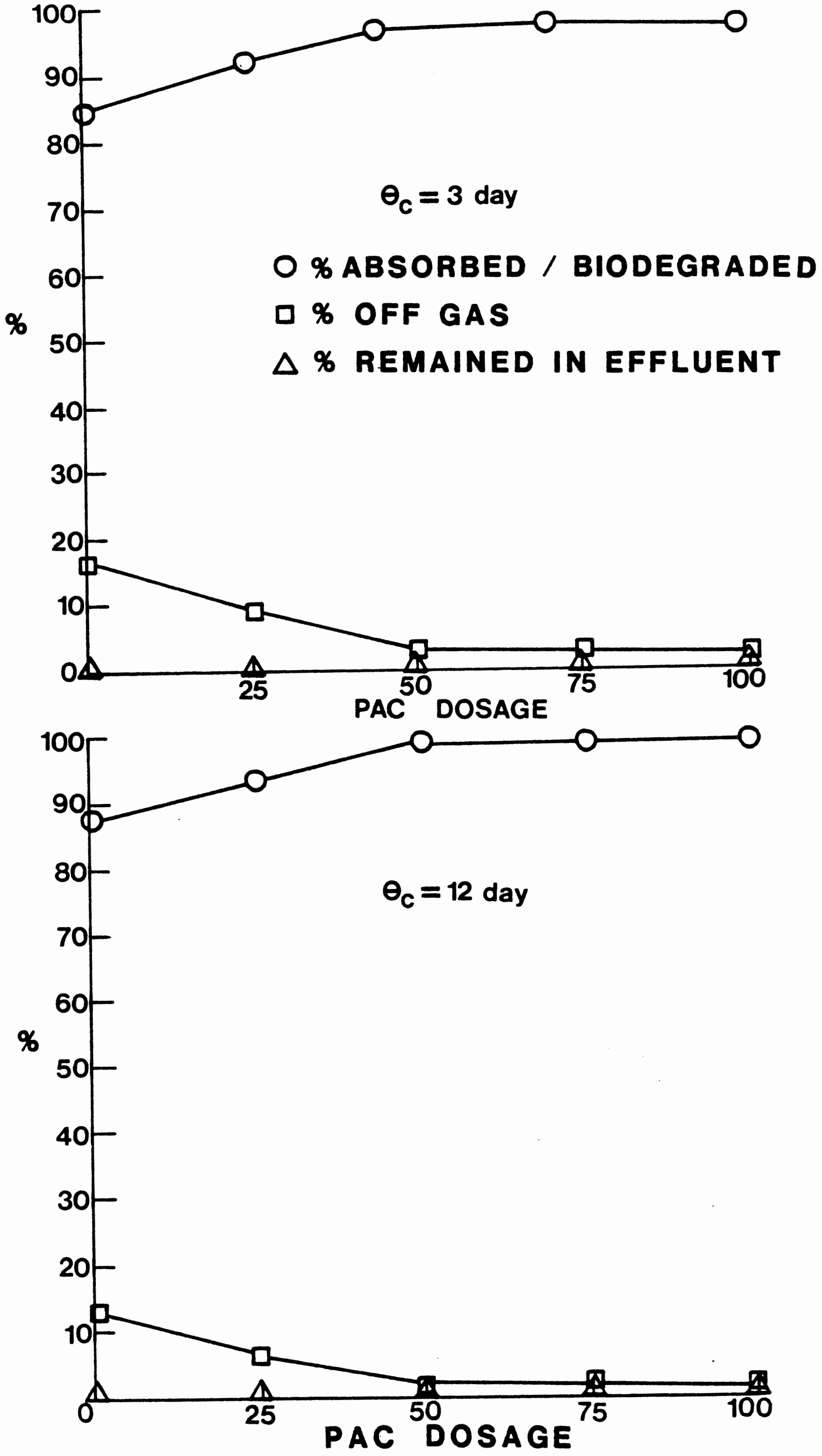
FATE OF TOLUENE

PAC dosage mg/ℓ	Influent mg/ℓ	% Toluene Remaining in Effluent		Total Percent Removed		Percent Stripped		Percent Adsorbed and Biodegraded	
		I	II	I	II	I	II	I	II
0	80	0.20	0.05	99.80	99.95	15.7	12.6	83.9	87.3
25	56	0.16	0.05	99.85	99.95	9.0	6.4	90.7	93.5
50	92.5	0.03	0.015	99.97	99.98	2.70	1.0	97.2	98.96
75	78.5	0.02	0.005	99.98	99.99	2.0	1.0	97.96	98.98
100	80	0.005	0.0025	99.99	99.99	2.0	1.0	97.98	98.98

I = θ_c = 3

II = θ_c = 12

Figure 22. Removal of Toluene in PAC Systems.


100
90
80
70
60
50
40
30
20
10
0
%
θc = 3 day
○ % ABSORBED / BIODEGRADED
□ % OFF GAS
△ % REMAINED IN EFFLUENT
25
50
75
100
PAC DOSAGE
100
90
80
70
60
50
40
30
20
10
%
θc = 12 day
0
25
50
75
100
PAC DOSAGE

administered toluene found to be degraded or adsorbed increased from 87 to 99.9 percent.

Ethylbenzene

In this part of the study, 80 mg/ℓ ethylbenzene was added to the base mix feed and used as a synthetic wastewater. Two units were operated, one at a θ_c equal to 3 day and the other operated at θ_c equal to 12 day. Both units were subjected to carbon dosage of 5, 10, 20, 30, 35, and 50 mg/ℓ (based upon influent flow rate). At each carbon dosage condition, the biological units were operated until steady state was achieved with respect to MLVSS and substrate analysis. Figures 23, 24, 25, and 26 present mean steady state influent and effluent substrate concentrations obtained for both units at various carbon dosages for BOD, COD, TOC, and ethylbenzene respectively. These results are also summarized in Table XV. Mixed liquor volatile suspended solids concentrations are also presented for both units (3 and 12 day). Figures 22, 23, and 24 show that additional reduction of effluent substrate concentration was minimal beyond a 35 mg/ℓ powdered activated carbon (PAC) dosage. The 35 mg/ℓ PAC dosage reduced effluent BOD, COD, and TOC to 1.80, 29 and 18.5 mg/ℓ in the 3 day unit, while they were 2.2, 40 and 40 before addition of any PAC. The percent reduction after addition of PAC for BOD, COD, and TOC was 18, 27.5 and 53%, respectively.

For the 12 day unit, it can be seen that 35 mg/ℓ PAC reduced BOD, COD, and TOC substrate concentration 37.5, 39, and 53% (when compared with 0 mg/ℓ PAC). Figure 25 shows that the effluent ethylbenze concentration decreased from 140 μg/ℓ to 5 μg/ℓ (additional 5% reduction) with only 35 mg/ℓ PAC.

Figure 23. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of Activated Sludge Systems (BOD_5) Receiving a Wastewater Containing Ethylbenzene.

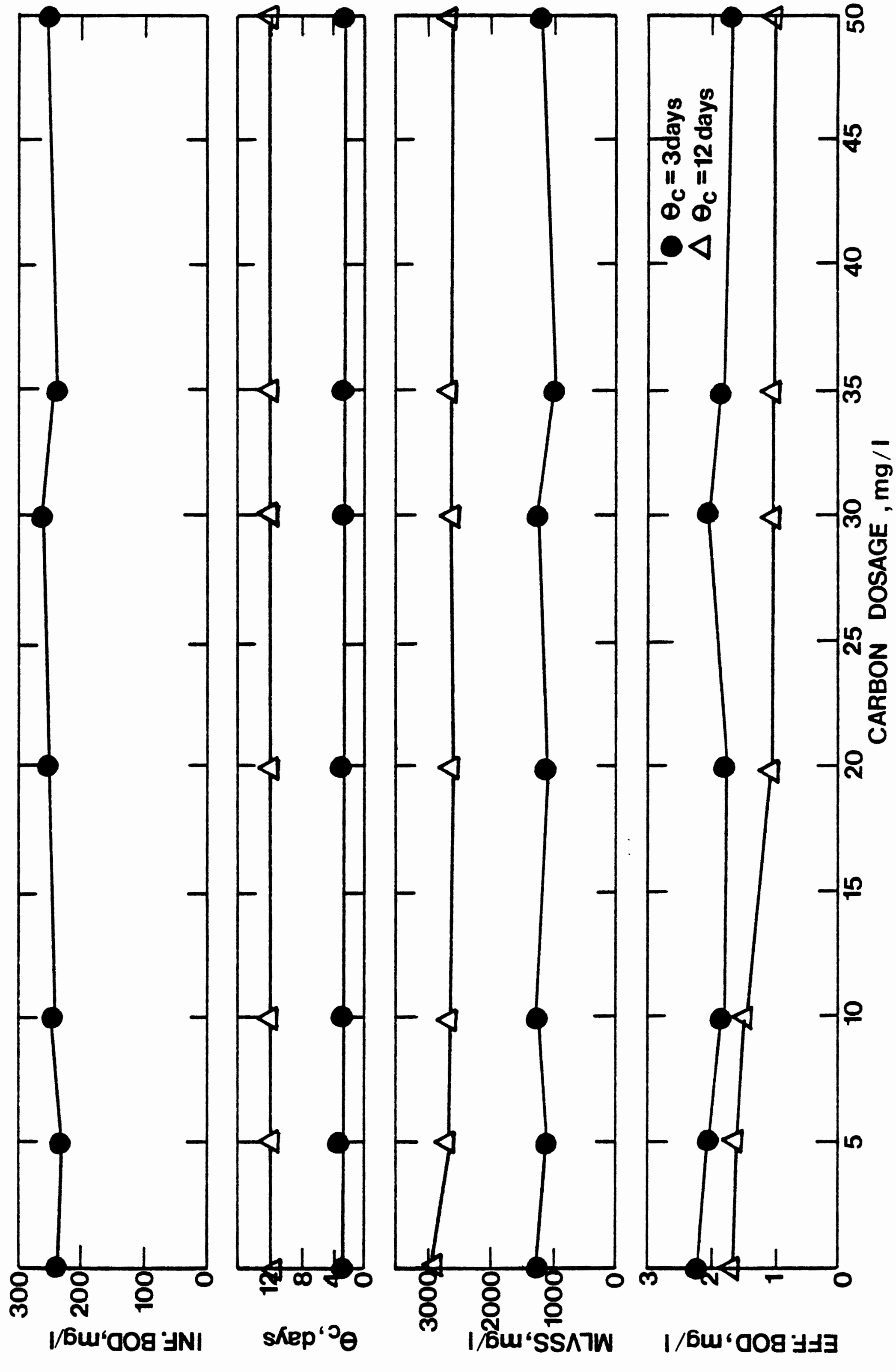

INF. BOD, mg/l
300
200
100
0
θ_c, days
12
8
4
0
MLVSS, mg/l
3000
2000
1000
0
EFF. BOD, mg/l
3
2
1
0
● θ_c = 3days
△ θ_c = 12 days
5
10
15
20
25
30
35
40
45
50
CARBON DOSAGE, mg/l

Figure 24. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of Activated Sludge Systems (COD) Receiving a Wastewater Containing Ethylbenzene.

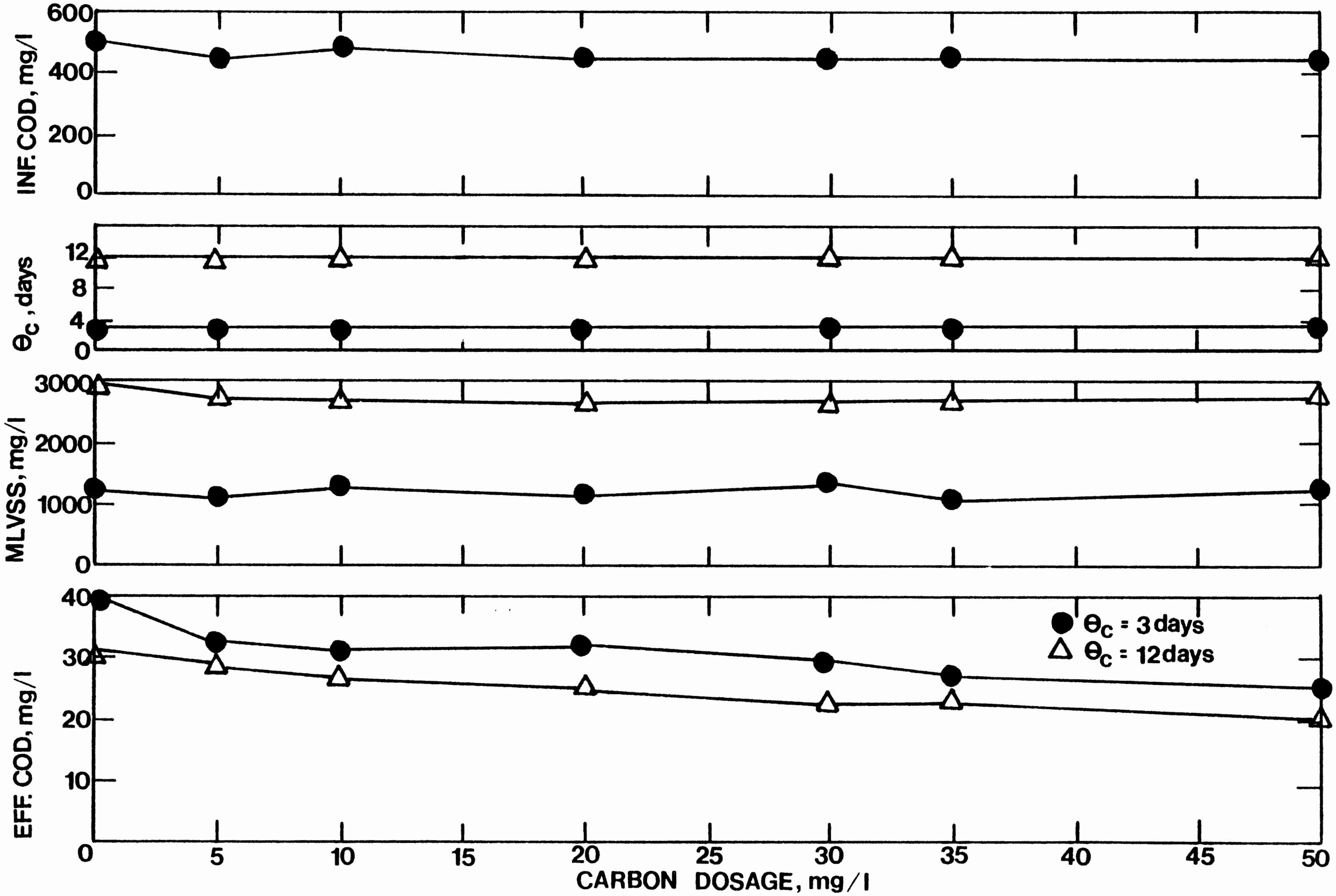

INF. COD, mg/l
600
400
200
0
θc , days
12
8
4
0
MLVSS, mg/l
3000
2000
1000
0
EFF. COD, mg/l
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
50
CARBON DOSAGE, mg/l
● θc = 3 days
△ θc = 12 days

Figure 25. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of Activated Sludge Systems (TOC) Receiving a Wastewater Containing Ethylbenzene.

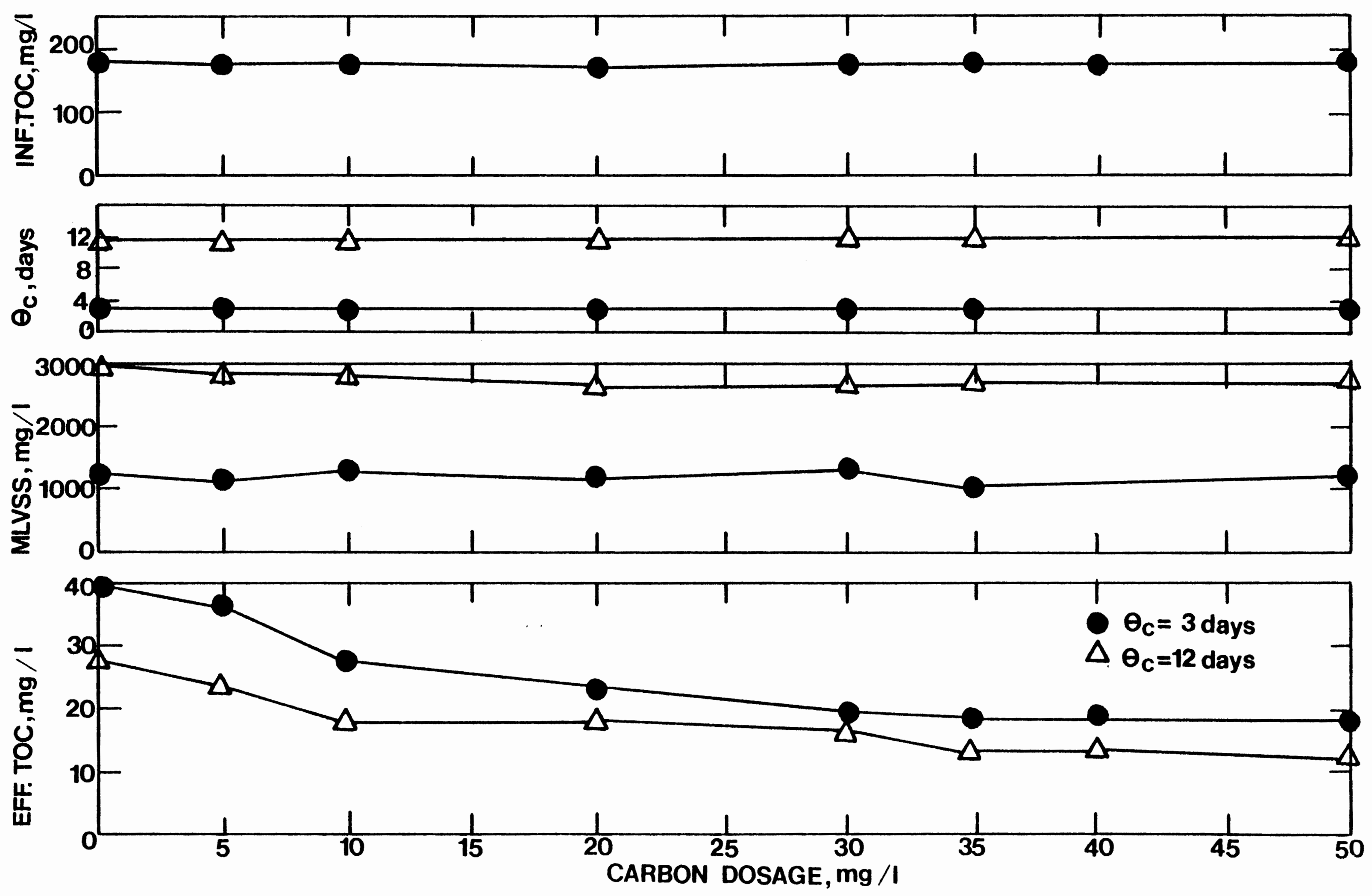

INF.TOC, mg/l
200
100
0
θ_c, days
12
8
4
0
MLVSS, mg/l
3000
2000
1000
0
EFF. TOC, mg / l
40
30
20
10
0
5
10
15
20
25
30
35
40
45
50
CARBON DOSAGE, mg / l
● θ_c = 3 days
△ θ_c = 12 days

Figure 26. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon Effluent Ethylbenzene Concentration of Activated Sludge Systems Receiving a Wastewater Containing Ethylbenzene.

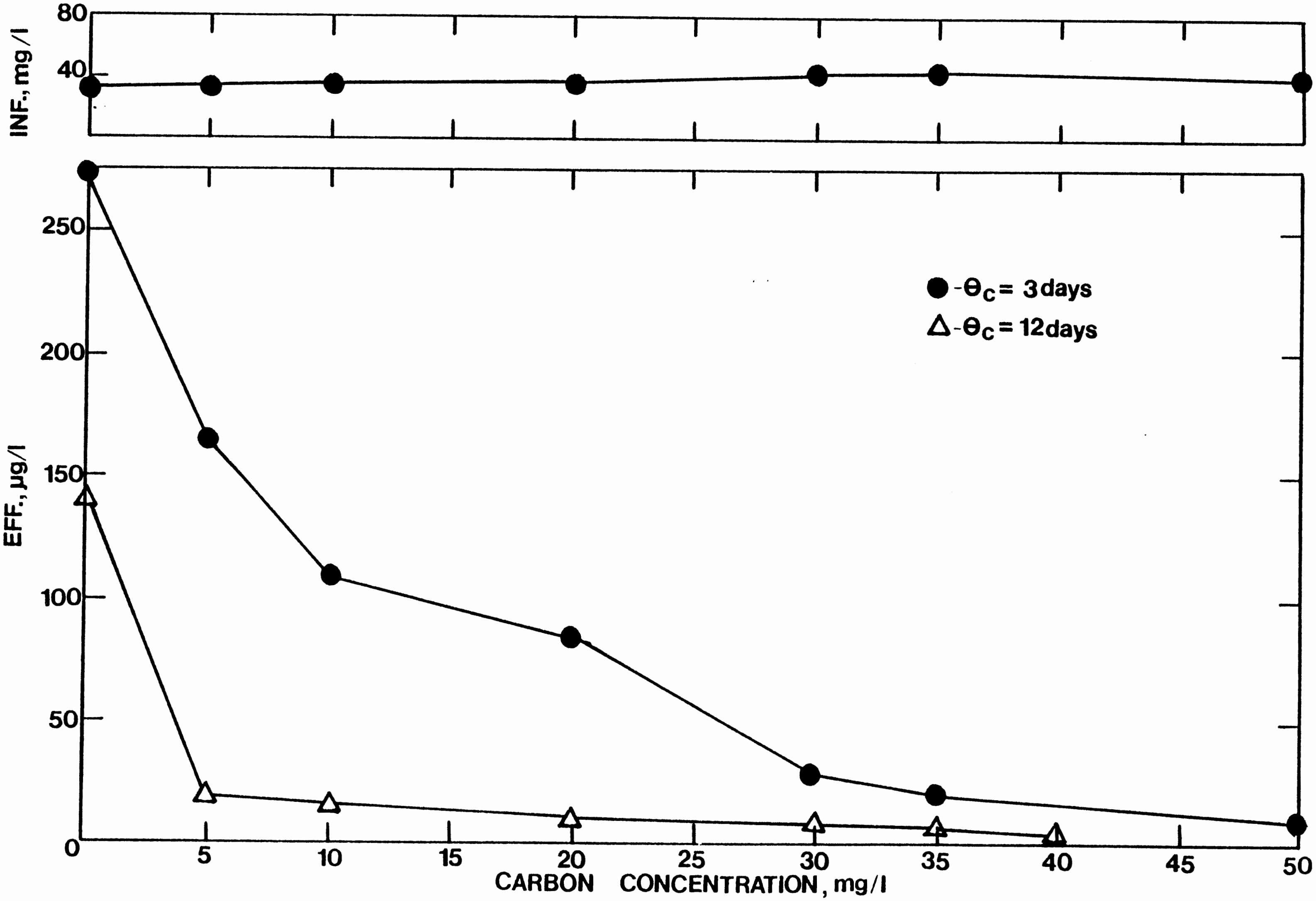

80
40
INF., mg/l
250
200
150
100
50
0
EFF., μg/l
● -θc = 3 days
△ -θc = 12 days
5
10
15
20
25
30
35
40
45
50
CARBON CONCENTRATION, mg/l

TABLE XV

MEAN VALUE OF EFFLUENT CONCENTRATION AND BIOLOGICAL SOLIDS FOR ETHYLBENZENE

Carbon dosage mg/ℓ	Mean Value									
	BOD_5 mg/ℓ		COD mg/ℓ		TOC mg/ℓ		MLVSS mg/ℓ		GC µg/ℓ	
	3 day	12 day	3 day	12 day	3 day	12 day	3 day	12 day	3 day	12 day
0	2.2	1.60	40	32	40	28.5	1000	2946	275	140
5	2.0	1.60	32	29	36	27.0	1096	2840	165	19
10	1.8	1.50	32	29	27.5	17.5	1280	2792	110	16
20	1.75	1.02	32	25	21.0	18.0	1070	2568	85	10
30	2.0	1.00	29	25	19.5	16.0	1304	2664	26	8
35	1.80	1.00	29	23	18.5	13.5	1000	2640	20	5
50	1.70	1.00	29	20	18.5	12.5	1200	2800	10	ND

MLVSS for the 3 day unit were 1000 mg/ℓ when the carbon dosage was 0 but increased to 1200 mg/ℓ when the carbon dosage was increased to 50 mg/ℓ. For the 12 day unit, the MLVSS were 2946 when no carbon was added and slightly decreased to 2800 mg/ℓ when 50 mg/ℓ carbon was added, which is not a significant change.

Tests were also conducted to determine the fate of ethylbenzene as it passes through biological treatment process. Influent, effluent and off-gas analyses were performed for each θ_c during each of the carbon dosing periods. Table XVI and Figure 27 present the results of the analyses incorporated to determine the fate of the ethylbenzene. The heading "percent" is used to denote the percentage of the ethylbenzene fed during the test period that was found in a particular area (effluent, off-gas, or adsorption and biological removal). For the 3 day θ_c unit, as the carbon dosage was increased from zero to 35 mg/ℓ, the percent of administered ethylbenzene found in the effluent decreased from 0.8 to 0.5. The percent of administered ethylbenzene found in the off-gas did not change during the same carbon dosing periods. By difference, the percent found to be degraded or adsorbed increased from 85.8 to 86.3.

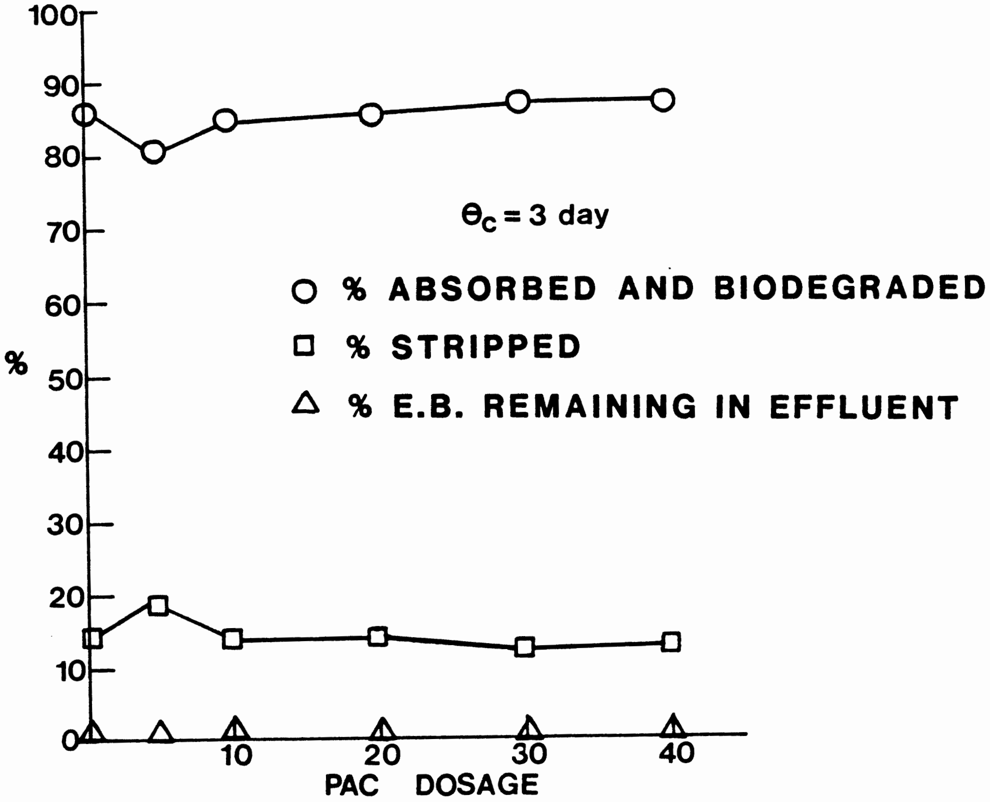
For the 12 day θ_c system, as the PAC dosage was increased from zero to 35 mg/ℓ, the percent of ethylbenzene administered which was found in the effluent, decreased from .04 to .01 for the Off-gas. The ethylbenzene found no significant change as powdered activated carbon dosage was increased from zero to 35 mg/ℓ. By difference, the amount of the administered ethylbenzene found to be degraded or adsorbed increased from 85.8 to 86.3 percent, which is not significant.

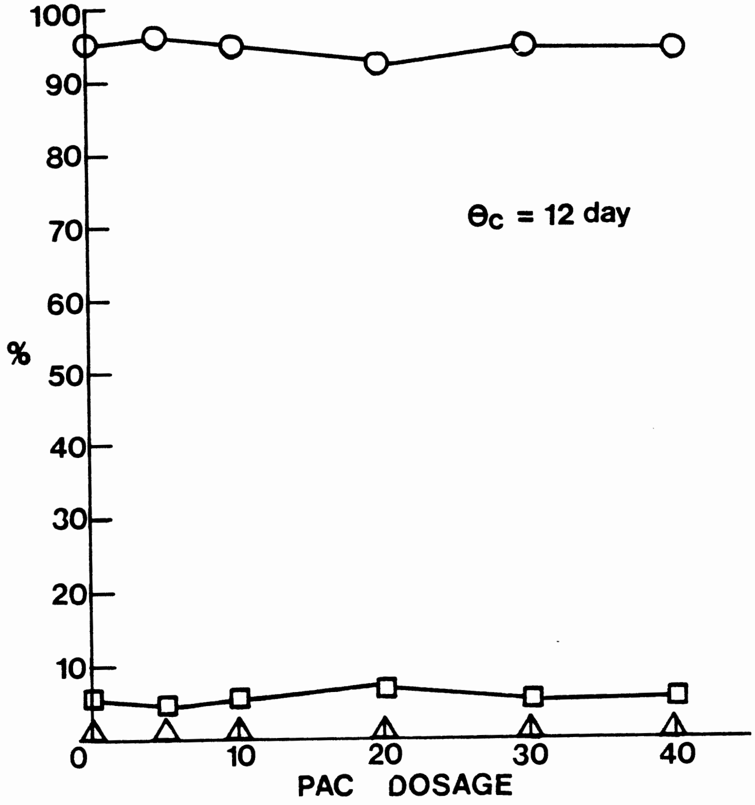
TABLE XVI

FATE OF ETHYLBENZENE

PAC dosage mg/ℓ	Influent mg/ℓ	Percent Ethylbenzene Remaining in Effluent		Total Percent Removed		Percent Stripped		Percent Adsorbed and Biodegraded	
		I	II	I	II	I	II	I	II
0	35	0.8	.04	99.2	99.6	13.4	5.0	85.8	94.6
5	35	0.5	.06	99.5	99.94	19.2	4.2	80.3	95.7
10	35	0.33	.05	99.67	99.95	14.6	5.3	85.1	94.6
20	38	0.23	.03	99.77	99.97	14.5	7.4	85.3	92.6
30	42	.06	.02	99.94	99.98	12.2	5.2	87.5	94.8
35	42	.05	.01	99.95	99.99	13.6	5.0	86.3	94.1

Figure 27. Removal of Ethylbenzene in PAC Systems.


100
90
80
70
60
50
40
30
20
10
0
%
10
20
30
40
PAC DOSAGE
θ_c = 3 day
○ % ABSORBED AND BIODEGRADED
□ % STRIPPED
△ % E.B. REMAINING IN EFFLUENT


100
90
80
70
60
50
40
30
20
10
0
%
10
20
30
40
PAC DOSAGE
θ_c = 12 day

1, 2 Dichloroethane

1,2 ichloroethane was the last individual priority pollutant investigated in the second phase. 1,2 ichloroethane is a halogenated hydrocarbon while the first three compounds were aromatics. Again, two bench scale internal recycle activated sludge units were operated under steady state conditions with 200 mg/ℓ 1,2 dichloroethane being added to the base mix and used as a feed for both units. One of the units was operated at a three day θ_c while the other was maintained at a 12 day θ_c. Carbon dosages of 0, 100, 300, 600, 1200 and 1600 mg/ℓ were added (based upon influent flow rates).

The result of BOD, COD and TOC effluent analyses for both units are presented in Figures 28, 29, and 30 respectively. These figures also present influent and MLVSS concentrations. Table XVII summarizes the analytical data taken for both units for all carbon dosages. It can be seen from these figures that beyond a carbon dosage of 600 mg/ℓ very little additional removal of BOD, COD and TOC occurred. For the 3 day θ_c unit BOD concentrations were reduced from 2.65 (during 0 mg/ℓ carbon) to 1.57 mg/ℓ (600 mg/ℓ PAC) while COD was reduced from 32 mg/ℓ to 18 mg/ℓ and TOC was reduced from 29 mg/ℓ to 10 mg/ℓ.

Similarly for the 12 day θ_c unit, when comparing the zero and the 600 mg/ℓ carbon dosage, BOD concentrations were reduced from 1.62 to 0.60 mg/ℓ while COD was reduced from 30 mg/ℓ to 10 mg/ℓ and TOC was reduced from 28.0 to 9.0 mg/ℓ.

When comparing the effluent substrate concentrations of the 3 day and 12 day units between the zero and 600 mg/ℓ carbon dosages, the 12 day effluent BOD was 1 to 2 mg/ℓ effluent COD was 20 to 8 mg/ℓ lower than

Figure 28. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of Activated Sludge Systems (BOD) Receiving a Wastewater Containing 1,2 Dichloroethane.

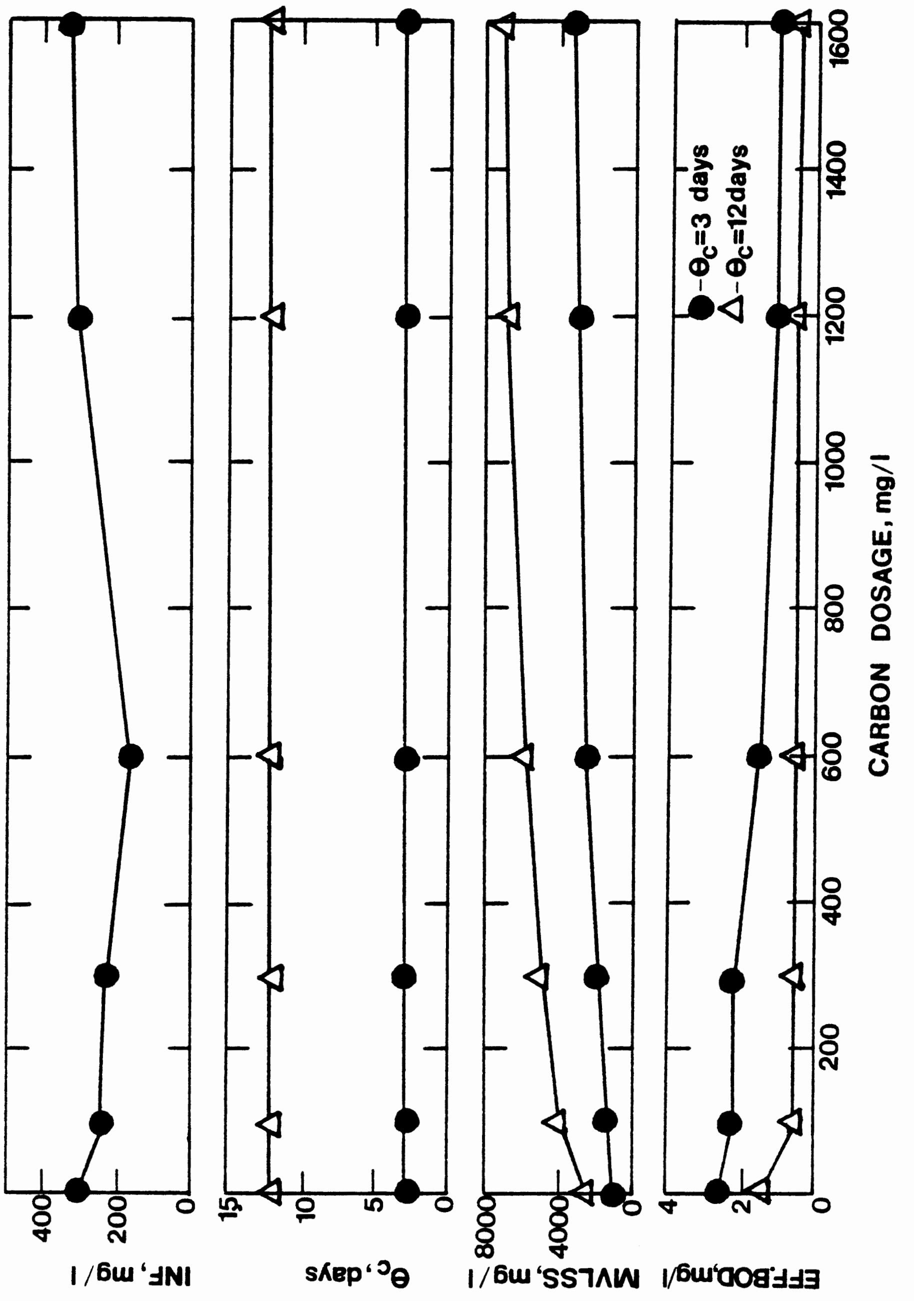

INF, mg/l
400
200
0
θc, days
15
10
5
0
MVLSS, mg/l
8000
4000
0
EFF.BOD, mg/l
4
2
0
200
400
600
800
1000
1200
1400
1600
CARBON DOSAGE, mg/l
● - θc=3 days
△ - θc=12days

Figure 29. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of Activated Sludge Systems (COD) Receiving a Wastewater Containing 1,2 Dichloroethane.

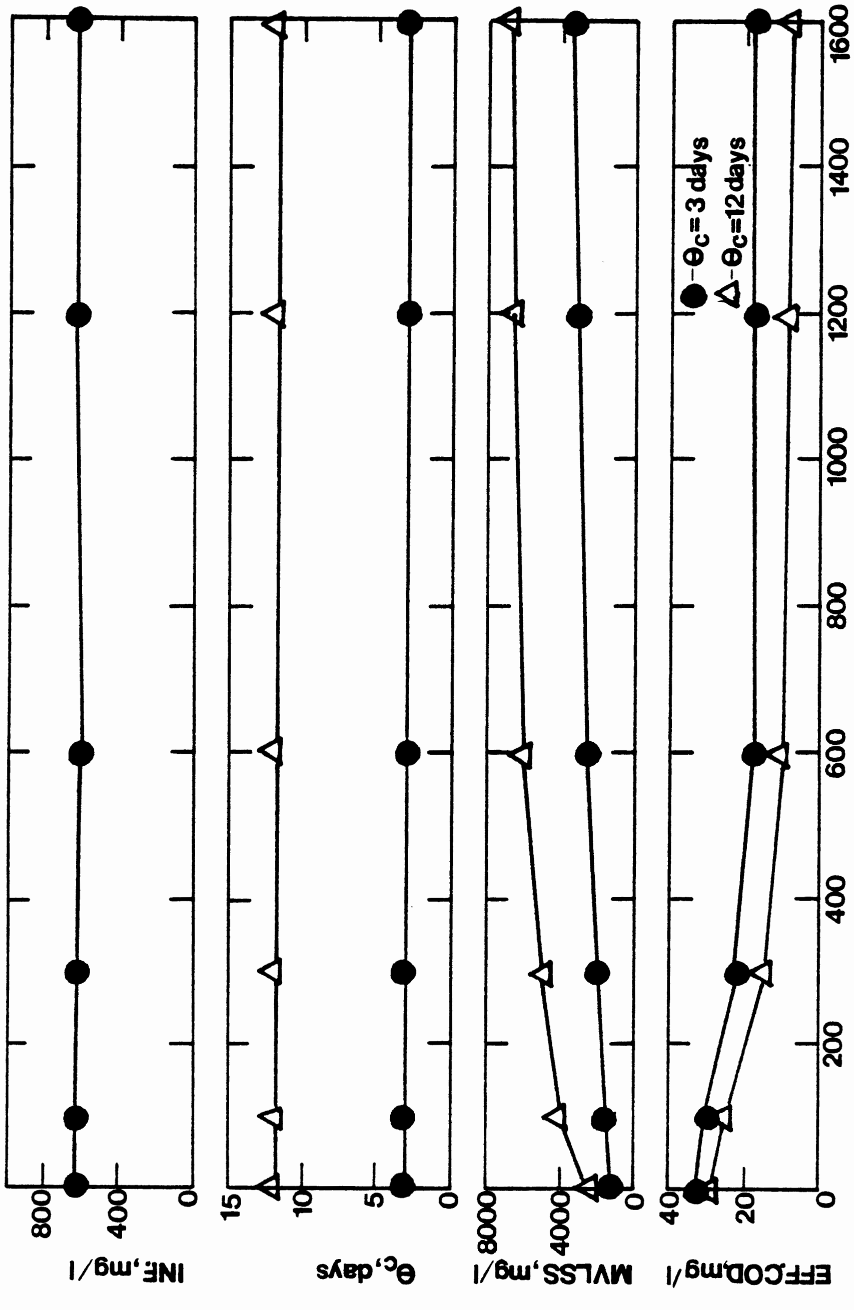

INF, mg/l
800
400
0
θc, days
15
10
5
0
MVLSS, mg/l
8000
4000
0
EFF.COD, mg/l
40
20
0
0
200
400
600
800
1000
1200
1400
1600
CARBON DOSAGE mg/l
● - θc = 3 days
△ - θc = 12 days

Figure 30. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of Activated Sludge Systems (TOC) Receiving a Wastewater Containing 1,2 Dichloroethane.

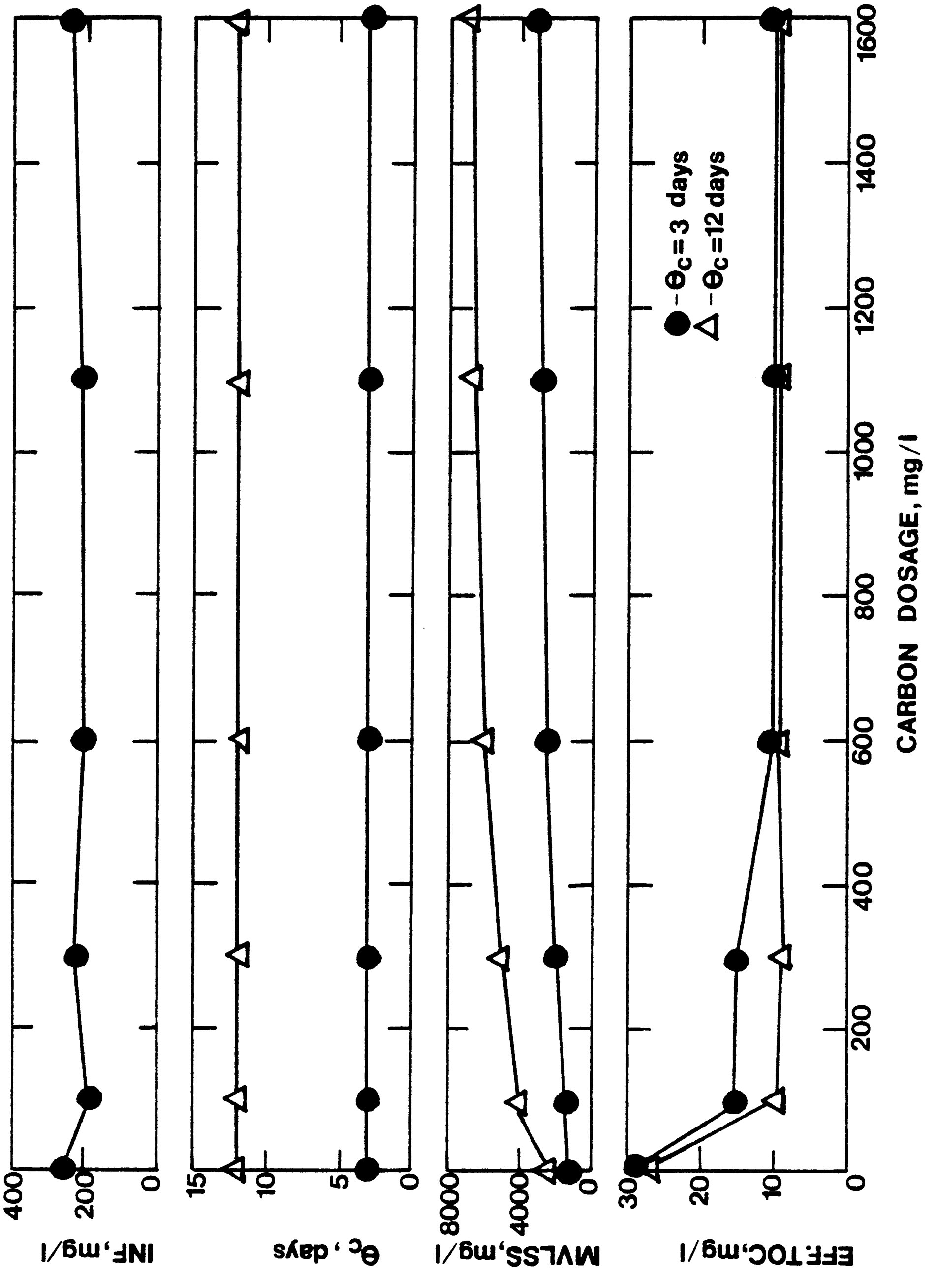

INF, mg/l
400
200
0
θc, days
15
10
5
0
MVLSS, mg/l
8000
4000
0
EFF.TOC, mg/l
30
20
10
0
200
400
600
800
1000
1200
1400
1600
CARBON DOSAGE, mg/l
● - θc=3 days
Δ - θc=12 days

TABLE XVII

MEAN VALUE OF EFFLUENT CONCENTRATION AND BIOLOGICAL SOLIDS FOR 1,2 DICHLOROETHANE

PAC dosage mg/ℓ	Mean Value									
	BOD mg/ℓ		COD mg/ℓ		TOC mg/ℓ		MLVSS mg/ℓ		GC mg/ℓ	
	I	II	I	II	I	II	I	II	I	II
0	2.65	1.62	32	30	29.0	28.0	1000	2500	9.0	8.25
100	2.23	0.60	30	25	15.0	10.0	1444	3908	8.0	7.75
300	2.40	0.60	22	15	15.0	10.0	1844	5172	7.0	7.0
600	1.57	0.60	18	10	10.0	9.0	2388	5172	6.0	6.5
1200	1.07	0.59	18	10	9.5	9.0	3100	6400	6.0	7.45
1500	1.0	0.55	18	8	7.5	9.0	3590	7384	4.5	2.95

the 3 day unit while the 12 day effluent TOC was generally 1 mg/ℓ lower than the 3 day unit.

1,2 dichloroethane analytical results are presented in Figure 31 for both units. Both the 12 day and the 3 day effluent exhibited the same trends with respect to carbon dosage both initially being 8 or 9 mg/ℓ and being reduced to 1.5 to 2.5 mg/ℓ when the carbon dose was increased to 2500 mg/ℓ . There was very little additional 1,2 dichloroethane removal realized by increasing the PAC dosage from 2000 to 2500 mg/ℓ. There seemed to be very little difference between the effluent 1,2 DCE concentrations of the 3 day and 12 day unit at corresponding carbon dosages.

MLVSS concentrations during this part of the study showed drastic increases due to the large carbon doses administered. The initial MLVSS for the 3 day unit was 1000 mg/ℓ while the MLVSS was 3600 mg/ℓ during the 1500 mg/ℓ carbon dosage. The 12 day unit had an initial MLVSS concentration of 2500 and, after 1500 mg/ℓ PAC addition, the MLVSS concentration was 7400 mg/ℓ.

Tests were also conducted to determine the fate of 1,2 dichloroethane as it passes through biological treatment process. Influent, effluent and off-gas analysis were performed for each θ_c during each of the carbon dosing periods. Table XVIII and Figure 32 present the results of the analysis incorporated to determine the fate of the 1,2 dichloroethane. The heading "percent" is used to denote the percentage of the 1,2 dichloroethane fed during the test period that was found in a particular area (effluent, off-gas, or adsorption and biological removal). For the 3 day θ_c unit, as carbon dosage was increased from zero to 1500 mg/ℓ, the percent of administered 1,2 dichloroethane found

Figure 31. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Effluent 1,2 Dichloroethane Concentration of Activated Sludge Systems Receiving a Wastewater Containing 1,2 Dichloroethane.

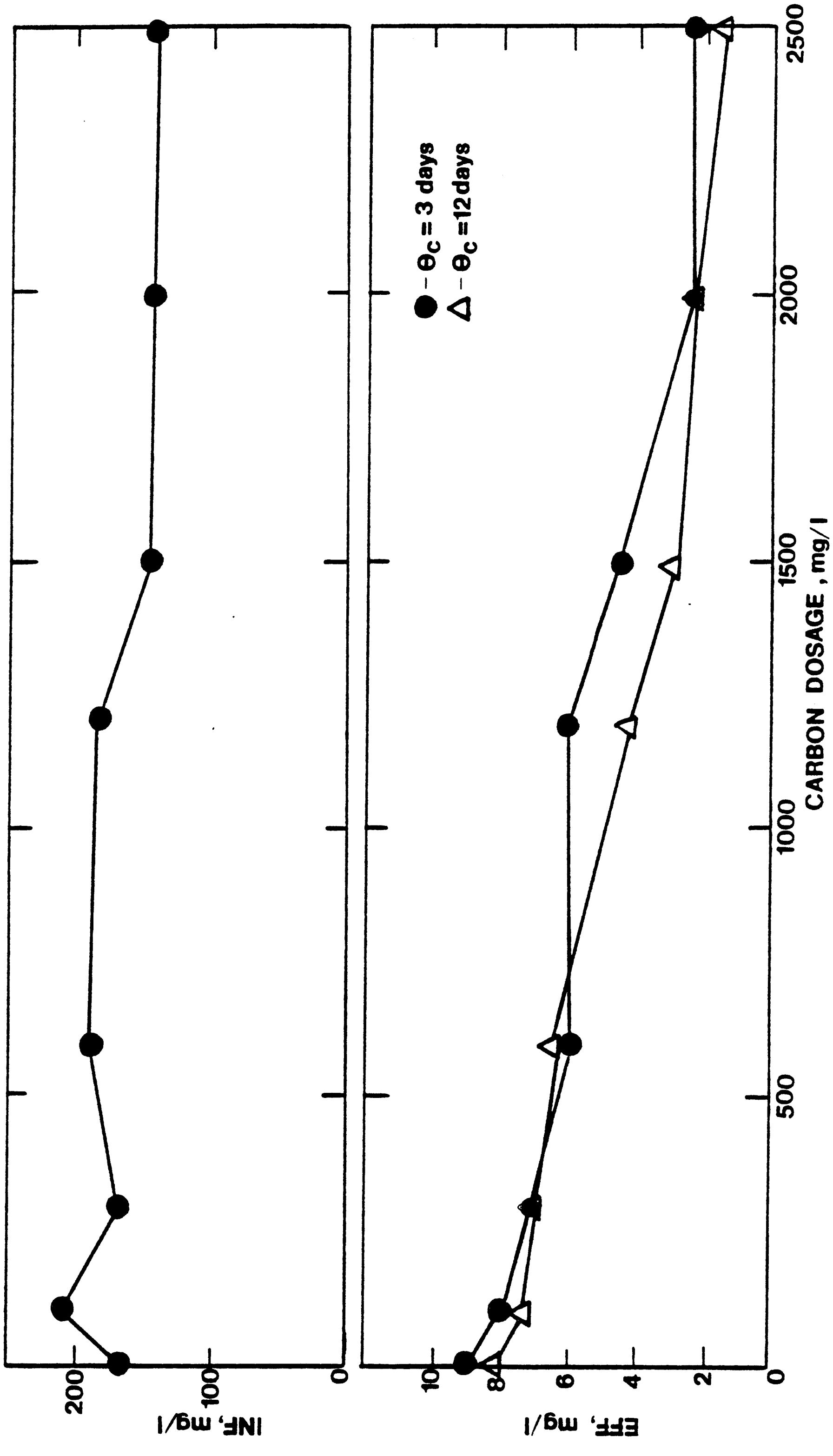

INF, mg/l
200
100
0
EFF, mg/l
10
8
6
4
2
0
0
500
1000
1500
2000
2500
CARBON DOSAGE, mg/l
● - θ_c = 3 days
Δ - θ_c = 12 days

TABLE XVIII

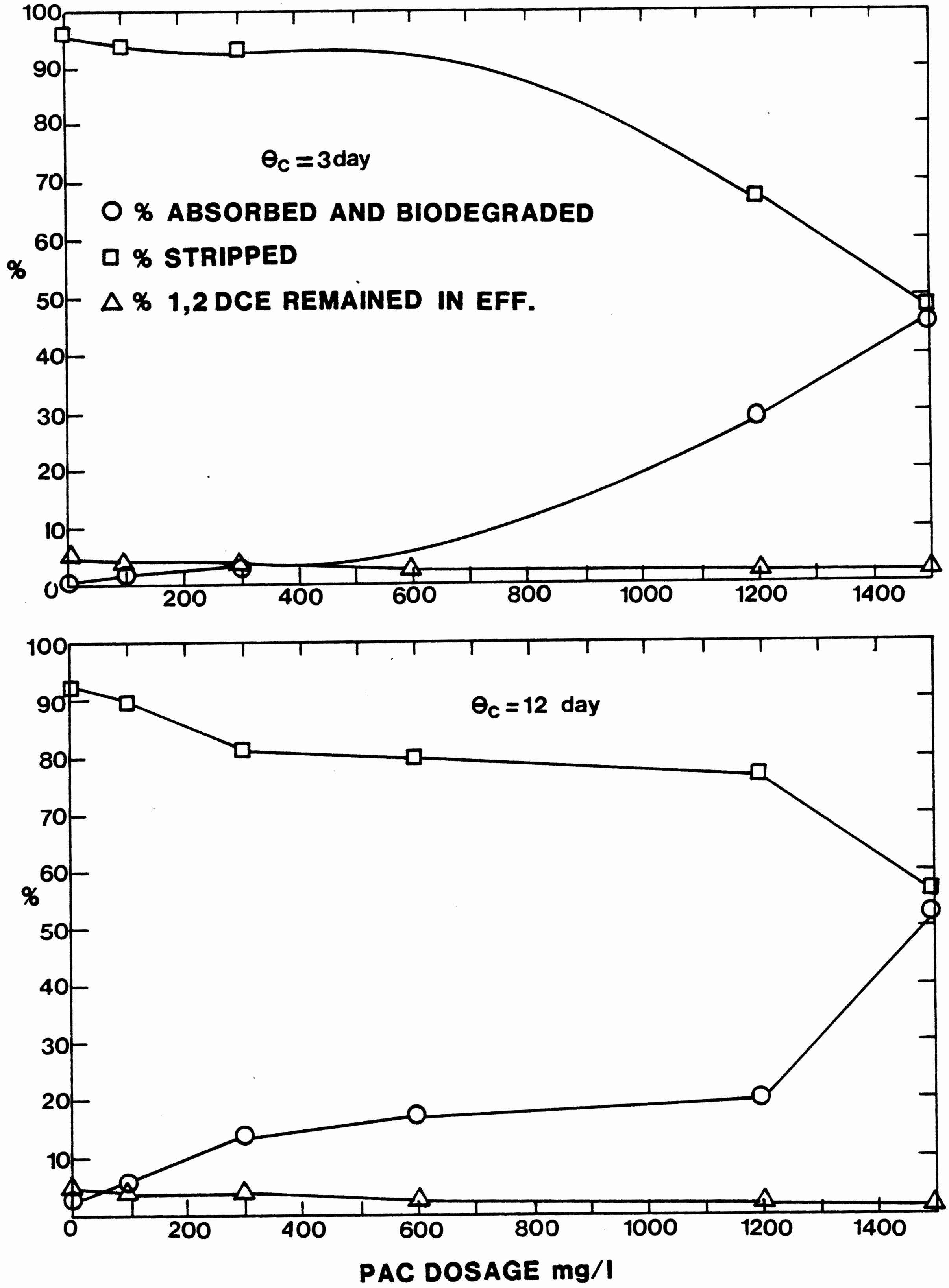
FATE OF 1,2 DICHLOROETHANE

PAC dosage mg/ℓ	Influent mg/ℓ	Percent 1,2 Dichloroethane remaining in effluent I	II	Total Percent Removed I	II	Percent Stripped I	II	Percent Adsorbed and Biodegraded I	II
0	165	5.5	5.0	94.5	95.0	95.9	92	0	3.0
100	185	4.3	4.1	95.7	95.8	93.6	89.7	2.1	6.1
300	165	4.3	4.3	95.7	95.7	93.0	81.7	2.7	14.0
600	187	3.2	3.5	96.8	96.5	65	79	31.8	17.5
1200	185	3.20	2.4	96.8	97.5	68.5	77.0	28.3	20.5
1500	145	3.1	1.95	96.9	98.0	48.4	46.0	48.5	52.0

I = θ_c = 3

II = θ_c = 12

Figure 32. Removal of 1,2 Dichloroethane in PAC Systems.


100
90
80
70
60
50
40
30
20
10
0
%
θc = 3day
○ % ABSORBED AND BIODEGRADED
□ % STRIPPED
△ % 1,2 DCE REMAINED IN EFF.
200
400
600
800
1000
1200
1400
θc = 12 day
0
PAC DOSAGE mg/l

in the effluent decreased from 5.5 to 3.1. The percent of administered 1,2 dichloroethane found in the off-gas decreased from 96 to 48.4 during the same carbon dosing periods. By difference, the percent found to be degraded or adsorbed increased from 0 to 48.5 percent.

For 12 day θ_c system, as the carbon dosage was increased from zero to 1500 mg/ℓ, the percent of the 1,2 dichloroethane administered which was found in the effluent decreased from 5.0 to 1.95. For the off-gas the 1,2 dichloroethane recovered decreased from 92 to 46.0 percent as the PAC dosage was increased from zero to 1500 mg/ℓ. By difference, the amount of the administered 1,2 dichloroethane found to be degraded or adsorbed increased from 3.0 to 52.0 percent.

Combined Priority Pollutants

During the latter part of the second phase of this investigation it was decided that a combination of four priority pollutants be added to the base mix feed and then be administered to two bench scale activated sludge units which would be operated at two different mean cell residence times (3 and 12 days).

The four priority pollutants selected for study were 1,2 dichloroethane, benzene, toluene, and ethylbenzene. Each were present in the feed at a concentration of 50 mg/ℓ. Varying carbon dosages (5.0, 10, and 25 mg/ℓ) were tested. The units were allowed to reach steady state and then analyzed for effluent quality. Figures 33, 34, 35, and 36 present the mean steady state values for influent and effluent substrate analyses for BOD, COD, TOC, and specific priority pollutants, respectively, for each of the carbon dosages tested. In addition, MLVSS data for both of the units are presented. These results are also summarized in Table XIX.

Figure 33. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of Activated Sludge Systems (BOD_5) Receiving a Wastewater Containing Priority Pollutants.

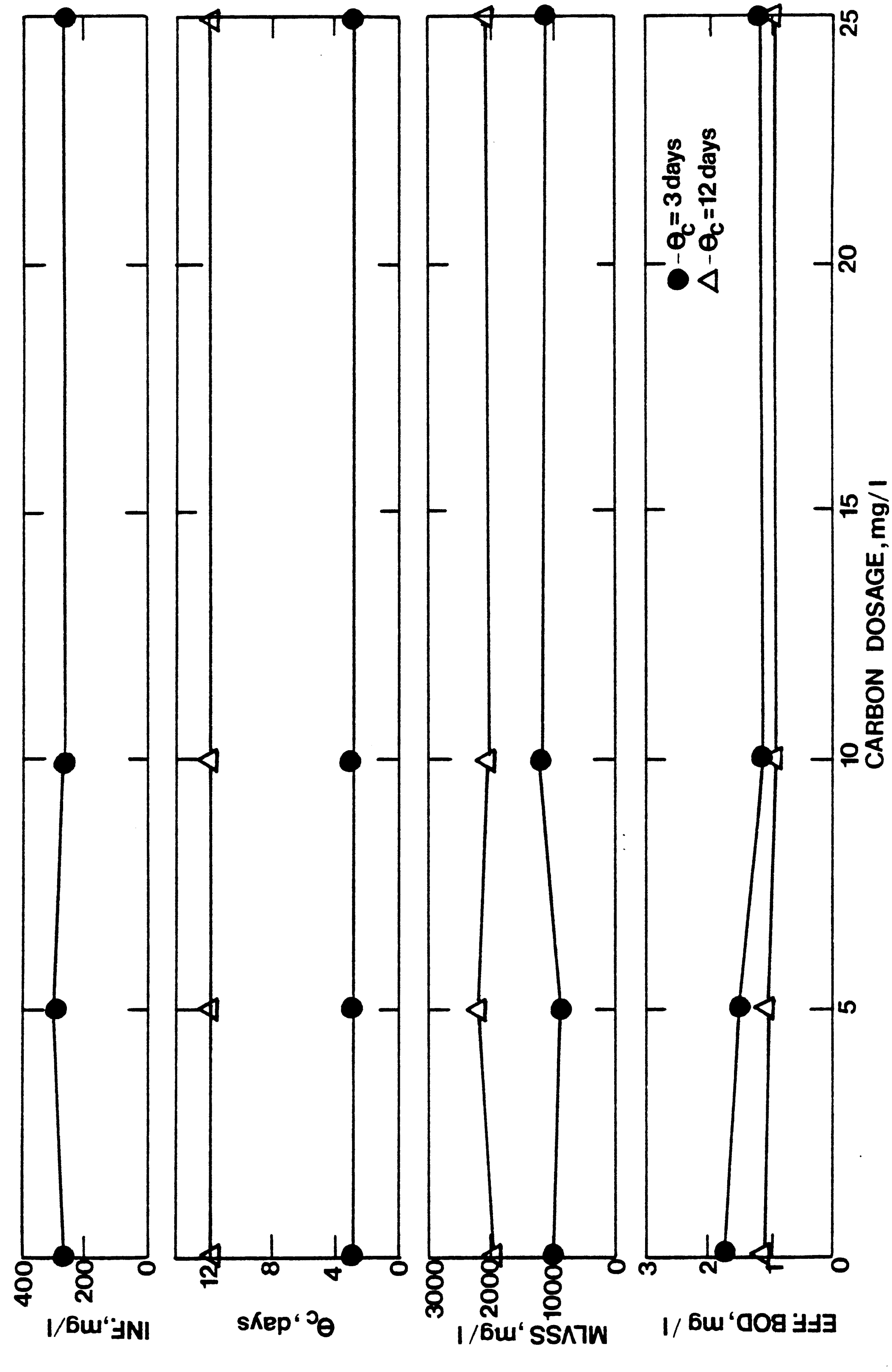

INF, mg/l
400
200
0
θc, days
12
8
4
0
MLVSS, mg/l
3000
2000
1000
0
EFF BOD, mg/l
3
2
1
0
0
5
10
15
20
25
CARBON DOSAGE, mg/l
● - θc = 3 days
Δ - θc = 12 days

Figure 34. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of Activated Sludge Systems (COD) Receiving a Wastewater Containing Priority Pollutants.

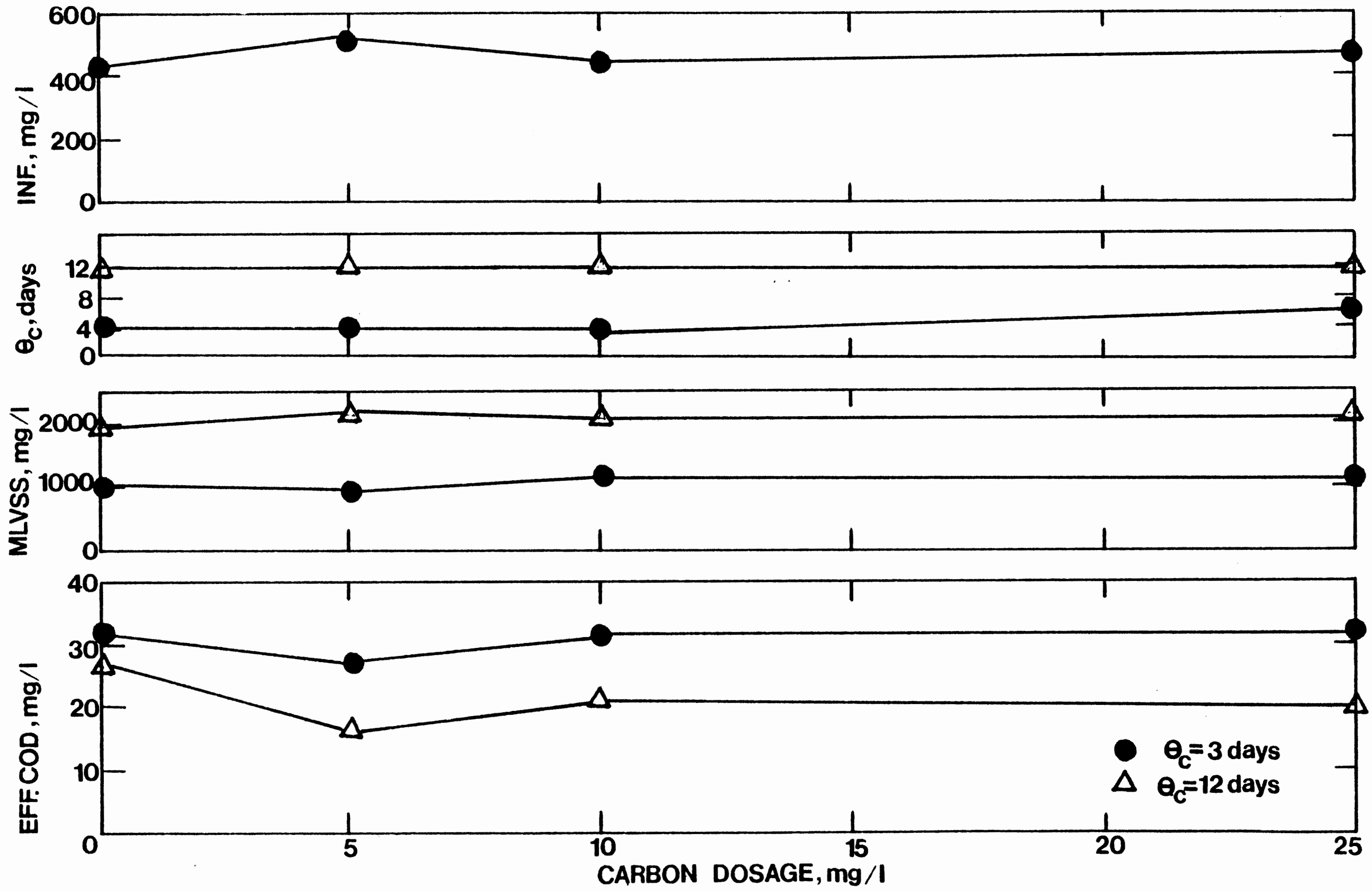

600
400
200
0
INF., mg/l
12
8
4
0
θ_c, days
2000
1000
0
MLVSS, mg/l
40
30
20
10
0
EFF. COD, mg/l
0
5
10
15
20
25
CARBON DOSAGE, mg/l
● θ_c= 3 days
△ θ_c=12 days

Figure 35. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Performance of Activated Sludge Systems (TOC) Receiving a Wastewater Containing Priority Pollutants.

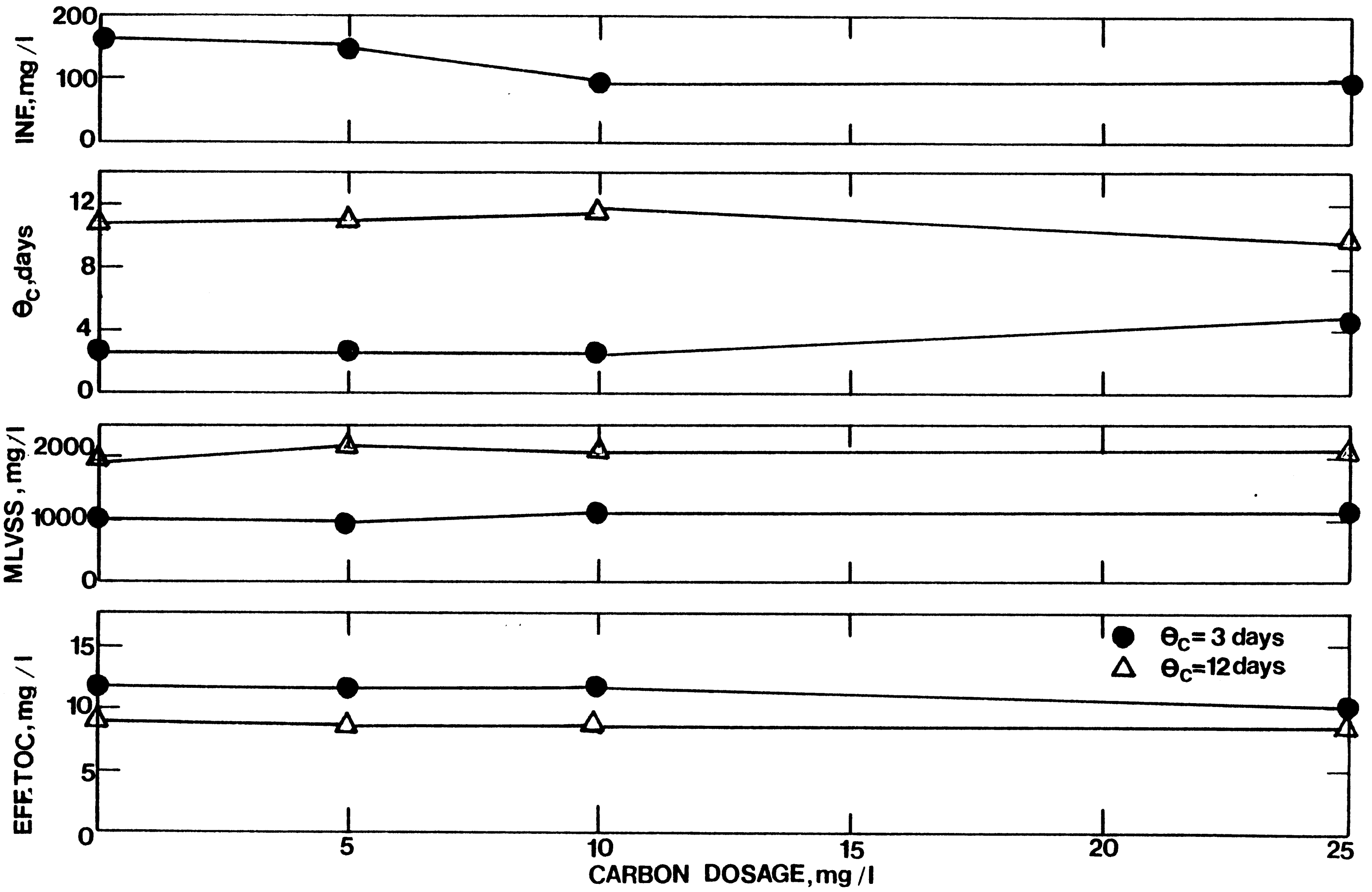

INF.,mg /l
200
100
0
θ_c,days
12
8
4
0
MLVSS, mg /l
2000
1000
0
EFF.TOC, mg /l
15
10
5
0
● θ_C= 3 days
△ θ_C=12 days
5
10
15
20
25
CARBON DOSAGE, mg /l

Figure 36. The Effect of Powdered Activated Carbon Dosage (PAC) and θ_c upon the Effluents of Combined Priority Pollutants Concentration of Activated Sludge Systems Receiving Wastewater Containing Four Priority Pollutants (Benzene, Toluene, Ethylbenzene, 1,2 Dichloroethane).

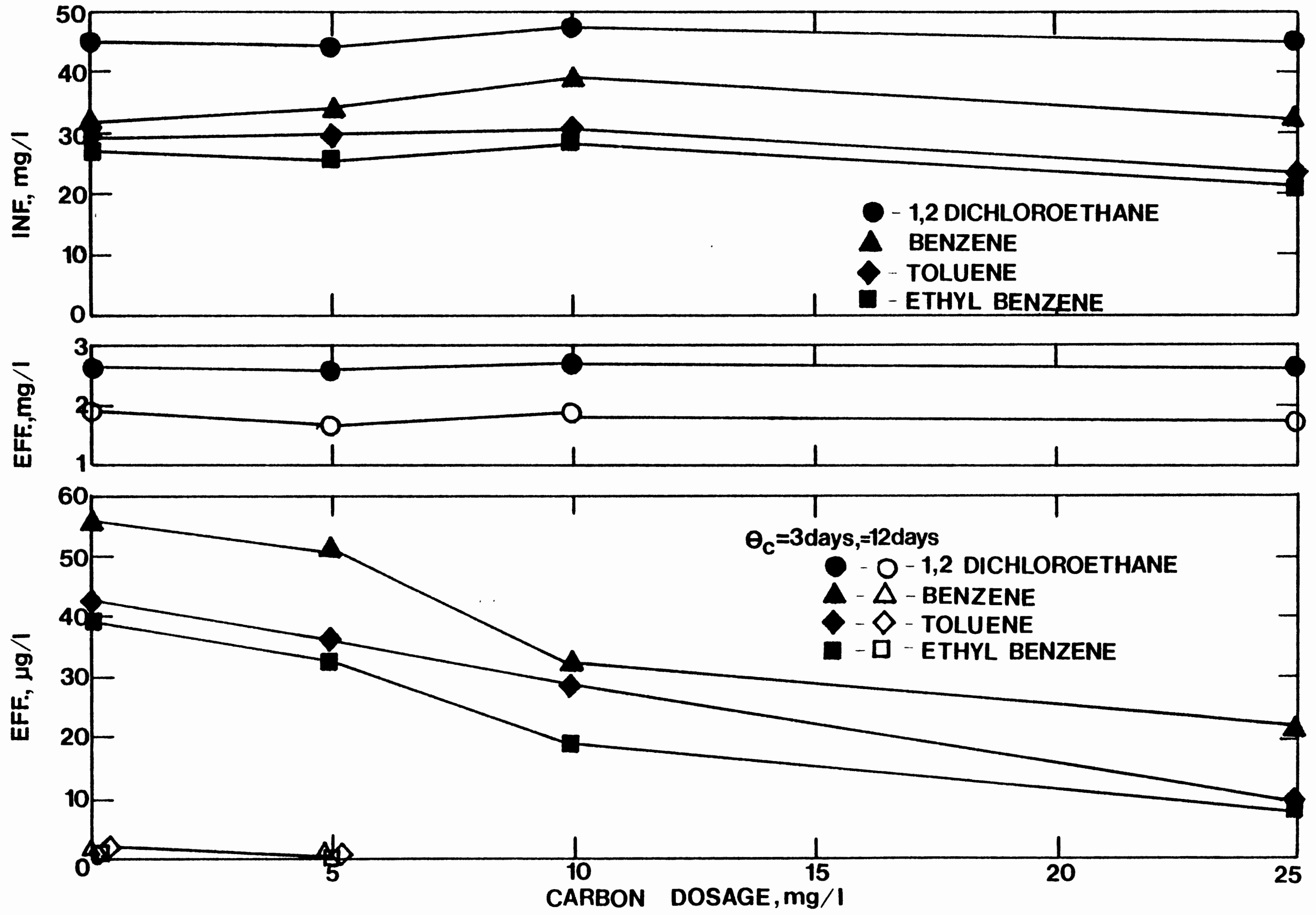

INF., mg/l
50
40
30
20
10
0
● - 1,2 DICHLOROETHANE
▲ BENZENE
◆ - TOLUENE
■ - ETHYL BENZENE
EFF.,mg/l
3
2
1
EFF., µg/l
60
50
40
30
20
10
0
5
10
15
20
25
Θ_c=3days,=12days
● - ○ - 1,2 DICHLOROETHANE
▲ - △ - BENZENE
◆ - ◇ - TOLUENE
■ - □ - ETHYL BENZENE
CARBON DOSAGE, mg/l

TABLE XIX

MEAN VALUE OF EFFLUENT CONCENTRATION AND BIOLOGICAL SOLIDS FOR COMBINED UNIT

Carbon dosage mg/ℓ	Mean Value															
	BOD mg/ℓ		COD mg/ℓ		TOC mg/ℓ		MLVSS mg/ℓ		GC							
									1,2 DCE mg/ℓ		Benzene mg/ℓ		Toluene µg/ℓ		Ethylbenzene µg/ℓ	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
0	1.8	1.20	32	28	13.5	8.5	1012	1952	2.65	2.05	37.0	2.0	43.0	20	39.0	2.0
5	1.56	1.26	27	12	13.5	7.5	952	2244	2.60	1.70	52.0	2.0	37.0	ND	32.5	2.0
10	1.26	1.22	32	22	13.5	8.5	1100	2166	2.70	1.90	32.5	ND	29.0	ND	17.0	ND
25	1.20	1.2	35	20	13.5	8.5	1138	2316	2.60	1.80	21.0	ND	9.0	ND	8.5	ND

It can be seen from Figures 30, 31, and 32 that PAC addition into the two reactors (3 and 12 day) did not result in much additional removal of BOD, COD, and TOC.

For the 3 day unit the only noticeable change was on removal of BOD after the addition of 10 mg/ℓ PAC. Here the concentration of BOD was reduced from 1.8 mg/ℓ to 1.26 mg/ℓ (an additional 30% reduction). No change in effluent COD and TOC concentrations occurred after the addition of PAC.

In the case of the 12 day unit, there were no changes in BOD and TOC concentration after addition of carbon. The only marked change occurred in effluent COD concentration where there was an additional reduction in COD with increasing carbon dosage. After the addition of 10 mg/ℓ PAC, the effluent COD was reduced by 6 mg/ℓ (28%) over the operational period where no carbon was added.

Figure 36 which shows the effluent comparison between the 3 and 12 day unit, also shows additional effluent priority pollutants (1,2 dichloroethane, benzene, toluene, and ethylbenzene) reduction due to PAC addition. For the 3 day unit effluent, an additional reduction of 63, 80 and 78% in benzene, toluene, and ethylbenze concentrations, respectively, when comparing effluent concentrations during the zero mg/ℓ PAC operational period with the 10 mg/ℓ or PAC period. Effluent 1,2 dichloroethane concentration showed negligible reduction even after 25 mg/ℓ PAC addition. PAC dosages in excess of 10 mg/ℓ had very little additional impact on effluent substrate concentrations.

For the 12 day unit very little change can be seen in the effluents concentration after addition of 5 mg/ℓ PAC. In fact, a maximum reduction of only 2 μg/ℓ benzene, toluene, and ethylbenzene occurred after addition of 5 mg/ℓ PAC.

Mean mix liquor volatile suspended solids for the 3 day unit was 1012 mg/ℓ when the carbon dosage was zero mg/ℓ and increased to 1100 mg/ℓ when the carbon dosage was increased to 10 mg/ℓ . For the 12 day unit a small change can also be seen between zero mg/ℓ carbon (952 mg/ℓ VSS) and 10 mg/ℓ. This increase was only 200 mg/ℓ.

Tests to determine the fate of all four compounds (benzene, toluene, ethylbenzene, and 1,2 dichloroethane) through the biological treatment process were also conducted. The results of these tests for the various carbon dosages are presented in Table XX and Figures 37 and 38. For the θ_c of 3 days, the percentage of the administered benzene recovered in the effluent decreased from 0.17 to 0.08 percent as the carbon dose increased from 0 to 10 mg/ℓ. Similarly, for the same carbon dosage period, the percentage recovered in the effluent decreased from 0.13 to 0.09 for toluene, 0.14 to 0.07 for ethylbenzene and from 5.9 to 5.6 for 1,3 dichloroethane. For the 12 day unit, the percent recovery of the priority pollutants in the effluent decreased from 0.006 to no detectable levels for benzene, toluene, and ethylbenzene, and from 5.9 to 5.6 for 1,2 dichloroethane, as carbon dosage increased from zero to 10 mg/ℓ.

For the percent of priority pollutants recovered in the off-gas analyses of the 3 day θ_c unit, as the carbon dosage was increased from zero to 10 mg/ℓ, the benzene stripped was reduced from 15.5 to 14.7, the toluene stripped was reduced from 15 to 14.3. The ethylbenze stripped was reduced from 13 to 10 and the 1,2 dichloroethane percentage stripped was reduced from 95 to 85. For the percent of priority pollutants recovered in the off-gas analyses of the 12 day θ_c unit, as the PAC dosage was increased from zero to 100 mg/ℓ, the benzene stripped was reduced from 12.4 to 12.0, the toluene stripped was increased a little from 15.0 to 15.6, the ethylbenzene was reduced from 15.2 to 12.5, and the 1,2 dichloroethane percentage stripped was reduced also from 99 to 95.

Figure 37. Removal of Priority Pollutants in Powdered Activated Carbon Systems (PAC) (θ_c = 3 day).

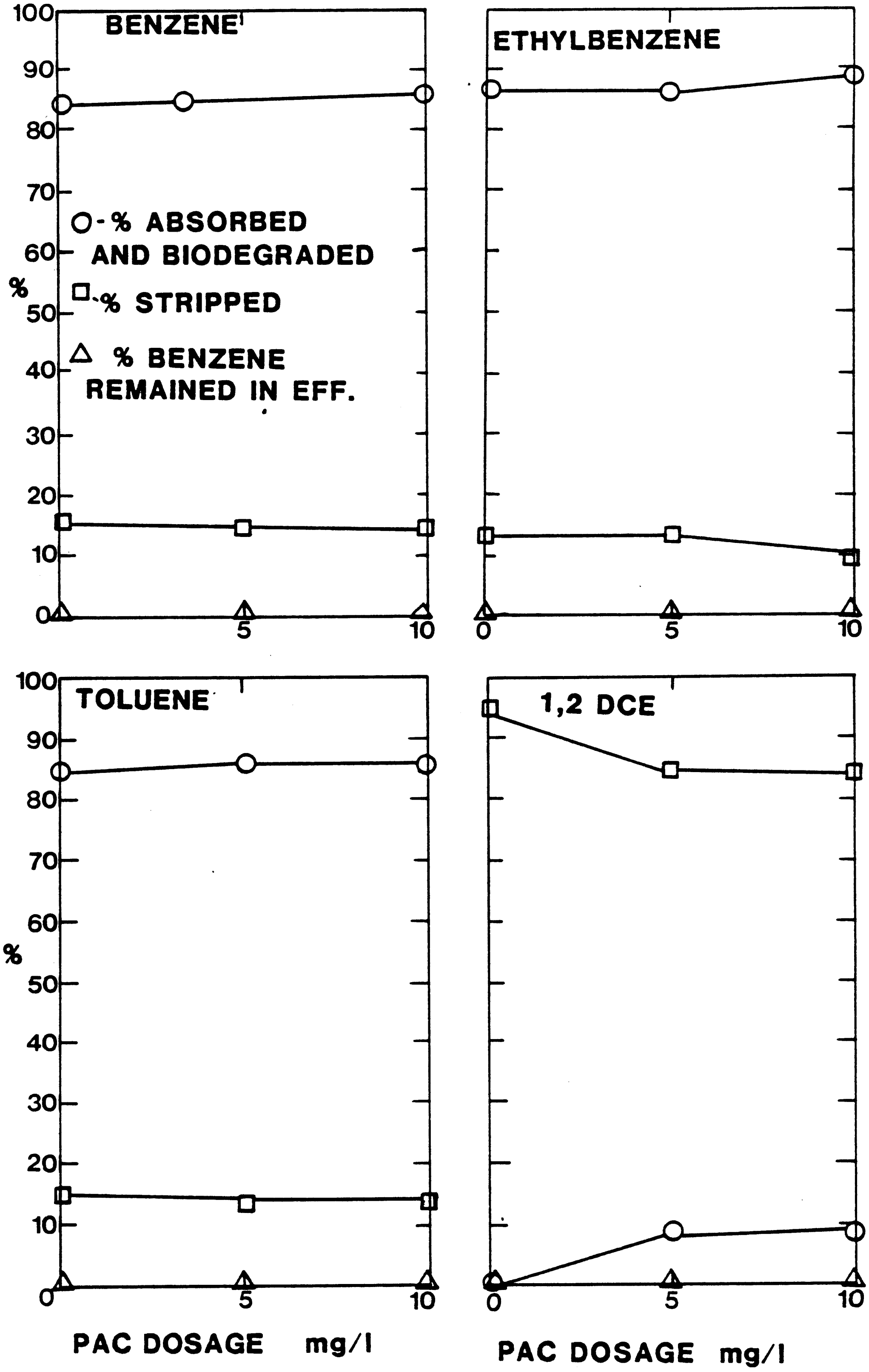

BENZENE
ETHYLBENZENE
TOLUENE
1,2 DCE
○ - % ABSORBED AND BIODEGRADED
□ - % STRIPPED
△ % BENZENE REMAINED IN EFF.
%
100
90
80
70
60
50
40
30
20
10
0
5
10
PAC DOSAGE mg/l
PAC DOSAGE mg/l

Figure 38. Removal of Priority Pollutants in Powdered Activated Carbon (PAC) Systems (θ_c = 12 day).

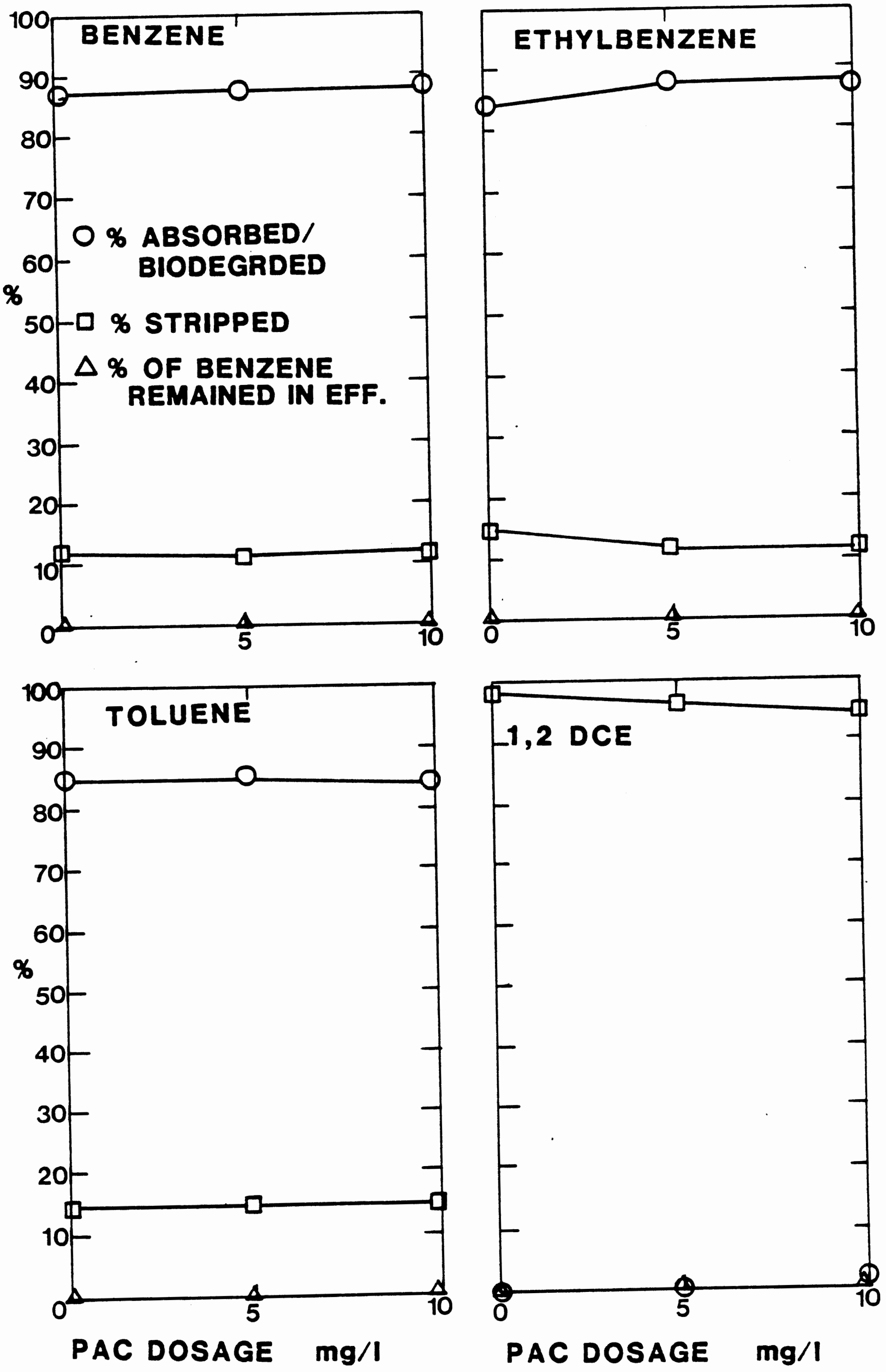

BENZENE
ETHYLBENZENE
TOLUENE
1,2 DCE
○ % ABSORBED/ BIODEGRDED
□ % STRIPPED
△ % OF BENZENE REMAINED IN EFF.
%
100
90
80
70
60
50
40
30
20
10
0
5
10
PAC DOSAGE mg/l

TABLE XX

FATE OF COMBINED PRIORITY POLLUTANTS (BENZENE, TOLUENE, ETHYLBENZENE AND 1,2 DICHLOROETHANE)

PAC dosage mg/ℓ	Influent mg/ℓ	Percent P.P. Remaining in Effluent		Total Percent Removed		Percent Stripped		Percent Adsorbed and Biodegraded	
		I	II	I	II	I	II	I	II
Benzene									
0	38.5	0.175	0.006	99.8	99.99	15.5	12.4	84.3	87.6
5	34.0	0.152	0.006	99.85	99.99	15.2	12.0	84.6	88.0
10	39.4	0.082	ND	99.9	>99.99	14.7	12.0	85.2	88.0
Toluene									
0	32.0	0.135	0.006	99.85	99.99	15.0	15.0	84.85	85.0
5	30.0	0.124	0.006	99.87	99.99	13.4	15.0	86.5	85.0
10	31.5	0.092	ND	99.99	>99.99	14.3	15.6	85.7	84.4
Ethylbenzene									
0	28.0	0.14	0.007	99.85	99.99	13.0	15.2	86.8	84.6
5	26.0	0.125	0.007	99.87	99.99	13.8	11.7	86.1	88.3
10	29.0	0.067	ND	99.93	>99.99	10.0	12.5	89.9	87.5
1,2 Dichloroethane									
0	45.0	5.90	4.55	94.0	95.5	95.0	99.0	0.0	0.0
5	44.0	5.90	3.9	94.0	96.0	85.0	96.5	9.0	0.0
10	48.0	5.60	3.6	94.4	96.5	85.4	95.0	9.0	1.5

CHAPTER V

DISCUSSION

The purpose of this study was to determine the effect of powdered activated carbon addition to an activated sludge system receiving wastewater containing organic priority pollutants. Performance of both PACT and conventional activated sludge were studied under identical conditions during the transient and steady state period following the addition of organic priority pollutants. In addition, a secondary aim was to find the effect of increasing the dosage of activated carbon under similar conditions to find the effect of activated carbon on effluent quality.

One of the organic pollutants which was studied more in depth than the other compounds is benzene. The result of the addition of various contentrations of benzene in a step-wise fashion to PACT and a control unit are shown in Chapter IV (Figure 2 to Figure 15).

The PACT system removed more BOD and exhibited less variability in the day to day effluent BOD. This is evident during the transient and steady state after each step increase in dosage of benzene. Even though the mechanism of removal in the PACT system has not been fully ascertained, one can expect the following removal mode in the PACT system. In the PACT system the activated carbon adsorbs the organics and retains them while they are biodegraded by the biomass. In the conventional system the period for which the organics are kept in contact with the biomass is shorter in the PACT system. So those organics which slowly biodegradate and intermediates which will pass through in a conventional system will be retained in the PACT system. However, during the transient immediately following a step increase in dosage of priority pollutants substrate will leak into the effluent either as original substrate or its derivatives and intermediates unless the biomass responds instantaneously.

In the case of the PACT system the carbon can adsorb the organics and retain them long enough for the biomass to biodegrade them, but it can have an adverse effect on biomass depending on the nature of the compound. If the organic is a toxic compound which is detrimental to the biomass, then the PACT system by concentrating it and keeping in close proximity with the biomass may worsen the situation. However no such effect was observed in the present study and throughout the study the BOD of the PACT system was lower than the control and exhibited less variability. Now the question arises, if so, by what amount and do we need to switch over to the PACT system. Based on this investigation, the differences in the order of ± 5 mg/ℓ BOD_5 and both the systems never exceeded a BOD_5 value of 10 mg/ℓ ; so for the systems receiving a Benzene dosage of 5 mg/ℓ to 150 mg/ℓ, it is not necessary to use the PACT system for BOD_5 removal.

The degree of improvement in effluent quality does not justify the increased cost of the PACT system. Based on the results shown in Figures 8 to 15 it is indicated that increased cell age from 2 day to 5 day helped the conventional system to provide better effluent quality (BOD). In the PACT system the effect of cell age is minimal. This is due to the fact that at the cell age of θ_c 2 day itself, the BOD_5 is brought down to very low value of less than 2 mg/ℓ. So the effect of further increase in cell age is minimal. The effect of cell age might have been more pronounced at cell age lower than 2 day.

The effluent COD and TOC during transient and steady state are shown in Figures 2-10. Again it is evident that the effluent COD and TOC were always lower in the PACT system than in control. The ratio of BOD to COD was 1 to 20 in the PACT system, and 1 to 10 in the control system. This indicates the relatively higher non-biodegradable, low-oxidisable fraction of organics present in the effluent. The normal ratio in a typical domestic waste is 1:2.

The lower effluent COD in PACT is partly due to the adsorption process, and the remaining of COD in the effluent indicates that there is considerable amount of non-biodegradable and non-adsorbable intermediates in the effluent. The COD to TOC ratio was about 1:1 to 1:2 in both systems and at both cell ages. This indicates the relatively well-oxidized constituencies in the effluent.

The amount of benzene in the effluent was very low, in the order of 5-10 μg/ℓ in PACT and 10-20 μg/ℓ in control (Figures 4-14) at a dosage of 150 mg/ℓ. During transient also the concentration rose to 130 μg/ℓ, but the final steady stage condition was less than 10 μg/ℓ in control and PACT. This is a clear indication that benzene is being biodegraded completely or converted to an intermediate.

All the results discussed above clearly indicate there is a difference between PACT and control in terms of COD, TOC, and BOD_5, but at the same time, for a benzene dosage of 150 mg/ℓ and below, there is no need to use the PACT system because the difference is very minimal and does not justify the increased cost.

In the second part of this investigation varying dosages of PAC were administered to the activated sludge which operated at a 3 and 12 day θ_c, and received a wastewater comprised of synthetic wastewater along with benzene or ethylbenzene or toluene or 1,2 DCE as well as a combination of all the above. It was found that PAC addition not only improved the effluent quality but also was responsible for reducing off-gas emission for benzene and toluene (Figure 22). It was found in the case where 1,2 dichloroethane was administered to the activated sludge system, air stripping accounted for virtually all of the removal of this compound. PAC addition not only slightly improved the effluent quality, but greatly reduced the off-gas emission of this compound.

In the case of combination of priority pollutants, which were four priority pollutants administered to the activated sludge system, the results are a little more complex. For both θ_cs (3 and 12) very little reduction in effluent COD and TOC concentrations were noted as the PAC concentrations increased slightly up to a carbon dosage of 10 mg/ℓ. For toluene, ethylbenzene, and benzene, a 10 mg/ℓ PAC dosage seemed to be the optimum dosage. Very little benefits were achieved when the PAC dosage was increased further.

Virtually no reduction in effluent 1,2 DCE concentration was noted as the PAC concentrations were increased from 0 to 25 mg/ℓ. In all cases, however, for corresponding carbon doses, the 12 day unit was able to achieve lower effluent BOD, COD, and TOC concentrations relative to the 3 day unit. Very low effluent benzene, toluene, and ethylbenzene concentrations were observed for the 12 day unit even when no carbon was added while measurable concentrations were present in the 3 day unit effluent even during the addition of 25 mg/ℓ dosage.

For off-gas emissions in the combined unit very little effect was noted upon toluene, benzene, and ethylbenzene stripping for both 3 and 12 day units as the PAC dosage was increased from 0 to 25 mg/ℓ . Over all, it seems that addition of activated carbon will help to improve the effluent quality marginally or substantially depending on the condition. Further, in some instances the PACT system could provide the comparable effluent quality at lower θ_c. The one need is to take into account the number of economical conditions before selecting the PACT system.

1. Cost of activated carbon.
2. Cost of regeneration of carbon (80-90%).
3. Increased cost of aeration due to decrease in oxygen transfer to the system.

CHAPTER VI

CONCLUSIONS

Based upon the results of these studies, the following conclusions may be drawn in regard to the addition of powdered activated carbon (PAC) to the activated sludge system.

The PACT process improved effluent quality in terms of BOD_5, COD, and TOC and exhibited less variability during the transient and steady state conditions. High cell age (SRT) helps the conventional system to provide a better effluent quality. However in the case of the PACT process the effect of cell age is minimal.

For the system receiving a benzene dosage of 5 mg/ℓ to 150 mg/ℓ it is not necessary to use powdered activated carbon because the benzene leakage into the effluent for both systems (PACT and conventional activated sludge) were almost the same, therefore, the cost increase of the PACT process is not justified.

It was observed that the amount of acclimation experienced by the system was a factor governing the amount of benzene leakage into the effluent.

Toluene, ethylbenzene, and benzene were administered to the activated sludge system and were removed by both stripping and biological oxidation. It was found that powdered activated carbon not only improved the effluent quality but also was responsible for reducing off-gas emission for benzene and toluene.

It was found in the case where 1,2 Dichloroethane was administered to the activated sludge system that air stripping accounted for virtually all of the removal of this compound.

Priority pollutant concentration in the effluent of the PACT system was always lower than in the effluent of the conventional activated sludge system.

The PACT system may be used for wastewater with priority pollutants wherever the benefits of improved effluent quality can offset the increased cost due to powdered activated carbon addition and regeneration of PAC.

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VITA 2

Ali Fazel

Candidate for the Degree of

Doctor of Philosophy

Thesis: THE REMOVAL PERFORMANCE OF POWDERED ACTIVATED CARBON (PAC) IN REMOVING SELECTED ORGANIC PRIORITY POLLUTANTS IN AN ACTIVATED SLUDGE PROCESS

Major Field: Civil Engineering

Biographical:

Personal Data: Born in Tehran, Iran, July 24, 1950, the son of Mr. and Mrs. Mahmoud Fazel.

Education: Graduated from Hadaf High School, Tehran, Iran in May, 1971; received a Licentiate from Arak College of Sciences, Arak, Iran, December, 1974; received Master of Environmental Science degree from the University of Oklahoma, Norman, Oklahoma, December, 1978; completed requirements for Doctor of Philosophy degree at Oklahoma State University in July, 1983.

Professional Societies: Water Pollution Control Federation (WPCF), American Water Works Association (AWWA), National Society of Professional Engineers (NSPE), Oklahoma Society of Professional Engineers (OSPE), Air Pollution Control Association (APCA).

Professional Experience: Construction Engineer's Assistant (1974-1975), National Oil Company, Tehran, Iran. Graduate research assistant (1979-1983), Oklahoma State University.