1987

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Saleh Mohammed Al-Muzaini
University of Rhode Island

Recommended Citation

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TREATMENT OF REFINERY WASTEWATERS USING VARIOUS MODIFIED ACTIVATED SLUDGE PROCESSES

BY

SALEH MOHAMMED AL-MUZAINI

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CIVIL AND ENVIRONMENTAL ENGINEERING

UNIVERSITY OF RHODE ISLAND

1987

DOCTOR OF PHILOSOPHY DISSERTATION

OF

SALEH MOHAMMED AL-MUZAINI

Approved:

Dissertation Committee

Major Professor Len G Thien

William R. Wright

Raymond M. Wright

A A Michel

Dean of the Graduate School

UNIVERSITY OF RHODE ISLAND

1987

ABSTRACT

Biological prosesses for treating refinery industry wastewater for re-use were studied. A pilot-scale biological reactor was constructed to simulate the activated sludge treatment process.

Actual refinery industry wastewater collected from a regional refinery and spiked with additions of selected priority organics was fed at a rate of 1.3 liters/hour into a 6-liter pilot plant having a hydraulic retention time of 4 hours. Activated sludge (AS) which was augmented by additions of powdered activated carbon (PAC) at dosages of 10, 50 and 120 mg/L was evaluated. The AS process removed 70-80% of the BOD_5, COD and TOC. With the addition of PAC, removal efficiencies of the indicator compounds rose to 80-95%. The sludge physical parameters and kinetic constants were determined with and without the addition of PAC to the AS.

PAC additions to the AS increased the amount of biomass in the reactor. Volatile compounds (benzene, chloroform, ethylbenzene, toluene, m-xylene and o-xylene) were removed from the reactor by volatilization which occurred from air stripping. PAC alone (without AS) was primarily responsible for removing base and acid/neutral-extractable compounds (2,4-dimethylphenol, fluorene, naphthalene and pyrene).

ACKNOWLEDGMENTS

This investigation was supported by a grant from the Kuwait Environmental Protection Council and the Kuwait Institute for Scientific Research.

The author wishes to extend his appreciation to his advisor, Dr. Leon Thiem and to Dr. Raymond Wright and Dr. William Wright for their assistance. Also the author would like to thank Sam Huston for his help in bringing wastewater from Pennsylvania to Rhode Island, George Huston for assistance with the mechanical apparatus and to my family for their understanding.

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GLOSSARY

AAS	Atomic adsorption spectrophotometry
AS	Activated Sludge
API	American Petroleum Institute
BOD_5	Biochemical oxygen demand, mg/L
C	Equilibrium carbon concentration, mg/L
C_I	Influent carbon concentration, mg/L
COD	Chemical oxygen demand, mg/L
D	Daily carbon dosage, mg/L
DOC	Dissolved organic carbon, mg/L
Efft	Effluent, concentration, ug/L
Effy	Efficiency of the system
EPA	U.S. Environmental Protection Agency
EPC	Kuwait Environmental Protection Council
EPC	Environmental Protection Center
GC	Gas Chromatography
GPM	Gallon per minute, GPM
HDT	Hydraulic detention time, hours
HRT	Hydraulic retention time, hours
Inft	Influent, concentration, ug/L
k	Maximum rate of substrate utilization, day^{-1}
k_d	Endogenous decay coefficient, day^{-1}
K_s	Half velocity constant, mg/L of BOD_5 or COD
KNPC	Kuwait National Petroleum Company
MGD	Million gallons per day, MGD

MLSS	Mixed liquor suspended solids, mg/L
MLVSS	Mixed liquor volatile suspended solids, mg/L
N	Number of reactors
PAC	Powdered activated carbon
pH	Reciprocal of the Logarithm of the Hydrogen Ion Concentration
PIC	Petroleum Industrial Companies
Q	Flow rate, L/hr
Q_e	Effluent flow rate, L/hr
Q_o	Influent flow rate, L/hr
Q_r	Return flow rate, L/hr
Q_u	Under flow rate, L/hr
Q_w	Sludge wasting flow rate, L/hr
r_g'	Net growth rate of biomass, mg/L
r_g	Rate of bacterial growth, mg/L day
r_{su}	Substrate utilization rate, mg/L
S	Substrate concentration, mg/L
S_e	Effluent substrate concentration, mg/L
S_o	Influent substrate concentration, mg/L
SAA	Shuaiba Area Authority
SEM	Scanning Electron Microscopy
SIA	Shuaiba Industrial Area
SRT	Sludge retention time, days
S_r	Return cell concentration, mg/L
S_u	Underflow substrate concentration, mg/L
SS	Suspended solids concentration, mg/L

t	Number of days
TDS	Total dissolved solids, mg/L
TKN	Total Kjeldahl nitrogen
TOC	Total organic carbon, mg/L
TSS	Total suspended solids, mg/L
u'	Net specific growth rate, day^{-1}
u	Specific growth rate, day^{-1}
U	Specific substrate utilization rate, gm/gm-day
u_m	Maximum specific growth rate, day^{-1}
V	Volume, L
VSS	Volatile suspended solids, mg/L
W	Weight of carbon, mg
X	Concentration of cells, mg/L
X_e	Biomass concentration in the effluent, mg/L
X_o	Biomass concentration in the influent, mg/L
X_r	Return cell concentration, mg/L
X_u	Biomass concentration in the underflow, mg/L
X_w	Wasting cell concentration, mg/L
Y	Maximum growth yield, mg VSS/mg-BOD_5 or COD
θ_c	Sludge age, days
θ_h	Hydraulic retention time, hours

1. INTRODUCTION

The Shuaiba Industrial Area (SIA) is Kuwait's first and largest industrial complex and one of the largest industrial areas in the Arabian Gulf. It produces about 6 MGD of refinery industry wastewater which is discharged directly to the Arabian Gulf without extensive treatment.

1.1 Shuaiba Industrial Area Site Description

Shuaiba Industrial Area (SIA) is located about 50 km south of Kuwait City, Kuwait as shown in Figure 1.1. The total area of SIA (both its Eastern and Western Sectors) is about 22.98 million sq. meters. This study focuses only on the Eastern Sector. Figure 1.2 presents the Shuabia Industrial Area. The Eastern sector of the SIA has twelve major industries, including a petrochemical company, two refineries, two desalination power plants, a melamine company, an industrial gas corporation, a paper products company, two steam electricity generating stations in addition to several other industries. The key to Figure 1.2, which represents the industry locations, is presented in Table 1.1.

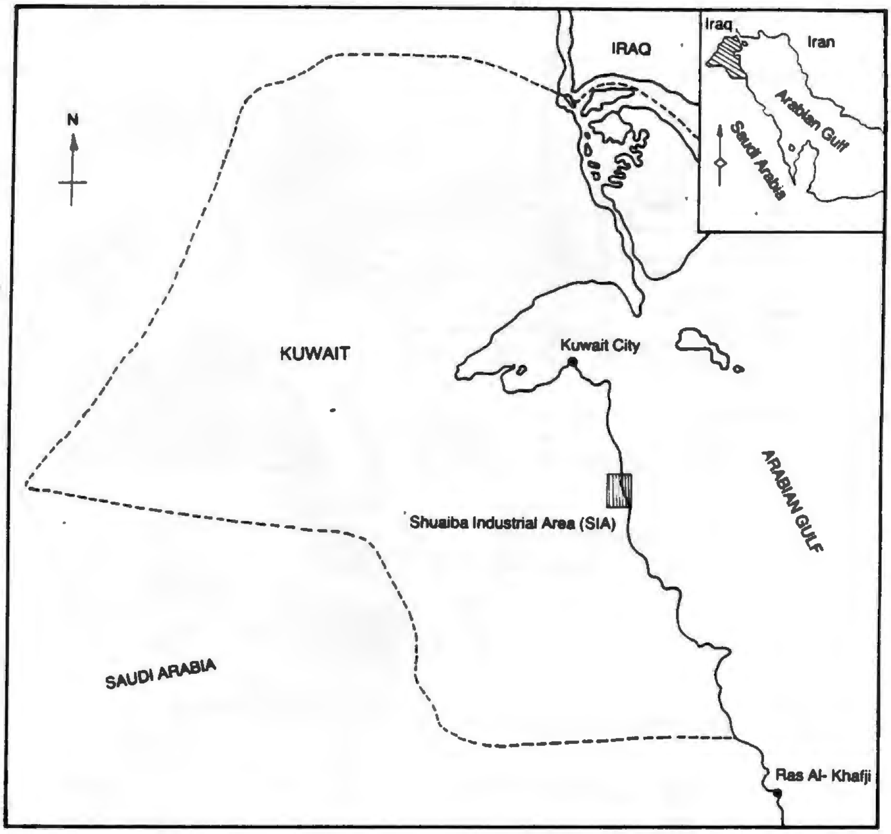


Figure 1.1 Location of the Shuaiba Industrial Area with Respect to Kuwait City and Arabian Gulf

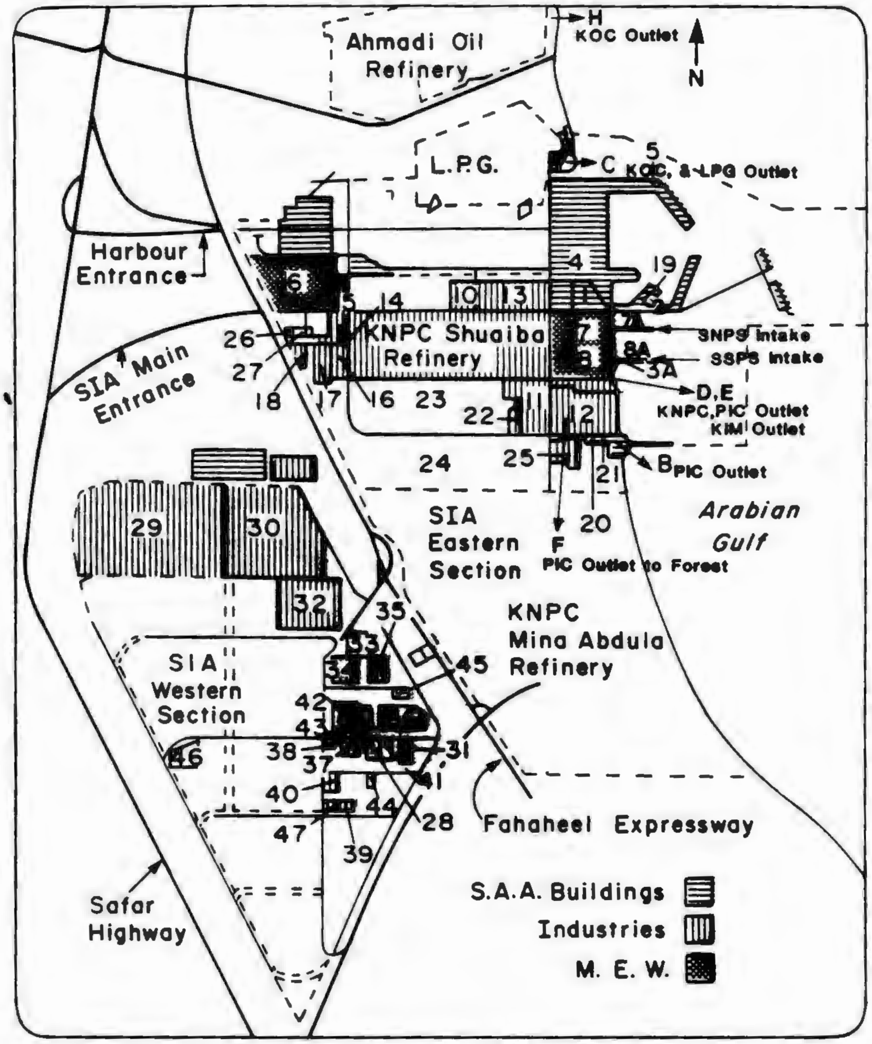


Figure 1.2 Shuaiba Industrial Area

Table 1.1 Key to Shuaiba Industrial Area

Key No.	Description
	EASTERN SECTION
1 -	S.A.A. Buildings
2 -	Barge Harbour
3 -	Cooling Water Intakes and Pumping Station A,B,C
4 -	Environment Protection Center
5 -	Shuaiba Harbour Expansion Project
6 -	Ministry of Electricity and Water
7 -	Shuaiba North Power and Water Production Station
8 -	Shuaiba South Power and Water Production Station
9 -	K.N.P.C. (Shuaiba Refinery)
10-	K.N.P.C. (Lube Oil Blending Plant)
11-	P.I.C. (Fertilizer Division, Plant A)
12-	P.I.C. (Fertilizer Division, Plant B)
13-	Kuwait Cement Company
14-	Shuaiba Paper Products Company S.A.K.
15-	Packaging and Plastic Industries Company.
16-	Dresser (Kuwait) S.A.K.
17-	KREMENCO
18-	Kuwait Petrochemical Products Co. (Sulphur Factory)
19-	United Fisheries of Kuwait Co. Corporation
20-	Kuwait Industrial Gases Corporation
21-	Refrigeration and Oxygen Co. Ltd.
22-	Kuwait Melamine Industries Company
23-	Proposed Site of Aromatics Project Plant
24-	Proposed Site of Olefins Project Plant
25-	Salt & Chlorine Division
26-	Shuaiba Post Office
27-	Industrial Medical Centre

Table 1.1 (continued) Key to Shuaiba Industrial Area

Key No.	Description
	WESTERN SECTION
28-	The Gulf Paper Manufacturing Co.
29-	N.I.C. (Sand Quarry)
30-	N.I.C. Lime Products Factory
31-	Kuwait Insulating Material Manufacturing Co.
32-	Kuwait Asbestos & Plastic Industries (N.I.C)
33-	Sanitary Ware Company
34-	Kuwait Precast System Co.
35-	Real Estate Con. and Fabrication Co.
36-	Kirby Building Systems, Kuwait.
37-	Al-Rabiah International Contracting Co.
38-	Kuwait Gypsum Manufacturing & Trading Co.
39-	Kuwait Blanket Manufacturing Co.
40-	Kuwait Chemical Manufacturing Company
41-	Gulf Glass Manufacturing Co.
42-	National Automotive Manufacturing & Trading Co.
43-	The Kuwait-Italian Steel Structures Co.
44-	Kuwait Lube Oil Co.
45-	The Kuwait Desalination Plants Fabrication Co.
46-	Kuwait Oil Tanker Company
47-	Kuwait Silicone Products Company

1.1.1 Existing Water Quality

Most of the industries in SIA are located near the shore of the Arabian Gulf, and discharge their wastewater directly into the Gulf after partial treatment or without any treatment. The pollutants remain in the water and because the seawater intakes of the two desalination plants (7A and 8A in Figure 1.2) are close to the outlet of these industries (B, C, D, and E in Figure 1.2), the pollutants may enter the water intakes of the desalination plants.

The inshore water of SIA is very shallow. The water depth offshore of SIA averages about 5 meters within 1 km from the coast line. Thus, most discharged pollutants are not well mixed or diluted with sea water (58).

The discharged industrial wastewaters in the SIA inshore water are diluted with seawater from the cooling water from the pumping stations. The concentration of pollutants in the wastewater will be affected by mixing with seawater in that the concentrations are reduced but the mass loading of the organic pollutants will not be reduced.

The main pollutants discharged by the existing industries in the SIA include the following: a high concentration of ammonia, heavy metals such as chromium, highly-colored wastes; large amounts of oil and grease;

urea, hydrogen sulfate; high temperature; and toxic organic chemicals. The measured and calculated values of the main pollutants are summarized in Table 1.1.1.

1.1.2 Present Wastewater Treatment

Presently, each plant in the SIA has its own on-site treatment plant. The industrial wastewater treatment in the PIC consists of 1) a hydrolyzer to purify the high ammonia and urea, 2) neutralizing pits for neutralizing and mixing operations, and 3) oil skimmer units. The hydrolyzer treats the wastewater efficiently, except during a plant shutdown when the raw wastewater is diverted to the neutralizing pit, to the forest, or as overflow to the sea. The chemical and surface drain waters are diluted with the seawater used in cooling and then mixed with refinery industry wastewater. This mixture then goes directly to the Gulf. The main contaminants are oil, NH_3, COD and urea.

At the KNPC refinery, the wastewater is collected in different drainage basins. The ammonia wastewater drain collects the wastewater contaminated with high ammonia and diverts it to the ammonical water treatment process. The sour water (with a high concentration of hydrogen sulfate) is collected and routed to the sour stripping unit, where the pre-treated water goes to the oil separator known as

Table 1.1.1 Industrial Wastewater Flows and Pollution Loads in the SIA. (Source: Ref. No. 58).

Sea Outlet Point	Industry	Flow Rate (m^3/h)		Average Pollution Load* (kg/d)									
		Max	Av	COD	TSS	TKN	Urea	NH_4N	Oil	H_2S	Cr	Temp	pH
D	KMI	30	15	100	1500	1800	50	700	3	0	0.4	32	9.4
B	PIC (South Surface Drain)	70	50	300	-	(80)	10	70	4	0	0.6	29	8.8
E	PIC (Chemical Drain B)	70	70	500	-	(400)	90	300	30	0	0.2	60	8.8
E	PIC (North Surface Drain B)	70	20	700	-	(400)	280	40	0	0	0.1	25	8.5
E	PIC A Surface Drain	90	25	800	-	(100)	40	50	210	0	tr	40	6.5
E	KNPC (API)	-	150	1800	(180)	(300)	0	280	480	60	1.6	55	10.0
C	KOC (LPG South)	20											
C	KOC (LPG South) Oily Water	60	50	1200	-	-	0	0	7	0	tr	40	7.5
G	KOC & LPG North (Chemical Drain)	10	5	50	-	-	0	0	3	0.1	0	33	7.6
H	KOC + LPG North Zone (Oily Water Effluent)	50	21	600	-	(20)	0	20	30	2	tr	39	8.2
F	PIC (Neutralizing Pit Effluent)	80	50	400	0	3700	3300	400	35	0	tr	66	8.8

*Assuming maximum production
( ) Estimated value

tr = trace

the API. The surface drain effluent is also routed in the API. The overflow of this pit is diluted with cooling sea water and then routed to the Gulf. The main contaminants of this effluent are high COD, NH_3, H_2S, oil and organic compounds.

However, the effluent of the National Refinery at Mina Abdullah has no affect on the Arabian Gulf water quality, because this wastewater is routed into lagoons located in the desert. There is no data on the lagoon water quality.

Industrial wastewater from Kuwait Oil Refinery is collected in settling tanks, the effluent is diluted with cooling seawater and then routed to the sea. Effluent from the chemical sump is treated similarly. The main pollutants here are oil, organics, COD and heavy metals. The Melamine industry's wastewater consists of cooling tower effluent and boiler blowdown discharge into the drainage system. The main pollutants are NH_3, TKN and TSS.

With the present high concentrations of contaminants in the effluents and the high rate of wastewater produced and discharged into the Gulf, it appears without a doubt that the present treatment is not efficient nor is it sufficient to meet the recommended standards set by the SIA authority as shown in Table 1.1.2. Laboratory analyses have indicated that the wastewater carried high

Table 1.1.2 Recommended Ambient Marine Environment Quality Criteria for Inshore Waters Around Shuaiba, (Source: Ref. No. 58).

Parameter	Desirable Environmental Value	Maximum/Minimum Threshold Hazard Value	Typical Concentration for Measured Effluents ppm
PH	8.0	5.5 to 9.0	
Dissolved Oxygen	5.4 ppm	2.0 ppm	
COD	2.0 ppm	4.0 ppm	3.67
BOD_5	2.0 ppm	4.0 ppm	210.00
Total Hydro-Carbon	Not detectable	0.5 ppm (as in water bulk)	
Phenolics	0.05 ppm	0.10 ppm	
Detergents	0.05 ppm	0.20 ppm (as in	
Sulphides (H_2S)	0.005 ppm	0.01 sulphide ion)	
Ammoniacal Nitrogen (NH_3/+NH_4)	0.02 ppm	0.20 to 0.50 ppm (as ammonium ion)	3.35
Oxidised Nitrogen	0.40 ppm	0.80 ppm	
Total Nitrogen	0.50 ppm	1.30 ppm	
Inorganics Phosphates	0.001 ppm	0.02 ppm	
Cyanide	Not detectable	0.01 ppm	
Alkyl Mercury		0.0001 ppm	
Total Mercury		0.0001 ppm	
Arsenic	0.01 ppm	0.05 ppm	
Cadmium	0.001 to 0.01 ppm	0.03 ppm	
Lead	0.01 ppm	0.05 ppm	0.025
Chromium	0.05 ppm	0.10 ppm	1.20
Copper	0.001 to 0.01 ppm	0.05 ppm	0.052
Zinc	0.001 to 0.10 ppm	0.10 ppm	
Iron	0.05 ppm	0.30 ppm	1.25
Manganese	0.02 ppm	0.10 ppm	
Nickel	0.002 ppm	0.10 ppm	0.02
Coliform Bacteria	100 MPN/ML	2000 MPN/ML	

MPN = most probable number

levels of ammonia, oil, H_2S, urea, organic compounds, inorganic compounds and suspended solids. Presently these pollutants can have adverse effects on marine life. Some of these pollutants are carried into the desalination power plants due to the close proximity of the power plant intakes to the industry outlets. Treating high levels of pollutants with seawater dilution is not a solution to the problem. There are now plans to improve the present situation and lower pollutant loads by improving the primary treatment plants, but since the wastewater flows will also increase, the net improvement in water quality will not be significant. Therefore, this study was initiated to investigate methods of treating priority pollutants found in SIA refinery industry wastewater using a powdered activated carbon with activated sludge as a secondary treatment.

1.2 Objectives

1. To investigate the application of activated sludge (AS) with powdered activated carbon (PAC) additions to treat a refinery industry wastewater by bio-removal of both conventional and priority pollutants.

2. To determine the biological kinetic constants in terms of BOD_5, COD and TOC for the activated sludge and for the activated sludge with addition of PAC at different carbon dosages.

2. LITERATURE REVIEW

2.1 Activated Sludge Treatment Processes

Extensive studies on activated sludge (AS) treatment of refinery industry wastewater have demonstrated that organic pollutants could be removed by converting most organic pollutants to more stable inorganic forms such as CO_2 and H_2O or to cellular masses.

Stover et al. (64) investigated the fate and the treatability of specific organic compounds such as benzene, phenol, 1,2-dichloroethane, 1,2-dichloropropane and tetrachloroethane found in a complex industrial wastewater. An activated sludge reactor was used to treat a synthetic wastewater containing specific organic compounds individually or in various combinations. They found that the removal efficiencies were high for all compounds investigated. Compounds such as 1,2-dichloroethane, 1,2-dichloropropane, and tetrachloroethane were stripped from the biological reactor.

However, Kincannon et al. (39) have shown that in addition to those compounds, benzene, methylchloride and 1,2-dichlorobenzene were completely stripped under identical conditions without a biological treatment.

Travers et al. (69) investigated a completely mixed activated sludge reactor fed with an industrial wastewater containing a high concentration of fat and specifically to study its performance at different concentrations of dissolved oxygen (DO). They concluded that the fat present in the influent of wastewater will be degraded rapidly at higher DO concentrations (up to 4.0 mg/L) and the sludge contained few filamentous microorganisms and low fat content and settled readily.

Shaul et al. (56) studied the removal of azo dyes from wastewaters using an activated sludge process. They showed that dyes in wastewater could be removed both by adsorption onto biological sludge solids and by biological degradation.

However, Reitano (54) reported that activated sludge removed about 40-80% of the COD where COD in the feed was in the range of 500 to 50 mg/L and that microorganisms could grow in concentrations of phenol of up to 200 mg/L.

Gallagher et al. (26) discussed an activated sludge pilot plant for treating a pretreated gasification condensate containing high COD, phenols, and ammonia. The treated wastewater could be used as cooling tower makeup. They showed that an activated sludge pilot plant process with a higher sludge retention time (SRT) (20 to 30 days) was more stable and produced the highest quality effluent. In addition, there was a reduction in biodegradable organics in the range of 99% to 100%. To obtain removal of thiocyanate, cyanide and ammonia in the wastewater required a long SRT (>20 days) combined with an increase in the hydraulic retention time to 3 days.

Lovett et al. (44) have shown that an industrial wastewater with high phosphorus could be effectively treated by an activated sludge process using sludge ages from 5 - 20 days. The effluent produced was low in phosphorus and total Kjeldahl nitrogen (TKN). They suggest further that feeding wastewater reactors continuously produced high effluent COD removal (>98%).

2.2 Addition of Powdered Activated Carbon To Improve Activated Sludge Treatment

For many years PAC was little used in chemical plants to remove suspended solids, organic compounds, color and odors because there was insufficient information about carbon design units and operating conditions. Also, there was no well-defined method to regenerate the carbon for reuse. Presently, new design methods and different ways of applying carbon have resulted in an increased use of carbon materials in wastewater and chemical plants (6, 50, 71, 75).

When activated carbon comes in contact with organic materials in wastewater, it removes compounds selectively by a combination of adsorption of less polar molecules, straining of the larger suspended particles and deposition of colloidal material on the exterior surface of the activated carbon. Removal of soluble organic compounds depends on diffusion of the dissolved particles onto the carbon surfaces. For colloidal particles, internal diffusion is important. Adsorption, in general, is a result of forces of attraction at the surface of a particle that cause soluble organic materials to be attracted and held on the surface. The activated carbon has a large surface area per unit weight, which makes it an efficient adsorptive material. In a wastewater plant, activated carbon is used as a tertiary process following a conventional secondary treatment unit. The efficiency of carbon adsorption in wastewater plants will depend first of all on the quality and quantity of the waste to be treated (13, 52).

Activated carbon can be classified into two groups: powdered and granular. Powdered activated carbon is produced by activating pieces of wood, charcoal, coconut shells and peats.

PAC has several advantages over granular carbon:

1. Lower capital costs. PAC requires less valves, piping, or columns.
2. Greater ability than GAC to control hydrogen sulfide gas.
3. Minimal pretreatment cost.

Activated carbon has been shown to remove chemical compounds present in waters and wastewaters which exhibit toxic, carcinogenic, mutagenic or teratogenic properties.

Previous studies have shown that addition of PAC to an activated sludge system not only improved the system's removal of organic pollutants, but increased the efficiency of the AS processes (17, 37). The studies have also shown that in addition PAC will:

1. improve BOD and COD removals despite high organic loading,
2. adsorb toxic materials present in the waste without biological treatment,
3. reduce color, foam and detergents from reactor and clarifier effluents,
4. improve solids settling in reactors as well as in clarifier effluents,
5. perform better over a wide range of organic and hydraulic loads,
6. improve plant operation efficiencies and save on capital investments because no additional equipment is needed, and,
7. reduce phosphorus concentrations.

During the aerobic oxidation, PAC adsorbs the organic pollutants dissolved in the waste stream. The adsorbed pollutants are degraded when they come in contact with biological organisms as follows:

$$\text{Organic Pollutant} + \text{Bacteria} + O_2 \xrightarrow{N,P} CO_2 + H_2O + \text{cells}.$$

It has been proven that some organic pollutants present in a receiving water are potentially dangerous to human and animal life. It is very important to gather information and data on the biodegradability and chemical-physical treatability of these organic pollutants. Traditional treatment processes cannot meet the requirements for removal of all of the 129 organic compounds (see Appendix 1), but additions of PAC to the AS reactor were found to reduce influent levels of BOD, COD, TOC and several priority organics such as benzene, ethylbenzene and toluene.

Weber (79) reported that there is little information on the treatability of all of the priority pollutants present in the highly complex mixtures of organic compounds in refinery industry wastewater.

Adam (1) showed that additions of powdered carbon to a conventional activated sludge treatment system with an average BOD of 1,700 mg/L and a COD of 3,200 mg/L increased COD removal by 25% and BOD removal by 20% during a two-month study. Another test that Adams conducted was at a municipal plant receiving about 70% of its industrial flow from a textile dyeing and finishing mill. A primary clarification tank effluent and a trickling filter effluent were directed to a contact stabilization basin. The BOD of the influent varied between 90 and 350 ug/L. Powdered activated carbon was added at a dose of 20 to 25 ug/L based on the influent flow rate. After five months of operation, BOD removals increased from about 70% to 90%, and the solids settling improved.

De John et al. (15) have evaluated PAC (Hydrodarco) added to AS systems to treat four refinery wastewaters. They reported for the first experiment that BOD reduction was 82% and BOD removal reached about 90-95% when the carbon concentration reached 1,800-2,000 mg/L within the AS reactor. For their second experiment, they used a 12 MGD flow with TOC concentrations in the range of 100-1,000 mg/L. Carbon added at a dose of 100 mg/L produced a 20% reduction in the TOC in the wastewater; however, when the carbon dosage was increased to 500 mg/L the effluent BOD reached to 30 mg/L. Their third experiment was conducted at a 2.5 MGD plant treating a 550 mg/L COD refinery wastewater in a two-stage conventional activated sludge system. Carbon was added at the rate of 200 mg/L over a six-week period. Effluent solids and COD removal increased to 40% and BOD removal increased by as much as 90%. Their fourth experiment was conducted at a 2 MGD plant treating refinery wastewater with a wide range of pH fluctuations. A PAC level of 400 mg/L was added and maintained daily. They reported that there was improvement in the BOD, COD, and SS removals, which reached the 90-95% range and the plant was able to meet the 30 mg/L BOD effluent standard.

Leipzig et al. (43) investigated treatment of the Salsbury (South Africa) Industry wastewater in five bench-scale laboratory experiments, including (1) AS, (2) a carbon adsorption column, (3) PAC, (4) macroreticular resin adsorption and (5) solvent extraction. After a five-month study, they determined that when PAC was added to an activated sludge reactor with a HRT of 2 or 3 days, there was no difference in the performance. A daily carbon dosage of 167 mg/L added to a 2-day HRT reactor with a mixed liquor activated carbon concentration of 5000 mg/L not only allowed nitrification to occur but provided an increase in TOC and color removal were 80% and 60%, respectively.

Ferguson et al. (21) tested the addition of carbon to two activated sludge studies of batch and continuous-flow processes. A COD supplement was added to increase the COD concentration in the influent to about 200 mg/L. Hydrodarco H powdered activated carbon was used. From the batch study, they concluded that even when PAC in the reactor carbon was at a concentration of 90 mg/L there was poor removal of trichlorophenol. For their continuous study they found that a carbon dosage of 50 to 100 mg/L gave better performance than a unit that was receiving 95 mg/L of trichlorophenol with PAC of 150 mg/L. The sludge retention time had an effect on effluent quality. SRT values between 7 and 12 days were found to yield the highest effluent quality and increased trichlorophenol removal with a PAC dosage of 50 mg/L; at a carbon dosage of 150 mg/L, trichlorophenol was completely removed.

Chao et al. (8) developed three completely mixed, continuous flow, activated sludge reactors. The wastewater feed consisted of 75% coke-plant wastewater and 25% sanitary wastewater. Five PAC doses (200, 300, 500, 700 and 1,000 mg/L) were investigated with two HRT's. PAC added at a dose of 300 mg/L combined with shorter HRT's increased COD removals. They reported that addition of PAC at a dose of 300 mg/L not only improved cyanide removal but also reduced the sensitivity to fluctuations in the feed. They also pointed out that neither cyanide nor thiocyanate in the wastewater was adsorbable on the PAC.

DeWalle et al. (16) found that PAC dosages of 0, 50, 300, and 1,000 mg/L to a plug-flow activated sludge unit and to units maintained at sludge ages of 3,5,10 and 15 days would increase the percentage removal of organic matter. They reported that COD removal tended to be independent of sludge age.

Janeczek et al. (37) investigated the effect of PAC additions to six AS processes at doses of 250, 500, 1,000, 2,500 and 5,000 mg/L for treating coal gasification wastewater diluted to one-quarter strength, at which BOD, COD and TOC were 2,000, 4,425 and 2,000 mg/L, respectively and pH was between 7.8 and 7.9. The major organic constituent was phenol. They reported that 97% of the COD was removed by PAC and 52% of the COD was removed by a biological unit. Also 98% of phenol was removed by biological treatment but adding PAC increased its removal to about 99.99%.

Heath (34) concluded that adding PAC to a 30 to 40 MGD DuPont plant with a complex chemical wastewater removed over 96% of the BOD and over 80% of the DOC. Heath added that the plant achieved a solids concentration removal of about 40% in the clarifier. Organic removals increased at a carbon dose of 120 ppm and higher sludge ages (20 to 60 days). Also 90 - 95% of the volatile organics and acid-extractable compounds were removed but base/neutral compounds were not removed. He also showed that PAC could be regenerated successfully in a multiple-heath regeneration furnace.

Adams (2) studied the addition of powdered activated carbon to a 1 MGD municipal plant treating about 70% industrial wastewater from a textile dyeing and finishing mill. The influent BOD ranged from 90 mg/L to 350 mg/L, averaging 150 mg/L. The effluent solids and color averaged 26 mg/L and 248 APHA units respectively before carbon was added. The HRT was about 2.2 hours. Adams found that BOD removals were increased from 72 to 89% with an increase in the carbon dose from 20 to 25 mg/L. Also, adding PAC at an average rate of 19 mg/L increased solids settling by 20%. An equilibrium carbon dosage of 500 mg/L reduced the color from 670 to 320 APHA. Adams indicated that PAC could be regenerated using a wet air oxidation with reasonable losses of 6% to 30%.

Flynn et al. (22) examined three bench-scale treatment units using industrial wastewater. Two units operated as PAC units and the third one was a biological unit. The PAC units were operated at different sludge ages (8.5 and 9.2 days). Flynn et al. concluded that effluent quality improved with a sludge age of 9.2 days and/or increasing carbon dose to 150 mg/L. In addition, a high sludge age (9.2 days) and low carbon dose (124 mg/L) produced an effluent similar to that from a unit operated at a lower sludge age (8.5 days) and a higher carbon dose (150 mg/L).

Flynn (23) tested a theoretical steady state model which incorporated the additions of PAC to an activated sludge process treating a wastewater containing heavy metals, dissolved dyes and organic compounds. Three separate tests were conducted with carbon dosages of 50, 150, and 650 mg/L at sludge ages of between 8.5 and 9 days. He concluded that BOD removal could be successfully modeled using a conventional kinetic approach.

Osantowski (51) et al. conducted PAC/AS studies to treat a raw pharmaceutical wastewater with a high COD, for 83 days. The HRT's and SRT's were 3 days and 10 days, respectively. For the first test 208 and 827 mg/L of PAC were added; in the second test, 496 and 1520 mg/L of PAC were used. The tests showed that PAC additions improved the removal of COD to about 90% but had no affect on the soluble CBOD (S-CBOD) of the effluent.

Heath (35) reported that PAC was added to a 40 MGD industrial wastewater treatment plant. The performance of the PAC exceeded expectations for BOD and color removal which were measured as 96% and 68% respectively. Removal of DOC and toxic and hazardous substances were also high. Also, operation at a sludge age of over 25 days reduced the required PAC dose from more than 170 mg/L to 120 mg/L. Heath found that the PAC could be regenerated with an 80% yield and a recovery of 63% of its virgin carbon properties.

Heath (36) discussed a 40 MGD plant which used the DuPont PACT process to treat an industrial wastewater from a variety of sources, to produce an effluent with the quality that could be achieved from secondary/tertiary treatment processes. The PACT process has been able to achieve a higher degree of treatment than could be obtained with a conventional actived sludge system. The influent had a soluble BOD of 280 mg/L, a DOC of 205 mg/L, a TDS of 2000-5000 mg/L and a TSS of 258 mg/L. The PAC process used only 150 mg/L of carbon at a 8-day sludge age; it gave a BOD removal of over 95% and increased DOC removal from 62% to 85%. Both color and foam concentrations were reduced and sludge settling was improved. Volatile organics such as benzene or chloroform and toluene and acid extractables such as 2-chlorophenol and phenol were removed, but base/neutral compounds (1,2 dichlorobenzene, and 2,6 dinitrotoluene) were removed with less success. Also, some heavy metals were removed.

McKay et al. (47) investigated the adsorptive capacity of PAC (Filtrasorb) for a number of pollutants (phenol, chlorophenol, dodecylhydrogen sulphate salt, mercuric ions, and chromic ions) in an aqueous solution. The Langmuir constants (mg/g) have been determined and they were 213 for phenol, 434 for chlorophenol and 361 for dodecylhydrogen sulphate, 138 for mercuric ions, and 35 for chromic ions. Tests showed that the carbon capacities were particle size dependent and that differences in adsorptive capacities were linked to the solute-adsorbent bonding.

Garcia-Orozco et al. (27) investigated eight reaction units operated for 4 weeks at sludge ages of between 4 and 12 days. Carbon was added at 70 mg/L to the first four reactors and no carbon was added to the other four. 4,6 dinitro-O-Cresol (DNOC), a priority pollutant was increased in concentration from 0 to 27 mg/L during the 4 weeks that the experiment was performed. TOC concentrations of the influent changed from 650 to 27 mg/L. A second carbon dose of 175 mg/L was added after 4 weeks. The test results showed that the assumptions on which the overall removal model was based were satisfactory (operational parameter, carbon dosage and sludge age) and they did represent the behavior of the PAC/AS process. The biodegradation rate coefficient, K_b, increased, but Y decreased, based on TOC concentrations. Carbon adsorption and biodegradation were the two mechanisms responsible for the DNOC removal.

Stensel et al. (62) studied the removal of organics from a refinery wastewater using an 800-gallon aeration tank in a pilot plant with a liquid retention time of 14.3 hours. The feed to the aeration tank was 1 gallon per minute (gpm). They evaluated three processes for the removal of organics: filtration-activated carbon, biological treatment, and biological-filtration-activated carbon treatment. The design parameters for PAC were bed depth or contact time and organic loading. Stensel et al. showed that to maintain effluent quality at a COD of about 37 mg/L the operating time should be increased. Also, effluent from the biological treatment process had a higher organic loading due to poor adsorption of organics, but the activated carbon adsorption increased with increasing molecular weight and decreased with decreasing aqueous solubility and polarity.

Stenstrom et al. (63) investigated whether carbon additions would produce high effluent quality. Three experimental phases were conducted using five reactors. Four reactors were operated at a sludge age of 20 days and were fed with 100 mg of carbon per liter of wastewater feed. One reactor was left as a control. Tests showed that improvement in the effluent quality of the carbon-fed units over the non-carbon-fed unit ranged from 65% for soluble organics to 95% for phenolics. A carbon concentration of 200 mg/L yielded a high effluent quality. Stenstrom et al. also concluded that less carbon added at a 60-day sludge age was the same as a high concentration of carbon added at a 30-day sludge age.

Flynn et al. (24) demonstrated that adding powdered activated carbon (65% Nuchar SA and 35% Hydrodarco C) to a 40 MGD aerator tank seeded with an industrial activated sludge yielded a 77% BOD removal. Increasing sludge age and temperature reduced the effluent's dissolved organic carbon (DOC) concentrations from 70 to 30 mg/L and reduced the effluent's BOD from 30 to 8.4 mg/L. Changing the carbon dose from 190 to 125 mg/L worsened the quality of the plant effluent slightly; DOC went from 28.6 to 40.3 mg/L and BOD went from 9.6 to 18.8 mg/L. A low carbon dose (80 mg/L) with a long sludge age (29 days) produced an effluent quality equivalent to that of the PAC process (157 mg/L carbon and 7.3 days sludge age). Therefore, Flynn et al. concluded that a PAC process with a low carbon dose and a long sludge age would produce a high-quality effluent.

Grabowski (27) described an agreement between a municipal wastewater facility and Sun's Marcus Hook Refinery Co. in Delcora, PA, in which Delcora would treat Hook Refinery wastewater as a joint treatment. Delcora had a secondary treatment plant, consisting of an activated sludge basin, a clarifier and a disinfection unit (chlorination). Grabowski indicated that, utilizing joint treatment, the Hook refinery would be able to control the organic pollutants in their final effluent.

Wallace et al. (74) discussed a 50 gpm pilot plant using a solids-contact treatment, which operated for 24 hours per day to remove soluble organics from wastewater by adding PAC. They concluded that treatment with a PAC addition could remove more organic compounds than a single-stage treatment could. In a carbon system, a biological treatment was responsible for removal of more than 50% of the soluble organics. Also, in a system with less organics, the inorganic coagulant pretreatment could reduce the organic loading and in some cases eliminate the need for carbon additions.

Specchia et al. (60) reported that adding Norit SA-5 PAC at a concentration of 0.2 to 0.1 gm/L to a 500-m/l Warburg-type respirometer fed with wastewater from a cotton and synthetic cloth dye-works helped to increase the removal efficiency for COD from 55.8 to 75.6% and increased BOD removals from 78 to 98.5% Also, the nitrification - denitrification capacity of the system was increased. Adding PAC reduced bacteria growth and increased the biological removal rates. Data collected from the experiment were used to calculate the biological oxidation constants.

Kincannon et al. (39) conducted two experimental studies on both non-biological and biological activated sludge systems. They used a 3-liter activated sludge reactor with a 3.23-liter settling clarifier. The activated sludge system was operated at SRTs of 2,4 and 6 days and an HRT of 8 hours. 1,2 - dichloropropane, methylene chloride, benzene, ethylacetate, 1,2-dichloroethane, phenol and 1,2-dichlorobenzene was added to a synthetic wastewater. It was shown that all compounds were stripped except phenol. Higher removal efficiencies were achieved based on BOD and TOC.

Frohlich et al. (25) assessed the use of biophysical treatment technology to treat effluents from both the pharmaceutical and fine organic chemicals industries. The BOD and TOC of the influent were about 7,470 and 14,970 mg/L respectively. The system showed higher removals of COD, BOD, color, odor and nitrogen.

Zimpro (33) showed that addition of PAC in an activated sludge treatment would improve BOD removal from 58% to 97% and COD removal from 58% to 97%, but the suspended solids removal increased from 73% to 91%. Color was also reduced by between 150 to 500 APHA units. In the industrial sector, however, PAC reduced TOC and color by 93 and 98% while a biological treatment removed only 67 and 27%, respectively.

2.3 Priority Pollutants

Specific organic compounds found in wastewaters are known as "priority pollutants". In the literature, investigators were concerned with defining better analytical methods for measuring and making assessments on the presence of these chemical compounds. Keith et al. (38) summarized the steps taken by U.S. EPA to develop a program for the priority pollutants in order to establish effluent limitations as well as guidelines. In the program, there were 129 priority pollutants. Each compound was analyzed to determine a monitoring level in the industrial discharges.

Chapman et al. (9) investigated the fate and the effects of the 129 priority pollutants in the environment based on their chemical behavior. They suggested that selection of individual priority pollutants for a monitoring program should be based on their anticipated fate and their effects in the environment.

Kincannon et al. (40) studied two mechanisms for removal of toxic priority pollutants. A 3-liter, activated sludge, completely mixed reactor was used with a 3.23-liter settling compartment. The reactor was fed with a synthetic wastewater with a BOD between 250 and 300 mg/L. The activated sludge system was operated at 3 sludge ages (2, 4 and 6 days). The 2-liter batch reactor had a mean residence time of 3 days. Kincannon found that nitrogen compounds, phenols and oxygenated compounds were removed by biodegradation. Aromatic compounds were removed by a combination of stripping and biodegration. Halogenated hydrocarbons were removed only by stripping. The study also indicated that a completely mixed reactor had better removal of priority pollutants than a batch reactor. Kincannon et al. also found that the larger the Henry's Law Constant the smaller the concentration of the priority pollutants in the final effluent.

Weber et al. (79) studied the effectiveness of three types of PAC added to a completely mixed flow bioreactor which contained the organic compound, Lindane. All three types of PAC removed about 96% of the Lindane at a carbon dosage of 30 mg/L. However, increases in both sludge age (from 0.25 to 15 days) and retention time did not increase either COD removal or the Lindane concentration. Weber et al. concluded that removal of priority pollutant compounds depends entirely on their chemical properties.

Tabak et al. (66) presented protocols to study biodegradation of organic priority pollutants. In his program a GC instrument was adapted as a tool to identify the organic priority compounds. Total and dissolved organic carbon analytical procedures were outlined.

Unger et al. (70) explained that percentage removals of priority pollutants and heavy metals vary significantly among wastewater plants. Metal and organic removals ranged from 32 to 81% and from 52 to 87%, respectively. Percentage removal of priority organics or heavy metals vary from plant to plant and even from sample to sample. The activated sludge process showed better removal for heavy metals such as Cr, Cu, Hg, and Zn. The study suggested that removal treatments should be planned on a plant-by-plant basis.

Tabak et al. (65) studied the biodegradability of 114 organic priority compounds using a static-culture flask screening process. It contained 5 mg of yeast extract per liter of a synthetic medium with a 5 and 10 mg/L compound concentration. A 7-day static incubation period at 25^{o}C was used. Three weekly subcultures were done with the addition of domestic wastewater as a microbial source. To test the biodegradability, DOC and TOC were determined for each compound. Results showed that priority pollutants did not degrade under static-culture conditions and therefore a new methodology should be developed.

Baller, et al. (5) explained the approach which had been taken by EPA to develop methods to measure hydrocarbon and chlorinated organic solvents in wastewater down to a concentration of 1 ug/L. These methods are reliable in qualifying water-insoluble volatile organic compounds at a concentration as low as 0.5 ug/L.

Thomas et al. (68) discussed EPA methods for analyzing priority pollutants in water by chromatography and chromatography/mass spectrometry (GC/MS). They also described sampling, storage, apparatus, sample preparation and gas chromatography analysis.

2.4 Air Stripping

Air Stripping methods have been used by petrochemical companies to treat wastewaters containing high concentrations of volatile compounds. Studies showed that for wastes containing volatile organic compounds, air stripping is a sufficient method of removal.

Engelbrecht et al. (17) studied stripping kinetics for acetone and butanone (methyl ethyl ketone) compounds using an 8.0-liter aeration tank at various air flow rates. Removals of acetone and butanone by air stripping could be described as first order kinetics. They concluded that the inorganics in wastewater required for the biological treatment processes would have no effect on stripability of the volatile compounds. The unit air flow rate Ka, varies linearly with air flow.

Gaudy et al. (28) reported that first order stripping kinetics cannot be applied to all volatile compounds in all experimental conditions. The variables that most affect the overall transfer coefficient, Ka, are temperature, air flow, and tank geometry.

Gaudy et al. (29) investigated volatile organic compounds in a 28.3-liter activated sludge tank at various air flow rates starting with 100 ml/min/L and increasing to 1200 ml/min/L. They concluded that joint mechanisms (air stripping and biological processes) were fairly good to predict kinetic constants. However, kinetic constants have no effect on the removal by either stripping or biological processes. Removals by either air stripping or biological methods were entirely dependent on the processes.

2.5 Industrial Wastewater Reclamation and Reuse

For years, many countries in the world have begun to reuse domestic and wastewater. The role of using reclaimed wastewater will increase in the future as drinkable water becomes scarce and expensive. Wastewater is a valuable source and could be used when treated and managed properly.

Lauer et al. (42) explained that reused wastewater for potable water may become economically feasible with development of water treatment processes. In Denver, Colorado, a 1-MGD demonstration plant has been in operation for 3 years. The demonstration plant incorporated the following units: lime clarification, recarbonation, filtration, selective ion exchange, first-stage carbon adsorption, reverse osmosis, air stripping, ozonation and chlorine dioxide disinfection. Ion exchange and carbon regeneration furnaces were also included. Treated wastewater was used directly to irrigate landscapes and part of the water was used by the city for nonpotable uses. The project will be run for 5 years to study its performance. Upon completion, the authority will be able to answer many questions related to future water reuse.

Vuuren et al. (73) studied water reclaimed from a pond which had received a secondary effluent from a treatment plant. The pond water was treated by an algae separation unit and then by an active carbon adsorption unit. In 1976, an ammonia removal was implementated. They reported that the reclamation plant operated for a short period totaling 200 days and contributed about 1000 million liters of reclaimed water to the water supply network. Chemical and microbial analysis were done and strict monitoring was applied at all times.

DeBoer (14) explored the idea of using wastewater for reuse. Presently techniques are becoming available to convert wastewater to water safe for irrigation or to potable water. The public has still negative opinions on reused water. He stressed that the benefits of using a wastewater program are becoming known to the public. In

Arizona, for example, without reused water programs, growth would be limited due to water shortages. In California, ground water aquifiers are already recharged with wastewater and no health effects have been observed on the public who used the reclaimed water.

Bruvold (7) conducted a public survey about using reclaimed wastewater as either drinking water or for nonpotable purposes. From the results of the survey he suggested that the best way to achieve public acceptance would be through the news media, lectures and advertising. Most of the public believed that the technology exists to treat wastewater sufficiently for potable reuse; however, they opposed the use of reclaimed water for drinking but for other purposes it would be acceptable.

Goff et al. (31) reviewed the construction of the 5 MGD wastewater reclamation facility for the city of Chandler, Arizona. A new water supply was needed; therefore, reuse of the municipal wastewater was being considered as a source to meet rapid growth in the community. Investigations were conducted to determine the most feasible way to use the reclaimed water. The plan was to reuse the reclaimed water for a golf course, a greenbelt area, as well as for residential and commercial development.

Crook (12) discussed water reuse in California within the past few years. California encouraged such uses as irrigation. Irrigation accounted for approximately 80% of the total quantity of wastewater reclaimed. Health criterias were established for various uses including irrigation, impoundments, and groundwater recharge.

Corssmit (11) reported on financing plans and price schedules for reused water. For the reuse project to be successful, four feasibility tests should be followed: (1) the technical aspects of the project should be understood; (2) the project must be economically desirable in term of costs and benefits; (3) the revenues must exceed the total cost; and (4) public opinion should accept the reuse project. Corssmit also pointed out that a market analysis should be done to make sure that there are demands for reused water. McClure (46) believed that the technology exists to develop and to produce high-quality reused water from either municipal sewage plants or from industrial wastes. Several industries tried successfully to reuse their cooling water for inside purposes. A steel mill and plating industry utilized significant amounts of potable water during their normal processes. 80% of this water could be reclaimed with an on-site treatment. Of course, depending on the characteristics of the wastewater, recommended steps would be added to make the water satisfactory for reuse.

Nellor et al. (49) evaluated the effects on human health from using groundwater recharged with municipal wastewater. Before being recharged into the groundwater, the wastewater was blended with stormwater and river water. Nellor et al. estimated that the wastewater-plant produced about 250,000 acre- ft of water each year, of which 67,500 acre-ft were reused and the remainder was discharged to the ocean. Replenished water did not show any measurable adverse effects on either groundwater quality or the health of the people ingesting the reclaimed water.

Shannon et al. (55) explained that Odessa City, Texas relies completely on Colorado municipal water for its main water supply. The watewater plant provides approximately 40 MGD, however, the amount will be increased in the future. There are two water reclamation plants, a conventional activated sludge plant, and an oxidation-ditch activated sludge plant. Both of these plants discharged their treatment wastewater into landscapes where water either evaporates or percolates into the groundwater. A local industrial company uses secondary effluent for fire protection and cooling tower makeup, after the water is pre-treated by lime clarification, filtration and zeolite softeners. Shannon et al. indicated that the future plan was to reuse the municipal wastewater for either landscaping, irrigation or recharging ground-water.

Corneille (10) presented a master plan for wastewater reuse at Chino Hills Area, California. With the area expanding so fast, a water conservation program will be implemented to reduce the water supply requirement by 20% from normal usage. Therefore, the main objective was to maximize the use of reclaimed wastewater in order to make up for the 20% reduction in the water supply. The secondary treatment effluent disinfected with chlorine reclaimed water was used only for restricted landscape irrigation. For a densely populated area, he recommended that the quality of secondary effluent should be equivalent to a tertiary discharge. He claimed that reused water in lieu of potable water is currently economically attractive.

Culp et al. (13) explained that desalination plants provide coastal areas with the main supply of fresh drinking water. However, sea water contains about 3.5% dissolved salts plus a considerable amount of organic matter over 35 times as much foreign matter as secondary treatment plant effluents contain. For this reason and others, investments in desalination plants exceed the cost for a wastewater reclamation plant. They pointed out that the benefits from water reuse are not only to reuse the water but also to control pollution.

Most of the studies to date have concentrated on the removal of specific priority organics which were added to a synthetic waste. In addition many studies were constructed on a bench-scale and involved batch reactors. Of the studies using pilot-scale reactors, none investigated the compounds that were studied in this dissertation. All of the AS operating parameters utilized in this study simulate those in a full-scale operation and the priority pollutants selected for this study (benzene, chloroform, 2,4-dimethylphenol, ethylbenzene, fluorene, naphthalene, pyrene, toluene, m-xylene, and o-xylene) are those found in an actual refinery waste. A study such as this fills a significant gap in the literature on refinery industry wastewater treatment.

3. EXPERIMENTAL PROCEDURE

3.1 Equipment

The schematic of the PAC/AS pilot plant utilized in this study is shown in Figure 3.1.1. The pilot plant was manufactured by the Virtis Co. and it consists of 1) a 6-liter Pyrex glass reactor fitted with an air-tight stainless steel cover to prevent the escape of gasses, 2) a feed pump operated at 1.3 L/hr, 3) a 120-L feed storage tank also with an air-tight cover, 4) a PAC slurry pump, 5) a clarifier pump, 6) a clarifier with a settling compartment volume of 2 liters and 7) an effluent receiving tank. A 120-L holding tank with a turbine impeller mixer rotating at 50 rpm was used for the feed storage tank. To minimize the space in the holding tank, a floating plate was placed inside on the wastewater surface to keep the volatile organic compounds from escaping. The feed holding tank was air sealed (Figure 3.1.2). Two filters were connected to the effluent of the holding tank and they were in series. The first filter consisted of a chemical addition section and filtering fiberglass material. The second filter consisted of only a filtering fiberglass material.

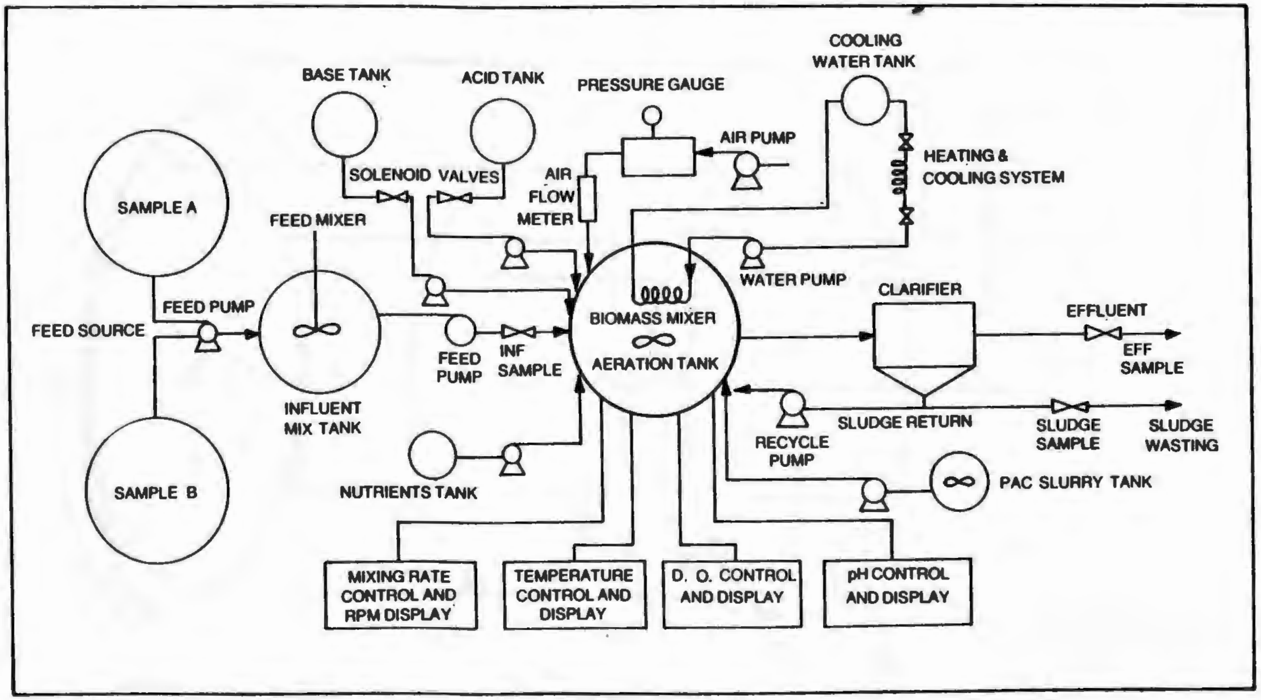


Figure 3.1.1 Schematic diagram of the Integrated PAC/AS Pilot Plant

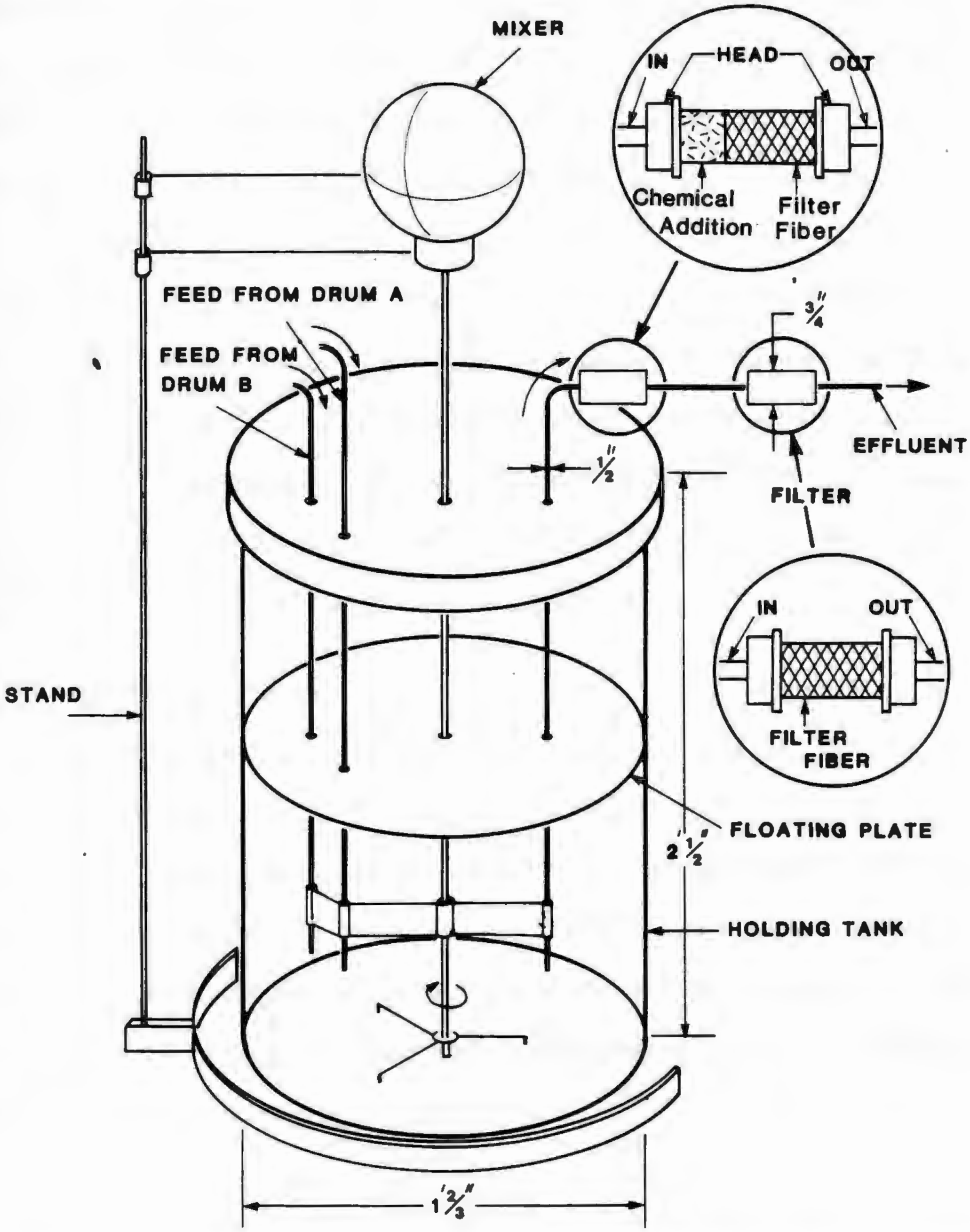


Figure 3.1.2 Schematic of the Holding Tank and Filters

The pilot plant was equipped with continuous monitoring and control devices for pH, temperature, air pressure, dissolved oxygen, agitation system, cooling unit, and acid and base control. The pilot plant clarifier was fabricated from a one-liter funnel-shaped glass tank (10^0 slope, 10 cm diameter, 68 cm high), as shown in Figures 3.1.3 and 3.1.4.

PAC, manufactured by the Calgon Corporation, Pittsburgh, PA was used for this study. It has a maximum of 75% of the particles passing through a 325-mesh screen. A BL type PAC recommended by the carbon manufacturer was selected for this study. The specifications for PAC were provided by the manufacturer (Table 3.1.1).

3.2 Experimental Steps

The experimental phases were run at 3, 6, 9 and 12 days sludge age (θ_c). These values are typical for conventional treatment processes. The characteristics of the refinery industry wastewater (physical and chemical parameters and organic loadings) were determined; they were identical to a discharged wastewater from a complex industrial area.

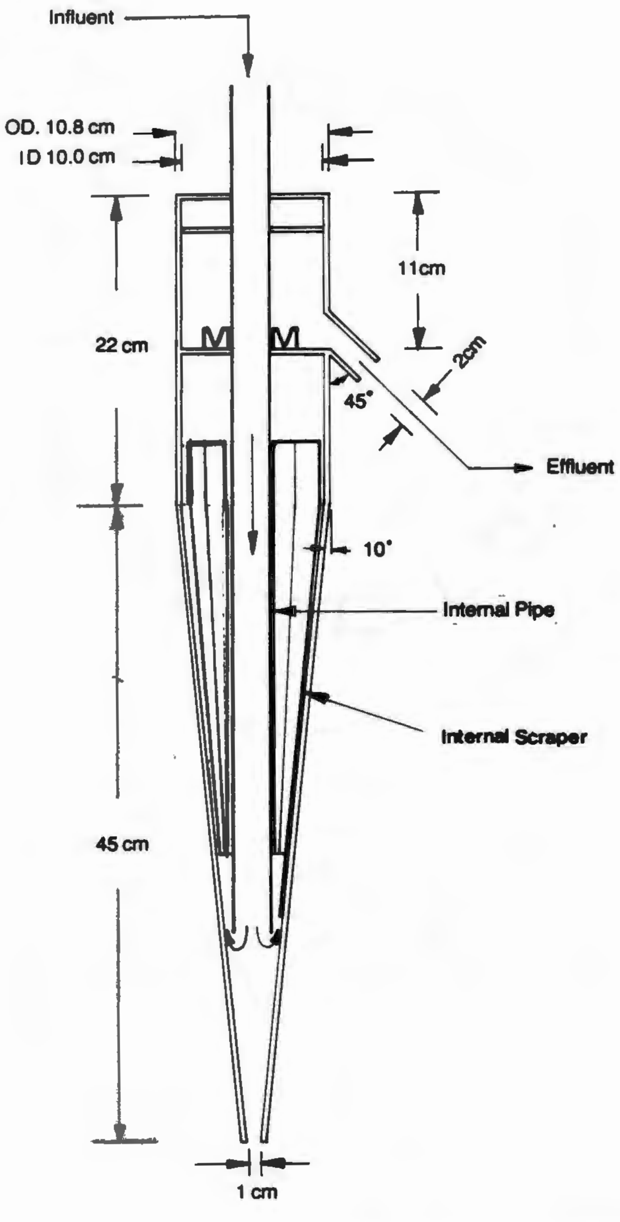


Figure 3.1.3 Schematic Diagram of the Experimental Clarifier Unit

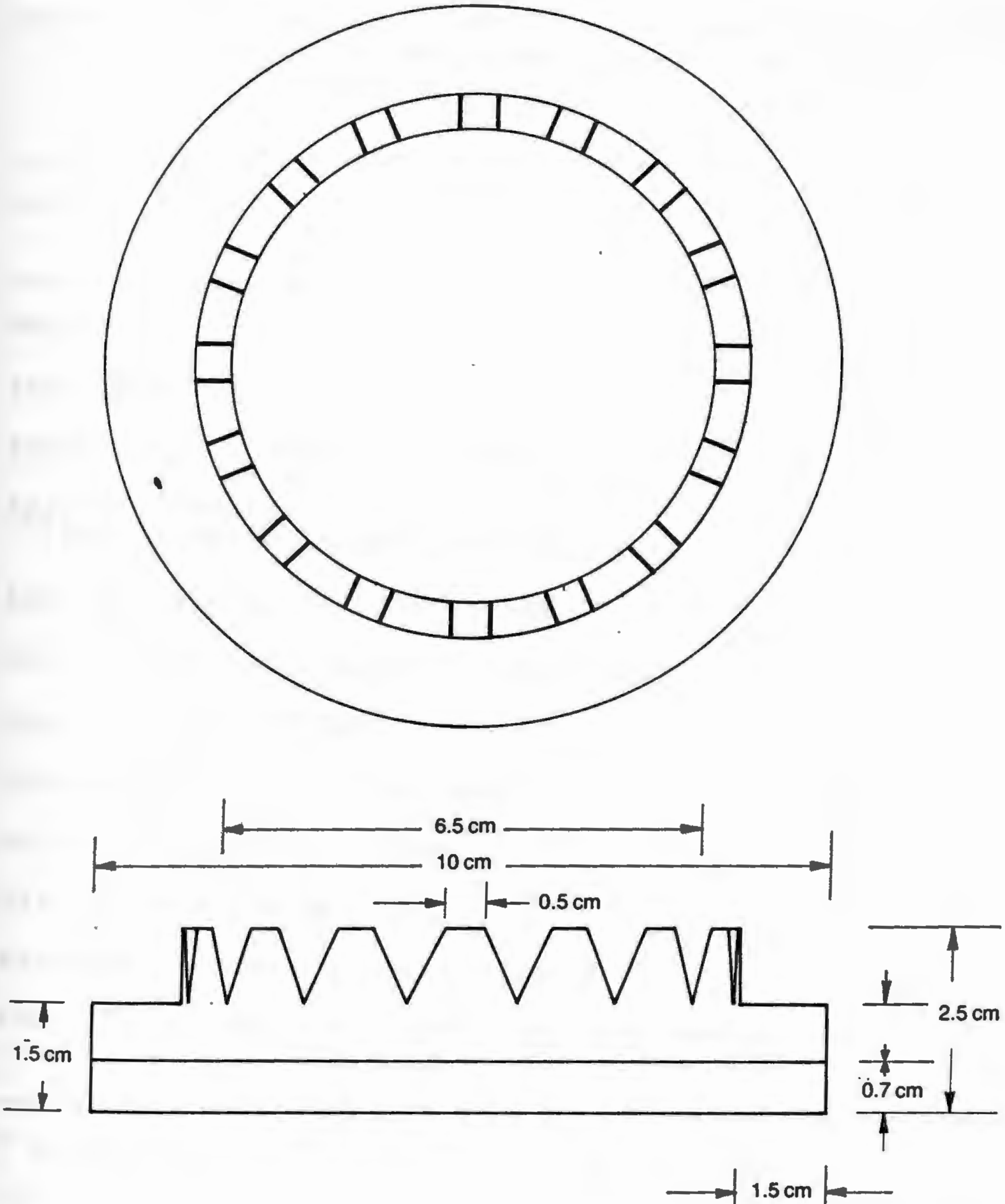


Figure 3.1.4 Schematic Diagram of the Weir Inside the Clarifier (not to scale)

Table 3.1.1 Physical Properties of the BL Type of Powdered Activated Carbon (Calgon Corporation, Pittsburgh, PA)

Specifications	Carbon Type BL
Manufacturer	Calgon
Base Material	Bituminous Coal
Total Surface Area (N2BET Method), m^2/g	1000-1100
Apparent Density (bulk density, dense packing), g/cc	0.51
Real Density He (displacement), g/cc	2.10
Pore Volume (within particle), g/cc	0.90
Specific Heat at 100°C	0.25
Iodine Number, minimum, mg/g	1000
Molasses Number, Minimum	230
Ash, maximum, wt %	8.5
Moisture, maximum as packed, wt %	2
*Wet Screen Analysis, minus 325 U.S. Mesh %	65.75

* U.S. Sieve Series; opening of 44 microns.

The hydraulic retention time ($\theta=V/Q$) in the aeration tank was designed to be around 4 hours. The clarifier effluent flow rate was approximately 20 ml/min (1.2 L/hr) and the recycling flow rate was about 0.10 L/hr. The design operating conditions of the biological pilot plant are listed in Table 3.2.1.

The temperature of the reactor was kept at $24^{\circ}C$ for all experimental phases and the pH was between 6.80 to 7.20. The air flow rate was kept at 2.0 L/hr which yielded a concentration of dissolved oxygen in the aeration tank in the range of 5 to 6 mg/L. The mixed liquor suspended solids (MLSS) concentration was in the range of 2,000 to 3,500 mg/L, and the mixed liquor volatile suspended solids (MLVSS) was about 1,500 to 3,000 mg/L. Solids were waste from the waste line in order to allow a more positive control of the sludge age than could be achieved by wasting from the reactor. During the test period 10, 50 and 120 mg/L of PAC were added to the influent. To make up for PAC lost along with the waste sludge, clarifier effluent and aeration tank samples, fresh PAC was added to the influent feed line once per day. The characteristic of the refinery industry watewater feed to the biological pilot plant was given in Tables 3.2.2 and 3.2.3.

Table 3.2.1 Operating Conditions of the Biological Pilot Plant

Reactor	
Volume	5.10 L
Hydraulic retention time, HRT	4.0 hr.
Air flow rate	1.5 L/hr
pH	6-8
Dissolved Oxygen (DO)	5-6 mg/L
Flow rate	1.3 L/hr
Agitation rate	100-300 rpm
Air pressure	3.0 psi
Temperature	24^{0}C
PAC dosages	10, 50, 120 mg/L
Holding Tank	
Volume	110 L
Mixing rate	50 rpm
Flow rate	1.3 L/hr
Clarifier	
Volume	2.5 L
Length	67 cm
Shape	cone
Top opening OD, ID	10.8, 10.0 cm
Lower Opening	1 cm

Table 3.2.2 Characteristics of the Refinery Industry Wastewater

Parameter	number of samples	Range low-high ug/L	Mean Value	Unit
Temperature	60	23-24	24°C	
pH	60	7.17-7.50	7.24	pH units
DO	60	4.5-6	5.0	mg/L
BOD_5	56	93-329	237.0	mg/L
COD	60	160-588	457.0	mg/L
TOC	60	35-847	272.0	mg/L
TSS	56	2000-3750	114.0	mg/L
VSS	56	5-185	105.0	mg/L
NH_3	56	15-70	40.0	mg/L
NO_2	56	0.01-0.10	0.05	mg/L
NO_3	56	0.54-1.94	0.91	mg/L
Orthophosphate	56	0.14-2.20	1.43	mg/L
Total Phosphate	56	0.10-0.46	0.28	mg/L
Chloride	3	206-260	260.0	mg/L
Oil and Grease	56	3-191	191.0	mg/L

Table 3.2.3 Chemical Composition of the Refinery Industry Wastewater Treated by the Pilot Plant

Parameter	number of samples	Range low - high ug/L	Mean Concentration ug/L
Acid Extractables			
2,4-Dimethylphenol	6	13-1,880	452
Base-Neutral Extractables			
Bis (2-ethylhexyl) phthalate	6	10-750	767
Fluorene	6	20-1,746	354
Naphthalene	7	33-6,933	1,358
Pyrene	5	27-33	32
Volatile Organics			
Benzene	4	620-3,696	2,074
Chloroform	4	1,260-1,952	1,725
Ethylbenzene	4	60-520	300
Toluene	4	460-3,500	1,699
m-Xylene	4	310-1,120	695
o-Xylene	4	460-1,260	857

3.3 Sampling Procedure

Samples for analyses (Table 3.3.1) were collected every 24 hours for 5 days for phase I and 3 days for phases II, III, and IV, for a continuous steady-state experiment. Composite samples were taken from the influent feed tank and the clarifier effluent. The sample containers were kept cool until the day of analysis. Composite samples of wasted mixed liquor were obtained from the wasting line before the daily volume of waste was measured and discarded. The contents of the holding tank, the aeration tank and the clarifier unit were mixed uniformly and completely before taking the sample. Parameters such as temperature, pH, air flow, and dissolved oxygen levels in the aeration tank were read directly from the pilot plant unit. Samples for mixed liquor and suspended solid were analyzed immediately after sampling. BOD_5, COD, TSS, and VSS were determined. Additional samples for analyses such as TOC, chloride, nutrients (nitrogen and phosphate), and oil and grease were done in the laboratory.

Microorganism growth and population dynamics were examined by both light microscopes and scanning electron microscopes (SEM). After changes in the parameters of each run, a period of three to four days was needed for

Table 3.3.1 Sampling and Analytical Work Schedule for the Biological Treatment Pilot Plant

Parameter	Influent	Reactor	Effluent	Frequency
	Sampling Location			
Temperature		X		Daily
pH	X	X		Daily
Air Flow	X			Daily
Flow Rate	X			Daily
DO		X		Daily
BOD_5	X		X	3 times/week
COD	X		X	3 times/week
TOC	X		X	3 times/week
<u>Suspended Solid</u>				
Volatile (MLVSS/VSS)	X	X	X	3 times/week
Fixed (TSS)	X	X	X	3 times/week
<u>Nitrogen</u>				
NH_3	X		X	3 times/week
NO_2	X		X	3 times/week
NO_3	X		X	3 times/week
Oil/Grease	X		X	3 times/week
Total Phosphate	X		X	3 times/week
Orthophosphate	X		X	3 times/week
<u>Organics</u>				
Volatile	X		X	Daily
Acid/Base Extractable	X		X	Daily

the biomass to reach steady-state conditions.

3.4 Analytical Methods

Selected priority organic compounds were analyzed according to the instructions given in the Federal Register (37, 81, 82). All other analyses were performed according to the Standard Methods for the Examination of Water and Wastewater (61).

TOC was measured using a TOC Model 700 analyzer made by O.I. Corporation. Ammonia was determined by the acidimetric method. Nitrite (NO_2) was measured using the diazotization method. Nitrate (NO_3) concentrations were determined by the bucine method. The stannous chloride method was used for both total phosphate and soluble orthophosphate. Chloride was measured by the argenometric method. Oil and grease method in the Standard Methods was modified as follows: A 150-ml sample was collected and actified to pH 2 or lower using 5 ml of concentrated HCl. The acidified sample was transferred to a separatory funnel and the sample container was washed with 10 ml of trichloro-trifluoro-ethane as a solvent, the wash liquid was then also transferred to the separatory funnel. Then the separatory funnel was shaken vigorously for 2 minutes and allowed to stand for 10 minutes or longer, so that the organic layers separated after excess gas venting.

The separatory layer was drained off through a funnel containing clean filter paper and the solution was collected in a distillation flask. Then the sample was extracted twice with 10 ml of solvent and the extractable materials were transferred to the distillation flask. The filter paper was washed with 10 to 20 ml of solvent and the washable liquid was transferred into the distillation flask. The distillation flask was placed in a water bath at 70°C for 15 minutes. The flask was then put in a desicator to cool for 30 minutes and was weighed.

The procedure for extracting the samples (base/neutral and acid extractables) and determining the selected priority organic pollutants are discussed in the following sections.

3.4.1 Sample Preparation

EPA base/neutrals and acid method 625 (72) describes the determination of organic compounds that are soluble and able to be measured by gas chromatography. Methylene chloride was used as a solvent to extract the dissolved organic compounds at a selected pH. The extract was dried and concentrated to a volume of 1 ml and analyzed by GC. The chromotographic conditions were modified for measuring the organic compounds at their concentrations in the refinery industry wastewater. (Tables 3.4.1.1, 3.4.1.2, 3.4.1.3, 3.4.1.4).

Table 3.4.1.1 Tekmar Model LSC-2 Conditions for Analysis of Purgeable Organic Compounds

Furnace	Range ambient to 350°. Rise time 200°C/min
Trap material	Tenax (Silica Gel/charcoal, 12" x 1/8")
Sample size	5 ml, medium porosity glass frits including 3-way manual valve for sample load, unload, front drain.
Times	Purge 15 min, Dry purge on timer set on 11. Desorb 4.0 min. Bake 7 min
Temperature readouts	Auto positions
Purge pressure	20 psi
Purge flow rate	40 ml/min
Bake temperature	180°C

Table 3.4.1.2 Gas Chromatographic Conditions for Photoionization Detection (PID)

Initial temperature	45°C
Final temperature	200 °C
Programming rate	8°C/min
Initial hold	3 min
Final hold	15 min
Detector temperature	250°C
Injection temperature	200°C
Carrier gas, He	40 ml/min
Column	60/80 Carbopack B 1% SP 1000 Glass

Table 3.4.1.3 Gas Chromatographic Conditions for Hall Electrolytic Detection (HALL)

Initial temperature	45°C
Final temperature	200°C
Program rate	8°C/min
Initial hold	3 min
Detector temperature	200°C
Injection temperature	200°C
Final hold	15 min
Carrier gas, He	40 ml/min
Reactor gas, H_2	50 ml/min
Column	60/80 Carbopack B 1% SP 1000, Glass

Table 3.4.1.4 Gas Chromatographic Conditions for Flame Ionization Detection (FID)

Initial temperature	50^{o}C
Final temperature	200^{o}C
Program rate	10^{o}C
Initial hold	2 min
Detector temperature	240^{o}C
Injection temperature	220^{o}C
Carrier gas, He	50 ml/min
Reaction gas, Air	0.2 l/min
Reactor gas, H_2	50 ml/ min
Mode	Splitless
Column	20m x 0.23 mm ID SE-54 fused silica capillary, custom made

The extraction procedure was as follows: The base/neutrals and acid extractable samples were collected from the influent and effluent at sample points in the biological pilot plant. Each 150 ml sample was collected and poured into a 250-ml separatory funnel. The pH of the sample was adjusted to above pH 11 by adding 1 ml of 10 N sodium hydroxide (NaOH). The sample was extracted three times with 10 ml of methylene chloride each time. The extracted sample in the separatory funnel was shaken for two minutes each time with periodic venting to release excess pressure produced by gases in the funnel. At least 10 minutes was allowed each time for the organic layer to separate from the water phase. The combined methylene chloride extracts contained the base/neutral extractables. The combined extract was poured through a drying column containing about 10 cm of anhydrous sodium sulfate, and then the extract was collected in the K-D concentrator. One or two clean boiling stones were added into the K-D concentrator and then the extract was placed into the prewetted Snyder Column. The K-D apparatus was placed in a hot water bath at 65-70°C and the concentrator tube was immersed in the hot water. The K-D apparatus was removed from the water bath when the apparent volume of the extract reached 1 ml. The apparatus was left to drain for at least 10 minutes. The Snyder Column was removed from the lower part. The lower flask with the concentrator tub was rinsed with 1 to 2 ml of methylene chloride. The concentrated liquid was collected in a 1 ml vial and was ready to be injected to the GC instrument. The pH of the aqueous layer left from the base/neutral extraction was readjusted to less than 2 by addition of approximately 1 ml of sulfuric acid (1+1). The aqueous phase was extracted three times with 10 ml of methlylene chloride each time. The combined extracts contained the acid extractables and were then treated in exactly the same way as the base/neutral extractables.

To estimate the amount of powdered activated carbon PAC present in the MLVSS the following procedure was utilized by the Zimpro Inc. Laboratory, Wisconsin (82). The procedure is applicable only to the wastewater carbon/biomass from an integrated powdered PAC and AS process. The procedure is known as nitric acid digestion and it yields an estimate of PAC in a carbon/biomass slurry. The determination of biomass and carbon was done by comparing the VSS of a nitric acid digested sample with the normal VSS and finding the ratio between activated carbon and biomass solid. The procedure for biomass determination in a nitric acid digestion sample was as follows:

1. Run normal suspended solids tests using a 10 ml sample, dry it at 600°C for one hour, then measure the suspended ash.
2. To another 10 ml aliqout of the sample, add 20 ml of concentrated nitric acid.
3. Heat the acidified sample to just under boiling.
4. Continue heating until the sample volume has been reduced to approximately 10 ml.
5. Cool the sample to room temperature.
6. Determine the suspended solids and ash on the digested sample.
7. Calculate the results.
8. The carbon and biomass concentrations could be determined as follows:

$$\text{Carbon, g/L} = \frac{C-D}{0.95}$$

$$\text{Biomass, g/L} = A-(B+\text{Carbon})$$

where

A = Normal suspended solids, g/L

B = Normal suspended ash, g/L

C = Nitric acid treated suspended solids, g/L

D = Nitric acid treated suspended ash, g/L

0.95 = Carbon factor

3.5 Seeding Refinery Industrial Wastewater

Initially, refinery industry wastewater was seeded with seed organisms obtained from the South Kingstown Wastewater Treatment plant in Narragansett, Rhode Island. Five ml of clarifier activated sludge was obtained and acclimated to the refinery industry wastewater. The suspended solid concentration in the clarifier was in the range of 2,000-3,000 mg/L. Ammonia, sulfate $[(NH4)_2\ SO_4]$ and potassium phosphate $[K_2\ H\ PO_4]$ were added as N and P nutrient sources. The refinery industry wastewater was fed directly into the seeded activated sludge aeration tank continuously. Parameters such as pH, temperature, dissolved oxygen and nutrient concentrations were kept constant. The biological pilot plant required between 4 and 5 weeks to reach a MLSS concentration of 2,200 mg/L.

3.6 Start-up of the Biological Pilot Plant

The biological pilot plant was operated continuously after being seeded, and achieved the steady-state conditions based on the MLVSS and MLSS measurements. To keep the concentration of priority organic compounds in the holding tank high enough to be detected by a GC instrument, organic materials had to be added and dissolved uniformly in the feed tank. Two filters were connected to the effluent of the feed tank in order to trap any suspended particles and organic materials from getting into the aeration reactor tank. The hydraulic retention time (HRT), and sludge age (SA) or sludge retention time (SRT) of the biological pilot plant were controlled at 4 hours and 3, 6, 9, 12, days respectively. Daily wasting of mixed liquor was performed once per day through the wasting sludge point to control the sludge age. PAC was added directly to the aeration tank. The concentration of PAC was calculated based on the required PAC concentration in the mixed liquor.

4. CHARACTERIZATION OF THE STANDARD REFINERY WASTEWATER

4.1 Data Collection

During the summer of 1985, a study was conducted in the Shuaiba Industrial Area (SIA) to determine the chemical composition, flow rates, and discharge points for industries in the SIA (67). The Kuwait National Petroleum Company Refinery (KNPC) and the Petrochemical Industrial Companies (PIC) plants A and B are considered the major sources of wastewater discharged directly into the Arabian Gulf. Composite samples were collected from the Shuaiba Industrial Area at the discharge points at a location prior to mixing with seawater. These samples were analyzed for BOD_5, COD, nitrates, nitrites, ammonia, pH, phenol, oil and grease, and selected heavy metals such as chromium (Cr^{+6}), copper (Cu), iron (Fe), lead (Pb), and nickel (Ni). The analyses were conducted according to Standard Methods (61). The results of these analysis are presented in Table 4.1.1.

The hydraulic flow survey showed that the mean daily flow to the KNPC API separator was about 960 gpm, but the flow to the PIC neutralizing basin was approximately 63 gpm. There was no change in the pattern of the wastewater flow at night or during the weekends in both the operation of the KNPC Refinery and PIC Fertilizer Company, Plant B. Chemical analyses of grab composite samples were made

Table 4.1.1 Results of Analysis for the Composite Samples From the KNPC-API Separator and PIC Plant B.

Parameter	Sample Number (Date) 1 (6/4/85)	2 (6/17/85)	3 (6/30/85)	Average Concentration (mg/L)
NH_3-N	3.35	3.13	2.85	3.11
NO_3-H	0.38	0.026	0.003	0.14
NO_2-N	0.13	0.026	0.010	0.055
Phenol	0.62	3.25	4.91	2.97
COD	375.7	592.2	132.2	367.0
BOD_5	320	100	-	210
Oil and Grease	2.60	150	95	82
Sulphides	3.42	0.078	3.89	2.46
Fe	1.39	0.88	1.50	1.25
Cr^{+6}	0.084	1.88	1.63	1.20
Pb	0.019	0.032	0.024	0.025
Cu	0.084	0.041	0.031	0.052
Ni	-	0.022	0.017	0.020

every other week over a one-month period. The results of these analyses are presented in Table 4.1.1, on page 65.

The composite samples were also analyzed for their organic priority pollutant composition. The analyses were conducted according to the USA Environmental Protection Agency Method No. 601 for purgeable halocarbons, Method No. 602 for purgeable aromatics (19, 20) and Method No. 625, for dissolved organic compounds. A GC was used to measure the concentrations of dissolved organic pollutants. The results are presented in Tables 4.1.2 and 4.1.3.

4.2 Selection of Priority Pollutants

According to the regulatory agency (Kuwait Environmental Protection Council), there are several factors which should be considered to determine the selection of priority pollutants. These factors are as follows: (1) toxicity in the water, (2) presence in the water, (3) highest concentration in the water, (4) frequency of occurance, and (5) effects on human and aquatic life.

Samples were collected from SIA and analyzed for pollutants. For the determination of the organic pollutants, GC-MS was used to identify the priority pollutants. The analyses showed that the following compounds were present:

Table 4.1.2 Extractable Organic Compounds Found in KNPC API Effluent

Compound	Average Concentration ug/L	Extractable Fraction
Naphthalene	121.0	Base/Neutral
2,4-Dimenthyl Phenol	50.4	Acid/Neutral
Phenol	25.2	Acid/Neutral
Fluorene	16.0	Base/Neutral
Pyrene	10.0	Base/Neutral
Chrysene	6.0	Base/Neutral
Bis (2 - Ethyl Hexyl) Phthalate	10.0	Base/Neutral

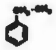
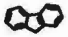
Table 4.1.3 Halocarbon and Aromatic Compound Concentrations Found in Wastewater of KNPC API Separator Effluent.

Compound	Concentration (ug/L)
Chloroform	740
Benzene	560
Toluene	660
Ethylbenzene	120
Xylene	500

benzene, bis (2-ethylhexyl) phthalate, chloroform, chrysene, 2,4-dimethylphenol, ethylbenzene, fluorene, naphthalene, pyrene, and xylene. A list of all organic priority pollutants found in SIA is given in Tables 4.1.2 and 4.1.3.

The selection of organic priority compounds for this study was not only based on the relative toxicity, but on their presence in the SIA discharge wastewater. Taking into account the utilization of seawater for drinking water after desalination, the following priority pollutants were selected for this study: benzene, chloroform, 2,4-dimethylphenol, ethylbenzene, fluorene, naphthalene, pyrene, toluene, and xylene. Table 4.2.1 shows the different chemical and physical characteristics of the selected compounds. Several wastewater characteristics were also identified including BOD_5, COD, TOC, TSS, nitrogen, and pH.

Table 4.2.1 Chemical and Physical Characteristics of Selected Priority Organic Pollutants

Compound Name	Benzene	Chloroform	2,4-Dimethyl phenol	Ethyl-benzene	Fluorene	Naphathalene	Pyrene	Toluene	Xylene
Formula	C_6H_6	$CHCl_3$	$C_8H_{18}O$	C_8H_{10}	$C_{13}H_{10}$	$C_{10}H_8$	$C_{16}H_{10}$	C_7H_8	$CH_3C_6H_6CH_3$
Structure									
Molecular Weight	78.12	119.38	122.20	106.16	116.20	128.20	202.30	92.13	106.20
Boiling Point, °C	80.10	61.70	210.90	136.20	293-295	218	393	110.60	144
Melting Point, °C	5.5	-63.5	27-28	-94.9	116-117	80	150	-95	-25.2
Vapor Pressure at 20°C, P_v (torr)	95.2 (25°C)	150.5 (20°C)	0.062 (25°)	7 (20°C)	$7.1X10^{-4}$	0.087 (25°C)	$2.5X10^{-6}$ (25°C)	28.7 (20°C)	10
Solubility in water S_{wl} (PPM)	1.78×10^3 (25°C)	8.20×10^3 (20°C)	590 (25°)	152 (20°C)	1.69 (25°C)	31.7 (25°C)	0.13 (25°C)	534.8 (25°C)	Insoluble
Henry's Law Constant (atom M^3/mde)	5.5×10^3	2.88×10^{-3}	1.7×10^{-5}	6.6×10^{-3}	6.4×10^{-5}	4.6×10^{-4}	5.1×10^{-6}	$6.66X10^{-3}$	6.12×10^{-3}
Octanol/water Unitless	135	91	200	2.2×10^3	1.5×10^4	1.95×10^3	8.0×10^4	620	Not Available
Ionization Constant	pK-NER	pK-NER	10.60	pK-NER	pK-NER	pK-NER	pK-NER	pK-NER	Not Available
Reeration Rate Ratio K_v/K_v	0.574	0.583	NAV	0.489	NAV	NAV	NAV	0.526	NAV

Note: NAV = not applicable for calculating the rate constant for volatization
pK-NER = pKa or pKr is not environmentally relevant for fate of chemicals

5. PRIORITY ORGANICS REMOVAL PROCESSES

To study the treatability and the fate of each selected organic compound in the industry refinery wastewater treatment process, each characteristic of each compound should be known as presented in Table 4.2.1. Some of these selected organic compounds will be affected by stripping, biological oxidation and adsorption processes.

A series of experiments was designed to investigate the removal of the selected priority pollutants as shown in Figure 5.1

5.1 Activated Sludge

The first experiment was to use AS for biological oxidation and to evaluate the effectiveness of the activated sludge in reducing organic pollutant concentrations in the refinery industry wastewater.

Initially, the activated sludge was acclimated to the refinery industry wastewater, and the acclimation period took approximately 4 to 5 weeks. The AS reactor was operated at an HRT of 4 hours. The steady-state condition was judged to have been reached when the effluent substrate concentration became steady over a long period.

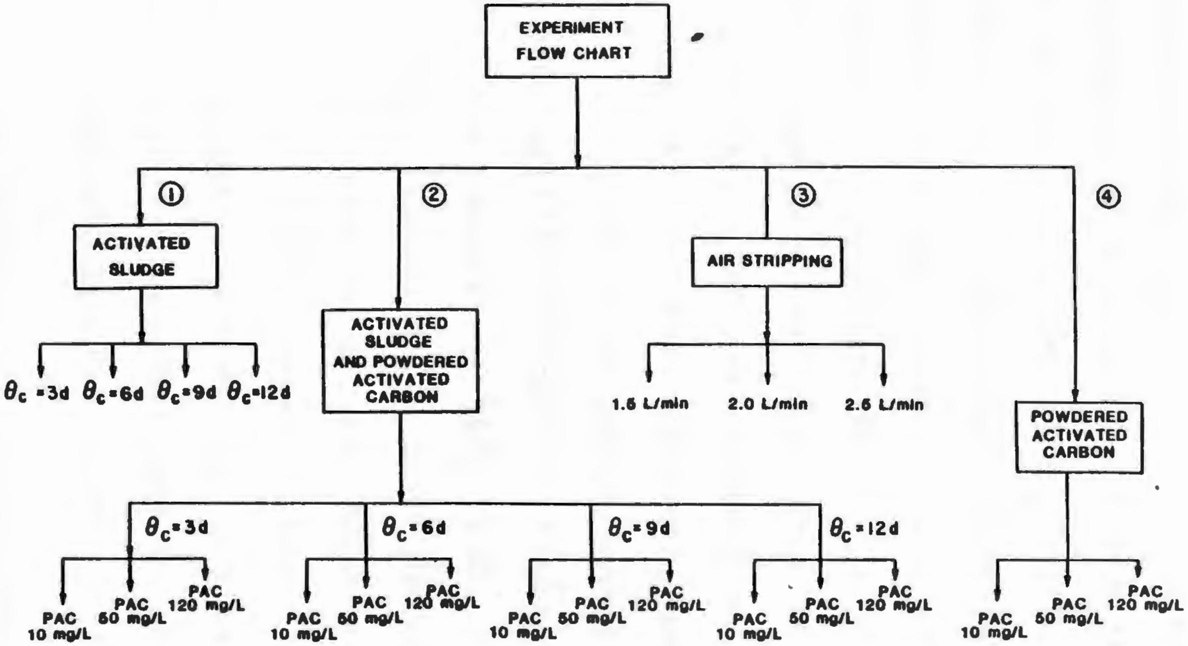


Figure 5.1 Experimental Steps

The aeration reactor tank was continuously fed with wastewater at a rate of 1.3 l/h and contained total suspended solids of 114 mg/l. In the aeration reactor tank, the DO was maintained at 5.0 mg/l, and the pH was kept between 6.80 to 7.20 by adding either 0.25 H_2SO_4 or 0.5 N NaOH to the mixed liquor. The θ_c was kept at 3, 6, 9 and 12 days. For each run, θc was controlled by wasting a suitable volume of mixed liquor from the sludge wasting line once per day. Data of interest were collected and analyzed from the influent, effluent, aeration tank and mixed liquor for a period of approximately 5 weeks.

The biological treatment process was examined by determining the removal of BOD_5, COD, TOC and selected priority organic compounds. Experimental parameters of the pilot plant such as DO, pH, temperature, and sludge retention time (SRT) were measured and recorded. Microscopic examination of the activated sludge was carried out several times each week to observe changes in the concentration and species of microorganisms.

5.2 Integrated Powdered Activated Carbon (PAC) and Activated Sludge (AS)

In this experiment, PAC in a slurry form was introduced into the aeration tank over a period of about two days to reach a constant level for each dosage.

The amount of carbon that was added to the reactor was calculated as follows:

$$\frac{W}{N} = D\ t\ V$$

where

W is the weight of carbon, in mg;

N is the number of reactors;

D is the daily carbon dosage, in mg/L;

t is the number of days until the next sample is taken, and

V is the volume of the reactor, in L/reactor.

Once the carbon reaches the aeration tank, its concentration increases until equilibrium is reached. The equilibrium carbon concentration in the aeration tank can be calculated, assuming a constant proportion of carbon and sludge in all streams as follows:

$$C = \frac{C_I \theta_c}{\theta_h}$$

The PAC experiments investigated 3 carbon dosages (10, 50, and 120 mg/l) at 4 mean cell residence times (3, 6, 9 and 12 days). The HRT time was held constant at 4 hours. A suitable amount of PAC was added once per day to maintain a constant PAC concentration in the system since some PAC was lost in the excess sludge wasting, the clarifier effluent, and the recycling line. The effect of each dosage of PAC on the activated sludge biomass and the percentage removal of the selected priority organic pollutants was investigated. Biological growth occurring on PAC was observed. Table 3.3.1 shows the frequency of sampling. This experiment was run for approximately 60 days.

PAC additions increased the stability of the aeration tank mixed liquor, increased the MLSS concentration, and improved the clarifier effluent quality.

5.3 Air Stripping and Adsorption

A third experiment was conducted to evaluate the stripping and adsorption characteristics of the selected priority pollutants in the absence of biological activity. This part of the study used the same biological pilot plant. Initially, the aeration tank and clarifier unit were cleaned, then the reactor tank and clarifier compartment were filled with distilled water. The refinery industry wastewater was pumped from the feed tank to the aeration tank, at a rate of 1.3 l/h to provide a HRT of 4 hours in the activated sludge reactor. The temperature of the reactor was kept at 23^{o}C and the pH at 6.8. The air flow rate was maintained at 2 l/h. It took about two days for the distilled water to be completely replaced by refinery industry wastewater, as determined by measuring the TOC level as a function of time. The experiment was run at air flow rates of 1.5, 2.0, and 2.5 l/hr to observe the stripability of the selected organic compounds, determined by measuring TOC and COD as a function of time and air flow rates. Influent and effluent samples were collected over a 15-day period for analysis. After this experiment was completed, the refinery industry wastewater in the reactor was analyzed to identify the remaining organics

5.4 Integrated Powdered Activated Carbon (PAC) in the Absence of Activated Sludge

In this experiment, the amounts of TOC, COD and selected priority organic pollutants removed in the activated sludge experiment above were compared with the amounts due to adsorption onto PAC. The 6-L pilot plant reactor was filled with the refinery industry wastewater to the 5.2-L mark and no activated sludge was added. Then the refinery industry wastewater was pumped continuously at a flow rate of 1.3 l/h. The experimental conditions were the same as in the second experiment, but no biomass was added. PAC was added at 10, 50 and 120 mg/l, the same concentration as in the second experiment. The pilot plant was operated for 24 hours; then samples were collected for COD, TOC and selected priority organic pollutant analysis. The experiments lasted for two weeks.

6. BIOLOGICAL ANALYSIS

Activated sludge is a mixed biological culture composed mostly of bacteria, protozoans, rotifers and fungi. Bacteria are mostly responsible for degrading the dissolved organic matter in the wastewater to microbial cell tissue and oxidized end products (mainly CO_2 and water). However, the protozoans and rotifers are responsible for removing the dispersed bacteria, which have not settled.

The general formulas describing aerobic processes in the AS reactor tank are as follows:

Oxidation

$$\text{Biomass} + O_2 + \underset{(\text{COHNS})}{\text{Organic matter}} \longrightarrow CO_2 + NH_3 + \text{Energy} + \text{end product}$$

Synthesis

$$\text{COHNS} + \text{Bacteria} + \text{Energy} \longrightarrow \underset{(\text{new cell})}{C_5H_7NO_2}$$

Respiration

$$C_5H_7NO_2 + 5O_2 \longrightarrow 5\ CO_2 + NH_3 + 2H_2O + \text{energy}$$

To produce the desired effluent quality, the temperature, the reactor basin volume, and the MLSS concentration must be adjusted and carefully controlled to achieve high BOD_5 and TOC removal.

Also, with refinery industry wastewater entering the reactor tank, the potential exists for inhibition of the AS processes. Heavy metals such as cadmium, chromium, copper, lead, nickel, and zinc react with microorganisms and inhibit their metabolism. Organic compounds also can be toxic to the AS.

In addition, any nutritional deficiency will affect bacterial growth. Therefore, it is important that the concentration of nutrients in the feed line be checked and adjusted if necessary.

6.1 Initial Biomass Seeding

The activated sludge was acclimated in the pilot plant by using a mixed liquor seed from the South Kingstown Wastewater Treatment Facility, as described in Section 3.5 of this report. The contents of the mixed liquor seed and of samples of the AS were measured as the MLSS and the MLVSS. The AS was sampled every three days after seeding and these are graphed in Figure 6.1.1.

In the first three days after seeding, the MLSS and the MLVSS concentration dropped from 2,000 (in the seed) to 380 mg/l and from 1,800 (in the seed) to 250 mg/l

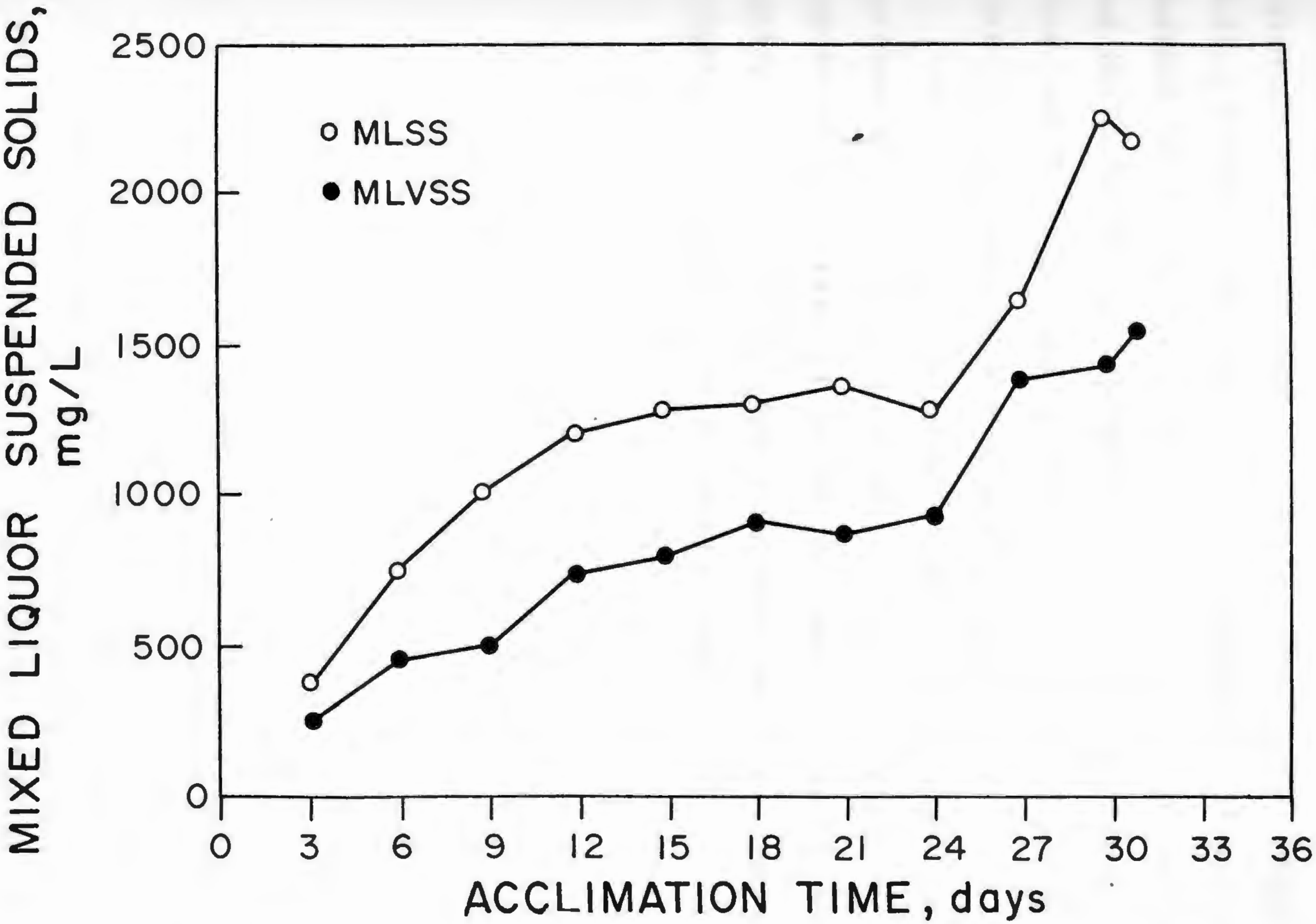


Figure 6.1.1 Suspended Solids Concentration in the Reactor Unit

respectively, (Figure 6.1.1). By day 6 after seeding, MLSS and MLVSS increased due to accumulation of bacteria. Between day 6 and day 24, the concentrations of both MLSS and MLVSS gradually increased to a steady concentration. Then both MLSS and MLVSS rose to peak values of 2,200 mg/L (day 31) and 1,500 mg/L (day 31), respectively.

After 31 days of operation, the system became acclimated to the refinery waste. The build up of MLSS and MLVSS from days 31 to 64 is shown in Figure 6.1.2; during the activated sludge phase MLSS and MLVSS decreased slightly and then increased fairly steadily.

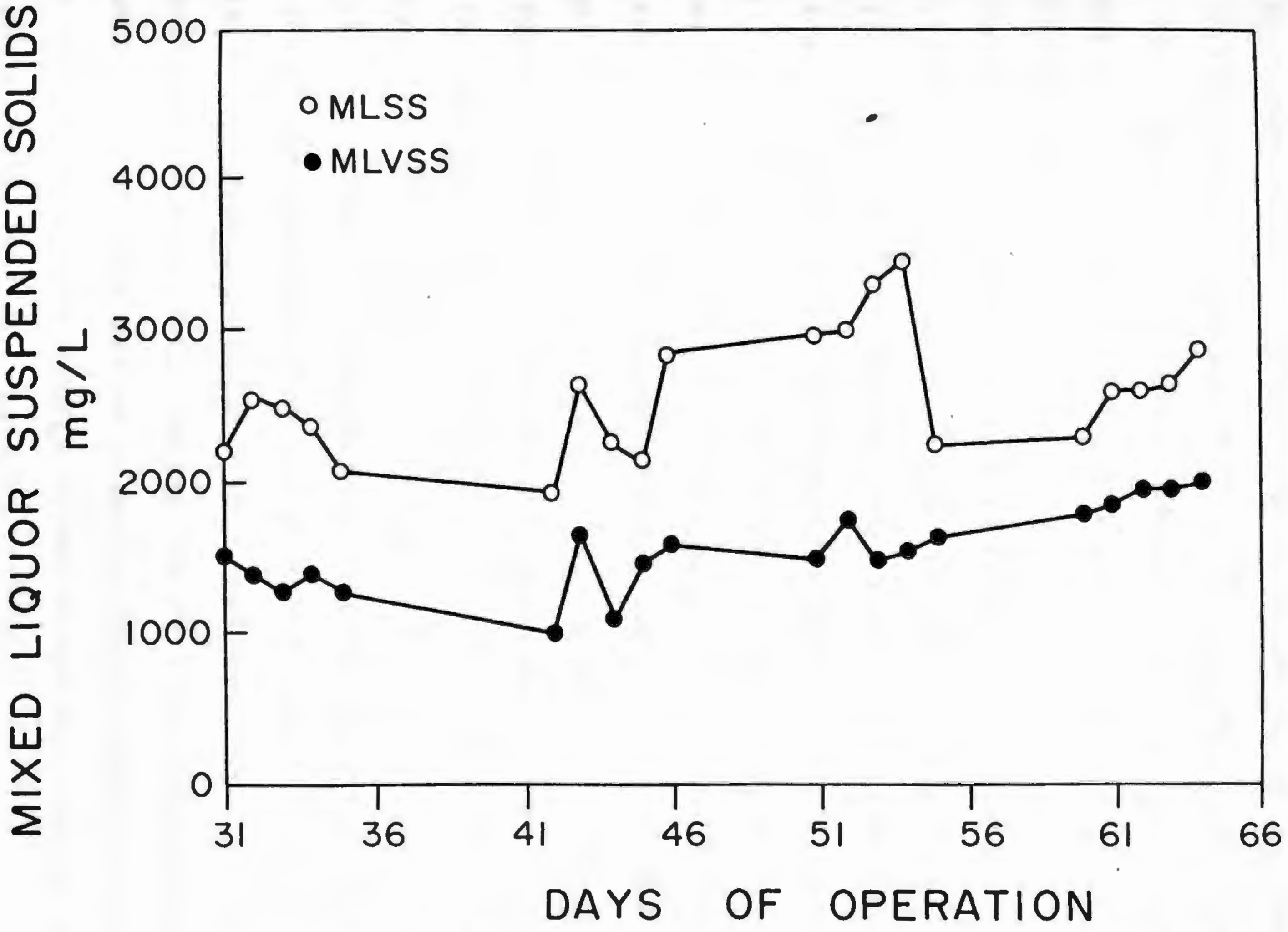


Figure 6.1.2 Aeration Tank Suspended Solids Concentration During Activated Sludge Phase

During the addition of PAC to the AS, the MLSS and MLVSS concentrations in the reactor appeared to increase as sludge age increased for each experiment (Figure 6.1.3). Moreover, a higher concentration of PAC in the reactor may increase the population and the mass of microorganisms.

The TSS and VSS in the clarifier effluent were plotted against the day of operation for 31 to 64 (the AS period; Figure 6.1.4) and for days 64 to 125 (the PAC/AS period; Figure 6.1.5). The concentration of both TSS and VSS increased as the sludge age increased, but not dramatically, the peak TSS level was 110 mg/l on day 61, during the activated sludge phase, while TSS reached a peak of 210 mg/l on day 83. This fluctuation in the effluent suspended solids probably occurred as a result of malfunctioning of the internal scraper for the clarifier unit. On the average both the TSS and VSS for the clarifier effluent were maintained between 30 and 60 mg/l. No solids were removed from the system during the first 30 days of operation, except those solids lost from the clarifier effluent unit. During the next two experiments, however, solids were wasted from the sludge wasting point; the amount of wasted sludge depended on the sludge age being maintained in the reactor.

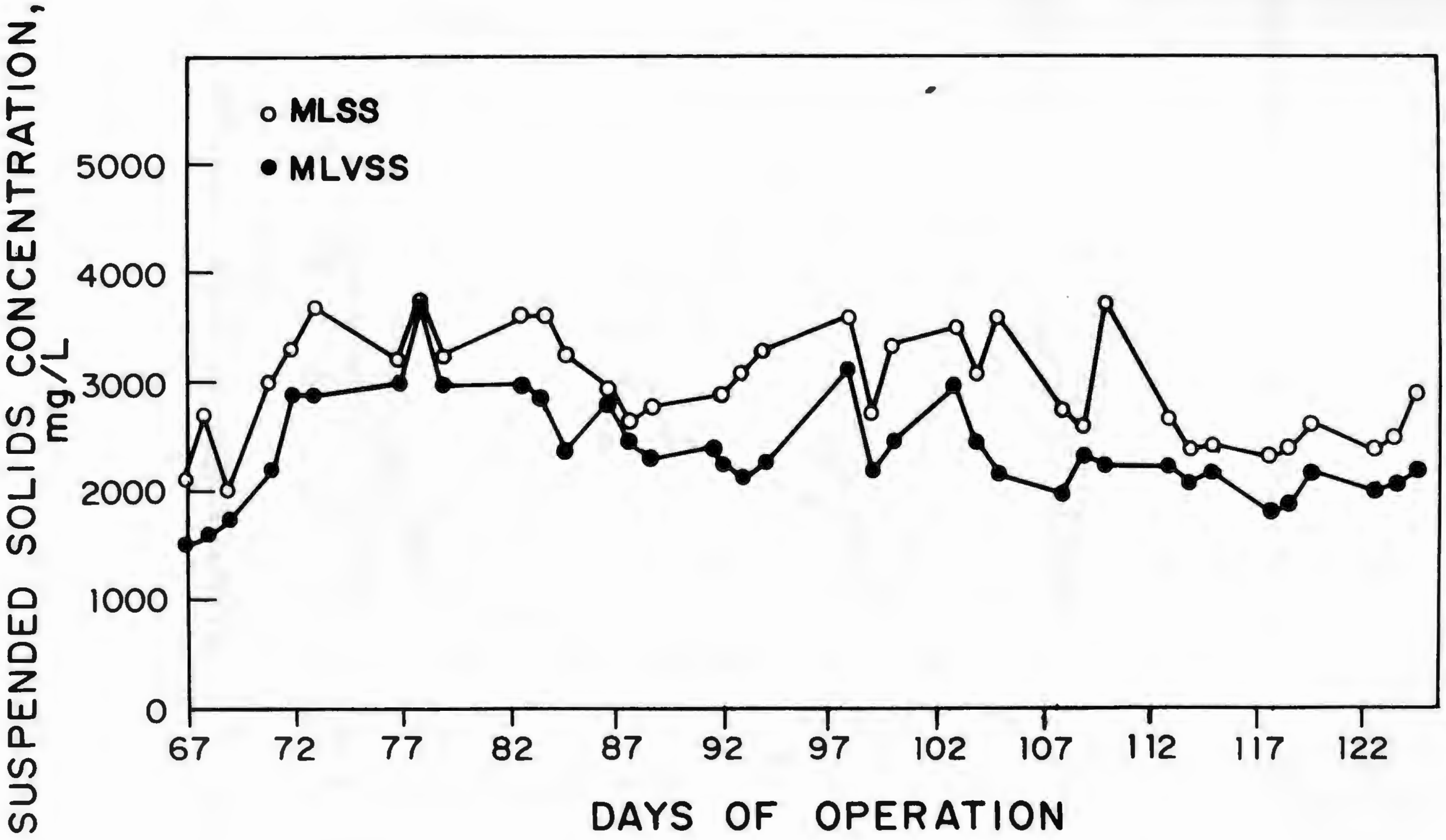


Figure 6.1.3 Areation Tank Suspended Solids During PAC/AS Phase

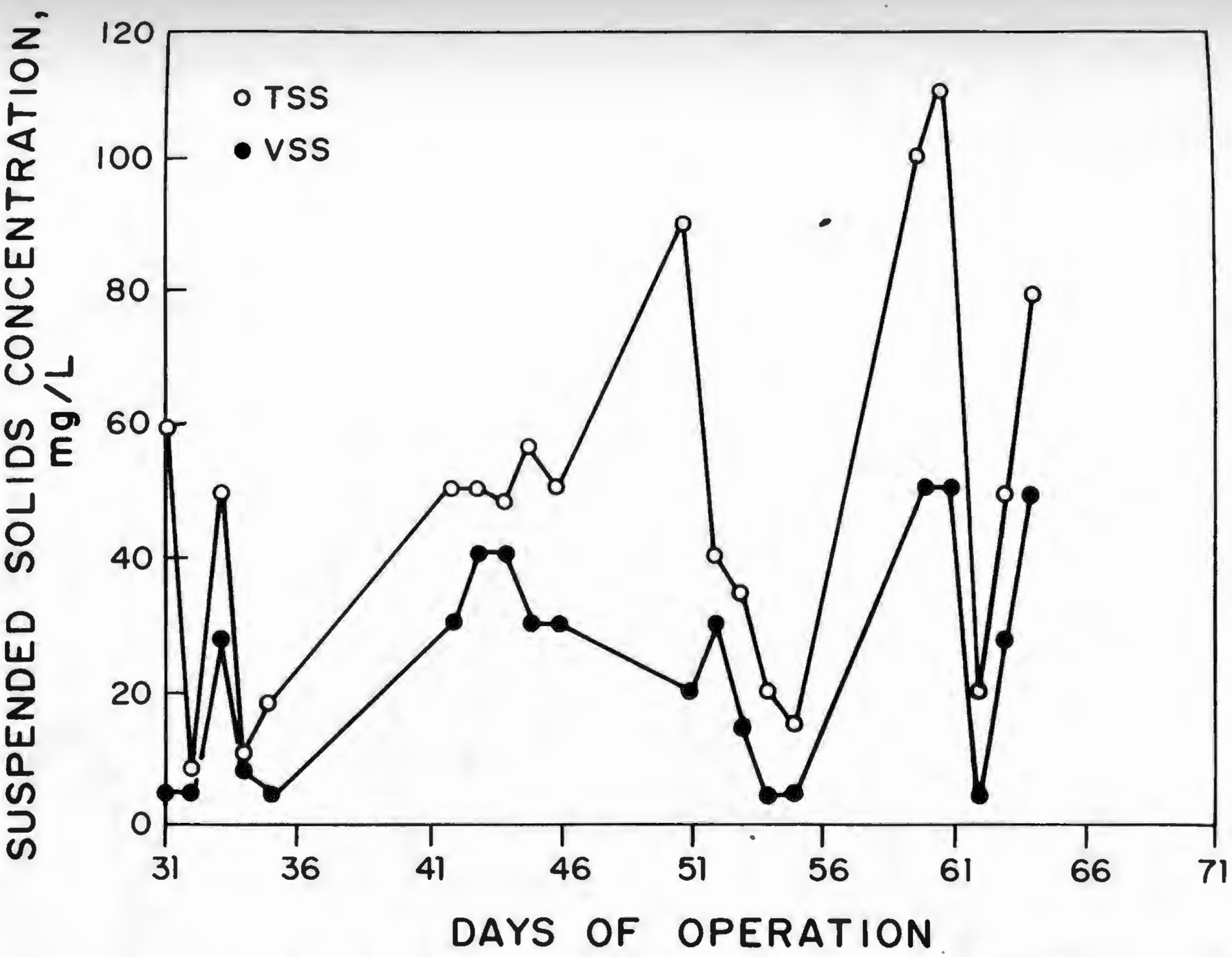


Figure 6.1.4 Clarifier Suspended Solids Effluent During Activated Sludge Phase

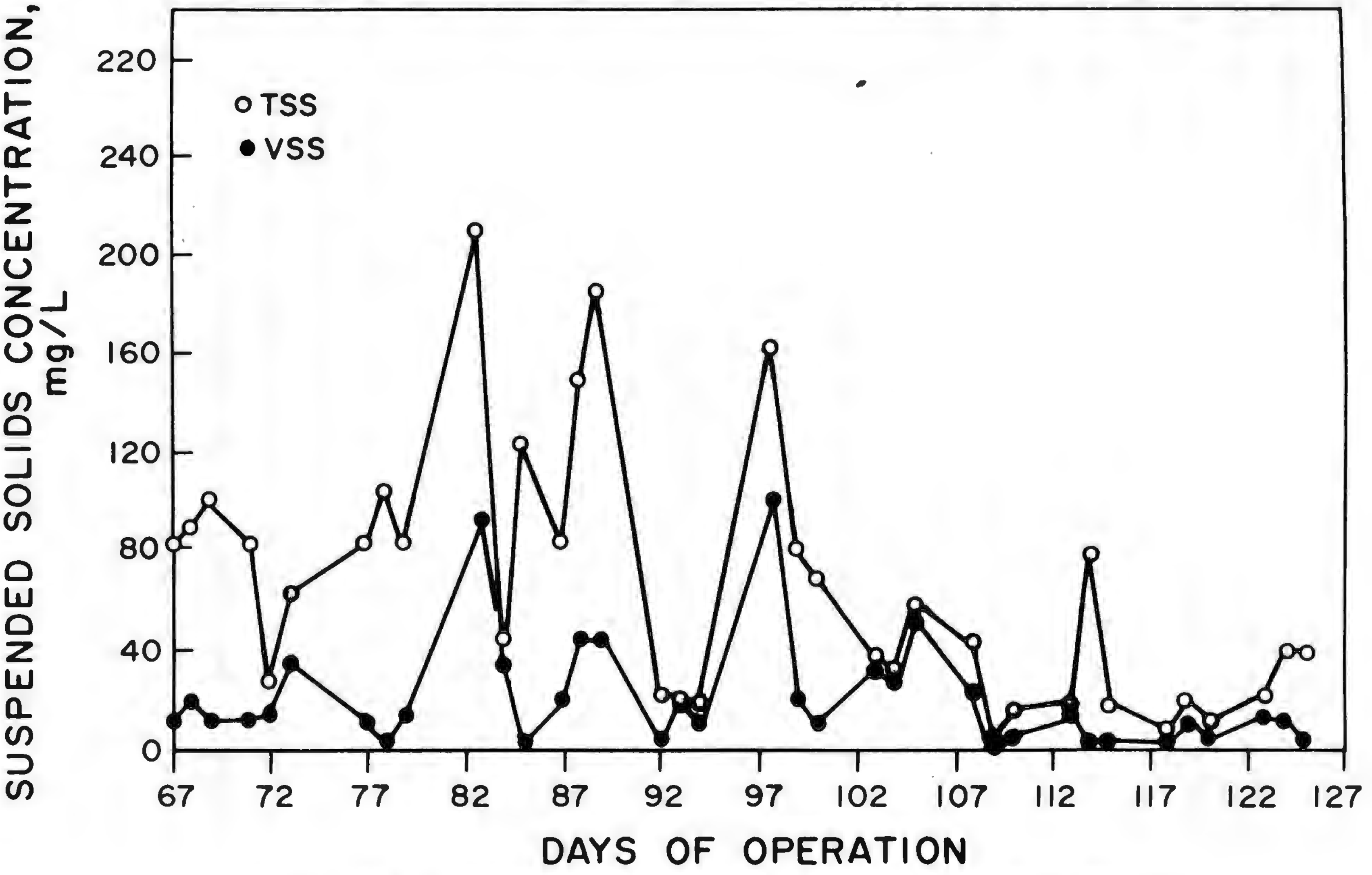


Figure 6.1.5 Claifier Suspended Solids Effluent During PAC/AS Phase

6.2 Biological Model

To come up with a model to describe the biological growth in the AS under the conditions of complete mixing, a typical scheme (shown in Figure 6.2.1) was examined. The influent feed from a holding tank entered the aeration tank and mixed with the recycled sludge from the clarifier. The microorganisms were provided with refinery industry wastewater as a substrate source. The pH was kept in the range of 6.8 to 7.2 and the temperature was kept at 24°C. The dissolved oxygen concentration was in the range of 5-6 mg/L and nutrients were added as needed. The hydraulic retention time (HRT) was kept at 4 hours; which established a MLSS level of 1500 to 2000 mg/L (77). Biological activity in the reactor tank reduced the BOD_5 concentration, resulting in an increase in bacterial cell numbers (or MLVSS) in the reactor. The solids in the clarifier unit were concentrated in the bottom of the clarifier. A fraction of the solids were recycled to the reactor as a return sludge to keep a constant concentration of MLSS in the reactor. Another fraction was wasted from the system each day from the clarifier underflow to maintain a sludge age of 3,6,9, and 12 days.

A mass balance for the biomass in the entire system can be written as:

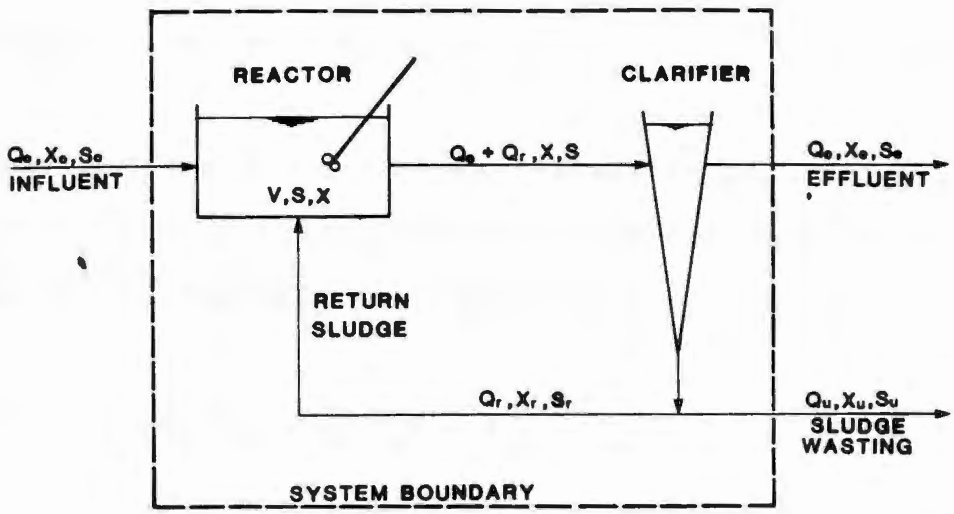


Figure 6.2.1 Complete Mix Activated Sludge Model

Accumulation of biomass in the system		Inflow of biomass to the system		Outflow of biomass from the system		Net growth of biomass the system
	=		-		+	

The equation for the biomass is:

$$\frac{dX}{dt} V = Q_o X_o - (Q_e X_e + Q_w X_w) + V r_g' \tag{6.2.1}$$

Assuming that the biomass concentration in the influent is zero and that a steady-state condition ($dX/dt=0$) is reached in the reactor, then Equation 6.2.1 becomes

$$0 = -\frac{1}{V} (Q_e X_e + Q_w X_w) + r_g' \tag{6.2.2}$$

or

$$\frac{1}{V} (Q_e X_e + Q_w X_w) = r_g' \tag{6.2.3}$$

r_g' is an expression defined by Metcalf (48):

$$r_g' = -Yr_{su} - k_d X$$

by definition, then the above equation becomes

$$\frac{1}{V} (Q_e X_e + Q_w X_w) = - Yr_{su} - k_d X \tag{6.2.4}$$

Dividing both sides of Equation 6.2.4 by X yields

$$\frac{1}{VX}(Q_e X_e + Q_w X_w) = - \frac{Yr_{su}}{X} - k_d \tag{6.2.5}$$

Since

$$\frac{1}{\theta_c} = - \frac{Yr_{su}}{X} - k_d \tag{6.2.6}$$

By definition, then Equation 6.2.5 becomes

$$\frac{1}{\theta_c} = \frac{1}{VX}(Q_e X_e + Q_w X_w) \qquad (6.2.7)$$

This equation can be rearranged to yield

$$\theta_c = \frac{VX}{(Q_e X_e + Q_w X_w)} \qquad (6.2.8)$$

However, the biomass in the effluent is very small compared to the biomass at other points in the system. Therefore,

$$\theta_c = \frac{VX}{Q_w X_w} \qquad (6.2.9)$$

where θ_c is called the mean cell residence time or sludge age.

Another important parameter in the design and operation of the reactor is the efficiency, defined as:

$$\text{Effy} = \frac{(S_o - S_e)}{S_o} \times 100\% \qquad (6.2.10)$$

6.3 Biokinetic Constants

In a biological system where all environmental needs are provided the bacteria will increase in number. The growth rate can be expressed as:

$$\frac{dX}{dt} = r_g = uX \tag{6.3.1}$$

Metcalf (48) showed that there are relationships between substrate nutrients for the microorganisms to grow. In a continuous culture, however, the growth of microorganisms can be limited to show the limiting effect of nutrients on substrate. This growth can be described as follows:

$$u = \frac{u_m S}{S+K_s} \tag{6.3.2}$$

When the activated sludge was operated under steady conditions, the biological growth rate equaled the rate of biomass losses in the effluent and waste sludge. If U is inserted as the symbol for specific substrate utilization, $-r_{su}/X$, in Equation 6.2.6 the equation becomes a

$$\frac{1}{\theta_c} = YU - k_d \tag{6.3.3}$$

At steady state conditions, the substrate utilization rate, r_{su}, and the specific substrate utilization rate, U, are constants and could be defined as:

$$r_{su} = -\frac{S_o - S_e}{\theta_h} \tag{6.3.4}$$

Thus,

$$U = -\frac{r_{su}}{X} = \frac{S_o - S_e}{\theta_h X} \qquad (6.3.5)$$

Substituting $\frac{(S_o - S_e)}{\theta_h X}$ for U in Equation 6.3.3 yields

$$\frac{1}{\theta_c} = Y \frac{(S_o - S_e)}{\theta_h X} - k_d \qquad (6.3.6)$$

Plotting $\frac{1}{\theta_c}$ against $\frac{(S_o - S_e)}{\theta_h X}$ one obtains a straight line with slope Y and intercept k_d.

The term u_m in Equation 6.3.2 can be defined as:

$$u_m = kY \qquad (6.3.7)$$

If the value of u from Equation 6.3.1 is substituted in Equation 6.3.2, the resulting expression for the rate of growth is

$$r_g = \frac{u_m S X}{K_s + S} \qquad (6.3.8)$$

Metcalf (48) showed that because of the quantity of new cells produced for a given substrate, the following relationships have been developed between the rate of substrate utilization and the rate of growth as follows:

$$r_g = -Y r_{su} \qquad (6.3.9)$$

The terms r_g in Equation 6.3.8 is substituted in Equation 6.3.9; the rate of substrate utilization can be defined as follows:

$$r_{su} = - \frac{u_m}{Y} \frac{X \; S}{(K_s + S)} \qquad (6.3.10)$$

In Equation 6.3.10 the term u_m/Y is replaced by the term k, and S equals to S_e; then

$$r_{su} = - \frac{k \; X \; S_e}{(K_s + S_e)} \qquad (6.3.11)$$

Substituting:

$$- \frac{(S_o - S_e)}{\theta_h}$$ for r_{su} in Equation 6.3.11 gives

$$\frac{S_o - S_e}{\theta_h} = \frac{k \; X \; S_e}{K_s + S_e} \qquad (6.3.12)$$

Dividing both sides by X yields

$$\frac{S_o - S_e}{\theta_h X} = \frac{k \quad S_e}{K_s + S_e} \qquad (6.3.13)$$

Taking the inverse of Equation 6.3.13 gives

$$\frac{\theta_h X}{S_o - S_e} = \frac{K_s}{k \; S_e} + \frac{S_e}{k \; S_e}$$

or

$$\frac{\theta_h X}{S_o - S_e} = \frac{K_s}{k} \; \frac{1}{S_e} + \frac{1}{k} \qquad (6.3.14)$$

By plotting $\frac{\theta_h X}{S_o - S_e}$ vs. $\frac{1}{S_e}$ one obtains a straight line with slope $\frac{K_s}{k}$ and intercept $\frac{1}{k}$.

6.4 Determination of Kinetic Coefficients.

The value of the kinetic coefficient k, the maximum rate of substrate utilization per unit mass of microorganisms (day $^{-1}$); K_s, the half-velocity constant (mg/L of BOD_5 or COD or TOC); k_d, the endogenous decay coefficient (day^{-1}); and Y, the maximum yield coeffiencient (day $^{-1}$) were determined for both the AS experiment and the experiment in which PAC was added to the AS. The procedure was to operate the reactor at different MLVSS concentrations in the range of 1500 - 3000 mg/L at several sludge ages (3, 6, 9, and 12 days) under steady-state conditions. Temperature, pH, dissolved oxygen concentration and θ were held constant throughout the experiments. The average values of 1) flow rates (Q), 2) influent BOD_5, COD and TOC as S_o, 3) effluent BOD_5, COD and TOC and as S_e, and 4) the concentrations of the biomass in the reactor as X were determined through frequent measurements. From the data obtained, the sludge age (θ_c) was calculated by Equation 6.2.9 and U values were obtained by Equation 6.3.5. By substituting these values into Equations 6.3.6, and 6.3.14 the biokinetic constants were determined.

6.5 Microscopic Analysis of Activated Sludge

6.5.1 Materials and Methods

A Zeiss photomicroscope was used at a magnification level of 160X and a phase contrast of 40X/1.25 to examine AS samples for the presence of microorganisms either attached to other cells or as free swimmers in the solution. Five samples (each about 2 ml) were collected directly from the reactor and placed in 5 ml test tubes. It was important to fill each test tube less than halfway to allow adequate air space. Immediately after collection, the sample was analyzed, beginning with 160X phase contrast microscopy, which requires only a small volume of sample (< 1 ml). Each sample was placed on a glass slide and covered with a thin glass cover; no special preparation such as staining was required. The sample was examined at a magnification of 160X for the types, relative amounts, and growth of microorganisms in the AS. No attempt was made in this study to estimate the total number or the sizes of each microorganism.

6.6 Biogrowth on Powdered Activated Carbon (PAC)

The PAC surfaces are excellent sites for microorganisms to grow on. The PAC surfaces enrich the concentration of organic compounds as well as provide excellent places for microorganisms to be protected from fluid shear forces. As reported in previous studies, (30, 41, 80), biological growth on PAC improved the removal efficiency of organic compounds found in refinery industry wastewater. Thus, microorganisms in the reactor can oxidize certain organic compounds on the surfaces of PAC particles and this reduces the organic concentrations and the organic loading on the carbon. Formation of a biofilm on the carbon particles may affect the adsorption rate; therefore, the biomass may act as a barrier and, in the end, reduce the transport rate of dissolved organics to the carbon surface (81). Scanning electron microscopy (SEM) was used as a tool to examine the carbon particles and to observe the relationships between the PAC and the attached growth. Thus, one could observe the type of organisms and the attachment structures that the organisms could build on the carbon particles (82).

6.6.1 Materials and Methods

In this experiment, PAC type BL (Calgon Corporation) was used. (For more information, see Table 3.1.1). PAC was added to the reactor in a slurry form. Carbon particle samples were collected directly from the reactor under conditions of complete mixing. At the time of sample collection, the reactor had PAC concentrations of 50 and 120 mg/L. No samples were collected for PAC particles at a reactor concentrations of 10 mg/L, because the biogrowth mass on the PAC particles was not abundant. After collection, the carbon samples were removed and fixed, as described below.

The collected samples were fixed and prepared for scanning electron microscopy (30, 41, 80). The PAC particles were immersed for two hours in 2 ml of a 70:30 mixture of 2.5% glutaraldehyde and pH 7.3 buffer solution. The carbon samples were then transferred into 0.1 M sodium phosphate buffer (pH 7.3) for one hour. Excess buffer solution was removed from the PAC particle samples, but a small amount was left to cover the specimen; the sample was then kept in a refrigerator at 4°C until the next step, fixation. The carbon particle samples were resuspended in 2% osmium oxide (OsO_4) in 0.1 M sodium phosphate buffer (pH 7.3) for 3 hours. Then the PAC particles were washed five time with ethanol (50, 70, 80, 90 and 100%). Samples were dried in a 1:1 100% ethanol amylacetate solution and stored for 24 hours in amylacetate.

A DCP - L critical point dryer was used to dry the fixed samples. Then the PAC particles were mounted on aluminum stubs and coated with gold to increase the conductivity of the biological materials. The PAC particle samples were examined in a scanning electron microscope at 20-25 KV with a resolution of 10 nm. For control samples (virgin carbon), the fixation, dehydration and drying steps were eliminated; the carbon particle samples were glued to the stubs and then coated with gold (about 2nm thick) before SEM.

7. RESULTS

7.1 Description and Evaluation of Biokinetic Constants

Using the data from the reactor, plots were made to determine the biokinetic constants of the refinery industry wastewater.

The biokinetic constants were defined in terms of BOD_5, COD and TOC. Each constant was obtained for the first two experiments with AS alone at first and then with the addition of PAC to the AS. The linearization of the experimental data collected is presented in Figures A.2.1 - A.2.24 in Appendix 2. The data were scattered around the best-fit line. This scattering of the data is typical of this type of analysis. The lines were drawn using the least square method. The straight-line analysis yielded k, K_s, k_d and Y according to Equations 6.3.6 and 6.3.14.

Table 7.1.1 presents the biokinetic constants in terms of BOD_5, COD and TOC, which are considered to be the substrate concentration in the reactor. The MLVSS are used as a measure of microbial solids concentrations. The values of the biokinetic constants for the wastewater (Table 7.1.1) were different from typical values (Table 7.1.2).

Table 7.1.1 Biokinetic Constants for the Modified Activated Sludge Pilot Plant

Constant	Units	PAC Concentrations (mg/L)	BOD_5	COD	TOC
k	day^{-1}	0	2	2.40	0.18
		10	2	2.50	1.0
		50	0.65	1.33	0.75
		120	0.82	1.80	0.64
K_s	mg/L BOD_5 or COD	0	75	80	7.2
		10	13	40	24.0
		50	15	89	30.0
		120	33	4	16.0
k_d	day^{-1}	0	0.42	0.46	0.59
		10	0.14	0.20	0.15
		50	0.22	0.46	0.32
		120	0.28	0.04	0.34
Y	mg VSS per mg BOD_5 or COD	0	1.00	0.62	0.86
		10	1.00	0.33	0.83
		50	2.50	0.80	0.80
		120	1.2	0.60	1.00

Table 7.1.2 Typical Values for Biokinetic Constants for the Activated Sludge at $20^{\circ}C$ (Ref no. 48).

Constant	Units	Range	Typical Value
k	day^{-1}	2-10	5.0
K_s	mg/L BOD_5	25-100	60
	mg/L COD	15-70	40
k_d	day^{-1}	0.04-0.075	0.06
Y	mg VSS/mg BOD_5	0.4 -0.8	0.6
	mg VSS/mg COD	0.25-0.4	0.4

The AS results for k measurements falls outside the range. K_s tend to fall within the range of literature and the values for k_d and Y are higher than typical values.

The high value of Y suggests high rates of sludge production. As can be observed in Table 7.1.1, biokinetic constants can differ from typical values for two possible reasons; 1) the biokinetic constant values depend on the type of wastewater, and 2) the values of the biokinetic constants depend entirely on the operating conditions of the reactor, such as temperature, sludge age and carbon dosages (24).

PAC present in the reactor has an effect on the value of the biokinetic constants. The presence of PAC can reduce the concentration of the AS; therefore, the kinetic values calculated with PAC would be less than the typical literature values for AS without PAC additions. Also, the biomass activity which occurs in the PAC pores is controlled by the substrate mass transfer into the pores (60).

7.2 Experiment 1: Activated Sludge Treatment Process

A series of experiments were carried out at sludge ages of 3, 6, 9 and 12 days. Each experiment lasted at least 5 days under steady state conditions. The hydraulic retention time (HRT) was kept at 4 hours for the duration of the test program. Ammonium sulfate and potassium phosphate were added as nutrient sources (N and P).

Experiment 1 was conducted at a sludge age (θ_c) of 3 days. Table 7.2.1 summarizes the biological treatment experimental findings when the MLSS was about 2,198 mg/L and the MLVSS was about 1,300 mg/L. Other parameters such as NH_3, NO_2, NO_3 phosphate and oil/grease were determined.

Biological parameters were also determined for sludge ages of 6, 9, and 12 days, (Tables 7.2.2-4, respectively). These data show increases in the MLVSS and MLSS concentrations as the sludge age increases. This is due to 1) increases in the activity of the biomass in the reactor and 2) the fact that the amount of wasted sludge was less than at a 3-day sludge age.

Table 7.2.1 Biological Treatment of Refinery Industry Wastewater by Activated Sludge, Sludge Age (θ_c) = 3 days (All concentrations are in mg/L)

		Supended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
8/31	1	1,520	2,196	5	60	35	30	0.20	0.07	0.54	0.06	3.0	0.17	2.20	1.22	191	127
9/1	2	1,420	2,584	5	8	43	32	0.32	0.03	0.61	0.16	2.0	0.04	1.79	0.66	28	6
9/2	3	1,560	2,492	28	50	30	20	0.28	0.02	0.20	0.07	3.0	0.02	2.44	0.43	33	7
9/3	4	1,380	2,370	9	10	24	8	0.46	0.02	1.32	0.38	0.94	0.67	0.27	0.20	61	15
9/4	5	1,300	2,198	5	18	30	7	0.40	0.02	0.50	0.05	0.22	0.20	1.50	0.15	81	8

Table 7.2.2 Biological Treatment of Refinery Industry Wastewater by Activated Sludge, Sludge Age (θ_c) = 6 days (All concentraions are in mg/L).

		Supended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
9/11	6	1,020	1,918	30	50	15	3	0.90	0.13	0.77	0.46	3.46	0.58	1.88	0.27	52	30
9/12	7	1,620	2,640	40	50	20	8	0.40	0.10	0.11	0.20	3.76	0.40	1.32	0.32	54	46
9/13	8	1,120	2,250	40	48	23	10	0.50	0.16	0.32	0.08	3.11	0.04	0.10	0.01	68	61
9/14	9	1,480	2,674	30	56	32	21	0.60	0.14	1.49	0.65	3.25	0.62	0.46	0.38	65	28
9/15	10	1,596	2,840	30	50	32	17	0.70	0.10	3.18	0.04	3.07	0.72	0.16	0.08	116	71

Table 7.2.3 Biological Treatment of Refinery Industry Wastewater by Activated Sludge, Sludge Age (θ_c) = 9 days (All concentrations are in mg/L).

		Supended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
9/20	11	1,500	2,980	20	90	44	30	0.08	0.04	1.20	0.68	1.35	0.70	0.14	0.12	30	21
9/21	12	1,760	3,000	30	40	40	33	0.18	0.04	0.16	0.02	4.62	0.76	2.64	1.98	50	19
9/22	13	1,500	3,300	15	35	15	3	0.12	0.02	0.80	0.16	4.14	0.28	2.64	1.14	92	40
9/23	14	1,540	3,460	5	20	20	1	0.16	0.02	0.40	0.03	3.16	0.01	1.18	1.51	15	3
9/24	15	1,640	2,220	5	15	10	1	0.20	0.14	1.36	0.72	5.30	0.48	3.60	1.80	62	27

Table 7.2.4 Biological Treatment of Refinery Industry Wastewater by Activated Sludge, Sludge Age (θ_c) = 12 days (All concentraions are in mg/L).

		Supended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
9/29	16	1,580	1,800	50	100	13	1	0.46	0.20	1.12	0.60	3.14	0.07	1.50	0.52	15	2
9/30	17	1,596	1,850	50	110	11	0	0.36	0.01	0.57	0.48	3.63	0.65	2.40	1.18	63	20
10/1	18	1,920	1,940	5	20	12	1	0.60	0.04	1.04	0.60	1.52	0.01	1.60	0.42	10	3
10/2	19	1,960	2,672	28	50	50	34	0.36	0.04	0.77	0.39	2.21	0.35	1.53	0.44	18	1
10/3	20	2,040	2,890	50	81	43	42	0.04	0.02	1.10	0.50	1.12	0.10	1.47	0.30	45	12

Tables 7.2.5-8 show the calculated results of experiment 1. The BOD_5 concentration in the effluent was in the average of 24 mg/L, giving a reduction in BOD_5 of about 80%. Figure 7.2.1 shows the variation in the influent and effluent BOD_5 concentrations throughout the test period. In general, the reduction in BOD_5 was about 80%. Even though the experiment was run at different sludge ages, the reduction in the BOD_5 concentration was almost the same. This demonstrated that typical biological treatment will remove approximately 80% BOD_5 for this waste. A greater reduction would be seen if the influent BOD_5 concentration was consistent during the test period. The variation in the feed composition will affect the biomass activities to reduce BOD_5 concentration. However if the feed composition was low, the percent of BOD_5 removal would be high, and all substrate utilization would occur in the reactor. Another factor which can contribute to lower BOD_5 removals is the oxygen demand exerted by high concentrations of organic pollutants.

Figure 7.2.2 shows the changes in the strength of TOC throughout the test period. The decline in TOC strength could be a result of concentration reduction in chemical compounds in the stored industrial wastewater. As can be seen from the results shown in Tables 7.2.5-8, biological treatment could achieve as high as 80% reduction with a TOC concentration in the effluent of less than 25 mg/L.

Table 7.2.5 Activated Sludge Performance in Experiment 1
Sludge Age (θc) = 3 days

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
1	160	88	45	356	90	75	47	15	68
2	183	22	88	329	78	76	39	15	62
3	150	27	82	522	100	80	50	18	64
4	160	22	86	380	80	79	48	13	73
5	147	21	86	313	52	83	41	14	66

Table 7.2.6 Activated Sludge Performance in Experiment 1 Sludge Age (θc) = 6 days

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
6	200	25	88	353	81	77	38	16	58
7	142	26	82	290	78	73	54	25	54
8	144	20	86	386	70	82	53	21	60
9	121	15	88	333	60	82	49	13	74
10	126	10	92	288	61	79	56	25	55

Table 7.2.7 Activated Sludge Performance in Experiment 1
Sludge Age (θc) = 9 days

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
11	82	11	87	292	58	80	45	12	73
12	100	20	80	310	71	77	30	11	63
13	135	16	88	354	79	78	31	11	65
14	173	16	91	294	60	80	42	10	76
15	151	15	90	300	67	78	62	15	76

Table 7.2.8 Activated Sludge Performance in Experiment 1
Sludge Age (θc) = 12 days

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
16	203	19	90	360	50	89	40	9	78
17	170	15	91	328	54	84	42	10	76
18	139	15	89	353	48	86	53	12	77
19	140	16	89	337	50	85	40	9	78
20	148	10	93	372	48	87	40	10	83

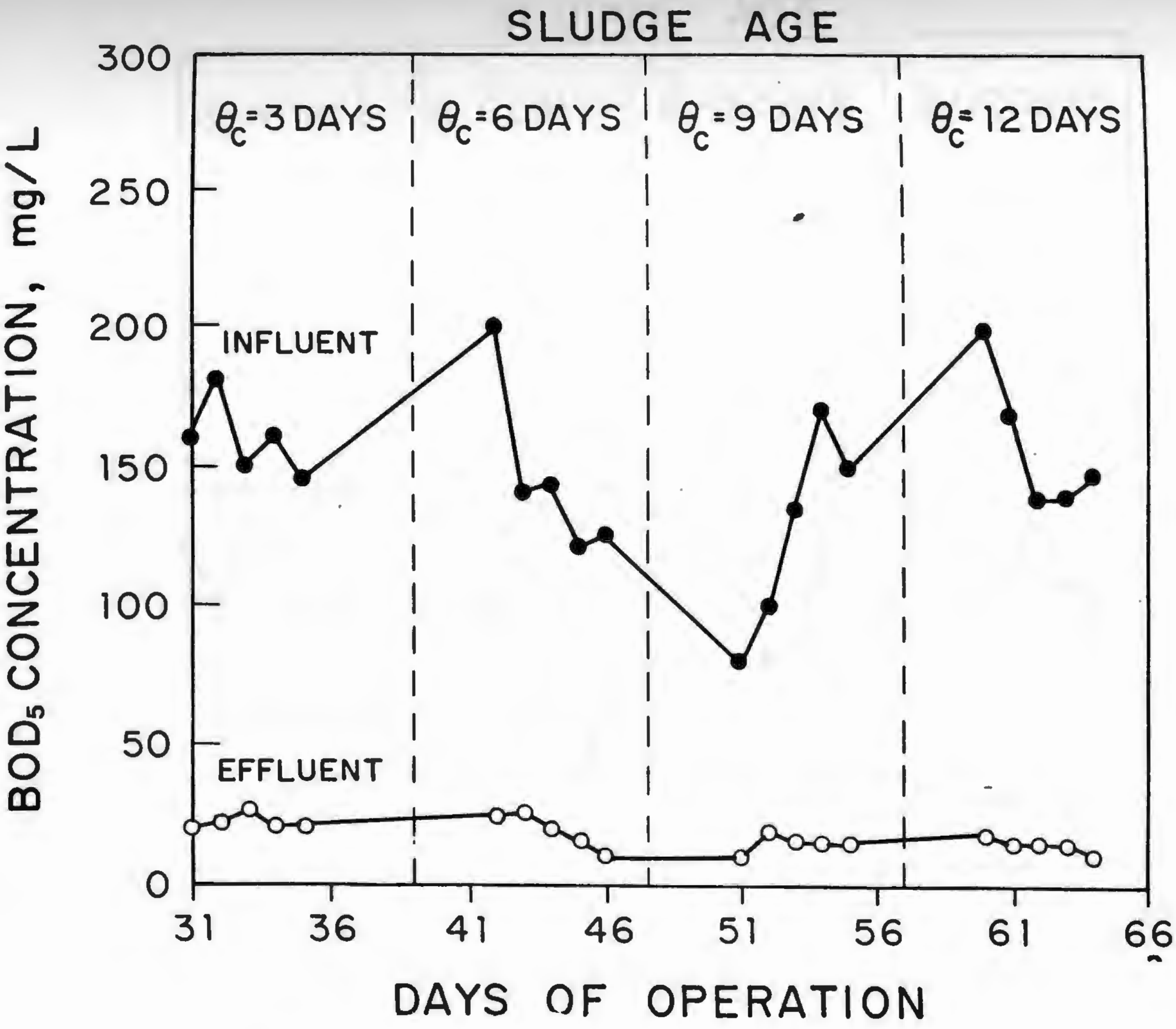


Figure 7.2.1 BOD_5 Removal by Activated Sludge

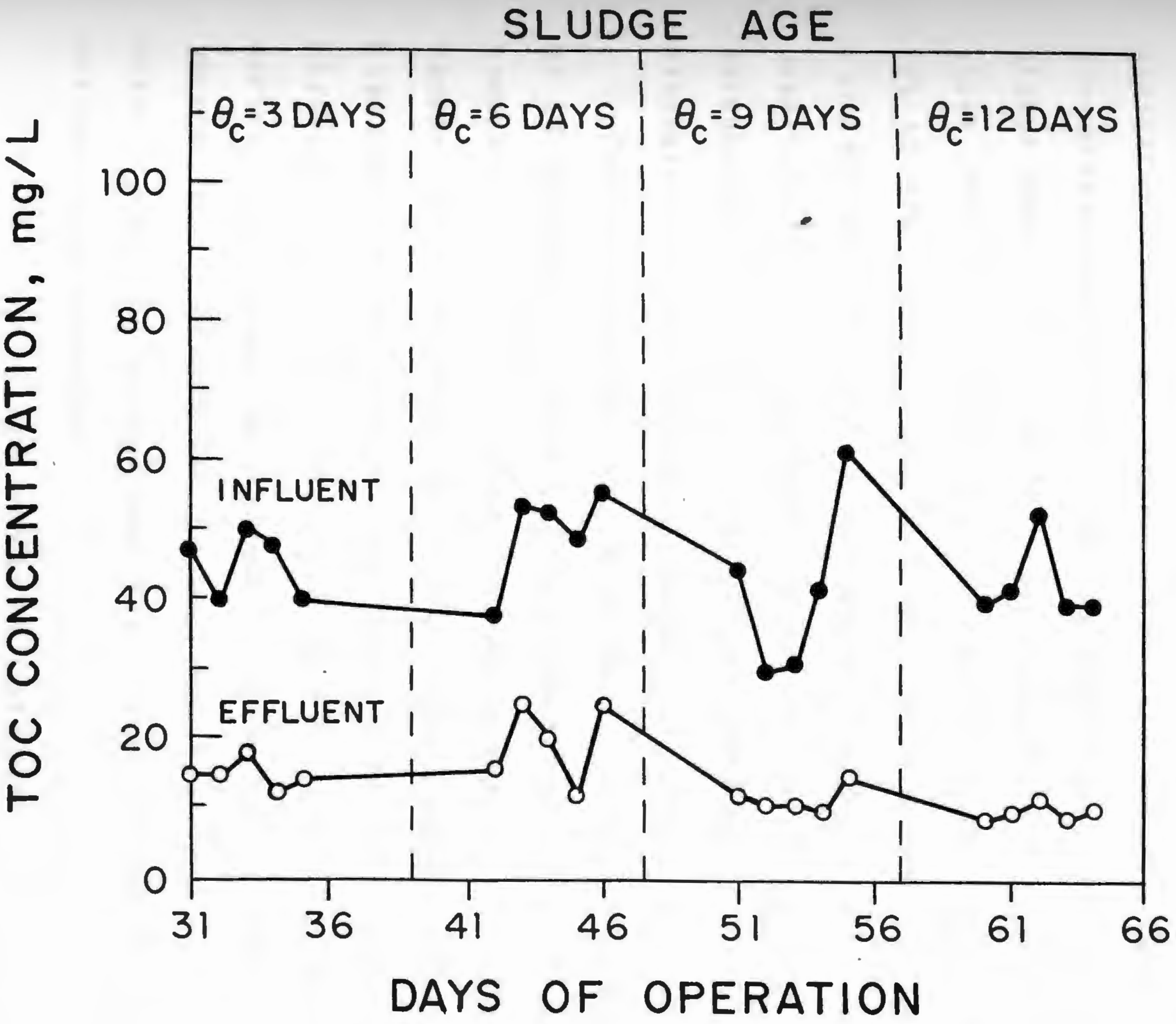


Figure 7.2.2 TOC Removal by Activated Sludge

Figure 7.2.3 illustrates the variation in the influent and effluent COD concentration throughout the activated sludge experiment. Tables 7.2.5-8 present COD concentrations through the AS experiments at various sludge ages (3,6,9 and 12 days) respectively. The table shows that the reduction in COD concentration ranged from 70% to 89%. With this level of reduction, the effluent concentration is still above 50 mg/L which is unsatisfactory. The reason would be the changes in the strength of the feed as a result of combined chemical and biological oxidation of the stored wastewater.

Tables 7.2.9-12 show the priority pollutants removal by AS treatment. With a high concentration of organic compounds in the feed flow, the AS treatment was able to remove on the average for 2,4-dimethylphenol, fluorene, naphthalene and pyrene are 90%, 77%, 68% and 67%, respectively. The reduction in the priority during various sludge ages were shown in Appendix 3. These data showed that the effluent quality remained almost steady even though the system was not being fed at constant effluent concentration.

Tables 7.2.13-16 present data on the priority pollutants removed by AS treatment at various sludge ages (3,6,9, and 12 days), respectively. These pollutants are benzene, chloroform, ethylbenzene, toluene, m-xylene and

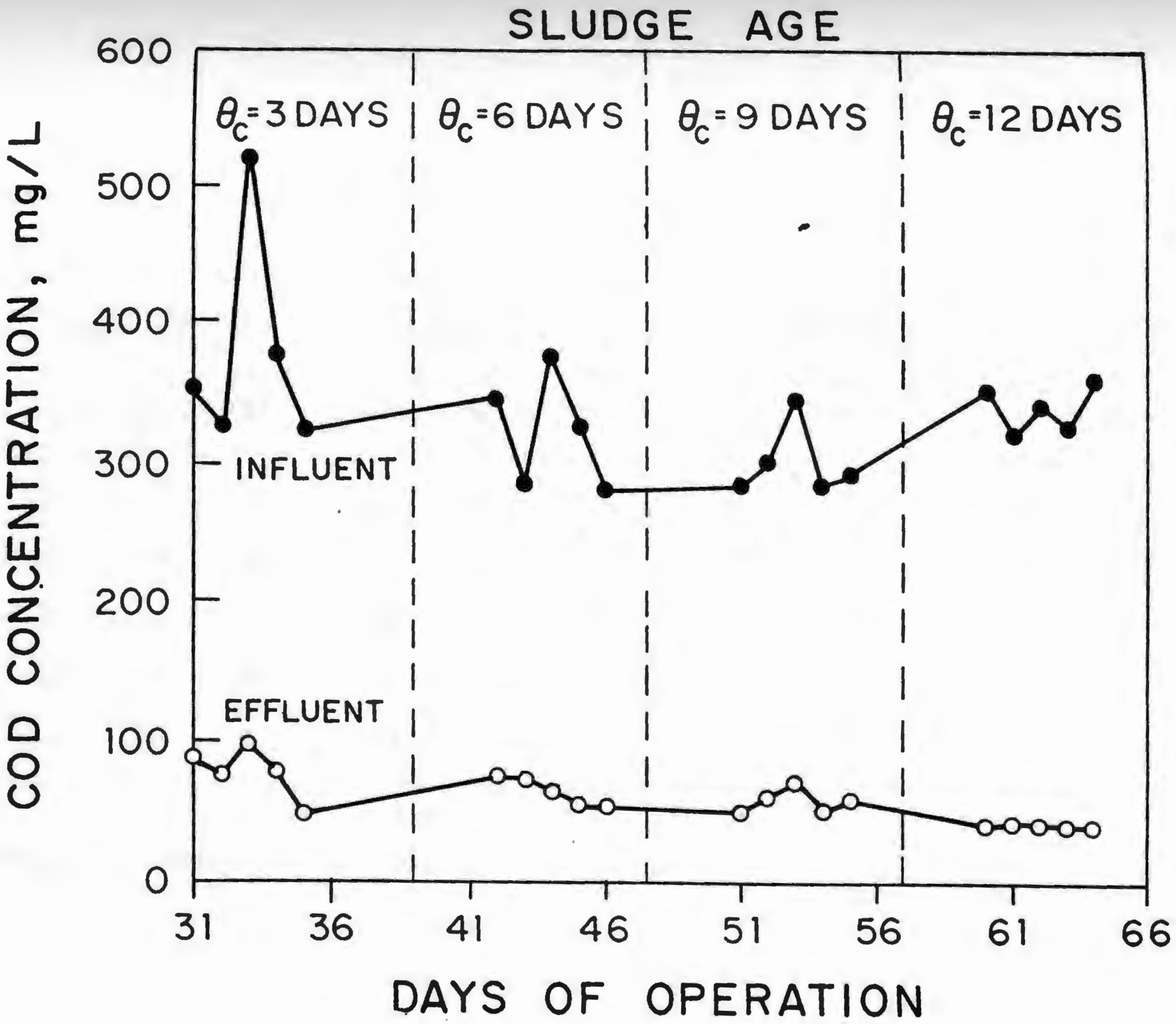


Figure 7.2.3 COD Removal by Activated Sludge

Table 7.2.9 Priority Pollutants Removal by Activated Sludge, Sludge Age (θc) = 3 days

		2,4-Dimethlphenol			Fluorene			Naphthalene			Pyrene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
8/31	1	570	27	95	139	30	78	33	19	42	27	ND	>63
9/1	2	533	33	94	133	10	92	300	11	96	28	ND	>64
9/2	3	100	33	67	20	ND	>50	40	20	50	20	ND	>50
9/3	4	260	27	90	40	10	75	40	9	78	24	ND	>58
9/4	5	267	20	92	27	11	60	92	18	80	26	ND	>62

ND = None detectable, detectability >10 ug/L

Table 7.2.10 Priority Pollutants Removal by Activated Sludge, Sludge Age (θc) = 6 days

		2,4-Dimethlphenol			Fluorene			Naphthalene			Pyrene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
9/11	6	1,887	300	84	67	10	85	300	10	97	30	10	67
9/12	7	333	27	92	27	ND	>63	198	ND	>97	27	11	60
9/13	8	334	73	78	53	ND	>81	1,000	33	97	27	12	56
9/14	9	1,667	266	84	33	13	61	133	10	92	29	10	66
9/15	10	867	133	85	37	12	68	200	33	84	30	12	60

ND = None detectable, detectability >10 ug/L

Table 7.2.10 Priority Pollutants Removal by Activated Sludge, Sludge Age (θc) = 6 days

		2,4-Dimethlphenol			Fluorene			Naphthalene			Pyrene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
9/11	6	1,887	300	84	67	10	85	300	10	97	30	10	67
9/12	7	333	27	92	27	ND	>63	198	ND	>97	27	11	60
9/13	8	334	73	78	53	ND	>81	1,000	33	97	27	12	56
9/14	9	1,667	266	84	33	13	61	133	10	92	29	10	66
9/15	10	867	133	85	37	12	68	200	33	84	30	12	60

ND = None detectable, detectability >10 ug/L

Table 7.2.11 Priority Pollutants Removal by Activated Sludge, Sludge Age (θc) = 9 days

		2,4-Dimethlphenol			Fluorene			Naphthalene			Pyrene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
9/20	11	1,140	73	94	35	17	51	147	20	86	13	ND	>30
9/21	12	440	20	95	133	24	82	280	21	93	32	13	60
9/22	13	387	27	93	153	17	89	280	23	92	32	13	60
9/23	14	1,000	33	97	80	13	84	200	23	89	13	ND	>20
9/24	15	1,090	146	87	167	23	86	1,200	127	89	12	ND	>17

ND = None detectable, detectability >10 ug/L

Table 7.2.12 Priority Pollutants Removal by Activated Sludge, Sludge Age (θc) = 12 days

		2,4-Dimethlphenol			Fluorene			Naphthalene			Pyrene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
9/29	16	547	25	95	174	40	77	933	33	96	41	14	66
9/30	17	404	27	93	207	40	81	1,533	27	98	27	12	56
10/1	18	217	17	92	247	41	83	1,867	33	98	27	15	44
10/2	19	492	24	94	400	23	94	1,867	27	99	110	13	88
10/3	20	613	33	95	320	40	88	2,268	43	98	100	14	80

Table 7.2.13 Volatile Organics Removal by Activated Sludge Treatment, Sludge Age (θc) ≈ 3 days

		Benzene			Chloroform			Ethylbenzene			Toluene			m-Xylene			o-Xylene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
8/31	1	1,200	ND	>99	900	30	97	125	ND	>92	200	ND	>95	530	ND	>98	720	ND	>99
9/1	2	330	ND	>97	460	25	95	10	ND	ND	220	ND	>98	640	ND	>98	580	ND	>98
9/2	3	640	ND	>98	730	60	92	80	ND	>88	620	ND	>98	280	ND	>96	370	ND	>97
9/3	4	980	ND	>99	1,440	80	94	250	ND	>96	1,000	ND	>99	400	ND	>98	560	ND	>98
9/4	5	1,956	20	100	1,691	120	93	460	ND	>98	1,767	65	>96	700	ND	>99	960	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.2.14 Volatile Organics Removal by Activated Sludge Treatment, Sludge Age (θc) = 6 days

		Benzene			Chloroform			Ethylbenzene			Toluene			m-Xylene			o-Xylene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
9/11	6	1,761	ND	>99	1,952	ND	>99	210	ND	>95	1,295	ND	>99	600	ND	>98	780	ND	>99
9/12	7	120	ND	>92	1,800	ND	>99	100	ND	>90	120	ND	>92	300	ND	>97	200	ND	>95
9/13	8	960	ND	>99	1,718	40	98	300	ND	>97	910	ND	>99	500	ND	>98	610	ND	>98
9/14	9	840	ND	>99	1,624	180	89	300	ND	>97	870	ND	>99	500	ND	>98	630	ND	>98
9/15	10	1,130	ND	>99	1,780	70	96	410	ND	>98	1,240	ND	>99	900	ND	>99	1322	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.2.15 Volatile Organics Removal by Activated Sludge Treatment, Sludge Age (θ_c) = 9 days

		Benzene			Chloroform			Ethylbenzene			Toluene			m-Xylene			o-Xylene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
9/20	11	620	ND	>98	1,785	158	91	60	ND	>83	460	ND	>98	310	ND	>97	460	ND	>98
9/21	12	890	ND	>99	1,212	10	99	220	ND	>95	640	ND	>98	360	ND	>97	460	ND	>98
9/22	13	210	ND	>95	1,744	80	95	60	ND	>83	120	ND	>92	100	ND	>90	10	ND	ND
9/23	14	247	ND	>96	2,072	66	97	900	ND	>99	233	ND	>96	1,097	ND	>99	1,475	ND	>99
9/24	15	709	ND	>99	1,877	ND	>99	640	ND	>98	616	ND	>98	760	ND	>99	980	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.2.16 Volatile Organics Removal by Activated Sludge Treatment, Sludge Age (θ_c) = 12 days

		Benzene			Chloroform			Ethylbenzene			Toluene			m-Xylene			o-Xylene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
9/29	16	2,219	ND	>99	1,904	90	95	408	ND	>98	1,550	ND	>99	750	ND	>99	930	ND	>99
9/30	17	1,976	ND	>99	2,054	300	85	500	ND	>98	1,450	ND	>99	920	ND	>99	1,080	ND	>99
10/1	18	1,620	ND	>99	2,043	80	96	680	ND	>99	1,340	ND	>99	1,337	ND	>99	1,520	ND	>99
10/2	19	970	ND	>99	1,834	10	99	820	ND	>99	480	ND	>98	750	ND	>99	1,040	ND	>99
10/3	20	490	ND	>98	1,637	40	98	220	ND	>95	400	ND	>98	340	ND	>97	440	ND	>98

ND = None detectable, detectability >10 ug/L

o-xylene. These compounds found to be air stripped from the reactor by the air flow (Section 7.5). There were no increases in the percentage removals of the volatile due to the AS.

7.3 Experiment 2: Activated Sludge with Powdered Activated Carbon

To enhance the AS process, PAC was added to the reactor tank in various concentrations over a period of 5 weeks. The PAC concentrations that were maintained in the AS reactor were 10, 50, and 120 mg/L.

The additions of PAC into the reactor resulted in changes in the MLVSS concentration from those measured in the AS process without PAC (experiment 1). The MLVSS results are shown in Tables 7.3.1-12. All additions of PAC resulted in increases in the MLVSS from those measured for the AS without PAC. At a θ_c of 3 days, and PAC concentrations of 10 mg/L, 50 mg/L, and 120 mg/L there was an initial increase in the MLVSS concentration up to a PAC concentration of 50 mg/L and a slight decrease at 120 mg/L. For all of the other θ_c values (6, 9, and 12 days) and all PAC concentrations, the MLVSS at first increased over the AS values and then showed a decrease as the PAC concentrations increased.

The concentrations of selected nutrients (nitrogen and phosphorus) in the influent and effluent were measured three times per week and these values are presented in Tables 7.3.1-12. The influent concentrations of the nutrients were high enough to satisfy the biomass requirements as reported in reference (75).

Oil and grease concentrations in the influent and

Table 7.3.1 Activated Sludge and PAC Performances in Experiment 2 when θ_c = 3 days and PAC = 10 mg/L, All Concentrations are in mg/L.

		Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
Date	Run	Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
10/16	21	1,500	2,100	11	85	54	43	0.06	0.01	1.52	0.28	0.25	0.06	0.14	0.04	29	9
10/17	22	1,600	2,700	20	90	30	24	0.04	0.03	0.78	0.20	0.42	0.18	0.22	0.18	29	10
10/18	23	1,740	2,032	11	100	51	41	0.02	0.01	1.04	1.02	0.42	0.06	0.16	0.14	29	10

Table 7.3.2 Activated Sludge and PAC Performances in Experiment 2 when θ_c = 6 days and PAC = 10 mg/L, All Concentrations are in mg/L.

		Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
Date	Run	Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
10/20	24	2,220	3,000	12	86	37	30	0.08	0.01	0.48	0.06	0.14	0.07	0.12	0.06	62	40
10/21	25	2,920	3,314	15	30	51	44	0.10	0.03	0.07	0.01	0.30	0.01	0.28	0.09	115	14
10/22	26	2,880	3,696	35	64	60	30	0.07	0.04	0.36	0.12	1.0	0.03	0.31	0.12	85	4

Table 7.3.3 Activated Sludge and PAC Performances in Experiment 2 when θ_c = 9 days and PAC = 10 mg/L, All Concentrations are in mg/L.

		Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
Date	Run	Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
10/26	27	3,060	3,200	11	85	70	50	0.11	0.03	1.94	1.90	1.0	0.02	0.24	0.08	47	19
10/27	28	3,750	3,780	5	105	64	50	0.16	0.02	2.0	1.20	0.60	0.16	0.29	0.19	43	9
10/28	29	3,020	3,270	15	85	33	23	0.13	0.02	2.17	2.04	0.28	0.14	0.14	0.10	55	28

Table 7.3.4 Activated Sludge and PAC Performances in Experiment 2 when θ_c = 12 days and PAC = 10 mg/L, All Concentrations are in mg/L.

		Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
Date	Run	Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
11/1	30	3,022	3,540	91	210	22	16	0.02	0.01	2.92	0.61	1.40	0.16	0.14	0.10	55	28
11/2	31	2,922	3,620	35	44	17	13	0.05	0.01	2.0	0.40	0.38	0.07	0.24	0.22	102	99
11/3	32	2,400	3,326	5	125	21	17	0.04	0.02	0.73	0.52	0.34	0.28	0.20	0.18	35	11

Table 7.3.5 Activated Sludge and PAC Performances in Experiment 2 when θ_c = 3 days and PAC = 50 mg/L, All Concentrations are in mg/L.

		Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
Date	Run	Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
11/5	33	2,880	2,920	20	85	26	22	0.72	0.52	4.16	2.56	1.78	0.40	0.09	0.05	86	37
11/6	34	2,520	2,660	47	150	28	20	0.18	0.12	2.24	1.04	1.26	0.12	0.20	0.09	43	32
11/7	35	2,334	2,800	45	185	24	19	1.0	0.11	1.68	1.28	0.22	0.02	0.18	0.10	140	44

Table 7.3.6 Activated Sludge and PAC Performance in Experiment 2 when θ_c = 6 days and PAC = 50 mg/L, All Concentrations are in mg/L.

Date	Run	Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
		Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
11/10	36	2,440	2,920	5	25	26	22	1.0	0.24	1.92	0.16	1.20	0.10	0.20	0.16	61	25
11/11	37	2,140	3,168	20	21	29	22	0.40	0.34	1.60	0.80	1.25	0.17	0.30	0.23	91	49
11/12	38	2,240	3,380	10	22	26	24	0.60	0.44	1.92	1.60	1.60	0.12	0.24	0.10	21	16

Table 7.3.7 Activated Sludge and PAC Performances in Experiment 2 when θ_c = 9 days and PAC = 50 mg/L, All Concentrations are in mg/L.

Date	Run	Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
		Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
11/16	39	3,160	3,636	100	160	35	10	0.38	0.10	2.0	0.20	1.12	0.11	0.34	0.10	53	18
11/17	40	2,200	2,760	20	80	33	22	0.16	0.14	1.8	0.60	1.28	0.14	0.48	0.15	40	37
11/18	41	2,440	3,384	10	70	24	11	0.16	0.12	2.43	1.71	1.43	0.40	0.48	0.24	92	42

Table 7.3.8 Activated Sludge and PAC Performance in Experiment 2 when θ_c = 12 days and PAC = 50 mg/L, All Concentrations are in mg/L.

		Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
Date	Run	Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
11/21	42	3,020	3,568	35	40	29	18	2.15	1.52	2.24	2.00	1.26	0.18	0.20	0.10	92	40
11/21	43	2,480	3,274	30	36	30	20	3.10	1.41	2.08	1.44	1.14	0.08	0.62	0.10	45	19
11/23	44	2,140	3,676	59	60	102	83	2.10	1.65	2.64	2.48	1.44	0.83	0.62	0.15	14	11

Table 7.3.9 Activated Sludge and PAC Performances in Experiment 2 when θ_c = 3 days and PAC = 120 mg/L, All Concentrations are in mg/L.

		Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
Date	Run	Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
11/26	45	2,080	2,754	24	45	77	70	1.28	0.18	2.62	2.06	1.32	0.20	0.77	0.08	28	20
11/27	46	2,380	2,620	3	5	74	62	1.04	0.11	1.68	0.36	1.42	0.40	0.96	0.16	58	13
11/28	47	2,280	3,788	5	18	57	39	1.84	0.08	3.76	1.40	1.35	0.34	0.85	0.15	27	21

Table 7.3.10 Activated Sludge and PAC Performances in Experiment 2 when θ_c = 6 days and PAC = 120 mg/L, All Concentrations are in mg/L.

		Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
Date	Run	Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
12/1	48	2,280	2,700	15	20	54	30	1.60	0.80	2.72	1.80	2.54	0.48	1.80	0.10	27	21
12/3	49	2,100	2,400	5	80	31	20	0.52	0.13	3.4	0.75	2.58	0.56	1.0	0.18	23	8
12/4	50	2,200	2,450	5	20	31	20	2.40	0.07	2.96	1.00	2.66	0.58	0.94	0.08	31	14

Table 7.3.11 Activated Sludge and PAC Performances in Experiment 2 when θ_c = 9 days and PAC = 120 mg/L, All Concentrations are in mg/L.

		Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
Date	Run	Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
12/7	51	1,800	2,350	5	10	34	16	0.80	0.22	3.52	2.16	2.40	0.56	1.40	0.15	25	17
12/8	52	1,894	2,400	12	20	25	14	0.12	0.10	2.40	1.20	1.5	0.64	0.92	0.06	17	12
12/9	53	2,200	2,648	5	15	24	11	0.32	0.08	2.24	0.92	1.48	0.44	0.24	0.10	15	10

Table 7.3.12 Activated Sludge and PAC Performances in Experiment 2 when θ_c = 12 days and PAC = 120 mg/L, All Concentrations are in mg/L.

Date	Run	Suspended Solids				NH_3		NO_2		NO_3		Total Phosphate		Ortho-Phosphate		Oil and Grease	
		Reactor		Effluent													
1986	No.	MLVSS	MLSS	VSS	TSS	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft	Inft	Efft
12/12	54	2,090	2,400	15	28	21	8	0.12	0.08	3.44	1.66	1.58	0.44	1.25	0.06	21	15
12/13	55	2,100	2,500	11	40	24	7	0.12	0.09	3.76	2.08	2.25	0.90	0.91	0.06	21	10
12/15	56	2,694	2,950	5	40	26	11	0.34	0.26	4.80	3.04	2.79	0.35	0.91	0.07	27	26

effluent were also measured 3 times each week and are reported in Tables 7.3.1-12. The influent oil and grease concentrations were below the levels found to be toxic (100 mg/L) by other researchers (75).

BOD_5 removals were enhanced by PAC additions. The PAC concentration present in the AS reactor did not appear to effect the percentage removals of BOD_5. A concentration of 10 mg/L of PAC enhanced BOD_5 removals within the AS reactors about as well as a PAC concentration of 50 or 120 mg/L. With the exception of a PAC concentration of 10 mg/L which showed a slight improvement in BOD_5 removals as θ_c increased, there was no significant increase in the removal percentages as θ_c was increased to 12 days. This data is presented in Tables 7.3.13-24. The influent and effluent concentrations versus day of operation are plotted in Figures 7.3.1-7.3.3. The effluent percentage removals versus θ_c are plotted in Figure 7.3.4.

COD removals were improved, compared to AS, by the additions of all concentrations of PAC. With the exception of θ_c equal to 3 days, the highest percentage removals were at a PAC concentration of 10 mg/L. For all θ_c values, the lowest percentage removals of COD occurred at a PAC concentration of 50 mg/L. As θ_c increased, the percentage removals of COD increased, with the exception of a PAC concentration of 120 mg/L, in which case there

Table 7.3.13 BOD_5, COD, and TOC Removals in Experiment 2 when θ_c = 3 days and PAC = 10 mg/L

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
21	213	35	84	510	70	86	168	24	86
22	214	28	87	480	74	85	160	20	88
23	242	27	89	504	72	86	182	28	85

Table 7.3.14 BOD_5, COD and TOC Removals in Experiment 2 when θ_c = 6 days and PAC = 10 mg/L

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
24	321	26	92	564	31	95	245	19	92
25	332	30	91	550	32	94	200	13	94
26	348	28	92	530	27	95	221	25	89

Table 7.3.15 BOD$_5$, COD and TOC Removals in Experiment 2 when θ_c = 9 days and PAC = 10 mg/L

Run No.	BOD$_5$			COD			TOC		
	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
27	350	22	94	550	30	95	170	16	91
28	340	20	94	548	26	95	180	17	91
29	345	24	93	552	20	96	184	18	90

Table 7.3.16 BOD$_5$, COD and TOC Removals in Experiment 2 when θ_c = 12 days and PAC = 10 mg/L

Run No.	BOD$_5$			COD			TOC		
	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
30	320	21	93	478	20	96	151	17	89
31	300	18	94	420	15	96	144	14	90
32	344	24	93	488	25	95	158	14	91

Table 7.3.17 BOD_5, COD and TOC Removals in Experiment 2 when θ_c = 3 days and PAC = 50 mg/L

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
33	305	29	90	976	210	79	847	36	96
34	304	29	90	416	100	76	135	28	79
35	302	22	93	776	200	74	119	29	76

Table 7.3.18 BOD_5, COD and TOC Removals in Experiment 2 when θ_c = 6 days and PAC = 50 mg/L

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
36	320	29	87	796	192	76	554	45	83
37	213	25	88	516	160	69	123	21	83
38	248	10	96	488	100	80	127	18	86

Table 7.3.19 BOD_5, COD and TOC Removals in Experiment 2 when θ_c = 9 days and PAC = 50 mg/L

Run No.	BOD_5 Inft (mg/L)	BOD_5 Efft (mg/L)	BOD_5 Effy (%)	COD Inft (mg/L)	COD Efft (mg/L)	COD Effy (%)	TOC Inft (mg/L)	TOC Efft (mg/L)	TOC Effy (%)
39	245	21	91	560	132	76	213	19	91
40	255	22	91	420	68	84	232	21	90
41	257	22	92	776	116	85	232	20	91

Table 7.3.20 BOD_5, COD and TOC Removals in Experiment 2 when θ_c = 12 days and PAC = 50 mg/L

Run No.	BOD_5 Inft (mg/L)	BOD_5 Efft (mg/L)	BOD_5 Effy (%)	COD Inft (mg/L)	COD Efft (mg/L)	COD Effy (%)	TOC Inft (mg/L)	TOC Efft (mg/L)	TOC Effy (%)
42	205	21	90	496	128	74	203	16	92
43	278	20	93	404	56	86	214	15	93
44	235	19	92	804	120	85	225	18	92

Table 7.3.21 BOD_5, COD and TOC Removals in Experiment 2 when θ_c = 3 days and PAC = 120 mg/L

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
45	292	26	91	360	30	92	191	13	93
46	255	30	88	540	50	91	205	17	92
47	300	28	91	624	70	89	260	20	92

Table 7.3.22 BOD_5, COD and TOC REmovals in Experiment 2 when θ_c = 6 days and PAC = 120 mg/L

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
48	295	30	90	360	35	90	188	17	91
49	249	24	90	356	25	93	184	13	93
50	222	21	91	515	60	88	188	15	92

Table 7.3.23 BOD_5, COD and TOC Removals in Experiment 2 when θ_c = 9 days and PAC = 120 mg/L

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
51	216	18	92	283	35	88	193	14	93
52	24	15	93	440	42	90	174	13	93
53	214	27	88	388	37	90	103	9	91

Table 7.3.24 BOD_5, COD and TOC Removals in Experiment 2 when θ_c = 12 days and PAC = 120 mg/L

	BOD_5			COD			TOC		
Run No.	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)	Inft (mg/L)	Efft (mg/L)	Effy (%)
54	200	18	91	348	33	91	157	9	94
55	195	16	92	380	32	92	159	11	93
56	205	20	90	352	34	90	158	10	94

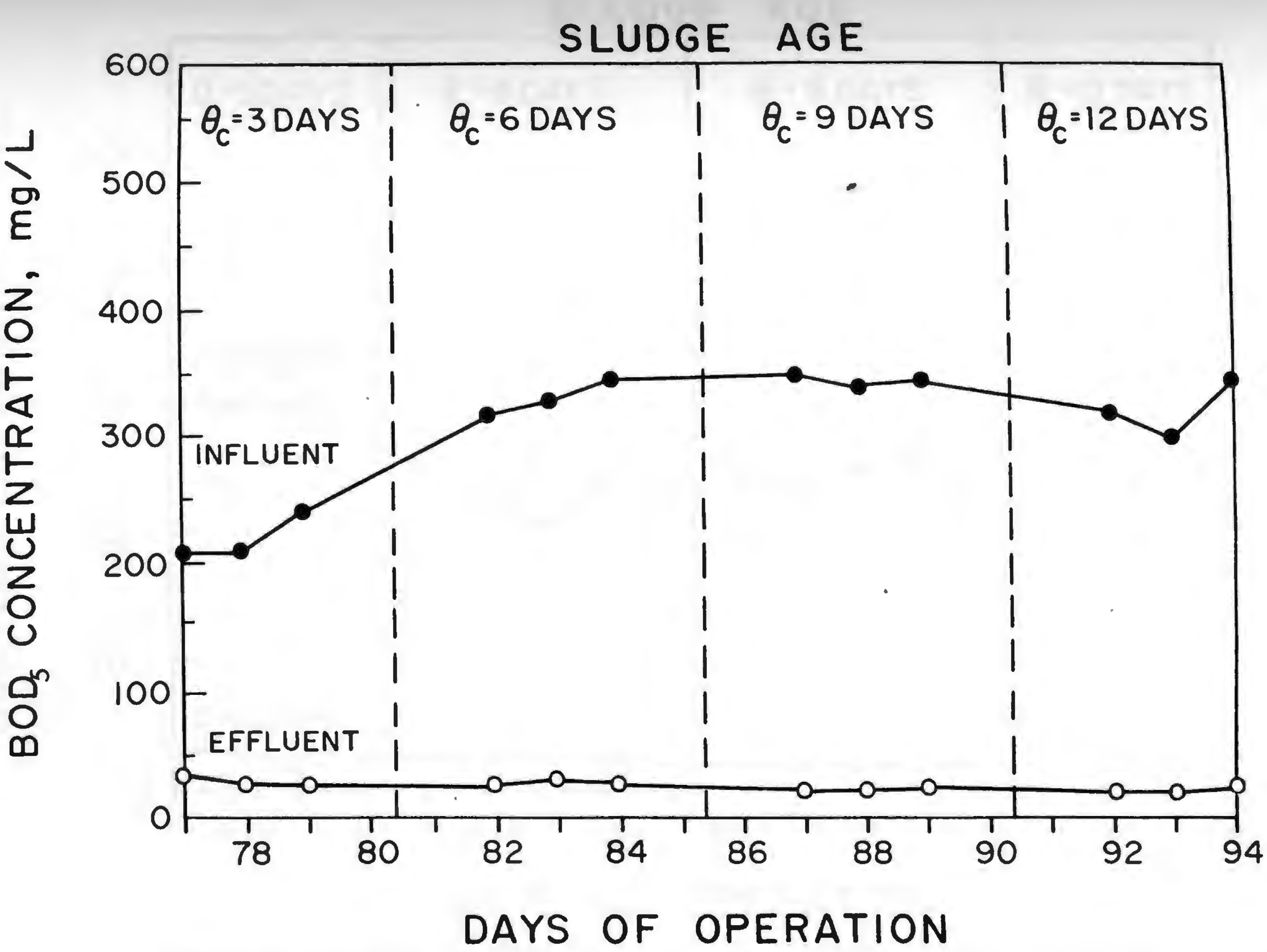


Figure 7.3.1 BOD_5 Removal by Activated Sludge and Powdered Activated Carbon PAC=10 mg/L

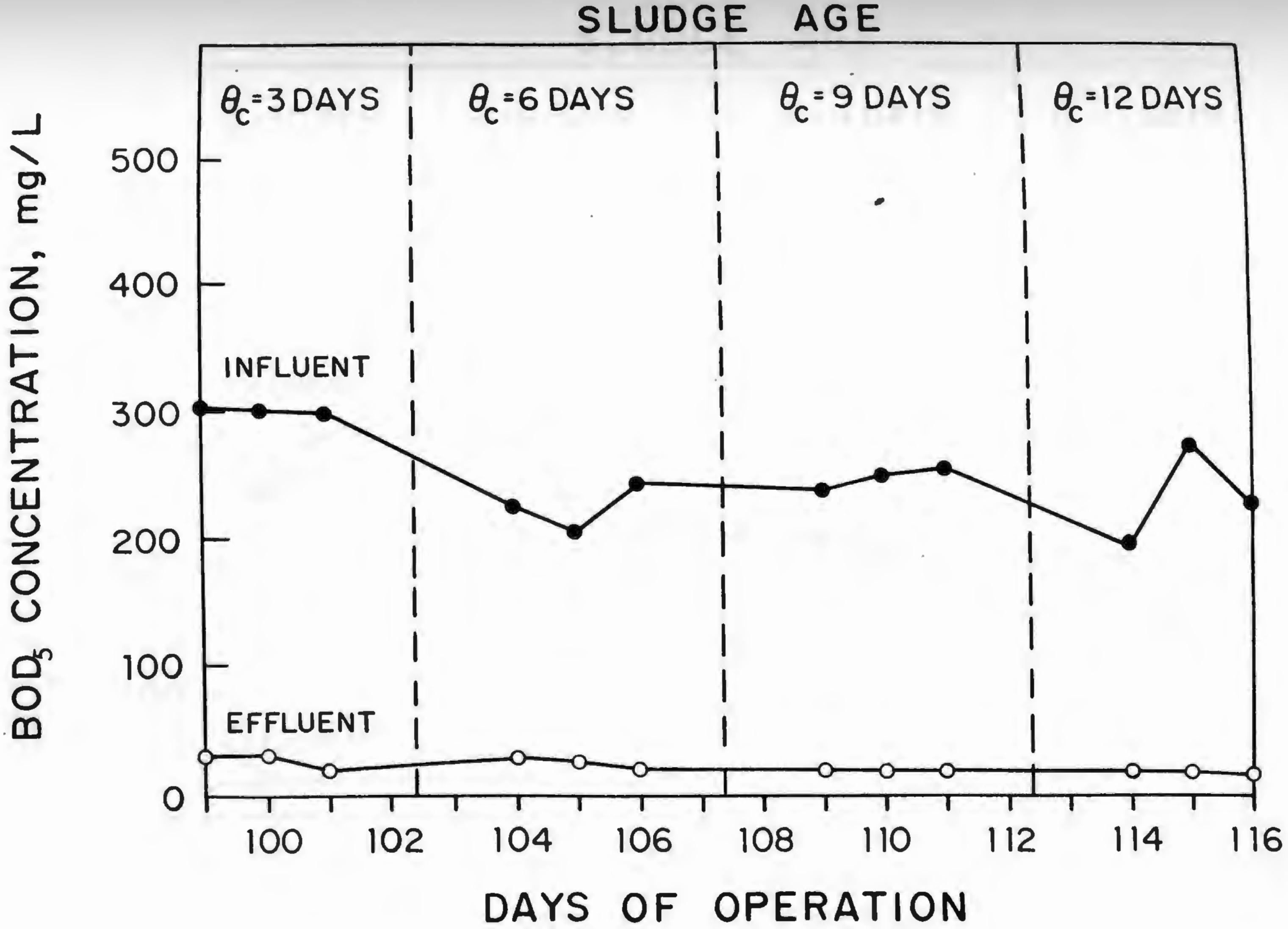


Figure 7.3.2 BOD_5 Removal by Activated Sludge and Powdered Activated Carbon PAC=50 mg/L

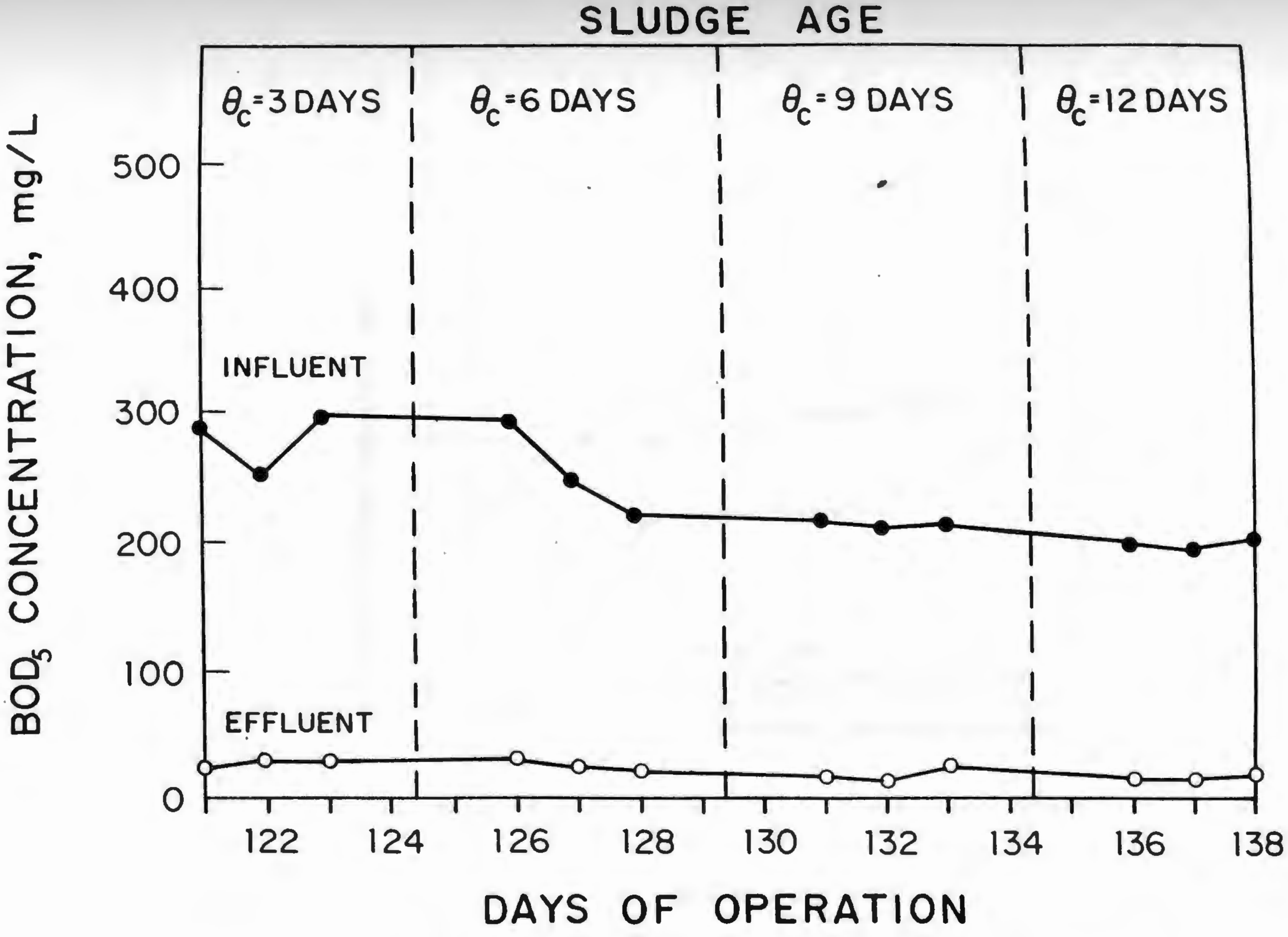


Figure 7.3.3 BOD_5 Removal by Activated Sludge and Powdered Activated Carbon PAC=120 mg/L

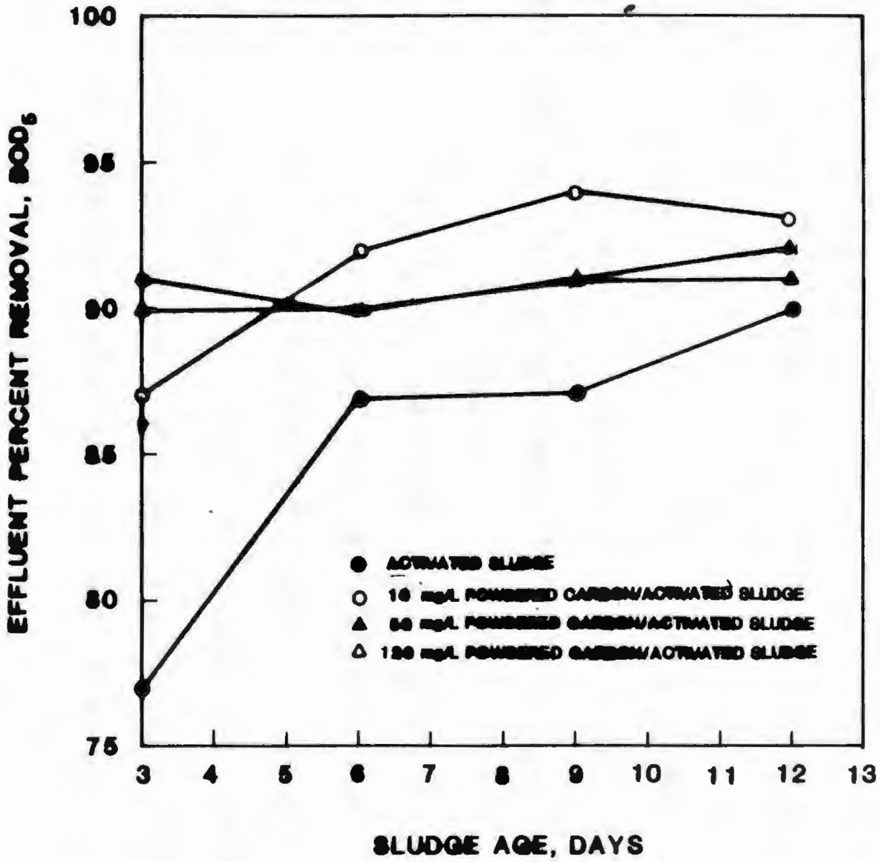


Figure 7.3.4 Effect of Sludge Age on BOD$_5$ Removal

was essentially no change in the percentage removals as θ_c was increased. AS can be seen that no change observed in the COD percent removal as θ_c increased from 6 days to 12 days, at a PAC concentration of 10 mg/L. These data are presented in Tables 7.3.13-24. The influent and effluent concentrations versus day of operation are plotted in Figures 7.3.5-7 and COD percentage removals versus θ_c are plotted in Figure 7.3.8.

TOC percentage removals were increased, in comparison 'to AS, by the additions of all concentrations of PAC. The highest TOC percentage removals occurred at a PAC concentration of 120 mg/L for all θ_c values. In general, TOC percentage removals increased with an increase in θ_c for all PAC concentrations with the exception of a PAC concentration of 10 mg/L. These data are presented in Tables 7.3.13-24, influent and effluent TOC concentrations versus days of operation are plotted in Figures 7.3.9-11, and effluent percentage removals versus θ_c are plotted in Figure 7.3.12.

Removals of priority organic pollutants (2,4 dimethylphenol, fluorene, naphthalene and pyrene) were investigated for various PAC reactor concentrations and sludge ages. Data for this experiment are presented in Tables 7.3.25-36 and plotted in Figures A.4.1-12.

The additions of PAC to the AS reactor resulted in a slight enhancement of 2,4 dimethylphenol removals at the

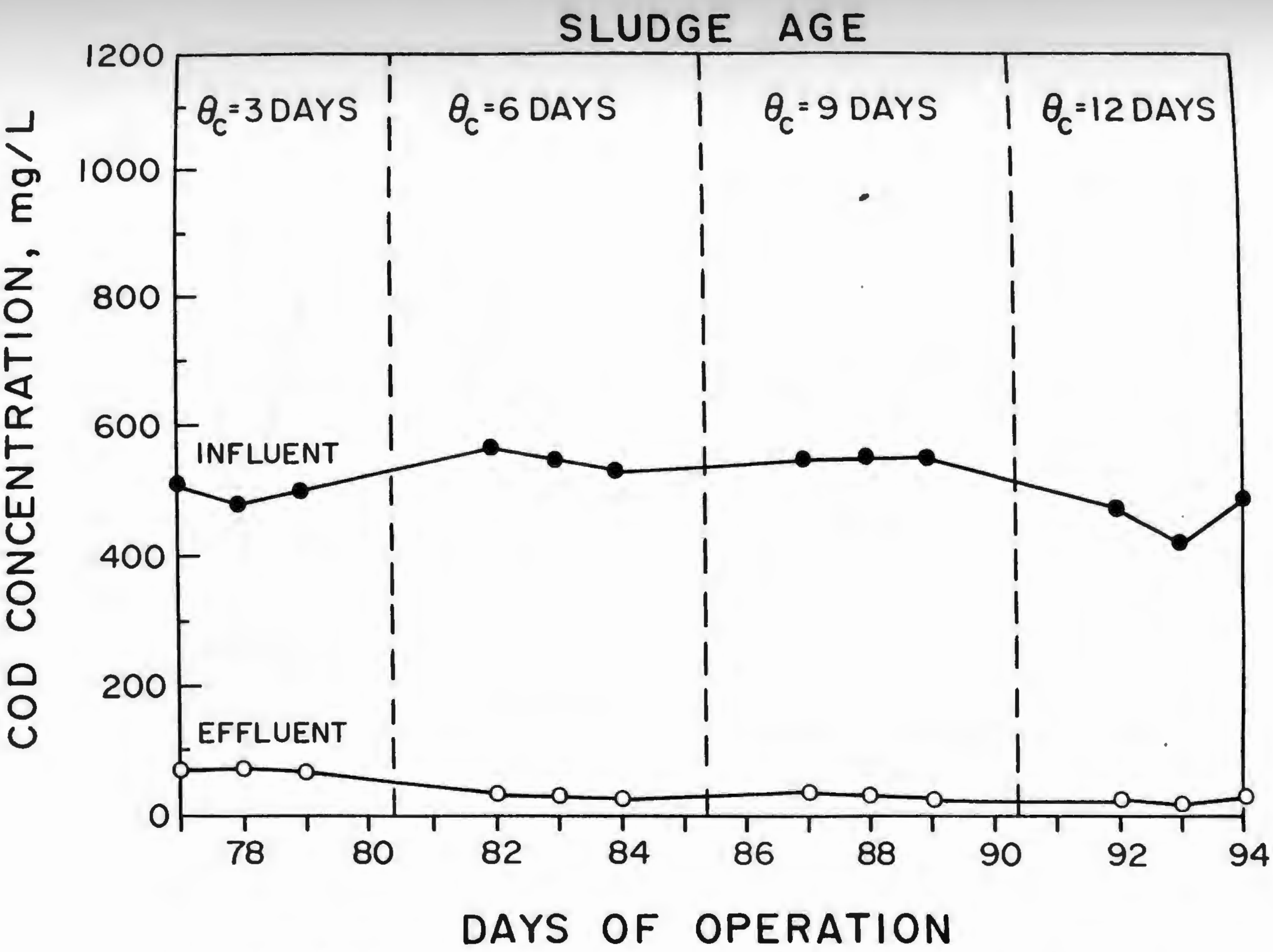


Figure 7.3.5 COD Removal by Activated Sludge and Powdered Activated Carbon PAC=10 mg/L

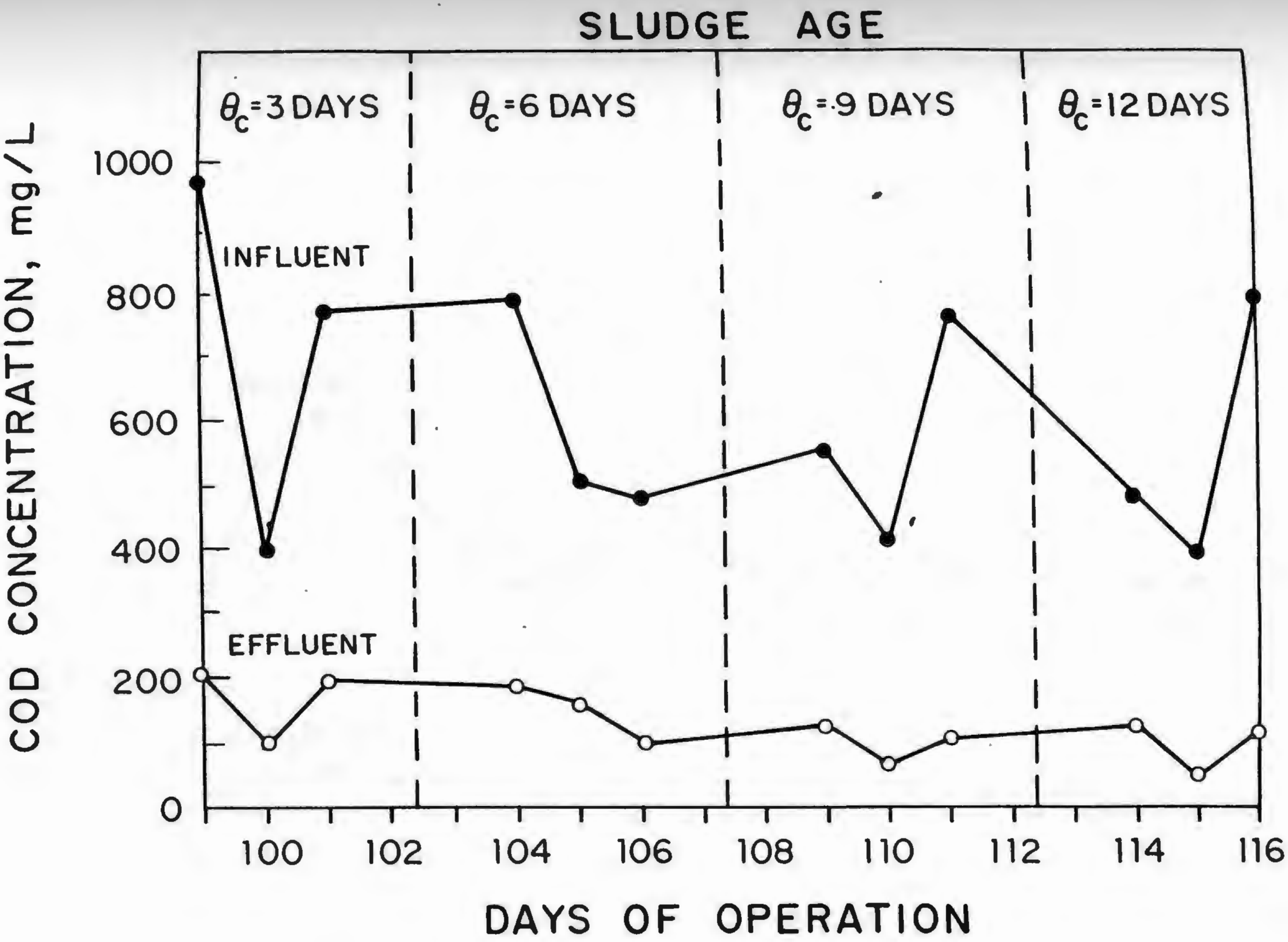


Figure 7.3.6 COD Removal by Activated Sludge and Powdered Activated Carbon PAC=50 mg/L

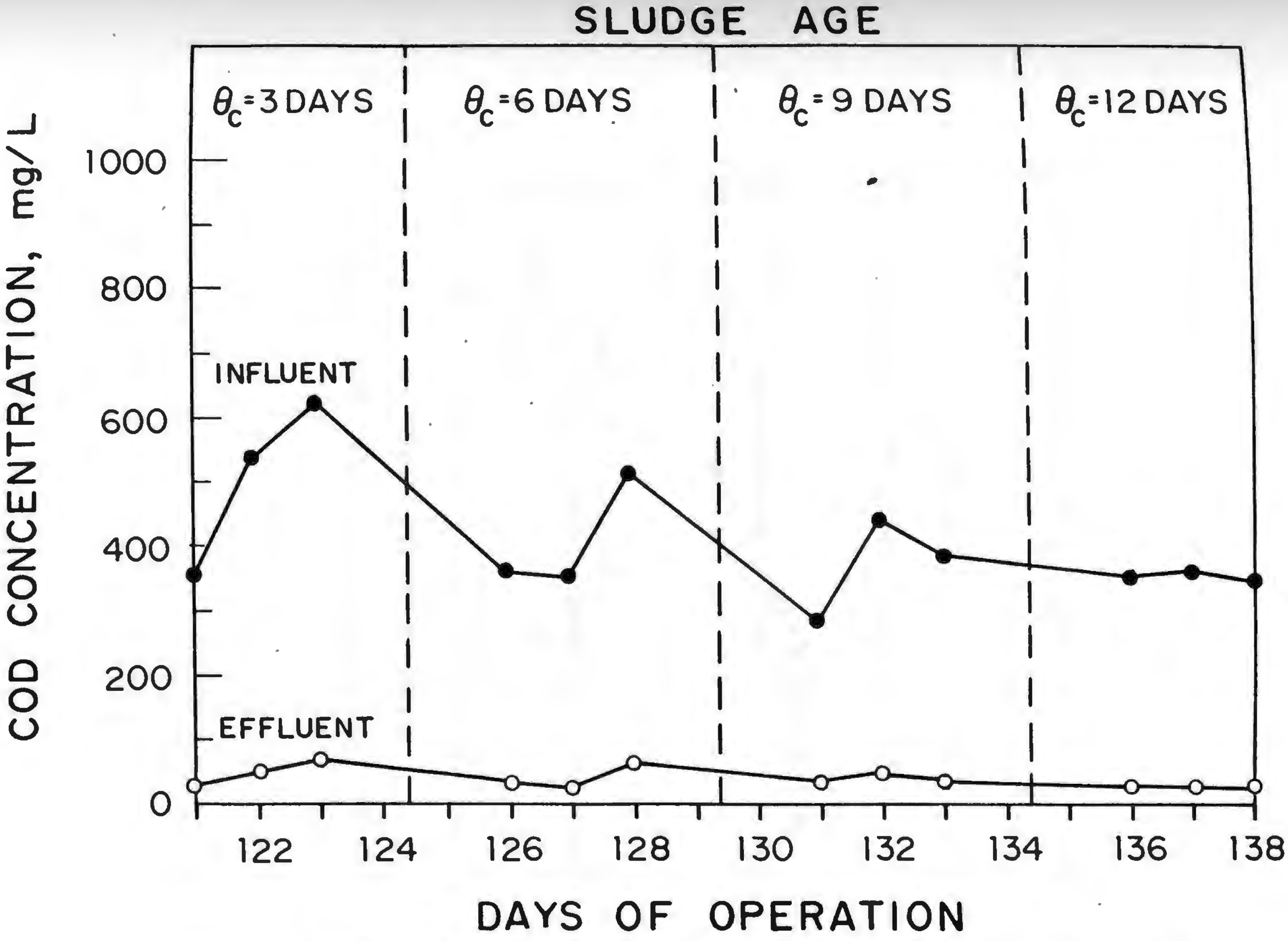


Figure 7.3.7 COD Removal by Activated Sludge and Powdered Activated Carbon PAC=120 mg/L

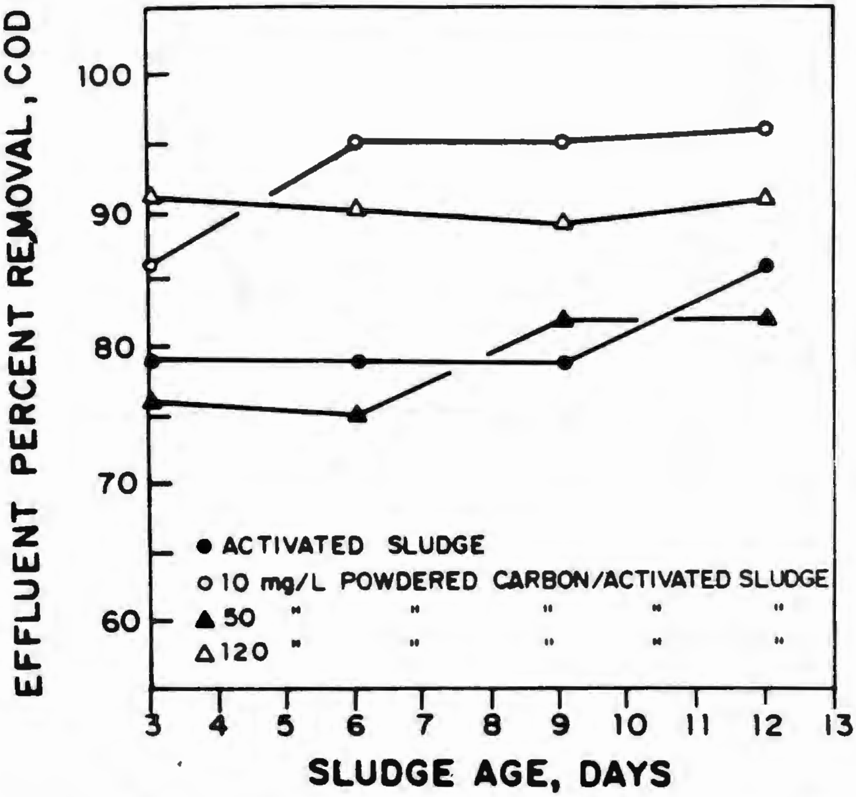


Figure 7.3.8 Effect of Sludge Age on COD Removal

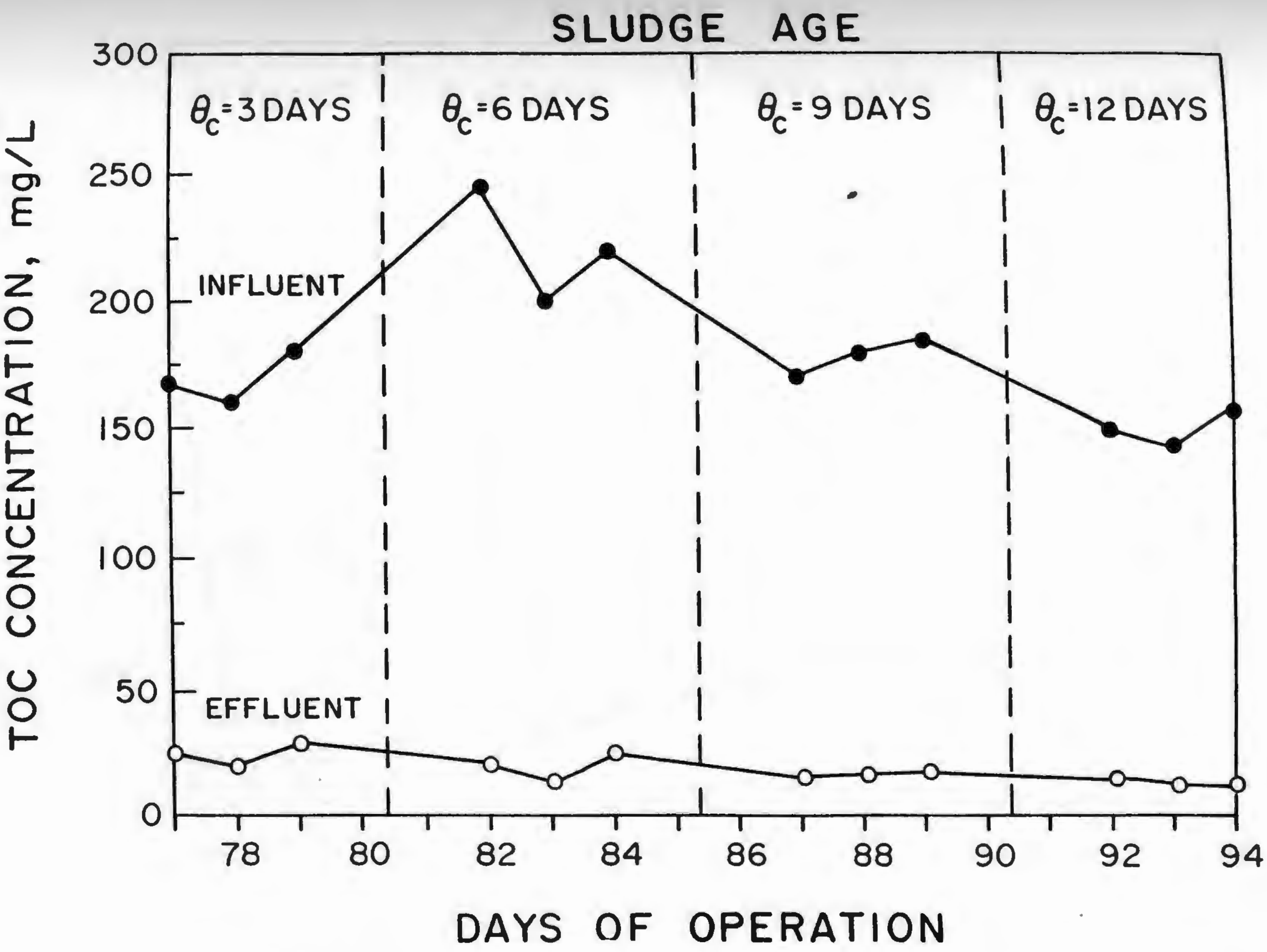


Figure 7.3.9 TOC Removal by Activated Sludge and Powdered Activated Carbon PAC=10 mg/L

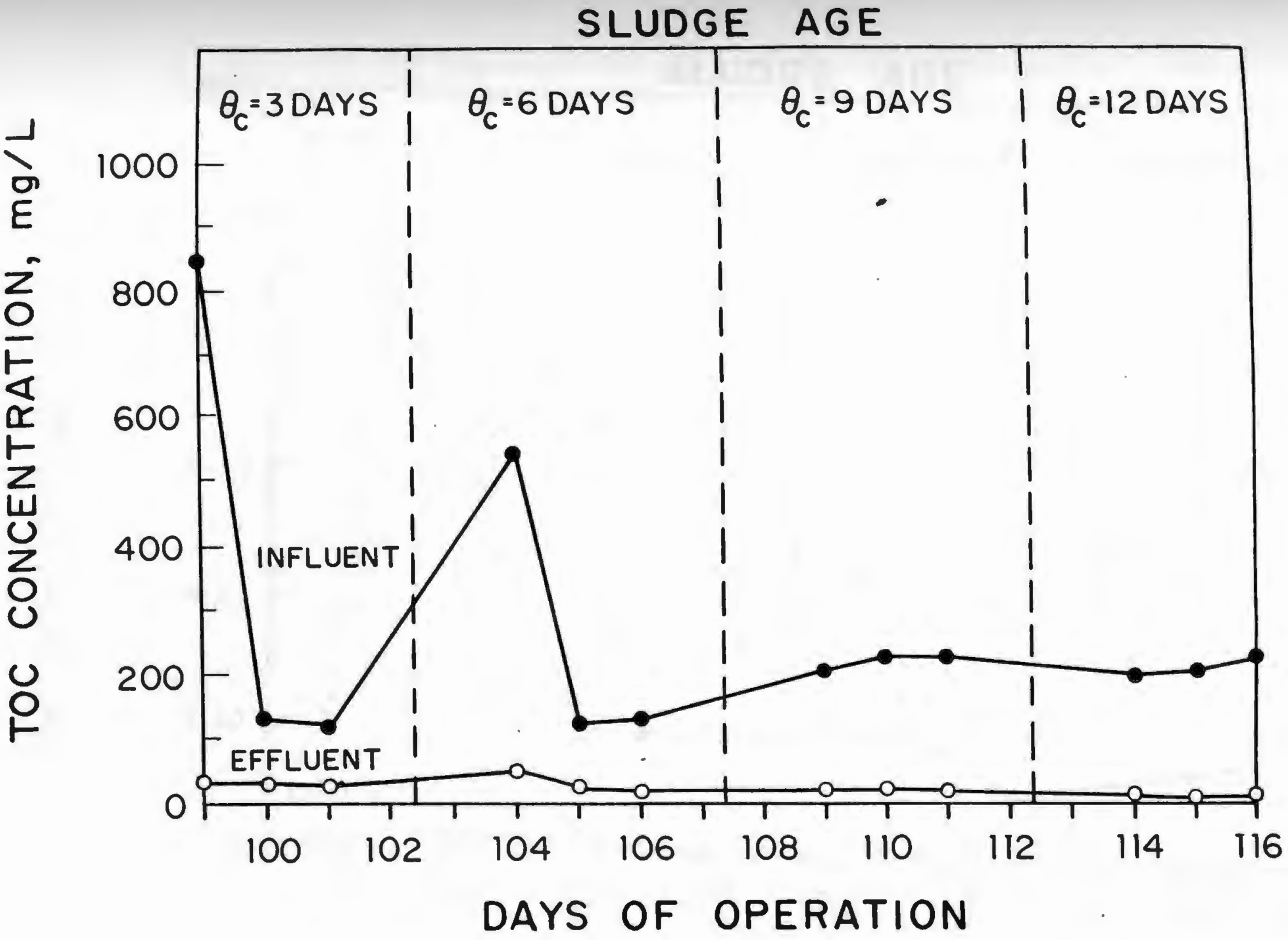


Figure 7.3.10 TOC Removal by Activated Sludge and Powdered Activated Carbon PAC=50 mg/L

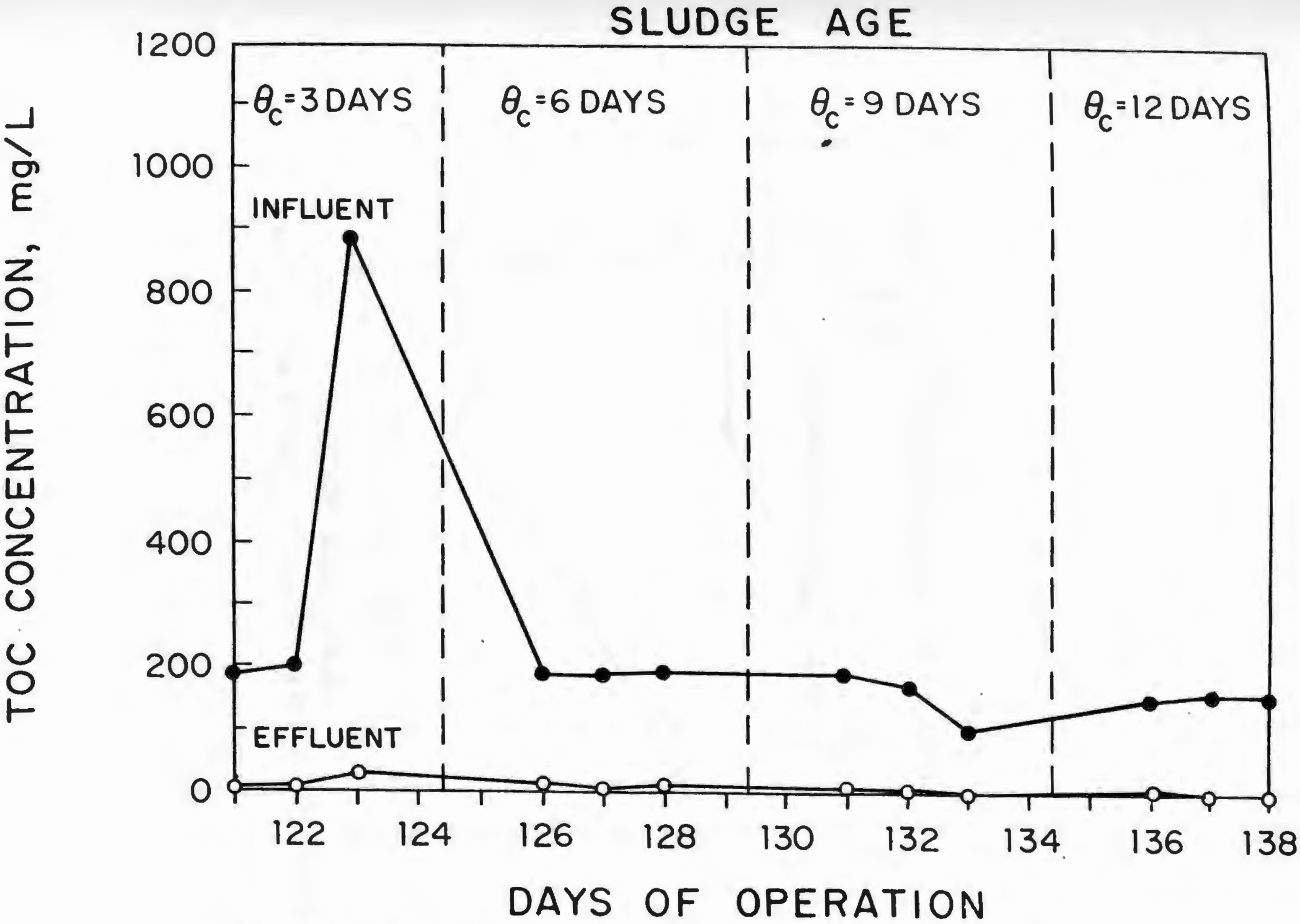


Figure 7.3.11 TOC Removal by Activated Sludge and Powdered Activated Carbon PAC=120 mg/L

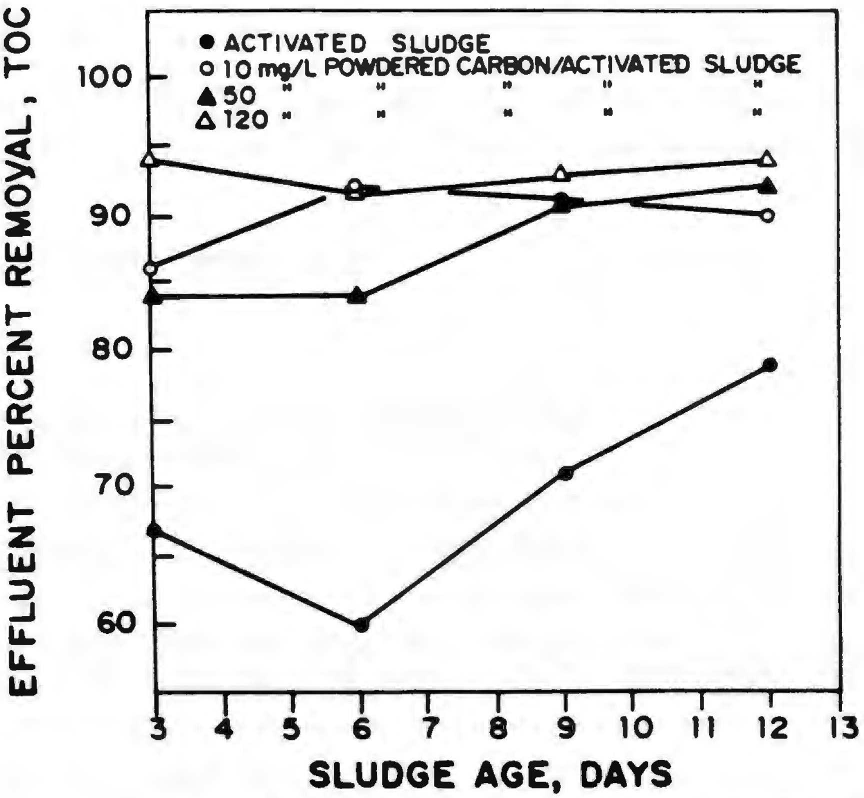


Figure 7.3.12 Effect of Sludge Age on TOC Removal

Table 7.3.25 Priority Pollutants Removal, Experiment 2 when θ_c = 3 days and PAC = 10 mg/L

Run No.	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
21	87	27	69	33	16	52	107	27	75	27	20	26
22	133	10	92	23	17	26	240	21	92	ND	ND	ND
23	933	33	96	105	13	88	467	27	94	87	12	86

ND = None detectable, detectability >10 ug/L

Table 7.3.26 Priority Pollutants Removal, Experiment 2 when θ_c = 6 days and PAC = 10 mg/L

Run No.	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
24	560	166	70	280	32	86	947	33	97	27	20	26
25	2,112	113	95	146	10	93	933	28	98	39	13	67
26	2,848	140	95	93	39	58	733	19	84	30	26	13

Table 7.3.27 Priority Pollutants Removal, Experiment 2 when θ_c = 9 days and PAC = 10 mg/L

	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
27	1,974	112	94	300	37	88	1,500	27	98	105	17	84
28	1,840	33	98	493	130	74	1,000	67	93	260	27	90
29	168	13	92	200	13	35	93	27	71	32	20	38

Table 7.3.28 Priority Pollutants Removal, Experiment 2 when θ_c = 12 days and PAC = 10 mg/L

	2,4-Dimethylphenol			Fluorene			Naphtalene			Pyrene		
Run No.	Inft (ug/l)	Efft (ug/L)	Effy (%)	Inft (ug/l)	Efft (ug/L)	Effy (%)	Inft (ug/l)	Efft (ug/l)	Effy (%)	Inft (ug/l)	Efft (ug/l)	Effy (%)
30	3,867	27	99	233	27	88	733	66	91	28	20	29
31	2,113	40	98	140	32	77	867	87	90	27	19	30
32	1,700	33	98	207	40	81	1,200	47	96	27	20	26

Table 7.3.29 Priority Pollutants Removal, Experiment when θ_c = 3 days and PAC = 50 mg/L

	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
33	9,933	140	99	279	57	80	7,600	493	94	47	20	57
34	1,500	32	98	167	35	79	1,200	33	97	27	10	63
35	5,333	80	99	128	10	92	853	40	95	ND	ND	ND

ND = None detectable, detectability >10 ug/L

Table 7.3.30 Priority Pollutants Removal, Experiment 2 when θ_c = 6 days and PAC = 50 mg/L

	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
36	4,772	30	99	33	ND	>70	1,172	53	95	41	ND	>76
37	9,065	20	99	48	ND	>79	40	13	68	ND	ND	ND
38	8,720	12	99	147	57	61	1,000	227	77	27	ND	>63

ND = None detectable, detectability >10 ug/L

Table 7.3.31 Priority Pollutants Removal, Experiment 2 when θ_c = 9 days and PAC = 50 mg/L

	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
39	7,553	433	94	33	ND	>70	733	203	72	31	15	52
40	3,000	253	92	47	ND	>79	279	ND	>96	22	ND	>55
41	6,660	33	99	533	ND	98	733	158	78	27	ND	>63

Table 7.3.32 Priority Pollutants Removal, Experiment 2 when θ_c = 12 days and PAC = 50 mg/L

	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
42	7,847	12	99	140	40	71	580	27	95	16	10	38
43	2,845	23	99	251	13	95	373	15	96	17	14	18
44	746	92	88	297	20	93	267	13	95	39	15	62

Table 7.3.33 Priority Pollutants Removal, Experiment 2 when θ_c = 3 days and PAC = 120 mg/L

	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
45	7,953	10	99	167	ND	>94	533	17	97	10	ND	-
46	7,293	13	99	207	13	94	920	53	94	20	ND	>50
47	2,093	27	99	340	ND	>97	4,667	27	99	40	12	70

ND = None detectable, detectability >10 ug/L

Table 7.3.34 Priority Pollutants Removal, Experiment 2 when θ_c = 6 days and PAC = 120 mg/L

	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
48	3,300	160	97	113	ND	>91	933	ND	>99	10	ND	-
49	6,747	387	94	167	10	94	733	ND	>99	13	ND	>23
50	5,693	ND	>99	120	12	90	733	20	97	27	ND	>63

ND = None detectable, detectability >10 ug/L

Table 7.3.35 Priority Pollutants Removal, Experiment 2 when θ_c = 9 days and PAC = 120 mg/L

	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
51	6,473	17	99	153	ND	>93	733	47	94	17	ND	>44
52	4,187	17	99	73	ND	>86	293	16	95	87	ND	>77
53	3,953	33	99	207	13	94	257	13	95	13	ND	>23

ND = None detectable, detectability >10 ug/L

Table 7.3.36 Priority Pollutants Removal, Experiment 2 when θ_c = 12 days and PAC = 120 mg/L

	2,4-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
54	6,613	327	95	133	20	85	293	17	94	27	ND	>63
55	5,200	33	99	67	17	75	200	ND	>95	27	12	56
56	11,367	667	94	47	ND	>79	2,467	127	95	33	11	67

ND = None detectable, detectability >10 ug/L

50 and 120 mg/L PAC concentrations at all sludge ages over the removals obtained from the AS alone. There appeared to be no advantages in terms of 2,4 dimethylphenol removals to maintaining a long θ_c with the exception of a PAC concentration of 10 mg/L.

Fluorene percentage removals could only be increased over that resulting from AS alone by a PAC concentration of 120 mg/L in the AS reactor. There appeared to be no trend which could be observed of percentage removals of fluorene versus θ_c.

As was the case for fluorene, the percentage removals of naphthalene only showed an enhancement over the AS removals at a PAC concentration of 120 mg/L. Changes in θ_c did not appear to improve the percentage removals of napthalene.

No percentage removal trends in terms of PAC concentrations and θ_c values could be observed for pyrene.

The results of the study on the removals of the volatile compounds (benzene, chloroform, ethylbenzene, toluene, m-xylene and o-xylene) are presented in Tables 7.3.37-48. Since these compounds were studied in section 7.5 and found to be air stripped from the reactor by the air flow, there were no increases expected and no increases observed in the percentage removals of the volatile compounds due to the addition of PAC to the AS reactor.

Table 7.3.37 Volatile Organics Removal, Experiment 2 when θ_c = 3 days, PAC = 10 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
21	4,367	ND	>99	2,692	500	81	1,333	ND	>99	2,983	ND	>99	1483	ND	>99	3,498	ND	>99
22	3,300	20	99	2,503	277	89	630	30	95	2,183	18	99	940	ND	>99	490	ND	>98
23	3,065	ND	>99	2,439	512	80	1,040	ND	>99	4,080	ND	>99	1,251	ND	>99	2,750	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.3.38 Volatile Organics Removal, Experiment 2 when θ_c = 6 days, PAC = 10 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
24	4,379	ND	>99	2,593	90	97	1,125	ND	>99	2,883	ND	100	3,274	ND	100	4,442	ND	>99
25	4,216	ND	>99	2,445	325	87	1,578	ND	>99	3,950	ND	100	2,863	ND	100	5,081	ND	>99
26	3,941	ND	>99	2,596	325	87	1,656	ND	>99	3,067	ND	100	700	ND	100	1,859	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.3.39 Volatile Organics Removal, Experiment 2, when θ_c = 9 days, PAC = 10 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
27	2,430	ND	>99	2,145	130	94	1,027	ND	>99	1,600	ND	>99	660	ND	>98	960	ND	>99
28	1,600	ND	>99	1,442	20	99	938	ND	>99	1,500	ND	>99	630	ND	>98	700	ND	>99
29	2,011	ND	>99	1,929	240	88	190	ND	>95	1,142	ND	>99	560	ND	>98	1,130	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.3.40 Volatile Organics Removal, Experiment 2, when θ_c = 12 days, PAC = 10 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
30	3,397	ND	>99	2,290	45	98	440	ND	>98	2,733	ND	100	1,326	ND	>99	1,784	ND	>99
31	2,516	ND	>99	2,185	190	91	160	30	81	1,743	30	100	330	120	64	1,160	ND	>99
32	2,284	ND	>99	2,178	40	98	110	ND	>91	900	ND	>99	60	ND	>83	40	ND	>75

ND = None detectable, detectability >10 ug/L

Table 7.3.41 Volatile Organics Removal, Experiment 2, when θ_c = 3 days, PAC = 50 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
33	3,487	ND	>99	1,950	18	99	392	ND	>97	2,283	ND	>99	500	ND	>98	1,020	ND	>99
34	2,919	ND	>99	1,995	ND	99	200	ND	>95	1,967	ND	>99	850	ND	>99	1,470	ND	>99
35	910	ND	>99	1,795	10	99	10	ND	ND	380	ND	>97	418	ND	>98	280	ND	>96

ND = None detectable, detectability >10 ug/L

Table 7.3.42 Volatile Organics Removal, Experiment 2 when θ_c = 6 days, PAC = 50 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
36	2,708	ND	>99	2,106	22	99	378	ND	>97	1,600	ND	>99	413	ND	>98	800	ND	>99
37	2,805	ND	>99	2,085	80	96	660	ND	>98	1,917	ND	>99	700	ND	>99	1,200	ND	>99
38	3,065	ND	>99	2,132	21	99	690	ND	>99	2,283	ND	>99	1,233	ND	>99	2,171	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.3.43 Volatile Organics Removal, Experiment 2, when θ_C = 9 days, PAC = 50 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
39	2,530	ND	>99	2,043	20	99	100	ND	>90	1,998	ND	>99	340	ND	>97	100	ND	>90
40	2,592	ND	>99	2,025	130	93	560	ND	>98	1,850	10	99	800	ND	>99	810	ND	>99
41	2,661	ND	>99	2,092	20	99	330	ND	>97	2,050	ND	>99	1,217	ND	>99	2,013	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.3.44 Volatile Organics Removal, Experiment 2, when θ_c = 12 days, PAC = 50 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
42	1,411	20	99	1,800	10	99	470	ND	>98	740	ND	>99	719	ND	>99	140	ND	>93
43	144	ND	>93	1,912	20	99	178	ND	>94	920	ND	>99	500	ND	>98	1,040	ND	>99
44	1,160	ND	>99	1,823	20	99	50	ND	>80	583	ND	>98	340	ND	>97	720	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.3.45 Volatile Organics Removal, Experiment 2 when θ_c = 3 days, PAC = 120 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
45	1,719	ND	>99	2,145	ND	>99	200	ND	>95	1,383	ND	>99	648	ND	>98	1,240	ND	>99
46	1,190	ND	>99	1,968	ND	>99	300	ND	>97	1,020	ND	>99	480	ND	>98	848	ND	>99
47	2,741	ND	>99	2,426	30	99	300	ND	>97	1,600	ND	>99	620	ND	>98	890	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.3.46 Volatile Organics Removal, Experiment 2, when θ_c = 6 days, PAC = 120 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
48	960	ND	>99	2,069	ND	>99	120	ND	>92	270	ND	>96	40	ND	>75	110	ND	>96
49	1,816	ND	>99	2,229	10	99	122	ND	>92	970	ND	>99	410	ND	>98	550	ND	>98
50	2,430	ND	>99	2,345	38	98	140	ND	>93	1,360	ND	>99	750	ND	>99	850	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.3.47 Volatile Organics Removal, Experiment 2, when θ_c = 9 days, PAC = 120 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
51	1,573	ND	>99	2,495	78	97	482	ND	>98	740	ND	>99	500	ND	>98	220	ND	>95
52	810	ND	>99	1,926	ND	>99	20	ND	>50	280	ND	>96	260	ND	>96	410	ND	>98
53	810	ND	>99	1,924	ND	>99	50	ND	>80	383	ND	>97	190	ND	>95	240	ND	>96

ND = None detectable, detectability >10 ug/L

Table 7.3.48 Volatile Organics Removal, Experiment 2, when θ_c = 12 days, PAC = 120 mg/L

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
54	1,020	ND	>99	2,180	60	97	50	10	80	383	ND	>97	325	ND	>97	520	ND	>98
55	940	ND	>99	2,253	10	99	30	ND	>67	385	ND	>97	220	ND	>95	280	ND	>96
56	2,238	ND	>99	2,283	60	97	380	ND	>97	1,417	ND	>97	1,040	ND	>99	1,658	ND	>99

ND = None detectable, detectability >10 ug/L

7.4 Evaluation of Biological Growth in Experiments 1 and 2

7.4.1 Light Microscopic Analysis

One important method for determining the viability of and any visible changes in the AS microbial population is an examination by use of a light microscope. Throughout the duration of this study, daily samples of the AS biomass were collected from the reactor and immediately viewed under the light microscope.

Chronological observations of the AS biomass were used by several researchers to document the acclimation period that is typically required for industrial biological treatment processes. Reitano (54) in a study to measure the potential of the AS process to treat a refinery waste, utilized a periodic microscopic examination of the biomass to determine the length of the acclimation phase for the bacteria.

The AS biomass utilized in each of of the experiments was originally collected from the South Kingstown Waste Treatment Facility (SKWTF) prior to the start of this study. An initial observation of this biomass immediately after collection revealed a diverse population of microorganisms typical of those found in a domestic AS including bacteria, rotifers, algae, fungi and ciliates.

The AS biomass collected from the SKWTF was transferred into the pilot-scale reactor and fed with the industrial refinery wastewater. After 24 hours of operation there was a decrease in the AS biomass population density from an initial MLVSS concentration in the range of 1,800 mg/L to approximately 250 mg/L MLVSS. An examination under the light microscope after 24 hours of operation revealed a high percentage of protozoa followed by ciliates and bacteria.

A photomicrograph of the AS sample which was examined on day 2 of operation is shown in Figure 7.4.1.1. This photomicrograph represents a typical microorganism population consisting primarily of protozoa. By themselves, protozoa consume bacteria and suspended organic matter and thus do not directly metabolize the dissolved organic fraction.

After two weeks of operation the MLVSS showed a slight increase from 1,520 to 1,596 mg/L. During this operational time the biomass was in a period of acclimation with an apparent mass balance between the dying microorganisms and the acclimated organisms. Not only was there a slight change in the total mass of microorganisms, but there was also a rearrangement in the types of microorganisms. A decrease in the number of protozoa and a corresponding increase in both the number of ciliates and the bacteria in the AS sludge was noted. Examples of the typical microorganisms present after two weeks of operation are shown in Figures 7.4.1.2 through

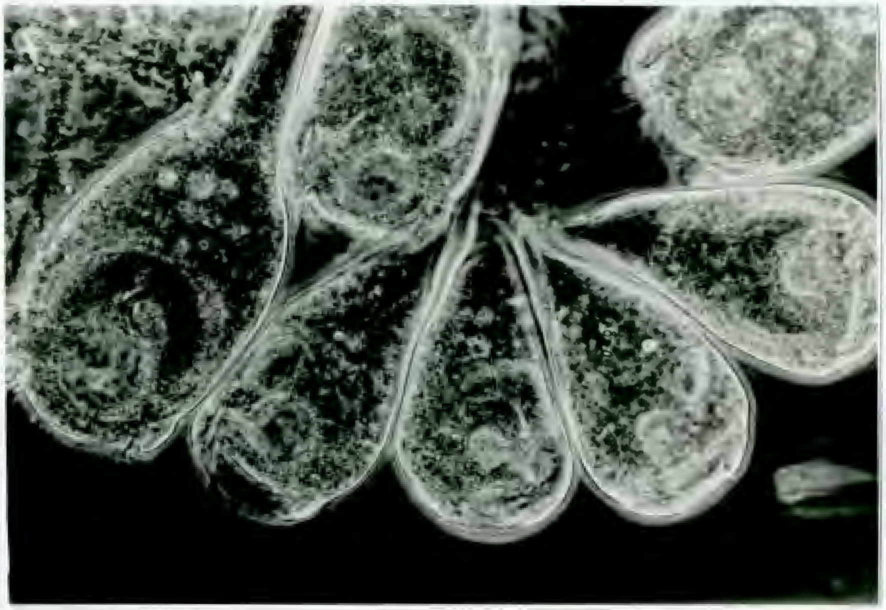


Figure 7.4.1.1 Photomicrograph of protozoa in a raw aerated wastewater (160X)

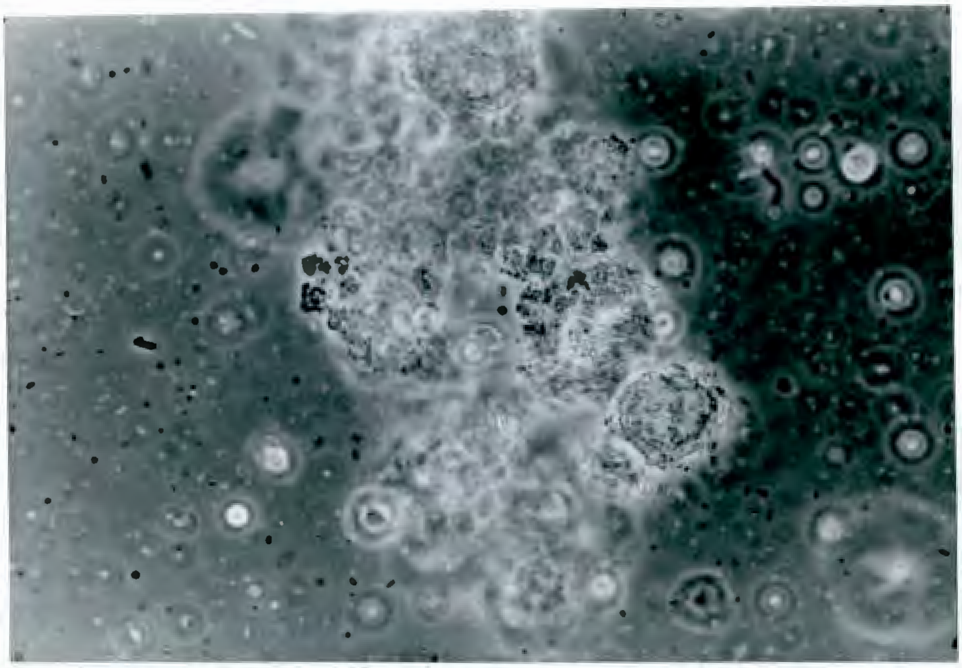


Figure 7.4.1.2 Photomicrograph of filamentous floc (bacteria) in the activated sludge (160X)

7.4.1.5. The relative increase in the numbers of bacteria is a positive sign that acclimation of the system was occurring.

Rotifers started to appear after the third week of operation. The reappearance and increase of the rotifers was an additional indication of the acclimation of the AS to the industrial refinery wastewater. The MLVSS concentration also showed an increase from 1,580 mg/L to 2,040 mg/L in the period between week 2 and week 3. A photomicrograph of a rotifer in the activated sludge is shown in Figure 7.4.1.6.

Acclimation of the AS biomass was reached approximately at the end of the fourth week. This was confirmed by both a relative increase in the bacteria, as well as a leveling off in the MLVSS concentration. Since the bacteria are the species responsible for the metabolism and removal of the dissolved organics, a biomass with a high relative concentration of bacteria is necessary for dissolved organics removal. A photomicrograph of the dispersed bacteria observed at the end of the fourth week is shown in Figure 7.4.1.7.

A summary of the changes in the population of the microorganisms is illustrated in Figure 7.4.1.8. The microorganism population in the AS did not change substantially after the acclimation period which occurred approximately 31 days from the start-up of the AS reactor.

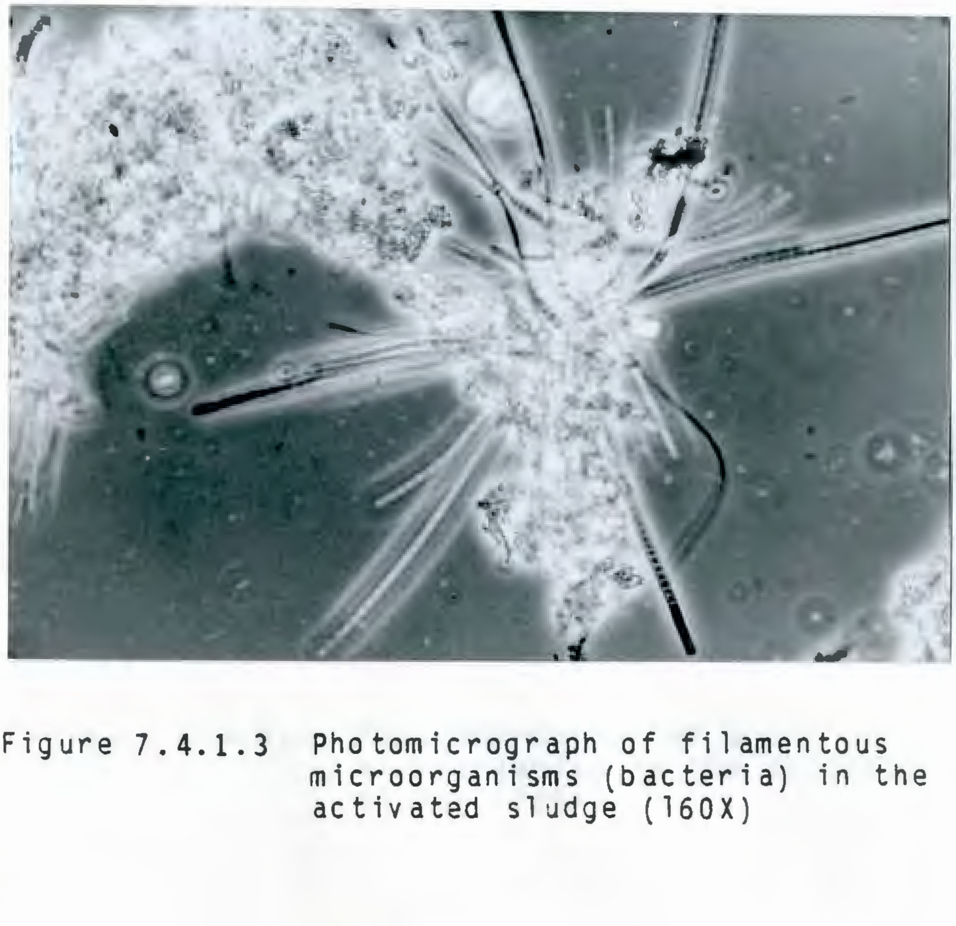


Figure 7.4.1.3 Photomicrograph of filamentous microorganisms (bacteria) in the activated sludge (160X)

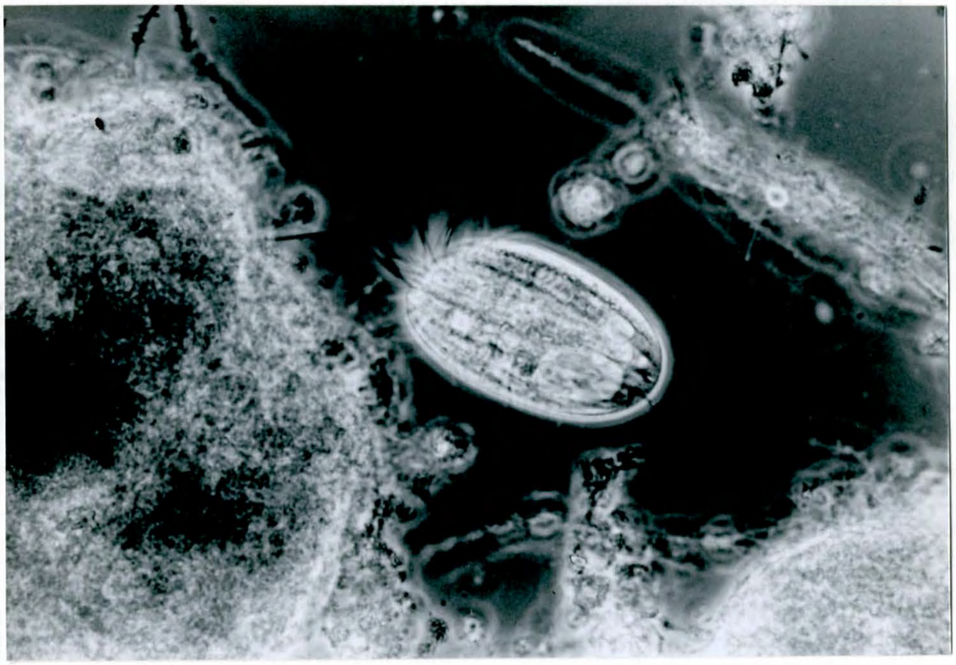


Figure 7.4.1.4 Photomicrograph of a ciliate microorganism in the activated sludge (160X)

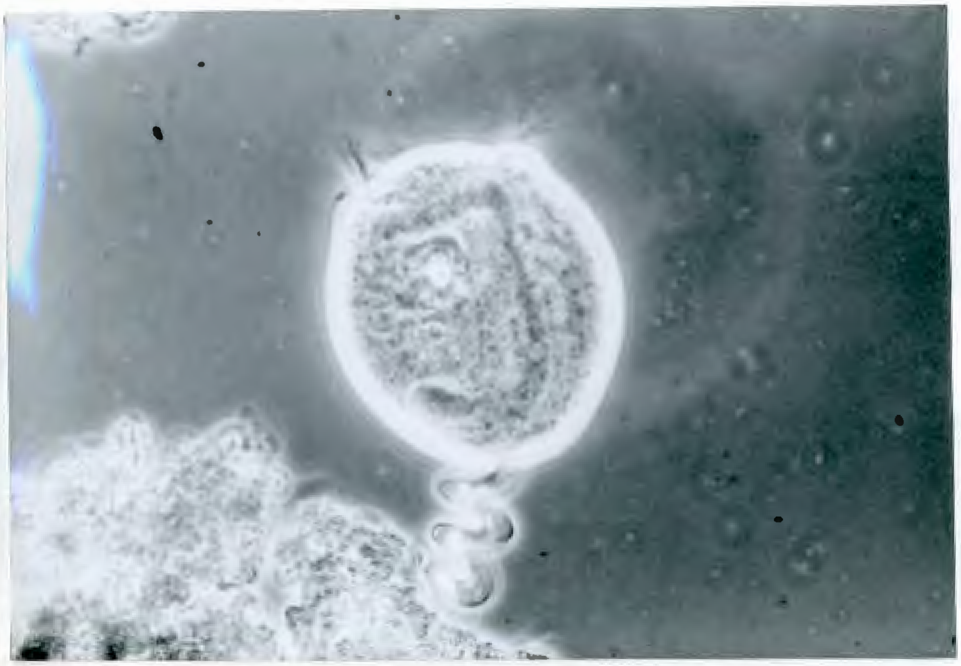


Figure 7.4.1.5 Photomicrograph of a ciliate in the activated sludge (160X)

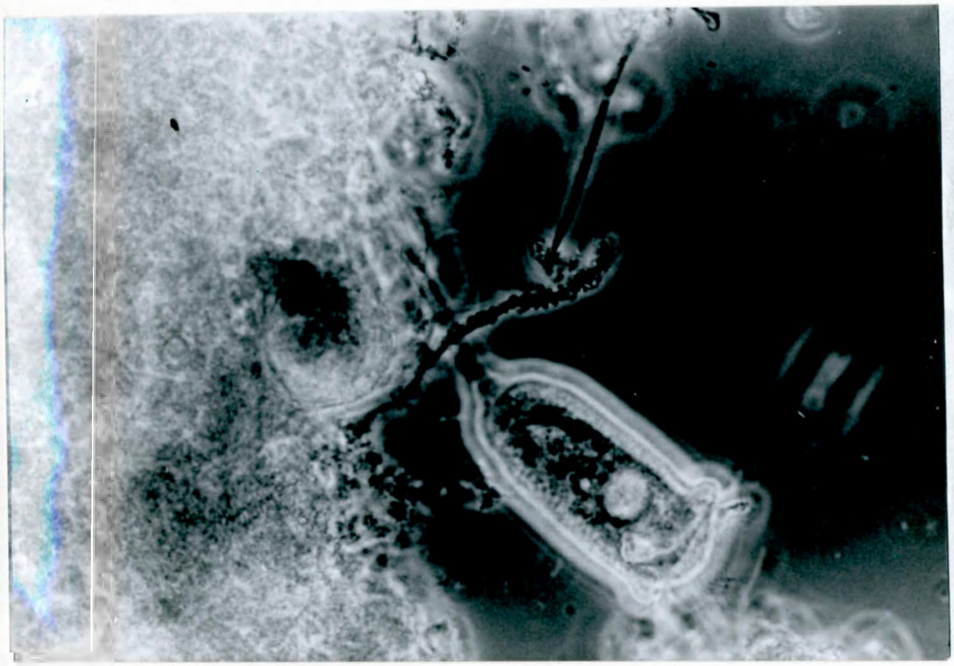


Figure 7.4.1.6 Photomicrograph of a rotifer in the activated sludge (160X)

Figure 7.4.1.7 Photomicrograph of dispersed bacteria in the activated sludge (160x)

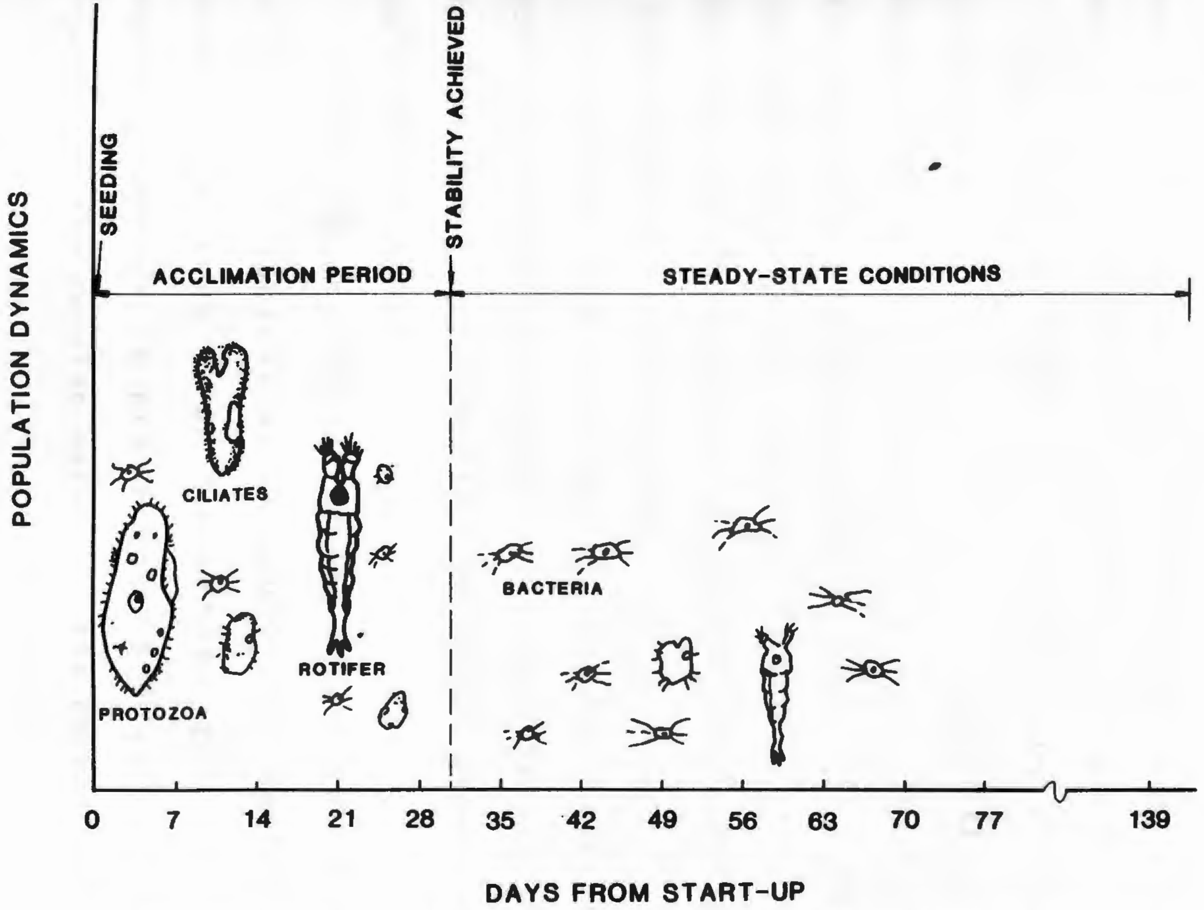


Figure 7.4.1.8 Changing Microorganism Population in the Aeration Tank

7.4.2 Scanning Electron Microscopic Analysis

When PAC has been added to the AS, an additional dissolved organic removal mechanism, adsorption, occurs in conjunction with biological oxidation. Not only does the PAC adsorb dissolved organics, but the high surface area of the carbon is an ideal site for fixed film bacteria to adhere to.

Microscopic analysis using a light microscope is sufficient for observing the relative population dynamics which occur within the AS. However, to observe the interactions between bacteria and PAC, very high magnifications, on the order of 25,000 X, are necessary. These magnifications are only possible through the use of a scanning electron microscope.

A series of PAC/AS samples were collected such that bacterial growth on the PAC could be observed at various operation times. Increases in bacterial growth on the PAC could then be noted.

A SEM photomicrograph of the virgin carbon was taken to provide a control which would show carbon surfaces which were free from bacterial growth. Such a photomicrograph is presented in Figure 7.4.2.1 and illustrates the angular nature of the carbon surface.

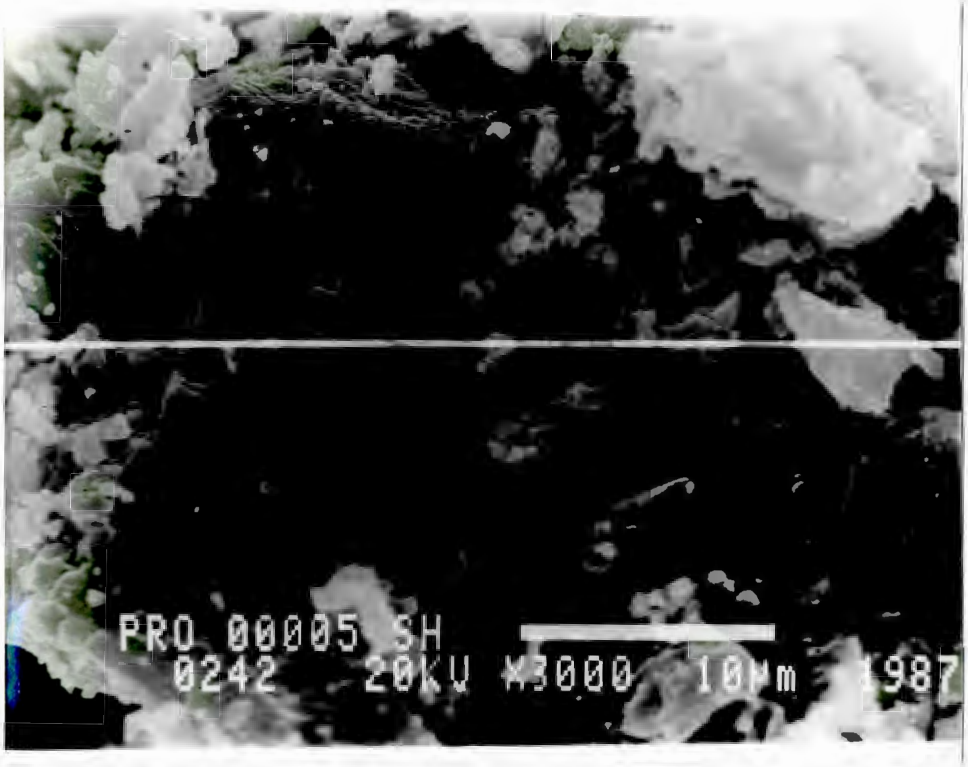


Figure 7.4.2.1 Scanning electron micrograph of the surface of virgin PAC particles without biological growth

The first SEM observation of a sample of the PAC that was in contact with the AS was taken after 44 days of operation. At the time the PAC/AS sample was collected, the PAC concentration in the AS reactor was equal to 120 mg/L and θ_c was equal to 3 days. Two photomicrographs were taken of the same PAC/AS sample using magnifications of 3,000 and 5,000 X. At a magnification of 3,000 X (Figure 7.4.2.2) a variety of microorganisms are shown to be attached to the surfaces of the PAC. Also visible in this photomicrograph are PAC surfaces which are free of microorganisms. At the higher magnification of 5,000 X (Figure 7.4.2.3) several rod shaped bacteria are shown which are attached to the PAC surfaces.

After a period of 56 days of operation another sample was withdrawn from the AS reactor and examined under the SEM. The operating conditions within the AS reactor when this sample was withdrawn were the same as the preceding sample except for a θ_c equal to 12 days. An overall photomicrograph of the PAC/AS at a magnification of 3,000 X is reproduced in Figure 7.4.2.4. The PAC within this photomicrograph is completely covered with a layer of rod-shaped bacteria. When the magnification was increased to 25,000 X (Figure 7.4.2.5) the attachment of the individual rod-shaped bacteria to the PAC surface could be seen. It appears from this photomicrograph that not all of the PAC surface is covered with bacteria, which means that some of

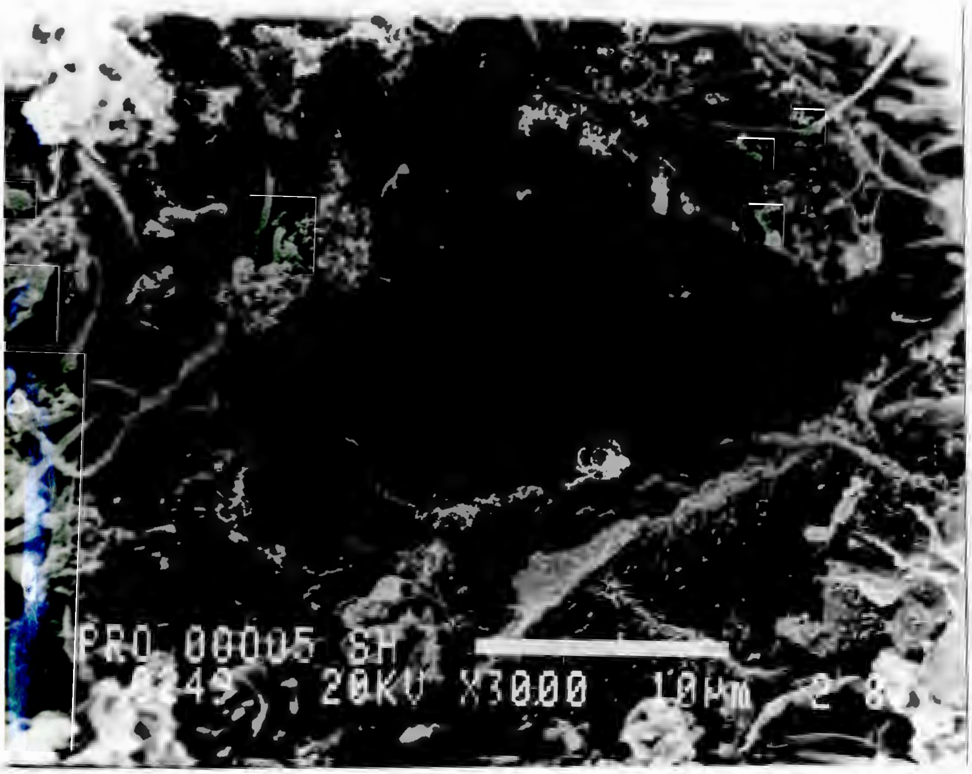


Figure 7.4.2.2 Scanning electron micrograph of PAC particles exposed to refinery industry wastewater for 44 days (rod-shaped bacteria were attached, PAC dosage 120 mg/l, sludge age 3 days).

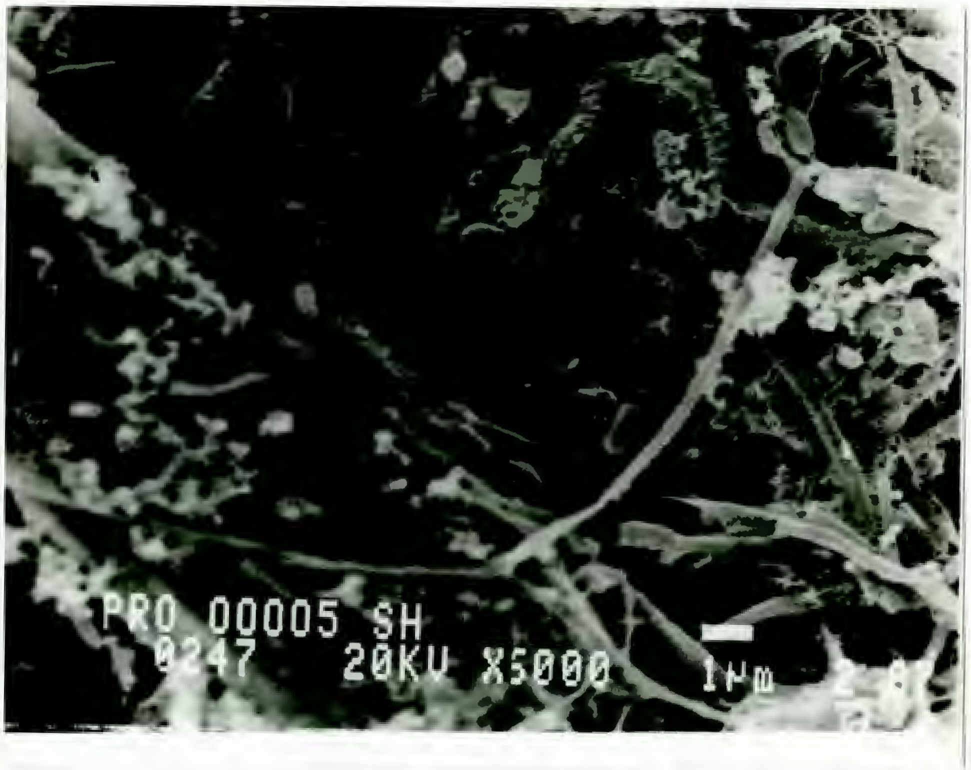


Figure 7.4.2.3 Scanning electron micrograph of PAC particles exposed to refinery industry wastewater for 44 days (rod-shaped bacteria are present in the wastewater, PAC dosage 120 mg/l; sludge age 3 days).

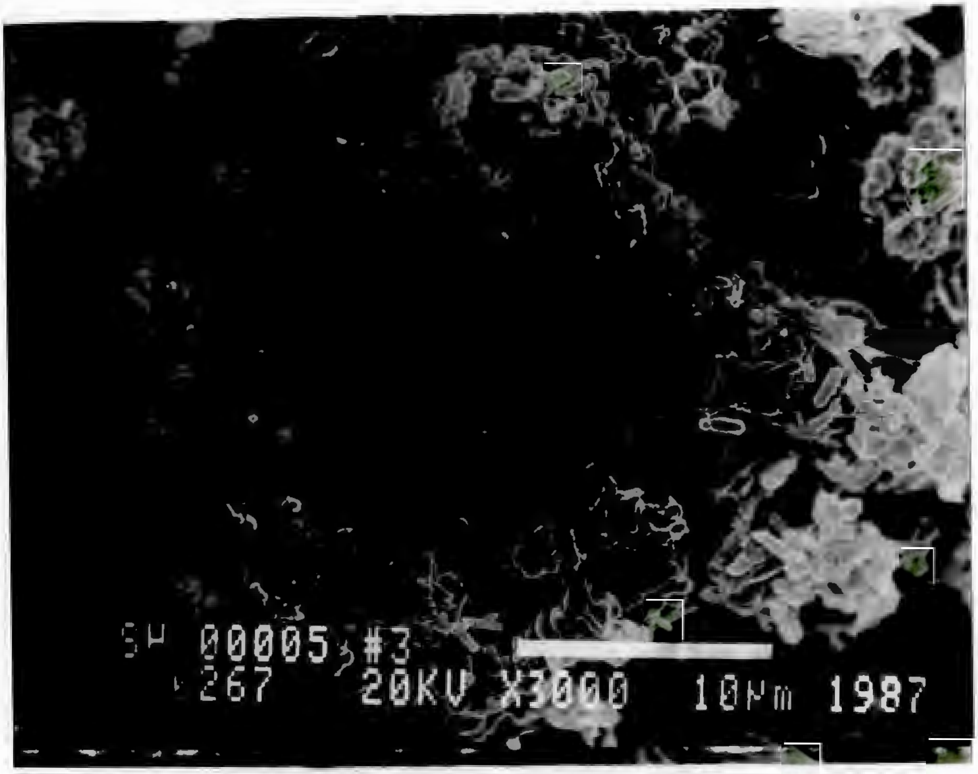


Figure 7.4.2.4 Scanning electron micrograph of PAC particles exposed to refinery industry wastewater for 56 days in a complete mixed reactor, (rod-shaped bacteria are growing on the PAC particles, PAC dosage 120 mg/l; sludge age 12 days).

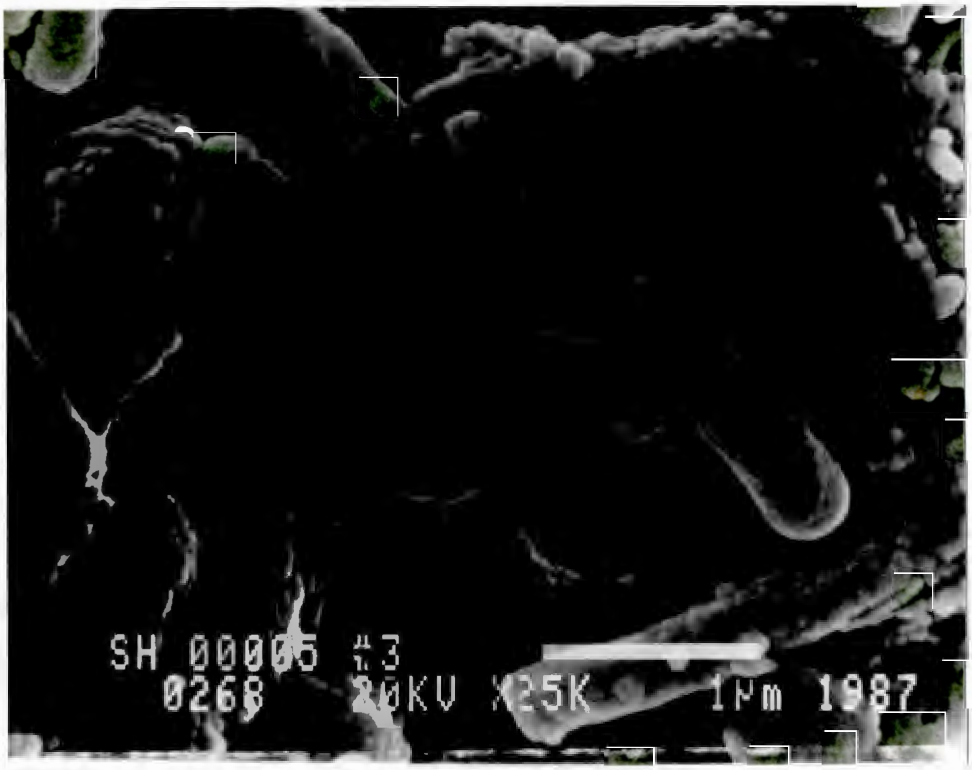


Figure 7.4.2.5 Scanning electron micrograph of PAC particles exposed to refinery industry wastewater for 56 days in complete mixed reactor, with 120 mg/L of carbon, (rod-shaped bacteria are growing on PAC particles).

the PAC surfaces were available for adsorption.

7.5 Experiment 3: Air Stripping Process

Within the conventional AS treatment process several dissolved organic removal mechanisms operate. The two major removal mechanisms are biological oxidation and air stripping. Air stripping can occur as dissolved organics are transferred from the liquid phase to the vapor phase during the aeration process. Experiment 3 was conducted in order to measure the potential air stripping of the following six compounds: benzene, chloroform, ethylbenzene, toluene, m-xylene and o-xylene. Each of these compounds is categorized as a volatile organic compound by the US EPA.

Three separate air flow rates were studied: 300, 400, and 500 ml/min/L. Each of these flow rates corresponded to the typical pilot plant air flow rates that were utilized during this study to maintain the dissolved oxygen concentration within the optimal range of 5 to 6 mg/L.

A wide range of concentrations for each of the six organic compounds was studied: benzene 360-1,903 ug/L, chloroform 1,673-2,383 ug/L, ethylbenzene 20-340 ug/L, toluene 100-1,433 ug/L, m-xylene 40-740 ug/L, and o-xylene 65-670 ug/L. The results of these experiments are presented in Tables 7.5.1 to 7.5.3. With the exception of the concentration of the chloroform effluent at a flow rate of 400 ml/min/L of 50 ug/L, all other effluent concentrations were below 10 ug/L which was the detection limit for each of the volatile organics.

The air stripping results that were reported above are similar to a study by Kincannon et al. (40) in which they observed that for an influent which consisted of a mixed industrial wastewater the volatile compounds which have Henry's Law Constants larger than 10^3 atom-m^3/mole are stripped from the AS reactor. Henry's Law Constants for benzene is 5.5 X 10^3 atom-m^3/mole, whereas the other volatile compounds have constants in the range of 10^{-3} atom-m^3/mole. Thus benzene is more easily stripped than the other volatile compounds that were studied.

7.6 Experiment 4: PAC Without Activated Sludge

The purpose of experiment 4 was to quantify the removals of each of the compounds previously studied, with the exception of BOD_5, which would result only from adsorption by the PAC present in the reactor. In order to accomplish this, the pilot plant was operated exactly as it was for the previous experiments except for the elimination of the biomass in the reactor. The PAC concentration in the reactor was maintained at 10 mg/L, 50

Table 7.5.1 Percent Stripping of Volatile Compounds in Nonbiological System, Experiment 3, air flow rate = 300 ml/min/L.

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
57	1,800	ND	>99	2,383	ND	>99	318	ND	>97	1,350	ND	>99	440	ND	>98	584	ND	>98
58	1,806	ND	>99	2,339	ND	>99	330	ND	>97	1,383	ND	>99	360	ND	>97	270	ND	>96
59	1,903	ND	>99	2,353	ND	>99	318	ND	>97	1,400	ND	>99	460	ND	>98	670	ND	>99

ND = None detectable, detectability >10 ug/L

Table 7.5.2 Percent Stripping of Volatile Compounds in Nonbiological System, Experiment 3, air flow rate = 400 ml/min/L.

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
60	1,790	ND	>99	2,295	ND	>99	340	ND	>97	1,433	ND	>99	530	ND	>98	390	ND	>97
61	1,774	ND	>99	2,299	ND	>99	340	ND	>97	1,383	ND	>97	700	ND	>97	740	ND	>97
62	440	ND	>99	2,341	50	98	20	ND	>50	100	ND	>90	70	ND	>86	80	ND	>88

ND = None detectable, detectability >10 ug/L

Table 7.5.3 Percent Stripping of Volatile Compounds in Nonbiological System, Experiment 3, when air flow rate 500 ml/min/L.

	Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
63	340	ND	>97	1,784	ND	>99	180	ND	>94	160	ND	>94	60	ND	>83	80	ND	>88
64	360	ND	>97	1,673	ND	>99	ND	ND	ND	182	ND	>95	90	ND	>89	150	ND	>93
65	360	ND	>97	1,781	ND	>99	20	ND	>50	200	ND	>95	40	ND	>75	65	ND	>85

ND = None detectable, detectability >10 ug/L

mg/L and 120 mg/L during each individual phase of the investigation. At each PAC concentration, the influent and effluent concentrations of all previously studied compounds were measured.

As the concentration of the PAC in the reactor was increased from 10 mg/L to 50 mg/L and finally to 120 mg/L the COD removals increased from approximately 56% up to a maximum of 83% (Tables 7.6.1-3 and Figure 7.6.1). However, when these COD removals are compared to the removals which resulted from the combination of AS and PAC, which averaged about 87% and were similar at all PAC dosages, it could be noted that from a PAC concentration of 10 mg/L up to a PAC concentration of 120 mg/L the percentage removal improvement was constant.

TOC removals were measured and the results are presented in tabular form in Tables 7.6.1-3 and in graphical form in Figure 7.6.2. The curve which depicts the influence of various dosages of PAC on the TOC removals showed a dependence on the PAC reactor concentration as the TOC removals increased from 43% at a PAC concentration of 10 mg/L up to 76% for a PAC concentration of 120 mg/L. A similar but less pronounced trend was evident for the PAC/AS system in that removals increased from 82% with no additions of PAC up to 90% at the highest PAC reactor concentration.

Table 7.6.1 COD and TOC Removal Efficiencies in Experiment 4, When PAC = 10 mg/L.

Date 1986	Day No.	COD Inft (mg/L)	COD Efft (mg/L)	COD Effy (%)	TOC Inft (mg/L)	TOC Efft (mg/L)	TOC Effy (%)
12/20	66	419	134	68	25	13	48
12/21	67	1,000	518	48	336	157	53
12/22	68	549	257	53	33	33	28

Table 7.6.2 COD and TOC Removal Efficiencies in Experiment 4, When PAC = 50 mg/L.

Date 1986	Day No.	COD Inft (mg/L)	COD Efft (mg/L)	COD Effy (%)	TOC Inft (mg/L)	TOC Efft (mg/L)	TOC Effy (%)
12/23	69	584	104	82	56	14	75
12/24	70	588	100	83	39	12	69
12/25	71	592	77	87	48	15	69

Table 7.6.3 COD and TOC Removal Efficiencies in Experiment 4, When PAC = 120 mg/L.

Date 1986	Day No.	COD Inft (mg/L)	COD Efft (mg/L)	COD Effy (%)	TOC Inft (mg/L)	TOC Efft (mg/L)	TOC Effy (%)
12/26	72	552	100	82	37	9	76
12/27	73	552	104	81	28	17	40
12/28	74	524	80	85	25	22	12

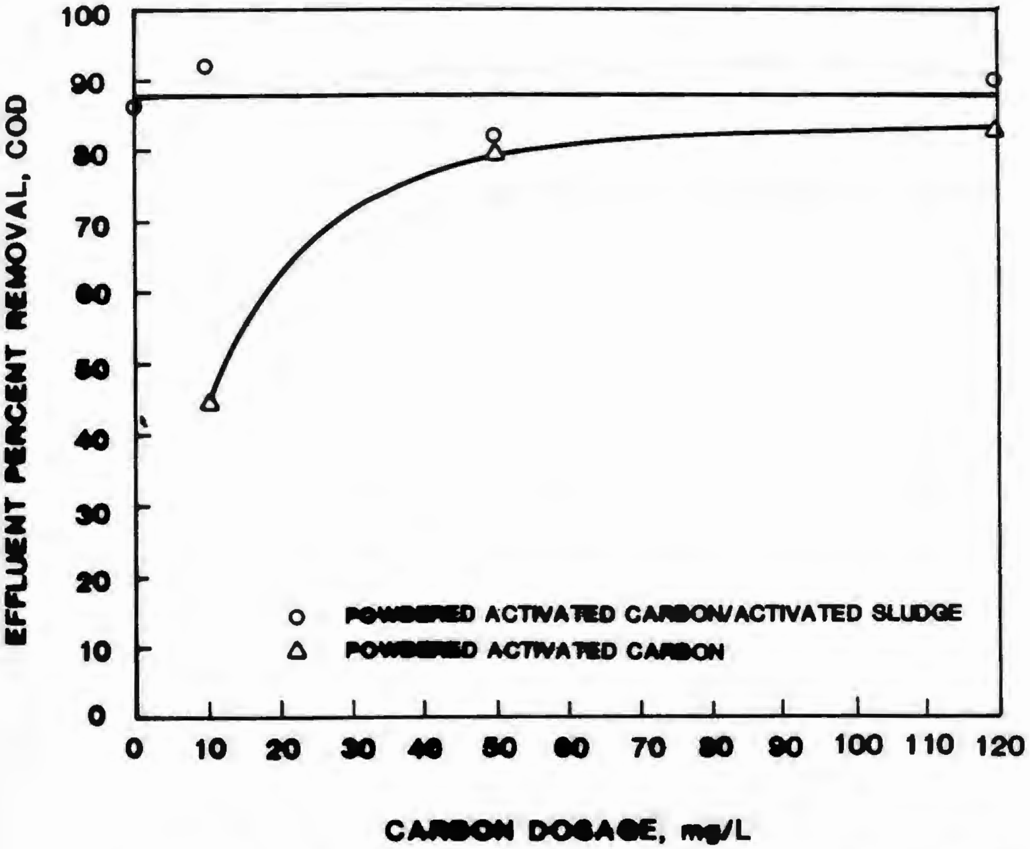


Figure 7.6.1 A Comparison of COD Removal by PAC and PAC/AS

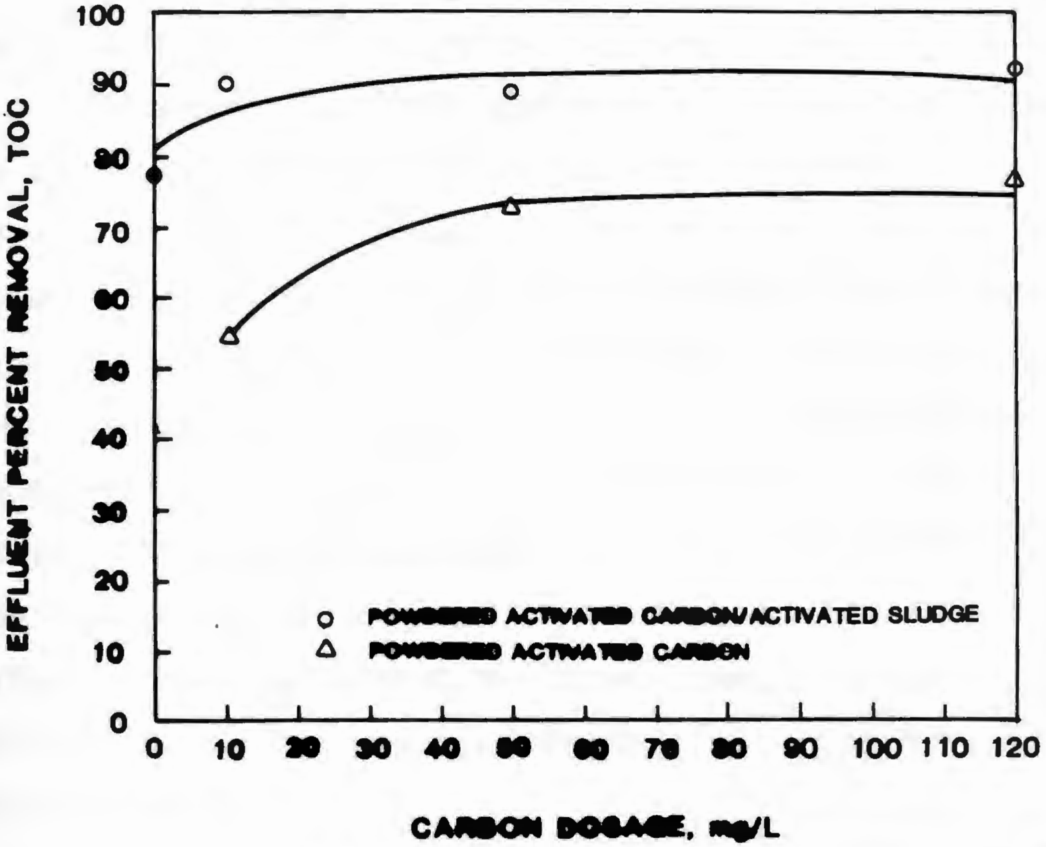


Figure 7.6.2 A Comparison of TOC Removal by PAC and PAC/AS

Removal of the remaining priority organic pollutants (2,4 dimethylphenol, fluorene, napthalene and pyrene) by adsorption was studied and the results are presented in Tables 7.6.4-6 and Figures 7.6.3-6. The influent concentrations of 2,4 dimethylphenol, fluorene, naphthalene and pyrene ranged from 1,040-9,707 ug/L, 80-533 ug/L, 100-4,093 ug/L, and 13-113 ug/L, respectively. Due to the extreme variability of the influent organic concentration there did not appear to be a correlation between the PAC concentration in the reactor and the effluent concentration. The compound 2,4 dimethylphenol effluent concentration appeared to be relatively insensitive to wide swings in the influent concentration, whereas the effluent concentrations of the other compounds appeared to somewhat track the highest variations in the influent concentrations.

The adsorption of the priority organic compounds that were previously studied was investigated. The percentage removals of each of the volatile compounds (benzene, chloroform, ethylbenzene, toluene, m-xylene and o-xylene) during this experiment ranged from a low of 67% for ethylbenzene to greater than 90% for each of the other compounds (Tables 7.6.7-9). This was due to the fact that the volatile compounds are easily air stripped under the operating conditions which exist in the reactor as shown in section 7.5.

Table 7.6.4 Priority Organic Pollutants' Removal Efficiencies in Experiment 4, when PAC = 10 mg/L.

Date	Day	2,4,-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
1986	No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
12/20	66	1,806	93	95	100	ND	>90	1,200	70	94	ND	ND	ND
12/21	67	9,707	180	98	80	20	75	4,093	373	91	ND	ND	ND
12/22	68	1,040	47	95	533	13	98	1,867	233	88	113	20	82

ND = None detectable, detectability >10 ug/L

Table 7.6.5 Priority Organic Pollutants' Removal Efficiencies in Experiment 4, when PAC = 50 mg/L.

Date	Day	2,4,-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
1986	No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
12/23	69	4,924	253	95	111	3	97	1,267	25	98	13	ND	>23
12/24	70	4,920	153	97	187	13	93	533	87	84	ND	ND	ND
12/25	71	4,506	33	99	220	49	78	573	120	77	ND	ND	ND

ND = None detectable, detectability >10 ug/L

Table 7.6.6 Priority Organic Pollutants' Removal Efficiencies in Experiment 4, when PAC = 120 mg/L.

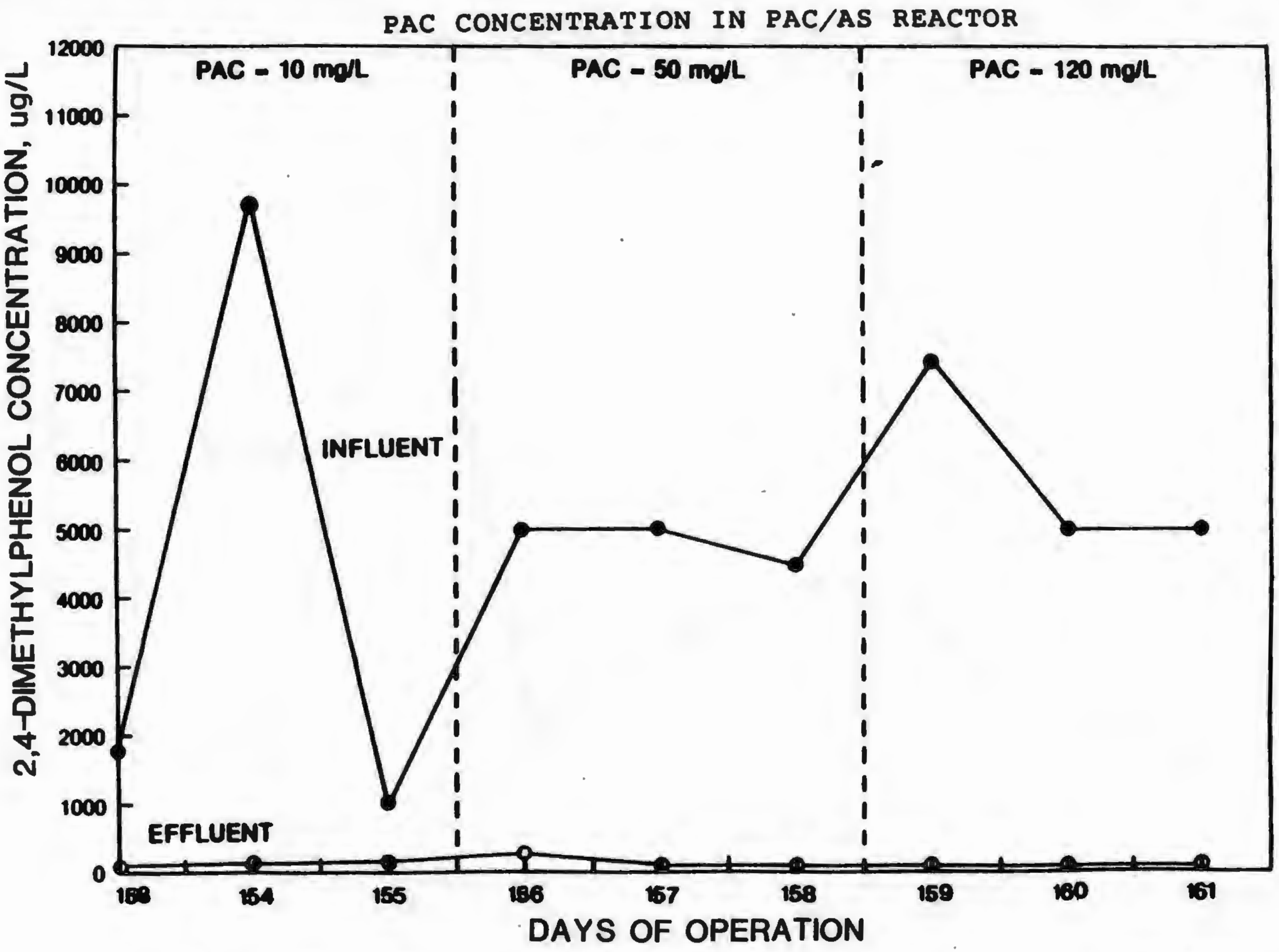
Date	Day	2,4,-Dimethylphenol			Fluorene			Naphthalene			Pyrene		
1986	No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
12/26	72	7,440	13	99	187	ND	>95	600	23	96	ND	ND	ND
12/27	73	4,936	15	99	132	ND	>92	933	8	99	ND	ND	ND
12/28	74	4,930	27	99	107	ND	>91	100	24	98	ND	ND	ND

ND = None detectable, detectability >10 ug/L

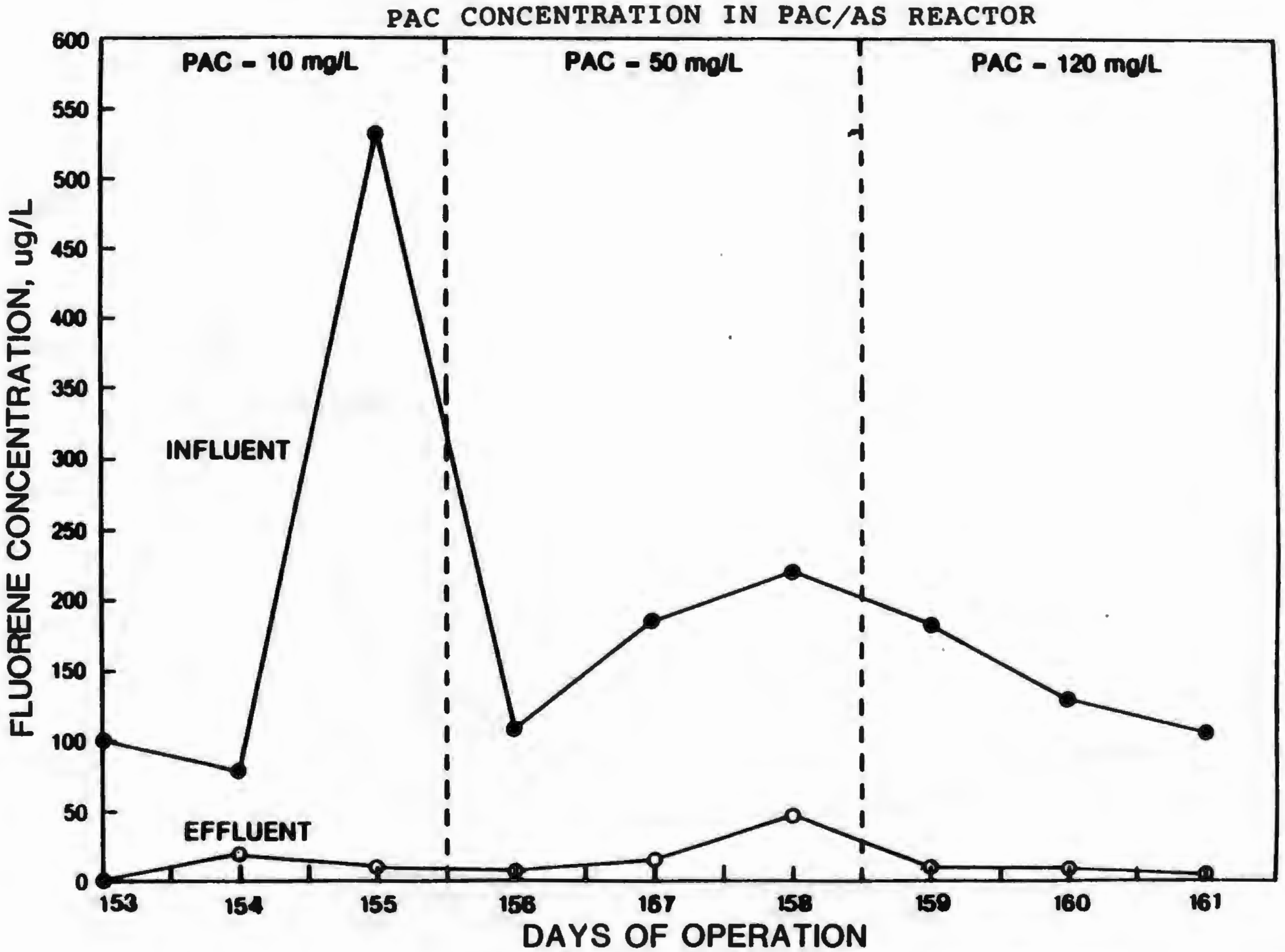
Table 7.6.7 Volatile Compounds Removal Efficiencies in Experiment 4, when PAC = 10 mg/L.

		Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
12/20	66	1,320	ND	>99	2,190	ND	>99	50	ND	>80	700	ND	>99	120	ND	>92	240	ND	>96
12/21	67	1,383	ND	>99	2,239	ND	>99	60	ND	>83	640	ND	>98	180	ND	>94	240	ND	>96
12/22	68	2,092	ND	>99	2,468	90	96	560	ND	>98	3,067	ND	>99	1,076	ND	>99	800	ND	>99

ND = None detectable, detectability >10 ug/L

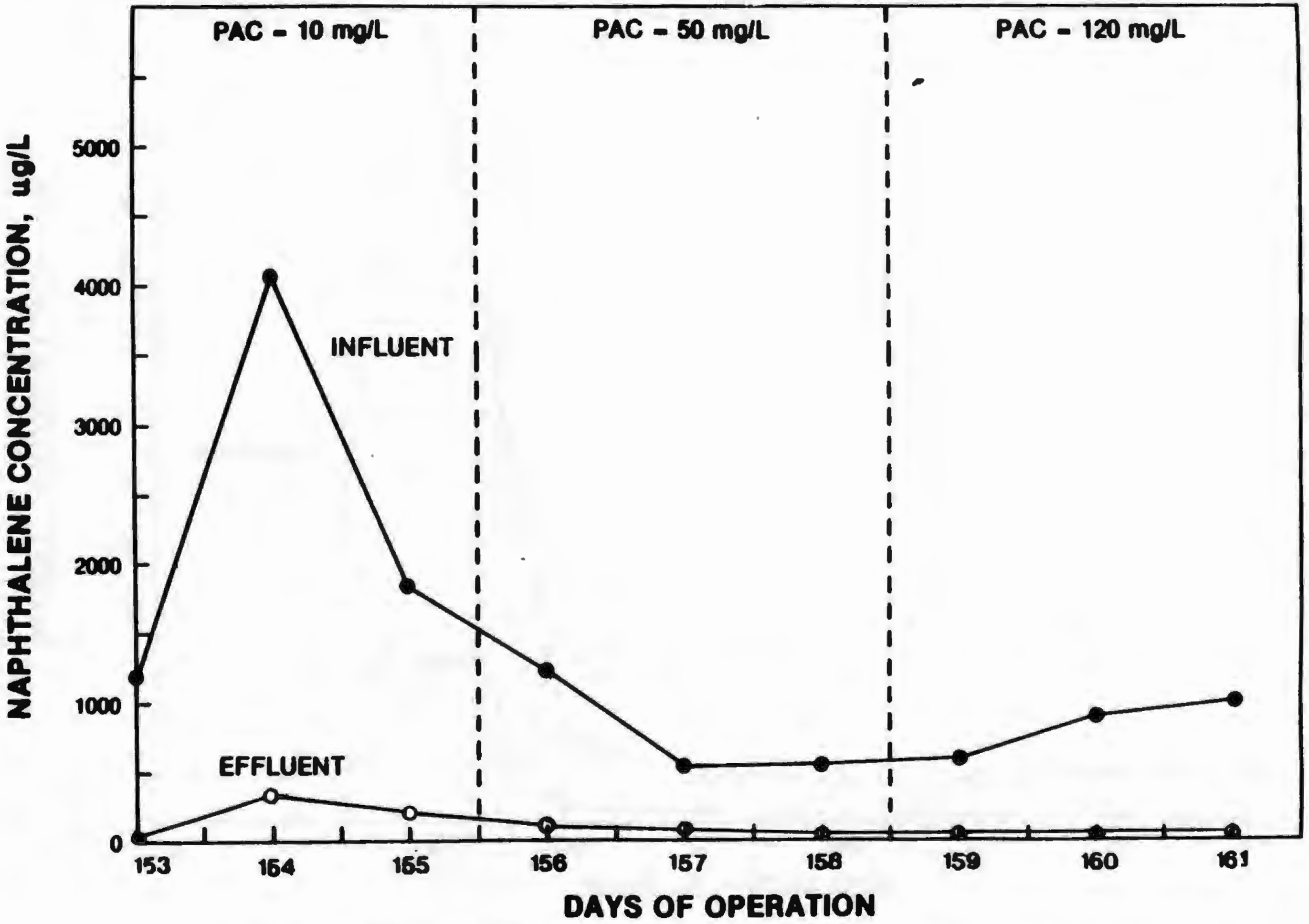


7.6.3 2,4-Dimethylphenol Removal by Powdered Activated Carbon

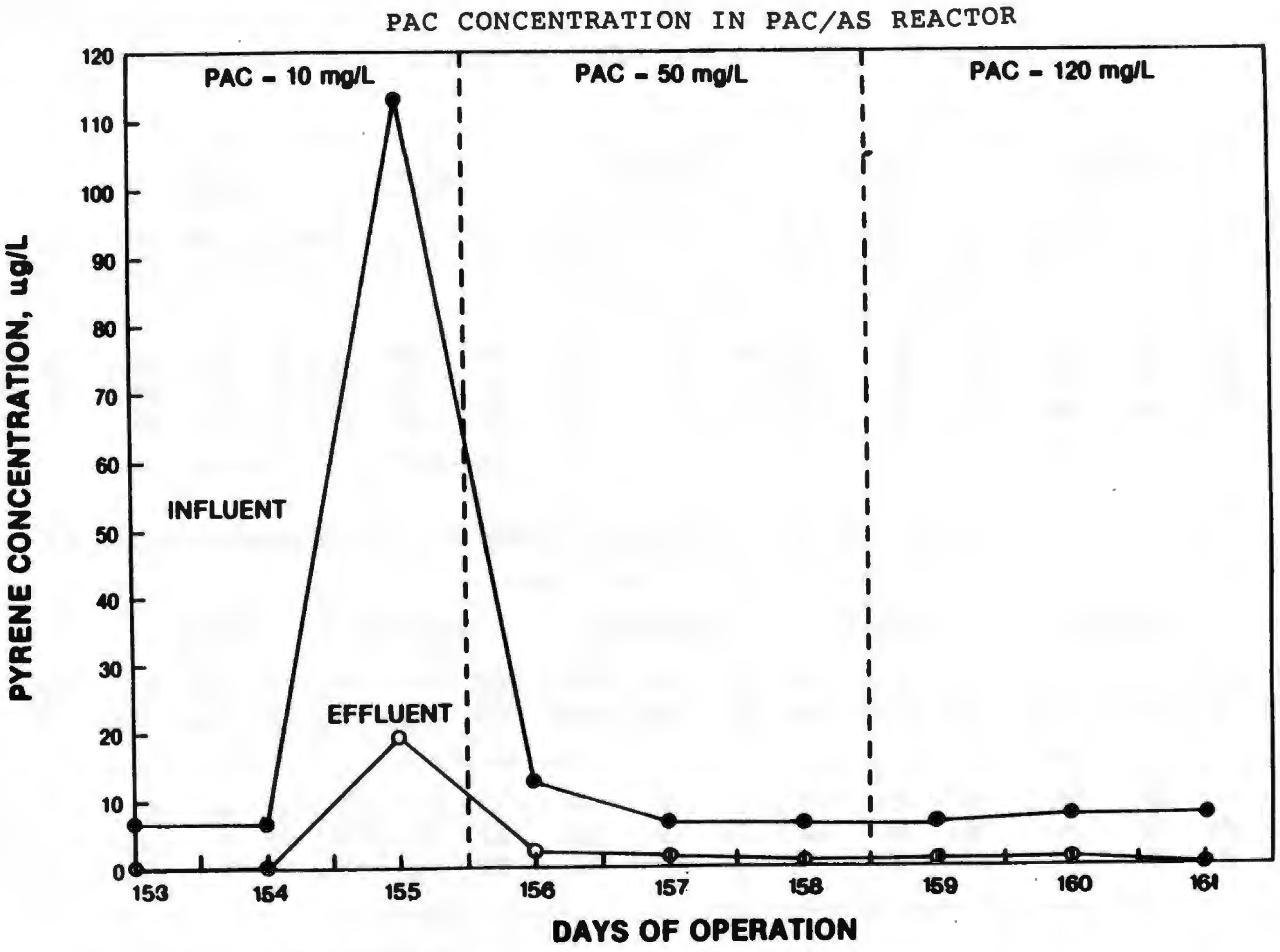


7.6.4 Fluorene Removal by Powdered Activated Carbon

PAC CONCENTRATION IN PAC/AS REACTTOR



7.6.5 Naphthalene Removal by Powdered Activated Carbon



7.6.6 Pyrene Removal by Powdered Activated Carbon

Table 7.6.8 Volatile Compounds Removal Efficiencies in Experiment 4, when PAC = 50 mg/L.

		Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
12/23	69	3,503	ND	>99	3,083	500	84	160	ND	>94	2,517	ND	>99	730	ND	>99	890	ND	>99
12/24	70	2,951	ND	>99	2,688	301	89	160	ND	>94	2,133	ND	>99	560	ND	>98	800	ND	>99
12/25	71	659	ND	>98	2,505	360	86	30	ND	>67	510	ND	>98	560	ND	>98	370	ND	>99

Table 7.6.9 Volatile Compounds Removal Efficiencies in Experiment 4, when PAC = 120 mg/L.

		Benzene			Chloroform			Ethylbenzene			Toluene			M-Xylene			O-Xylene		
Date 1986	Run No.	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)	Inft (ug/L)	Efft (ug/L)	Effy (%)
12/26	72	2,735	ND	>99	2,679	570	100	190	ND	>95	2,000	ND	>99	1,183	ND	>99	1,663	ND	>99
12/27	73	2,279	ND	>99	2,597	80	100	30	ND	>67	1,660	ND	>99	865	ND	>99	1,440	ND	>99
12/28	74	1,638	ND	>99	2,544	224	100	30	ND	>67	1,133	ND	>99	643	ND	>98	650	ND	>98

ND = None detectable, detectability >10 ug/L

8. CONCLUSIONS

1. Activated sludge biomass that has been collected from a municipal wastewater treatment facility can be acclimated in a period of 31 days to treat a refinery industrial wastewater.

2. Various stages in the activated sludge biomass acclimation period could be identified by a periodic microscopic examination of the microorganism population.

3. PAC provided a favorable site for the attachment of bacteria.

4. The conventional pollutants (BOD_5, COD and TOC) which are present in a refinery industrial wastewater can be removed by the activated sludge process and this removal can be enhanced by PAC additions to the AS reactor.

5. Priority organic compounds (2,4 dimethylphenol, fluorene, naphthalene and pyrene) were removed by the AS process, PAC additions to the AS reactor improved percentage removals with the exception of pyrene.

6. Volatile organic compounds (benzene, chloroform, ethylbenzene, toluene, m-xylene and o-xylene) were air stripped from the reactor.

9. RECOMMENDATIONS

1. Since concentrations of oil and grease greater than were investigated in this study could be present in a refinery industrial influent especially during API separator upset periods, the effects of these high oil and grease levels on the activity of the biomass should be investigated.

2. An investigation should be conducted on the effects of maintaining a DO concentration in the AS reactor in the range of 2 mg/L.

3. It is possible that if a PAC/AS scheme were to be constructed in Kuwait to treat the wastewaters from the SIA petrochemical complex, a significant fraction of the total flow would consist of sanitary wastewater. Possible effects of the additions of the sanitary wastewaters should be investigated.

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APPENDICES

Appendix 1

A List of Priority Pollutants

Priority Pollutant Compounds

Compound Name		Mole Wt
1.	*acenaphthene	154
2.	*acrolein	56
3.	*acrylonitrile	53
4.	*benzene	78
5.	*benzidine	184
6.	*carbon tetrachloride (tetrachloromethane)	154
	*Chlorinated benzenes (other than dichlorobenzenes)	
7.	chlorobenzene	113
8.	1,2,4-trichlorobenzene	181
9.	hexachlorobenzene	
	*chlorinated ethanes (including 1,2-dichloroethane, 1,1,-thrichloroethane and hexachloroethane)	
10.	1,2-dichloroethane	99
11.	1,1,1-trichloroethane	133
12.	hexachloroethane	237
13.	1,1-dichlorethane	99
14.	1,1,2-trichloroethane	133
15.	1,1,2,2-tetrachloroethane	168
16.	chloroethane	65
	*Chloroalkyl ethers (chloromethyl, chloroethyl and mixed ethers)	
17.	bix(chloromethyl) ether	
18.	bix (2-chloroethyl) ether	137
19.	2-chloroethyl vinyl ether (mixed)	
	*chlorinated naphthalene	
20.	2-chloronaphthalene	163
	*chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)	
21.	2,4,6-trichlorophenol	197
22.	parachlorometa cresol	
23.	*chloroform (trichloromethane)	119
24.	*2-chlorophenol	129

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*Specific compounds and chemical classes as listed in original Consent Decree

	*dishlorobenzenes	
25.	1,2-dichlorobenzene	147
26.	1,3-dichlorobenzene	147
27.	1,4-dichlorobenzene	147
	*Dichlorobenzidine	
28.	3,3-dichlorobenzidine	
	*Dichloroethylenes (1,1-dichloroethylene and 1,2-dichloroethylene)	97
29	1,1-dichloroethylene	97
30.	1,2-trans-dichloroethylene	97
31.	*2,4-dichlorophenol	163
	*Dichloropropane and dichloropropene	
32.	1,2-dichloropropane	113
33.	1,2-dichloropropylene (1,3-dichloropropene)	111
34.	*2,4-dimethylphenol	122
	*Dinitrotoluene	
35.	2,4-dinitrotoluene	182
36.	2,6,dinitrotoluene	182
37.	*1,2-diphenylhydrazine	184
38.	*ethylbenzene	106
39.	*Fluoranthene	202
	*Haloethers (other than those listed elsewhere)	
40.	4-chlorophenyl phenyl ether	
41.	4-bromophenyl phenyl ther	
42.	bis (2-chloroisopropyl) ether	
43.	bis (2-chloroethoxy)methane	
	*Halomethanes (other than those listed elsewhere)	
44.	Methylene chloride (dichloromethane)	85
45.	methy chloride (chloromethane	50
46.	methybromide (bromomethane)	95
47.	bromoform(tribromomethane)	253
48.	dichlorobromomethane	164
49.	trichlorofluoromethane	139
50.	dichlorodifloromethane	121
51.	chlorodibromomethane	208
52.	*hexachlorobutadene	261
53.	*hexachlorocyclopentadiene	273
54.	*isophorone	138
55.	*naphthalene	128
56.	*nitrobenzene	123

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*Specific compounds and chemical classes as listed in original Consent Decree

	*Nitrophenols (including 2,4-dinitrophenol and dinitrocresol)	
57.	2-nitrophenol	139
58.	4-nitrophenol	139
59.	*2,4-dinitrophenol	184
60.	4,6-dinitro-o-cresol	198
	*Nitrosamines	
61.	N-nitrosodimethylamine	74
62.	N-nitrosodiphenylamine	198
63.	N-nitrosodi-n-propylamine	130
64.	*pentachlorophenol	266
65.	*phenol	94
	*Phthalate esters	
66.	bis (2-ethylhexyl) phthalate	
67.	butyl benzyl phthalate	310
68.	di-n-butyl phthalate	
69.	Di-n-octyl phthalate	
70.	diethyl phthalate	
71.	dimethyl phthalate	
	*polynuclear aromatic hydrocarbons	
72.	benzo(a)anthracene (1,2-benzathracene)	243
73.	benzo(a)pyrene (3,4-benzopyrene)	
74.	3,4-benzofluoranthene	
75.	benzo(k)fluoranthene (11,120 benzofluoranthene)	
76.	chrysene	228
77.	acenaphthylene	152
78.	anthracene	178
79.	benzo(ghi)perylene (1,12-benzoperylene)	
80.	fluorene	166
81.	phenanthrene	178
82.	dibenzo(a,h)anthracene (1,2,5,6-dibenzanthracene)	
83.	ideno (1,2,3-cd) pyrene (2,3-o-phenylenepyrene)	
84.	pyrene	202
85.	*tetrrachloroethylene	166
86.	*toluene	92
87.	*trichloroethylene	132
88.	*vinyl chloride (chloroethylene)	63

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*Specific compoiunds and chemical classes as listed in original Consent Decree

	Pesticides and Metabolities	
89.	*aldrin	365
90.	*dieldrin	381
91.	*chlordane (technical mixture & metabolities)	410
	*DDt and methabolities	
92.	4,4-DDT	
93.	4,4-DDE (p,p-DDX)	
94.	4,4-DDD (p,p-TDE)	
	*endosulfan and metabolities	
95.	a-endosulfan-Alpha	
96.	b-endosulfan-Beta	
97.	endosulfan sulfate	
	*endrin and metabolities	
98.	endrin	381
99.	endrin aldehyde	
	*heptachlor and metabolities	
100.	heptachlor	373
101.	heptachlor epoxide	394
	*hexachlorocyclohexane (al insomers)	
102.	a-BHC-Alpha	291
103.	b-BHC-Beta	291
104.	r-BHC (lindane)-Gamma	291
105.	g-BHC-Delta	291
	*polychlorinated biphenyls (PCBs)	
106.	PCB-1242 (Archlor 1242)	
107.	PCB-1254 (Arochlor 1254)	
108.	PCB-1221 (Arochlor 1221)	
109.	PCB-1232 (Arochlor 1232)	
110.	PCB-1248 (Arochlor 1248)	
111.	PCB-;260 (Arochlor 1260)	
112.	PCVB-1016 (Arochlor 1016)	
113.	*Toxaphene	
114.	*Antimony (Total)	
115.	*Arsenic (Total)	
116.	*Asbestos (Fibrous)	
117.	*Beryllium (Total)	
118.	*Cadmium (Total)	
119.	*Cadmium (Total)	
120.	*Copper (Total	

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*Specific compounds and chemical classes as listed in original Consent Decree

121. *Cyanide (Total)
122. *Lead (Total)
123. *Mercury (Total)
124. *Nickel (Total)
125. *Selenium (Total)
126. *Silver (Total)
127. *Thallium (Total)
128. *Zinc (Total)
129. *2,3,7,8 - tetrachlorodibenzo-p-dioxin (TCDD)

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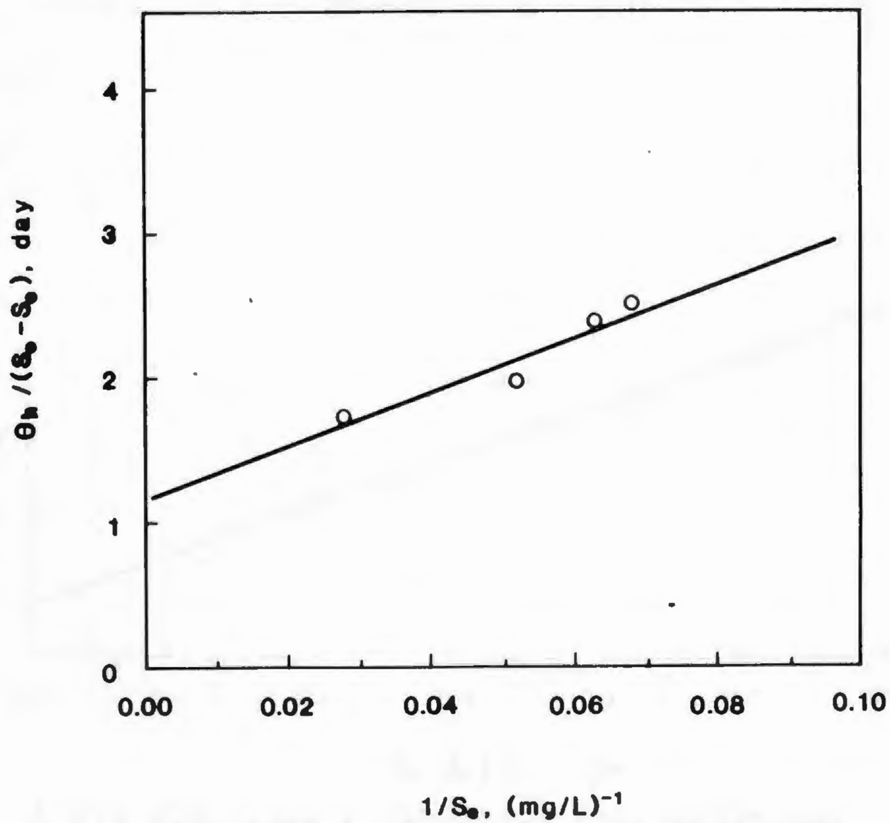
*Specific compounds and chemical classes as listed in original Consent Decree

Appendix 2

Experiment 1: Figures for Bio-Kinetic Constants



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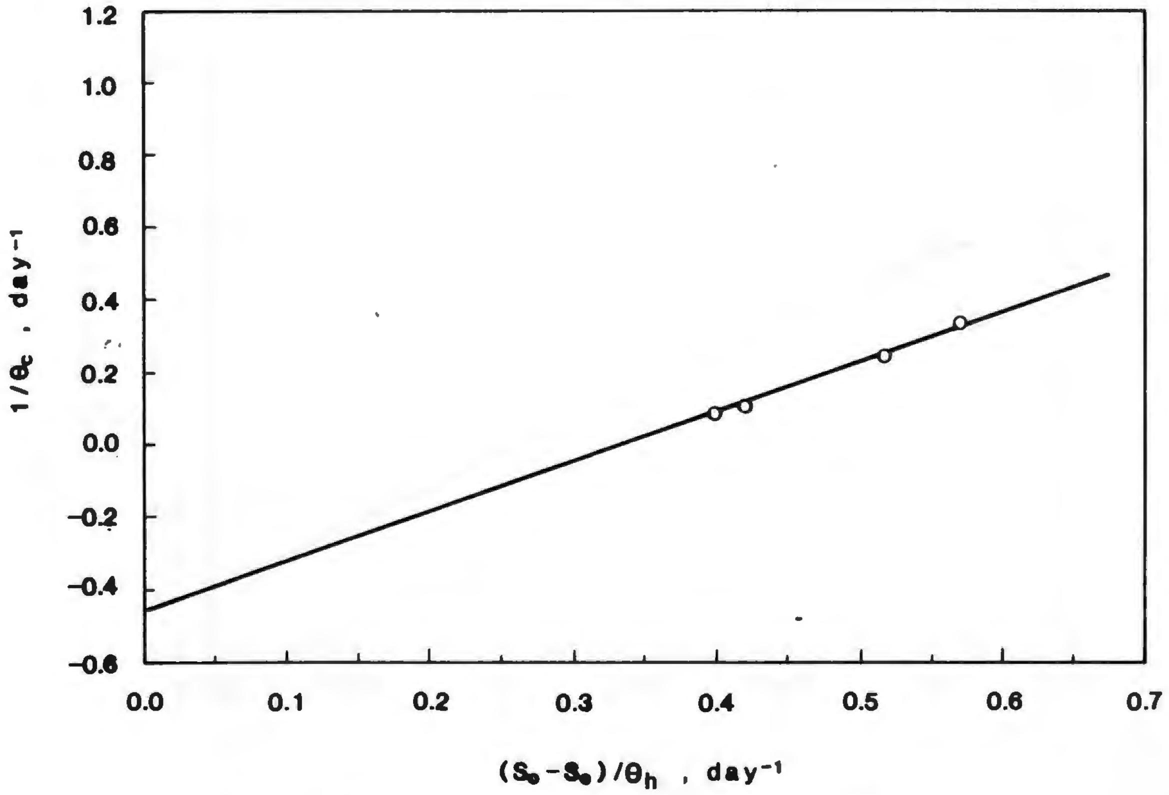

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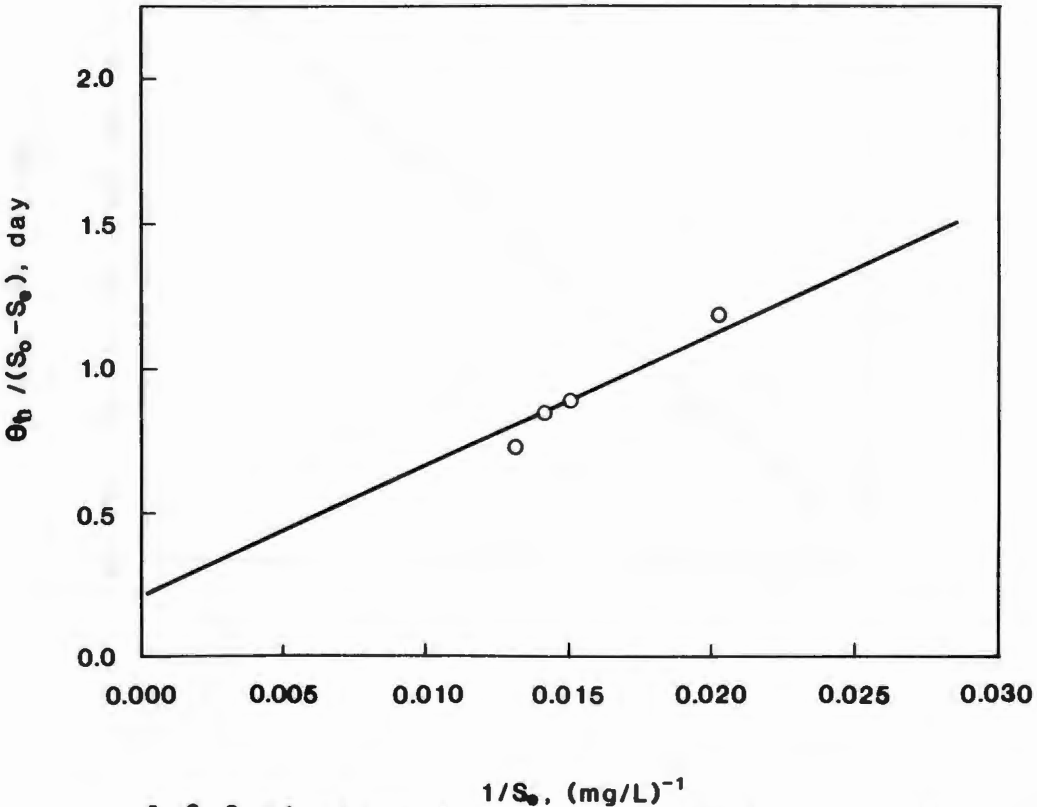

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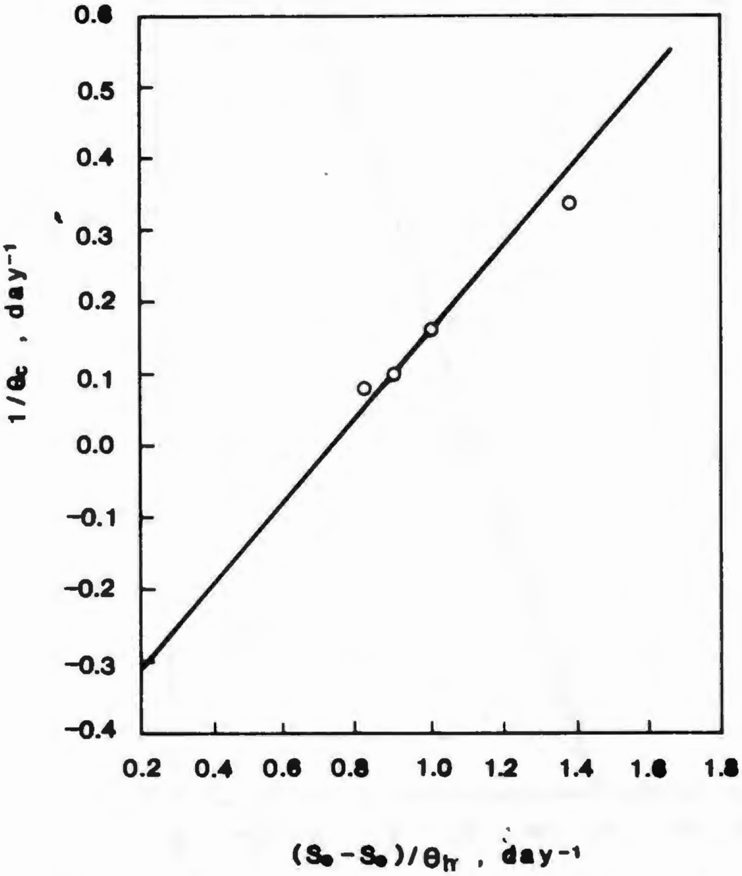

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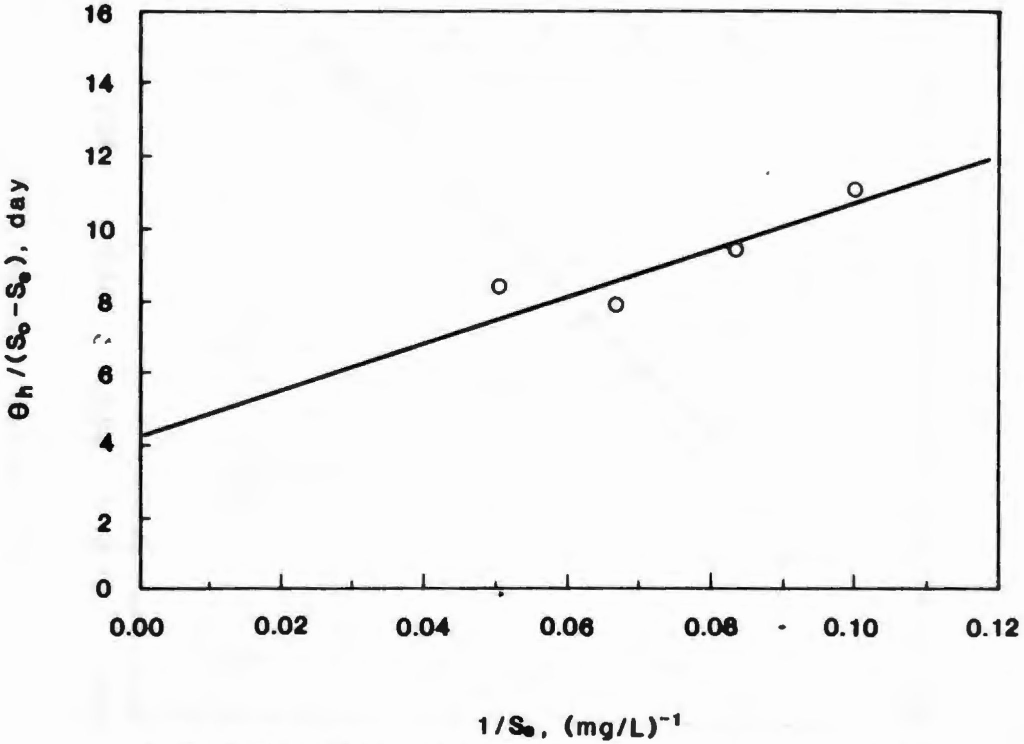
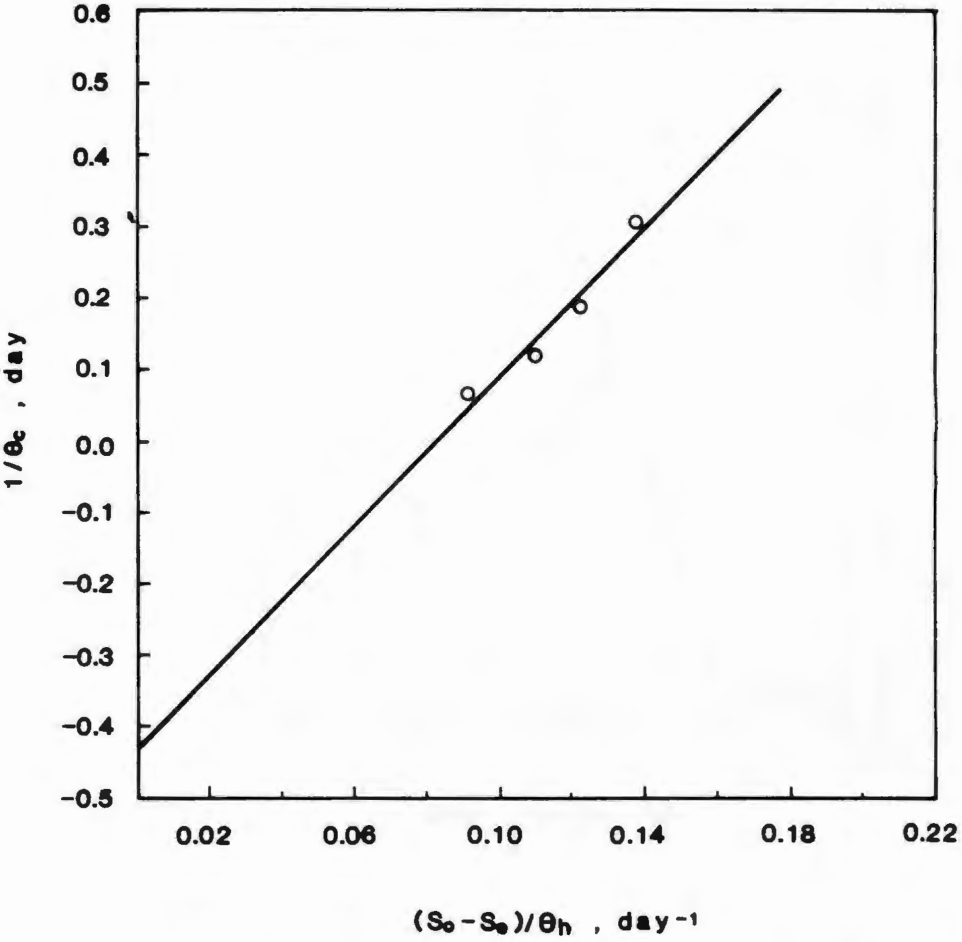


A.2.5 Bio-kinetic Constants Evaluation,TOC



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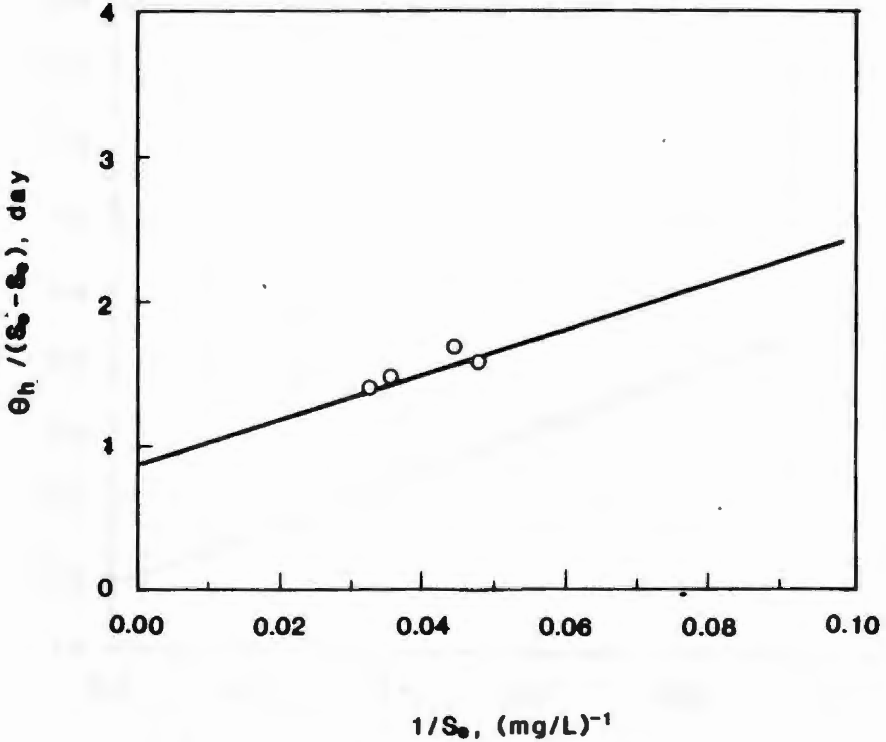
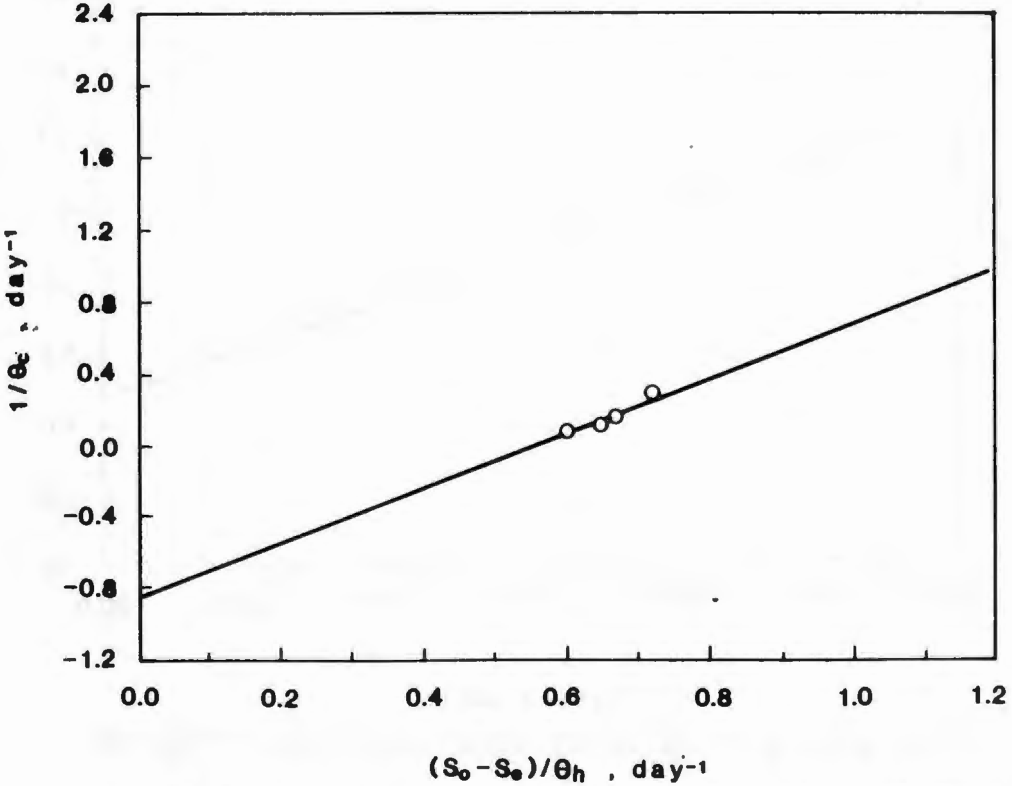


A.2.7 Bio-kinetic Constants, PAC=10 mg/L,BOD



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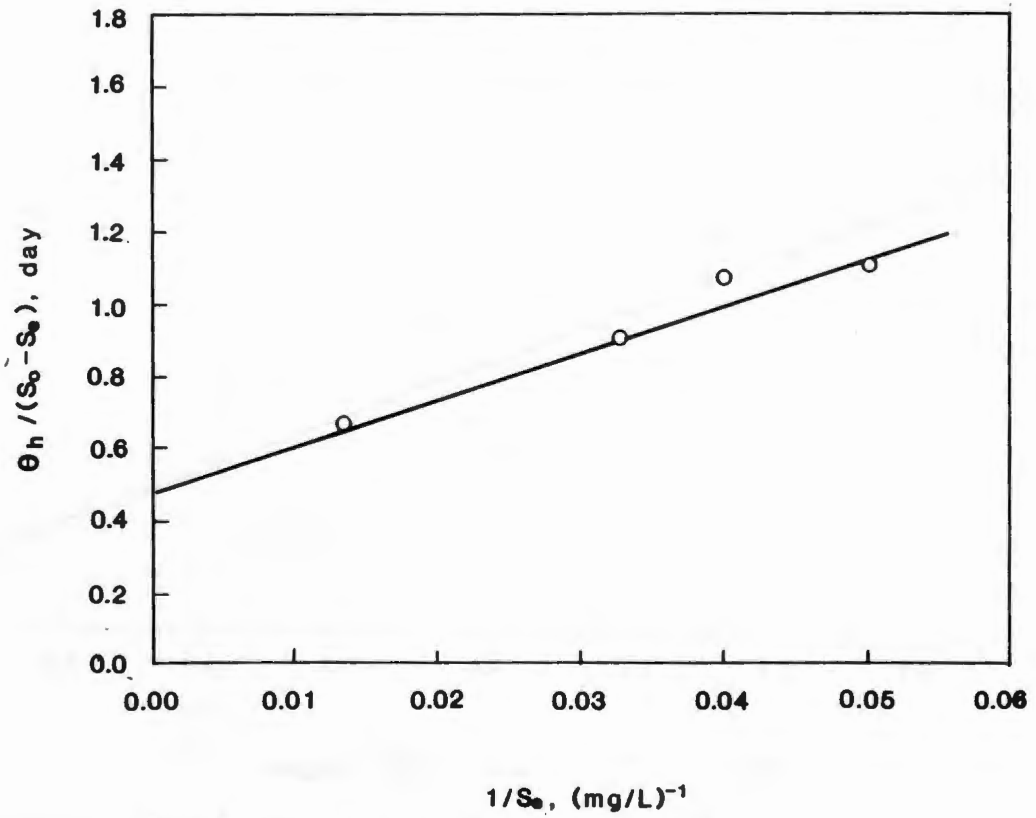

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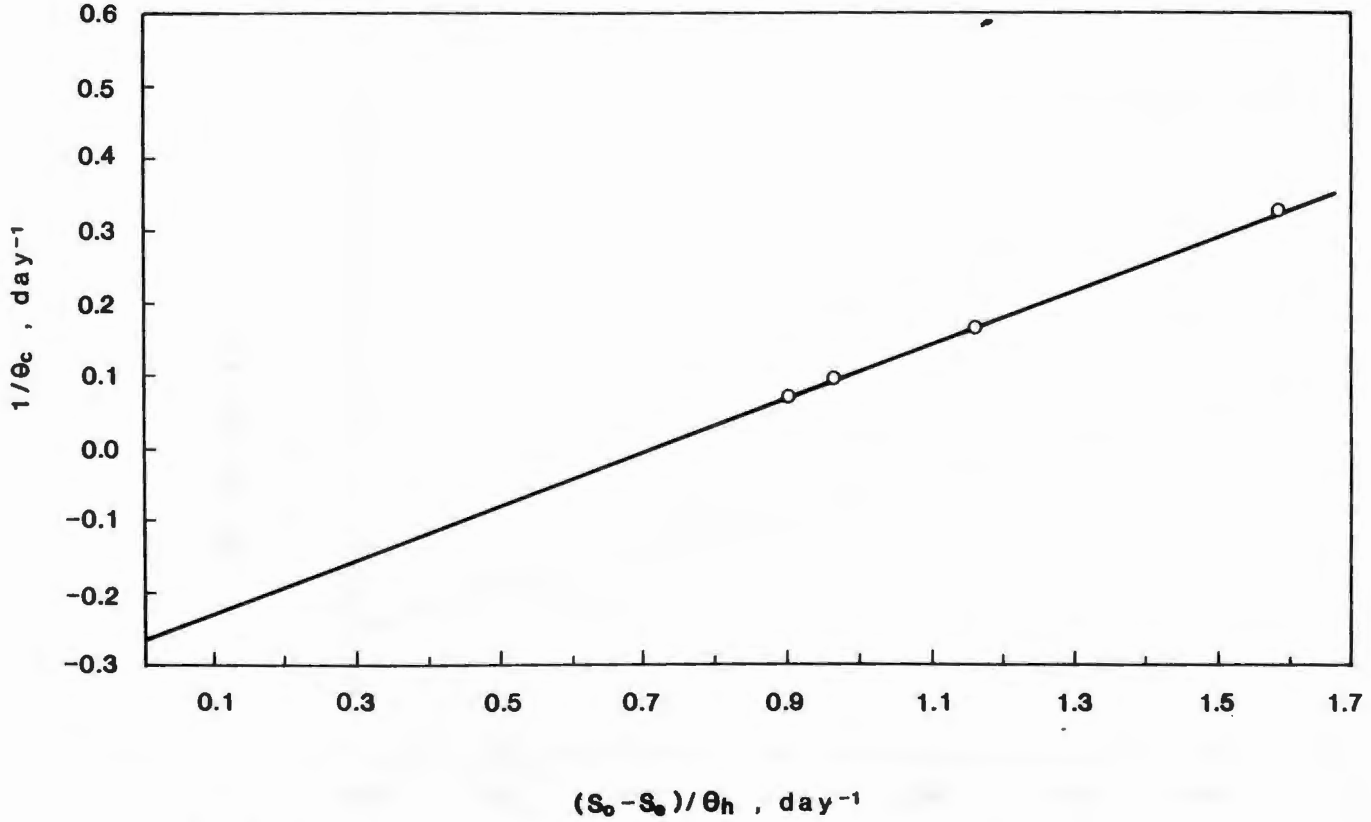

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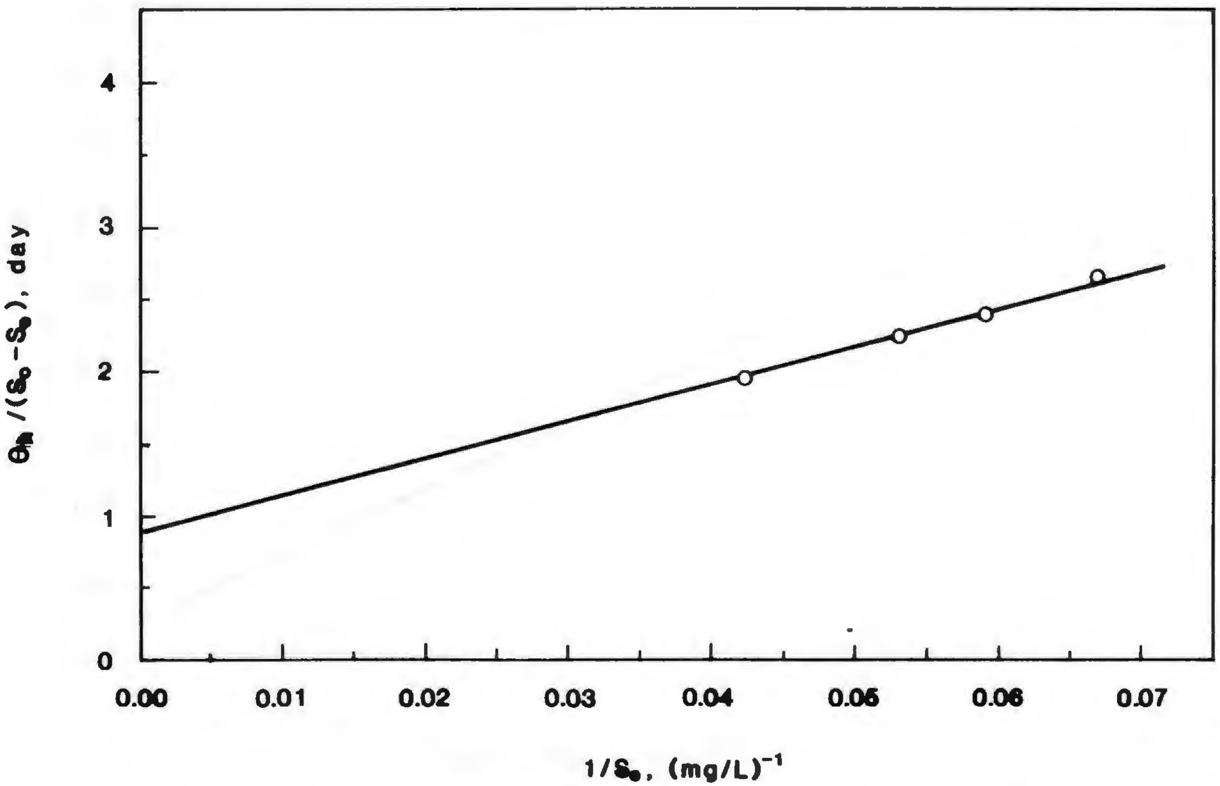

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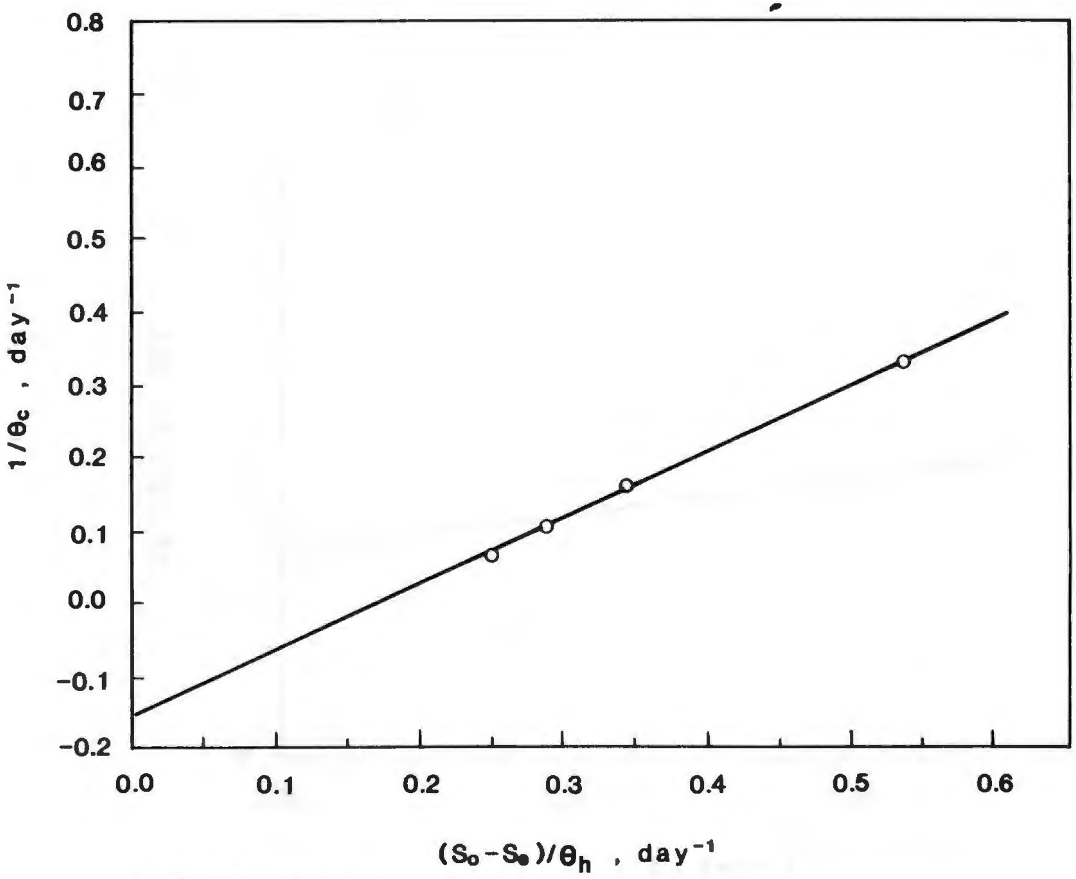

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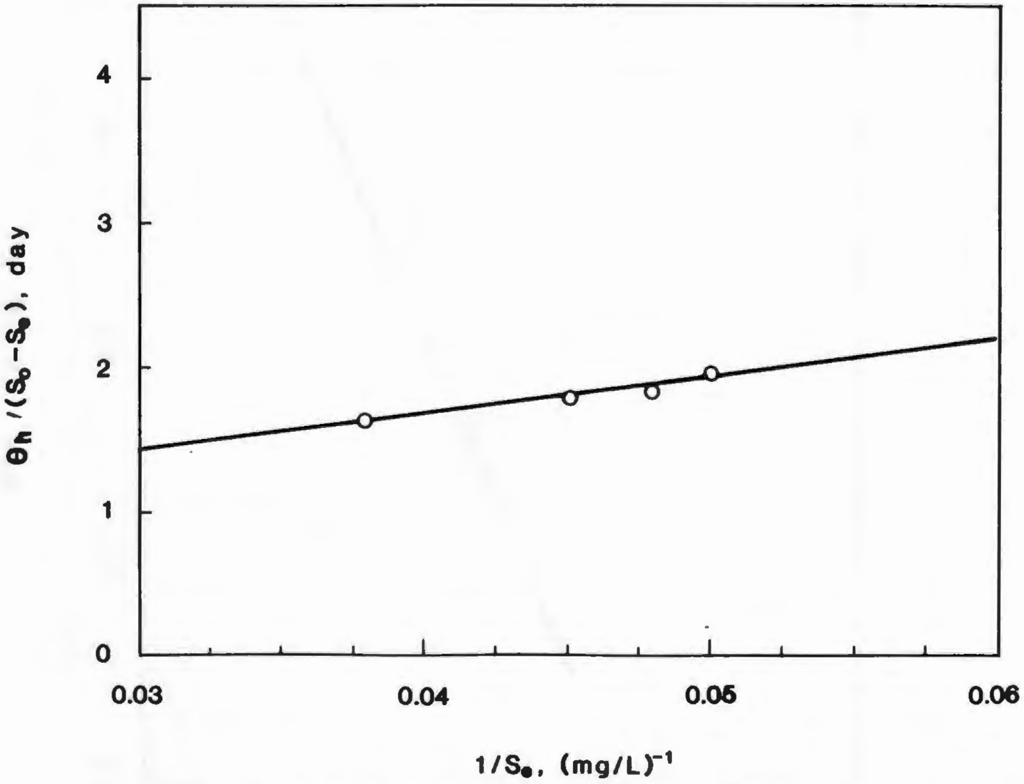

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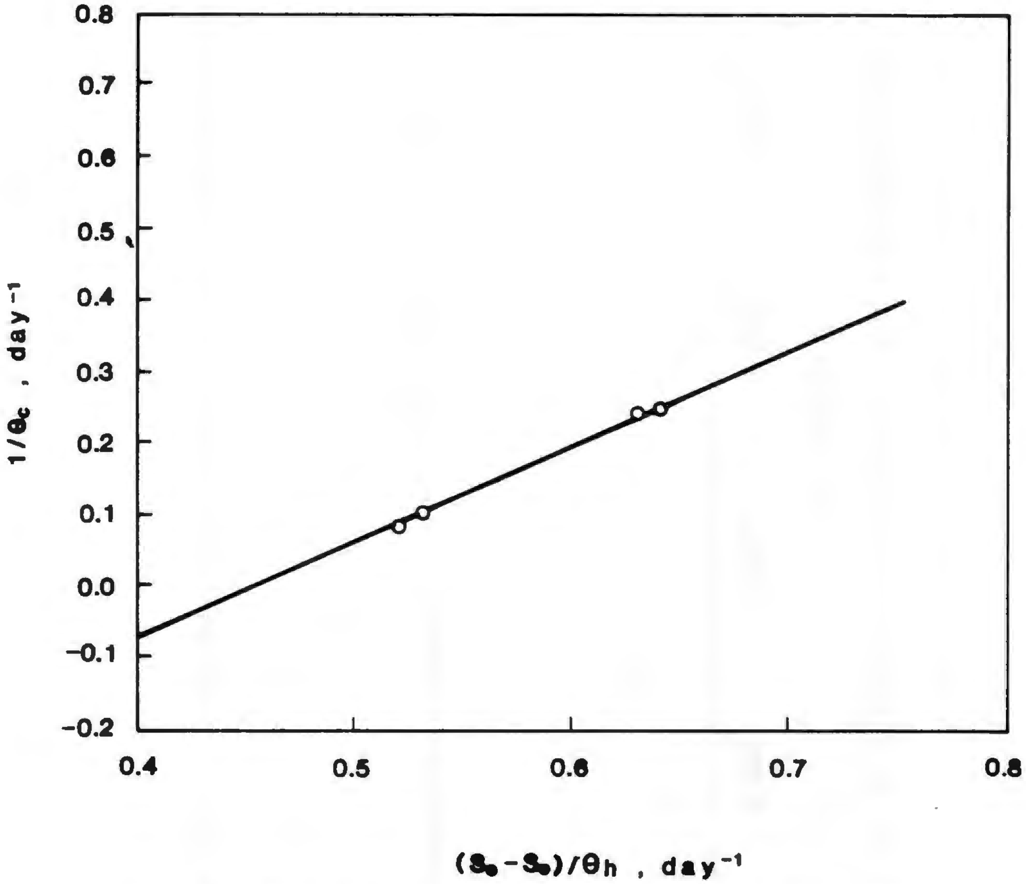

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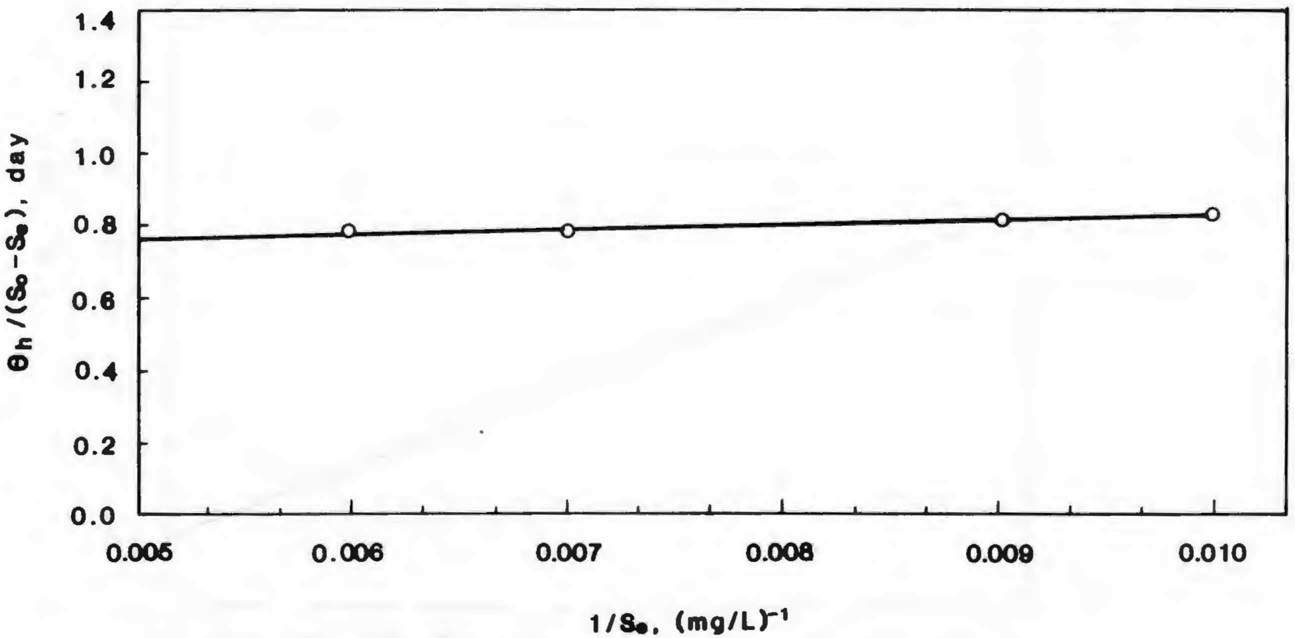

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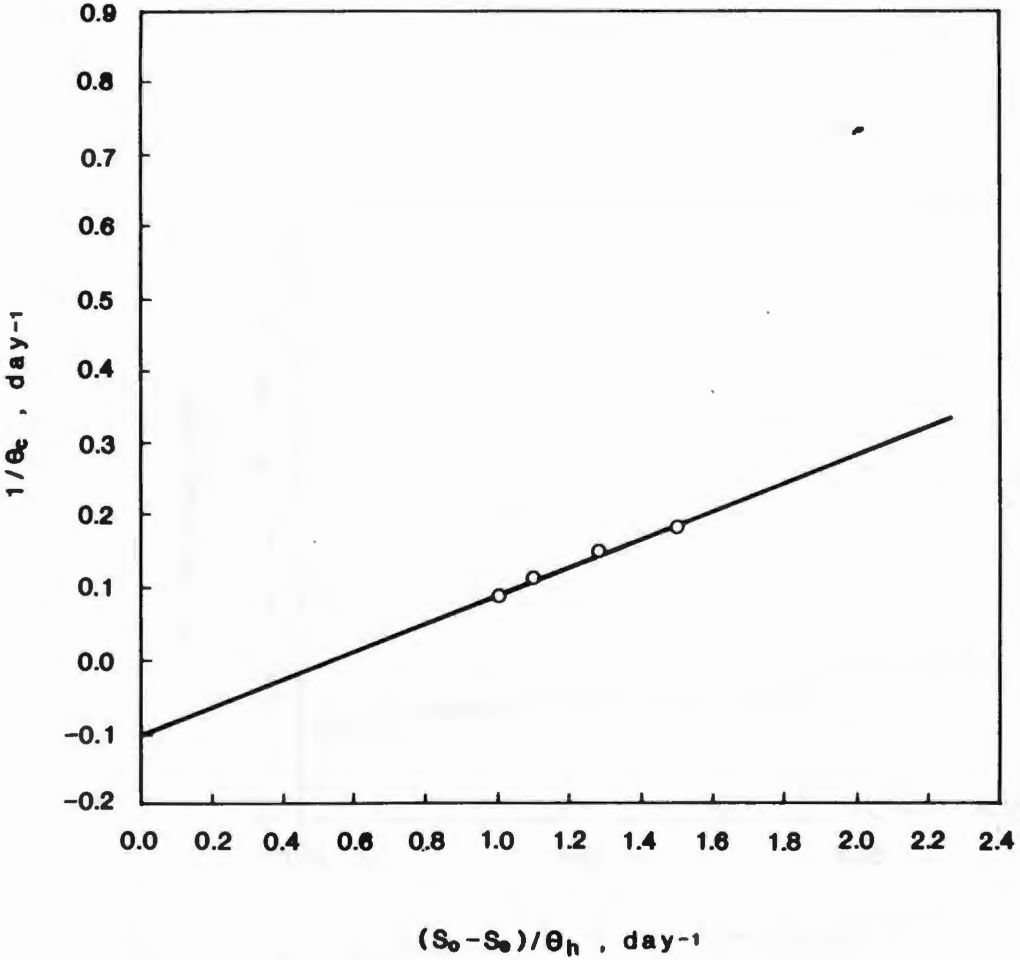

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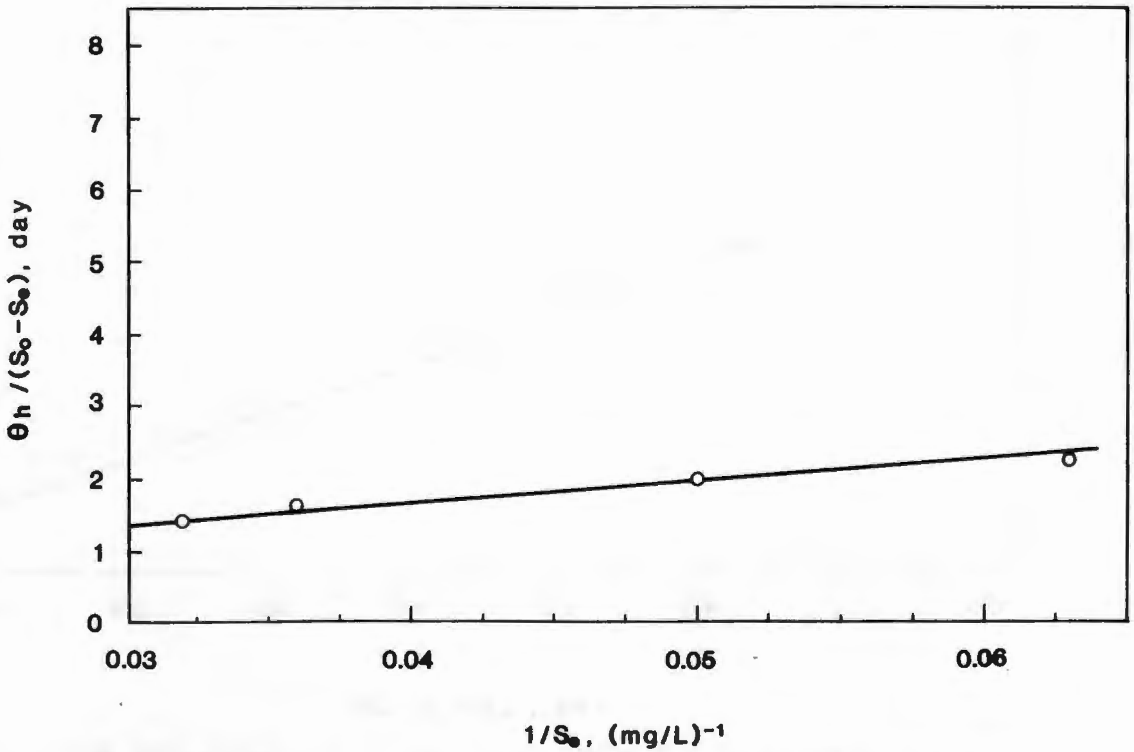
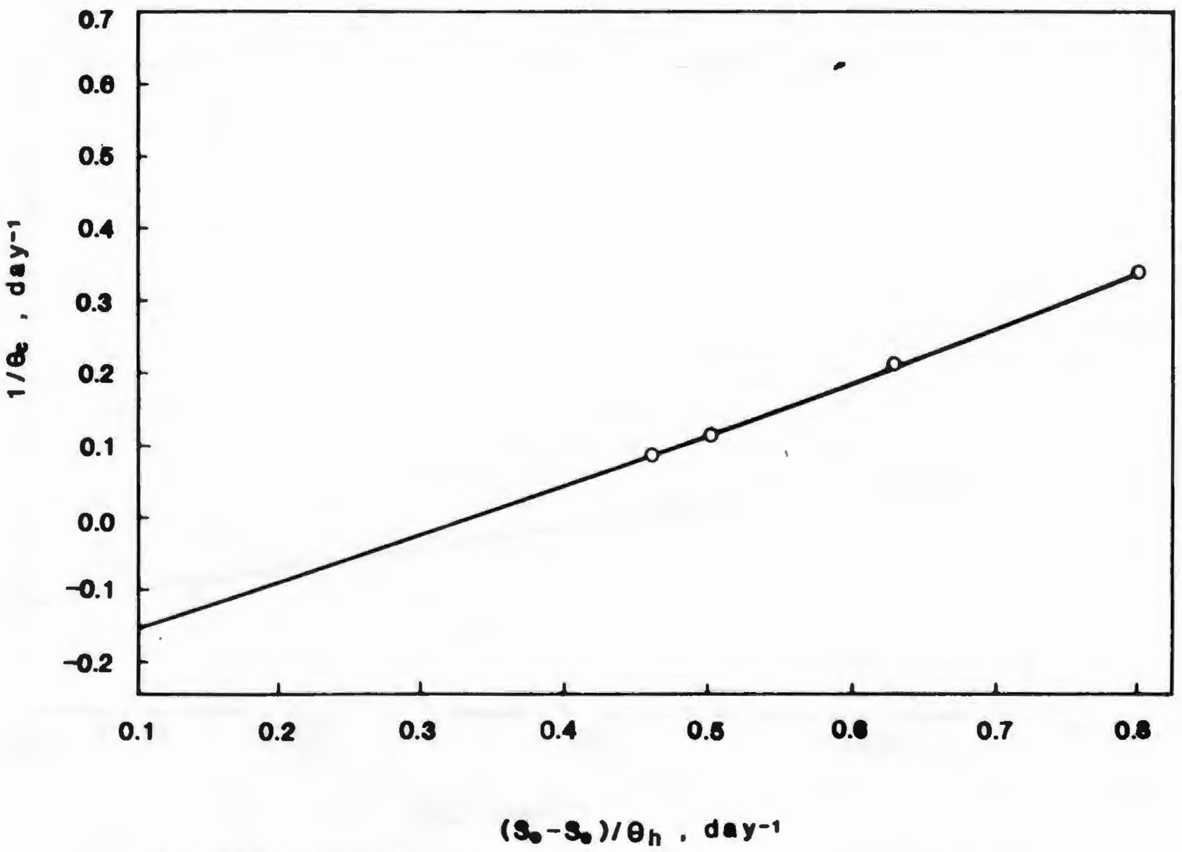
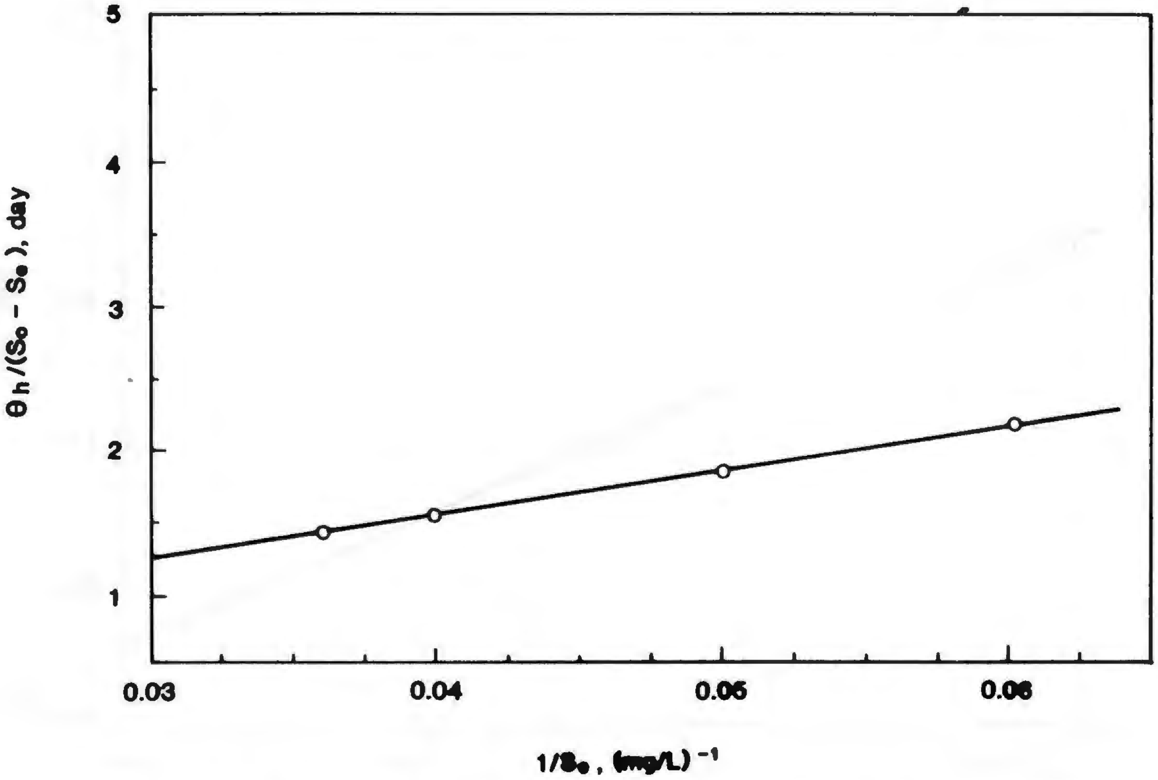


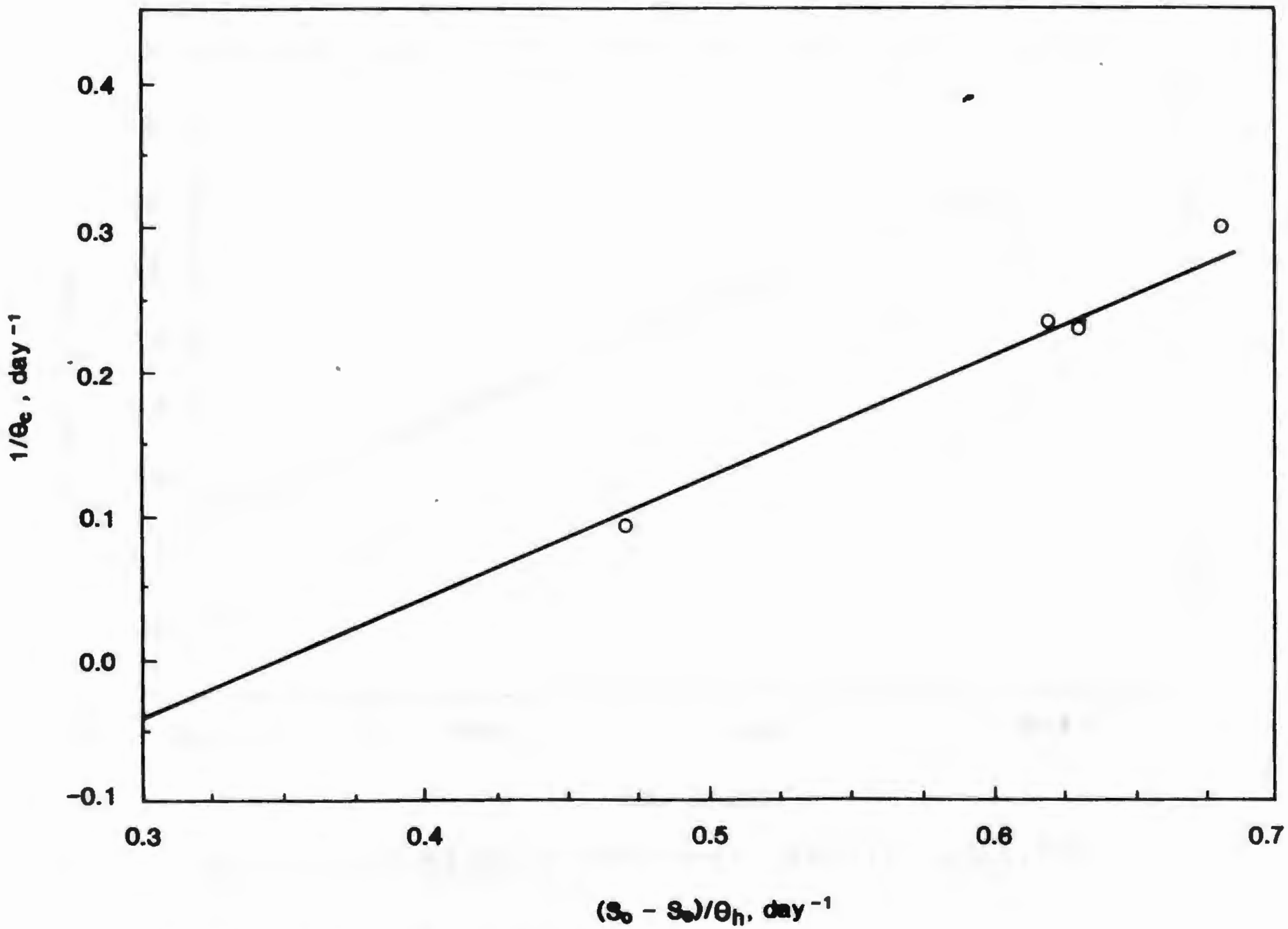
A.2.17 Bio-kinetic Constants, PAC=50 mg/L,TOC



A.2.18 BIO-kinetic Constants, PAC=50 mg/L,TOC



A.2.19 Bio-kinetic Constants, PAC=120 mg/L,BOD



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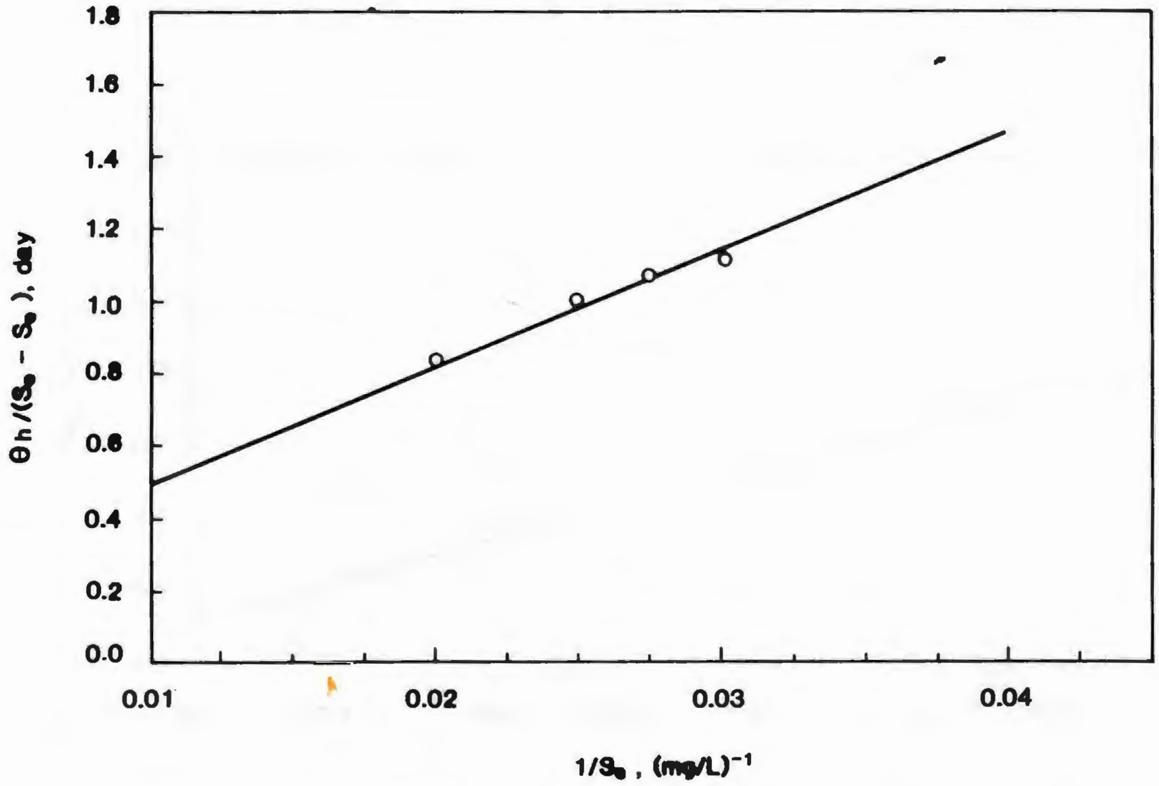

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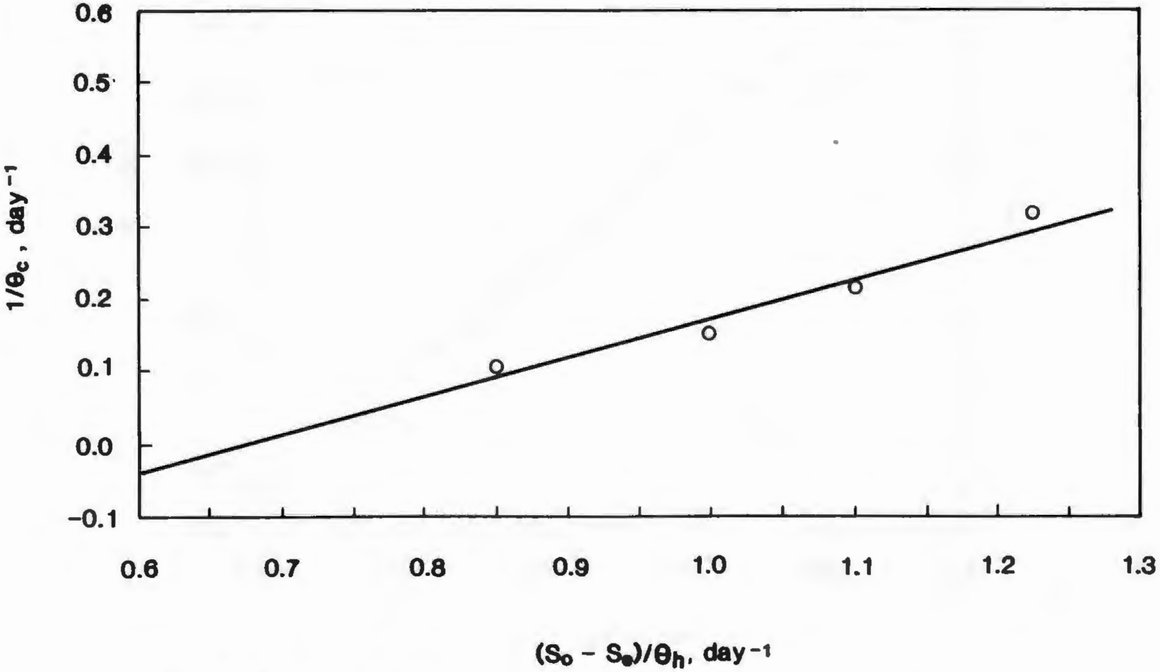

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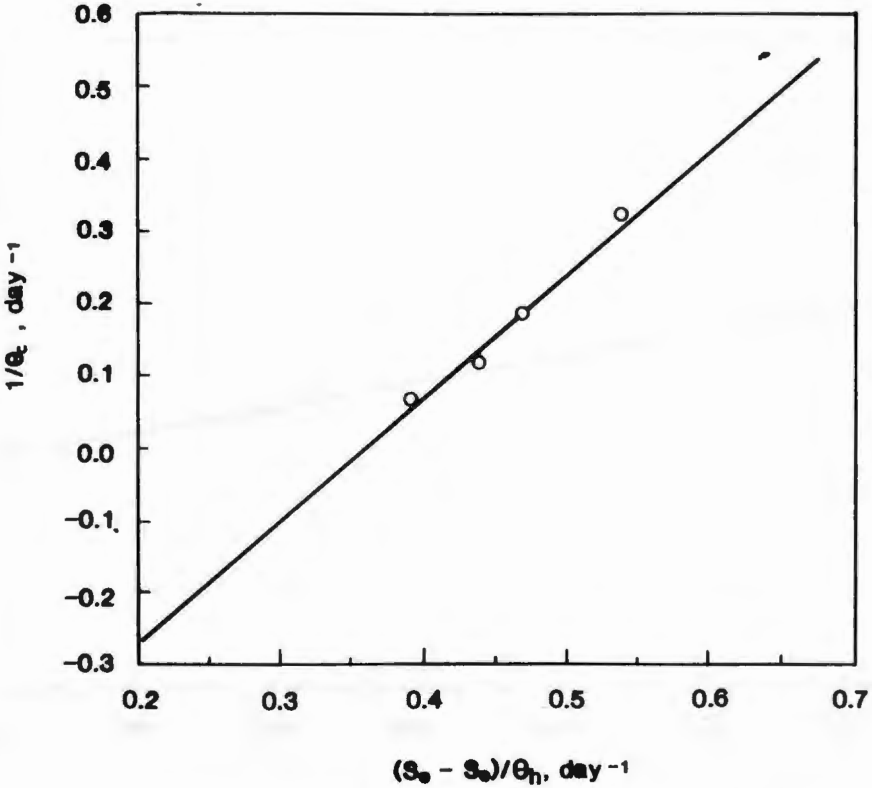

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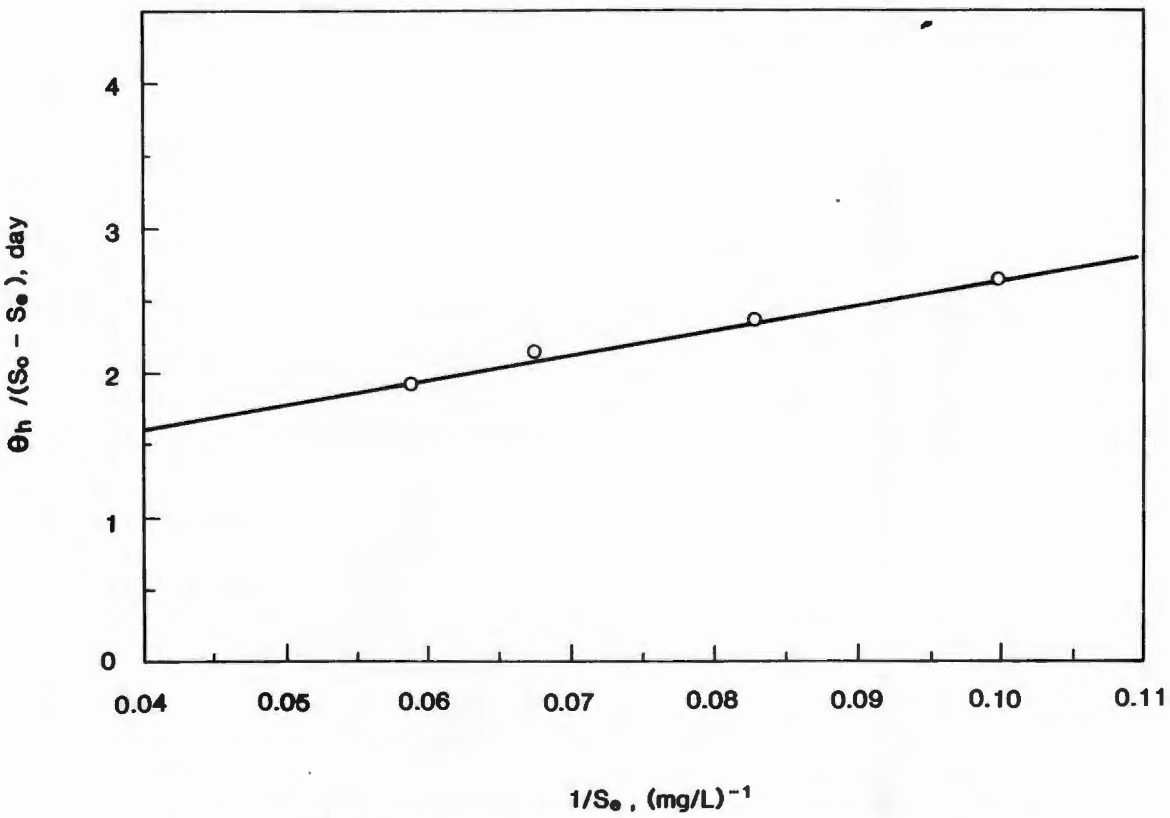
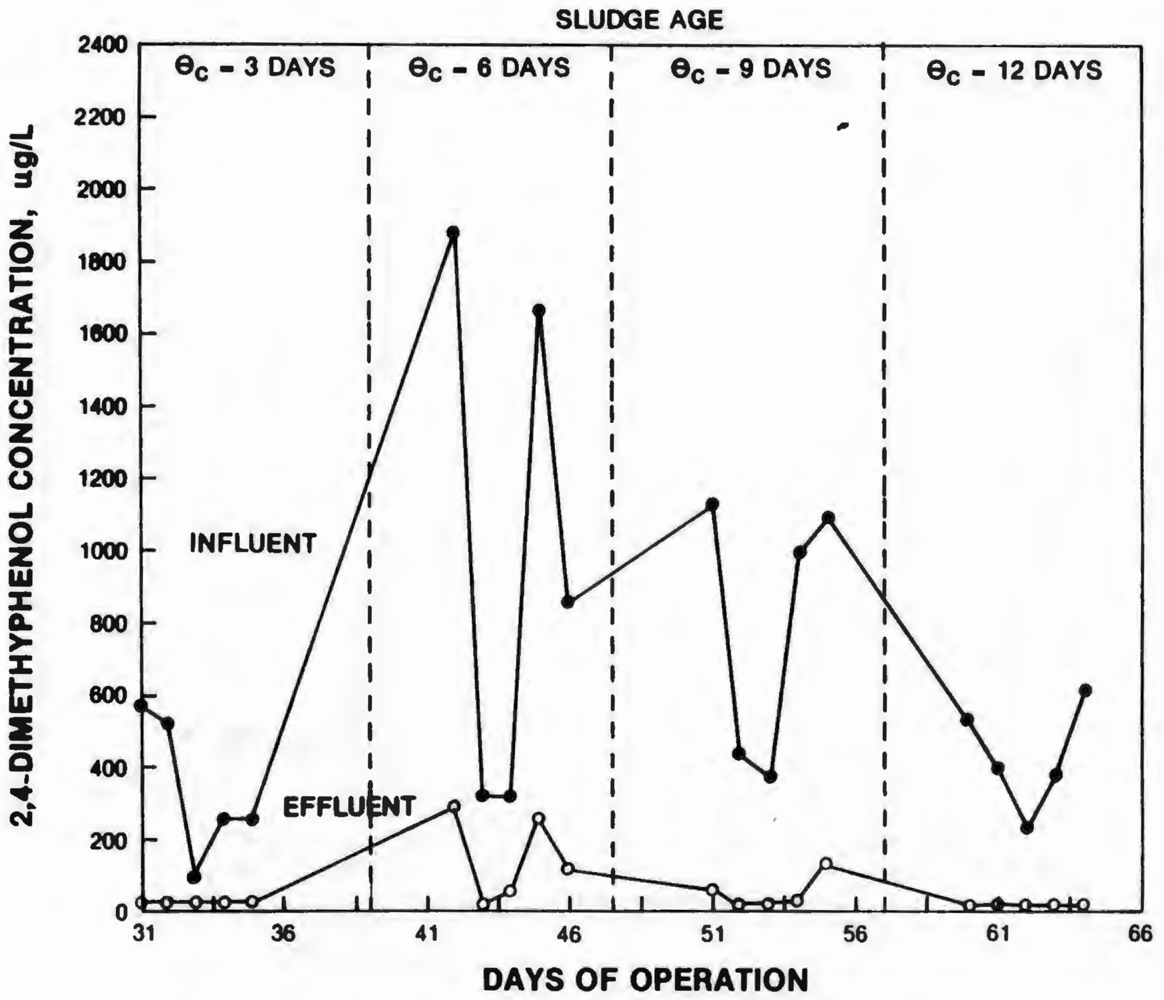


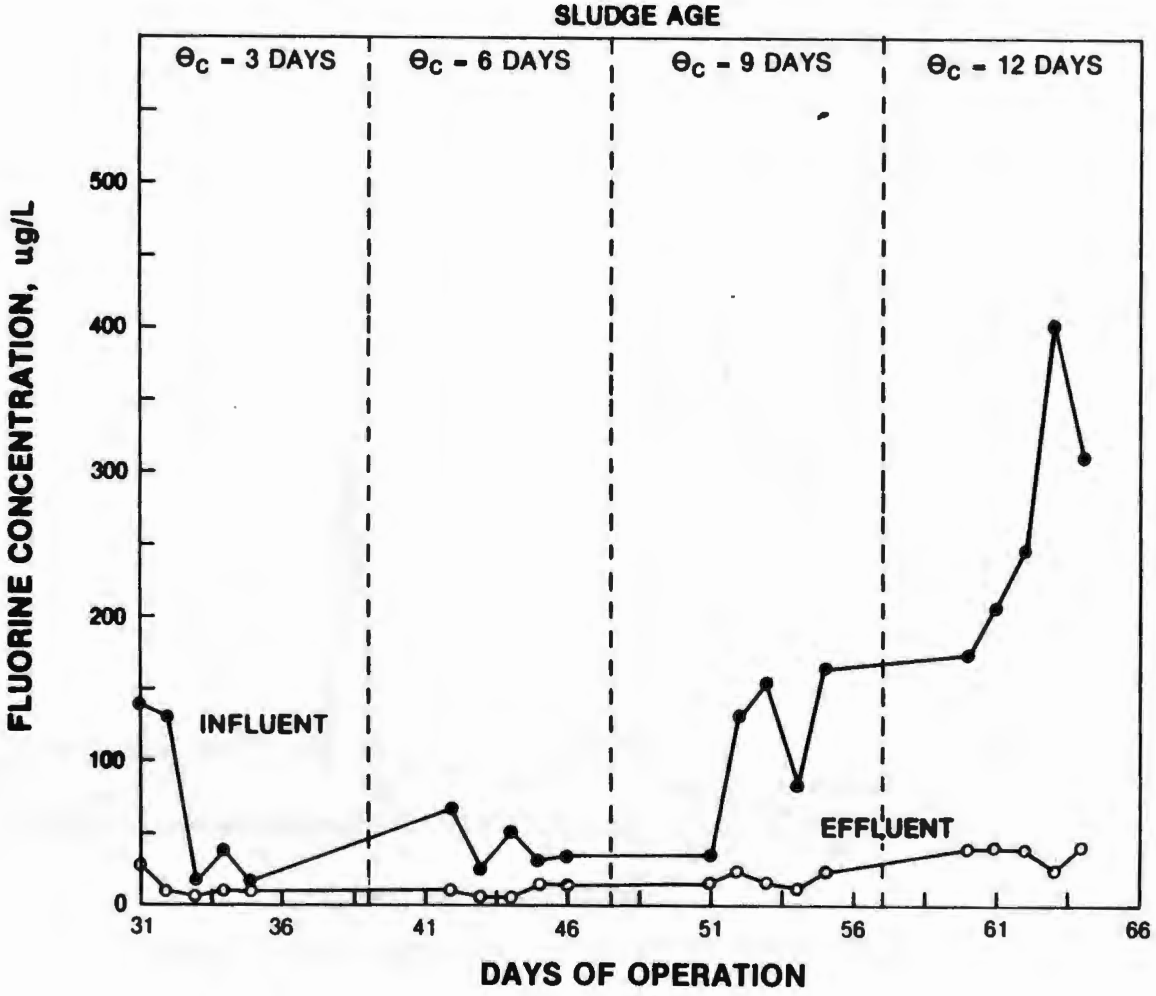
A.2.24 Bio-kinetic Constants, PAC=120 mg/L,TOC

Appendix 3

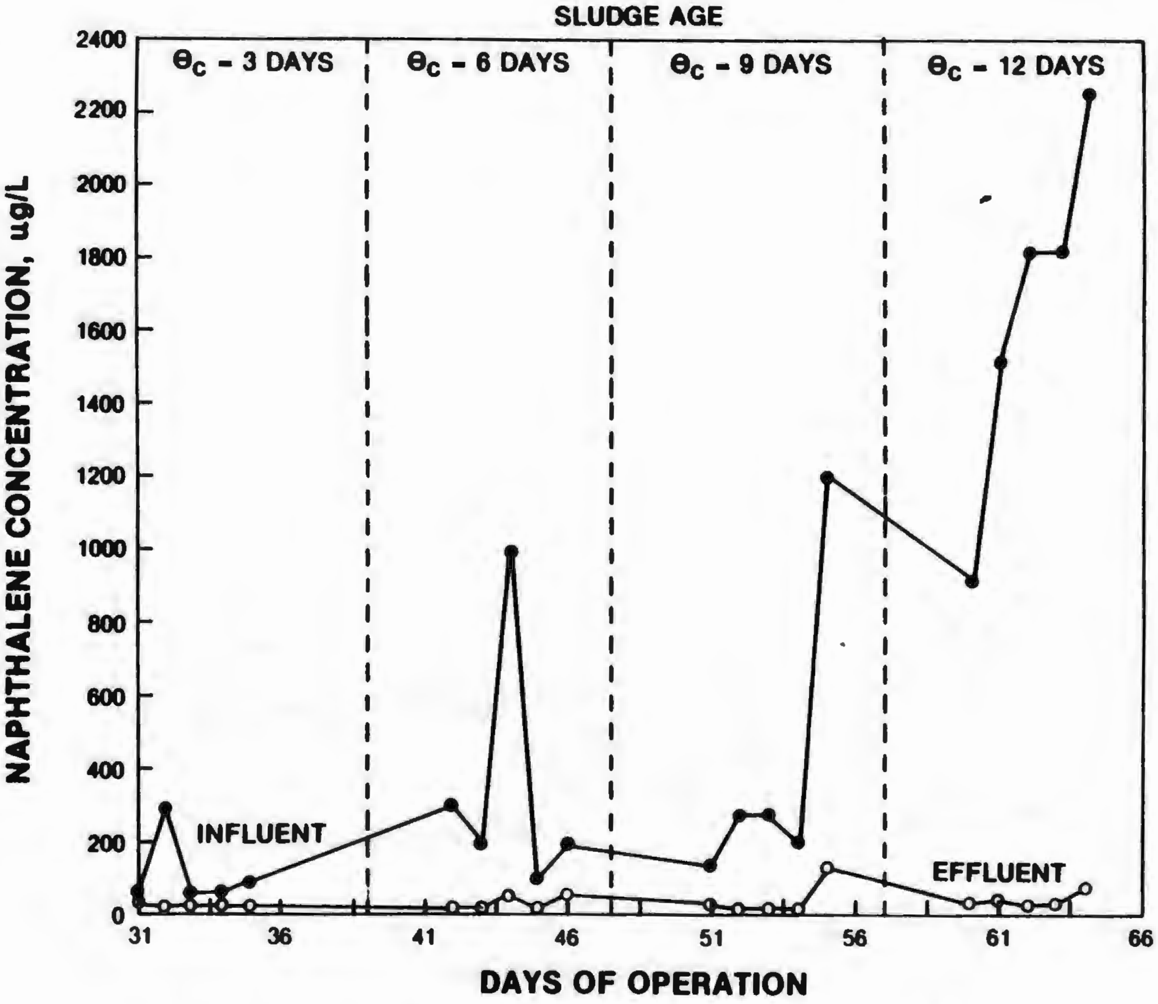
Experiment 1: Figures for Priority Pollutants Removal



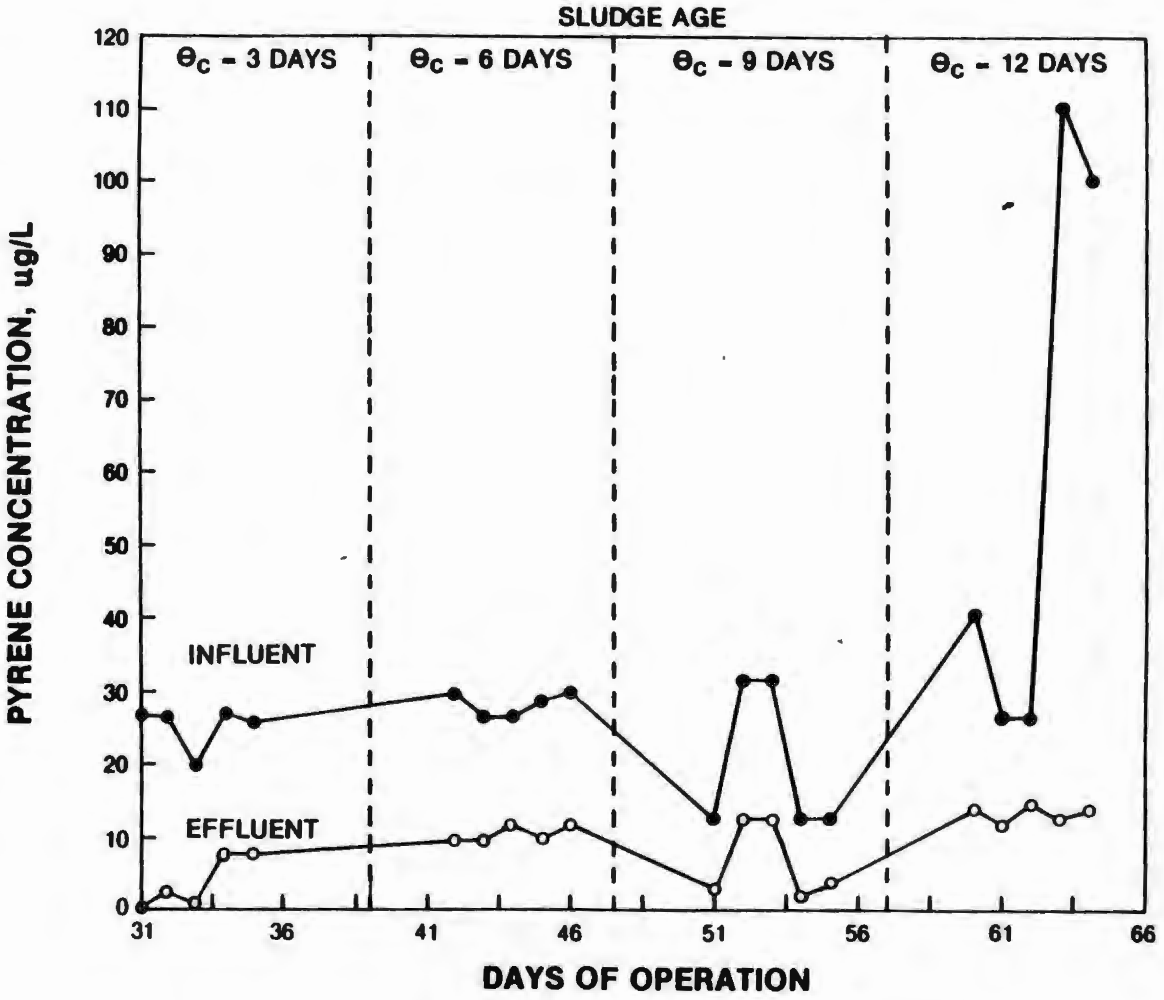
A.3.1 2,4-Dimethylphenol Removal by Activated Sludge



A.3.2 Fluorene Removal by Activated Sludge



A.3.3 Naphthalene Removal by Activated Sludge

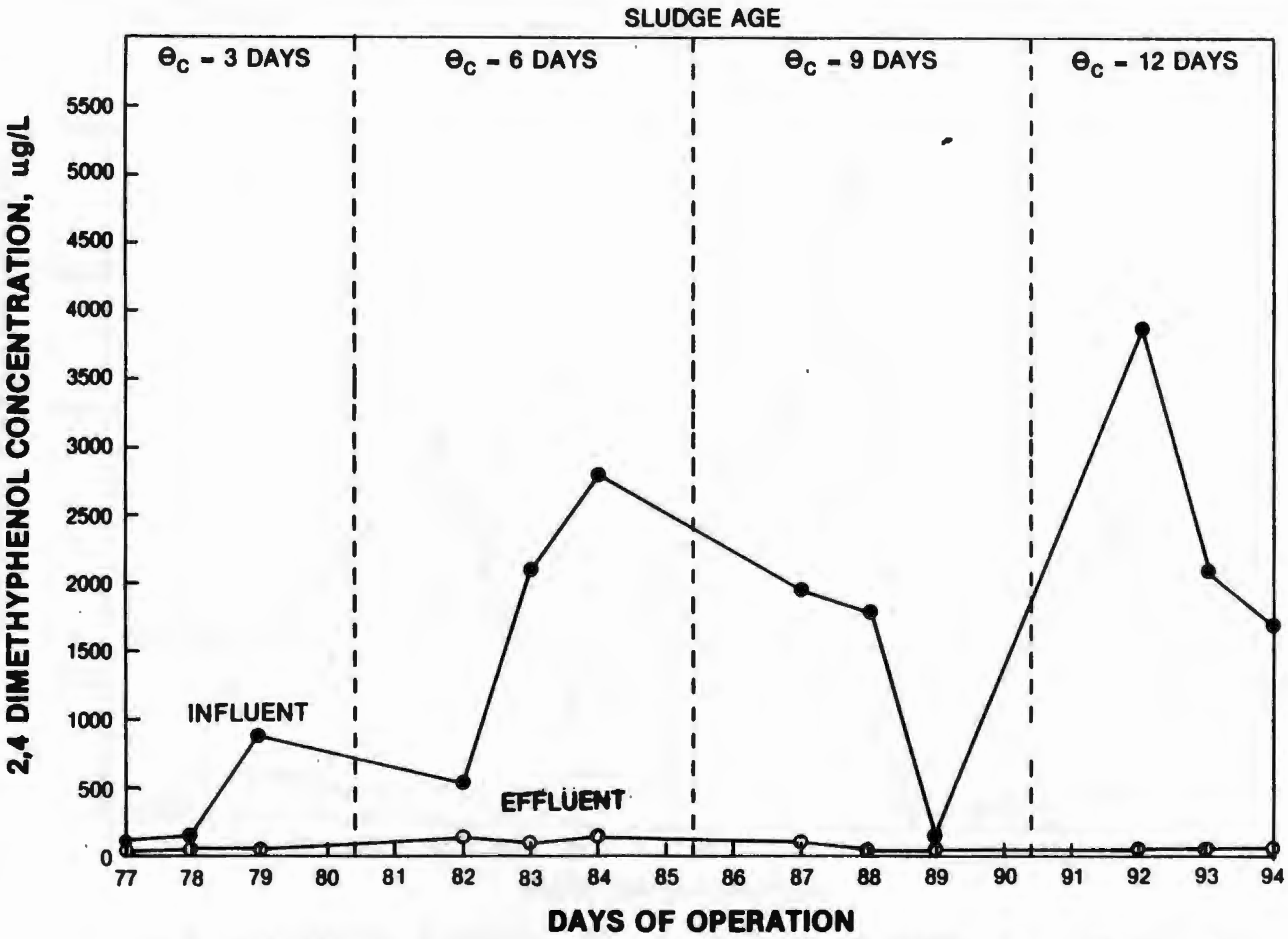


A.3.4 Pyrene Removal by Activated Sludge

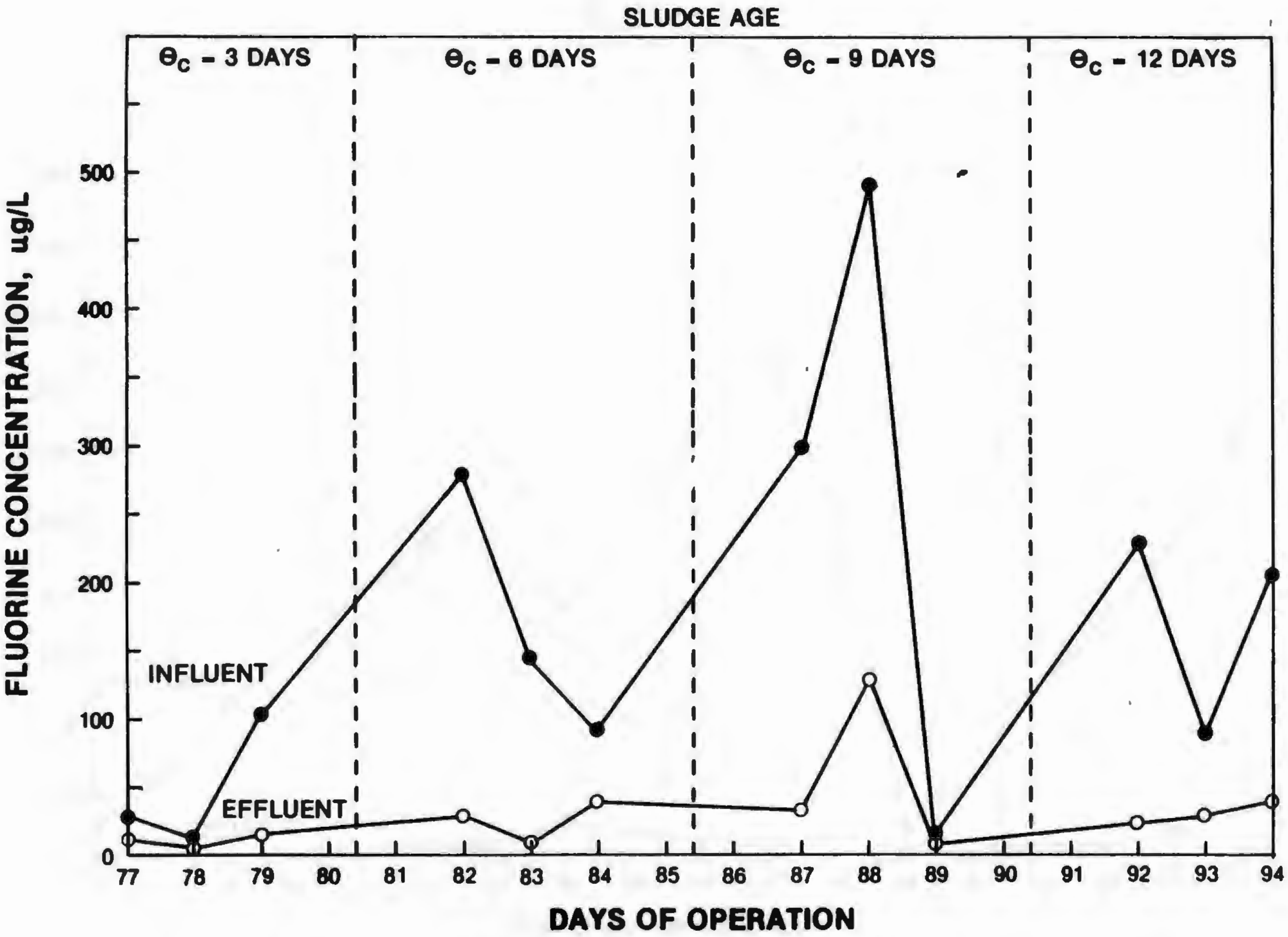
Appendix 4

Experiment 2: Figures for Priority Pollutants Removal

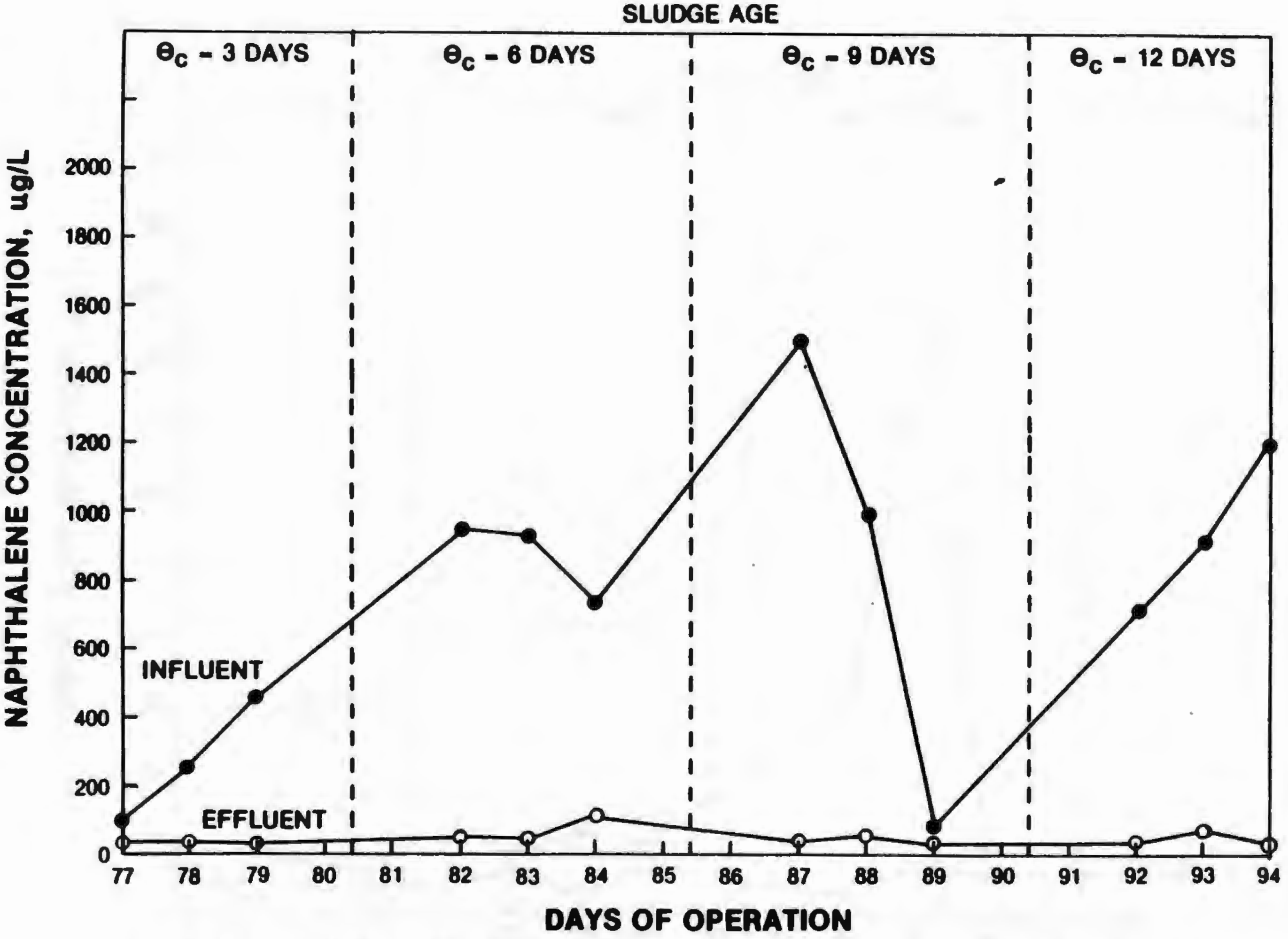
PAC= 10, 50, and 120 mg/L



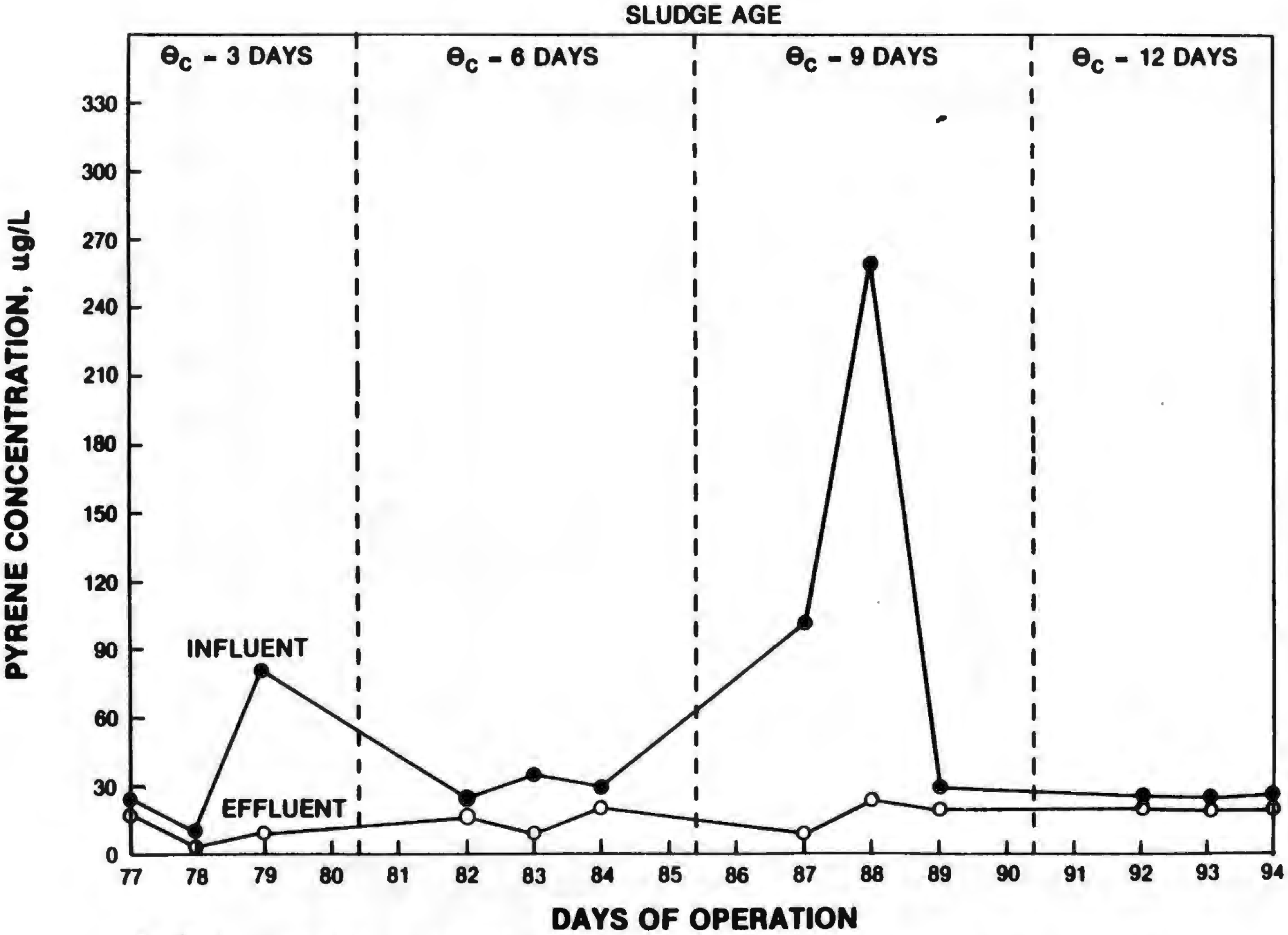
A.4.1 2,4-Dimethylphenol Removal by Activated Sludge and Powdered Activated Carbon PAC=10 mg/L



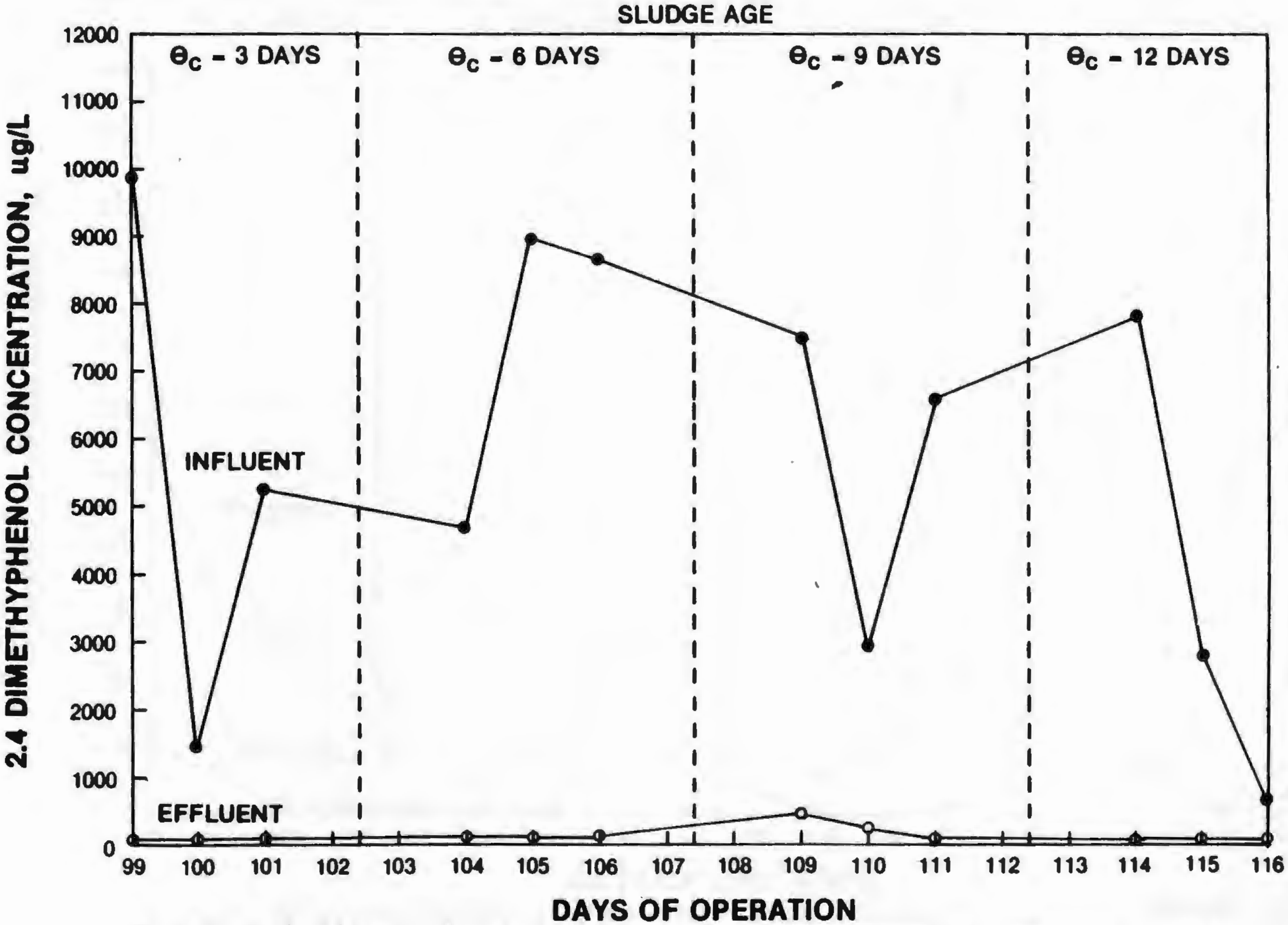
A.4.2 Fluorene Removal by Activated Sludge and Powdered Activated Carbon PAC=10 mg/L



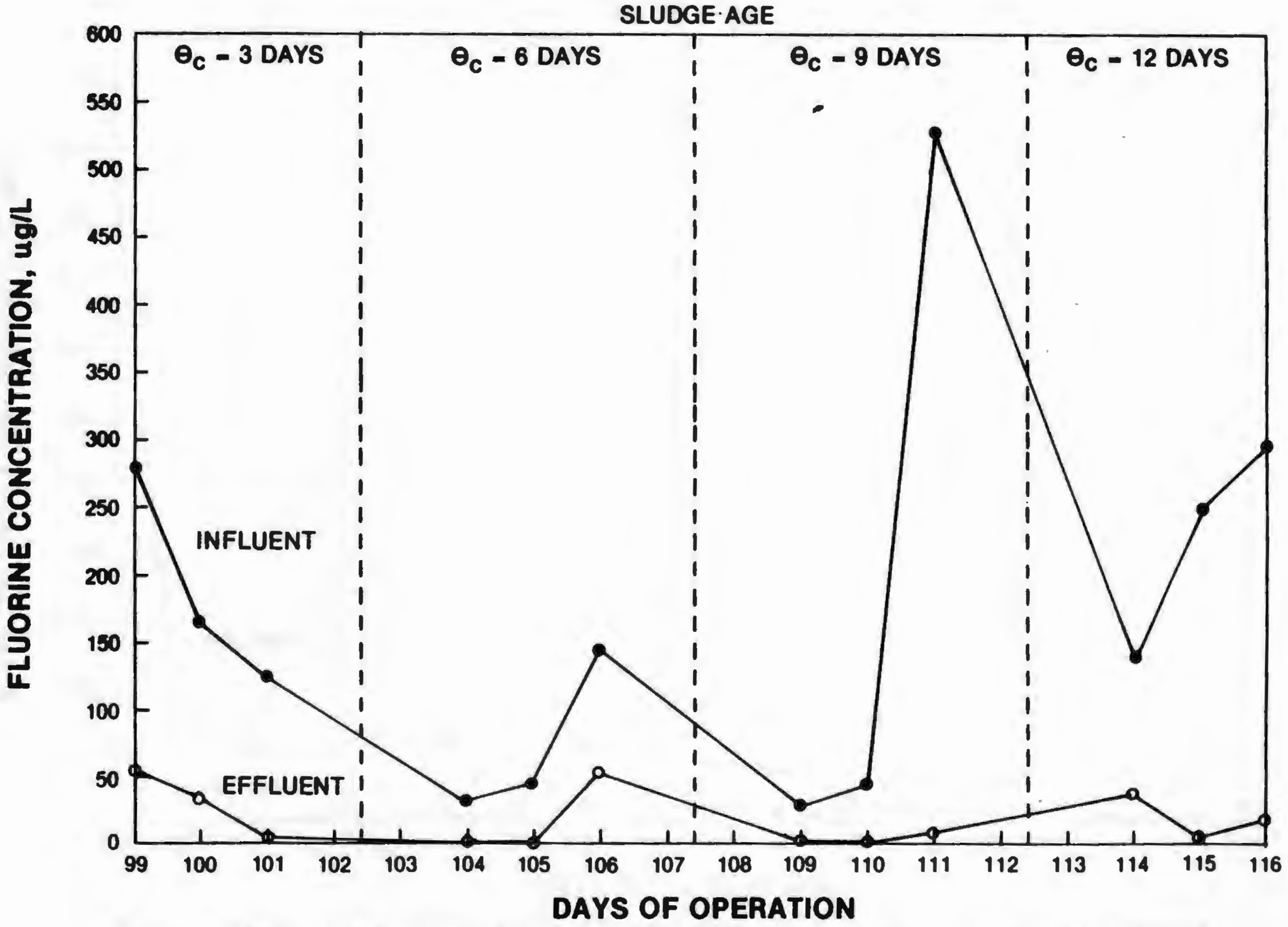
A.4.3 Naphthalene Removal by Activated Sludge and Powdered Activated Carbon PAC=10 mg/L



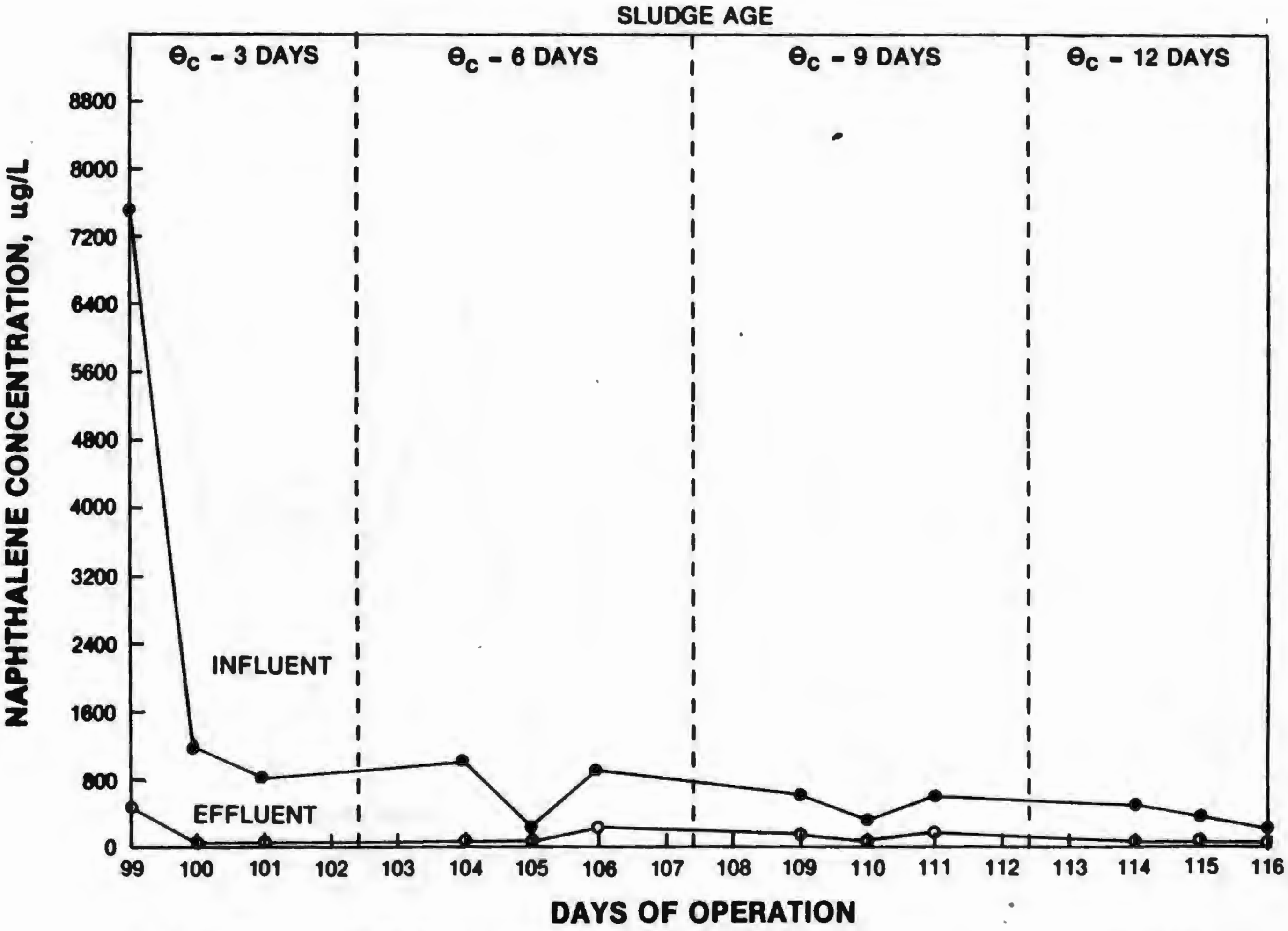
A.4.4 Pyrene Removal by Activated Sludge and Powdered Activated Carbon PAC=10 mg/L



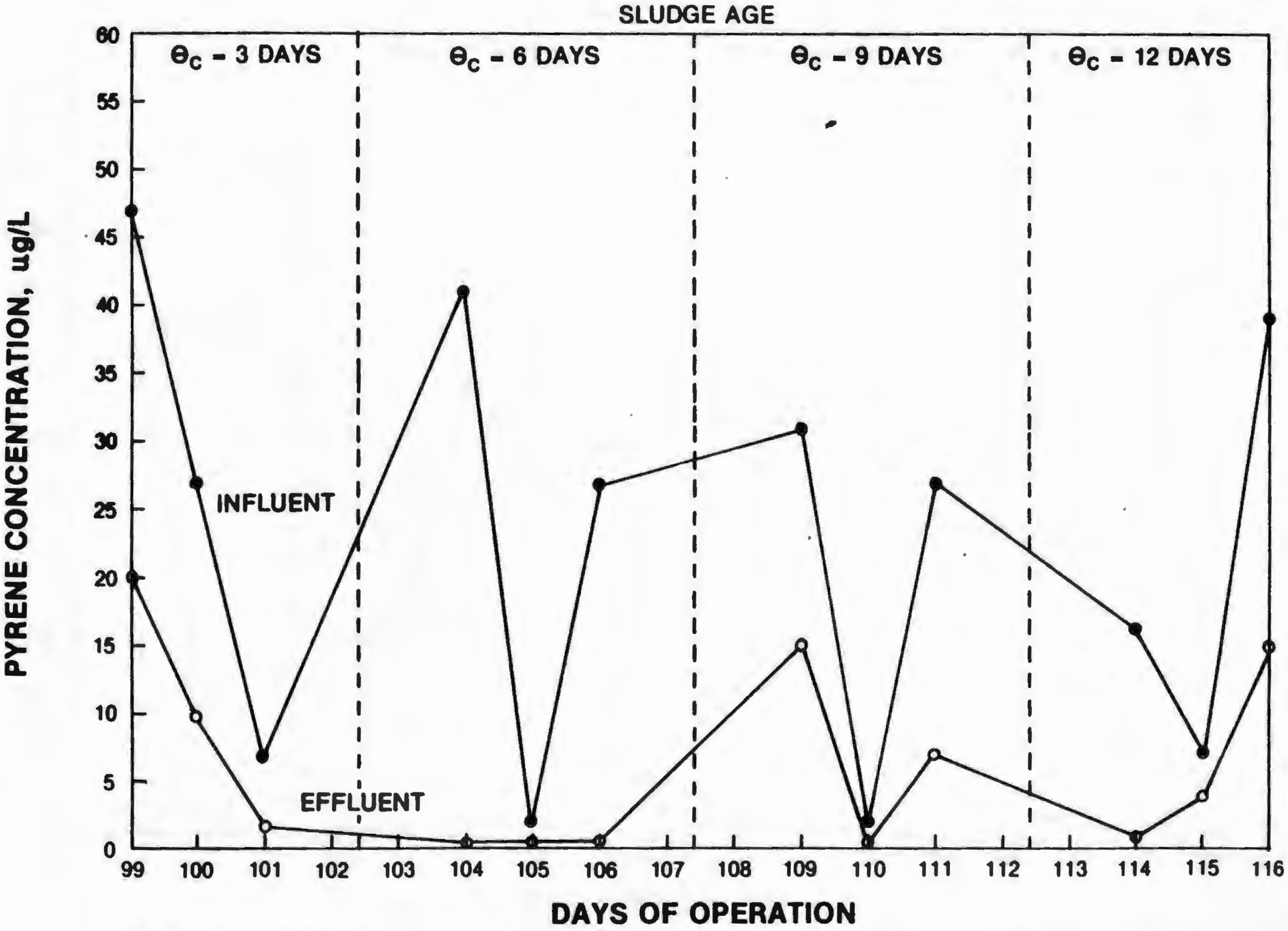
A.4.5 2,4-Dimethylphenol Removal by Activated Sludge and Powdered Activated Carbon PAC=50 mg/L



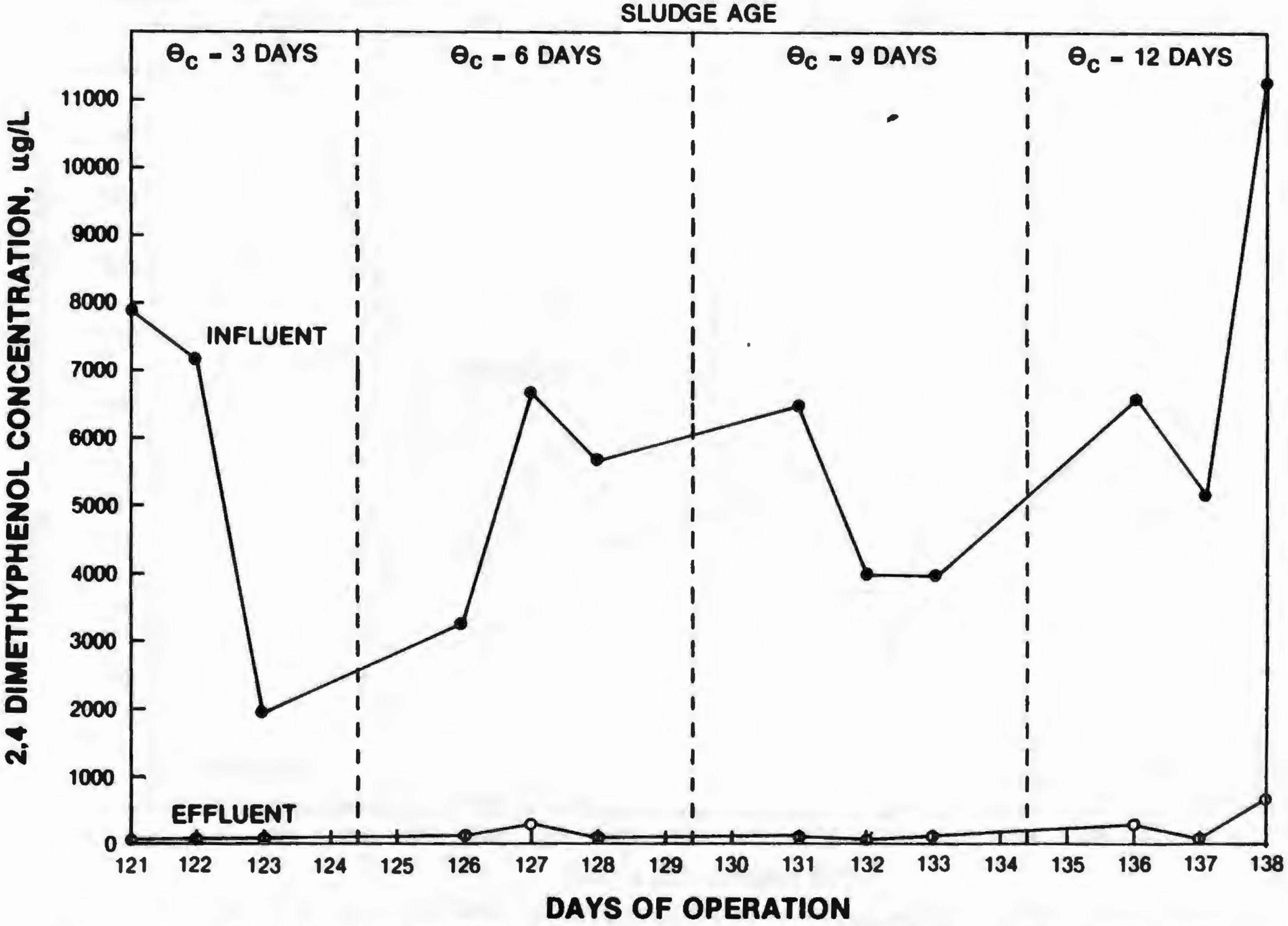
A.4.6 Fluorene Removal by Activated Sludge and Powdered Activated Carbon PAC=50 mg/L



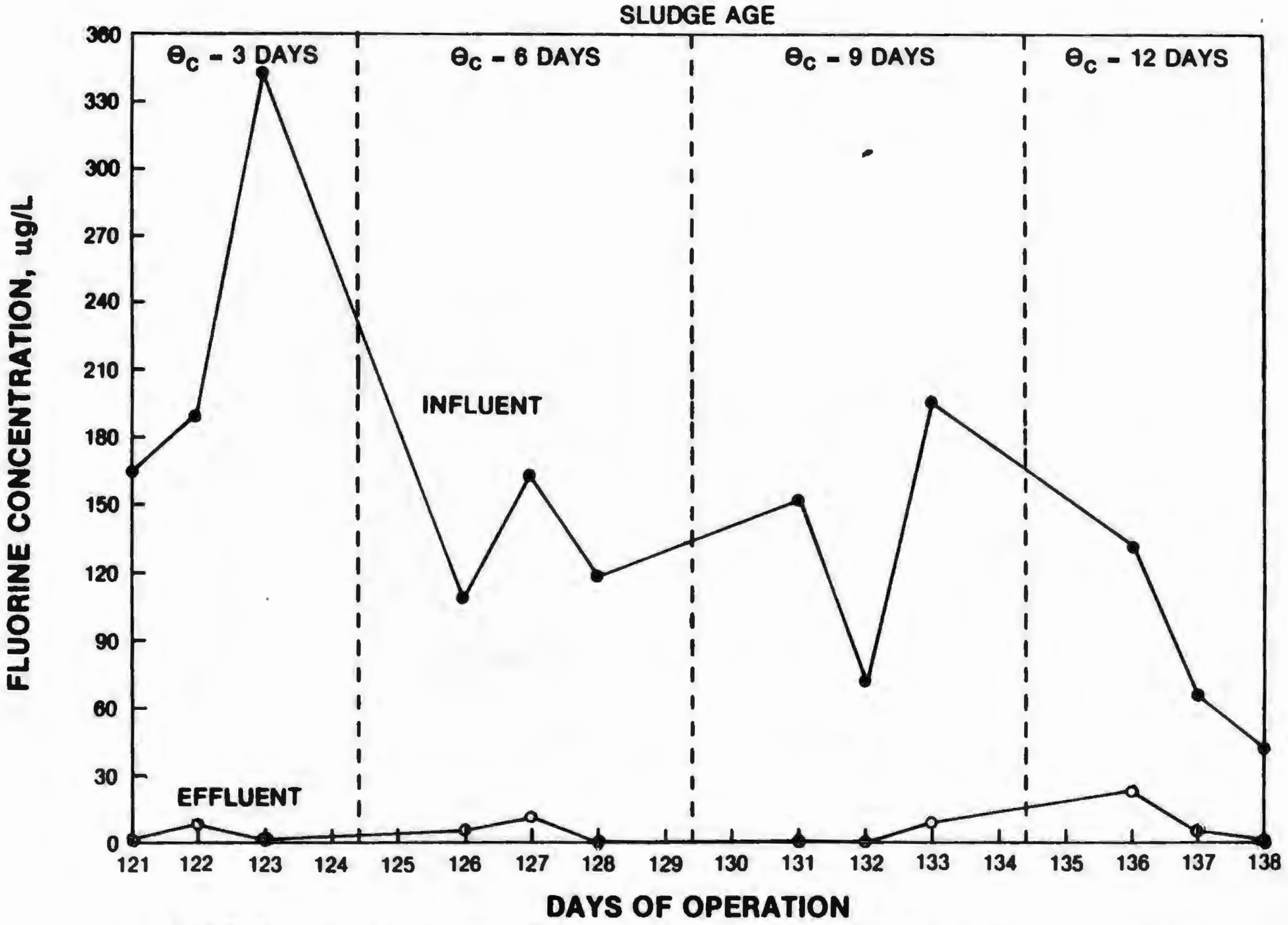
A.4.7 Naphthalene Removal by Activated Sludge and Powdered Activated Carbon PAC=50 mg/L



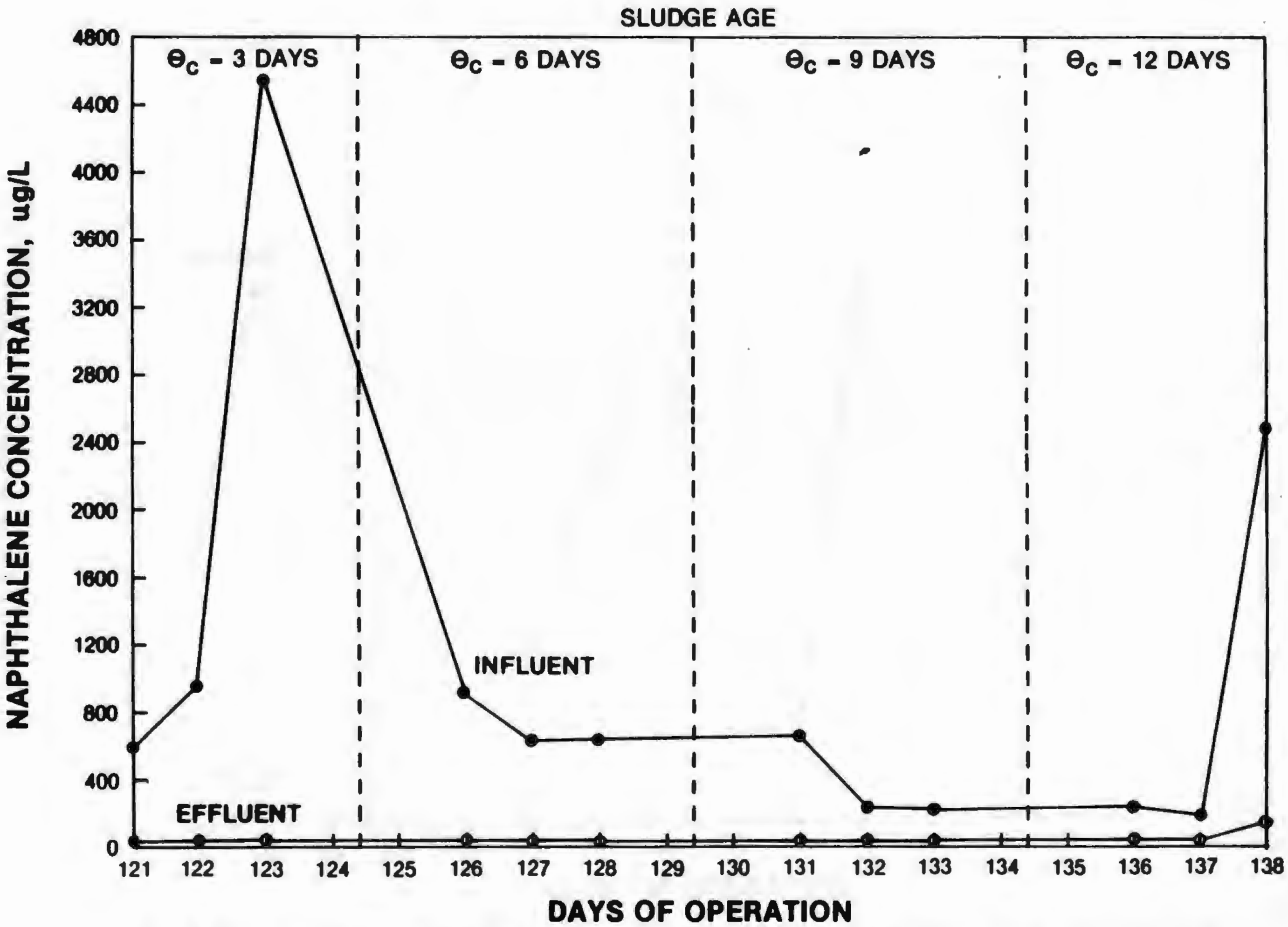
A.4.8 Pyrene Removal by Activated Sludge and Powdered Activated Carbon PAC=50 mg/L



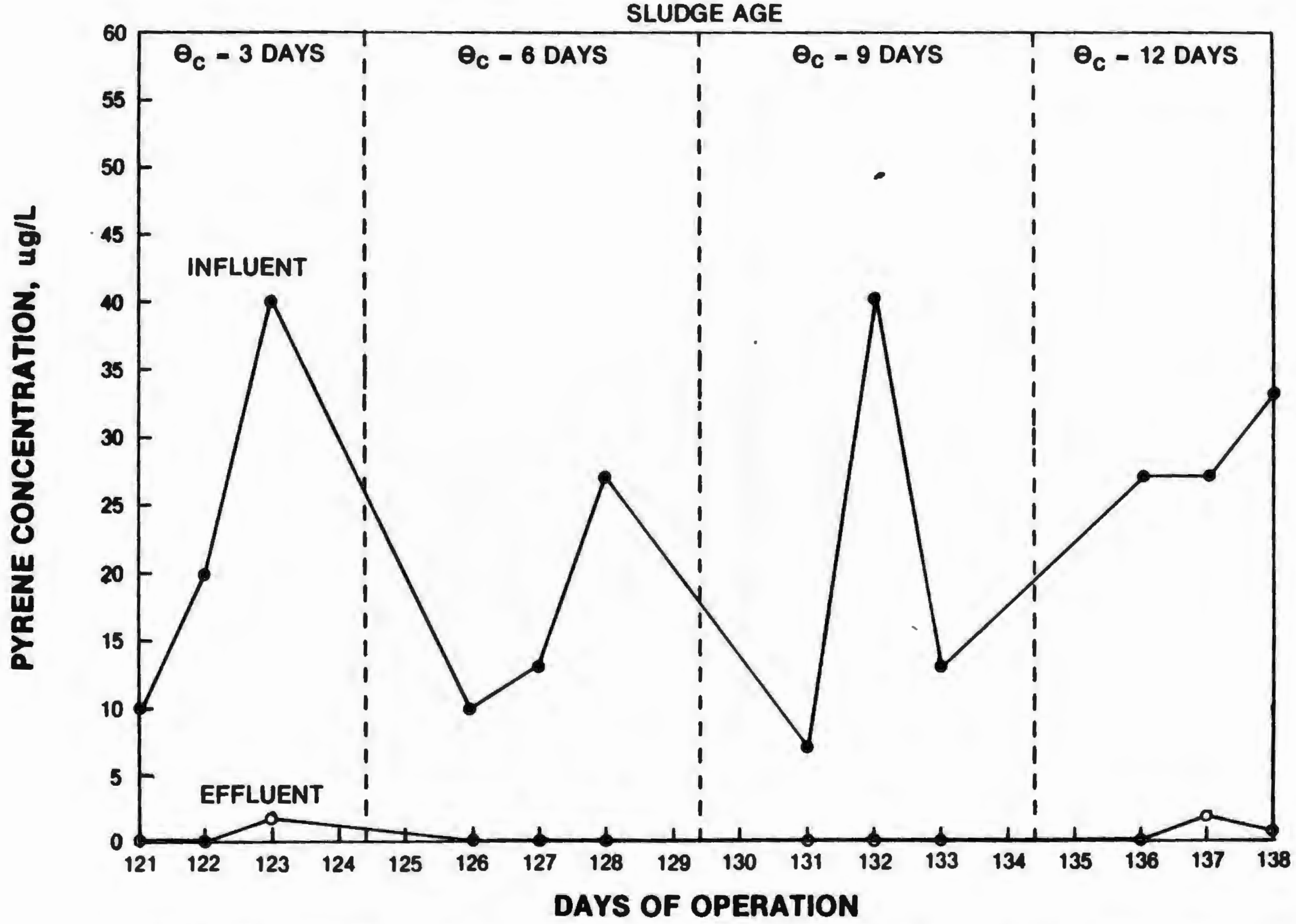
A.4.9 A.4.9 2,4-Dimethylphenol Removal by Activated Sludge and Powdered Activated Carbon PAC=120 mg/L



A.4.10 Fluorene Removal by Activated Sludge and Powdered Activated Carbon PAC=120



A.4.11 Naphthalene Removal by Activated Sludge and Powdered Activated Carbon PAC=120 mg/L



A.4.12 Pyrene Removal by Activated Sludge and Powdered Activated Carbon PAC=120 mg/L

Appendix 5

Modification of Purgeable Halocarbons Method 601

Method for Purgeable Halocarbons

This method is a modification of the EPA Test Method No. 601.

Compounds Determined by this Method

1. Chloroform

Method Summary

A 5 ml water sample is purged with helium gas at ambient temperature. Concentrations of halocarbons in water greater than 10 ug/L can be detected using gas chromatography. The halocarbons in the resulting vapor are trapped on a sorbent trap. After purging is completed, the trap is heated and backflushed with inert gas to absorb the halocarbons and transporting them to a GC column where they are separated and analyzed with a Hall detector.

Apparatus and Materials

- Tekmar LSC-2 purgeable unit
- Tracor 565 with 700A Hall Electrolytic Conductivity Detector
- GC Column - 1% SP-1000 on Carbopack B (60/80 mesh), 8 feet glass

- Three state trap: Tenax/Silica gel/Charcoals (12" X 1/8")
- Distilled water

Standard Preparation

Stock standards are prepared at the beginning of the test. Positive confirmation for the standard was made by spiking the GC.

Each standard is prepared as follows: A 10 ml ground glass stoppered volumetric flash is filled to about 9.8 ml of methanol and allowed to stand unstoppered for 10 minutes before weighing to the nearest 0.1 mg. A 100 ul syringe is used to add 2-3 drops of each liquid standard to the methanol. The drops must not contact the neck of the flask. The flask is reweighed, diluted to volume. Secondary dilution of each stock of 1/10 in distilled water is made. Working standards are prepared by adding 1 ml of the stock solution to 100 ml of distilled water. Dilutions of secondary solution are prepared yielding standards around 10 ug/L or higher. Working standard are stored in 40 ml teflon lined screw cap vials until used on the same day.

Sampling

Samples are collected in triplicate in 40 ml screw cap vials with teflon lines septa. The vials are filled so that no headspace remains. Then, samples are refrigerated in the laboratory.

Standard and Sample Analysis

A 5 ml syringe is filled with sample and the sample is then loaded into the Tekmar sampler. The sample is purged at room temperature for 15 minutes with helium at 40 ml/min, then desorbed at 200°C for 4 minutes with helium at 30 ml/min. The trap is baked at 180°C for 7 minutes. The GC conditions for HALL are the following:

Initial temperature	45°C
Final temperature	200°C
Program rate	8°C/min
Initial hold	3 min.
Detector temperature	200°C
Injection temperature	200°C
Final hold	15 min.
Carrier gas, He	40 ml/min
Reaction gas, H_2	50 ml/min

External Standard Quantitation

Compounds are quantitated by comparing sample peak areas and standard peak areas. Peaks are identified by retention time.

Quality Control

1. A method blank is run every day to make the system is free of interferences.
2. Standards are run for Retention Times to evaluate laboratory data quality.
3. EPA Quality Control Check Samples are run to insure the accuracy of our analytical system.

Appendix 6

Modification of Volatile Aromatics Method 602

Method for Volatile Aromatics

This method is a modification of the EPA Test Method No. 602.

Compound Determined by this Method

1. Benzene
2. Ethylbenzene
3. Toluene
4. M-Xylene
5. O-Xylene

Method Summary

A 5 mL water sample is purged with helium at ambient temperature. The aromatics in the resulting vapor are trapped on a sorbent trap. The trap was rapidly heated and backflushed, desorbing the aromatics and transporting them to a GC column where the were separated and analyzed with a PID. Concentrations of volatile aromatics in wastewater greater than 10 ug/L can be detected at ambient temperature. Initially positive samples were confirmed by GC/MS. Positive confirmation for sample was made by spiking the GC as well.

Apparatus and Materials

- Tekmar Model LSC-2
- Tracor Model No. 565 with Photoionization Detector (PID)
- GC Column - 1% SP-1000 on Carbopack B (60/80 mesh), 8 feet glass
- Three state trap: Tenax/Silica gel/Charcoals (12" X 1/8")
- Organic Free water

Standard Preparation

Stock standards are prepared. A 10 ml ground glass-stoppered volumetric flask is filled with 9.8 ml of methanol and allowed to stand unstoppered for 10 minutes or until all alcohol wetted surfaces have dried before weighing to the nearest 0.1 mg. A 100 ul syringe is used to add 3 drops of each liquid standard to the methanol. The drops must not contact the neck of the flask. The flask is re-weighed, diluted to volume, stoppered and mixed by inverting the flask several times. The concentration calculated in ug/uL or in gm/ml. Stock standard solutions transferred into a Teflon-sealed screw-cap bottle and stored in the freezer. A secondary dilution of stock solution is prepared. Dilution standards are prepared by adding 1000 ul of stock solution to 100 ml of distilled water. Working standards are prepared and stored in a 100 ml or in a 50 ml flask until used on the same day.

Sampling

Samples are collected in triplicate in 40 ml screw cap vials with teflon lined septa. The vials are filled so that no headspace remains.

Standard and Sample Analysis

5 ml syringe is filled with sample and then loaded into the Tekmar sampler. The sample is purged at room temperature for 15 minutes with helium at 40 ml/min., then desorbed 200°C for 4 minutes with helium at 40 ml/min. Then the trap is baked at 180°C for 7 minutes. The sampler is rinsed with distilled water. The GC conditions for PID are the following:

Initial temperature	45°C
Final temperature	200°C
Program rate	8°C/min
Initial hold	3 min.
Detector temperature	250°C
Injection temperature	200°C
Final hold	15 min.
Carrier gas, He	40 ml/min
Detector	PID

External Standard Quantitation

Peaks are identified by retention time. Compounds are quantified by comparing peak area and daily run standard peak areas. All sample (> 10 ug/L) are identified and their concentrations are determined and recorded.

Quality Control

1. A method blank is run every day to make sure that the system is free of interferences.
2. Standards are run for retention times to allow detection of any potential problems.
3. EPA Quality control check samples are run to insure the accuracy of our analytical system.

Appendix 7

Water Analysis in the Shuaiba Industrial Area

Analysis of Cooling Seawater at the Shuaiba Industrial Area. (Source: Ref. No. 59).

Parameter	Concentration
Neutral Electrical Conductivity micromhos at $20^{\circ}C$	70,000-72,500
Total Dissolved Solids (TDS), ppm	44,400-45,985
pH	8.6-9.0
Free Causticity, ppm as NaoH	Nil
Total " "	Less than 5
Total Alkalinity, ppm as $CaCO_3$	130-140
Total Chlorides, ppm as CL	21,500-22,630
Total Sulphates, ppm as SO_4	3,100-3,300
Total Hardness, ppm as $CaCO_3$	8,400-8,500
Peranent Hardness, ppm as $CaCO_3$	8,300-8,400
Temporary Hardness, ppm as $CaCO_3$	100-500
Calcium Hardness, ppm as Ca++	500-500
Magnesium Hardness, ppm as Mg++	1,740-1,760
Total Free and Combined Ammoniacal Nitrogen, ppm NH_3	0.5-10.0
Total Silica Soluble and Suspended, ppm as SiO_2	5-50
Phosphate, ppm as PO_4	-
Chlorine, ppm as CL_2 (after Chlorination)	2.5
Total Iron, ppm as Fe^{+3}	-
Sodium, ppm as Na^+	-
Critical Temperature of Cooling Seawater, $^{\circ}C$	32
Free Carbon Dioxide, ppm CO_2	-

Drinking Water Analysis, Shuaiba Power and Water production Plants. (Source: Ref. No. 59).

Parameter	Concentration
pH	7-8.5
TDS	500 mg/L
Chloride	150-200 mg/L
Sulphate	200-280 mg/L
Total Hardness	100-120 mg/L as $CaCO_3$
Total Iron	0.01-0.30 mg/L
Residual Chlorine	0.5 mg/L
Fluoride	0.7-1 mg/L
Conductivity	700-850 micromhos/cm

Analysis of Distilled Water Production By Shuaiba Power and Water Production Plants (Source: Ref. No. 59).

Parameter	Concentrations (ppm) Normal	Maximum
Neutral Electrical Conductivity in micromhos at 20°C	5.0	50.0
Calculated Total Dissolved Solids (TDS) (Based on 0.60 ppm/umhos)	3.0	30.0
pH	6.8-7.0	9.0
Free Causticity as NaOH	ND	ND
Total Causticity as NaOH	ND	4.0
Total Chloride as Cl^-	2.0	20.0
Total Alkalinity as $CaCO_3$	Trace	10.0
Total Sulphate as SO_4	"	5.0
Total Hardness as $CaCO_3$	"	10.0
Free Carbon Dioxide as CO_2	0.10	0.10
Total Iron	0.05	0.10
Silica as SiO_2	0.05	0.10
Total Ammoniacal Nitrogen (Free and Saline) as NH_3	0.02	2.0