Characterization and treatment of a petrochemical wastewater for reuse

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Civil Engineering

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Abstract

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Batch scale granular activated carbon adsorption studies conducted on phosphate stream wastewater indicated that low values of initial pH and temperatures are favorable for adsorption. A nonadsorbable portion of organics was found to be ubiquitious to this specific wastewater. Bench scale ozonation studies were also conducted by varying the experimental conditions such as, detention time, gas flowrate, initial pH and temperature. The maximum reduction in terms of total organic carbon was 32.5 percent at a pH of 11.4 and temperature of 60?-C. The experimental data fitted well to a first order equation. Furthermore, the combined ozone/activated carbon was found to remove upto 81 percent of total organic carbon from the phosphate stream wastewater.

Biological treatment of the final effluent in sequencing batch reactors (SBRs) removed 94 percent of biological oxygen demand. The optimum total suspended solids concentration was less than 5 mg/L for the effluent of SBRs. The introduction of fill and anoxic react periods into an SBR cycle was found to improve the quality of the biologically treated effluent.

Characterization and Treatment of a Petrochemical Wastewater for Reuse

by

Mohammed Misbashuddin

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

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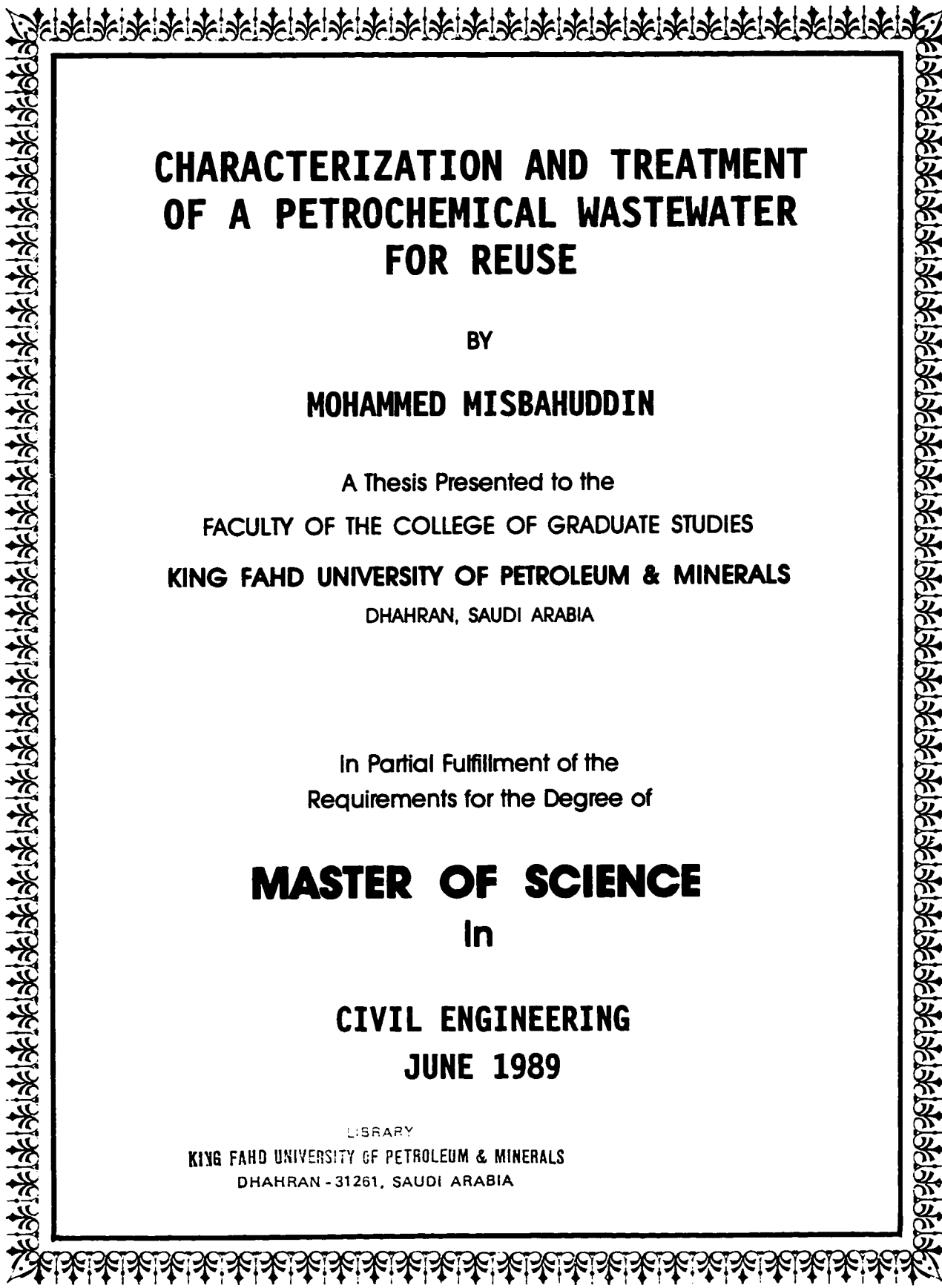
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OF A PETROCHEMICAL WASTEWATER
FOR REUSE

BY

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This thesis, written by

MOHAMMED MISBAHUDDIN

under the direction of his thesis committee, and approved by all the members, has been presented to and accepted by the Dean, College of Graduate Studies, in partial fulfillment of the requirements for the degree of

·MASTER OF SCIENCE IN CIVIL ENGINEERING

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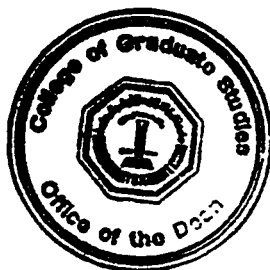
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Date : Feb. 3rd 1990

Dedicated

To

My Beloved Parents

ACKNOWLEDGEMENT

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خلاصة الرسالة

اسم الطالب الكامل : محمد مصباح الدين .

عنوان الدراســـــة : تحديد وتنقية مياه من مخلفات الصناعات البتروكيماوية
لأجل اعادة الاستعمال .

التخصـــــــص : هندسة مدنية .

تاريخ الشهـــــادة : يونيو ١٩٨٩م .

لقد تم اجراء دراسة مخبرية لدراسة الخواص والقابلية للتنقية على مياه
المخلفات البتروكيماوية الناتجة من الشركة السعودية للصناعات البتروكيميائية
(صدف) في الجبيل ، المملكة العربية السعودية .

خلال عملية مسح نوعية المياه كانت تؤخذ عينات كل ساعة من قناة الفوسفات
وكذلك الخارج النهائي للمصنع .

دلت نتائج المسح ان هذه المياه تحتوي على كمية قليلة من المواد العضوية ولكن
بتركيزات مختلفة . حيث كان معدل الكربون العضوي الكلي لقناة الفوسفات والقناة
النهائية ٧٣ مللجرام/ل و ٦٥ مللجرام/ل على الترتيب .

وقد دلت دراسات على الامتصاصية لقناة الفوسفات بواسطة الكربون المنشط
الحبيبي أن قيم ابتدائية متدنية من درجة الحموضه و الحرارة تحسن من الامتصاص .
هذا وقد تم عمل دراسات أوزونية مصفرة وذلك بتغيير الظروف المخبرية مثل وقت
التعرض ، تدفق الغاز ، درجة الحموضة الابتدائية وكذلك درجة الحرارة .

هذا وقد كانت الازالية الاعظمية في هيئة الكربون العضوي ٣٢ر٥٪ في درجة

حموضه ١١.٤ وعند درجة حرارة ٦٥° . وقد تم توقيع القيم المخبرية جيدا على المنحنى
الدال على معادلة الدرجة الاولى ، بالاضافة الى ذلك فقد وجد ان الاوزون والكربون
المنشط يذيل حوالي ٨١٪ من الكربون العضوي الكلي لمسار الفوسفات .

هذا وقد وجد ان المعالجة البيولوجية للقناة النهائية في احواض متتابعة تزيل
٩٤٪ من المتطلبات العضوية للأوكسجين (BOD) . وكان معدل كمية العوالق الكلية أقل
من ٥ مللجرام /ل . إن ادخال أوقات للملى والمعالجة الغير هوائية على نظام المعالجة
أدى الى تحسين نوعية المياه الخارجة المعالجة بيولوجيا .

درجة الماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
الظهران – المملكة العربية السعودية

ABSTRACT

NAME : MOHAMMED MISBAHUDDIN

TITLE : CHARACTERIZATION AND TREATMENT OF A

PETROCHEMICAL WASTEWATER FOR REUSE

MAJOR : CIVIL ENGINEERING

DATE : JUNE, 1989

Characterization and treatability studies on a bench scale were carried out for the petrochemical wastewater of saudi petrochemical company (SADAF) at Al-Jubail, Saudi Arabia. During wastewater quality survey, hourly samples were collected from the phosphate stream and the final effluent of the plant. The results of the analysis indicate that the wastewaters are low in organic content but variable in concentrations. The average total organic carbon for the phosphate stream and the final effluent were 73 mg/L and 65 mg/L, respectively.

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MASTER OF SCIENCE

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

Dhahran, Saudi Arabia.

Chapter 1

INTRODUCTION

This study was carried out to investigate the treatment of petrochemical wastewater for reuse purposes from Saudi Petrochemical Company (SADAF) at Madinat Al-jubail Al-Sinaiyah, Saudi Arabia. The petrochemical complex utilizes Saudi Arabia's two basic resources, natural gas and salt, to produce ethylene, crude industrial ethanol, styrene, ethylene dichloride and caustic soda.

SADAF produces on an average 5000 cubic meters per day of wastewater, which is the result of different activities taking place within the plant. The phosphate stream wastewater constitutes 40% of the total flow and posess high phosphate levels. Presently, the phosphates are removed with lime in plant's phosphate removal system. The average total organic carbon (TOC), total Kjeldahl nitrogen (TKN) and total phosphorous (Total-P) after the phosphate removal were 73, 2.6 and 27 mg/L, respectively. The removal of oil and grease, and suspended solids for the plant's wastewater is accomplished by the standard corrugated plate interceptor (CPI) separators and dissolved air flotation (DAF) system. The average TOC, TKN, and total-P values for plant's final effluent were 65, 0.8 and 19 mg/L, respectively. The concentration of heavy metals are also below the limiting levels. Hence the treatment of the wastewater for reuse within the plant can be considered as a choice of interest.

Petrochemical wastewaters are considered to be the complex and hard to treat among the complex industrial wastes. The consituents of the petrochemical wastewaters were also found to be highly industry specific. Therefore, each wastewater has to be characterized extensively and viable processing technologies have to be evaluated for recycling and reuse.

Some of the processes that are commonly employed for the treatment of petrochemical wastewaters are air stripping, activated carbon adsorption, oxidation with ozone, and biological treatment. These processes have long been employed with high pollutant removal efficiencies. Recently, Eckenfelder [1] also discussed the processes that are used for the treatment of petrochemical wastewaters and identified the above mentioned processes as the viable treatment methods.

Air stripping is a unit process for removing volatile organic compounds and has been shown to remove certain organics from petrochemical wastewaters [2,3]. Activated carbon adsorption is often employed for the removal of non-biodegradable and specific compounds, such as phenols, from industrial wastewater which contain relatively small concentration of specific organic species. Investigators have presented data on the adsorption of pure compounds [4] as well as on the petrochemical wastewaters [5]. Ozone has the potential for removing from wastewaters those organic substances that are resistant to other treatment methods. Ozonation process is often employed in combination with either activated carbon or some biological process. The biological treatment of petrochemical wastewaters was reported as early as 1952 [6] and the removal mechanism of biochemical oxygen demand (BOD) and the process design has been well established [1].

All the processes mentioned above were investigated on bench scale laboratory units in this study for the treatment of SADAF wastewater. This will generate information for conducting the pilot scale studies which will lead ultimately to the consideration of recycle and reuse.

The biological treatability of SADAF wastewater was conducted in sequencing batch reactors (SBRs) which is an innovative treatment technology. SBR is a revival of the batch activated sludge process and has better process control due to advances in automation when compared to the other biological treatment methods.

Chapter 2

LITERATURE REVIEW

2.1 Petrochemical Industry

Petrochemical is a broad term and is used to define a variety of organic chemicals. In general, petrochemicals are considered to be those products or components which arise primarily from the chemical processing of petroleum and natural gas hydrocarbons [7]. Petrochemicals are used in a wide variety of products, including plastics, synthetic fibers, synthetic rubbers, resins, plasticizers, synthetic detergents, a variety of automated chemicals, and numerous other products.

Ruggers [8] has defined " basic petrochemical processes " as those which use previously unreacted hydrocarbons and are used to produce new chemicals. Such primary reactions may produce some 200 industrial products. These in turn may form the " charge stock " for processess producing thousands of new chemicals and finished products. One of the unique characters of the petrochemical industry is that it is defined by the considerations of its raw materials rather than by its finished products.

A survey of the processess associated with the industrial processing of petrochemicals in the united states was under taken by Hedley *et. al.* [9] for US Environmental Protection Agency. The study identified 11 basic petrochemicals

used in producing the great majority of synthetic organic products. They were ethylene, benzene, methane, propylene, toulene, xylenes, butylenes, acetylenes, naphthalene, n-parrafins, and creserols.

Many potential hazardous compounds released into the environment are believed to be created during the processing of petrochemicals. Hence the industry faces challenges on two fronts with regard to environmental quality: (1) pollution resulting from the synthesis of a product, and (2) pollution resulting from the product itself.

Wright [10] has grossly classified the sources of waste from such petrochemical industry operations as : (a) by-product formation, (b) side reactions (unwanted products), (c) incomplete reactions, and (d) mechanical loss problems. Often the by-products are marketable commodities and their appearance in the waste streams may be directly related to the market conditions in the particular locale. The amount of unwanted products arising through side reactions is subject to some control and may become of decreasing importance as research in organic synthesis progresses. Incomplete reaction is in general the result of impurities in the raw material and the intrinsic equilibrium of the particular reactions in question. Many times, the resulting process stream is subjected to recycling at some point in the process. The amount of practicable recycling is related to the cost of raw materials and the amount of dilution water available for waste disposal. Any process is subjected to mechanical loss problems arising through human error and equipment failure. These are best handled through operational control. An excellent treatise of the subject of the sources of pollution in the petrochemical companies can be found in the book by Bechock [11].

Petrochemical wastewaters are considered one of the complex and hard to treat among the industrial wastes. The characteristics of the wastewater also differ widely as shown in Tables 2.1 [12]. It can be seen that the COD value in case of high level petrochemical wastewater is 17,500 mg/L which is 25 times higher than for the low level wastewater of 700 mg/L. The concentration of nitrogen and sulfates for high level wastewater were 3,500 mg/L and 10,000 mg/L respectively. Also the concentration of phenol are very high, i.e., 850 mg/L. These type of wide variation in characteristics are not common in case of either domestic or many other industrial wastewaters.

However, due to improved source of raw materials, proper process design, good house keeping and segregation of waste streams, the quality of the effluents have improved over the years.

2.2 Activated Carbon Adsorption

Guisti, Conway and Lawson [4] conducted adsorption and isotherm studies on 93 different petrochemicals. The study emphasized the behavior of activated carbon according to the functionality, molecular weight, branching, solubility and polarity of the organic chemicals. Results of their study indicate increased adsorption with increased molecular weight, and the adsorption declined with decreased molecular weight and decreased molecular polarity, solubility, and branching. For straight chained organics the affinity to carbon was found to be in the following order for petrochemicals :

Undissociated organic acids > aldehydes > esters > ketones > alcohols > glycols

In addition, they reported a decrease in adsorption with increasing total surface

Table 2.1 : Characteristics of Petrochemical Wastewaters [12].

Parameter*	Concentration				
	High Level(a)[1]	High Level(b)[2]	Medium Level[1]	Low Level[1]	Montcs[1]
COD	17,500	12,000	1,500	700	260
BOD			1,300	600	150
Total Organic N	3,500		0	0	
Nitriles	300	0	0	0	
pII	5.4	10.8	5	7.5	
Oil	10	150	500		
Phenol	1	850	65	7	
Sulfides	0	0	5	2	
Total Alkalinity	750	2,000		100	
Sulfates	10,000	1,800	0	0	650
TSS	16,000	8,000	40	500	
Chlorides					190

* Parameters are expressed in mg/L

[1] R.D. Sadow, Journal WPCF, 38(3) : 478,1966.

[2] G.E. Montes et al, Sewage Ind. Wastes, 28(4) : 507, 1956.

acidity of the carbon and an increased adsorptive capacity for synthetic organics. In their study they have found that that the reduction for alcohols; methanol and ethanol were 3.6 and 10 percent respectively, as compared to 95.5 percent reduction in case of n-hexanol.

Due to the need for developing a simple analysis, Reimers *et. al.* [13] conducted experimental work to quantify the affinity of selected organics for activated carbon with specific reference to carbon chain length, aromaticity and functional groups. The order of preference was as follows:

Aromatic acids> aliphatic acids and alcohols> aniline > aliphatic amines> phenol

An important observation was that aromatics did not always sorb better than aliphatics, since the affinity for carbon was greatly affected by substituent groups on aromatic rings and by functional groups associated with aliphatics. These findings confirmed literature reports with respect to solubility and acid dissociation of synthetic organics. An extension of the information base was realized by consideration of acidic and basic aliphatic polymers. Further, a decrease was observed in the adsorptive capacity of at least 1000-fold when pH fluctuations caused charging of the polymer functional groups.

The findings recommended a study of the waste characteristic which may be used in the development of feasibility analysis for the affinity of aqueous organics to carbon. The proposed characteristics include: total organic carbon, total acidity (pII range of 4-7) minus inorganic carbon acidity, organic nitrogen, and aromaticity. El-Dib and Badawy [14] investigated the adsorption on granular activated carbon of four hydrocarbons; benzene, toulene, o-xylene, and ethylbenzene and found that the data conform to Freundlich isotherm.

The application of carbon adsorption in petrochemical industry can be at two points in the process train. It can be used as a tertiary treatment step to remove refractory compounds before or after conventional biological systems. Ford [15] evaluated the applicability at both the points. The results of the study was based on the treatability studies conducted by the author at eight refineries and petrochemical installations. The data tabulated from the study indicated that the BOD for effluents of activated sludge treatment, total carbon treatment, and combined activated sludge/carbon treatment was found to be in the range of 20-50 mg/L, 40-100 mg/L and 5-30 mg/L, respectively. The influent BOD range was 250-350 mg/L. These values show that the removal efficiency of activated sludge treatment is better than that of the carbon treatment.

Ford and Buercklin [16] also discussed the applicability of activated carbon at the two points. Based on the extensive experimental work undertaken by them on the pilot scale for the treatment of refinery and petrochemical wastewaters, they have suggested pilot scale studies for evaluating the application of activated carbon for a particular application. The results of combined biological treatment and carbon adsorption for petrochemical wastewaters as given by Ford and Buercklin [16] are shown in Fig. 2.1. The effluent quality at different stages is expressed in terms of BOD/COD ratio in the figure. The BOD/COD ratio of the wastewaters remained unchanged when wastewaters were subjected to activated carbon adsorption. However, the BOD/COD ratio decreased considerably after the biological treatment. This may be due to the reduction of biodegradable organics from the wastewater. The authors hypothised further that the biological/carbon treatment in series will be the most prevalent application in future.
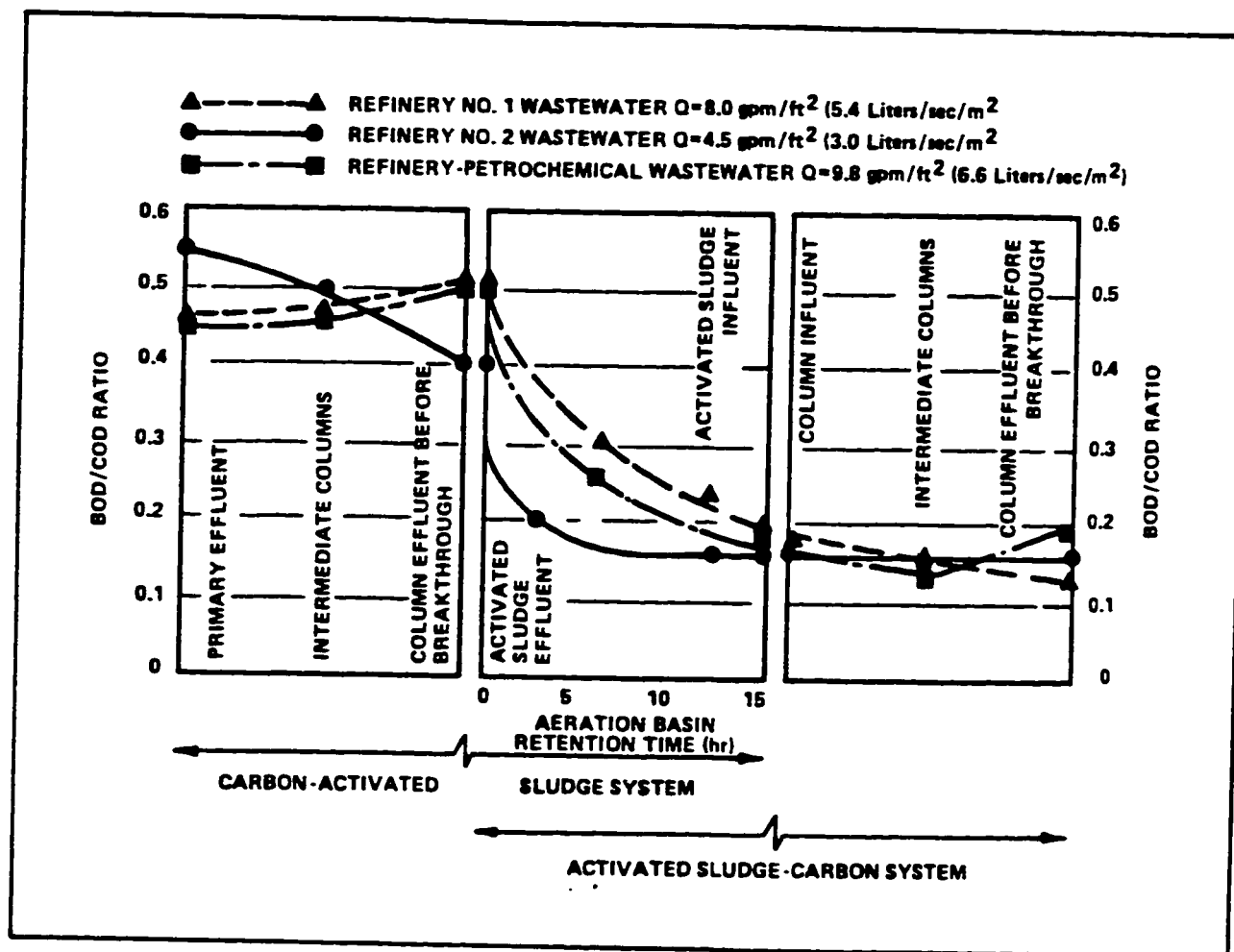
Fig. 2.1 : Organic Selectivity Through Combined Activated Carbon -
Biological Treatment Systems [12].

In order to establish the feasibility of using activated carbon as an advanced treatment process for petrochemical wastewaters, pilot scale experimental work using both Granular Activated Carbon (GAC) and Powdered Activated Carbon (PAC) was undertaken by Guarino et. al. [5]. The results showed that GAC system was far superior than the PAC system. The effluent COD from PAC averaged 300 mg/L whereas the effluent COD for GAC was 100-150 mg/L ; the influent COD was approximately 750 mg/L in both the cases. The study also found out a considerable reduction in the concentrations of heavy metals and priority pollutants.

2.3 Ozonation

Ozone has been proposed as an oxidizing agent for phenols, cyanides and unsaturated organics [17-23]. Neigowski [17] studied the oxidation of phenol with ozone and found that at optimum pH of 12.0 the oxidation was virtually complete. This value is close to the optimum value of 11.4 as given by Anon [19]. Eisenhauer [21] found that the pH of the wastewater decreased as the reaction proceeded. He also concluded that the phenol removal increased by : increasing the flow rate; reducing gas bubble size; increasing the concentration of ozone and increasing the gas liquid contact time. In another study by Eisenhauer, [22] higher temperatures were found to favor the oxidation of phenols. Thiocyanates and cyanides were found to be effectively oxidized in the wastewater containing phenols [18] .

Kwie [24] evaluated ozone treatment of three wastestreams from a synthetic polymer plant containing high concentrations of unsaturated organics. As much as 90% COD removal was found in case of a waste containing unsaturated

hydrocarbons at an optimal pH of 12.6 [25]. The oxidation of organic matter with ozone, in terms of TOC reduction from a petroleum refinery wastewater was studied by Schwartz et. al. [26]. They found a reduction of 5.5, 10.4 and 26.4 percent for ozone dosages of 26, 60, and 159 mg/L, respectively. The initial TOC in all the cases were 81.5 mg/L. Study conducted by Buys and Renolds [27] on the biologically treated petrochemical effluents revealed that ozonation caused a decrease in organic content measured as COD. Also a reduction in the nonadsorbable portion of the COD was observed.

2.4 Biological Treatment

The success of activated sludge for the treatment of petrochemical wastewater was demonstrated as early as 1952 [6]. The study carried out on the bench scale showed upto 90% BOD and phenol removal. The waste contained petrochemicals such as benzene, toulene, alcohols, ketones and cresylic acids. Results of another laboratory scale activated sludge unit [28] operated on extended aeration mode showed the influent BOD of 1950 mg/L was reduced to 20 mg/L. Huber [29] achieved the effluent phenol concentrations of 0.1 mg/L for acetylene and ethylene wastes. Shannon [30] discussed the origin, handling and treatment of process waste streams in the petrochemical complex of Dow company, Michigan, U.S.A. The activated sludge treatment of ethylene and polyethylene wastes were preceded by trickling filter. Ninety nine percent removal of BOD was obtained for an influent BOD concentration of 85 mg/L. However, the removal efficiency in terms of COD was 62.5 %. In a large petrochemical complex manufacturing ethylene and propylene, Sadow [31] reported equal removal efficiencies in term of BOD and COD. However the difference between the influent BOD and COD was less than

15%. Table 2.2 depicts some values for the activated sludge treated effluents. Table 2.2 shows that the total solids even after biological treatment for refinery wastewaters were 3000 mg/L. High COD values (approximately 100 mg/L) can be observed for average BOD of 3 mg/L. This shows that although BOD effluent of 3 mg/L can be achieved the COD concentrations were very high.

The use of bioaugmentation in the activated sludge treatment of refinery and petrochemical wastes was suggested by Christiansen [32]. The technology involves the use of mutant bacterial culture. Case histories were reported in which these bacterial cultures resulted in achieving high nitrification, MLSS build-up, and an excellent improvement in the settling characteristics of the waste. Hamer [33] discussed the philosophies and strategies to be adopted for successful biotreatment of petrochemicals.

Next to the activated sludge, the other most popular and outstanding aerobic biological treatment systems are the trickling systems in the trickling filter. The removal efficiency of trickling filter is usually less than that of the activated sludge systems. Hence it is often used in conjuction with either the activated sludge or aerated lagoon system for industrial waste treatment. In this way they reduce the organic load to the system that follows. Trickling filters using plastic media reduced 50% of the organic load before subsequent treatment by the activated sludge in the Dow chemical company, USA [30].

Sadow [31] reported the use of trickling filter in treating sour waters of the petrochemical company manufacturing ethylene derivatives. The filter media consists of rockstone. Removal of 60-75% was observed for influent COD of 1500 mg/L. Brush and Wheeler [34] studied the treatment of petrochemical waste on

Table 2.2 : Characteristics of Refinery and Petrochemical Secondary Effluents.

Constituent (mg/L)	Refinery		Petrochemical
	Activated Sludge	Extended Aeration	Extended Aeration
Total Solids	2,900	3,000	
Suspended Solids	14	17	
Volatile Suspended Solids	10	10	
BOD	2	4	11
COD	99	112	132
Chlorides		1,640	
pH	6.8	6.6	7.9

Source : W.W. Eckenfelder, Water Quality Engineering for Practising

Engineers Barnes and Noble, New York, 1970.

trickling filters with different organic loadings.

2.4.1 Kinetics of Biotreatment

The kinetics of the biological treatment is well established. The rate of growth of micro-organisms in a batch system can be described by one of the following equations :

$$\frac{dX}{dt} = \mu X - k_d X \qquad (2.1)$$

where,

X = concentration of micro-organism, mass/unit volume

μ = specific growth rate, $time^{-1}$

k_d = endogenous decay coefficient, $time^{-1}$.

Expression for the specific growth rate as proposed by Monod is the most widely used and can be expressed as :

$$\mu = \mu_m \frac{S}{K_S + S} \qquad (2.2)$$

where,

μ = speicific growth rate, $time^{-1}$

μ_m = maximum specific growth rate, $time^{-1}$

S = concentration of growth limiting substrate in solution, mass/unit volume

K_S = half-velocity constant, substrate concentration at on half the maximum growth rate, mass/unit volume.

Eckenfelder [1] has provided the following design relationship for activated sludge treatment of petrochemical wastewaters:

$$\frac{S_o - S}{X_v t} = K\frac{S}{S_o} \quad (Kinetics)$$

$$\Delta X_v = a(S_o\text{-}S)\text{-}bX_d X_v \quad (Sludge\,Yield)$$

$$O_2/day = a'(S_o\text{-}S) + b'X_d X_v \quad (Oxygen\,Requirement)$$

$$N = 0.123\frac{X_d}{0.8}\ \Delta X_v + 0.07\frac{0.8\text{-}X_d}{0.8}\Delta X_{x_v} \quad (Nutrient\,Requirement)$$

$$P = 0.026\frac{X_d}{0.8}\ \Delta X_v + 0.01\frac{0.8\text{-}X_d}{0.8}\Delta X_x$$

Where,

S_o = influent BOD

S = effluent BOD

X_v = MLVSS

t = aeration time

a = sludge yield coefficient

a' = oxygen coefficient

X_d = degradable fraction of VSS

b = endogenous coefficient

b' = endogenous oxygen coefficient

K = kinetic rate coefficient

Table 2.3 is a summary of the design parameters for petrochemical wastewaters [1]. It can be seen from Table 2.3 that the reaction rate constant K varies between 0.59 to 4.90 on BOD basis and from 2.7 to 7.97 on COD basis. It can also be seen from the table that the residual COD varies from 22-106 mg/L.

Table 2.3 : Biological Treatment Coefficients for Petroleum and Petrochemical Wastewaters [1].

| Plants | Organic Removal Rate k* (days) | | Sludge Growth Coefficients | | | | Oxygen Requirement Coefficients | | | | Residuals |
	BOD	COD	BOD Basis a	BOD Basis b	COD Basis a	COD Basis b	BOD Basis a'	BOD Basis b'	COD Basis a'	COD Basis b'	COD (mg/L)
1	4.15	2.74	--	--	--	--	--	0.57	0.1	106	53
2	--	7.97	--	--	0.5	0.06	--	--	0.6	0.11	100
3	--	5.86	--	--	0.5	0.06	--	--	0.34	0.06	22
4	--	2.92	0.5	0.08	0.44	0.10	--	--	0.35	0.08	***
**5	--	5.0	--	--	0.26	0.03	0.47	--	0.46	0.05	100
6	0.59	--	0.5	0.05	--	--	--	0.28	--	--	--
7	4.90	7.79	--	--	0.2	0.08	--	--	0.40	0.01	76
8	--	7.24	--	--	0.43	0.10	--	--	0.52	0.14	82

* At 24°C

**Pilotscale

***TOD

2.4.2 Biological Treatment in Sequencing Batch Reactors (SBRs)

The continuous flow conventional treatment systems treated different wastewaters successfully for many decades. They require minimum supervision and maintenance. However, wastewaters containing refractory, inhibitory or slowly degradable compounds make the system ineffective. Hence extensive efforts were made by the researchers to develop process modification offering improved treatment potential. One of the promising options is the sequencing batch reactor (SBR) system.

An SBR has a time cycle with five distinct periods, namely; FILL, REACT, SETTLE, DRAW, and IDLE. These periods has been named according to the primary function. During FILL, wastewater is fed to the reactors containing mixed liquor from previous cycle, and during this period the reactor contents are mixed but not always aerated. The REACT is the time required for the desired reactions to take place. A combination of anoxic and aerobic periods can prevail during this period. SETTLE is the time for microorganisms to settle under gravity in quiescent conditions. DRAW is the time required to discharge the treated effluent. IDLE is the waiting period for the reactor from the end of DRAW to the beginning of refilling. A schematic representation of the reactor condition in different modes as given by Ying et. al. [35] is shown in Fig. 2.2.

The five periods of an SBR may overlap, and one or two steps may be skipped depending upon the requirement for a particular treatment. For example, the idle period may be omitted and filling can begin immediately after completion of the draw period of the last SBR cycle. The operating characteristics of SBR systems are described in detail in an overview paper by Irvine and Bush [36].
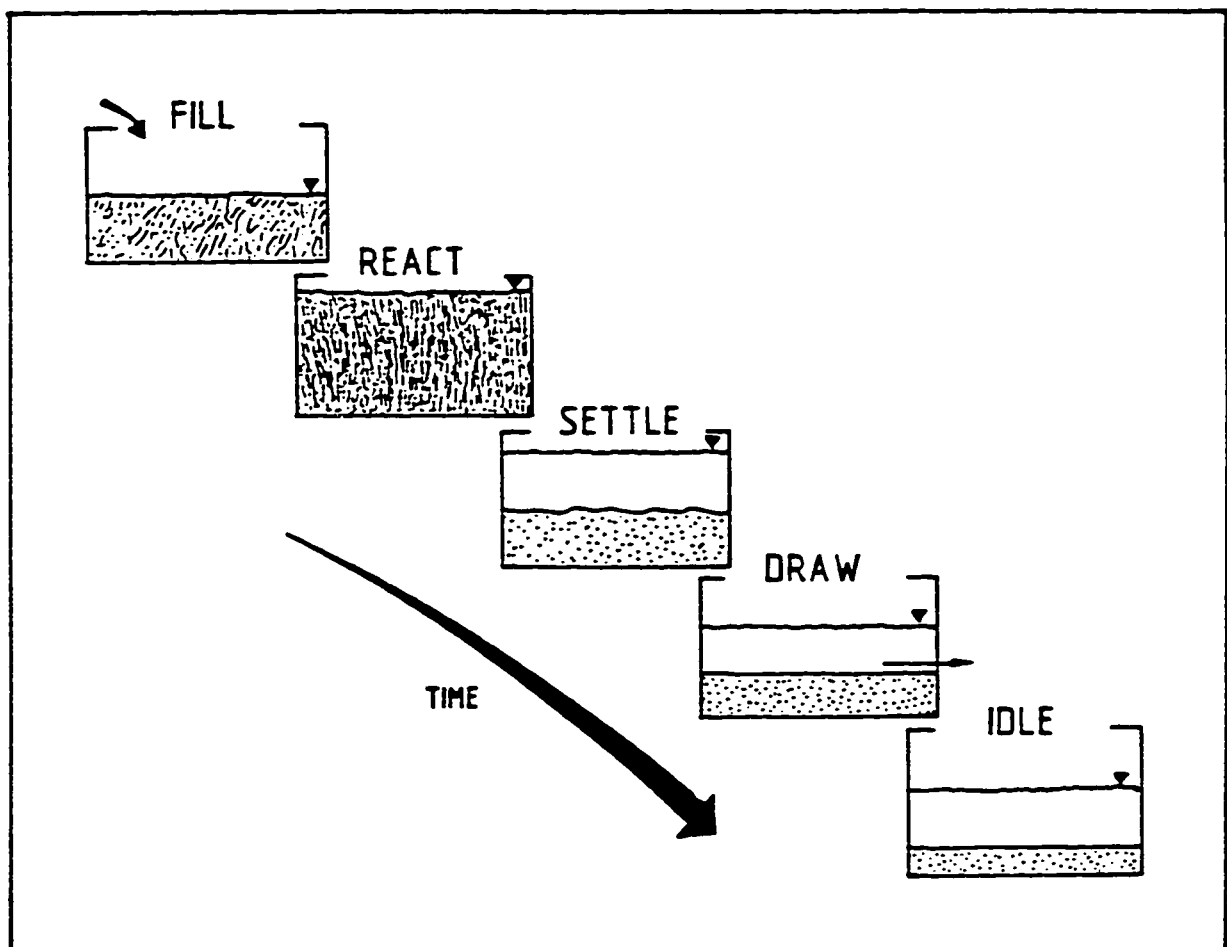
Fig. 2.2 : Illustration of SBR Biotreatment Technology [35].

SBR system has several advantages over conventional continuous flow systems [36-43]. Its ability to effectively remove BOD and suspended solids [40] , nitrification [44-46] ,denitrification [46,47] , and biological phosphorous removal [48,49] , in a single tank is noteworthy. In SBRs, equalization, reaction and clarification takes place in one reactor, saving considerable capital and O&M costs. The flexibility of operation of individual SBR periods allow manipulation of operating strategy to suit various treatment requirements. Hence it was demonstrated for the successful treatment of municipal wastewaters [40,41] , industrial wastewaters [50] , hazardous wastes [51] , and treatment of toxic landfill leachates [35,52].

A full scale demonstration plant for the treatment of municipal wastewater at Culver, Indiana, U.S.A achieved effluent 5-day BOD, SS and P concentrations of 10, 8 and 0.6 mg/L [40], respectively. Hsu [53] investigated the application of SBR to petrochemical wastewater. The BOD of 242 mg/L of the petrochemical wastewater was reduced to less than 10 mg/L. The SBR also reacted well to phenolic shock loading after acclimatization. Phenols were degraded from initial concentrations ranging from 200-295 mg/L to less than 0.1 mg/L. He found that the performance of SBR is comparable or slightly superior to that of the conventional activated sludge system.

2.5 Recycle and Reuse of Petrochemical Wastewater

Many petrochemical industries are evaluating the efficiencies of the physico-chemical and biological treatment processes to treat their wastes for reuse. But very little data is published in the technical literature. Rebhun [54] reported the

use of tertiary treated municipal effluent in Haifa refinery and petrochemical complex. The tertiary treatment process consists of lime precipitation to remove phosphorous along with reductions in BOD alkalinity and calcium. Davis [55] investigated the possibility of recycling treated process wastewater into cooling water makeup and concluded that the effluent can be recycled provided the treatment is economical.

Refinery wastewater was subjected to a tertiary treatment, which consist of a combination of ozonation, activated carbon adsorption and biological activated carbon (BAC) systems [26]. The purpose of the study was to evaluate these systems to make the wastewater fit for reuse. It was found that high and uneconomical dosages of ozonation (159 mg/L) were required to reduce the TOC content from 81.5 to 60.0 mg/L. Further, the ozone dosages of 26 mg/L and 60 mg/L increased the carbon usage rate by 30 and 50%, respectively. Hence it was also concluded that the expenditure to operate a BAC system for this particular case was very high.

Chapter 3

OBJECTIVES

The main objectives of this study were the characterization of the petrochemical wastewater from SADAF and its treatability by physico-chemical and biological processes.

The specific objectives are :

(i)   to characterize wastewater from two streams, i.e., phosphate stream and plant's final effluent for physical, chemical and biological characteristics,

(ii)   to evaluate the feasibility of removing volatile organic compounds constituting the TOC of the phosphate stream wastewater by air stripping,

(iii)   to conduct batch scale activated carbon adsorption studies for the removal of TOC from the phosphate stream wastewater,

(iv)   to conduct bench scale ozonation experiments for the removal of TOC from the phosphate stream wastewater, and,

(v)   to evaluate biological treatability of plant's final effluent in sequencing batch reactor (SBR) system.

Chapter 4

MATERIALS AND METHODS

4.1 Source of Wastewater

The wastewater for the present study was collected from two locations in SADAF, referred as phosphate stream and the final effluent. The phosphate stream comprises of the condensate from crude industrial ethanol (CIE) plant and boiler blowdown from utility and ethylbenzene/styrene plants which constitute more than 40% of SADAF's total flow of 5000 cubic meters per day. The wastewater which is high in phosphate and organics is treated at present in plant's phosphate removal system.

The system consists of flocculator/clarifier to which the wastewater is fed with lime, ferric chloride and polyelectrolyte solution. Lime reacts with the dissolved phosphate to form calcium phosphate. The calcium phosphate being insoluble in water is removed with the help of a coagulant (ferric chloride) and the coagulant aid (polyelectrolyte solution).

The effluent from the phosphate removal system is combined with the other discharges from each operating unit of the plant. The combined wastewater is then given a primary treatment before it is discharged to the industrial sewer line

of Royal Commision for Al-jubail. The primary treatment step consists of pII adjustment, oil & grease and settleable solids removal in corrugated plate interceptor (CPI) separators followed by an optional coagulation/flocculation. The final stage treatment is the clarification of the effluent by dissolved air floatation (DAF) process. Fig. 4.1 shows the process flow diagram for primary treatment at SADAF and the sampling locations.

4.2 Sampling Technique

For hourly grab samples automatic samplers manufactured by Manning Technologies Inc., U.S.A were installed at the two locations. The samplers which were operated with 12 V DC battery had facilities to set the desired collection frequency and volume of the sample. The samplers were equipped with 24 individual bottles for sample collection. The bottles were numbered from 1 to 24 to indicate the time of collection. The bottles were replaced with fresh bottles everyday around 10 A.M. when all the bottles were full.

A bypass line at both the locations was created and made to pass continuously through a fixed tank consisting of a plastic carboy which holds a little greater than 1 L of wastewater at a time. The extra volume of liquid was kept to avoid sucking of air by the sampler. The flow rate of wastewater into the tank was adjusted so as to keep the contents well mixed at all times. The hose of the sampler was inserted into this tank, so that the sampler can suck exactly 1 L of wastewater at a preset frequency. The sampling frequency was adjusted at every one hour for all the grab samples collected. The wastewater survey was conducted for 10 days of the normal plant operation.
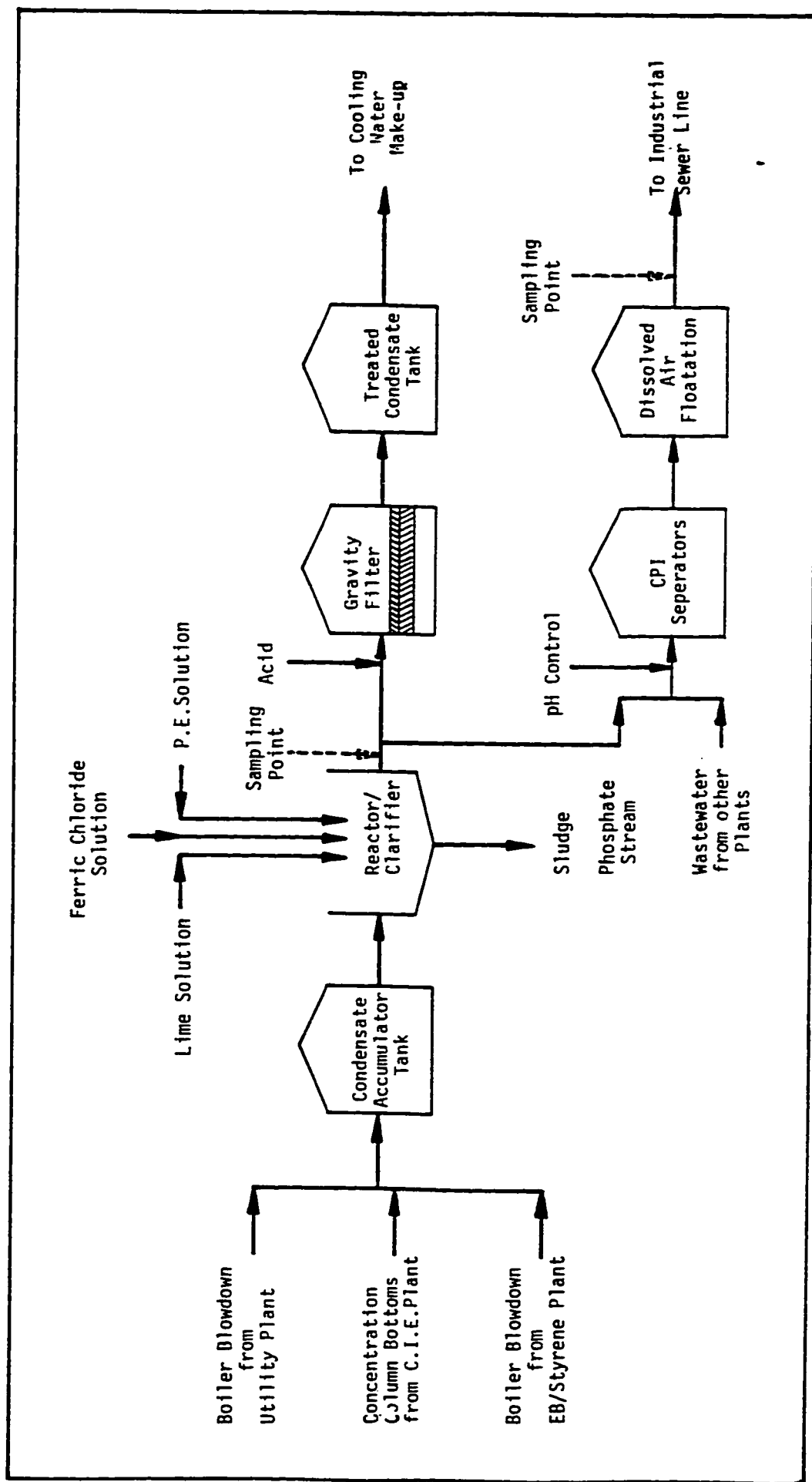
Fig. 4.1 : Process Flow Diagram for the Primary Treatment at SADAF.

The composite samples were collected in 20 L capacity plastic carboys. In order to obtain equal volume of wastewater per day, the flow rate of the bypass line for the wastewater streams was controlled with help of a stop cock and regulated at 12.5 mL/min. This flowrate gives approximately 18 L of sample in a period of 24 hours.

4.3 Sample Analysis and Storage

Analysis of the samples was carried out immediately after they were brought to the laboratory to determine some of the water pollution parameters like pH, BOD, TOC, etc. The estimation of other parameters was done after finishing the sampling program. The samples were preserved in the laboratory refrigerators according to the sample preservation methods recommended by the U.S. Environmental Protection Agency [56] . These are listed in Table 4.1.

4.4 Experimental Set-Up and Procedure

4.4.1 Activated Carbon Adsorption

The following experimental procedure was adopted for batch studies :

1. The granular Carbon (10-18 mesh manufactured by BDH Chemical Company, U.K) was pulverized so as to pass U.S. Standard sieve size 200 mesh and retained on 400 mesh. It was washed once with dilute HCl and then several times with distilled water. It was dried in the oven at 150°C for 3 hours and then put in the dessicator for cooling.

Table 4.1 : Recommendations for Sample Preservation [56].

Parameter	Preservative	Maximum Holding Period
Calcium	None required	7 days
Chemical Oxygen Demand	2 ml H_2SO_4 per liter	7 days
Chloride	None Required	7 days
Metals, Total	5 ml HNO_3 per liter	6 months
Nitrogen, Ammonia	40 mg $HgCl_2$ per liter-4°C	7 days
Nitrogen, kjeldahl	40 mg $HgCl_2$ per liter-4°C	Unstable
Nitrogen, Nitrate-Nitrite	40 mg $HgCl_2$ per liter-4°C	7 days
Oil and Grease	2 ml H_2SO_4 per liter-4°C	24 days
Organic Carbon	2 ml H_2SO_4 per liter (pH 2)	7 days
Phosphorous	40 mg $HgCl_2$ per liter-4°C	7 days
Solids	None available	7 days
Specific Conductance	None required	7 days
Sulfate	Refrigeration at 4°C	7 days

2. The Carbon was then weighed according to the dosages of 0.05, 0.10, 0.25, 0.50, 1.0, 2.5, 5.0 and 10.0 grams and transferred into 250 mL reagent bottles.

3. The sample was filtered with Whatman # 44 filter paper using buchner funnel. The caps of the bottles were held tight by putting adhesive tape. 100 mL of filtered sample was then poured into each of these bottles and the carbon was wetted manually by shaking.

4. The bottles were then arranged in a shaker (water bath shaker if temperature control was required) and shaken well on low speed for 6 hours.

5. After the required time has elapsed the carbon was removed by vacuum filtration through millipore filters with 0.45 μm membrane filter.

6. The TOC of the filtrate for different dosages of carbon was determined. One reagent bottle, containing only sample and no carbon, as a control, was subjected to the same conditions as for other bottles. The difference between the TOC's of the control and other sample bottles gives the reduction in TOC for that particular dosage of carbon.

The GAC used for dynamic studies was of 10-18 mesh size and was given pretreatment by washing with dilute HCl and then with distilled water. It was then dried in the oven for 3 hours at 150°C. Before it was fed into the columns in the form of slurry, it was soaked for 24 hours in distilled deionized water at room temperature for degassification.

As the sample contained a lot of suspended solids it was filtered through a whatman # 44 filter paper by using Buchner funnel. All the dynamic studies were carried at neutral pH and at room temperature of 20° – 22°C.

The column for the dynamic study was made of clear plexiglass. The column was one inch in diameter and 2 ft long. The sample was fed with small size masterflex pumps manufactured by Cole-parmer, Chicago, U.S.A. The columns were set-up individually and were operated in the downflow mode. Fig. 4.2 and Plate 1 shows the set-up for the Dynamic Column Studies.

4.4.2 Ozonation

The details of the experimental set-up for the ozonation studies are shown in Fig. 4.3. The reactor for the semi-batch ozonation study was made of clear plexiglass cylinder having 2.5 inches (62.5 mm) internal diameter and 25 inches (625 mm) in height. Its capacity was approximately 2 litres. The thickness of the reactor was 1/4 inch and it was closed at both the ends by 1/2 inch thick plane plexiglass circular disks. Grooves were cut in the disks to fit the cylinder. A ring shape rubber gasket was provided at the intersection between the cylinder and the disks to avoid leakage of water.

Compressed air from the cylinder after passing through a column of dry silica gel was fed to the Welsbach T-816 ozonator (Plate 2). The ozonator pressure and voltage were maintained at 8 psig and 100 volts respectively. The flow rate of the generated Air/Ozone mixture to reactor was 4 L/min, unless otherwise mentioned. This mixture was supplied at the bottom of the reactor through a medium porosity glass fritted diffuser.

The concentration of ozone in the gas phase was determined by opening the sample valve and passing 0.25 L/min of gas through a 500 mL gas washing bottle containing 400 mL of a 2% potassium iodide solution. After approximately 3 liters of gas had passed through the gas washing bottle, the solution was acidified and
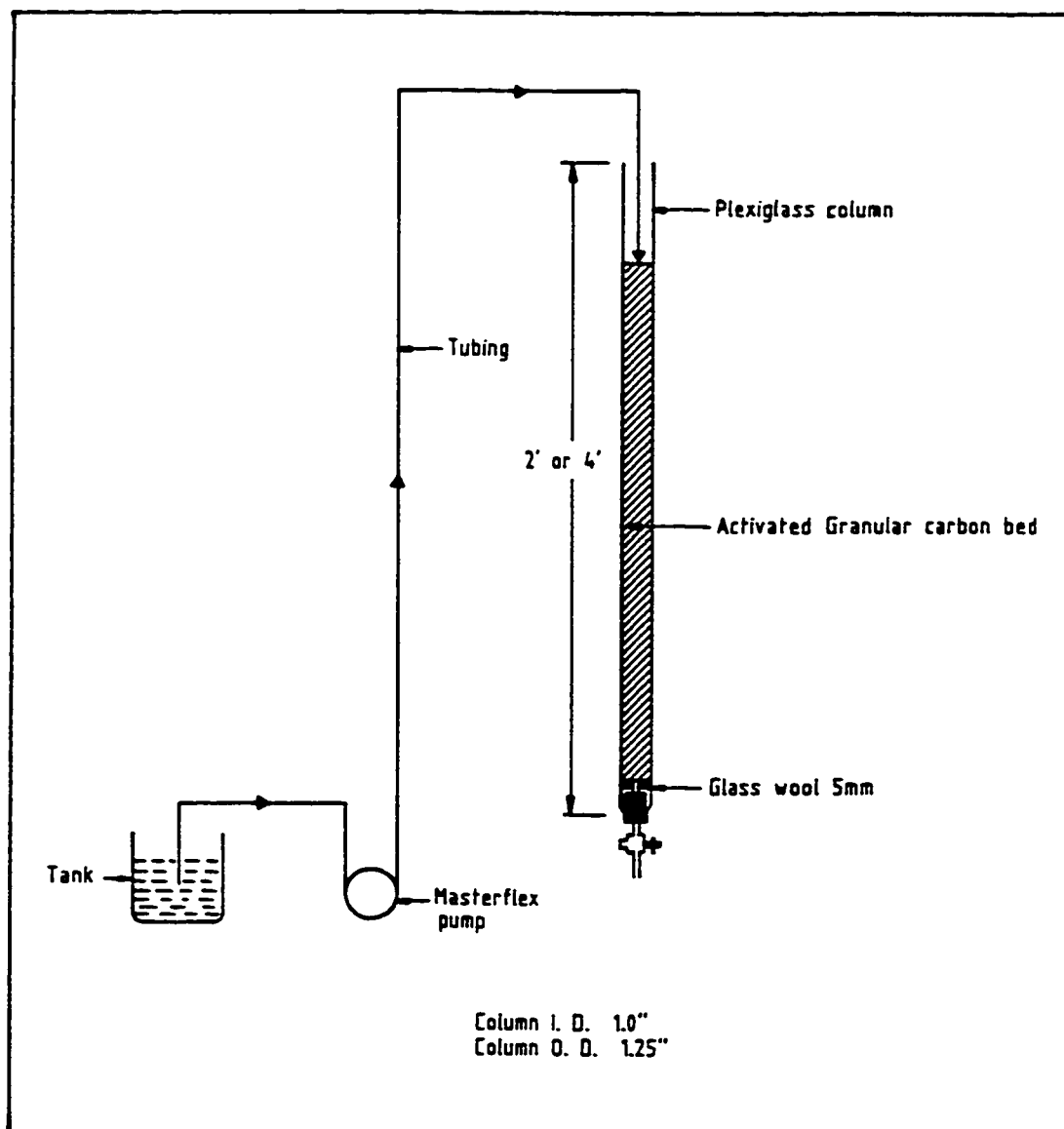
Fig. 4.2 : The Experimental Set-up for Continuous Flow GAC Study.
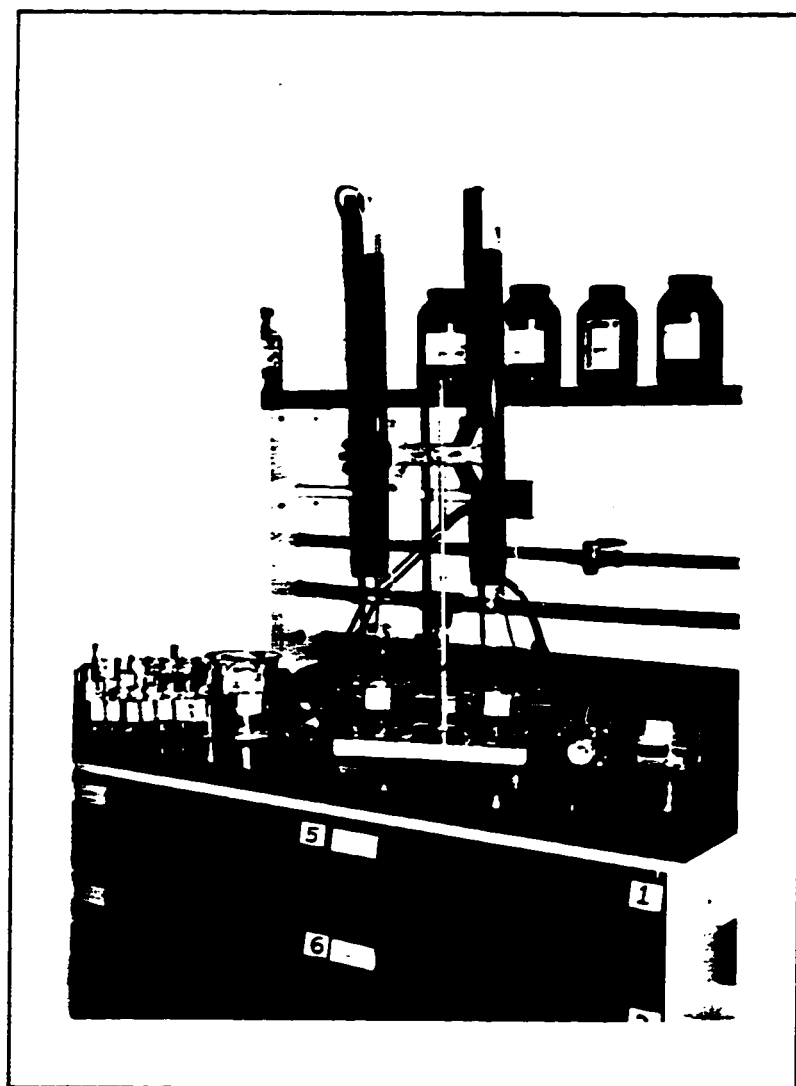
Plate 1 : **Experimental Set-up for Continuous Flow GAC Study.**
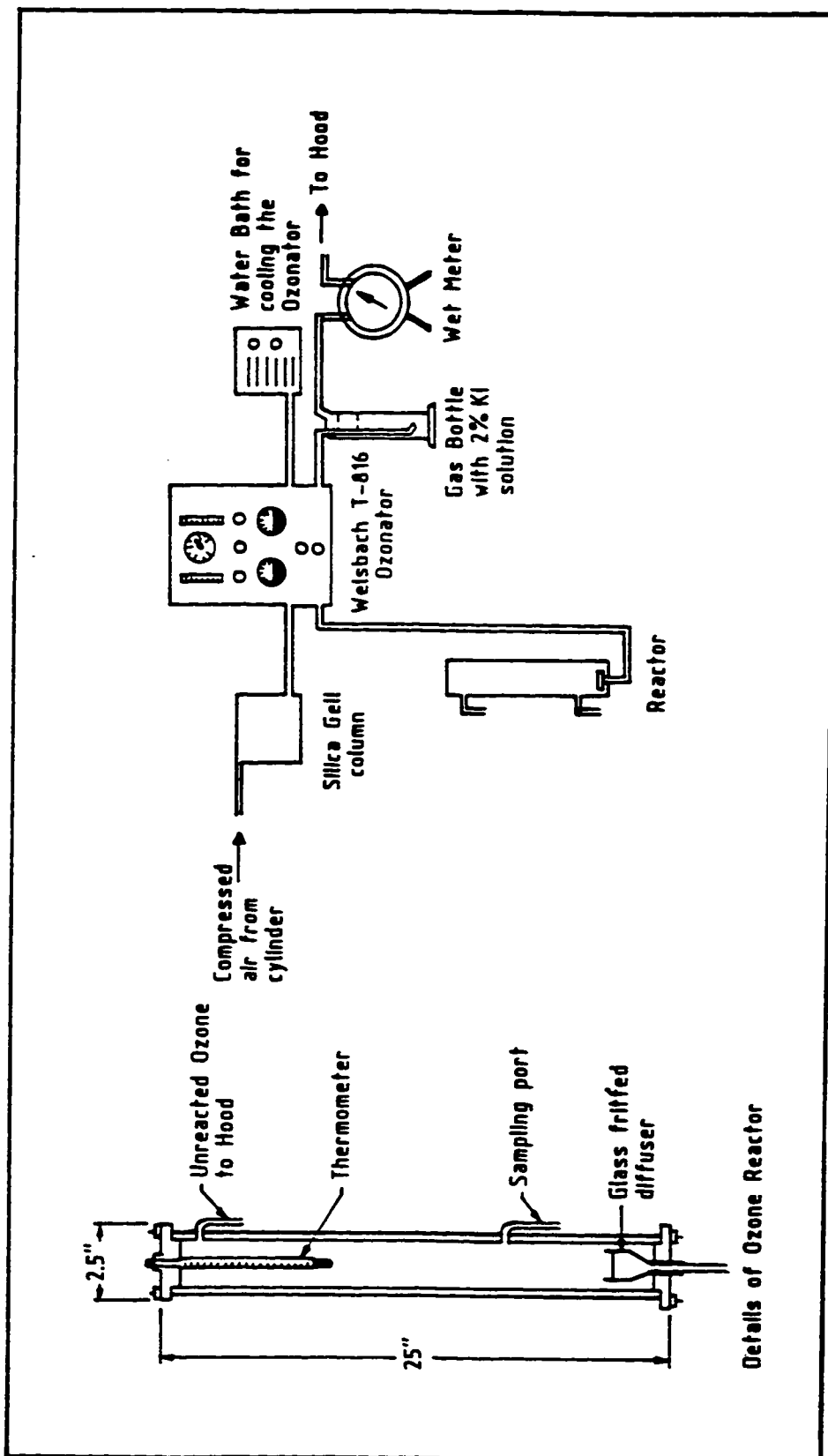
Fig. 4.3 : The Experimental Set-up for the Ozonation Study.
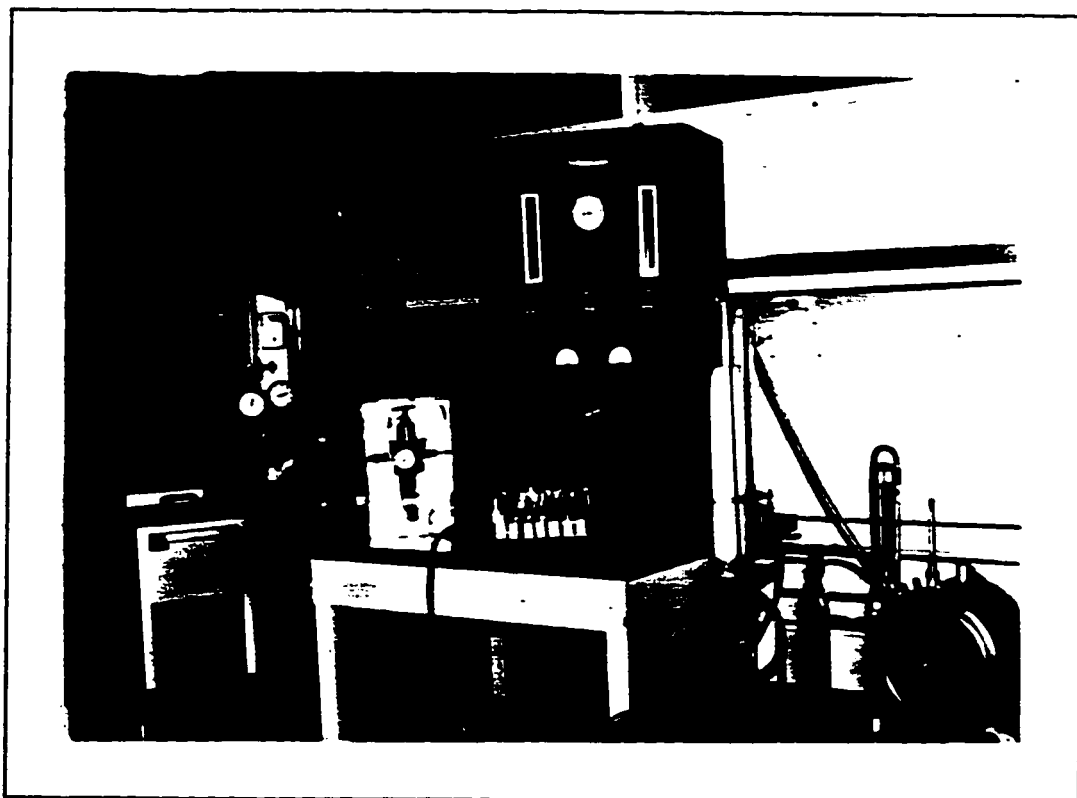
Plate 2 : Experimental Set-up for Ozonation Study.

titrated with standardized sodium thiosulfate solution according to the procedure given in *Standard Methods* [57].

4.4.3 Biological Treatment

The experimental setup for a SBR is shown in Fig. 4.4 consists mainly of four reactors (SBR-1, SBR-2, SBR-3, and SBR-4) mounted on a wooden bench. The reactors 3.5 inches internal diameter and 10 inches in height were made of 0.25 inch thick plexiglass. The total volumetric capacity of each reactor was 1.5 L. The reactors were calibrated so that the least count for volume measurement was equal to 10 mL.

Small motors manufactured by Dayton Elec. Mfg., Chicago and operated on 110 V AC supply with a speed of 120 rpm were mounted on the top of each reactor. The shaft of the motor was connected to a steel rod 8 inches long. The steel rod had two thick plastic blades one at the bottom of the rod and the other at the centre. The two blades were fixed perpendicular to each other.

Medium porosity diffusers were fixed at the bottom of each reactor. The diffusers were connected through 0.75 inch tygon tubes to a common air supply. The air supply to each of the reactors was controlled through pinch corks. The air requirement for the experiment was fulfilled by the service line supplying the laboratory from a central unit. Dry and particulate free air was obtained by passing the air first through an oil trap and then from a conical flask as shown in the Fig. 4.4. The oil trap arrangement has a pressure gauge attached to it, which measures the applied air pressure. The flask contained dry silica gel with glass plugs fitted at the inlet and outlet ends. Purified air passes through a flow meter, for measuring the applied air, before it goes and is distributed equally to the
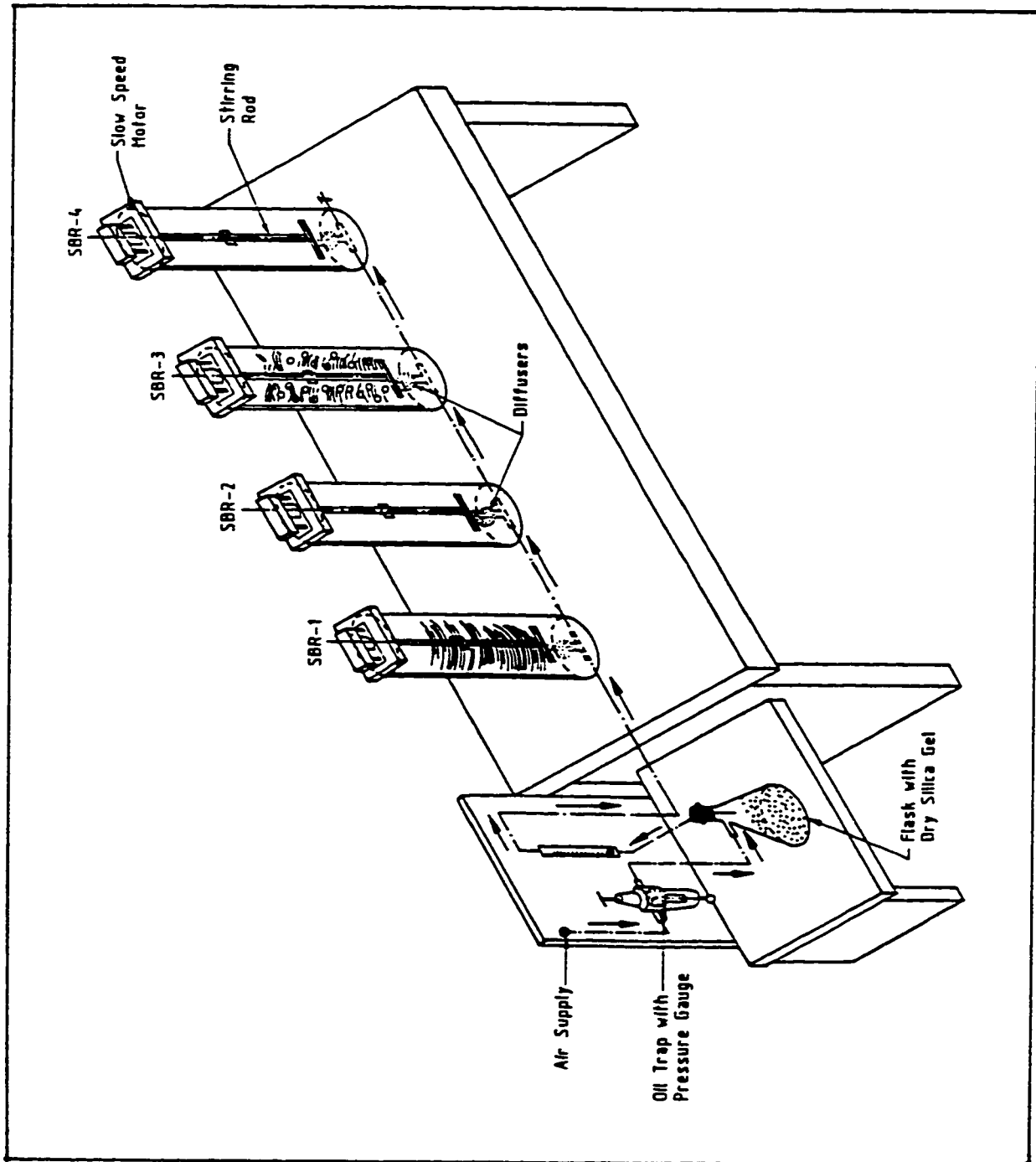
Fig. 4.4 : The Experimental Set-up for Biological Treatment.

reactors.

Automatic timers manufactured by REX Zeitschaller, West Germany were employed to regulate working of peristaltic pumps, mixers and air pumps for on phase II of the biological treatment study. The maximum volume of wastewater at which the reactors were operated i.e., during react period was 1200 mL. During the react period purified air was applied at a uniform flow rate of 600 mL/min to each of the reactors. This air was enough to keep the biological solids in suspension apart from the air requirement of organisms.

The dissolved oxygen was checked periodically and was maintained above 2 mg/L. The mixed liquor suspended solids (MLSS) sticking to the sides of the reactor above the 1200 mL mark was scraped from time to time with the help of a rubber spatula. At the end of the react period some distilled water was added to make-up the losses due to evaporation. Appropriate MLSS was wasted at the end of each day for all the reactors. The react period was terminated by shutting off the air supply. The microorganisms were then allowed to settle for 1 hour by gravity and 900 mL of the treated effluent was then removed by suction. Immediately the volume taken out was replaced with fresh wastewater and the react period initiated by letting the air to flow. The whole operation of drawing and filling took less than 5 minutes.

4.5 Analytical Techniques

Measurements of all physical, chemical and biological parameters for characterization and treatment studies were made in accordance with the methods given in the Standard Methods [57] with slight modification wherever necessary.

The total organic carbon (TOC) determinations were performed on a Beckman Model 915A (Fullerton, Ca.) Total Organic Carbon Analyser, using $20\mu L$ samples. The TOC values were determined according to the procedure recommended in Beckman Manual. The concentration of ions and heavy metals were determined by Perkin Elmner Model 4000 Atomic Absorption Spectrophotometer.

The calibration curves used for the determining TOC, phosphate and sulphate are included in APPENDIX A.

Chapter 5

RESULTS AND DISCUSSION

5.1 Characterization of Wastewater

characterization studies were carried out on phosphate stream wastewater and final effluent of Saudi Petrochemical Company (SADAF). The phosphate stream is a segregation of condensate from crude industrial ethanol (CIE) plant and boiler blowdown from the ethylbenzene/styrene (EB/S) and utility plants. The wastewater for the final effluent is due to the activities in ethylene, chlor alkali and ethylene dichloride plants and aggregation of phosphate stream wastewater.

Most of the wastewater in the phosphate stream is from the CIE plant. CIE is produced by the direct hydration of ethylene under controlled reactor conditions as follows:

$$C_2H_2 \quad + \quad H_2O \quad = \quad C_2H_5-OH \quad + \quad K.\ Cal.$$

$$Ethylene \qquad Water \qquad Ethyl\ Alcohol$$
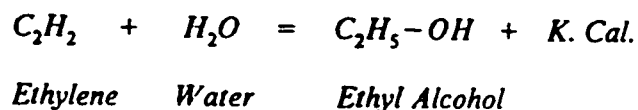
The predominant side products in the process are diethyl ether, higher alcohols, acetaldehyde, crotonaldehyde, cuprene, and polymers.

The ethylbenzene is produced due to the reaction between benzene and ethylene in alkylation reactor as :

$$ \bigcirc\!\!\!\!O \quad + \quad CH_2 = CH_2 \quad = \quad \bigcirc\!\!\!\!O^{-CH_2-CH_3} $$

Benzene   *Ethylene*   *Ethylbenzene*
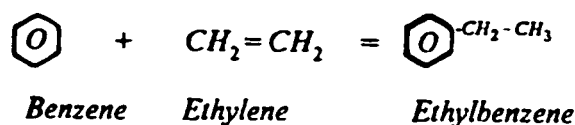
Dehydration of ethyl benzene leads to styrene as follows:

$$ \bigcirc\!\!\!\!O^{-CH_2-CH_3} \quad = \quad \bigcirc\!\!\!\!O^{-CH-CH_2} \quad + \quad H_2 $$

Ethylbenzene   *Styrene*
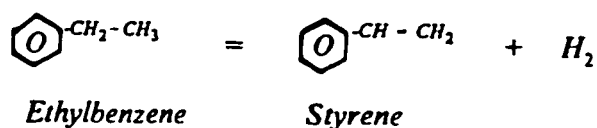
The organic constituents of phosphate stream were expected to be comprised of some raw materials, products and co-products escaping the process along with the impurities like higher alcohols, aldehydes, ketones and ethylene polymers. The plants final effluent too was thought to be contaminated with variety of organic chemicals generated due to various activities taking place in the complex.

For characterization studies the water pollution parameters like pH, conductivity, total organic carbon (TOC) and chemical oxygen demand (COD) were measured for hourly individual samples collected. This gives the hourly variation of the parameters measured.

One-day composite samples were then prepared by adding 100 mL each of wastewater from the 24 individual samples for that day. These 1-day composite samples were then analyzed for 5-day biochemical oxygen demand (BOD) , total solids, volatile solids, total suspended solids (TSS), volatile suspended solids (VSS), total-phosphate, ortho-phosphate, total Kjeldahl nitrogen (TKN), ammonia nitrogen, (NH_4-N) , chloride and sulfate. Heavy metals, iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), nickel (Ni), lead (Pb), chromium (Cr) and cadmium

(Cd) were measured for 1-day composite samples. The ions, calcium (Ca), magnesium (Mg), Sodium (Na), and Potassium (K) were also determined for the one-day composite samples.

The average hourly variation in PII values of the phosphate stream wastewater and final effluent is shown in Fig 5.1. The pH of the phosphate stream wastewater ranged between 10.4 and 11.5. The high PH value of the phosphate stream is due to the addition of lime for precipitating the phosphate present in the wastewater. The variation in PH values at different time intervals may be due to lime addition in varying quantities, which are calculated according to the amount of phosphates to be precipitated. It can also be seen from Fig 5.1 that the PH of the final effluent is around the neutral value of 7.0. This is due to pH adjustment prior to the sampling location.

The average hourly variations of TOC for the phosphate stream wastewater and final effluent are shown in Fig 5.2. In case of both the wastewaters maximum average TOC values of 95 mg/L was noticed around 2 PM. Fig 5.3 gives the daily average values of TOC for a one week period.

The solids concentration in the phosphate stream wastewater comprise mostly of the unsettled calcium phosphate sludge which gives high values for the suspended solids (Fig 5.4). The appearance of high suspended solids in the wastewater can be attributed to either improper lime dosage or faulty clarifier design. The average total dissolved solids (TDS) concentration for the final effluent ranged between 500 mg/L and 800 mg/L. Fig 5.5 shows the diurnal variation of solids for the final effluent. The conductivity of all the samples for the final effluent was monitored so as to get an approximate indication of the
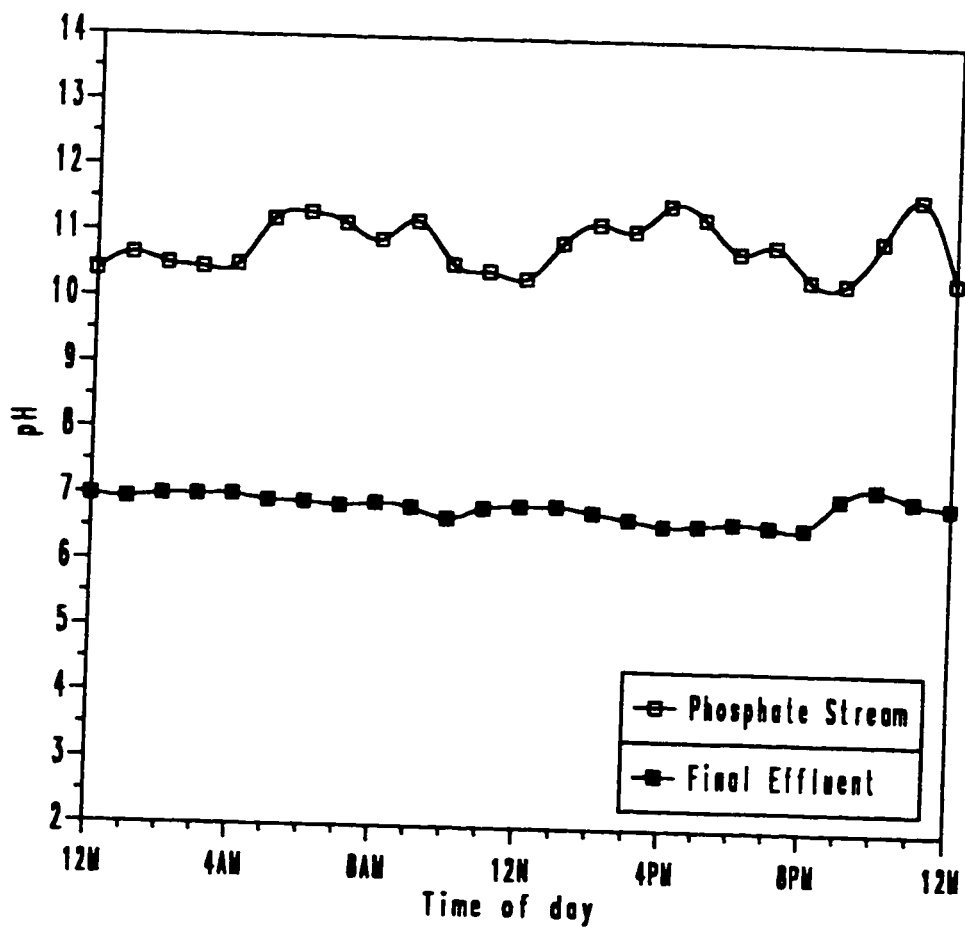
Fig. 5.1 : Average Hourly Variation in pH of Phosphate Stream Wastewater and Final Effluent.
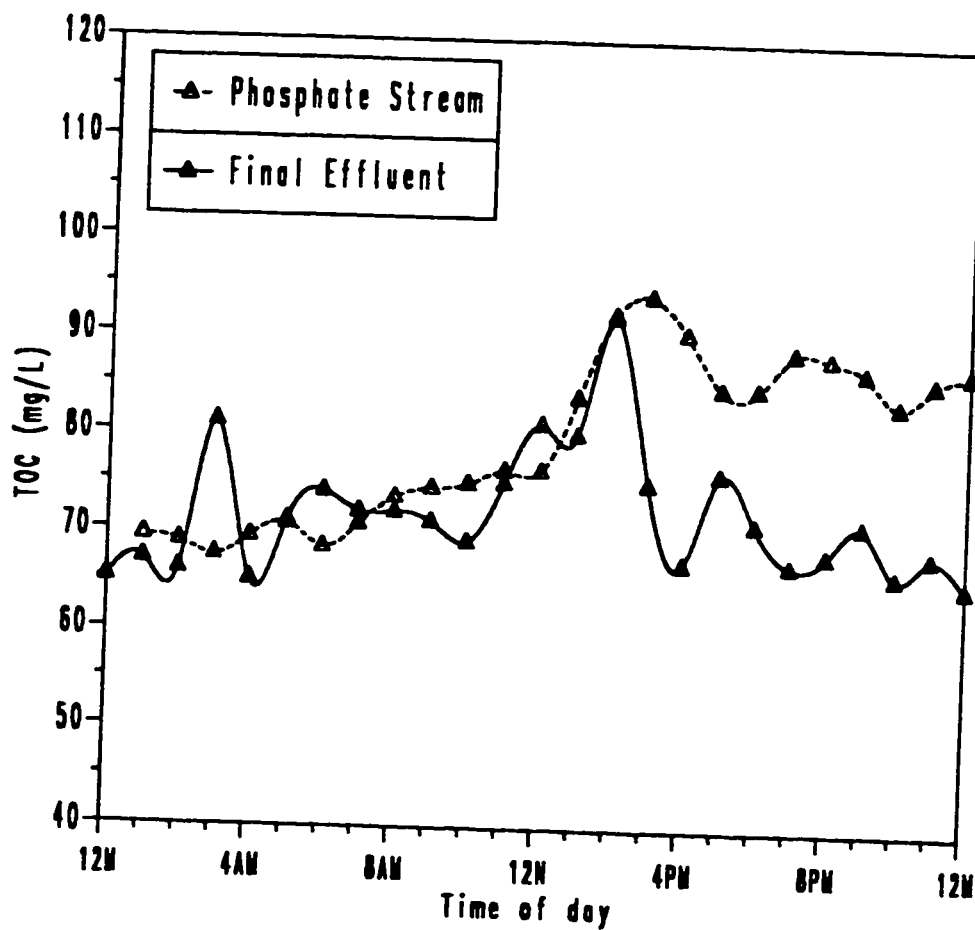
Fig. 5.2 : Typical Hourly Variation in TOC of Phosphate Stream Wastewater and Final Effluent.
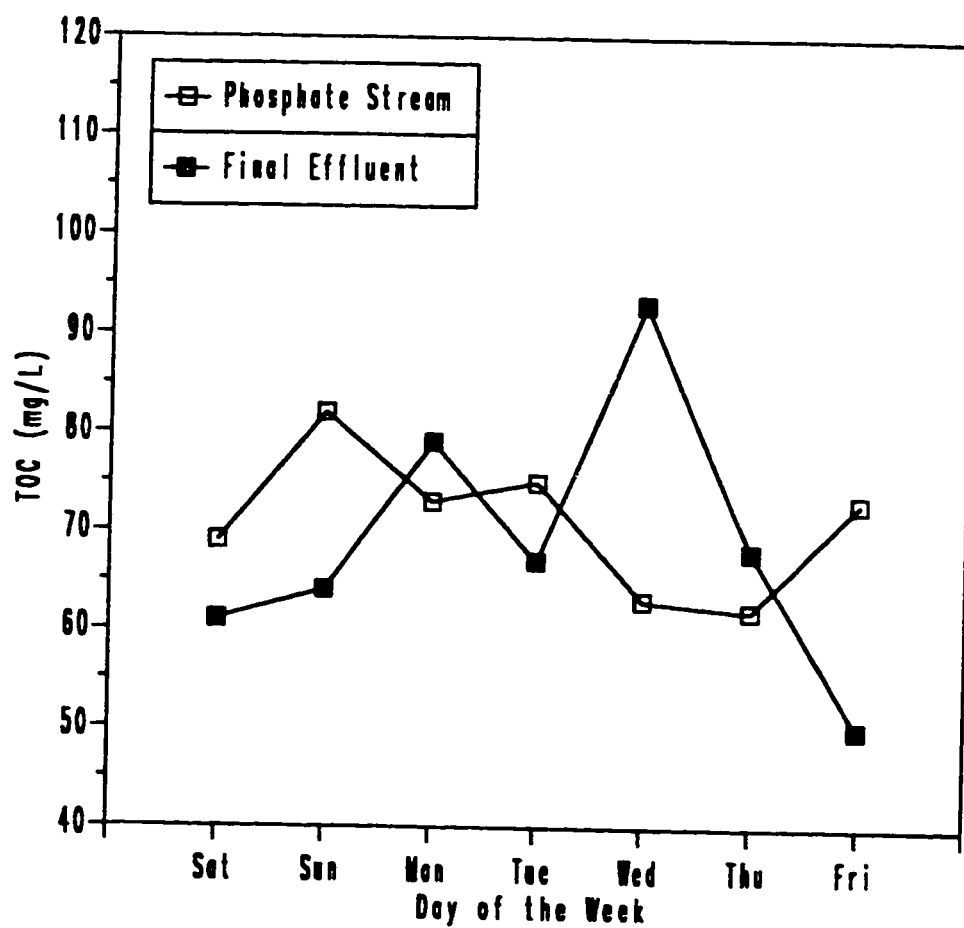
Fig. 5.3 : Average Diurnal Variation in TOC of Phosphate Stream Wastewater and Final Effluent.
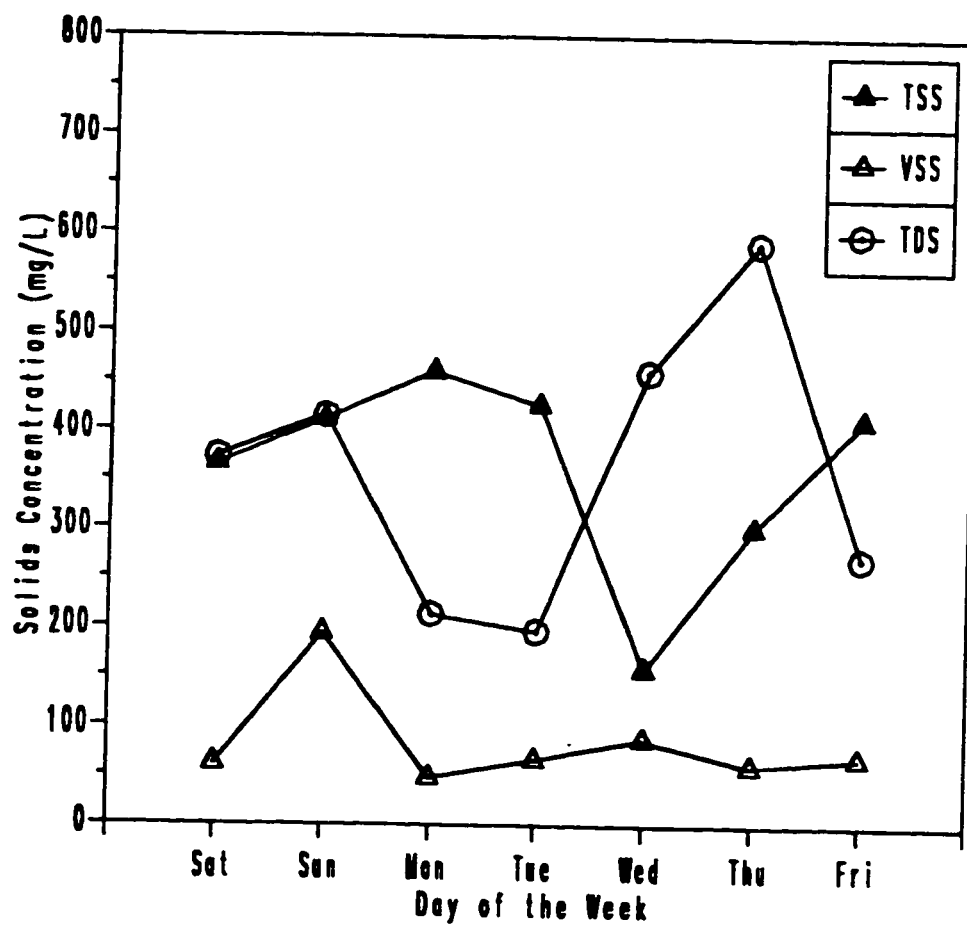
**Fig. 5.4 : Average Daily Variation of Solids in Phosphate
Stream Wastewater.**
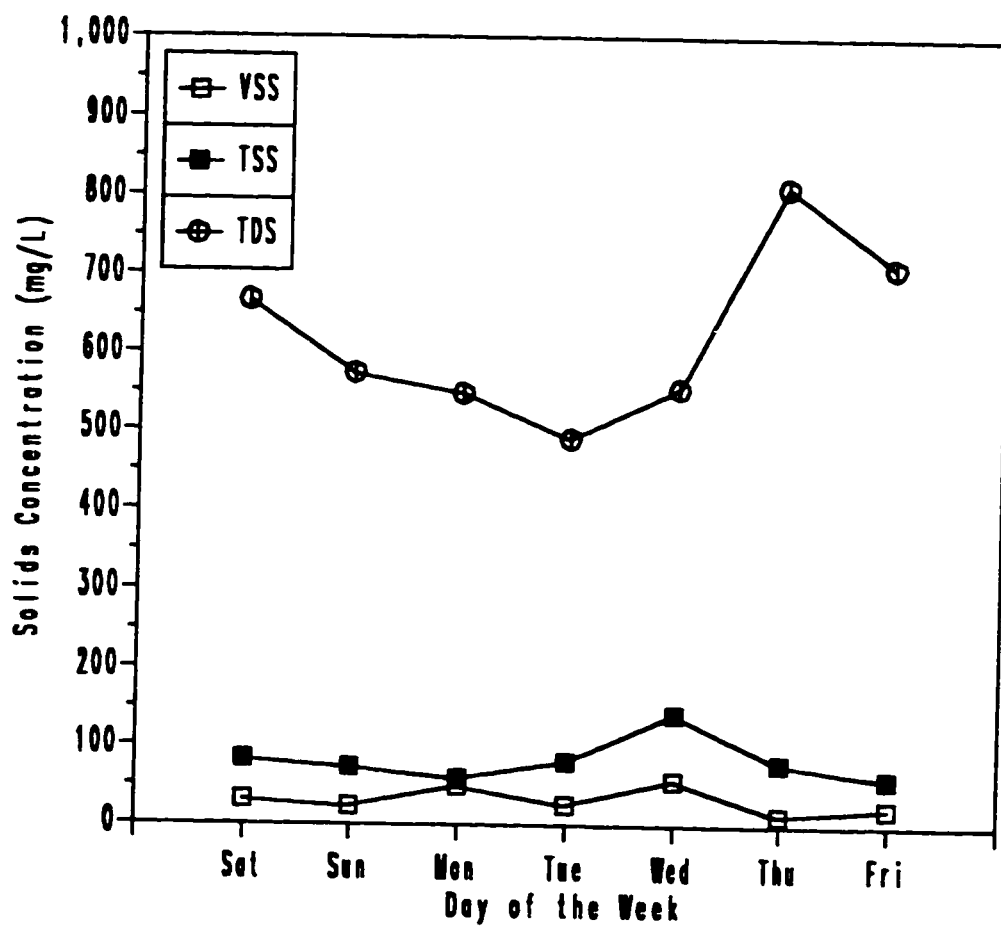
Fig. 5.5 : Average Daily Variation of Solids in Final Effluent.

variation of dissolved solids in the wastewater. The conductivity too, varied with time with a peak in the afternoon time (see Fig 5.6).

The concentrations of ortho-phosphate and total phosphates in both the streams are as shown in Fig 5.7. The average diurnal phosphate concentrations in phosphate stream wastewater did not vary significantly and averaged 1.4 mg/L and 27 mg/L as ortho-P and total-P, respectively. This value indicates proper working of the clarifier in terms of phosphate removal. However, as shown in Fig 5.7, the diurnal average concentrations of phosphates in the final effluent varied significantly as opposed to the nearly constant values in case of phosphate stream. This shows that phosphates may be added to the final effluent from other streams of the plant. The variation of total-P in the final effluent was from 11 mg/L to 24 mg/L, whereas the ortho-P varied between 3.5 mg/L to 8.0 mg/L.

The nitrogen content in both the streams were measured in terms of total Kjeldahl nitrogen (TKN), ammonia nitrogen NH_4-N and (nitrate + nitrite)-nitrogen for the one day composite samples of both the streams. The nitrogen content in terms of the TKN averaged 0.8 mg/L and 2.6 mg/L, respectively, for the phosphate stream and the final effluent. The ammonia nitrogen could not be detected in samples of the phosphate stream. Furthermore, no (nitrate + nitrite) nitrogen could be detected in both the streams.

The concentration of heavy metals Fe, Mn, Pb, Zn, Cr did not vary significantly as shown in Figures 5.8 and 5.9. However, variations in the concentration of Fe was observed in both the streams. The variation in the phosphate stream wastewater was between 0.6 to 1.2 mg/L, whereas, a variation of 0.6 to 1.4 mg/L was observed in case of the final effluent. Ionic concentrations of
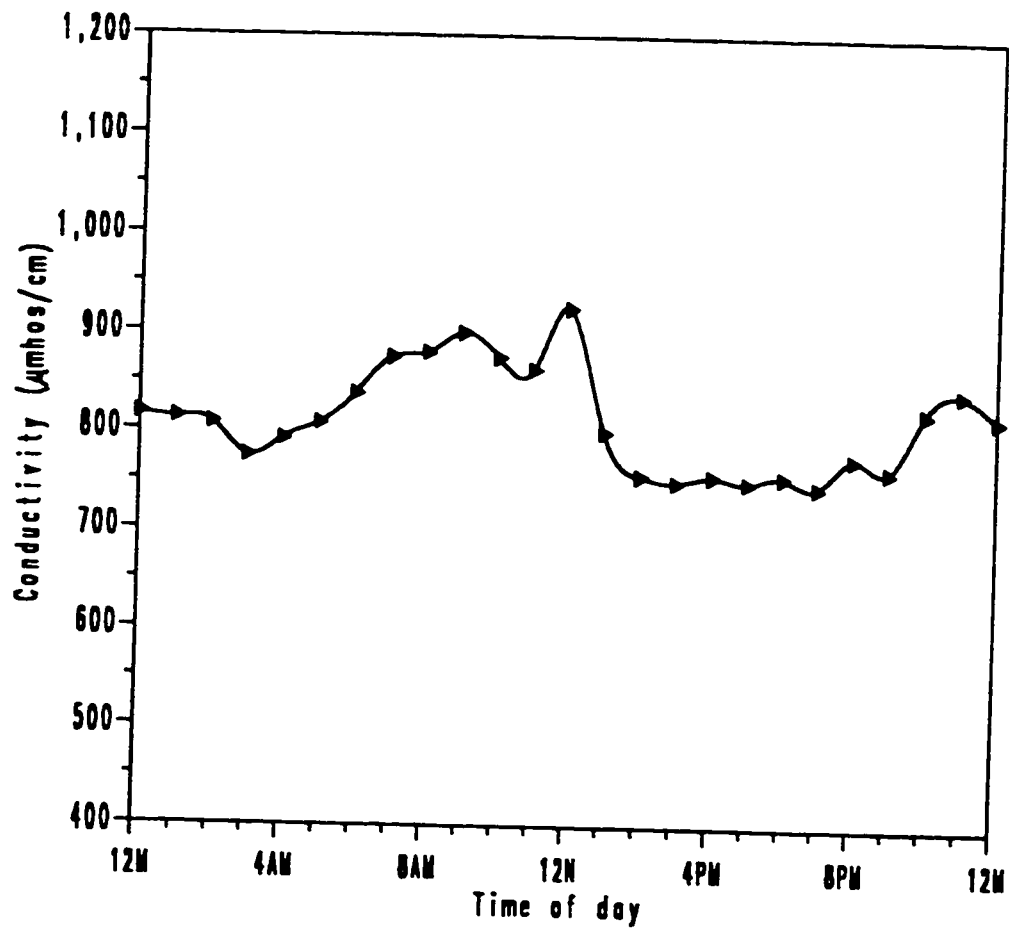
**Fig. 5.6 : Average Hourly Variation in Conductivity of
Final Effluent.**
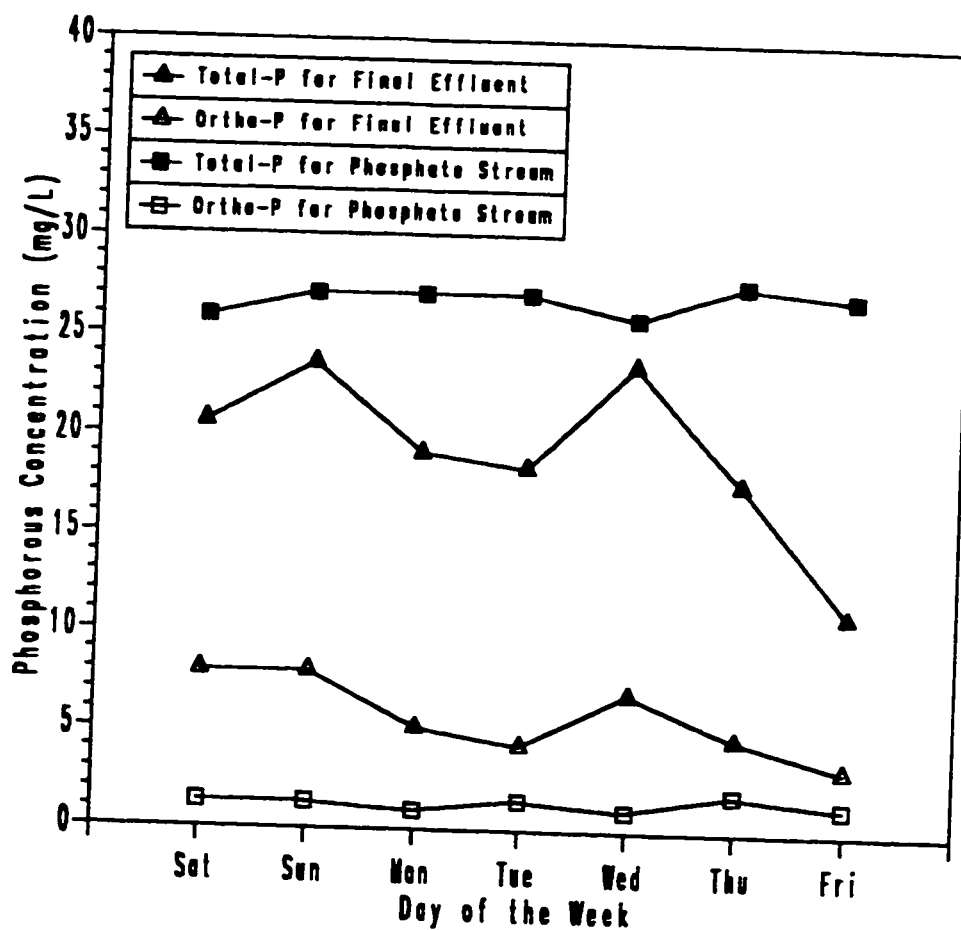
Fig. 5.7 : **Average Diurnal Concentration of Phosphorous in Phosphate Stream and Final Effluent.**
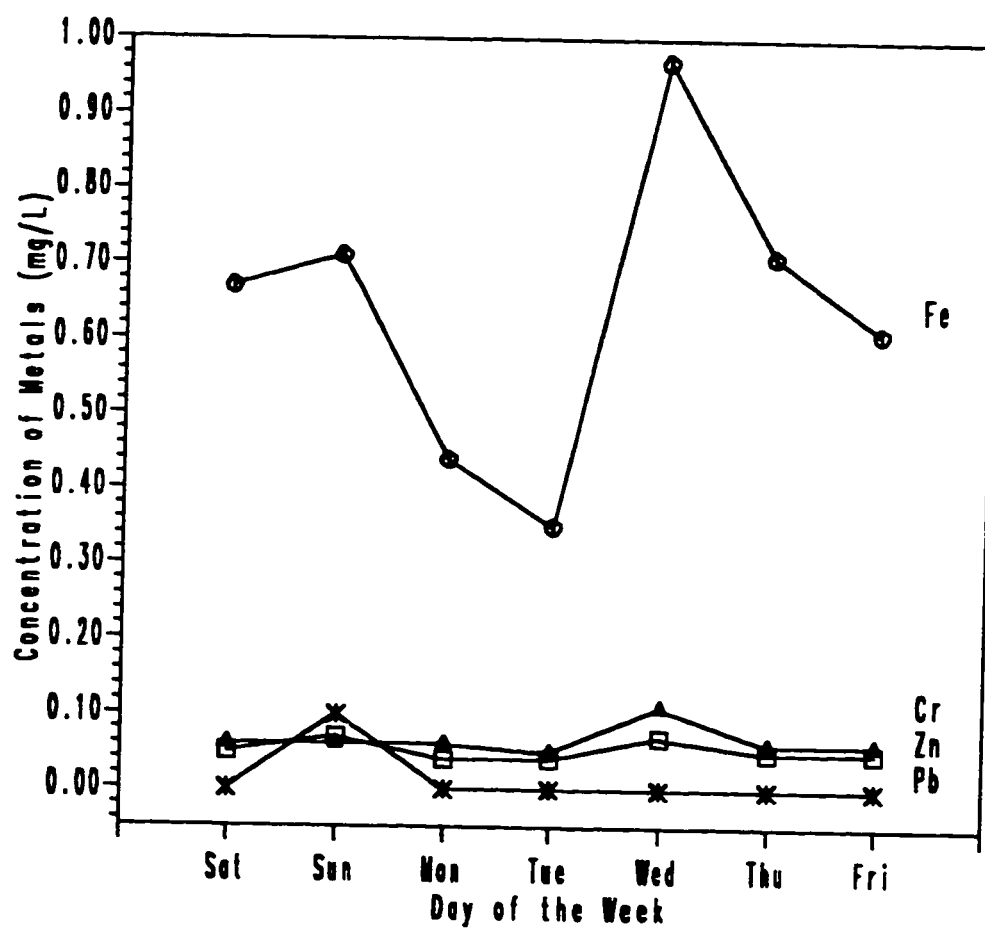
Fig. 5.8 : Average Diurnal Concentration of Heavy Metals in Phosphate Stream Wastewater.
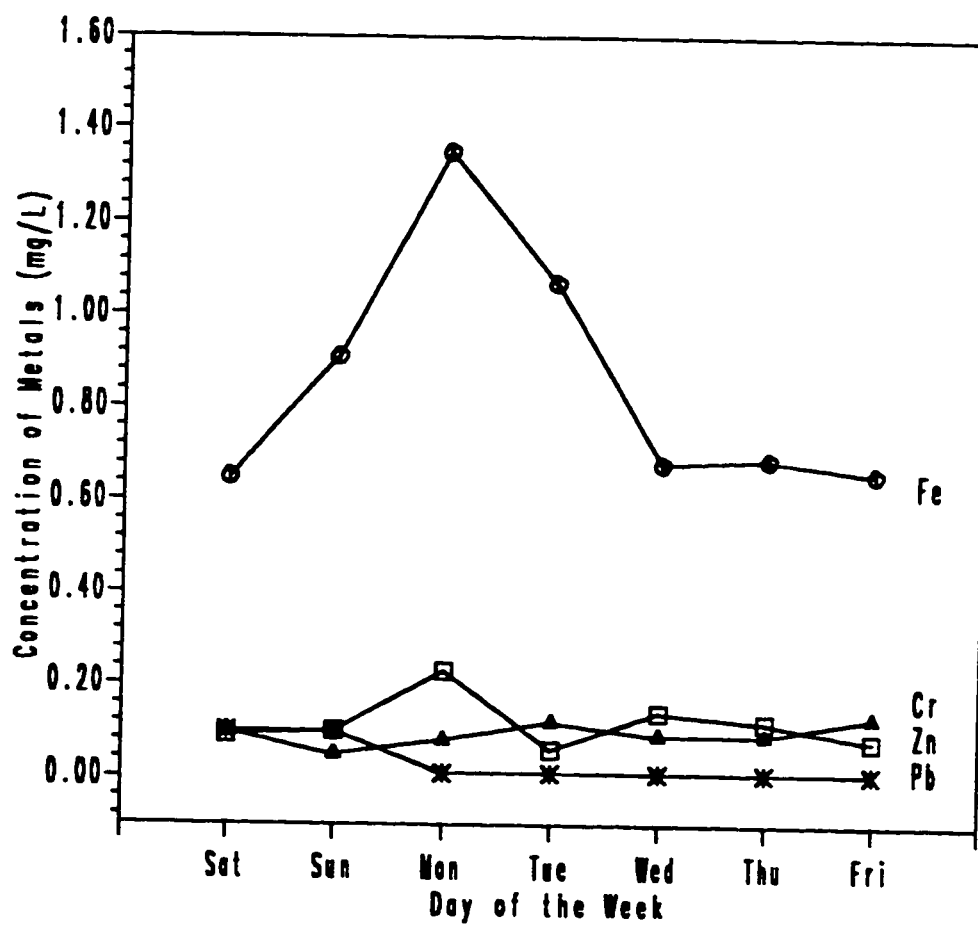
Fig. 5.9 : Average Diurnal Concentration of Heavy Metals in Final Effluent.

Ca, Mg, Na and K were also measured for one-day composite samples of both the wastewaters. The results are plotted in Figures 5.10 and 5.11. The average values and ranges of all the parameters discussed above for the phosphate stream wastewater and final effluent along with the chloride and sulfate concentrations are summarized in Table 5.1 and 5.2, respectively.

Relation between BOD, COD and TOC

Establishment of a constant relation between the parameters BOD, COD and TOC can save a considerable amount of time because of the rapidity of measurement of one parameter over the other. Hence an attempt was made to establish the relation between the aforementioned parameters.

The average COD/TOC ratio for the phosphate stream wastewater and final effluent was found to be 2.51 and 3.38 respectively. Stoichiometrically the COD/TOC of a wastewater would be expected to approximate the molecular ratio of oxygen to carbon [58] i.e , (32/12 = 2.66). Theoretically, the ratio limits would range from zero, when the organic material is resistant to dichromate oxidation, to 5.33 for methane or lightly higher when inorganic reducing agents are present.

A great variability between the calculated and measured COD/TOC values for pure compounds was also reported [58]. For example, for petrochemicals ethanol, methanol and benzene, the calculated COD/TOC was found to be 3.35, 3.89 and 0.84 respectively. Hence when the constituents of a wastewater are like compounds mentioned above a constant COD/TOC value cannot be established. The variation of the concentration of the compounds may shift the COD/TOC ratio to a considerable extent.
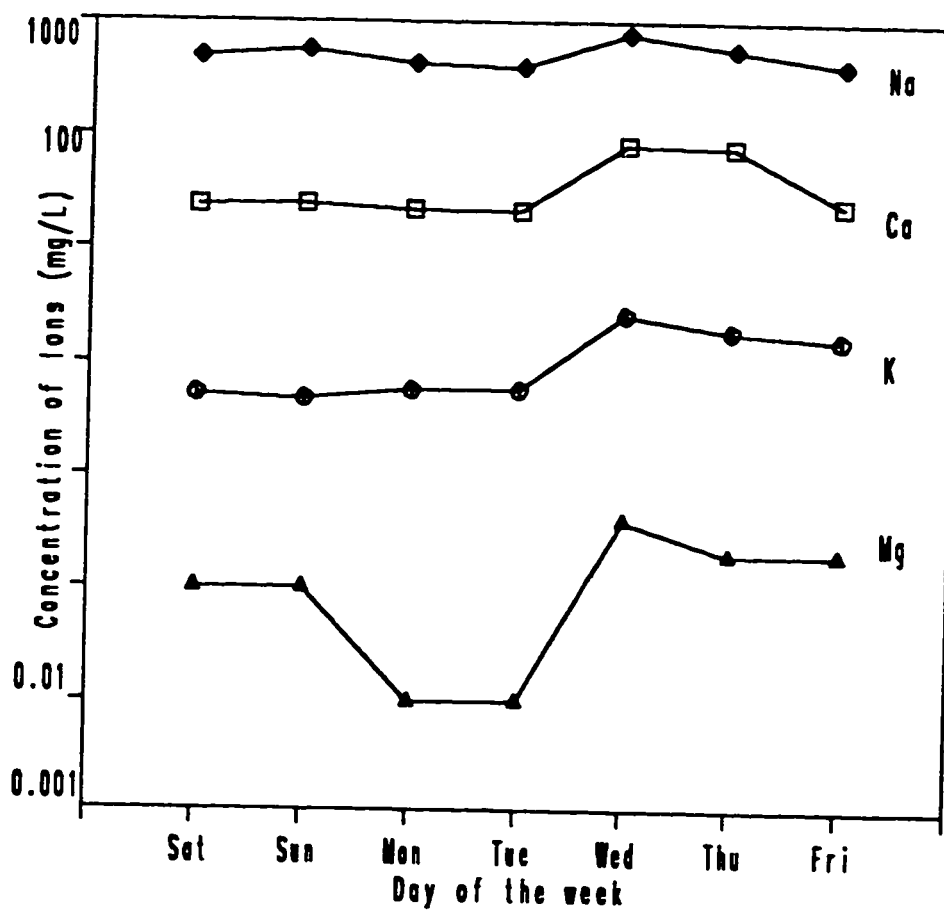
Fig. 5.10 : Average Diurnal Concentration of Ca, Mg, Na and K in Phosphate Stream Wastewater.
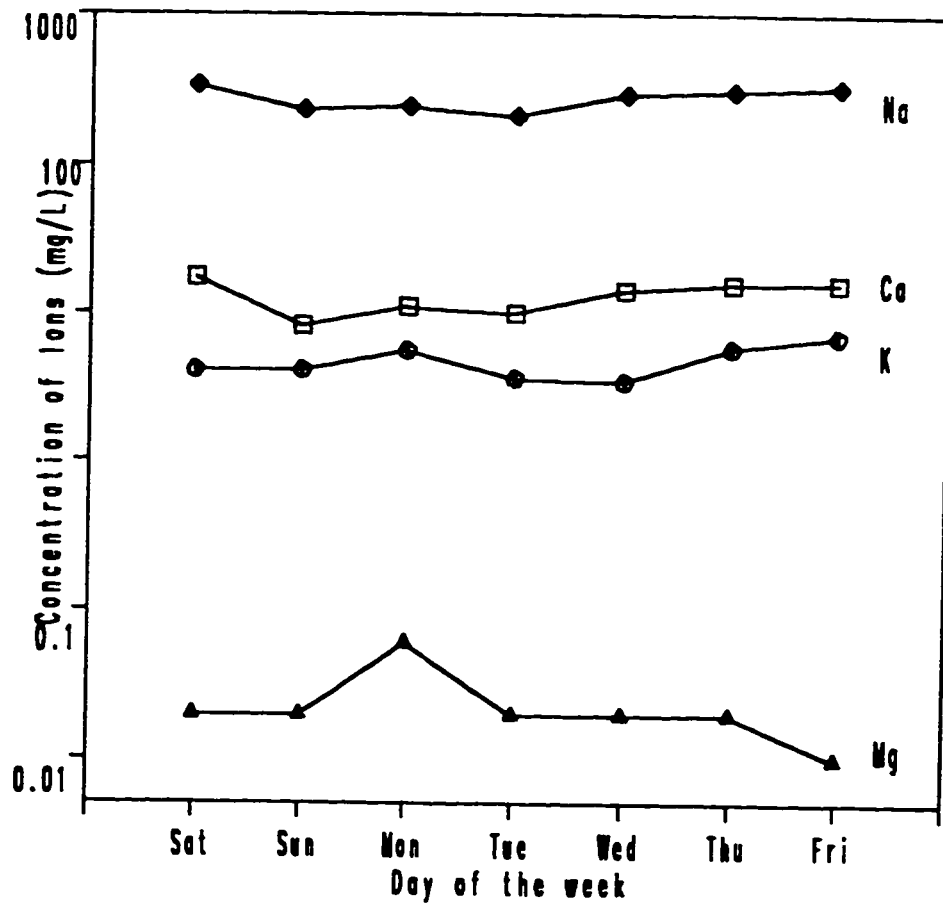
Fig. 5.11 : Average Diurnal Concentration of Ca, Mg, Na and K
in Final Effluent.

Table 5.1 : Characteristics of Phosphate Stream Wastewater.

Parameter	Values	Range
pH	--	10.2-11.5
Conductivity, μmhos/cm	650	560-875
Temperature, °C	50	--
Flow rate, m³/d	1950	--
Total Organic Carbon (TOC)	73	63-98
Chemical Oxygen Demand (COD)	183	135-434
Biological Oxygen Demand (BOD)	56	45-68
Total Solids	725	619-891
Volatile	144	133-150
Fixed	581	442-787
Suspended Solids	333	196-590
Volatile	72	48-192
Fixed	2615	165-529
Total Kjeldahl Nitrogen (TKN)	0.8	0.2-1.6
Ammonia Nitrogen	nil	--
(Nitrate + Nitrite) Nitrogen	nil	--
Total Phosphorous	27	23-21
Ortho-phosphorous	1.4	1.0-1.9
Sulfate	230	128-342
Chloride	19	14-26
Calcium (Ca)	40	35-83
Magnesium (Mg)	8	6-14
Sodium (Na)	522	392-783
Potassium (K)	1.2	0.6-2.7
Iron (Fe)	0.72	0.35-0.97
Manganese (Mn)	0.02	0.01-0.04
Copper (Cu)	0.02	0.01-0.04
Zinc (Zn)	0.05	0.04-0.08
Lead (Pb)	0.01	0.01-0.01
Chromium (Cr)	0.06	0.05-0.11

N.B:- Parameters not expressed are in mg/L except pH.

Table 5.2 : Characteristics of Final Effluent.

Parameter	Values	Range
pH	--	6.2-7.6
Conductivity, μmhos/cm	875	746-925
Temperature, °C	30	--
Flow rate, m³/d	4800	--
Total Organic Carbon (TOC)	65	33-119
Chemical Oxygen Demand (COD)	220	74-386
Biological Oxygen Demand (BOD)	69	56-84
Total Solids	676	570-774
Volatile	82	59-124
Fixed	594	489-711
Suspended Solids	30.5	18-62
Volatile	24	13-56
Fixed	16.5	9-38
Total Kjeldahl Nitrogen (TKN)	2.6	1.2-3.8
Ammonia Nitrogen	0.8	0.2-2.4
(Nitrate + Nitrite) Nitrogen	nil	--
Total Phosphorous	19	11-28
Ortho-phosphorous	6.1	3.2-7.9
Sulfate	253	201-286
Chloride	172	148-213
Calcium (Ca)	14.5	8.1-17.3
Magnesium (Mg)	16	12-22
Sodium (Na)	290	215-339
Potassium (K)	5.7	3.4-6.9
Iron (Fe)	0.95	0.65-1.45
Manganese (Mn)	0.02	0.01-0.04
Copper (Cu)	0.02	0.01-0.06
Zinc (Zn)	0.02	0.04-0.20
Lead (Pb)	0.01	0.01-0.01
Chromium (Cr)	0.08	0.05-0.13

N.B:- Parameters not expressed are in mg/L except pH.

The range of COD/TOC for the phosphate stream wastewater and the final effluent was 1.55 to 4.74 and 1.31 to 4.98 respectively. The variability in the COD/TOC values indicates that the constituents of the wastewater were inconsistent. This can be a valuable aid in predicting the organic loads to various treatment processes.

The COD vs TOC values for the phosphate stream wastewater and final effluent are plotted in Fig's 5.12a and 5.12b, respectively. A remarkably good straight line fit was achieved for the final effluent whereas there was a scatter in the data points for the phosphate stream wastewater. The scatter again indicates a great variability in the constituents which does not give the calculated COD/TOC values. In Table 5.3 the COD/TOC values for these two streams are compared with the values available in literature for petrochemical wastewaters. As seen from Table 5.3 the COD/TOC ratios for SADAF wastewater do not correlate well with the values reported in the literature.

The average BOD/COD ratio was found to be 0.31 for both the stream for the composite samples obtained during wastewater survey. The low value of BOD/COD ratio indicates the presence of low concentrations of readily biodegradable compounds. The ranges of BOD and COD also suggest that, while the concentrations of biodegradable compounds are relatively constant, the non-biodegradable portion varies to a great extent. Table 5.3 shows the BOD/COD ratio of the wastewaters and other petrochemical wastewaters as found in the literature.

Similarly the average BOD/TOC ratios were found to be 1.06 and 0.78 for the final effluent and phosphate stream, respectively. The BOD/TOC ratios for
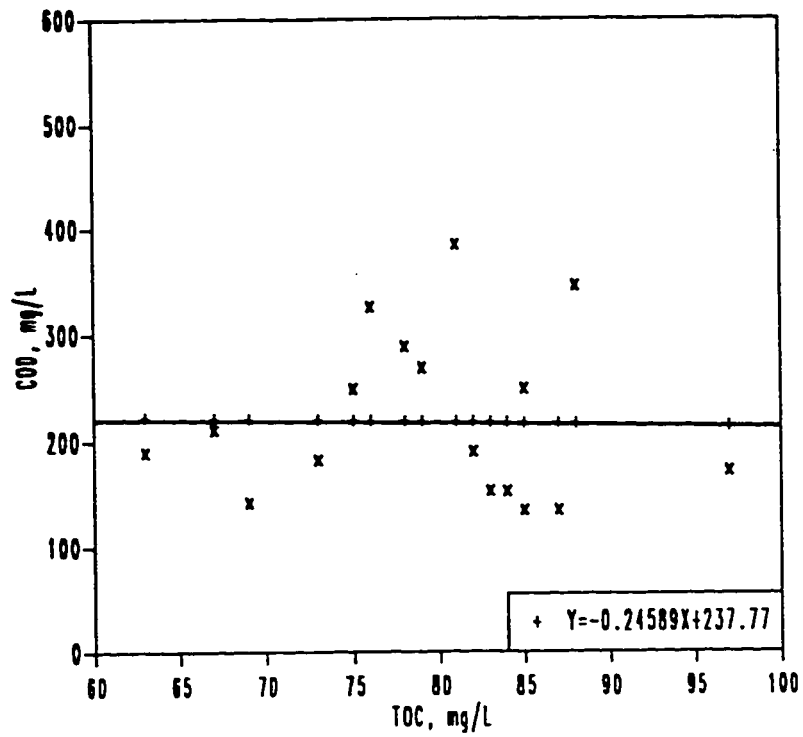
Fig. 5.12a : Correlation of TOC and COD for Phosphate
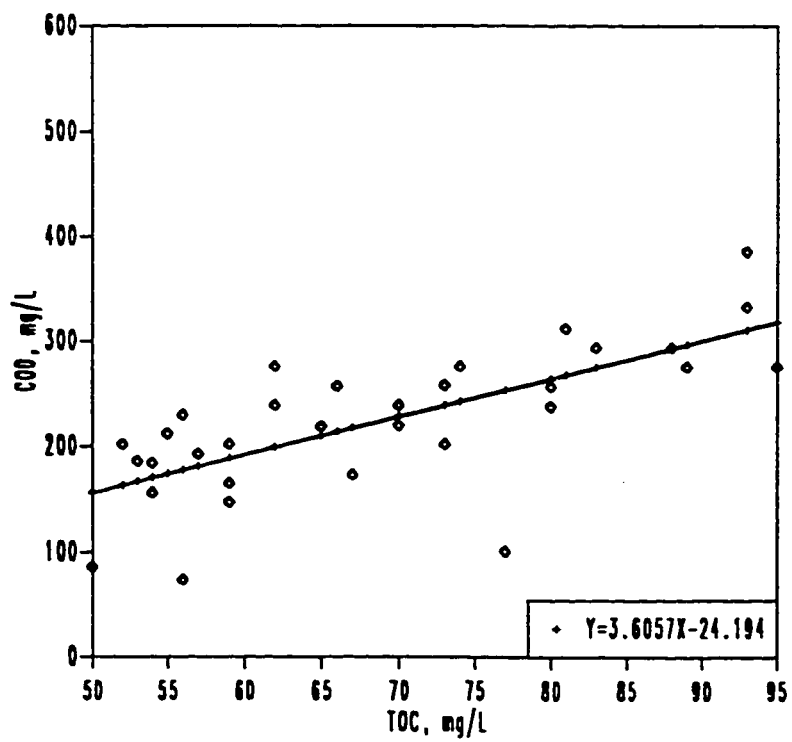
Fig. 5.12b : Correlation of TOC and COD for Final Effluent.

Table 5.3 : Comparison of Oxygen Demand and Organic Carbon in SADAF
with other Petrochemical Wastewaters.

Reference	BOD	COD	TOC	BOD:COD	COD:TOC	Remarks
Present Study	56	183	73	0.30	2.51	Phosphate Stream
Present Study	69	220	65	0.31	3.88	Final Effluent
Eckenfelder [1]	100	300		0.33		Average Values
Fckenfelder [1]	300	675		0.44		Average Values
Sadow [31]	1300	1500		0.87		Medium Level
Sadow [31]	600	700		0.86		Low Level
Ford et. al. [58]		3310	900		3.32	
Ford et. al. [58]				2.70		
Montes [59]	150	260		0.58		

petrochemical wastewaters are not available in the literature This may be due to the diversity of the wastewater constituents. However, a BOD/TOC value of 1.35 to 2.62 is often used for the domestic wastewater [60].

5.2 Air Stripping

A preliminary investigation was conducted for the removal of volatile organic compounds from phosphate stream wastewater. The phosphate stream wastewater contained a lot of suspended solids which would interfere in the TOC analysis and hence it was first filtered through a Whatman # 44 filter paper. The sample pH was not changed and was as is pH (11.4) and the temperature was at an ambient value of 22°C.

The reactor for the air stripping was the same as was used for the ozonation studies. Humidified air was passed through a column of dry silica gel to remove any impurities present in air. The flow rate of air was maintained at a constant value of 2 L/min.

The results of the feasibility test conducted at an ambient temperature of 22°C did not give good response and the removal of TOC was less than 2 percent. Since the phosphate stream wastewater at the plant was at high temperature (around 50°C) the sample temperature was also raised to 50°C. The result of the study is shown in Fig 5.13. From this figure it can be seen that TOC reduced from 75.5 mg/L to 70.0 mg/L at the end of 2 hours of aeration.

Since the response of air stripping process was found to be poor, further studies were not carried out in this area.
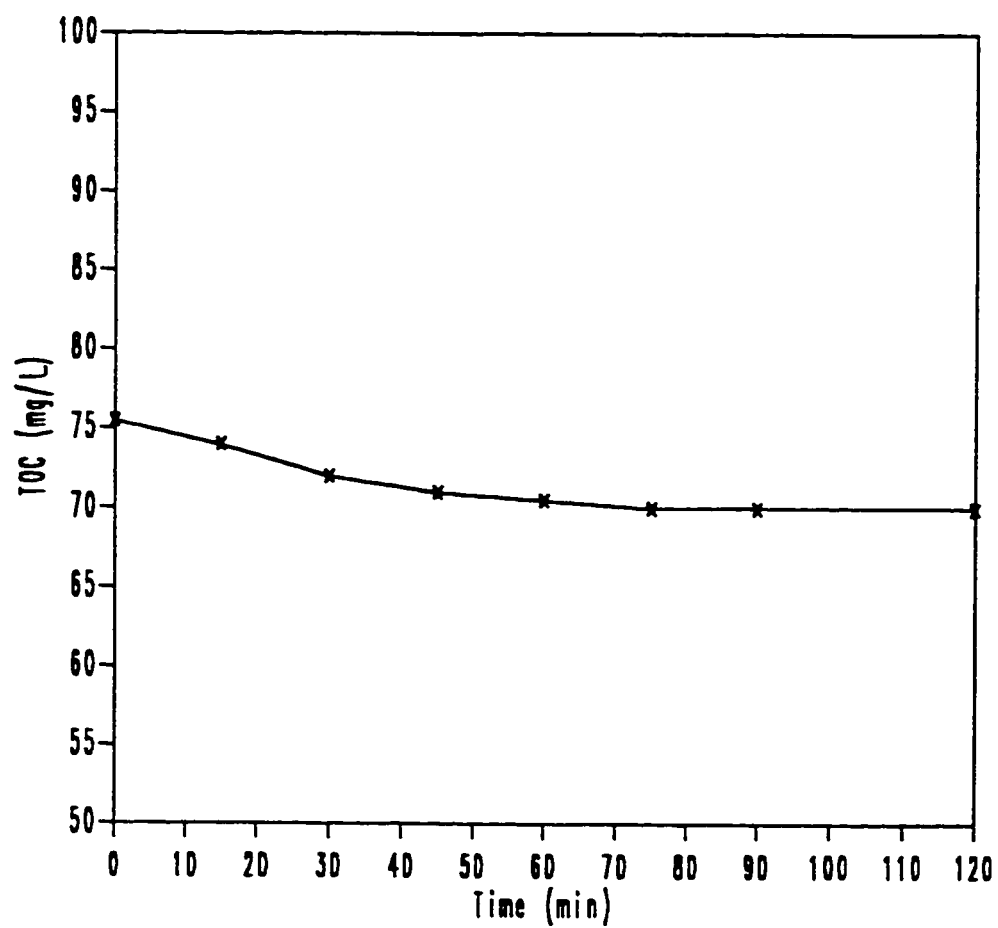
**Fig. 5.13 : Feasibility Study for Air Stripping of TOC
from Phosphate Stream Wastewater.**

5.3 Activated Carbon Treatment

5.3.1 Equilibrium Time

The determination of equilibrium time is important before conducting the adsorption isotherm studies. Equilibrium time in general depends upon a number of factors such as feed concentration, temperature, and the liquid phase and intraparticle mass transfer rates [61]. Usually intra particle diffusion controls the adsorption rate and will determine the required equilibrium time for a given wastewater. The results of the equilibrium studies are shown in Fig. 5.14, which was conducted by contacting 100-mL aliquots of wastewater with 10 g of pulverized carbon. Analysis of the results indicate that equilibrium was almost reached within the first two hours of the contact time and there was practically no adsorption after three hours. These results are in confirmation of the observations made by Wagner and Jula [62]. They have observed that, 1 to 2 hours are sufficient to reach equilibrium for most industrial wastes. In another study Crittenden *et. al.* [61] recommended five to seven days for adsorption studies. However, in this study six hours of contact time was chosen for conducting isotherm tests to ensure complete equilibrium for different pH values and temperatures.

5.3.2 Feasibility Test

A batch adsorption isotherm test was conducted for determining the feasibility of activated carbon for the removal of TOC from the wastewater. The pH of the wastewater was 11.4 (as is pH) and room temperature was 22°C. The Freundlich isotherm model which is most often employed in the wastewater treatment was
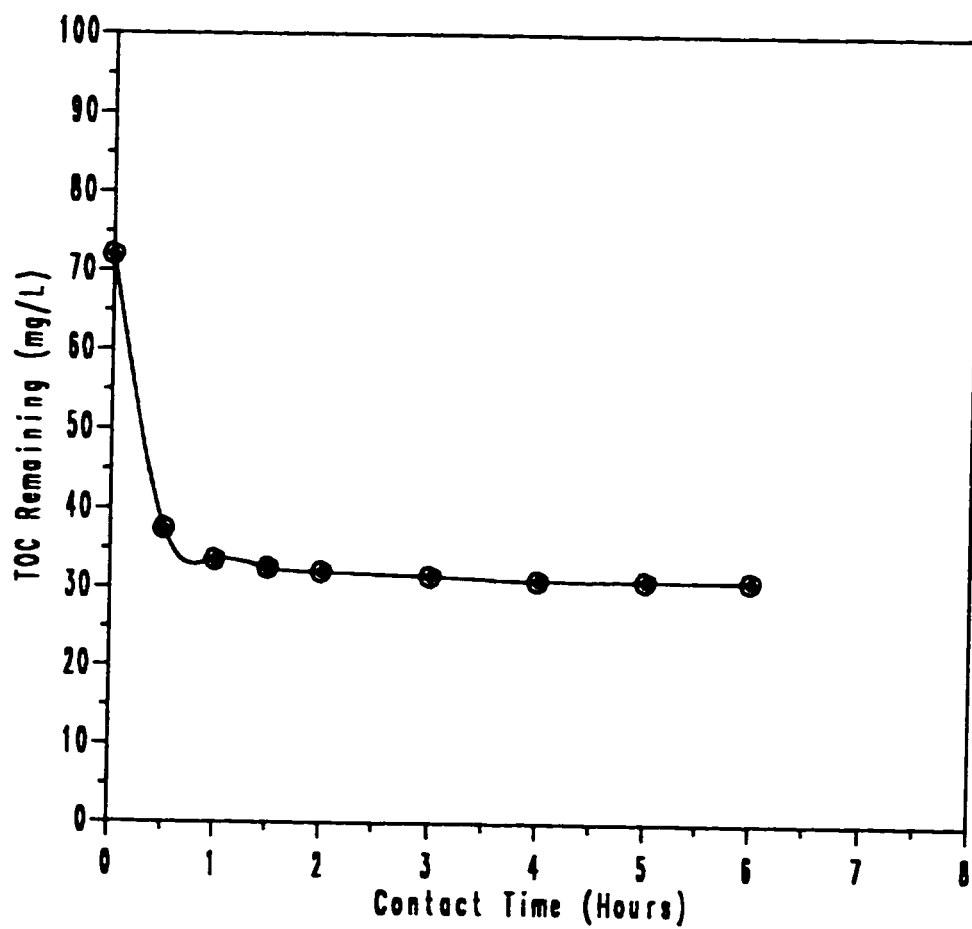
Fig. 5.14 : Equilibrium Adsorption of TOC from Phosphate Stream Wastewater by Activated Carbon.

utilized to correlate the adsorptive capacity (X/M, mg of TOC adsorbed/g of carbon) with the equilibrium concentration of TOC (C, mg/L) for the purpose of estimating the treatment capacity of the carbon for this specific wastewater. The Freundlich isotherm model has the following form [63]:

$$X/M = kC^{\frac{1}{n}}$$ (5.1)

where,

X   = Amount of TOC absorbed

M   = Weight of carbon

C   = Equilibrium concentration of TOC in wastewater

k,n = constants, characterizing the adsorption isotherm.

The plotted data are shown in Fig. 5.15. Sample calculations for the plot parameters are shown in Appendix-B. The shape of the isotherm correspond to a non-linear form with multiphase adsorption. A non adsorbable portion of the TOC was also noticed from the isotherm plot. The non-linear adsorption isotherm pattern obtained may be due to the presence of different species of organics constituting the TOC which exhibits different adsorbabilities [64]. As one species, which dominates the shape of the isotherm, is completely adsorbed, a species remaining in solution exhibits its adsorbability characteristic and the isotherm plot abruptly changes to reflect the new adsorbability. Examination of Fig. 5.15 indicate that the more adsorbable solutes have been removed in the first phase and the less adsorbable solutes in the second phase as evident from the slopes of the isotherms. The nonadsorbable portion of TOC may consist of primary alcohols, aldehydes, ketones and other organics that may be present in the wastewater that has very little affinity to activated carbon adsorption as found by Guisti et. al. [4].
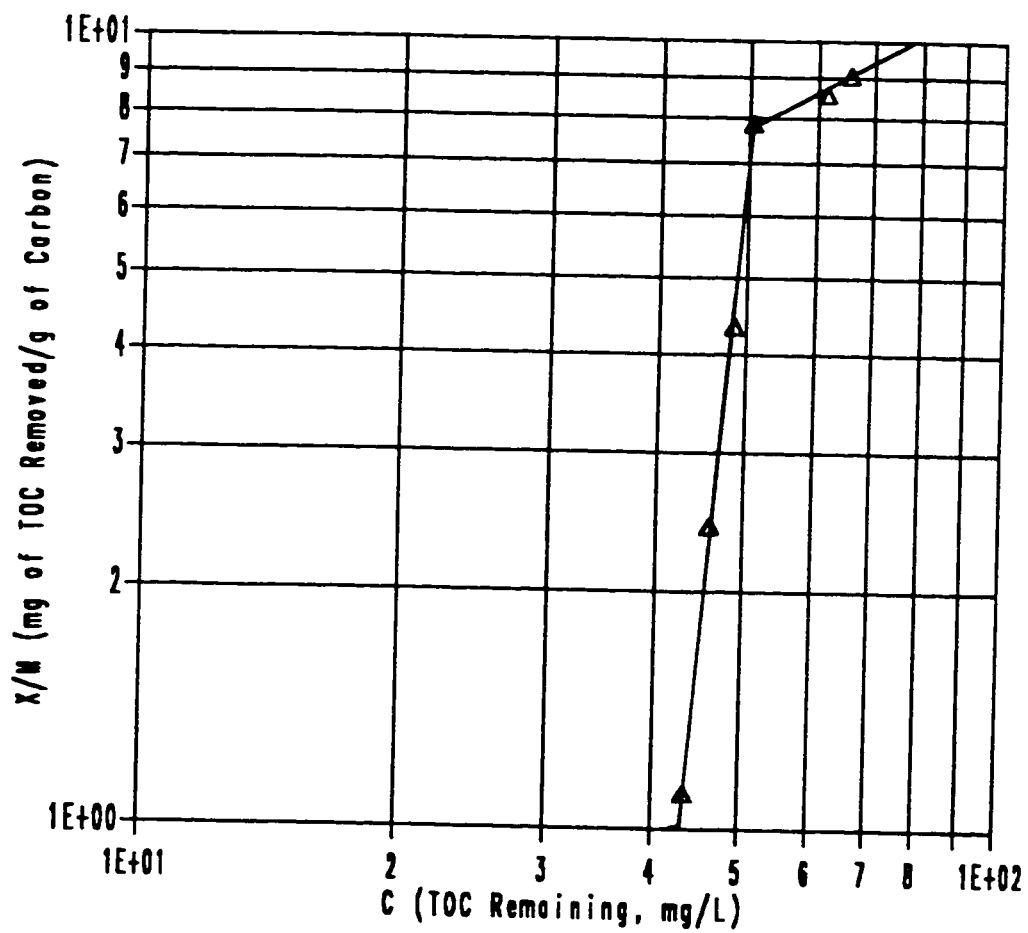
Fig. 5.15 : Removal of TOC from Phosphate Stream Wastewater by
Activated Carbon Adsorption.

5.3.3 Effect of pH

Adsorption isotherms were also determined at different values of pH i.e., 4.0, 7.0 and 12.0 to find the optimum pH value for the treatment; the initial pH values were adjusted by the addition of dilute HCl. The adsorption isotherms are shown in Fig. 5.16. The removal of TOC was 33, 62 and 68 percent for initial pH of 4.0, 7.0 and 12.0, respectively, indicating that lower pH values are favorable for adsorption for this specific wastewater. This suggests the presence of organic acids [65] the adsorption of which were promoted due to the lowering of the pH. The increased adsorption can also be attributed to the compositional change due to changes in pH in which the formation of more adsorbable compounds might have taken place.

5.3.4 Effect of Temperature

Fig. 5.17 shows the adsorption isotherms for temperatures of 10, 30 and 60°C. The removal of TOC increased from 49 to 73 percent when the temperature was lowered from 60 to 10°C. As seen from isotherm results (Fig. 5.17 and Table 5.4) although maximum removal at all carbon dosages occurred for lower temperatures the isotherm deviated from linearity as we go from higher temperature of 60°C (correlation coefficient 0.98) to lower temperature of 10°C (correlation coefficient 0.88) suggesting selective adsorption at lower temperatures. Investigators have found increased adsorption at lower temperatures. Ford [65] observed that the low adsorption at higher temperatures are due to the exothermic nature of the adsorption reactions, whereas, Wagner and Jula [62] hypothesized that increased adsorption at lower temperatures to the fact that equilibrium capacities of the adsorbates being inversely proportional to temperature. However, in some cases
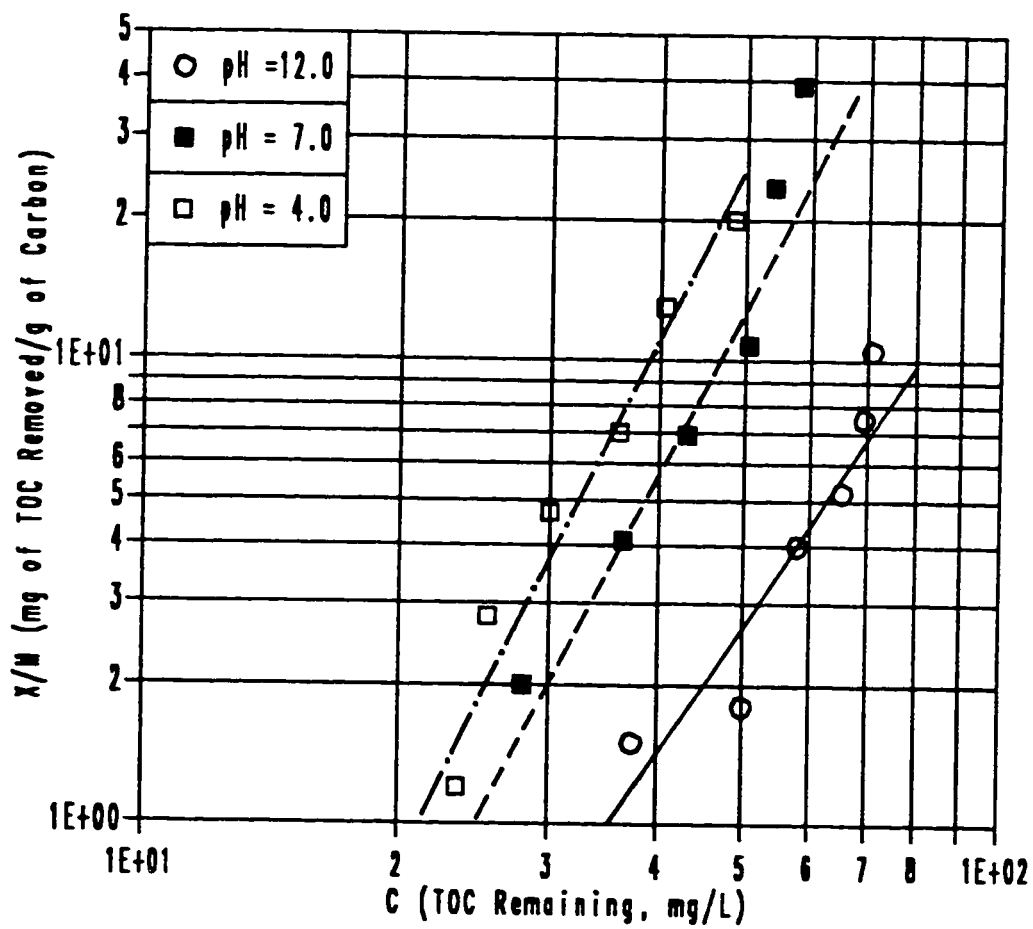
**Fig. 5.16 : Effect of pH on TOC Removal by Activated
Carbon Adsorption.**
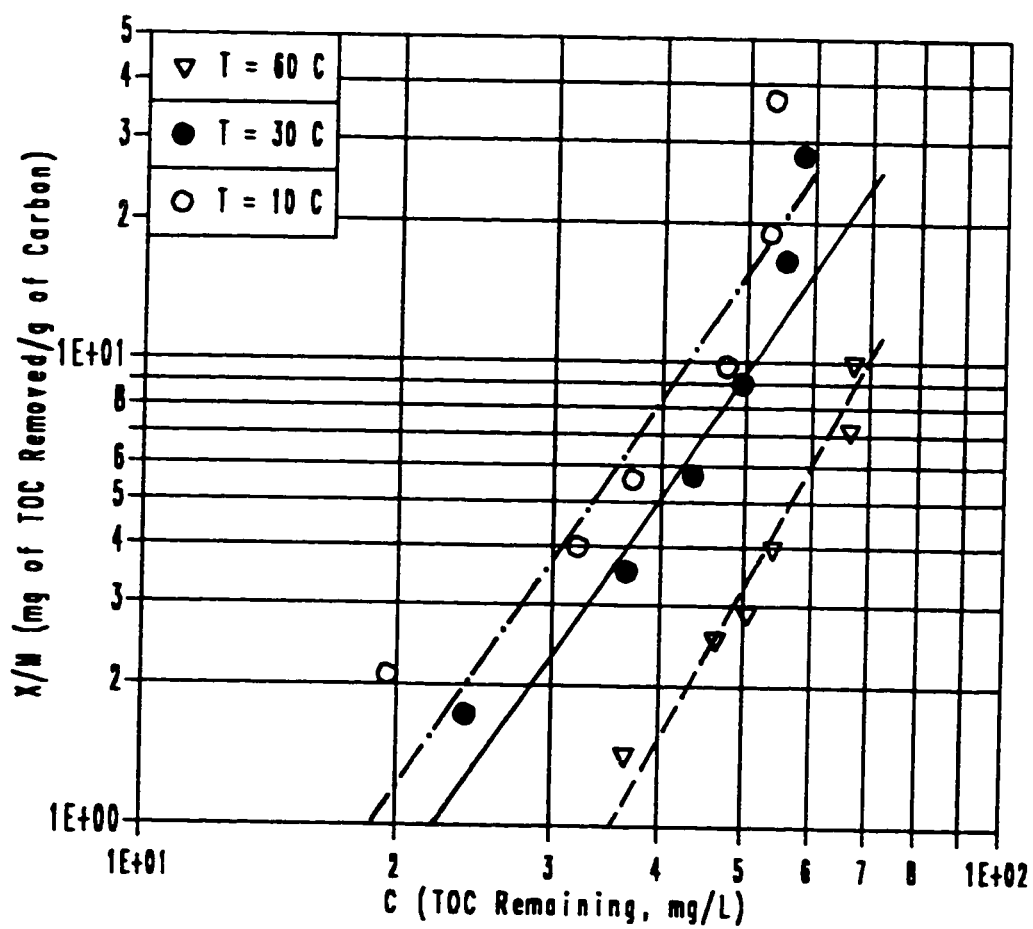
Fig. 5.17 : Effect of Temperature on TOC Removal by Activated Carbon Adsorption.

Table 5.4 : Freundlich Isotherm Coefficients at Different Values of pH and Temperature.

Temp. °C	pH	K	n	r	$\bar{C}$	$\overline{X/M}$
22	4.0	4.8×10^{-6}	0.25	0.98	21.1	145
22	7.0	4.0×10^{-6}	0.26	0.97	24.7	66
22	12.0	2.5×10^{-5}	0.34	0.94	35.7	35
10	7.0	9.4×10^{-4}	0.40	0.88	18.4	42
30	7.0	1.1×10^{-4}	0.34	0.95	21.8	35
60	7.0	2.2×10^{-5}	0.33	0.98	33.8	11

r = Correlation Coefficient
$\bar{C}$ = Equilibrium Concentration of TOC at X/M = 1
$\overline{X/M}$ = (X/M) at Initial TOC Concentration

the temperature was found to increase diffusion rates; thereby increasing adsorption rates [62].

5.3.5 Column Adsorption

A preliminary continuous column study was conducted in order to investigate the removal of TOC in continuous column as compared to batch tests. Previous workers [15,16] have reported increased adsorptive capacity in continuous columns and attributed this increase to the biological activity and the availability of higher number of adsorption sites for preferential adsorption. The column (25 mm diameter and 300 mm long) was operated in the downflow mode at three different flowrates. The GAC used for dynamic studies was of 10-18 mesh size and was given pretreatment similar to the batch tests. Before it was fed into the columns in the form of slurry, it was soaked for 24 hours in distilled deionized water at room temperature for degassification. All the dynamic studies were carried at neutral pH and at room temperature of $22°C$.

Three flow rates of 10, 20 and 30 mL/min , respectively, corresponding to 0.5, 1.0 and 1.5 gpm/ft^2 of loading were studied. The experiments were conducted for 90 min each and the results were plotted as shown in Fig. 5.18. The lower flow rate gave better performance as expected. However, at the end of 90 minutes the effluent in all the three cases contained approximately 25 mg/L of TOC, indicating that preferential adsorption took place which resulted in low effluent TOC when compared to batch tests.
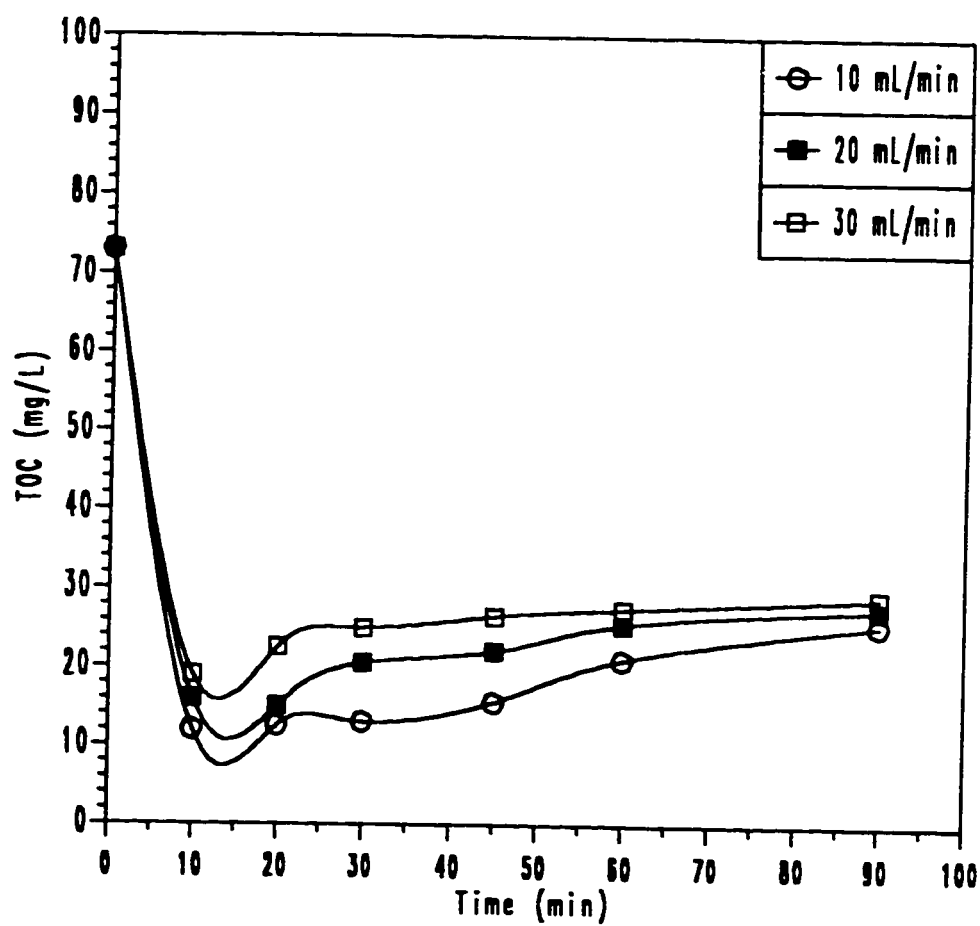
Fig. 5.18 : Effect of Flowrate on TOC Removal by Continuous Column Adsorption.

5.4 Treatment with Ozone

5.4.1 Effect of Gas Flowrate on TOC Removal

In order to find out the effect of mass transfer on the removal of TOC, ozone gas was applied at two different flowrates of of 2 L/min and 4 L/min , respectively to wastewater samples of one liter each for a period of 2 hours. The initial pH and temperature for both the experiments were kept at 7.0 and 22°C , respectively. The ozone concentration in both the experiments did not vary significantly and averaged 17.5 mg/L . The amount of ozone corresponding to this concentration was 2.1 g/hour and 4.2 g/hour respectively, for 2 L/min and 4 L/min flowrates.

As shown in Fig. 5.19 the rates of TOC removal were essentially the same for both the gas flowrates. This shows that the rate of TOC removal is not mass transferred limited. The data fitted well to a first order expression expressed by the following equation :

$$\frac{dTOC}{dt} = -k\,(TOC) \tag{5.2}$$

Where,

(TOC) is the concentration of organics in mg/L at time t, and

k is the first order reaction rate constant, hour^{-1}.

5.4.2 Effect of Ozonation on pH of Wastewater.

For both the gas flowrates studied the pH of the wastewater shifted slightly upwards from neutrality and then decreased to an appreciable level as shown in Fig. 5.20. In 2 L/min run the pH first increased to 7.4 and came down to 4.5 at the end of 2 hours of ozonation. For the same period of ozonation, 4 L/min of gas
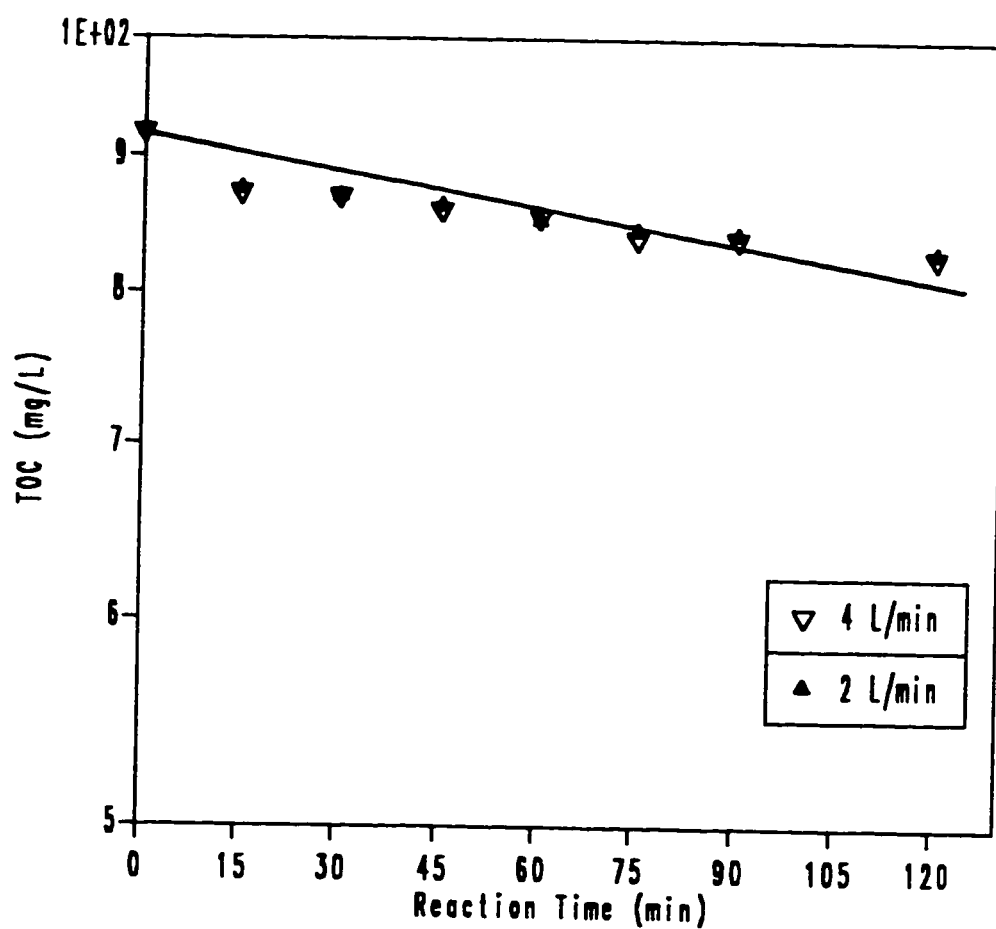
Fig. 5.19 : Removal of TOC from Phosphate Stream Wastewater by Ozone at two Different Flowrates (pH = 7.0; T = 22°C).
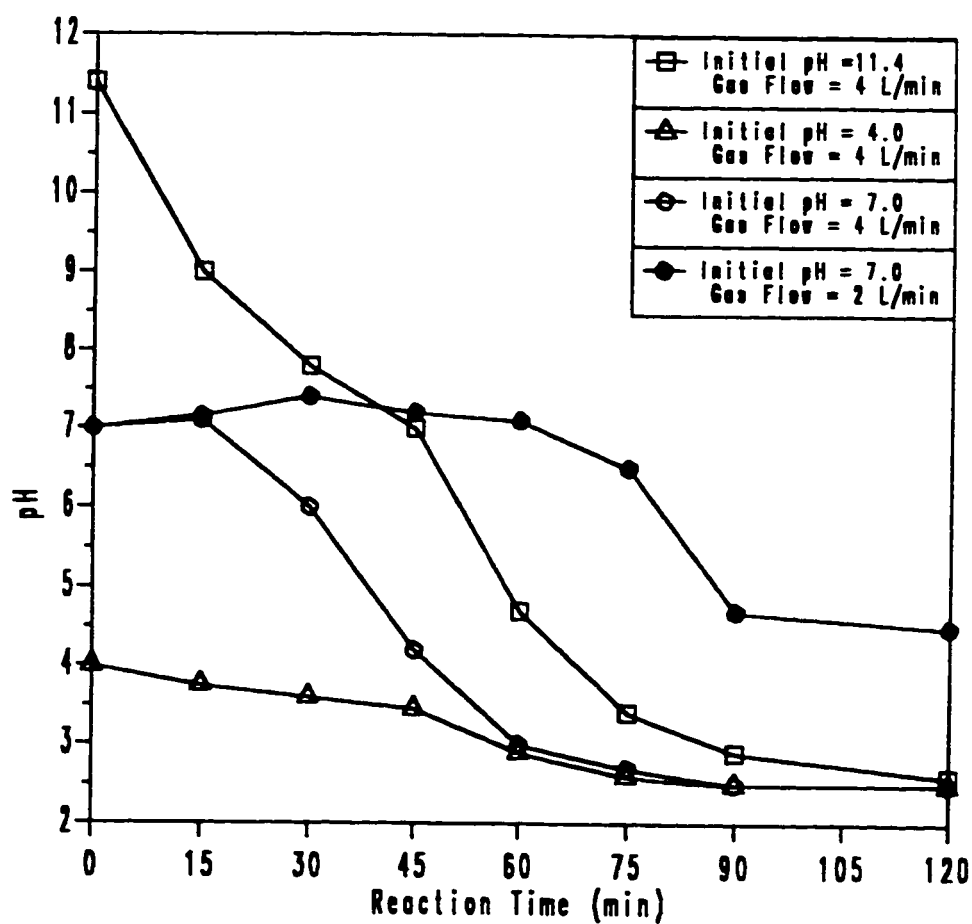
Fig. 5.20 : **Effect of Gas Flowrate on pH of Wastewater and pH Changes During Ozonation at 22°C.**

flowrate resulted in changing the pH first to 7.1 and dropping rapidly to 2.5. The increase in the pH initially can be attributed to the gas stripping of carbon dioxide from the system. The decrease in the pH may be due to the formation of organic acids like acetic acid, resulting from the ozone oxidation of alcohols, aldehydes, etc., known to be present in the wastewater. Eisenhaur [22] studied the ozonation of phenolic wastes and found that the initial pH values in the range of 3.0 to 9.14 decreased as reaction proceeded to values of 3.0 to 3.5. Kirk et. al. [67] conducted pilot plant studies on the tertiary treatment of municipal wastewater and also found the pH to decrease consistently.

The difference in the final pH values for the two flowrates indicate that the ozone oxidation reactions for this wastewater, leading to the formation of organic acids are mass transferred limited. Also, samples with initial pH of 4.0 and 11.4 were found to be reduced to pH of approximately 2.5 at the end of 2 hours of ozonation (Fig. 5.20).

5.4.3 Effect of Initial pH

Wastewater samples were adjusted at four different pH values of 4.0, 7.0, 10.0 and 11.4 in order to evaluate the effect of initial pH upon TOC removal. In all the tests the temperature was at an ambient value of $22°C$. In all the four tests, after approximately two hours there were small reduction in the TOC values. The TOC values at the end of each reaction time is shown in Fig. 5.21. Fig. 5.22 shows the first order regression curve for the TOC reductions at different initial pH values. As seen from the Fig. 5.21, ozonation at an initial pH value of 4.0 resulted in the smallest reduction in TOC. The maximum removal of TOC occurred at the highest pH value studied i.e., 11.4. Neigowski [17] studied the oxidation of phenol with
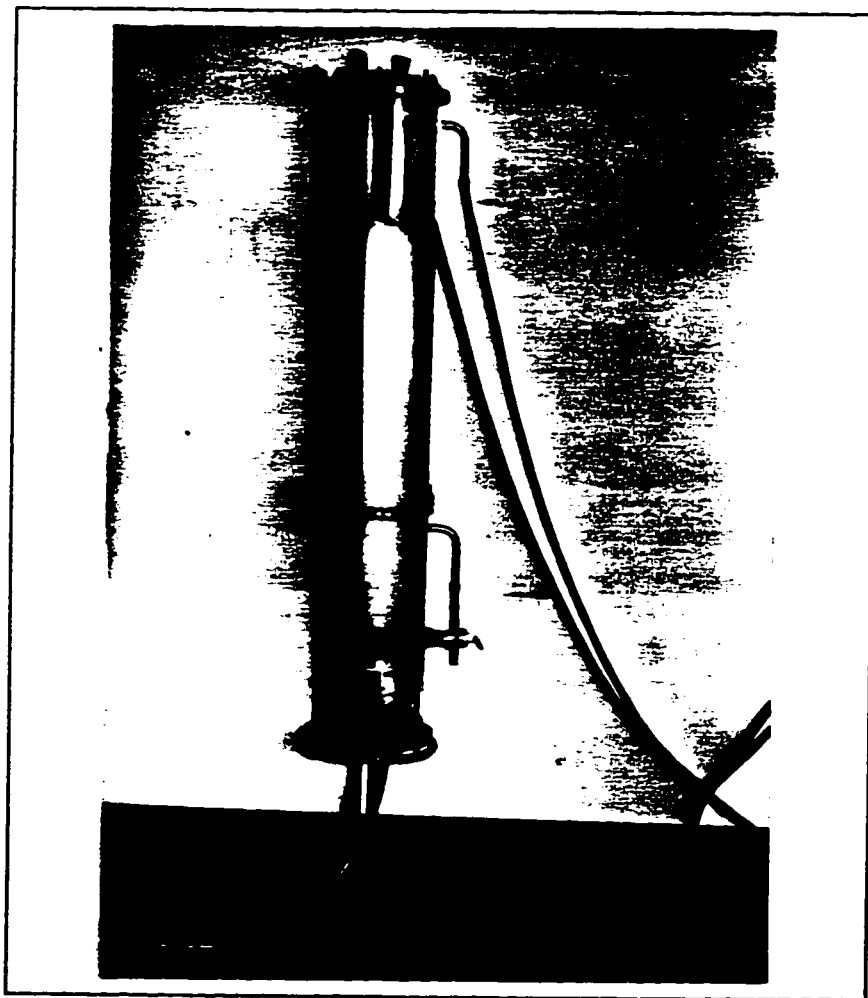
**Plate 3 : Reactor Showing the Foam Produced During Ozonation of
Phosphate Stream Wastewater.**
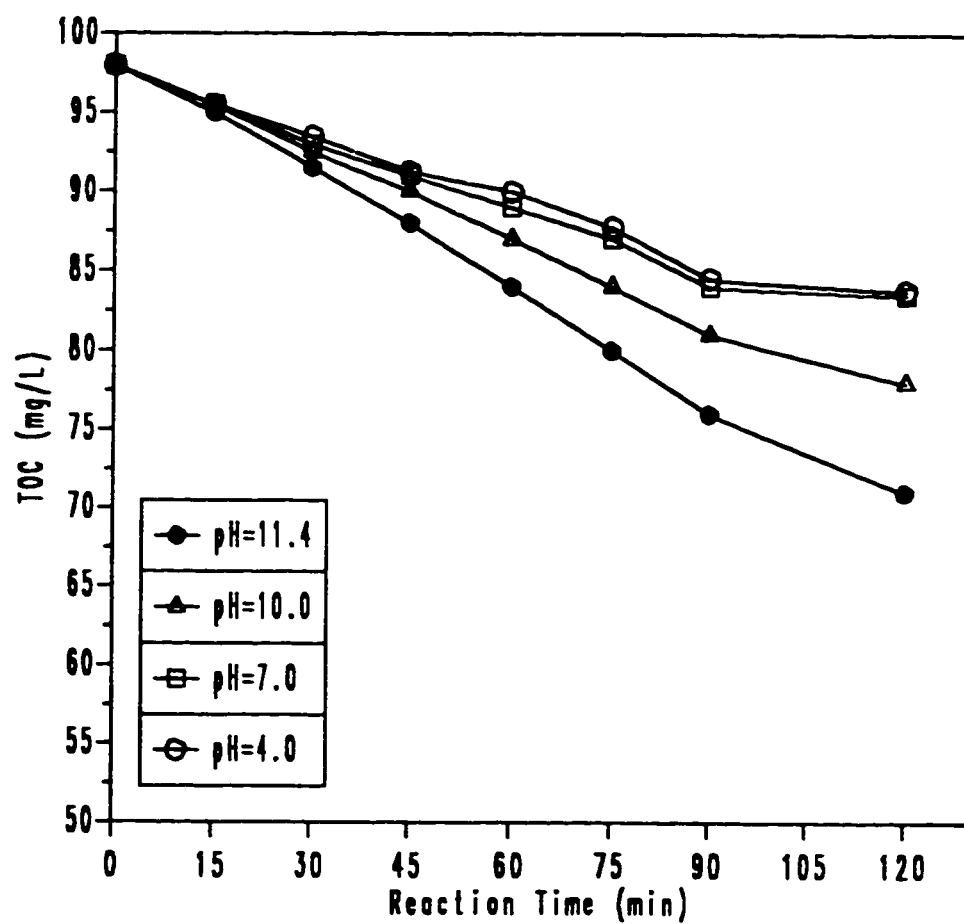
Fig. 5.21 : **Removal of TOC with Ozone at Various Values of Initial pH and Temperature of 22°C.**
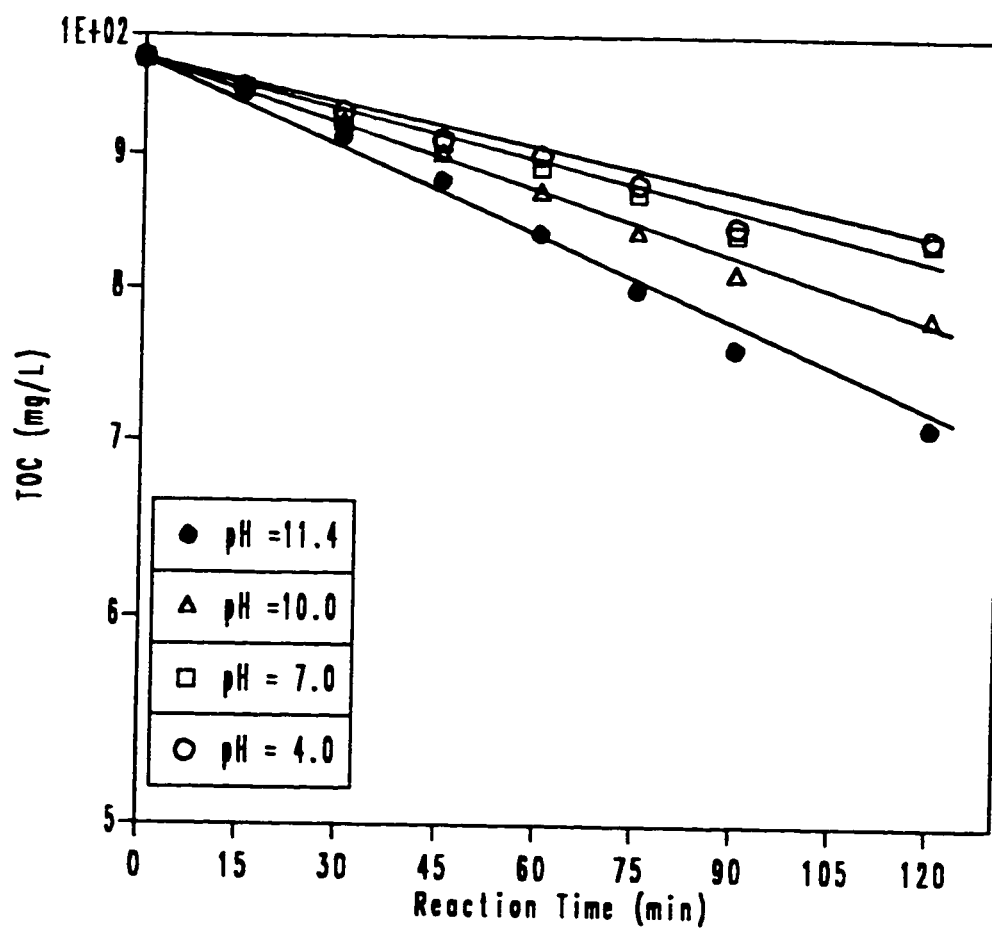
Fig. 5.22 : Effect of Initial pH on TOC Removal by Ozone for a First Order Equation.

ozone and found that at optimum pH of 12.0 the oxidation was virtually complete, and this value is close to the optimum value of 11.4 as given by Anon [19]. Kwie [68] evaluated ozone treatment of three wastestreams from a synthetic polymer plant containing high concentrations of unsaturated organics. As much as 90% COD removal was found in case of a waste containing unsaturated hydrocarbons at an optimal pH of 12.6 [25]. The oxidation of organic matter with ozone, in terms of TOC reduction from a petroleum refinery wastewater was studied by Schwartz et. al. [26]. They found a reduction of 5.5, 10.4 and 26.4 percent for ozone dosages of 26, 60, and 159 mg/L respectively. The initial TOC in all the cases were 81.5 mg/L . The increased removal of organics at higher pH values are evident from literature. This is due to the fact that the reactivity of ozone is maximum at higher pH values. Moreover, at high pH values the ionization of constituents might take place allowing for an electrophillic attack by ozone.

5.4.4 Effect of Temperature

Samples were ozonated for two hours at elevated temperatures of 25, 40 and 60°C to investigate the TOC removal at higher temperatures. The initial pH was not changed and was kept at 11.4 for all the tests, since higher removal of TOC was observed at this pH in the previous tests. Fig. 5.23 shows the TOC values at the end of each reaction time. The data fitted well to a first order equation as shown in Fig. 5.24. Greater reductions were obtained for higher values of temperatures studied. Eisenhaur [22] also found that higher temperatures favor oxidation of phenols by ozone.

Table 5.5 gives the TOC and COD removals along with the pH changes at the end of two hours of ozonation for different initial pH values and temperatures.
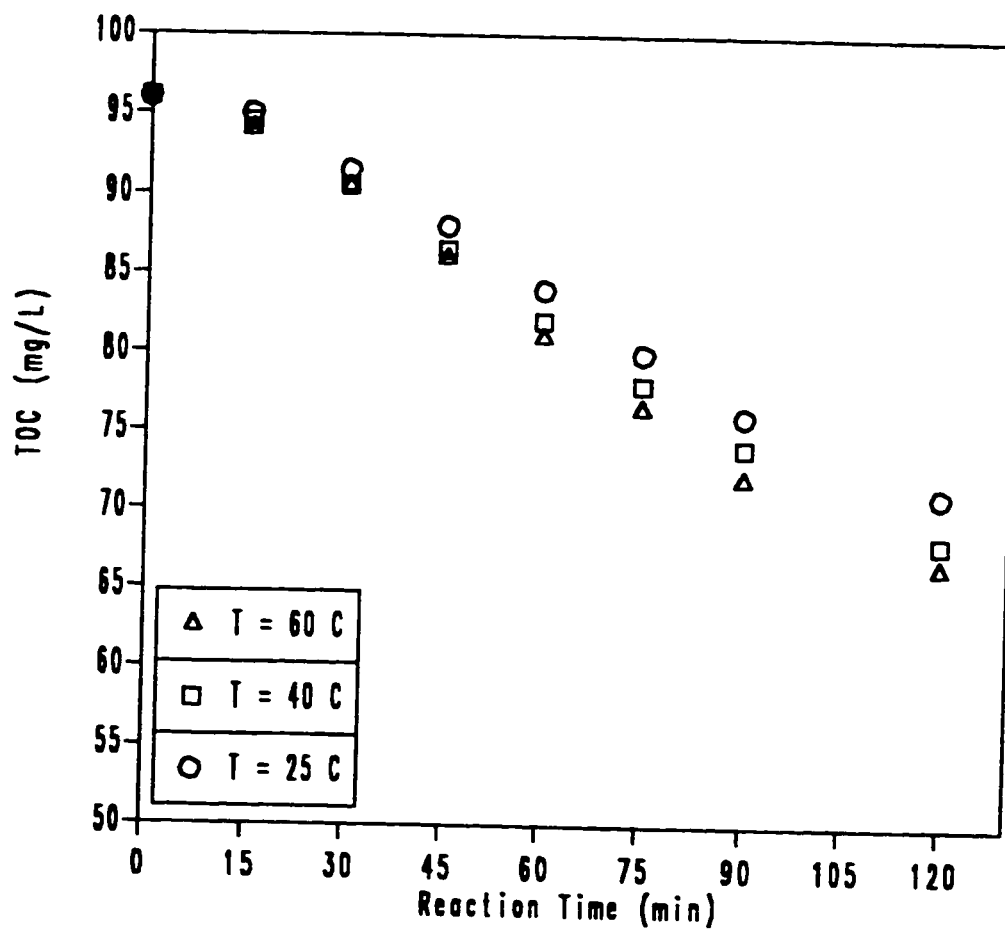
Fig. 5.23 : Removal of TOC by Ozone at Different Temperatures and at Initial pH of 11.4.
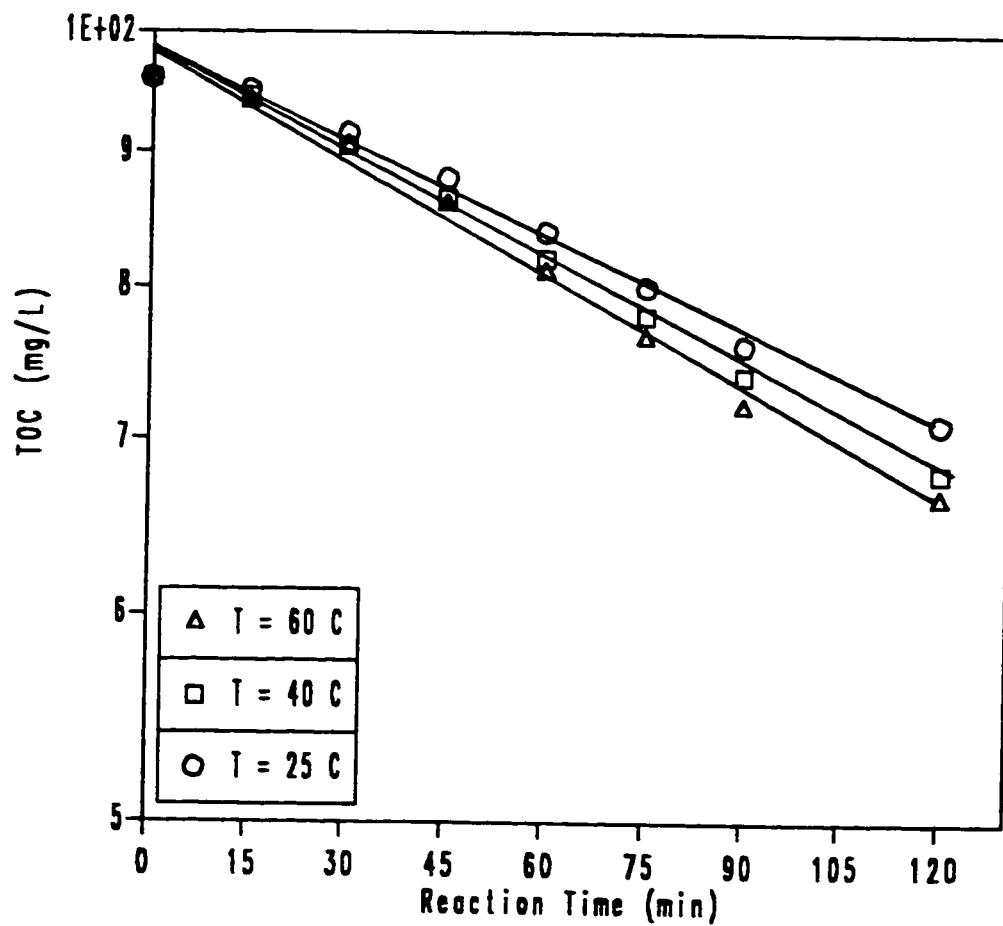
Fig. 5.24 : Effect of Temperature on TOC Removal by Ozone for a First Order Equation.

Table 5.5 Removal of TOC, COD and pH Changes During 2 Hours of Ozonation for Different Initial pH Values and Temperature

TEMPERATURE (°C)	INITIAL pH	FINAL pH	TOC REMOVED (%)	COD REMOVED (%)	FIRST ORDER RATE CONSTANT k hr⁻¹
22	4.0	2.5	9.4	16.1	0.11
22	7.0	2.5	13.0	24.2	0.12
22	10.0	2.8	18.8	26.7	0.17
22	11.4	3.4	26.1	35.5	0.23
25	11.4	3.2	27.6	37.2	0.23
40	11.4	2.6	30.6	40.3	0.25
60	11.4	2.5	32.5	42.3	0.27

The first order reaction rate constants as calculated from equation 5.2 are also given in Table 5.5. As shown in the table the TOC removal increased from 9.4 to 26.1 percent when the pH was changed from 4.0 to 11.4. The corresponding COD removal was 16.1 and 35.5 percent, respectively. Similarly, when the temperature was raised from 25°C to 60°C the TOC removal increased from 27.6 to 32.2 percent, respectively. The corresponding COD removal was increased from 37.2 to 42.3 percent.

5.5 Combined Ozone and Activated Carbon Treatment

In order to find out the effect of ozonation on the adsorptive capacity of the activated carbon and assess the combined removal of TOC both batch scale and continuous scale experiments were conducted at room temperature of 22°C. The wastewater was ozonated for one hour at neutral pH of 7, and at a gas flowrate of 2 L/min with an ozone concentration of 17.5 mg/L in the gas phase The adsorption isotherms for the ozonated and unozonated samples in a batch test are plotted according to the Freundlich isotherm (Fig. 5.25). As seen from the isotherms the adsorption for the unozonated sample follow a multiple phase or nonlinear pattern. Whereas, dissimilar adsorption characteristics are displayed by the components present in the wastewater after ozonation. Furthermore, there seems to be a reduction (16 percent)in the non adsorbable residue from the wastewater.

As shown in Fig. 5.25 ozonation improved the adsorption of TOC from the wastewater. However, ozonation also decreased the TOC of the wastewater as is evident from previous discussions. Therefore, the improvement in adsorbability of the remaining components (after ozonation) comprising TOC could be caused
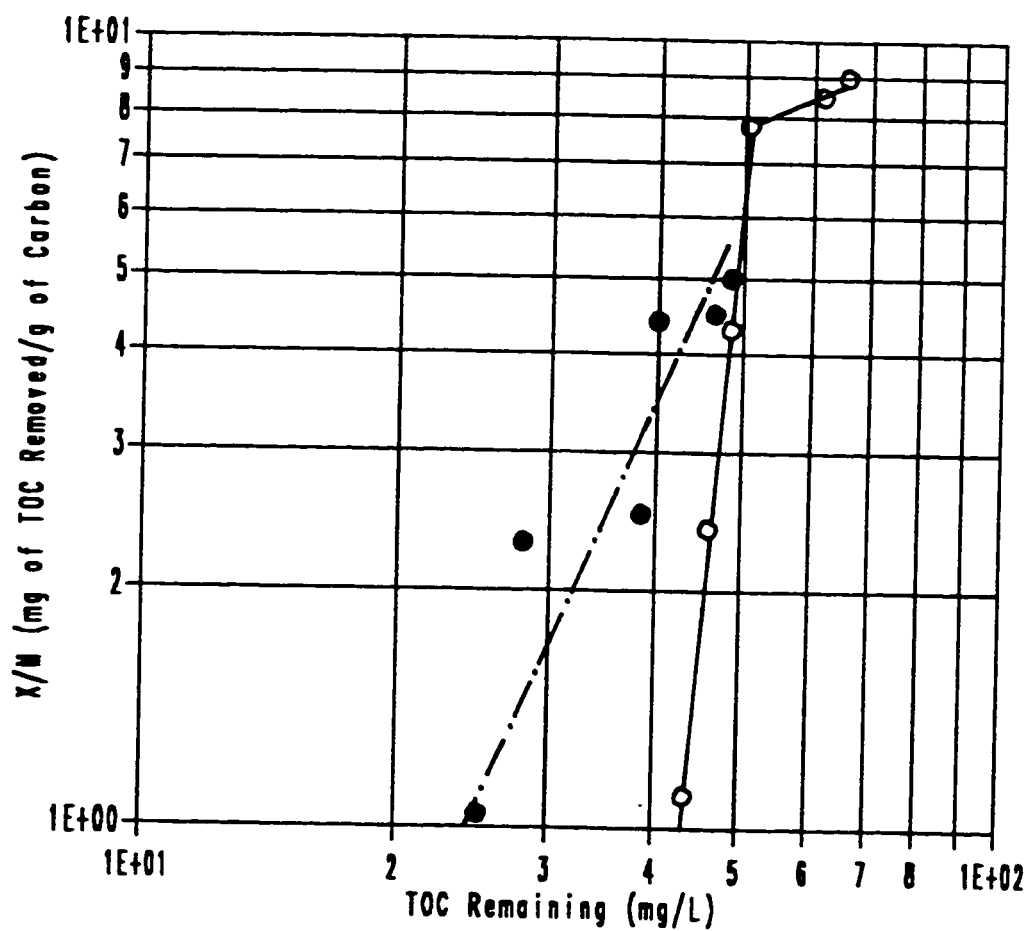
Fig. 5.25 : Adsorption Isotherms for Ozonated and Un-Ozonated
Phosphate Stream Wastewater.

either by a reduction in the overall concentration of the components or by a compositional change wherein the adsorbability of each component is altered by selective removal of components by ozonation or by both. The compositional change is evident as the pH of wastewater decreased for all the ozonation studies. Hence it may be concluded that the increased adsorption after ozonation is due to both the compositional change and reduction of various components comprising TOC of the wastewater.

The reduction in the TOC of the ozonated and unozonated sample in a continuous column study is shown in Fig. 5.26. The data show that the adsorptive capacity of carbon is increased due to ozonation of the wastewater. One of the main factors for the increased removal of organics might be the formation of organic acids during ozonation, which are more adsorbable to activated carbon than alcohols, aldehydes, etc., as reported by Guisti et. al. [4].

5.6 Biological Treatment in SBRs

5.6.1 Acclimatization of Wastewater

Acclimatization of industrial wastewater is essential for its treatability. One of the popular methods by which a viable culture of microorganisms can be developed is by using the mixed liquor from a biological treatment plant. The mixed liquor and sewage used during acclimatization period were obtained from North Aramco wastewater treatment plant, Dhahran. The acclimatization period was for a total of six weeks. In the first week only raw sewage was fed to the reactors. In the following weeks wastewater was introduced first by adding 25% and then increasing by 25% in each week. The reactors received 100% wastewater in the
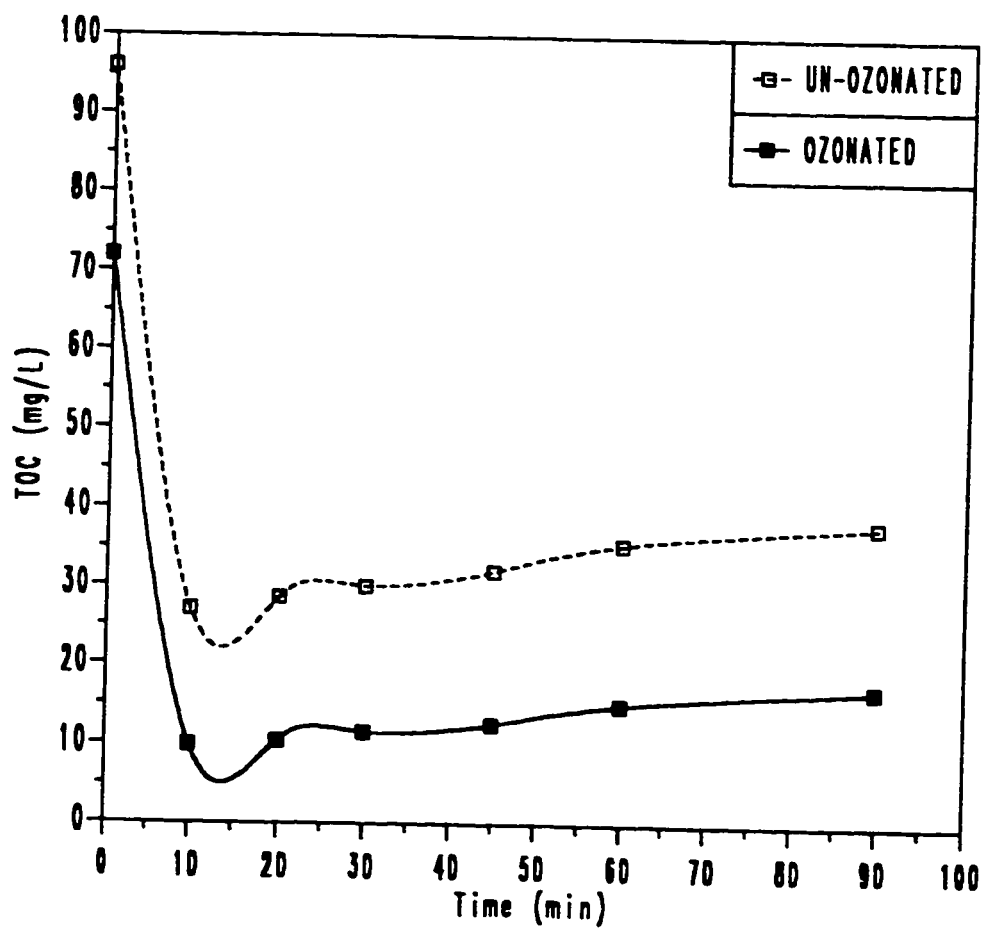
Fig. 5.26 :   Removal of TOC by Combined Ozonation and Activated Carbon Adsorption.

fifth week. The Sample mixing schedule for the acclimatization of the wastewater is summarized in Table 5.6. Then the reactors were operated for additional one week to allow steady state conditions to be reached.

Four reactors were started with an initial MLSS concentration of 1500 mg/L The feeding periods for these reactors were 24, 12, 8 and 6 for SBR-1, SBR-2, SBR-3 and SBR-4, respectively. The reactor operating strategy for the reactors is shown in Fig. 5.27. The reactors were fed in a batch mode (0 hour fill time) and the reaction started by actuating the aeration equipment. The air supplied to these reactors was constant at 900 mL /min At the end of the react period water was added to make-up the volume lost due to evaporation. Then air was stopped and the contents of the reactors were allowed to settle in quiescent environmental conditions by gravity. At the end of 30 min the volume of settled sludge was recorded from which the SVI was calculated by dividing with the dry weight of MLSS. The settling time was kept constant at one hour. At the end of the settling period 900 mL the supernatant from each of the reactors were removed by suction and immediately the volume was replaced with fresh sample. Reaction period was started again with the activation of aeration.

No mixed liquor was wasted at the end of react period during the acclimatization study, except 10 mL , drawn for the determination of MLSS and MLVSS concentrations in each of the reactors. The supernatant was then analyzed for TSS, VSS and BOD on a daily basis. Other parameters COD , nitrogen, phosphorus, and DO were measured periodically.

Table 5.6 : Sample Mixing Schedule for Acclimatization of Wastewater.

Raw Sewage (%)	Wastewater (%)	Time (Weeks)
100	0	1
75	25	1
50	50	1
25	75	1
0	100	2

Initial MLSS Concentration = 1500 mg/L.
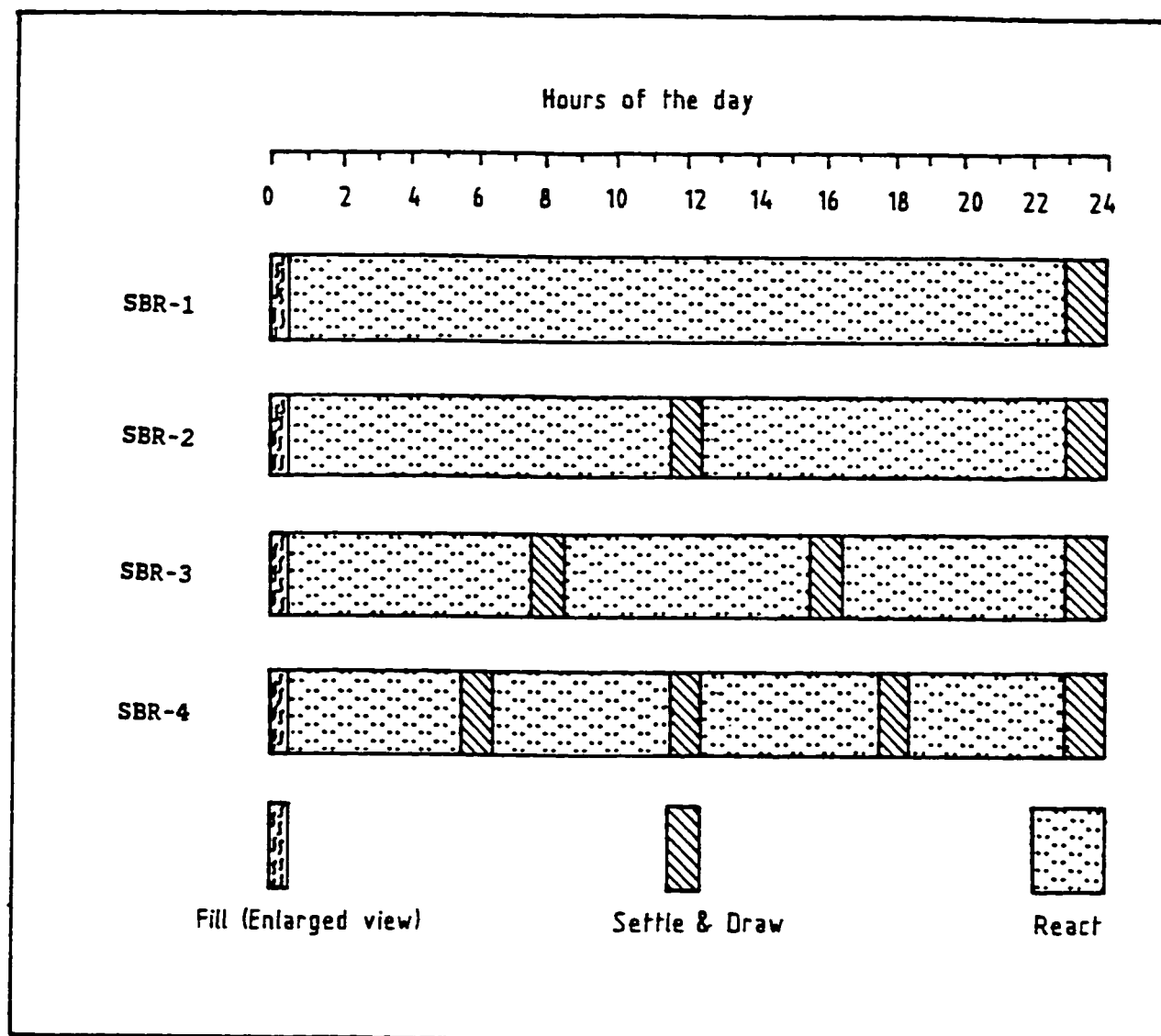
Fig. 5.27 : Reactor Operating Strategies for Acclimatization and
Phase I Batch Study.

All the reactors behaved with a gradual buildup of MLSS. SBR-1 which was fed only once in a day did not show a rapid buildup of MLSS when compared with other reactors. SBR-4 which was fed four times a day showed a rapid increase in MLSS. The MLSS concentration in SBR-4 increased to 5500 mg/L at the end of second week. Whereas, in SBR-1 the maximum MLSS achieved was 2600 mg/L during the same time period. Results of analysis showed that the MLSS towards the end of the week reached to a maximum level and as soon as the percentage of wastewater was increased the MLSS concentration was impaired. However, growth of microorganisms increased with time. The buildup of mixed liquor suspended solids during acclimatization period for the four reactors are shown in Fig's 5.28 to 5.31.

The reactors were operated for an additional two weeks after the period of four weeks. Periodical monitoring of the cell concentration showed an increase in the microorganisms. The optimum operational condition was attained by the system after a period of six weeks operation. It was indicated by the low effluent BOD and solids, expected MLSS values and low SVI(Fig's 5.28 to 5.34 and Table 5.7). Hence, a viable culture of microorganisms was assumed to have developed at that stage. The whole operation of acclimatization took a total of 6 weeks. Literature [69,70] also suggests that a total of 4-8 weeks are required to develop a stable mixed liquor concentration of 3000-4000 mg/L for petrochemical wastewaters.

5.6.2 SBR Treatment (Phase I Batch Study)

The experimental procedure and the operating strategy for this phase of the study was similar to the acclimatization procedure. In this phase of the study approximately 50 mL /day of the reactor solids were wasted at the end of each
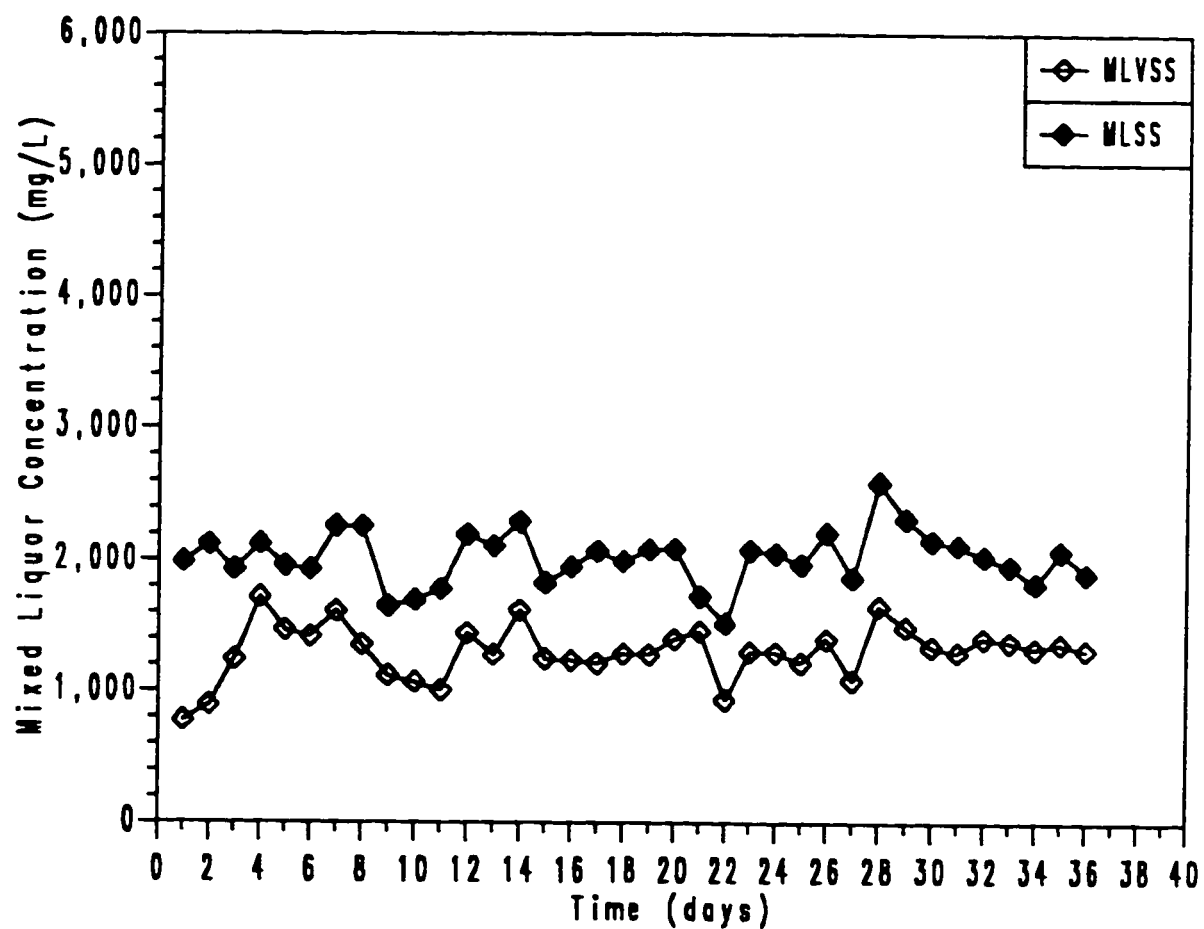
Fig. 5.28 : Mixed Liquor Concentration During Acclimatization
in SBR-1.
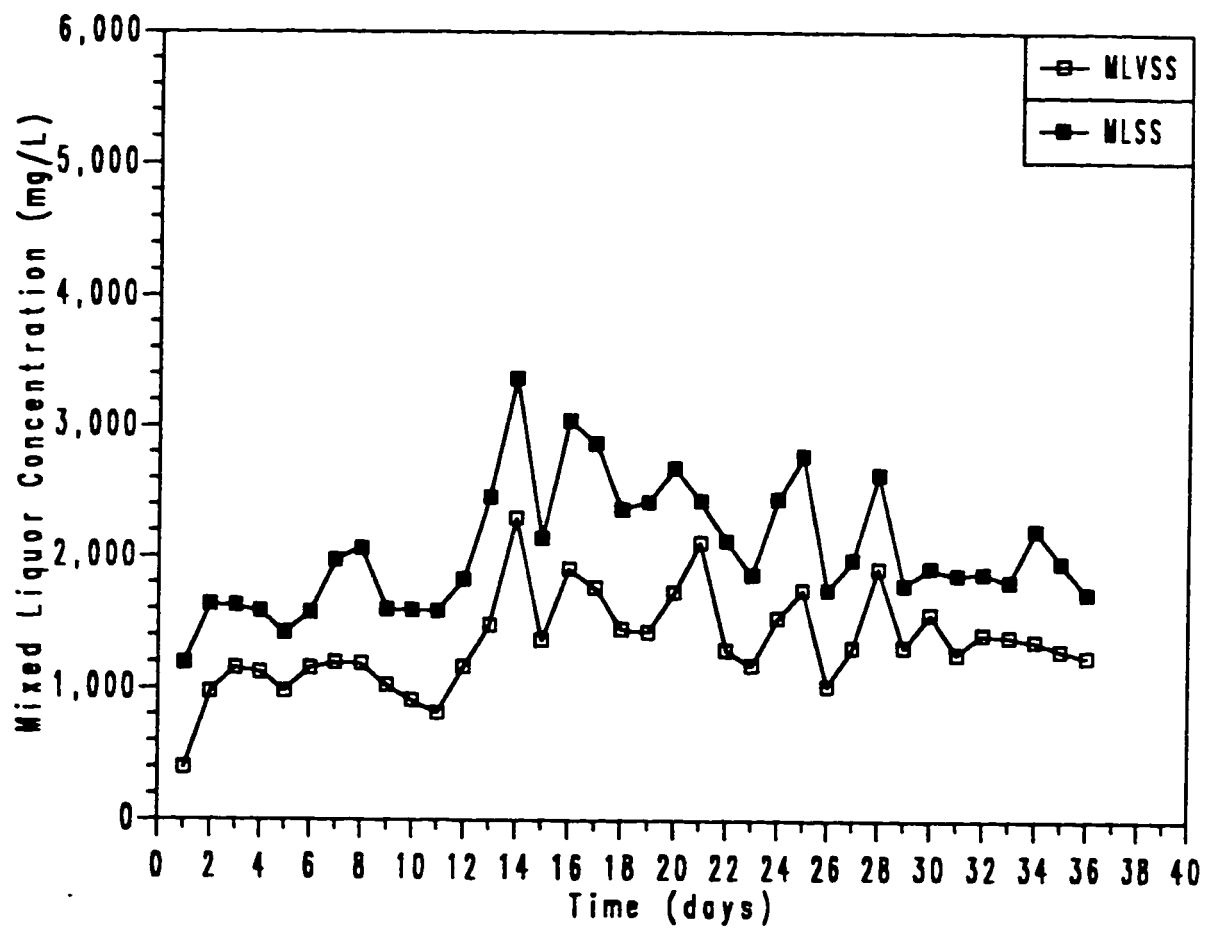
**Fig. 5.29 : Mixed Liquor Concentration During Acclimatization
in SBR-2.**
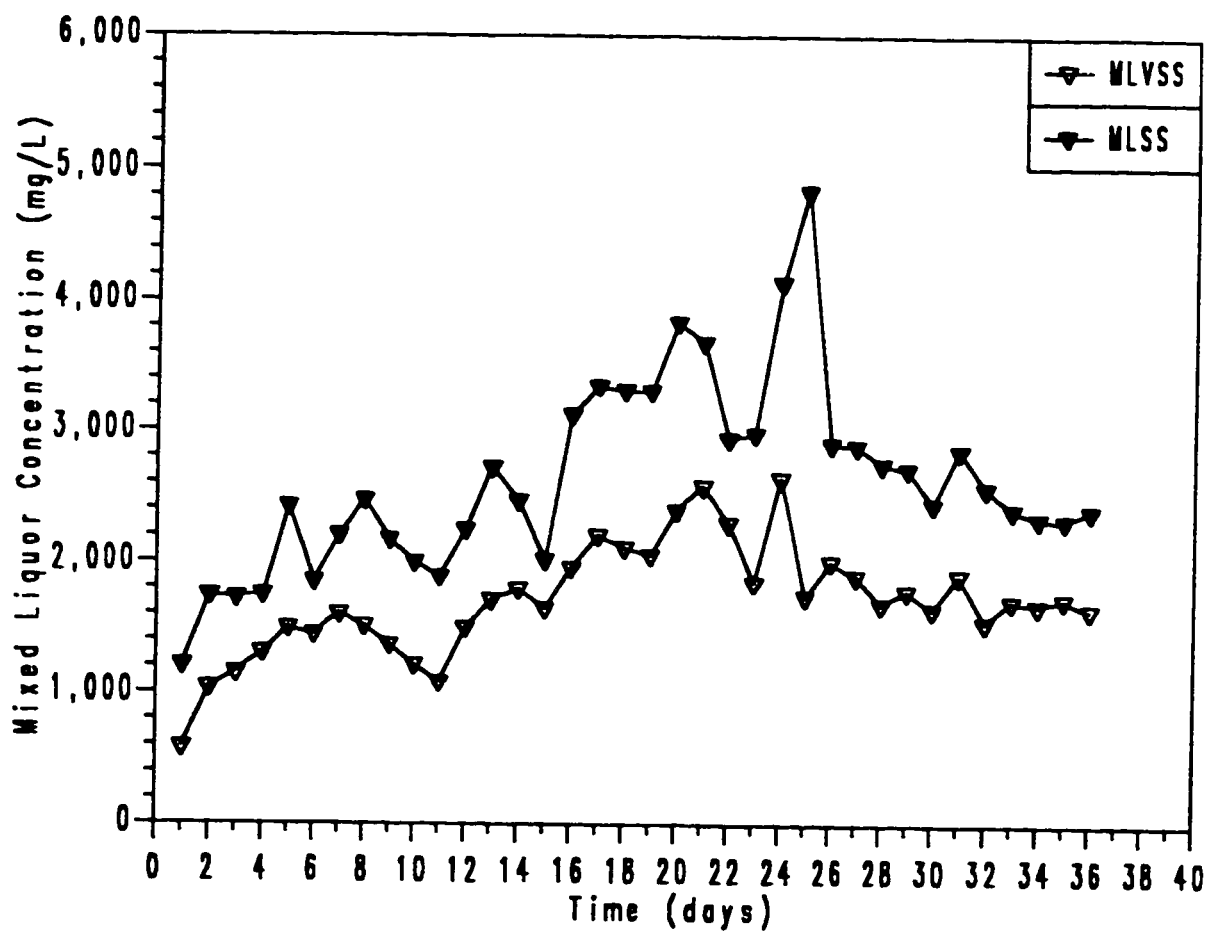
Fig. 5.30 : Mixed Liquor Concentration During Acclimatization in SBR-3.
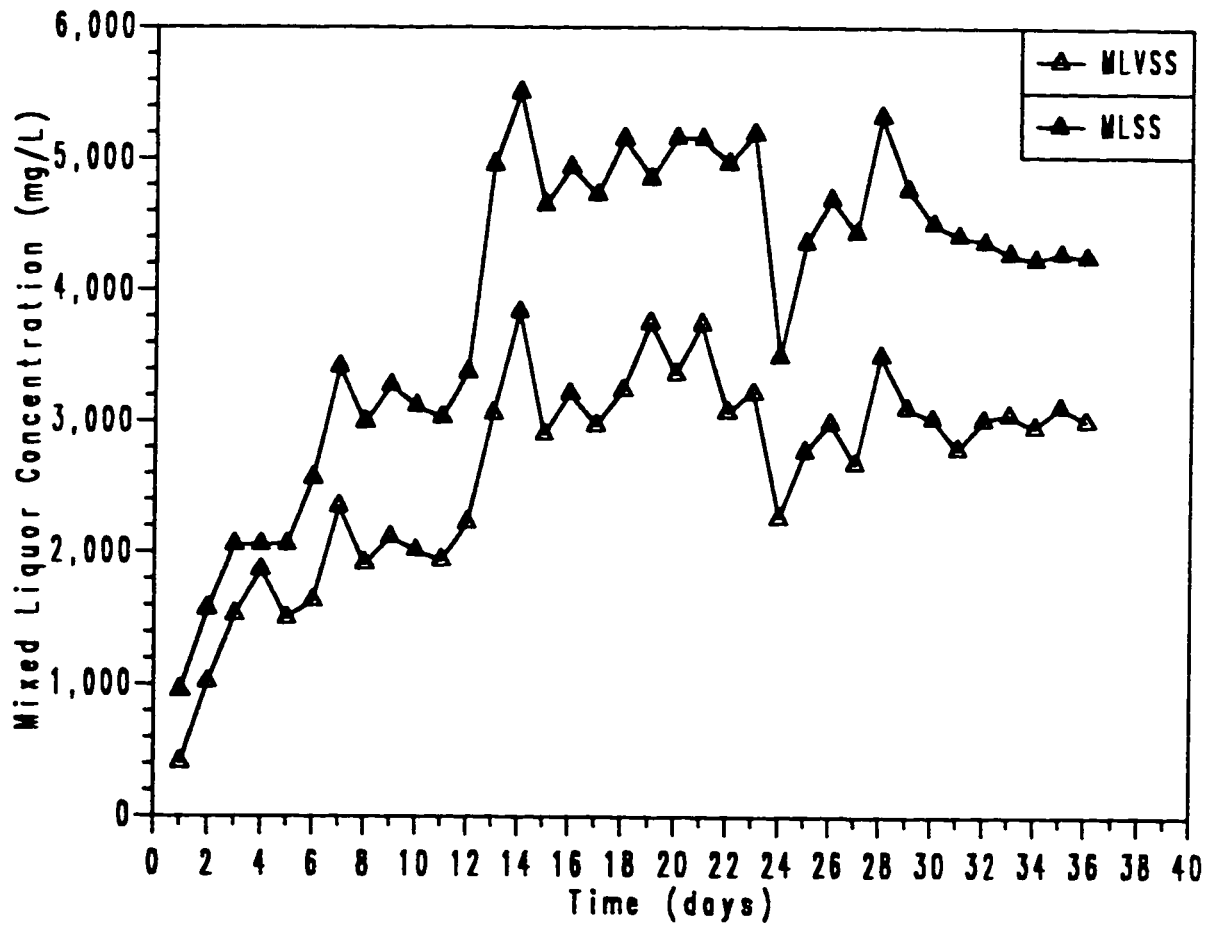
Fig. 5.31 : Mixed Liquor Concentration During Acclimatization in SBR-4.
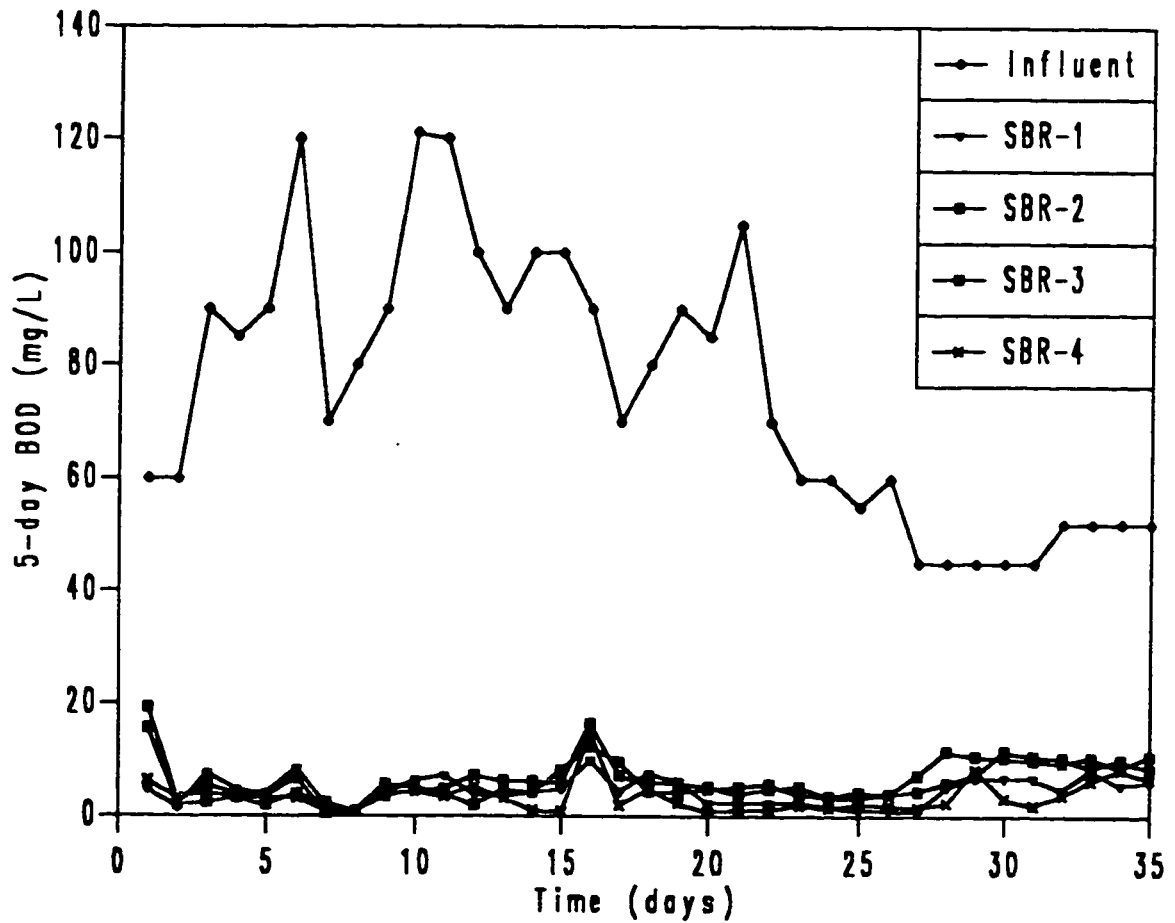
Fig. 5.32 : Influent and Effluent BOD Concentrations in SBRs
During Acclimatization.
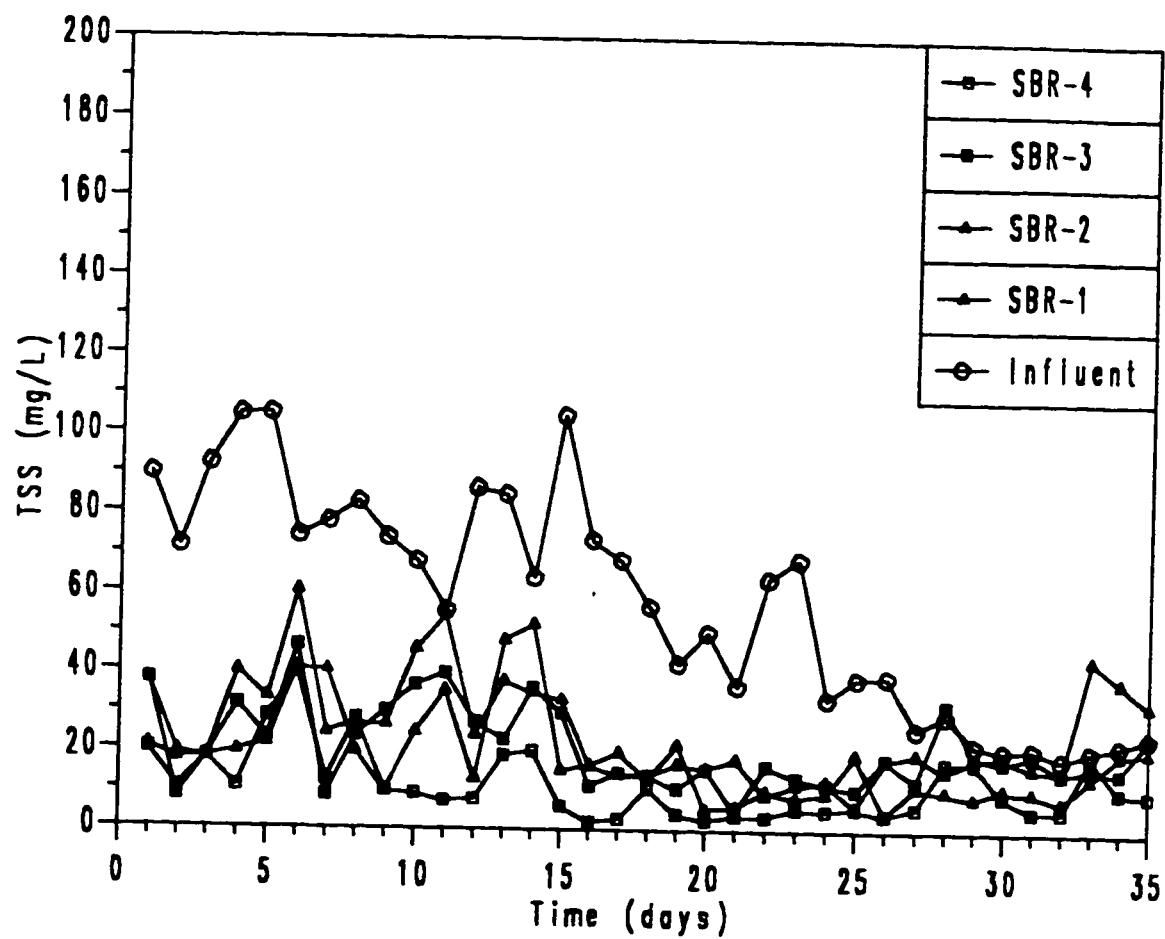
Fig. 5.33 : Influent and Effluent BOD Concentrations in SBRs
During Acclimatization.
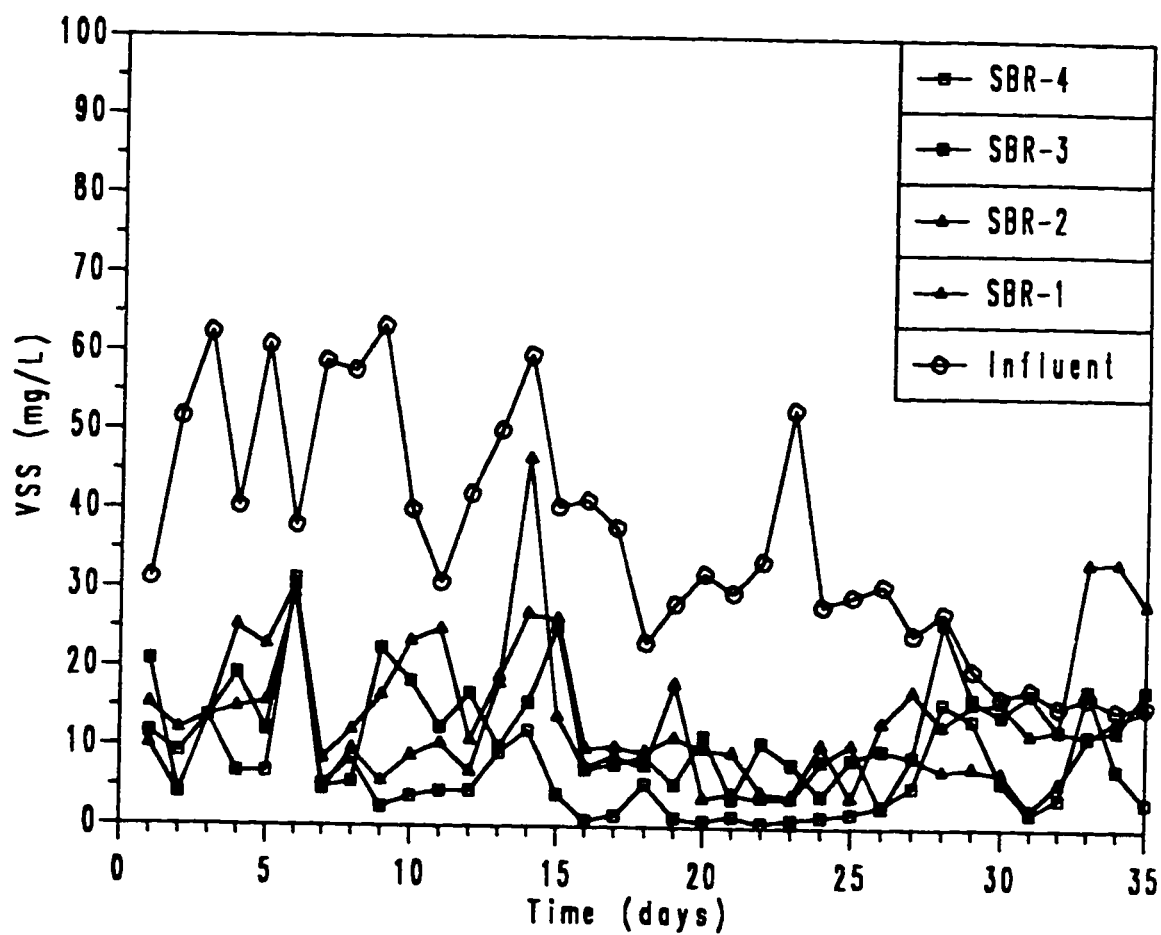
Fig. 5.34 : Influent and Effluent VSS Concentrations in SBRs
During Acclimatization.

Table 5.7 : The Performance of Reactors During Acclimatization

REACTOR	SBR-1	SBR-2	SBR-3	SBR-4
MLSS (mg/L)	2026 (1518-2590)	2085 (1188-3364)	2629 (1210-5134)	4000 (956-5504)
MLVSS (mg/L)	1309 (770-1716)	1368 (394-2298)	1704 (586-2640)	2662 (408-3836)
Influent BOD (mg/L)	73 (45-120)	73 (45-120)	73 (45-120)	73 (45-120)
Effluent BOD (mg/L)	4.6 (0.8-10.)	6.43 (0.8-19.2)	6.5 (0.8-16.4)	4.13 (0.8-14.8)
Influent TSS (mg/L)	57.6 (18.7-105.)	57.6 (18.7-105.)	57.6 (18.7-105.)	57.6 (18.7-105.)
Effluent TSS (mg/L)	18.4 (5.4-52.)	24.5 (6.2-60.0)	20.7 (5.-46.4)	11.4 (2.0-39.6)
Influent VSS (mg/L)	36.05 (15.1-63.2)	36.05 (15.1-63.2)	36.05 (15.1-63.2)	36.05 (15.1-63.2)
Effluent VSS (mg/L)	11.2 (2.4-46.)	15.4 (3.8-33.7)	17.3 (3.6-30.4)	6.5 (0.6-31.2)
Sludge Volume Index	158.4 (122-206)	80 (40-119)	72 (38-116)	114 (66-202)

day. This corresponds to an apparent solids retention time (SRT) or sludge age of 24 days. The reactor condition for phase I study is shown in Table 5.8 ⁻

The acclimated seed corresponding to F/M (food to microorganism) ratio of 0.2 was retained into each of the reactors. A F/M ratio of 0.2 was chosen, as it is an intermediate F/M value between the extended aeration and conventional activated sludge systems. The mixed liquor volatile suspended solids was calculated using the relation :

$$F/M = \frac{BOD}{MLVSS \times t}$$ (5.3)

where,

F/M = food-to-microorganism ratio, mg of BOD per day per mg of MLVSS

t = the detention time in days

MLVSS = mixed liquor volatile suspended solids, mg/L

For a F/M ratio of 0.2 and an average BOD concentration of 48 mg/L in the wastewater the MLVSS concentration in the four reactors SBR-1, SBR-2, SBR-3 and SBR-4 worked out to be 240, 360, 480 and 960 mg/L , respectively. Based on approximate MLVSS/MLSS ratio of 0.6, observed during acclimatization, the MLSS concentrations in the four reactors were kept at 400, 800, 1000 and 1600 mg/L , respectively. The sludge wastage (50 mL) was accomplished at the end of each day. The volume of sludge wasted was 50 mL/day and this value was chosen on the assumption that 50% of BOD is converted to cells.

Table 5.9 gives a summary of the results for the first phase of the study which was carried out after acclimatization. The summary includes the average values of MLSS, MLVSS, TSS, VSS, BOD and the sludge volume Index (SVI). The range

Table 5.8 : Reactor Condition for Phase I Study.

Parameter	Reactor			
	SBR-1	SBR-2	SBR-3	SBR-4
F/M Ratio	0.2	0.2	0.2	0.2
MLSS (mg/L)	400	800	1000	1200
Sludge Wastage	50	50	50	50
Cycle Length (hrs)	6	8	12	24
Aeration Time (hrs)	5	7	11	23
Settle & Draw (hrs)	1	1	1	1

Table 5.9 : The Performance of Reactors For Phase I Study

REACTOR	SBR-1	SBR-2	SBR-3	SBR-4
MLSS (mg/L)	439 (306-586)	809 (571-1096)	1068 (638-1289)	1721 (1490-1997)
MLVSS (mg/L)	310 (202-444)	554 (400-800)	806 (464-954)	1286 (1070-1529)
Influent BOD (mg/L)	50 (48-52)	50 (48-52)	50 (48-52)	50 (48-52)
Effluent BOD (mg/L)	3.0 (0.8-10.)	4.7 (0.8-19.2)	5.1 (0.8-16.4)	6.9 (0.8-14.8)
Influent TSS (mg/L)	22.2 (18.6-24.5)	22.2 (18.6-24.5)	22.2 (18.6-24.5)	22.2 (18.6-24.5)
Effluent TSS (mg/L)	9.1 (3.6-20.4)	12.0 (8.6-22.2)	11.4 (8.4-18.4)	11.0 (6.2-18.2)
Influent VSS (mg/L)	16.4 (12.8-19.6)	16.4 (12.8-19.6)	16.4 (12.8-19.6)	16.4 (12.8-19.6)
Effluent VSS (mg/L)	5.4 (2.2-14.2)	6.8 (2.6-10.2)	6.9 (3.2-10.2)	6.6 (3.2-15.0)
Sludge Volume Index	136 (118-173)	64 (44-102)	67 (45-89)	104 (78-131)

values for the parameters mentioned above are included in the parentheses. The reported values in the table are the averages taken over a period of one and a half month. The range for each parameter is included in the parenthesis.

MLSS

The concentration of MLSS in all the four reactors increased with time. SBR-4 which was fed more frequently (shortest cycle time of 6 hours) showed a rapid increase in the concentration of MLSS. SBR-1 (longest cycle time of 24 hours) did not show a rapid growth although the concentration of microbial cells in the SBR-1 correspond to a F/M ratio of 0.2 like other reactors. This may be due to the fact that the sludge wastage was not accomplished at the end of each operating cycle. Instead, the sludge wastage was done at the end of each day which correspond to 1, 2, 3, and 4 cycles for SBR-1, SBR-2, SBR-3, and SBR-4, respectively. Thus the concentration of MLSS in SBR-4 gets compounded resulting in higher value of 1721 mg/L (see Table 5.9). This effect can also be visualized from Fig. 5.35 in which the MLSS concentration is above the 1600 mg/L most of the time. Although variations occured for MLSS for SBR-2 and SBR-3, the average values of 809 mg/L and 1068 mg/L were similar to the theoretical calculated values of 800 mg/L and 1000 mg/L for SBR-2 and SBR-3, respectively. Moreover the MLSS concentration in SBR-1 was the lowest because of long endogenous respiration. Fig. 5.36 shows the MLVSS concentration in SBRs.

Effluent BOD

The influent and effluent BOD concentrations for the first phase of the study are plotted in Fig. 5.37 The influent to the SBRs was the wastewater that was left after the characterization study and the 24-hour composite samples collected
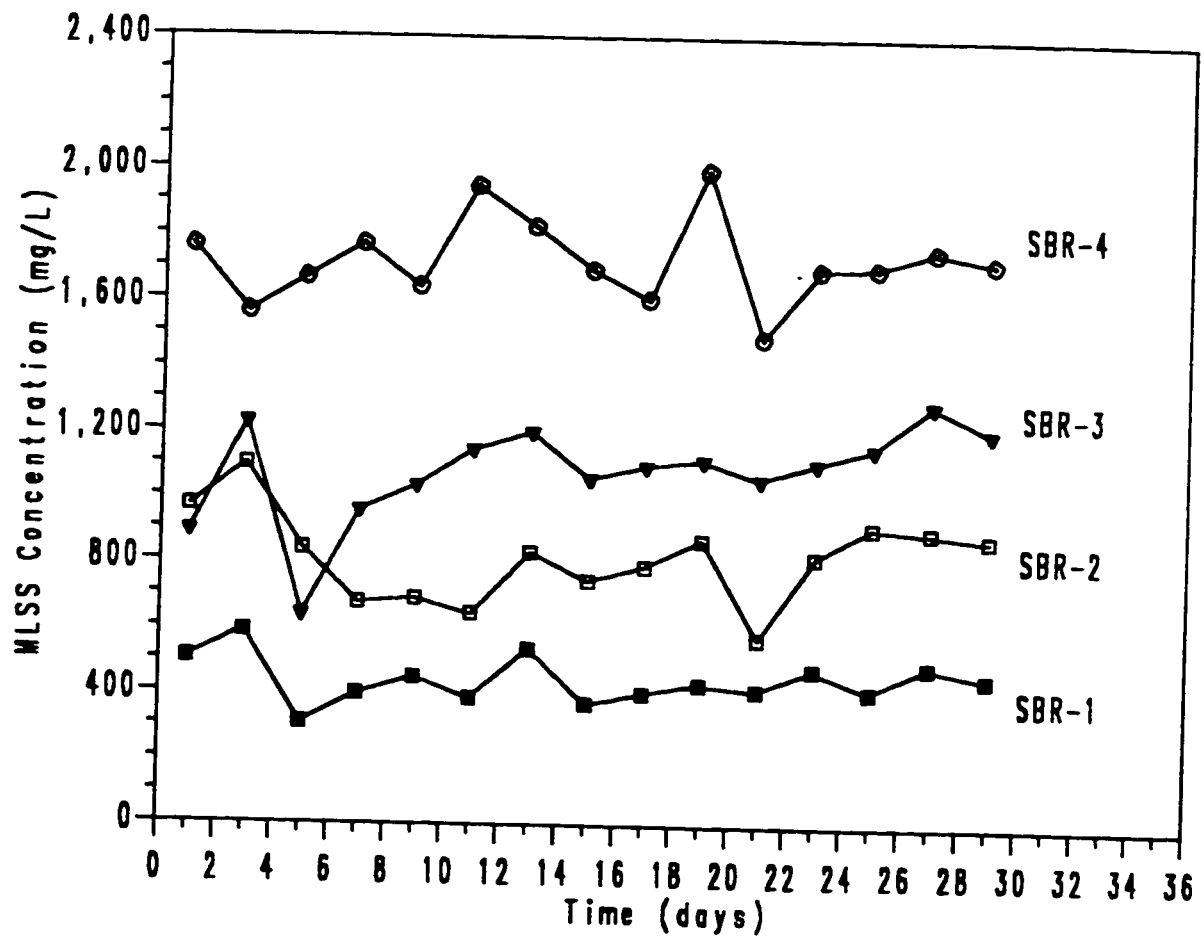
Fig. 5.35 : **Concentration of Mixed Liquor Suspended Solids in the SBRs (Phase I).**
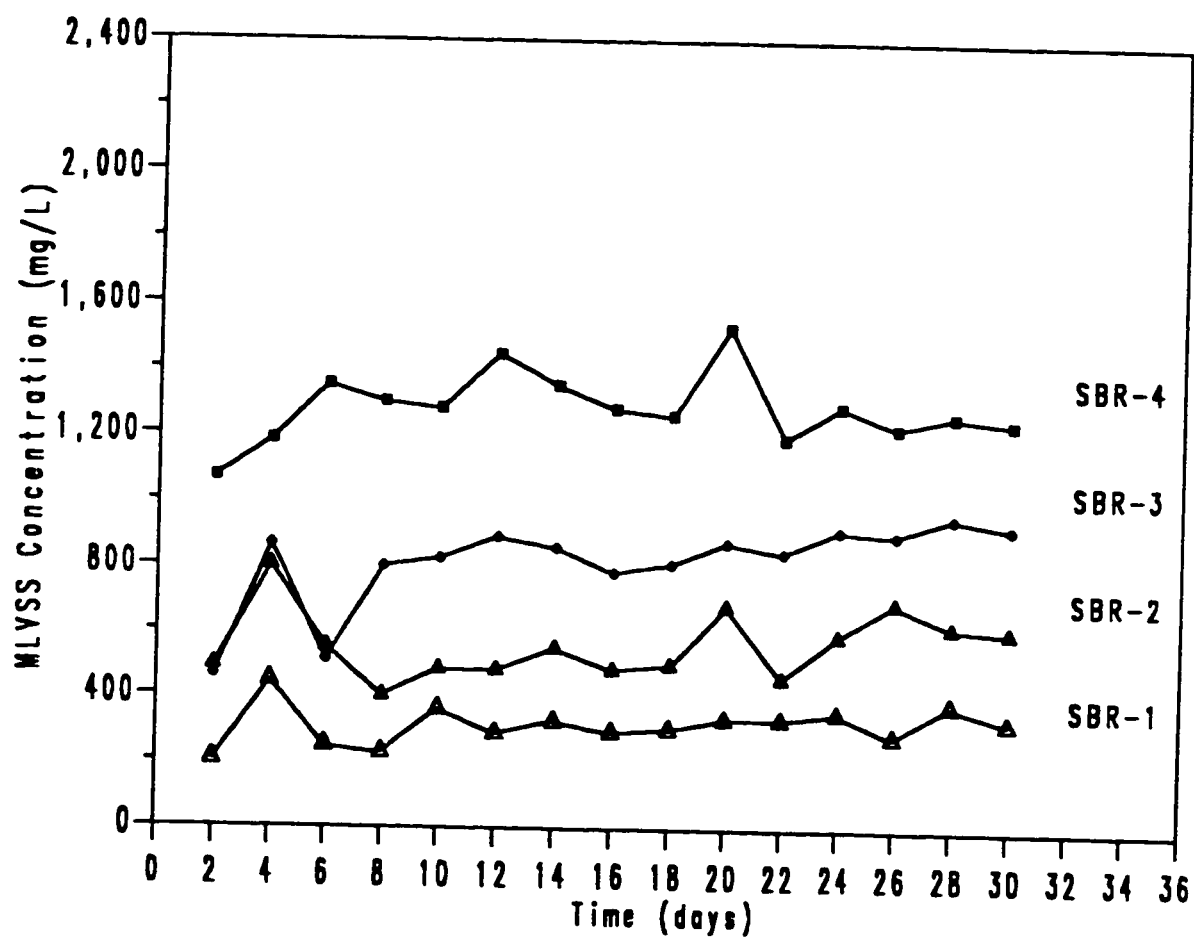
Fig. 5.36 : Concentration of Mixed Liquor Volatile Suspended Solids in the SBRs (Phase I).
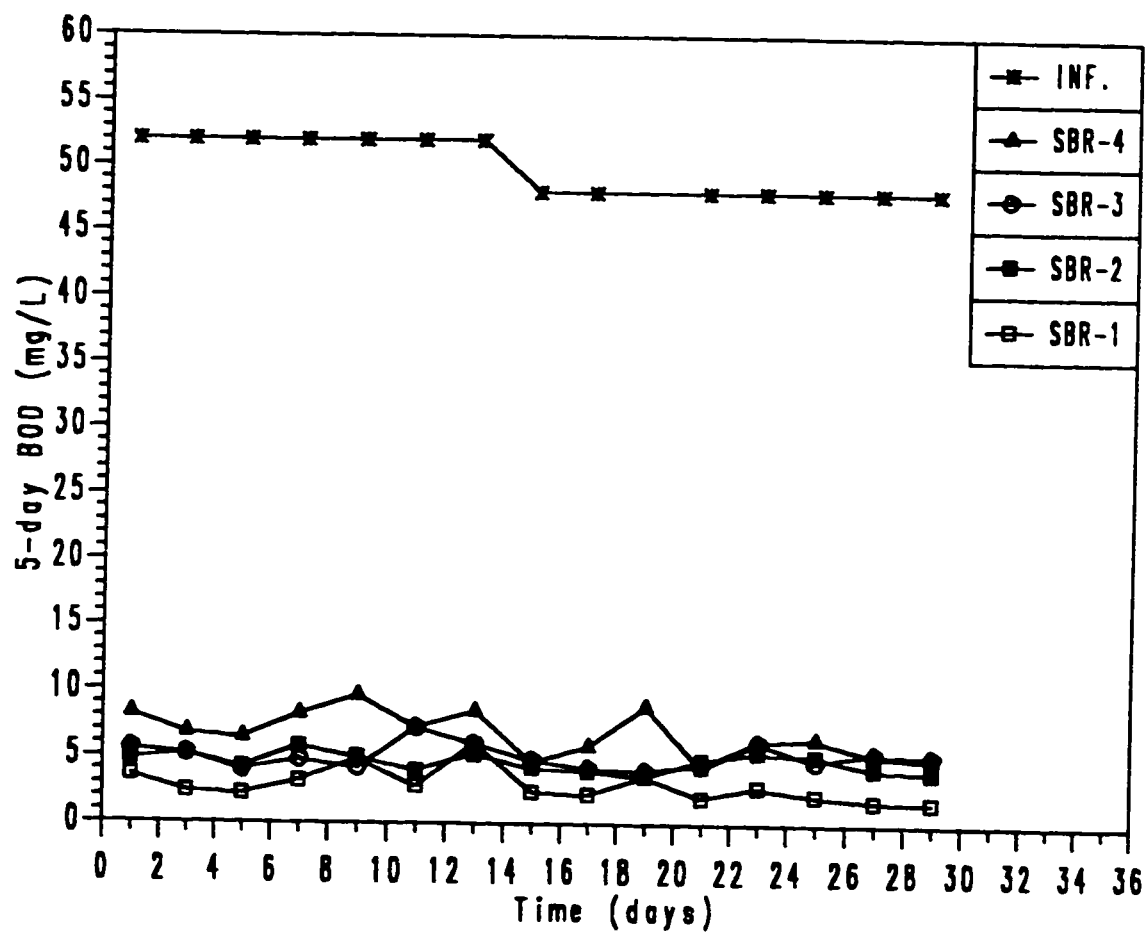
Fig. 5.37 : Concentration of Effluent BOD in the SBRs (Phase I).

thereafter.The concentration of influent was found to be 52 mg/L when the phase I study was started. After two weeks another composite sample was procured with BOD of 48 mg/L . As seen from Table 5.9 and Fig. 5.37 the quality of the effluent in terms of BOD deteriorated from SBR-1 (aeration time 23 hours) to SBR-4 (aeration time 5 hours). In SBR-1, consistently low values of BOD with an average of 3.0 mg/L was obtained. Whereas, the average BOD for SBR-4 was 6.9 mg/L . This result was expected, however, due to small variations in BOD values the difference was insignificant. The performance of SBR-2 (11 hours of aeration) and SBR-3 (7 hours of aeration) were comparable to SBR-1 in terms of degradation of organic matter.

Effluent SS

Among the four SBRs, SBR-1 which was operated with the longest cycle time (1 cycle/day), produced the lowest suspended solids. The average suspended solids for one month period was 9.1 mg/L for TSS and 5.4 mg/L for VSS, respectively, as shown in Table 5.9. Fig.'s 5.38 and 5.39 , give the plots of TSS and VSS for the four reactors. As shown in Fig 5.38, the TSS concentration for SBR-1 was very low in first five days and then it increased for the remaining period of the study. SBR-1 with one cycle per day producing effluent with lowest TSS showed that apparently there was no break-up and dispersion of biological flocs due to long period of aeration (23 hours) for SBR-1.

Consistently higher values of TSS and also VSS were observed in the SBR-2, and SBR-3. The average TSS for SBR-2 and SBR-3 were 12.0 mg/L and 11.4 mg/L , respectively. Physical examination also showed the presence of dispersed cells in the reactors. The flow of air for all the reactors was checked and found to be equal
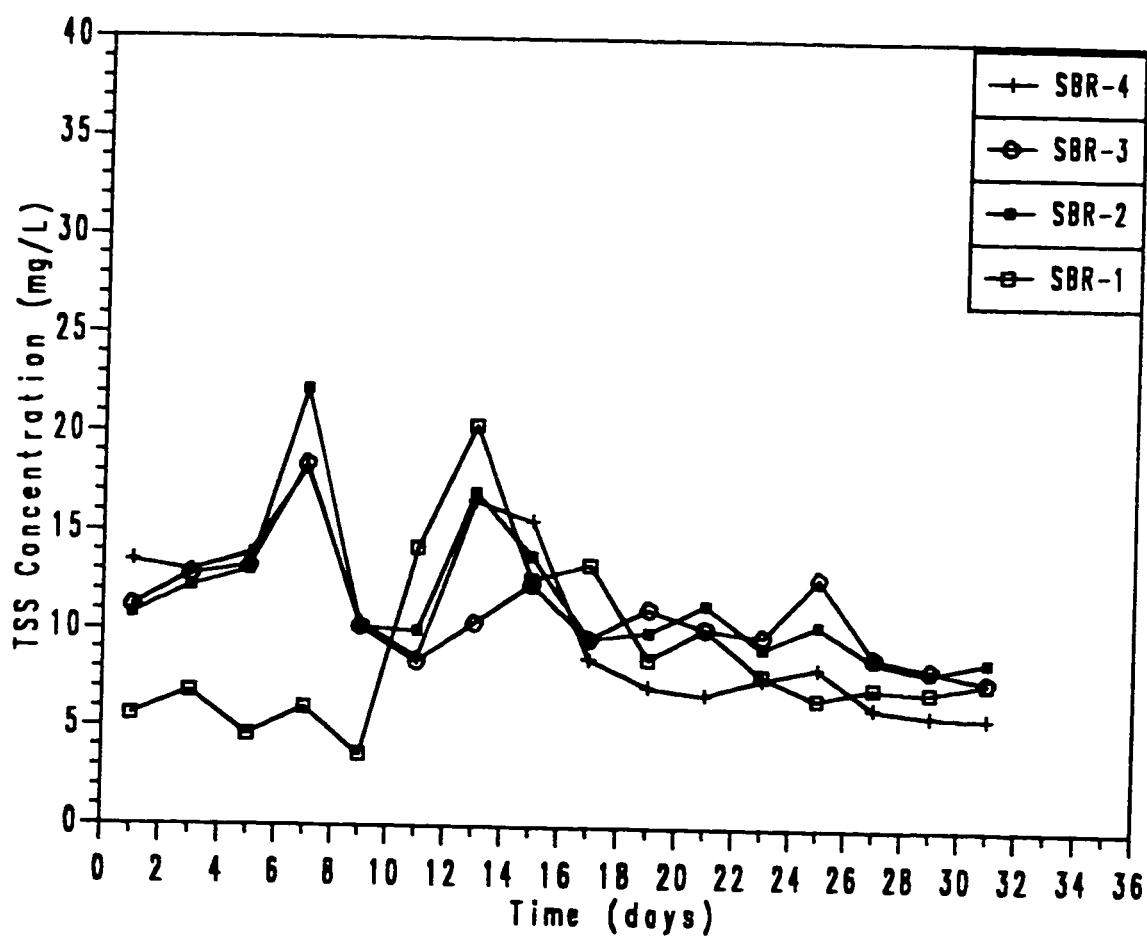
**Fig. 5.38 : Concentration of Effluent Total Suspended Solids
in the SBRs (Phase I).**
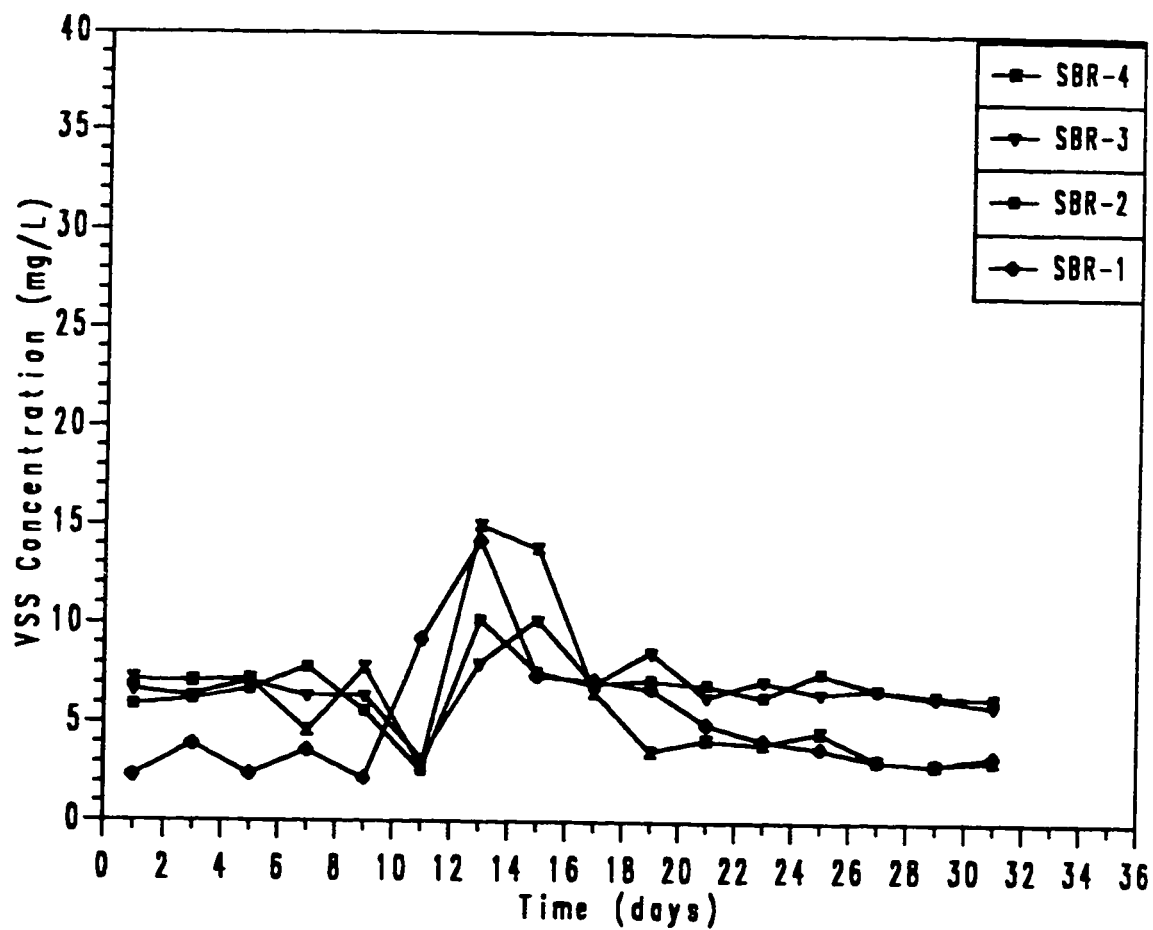
**Fig. 5.39 : Concentration of Effluent Total Volatile Suspended Solids in the SBRs (Phase I).**

for all the reactors. The second observation for reactors SBR-2 and SBR-3, was that the sludge blanket produced was very compact. This resulted in the yield of low SVI values of 64 mL/g and 67 mL/g for SBR-2 and SBR-3, respectively (see Fig 5.40 and Table 5.9). The SVI for the other reactors i.e., SBR-4 and SBR-1, were 137 mL/g and 104 mL/g , respectively. Although a firm reason for the high concentration of TSS in the SBR-2 and SBR-3 could not be given, however, it can be attributed to the development of the compact sludge. Hoepker and Schoeder [71] found that batch systems with compact sludges produce dispersed cells resulting in high TSS values. This phenomenon was hypothesized by Irvine et. al. [72] as due to the crowding out of the filamentous organisms resulting in well compacted sludges of the filament free cultures. However, the design objective should be to combine minimum effluent SS concentrations with maximum sludge compactability and that these two factors were found to be inversely related [71].

Nutrient Removal

The concentration of nitrogen and phosphorous were not determined daily but were analyzed only once in a week. Periodical measurement of DO in all the four reactors showed a value greater than 2 mg/L , a condition necessary for nitrification. Table 5.10 shows the influent and effluent concentrations of nitrogen and phosphorous which is the average of six readings. As can be seen from Table 5 the total nitrogen measured as TKN decreased from 2.8 mg/L to 1.2 mg/L and 2.1 mg/L in SBR-1, and SBR-4, respectively. The decrease in influent nitrogen can be attributed to the utilization of nitrogen for the cell synthesis plus the conversion of organic nitrogen to ammonia nitrogen and subsequently to nitrite and nitrate nitrogen. A mass balance on the various forms of nitrogen showed that the loss of nitrogen from the system is insignificant. This indicates that no denitrification took
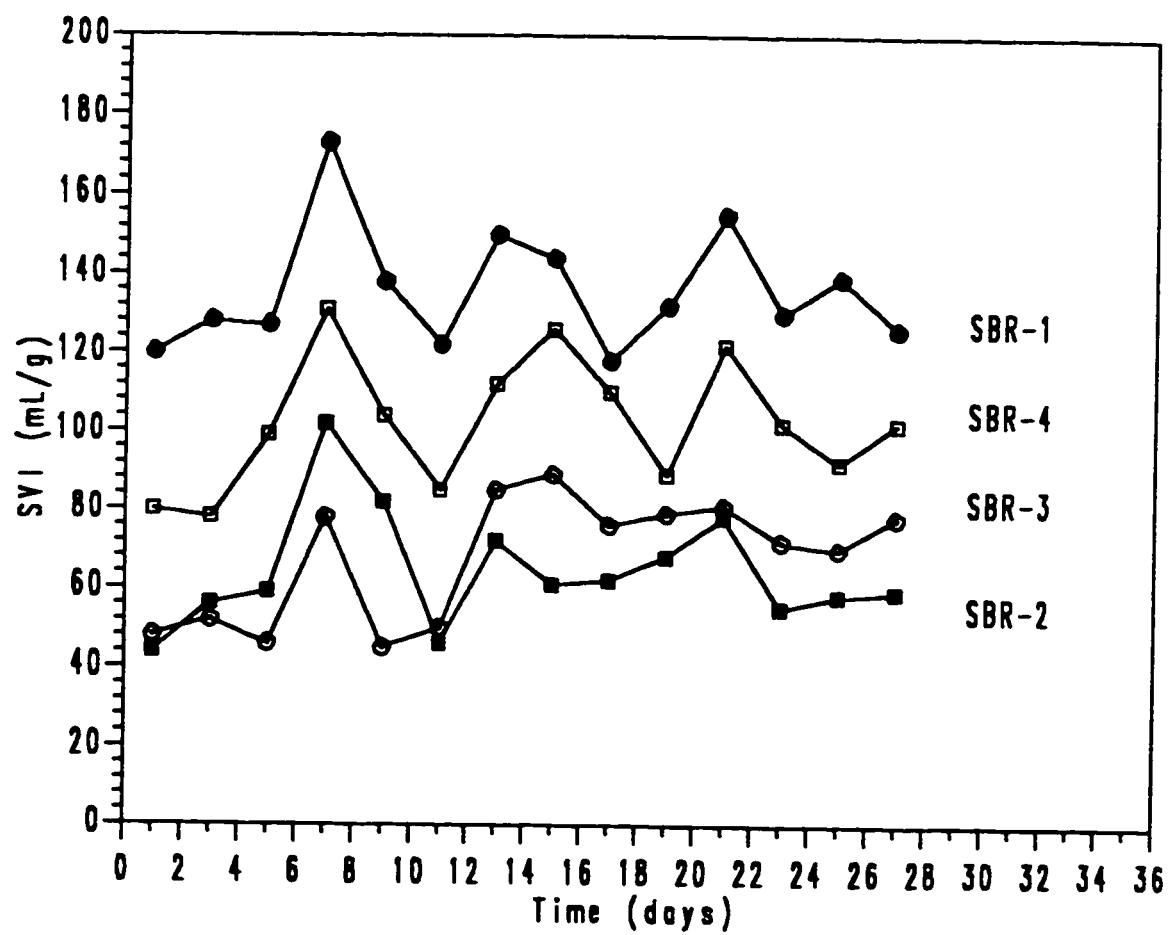
Fig. 5.40 : Sludge Volume Index in the SBRs (Phase I).

Table 5.10 : Nutrient Removal Efficiencies in the Reactors.

Parameter (mg/L)	Reactor			
	SBR-1	SBR-2	SBR-3	SBR-4
Total Nitrogen				
Influent	2.8	2.8	2.8	2.8
Effluent	1.2	1.6	1.9	2.1
Ammonia Nitrogen				
Influent	0.8	0.8	0.8	0.8
Effluent	0.6	0.5	0.5	0.4
Oxidized Nitrogen *				
Influent	0.0	0.0	0.0	0.0
Effluent	1.8	1.5	1.2	1.1
Total Phosphorous				
Influent	14.0	14.0	14.0	14.0
Effluent	11.2	11.8	12.4	12.4

* (Nitrite + Nitrate) Nitrogen

place in the reactors. This result was expected as the DO concentration in all the reactors were above 2.0 mg/L , whereas, for denitrification DO concentration should be less than 0.5 mg/L [36]. The maximum phosphorous concentration removal was attained in SBR-1 in which the concentration of 14 mg/L of total-P was reduced to 11.2 mg/L . Again, the high removal of phosphorous in SBR-1 can be attributed to the long aeration time of 23 hours.

5.6.3 SBR Treatment (Phase II Semi-Batch Study)

One of the special features of an SBR is its flexibility to operate both under aerobic and anoxic conditions. The most pertinent problems faced during the biological treatment of industrial wastewaters is the quality of effluent in terms of high TSS values. The operation of a SBR alternatively in aerobic and anoxic conditions is one of the potential solutions to the SS concentrations of the effluent from industries. Irvine et. al. [72] used an anoxic period to minimize oxygen uptake rates during the fill portion of the cycle and found that both effluent quality and sludge compactability improved. This anoxic period would be expected to decrease the filamentous organism population because of the higher organic concentrations when aeration was started. Thus, a method of coupling two phenomena, i.e., reducing the concentration of SS in the effluent and at the same time having compact sludges, may be feasible. Hoepker and Schoeder [71] also found that prolonging of the fill period reduced TSS concentration in the effluent.

Hence the phase II study was carried out by fixing the SBR cycle time of 8 hours as determined by the optimum operating conditions in Phase I Study. One hour each was fixed for FILL, SETTLE, and DRAW. The only operational condition varied was the REACT period with anoxic and aerobic conditions. The reac-

tor operating strategies for Phase II study are shown in Fig 5.41. The manual accomplishment of this task was not feasible and hence automatic timers were installed to control the aeration pumps. These timers were programmed according to the reactor operating strategy as given in Fig 5.41.

Table 5.11 gives a summary of the results for this phase of the study. The MLSS, MLVSS, influent and effluent BOD, effluent TSS and VSS along with the SVI values for the four reactors are plotted in Fig.'s 5.42 to 5.47. Fig.'s 5.42 and 5.43 show the MLSS and MLVSS concentrations for the four reactors. It can be observed from these figures that lower values of MLSS were encountered for SBR-4 when compared to SBR-1, SBR-2, and SBR-3. The average MLSS concentration for SBR-4 was 900 mg/L when compared to 1136 mg/L for SBR-1. The effluent BOD of 8.9 mg/L suggested that an aeration time of 2 hours provided in SBR-4 was insufficient. This resulted in high effluent BOD and very low yield of the cells. Moreover, the suspended solids concentration in the effluent was also higher (12.6 mg/L as against 5.2 mg/L in SBR-3) suggesting that the substrate was not fully utilized.

The performance of SBR-1 in terms of BOD removal was better than other three SBRs. This was due to the relatively longer aeration time (5 hours). However, the performance of SBR-2 (4 hours aeration) and SBR-3 (3 hours aeration) with approximately 5.5 mg/L of BOD in both the SBRs was comparable to SBR-1 (BOD of 4.4 mg/L) in terms of organic matter degradation. However, the TSS and VSS concentrations in SBR-2 and SBR-3 could be considered as optimum for the treatment of SADAF wastewater.
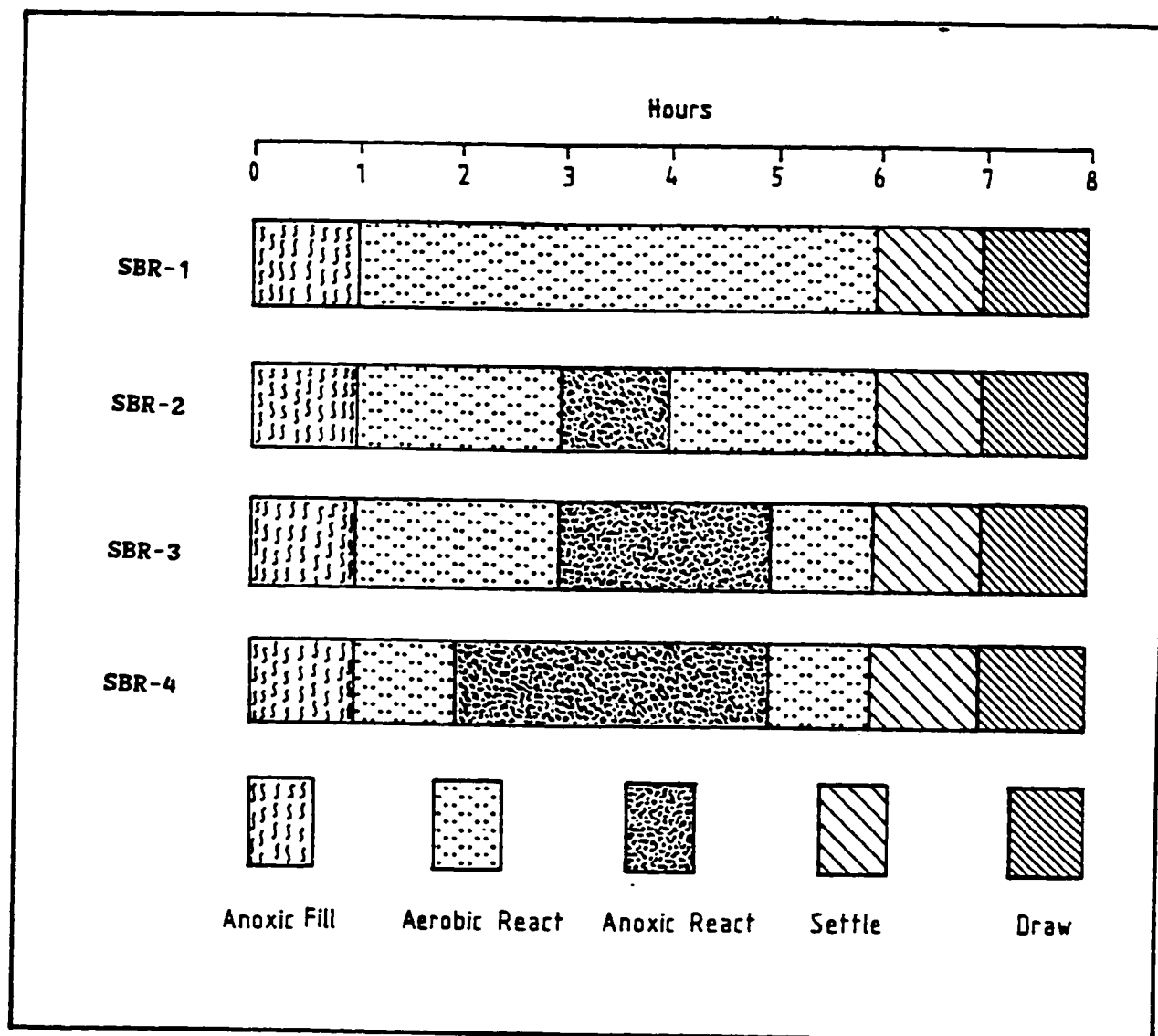
Fig. 5.41 :   Reactor Operating Strategies for Phase II
Semi-Batch Study.

Table 5.11 : The Reactor Condition for Phase II Study

REACTOR	SBR-1	SBR-2	SBR-3	SBR-4
F/M Ratio	0.2	0.2	0.2	0.2
MLSS (mg/L)	1000	1000	1000	1000
Sludge Wastage (ml/day)	50	50	50	50
Cycle Length (hrs)	8	8	8	8
Fill (hrs)	1	1	1	1
Aerobic React (hrs)	5	4	3	2
Anoxicc React (hrs)	0	1	2	3
Settle (hrs)	1	1	1	1
Draw (hrs)	1	1	1	1

Table 5.12 : The Performance of Reactors For Phase II Study

REACTOR	SBR-1	SBR-2	SBR-3	SBR-4
MLSS (mg/l.)	1136 (992-1289)	1057 (862-1257)	1111 (899-1239)	990 (805-1181)
MLVSS (mg/l.)	780 (627-938)	802 (633-922)	813 (719-929)	689 (557-8019)
Influent BOD (mg/l.)	56 (50-56)	56 (50-56)	56 (50-56)	56 (50-56)
Effluent BOD (mg/l.)	4.4 (2.6-8.6	5.5 (4.2-9.6)	5.4 (5.2-7.8)	8.9 (7.8-14.8)
Influent TSS (mg/l.)	22.8 (18.6-24.2)	22.8 (18.6-24.2)	22.8 (18.6-24.2)	22.8 (18.6-24.2)
Effluent TSS (mg/l.)	8.2 (5.4-12.2)	5.9 (3.6-10.0)	5.2 (3.4-10.0)	12.6 (10.2-16.2)
Influent VSS (mg/l.)	16.1 (14.2-18.3)	16.1 (14.2-18.3)	16.1 (14.2-18.3)	16.1 (14.2-18.3)
Effluent VSS (mg/l.)	6.0 (3.6-7.9)	4.2 (2.4-7.1)	3.7 (2.4-6.7)	9.9 (7.8-13.1)
Sludge Volume Index	69 (59-78)	65 (58-72)	57 (46-78)	59 (42-86)
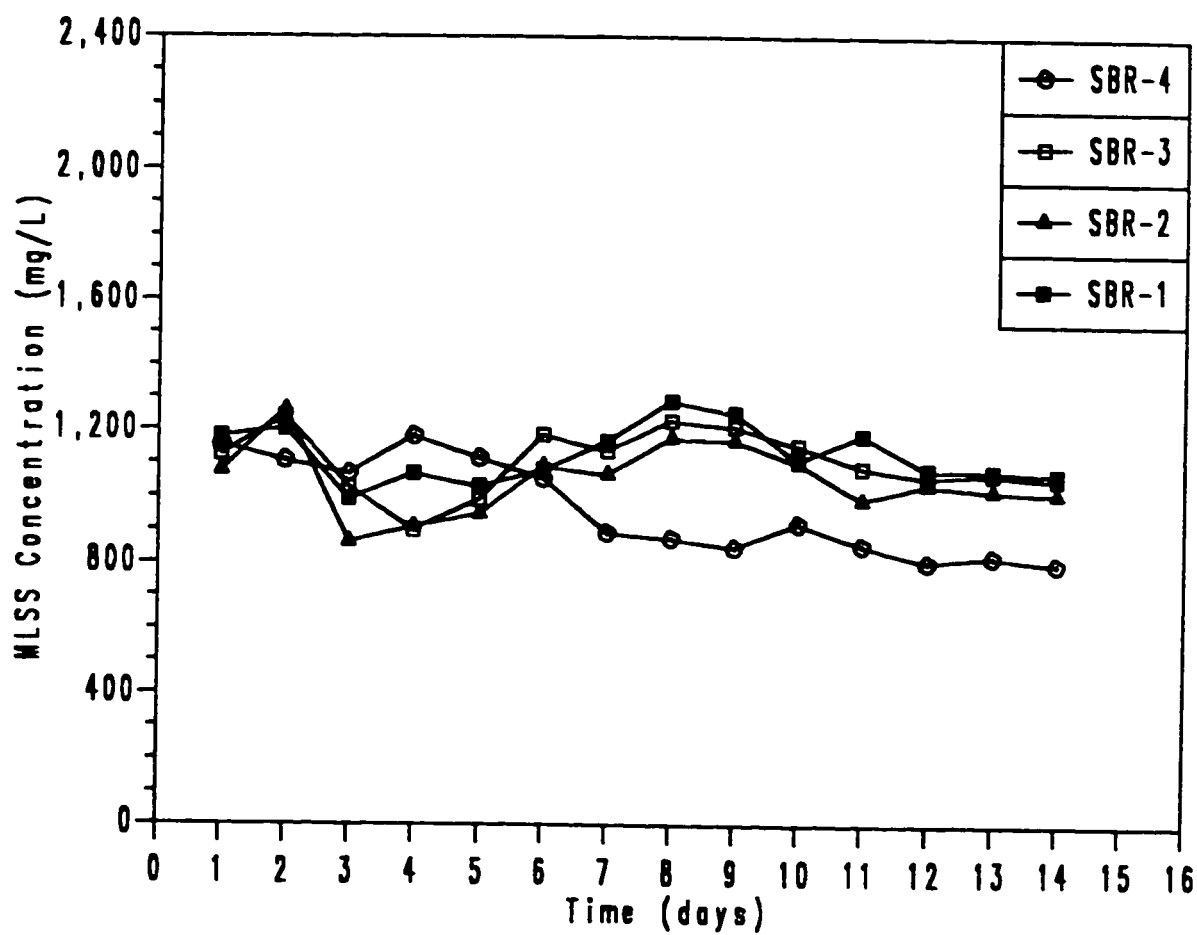
Fig. 5.42 : Concentration of Mixed Liquor Suspended Solids in the SBRs (Phase II).
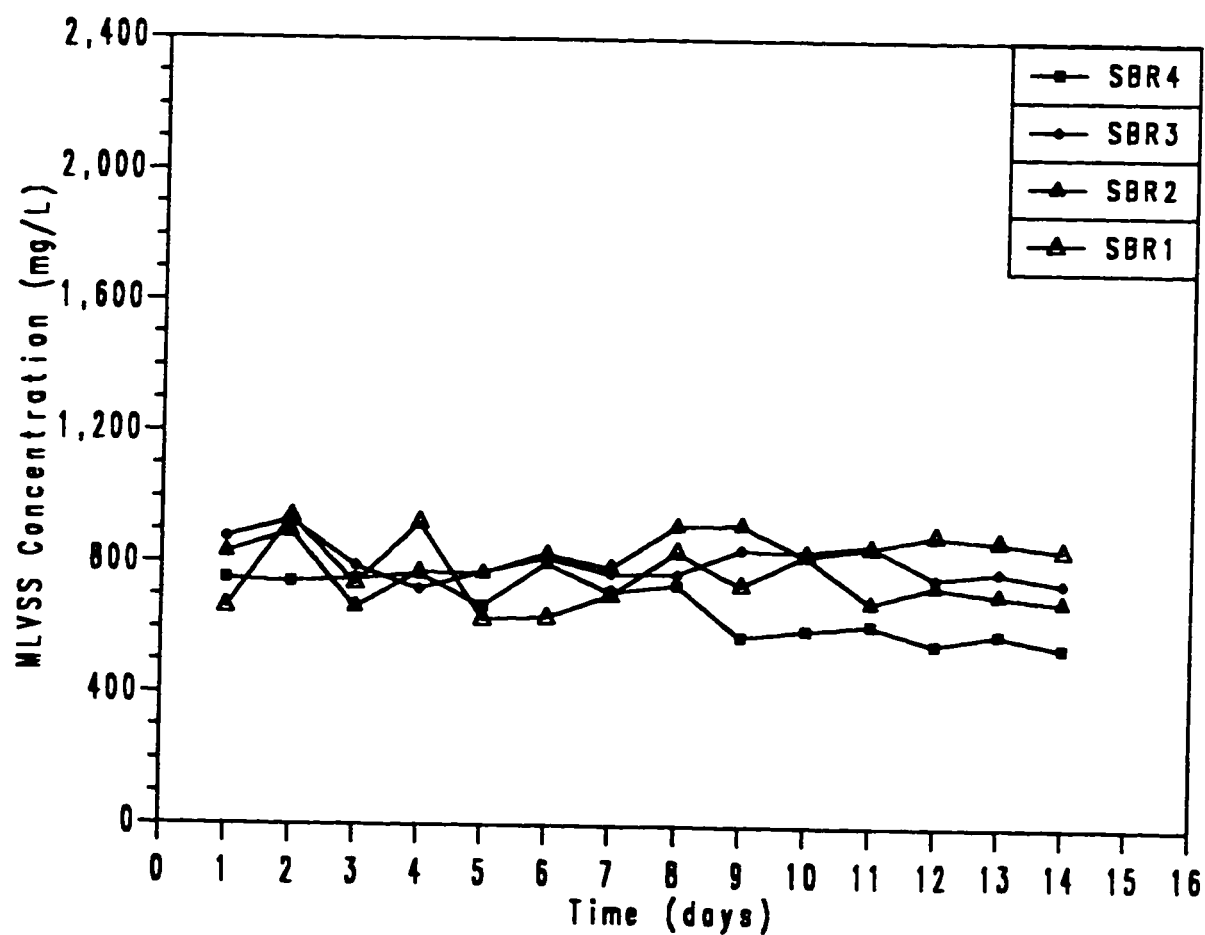
Fig. 5.43 : Concentration of Mixed Liquor Volatile Suspended
Solids in the SBRs (Phase II).
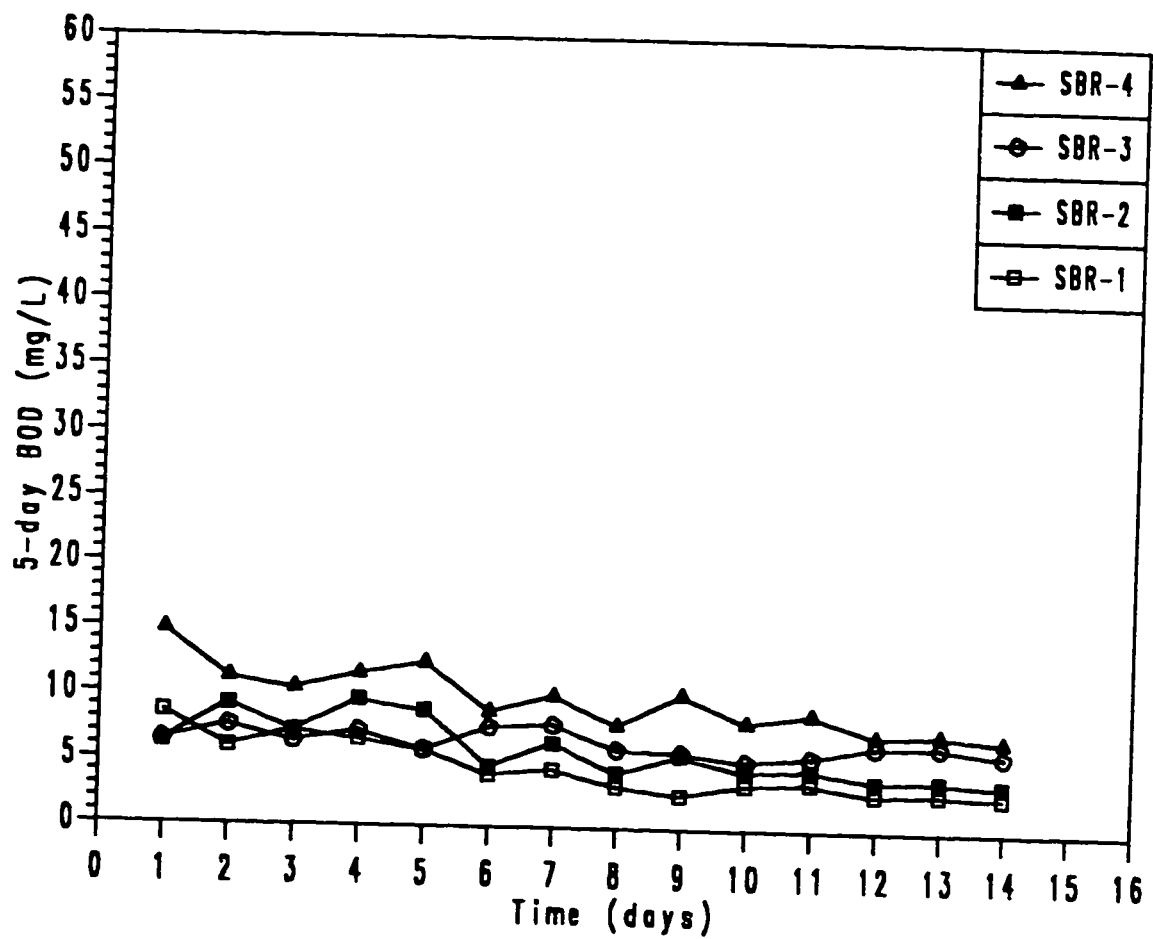
Fig. 5.44 : Concentration of Effluent BOD in the SBRs (Phase II).
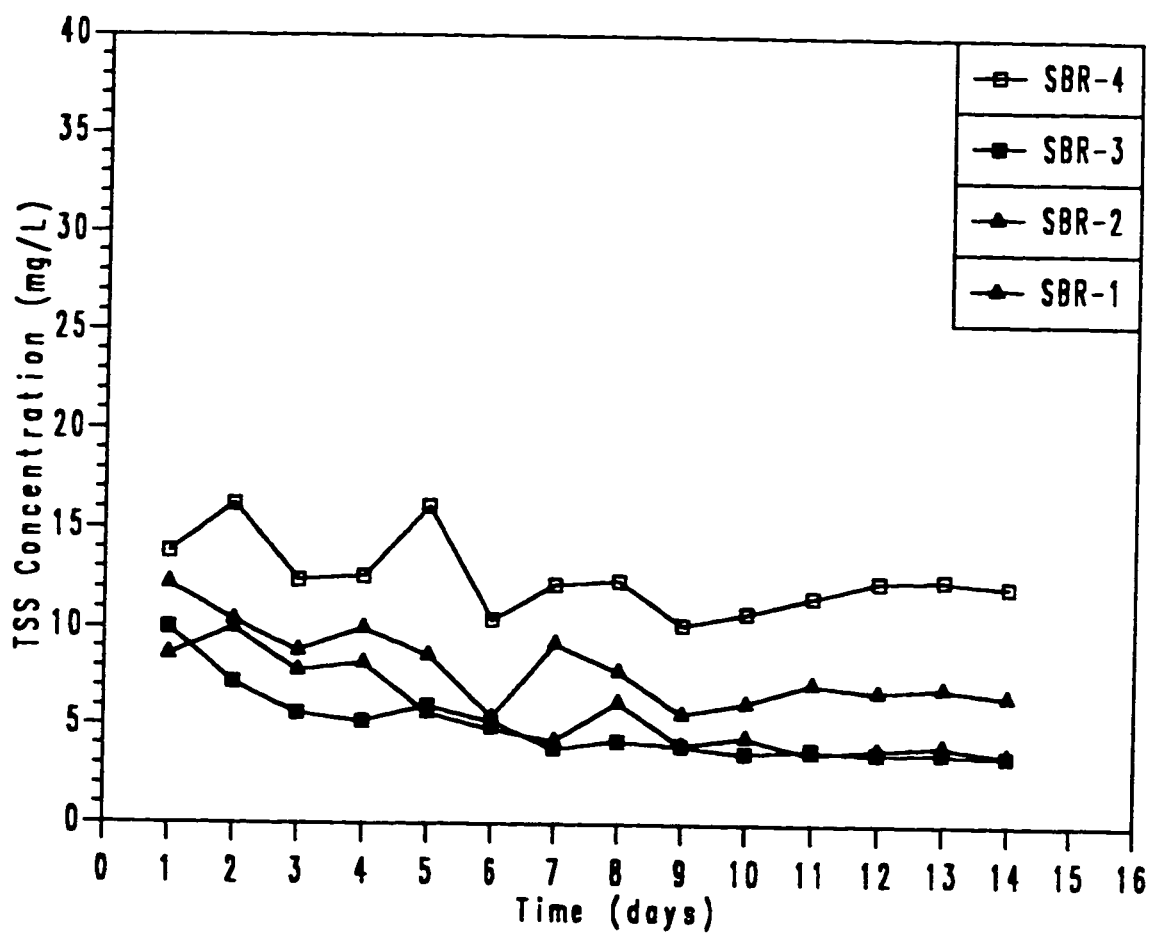
Fig. 5.45 : Concentration of Effluent Total Suspended Solids in the SBRs (Phase II).
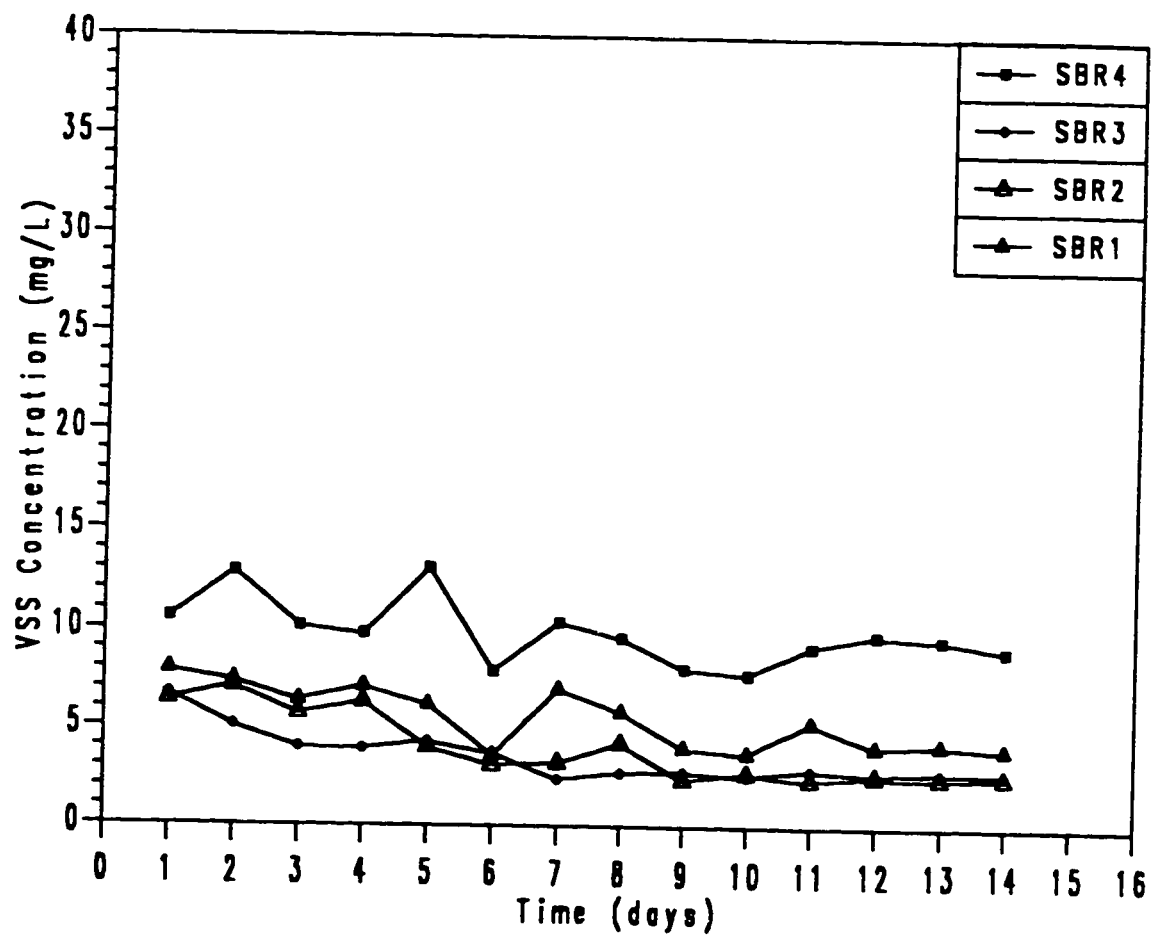
Fig. 5.46 : Concentration of Effluent Volatile Suspended Solids in the SBRs (Phase II).
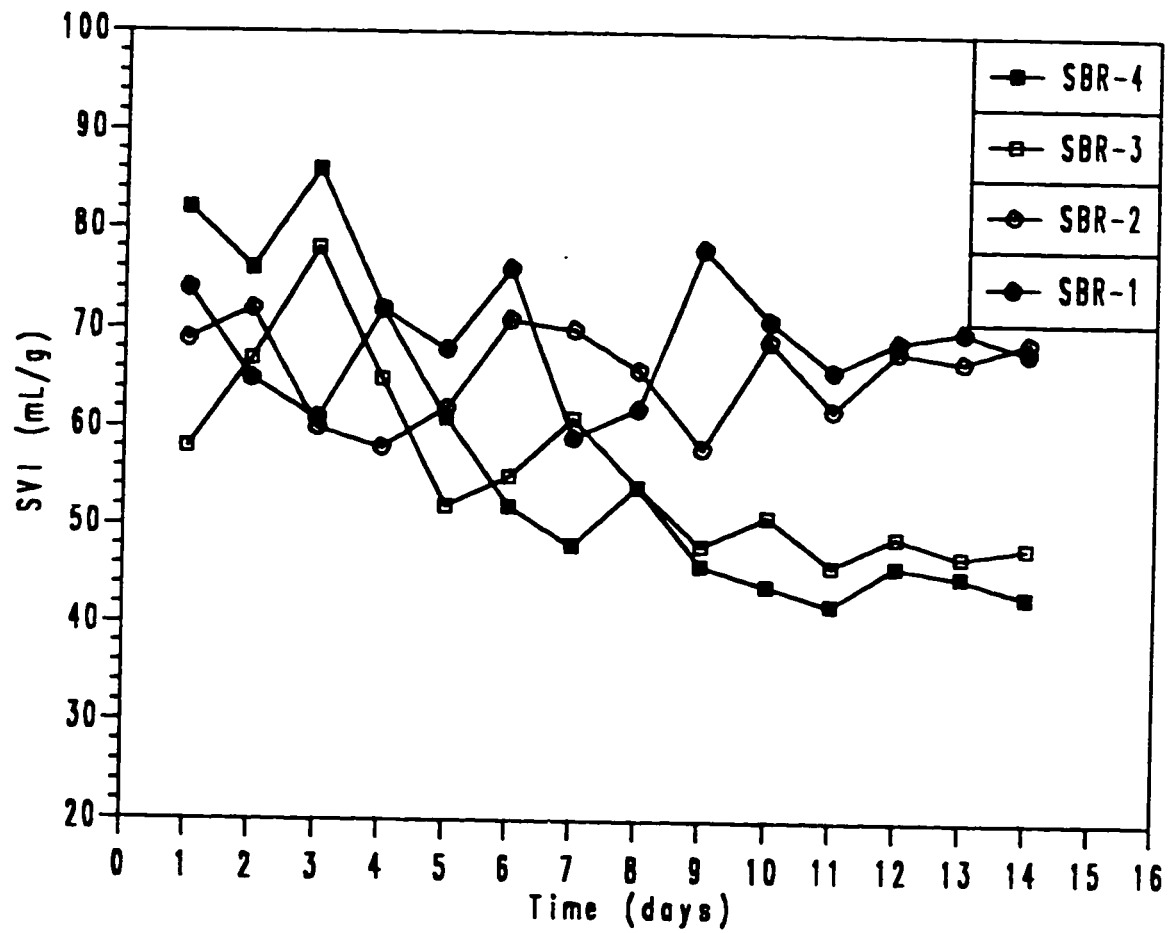
Fig. 5.47 : Sludge Volume Index in the SBRs (Phase II).

5.6.4 Treatment Efficiency in SBRs

The treatment efficiencies of SBRs in this study were compared to the removal efficiencies of other biological systems dealing with petrochemical wastewaters as given in the literature (Table 5.13). As seen from Table 5.13 the maximum removal efficiencies attained in the present study were 94% and 87% with respect to BOD and COD, respectively. Hsu [53] attained 97% removal of BOD using SBRs. The BOD concentration of 242 mg/L was reduced to 8 mg/L . However, the type of processes and/or products of the petrochemical industry was not given which makes the comparison difficult. The moderate removal efficiency attained in the present study suggests the presence of slowly degradable compounds. Shannon [30] obtained 99% removal efficiency for activated sludge treatment of a petrochemical waste. The BOD of 85 mg/L was reduced to 10 mg/L , however, the removal efficiency in terms of COD was reported to be very low (62.5%). It can be further noted from Table 5.13 that although the maximum BOD removals are the same for most of the wastewaters, the treatment efficiencies in terms of COD are highly variable. This can be due to the presence of varying amounts of compounds that are resistant to biodegradation.

5.7 Quality Criteria for Cooling water

The major problems in the industrial cooling systems as related to water quality are : scaling; corrosion; and biofouling [54]. The scaling is caused mainly by the carbonates of calcium and magnesium and to some extent by calcium sulfate due to their low solubilities. The main causes of corrosion are the concentrations of TDS and chlorides. These are controlled in the recirculating cooling systems by

Table 5.13 : Comparison of Biological Treatment Efficiency of SADAF with Other Petrochemical wastewaters.

Method	Product/Process	BOD			COD			Reference
		Influent	Effluent	%Removal	Influent	Effluent	%Removal	
SBR	Ethylene,Ethanol, Ethylbenzene,Styrene	52	3	94	174	22	87	present study
SBR	Petrochemical	242	8	97				Hsu [19]
AS	Ethylene,Propylene, Benzene	600	90	85	700	105	85	Sadow [23]
AS	Ethylene,Propylene, Benzene,Butadiene	85	10	99	200	75	63	Shannon [29]
AS	Ethylene,Glycols, Morpholene,Ethers	1950	20	99	7970-8540	5120-5950	25-40	Ford [30]
AS	Benzene,Toulene, Alcohols,Ketones	1100	55-100	90-95	700	105	85	Coe [31]

SBR = Sequencing Batch Reactor; AS = Activated Sludge

concentration cycles, i.e., blow down. The maximum concentration of the TDS or chlorides to which the cooling systems are operated is generally the allowable discharge concentration by the regulatory authorities (3000 mg/L of max. TDS allowed by Royal Commission Al-Jubail). The corrosion inhibitors are also added to reduce the corrosion of equipment. According to Rebhun and Angel [54] biogrowth in the cooling systems was observed both as attached biomass and as dispersed organic SS, however, it can be controlled by proper pretreatment of the water to reduce the organic matter and nutrient or by the use of biocides. The latter is used in the case of small substrate concentrations.

Table 5.14 shows the influent and effluent charcteristics of the phosphate stream wastewater and the final effluent. The effluent under the phosphate stream wastewater refers to the combined adsorption and ozone treated wastewater; whereas, in case of plant's final effluent it refers to the SBR biologically treated wastewater. The cooling water quality criteria required at SADAF and the analysis of a tertiary treated secondary effluent which is now being used in a large petrochemical complex [54] is also presented. The untreated phosphate stream wastewater from SADAF is an excellent candidate to be used as cooling water make-up as indicated by low values of chlorides, TDS, etc., except for the high TOC levels. The combined ozonation/carbon adsorption, however, reduced the TOC concentrations of 96 mg/L to below 15 mg/L , which is still higher than the 10 mg/L limit set by SADAF for cooling purposes. Hence, the treated wastewater can be used in combination with fresh water for the cooling purposes. However, as shown in Table 5.14, the COD of 80 mg/L of the tertiary treated secondary effluent is more than 73 mg/L of COD for the ozonated carbon treated wastewater which suggests that the wastewaters can be tried as a sole source of cooling water

Table 5.14 : Cooling Water Criteria in Petrochemical Industry

parameter	Phosphate Wastewater		Plant's Effluent		Cooling Criteria at SADAF	Treated Secondary Effluent (5)
	Influent	Effluent	Influent	Effluent		
pH	10.2-11.5	7.0	6.2-7.6	7.0	6.2-6.8	10.5
Conductivity	650	650	875	875	2500	
Alkalinity	120		50			250
Chlorides	19	19	172	172	150	150
TDS	392	392	646	646	3000	350
BOD	56		52	3.0		10
COD	183	73	174	22		80
TOC	73	18	72	12	10	
Nitrogen	0.8	0.8	2.6	1.8	20	25
Phosphate	27	27	19	12		0.2

N.B:- All values are in mg/L except pH and conductivity.

make-up with a rigorous monitoring of the biological activity.

The SBR biological treatment produced a good quality effluent with respect to removal of organic matter; i.e., BOD, COD and TOC of 3, 22, and 12 mg/L, respectively. This effluent can also be considered for reuse in the cooling water system. However, the TDS and chloride concentrations of 875 and 172 mg/L, respectively, are slightly higher to those of the phosphate stream wastewater and SADAF's cooling water criteria. These slightly high concentrations of TDS and chlorides may lead to higher number of blowdowns.

Chapter 6 .   -

SUMMARY AND CONCLUSIONS

6.1 Summary of Results

A summary of all the results obtained from this study for different processes, namely; air stripping, activated carbon adsorption, ozonation, combined activated carbon/ozonation for the treatment of phosphate stream wastewater and biological treatment of the plant's final effluent in sequencing batch reactor system is given in Table 6.1.

The performance of air stripping process was poor, i.e., with less than 10 percent removal of TOC even at an elevated temperature of 50°C. Granular activated carbon adsorption reduced TOC concentration by 62.2 percent, i.e., from 74.0 mg/L to 28.0 mg/L in continuous flow studies. The removal was 66.6 percent with respect to COD. It was noticed that there was no great change in the COD/TOC ratios when the wastewater was subjected to granular activated carbon adsorption.

Ozonation of the phosphate stream wastewater resulted in a decrease of TOC and COD contents by 32.5 and 42.3 percent, respectively. The pH value was 11.4 and the temperature was 60°C for a detention period of 2 hours and ozone dosage of 17.5 mg/L.

Table 6.1 : The Relative Efficiencies of Air Stripping, Activated Carbon Adsorption, Ozonation and Biological Treatment for SADAF Wastewater

Sample	TOC (mg/L)	COD (mg/L)	BOD (mg/L)	REMARKS
Phosphate Stream				GAC column study
Before GAC adsorption	74.0	204		Down flow mode
After GAC adsorption	28.0	68		Loading = 1.0 gpm/ft²
Removal (%)	62.2	66.6		Sample at pH = 7.0, t = 22°C
				Semi - batch ozonation
Before ozonation	96.0	434		Ozone dosage = 17.5 mg/L
After ozonation	64.5	251		Detention time = 2 hours
Removal (%)	32.5	42.3		Sample at pH = 7.0, t = 60°C
Before GAC/ozonation	96.0	434		The conditions are
After GAC/ozonation	18.0	96		Combination of the
Removal (%)	81.2	77.9		Above two processes except t = 22°C
Before Air stripping	75.5	196		Diffused Aeration
After Air stripping	70.0	177		Detention time = 2 hours
Removal (%)	7.0	9.7		pH = 7.0, t = 50°C
Final Effluent				
Before biological treatment	71	174	52	
After biological treatment	12	22	3.0	
Removal (%)	83	87	94	

The combined ozone/activated carbon adsorption achieved upto 8J.2 percent of TOC removal. The corresponding COD removal was 77.9 percent. Under the limitations of the batch tests it can be concluded that the combined ozonation/granular activated carbon adsorption can be considered as a potential candidate for the treatment of phosphate stream wastewater for reuse purposes. However, it should be remembered that on site pilot scale studies have to be carried out before implementing any program for the full scale treatment.

The biological treatment of the final effluent achieved upto 94, 87 and 83 percent removal of BOD, COD and TOC, respectively. This indicates that the biological treatment of the SADAF's final effluent is feasible in an SBR.

6.2 Conclusions

Phosphate Stream Wastewater

The following conclusions may be drawn based on the adsorption and ozonation studies of the phosphate stream wastewater :

1. An appreciable non-adsorbable portion (49-27%) of TOC was noticed for different values of pH and temperature.

2. The TOC removal was 62% at a pH of 7.0 through adsorption, however, it increased from 33 to 68% when the pH was changed from 12.0 to 4.0.

3. The adsorption of TOC was 49, 66 and 73%, respectively, at the temperatures of 60, 30, and 10°C at a given pH of 7.0.

4. The TOC removal by ozonation increased from 9.4 to 26% when the pH was

changed from 4.0 to 11.4. This indicates that pH has a pronounceed effect on ozonation of this wastewater.

5. The TOC removal by ozonation increased from 27.6 to 32.5% when the temperature was raised from 25 to 60°C.

6. The adsorptive capacity of the activated carbon increased for the ozonated samples as is evident from both the batch and continuous flow tests. This can be due to the formation of organic acids which are more adsorbable when compared to alcohols, aldehydes, etc. present in the wastewater.

7. The wastewater can be reused as a cooling water make-up along with fresh water after ozonation and activated carbon treatment.

Final Effluent

The following specific conclusions may be drawn about the biological treatability of the final effluent.

8. The SBR biological treatment seems to be a feasible method for the reduction of BOD from SADAF's final effluent. A good quality effluent with BOD and TSS concentrations of 5 mg/L each can be achieved by selecting a suitable reactor operating strategy.

9. The results of the analysis of the phase I study indicate that the optimum total cycle time for the treatment of SADAF's final effluent is in the range of 8 to 12 hours. The effluent BOD for these cycle times is comparable to the reactor with 24 hours of total cycle time.

10. In the phase I study it was observed that the SVI values for the SBR-2 and

SBR-3 were lower than for SBR-1 and SBR-4. This is due to the development of compact sludge in SBR-2 and SBR-3 when compared to other two reactors. This phenomena also lead to the higher concentrations of TSS in the effluent of SBR-2 and SBR-3.

11. The introduction of anoxic conditions in the phase II study, during the fill period, reduced the TSS concentration in the effluent discharged from the SBRs.

12. The performance of SBR-4 in the phase II study was poor in terms of the effluent quality. This may be due to the prolonged anoxic react period.

Chapter 7

RECOMMENDATIONS

Based upon the results of the present bench scale studies, more comprehensive studies at pilot scale can be carried out at the plant site for which the following recommendations have been forwarded.

1. Batch adsorption studies have shown that the phosphate stream wastewater contains compounds that are not amenable to activated carbon. Identification and quantification of these compounds, and employment of another adsorbent in series, can enhance the organic removal efficiency. The adsorbents that can be used are microporous polymers and site specific silicalites.

2. Ozonation of wastewater in the presence of certain catalysts was found to increase the TOC removal efficiencies from certain industrial wastewaters. Catalysts, such as, metal oxides should be tried for this specific wastewater.

3. Biological treatment in sequencing batch reactors (SBRs) removed upto 94 percent of BOD and 87 percent of COD with effluent TSS of less than 5 mg/L. The biological treatment of final effluent in SBRs seems to be viable method due to its flexibility, especially, taking into consideration the variable nature of wastewater. Pilot scale studies can be carried out with different organic and shock loadings with compounds that may be expected to join the effluent during leaks.

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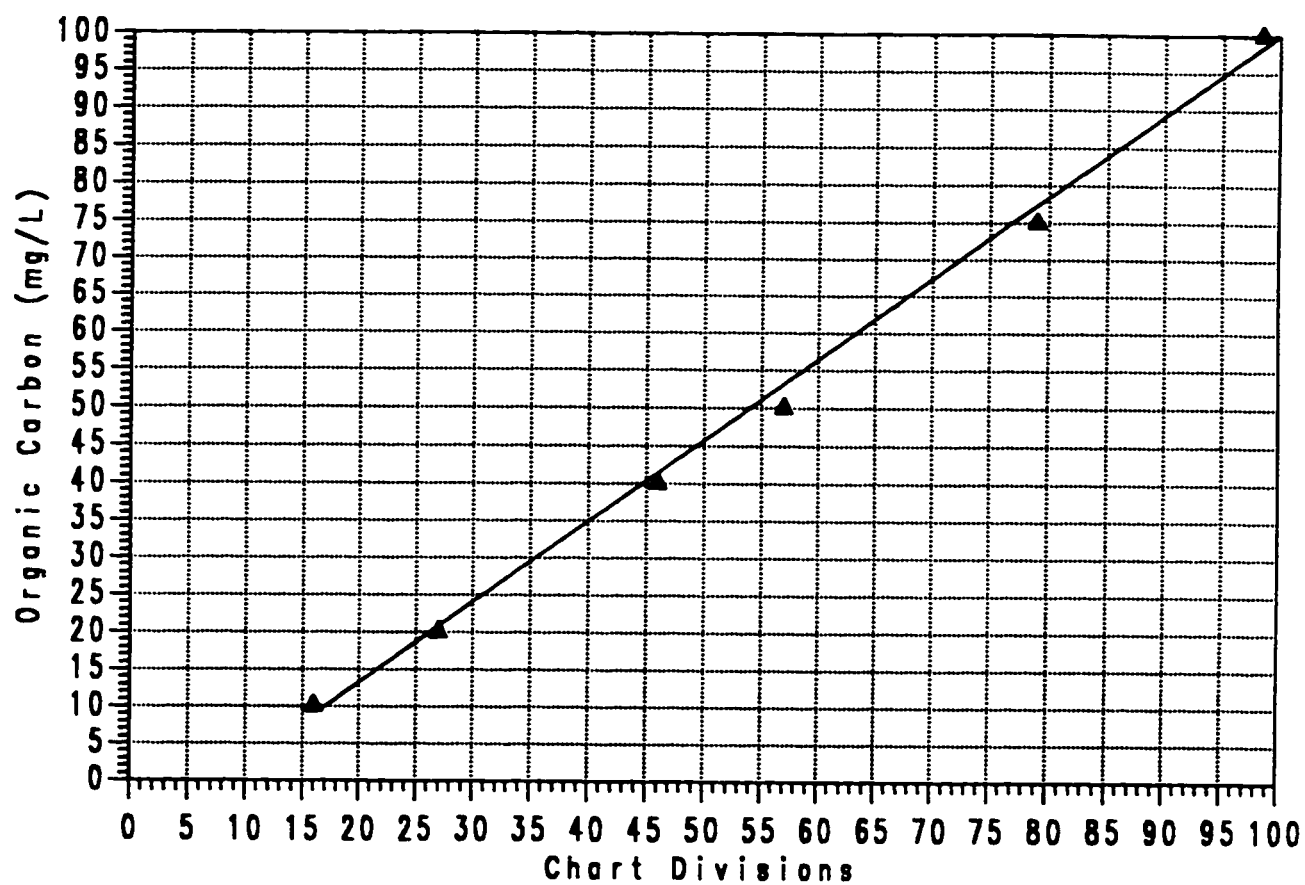
APPENDIX-A

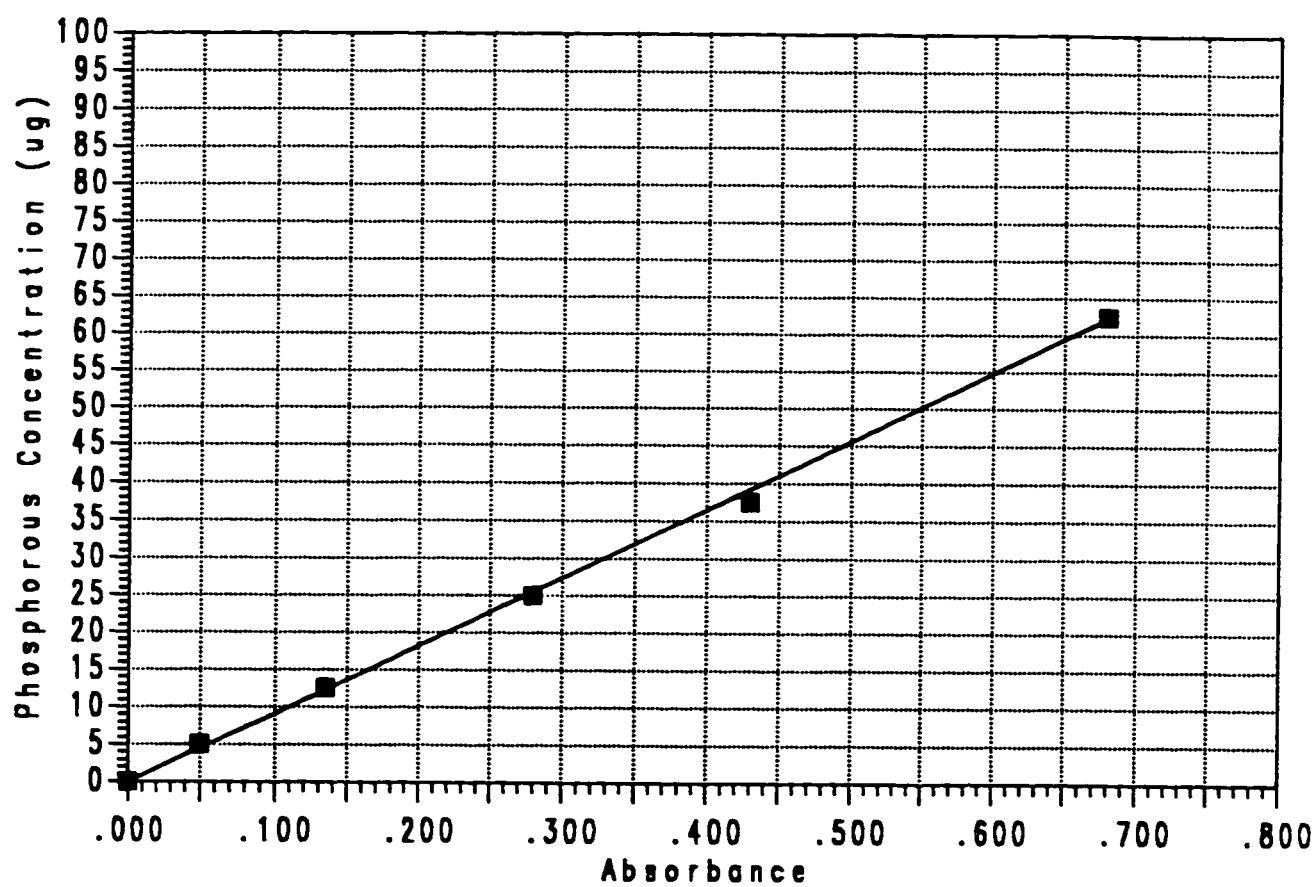# CALIBRATION CURVES

Fig. A.1 : Calibration Curve for TOC Measurement.

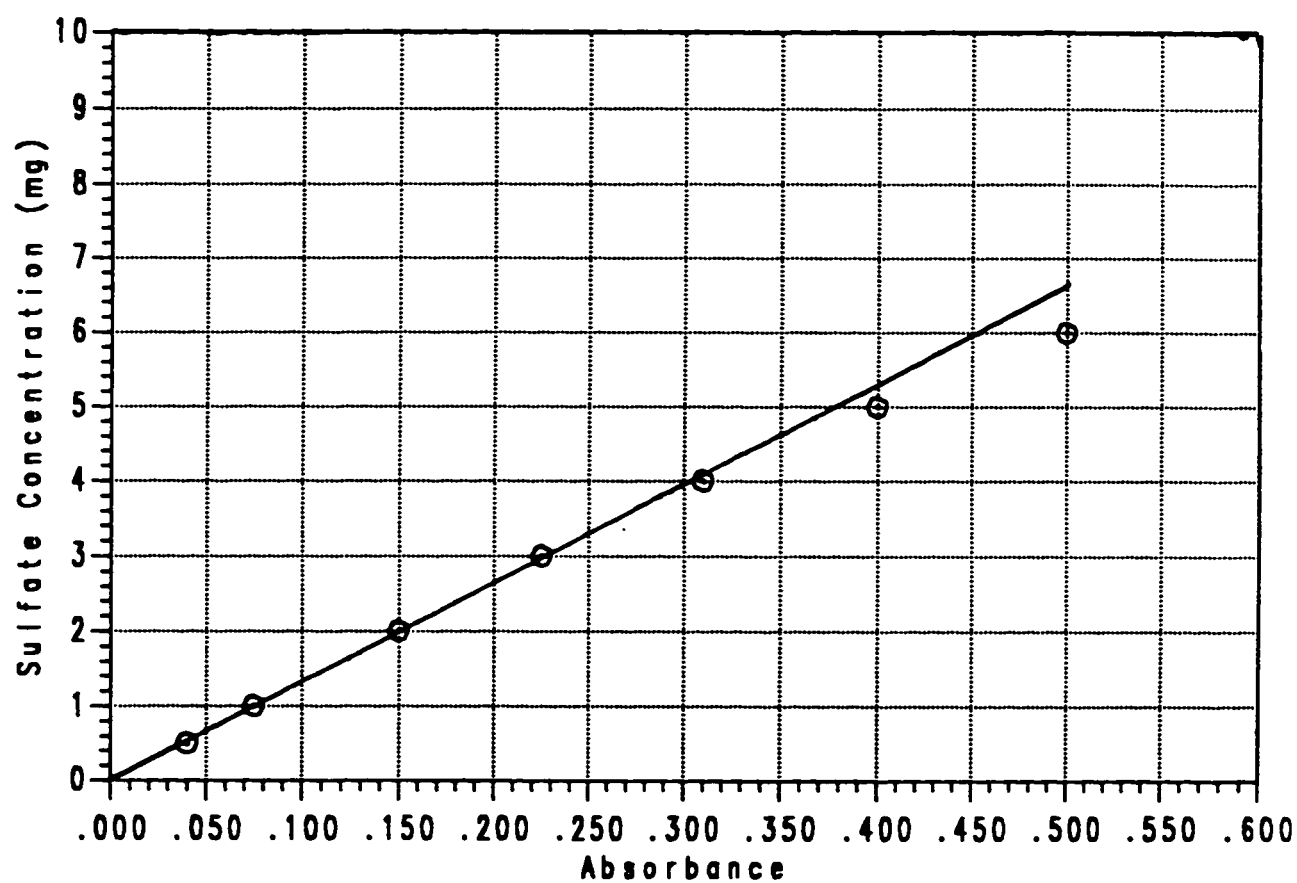**Fig. A.2 : Calibration Curve for Phosphorous Measurement.**

Fig. A3 : Calibration Curve for Sulfate Measurement.

APPENDIX-B

SAMPLE CALCULATIONS

ACTIVATED CARBON ADSORPTION

(Data Sheet for Batch Tests)

Experiment # : C1   Date : ....

Sample pH : 11.4   Sample Temperature : 22.5°C

Title : Feasibility of Activated Carbon to Remove Organics from Phosphate Stream Wastewater

S. No.	Wt. of Carbon M (gms)	Amount of Carbon Remaining in Solution			TOC Adsorbed per 100 mL X (mg/L)	$\frac{X}{M} \left(\frac{mg}{g} \right)$
		Total Carbon (mg/L)	Inorganic Carbon (mg/L)	TOC (mg/L)		
Control	0.00	90.0	20.0	70.0	-	-
1	0.05	80.0	14.5	65.5	0.45	9.00
2	0.10	79.0	17.5	61.5	0.85	8.50
3	0.25	75.0	24.5	50.5	1.95	7.80
4	0.50	56.0	7.5	48.5	2.15	4.30
5	1.00	59.0	13.0	46.0	2.40	2.40
6	2.50	56.0	12.5	43.5	2.65	1.06
7	5.00	40.0	17.0	23.0	4.70	0.94
8	10.00	38.5	17.0	21.5	4.85	0.48

N.B:- Volume of Sample taken = 100 mL