

**Sequencing Batch Reactor Treatment of Oily Wastewater
from Can Manufacturing and Gasoline Tank Bottoms**

by

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1.0 Introduction

Because the daily energy demand has increased dramatically, the oil industry has grown to be the largest industry in the world. In 1981, world oil production was 55.9 million barrels per day [1], 25% of which was consumed by the United States alone.

As a result of the high consumption of oil, oil-related pollution has become a more severe problem during this decade. The biological effect of oil toxicity on birds, marine life, and the whole ecosystem can be seen in many areas in the world [1],[2].

About 2-5 million tons of oil enter the world waters every year resulting in various environmental pollution effects. Half of the oil pollution is caused by used motor and industrial oil [1], and this makes it necessary to reduce oil pollution in water by recycling wasted oil, although it is a complicated process.

At the headquarters of Environmental Technology Southeast Inc. at Jacksonville, FL., waste oils are picked up at various disposal spots and transported to the treatment site of the company.

The waste oil to be treated contains a high percentage of water, and the wastewaters have to be treated for oil separation before discharge to municipal sewage system.

The Sequencing Batch Reactor (SBR) activated sludge process is used for the wastewater treatment. Before this investigation started, however, the concentrations of organic substrate in the effluent, as measured by BOD₅ and COD, were often higher than those in the influent because of bad operating conditions, and this made the SBR process ineffective.

The major objective of this study, therefore, was to identify optimal operating conditions for the SBR system to achieve high removal of organic matter from oily wastewaters.

2.0 Literature Review

Research conducted by Irvine and his co-workers has revitalized interest in batch or fill-and -draw systems for wastewater treatment. The Sequencing Batch Reactor (SBR) process is an alternative to conventional Continuous-Flow activated sludge treatment of wastewater for rural areas and small communities.[3-14]

The basic batch process concept can be traced back to 1914, when Arden and Lockett showed the efficiency of nitrification in a biological mass remained batch reactor. The term of "Activated Sludge" was also put forward by Arden and Lockett, to describe the biological mass, and it is still used at the present time. However, the fundamental batch reactor system was not widely used. Instead, it was replaced by the present day Continuous-flow System (CFS). The failure of batch reactors was not because of the performance of the process, but rather, because it requires more sophisticated operation. The resulting higher labor cost inhibited the application of SBR wastewater treatment plants, but the system did have potential advantages over Continuous-Flow processes [3,12]

In early 1950s, batch biological reactors had their first resurgence in the United States through the work of Hoover Porge and his coworkers at the Eastern Regional Research Laboratory [3], but the resurgence failed to prevail in extent wastewater treatment option. Since 1976, Irvine and Richter [6-13] have demonstrated the possibility of SBR as an alternative to CFS through studies conducted by the University of Notre Dame, Indiana. The second resurgence of SBR is possible due to modern technologies such as microprocessors, level sensors and electric automatic controllers. Therefore, less labor is required than before.

2.1.1.1 Characteristics of SBR

One cycle of a Sequencing Batch Reactor process consists of five periods [6, 7, 9] REACT, SETTLE, DRAW and IDLE, as schematically shown in Fig. 1 During FILL, wastewater is introduced to a reactor until a desired maximum water volume is reached. Aeration or mechanical mixing is either on or off according to the operating strategies. Irvine [9,16] has demonstrated that anaerobic operation in the FILL phase can lower the maximum volumetric oxygen uptake rates (g/m^3d) and suppress filamentous growth. As a result, anoxic FILL is beneficial to the overall operational scheme. But the time should be carefully controlled because the substrates accumulated in a fill period that is too long need extended aeration time for stabilization.

The REACT period takes place without additional wastewater, but the addition of air or pure oxygen and mixing are necessary for continuation of substrate stabilization which was initiated during the FILL period. Though an extensive aeration period can result in high substrate removal [11] from waste, it also may result in high turbidity

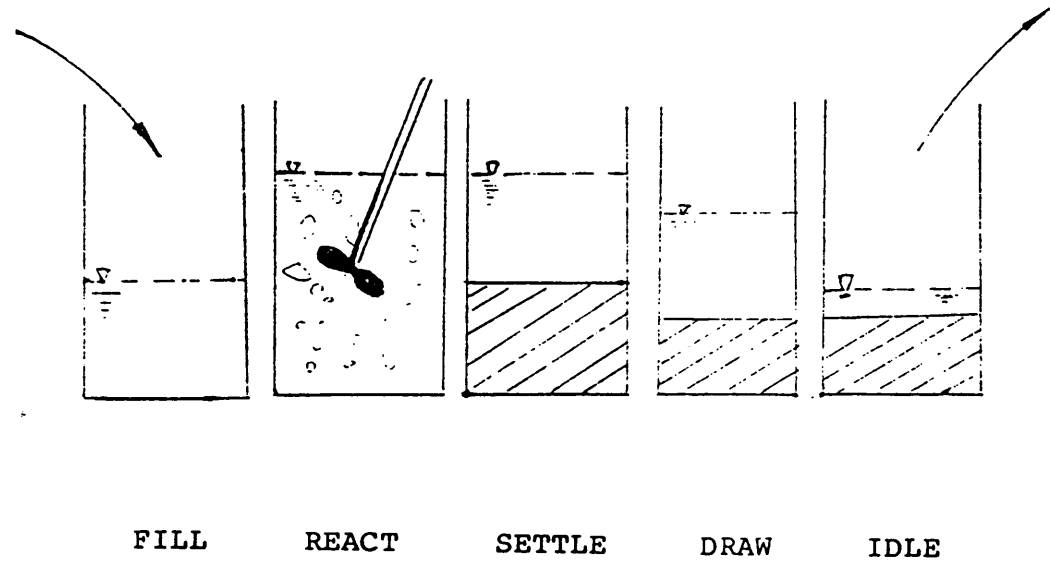
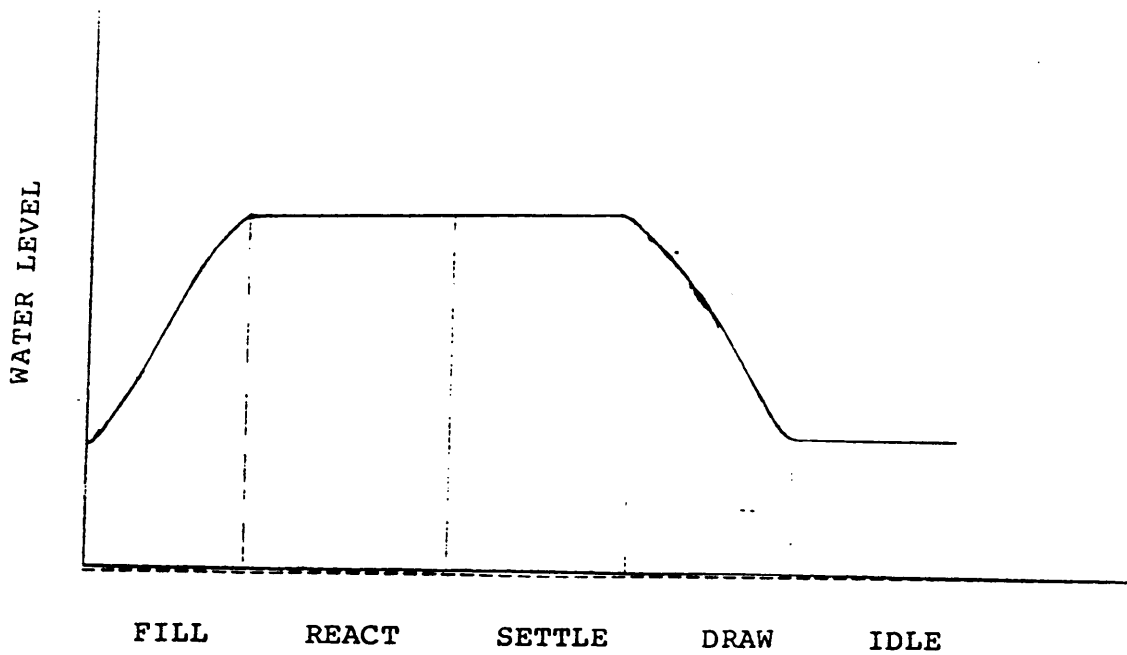


Figure 1. The four operating periods of an SBR cycle

in effluent. Nevertheless, proper selection of the length of this period can increase SBR treatment range and operating flexibility.

After organic reduction is completed during the REACT period, the activated sludge is separated from the liquid by sedimentation in the same basin during SETTLE period. Unlike CFS, no hydraulic motion exists during this period [14] and sludge settling occurs in nearly ideal quiescent conditions. The separated sludge is discharged during the DRAW period. The time interval between the end of DRAW period and the beginning of a new FILL period is the IDLE period. After a period of time of IDLE, the SBR is ready for another new cycle. To maintain the activity of the microorganisms in the reactor and sludge age control, activated sludge may be wasted either at the end of the REACT or during the IDLE period. The wasting frequency is determined by the net biomass increase in the system each day, and the capacity of the mixing and aeration equipment. Though a complete SBR cycle is composed of five discrete phases as described above, one or two phases may be either overlapping or omitted according to a particular treatment requirement.

An SBR system may have a single tank or multiple tanks depending on the influent flow and the desired quality of the effluent. For small communities one tank system usually is enough.

2.1.1.2 SBR Kinetic Responses

Even though the SBR process is an unsteady-state system, the kinetic response is similar to that of the Continuous-Flow process. The mass balances for flow, wastes and organisms can be presented with the following equations [14, 15, 16]:

During FILL period, the flow balance can be expressed as :

$$\frac{dV}{dt} = q; V(0) = V_0 \quad (1)$$

Waste balance can be expressed as :

$$\frac{dV C_s}{dt} = qC_{s0} + V r_{(fs)}; C_s(0) \text{ known} \quad (2)$$

Biomass balance can be expressed as :

$$\frac{dV C_b}{dt} = qC_{b0} + V r_{(fb)}; C_b(0) \text{ known} \quad (3)$$

After FILL, since there is no flow into or out of the reactor during the aeration period, the mass balance for a specific component can be mathematically expressed as following.

$$\frac{dV C_i}{dt} = kC_i \quad (4)$$

Where

V_0 = the volume of liquid at zero time in (m^3)

$C_s(0)$ = the waste concentration at zero time in (mg/l);

$C_b(0)$ = the organic concentration at zero time in (mg/l);

V = the liquid volume at any time, in (m^3);

C_{s_0} = the raw waste concentration, in (mg/l);

C_{bs} = the raw waste organisms concentration, in (mg/l);

r_n = the rate of formation of the i th component, in (mg/l d)

$$r_n = Y_{1,i}r_1 + Y_{2,i}r_2$$

where

r_1 and r_2 = the rates of reaction for first, and second reactions respectively, in (mg/l.d)

$Y_{i,j}$ = the stoichiometric coefficient for the i th component in j th reaction, in (mass/mass)

In an SBR system, the organic transfer coefficient can be used to evaluate the system performance, which is defined by the following equation [17, 18,19].

$$K = \frac{C_0 - C_e}{C_e T_e} \quad (5)$$

where

K = organic transfer rate coefficient, time ;

C_0 = initial organic concentration entering reactor, mg/l;

C_e = organic concentration in reactor at time T_e , mg/l;

T_e = equilibrium time.

Figure 2. schematically shows determination of the organic transfer rate coefficient.[17,18]

2.1.1.3 SBR Studies and Applications

The desired removals of organic carbon, and suspended solids, were achieved using an SBR system to treat landfill leachate, generated by Hyde Park, New York Landfill Site [21, 21]. The SBR treatment of the leachates mixing with chemical manufacturing wastewater was investigated by W. Ying and his associates using three different size reactors (1-L, 2-L, and 500-L reactors).

The nutrients requirement study conducted in the two smaller SBRs showed the optimum TOC : $\text{NH}_4\text{-N}$: $\text{PO}_4\text{-P}$ ratio of 75 :5:1 for the best treatment of high TOC containing leachate. Also, nitrification and denitrification were obtained without aeration during the last two hours of the REACT period. Eighty-six percentage of influent total organic carbon (TOC) was removed. The initial TOC concentration was 8135 mg/l.

The pilot-scale SBR treatment study was performed using 2-day and 5-day Hydraulic Retention Times (HRT) with MLSS concentrations of 5000 and 10000 mg/l in the 500 – L reactors. The results indicated that the system, with longer HRT ,and higher

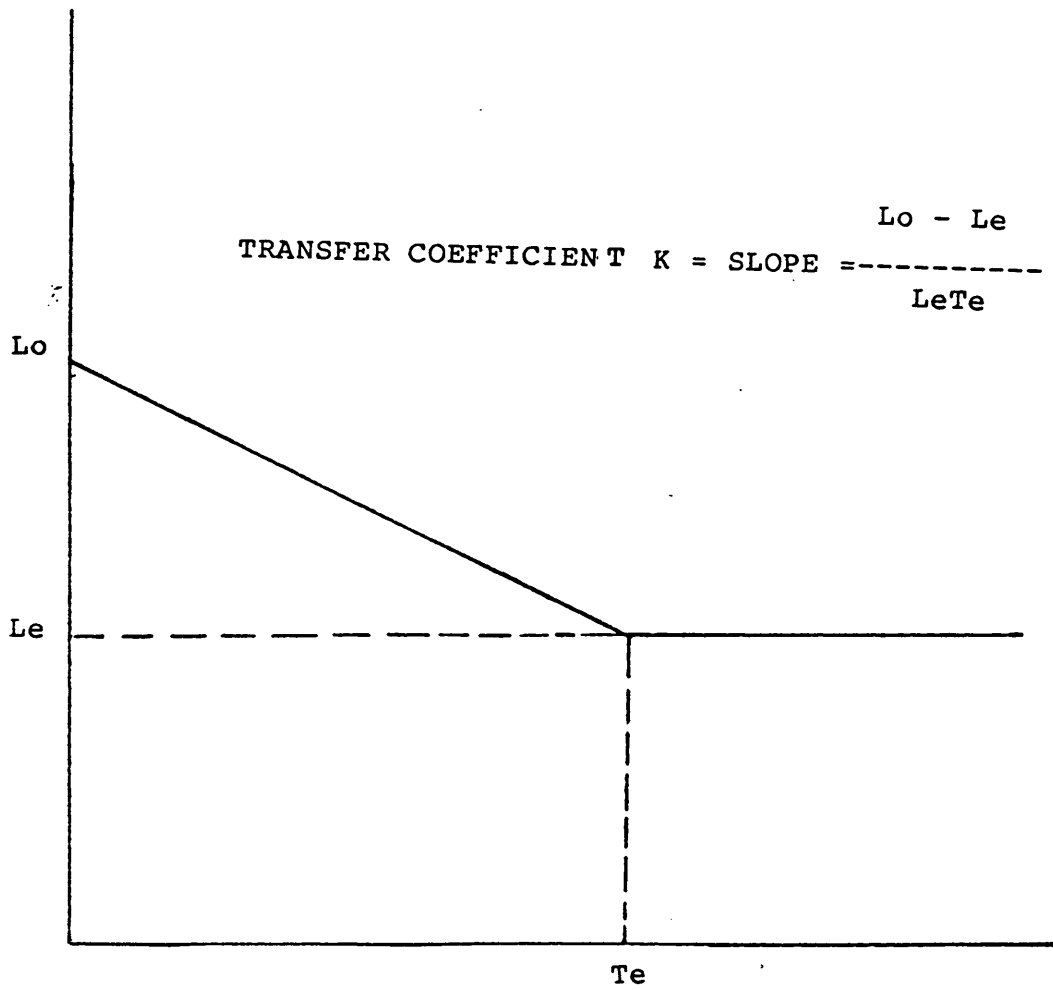


Figure 2. Determination of the organic transfer coefficient

MLSS concentration, generated the better effluent quality. However the TOC removal decreased, being compared with those of smaller scale reactors. The author considered that the dissolved oxygen (DO) concentration in mixed liquor was very critical for the TOC and COD reduction. DO concentration had to remain at least 1 mg/l through the aeration period. In the experimental reactors, high effluent total suspended solids (TSS) concentrations was produced. The concentration was greater than 250 mg/l.

Ying and his co-workers [22] indicated, in another investigation of the landfill leachate, that powdered activated carbon (PAC) addition to SBRs significantly improved the wastewater treatment efficiency. The TOC concentration was reduced from 3570 mg/l to 190 mg/l (ranging from 121 to 280 mg/l) in the effluent, and the phenol concentration was reduced from 820 mg/l to less than 3 mg/l in the effluent.

Irvine [6], in his work, concluded that nitrification and denitrification occurred simultaneously during FILL and REACT periods. An effluent Ammonia nitrogen of 1-2 mg/l was achieved in that investigation.

E. H. Hsu [23] performed a study of petrochemical wastewater treatment by an SBR, which exhibited that the SBRs were comparable, or in some cases slightly superior to CFS in terms of organic removal and nitrification. However, a high concentration of suspended solid in the effluent resulted because of the high strength of the waste. In contrast, Irvine [6] indicated that, when a relatively long detention time such as 24 to 26 hours is used, activated sludge can settle well.

E. H. Hsu also demonstrated that MLSS concentration for a shorter cycle with less sludge wasted was higher than that for a longer cycle with more sludge wasted. A

peak MLSS concentration occurred in the SBR about 16 to 17 hours after feeding. Meanwhile, the removal of about 90% BOD₅ was attained during the period. With additional aeration, the MLSS concentration declined due to cell decay.

It was reported by Hsu that the shorter the solid retention time, the higher the effluent suspended solids for the same influent wastewater. One batch with a retention time of 10 days produced the highest effluent TSS (21 mg/l), while another one with a retention time of 20 days produced the lowest effluent TSS (11 mg/l). The range is very small, however, when all concentrations are considered. Subsequently, the author found no significant effects of extended aeration on dispersion of the biological flocs, which would result in a high turbid effluent.

Hoepker and Schroeder, and Li [24, 25] indicated that the organic loading in SBRs strongly affects the TSS concentration in the effluent. The results in Hoepker and Schroeder's work showed that TSS concentrations of less than 30 mg/l were produced by SBRs with influent TOC concentrations of less than 170 mg/l, while a 640 mg/l effluent TSS concentration was observed from an SBRs receiving TOC concentration of 1280 mg/l. Dispersed growth of biological cells occurred, in the latter reactor.

It was also reported by Hoepker and Schroeder that the total suspended solids in the effluent could be reduced from an average of 270 to 55 mg/l when the wastewater was fed to the SBRs over a period of about eight hours. In the work performed by Hsu [23] the same result was observed. In addition, the effluent TSS concentration may be reduced by adding certain flocculants. In 1977, Rea [26] presented results showing that the addition of a polymer, Calgon WT 300, at the application dosage of

1 mg/l, produced effluent TSS concentrations of 30 mg/l. In that case, the oily wastewater was held in the basin for 7-40 days.

R. G. Smith et al [27] investigated using SBRs to treat leachate generated from Georgswerder landfill site, Hamburg, West Germany. Two sequencing stages of SBRs (Stage 1 and 2) were used to treat a synthetic leachate. Stage 1 was a suspended-growth SBR system, while Stage 2 was a fixed process, the latter was termed a Sequencing Batch Fixed-Film Reactor by the authors. The results showed that during first 6 hours of aeration time ammonia nitrogen removal was completed. Microscopic examinations presented both nitrosomonas and nitrobacter existing in the systems. The COD was removed rapidly at the beginning of reaction, and then decreased. The degradation of the COD followed first order kinetics, with greater than 90% COD removals. It was quite interesting that the system sludge volume (SV_{30}) decreased steadily throughout aeration period in the process.

2.1.1.4 Advantages and disadvantages of SBR

The advantages of SBR can be summarized as the following:

.The batch reactors behave as ideal plug flow reactors with respect to kinetic responses.

.Clarification and reaction are completed in the same basin without the additional maintenance of another tank, which saves space, construction, and labor.

.The internal equalization characteristics of SBRs provide the capability for handling complex incoming wastewaters and fluctuating organic loadings.

.Because the discharge is periodic, wastewater can be held in the tank until the predetermined effluent quality is obtained, and the operating tanks can be taken on and off line as desired. Therefore the process has a high feasibility for operation.

.Finally, the savings on energy and, consequently on operating costs can be achieved as a result of reduced aeration and sludge recycle equipment. If an automatic control system is used, the SBR process can be operated without a skilled operator.

An SBR process has the obvious benefits as indicated above; however, it still has some disadvantages. Otherwise it could be applicable for wide use instead of being limited in small communities. The disadvantages mainly include:

.In some cases SBR processes produce poor sludge settling characteristics with high turbidity in the effluent [28].

.Unfortunately, the well-developed operation criteria, such as hydraulic detention time, sludge age, and sludge volume index (SVI), which are used for CFS are not very applicable to SBR systems, which has discouraged extensive use. Further studies are required for the SBR processes to be a truly reliable alternative to CFS.

2.1.1.5 Overall Oily wastewater biological treatment methods

Oily wastewater biological treatment units include activated sludge systems, trickling filters, aerated lagoons, and waste stabilization ponds. However, the activated sludge

process is the most effective biological treatment process with respect to BOD₅ removal. For petroleum wastes [29], the activated sludge process can achieve substrate reduction efficiency of 79-95% for BOD₅, 30-71% for COD, and 65-99% for phenols. It has been reported that a wide range of organic loadings to activated sludge processes will affect the efficiency of BOD and COD removal and biomass settleability [30]. These effects are illustrated in Fig.3.

The treatment efficiency of oily wastewater by an activated sludge unit is also greatly affected by certain parameters, such as temperature, hydrogen ion concentration (pH) and nutrients .

Temperature effects on activated sludge systems are related to oxygen variation, microbial mass, and to substrate biological degradation rates. High temperature loadings cause a decrease in oxygen solubility as well as an increase in oxygen utilization. Fig. 4 shows that temperature change resulted in the change of COD removal for a petrochemical waste.

An optimal operating temperature range for an activated sludge system is 20 – 30°C, though some systems may perform well when the temperature exceeds 38°C by using thermophilic bacteria [30]. In conventional operating conditions, high temperature systems usually make it difficult for solid-liquid separation and a cloudy effluent normally results.

The activity of microbes is influenced by the pH values in an activated sludge system. A suitable pH range is 6-8 for proper function of the microorganisms.

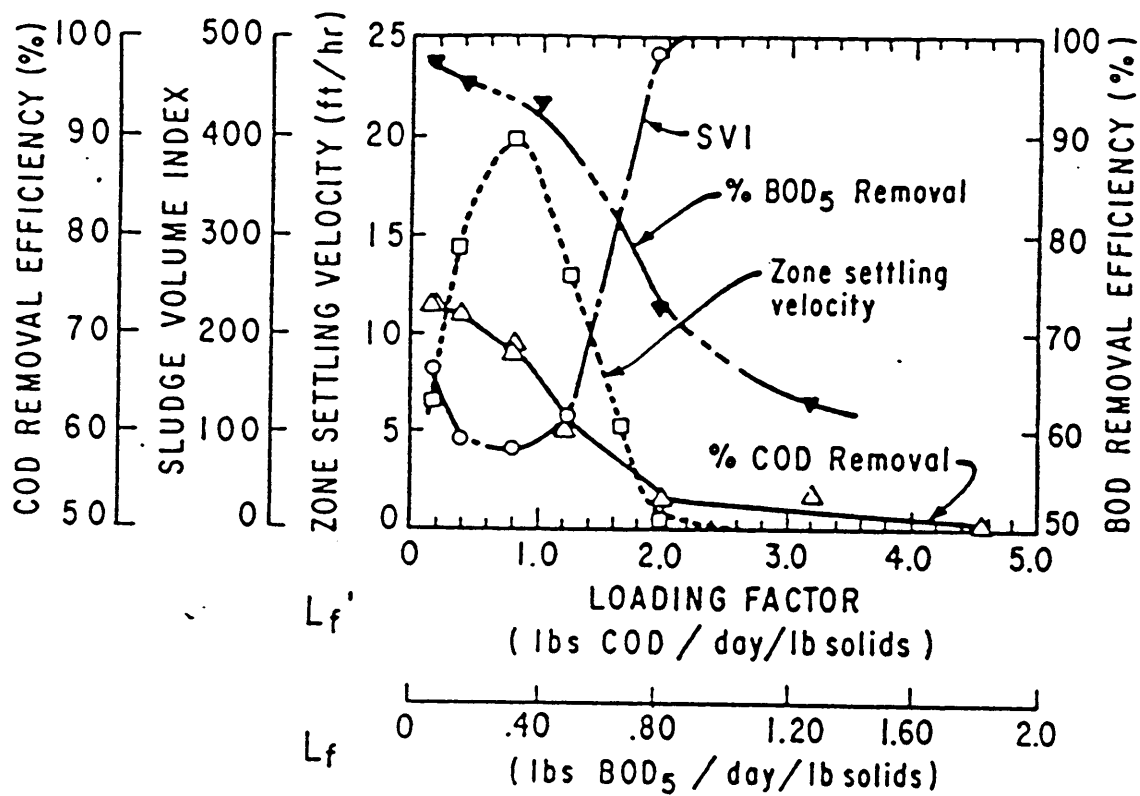


Figure 3. Parameter response to organic loading --Petrochemical waste (After Ford) [30]

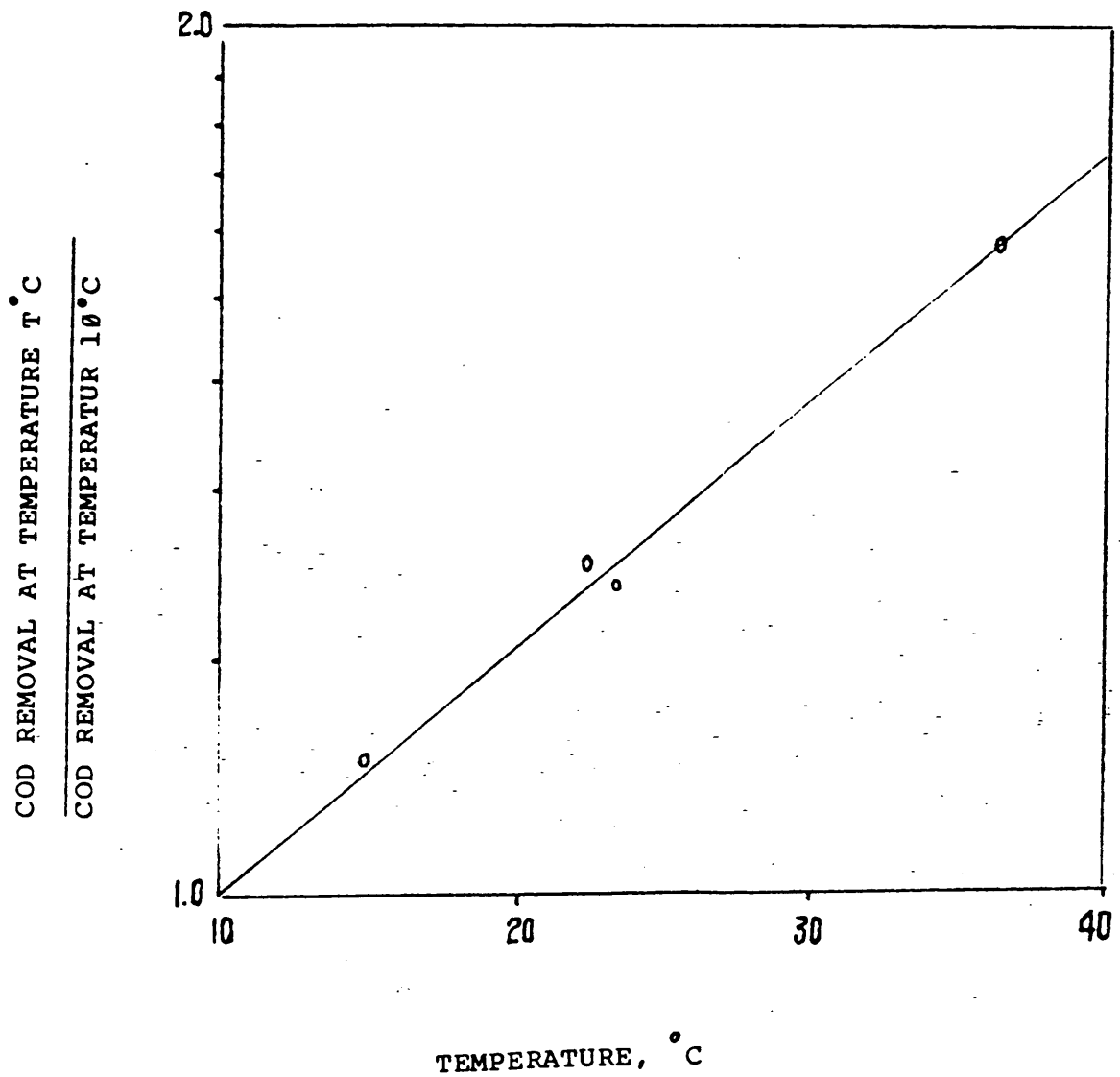


Figure 4. Temperature effect on COD removal (After Jones) [25]

Nutrients, especially nitrogen and phosphorus, are required for the growth of microorganisms in an activated sludge system. If nitrogen and phosphorus are insufficient, the biological degradation rate of organic matters will decrease and the growth of filamentous microorganisms may occur, which makes it difficult to separate the solids from the water. As a rule of thumb, nutrient balance should be maintained in the level of 5 mg nitrogen and 1 mg of phosphorous for every 100 mg of BOD₅ [31].

Ammonia and ammonium ion are the most available nitrogen sources to microorganisms, while, if organic nitrogen, nitrites and nitrates are used as nitrogen sources, extra energy is required for microorganisms to break down and reduce these compounds to ammonia nitrogen [25].

Phosphate phosphorus is the most readily available phosphorus form for microorganisms.

In the process of biological wastewater treatment, bacteria are the primary decomposers of substrates. Therefore, the efficiency of treatment is significantly dependent upon bacterial growth and metabolism of the organic materials.

It is important to know that in a batch system the bacterial growth pattern based on the mass of microorganisms with time is divided into four phases [32] as shown in Fig. 5.

1. Lag phase: The lag phase represents the time required for the bacteria to acclimate to a new environment.

2. **Log Growth Phase:** The log growth phase is characterized by the high activity of microorganisms. Sufficient food is available for the organisms; therefore the ability of the organisms to process the food is the main factor to be considered. Shock loads can change the bacterial activity from one stage to the another.
3. **Declining Growth Phase:** During this phase the rate of growth, and then the mass of organisms decreases as a result of limited available food.
4. **Endogenous Phase:** Because the food reaches the minimum level, the mass of organisms decreases and at the same time the death of some organisms results the release of nutrients which are used by the remaining organisms for growth.

The log growth phase near declining phase is commonly desired for wastewater treatment because of the high activity of organisms during this stage.

2.1.1.6 Special Concerns of Oil and Heavy Metals

Oily wastewaters are typically characterized by both high oil content of oil and high concentrations of organic materials. Oil waste frequently include some toxic materials, such as phenols and aromatic hydrocarbons in addition to hydrocarbons. When used oils from motors and vehicles are to be treated, special attention is needed. Many additives are added into the oil to prevent motors from oxidation and rust, and to withstand high temperatures [1]. The additives include compounds of barium, calcium, zinc, magnesium chlorine, etc., some of which are harmful to the growth of microorganisms. High sulfide content also may be toxic to organisms. On the other

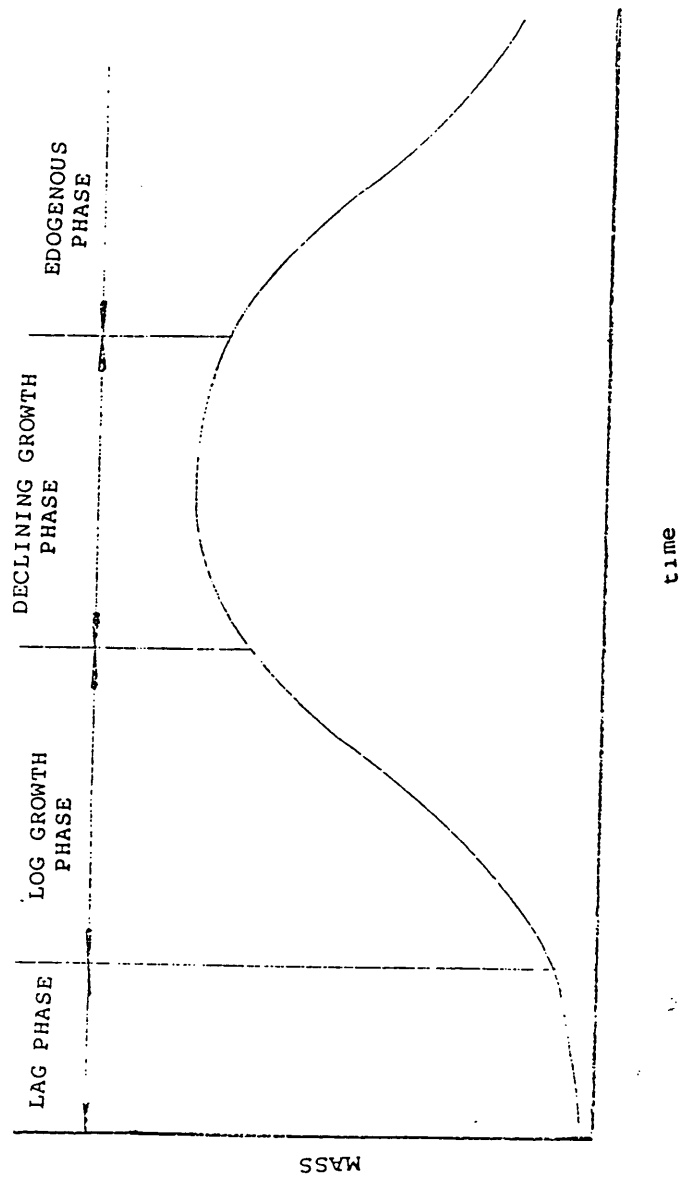


Figure 5. Microorganisms growth pattern

hand, the sulfides can react with dissolved oxygen, and thus reduce the oxygen available for biological oxidation in a treatment process.

Oils exist in wastewaters as low soluble materials, which makes it difficult for the microorganisms to metabolize them [1,23]. The insoluble materials associated with nonbiodegradable oily matters tend to accumulate in the biological treat process and subsequently result in solids settling problems because of their low specific gravity.

Sierp and Fransemeier [33] claimed in their investigation that copper at a concentration of 1 mg/l had a detectable influence in increasing effluent turbidity and decreasing the extent of nitrification, but showed only a slight impact on the efficiency of BOD removal.

Barth [34] reported that small amount of heavy metals significantly reduced biological treatment efficiency, but, after certain time, either low or higher dosage of metal did not greatly affected the treatment efficiency. Fig. 6 shows the effects the metal dosage on general wastewater treatment. However, heavy metals, with either lower or higher concentrations significantly inhibited nitrifying organisms. Lower oxygen requirement was found in metal-loaded sludge by by being compared to that in control unit, The biological transformation of ammonia to nitrate was inhibited. The nitrifying organisms were unable to acclimate heavy metals.

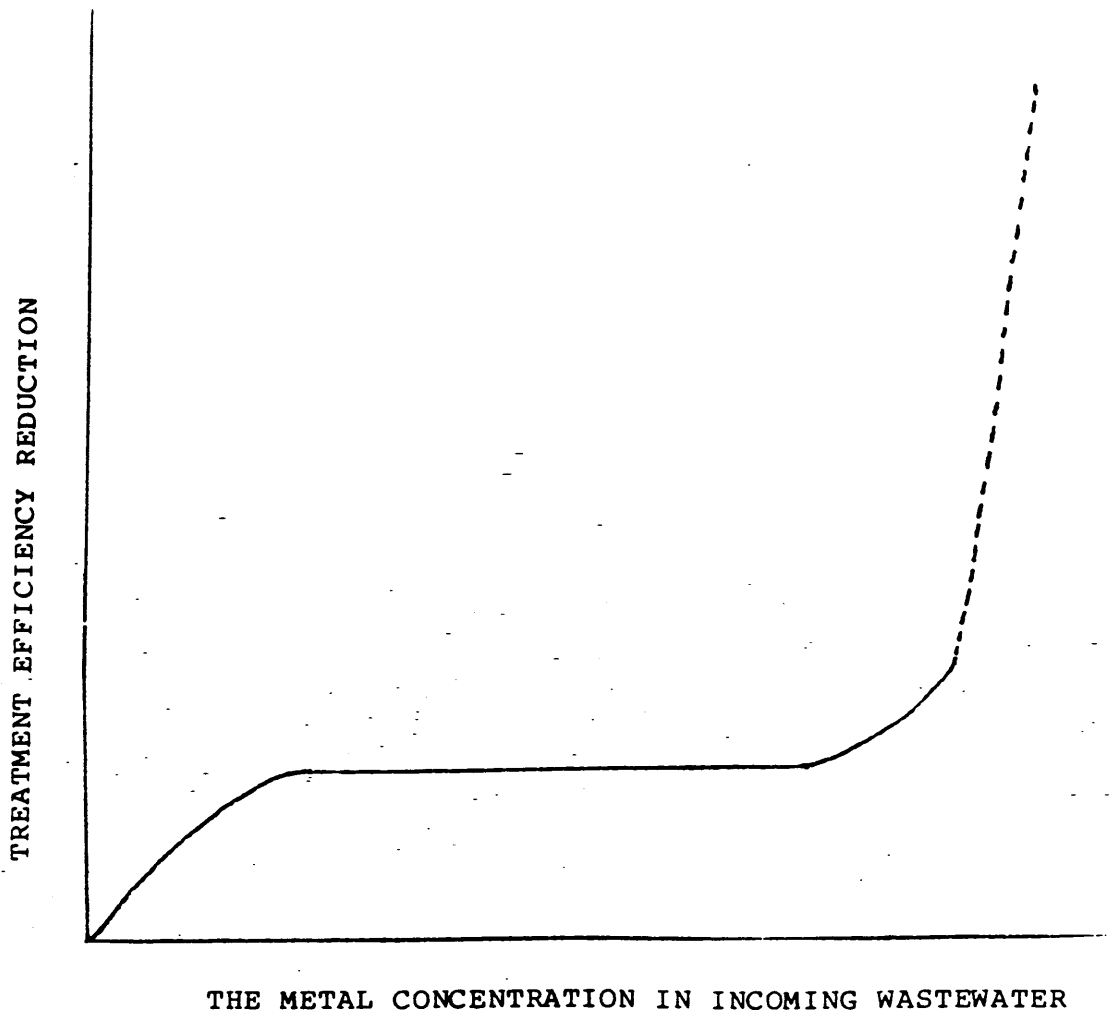


Figure 6. Effect of heavy metal dosage on activated sludge system: This figure is adopted from Barth [30].

3.0 Methods and Materials

The methods and materials used in the performance of this full-scale study of the treatment of high-strength industrial wastewaters by a sequencing batch reactor system are described in detail in this chapter.

3.1.1.1 Study Area Description

This study was performed at the headquarters of Environmental Technology Southeast Co. Inc., located at Jacksonville, Florida. Environmental Technology Southeast is a comprehensive industrial and petroleum waste engineering and service firm specializing in oil recovery and petroleum related waste disposal. The wastes to be treated were transported from customers to the plant site by the Company's transportation division and unloaded into oil recovery facilities where recoverable oil was extracted for recycle. The associated waste waters had to be treated to acceptable limits prior to discharge into the local Public Owned Treatment Works (POTW) via the municipal sewer. Physical and chemical methods were applied for oil separation from the incoming waste and an activated sludge Sequential Batch Reactor (SBR)

system was used to treat the associated water. The company was processing wastewater from more than fifty companies during the period of this investigation.

3.1.1.2 Overview of the Raw Waste and Treatment Process

A wide variety of oily wastewaters were treated during the period of this project. They were oil containing wastes from petroleum industries, cooling and process water from can manufacturing, waste gasoline from gasoline storage tanks, ship bilge water from shipyards, contaminated water from oil spills, and wastewaters from groundwater clean-up sites. The average pH value of the equalized raw water was 6.84 (ranging from 4.94 to 11.7), the viscosity was 20 with an average water content of 80.8% (ranging from 10 to 98%), and the flash point was greater than 140°F .

The raw waste samples were analyzed for the acceptance of all the wastes in accordance with hazardous waste regulations. The main concern was Polychlorinated biphenols (PCBs). The acceptable wastes were then unloaded from trucks into storage tanks via a decanter, and the decanted oil was directly pumped to oil storage tanks. Chemicals were added to the oil in the storage tanks and the oil was distilled, resulting in high quality oil for sale and reuse. The oily water separated by decanting was drained into an equalization tank (Tank 19) through an oil / water separator. The accumulated oil layer in the separator was transferred to a sludge thickening tank. Tank 19 was a pretreatment facility for the SBR. Chemicals such as polymers or ferric chloride were added to the wastewater in Tank 19 for removal of suspended and emulsified oil by mixing and settling when Dissolved Air Flotation (DAF) was not available. The pretreated wastewater in Tank 19 was pumped into SBR tanks for biological treatment. After the four periods of SBR system : FILL, REACT, SETTLE,

DRAW, the treated and clarified effluent was discharged to the sanitary sewer under a permit from the City of Jacksonville.

The process facilities existed before this project was started, and the process flowsheet of the plant is shown in Fig. 7.

3.1.1.3 Sequencing Batch Reactor Treatment Facility

The SBR system had been in use since Oct. 1986, when this study was started April 15, 1987. The system had two tanks available for the treatment process, and they were used alternatively. The two tanks were situated in horizontally and numbered 16 and 18. The maximum capacity of tank 16 was 20,000 gals, it was 10 feet and 6 inches in diameter and 32 feet in length, and was equipped with one manhole and two couplings. Tank 18 had a capacity of 19,000 gals, a diameter of 10 feet and 6 inches, and a length of 29 feet and 6 inches. Figure 8 is a photograph of the SBR facilities.

Air used for mixing and aeration was supplied by a 10 HP Roots Blower ER, model 865-112-1020. The connection between the blower and the SBR tanks was a 2"-diameter manifold pipe. Thirty-inch long pipes 1 inch in diameter with holes every 6 inches, were used as air diffusers and located at the bottom of the tanks. The oxygen in the wastewater was maintained at 2 mg/l or higher during aeration. The aeration pump was controlled by a timer, working either continuously or intermittently, throughout the experiments. Fig. 9 is a drawing of an SBR tank.

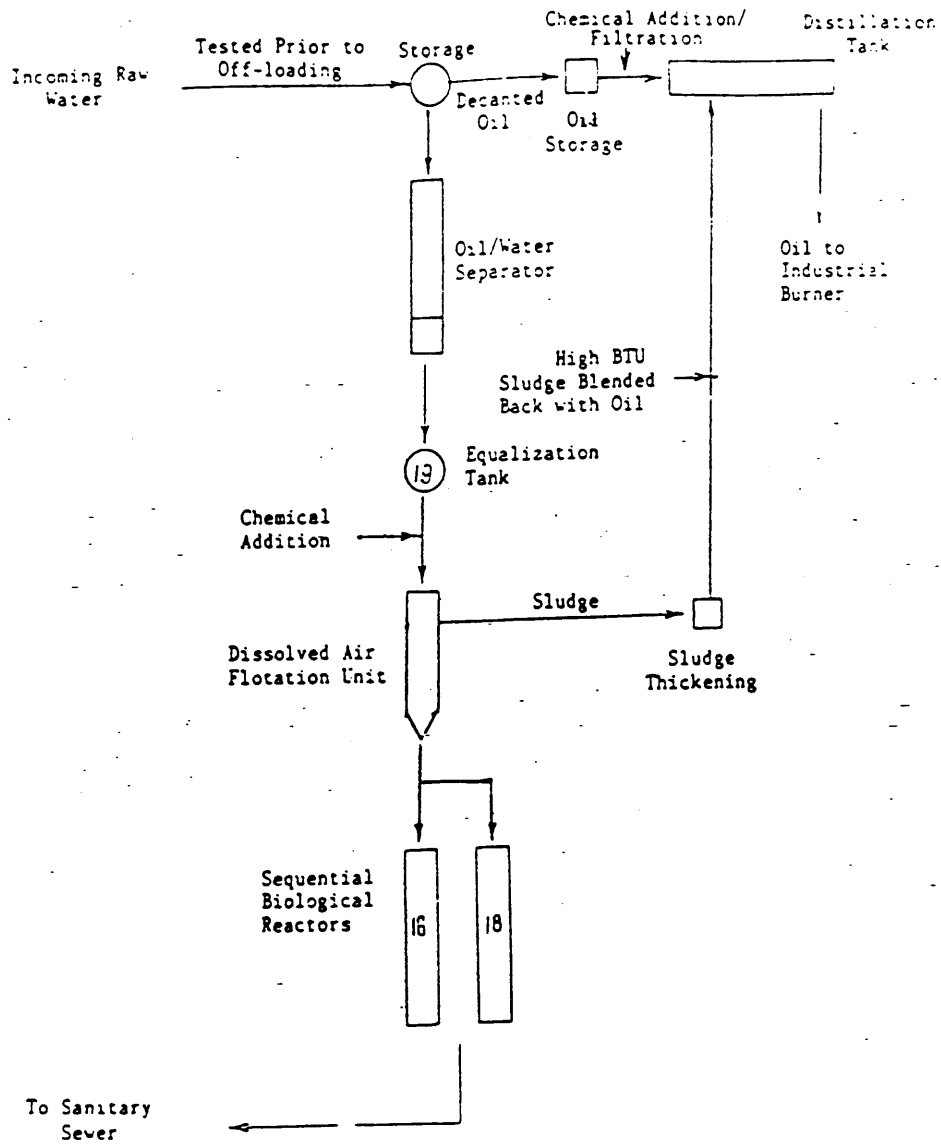


Figure 7. The oily wastes treatment flowsheet

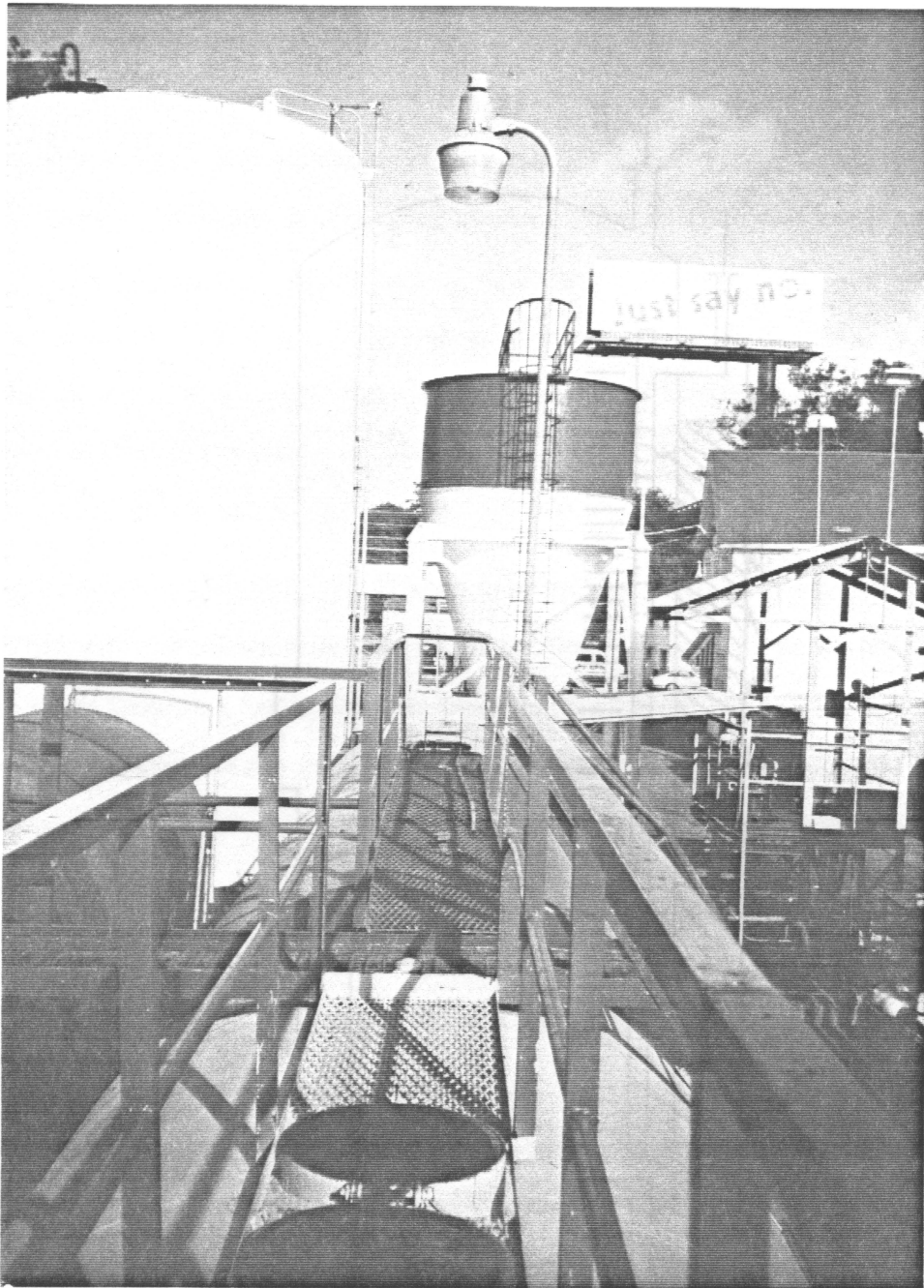


Figure 8. Sequencing batch reactor facilities

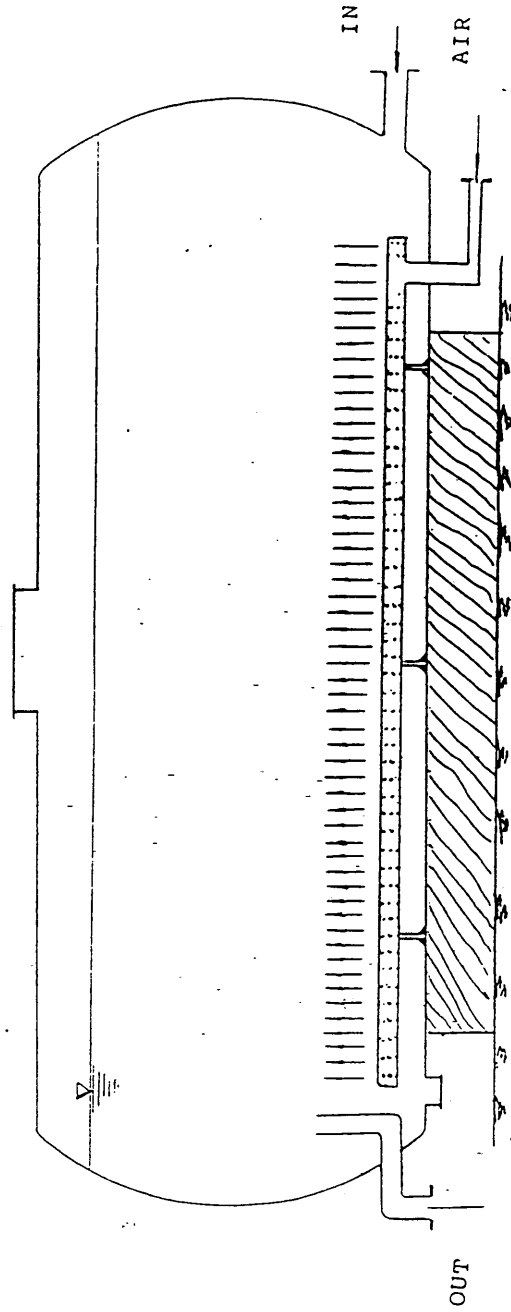


Figure 9. The drawing of an SBR tank

3.1.1.4 Experimental Design

In the first place, a comprehensive treatability experiment was conducted to define the optimum strategies for achieving maximum organic reduction under various SBR operating and cycle schedules, and to quantify the amount of nutrients required during treatment. Several operating strategies were undertaken from May to October in 1987. In total, thirty cycles were run under different operating schedules using the range of parameters shown in Table 1.

Ammonia Nitrate (NH_4NO_3) and Trisodium phosphate (Na_3PO_4) in solid form were used as nitrogen and phosphorus sources for nutrient requirement. Some chemicals such as Ferric Chloride (FeCl_3), Calcium Chloride (CaCl_2) and Alum ($(\text{Al}_2\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) were selected to improve the activated sludge settling characteristics during this study. A listing of the operating conditions for all thirty experiments is given in Table 1, Appendix A.

3.1.1.5 Treatment Procedure by SBR System

A particular microorganism seed provided by Sybron Biochemical Company Inc., was selected for the oily wastewater biological treatment by the SBR system. The seed contained *Pseudomonas* and *Bacillus* species that had been in the culture and were cultivated particularly for oil and phenol degradation.

Before the SBR system start-up, the microbes in dry form stored with grounded grain, were fed into a laboratory bench reactor with either diluted wastewater or SBR

Table 1. Various operating strategies for the SBR investigation

Aeration Pattern	Continuous	Intermittent
Cycle Length (days)	1-5	1-5
HRT (days)	11-8	11-8
Approximate SRT (days)	10-50	10-50

effluent. The addition of nitrogen and phosphorus compounds and continuous aeration were required for the microorganisms to acclimate to the industrial wastewaters. After two hours, the acclimated culture was transferred to full-scale SBR tanks for another 3 weeks acclimation to the incoming wastewaters. The microbial mass gradually increased until the desirable microorganism population was reached, and then the SBR system was ready to receive the wastewaters.

SBR systems were operated through five discrete periods each treatment cycle, as described in Chapter 2. During Fill period, the pretreated wastewaters were pumped from Tank 19 to Tank 16 or 18 at a constant flow rate. It usually took one to two hours to fill a tank with the average loading of 15,000 gallons (ranging from 10,000 to 18,000 gals) per cycle. Influent grab samples were collected from the discharge port of Tank 19 for the selected parameter analyses. No aeration and mixing were supplied during the FILL period, to insure anoxic conditions. Once the FILL period was completed, the REACT period began. An aeration blower was turned on with either continuous aeration or sequencing aeration controlled by a timer. The air bubbles were released from a pipe system to supply the oxygen requirement and the necessary mixing of the treatment system. When a timer was used, various intermittent aeration patterns were used, such as 15 minutes on, 15 minutes off; 45 minutes on, 30 minutes off; and 60 minutes on, 15 minutes off.

The NH_4NO_3 and Na_3PO_4 in solid form as nutrient supplement were added manually. A C :P:N ratio of 100 :5:1 as BOD_5 :TKN:TP or 200:5:1 as COD:TKN:TP , was desired for SBR processing. During the study, due to the variation of incoming waters, various amount of nitrogen and phosphorus compounds were added resulting in different ratios as presented in Chapter IV.

Influent grab samples were analyzed for Chemical Oxygen Demand (COD), 5-day Biochemical Oxygen Demand (BOD₅), Nitrate-Nitrogen (NO₃ -N), Total Phosphorus (TP), Phenols, Total Kjeldahl Nitrogen (TKN), Oil and Grease, Alkalinity and Hydrogen Ion Concentration (pH). The analysis was performed on site right after the samples were collected on the plant. The Mixed Liquor Suspended Solids (MLSS), Mixed Liquor Volatile suspended solids (MLVSS), and pH were monitored during aeration for activated sludge quality observation. Later in the investigation, changes in filtered Mixed Liquor COD (MLCOD), filtered Mixed Liquor BOD₅ (MLBOD₅), Phenol concentration and Zone Settling Velocity (ZSV) were measured during treatment.

When the REACT period was completed, the blower was shut off and the system was kept in quiescent for two hours during the SETTLE period. Periodically, some chemicals were added 15 minutes before aeration was turned off to assist solids-liquid separation. If desired, mixed liquor could be wasted after some chemicals were added to obtaining sludge age. The sludge age in SBR system does not mean much because of the unsteady state during treatment.

Jar tests were required for determining the dosage of chemical supplements. The composite reactor mixed liquor samples for the jar test were collected by using an eleven-foot-long plastic column. The addition of three types of chemicals were studied. They were Calcium Chloride, Ferric Chloride , and Alum. 100 ml mixed liquor samples were stirred by hand for about 15 minutes and then settled for 30 minutes in a 500 ml beaker. After the chemicals were added, solids concentration in supernatant was measured to evaluate the coagulation efficiency of each chemical added. After jar tests, the most effective chemical based on economics was picked up for the full-scale SBR application.

After two hours of settling, the activated sludge had separated from the water, and the supernatant was discharged from the SBR tanks. This DRAW period lasted either two to three hours if discharged by a pump, or six hours if discharged by gravity. The activated sludge was left in the tank bottom for the next batch.

The IDLE period time was dependant on whether or not incoming wastewaters were available on the treatment plant. Usually the time was twelve to twenty-four hours. During IDLE period, aeration was supplied to the system to maintain an aerobic activated sludge culture.

3.1.1.6 *Glassware Preparation and Analyses Apparatus*

The glassware used for the tests were washed by Dawn detergent and rinsed with tap water and then deionized water, except glassware for TKN, and TP analysis, which was washed by 10% Hydrochloric acid and rinsed with tap water and then deionized water.

A Mettler balance was used for all sample weighing. A Spectronic 20 Model Bausch & Lomb spectrometer was the instrument used for spectrophotometric analysis.

A YSI model 58 meter, manufactured by Yellow Springs Instrument Co. Inc. was used to determine dissolved oxygen (DO). pH measurements were made with a Corning pH meter, Model 125.

A HACH COD digester was used for COD tests.

3.1.1.7 Sample Analyses

Samples were analyzed for several parameters They were 5-day Biochemical Oxygen Demand (BOD₅), Chemical Oxygen Demand (COD), Oil and Grease, Total Recoverable Phenols, Total Kjeldahl Nitrogen(TKN), Total Phosphorus (TP), Nitrate Nitrogen (NO₃ -N), Alkalinity, pH, Total Suspended Solids (TSS), Mixed Liquor Suspended Solids (MLSS), and Mixed Liquor Volatile Suspended Solids (MLVSS).

The BOD test method was adopted from *Standard Methods for the Examination of the Water and Wastewater* [38]. Because of the high concentrations in the industrial wastewaters, various dilution factors were necessary. More than three dilution factors were made for every sample. The DO meter was calibrated every day by the air calibration method recommended by the Yellow Springs Co. Inc., and the probe membrane was changed once every two weeks. Sometimes the membrane was changed more often in case of unstable calibration. A standard solution made of glucose and glutamic acid was used to check the accuracy of the procedures.

The COD test was performed in accordance with *Procedures for Water and Wastewater Analysis* [39] issued by the HACH Company in 1986. Sample was diluted ten times before digestion, and the digested sample was measured by spectrophotometric method while still in the original vial. Method accuracy was checked using Potassium Hydrogen Phthlate standard solution.

The method used for oil and grease test can be found in detail in *Standard Methods for the Examination of Water and Wastewater* [38]. Sample was extracted three times

by Fluorocarbon-13 solvent and then evaporated at 70° c in a boiling flask. The weight gain of the flask was calculated to determine the concentration of the oil and grease.

Phenols were measured in accordance with *Standard Methods for the Examination of Water and Wastewater* [38]. Sample was pretreated by chloroform to eliminate oil interference. Spectrophotometric method was applied to determine the concentration from the standard curve presented in Appendix B, Figure B-1.

The TKN test was adapted from *Procedures for Water and Wastewater Analysis (HACH 1986 edition)* [39]. Standard addition method was used for method accuracy check.

The TP measurement method was also adopted from *Procedures for Water and Wastewater Analysis (HACH 1986 edition)* [39]. The sample was digested on a hot plate after the addition of Sulfuric acid and Nitric acid on a hot plate. The accuracy was checked by standard addition.

The method for the Nitrate Nitrogen test is detailed in *Procedures for Water and Wastewater Analyses* [39] and method accuracy was checked by standard additions.

The alkalinity was measured in accordance with *Standard Methods for the Examination of Water and Wastewater* [39].

Total Suspended Solids, Mixed Liquor Suspended The TSS, MLSS and MLVSS measurements were determined in four steps:

- 1)filtration of samples through a 5.5cm. micro-glassfiber filter;

2) evaporation in an oven with a temperature of 105° c or combustion in a furnace at 500° c.

3) cooling in a desiccator for an hour;

4) weighing of the residual and calculation of the sample concentration.

The details can be found in *Standard Methods for Examination of Water and Wastewater, 15th edition* [38].

3.1.1.8 Settling Characteristics

The Sludge Volume Index (SVI) and Zone Settling Velocity (ZSV) were used to measure the sludge settling characteristics. The SVI test was performed by the following procedure: 1,000 ml mixed liquor was poured into a one-liter graduated cylinder. The height of the sludge blanket was measured after 30 minutes of settling in the cylinder. The SVI was calculated as:

$$\text{SVI} = \frac{\text{settled sludge volume, ml, x 1000}}{\text{total suspended solids concentration, mg/l}}$$

The ZSV test was performed by the following procedure: 1,000 ml mixed liquor was poured into a one-liter graduated cylinder. The height of solids-liquid interface in interval of 1 minute was recorded until 30 minutes of

settling. The interface height in inches with the settling time was plotted and the settling rate was calculated as the slope of the plotted straight line.

When Ammonium Nitrogen, Orthophosphate phosphorus, Zinc and Copper tests were performed, HACH's procedures were chosen. Filtered mixed liquor Phenols measured during aeration period were checked using Phenol test kit distributed by Fisher.

4.0 Results and Discussion

The results of the experiment of a full-scale SBR system for the treatment of oily wastewater and discussion of the results are presented in this chapter. The raw data collected from the thirty SBR experiments during the investigation are summarized in Appendix A.

4.1.1.1 *Wastewater Characteristics*

Table 2 presents the average concentrations and ranges of selected parameters of the wastewaters treated during the study. A review of the data in the table indicates that the influent concentrations of BOD₅ and COD were very high and had a wide variation. In addition, a low ratio of BOD₅: COD (an average of 0.34) was observed, indicating a high fraction of non-biodegradable materials contained in the wastewaters. In some cases, a greenish influent resulted from high concentrations of zinc and copper. The concentrations of zinc and copper were related to the wastewater from can manufacturing. Several thousand milligram per liter zinc and copper were added into cooling water during can manufacturing procedure. High

concentrations of heavy metals may inhibit biological activity of the organisms, because the tolerant concentration of the microorganism culture was approximately 1 mg/l, either for zinc or copper, according to the recommendations by the Sybron Biochemical Corporation.

The concentrations of oil & grease and phenols were high and needed separate measurement. It also can be seen that the nitrogen and phosphorus contents of the influent were low compared to the concentration of organic materials; therefore the addition of nutrients was necessary to meet the normal nutrient requirements for microbial metabolism.

Table 3 is a summary of the SBR performance data prior to when the study was conducted, and it also included the results from the start-up period of this investigation. It can be seen that the effluent concentrations were sometimes higher than those of the influent because of non-optimal operating conditions. Therefore, first of all, an optimal operating conditions had to be determined.

4.1.1.2 The Effects of Operating Conditions on Substrate Reduction

Three different aeration modes were used to determine the optimal aeration style for substrate biodegradation with various levels of nutrients supplement. The variable additions of nitrogen and phosphorus compounds produced three average BOD_5 :TKN : TP ratios of 32 : 7.6 : 1 ; 108 : 8 : 1 and 250 : 6.5 : 1 throughout the investigation. According to the different ratios the operating conditions were designated as three strategies: Unit 1 stands for the BOD_5 : TKN : TP ratio of 32 : 7.6 : 1; Unit 2 stands for

Table 2. The average wastewater characteristics of SBR influent *

	Average	Range
BOD	2927	708-7320
COD	9196	2710-24800
Oil & Grease	191	20-483
Phenols	6.7	4.7-8.6
TP	7.85	0.13-43
TKN	147	10-710
NO -N	8.3	0.7-33
Alkalinity	725	80-2168
pH	6.7	4.7-8.6
TSS	431	5-4720
Cu	6.33	0.05-21
Zn	9.7	0.5-26

* All data except pH reported as mg/l, (ppm)

Table 3. Performance of the E.T.S. SBR before the investigation

BATCH	SAMPLE	BOD	COD	OIL&GREASE	PHENOLS
1	I	391	2837	--	.5
	E	661	3170	146	4.03
2	I	2079	4395	99	27
	E	2385	4470	107	10
3	I	2365	8440	101	4.7
	E	1735	7540	59	6
4	I	2533	5200	39	27
	E	1500	4170	47	24
5	I	2584	6645	33	12
	E	1269	3810	20	14

WHERE I= influent; E= effluent . concentration in mg/l

BOD₅:TKN:TP ratio of 108 : 8 : 1; and Unit 3 stands for BOD₅: TKN : TP ratio of 250 : 6.5 : 1.

The BOD₅ removals achieved under various aeration modes, which included continuous and intermittent aeration patterns, are shown in Fig. 10 through Fig. 12, and COD removals are shown in Fig. 13 through Fig. 15. It should be mentioned here that the data collected from Tank 16 is not interpreted in the paper because the tank was only a substitute for Tank 18 when the incoming water contained a high portion of can manufacturing waste. The interests of the investigation later focused on the oily wastewaters from the waste oil production customers other than from can manufacturing industry. The can manufacturing wastes also often lowered the system treatment efficiency because of high strength organics. It is interesting to note, that the BOD₅ removal in the batches of intermittent aeration mode were higher than those in the batches of Continuous aeration mode, except for that in Unit 1.

The results shown in Fig.10 indicate that higher BOD₅ removal was achieved under continuous aeration conditions, which may be because of the nitrogen and phosphorus were not limiting the system. Therefore, growth was not nutrient limited and the activated sludge removed the maximum amount of BOD possible for the operating conditions. Therefore, the rates of microbial oxidation and reduction were not dependent on the nutrients but BOD removal became limited by the amount of dissolved oxygen available to the activated sludge during treatment. More oxygen was supplied by continuous aeration than by intermittent aeration and BOD removal during continuous aeration was greater than that accomplished with intermittent aeration.

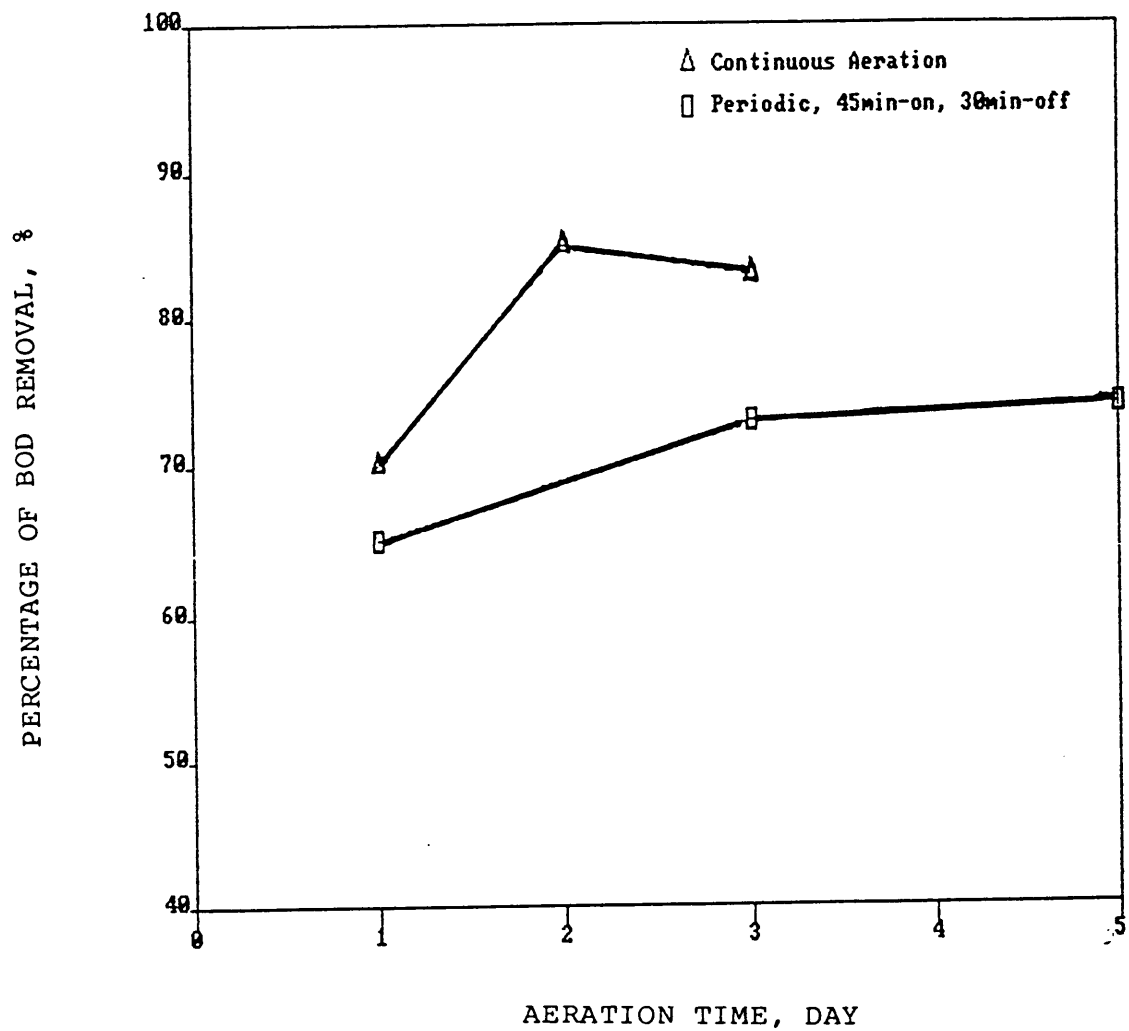


Figure 10. BOD removal at a C : N : P of 32 : 7.6 : 1

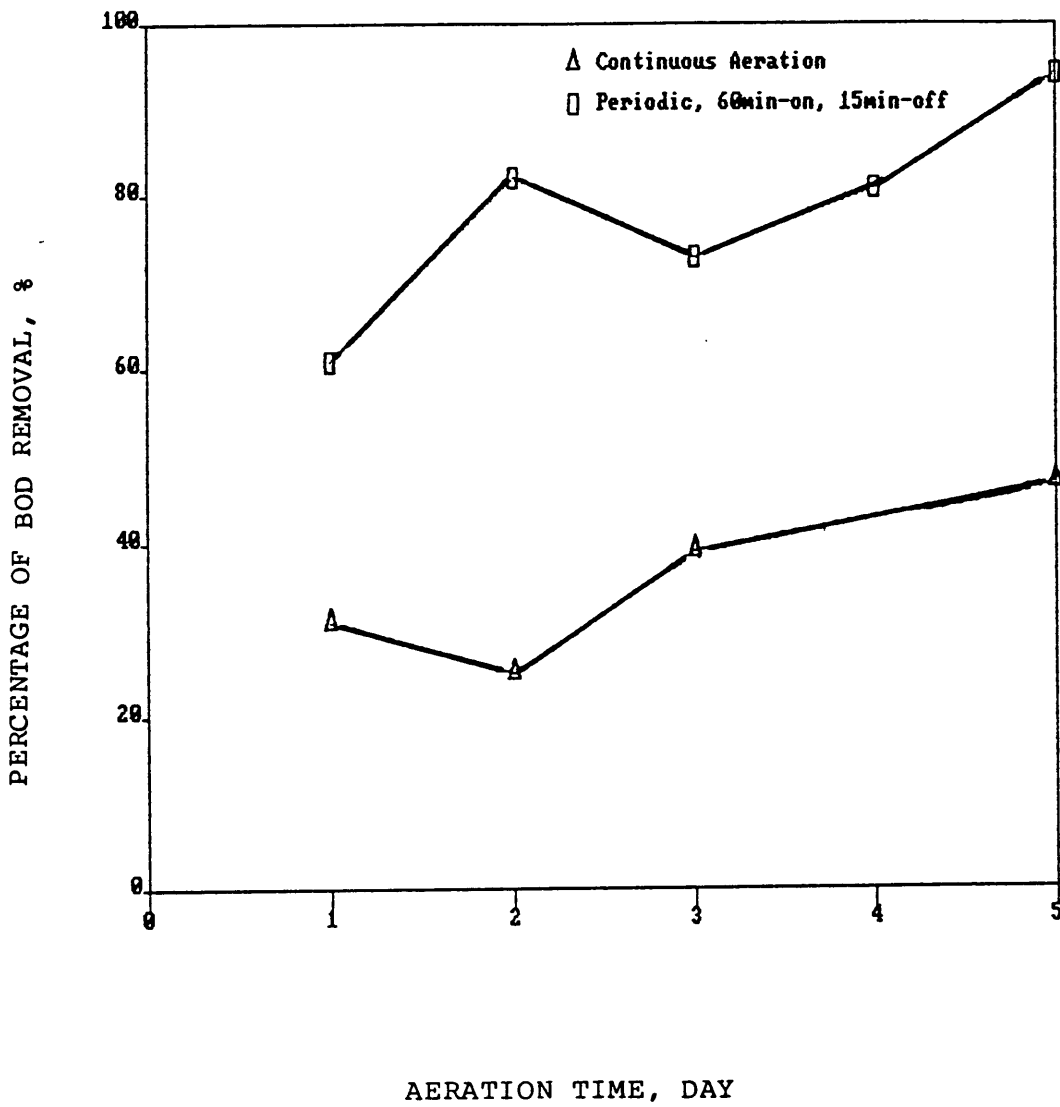


Figure 11. BOD removal at a C : N : P of 108 : 8 : 1

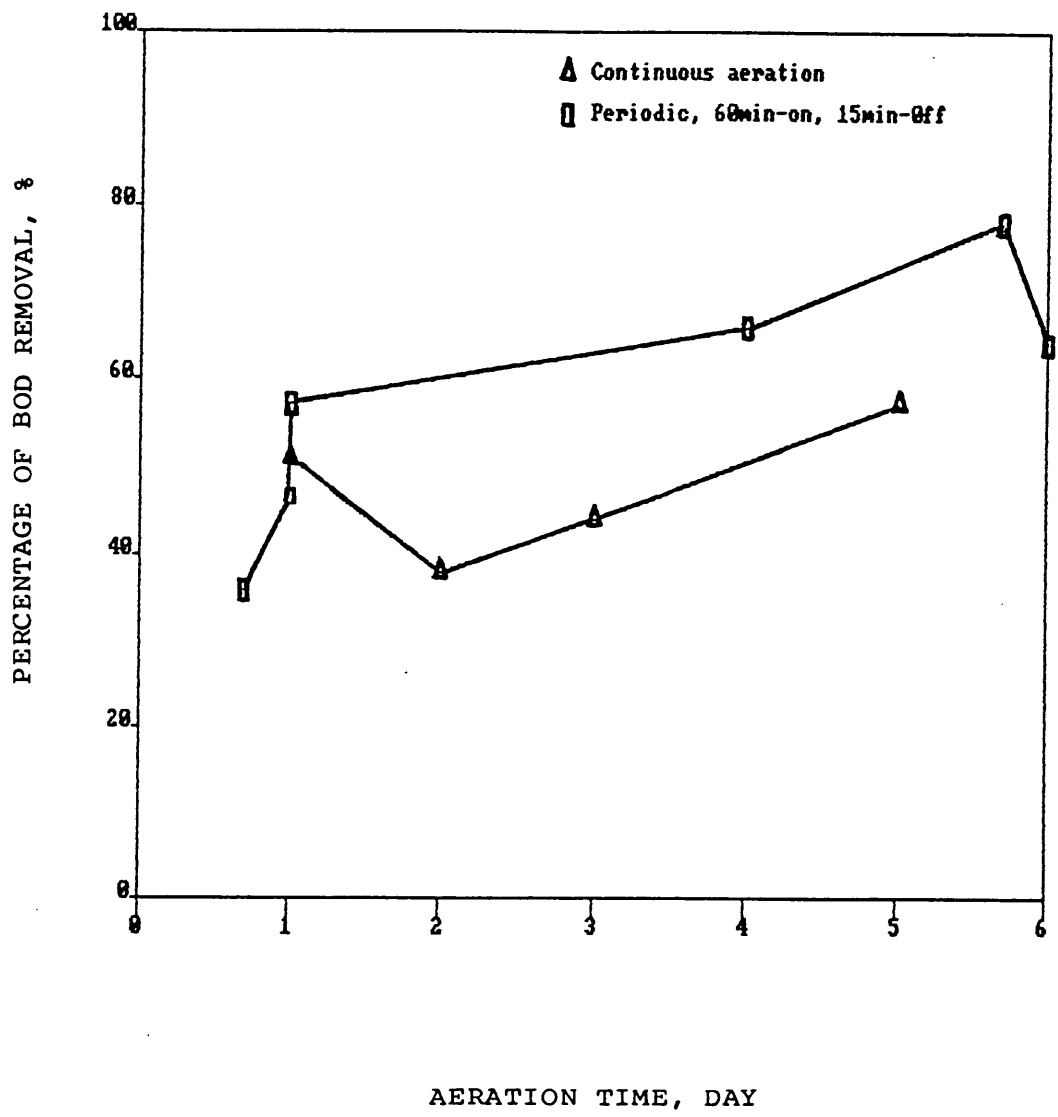


Figure 12. BOD removal at a C : N : P ratio of 250 : 6.5 : 1

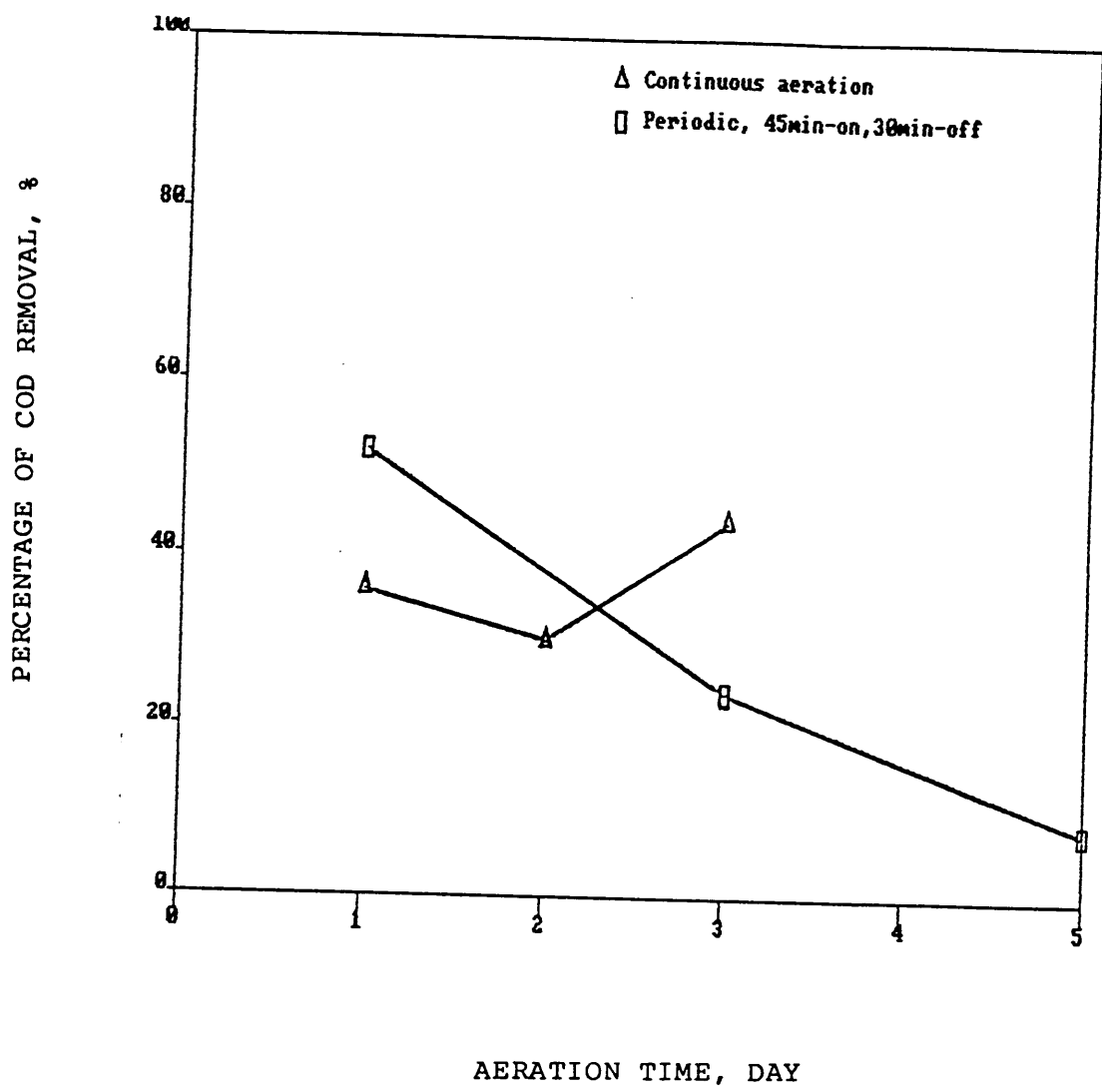


Figure 13. COD removal at a C : N : P ratio of 32 : 7.6 : 1

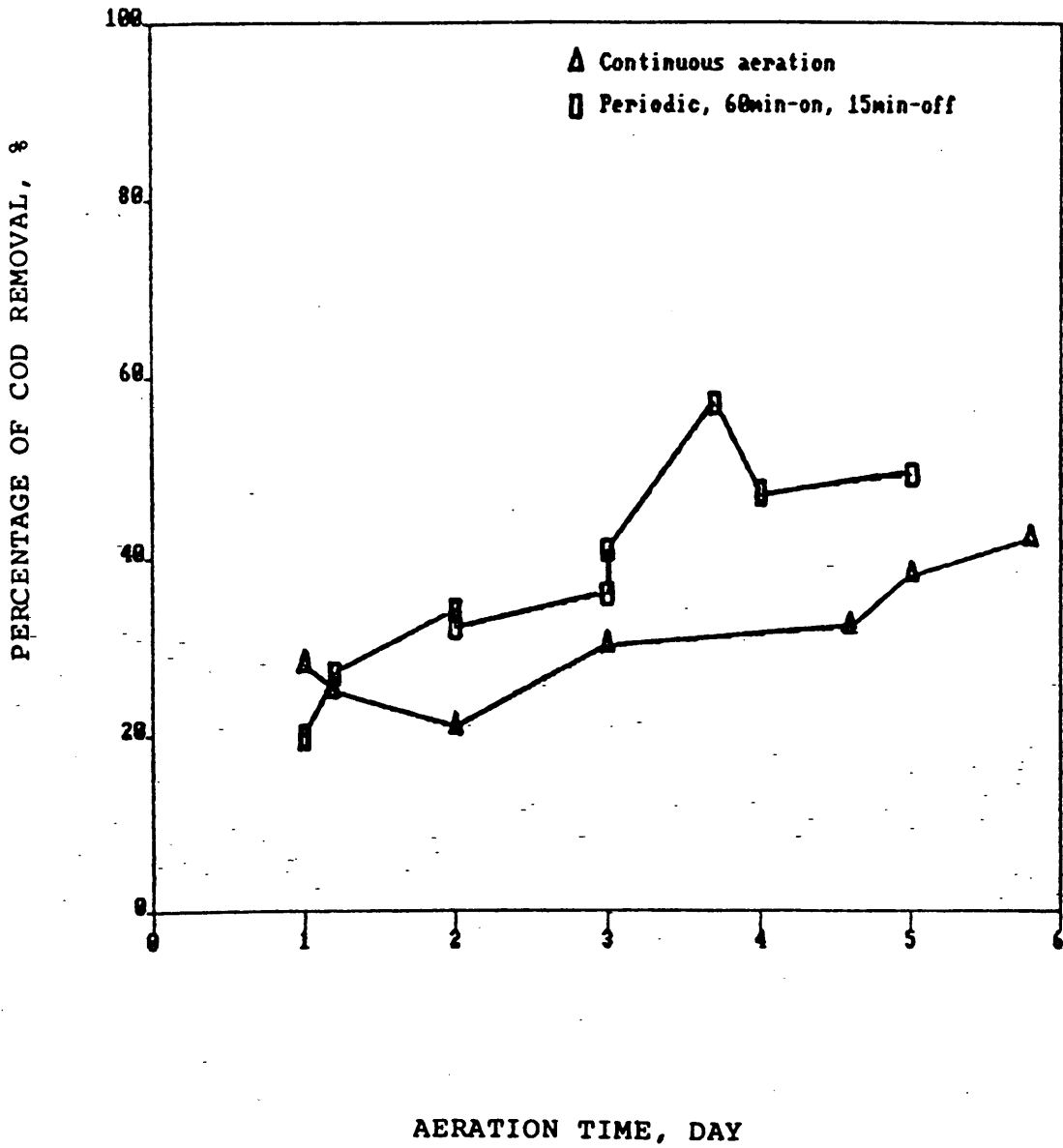


Figure 14. COD removal at a C : N : P ratio of 108 : 8 : 1

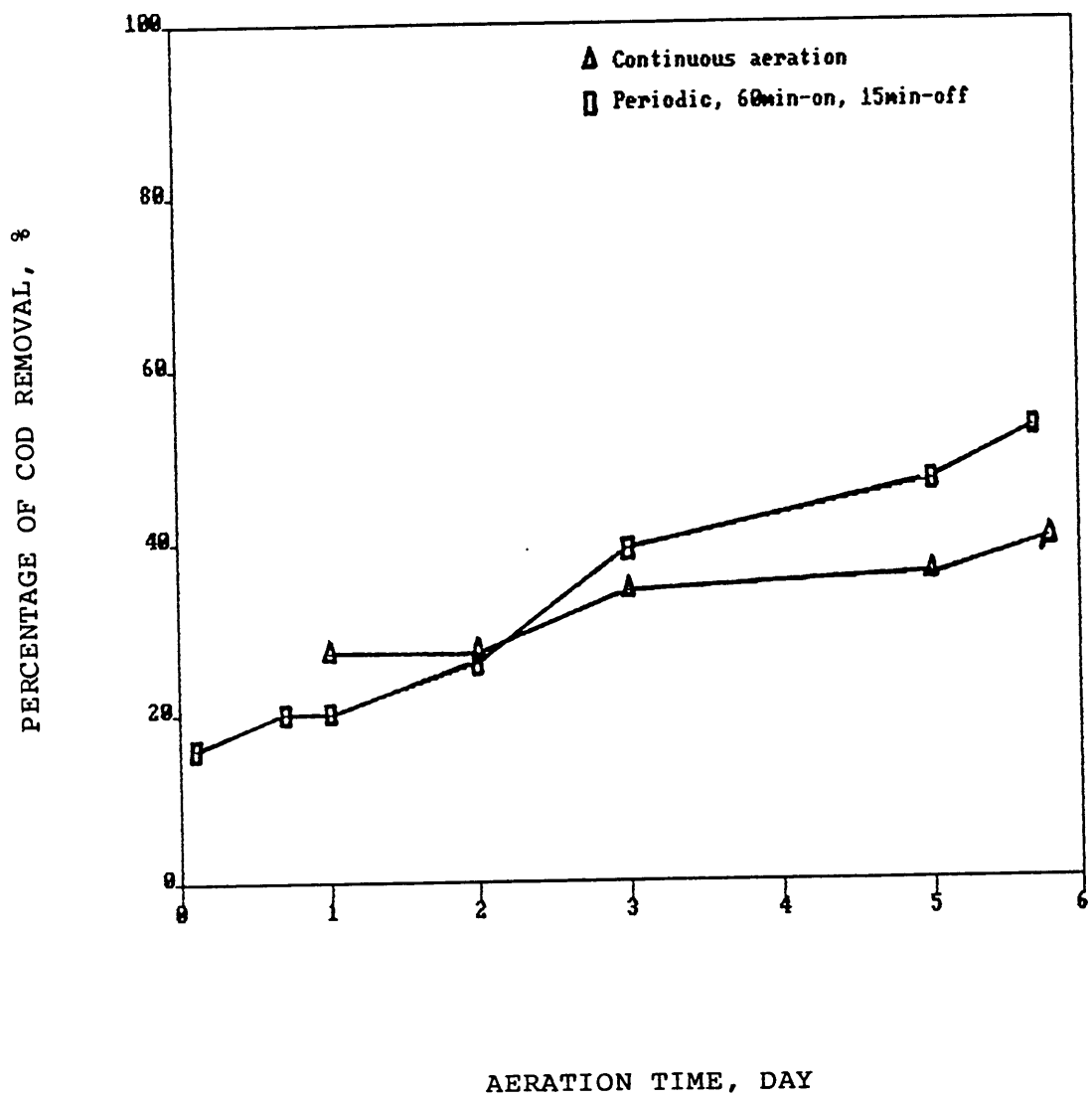


Figure 15. COD removal at a C : N : P ratio of 250 : 6.5 : 1

The nutrients added to the unit described by Figure was in excess and could not be completely utilized by the microbes. As a result the concentration of TKN and TP in the effluent were quite high as shown in Table 4. The overdosing of nutrients resulted in maximum BOD removal, energy consumption, and high nutrient concentration in the effluent. In contrast to continuous aeration, intermittent aeration controlled by a timer showed more efficiency in term of BOD₅ and COD removal in the higher BOD₅:TKN:TP ratio experiments, even though sometimes the concentration of DO less than 1 mg/l was observed during the REACT period. The phenomena may have resulted from the nutrient deficiency, which was more acute when the system was continuously aerated.

It is proposed that BOD removal, illustrated in Figure 11 and 12, was greater with intermittent aeration, compared to continuous aeration, because nutrients were limiting in both systems. Some anoxic and anaerobic metabolism occurred during intermittent aeration, and in less cell production, because anoxic/anaerobic metabolism is less efficient than aerobic metabolism. Nutrient requirements are directly proportional to cellular production. Therefore, the amount of nutrients needed for the same amount of BOD removal was less in the intermittently aerated system compared to the continuously aerated system, because both were nutrient limited, the BOD removal in the intermittent system was greater than that in the continuously aerated system. The average MLSS concentration in continuous aerated batches was 3908 mg/l, while it was 2023 mg/l in intermittent aerated batches. This illustrates the difference in sludge production in two systems. organic materials need to measured with time.

Table 4. The effluent concentration of TKN and TP in the batches with C : N : P of 32 : 7.6 : 1^{*}

No of batch		NH ₄ NO ₃ Addition (mg/l)	TKN (mg/l)	Na ₃ PO ₄ Addition (mg/l)	TP (mg/l)
9	I	255	710	54	17.3
	E		423		14.2
10	I	247	10	52	0.53
	E		200		22
11	I	255	24	54	1.36
	E		172		4.96
14	I	255	90	54	12.6
	E		314		14.7
17	I	291	508	77	0.16
	E		1016		9.09

* I = influent; E = effluent

The characteristics of the incoming wastewater also significantly influenced the SBR treatment efficiency. Wastewater from can manufacturing contained very high concentrations of organic matter, which were hard for the bacteria to degrade and assimilate, while wastewater from oil storage tanks were biodegraded more easily by bacteria. Table 5 is a listing of the BOD₅ removals, effluent nitrogen, and effluent phosphorus under various waste ratios of can manufacturing wastes over tank bottom wastes, and different heavy metal levels.

The removal of oil and grease and phenols under different operation conditions is summarized in Table 6. It is apparent that the removal of both oil and grease and phenols was usually better under intermittent aeration conditions. It also can be seen that the removal of oil and grease decreased with extended aeration time. Under continuous aeration condition the nutrients overdosed experiments (Unit 1) show benefit to phenols removals, but the removal of oil and grease was worse than those of Unit 2 and 3.

In spite of the wide variety of conditions throughout the study, the ranges of removal were 39-57% for COD; 56-94% for BOD₅; 73-98% for oil & grease and 22-97% for phenols.

The pH values and alkalinity concentrations generally increased during treatment. This was most likely because of denitrification in the system. It is well-known that denitrification produces alkalinity.

Table 5. Changes in BOD removals with changes in wastewater characterization

Batch	Waste* Ratio C/T	BOD ₅ COD	Copper mg/l	Zinc mg/l	BOD:N:P	Influent BOD ₅ mg/l	Effluent BOD ₅ mg/l	BOD ₅ mg/l	Removal %	Effluent TKN mg/l	Effluent Nitrogen NO ₃ -N mg/l	Effluent TP mg/l
1	1:1.8	357	187	15.6
2	1:4.0	0.084	20:4.5:1	434	433	77	18	21	0.5	6.7
3	1:1.5	578	109	1.6
4	1:4.0	2084	240
5	1:5.7	0.086	71.5:9:1	2121	2133	34	6.6
6	1:4.0	0.34	125:6.3:1	7320	4470	2850	39	2070	15.2	6.1
7	1:4.0	0.35	71:4:1.0	4470	2187	863	19	197	21.7	20
8	1:4.0	0.26	197:13:1.0	3607	1081	1420	39	423	9	14.2
9	1:4.0	0.26	197:13:1.0	3607	2180	2526	70	580	4.6	5.2
10	100%T	0.37	20:4.7:1	1151	165	984	85	200	22
11	100%T	0.2	10:5:1.0	822	138	684	83	172	14.5	5
12	1:1.5	0.31	1067	153	914	86	6.5
13	1:2.3	0.36	6	3	3010	378	2632	87	5.2
14	1:3.0	0.6	21	12	32:5:3:1	3150	2048	1102	35	392	8.7	26.4
15	1:4.0	0.3	13	6	36:5:2:1	2400	651	1749	73	314	32.7	14.7
16	1:19:0	0.28	7	26	14:5:1.0	881	81	800	91	188	9.4	5
17	1:4.0	558
18	1:1.0	0.23	33	26	12:13:1.0	708	182	526	74	1016	0.97	9.09
19	100%T	0.24	50:10:1.0	858	301	557	65	100	4.7
20	100%T	0.24	50:10:1.0	858	294	564	66	95	7.4	12.5
21	1:4.0	0.21	2	21	39:6:1.0	934	471	463	50	30	17
22	1:4.0	0.25	135:12:1.0	2586	1140	1140	56	144	5.2
23	1:4.0	0.57	227:6.7:1	5080	1830	2960	66	118	12.3	12.3
24	1:0.2	0.38	2.5	6.6	220:4.6:1	4460	1500	3250	64	68	6.3	10.3
25	100%T	0.46	77:6.2:1	1750	235	1575	87	55	8.7	4.3
26	1:4.0	0.46	340:5:1.0	6160	1340	4810	78	44	2.1
27	1:1.0	0.41	198:10:1.0	4580	1916	2664	58	98*	0.6
28	1:4.0	0.27	116:1:1.0	1635	550	1085	66	34	3.5
29	100%T	0.49	108:2:1.0	3210	828	2382	74	84	1.4	6.4
30	100%T	0.49	108:2:1.0	3328	204	3124	94	0.8	7.5	4.2

* "C" ----- Can manufacturing wastewater

"T" ----- Tank bottom wastewater

Table 6. Removal of oil & grease and phenols in various conditions *

Nutrient Ratios	Aeration Time (d)	Type of Aeration			
		Continuous		Intermittent	
		O & G	Phenols	O & G	Phenols
C:N:P	1	57	81	70	89
32:7.6:1	3	61	95	65	97
	5	--	--	40	96
	2	81	52	--	--
C:N:P=	2	--	66	--	--
108:8:1	5	91	42	81	98
	7	--	--	64	81
C:N:P=	4	--	--	81	90
250:6.5:1	6	84	47	81	94

* The Oil & Grease and Phenol numbers are percentage(%)

4.1.1.3 Substrate Removal Rate Studies

A study was conducted to monitor changes in the concentration of the wastewater components during treatment and to determine the substrate degradation rate in terms of BOD₅. The results of the variation of COD, BOD₅, Phenols and NO₃ –N with aeration time for different batches are plotted in Fig. 16, 17, 18, and 18. The initial concentration of each parameter was calculated accounting for the wastewater left in previous batch. Figures 16 and 17 show that the removals of COD and BOD₅ were in accordance with first-order rate kinetics, i.e. with a relatively rapid reduction at the beginning of the reaction period. Table 6 presents the calculated organic transfer rate coefficient, which has been defined in the previous chapter, in terms of BOD₅ degradation for four SBR cycles. From a comparison of the four batches, it is apparent that batch 30 has the highest degradation rate with BOD₅ removal of 94% under the operating condition of intermittent aeration and less nutrients addition. In fact, phosphorus was added twice into the batch, once at the beginning of aeration and second after 96 hours of aeration time.

Fig.20 shows the variation of filtered orthophosphate phosphorus versus time for batch 30 . Though the highest BOD₅ reduction was achieved in batch 30, no other conclusions can be made.

Fig. 18 indicates the degradation of phenols was divided into two stages. During the first day of aeration, phenols were reduced rapidly, while during day 1.5 to 3 the concentration was almost the same, followed by another reduction peak. This implies that, at the start there were some groups of simple phenols compounds were readily

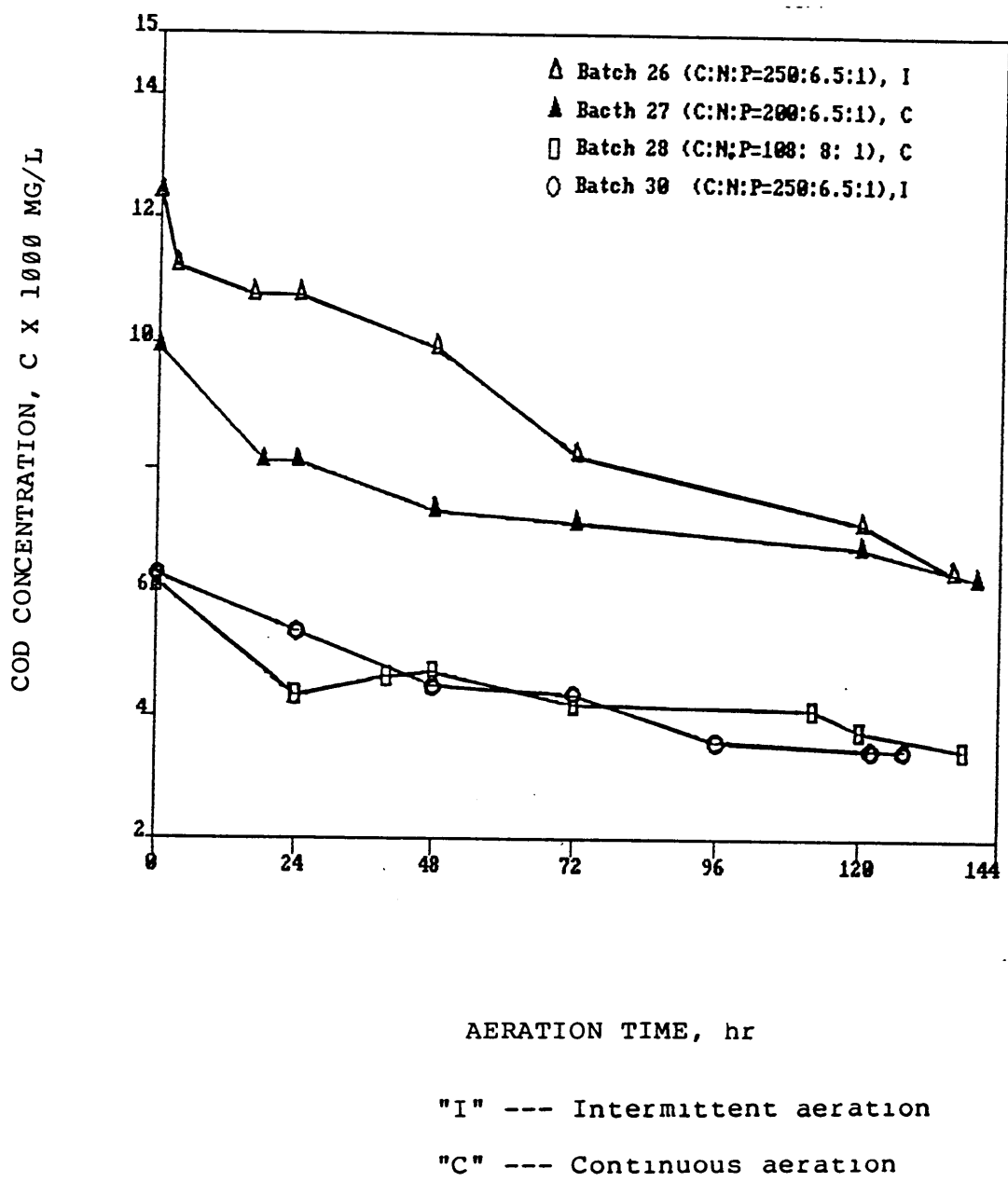


Figure 16. Changes in COD with aeration time

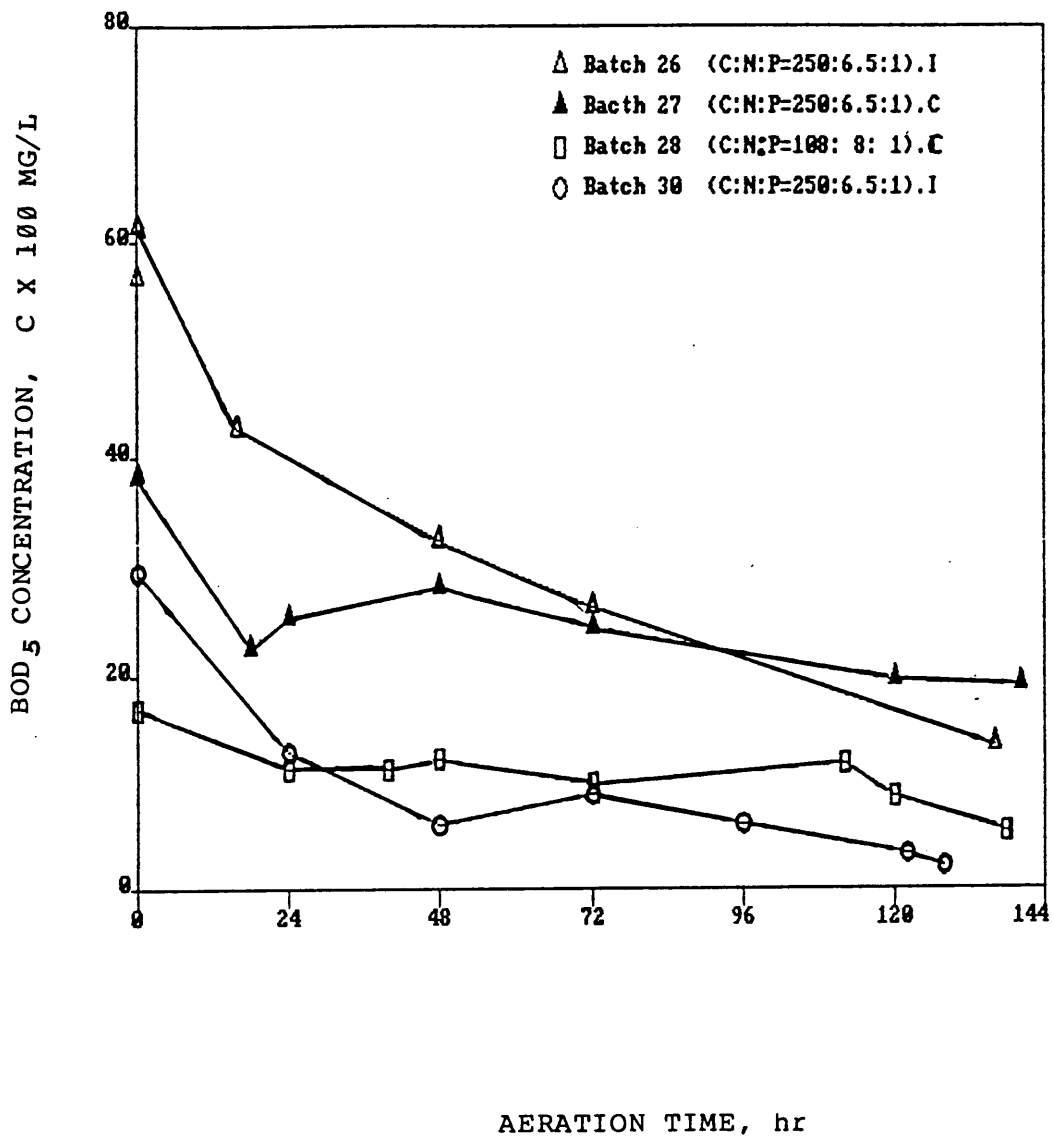


Figure 17. Changes in BOD with aeration time

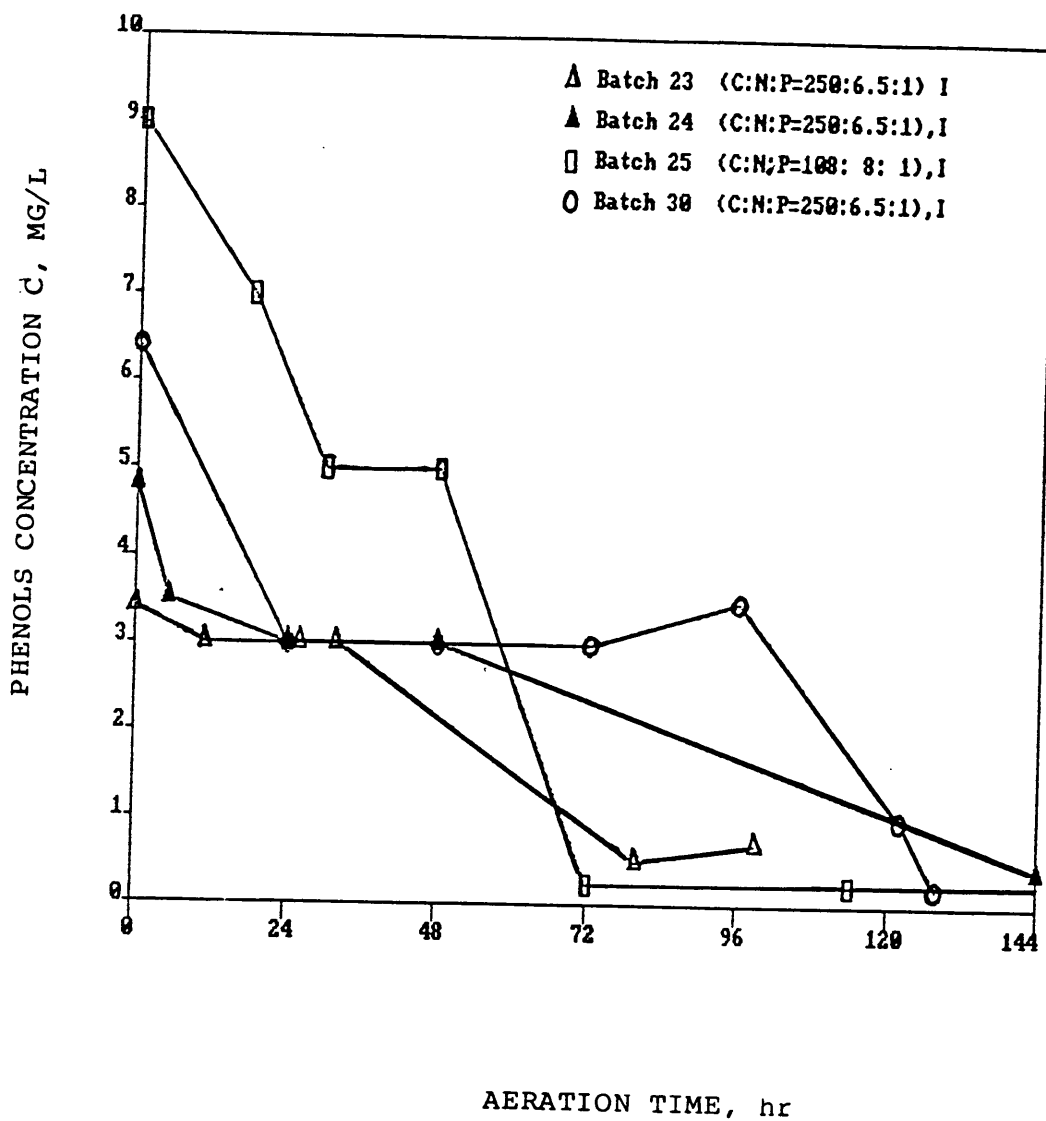


Figure 18. Changes in phenol concentration with aeration time

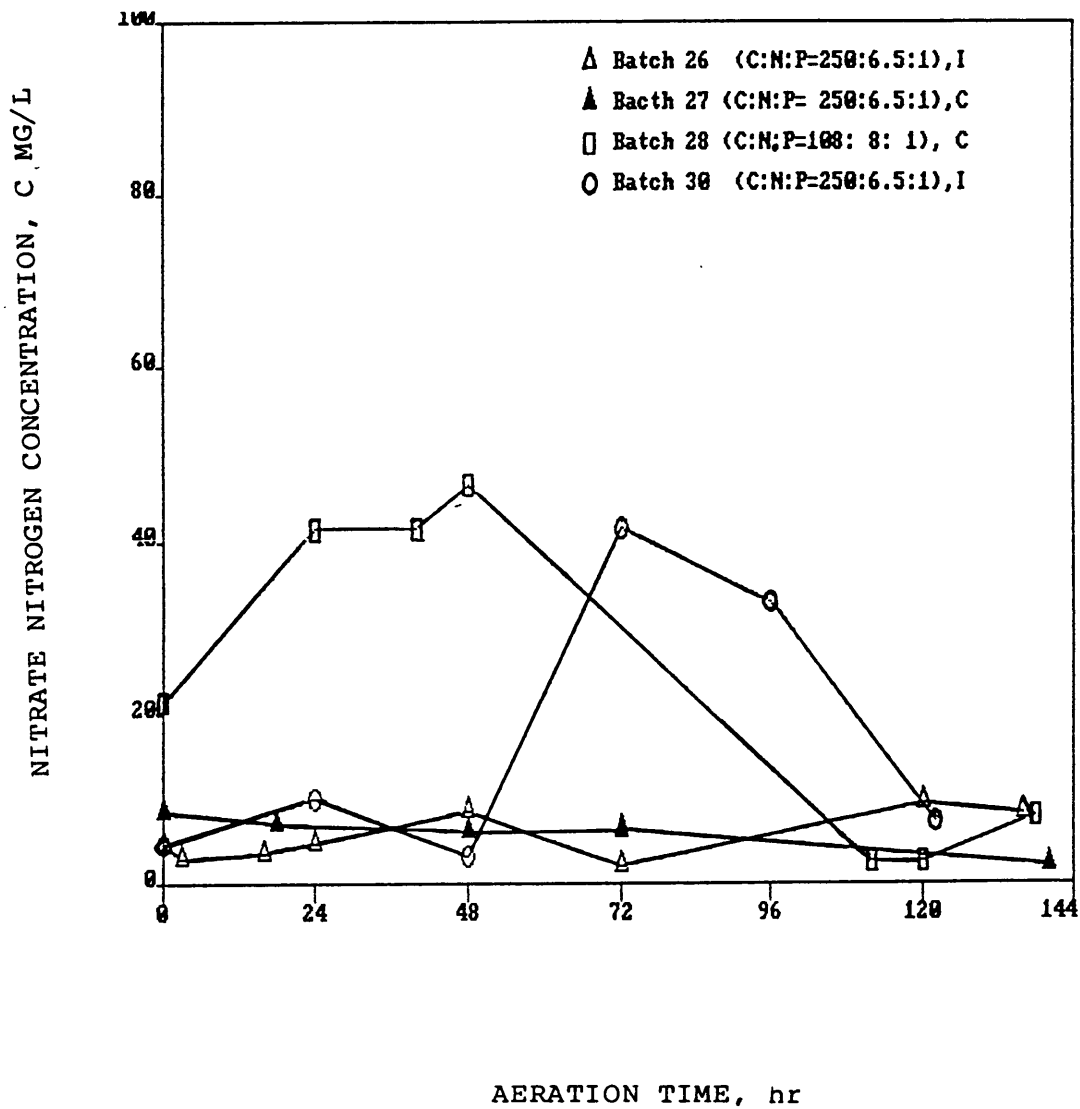


Figure 19. Changes in nitrate nitrogen concentration with aeration time

Table 7. Organic transfer coefficient values for four experiments

Batch	26	27	28	30
K (hr ⁻¹)	0.022	0.038	0.032	0.43

reduced, but the higher molecular phenol containing material have to be broken down to simple compounds before phenol destruction could occur.

Inconsistent results were obtained in the nitrate nitrogen change studies, as shown in Fig.19. However, it was true that nitrification and denitrification occurred simultaneously during aeration time. The relationship between aeration patterns and nitrification are not significant. The DO level was not constantly monitored during aeration time, so that it was not sure if the continuous aeration processes had sufficient DO in activated sludge, because of the high organic loading of the SBR processes. Also, the heavy metal concentrations changed for batches, which made it difficult interpret the results.

In batch 28, the high nitrate nitrogen concentration increased during 48 hours aeration time and then the dropped quickly afterwards in Batch 28 under continuous aeration condition. This may be due to the low organic degradation in the system. The batch's organic transfer coefficients was 0.032 hr^{-1} , which was lower than that of Batch 30, as shown in Table 7. In batch 28 the BOD_5 concentration was 1170 mg/l after 112 hours aeration time, when the initial BOD_5 was 1635 mg/l. In Batch 30, of which the highest BOD_5 removal was achieved, the remaining BOD_5 was 610 mg/l after 48 hours aeration time, when the initial concentration was 3328 mg/l. Therefore the phenomena occurring in Batch 28 probably can be explained as following presents. Because the remaining BOD_5 was still high, organism oxygen uptake rate in the sludge may be high, though aeration was on for almost 5 days. The difference of oxygen uptake rate and oxygen transfer rate in the system may lead unsatisfying oxygen level for organism assimilating. Therefore denitrification may occur. On the other hand the heavy metals may effect nitrifying bacteria in the system. Batch 28 was

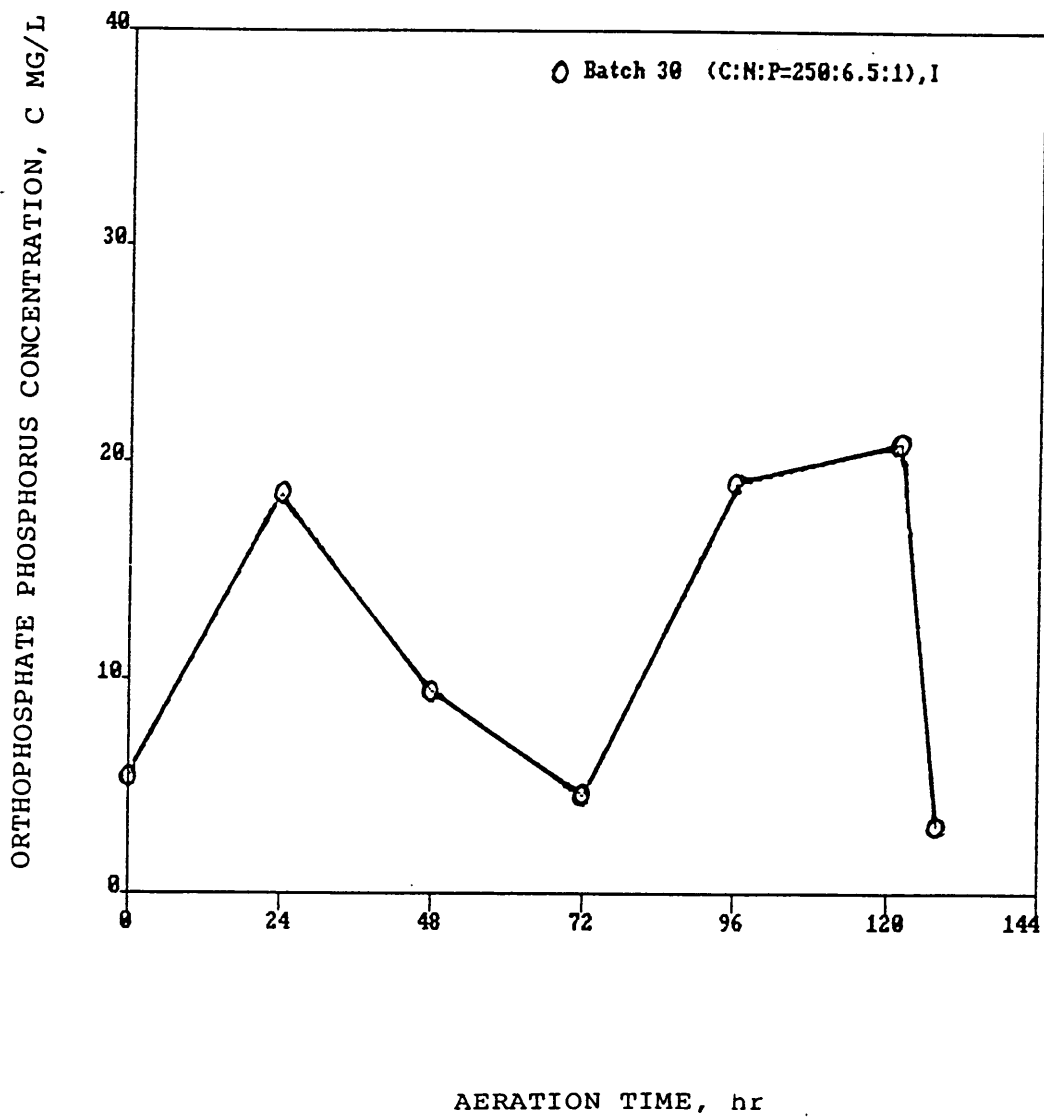


Figure 20. Changes in orthophosphate phosphorus with aeration time

composed of 20% can manufacturing wastewater, which generally contributed higher zinc and copper concentration to the wastewaters. Being compared with Batch 28, Batch 30 was composed of 100% oily waste from shipyards. Though, nitrate nitrogen increased during the period of 48 hours aeration time in Batch 28, it may be because of the nitrogen addition at the beginning of aeration period. The above stated assumption was not confirmed in this investigation, because the ammonium nitrogen could not be accurately measured because of the color in the mixed liquor filtrate. The dilution factor was as high as 20,000 times, which was unsatisfied to be used herein.

The reduction of oil & grease with aeration time was observed for Batch 26 and is as shown in Fig.21. The data show that very rapid removal of oil & grease occurred at the beginning of aeration period and was virtually complete after 24 hours.

The impact of the REACT period on sludge production was investigated during the study. Unfortunately, the operating conditions often changed and consistent results were not achieved. Nevertheless, it was noted that the concentration of MLSS generally increased rapidly at the beginning of the aeration period and then dropped until another MLSS increasing period was obtained, as shown in Fig. 22. The initial concentration of MLSS in Fig. 22 was measured after FILL period. The mixed liquor averaged almost 27,000 mg/l, 76% of which was volatile content.

The fluctuation of the MLSS concentration with aeration time may reflect the microbial growth pattern during different periods, but the two high growth stages occurred in the monitoring also may imply that there was a high fraction of slowly biodegradable substrate in the wastewater, which was evidenced by different removal of COD and BOD₅.

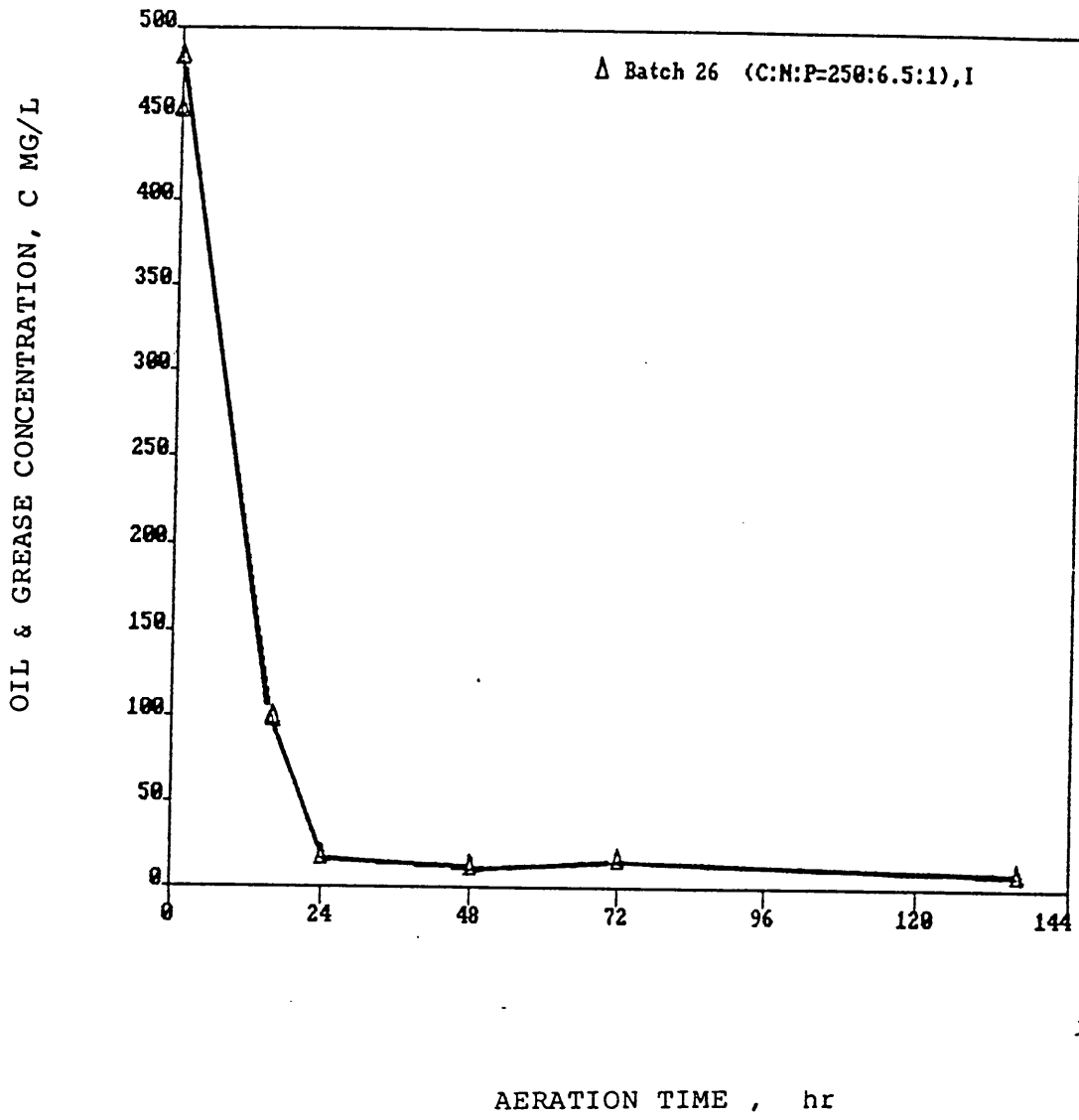


Figure 21. Removal of oil & grease with aeration time

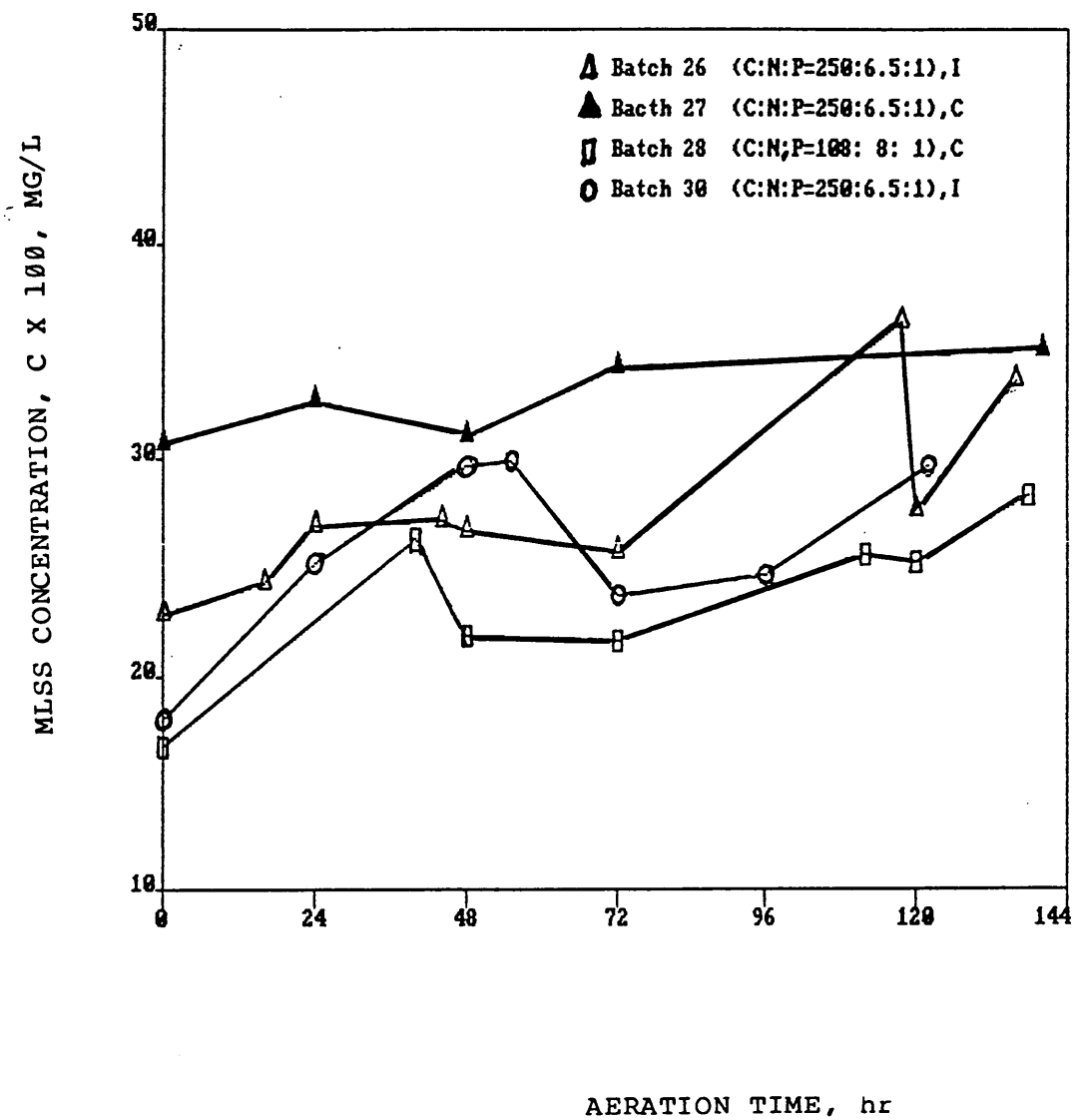


Figure 22. Changes in MLSS concentration with aeration time

4.1.1.4 Settling Characteristics

Zone Settling Velocity (ZVS) and SVI tests were conducted during the investigation to measure changes in the activated sludge settling characteristics. Fig.23 and 24 present the results of ZSV and SVI measurement with aeration time for four different batches. Throughout the experiments the SVI values were quite low. According to the experiences obtained during the study the higher SVIs produced low better effluent TSS. Generally, when ZSV was lower, the fraction of large flocs in sludge was higher, and the SVI was slightly higher. When ZSV was higher, the fraction of large flocs was lower, and the SVI was lower with more compacted sludge. If the fraction of large flocs was extremely low, the ZSV tests were even hard to perform because the large flocs settled down to bottom of the cylinder within about 1 to 5 minutes, resulting low SVI. The ZSV and SVI results of Batch 26 presented in Fig 23 was an example of straight decrease of ZSV and decrease of SVI. During aeration time of 2 to 5 days the ZSV could not be measured. The effluent TSS of Batch 26 was 540mg/l. This observation was not fully understood at this time. Microscopic examination of the sludge revealed many individual organisms, very few flocculating particles, and no protozoa. However the

results were not accurate because the sample was transferred from Jacksonville to Blacksburg within two days.

According to Michael Winkler [35], when operating at long sludge age (greater than 6 days), "pin-point" flocs easily formed and led to poor sludge settling characteristics. Deflocculation also may occur because of low mixed liquor DO, low pH, or shock toxic loadings.

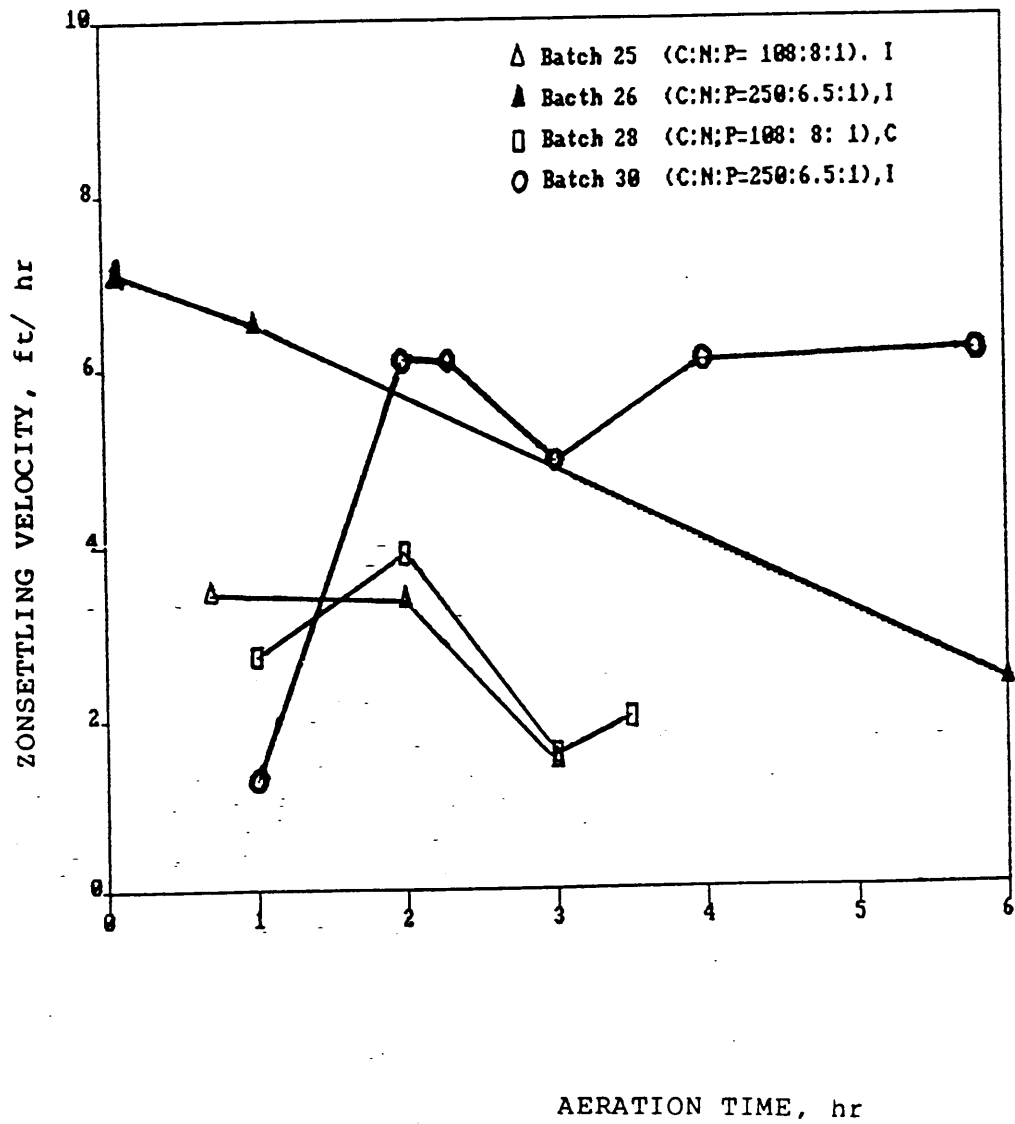


Figure 23. Changes in ZSV during aeration time

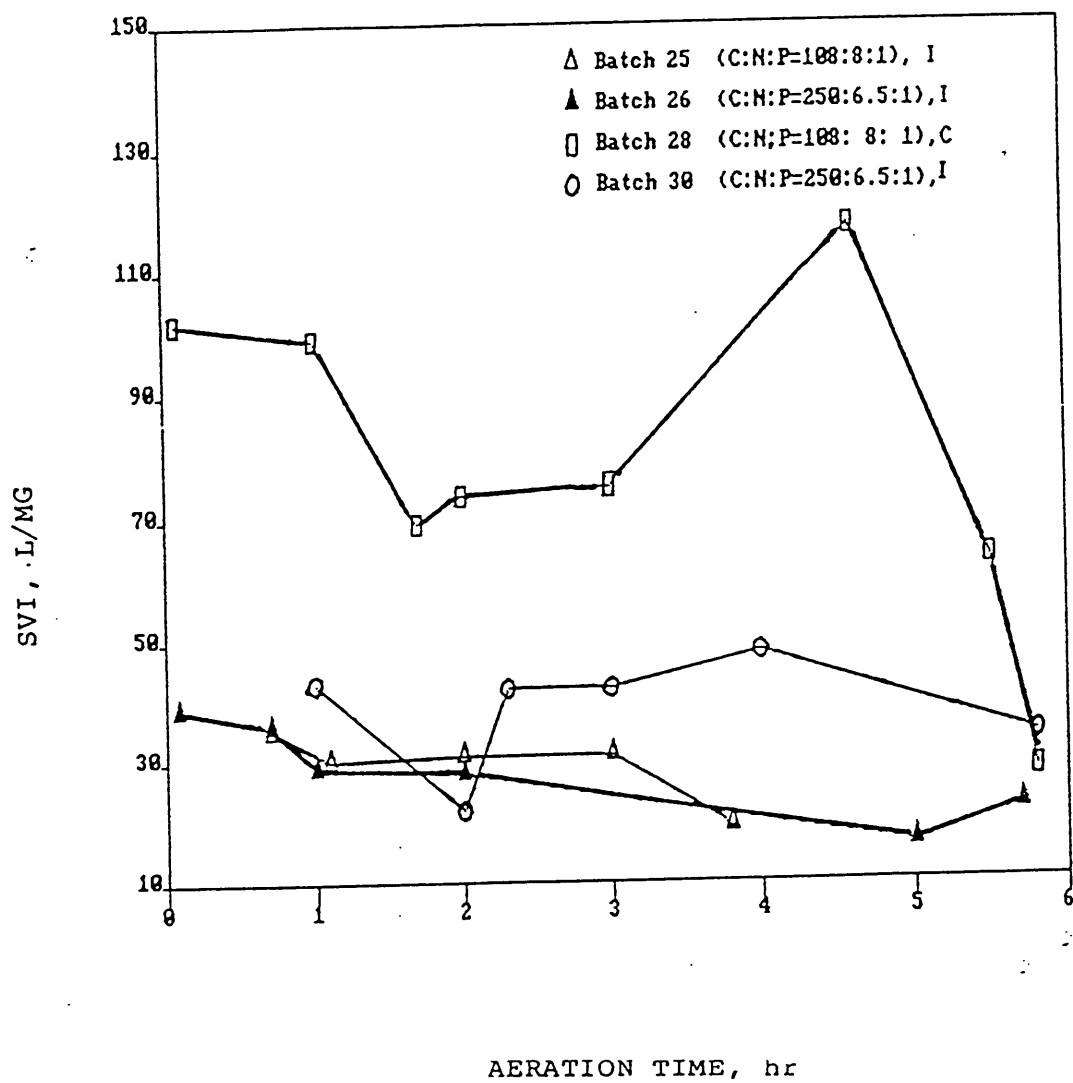


Figure 24. Changes in SVI during aeration time

During these experiments, the sludge age ranged from 10 to 50 days which may be one factor which caused the "pin-point" flocs and deflocculation. The low DO level of less than 1 mg/l was often found. The toxic shock of phenols and heavy metals on the microorganism was probably significant, because of the FILL period was only about 2 to 3 hours, and then the accumulated toxic materials exceeded the microbial degradation rate.

Hoeper and Schrieder [24] reported that the high organic loadings to a batch reactor resulted in high TSS concentrations in the effluent. The relationship between organic loading and activated sludge was also reported by other investigators [36, 37]. It is interesting to note that regardless of the operation conditions in the present investigation, the effluent TSS concentration was dependent on the organic loadings, as can be seen from Fig. 25. The probability of low TSS occurring with low organic loading was greater than that with high organic loading.

To obviate the difficulties of separating the solids from the water, chemicals were used to flocculate the dispersed particles in supernatant. In general, the addition of chemicals improved the effluent quality in terms of TSS; however, it did not significantly contribute to the removal of organic materials, which can be seen from laboratory jar tests. Table 7 and 8 demonstrates the effects of chemical addition on effluent TSS. The COD presented in Table 7 is total COD concentration. The efficiency of flocculation also was compared among the three chemicals. Even though the optimal dosages were not achieved, it still can be seen that Ferric Chloride and Alum improved flocculation and separation more significantly than Calcium Chloride. The same results were also obtained during actual SBR processes. Calcium Chloride was used for the improvement of the sludge settling characteristics according to Dr. C.

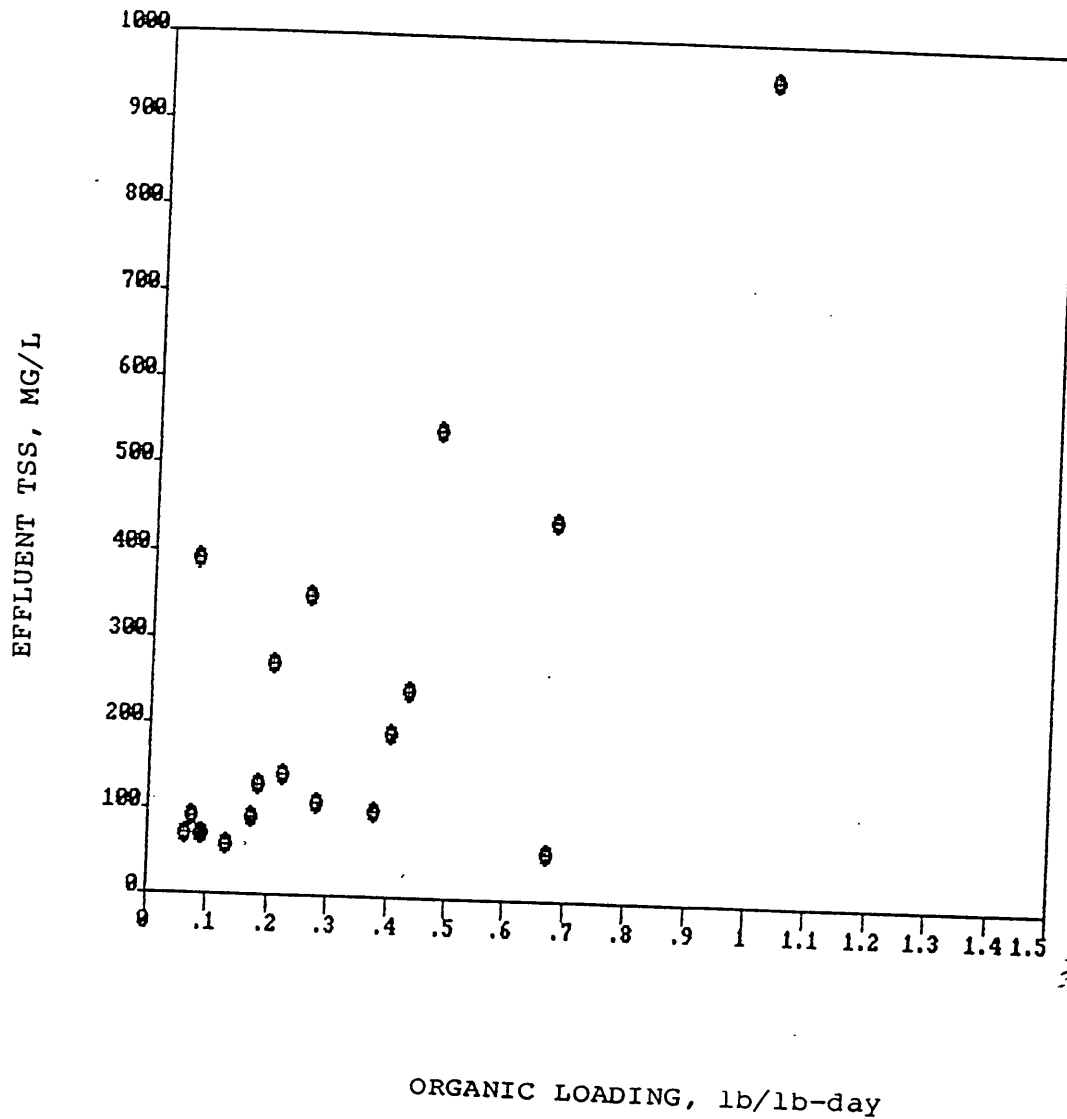


Figure 25. The effects of organic loading on effluent TSS

W. Randall's recommendation. During the first seven batches the Calcium Chloride did affect the effluent TSS, resulting low effluent TSS. Before CaCl_2 was added the supernatant was visually very turbid and the turbidity was obviously reduced after the addition of the compound. In Batch 2 the effluent TSS decreased from 160 to 70 mg/l with the addition of 88 lbs CaCl_2 into 18,500 gals wastewater. But from Batch 8 on Calcium Chloride was no more efficient and the combination of Calcium Chloride and Ferric Chloride had to be applied together. The question of whether sodium ion concentration in the wastewater was high or low could not be proved, because the sodium concentration was not measured during the experiments. Therefore the mechanism of the effect of calcium on the improvement of sludge settling could not be addressed here. However the other effects of the chemical addition on activated sludge were not investigated during this study. In future, it may be interesting to determine how the chemicals could effect the microorganism activity and biochemical mechanisms.

Table 8. The flocculation test (1)

	Dosage (ppm)	pH	TSS (ppm)
----- Supernatant TSS= 500mg/l, in control sample -----			
CaCl ₂	500	6	1000
	1000	6	1020
	2000	6	920
	3000	6	2158
FeCl ₃	240	7.3	---
	480	6.8	280
	960	4.5	65
	2400	4	--
Alum	100	6	50
	200	3.8	50
	500	3.8	205
	1000	3.8	330

Table 9. The flocculation test (2)

Initial MLSS = 3630 mg/l; FCOD = 8330 mg/l; TSS = 760 mg/l

	Dosage mg/l	pH	TSS mg/l	COD mg/l
CaCl ₂	220	7	890	8670
	670	7	1040	8330
	1100	7	1050	10480
	2014	7	1130	8440
	5092	6.8	1260	15150
FeCl ₃	40	7	250	7540
	80	7	340	7980
	120	7	480	8210
	160	--	280	9650
Alum	218	7.2	670	13080
	592	7	590	6550
	820	7	1046	7650
	1120	6	2020	7650
	1502	5	5143	7540

5.0 Conclusions and Recommendations

This study was a full-scale investigation of SBR for the treatment of oily wastewater with determination of the effects of different operating conditions on process performance. It was demonstrated that under a rather complex situation, the performance of the SBR could be significantly improved, compared to the results prior to the study. In contrast to the low COD reduction, significantly higher BOD₅ removals were achieved. When the waste was only composed of wasted oils, the BOD₅ in the effluent averaged 179 mg/l for an average removal of 87%. Also, good reductions of phenols and oil & grease were attained during the study.

Based on a thorough evaluation of the results the following specific conclusions are made.

- . Continuous aeration accomplished greater BOD removal than intermittent aeration when nutrients were not limiting.

- . Intermittent aeration of the SBR system produced a better quality effluent than continuous aeration when nutrients were limiting. This occurred because

biomass production was less in the intermittently aerated system and, therefore, the nutrient requirements were less, which permitted more BOD removal for the nutrients available.

. Better treatment was obtained when the BOD₅:N:P ratio was at least 100:5:1 or less.

. High organic loadings to the SBR resulted in very high growth rates and promoted the production of dispersed particles, which in turn contributed to high concentrations of TSS and Total BOD₅ in the effluent.

. In an SBR system, the aeration time is a very important parameter for the removal of substrates. This study showed that extended aeration times would usually increase the reduction of phenols and BOD₅.

. The effluent TSS concentration from the SBR effluent was highly dependent on the organic loading, but chemical addition to the activated sludge reduced the effluent TSS concentration.

The following recommendations can be made:

. This SBR system still has some operating problems which have not been resolved. Nutrients were added in solid form which may have reduced their availability for microorganism use. The phosphorus chemicals were hard to dissolve in water. A high residue of inorganic particles may remain in the tank as a result of undissolved phosphorus containing chemicals. It is suggested that other forms of phosphorus such as phosphorus acid should be tried.

. Sludge should be more regularly wasted to obtain MCRT control. This means that close supervision will be needed. However, wasting needs to occur only at the end batch treatment period.

. If possible the plant needs to have an adjustable pump to feed wastewater for better control of the operating mode. During these experiments, the FILL period was unadjustable; the benefit of a long FILL stage could not be introduced to the system.

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Appendix A. The raw data collected during the investigation of full-scale SBR treatment of the oily wastewaters.

Table A-1. The Operating Conditions for the Thirty Batches*

Batch	A.T. (hr)	NH ₄ NO ₃	Na ₃ PO ₄	Time	Chemical Addition	Initial	A.P.
1	24	2.0	0.2	E	NO	5950	C
2	72	0.9	0.1	E	CaCl ₂	2380	C
3	20	1.1	0.11	E	CaCl ₂	8210	C
4	26	1.03	0.11	E	CaCl ₂	-----	C
5	8	1.7	0.18	E	CaCl ₂	-----	C
6	24	0.94	0.1	E	CaCl ₂	1080	C
7	24	1.9	0.4	E	CaCl ₂	4410	C
8	24	3.1	0.7	E	CaCl ₂	-----	C
9	72	2.1	0.2	E	FeCl ₃	3030	C
10	65	2.1	0.2	E	CaCl ₂	4890	C
11	72	2.1	0.2	B	FeCl ₃	3100	C
12	48	2.1	0.2	B	FeCl ₃	795	C
13	68	2.1	0.2	B	FeCl ₃	2130	C
14	144	2.1	0.2	B	FeCl ₃	2590	I
15	72	2.1	0.2	B	FeCl ₃	1880	I
16	504	2.4	0.2	E	FeCl ₃	580	I
17	68	2.1	0.2	E	FeCl ₃	1990	I
18	120	3.0	0.6	E	FeCl ₃	2190	I
19	24	0.6	0.12	NO	NO	940	I
20	96	0.6	0.12	NO	NO	2640	I
21	120	0.5	0.1	NO	NO	834	I
22	72	0.47	0.1	NO	NO	-----	I
23	99	0.47	0.1	E	Alum	1660	I
24	144	0.9	0.2	E	FeCl ₃	2290	I
25	114	0.85	0.2	E	Alum	2870	I
26	136	0.5	0.1	E	FeCl ₃	2300	I

(table 1 continued)

27	140	0.6	0.1	E	Alum	3.3	3070	C
28	138	0.6	0.1	E	Alum	3.3	1670	C
29	168	0.6	0.1	E	Alum	2.0	2540	I
30	127	0.5	0.1	E	Alum	2.9	2224	I

* In the table " A. T. " == AERATION TIME;
" A. P. " == AERATION PATTERN;
" E " == THE END OF AERATION PERIOD;
" B " == THE BEGINNING OF AERATION PERIOD;
" I " == INTERMITTENT AERATION;
" C " == CONTINUOUS AERATION;
" NO " == NO CHEMICAL ADDITION.

Table A-2 Alkalinity, pH, TKN, TP, and TSS data for thirty batches.

Batch	Alkalinity		pH		TSS		TKN		TP		Influent Capacity (gal)
	(mg/l)				(mg/l)		(mg/l)		(mg/l)		
	I	E	I	E	I	E	I	E	I	E	
1	---	187	--	7.6	---	100	---	187	---	15.2	10,500
2	114	847	7.7	7.0	2010	70	117	21	25.6	6.7	18,000
3	---	648	---	5.1	8210	330	---	109	----	1.6	16,500
4	---	---	---	4.8	----	240	---	---	----	---	10,000
5	998	682	6.5	6.7	4720	290	72	34	8.6	6.6	18,000
6	840	977	6.1	7.0	170	150	141*	207	5.7*	6.1	18,000
7	2168	1629	8.6	8.1	160	960	150	197	9.1	20	16,000
8	80	1119	7.0	7.8	180	190	710*	423	17.3	14.2	16,000
9	80	1364	7.0	7.5	180	130	710	580	17.3	5.2	16,500
10	407	519	6.3	7.3	---	170	10	200	0.53	22	16,000
11	231	489	6.6	7.6	60	70	24	172	1.4	5.0	16,000
12	356	---	6.1	7.6	22	55	---	---	---	---	16,000
13	824	---	7.2	7.8	32	390	---	---	---	---	15,000
14	936	---	7.4	7.9	245	270	260	392	43	264	16,000
15	672	---	7.2	7.9	105	240	90	314	12.6	14.7	14,000
16	234	623	6.4	7.8	130	90	28	188	2.9	5.0	14,000
17	1283	---	---	7.0	---	130	---	---	---	---	12,000
18	499	824	7.3	8.1	5	70	508	1016	0.16	9.09	15,000
19	550	835	6.9	8.3	110	140	94	100	2.6	4.7	15,000
20	550	936	6.9	8.3	110	30	94	95	2.6	12.5	17,000
21	274	---	6.3	7.6	20	350	45	30	4.1	17.0	18,000
22	370	380	5.7	7.2	785	110	154	144	5.2	1.9	18,000
23	1383	---	7.3	8.0	330	440	76	118	7.6	12.3	9,5000
24	1394	1003	6.4	8.0	140	100	96	68	8.4	10.3	10,000
25	486	359	6.0	7.0	70	60	48	34	2.8	3.5	17,000
26	1740	1457	6.8	7.8	---	---	168	44*	7.54	2.1	16,000
27	1415	1436	6.0	7.2	980	350	166	98*	9.1	0.6	14,000
28	274	470	4.7	7.4	190	90	90	34	0.1	3.5	15,000
29	137	337	4.7	7.4	170	130	14	84	17	6.4	17,000
30	538	475	7.0	7.6	170	110	200	0.8	5.4	4.2	17,000

* filtered sample

Table A-3 COD, BOD, Oil & Grease, Phenols, and NO₃-N concentrations for thirty batches

Batch	COD (mg/l)		BOD ₅ (mg/l)		O & G (mg/l)		Phenols (mg/l)		NO ₃ -N (mg/l)	
	I	E	I	E	I	E	I	E	I	E
1	-----	4170	-----	375	-----	---	-----	0.36	---	---
2	30300	9022	434	433	1111	158	-----	-----	---	---
3	18800	8900	-----	570	-----	---	-----	-----	---	---
4	-----	-----	-----	2034	-----	---	-----	-----	---	---
5	24800	14500	2121	2133	12829	216	-----	-----	---	---
6	21600	17250	7320	4470	362	157	33.8	6.4	0.7	15.2
7	12900	25800	4895	3548	226	542	37	43	12	20.7
8	14060	17800	3607	2187	316	261	6.4	2.6	---	9
9	-----	8920	-----	1080	---	213	---	2.8	---	4.6
10	3060	2130	1151	167	101	70	7.1	3.5	---	---
11	2710	1530	822	138	188	74	2.1	0.1	3.9	14.5
12	3450	2520	1067	153	61	13	2.5	0.5	1.5	6.4
13	8440	5810	3010	378	114	93	6.3	0.7	19	5.38
14	5280	5120	3150	2048	295	173	69	55	8.7	---
15	7130	5451	2400	651	187	66	17.5	0.5	---	32.7
16	3170	1470	881	81	91	12	8.8	0.2	1.1	9.4
17	6460	4710	---	558	34	26	8.8	0.2	---	-----
18	3030	2770	708	182	20	12	12.5	0.5	---	0.97
19	3450	2900	858	301	67	35	10	1.0	---	---
20	-----	1650	-----	294	---	20	---	1.2	---	---
21	4470	3980	934	471	39	36	11.2	5.0	---	---
22	10200	6370	2586	1140	471	44	17.6	7.5	---	---
23	11380	7760	4460	1500	275	51	3.1	0.3	7.34	12.4
24	13280	8440	5080	1830	240	65	2.9	0.18	3.4	6.26
25	3810	1880	1750	235	124	23	9.8	0.16	16.0	8.56
26	13450	6370	6150	1340	483	7.5	9.2	7.2	---	---
27	11070	6260	4580	1916	195	31	14.8	1.9	---	---
28	5990	3450	1635	550	120	11	19	11	---	---
29	6500	3565	3210	828	44	16	7.8	1.5	3.5	1.4
30	6740	3450	3328	204	---	27	7.2	0.2	5.3	7.5

Table A-4. Changes of COD, BOD₅, MLSS, MLVSS, SVI, ZSV with aeration time

Batch	12						
Aeration time (hr)	COD	BOD ₅	MLSS	MLVSS	SVI	ZSV	pH
Initial	3450	877	795	510	63		6.2
24	2640		775	510	32		7.8
36	2520		825	570	30		7.6
Effluent	2520	153					

Table A-5. Changes of COD, BOD, MLSS, MLVSS, SVI, and ZSV with aeration time

Batch	13						
Aeration time (hr)	COD	BOD5	MLSS	MLVSS	SVI	ZSV	pH
Initial	8440	3010	2130	1860	33		7.1
16	6550		2360	1860	17		7.8
21	5990		2360	1680	19		
24			2550	1740	18		
40	5990		2460	1580	18		
43			2370	1710	20		
68	5810	378	4320	3000	47		7.6
162	4320	376	4720	3240	36		8.1

Table A-6. Changes of COD, BOD, MLSS, MLVSS, SVI, and ZSV with
aeration time

Batch		14						
Aeration time (hr)	COD (mg/l)	BOD ₅ (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	SVI	ZSV	pH	
Initial	5280	3150	2590	1860	27			
19			2310	1590				
44			3570	2440	20		8.2	
46			2800	1780	25		8.2	
48			2760	1910	24			
66			2900	1970	22			
72	5630		3140	2180				
144	5120		3160	2110	25			

Table A-7. Changes of COD, BOD, MLSS, MLVSS, SVI, and ZSV with
aeration time

Batch		18					
Aeration time (hr)	COD (mg/l)	BOD ₅ (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	SVI	ZSV	pH
Initial	3030	708	1590				
2	2900		2190	1420	27		
72			2020	1070			
96			1590	980	25		
119			2280	1330	22		
120			3410	1970	42		

Table A-8. Changes of COD, BOD₅, MLSS, MLVSS, SVI, and ZSV
with aeration time

Batch		23						
Aeration time (hr)	COD (mg/l)	BOD ₅ (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	SVI	ZSV	pH	
Initial	11380	4450						
7	9100		1660	1340				
11	9270		1830	1360			7.6	
26	11070		2330	1920			7.8	
32	7980		2304	1810				
80	7230		2170	1680				
99	7190		1910	1420			8.2	

Table A-9. Changes of COD, BOD, MLSS, MLVSS, SVI, and ZSV
with aeration time

Batch		24					
Aeration time (hr)	COD (mg/l)	BOD ₅ (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	SVI	ZSV	pH
Initial	13270	5050					
5	10480		2290	1670			
34	10060		2290	1670			
48	9150		2460	1790			
74	7870		2260	1680			
144	7540		2260	1680			

Table A-10. Changes of COD, BOD, MLSS, MLVSS, SVI, and ZSV
with aeration time

Batch	25						
Aeration time (hr)	COD (mg/l)	BOD ₅ (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	SVI	ZSV	pH
Initial	8310	1971	1519				
18	4020		2870	2000	35		
30	2770		2275	1705	30		
48	2580	678	2180	1560	32		8
72	2230		2280	1680	31		8
90	1650		2675	2035	19		

Table A-11. Changes of COD, BOD, MLSS, MLVSS, SVI, and ZSV
with aeration time

Batch	26							
Aeration time (hr)	COD (mg/l)	BOD ₅ (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	SVI	ZSV	pH	
Initial	13450	6150	2300	1700	39		6.8	
3	11230		2870	2000			7.0	
16	10770	4260	2430	1820	36		7.2	
24	10770		2690	2000	29		7.2	
44	9920		2720	1990	26		7.8	
48	8210	3250	2670	1910	28		7.8	
72		2640	2580	1960				
118			3630	2680	16			
120	7130		2760	2070	22		8.2	

Table A-12. Changes of COD, BOD₅, MLSS, MLVSS, SVI, and ZSV
with aeration time

Batch	Aeration time (hr)	COD (mg/l)	BOD ₅ (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	SVI	ZSV	pH
	Initial	11070	4580					
	18	8100	2250	3070	2210	52		6.0
	24	8100	2552	3270	2490	21		7.2
	48	7330	2830	3110	2250	25		7.3
	72	7130	2442	3420	2480	50		7.3
	120	6740	1947	3510	2620	30		7.3

Table A-13. Changes of COD, BOD, MLSS, MLVSS, SVI, and ZSV
with aeration time

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Batch	Aeration time (hr)	COD (mg/l)	BOD ₅ (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	SVI	ZSV	pH
	Initial	5990	1635	1670	1140	102		5.0
	24	4320	1122	2320	1760	99	2.7	5.5
	40	4630		2630	2050	69		6.3
	48	4710	1230	2900	1680	74	3.9	6.5
	72	4170	1000	2170	2060	75	1.6	7.0
	112	4100	1170	2570	1910	117	2.0	7.3
	120	3740	870	2530	1990	63		7.4
	After Chemical Addition			2830	2000	106		

Table A-14. Changes of COD, BOD, MLSS, MLVSS, SVI, and ZSV
with aeration time

Batch	30						
Aeration time (hr)	COD (mg/l)	BOD ₅ (mg/l)	MLSS (mg/l)	MLVSS (mg/l)	SVI	ZSV	pH
Initial	6740	3328	1800			1.3	7.0
24	5370	1294	2530	1710	43	1.3	7.4
48	4470	6100	2970	2100	44	6.1	7.2
72	4320	8850	2990	2040	42	6.2	7.4
96	3583	6210	2473	1764	48	4.9	7.6
122	3450	3660	2960	1140	34	6.1	7.6

Table A-15 Changes of oil & grease, NO₃-N , and phenols with aeration time

Batch		26			
Aeration time (hr)	Oil&Grease (mg/l)	Phenols (mg/l)	NO ₃ -N (mg/l)		
Initial	483	9.2	5.1		
3	---	---	3.0		
16	97	9.0	3.6		
24	16	10	4.7		
44	---	9.0	8.4		
48	10	9.0	2.2		
72	15	---	---		
120	7.5	7.2	9.4		

Table A-16 Changes of oil & grease, NO₃-N , and phenols with aeration time

Batch		27			
Aeration time (hr)	Oil&Grease (mg/l)	Phenols (mg/l)	NO ₃ -N (mg/l)		
Initial	195	15.2	7.02		
18	---	14.8	7.12		
24	---	13.0	6.5		
48	---	12.0	---		
72	---	10.0	---		
120	10	10.0	---		
140	30	7.88	2.2		

Table A-17 Changes of oil & grease, NO₃-N , and phenols with aeration time

Batch		28			
Aeration time (hr)	Oil&Grease (mg/l)	Phenols (mg/l)	NO ₃ -N (mg/l)		
Initial	120	19.0	28.4		
24	---	9.00	41.5		
40	23	---	41.5		
48	---	6.40	46.4		
72	47	8.00	---		
138	11	11	2.6		

Table A-18 Changes of oil & grease, NO₃-N , orthophosphorus,
and phenols with aeration time

Batch		30				
Aeration time (hr)	Oil&Grease (mg/l)	Phenols (mg/l)	NO ₃ -N (mg/l)	Ortho-P (mg/l)		
Initial	---	7.2	5.32	6.0		
24	---	3	9.94	18.6		
48	---	3	3.1	9.4		
72	---	3	41.5	4.6		
96	---	3.5	33	19		
122	---	1.0	7.46	20.8		

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**Sequencing Batch Reactor Treatment of Oily Wastewater
from Can Manufacturing and Gasoline Tank Bottoms**

by

Xiaochun Zhang

C. W. Randall

(ABSTRACT)

The performance of an SBR system applied for the biological treatment of oily wastewaters was investigated. Aeration time for the SBR application varied from one day to six days with either continuous or intermittent aeration. In term of the removals of BOD₅, oil & grease, and phenols, the efficiency of the SBR wastewater treatment system was improved significantly by operational changes. However, for the high strength wastewater with BOD₅ greater than 1000 mg/l, the effluent TSS concentration was high as a result of dispersed fine particles. Nutrient addition to the wastes was required due to the deficiency of nitrogen and phosphorus in the incoming wastes. A BOD₅:N:P ratio of 100:5:1 or less was suitable for good performance of the activated sludge SBR system. Extended aeration time increased the reduction of BOD₅, and phenols. Due to the high effluent TSS concentration, certain chemicals were added to the mixed liquor during this investigation. The addition of chemical improved the activated sludge settleability, and reduced the effluent TSS concentrations. This investigation also showed that the effluent TSS was strongly affected by the SBR system organic loading rates.

In spite of the wide variety of operating conditions and wastewater influent characteristics, the removals of substrates were 39-57% for COD, 56-94 % for BOD₅, 73-98 % for oil & grease, and 22-97 % for phenols, which was comparable to conventional

activated sludge treatment processes for oily wastes. The degradation rate of BOD_5 for the SBR treatment of the oily wastewaters followed first-order kinetics.