AN INVESTIGATION OF THE EFFECTS OF THE ADDITION OF POWDERED ACTIVATED CARBON TO THE ACTIVATED SLUDGE OF CELLULOSE ACETATE MANUFACTURING WASTEWATER

by

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(ABSTRACT)

Equilibrium powdered activated carbon (PAC) concentrations of 20, 160, and 280 mg/L in activated sludge reactors treating cellulose acetate manufacturing wastewater were found to enhance substrate removal. The improved substrate removal as measured by COD averaged 20 percent. The apparent mechanism of improved removal was the stimulation of greater biomass growth.

PAC addition increased the oxygen uptake rate (OUR), the observed cell yield coefficient (Y_{obs}) and the first order substrate removal coefficient (K_b) of the activated sludge system, which were operated at a temperature of 18^{o}C and a biological solids retention times of fourteen days. The addition of PAC also improved the sludge settleability but this resulted in higher effluent suspended solids concentration because zone settling velocity was the primary factor affecting effluent suspended solids.

A type of activated sludge bulking, known as jelly formation, plagued the biological reactors but nitrogen addition appeared to solve the problem.

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Chapter I

INTRODUCTION

In the past two decades, tertiary treatment has received a great deal of attention due to stringent effluent limitations imposed on industries to avoid the deterioration of the aquatic environment. Tertiary treatment, which is treatment beyond secondary biological treatment, includes among others, hyper-filtration, reverse osmosis, filtration and coagulation, and, of course, carbon adsorption.

The carbon adsorption process in a wastewater treatment system may either precede or follow the biological process in the treatment scheme; i.e., biological-carbon treatment or carbon-biological treatment. While the latter possesses many advantages, the former is commonly employed because it has the potential to reduce effluent suspended solids and/or color concentrations from conventional biological treatment processes. The carbon adsorption unit placed after secondary treatment is often referred to as a polishing unit.

In the past, granular activated carbon (GAC) has been used instead of powdered activated carbon (PAC) because it is easier to regenerate the granular carbon. Moreover, the United States Environmental Protection Agency in 1975 encouraged the use of columnar granular activated carbon as a polishing process by defining it as the Best Available

Technology Economically Achievable (BATEA) [35]. Unfortunately, GAC columns have been faced with the problems of biological adherence and growth on the carbon particles [8].

PAC has certain advantages over GAC. PAC is inexpensive compared to GAC. Scaramelli and DiGiano [58] reported 9 to 15 cents/pound versus 30 cents/pound of GAC. The small particle size of PAC reduces the intraparticle transport, thereby increasing the adsorption rates with shorter equilibrium time. Nevertheless, PAC has economic shortcomings. The major drawbacks are the capital cost of constructing a new reactor to mix PAC with the wastewater and additional operating cost induced by the need for coagulation before clarification after contacting PAC with wastewater. Thus, as initially used, a more efficient means of using PAC in upgrading treatment plant facilities was needed.

It was recently that Dupont developed the PACT process. The PACT process is a modified activated sludge treatment system in which PAC is added directly to the mixed liquor in the aeration vessel. Many industries and municipalities have applied this process successfully to meet stringent effluent standards [1, 49].

More stringent effluent quality standards may be imposed on a cellulose acetate manufacturing (Celco) plant located between Narrows and Pearisburg, Virginia, effective from July 1, 1985. The PACT process was being considered as a possible modification in an effort to upgrade performance of the treatment system.

Regardless of the potential merits of the PACT process, laboratory investigations and/or pilot plant studies were considered to be necessary before implementation. Wastewater characteristics vary from industry to industry, and there may be considerable in-plant variability. Moreover, the effects of PAC on activated sludge treatment of cellulose acetate manufacturing wastewater has not been documented adequately in the literature. The PACT process has been shown to be well suited for wastewaters containing adsorbable, toxic and poorly biodegradable organics [20, 22]. However, the Celco manufacturing wastewater contains highly biodegradable but poorly adsorbable organics, some of which are thought to be toxic. Flynn [21,24] reported that activated sludge and PACT processes remove rapidly biodegradable organics in equal amount. The benefits of PACT for treatment of the Celco wastewater are in doubt, and, therefore, there was a need to perform research to fill the void.

Several researchers have reported consistent increases in substrate removal [1, 17, 18, 20, 30, 34, 68] measured in terms of BOD_5, COD and TOC over a wide range of PAC dosages added to activated sludge units. Low carbon dosages, therefore, could represent a significant amount of saving by improving substrate removal without an increase in aeration basin volume. In addition, there exists a considerable controversy over the mechanism of substrate removal by PAC. Scaramelli and DiGiano [58] concluded that physical adsorption

is the controlling mechanism of enhanced substrate removal. On the other hand, Kalinske [34] showed that biological oxidation is increased by PAC resulting in a higher substrate removal as measured by COD. Other investigators [1, 24, 68] have claimed bioactivity and bioregeneration as the mechanism of enhanced substrate removal. Furthermore, the effect of PAC on the biokinetic constants of activated sludge unit is not entirely clear in the existing literature.

With the preceding in mind, the objectives of this research were as follows:

1. To ascertain whether PAC addition to activated sludge mixed liquor would enhance substrate removal as measured by COD and/or TOC of a highly biodegradable but poorly adsorbable wastewater from cellulose acetate manufacturing and, if so, to determine the mechanism of increased COD, BOD and TOC removal by PAC in the activated sludge process.
2. To ascertain whether PAC addition improves sludge settleability and reduces the effluent suspended solids from the activated sludge system.
3. To determine the ability of PAC to reduce the concentration of potentially toxic organics in the treatment plant effluent.
4. To examine the effect of PAC on the biokinetic constants of the activated sludge unit.

While performing this experimental study, jellied activated sludge, a strange phenomena, was observed in the experimental activated sludge units. Therefore, the secondary purposes of this research were:

a) To study the effect of nitrogen addition to the raw wastewater to see if nitrogen deficiency is a factor that causes jelly formation in the clarifier unit of the activated sludge process.

b) To examine the roles of increased loads of acetic acid and solvents on jelly formation in the activated sludge, and, finally,

c) To resolve the question of whether Mesityl oxide (MeO) is the cause of biological upsets often observed in the summer months at the Celco plant.

Chapter II

LITERATURE REVIEW

With increased interest in water pollution control over the past decade, activated carbon has become increasingly important in wastewater treatment. Activated carbon either in powdered or granular form can be applied in physicochemical processes or directly to the biological reactor. However, studies have shown that addition of powdered activated carbon (PAC) to the biological reactor is the cost effective approach to meet the increasingly stringent effluent limitations imposed on many industries [1, 8, 17, 18, 24, 49, 68].

Addition of powdered activated carbon to the sludge unit was developed by Dupont, and its patent name is PACT. A simplified diagram of PACT is depicted in Figure 1. The PACT process is suitable for aerobic biological process such as activated sludge, contact stabilization and aerated lagoon systems [56] (i.e. suspension of the powdered activated carbon in the aeration vessel through which the wastewater passes).

Several investigators [1, 15, 23, 56, 68] have reported numerous advantages of PAC addition to the sludge unit of an activated sludge process, which include:

- Enhancement of effluent water quality measured as BOD, COD, and TOC over a wide range of food to microorganisms (F/M) loadings.
- The settleability of sludge is greatly improved by PAC,

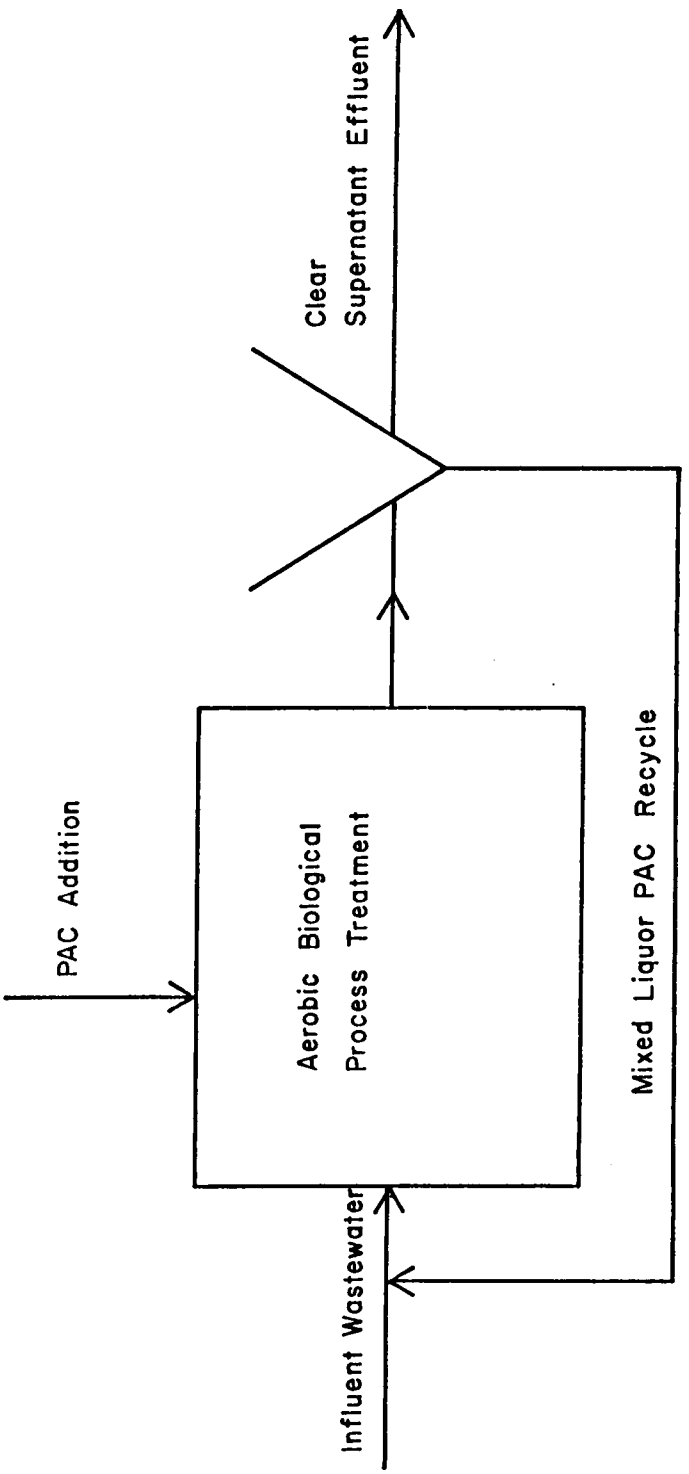


Figure 1. A simplified diagram of PACT.

thereby, reducing the effluent suspended solids, and producing a well-compacted dark sludge.

- It can increase the hydraulic capacity of existing treatment plants without capital intensive expansion programs.
- Process stability is ensured by resisting shock loads to the biological system.

The efficiency of PAC in a biological reactor is determined by equilibrium carbon concentration, hydraulic retention time (HRT) and biological solids retention times (BSRT).

The role of PAC with respect to these parameters, in improving the performance of the activated sludge process as stated in the literature is reviewed in this chapter under the following appropriate headings.

PAC Enhancements and Their Postulates

Most investigators [1, 14, 17, 20-22, 24, 34, 68, 76] report that there are benefits associated with the addition of PAC to the activated sludge process. One such benefit is enhanced organic substrate removal. All the investigators of the role of PAC in the activated sludge process agreed to this. However, the method by which PAC enhances substrate removal is a controversy among the investigators. There has been controversy over the mechanism of improved COD, TOC and BOD removal in a PACT system since its introduction by Dupont. It may be misleading to view the mechanism as bioactivity and adsorption acting independently [25].

In addition, the introduction of a conservative substance such as PAC into the aeration basin of a biological reactor may alter the biological operational characteristics, and, therefore, affect the kinetics of microbial activity. Several researchers have reported that the kinetic constant parameters are changed by addition of PAC to the activated sludge unit [22, 68, 76]. Considerable controversy exists in the literature on how these parameters are changed. The differences in the kinetic constant reported may be due to experimental design, data collection methods, and analysis techniques. Therefore, this section of the review will mainly lay emphasis on these aspects of PAC effects on the activated sludge unit.

Scaramelli and DiGiano [58] used two bench scale continuous flow activated sludge units of heterogeneous culture, one with PAC, and a control unit without PAC, and noted an increase in TOC removal, but concluded that physical adsorption was the controlling mechanism since there was no increase in oxygen uptake rate with the PAC unit plus no increase in the steady state Mixed Liquor Suspended Solids (MLSS) concentration. This conclusion is open to questions, however, because the data presented in their article were insufficient to justify this claim. The active biomass was not properly accounted for, and it was assumed that the addition of PAC did not alter the mixed liquor volatile suspended solids.

These investigators did not use SVI to measure the settleability of sludges with and without PAC. The investigators instead used settled volume to compare the two sludges. The sludge with PAC had the same settled volume as the control unit, and, thus, the authors claimed that PAC had no effect on the settleability of the sludge. This is questionable since neither zone settling velocity, nor effluent suspended solids were measured to compare the biomass-liquid separation of both units. The researchers, however, contended that the two sludge were of different densities. The MLSS concentrations with and without PAC were, respectively, 2350 and 1550 milligrams per liter (mg/L). These solids levels are not high enough to avoid the use of SVI. The sludges were similar, but the addition of a conservative substance, of course, increased the MLSS. Carbon is a weighting agent [56], and, the fact that sludges had different mass weights should have been the reason to use SVI in order to compare them on a unit weight basis. SVI decreases with increasing carbon dose [1, 17]. The data reported in their article concerning oxygen uptake rate (OUR) and the sludge settleability are summarized in Table 1.

Kalinske [34] investigated the effects of GAC on bioxidation using both batch, and continuous flow reactors. The GAC size was 12 x 40 mesh and it was added to a batch reactor that was fed with a glucose-nutrient-salt solution. The control unit was also fed with the same nutrient solution,

Table 1. Effects of 200 mg/L PAC after Scaramelli and DiGiano [48].

Oxygen Uptake Rate (mg/L-hr)		Settleability, ml	
Unit with PAC	Without PAC	PAC unit	Control unit
12.0	12.0	80	80
12.0	12.0	80	80
12.0	12.0	80	80
12.0	12.0	90	80
12.0	12.0		
12.0	12.0		
12.0	12.0		

and both systems were maintained at MLSS concentrations of 2000 to 2500 mg/L. However, the method of wasting was not clearly stated by the authors. After 1 and 2 hours, readings of COD were taken, and it was observed that the unit with GAC had better COD removal. The continuous flow reactor produced a similar result. Again, how wasting was performed with the continuous flow reactor was not clear in the article published. The author postulated that biological oxygen uptake rate was enhanced by carbon since there was no adsorption of glucose on the carbon. The investigator presented dissolved oxygen (DO) rather than oxygen uptake rate. The unit without PAC was observed to have a higher dissolved oxygen level.

Sundstrom et al. [70] studied the use of PAC to maintain process stability of an activated sludge system under transient conditions. In the experiment, glucose-nutrient salt solutions was fed to a mixed culture in a continuous flow reactor, one with PAC and the other without PAC. It was found in the study that the unit with PAC showed a substantial reduction in TOC and glucose as compared to the control unit. The investigators postulated that the decrease was not due to adsorption alone since glucose has a low affinity for carbon. In essence, PAC enhanced biodegradation of the organics. Unfortunately, data on oxygen uptake rate were not presented. Also in this study, the glucose loading was increased, and it was found that the control unit showed poor TOC removal.

However, when PAC was increased from 0 to 110 mg/L, effluent TOC decreased from 65 to 12 mg/L. In the same study, the investigators observed that PAC achieved a reduction of effluent TOC concentrations when a phenol impulse was applied to the system. For example, when a 1000 mg/L phenol impulse was applied to the systems, the unit with PAC indicated a TOC concentration of 33 mg/L while the unit without PAC had a 325 mg/L concentration. Thus, the unit PAC produced an effluent quality 10 times better than the biological unit when both units were subjected to shock loading. Therefore, the authors concluded that PAC can be employed to maintain good effluent quality in the presence of organic loading and toxic upsets.

Specchia and Gianetto [68] noted an increase in the purifying capacity of an activated sludge treatment plant fed with dyeworks wastewater when PAC was added. It was found in the study that the efficiency of the plant measured in terms of COD and BOD removal respectively, increased from 55.8 to 75.6 percent and 78 to 98 percent. In the study cited here, oxygen uptake rate was observed to increase at PAC levels of 200 and 1000 mg/L. The increase decreased with increased carbon dosages, and attributed this trend to a lack of substrate which imposed a limitation on bacterial growth. The authors postulated that the increase in PAC concentration induced more bacteria growth in PAC macropores. In the study, the authors did not state how wasting was performed and no BSRT was reported. Therefore, carbon was fed and wasted

indiscriminately. The authors stated that adsorption played an insignificant role in substrate removal, and, thus, concluded that bioactivity and bioregeneration were the mechanisms of enhanced substrate removal.

These authors reported that microbial decay coefficient and the cell yield coefficient decreased when PAC was added. This result may be misleading based on the fact that the data were collected over an unsteady state run. Moreover, the kinetic equation used was based on a steady state assumption. The decreased in cell yield coefficient indicates less biomass production which correlates directly with MLVSS. However, data on MLVSS were not presented, instead they reported MLSS. Therefore, the method by which MLVSS was determined is in question. This is important because there are conflicting approaches on the determination of MLVSS for PACT process in the existing literature [2, 17, 22, 40]. In the study reported by Specchia and Gianetto [68], the first order coefficient (k_b) with respect to substrate concentration was found to increase with PAC when compared with that without PAC. In their article, it was stated that the data used to determine the constant were collected over a steady state run. Nevertheless, the result of the kinetic parameter is highly questionable. The experiment was performed for four months. The first two months tested were performed without PAC and served as the control unit. The other two months were tested with PAC. Since these two runs were not operated in

parallel but at different periods, temperature effects could have caused the differences in the kinetic constants between the PAC, and without PAC runs. Unfortunately, the temperature of the data was not reported. This is important because Friedman and Schroeder [26] have shown that temperature affects the cell yield coefficient of the activated sludge process.

DeWalle et al. [17] used two bench scale activated sludge units to show an increase in COD removal at PAC levels of 50 mg/L and 300 mg/L. They reported an increase in COD removal of 15 percent at 5-day and 10-day BSRTS. The investigators obtained a 25 percent increase in COD removal at 300 mg/L PAC dosage at the two BSRT's cited herein. The authors noted that the rate increased less proportionally with increasing carbon dosages and attributed this trend to decreasing equilibrium concentration. The authors also indicated that improved in COD beyond the control unit was a function of hydraulic retention time.

In an attempt to postulate the mechanism by which PAC enhanced the COD removal, adsorption isotherm tests were performed with the PAC and the control units effluent by the authors. The investigators noted that the results were not satisfactory due to difficulty in removing carbon particles from the samples. As a consequence, column studies were conducted with the effluent of the control units, with upflow mode that caused the bed to expand almost 100 percent. It was

found in the study that 34 percent of the effluent organics as measured by COD from the 5-day control unit was removed, while the removal from the 10-day control unit was as large as 80 percent before breakthrough occurred. The authors postulated that physical adsorption alone could not account for the substrate removal attained by the biological reactors, since percentage improvements obtained with the column test were higher than 15 and 25 percent, respectively, obtained at 5-day and 10-day BSRT's.

In the study cited here, the MLVSS corrected for PAC was found to decrease on the addition of PAC to the biological reactors and attributed this trend to enhanced endogenous respiration. In addition, the reactors effluents were analyzed for aromatic hydroxyl, carbonyls total phosphorus, protein amino acid. It was observed that PAC enhanced the removal of all these groups. They also reported that there was more increase in the reductio of protein, amino acid, and carbohydrates in PAC unit operating at 5-day BSRT than that at 10-day BSRT and attributed this observation to differences in floc characteristics. Microscopic examinations of the sludges revealed that 5-day floc was more compact than the 10-day floc. It was, however, speculated by the authors that the diffusion of intermediates and all debris out of a more floc may be limited while the uptake of food may be enhanced.

Wu and Mahmud [77] examined the effects of PAC on the activated sludge units. These researchers, using batch

activated sludge units and carbon dosages of 1, 2, 3, and 10 gram per liter PAC showed an enhanced substrate removal, reported as TOC. It was observed that one gram per liter showed a tremendous increase in mg/L of TOC removal. When the carbon dosages were increased there was an increase in TOC removal but the improvement was marginal. Furthermore, carbon dose of 3 and 10 grams per liter showed an equal amount of substrate removal. The implication of this finding is that any further increase in PAC after a certain level represents an economical waste. In the study cited herein, the microbial decay coefficient was found to be relatively constant. The increasing carbon dosages also increased the cell yield coefficient. The implication of higher yield coefficient is more sludge production with increasing carbon dosages. The researchers attributed the increasing cell yield coefficients to increasing bacteria growth in the system. In essence, the bacteria were able to grow on powdered activated carbon. In the study, oxygen uptake rate was found to increase, and thus concluded that increase in bioactivity enhanced the substrate removed measured as TOC. However, the method by which MLVSS was determined was not stated in their article. In addition, SVI was found to decrease with increasing carbon dosage.

Ferguson et al. [20] using contact stabilization configuration with trichlorophenol found that the unit with PAC removed this compound whereas the control did not. A carbon dosage of 50 mg/L achieved a substantial removal of

tricholorophenol while 150 mg/L PAC accomplished total removal of this compound. In the experiment cited here, COD removal was better at 150 mg/L PAC than at 50 mg/L PAC with an absolute failure of removal in the control unit. The investigators postulated that adsorption of trichlorophenol by PAC enhanced the bioactivity. The meaning of this finding is, however, higher carbon dosages may reduce toxic effects of toxic organic compounds. In the same study, heavy metals such as copper, zinc, and lead were fed to the systems. For a copper dose of 3 mg/L, and 50 or 150 mg/L dosages of PAC the unit had an effluent soluble copper concentration of 0.25 mg/L while the control unit without PAC had 0.33 mg/L of soluble copper in the effluent while 150 mg/L showed 0.13 mg/L. Other heavy metals (zinc and lead) removals followed a similar pattern.

Furthermore, Ferguson et al. [20] experimented with the contact stabilization process using Seattle Metro wastewater and varied BSRT from 2 to 9 days, and observed an improvement in effluent quality with increasing sludge ages. The carbon dose used in the investigations was 150 mg/L.

Adams obtained a 25 and 20 percent improvement in COD and BOD removal, respectively, during the winter months by adding PAC to the activated sludge system treating ICI America polyols and derivative manufacturing wastewater. The author attributed these increases to synergistic effects of adsorption and biological regeneration. Also, in his study

total effluent suspended solids were substantially reduced on addition of 900 mg/L PAC.

Several researchers have reported improved in COD removal by PAC as a function of BSRT, hydraulic retention time, and carbon dosages [1, 17, 21, 22, 24, 27]. Mathematically, it is expressed as [27]

$$C_1 = C_o \ (\theta_c / \theta) \qquad [1]$$

where,

C_1 = Equilibrium PAC concentration in the bioreactor, mass volume^{-1}

C_o = Fresh feed of carbon slurry, mass volume^{-1} or influent PAC concentration, mass volume^{-1}

θ_c = BSRT, time

θ = HRT, time

Thus, Equation 1 demonstrates that mixed-liquor PAC concentration is directly proportional to the product of biological solids retention time and the feed of PAC to the aeration vessel of the activated sludge process. The implications of the equation is that equilibrium PAC concentrations can be increased by increasing the dose of carbon to the reactor, or the BSRT or both, and, by decreasing the hydraulic retention time. To put it in another form, it is more cost efficient to operate at high BSRT's and not at an excessively long hydraulic residence time. This is the best

approach in order to keep the carbon costs to the bare minimum. The preceedings indicates that the addition of PAC into the activated sludge unit introduces another parameter called the carbon detention time. The detention time of carbon is the time a mass of carbon remains in the biological reactor. Many investigators [1, 21, 22] have reported the carbon detention time to be equal to BSRT.

Flynn et al. [24] divided organic wastewater components into five distinct categories. Table 2 shows the wastewater component removability [21] based on biodegradability and adsorbability.

An examination of Table 2 indicates that non-biodegradable, non-adsorbable and slowly contact degradable wastewater organics cannot be removed by a PACT system or conventional activated sludge process. Fortunately, there are few or no organics with these combinations of characteristics [35]. Rapidly biodegradable organics are equally removed by activated sludge and PACT processes [21, 24]. Based on Table 2, another type of organics are non-biodegradable, adsorbable, and slowly biodegradable, adsorbable compounds. Flynn [24] noted that wastewaters containing these types of organics are efficiently degraded by the PACT process. The mechanism of removal of these compounds is a function of contact time [21, 35], In the form of a mathematical function, it is:

$$\text{RNBS or RSBA} = f(\theta) \qquad [2]$$

Table 2. Wastewater Component Removability [24]

Item	Adsorbably	Non-Adsorbable
Biodegradable	+	+
Non-biodegradable	0	
Slowly Contact Degradable	0	impossible

\+ = Removed by conventional activated sludge treatment and PACT system

0 = Removed only by PACT system

where,

RNBA = Removability of Non-Biodegradable Adsorbable Compound

RSBA = Removability of Slowly Biodegradable Adsorbably Compound

θ = Detention time of carbon

Removal occurs first by adsorbing the organics onto the surface of the carbon. The biomass (microbes) then partially degrades these adsorbed compounds with time. Thus, the carbon surface is also partially renewed. The implication of this is that enhanced removal of organics is due to the combination of effects of adsorption and bioactivity. Recall that in the conventional activated sludge process, these organics have a contact time equal to the hydraulic retention time. With the introduction of PAC, the detention time of the carbon is equal to BSRT, and, therefore, the contact time of the absorbed organics is also increased. It they are biodegradable, then bioregeneration is also increased. Thus, increasing BSRT will greatly enhance the removal of this organics at a particular carbon dose.

Flynn et al. [24] defined an apparent loading which is not equal to real loading. "An apparent loading is the amount of soluble organic material measured in terms of COD or TOC removed by a PACT system less the amount removed by a activated sludge unitoperating at the same BSRT, and divided by the carbon dose applied." The investigators used data taken from bench scale treatability testing units that were

fed industrial wastewater from the Dupont Chambers works located in Deep Water, New Jersey, and found that apparent loadings for PACT system were higher than that predicted form adsorption isotherms. They concluded that this phenomenon was the result of bioregeneration. Unfortunately, the enhancement of bioactivity in the PACT system due to adsorption was note indicated in their article [20]. It was also observed that the effluent TOC was enhanced with increasing sludge age or PAC concentrations or both. In other words, the fate of slowly biodegradable and adsorbable organics was an important factor in determining the effluent water quality. In the experiment, it was noted that a combination of low BSRT and high PAC concentration dose produced effluent water quality comparable to that produced by high BSRT and low PAC dose. In the same study cited herein, a better relationship between BSRT and effluent quality existed in PACT system than in a conventional activated sludge system. This observation can be attributed to the fact that the adsorbed microorganisms have BSRT equal to carbon detention time, rather than short hydraulic retention time to biodegrade the recalcitrant organic compounds. Finally, it was observed that apparent loading increased with BSRT, and, thus, lended a considerable support for the existence of bioregeneration.

Again, DeJohn and Black [15] classified organic molecules based on adsorbability as follows:

- Organic compounds which are tightly held by carbon and are not easily desorbed

- Compounds that readily desorbed, and are adsorbed on the carbon surface with difficulty
- Poorly adsorbably compounds

In addition, they divided the organic compounds into three categories based on susceptibility to biodegration:

1. compounds which are readily and rapidly biodegraded
2. slowly degraded organic molecules
3. difficult-to-degrade or recalcitrant organic molecules.

Using the above concepts , they developed an interaction of carbon and the microorganisms in PACT system, similar to Flynn [24], in an activated sludge system. Table 3 presents the interactions developed by the authors. The authors indicated that classes of compounds that are represented by box 1, 2 and 3 would be degraded with no difficulty by the microbes in a PACT system. Compounds that fall in Box 1, 4, and 7 are efficiently removed by carbon adsorption. However, compounds of box [1] are few in number, and one such example is O-Cresol [15]. Furthermore, compounds of Boxes 4, 5, and 6 are slowly biodegradable, and could not be removed effectively in a conventional activated sludge system. While compounds represented by Boxes 7, 8 and 9 are not biodegradable and may be toxic to microbes in some cases.

The author noted that the addition of PAC to the biological reactor increases the biomass level, and, therefore, acts as a weighting agent. The increase in biomass

Table 3. Microorganisms Interaction with Carbon in PACT System [15].

Box	Extent of Biodegradability	Adsorpability
1	Rapid	Strong
2	Rapid	Moderate
3	Rapid	Weak
4	Slow	Strong
5	Slow	Moderate
6	Slow	Weak
7	None	Strong
8	None	Moderate
9	None	Weak

plus higher retention time of slowly degraded compounds by the carbon gives more time for the organic compounds to be consumed biologically. These authors also reported that carbon will prevent the sludge from overflowing in the presence of high organic load which normally would lead to sludge bulking. Under low organic loads dispersed biofloc may result and PAC serves as a seed for floc formation preventing loss of solids. Lastly, the authors explained enhancement mechanism by PAC as localization and concentration of oxygen and organics due to adsorption on carbon surfaces, resulting in a more complete oxidation.

Table 4 summarizes the results of the effects of PAC addition to the activated sludge process. Table 4 indicates that few literature has reported biokinetic constants with respect to PAC addition. In the few of the articles published, K_s, the concentration saturation constant and K, the maximum specific substrate utilization constant were presented.

Monod's biological kinetics equation [5] is $q = KS/K_s+S$ and linearizing this equation, it then reduces to

$$1/q = (K_s/K)\ 1/s + 1/K \qquad [3]$$

A plot of Equation 1 will result in a straight line, with the slope as K_s/K and the intercept as $1/K$. Again, making the assumption that K_s is much greater then the substrate, Monod's kinetic equation reduces to

$$q = K_bS \qquad [4]$$

Table 4. Results of PAC addition to the activated sludge of different investigations.

Wastewater Type	Percent COD Improvement	Y_T Control Unit	Y_T PAC Unit	K_b Control L/mg-day	K_b Control PAC Unit L/mg-day	OUR Increase or Decrease	Equilibrium Carbon Dosage mg/L	BSRT Days	HRT Days	Temp. °C	Researcher	Postulates
Synthetic wastewater containing paint industry wastewater components	-	0.3[c]	0.38[c]	0.0083[+]	0.012[+]	Increase	1000	-	-	-	Wu and Mahmud [77]	Bioactivity
Synthetic wastewater containing paint industry wastewater components		0.3[c]	0.50[c]	0.0083[+]	0.015[+]	Increase	2000	-	-	-	Wu and Mahmud [77]	Bioactivity
Dye works wastewater	45	0.67	0.48[d]	0.000046	0.00032	Increase	800	-	-	-	Specchia & Gianetto [68]	Bioregeneration
Petroleum Refinery wastewater	-	0.16	0.08	-	-	Increase (by a narrow margin)	2500	50	0.75	-	Crame [14]	Physical Adsorption
Synthetic wastewater Glucose nutrient	15	Increased	Decreased	-	-	-	50	5	-	-	DeWalle et al. [17]	Bioactivity
Synthetic Wastewater Glucose nutrient	25	Increased	Decreased	-	-	-	300	10	-	-	De Walle et al. [17]	Bioactivity
Municipal Sewage	-	-	-	-	-	No increase or decrease	200	-	-	-	Scaramelli & DiGiano [58]	Adsorption
Synthetic	45	-	-	-	-	-	500	-	-	-	Kaluske [34]	Bioactivity
Synthetic wastewater containing paint industry wastewater components	-	0.3[c]	0.65[c]	0.0083[+]	0.021[+]	Increase	3000	-	-	-	Mu and Mahmud [77]	Bioactivity
Synthetic wastewater containing paint industry wastewater components	-	0.3[c]	0.66[c]	0.0083[+]	0.030[+]	Increase	3000	-	-	-	Mu and Mahmud [77]	Bioactivity

c = $\frac{\text{mg of biomass produced}}{\text{mg of TOC removed}}$

d = $\frac{\text{kg MLSS}}{\text{kg BOD}}$

\- not reported in the literature

\+ determined by K/Ks

It then becomes evident from Equations 3 and 4 that K_b (first order kinetic) is equal to K/K_s. It was on this basis that some of the K_bS' presented in the table were determined.

Flynn [22] showed that with temperature increases from 7°C to 20.5°C K_s (second order rate kinetic constant) increased respectively from 0.0230 to 0.130 milligrams per liter of MLVSS, and a steady decline occurred with an increases from 25°C to 31°C. In the same study the investigator used 151 mg/L of PAC at a temperature of 22°C to show that the K_s (second order kinetic rate constant) of a PAC unit was 0.0895 while the biological control unit had a value of 0.121. Thus, there was a decrease in the second order kinetic rate constant in terms of concentration. However, Flynn [21] reported that the error is within the limits of experimental error. In essence, the constants were equal, and postulated that it could be assumed that material which would be normally biodegraded in the absence of PAC will biodegrade at the same rate whether or not they are adsorbed. In other words, the organics will be removed in equal amount by PACT and conventional activated sludge process. This explanation is questionable since there is a significant difference between the parameters presented here in.

Approaches to the Determinations of the Parameters Induced by PAC

The introduction of PAC into the biological reactor changes some of the parameters such as MLSS and MLVSS. Interpretation of data on the effect of PAC on MLSS and MLVSS are not clear in the existing literature [2, 17, 22, 40]. Therefore, it is imperative to present the existing approaches on determining these parameters plus the carbon detention time induced by the PAC addition.

Flynn [22] modeled the biokinetics of the PAC reactor and developed the following equation to calculate the mixed liquor suspended solids:

$$X_T = C_o \left(\frac{\theta_C}{\theta} \right) + Y \left(\frac{S_o - S_e}{1 + K_d C} \right) \frac{\theta_C}{\theta} \qquad [5]$$

Where X_T = mixed Liquor Suspended Solids (mass per volume)

C_o = influent PAC concentration based on fresh feed (mass volume^{-1})

θ_C = BSRT

θ = HRT

Y = cell yield coefficient

S_o = influent substrate concentration (mass volume^{-1})

S_e = effluent substrate concentration (mass volume^{-1})

K_d = Microbial decay coefficient (time^{-1})

It is of interest to note that the second expression on the right hand side of Equation [5] was developed by materials balance for substrate without PAC at steady state. Similarily the first expression was developed on the basis of steady state using PAC as a conservative substance. The mathematical development of Equation [5] is presented in Appendix A. In the appendix, the detention time of carbon is also explained. The first equation is equal to the concentration of PAC in the mixed liquor suspended solids.

$$C_1 = C_O \left(\theta_C / \theta \right) \qquad [1b]$$

The investigator represented the active biomass as

$$X = X_T - C_1 \qquad [6]$$

Thus, Equation [1b] indicates that increasing BSRT with low HRT will result in high PAC mixed liquor concentration. Therefore, plant performance can be controlled by changing either carbon feed rate or BSRT. However, the steady state assumption of equation [1b] may not be true due to the fact that the wastewaters for which PAC addition is favored tend to vary significantly in hydraulic loading and in composition [2]. The latter may require adjustment in influent carbon dose while the former affects the detention time of carbon. Nevertheless, Flynn's [22] approach to determination of MLVSS

is more or less theoretical rather than experimental. The method should be confirmed experimentally, before it is extensively used.

Based on these considerations, Arbuckle and Griggs [2] proposed an equation similar to Lee and Johnson [40].

$$VSS_E = VSS - f\ (SS)\ X \qquad [7]$$

where, VSS_E = actual MLVSS representated as microbes

VSS = experimentally measured MLVSS

f = PAC fraction of total MLSS

SS = experimental value of MLSS

X = volatile fraction of PAC in MLVSS (to be performed separately with PAC)

The investigators discouraged the use of Equation [1b] to compute the PAC fraction of total MLSS. An attempt was made to develop a procedure that would actually differentiate biological MLVSS from MLVSS induced by carbon. The approach was to use a particular sludge (obtained from Kanaplaha Waste Treatment Plant, Gainesville, Florida) with previously determined MLVSS concentrations, and mix it with various concentrations of PAC. Thus, the percent concentration of PAC in the sludges ranged from 0 to 100 percent. The sludges were then subjected to different temperatures to determine the volitalization of PAC at different temperatures. Based on the data presented in the literature, the authors claimed that

data obtained at 400°C appeared closest to the "actual" data (550°C). Actual data here refers to MLVSS obtained as recommended by Standard Methods for Examination of Water and Wastewaters. Unfortunately, the data was not reported in their article. Nevertheless, the data were reported relatively (i.e. in terms of percentage). The authors, however, conducted further experiments using 400°C on the consideration that oxidation of PAC would be fastest at the highest temperature. The authors developed the following equation in their further study.

$$f = \frac{V_{400} - 0.9V_{550}}{X_{400} - 0.9X_{550}} \qquad [8]$$

Where,

V_{400} = fraction of MLSS at 400°C

V_{550} = MLVSS at 550°C

X_{400} = PAC fraction at 400°C

X_{550} = PAC fraction at 550°C

Equation [8] is highly questionable because of the temperature (400°C) used in their further investigation based on the data presented in their article. Table 5 represents the base for which the temperature (400°C) was selected. Table 5 indicates that the closest temperature was 350°C rather than 400°C.

Furthermore, Equation 8 was tested for only one biological sludge. In essence, more biological sludges should be tested to determine its suitability in accounting for MLVSS in a PACT

Table 5. Volatilization of PAC at Different Temperatures [2].

Temperature, °C	Actual Percent PAC			
	13.8	27.7	49.1	65.8
300	11.7	12.4	32.1	55.6
325	19.2	22.7	41.8	61.1
350	23.2	25.9	45.3	64.4
375	14.9	21.1	39.2	61.1
400	17.6	26.1	43.0	64.3

system. In addition, in the mathematical model developed, considerable error existed at low PAC when it was tested.

Another approach was that used by DeWalle et al. [17]. They stated that virgin PAC used in the study constantly volatizes 79 percent of its weight. It was on the assumption of constant volitalization that the MLVSS results were corrected.

Summary of Literature Review

Much work has been done on the addition of powdered activated carbon (PAC) to activated sludge systems. Little or no knowledge exists on the effects of PAC for biodegradable and poorly adsorbable organics in wastewaters. Moreover, the effects of PAC on the sludge of cellulose acetate manufacturing wastewater is not documented elsewhere in the literature.

Reported research has shown that PAC in the biological reactor enhances the removal of COD, BOD, and TOC. It aids settling and produces a compact, dark sludge. PAC also improves process stability in the presence of shock loadings to the system, and better effluent quality is attained over a wide range of F/M ratios. Various carbon dosages have been shown to substantially enhance substrate removal. The performance of PAC in the reactor is dependent upon BSRT, carbon dose rate and HRT. Increasing BSRT at constant PAC dose increasingly improves the removal of organics. The

addition of PAC into a biological reactor causes changes in parameters such as MLSS, MLVSS and introduces a new one, carbon detention time. The carbon detention time is equal to BSRT. Method of interpreting data on MLVSS is not clear in the existing literature.

Little literature exists on the effects of PAC on biokinetic constants. In the few articles published there exist differ- ences in the way PAC changes biokinetic constants. Considerable controversy exists in the literature over the mechanism of substrate removal. Based on the literature reviewed, it may be due to synergistic effects of bioactivity and bioregeneration.

Chapter III

MATERIALS AND METHODS

This experimental study was conducted in two distinct phases. The objective of the first phase was to determine the powdered activated carbon (PAC) with the highest removal capacity for the organics in the wastewater in order to maximize the efficiency of PAC in the biological reactor. This phase was comprised of equilibrium time studies, and an adsorption isotherm test. Following this, two bench-scale, heterogeneous culture, continuous-flow completely mixed activated sludge reactors operating in parallel with and without PAC were set up. The transport of wastewater, wastewater components, sampling site location, preservation, experimental materials, and procedures will be discussed in the following sections.

Wastewater Components, Sampling Point, and Transport

The wastewater used in the study was the cellulose acetate manufacturing wastewater from the Celco plant located between Narrows and Pearisburg, Virginia. The wastewater contained acetic acid, acetone, dimethyl ketone (DMK), and other solvents, and organic chemicals such as mesityl oxide (MeO), di-isobutyl (DIBK), methyl cynanide (CH_3CN), methylethylyketone (MEK), and benzene. This wastewater was used throughout the experimental study.

There were two wastewater sampling points at the Celco plant. The first sampling point was from the influent channel after screening but before equalization. The manhole is located near the sludge thickener and the laboratory building. The pH of the wastewater from this location fluctuated around 6.2 to 6.3. It was found that this wastewater does not represent the typical characteristics of wastewater entering the aeration basin. As a result, a new sampling point was established at the effluent point of the equalization basin where the pH was typically 4.7. Wastewater sampled at this point represented the influent wastewater characteristics of the aeration tank. This sampling point was used throughout the experimental study. However, both the first and second sampling points were used in the equilibrium time adsorption studies.

Each time the wastewater was collected, it was transported immediately to the Environmental Engineering laboratory, Department of Civil Engineering, Virginia Polytechnic Institute and State University, and stored at $4^{o}C$. In this way, the sample remained fresh each time it was used. Each batch of the wastewater was stored a maximum of one week. In other words, regardless of the amount of wastewater remaining in the refrigerator at the end of six days, a new sample wastewater was brought from the treatment plant and the old wastewater was thrown out. It was assumed in this study, that the COD lost due to storage and transport was negligible. In

addition, variation in pH during transportation and storage was also assumed to be insignificant.

Equilibrium Time Studies

The equilibrium time studies were conducted at two pH values. The pH values of the experiments were: the pH of the wastewater as collected and pH 7 which was obtained by adjustment with 0.5 N sodium hydroxide (NaOH) and 0.02 N sulfuric acid (H_2SO_4). Activated carbon obtained directly from the Celco plant was used for the equilibrium time adsorption studies. The carbon was originally in granular form, and, is used for acetone recovery by the manufacturing plant. The carbon was then ground with a mortar and pestle, and, sieved to a particle size between 0.0017 to 0.0029 inches. The geometric mean of the particles of carbon was 0.0022 inches using the mathematical formula:

$$D_{mp} = \sqrt{D_1 \, D_2} \ldots\ldots\ldots \qquad [14]$$

where,

D_{mp} = the mean particle size of carbon

D_1 = diameter of sieve opening no. 200

D_2 = diameter of sieve opening no. 300

The wastewater was first centrifuged [Beckman centrifuge Model J-21C) at 5 rpm for 10 minutes. The centrate was then filtered using 5.5 cm Whatman glass microfilter. The

wastewater was centrifuged, however, to ease the filtration of the samples.

Following this two one-liter beakers were used for each experiment, and 600 mL of the wastewater were added to each beaker. One beaker of the wastewater was left at the original pH, and the other was adjusted to a pH of 7.0. Both beakers were dosed with 120 mg of the powdered activated carbon (PAC) to obtain a carbon concentration in each beaker of 200 mg/L. The two beakers were then subjected to jar testing and samples were taken at the following time intervals: 1 min., 30 min., 45 min., 1 hr., 1.5 hr., 2 hr., 4 hr., 7 hr., 20 hr., and 24 hr. The jar test apparatus stirrers were allowed to revolve at 55 revolutions per minute. This speed was selected to provide good contact of PAC with the wastewater. The temperature of the test was maintained at 23 $\pm$ 1.5^{o}C by performing the experiment in the constant temperature room.

Adsorption Isotherm Test

The adsorption isotherm test was conducted to determine the carbon best-suited for treatment of the wastewater. Once the equilibratiom times (12 and 24 hours) and a pH value were selected, the adsorption isotherm study was performed. The centrifuged and filtered centrate wastewater was added to a two-liter beaker and the pH was then raised to 7.0. Following this, ten glass Erlenmeyer flasks were set up and 150 mL of the wastewater was added to each flask. Subsequently, the flasks were dosed with PAC according to Table 6.

Table 6. Various Carbon Dosages in Flasks Containing 150 mL Wastewater.

Flask No.	Carbon Dosage (mg/L)	Dosage (mg)
1	100	15.0
2	150	22.5
3	200	30.0
4	300	45.0
5	400	60.0
6	500	75.0
7	600	90.0
8	800	120.0
9	1000	150.0
10	2000	300.0

A control containing no PAC but the same quantity of wastewater was set up to ensure that removal of organics was primarily due to adsorption mechanisms. The flasks were tightly sealed with aluminum foil and placed on a rotating gang shaker without speed control. The speed of revolution was, however, sufficient to provide good contact of PAC with wastewater. At the end of twelve hours, samples were withdrawn from each of the flasks and they were set up again for the next twelve hours. At the end of the twenty-four hours, samples were again taken from the flasks. The samples were filtered to remove the particles of PAC and stored at 4°C. One to two drops of concentrated HCl acid was added to the samples to preserve them.

The adsorption tests were carried out at a constant temperature of 23 ± 1.5°C. The tests were performed using both Celco carbon and Nuchar WV-W, a product of WestVaco (Covington, VA). The Nuchar WV-W used had a particle size of 12 x 40 mesh but was reduced to a uniform particle size of 0.0022 inches. The carbon, based on the manufacturer's instruction, has the capability to remove residual and toxic organic substances, taste and odors. Also, it controls foam-causing synthetic detergents and has a catalytic effect on flocculation. It should be noted that Whatman filters (5.5 cm diameter) were used for all of the filtrations performed.

TOC Analytical Procedure

The samples collected from the equilibrium time studies and adsorption isotherm test were analyzed for TOC using a Dohrmann TOC analyzer (Division of Xertex, formerly EnviroTech, Santa Clara, CA; Model DC-50A/52A). The standard used for TOC was potassium hydrogen phthalate, KHP ($C_8H_5O_4K$). The KHP aqueous solution was stored at 4°C. Samples for TOC analysis and the KHP standard solution were allowed to warm to room temperature before performing the analyses. This was done to eliminate errors associated with liquid volume. Once the instrument was standardized with KHP aqueous solution, the samples collected were analyzed. Sample injections were made with a 50 microliter-syringe (Hamilton TP4050, Unimetrics Corp.; Calif.). To ensure adequate sensitivity of the instrument, 30 microliters of sample were injected for each analysis. All sample readings were taken in triplicate with a reproducibility of 3 ± 1 percent. The bottles used to store the samples for TOC analysis were brown, having rubber tops according to Standard Methods for Water and Wastewater Examinations.

Laboratory Scale Activated Sludge Process

This subsection describes the second phase of this experimental study. Following the adsorption studies, two laboratory scale, continuous-flow reactors with internal recycle were set up to operate in parallel. The reactors were

designated as R_A and R_B. R_A contained PAC while R_B was the biological control unit containing no PAC. Figure 2 illustrates the experimental design of the reactors.

This experiment originally intended to use a pump head that would divide the flow equally to the two reactors. The rationale behind this was to ensure equal feed rates to the reactors at all times. Regrettably, it was difficult to obtain such a pump. A close approximation to this approach, after Scaramelli and DiGiano [58], was attained by using a multiple pump head capable of pumping at a very slow rate. The Manostat Cassette pump head (Manostat Corp.; New York), in addition to gravity, was used to pump the influent wastewater from the carboy to the reactors. The influent wastewaters entering R_A and R_B had the same characteristics because they were from the same carboy.

The influent wastewater rate was 4.32 L/day, to obtain a hydraulic residence time in conformity with the Celco wastewater treatment plant hydraulic retention time. Thus, the hydraulic retention time was 3.8 days. It is believed that this feed rate was slow enough to ensure microbial degradation of all the biodegradable organics. The total volume of each was bioreactor was 16.5 liters. The reactors were supplied with air from air supply lines attached to the wall. For each reactor, air was passed through a Y-tubing connection containing two diffuser stones of the same size, into the aeration basins of the reactors.

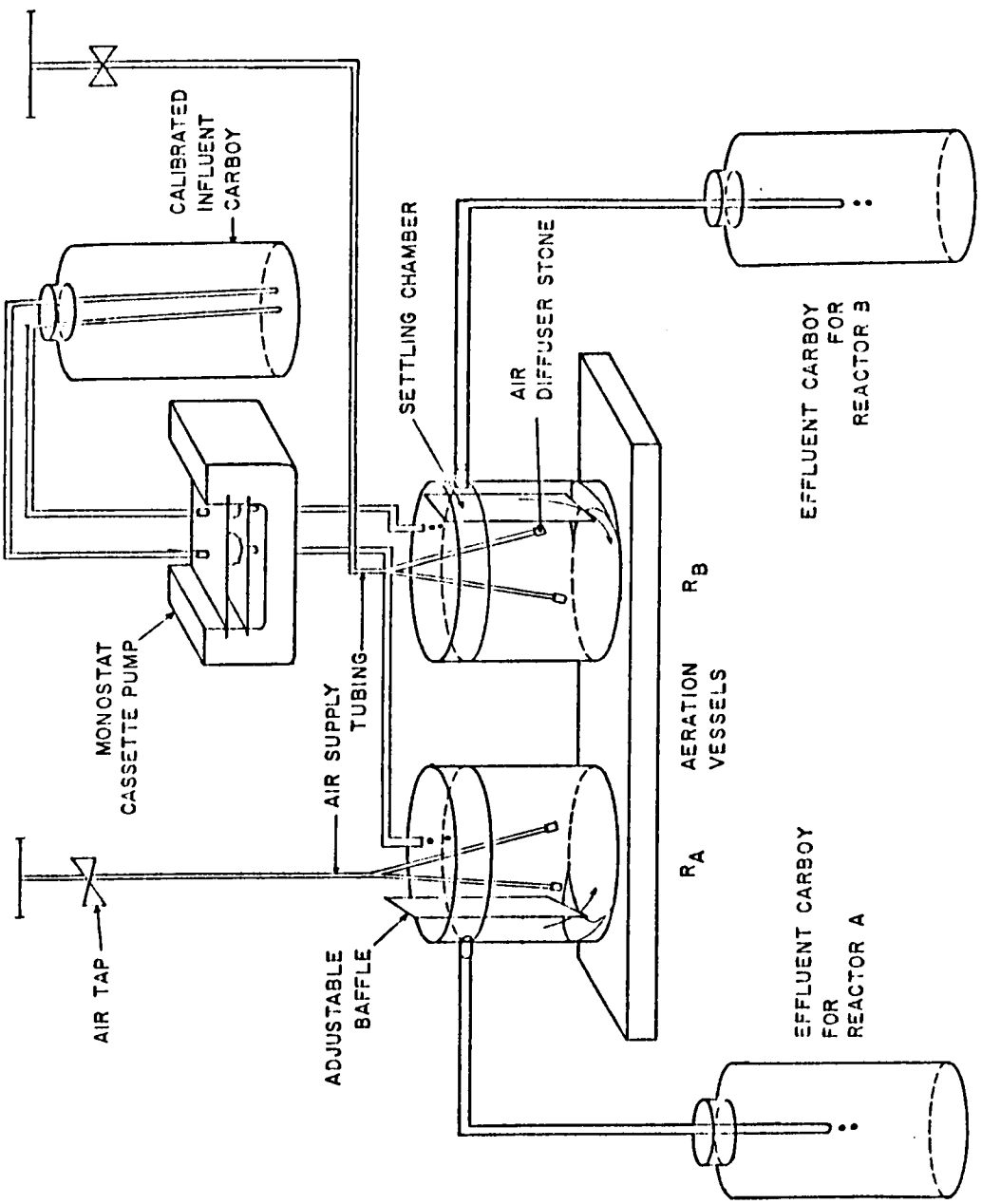


Figure 2. Experimental System.

The reactors had adjustable baffles with automatic recycle. The baffles were raised to the heights that allowed proper recirculation of sludge. The influent lines were changed every two weeks. These changes were made for the following reasons:

1. To prevent microbes from growing in the influent carboy and thus, avoid contamination by filamentous organisms of the substrate going into the reactors.
2. To prevent biodegradation of the wastewater in the carboy, to maintain the integrity of the kinetic model. The kinetic model assumes that influent substrate is essentially constant.

The effluent lines were connected behind the reactors, and were changed at monthly intervals. All tubing used was amber, thin wall tubing.

Investigational Parameters and Method of Sample Handling

The parameters monitored throughout the course of the experiments are shown in Table 7. In addition to the parameters shown here, microscopic examination of the biological sludges was performed for each of the reactors. The pH, dissoved oxygen concentration (DO), mixed liquor volatile suspended solids (MLVSS) and mixed liquor suspended solids (MLSS) were monitored almost daily.

A pH meter (Fisher, Pittsburgh, PA; Model 120) was used to measure the pH values of the aeration vessels and the influent

Table 7. Experimental Parameters Monitored

Influent Parameters	Effluent Parameters	Aeration Vessel Parameters
pH	pH	MLSS
COD	COD	MLVSS
TOC	TOC	DO
% acid	% acid	Temperature
acetone	acetone	pH
% solvent	% solvent	SVI
Mesityl oxide	Mesityl oxide	ZSV

and effluent wastewater samples. The pH meter was standardized with standard Fisher buffer solution (4, 7, 10) before daily measurements were performed. The buffer solutions were changed periodically. The standard DO concentration test was performed with an oxygen meter (YSI, Yellow Springs, OH; Model 54). The temperature of the aeration vessel was also measured with this instrument. Each time the DO level of one reactor was measured, the instrument was recalibrated. The same instrument was used to perform tests of oxygen uptake rate.

A 300 mL BOD bottle was used to measure the oxygen uptake rate. The BOD bottle was always kept in the constant temperature room so that the temperature of the mixed liquor from the aeration vessel when in the bottle was essentially equal to that in the aeration basin. In essence, there was no error due to temperature differential. The aeration vessel liquor was adequately displaced when the probe was inserted into the bottle. A magnetic stirrer was used only when it was necessary; i.e. inadequacy of stirring mechanism of the probe. Once the initial DO reading was stabilized, readings were taken at 15, 30, 45 seconds, 1 minute and, the rest of the time was distributed depending on the rate of oxygen utilization. Readings were taken until oxygen became limiting. A plot of DO against time was constructed, and the slope of the line of best fit was determined to be the oxygen uptake rate (OUR). The specific OUR was computed by dividing

the oxygen uptake rate by MLVSS in the aeration vessel.

Each time MLSS and MLVSS tests were performed, the baffle was removed, and the aeration tank was properly stirred to keep solids in suspension. The volume of the liquor used in the test depended upon the concentration of the liquor in the aeration vessel and it's filtrability. Simply stated, the test was performed according to Standard Methods for the Examination of Water and Wastewater.

A blank MLVSS was run for R_A at the various PAC equilibrium concentrations of the experiment. There were three equilibrium concentrations: 20, 160, and 280 mg/L. The blanks for each of the concentrations were prepared by proportioning the equilibrium PAC concentration. For example, at 280 mg/L PAC concentration with the reactor volume of 16.5 L, the amount of PAC in mass units was 4620 mg. Therefore, the amount of PAC added to 200 mL of distilled water was 56 mg. Thus, 56 mg of PAC in 200 mL of distilled water is equivalent to the equilibrium concentration of 280 mg/L in the reactor. Each blank was made in triplicate. The rest of the equilibrium concentrations of PAC were similarly treated. Thus, MLVSS was corrected for PAC by subtracting the blank value from the value obtained from the R_A.

The influent COD and TOC samples were unfiltered. Due to difficulty in standardizing the TOC analyzer, sample volumes of 30 mL were preserved by two drops of concentrated HCl acid, and stored at $4^{o}C$ with minimum delay. The storage time,

however, was a maximum of ten days. The TOC analyses were performed as outlined in the Standard Methods section titled TOC Analytical Procedure. The effluent TOC and COD samples were filtered through 5.5 cm diameter, 1.5 micrometer, Whatman filter paper. The filtrate was again filtered with 0.45 μm filter paper to remove all bacteria.

The filtered samples for COD were also stored at 4°C when there was a delay in COD analysis. For example, if it was envisaged that testing procedures could not be performed within 30 minutes, samples were properly covered with aluminum foil, and stored at 4°C. This was done to maintain the bactericidal and/or bacteriostatic conditions of the sample. The COD test was performed according to section 508 of Standard Methods for the Examination of Water and Wastewater with slight modifications. For any modification, the volume of concentrated sulfuric acid and the volume of the sample plus volume of the dichromate solution must be in ratio of 1 to 1, and, this was maintained [57]. A smaller volume of concentrated sulfuric acid decreases the oxidizing power of the solution with a considerable effect on the COD result. In addition, a large volume will result in a large blank consumption of dichromate.

Trial samples using 20 mL of the raw wastewater were tested as outlined by Standard Methods for the Examination of Water and Wastewater. At the end of the two hour trial, the samples were observed to be green, indicating that no

titration was needed. The implication of this result was that the COD concentration of the wastewater was greater than 1000 mg/L. Standard Methods only indicated a testing procedure for wastewaters with a COD value less than 1000 mg/L. Therefore, the testing procedure was modified as follows:

1. Each time the COD test was performed, only 10 mL of the influent sample was used. The sample was then diluted with distilled water, and also, the dilution factor was noted. The degree of dilution required was dictated by the COD concentration of the wastewater. To know whether the incoming wastewater to the system was high or low was based on experience. If a low COD value was anticipated, the wastewater (10 mL) was diluted by 40 mL of distilled water, resulting in a dilution factor of 5. In order to determine the actual value of the COD, the measured value was multiplied by the dilution factor, which is 5 in this example.
2. The volume of sulfuric acid used was 15 mL and that of potassium dichromate solution, 5 mL.
3. The COD of the wastewater was tested at different boiling times (45 minutes, 1 hour and 2 hours). In each case, two representative samples were prepared, indicating a total of six samples used for the test. These samples were simultaneously boiled, and ended the test at the various times indicated. It was

determined that the COD values for 45 min., 1 hr., and 2 hr. were, respectively, 3160, 3320, and 3359 mg/L. Taking the 2 hour value as the standard value, boiling for only 45 minutes resulted in 11.2 percent error while the 1 hour boiling time yielded an error of 1 per cent. The difference between the latter two may be error due to the reading of the concave meniscus of the liquid in the burette. Nevertheless, the percent error was compensated for by boiling for 1 1/2 hours. In essence, all COD titrations performed in this experiment were boiled for 1 1/2 hours rather than 2 hours.

It should be recalled that the effluent samples were tested according to Standard Methods, but were boiled for 1 1/2 hours. In addition, precautions were taken during the addition of concentrated sulfuric acid reagent to minimize the volatilization of low molecular weight acids contained in the wastewater.

The acetone, MeO, percent acid, and percent solvent loadings to the reactors were analyzed by the laboratory staff of the Celco manufacturing plant since the instrument to perform these tests was unavailable in the laboratory at VPI. The samples were stored at $4^{o}C$ in the refrigerator. However, the samples were frozen if they were to remain one to two weeks in the laboratory before sending them out for analyses.

The zone settling velocity test was begun by removing the baffle and mixing the aeration vessel completely to put all of the biological sludge in suspension. Sample was immediately withdrawn from the tank and transferred into a 1-liter graduated cylinder that was recalibrated in inches. The solid-liquid interface heights were taken at time intervals of 1, 5, 10, 15 minutes, and 1 or 2 hours, depending upon the settleability of the sludge. The recorded interface heights were then plotted against the time intervals, and the zone settling velocity (ZSV) was obtained by constructing a tangent to the curve. The SVI was sometimes taken at the same time as ZSV. A separate test was run occasionally. Regardless of whether SVI was run simultaneously with ZSV or not, the procedure was in conformity with Standard Methods.

It should be noted that the testing procedures described above apply to the reactors with and without PAC. Precautions were taken to ensure that samples from both reactors were similarly treated.

Start-up of Bioreactors

The sludge used for this study was activated sludge from the Celco cellulose acetate wastewater treatment plant. On July 11, 1984, the first sludge for the experiment was brought to the laboratory. The sludge was aerated, and then poured into the reactors. Regrettably, the reactors were run for only six days due to formation of a "jelly" that prevented the

sludge from settling. "Jelly", a strange phenomena, is a type of activated sludge bulking that makes the sludge in the clarifier gel and eventually float to the surface in the form of chunks of jelly. After floating, it becomes black with time, because the sulfate reduction that occurs when the sludge goes into an anaerobic state because oxygen cannot diffuse into the gelled sludge. The initially obtained sludge was eventually discarded.

As a consequence, a new sludge was brought from the plant on July 17, 1984. The reactors were then set up with this sludge. Unfortunately, the sludge condition at this time was not better than the first sludge. Using the concept that all conditions should be corrected before proceeding with experimental investigations, an attempt was made to define the problem, and nitrogen deficiency was proposed as a factor that was causing the "jelly" problem. Consequently, 15 mg/L of nitrogen was added in the form of ammonia chloride (NH_4Cl) for two weeks. Subsequently, nitrogen was added using an approach based on biomass production as recommended by Benefield and Randall [5].

$$\text{nitrogen requirement (mg/L)} = 0.122\,\Delta X \qquad [10]$$

$$\text{where } \Delta X = XV/\theta_c \qquad [11]$$

$$\text{nitrogen added in mg/L} = 0.122\,XV/Q\theta_c \qquad [12]$$

where,

X = MLSS in reactor, Mass Vol.$^{-1}$

θ_c = BSRT days

V = Aeration volume, volume

Q = Volumetric flow rate

In addition, the calculated value was scaled up by increasing the amount required by 8 mg/L.

Table 8 summarizes the sequence of nitrogen addition to the wastewater during the experimental study. The reactors were operated to steady state and the "jelly" was cleared up before the investigational study of the effects of PAC on the activated sludge was begun.

In addition to this problem, the reactors were foaming excessively to a point that the liquor from the aeration vessel were messing up the floor in the constant temperature room. Several problems exist with foaming:

- Loss of biomass from the reactors
- Constant removal of the foams manually which is cumbersome
- More importantly, the potential danger of fouling up the influent lines by microbes.

The foaming problem was, however, solved by adding a chemical anti-foaming agent into the influent carboy that reduced the surface tension of the liquor in the aeration vessels. It is worthwhile to note that the anti-foaming agent was not applied constantly throughout the experiment, rather it was added only when the foaming became undesirable.

Table 8. Sequence of Nitrogen Addition

Date	Nitrogen added (mg/L)
7/17 - 8/4	15
8/5 - 8/11	75
8/12 - 8/21	20
8/22 - 8/28	67
8/29 - 9/23	47
9/24 - 9/29	70
10/3 - 10/15	50-60
10/16 - 10/20	60
10/20 - 10/31	50
11/1 - 11/30	75

Method of PAC Addition to Reactor A

Based on the results of the adsorption isotherm test, neither Celco carbon nor Nuchar WV-W were used in the reactor. Instead Sorbonorit 3B supplied by the Celco plant was used in the experiment. A similar carbon Norit SA-5 was used by Specchia and Gianetto [68] to increase the purifying capacity of an activated sludge treatment plant fed with dye-works wastewater. The physical properties of Sorbonorit 3B are presented in Table 9.

The Sorbonorit was blended with an electric blender and dried at a constant temperature of 103°C. It was sieved and the particle size that was retained on sieve no. 300, but passes through sieve no 200, was used in the test. The respective sizes of the sieves were 0.0017 and 0.0029 inches. Thus, the mean diameter of the particles used was 0.0022 inches.

The initial PAC concentration added to the reactor was 20 mg/L. This amount was added daily for fourteen days, and the concentration of PAC built up to 280 mg/L. The PAC was added daily and wasted as a function of biological solids retention time. This equilibrium concentration was maintained in the reactor by wasting and replacing the amount until steady state was reached as measured by MLSS, COD, and TOC. Following the 280 mg/L experiment, a new equilibrium concentration of 160 mg/L was established by wasting daily without PAC replacement. Similarly, 160 mg/L of PAC was reduced to 20

Table 9. Physical Properties of Sorbonorit 3B

Properties	Typical Values
Bulk Density	400 g/L
Pellet Diameter	2.9 mm
Total Internal Surface Area[1]	1200 - 1300 mg/g
Voids, packed	0.4
Iodine No.	1000 - 1100

1. from benzene adsorption test

mg/L. Thus, the three experiments were performed at mixed liquor carbon concentrations of 280, 160, and 20 mg/L.

The relationship between the actual concentration of activated carbon in the reactor and the daily addition of carbon is summarized by the following mathematical development and the graphical illustration shown in Figure 3.

Mass of carbon added on the first day = $C_A V$ [13]

Mass of carbon wasted on the following day = $\frac{C_A V}{\theta_C}$ [14]

Note: $\frac{C_A V}{\theta_C}$ includes both intentional and inadvertant wasting

where θ_C and V are as defined previously

C_A is the concentration of PAC, mass volume $^{-1}$

Amount of PAC added on the second day:

$$CM = \frac{C_A V}{\theta_C} + C_A V \qquad [15]$$

Thus, new carbon concentration in the reactor at the end of the second day

$$CN = CM - \frac{C_A V}{\theta_C} + C_A V \qquad [16]$$

Replacing equations [13] and [14], respectively, as K and WS, equation [16] becomes

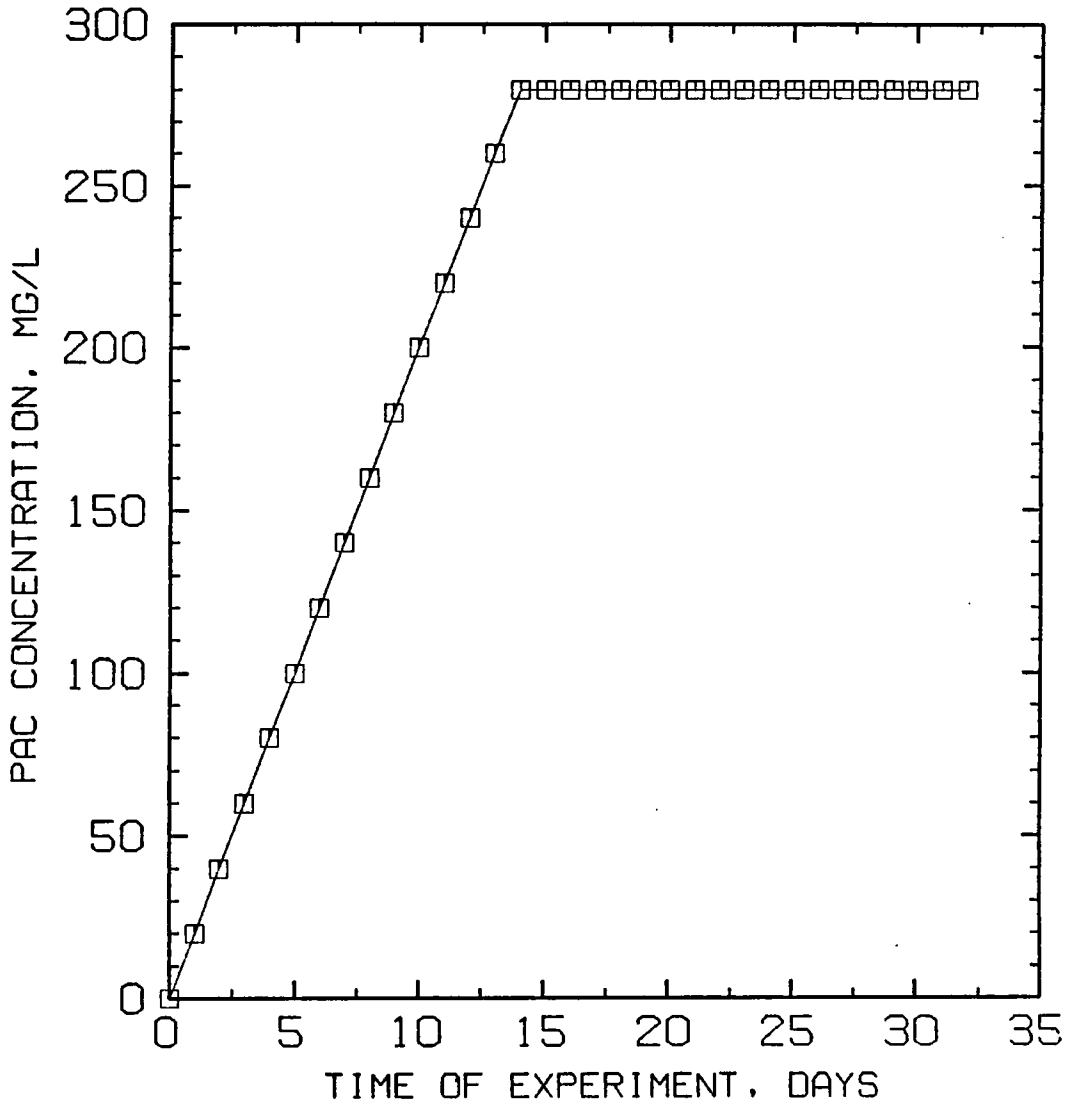


Figure 3. Build up of PAC in Bioreactor A.

$$CN = CM - WS + K \qquad [17]$$

Following the procedure of developing equation [17], CM is a function of WS and WS is dependent upon CN. Therefore, Equation [17] becomes

$$CN_i = CM_{i,i-1} - WS_{i,\ i-1} + jK \qquad [18]$$

CN_i = cumulative PAC concentration in the reactor at the end of i^{th} day, mass unit

i-1=j, cumulative number of times carbon was wasted.

Thus, at equilibrium, $CM_{i,i-1} = WS_{i,i-1}$ and Equation [18] becomes

$$CN_i = jK \qquad [19]$$

For example, at the first day when addition of PAC began, $CN_1 = CM_{1,0} - WS_{1,0} + jK$. $WS_{1,0}$ equal to zero because no wasting of PAC was performed, and i-1=0. $CN_1 = CM_{1,0} = C_AV$.

When wasting is performed without replacement, $CM_{i,\ i-1} = 0$ and Equation [18] reduces to

$$CN_i = jK - WS_{i,i-1} \qquad [20]$$

The method of PAC addition is shown in Appendix B with illustrations of applications of Equations [18] and [20].

Typical Experiment

The two laboratory scale activated sludge units were operated at a biological solids retention time (BSRT) of fourteen days. In order to maintain the BSRT constant, effluent suspended solids were determined daily for each unit. Based on this, the amount of manual wasting required for the reactors was calculated. The computation of BSRT was based on Monod's biological kinetic concepts developed by Lawrence and McCarty [39]. The BSRT, is defined as $X/\Delta x/\Delta t$ where X is the total MLSS wasted from the reactor, and $\Delta x/\Delta t$ is the total solids wasted from both the aeration vessel and the effluent weir.

$$\theta_c = \frac{X}{\Delta x/\Delta t} = \frac{XV}{Q_w X - (Q-Q_w)X_e} \qquad [21]$$

Where,

V = volume of the aeration vessel, liters

Q = influent flow rate, liters/day

Q_w = sludge wasting rate, liters/day

X_e = solids lost through the effluent line, mass volume^{-1}

The overflow $(Q - Q_w)$ leaving the clarifier was assumed to be Q. This assumption is true since no wasting was performed through the clarifier. Thus, Equation [21] reduces to

$$\theta_c = \frac{XV}{Q_w X + Q X_e} \qquad [22]$$

Solving Equation [22], Q_w becomes

$$Q_w = V/\theta_c - (X_e/X)\ Q \qquad [23]$$

The above Equation [23] was used to determine the wasting rate required each day.

The bioreactors were operated to steady state as measured by COD, specific oxygen utilization and MLSS before PAC was added. Each time an equilibrium carbon concentration was established in reactor A, it was allowed to reach a steady state, and data were collected over the steady state period.

When SVI and ZSV tests were made, and it was determined that only one liter of sludge was needed for wasting, the supernatant was returned to the aeration vessel to minimize hydraulic disturbances, and the concentrated sludge in the cylinder was wasted. Where the amount required for wasting was not one liter, the graduate cylinder was completely mixed to resuspend the sludge, the required amount was returned to the vessel, and the rest was discarded.

At the end of experimental measurements each day, the effluents in the two carboys were discarded. In other words, the effluent in the carboys represented a 24 hour composite sample. The influent volumetric flow rate was adjusted twice daily, in the morning and evening. Powdered activated carbon was added or replaced after wasting each day. The addition of PAC was the last operation in each day.

Chapter IV

RESULTS

This chapter presents the results of this investigational study. The data and figures will be presented in the order of the experiments performed. In addition, comments will be made concerning the data where appropriate.

Equilibrium Adsorption Time Studies

The data obtained for the equilibrium time studies are shown in Appendix C, Table C-1 to C-2. Data in Table C-1 are readings obtained from the equilibrium time study of wastewater with pH of 6.3 collected near the sludge thickener, and Table C-2 are readings obtained from the wastewater at pH of 4.7 from the effluent point of the equalization basin. The tables contains raw data measured experimentally. The equilibrium time curves are, respectively, indicated in Figures 4 and 5. The curves were obtained by drawing the line of best fit curve. It is of interest to note that Figure 5 had more scattered data points than Figure 4. Both curves indicate an unsteady adsoprtion and desorption. Thus, the curves posed the problem of selecting what the best equilibrium time is for this wastewater. Nevertheless, two equilibrium times: 12 and 24 hours were selected, which were the basis of the

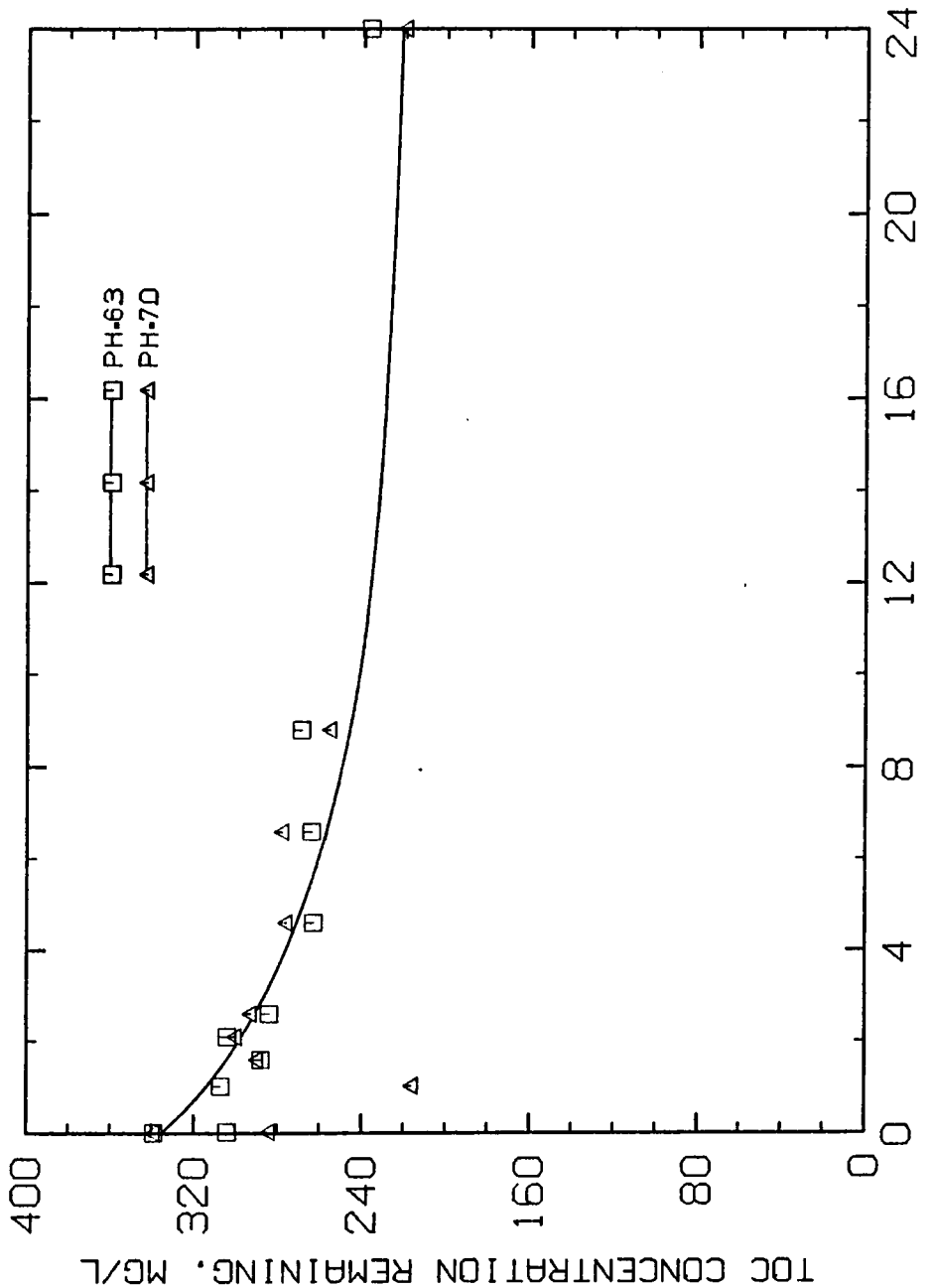


Figure 4. Equilibrium Time Study Curve for Wastewater pH of 6.3 and 7.0.

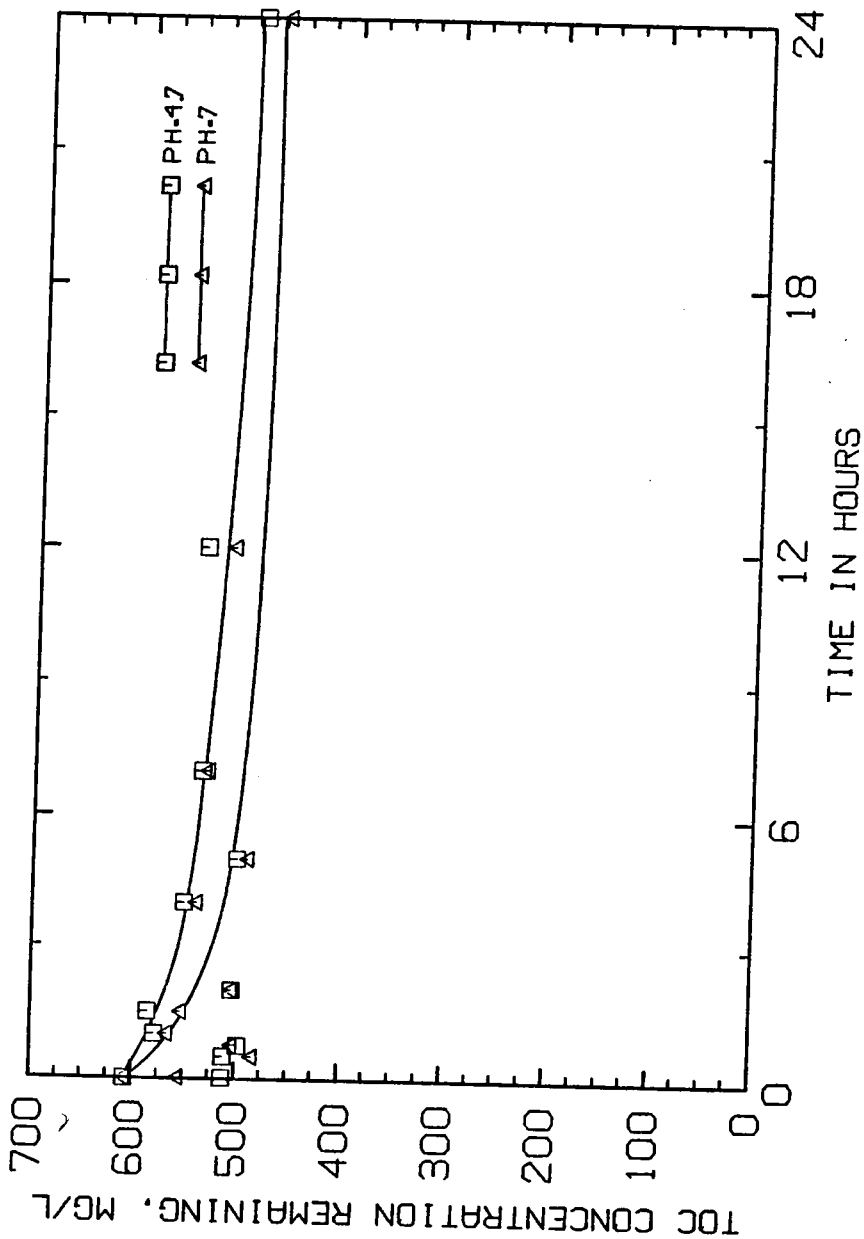


Figure 5. Adsorption Rate Curves for Wastewater pH of 4.7 and 7.0.

adsorption isotherm studies. In the graphs presented for each case, there are two curves, one at the pH of the wastewater, and the other at pH of 7.0 obtained by adjustment.

Regardless of the location where wastewater was collected, adsorption was better at pH 7. Appendix C, Table C-1 indicates lower TOC remaining in solution at the end of 24 hours at pH of 7. In the appendix table cited here, the lowest TOC concentration, which was 216 mg/L, was attained at pH of 7. Taking the averages of the TOC concentration remaining over the period of equilibrium time study, the average TOC concentration remaining at pH of 7 was calculated to be 268 mg/L, while that of pH equal to 6.3 was determined to be 280 mg/L. Furthermore, Appendix C, Table C-2 indicates that the lowest TOC remaining in solution at 24 hours was at pH 7. The lowest value was found to be 472 mg/L while that of pH 4.7 was 494 mg/L. Again, taking the averages of the data presented, pH 7 showed better adsorption than at pH of 4.7. These, in addition to the fact that the pH of the aeration basin fluctuates around 7, caused the adjustment of pH to 7 for the adsorption isotherm tests.

Adsorption Isotherm Tests

The result of adsorption isotherms are often correlated by Langmuir and Freundlich models. The Freundlich equation is represented as follows:

$$X/M = KC_e^{1/n} \quad [24]$$

where X/M = the amount of adsorbate per unit weight of carbon applied

n = constant, mg/L, and 1/n measures the intensity of adsorption (n must be greater than one for adsorption to be favorable).

C_e = is the concentration of solute remaining at equilibrium.

K = a constant that measures the adsorbent capacity and is temperature dependent. mg/mg.

The temperature dependent of K is evidence in the following equation.

$$K = RT\ e^{\Delta S/R} \quad [25]$$

where ΔS is the net change of entropy of adsorption , R is the Gas Law constant. The experimental data were reduced by the following equation.

$$X/M = [(C_o - C_e)/M]\ VI \quad [26]$$

Where X/M and C_e are as previously defined.

VI = Volume of the wastewater used in the test

M = Mass of carbon applied, mg.

C_o = Initial Concentration of TOC, mg/L.

The sample calculations are shown in Appendix D. The reduced data for 12 and 24 hours of equilibration are shown in Appendix Tables C-5 and C-6.

The plots of Freundlich Isotherm for 24 hours of equilibration are presented in Figure 6.

Table 10 summarizes the activated carbon correlation coefficients for the wastewater at pH of 7 based on experimental data. At 12 hours of equilibration, correlation coefficients for Celco and Nuchar WV-W were respectively determined to be -0.68 and -0.50, while at 24 hours, they were found to be -0.78 and -0.92, respectively. The negative signs can be dropped. It is placed here, however, to indicate the trend of adsorption. Simply stated, the sign implies inverse relationship (i.e. with increasing carbon dose, the concentration of TOC decreased and vice versa). In addition, the correlation constants evidenced that the true equilibrium for this wastewater was not 12 hours but 24 hours. Interestingly, equilibrium time of 12 hours was based on Figure 4, representing the wastewater with less complexity and, the adsorption isotherm test was performed with a more complex wastewater. Therefore, no attempt was made to plot the

Table 10. Activated Carbon Correlation Coefficients Based on Experimental Data.

Carbon Type	12 Hours	24 Hours
Celco	0.68	0.78
Nuchar WV-W	0.50	0.92

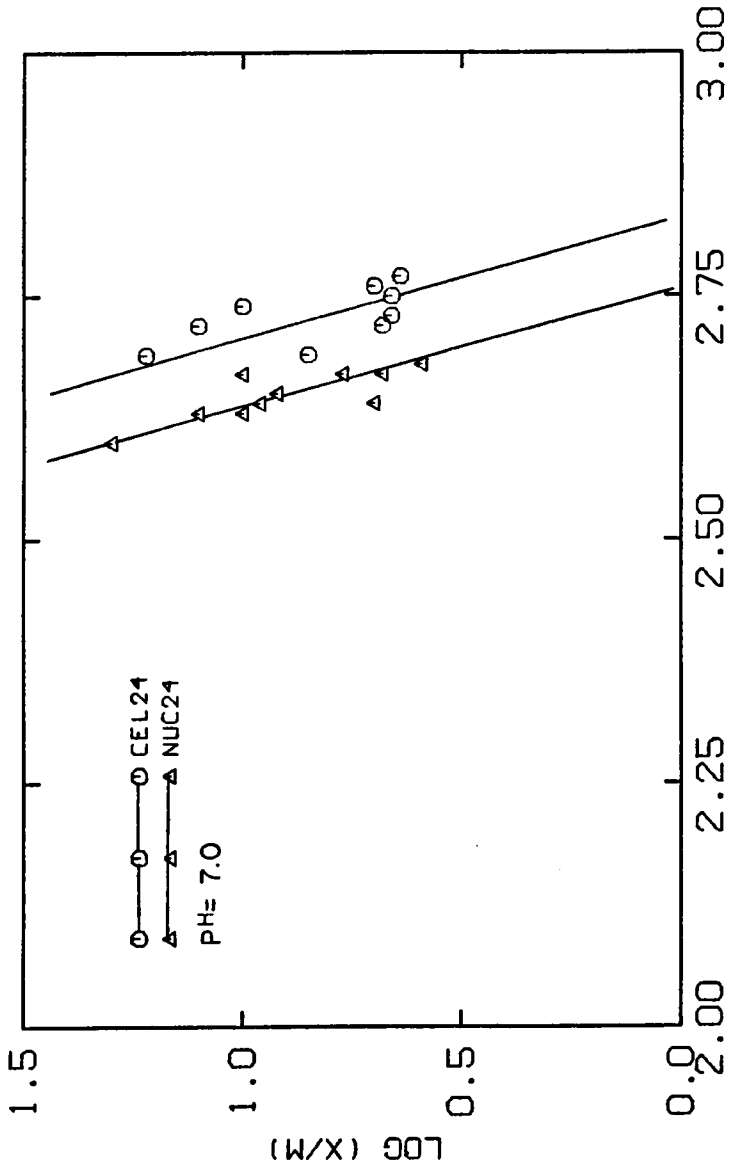


Figure 6. Freundlich Adsorption Isotherm Equilibrated at 24 hours.

Freundlich and Langmuir isotherms at this equlibrium time (12 hours).

The slopes of the Freundlich are very steep indicating small removal of the organics. No effort was made, however, to evaluate the constants.

An attempt was made to correlate the data with the Langmiur model. The Langmuir model is based on three fundamental assumptions [12].

Maximum adsorption is equal to one layer of adsorbate molecules on the adsorbent surface.

Energy of adsorption is essentially constant.

Molecular attractions between the adsorbate molecules are virtually absent

Thus, the Langmuir model is represented as

$$Y = \frac{x_m a C_e}{1 + aC_e} \qquad [27]$$

where

Y = X/M previously defined

a = Adsorption Energy Constant

C_e = as previously defined.

X_m = Monolayer of maximum adsorbate loading attainable.

Equation [27] is linearized into the following form

$$1/Y = 1/X_m + 1/X_m a \ (1/C_e) \qquad [28]$$

A plot of $1/Y$ against $1/C_e$ will result in a straight line with intercept as $1/X_m$ and the slope as $1/X_m a$.

The plots of Langmuir isotherms for this study are depicted in Figure 7 equilibrated at 24 hours. The graphs demonstrate that the data does not fit well to the Langmuir model. As a result, no attempt was made to evaluate the Langmuir Isotherm Constants.

To further shed light into the removability of the the organics in the wastewater, percent TOC removed was calculated for each mass of the carbon loading. Table C-9 in the Appendix contains the calculated values, and the plots of TOC removed are presented in Figures 8 and 9. For the Celco carbon, at 24 hours of equilibration, the percent TOC removed ranged from 4.0 to 19.0 while Nuchar WV-V showed a range of 5.0 to 21.0. At 12 hours of equilibration, Nuchar WV-W showed a maximum TOC removal of 17 percent and Celco carbon indicated 15 percent. The minimum values of TOC removed were respectively 9.8 and 2.9 percent. Both curves showed an unsteady rise in percent removal of TOC by the carbon used.

The two carbon types exhibited different patterns of TOC removal. Appendix Table C-9 and Figure 8 indicates that Nuchar WV-W removed readily most of the adsorbates by the end of 12 hours, followed with desorption and adsorption after 12 hours, and, attained the maximum

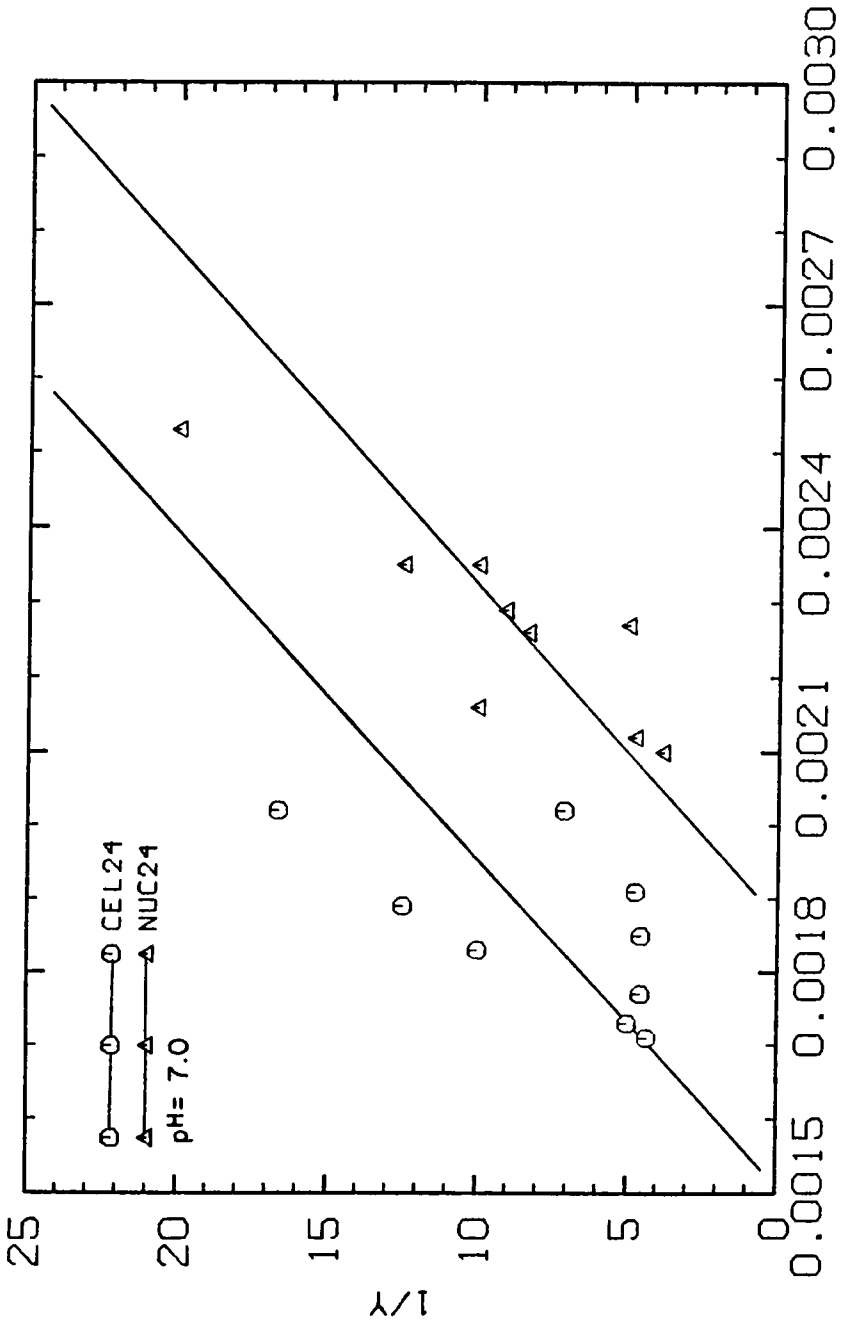


Figure 7. Langmiur Adsorption Isotherm Plots at Equilibrium Time of 24 Hours.

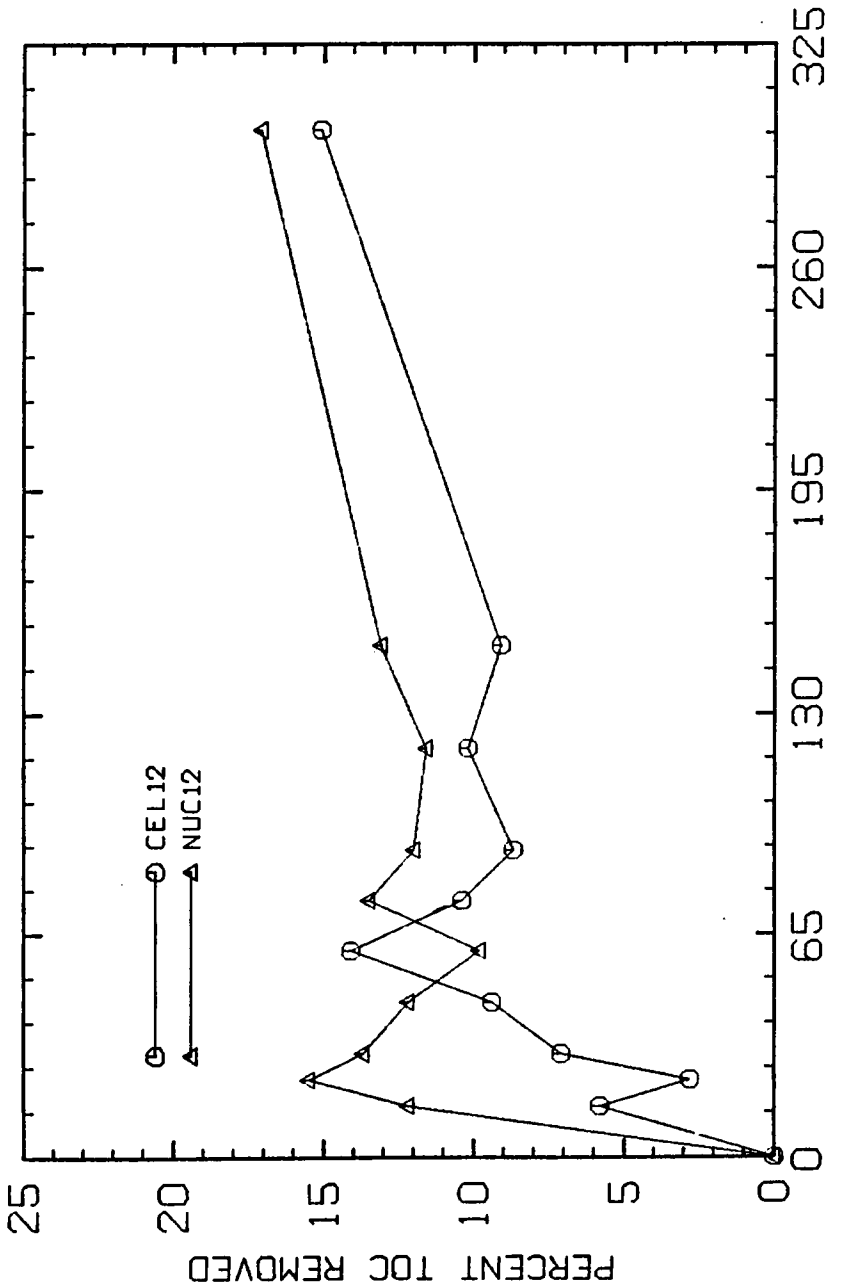


Figure 8. Plots Showing Percent TOC Removed by the Carbons With Wastewater Volume of 150 ml at Equilibrium Time of 12 Hours.

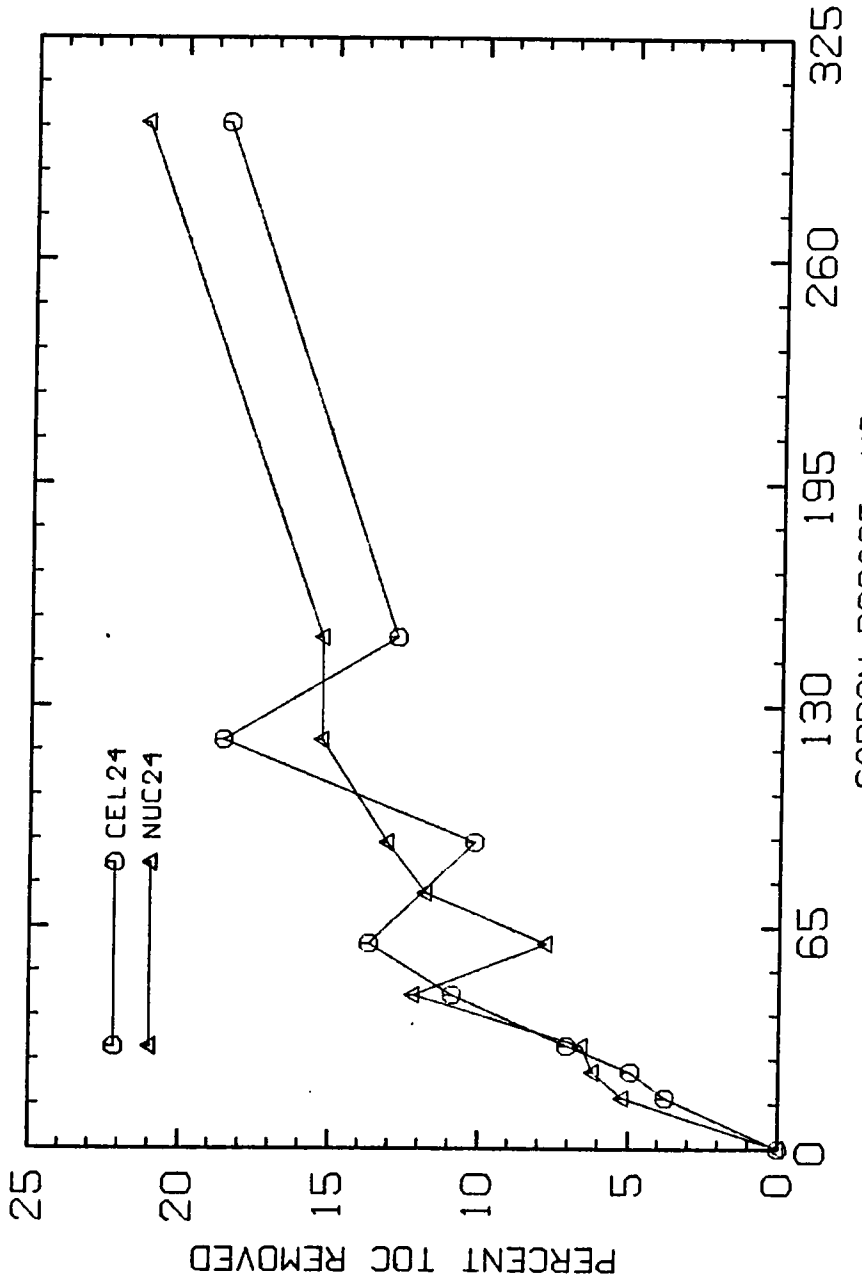


Figure 9. Plots showing percent TOC removed by the carbons with wastewater volume of 150 ml at equilibration of 24 hours.

percent removal at 24 hours. On the other hand, Celco carbon slowly removed the organics by the end of 12 hours with subsequent desorption and adsorption, and achieved the maximum removal at the end of 24 hours time. Nevertheless, the Nuchar WV-W carbon exhibited a consistent pattern in the TOC removed. Regardless, the percent TOC removed by the carbon was poor, indicating poor removability of the organics by physical adsorption mechanism.

Activated Sludge Process

This subsection introduces the results of the investigational study of the effects of activated carbon on the activated sludge units. During the investigational period, "jelly" was observed in both units, and, therefore, data collected during this period will be presented first with subsequent presentation of data collected when the addition of carbon to the reactors began. In addition, observations will be made concerning the data, and figures.

Jelly Formation

No data was collected from the experimental bioreactor units that were run from July 11 to 16, 1984, due to formation of jelly that caused the sludge not to settle at all. As a consequence, the experiment was terminated, and, the contents of the bioreactors were thrown down the drain.

However, when the new sludge was brought on July 17, 1984, parameters such as MLSS, MLVSS, and the pH of the sludge were taken immediately before the addition of the sludge into the units. The value of MLSS was 2340 mg/L with an MLVSS to MLSS ratio of 0.885. The pH was measured to be 8.4. These parametric measurements were made to give an idea as to the cause of jelly formation, based on the fact these parameters are good monitoring tools in an activated sludge process. Not only this, it is often a good practice to know what you started out with in order to identify any potential problems.

Once the reactors were set up for the second time, nitrogen addition was begun simultaneously. After three days, an improvement was noted in the units based on the researcher's observation. Nevertheless, sludge settleability tests were not performed because it would take nothing less than 10 hours to obtain a zone settling velocity curve. On the fifth day (7/22/84) of the run, there was a remarkable improvement, and therefore, full scale experimental measurements were begun. Table 11 shows the parameters measured before the commencement of powdered activated carbon addition to the bioreactor. The aeration pH of unit A was lower than that of Unit B as Table 11 indicates. The COD and TOC loadings to the system were fairly low. It should be noted that no wasting was performed during this period due to loss of solids through

Table 11. Parameters measured during the period of jelly formation.

Date	MLSS	MLVSS	% Volative SS	COD	TOC	pH*	DO
7/20/84	-	-	-	-	-	8.0	4.8
	-	-	-	-	-	8.2	4.8
7/21/84	-	-	-	-	-	8.0	5.5
	-	-	-	-	-	8.2	5.5
7/23/84	1750	1420	0.811	-	-	8.1	5.5
	1440	1280	0.889	-	-	8.2	5.5
7/24/84	1920	1480	0.771	[b]1520	[b]473	-	-
	2080	1750	0.841				
7/25/84	1740	1500	0.862	-	-	8.2	5.6
	1810	1490	0.823	-	-	8.2	5.6
7/26/84	1850	1510	0.816	[b]1740	[b]548	-	-
	2060	1560	0.757				
7/27/84	-	-	-	-	-	8.1	5.6
	-	-	-	-	-	8.2	5.6
7/28/84	1880	1510	0.803	2170	591	8.1	-
	1970	1460	0.741			8.2	
7/29/84	1860	1560	0.839	-	-	-	-
	1820	1450	0.797				
7/30/84	2040	1760	0.863	2340	645	8.2	-
	1890	1500	0.794			8.3	
7/31/84	2120	1640	0.774	-	-	8.1	6.5
	1930	1440	0.746			8.2	6.5
8/1/84	1940	1560	0.804	-	-	-	-
	1900	1400	0.758				

- Data were not taken
b Filtered influent COD and TOC
* Aeration vessel pH

NOTE: There are two data presented for a parameter in some instances. The first data correspond to Reactor A while the second data is for Reactor B. The temperature of both reactors averaged 17°C throughout the period of time indicated in the table.

the effluent weirs caused by jelly as evidenced by the MLSS data in Table 11, when compared with the initial concentration of MLSS. In addition, Table 11 indicates that steady state was reached before PAC addition was begun. Figure 10 presents the sludge volume index (SVI) determined for the reactors during this period. The SVI for unit A averaged 488 ml/gm while Unit B averaged 495 ml/gm, thus indicating a difference of 7.0 ml/mg which is within experimental error. Furthermore, microscopic examination of the sludge performed, revealed no filamentous organisms. Rather, protozoa were observed swimming in the sludges.

PAC Addition to the Activated Sludge Unit

Three equilibrium carbon dosages were experimented and will be presented in the order of the dosages to Reactor A (R_A).

Trial Run of 280 mg/L PAC

Figure 11 presents the mixed liquor suspended solids (MLSS) of R_A and R_B operating at biological solids retention time of fourteen days. The first thirteen days on the graph were at various equilibrium carbon dosages, and, therefore, the MLVSS of those days were not corrected for PAC. However, the rest of the MLVSS values during the trial run of 280 mg/L PAC were corrected for MLVSS. A

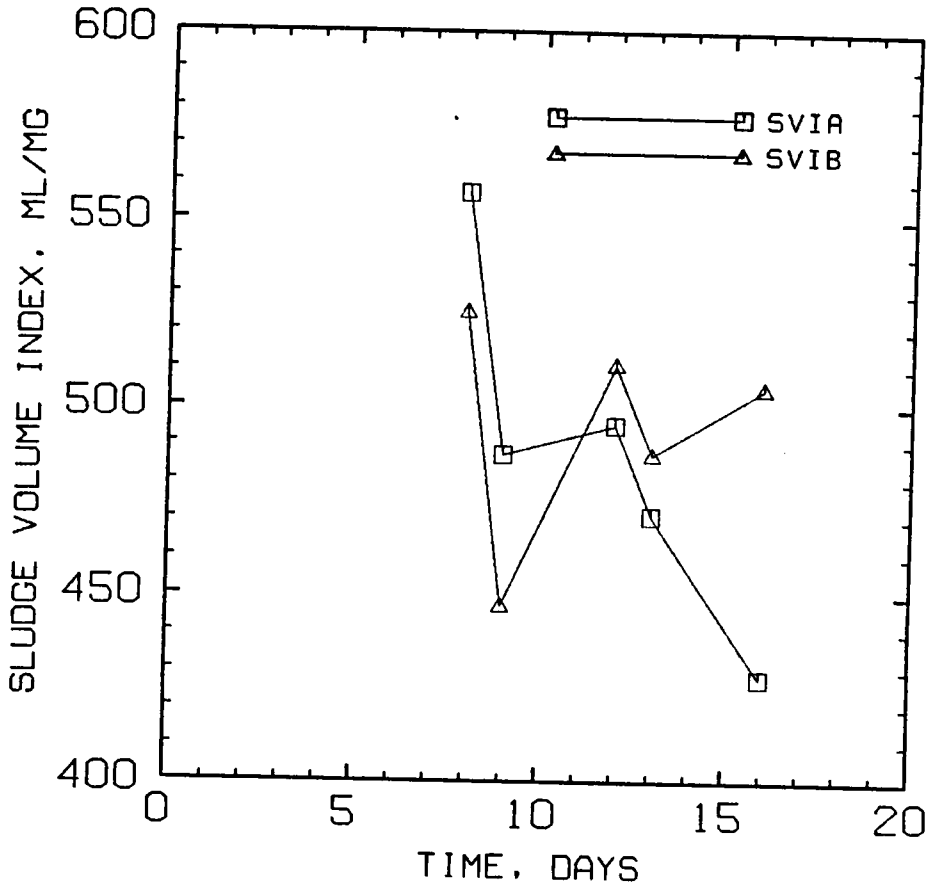


Figure 10. Sludge volume index for the bioreactors during the period of jelly formation.

blank test run at equilibrium carbon concentration of 280 mg/L resulted in 35 mg/L. The MLVSS was thus obtained by substracting this value from the actual MLVSS of R_A presented in Appendix E - Table E-1. Appendix E shows the whole experimental data in a reduced form throughout the investigational period of PAC additions to the reactor. However, b_1b_2 represent those data collected during the trial run of 280 mg/L PAC. Similarly, Table E-2 a_1a_2 indicates the data collected for the control unit (R_B) during the trial run.

Other important operating parameters such as pH, temperature and dissolved oxygen are shown in the appendix. The temperatures of both reactors averaged 18^{o}C during the run. The pH of the aeration vessel for R_A varied from 7.8 to 8.1 while that of R_B ranged from 7.7 to 8.2. In essence, the aeration pH of the vessels were essentially the same throughout the trial run of 280 mg/L. The dissolved oxygen in bioreactor A ranged from 4.8 to 7.0 mg/L, while that of bioreactor B ranged from 5.8 to 8.2 mg/L. Thus, sufficient dissolved oxygen was maintained in the system, based on the fact that dissolved oxygen (DO) must be greater than 2 mg/L to avoid the system from becoming oxygen limiting.

Table 11 indicates that MLSS was fairly high towards the end of jelly formation period, and this trend continued as evidenced by the graphs presented in Figure 11, which

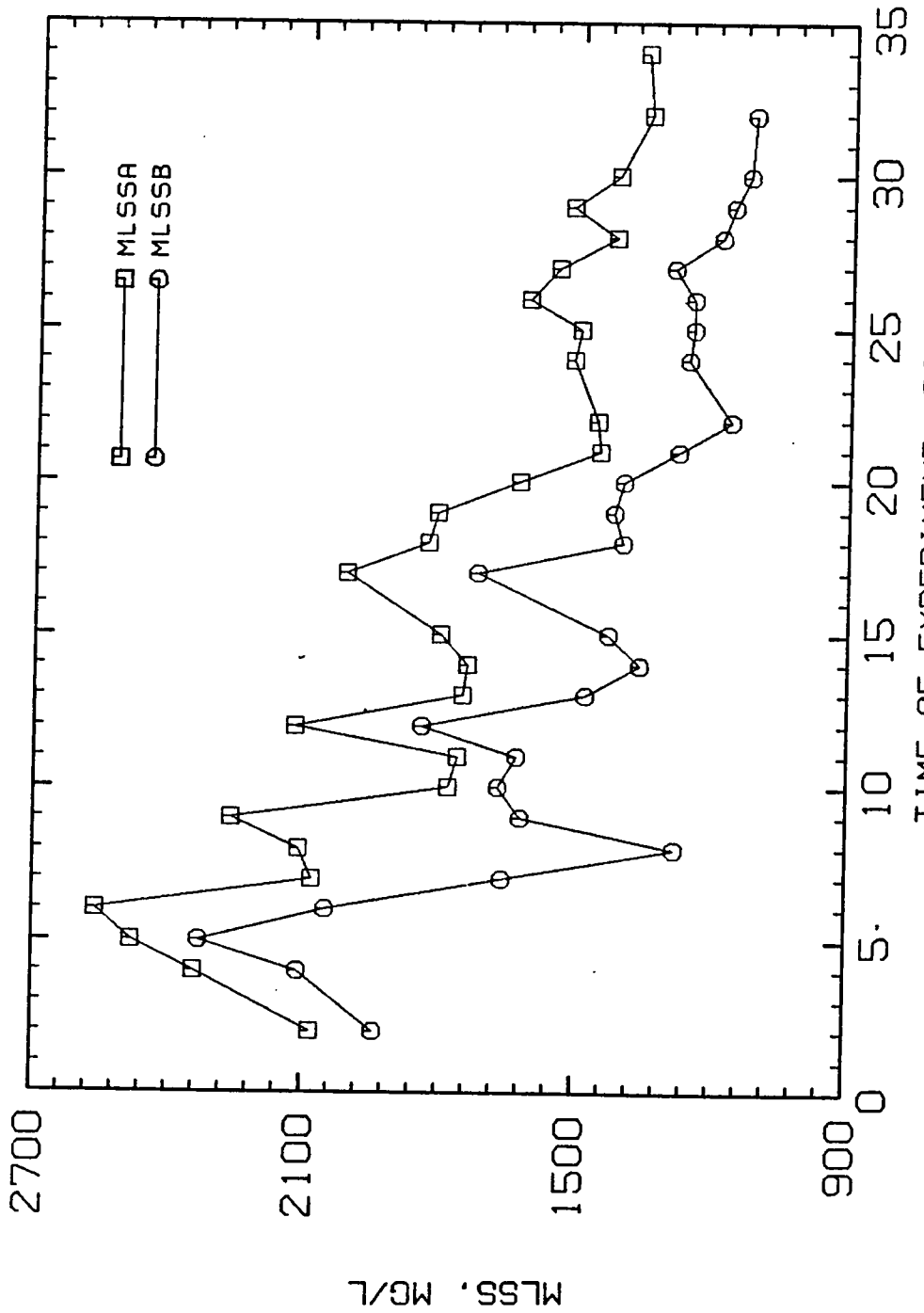


Figure 11. Operational MLSS for the bioreactors (R_A and R_B) at BSRT of 14 days during the trial run of 280 mg/L PAC.

indicated a high MLSS up to day 5 of PAC addition to the reactor. After then, there was a sharp decrease in MLSS in the reactors. Reactor B showed more decrease in both MLSS and MLVSS.

Figures 12 and 13 presents the COD and TOC loadings to the units plus the filtered effluent values. In the figures presented, the influent pH values of the wastewater are also indicated. High pH values corresponded to low COD and TOC values. Decreasing pH values corresponded to increasing COD and TOC values. Thus, the graphical shapes of COD and TOC followed a similar pattern. Increasing COD corresponded to increasing TOC values, indicating that correlation exists between these two parameters for this particular wastewater.

The first three data points on both graphs were data obtained at different powdered activated carbon concentrations. For instance, data obtained on day 2, 5, and 9 were not at equilibrium carbon concentrations of 280 mg/L. Based on the graphs presented here, there were steady increases in COD and TOC loadings to the reactors on day 2, 5 and 9. The effluent COD and TOC followed a similar pattern. The unit without PAC (R_B), however, showed higher effluent COD and TOC concentrations. After day 10, there was a sharp decrease in the effluent substrate concentrations for both units as evidenced by the figures presented. Nevertheless, Unit A showed a

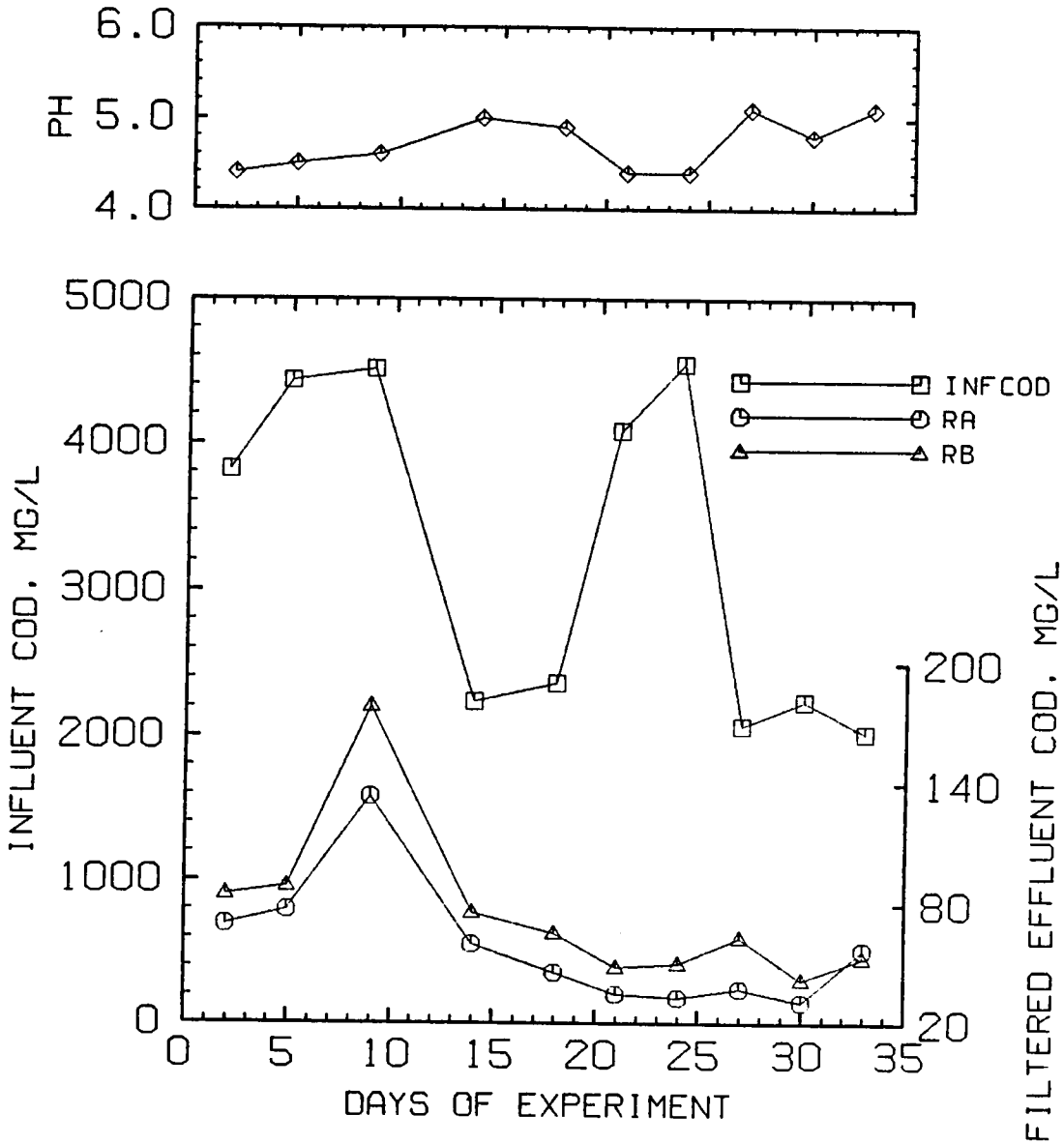


Figure 12. Comparative plots of effluent COD for the unit with 280 mg/L PAC and without PAC at BSRT of 14 days.

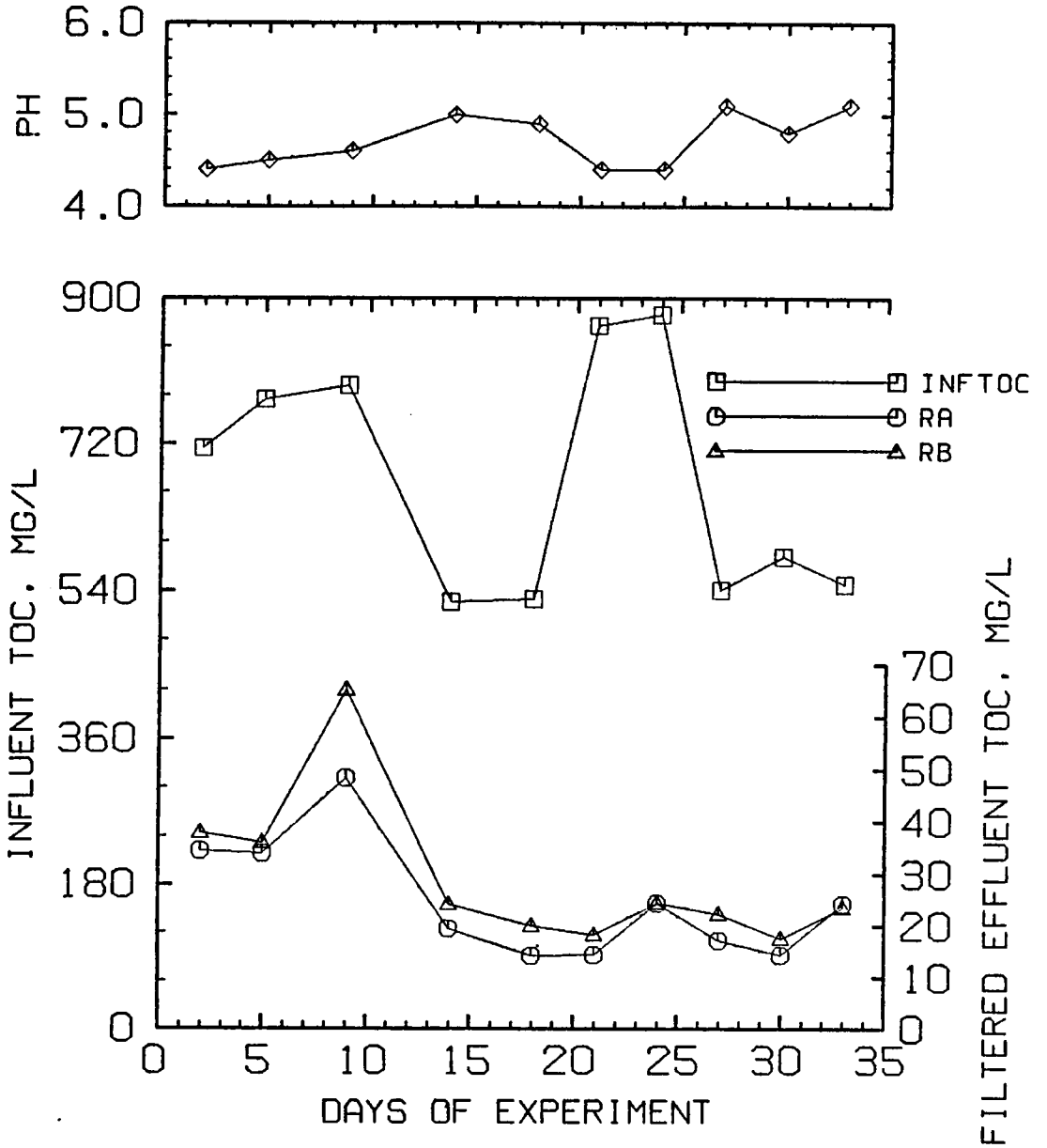


Figure 13. Comparative plots of effluent TOC for the unit with 280 mg/L PAC, and without PAC at BSRT of 14 days.

consistent better removal of substrates than Unit B - the control unit. The data shows that a steady state had been reached.

Reactor A containing 280 mg/L PAC had an average effluent COD of 42.7 mg/L while the control unit had 56.8 mg/L. The average COD removal improvement was calculated to be 14.0 mg/L (an average percent improvement of 24). Following the same computational procedure, average TOC removal for Unit A was 18.3 mg/L while Unit B was determined to be 21.4 mg/L. The average improvement in TOC removal was 3.2 mg/L with an average percent improvement of 16.3. Appendix Table F-1 summarizes the results of the computations.

Figure 14 shows comparative plots of oxygen uptake rate (OUR) and specific oxygen uptake rate (SPOUR) during the trial run of the carbon concentration. Again, the first two data points were collected at different carbon concentrations. The oxygen uptake rate decreased for both units beginning from day 9. In addition, there were an unsteady increase and decrease in oxygen uptake rate by the reactors with and without PAC. However, the unit with PAC maintained a consistent increase in oxygen uptake over Reactor B without PAC. The specific oxygen uptake rate (SPOUR) of both reactors were almost the same. It should be noted that the MLVSS used to compute SPOUR for Unit A was MLVSS corrected for PAC. The average increase in OUR

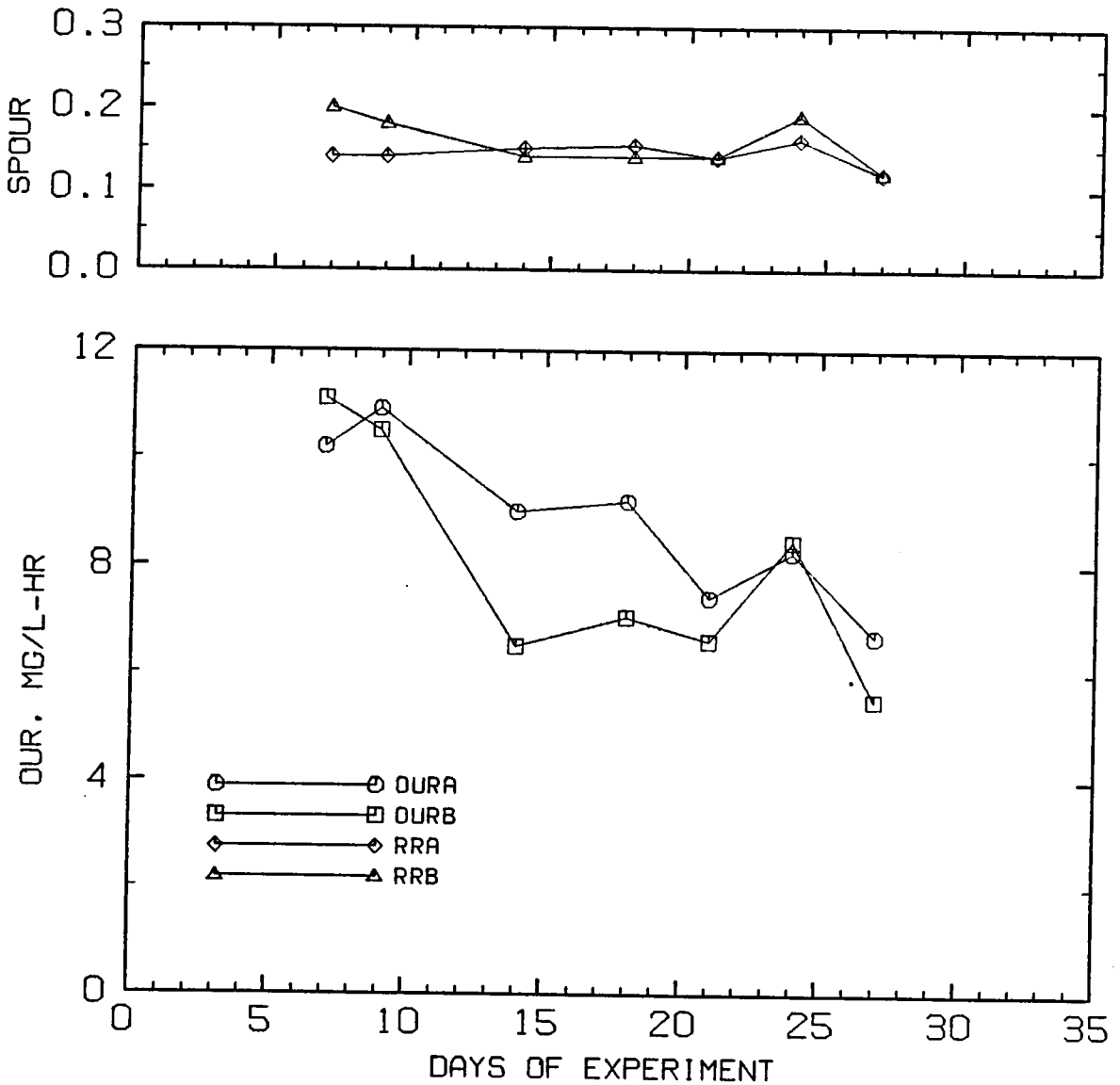


Figure 14. Comparative plots of oxygen uptake rate (OUR) and specific oxygen uptake (SPOUR) for R_A and R_B.

over the period was 1.33 mg/L-hr with corresponding percent increase of 22. The average OUR for Unit A was 7.79 mg/L-hr and Unit B averaged 6.47 mg/L-hr. The specific oxygen uptake rate (R_r) for R_A averaged 0.139 day^{-1} while R_B averaged 0.142, showing 2 percent increase over Reactor A which is significant. Table 12 summarizes the averaged parameters during the trial run of 280 mg/L PAC.

Comparative plots of SVI and zone settling velocity (ZSV) during this experiment are shown in Figure 15. At days 4 and 6, Unit B had better settling velocities than Unit A. On day 11, Unit A had better settling velocity than Reactor B. The SVI of Unit A showed consistently better results than Unit B. The graphs indicate that increasing SVI correlates with decreasing ZSV and vice versa. This is further evidence in their average computational values. For example, Unit A had an average SVI of 228 ml/gm with ZSV of 4.94 ft/sec, while Unit B average was 286 ml/gm with an average ZSV of 2.88 ft/sec; which is a typical indication of good correlation.

Carbon Dose of 160 mg/L

Once the steady state was reached in bioreactor A, the equilibrium carbon concentration was reduced from 280 mg/L to 160 mg/L by wasting without carbon replacement. It is of interest to note that this equilibrium carbon concentration was not arbitrarily selected. The selection

Table 12. Averages of the important parameters for the bioreactors during the trial run of 280 mg/L PAC.

Parameters	Average R_A	R_B
OUR, mg/L-hr	7.79	6.47
R_r, day^{-1}	0.14	0.14
MLVSS, mg/L	1340[b]	1110
COD effluent, mg/L	42.7	56.8
TOC effluent, mg/L	18.3	21.4
COD influent, mg/L	2820	2820
TOC influent, mg/L	639	639

R_r = SPOUR
b = Corrected for PAC

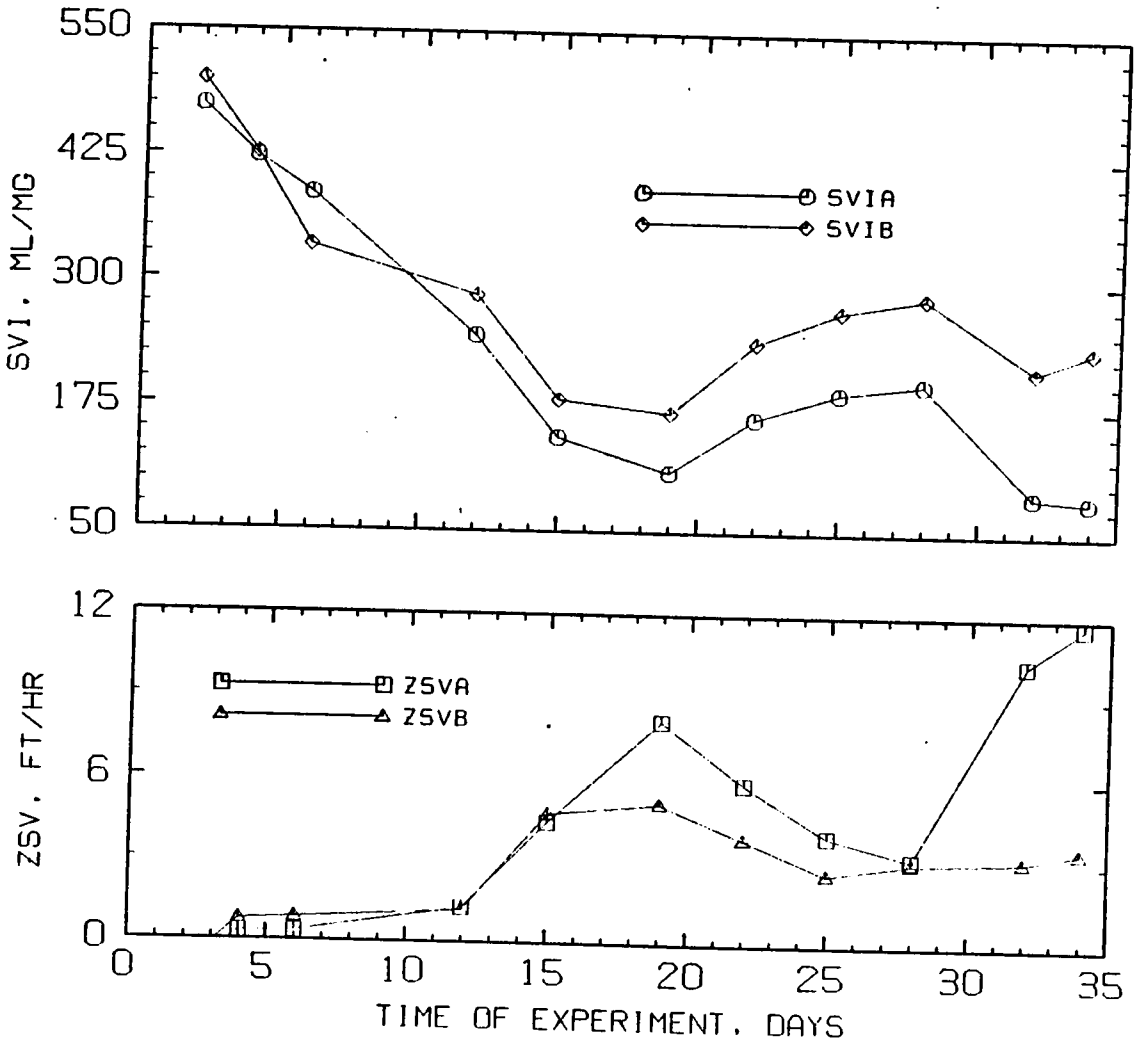


Figure 15. Plots of SVI and ZSV for the bioreactors with 280 mg/L PAC and without PAC.

was made based on the results presented in Figures 12 and 13. The first thirteen days the units contained different powdered activated carbon concentrations. Correlation with Figure 14 indicated that there were more substrate removal at a dose of 160 mg/L, and also resisted shock loading induced by high organic loading to the system.

Figure 12 indicates 15 mg/L of improved COD removal with 18 percent increase in COD removal on day 2. On day 5 corresponding to a carbon dose of 80 mg/L a marginal improvement in COD of 2 mg/L, or 2.25 percent, was observed when there was an increase with higher organic loading. At a carbon dose of 160 mg/L on day 9, the improvement in COD removal was 45 mg/L for a percent increase of 25.0 when the highest organic loading occurred. The TOC followed a similar pattern. A substantial TOC removal of 16 mg/L was also observed on day 9 corresponding to a carbon dose of 160 mg/L. These observations, plus the fact that the system at 160 mg/L of PAC concentration was not allowed to reach steady state, resulted in the selection of equilibrium PAC dose of 160 mg/L for further experimental investigation.

The operational MLSS of the bioreactors are shown in Figure 16. In the figure presented here, the MLSS of the reactors with and without PAC were consistent within the limits of test accuracy, indicating a steady state was reached. On day 67 for bioreactor B, there was a steep

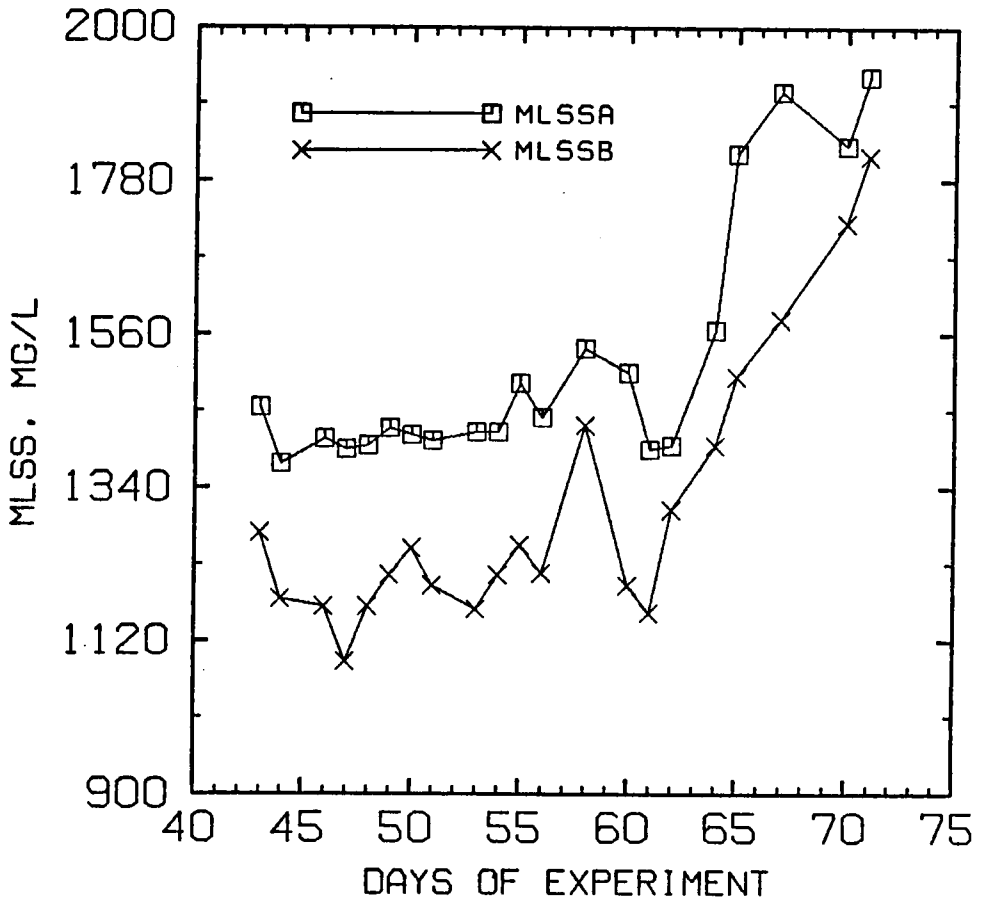


Figure 16. Plots of MLSS for Reactor A and Reactor B at carbon dose of 160 mg/L operating at BSRT of 14 days.

increase in both MLSS and MLVSS. This trend was also noted with bioreactor A on day 70. Thus, the reactors were going into a transient state and the experiment was, therefore, cut off. Appendix Table E-1 (b_3b_4) indicates data of MLSS and MLVSS collected for R_A plus other operating parameters such as pH, temperature and dissolved oxygen (DO). The temperature averaged 18°C over the period of time. The aeration pH varied from 7.4 to 8.0, which is the range at which most microorganisms function, while the dissolved oxygen concentration ranged from 4.3 to 6.5 mg/L indicating a sufficient oxygen concentration level in the reactor over the period of the run. It should be noted that other parameters obtained during the test are also summarized in the appendix table cited here. The blank PAC was, however, determined to be 33 mg/L for this equilibrium concentration. Appendix Table E-2 (a_3a_4) presents data collected for reactor B over the period of the run. The pH of the aeration vessel varied from 7.5 to 7.8 which is within good operational range. The temperature of reactor A averaged 18°C over the period of experiment while DO level ranged from 4.8 to 7.3 mg/L. It should be noted that it was only two days that DO was as high as 7.3 mg/L. The DO, therefore fluctuated around 6.0 mg/L most of the time.

Figures 17 present the comparative plots of COD removals for the bioreactors. With increasing COD loading the control unit showed a poorer effluent quality as

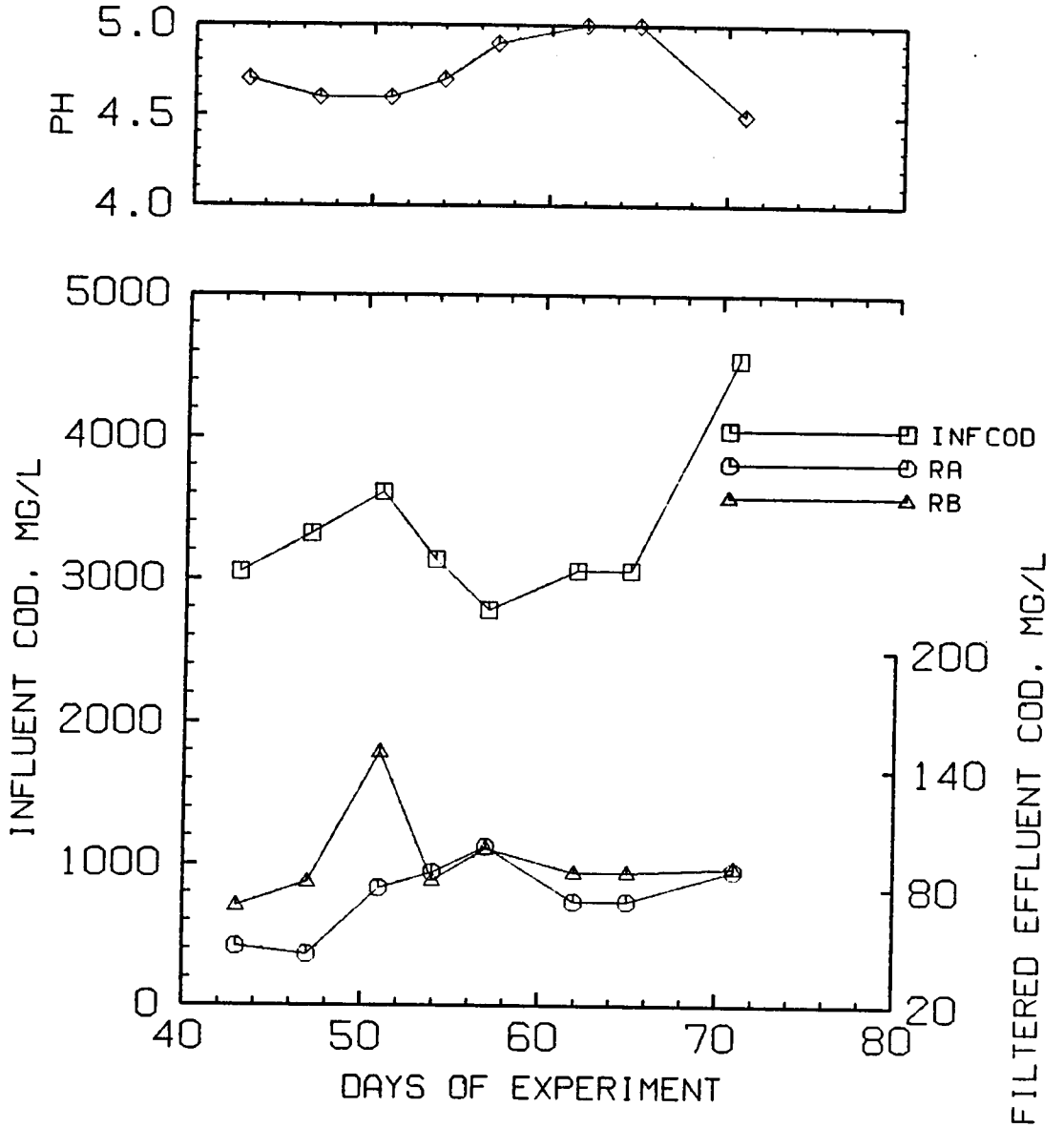


Figure 17. Plots of COD removal by the bioreactors during the trial run of PAC of 160 mg/L at BSRT of 14 days.

measured by COD. The unit with PAC followed a similar trend but poor performance was more pronounced on the unit without PAC. After day 51, Unit B effluent COD decreased to a point lower than that of Unit A on days 54 and 57. The improvement in COD on these days over bioreactor A was by a narrow margin, and therefore is within the limits of experimental error. From day 58, Unit A showed a consistent COD removal better than Unit B. Another feature of the graphs presented in Figure 17 is the relationship between the influent COD and effluent COD of the bioreactors. Bioreactor B showed an increase in effluent COD value with increasing COD loading and a decrease in effluent COD with decreasing COD loading. Reactor A, however, appeared to have a decrease in effluent COD value with increasing COD loading and vice versa. It was only one data point that did not follow this trend, and that was day 51 of this experimental study. The pH followed the pattern of increasing pH value with decreasing COD loading and vice versa. The average effluent soluble COD of the PAC unit was determined to be 73.9 mg/L as compared to 93.8 mg/L of the control unit indicating 20 percent improved COD removal over the period of the run. In terms of concentration, the improvement in COD removal was 20 mg/L. TOC measurements were terminated at day 57 because a relationship had been established between COD and TOC. The effluent TOC of Unit A showed a better TOC removal the Unit

B, consistently, over the period of the run TOC measurements were made.

Figure 18 is the plot of oxygen uptake rate and the specific oxygen uptake rate measurements made during the trial run of 160 mg/L PAC. Out of 9 experimental measurements during the run, Unit A had five data points of better oxygen uptake rate (OUR) than Unit B, while Unit B had four data points of better oxygen uptake than Unit A. In essence, the oxygen uptake rate was almost nearly equal as evidenced by the graphs presented. The averages of OUR readings collected over the period of experiment were determined for both reactors. It was found that OUR for Unit A was 8.73 mg/L-hr, while that of Unit B was 8.46, for a percent increase in OUR of 4 percent with PAC addition. Again, the specific oxygen uptake rate (SPOUR) of Unit B was almost higher than that of Unit A throughout most of the period of testing as Figure 18 shows.

Taking the averages of SPOUR taken over the period, Unit A value was 0.16 day $^{-1}$ and the Unit B value was 0.18 day^{-1}. In addition, out of the 9 experimentally determined data points shown in the figure, only three data points for Reactor A were observed to be higher than those of Reactor B.

Figure 19 presents the SVI and ZSV values obtained during the trial run of 160 mg/L PAC. The SVI of Unit A was consistently lower over the period than Unit B.

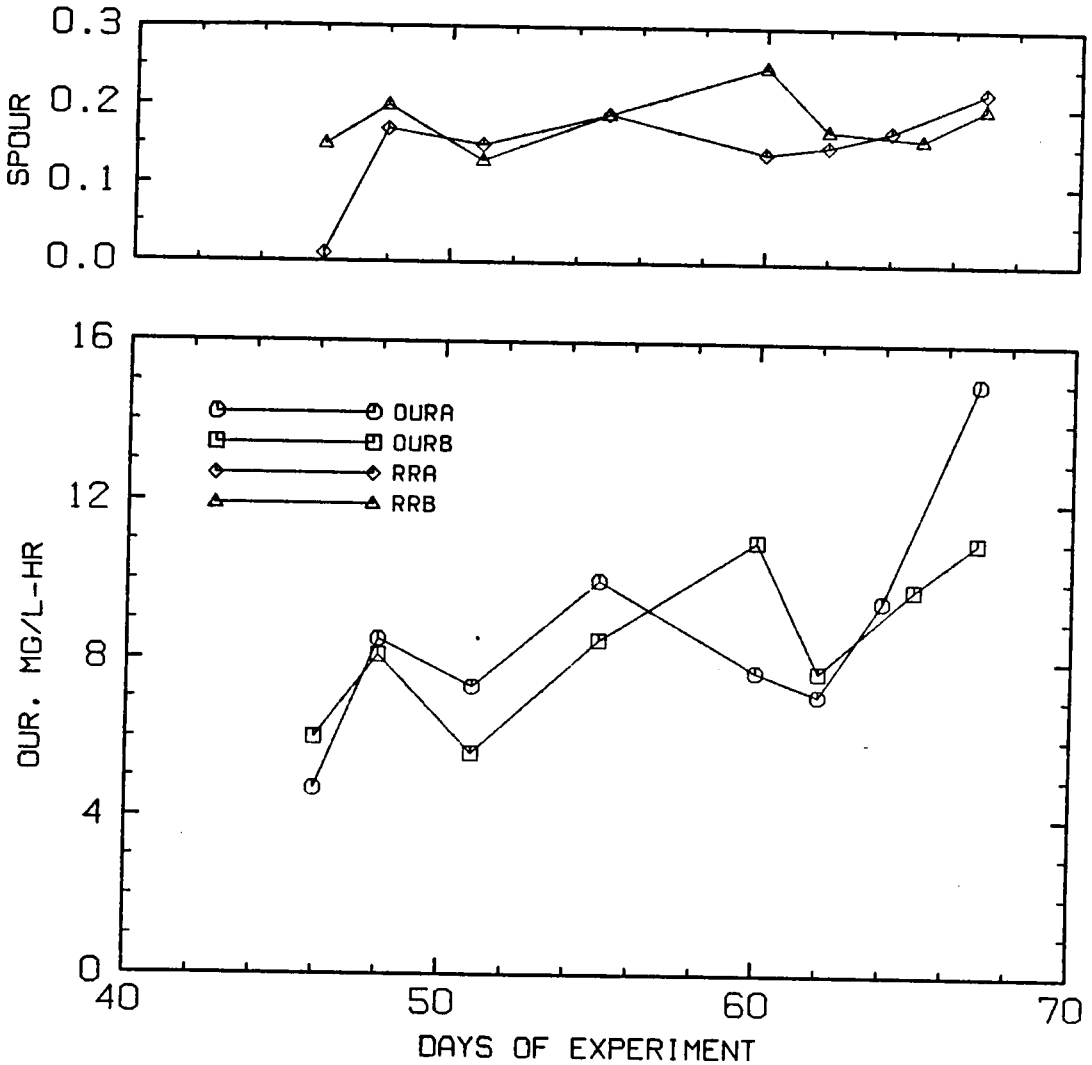


Figure 18. Plots of OUR and SPOUR during the trial run of PAC of 160 mg/L.

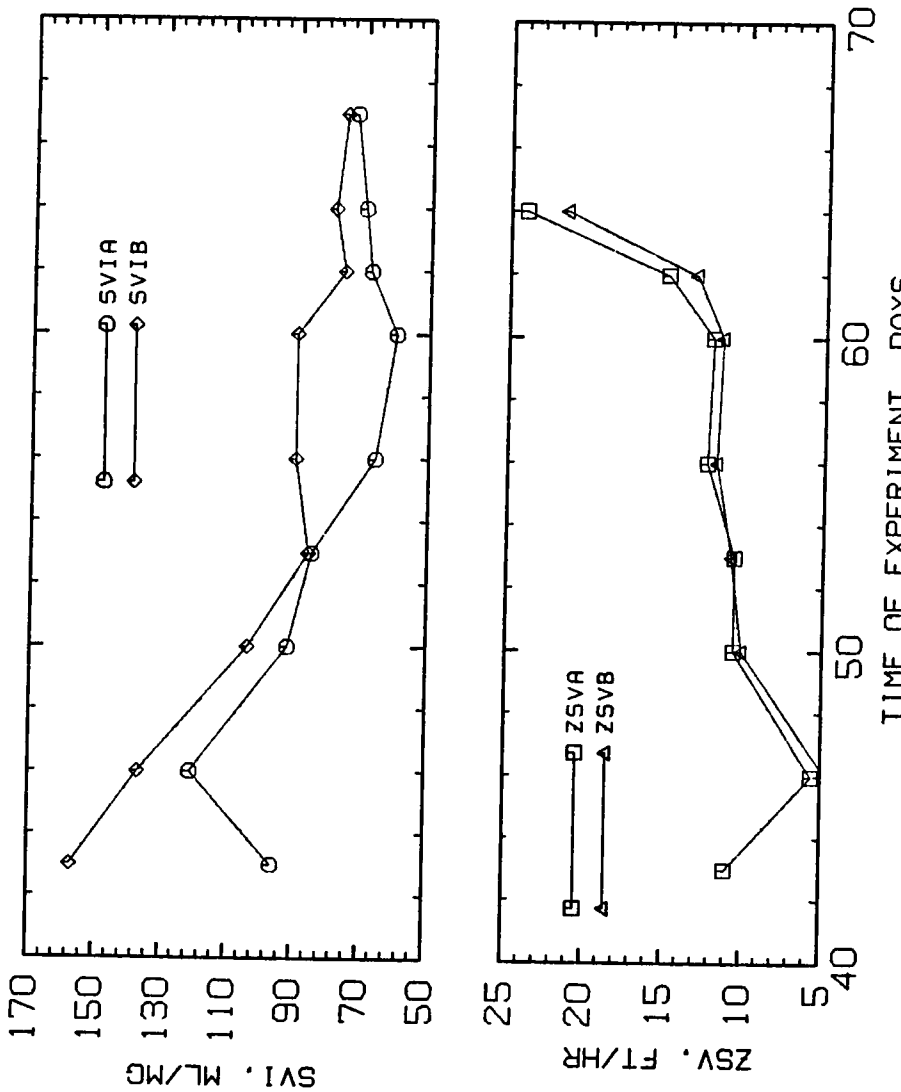


Figure 19. Plots of SVI and ZSV at PAC concentrations of 160 mg/L at BSRT of 14 days.

Likewise, the zone settling velocity (ZSV) was consistently higher for Unit A, except on day 53 where the values were essentially equal. The values of SVI for unit A ranged from 60 to 121 ml/mg with corresponding ZSV range of 24 to 5.6 ft/sec. The SVI values for Unit B varied from 76 to 157 ml/mg with corresponding ZSV range of 21.4 to 3.33 ft/sec.

Table 13 shows the averages of some of the important parameters measured during the test.

Experiment with 20 mg/L Equilibrium PAC Concentration

Once the 160 mg/L PAC experiment was terminated, 20 mg/L PAC was chosen for further investigational study. Consquently, the carbon concentration in the reactor was brought down from 160 mg/L to 20 mg/L.

It is imperative to note the observational characteristics of the bioreactors during the reduction of PAC concentrations before presenting the data collected over the period of the steady state. The units were not performing well, particularly the unit with PAC. The reactors were characterized by activated sludge bulking plus loss of solids through the effluent weirs. However, the author felt that proper attention was not given to the units, and attributed this observational phenomenon to improper flow adjustment with occasional malfunctioning of the pumping system. For instance, flow rates were observed

Table 13. Averages of Important Parameters Measured for 160 mg/L PAC Concentration Run.

Parameters	R_A	R_B
OUR, mg/L-hr	8.73	8.46
R_r, day^{-1}	0.16	0.18
MLVSS, mg/L	1340+	1190
Effluent COD, mg/L	73.9	93.8
Influent COD, mg/L	3520	3520

+ Corrected for PAC

to flow faster in the following morning after adjusting the flow on the previous day. This view was further evidenced by effluent wastewater in the effluent carboys for bioreactors A and B. The effluent in carboy A indicated a higher volume of effluent than carboy B. Carboy B also showed higher volume of the effluent in some instances. In few cases, the flow rate was checked only once a day. Once data collection was begun, precautionary measures were taken to ensure proper functioning of the biological units. Interestingly, this yeilded good results as revealed by microscopic examination of sludges from the units. Both units indicated good flocculant sludges. However, Unit A had better floc than Unit B.

The operational MLSS for the bioreactors collected over steady state are depicted in Figure 20. Both units exhibited low MLSS as indicated by Figure 20. The MLVSS data for Unit A were corrected for PAC. The blank PAC at equilibrium carbon concentration of 20 mg/L was determined to be 33 mg/L. The bouncing of data points in the graphs indicates steady state over the period of time shown. Appendix Table E-1 (b_5b_6) and Table E-2 (a_5a_6), respectively, presents data collected for reactors A and B. It should be noted here that these tables contain all the experimental data analyzed over this period. The DO for Reactor B ranged from 6.0 to 7.2. However, only one day did the dissolved oxygen reached 7.2. Therefore, DO

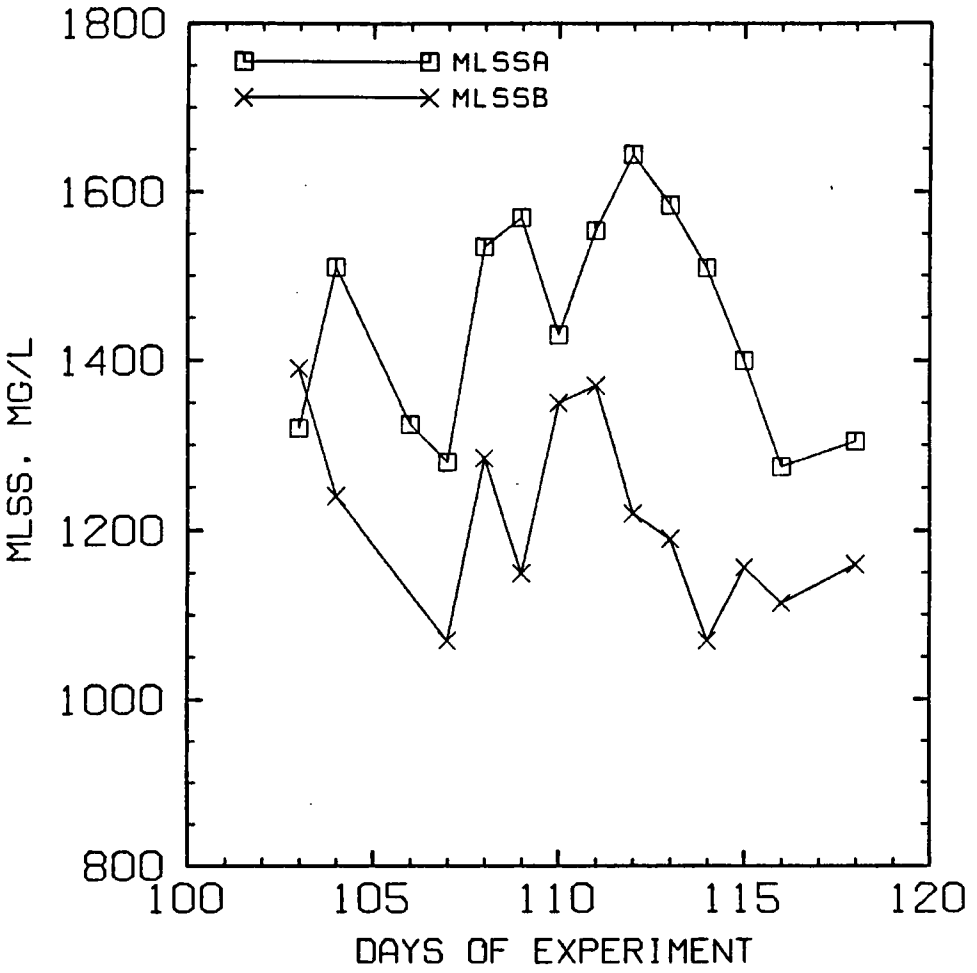


Figure 20. Operational MLSS of the bioreactors during PAC run of 20 mg/L at BSRT of 14 days.

fluctuated around 6.0. The temperature of the reactor averaged 18°C while pH of the aeration vessel varied from 6.6 to 7.2. It was only two days that the pH decreased to 6.6. Reactor A indicated a pH range of 7.1 to 7.7 for the aeration vessel during the trial run, and the temperature averaged 18.2°C. These data are typical indications of favorable environmental conditions for the reactors.

The plots of COD for the reactors and of pH of the influent wastewater are depicted in Figure 21. This figure did not show the effluent COD from reactor A on day 107 because of a discrepancy. The respective values for the units on that day were 532 mg/l and 137 mg/L of soluble COD indicating a substantial difference. The values cited here show that Unit B had four times better removal of COD than bioreactor A. This is an abnormal trend when compared with the results of the preceding experimental trials. A closer examination of Appendix F-1 (b_5b_6) reveals that DO level on that day was 3.3 mg/L, the lowest level of oxygen concentration in the reactors ever obtained during the whole period of this research. In Appendix E, Table E-2 (a_5a_6) shows that the dissolved oxygen (DO) level for reactor B on day 107 was 6.4 mg/L which was a typical value for DO exhibited by the units during this research. After day 107, effluent COD from bioreactor A was consistently lower than the bioreactor B effluent throughout the period of this trial run regardless of the influent COD into the

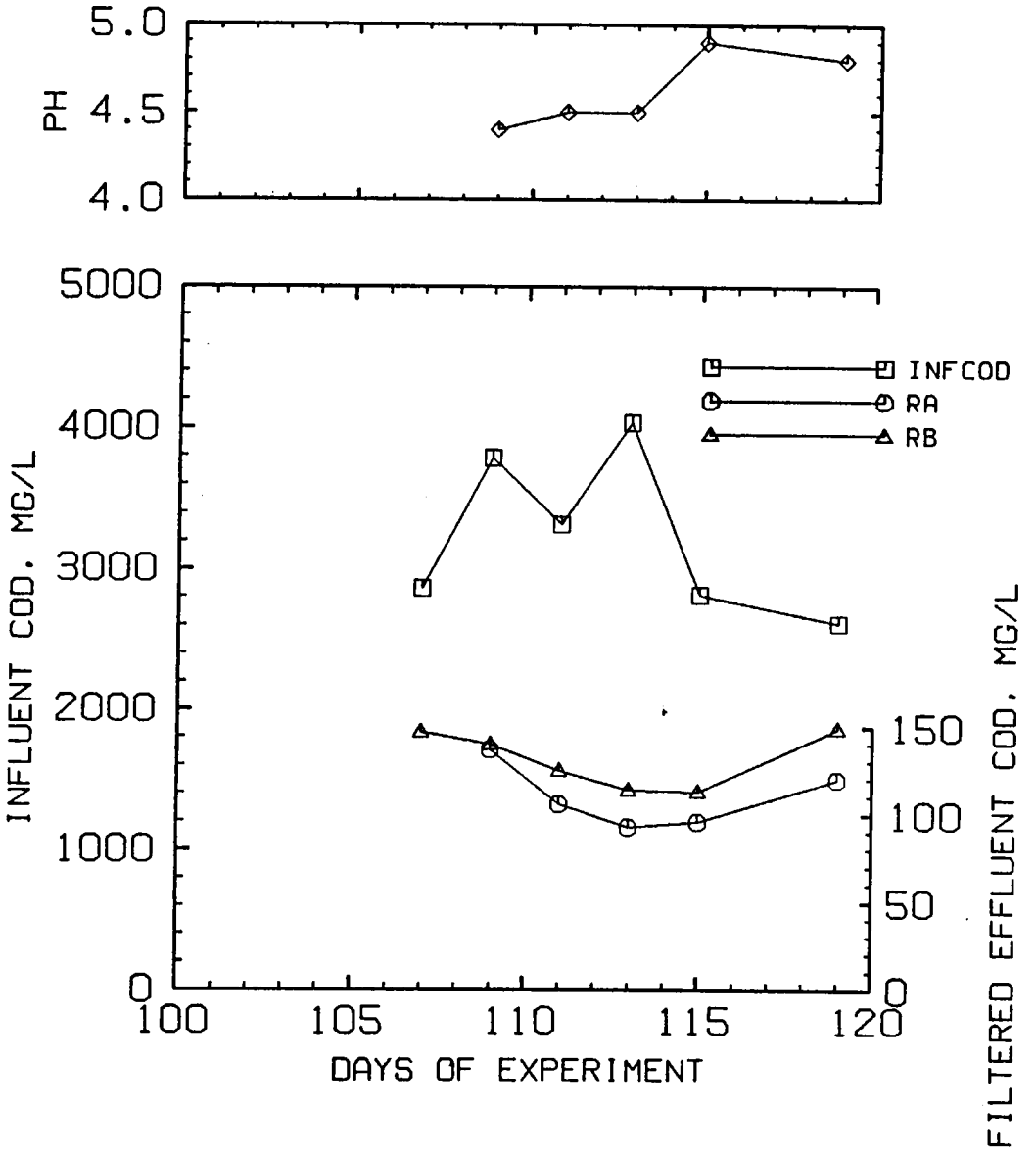


Figure 21. Comparative plot of COD removals at PAC does of 20 mg/L at BSRT of 14 days.

reactors. The average COD for Unit A was determined to be 110 mg/L excluding the data collected on day 107 while that of Unit B was found to be 128 mg/L. The increase in improved COD removal was 15 percent with increase of 18 mg/L. Appendix F, Table F-3, shows the daily computational improvements of the COD during the trial run.

Figure 22 presents the plots of oxygen uptake rate and specific oxygen uptake rate (SPOUR) for the bioreactors. Bioreactor A had higher oxygen uptake rate on days 109, 111,112, and 118 out of the six data points collected. Thus, Unit B OUR was higer than the OUR in reactor A on two days, i.e., days 114 and 116, as indicated by the graphs. The specific oxygen uptake rate (SPOUR) of Unit B indicated higher values than SPOUR of Unit B as evidenced in their average values over the period of the run. Reactor A averaged 0.24 day^{-1} of SPOUR, while Unit B averaged 0.28 day^{-1}. The average values of OUR were respectively 12.7 gm/L-hr and 11.43 mg/L-hr for reactors A and B. The marginal increase is 1.24 mg/L with percent increase of 12.5. Appendix F, Table F-3 summarizes the daily improvements in OUR exhibited by Bioreactor A. Table 14 presents the averages of the parameter measured during the run.

Figure 23 presents the comparative plots of SVI and ZSV for the bioreactors during the trial run of 20 mg/L PAC. For Unit A increase in ZSV on day 108 corresponded with a

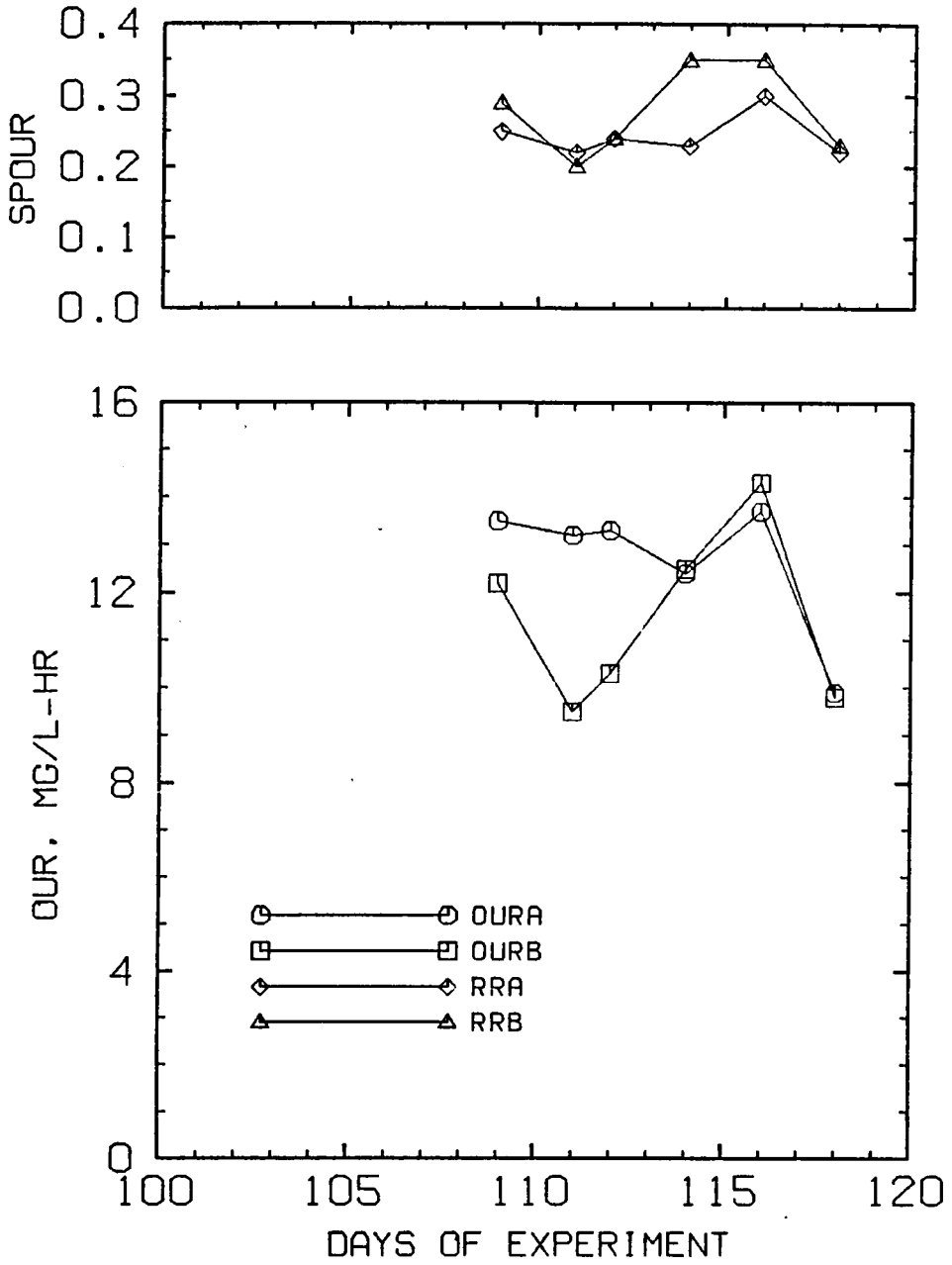


Figure 22. Plots of OUR and SPOUR for the trial run of PAC dose of 20 mg/L.

Table 14. Averages of the Parameters Measured During the Trial Run of 20 mg/L PAC.

Parameters	R_A	R_B
OUR, mg/L-hr	12.7	11.4
R_r, day^{-1}	0.24	0.28
MLVSS, mg/L	1224+	1015
Effluent COD, mg/L	110	131
Influent COD, mg/L	3320	3320

+ Corrected for PAC

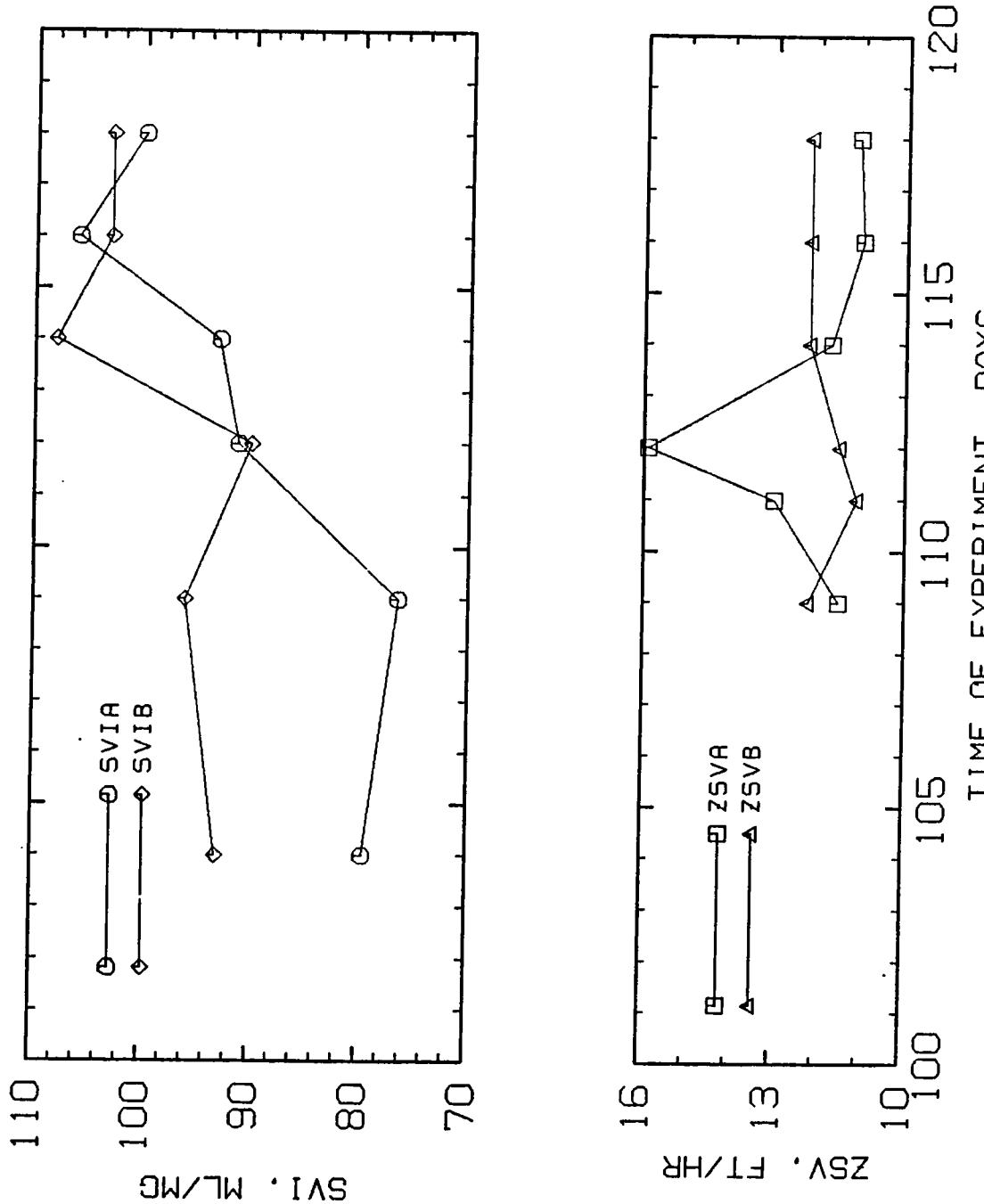


Figure 23. Plots of SVI and ZSV at PAC does of 20 mg/L.

decrease in SVI. On the other hand, on day 109, an increase in ZSV corresponded with a slight increase in SVI value. Similar variations were noted for Unit B but not much remarkable. The SVI for Unit A ranged from 61.9 to 106 ml/gm with corresponding ZSV of 15.9 to 11.0 ft/sec. However, no data on ZSV was collected for the lowest SVI value. Again, it does not mean that the highest SVI value corresponds to the lowest ZSV as indicated by the graphs. The SVI for Unit B ranged from 78 to 108 ml/gm corresponding to ZSV of 12.2 to 11.1 ft/sec. Considering the data shown here, there exists several discrepancies.

COD, TOC and pH

Based on Figures 11, 12, 16, and 21 a relationship exists between COD, TOC and pH for this particular wastewater. In the figures presented, increasing COD corresponds to increasing TOC and decreasing influent wastewater pH.

Presently, the industry does not monitor TOC. In addition to this, TOC analyses were not performed all through the investigational period. Therefore, an attempt was made to determine a statistical equation to predict the influent TOC of the wastewater. Since the industry only measures COD, the chemical oxygen demand was chosen to be the independent X variable while TOC was the dependent variable. Data collected over the period of the experiment

was used to draw the regression line depicted in Figure 24. The correlation coefficient (r) was computed to be 0.91. The determined statistical equation is shown below.

$$TOC = 0.138\ COD + 240 \qquad [29]$$

The above equation is with a standard error of estimate of ± 55 milligram per liter. The high correlation coefficient found here is indicative of a good relationship between these parameters.

However, environmental engineers often correlate by COD/TOC ratio. Table 15 shows the ratio of COD to TOC computed. An average value of 4.53 was determined. Either this average value or Equation [29] can be used to approximate TOC for this particular wastewater. Equation [29] has a shortcoming in that it can only be used for influent COD wastewater, and not for effluent COD. While COD/TOC ratio can be used for effluent COD, it is essential to note, however, that it may not give a good approximation. Nevertheless, it can be used to give a "rough" idea of effluent TOC where effluent COD is given.

The COD and pH showed a correlation factor of -0.85. The negative sign implies that with increasing pH, the COD loading to the units decreased and vice versa. It does not, however, mean that an increase in pH caused a decrease in COD loading. The meaning of this result will be

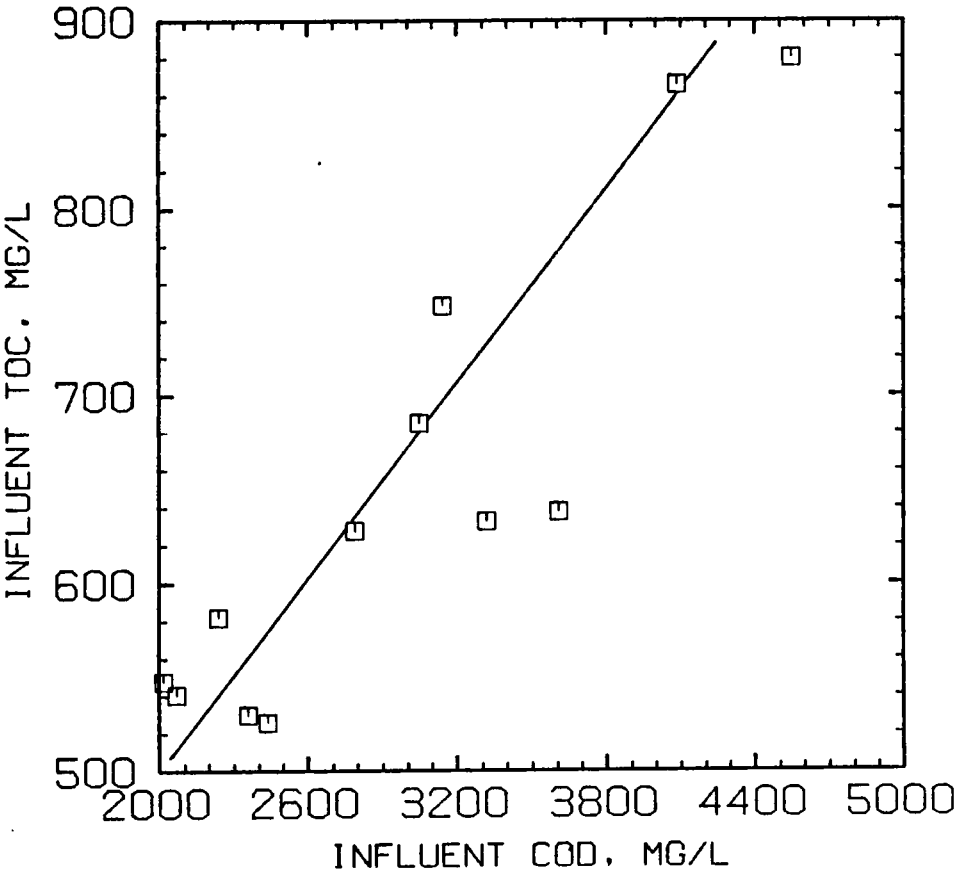


Figure 24. Determination of statistical equation between COD and TOC.

Table 15. Correlation between COD and TOC

	TOC	COD	COD/TOC
	526	2440	4.64
	530	2360	4.45
	866	4090	4.72
	880	4550	5.17
	541	2070	3.83
	582	2240	3.85
	548	2020	3.69
	685	3050	4.45
	633	3320	5.24
	638	3610	5.66
	748	3143	4.20
	628	2790	4.44
Average	650	2970	4.53

Note: all TOC and COD numbers are concentration in mg/L.

discussed in the following chapter. All the statistical computational procedures are shown in Appendix G.

Biokinetic Constants

A material balance for substrate around the bioreactors resulted in the following equation.

$$1/X\ (ds/dt)_u = Q(S_o-Se)/XV \qquad [30]$$

where

$1/X(ds/dt)_u$ = q, the specific utilization constant, day^{-1}

Q = Volumetric flow rate, liters/day

X = The active biomass in the system, mg/L

S_o = Influent substrate measured as COD, mg/L

S_e = Effluent substrate expressed as COD, mg/L

V = Volume of the aeration vessel in liters

A mathematical development of Equation [30] is presented in Appendix A.

Lawrence and McCarty (1970) [39] represented the substrate removal rate based on Monod's microbial kinetics as

$$(ds/dt)_u = KXS/K_S+S \qquad [31]$$

where

K = maximum rate of utilization of substrte per unit biomass, time $^{-1}$

K_s = saturation constant, mg/L

Dividing both sides of the equation by X, results in the following

$$1/X\ (ds/dt)_u = KS/K_s+S \qquad [32]$$

The bioreactors were assumed to be completely mixed in this study, and, therefore, the COD in the aeration vessel was essentially equal to the effluent COD. In addition, making the assumption that the effluent substrate measured as COD was infinitesimal as compared to the saturation constant, K_s, then Equation [32] reduces to

$$(ds/dt)_u/X = (K/K_s)S_e \qquad [33]$$

Replacing K/K_s by K_b, Equation [33] becomes

$$(ds/dt)_u/X = K_bS_e \qquad [34]$$

where

K_b is the specific utilization rate constant with units of

L/mg-day. It is also a first order kinetic constant.

Combining Equations [30] and [34], the following equation was formed.

$$Q(S_o-S_e)/XV = K_bS_e \qquad [35]$$

The observed cell yield coefficient is mathematically defined as

$$Y_{obs} = (dx/dt)/X \quad (ds/dt)/X \qquad [36]$$

$$Y_{obs} = \ /q = 1/\ _cq \qquad [37]$$

Equations [35] and [37] were used to evaluate the effects of PAC on the biokinetic constants.

The approach to the determination of the constants was to take the averages of the data collected over the period of each run. The data that are of importance were influent COD loading, effluent COD, and mixed liquor volatile suspended solids. The averages of these parameters are, however, presented in Tables 11, 13 and 14. Using these averages, the kinetic constants were determined for trial runs of 280 mg/L, 160 mg/L, and 20 mg/L. In addition, the values for the control units were also determined. It

should be noted that MLVSS used for bioreactor A was corrected for PAC. Sample calculations are shown in Appendix I-2.

Table 16 presents the biokinetic constants for PAC runs of 280, 160, and 20 mg/L along with their respective biological control values. For each of the runs, there was an increse in observed yield coefficient when compared with the control unit. With increase in equilibrium concentration, the observed yield coefficient increased. The increase was less proportional to increasing equilibrium carbon concentration. The control units followed a similar pattern as evidenced by Table 16. Increasing equilibrium carbon concentrations from 20 mg/L to 160 mg/L showed an increase in observed yield of only 0.002 while the control unit values had an increase of 0.074. Similarly, an increase in carbon concentration from 160 to 280 mg/L indicated an increase of 0.026 in observed yield while the control unit values showed a difference of 0.0154. Interestingly, the control units increases followed a consistent pattern during the study. To further elucidate the fact that the observed yield coefficient in this study increased less proportionally to carbon concentration in the reactors, the "actual" observed yield constants induced by PAC were calculated. The actual observed yield coefficients for 20, 160, 280 mg/L PAC were respectively found to be 0.0168, 0.014, and 0.022. Thus,

Table 16. Biokinetic Constants for Various Carbon Dosages and their Biological Control Values at Temperature of 18°C.

*Parameters	280 mg/L		160 mg/L		20 mg/L	
	R_A	R_B	R_A	R_B	R_A	R_B
Y_{obs}	0.132	0.110	0.106	0.0946	0.104	0.0872
$K_{b'}$ mg/L-day	0.0126	0.0114	0.00911	0.00803	0.00626	0.00640

*Parameters are expressed in terms of COD.

increasing PAC by 140 mg/L resulted in a decrease of the observed yield coefficient while increasing PAC by 120 mg/L resulted in an increase of the observed yield. It should be noted that the observed yield constants induced by PAC were determined by subtracting the control values from the PAC units.

The first order kinetic constant also increased with PAC addition except when the value for carbon dose of 20 mg/L. However, the difference is within the limits of experimental error. Taking the difference between the data presented in Table 16 for K_b PAC concentrations of 280, 160, and 20 mg/L caused K_b changes of .0012, .00105 and -.00019, respectively. Thus, decreasing the equilibrium carbon concentration tended to decrease the first order constant, K_b. In other words, increasing equilibrium PAC concentration increased the first order kinetic constant.

Chapter V

DISCUSSION

Major findings will be discussed in this chapter, in the order of presentation of the supporting data in the previous chapter.

Adsorption and Equilibrium Time Studies

Experiments with two different activated carbon showed that the cellulose acetate manufacturing wastewater is porrly adsorbable and the effluent TOC concentration could not be reduced to a reasonable level by activated carbon adsorption alone. Regardless of the amount of application of the carbon in the jar test, the TOC concentration of the wastewater could only be reduced from an average of 608 mg/L to about 528 mg/L. The adsorption could be improved a little by adjusting the wastewater pH to 7.0 before the batch adsorption tests, but even then the average TOC concentration remaining was 500 mg/L.

Freundlich isotherms were developed for both carbons, but the resulting graph lines were very steep, revealing that the TOC of the wastewater was composed of a small amount of strongly or moderately adsorbable material, and a large amount of weakly non-adsorbable material. Examples of poorly adsorbable compounds are acetic acid, ethanol,

and methanol, all of which were components of the wastewater. However, they are readily biodegradable. An example of a moderately adsorbable compound is acetone, and it was also a component of the wastewater. This compound is also slowly biodegradable [15], and this indicates a potential advantage of the use of PAC to treat the wastewater. The slowly biodegradable compound could be adsorbed by the activated carbon and would remain in the activated sludge system for an entire sludge age rather than just the wastewater hydraulic detention time. Thus, the microorganisms would have a much longer time to biodegrade the acetone, and organic removal could be enhanced.

Even though a third activated carbon was actually used for the PAC studies, the adsorption test studies show that the major benefits of adding carbon to an activated sludge system treating cellulose acetate wastewater are not likely to be related to organics adsorption. It seems more likely that any benefits observed would result from improved floc formation because the carbon particles act as floc nuclei, or improved settleability because the carbon adds weight to the flocs or the resulting flocs are larger.

In addition, the results indicate that an isotherm of this kind will result in a rapid breakthrough curve if applied as a carbon column.

Jelly Formation

Table 11 shows that experimental measurements were begun on July 23, 1984, while the units were started on July 17, 1984. The delay was because of jelly formation in the units. The table shows that the mixed liquor suspended solids concentration measured on July 23 was quite low when compared with the initial concentration of 2,340 mg/L. This indicates the poor performance of the units in the previous days when data were not collected. In addition, no wasting was performed due to the excessive loss of solids through the effluent weirs, another indication of poor settleability of the activated sludge at the initial stage of the investigation.

In addition, the units were started out with a pH of 8.4. Table 11, however, indicates lower pH values for the units after the initial period of time. Bioreactor A fluctuated around a pH of 8.0, while B fluctuated around a pH of 8.2. During the period of jelly formation, 15 mg/L of nitrogen was fed to the reactors. Unit A was, however, paid more attention than Unit B by breaking up the clumps of jelly, and returning them back to the aeration vessels. In addition, the volumetric influent flow rate of Unit A was adjusted higher than the flow entering Unit B indicating more inflow of nitrogen to bioreactor A. Once the conditions in Unit A improved, Unit B was given proper

attention by breaking up the clumps of jelly, and returning them back to the aeration vessel. Finally, the jelly was cleared from the units.

The breaking up of clumps of jelly and returning them to the vessels probably improved exposure of the microorganism to the incoming wastewater containing adequate nitrogen for their microbial synthesis. The pH differential between the units can be attributed to the higher influent concentration of nitrogen entering Reactor A. The nitrogen was added in the form of ammonium chloride (NH_4Cl), and was decomposed according to the

$$NH_4Cl \longrightarrow NH_4^+ + Cl^- \qquad [38]$$

$$NH_4^+ \longrightarrow NH_3 + H^+ \qquad [39]$$

Equation [38] was only a forward reaction for the following reasons

- Ammonium ions exist in solution at pH equal to or less than 9
- The pH of the initial mixed liquor was 8.4
- The influent wastewater pH varied from 4.6 to 4.9 during the period of the run.

It can be seen from the above that once the ammonium chloride was added to the wastewater, it dissociated and remained in the form of ammonium ion in the influent carboy and also in this form in the aeration vessel. Thus, Equation [39] was only biologically induced. In simple

terms, the microbes incorporated nitrogen into their cells as ammonia (NH_3), thus releasing hydrogen ion H^+ into the mixed liquor medium, which slightly depressed the pH of the aeration vessel. Therefore, the higher influent of nitrogen into bioreactor A initiated more microbial uptake of ammonia, and more release of hydrogen ion than bioreactor B. The greater release of hydrogen ion (H^+) in bioreactor A caused the pH differential exhibited by the system during the initial period of reactor operation. Regrettably, the influent wastewater flow rate of the two units were not noted during this period.

As the study progressed, the sludges settled considerably better based on the fact that the sludge did not settle at all when the experiment commenced. This result is clearly demonstrated in Figure 10. Thus, the results indicate that nitrogen played a substantial role in the settleability of the sludge, and the loss of jelly from the clarifier units. In addition, Table 11 shows that after July 23, 1984, the units exhibited a consistent build up of MLVSS and MLSS indicating better microbial activity in the units. The MLSS and MLVSS, however, did not reach the initial mixed liquor suspended solids concentration. Nevertheless, the conditions of the bioreactors were satisfactory before the investigational study of the effects of PAC on the sludge unit was begun.

Table 11 data show that the influent COD to the bioreactors was relatively low during the period of jelly formation study. However, Figure 12 shows that this trend changed at the beginning of the study of the effects of PAC on the activated sludge unit and the COD was twice as concentrated. The study commenced on August 3, 1984, and a new wastewater sample was brought from the wastewater treatment plant on that day. The reactors were fed with the new wastewater beginning August 4, 1984, day 2 as indicated in Appendix B. On day 3, the two bioreactors were observed to deviate from the "normal" trend. Normal trend here, refers to the performance after the jelly was cleared up from the reactors, but before the large increase in organic loading. The sludge settleability had been improving but the initial zone settling velocity tests, performed on day 4, showed a worsening of settleability. The settling curves obtained on August 6, 1984 are shown in Figure 25.

In the zone settling curves shown here, bioreactor A had about 2 hours of refloccuation time while bioreactor B had a reflocculation time of 20 minutes. These high reflocculation times are indicative of bulking sludge as evidenced by the zone settling velocities (ZSV) and sludge volume indexes. For instance, bioreactor A exhibited a ZSV of 0.29 feet per hour (ft/hr) with a SVI value of 424 ml/gm, while bioreactor B showed a ZSV of 0.76 feet per

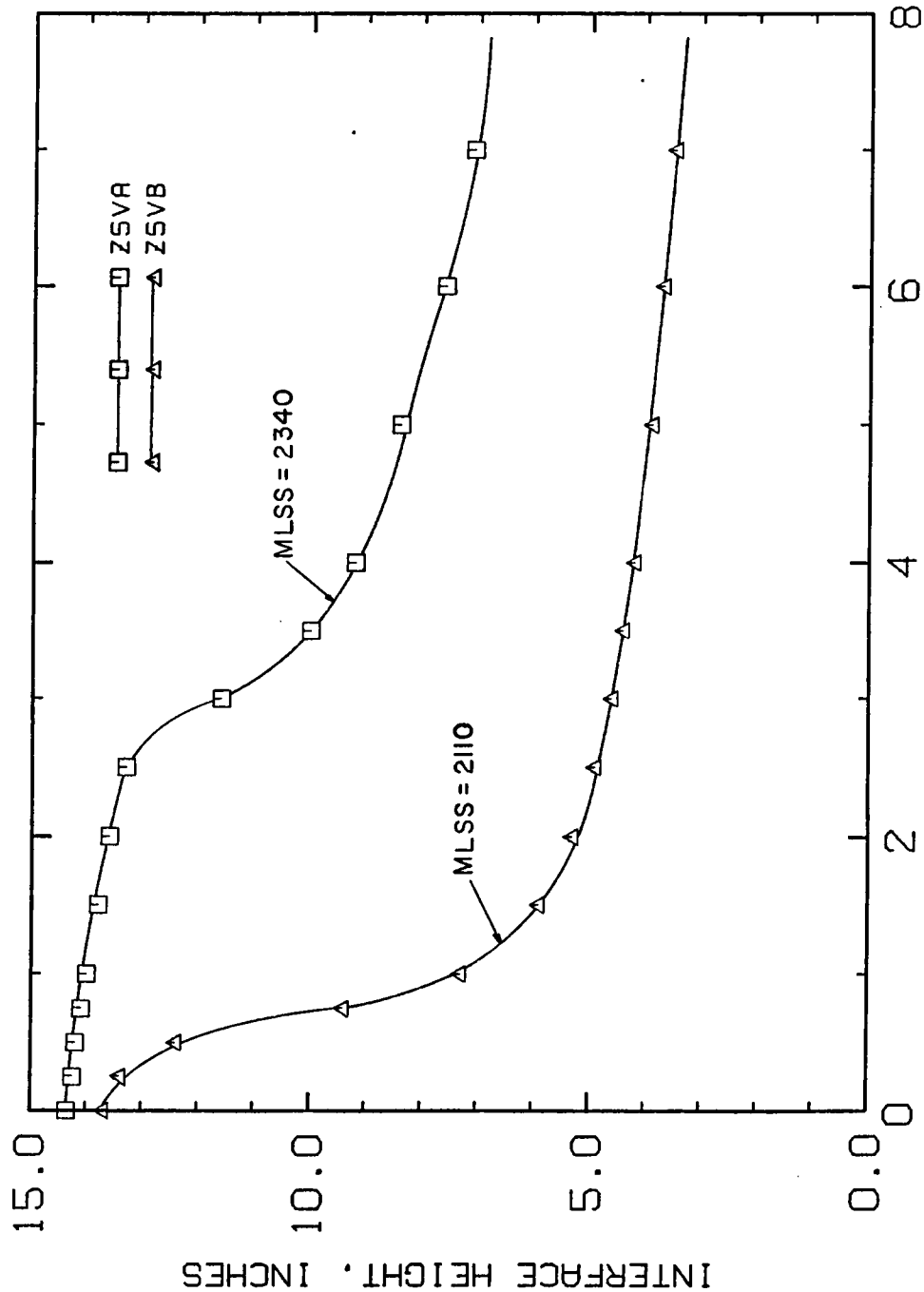


Figure 25. Plots of zone settling curves for the bioreactors with and without PAC for August 6, 1984.

hour with corresponding a SVI value of 427 ml/gm. The zone settling velocity test lasted for 7 hours as the graphs indicate, demonstrating the poor settling of the sludge.

A microscopic examination of the sludges performed on 8/8/84 revealed filamentous microorganism growth in the bioreactors. Unit A showed more filamentous growth than Unit B. The types of filamentous microorganisms were not established because the investigator had little or no knowledge of these types of microorganisms. A zone settling velocity test performed on this day indicated bulking sludges as shown in Figure 26. This time the reflocculation time of Unit A increased from 2.0 to 2.5 hours but that of Unit B decreased to 15 minutes. The zone settling velocity for R_A and R_B were respectively, 0.32 ft/hr and 0.85 ft/hr. However, the reflocculation time of Unit B still indicated a bulking sludge. Furthermore, the settling tests lasted for 9 hours as opposed to 7 hours on August 6, 1984.

At low dissolved oxygen (DO) concentration, some filamentous organisms will grow faster than zoological microorganisms and vice versa for high concentration [62]. It is known that if the oxygen concentration level in the reactor is much below the critical limit of 2 milligram per liter (mg/L), filamentous organisms may outgrow zoological organisms which would adversely affect the settling characteristics of the sludge. Apparently, the extended

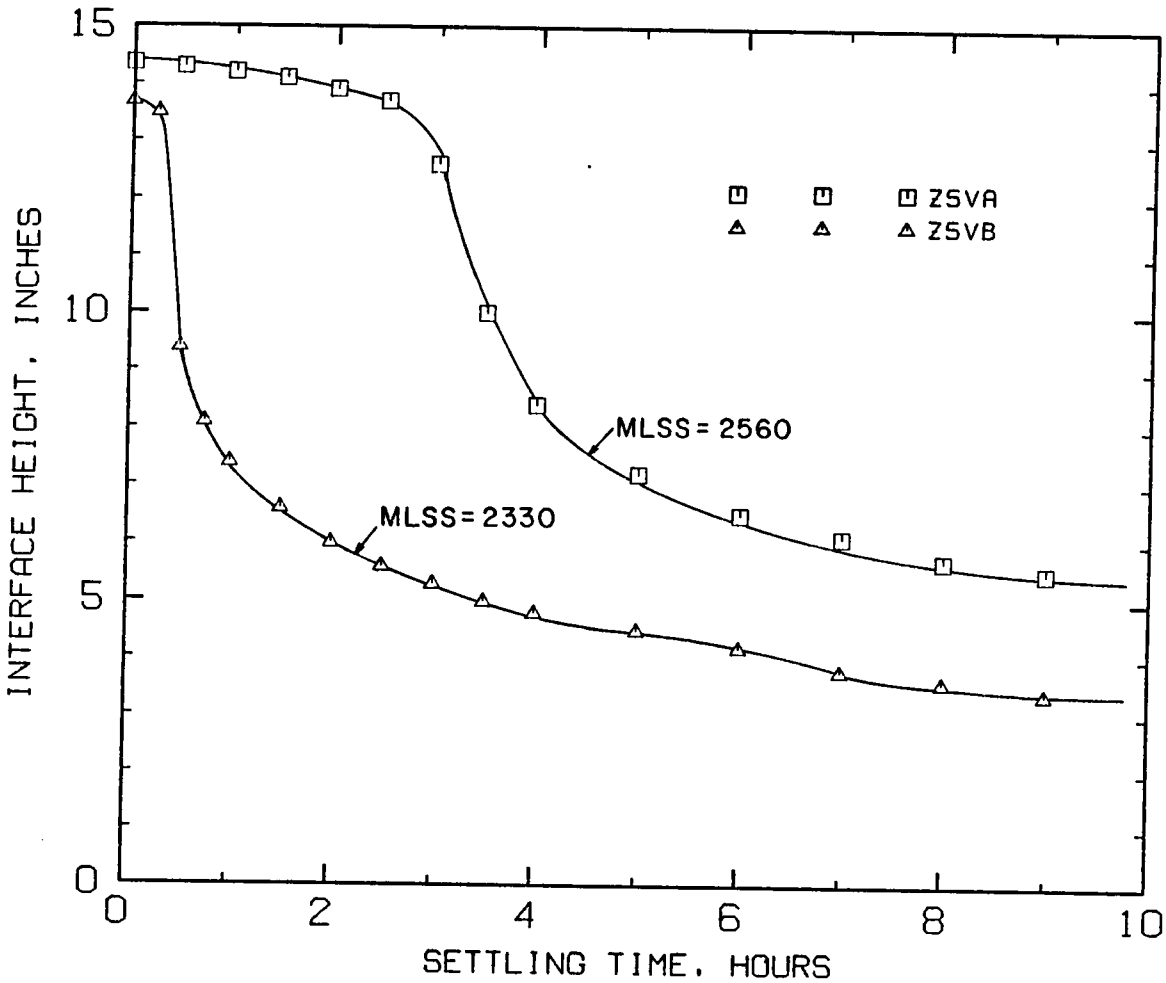


Figure 26. Plots of zone settling curves for the bioreactors on August 8, 1984.

filament of this type of microbe can produce a lot of drag force that can induce poor settling, and can mechanically hinder sludge consolidation. However, low DO was not the cause of the bulking experienced because the dissolved oxygen concentrations on those days were three times, or more, greater than 2 milligram per liter. It should be recalled that the dissolved oxygen in the reactors fluctuated around 6.0. Thus, low DO was not the cause of filamentous bulking experienced in this study.

A look at Figures 11 and 12 indicates that high organic loading was the cause of the system upset. The graphs indicate that the COD and TOC loadings were very high as compared to the influent TOC and COD values presented in Table 11. High organic loading caused by an increase in simple acids and alcohols, could result in nutrient deficiency, principally the nitrogen. The graphs shown in Figures 25 and 26 attest to this conclusion. The greater bulking tendency of Unit A was due to greater bacterial growth which created a need for more nitrogen for microbial synthesis, but no additional nitrogen was available.

The highest ZSV exhibited by bioreactor B on those days may be misleading, because the mixed liquor was dispersed during the test period. Unit A exhibited better biological flocs but they were not very good, based on microscopic examination. Figure 27 further demonstrates this fact. It

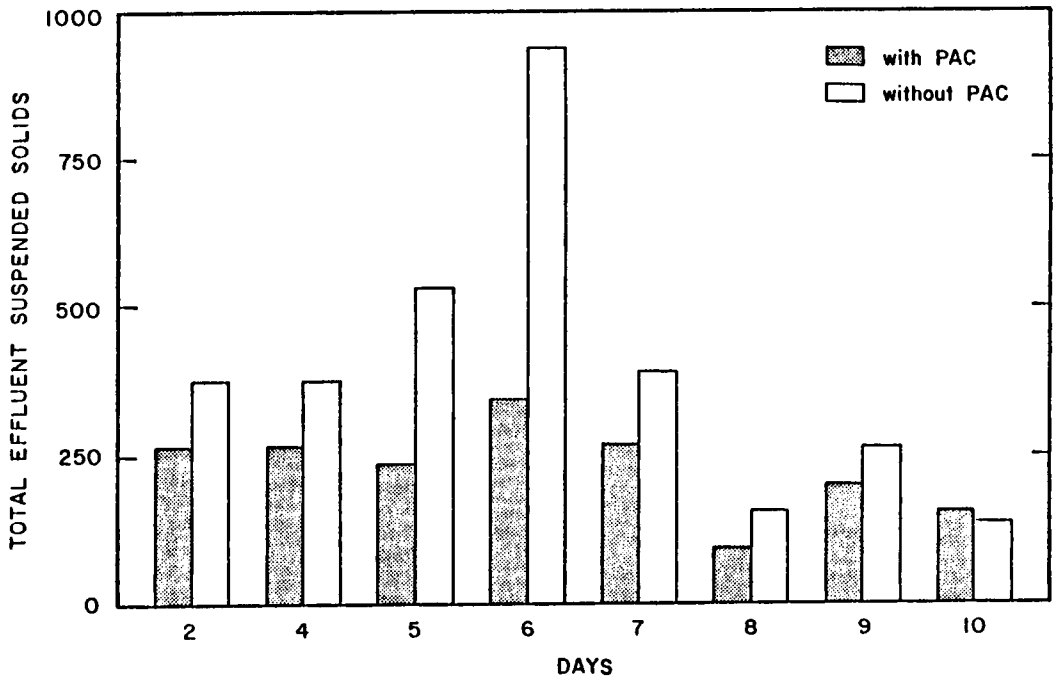


Figure 27. Total effluent suspended solids during the first shock organic loading at various carbon concentrations (20 mg/L to 180 mg/L).

summarizes the effluent suspended solids for each bioreactor during this period of biological upset. From the data presented in Figure 27, Unit B showed a high lost of solids through the effluent weir during the period of the shock organic loading. No wasting was performed for Unit B on days 5 and 6 because the suspended solids lost exceeded the computed value required for manual wasting. The effluent suspended solids from bioreactor A were also high. Figure 11 shows the sharp decrease in MLSS of the units after day 5, which can be attributed to the loss of solids through the effluent weirs caused by the organic shock loading. The results clearly indicate that carbon can reduce effluent variability in the presence of shock loading. This conclusion is also supported by Figures 11 and 12 which show that the effluent substrate concentrations from bioreactor A were significantly lower than those of bioreactor B on day 2 to day 10. Because of the high organic loading, the influent nitrogen was adjusted from 15 mg/L to 75 mg/L, and the conditions of the bioreactors returned to normalcy.

Interestingly, the Wastewater Treatment Plant was visited in the week of the biological upset in the laboratory units. It was found that the clarifier units of the treatment system were plagued with problem of jelly formation - very black chunks of sludges that were very slimy when touched. In addition, effluent standards were

grossly violated during the week [52] indicating the intensity of the upset. The plant, however, was not adding nitrogen to the influent wastewater, and was recalcitrant to do so regardless of the biological upset, and the problem, therefore, persisted.

Most of the staff of the Wastewater Treatment Plant contended that the mesityl oxide (MeO) was the cause of upset rather than nitrogen deficiency [52]. The results of this investigation cast considerable doubt on this theory. Nitrogen analysis performed on the raw wastewater on July 30, 1984 indicated total Kjeldahl Nitrogen (TKN) to be 0.28 mg/L. In essence, the wastewater contained no nitrogen. As a consequence, the test was discontinued, and, throughout the experiments it was assumed that the cellulose acetate manufacturing wastewater did not contain nitrogen.

Appendix H, Table H-5 to 7 shows the influent and effluent mesityl oxide (MeO) of the bioreactors obtained throughout the period of the investigation. Table H-5 indicates that influent MeO concentrations were 0.5 mg/L, 0.7 mg/L, and 0.5 mg/L on days 2, 9, and 15, respectively. The effluent from R_A on day 2 was 0.7 mg/L and from R_B was 0.6 mg/L. These high effluent values may be resulted from analytical errors but, regardless, the level of concentration was not believed to be high enough to cause biological upset of such a magnitude [52]. Celanese

personnel believe mesityl oxide is toxic to microorganisms at a concentration level of 2 mg/L [55] and the concentrations were below that level. Furthermore, days 9 and 5 indicated biodegradability of this compound. For example, the concentrations were reduced from 0.7 and 0.5 mg/L, respectively, to 0.3 mg/L for reactor A, and 0.2 mg/L for reactor B for both days. In the appendix table cited, the MeO was removed essentially in equal amounts by the reactors. If it were not biodegradable by the microbes, Unit B should have indicated little or no removal of this compound.

Tables H-6 and H-7 show that the influent concentrations of MeO were very low during most of the 160 mg/L and 20 mg/L PAC runs. Concentrations of 0.1 mg/L were actually too low to be detected [52]. These data indicate that MeO was not a factor in the biological upset of the reactors. It should be noted that the treatment plant experienced jelly formation over most of the summer period. While the laboratory units were jelly-free throughout the period of the investigation.

Appendix H, Table H-1 indicates that large increases in acetic acid, ethanol, acetone and methyl cyanide may have been the cause of the upset. Typically, increases in acetic acid, methanol and acetone are responible for high organic loadings. In addition, high levels of acetic acid and acetone may be associated with higher level of MeO

[53]. Unfortunately, data on acetic acids on days 2, 9, and 15 were not obtained. However, the ethanol values were very high and the acetone value was high on day 9. High acetic acid values were measured on days 21 and 24, corresponding to the high COD and TOC values shown in Figures 11 and 12. Again, the acetic acid concentrations were low on days 27 and 30 corresponding to low and TOC values. Thus, it can be deduced that acetic acids were high on days 2 and 9 because the TOC and COD values were high.

All compounds shown in Table H-1, Apendix H were completely biodegraded, except on day 9 when there was an effluent concentration of 3 mg/L acetone from bioreactor B. Acetone biodegradation is known to be slower than the other compounds [15]. Therefore, at relatively high levels of acetone, biodegradation may not go to completion in the biological unit without PAC, but might in the reactor with PAC because it would be adsorbed by the carbon and held in the system longer.

A comparison of Appendix H, Table H-3 with plots of COD presented in Figure 16 demonstrate that acetic acid and acetone, usually correlate well with COD. For example, on day 54 the COD concentration was 3140 mg/L while acetic acid and acetone were, respectively, 620 mg/L and 42 mg/L. Then, on day 71, acetic acid and acetone were, respectively 620 mg/L and 190 mg/L and the COD value was 4550 mg/L.

When acetic acid and acetone were low, COD values were also relatively low. However, on only one day (day 65) was this pattern not followed. Table H-4 and Figure 24 show a similar trend.

An experimental study set up by Kajornatuyudh in October 1984 does not fully support the findings of this investigation that nitrogen difficiency is the primary factor that causes jelly formation. He attempted to stimulate jelly formation in the laboratory by operating two reactors in parallel, one fed with nitrogen and the other without nitrogen. The feed wastewater and sludge was directly from the Celco Wastewater Treatment Plant. However, jelly was not formed in the unit without nitrogen addition, neither was it formed in the unit with nitrogen addition. This result was not a failure, however, because it gave additional clues to the cause of jelly formation. A postulate arising from it is given in the next paragraph.

Jelly is most frequently observed in the cellulose acetate wastewater treatment plant during the summer months [52]. Therefore, temperature may be an important factor in the cause of this phenomenon. This does not necessarily eliminate nitrogen deficiency as a factor, however. High temperatures would induce higher growth rates which could result in nitrogen deficiency if sufficient nutrient were not present to meet the increase in microbial activities. Also, at temperatures above the mesophilic range, the

mesophilic bacteria typically found in the activated sludge process may begin to fail metabolically. Such a failure could lead to the formation of excessive amounts of extracellular material and it could also lead to a shift in the types of microorganisms in the system.

The failure of Kajornaturyudh's experimental units to produce jelly formation could possibly be attributed to the low temperature of the test, which was about 18^{o}C. Thus, the conditions for jelly formation were not completely satisfied, and it did not occur.

Prior to the experiment mentioned, Kajornatuyudh experimented with the jellied activated sludge originally obtained, and fed it with synthetic wastewater [33]. Nitrogen was fed to the reactor in the form of a nitrate. It was found that the jelly disappeared just as it did in the experiments of this investigation when ammonium was added. These results do not eliminate the possibility that some of the organics in the wastewater that may be the primary cause of the jelly formation problem.

Based on the data collected in this study, acetic acid and acetone are likely stimulators jelly formation. Of these, acetic acid is the most likely based on the fact that acetone can be further oxidized in the presence of oxygen to form acetic acid as shown by the following equation [47]

$$\underset{\text{[Acetone]}}{CH_3\overset{\overset{O}{\|}}{C}CH_3} + 2O_2 \rightarrow CO_2 + H_2O + \underset{\text{[Acetic acid]}}{CH_3COOH} \qquad [40]$$

Acetic acid has been found to cause activated sludge filamentous bulking [72] at the Southerly Wastewater Treatment Plant in Columbus, Ohio. This plant was characterized by filamentous bulking with SVI values of 300 to 400 ml/gm during late summers - a period when wastewater temperature was 21°C and wastewater flow was low. It was concluded that neither low dissolved oxygen level nor nutrient deficiency was the cause, rather it was attributed to acetic acid. Bench scale units that consisted of 1-liter graduate cylinders operated in a fill-and-draw [72] mode to stimulate ideal plug flow were used in the investigation. The results of Sykes et al. are summarized in Table 17 with the conditions of the experiment. Based on the data shown here bulking occurred with acetate regardless of the operating BSRT. Interestingly, at high F/M (1.2) with DO level greater than 5.0 mg/L, bulking did not occur with Southerly wastewater only. In most experiments, bulking occurred only when a low/high DO level pattern was used. However, at the lowest BSRT and lower temperature (20°C) filamentous bulking occurred with high DO level. The results of this

Table 17. Laboratory bench scale investigation of the effects of acetic acid on Southerly wastewater [After Sykes et al, 1979].

Experiment No.	Wastewater Type	BSRT (days)	SVI ml/mg	F/M $\frac{g\ COD}{gMLSS\ day}$	Temp. °C	DO mg/L	COD (mg/L) Influent	COD (mg/L) Effluent	Type of Filamentuos Microbe
1	Southerly	15	80	0.89	30	> 6.0	220	40	None
1	Southerly & Acetate*	15	200	0.52	30	0.5/4.0[b]	1000	98	Schizothrix
2	Southerly	12.5	80	0.50	30	> 5.0	490	33	None
2	Southerly & Acetate*	12.5	58	1.2	30	> 5.0	1000	72	None
2	Southerly & Acetate*	12.5	220	0.45	30	0.5/5.0[b]	1000	67	Schizothrix
3	Southerly	10	100	0.40	20	> 7.0	500	38	Schizothrix
3	Southerly & Acetate*	10	110	0.540	20	> 7.0	1080	47	Schizothrix
3	Southerly & Acetate*	10	132	0.52	20	0.5/5.0[b]	1080	43	Schizothrix
3	Southerly & Acetate*	10	292	0.59	20	1.0/5.0[b]	1080	45	Schizothrix

* sodium acetate

b Low/high DO pattern [Ce]. DO was 4 hours below 0.5 mg/L followed by 7.0 hours above the value indicated and was fed once every 12 hours.

a DO was less than 1.0 mg/L for 12 hours and remained at level of 5.0 mg/L throughout the period of feed. Fed once every 12 hours.

pH of the reactors varied from 7.0 to 8.7.

laboratory investigation were then applied to a wastewater (Jackson Pike's settled wastewater) similar in characteristics to the Southerly wastewater. It was found that Schizothrix bulking occurred. Therefore, the conditions reported in the table are favorable for the propagation of Schizothrix microorganisms.

Thiothrix, a filamentous bacteria has been reported to cause activated sludge bulking [19]. These microorganisms are capable of oxidizing hydrogen sulfide (H_2S) and bisulfide ions to elemental sulfur. They like black and septic wastewater [19] and, thus the presence of H_2S can stimulate thiothrix growth and potentionally cause bulking sludge. Farquhar and Boyle [19] used plug flow reactors to show activated sludge bulking by thiothrix. In their study, the DO levels in the reactors were 1.6 and 4.6 mg/L with an operating F/M of 0.3 to 0.99 BOD_5/g MLVSS and influent sulfide concentrations of 0.06 to 1.9 mg/L. The SVI values reported due to thiothrix bulking were 145, 590, 582, and 872. Unfortunately, the temperature of the experiment was not reported in the article.

Substrate Removal at the Various PAC Dosages

Figures 11, 12, 16, and 21 indicate that PAC enhanced the removal of substrate as measured by COD and TOC. Appendix F indicates the computed improvement measured each day readings were taken. It is imperative to note that

Unit B was the fixed base for computation of improved COD removal and the percent improvement induced by PAC. Using the values in Appendix G, the bar graphs for the various equilibrium carbon dosages were drawn, and are depicted in Figures 28, 29 and 30.

Figure 28 shows that the 280 mg/L PAC system had greater COD removal everyday except one, and the effluent COD reading on that day is questionable, because the TOC values indicated improved substrate removal. Considering that TOC correlates well with COD for this wastewater, the COD measurement appears to be in error. Regardless, Unit A had better substrate removal over the period of the run than Unit B as evidenced by the data in Table 11, and figure 29 illustrates that the average improvement was 14 mg/L of COD for an effluent quality improvement of 24 percent.

Presented in Figure 29 is the bar graph representing the daily increase in COD removed and their percent improvements at PAC concentration of 160 mg/L. The comparative plots of COD removal with respect to the control unit are shown in Figure 16. This figure also appear to exhibit enhanced substrate removal by PAC. The bar graphs indicates two times where Unit B had slightly better substrate removal than Unit A, however, the PAC unit removed 20 mg/L more COD on the average for an effluent concentration improvement of 20 percent.

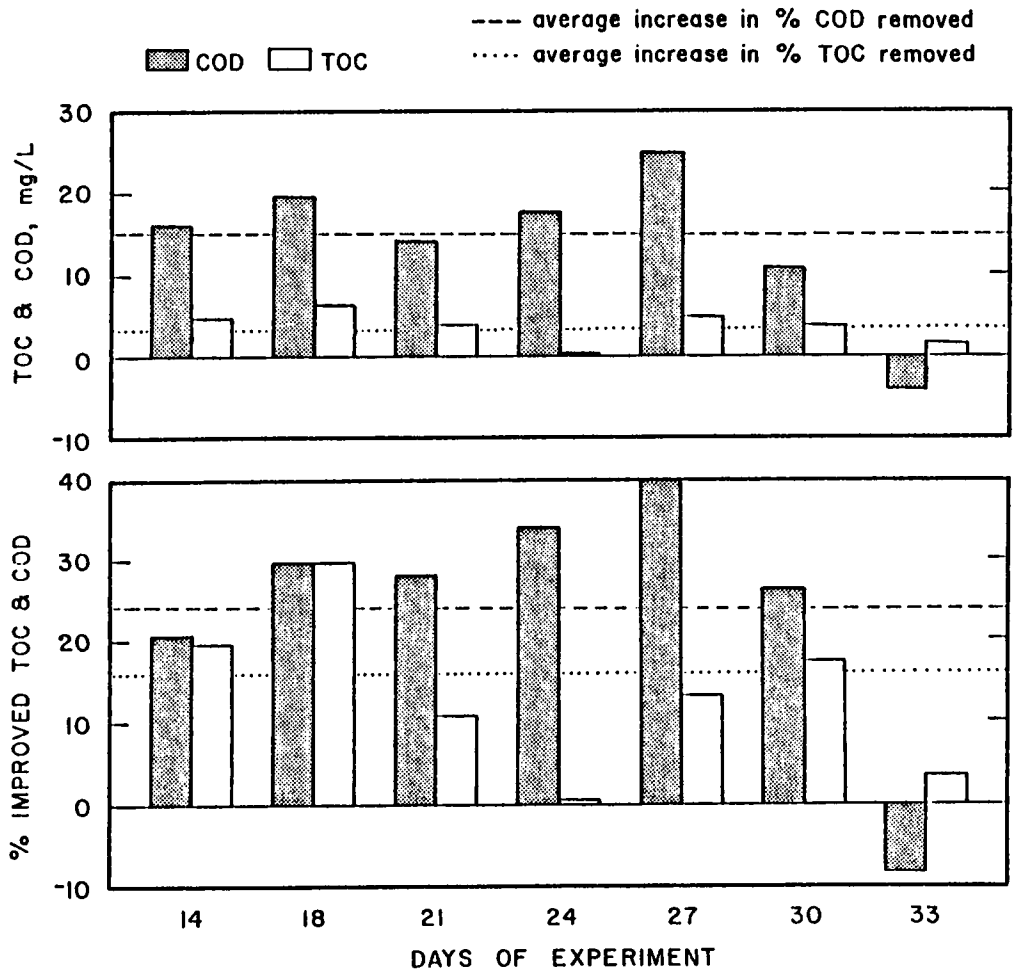


Figure 28. Enhanced substrate removal by PAC at equilibrium carbon concentration of 280 mg/L.

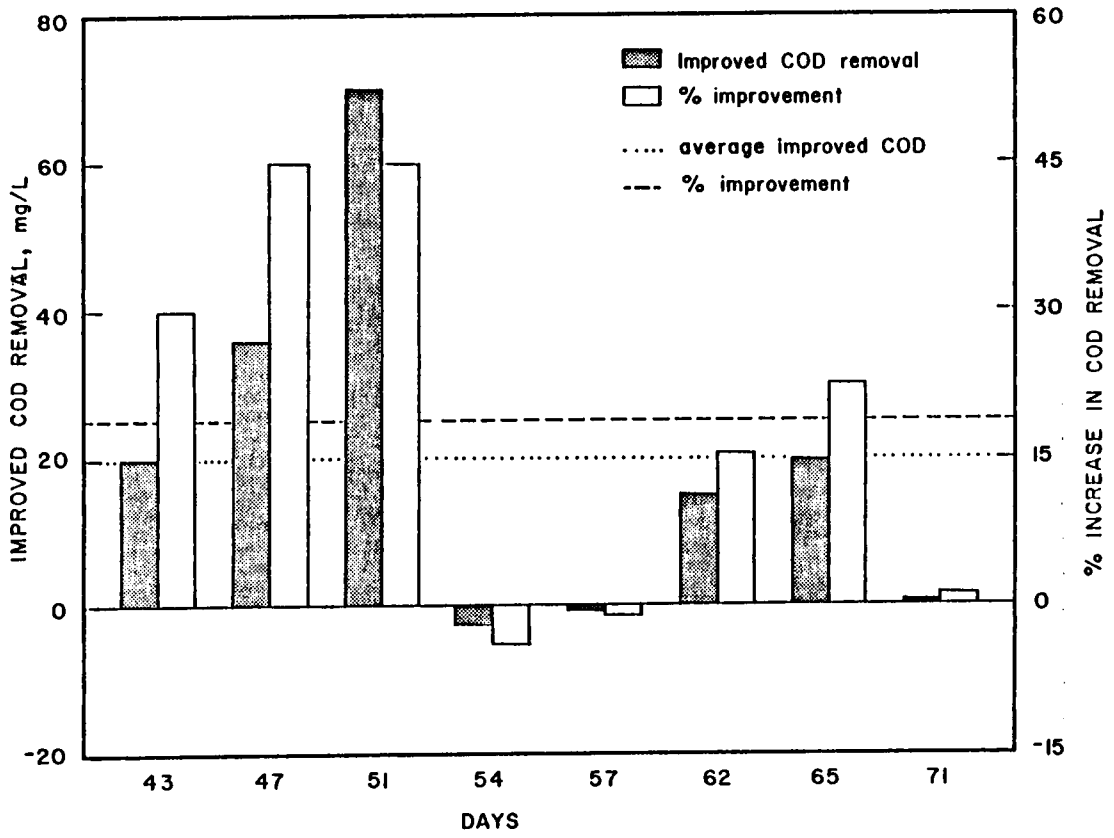


Figure 29. Enhanced COD removal by equilibrium carbon centrations of 160 mg/L.

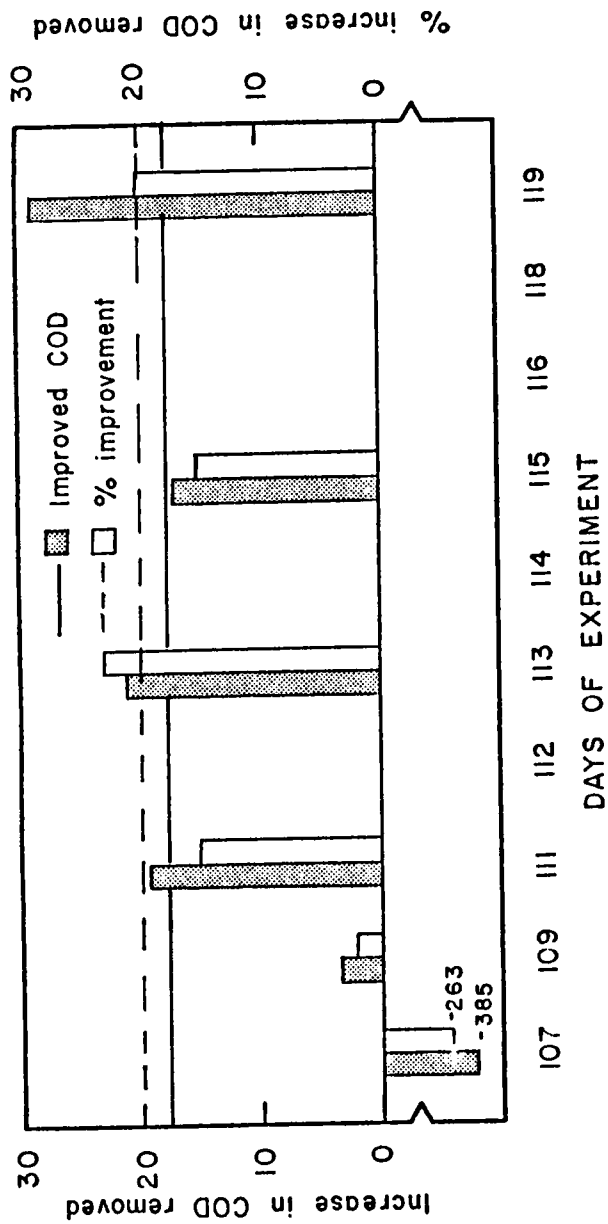


Figure 30. Enhanced COD removal by equilibrium PAC concentration of 20 mg/L.

Again, TOC analysis indicated that Unit A had better TOC removal than Unit B on the days COD removal appeared to be better in Unit B.

A look at the average COD loadings and food to microorganism (F/M) ratio over the period of the runs shows that the average influent COD to the system during the period of 280 mg/L PAC was 2820 mg/L while 3520 mg/L was the average for the 160 mg/L PAC run. Unit A at 280 mg/L PAC had a F/M of 0.55 while the control unit F/M was 0.67. During the 160 mg/L PAC run, Unit A F/M was determined to be 0.69 and it was 0.78 for the control unit. Clearly the units were subjected to higher organic loadings during the 160 mg/L PAC run, which may have caused greater effluent pertubations. At 280 mg/L PAC, the average COD effluent concentration were 42.7 mg/L with PAC and 56.8 mg/L without PAC. For the 160 mg/L run the PAC unit average was 73.9 mg/L, and control unit average was 93.8 mg/L. The higher effluent concentrations and higher variations in effluent quality, from the 160 mg/L PAC run, could logically be attributed to the higher F/M ratios.

Shown in Figure 30 is the bar graph for enhanced COD removal and percent COD improvements measured for the equilibrium carbon concentration of 20 mg/L PAC compared to the control. The first day of the experiment, day 107, the control reactor effluent was much better than the PAC reactor effluent, but the PAC unit performed increasingly better throughout the rest of the run.

Appendix E (B_5b_6) shows that the DO was 3.3 mg/L on day 107 - the lowest value ever measured during the investigation. On the day cited here, the flow rate entering bioreactor A was found to be higher than the influent volumetric flow rate of bioreactor B over an order of magnitude, due to malfunctioning of the pump or the pump was not properly adjusted. The author cannot actually account for which one was the major cause. Anyway, the effluent carboys were observed to have different volumes of the effluent liquid. The liquid volume of Unit A was found to be about three times higher than that of Unit B. Thus, bioreactor A had an organic loading within the 24-hour period that was approximately three times greater than the loading received by bioreactor B. This was reflected by the low DO measurement. Unfortunately, the oxygen uptake rate was not taken on that day. Once the situation was corrected, Unit A showed a better COD removal throughout the period of the investigation as evidenced by the bar graph. The average COD removal, and the percent COD removal are drawn on Figure 30.

Thus, this investigation indicated an enhancement of COD removal with PAC addition. The increases in COD removal were, 14 mg/L, 20 mg/L, and 18 mg/L at the respective equilibrium carbon concentrations of 280 mg/L, 160 mg/L, and 20 mg/L. The increase is not proportional to the equilibrium carbon concentrations indicating higher

carbon concentrations do not necessarily enhance substrate removal better than lower equilibrium carbon concentration. However, the influent concentration for the 160 mg/L run was considerably higher than for the 280 mg/L run and this could account for the difference between these two runs. It is interesting to observe that the percent COD removal predicted at earlier trial run (days 2 and 9) at equilibrium PAC concentrations of 20 mg/L and 160 mg/L were almost equal to that collected at these concentrations at their steady state runs. For example, percent improved COD removal on day 2 (20 mg/L PAC), was 18 percent as compared to 15 percent over the steady state run. In addition, day 9 (160 mg/L PAC) improved percent COD removal was 25 percent as compared to 20 percent over a steady state period.

Table 18 compares the results of this investigation in terms of substrate removal with the results of other investigators. The table indicates various types of wastewater used, and different operating conditions. Regardless of the operating conditions plus wastewater type, the table suggests that this investigation achieved an appreciable removal of organics.

The higher percentage shown in the table for some of the investigators may be due to the wastewater containing a substantial amount of slowly biodegradable but readily adsorbable organics. For example, Specchia and Gianetto

Table 18. A comparison of the results of enhanced COD removal with other investigators.

Wastewater Type	Improved COD Removal (mg/L)	Percent Improved Removal	Equil. PAC Conc. mg/L	BSRT (days)	HRT (days)	Type of Experiment	Temp. °C	Researcher	Reference No.
Dye Works Wastewater	256	45	800	C	C	Full scale	C	Specchia & Gianetto	68
Synthetic	C	15 25	50 300	5 10	1.05	Laboratory bench scale units	C	DeWalle et al.	17
Oil Refinery	26[d]	36[d]	100[b]	20	0.625	Pilot plant	31	Grieve et al.	27
Oil Refinery	C	21	500	C	C	Full scale	C	DeJohn & Black	15
Cellulose Acetate	14	24	280	14	4	Laboratory scale unit	18	This research[a]	a
Cellulose Acetate	20	20	160	14	4	Laboratory scale unit	18	This research[a]	a
Cellulose Acetate	18	15	20	14	4	Laboratory scale unit	18	This research[a]	a
Dupont Chambers	9.8	29	151	8.8	0.26	Laboratory scale unit	22	Flynn	21
Dupont Chambers	3.7	11	51	8.5	0.26	Laboratory scale unit	22	Flynn	21
Dupont Chambers	79	49	145	8.7	0.26	Laboratory scale unit	22	Flynn	21
ICI Polyols	C	25	1000	C	C	Full scale	Winter months	Adams	1

C = not reported in the literature
b = true equilibrium concentration = 3200 mg/L, determined by $C(\theta_c/\theta)$, i.e. 100 (20/.625) = 3200, since carbon was fed in form of a slurry.
d = average of the results of four different carbon types

[68] attributed the substantial amount of COD removal to the presence of hard to biodegraded organics, and, therefore, the efficiency of PAC was maximized. Powdered activated carbon is well suited to wastewaters containing adsorbable but poorly biodegradable organics [20,21]. Unfortunately, Specchia and Gianetto [68] did not report the biological solids retention time (sludge age) and this reduces the usefulness of their results.

Flynn's [21] high increase in percent COD removed may be misleading at a glance. It was noted in the article published that the biological control units were operated at a different BSRT. The BSRT of the control units were lower than those of the PACT unit by about 1.1 to 1.9 days. It is believed that lower biological solids retention times of poorly biodegradable organics will result in a poorer effluent COD based on the fact that they have lower contact times with the control units biomass. Nevertheless, the difference could not have enhanced the effluent COD of the control units, considerably.

The values reported by Grieve et al. [27] is considerably higher than the values found in this study. The temperature of operation was higher and the system was operated at a higher sludge age than the ones used during the investigation. The carbon was fed in the form of a slurry, and therefore, the true equilibrium carbon concentration would be higher as demonstrated by the following equation

$$C_e = C_o \left(\theta_c / \theta \right) \qquad [1c]$$

where the parameters are as previously defined. Thus, it is now evident that the results of this study is quite comparable to Grieve et al. 's result.

DeWalle et al. [17] and DeJohn and Black [15] findings are comparable to the results of the investigation. However, DeJohn and Black indicated unsatisfactory performance of their full scale units under the conditions reported in the table due to high influent oil concentrations (100 mg/L) into the aeration basin of the treatment plant.

DeWalle et al. [17] as the table indicates used synthetic wastewater which is highly biodegradable. In addition, the glucose used in the make up of the synthetic wastewater has a low affinity for carbon. Thus, the synthetic wastewater used was somewhat similar to cellulose acetate manufacturing wastewater based on biodegradability and poor affinity for carbon but good affinity for water. In this study, the removal rate was not very proportional to increasing carbon dosages a similar trend noted by DeWalle et al. [17].

Flynn [22] reported that rapidly biodegradable organics are equally removed by the activated sludge and PAC processes. Cellulose acetate contains a lot of

biodegradable organics based on the results of the biological control unit. The percent efficiency determined by (COD_{inf} - COD_{eff}/COD_{inf}) multiplied by 100 of the bioreactor B over the whole period of the investigational study was found to be 97. Thus, the improvement beyond the control units indicate that wastewaters contain a small amount of slowly biodegradable organics. It can equally also be deduced that the effluent from bioreactor B contains more refractory organic compounds than effluent from bioreactor A.

Oxygen Utilization at the Various PAC Dosages

The oxygen utpake rate in the PAC units was usually higher than the oxygen uptake rate in the control units. The average increase in the uptake rates, and the percent increases, for the three runs are given in Figures 31, 32, and 33. As the bar graphs show there were occasions when the control unit oxygen uptake rate was greater, but these were the exceptions.

Figure 31 shows that only on one occasion was the control unit oxygen uptake rate greater than the PAC unit uptake rate during the 280 mg/L PAC study. Also, the difference in readings on that day was very small and was well within the range of experimental error.

The data presented in Figure 32 show that there were two times out of seven when the control unit for the 160

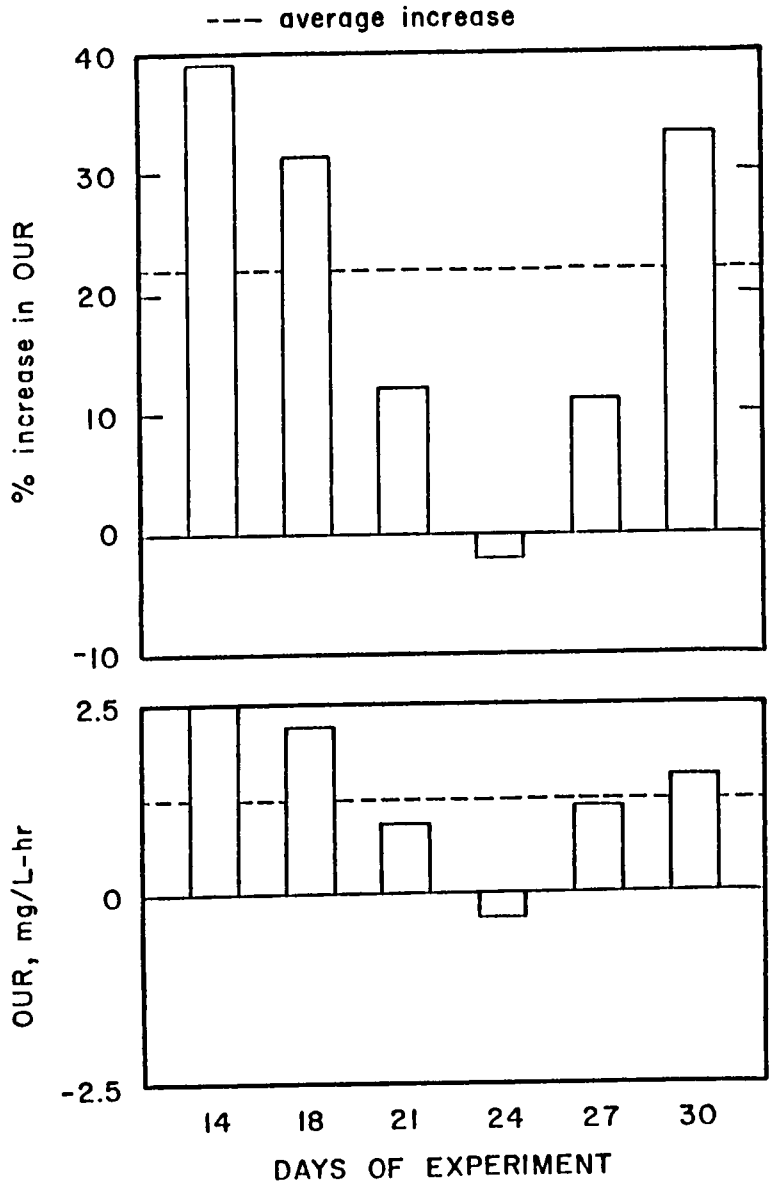


Figure 31. Improved OUR and percent improvement by Reactor A at PAC of 280 mg/L over Reactor B.

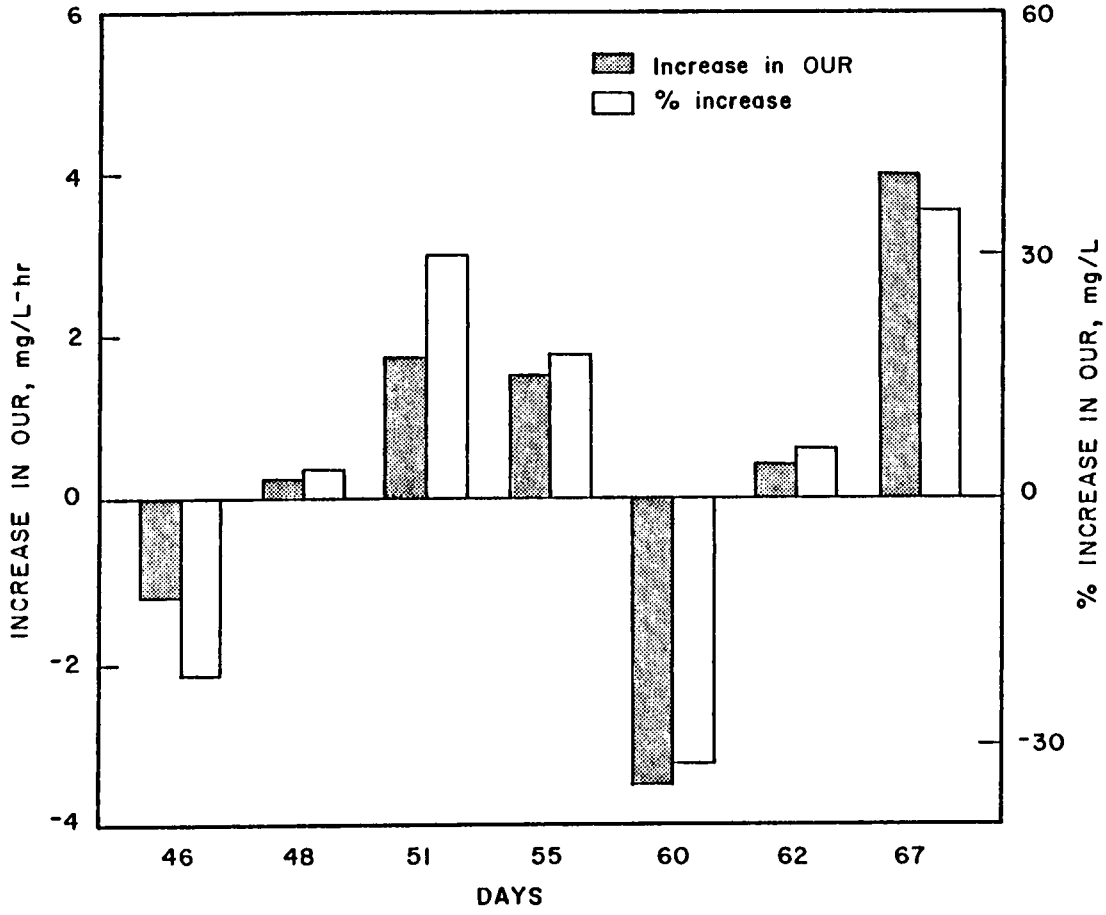


Figure 32. Improved OUR and percent improvement by Reactor A at PAC of 160 mg/L over Reactor B.

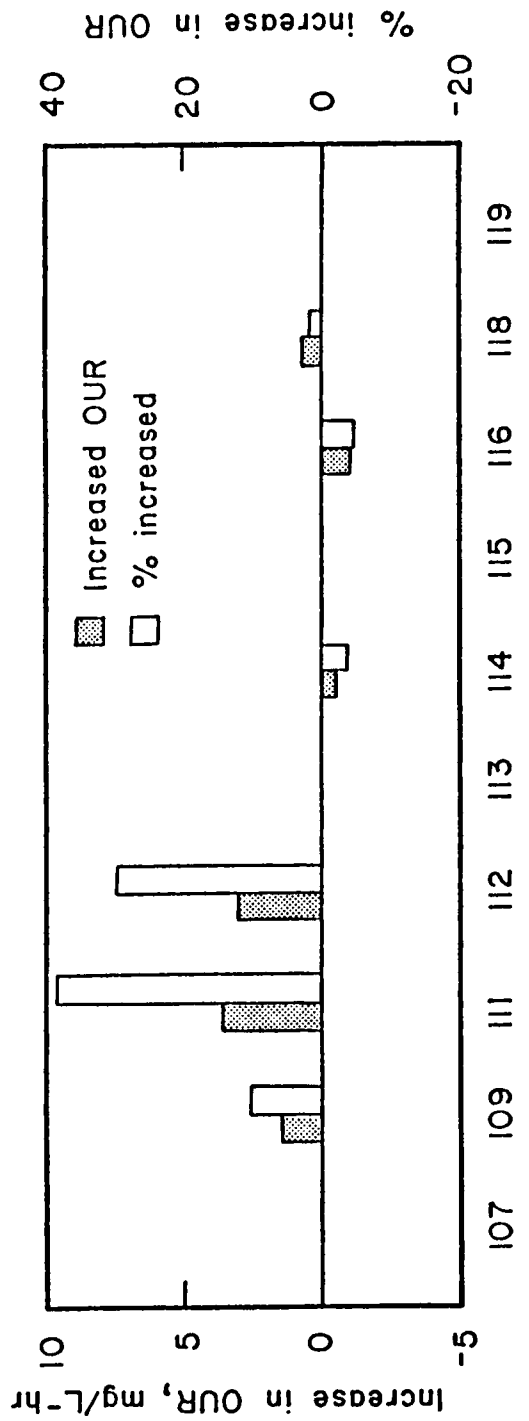


Figure 33. Trends of oxygen uptake rate increase by 20 mg/L PAC.

mg/L PAC experiment had a higher oxygen uptake than the PAC unit. Furthermore, the differences were substantially greater than the control unit on only three occassions, the average increase in the PAC unit oxygen uptake rate was only marginally higher than the control unit average.

Oxygen uptake rate increase measured during the 20 mg/L PAC experiment, illustrated Figure 33, show that the uptake rate of the control unit was greater on two occasions. However, the bar graphs show that the differences were small and within the limits of experimental error. In fact, the average OUR increase measured over the period of steady state was 1.3 mg/L-hr, which is quite substantial.

It can be seen, then, that the PAC units had a greater rate of oxygen utilization than the control units. To what can that be attributed? It should be noted that the biomass concentration in the PAC units was always greater thanthat in the controls. The average mixed liquor volatile suspended solids (MLVSS) for the bioreactors during the periods of steady state are given in Figure 34. The greater biomass in the PAC units would have been responsible for the greater oxygen utilization they exhibited.

The specific oxygen uptake rates (SPOUR) of the bioreactors shows that the PAC oxygen utilization rates were greater only because of greater biomass. The SPOUR value for the control units was always higher than that of

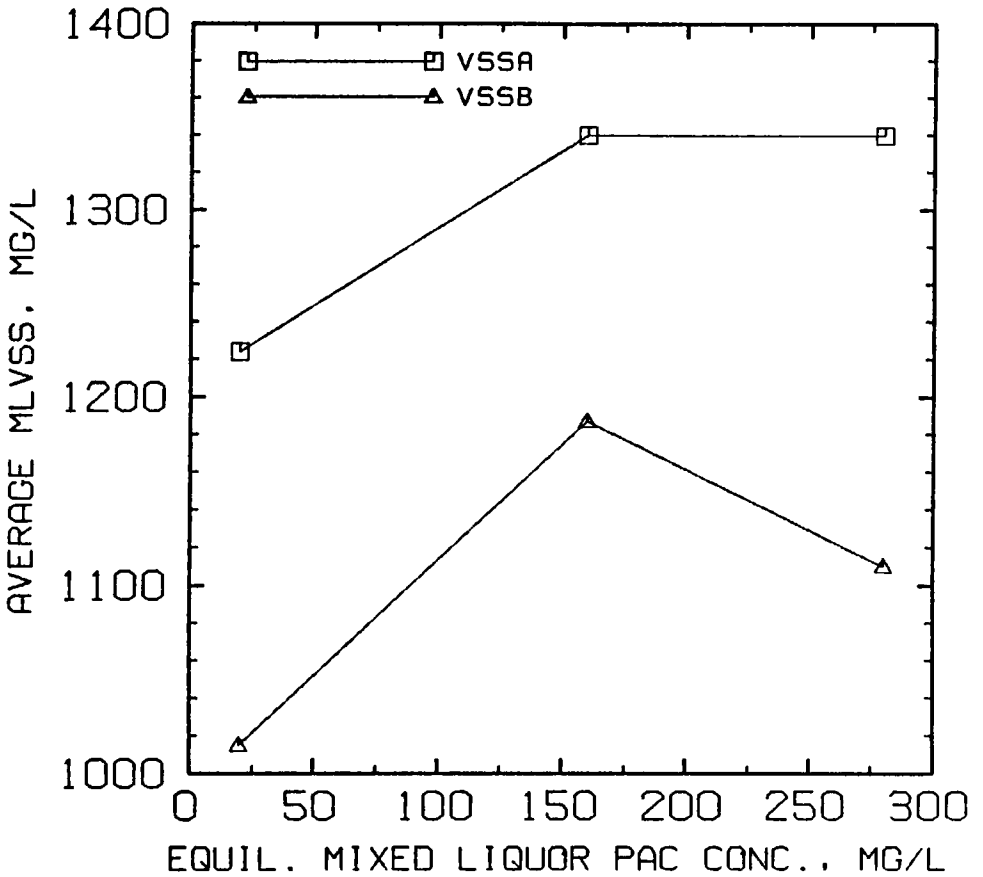


Figure 34. Average Mixed Liquor Volatile Suspended Solids of the bioreactors at various equilibrium carbon dosages operated at BSRT of 14 days.

the PAC units, showing that the control unit biomass was more active, even though it removed less substrate and used less total oxygen. Interestingly, the increase in the SPOUR difference between units was inverse to the PAC concentration in Unit A. This is the reverse of what it should be if the addition of PAC was responsible for the lesser SPOUR values in the PAC units. It was concluded that the SPOUR differences were because of the lesser MLVSS concentrations in the control units, which resulted in a higher F/M ratio.

Mechanism of Enhanced Substrate Removal

Results of the experiments showed that the units with PAC addition removed more COD than the control units. The effluent COD was always significantly less from the PAC units, but the improvement in mg/L could not be related to the PAC concentrations. However, when expressed as percent improvement, an apparent linear relationship with PAC concentration was obtained. But, extrapolation of the line to a PAC concentration of zero indicates that the PAC units were 14 percent more effective than the control untis in removing COD than the control untis, independent of the PAC in the untis. This data is illustrated by Figure 35.

Scaramelli and DiGiano [58] concluded that physical adsorption was a factor that produced a substantial improvement in effluent TOC on addition of PAC, but they

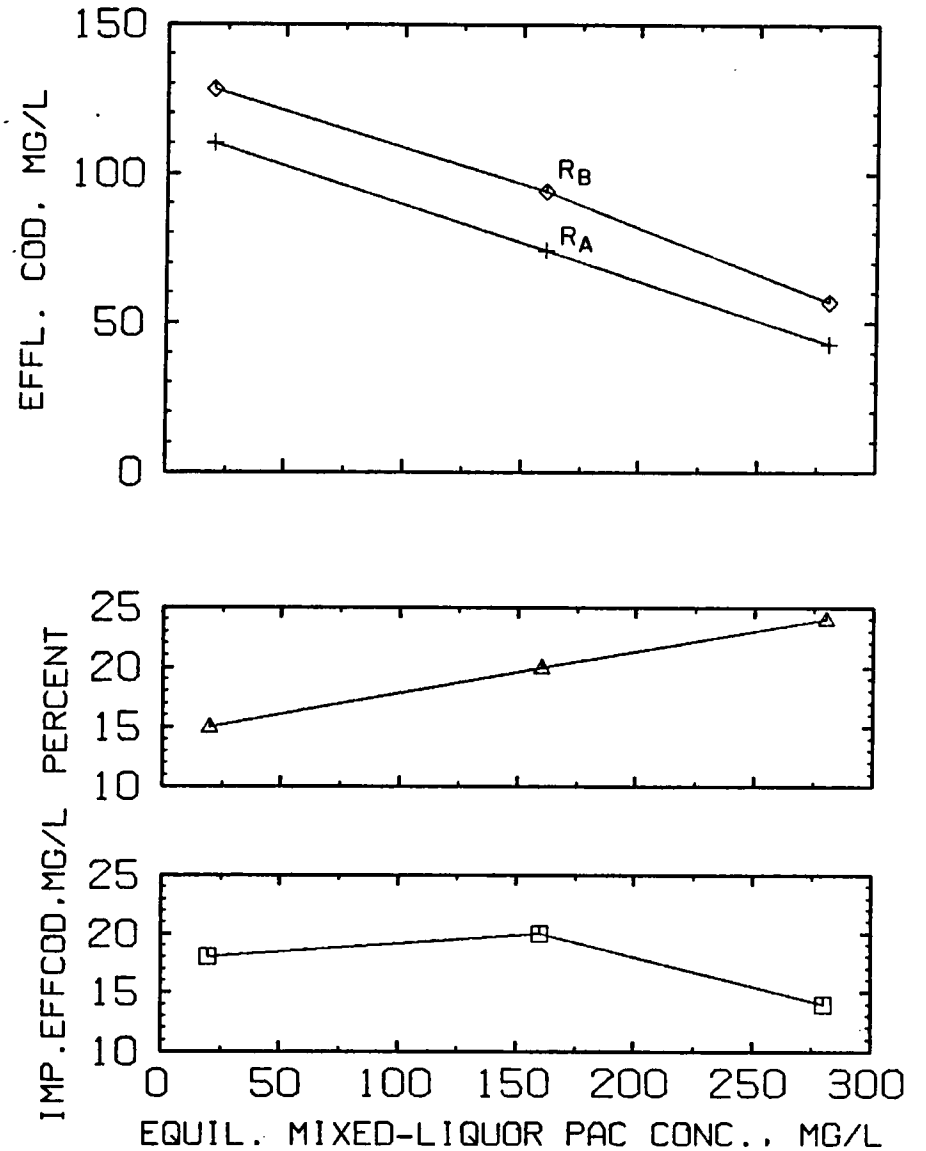


Figure 35. Effects of various PAC concentrations on the effluent COD at BSRT of 14 days.

measured no increases in oxygen uptake rate and steady state mixed liquor suspended solids (MLSS) during their study.

Specchia and Gianetto [68] postulated that increased bioactivity and bioregeneration were the mechanisms of enhanced substrate removal in their study, because oxygen uptake was found to increase on the addition of PAC to the sludge unit. Their conclusion is questionable, however, because the biomass production rate they reported for the PAC unit was lower than the control unit, as reflected in the growth yield factor shown in Table 21. Nonetheless, these authors postulated that PAC concentrations induced larger populations of bacteria in the PAC macropores even though their postulate was not supported by their data.

Crame [14] used apparent carbon loading as explained by Flynn [20] to postulate the mechanism of enhanced substrate removal in his investigation of the effects of powdered activated carbon on an oil refinery activated sludge wastewater process. Flynn observed that high apparent TOC and/or COD carbon loading was an indicator of increased biological regeneration. Crame, however, reported his apparent TOC loading to be 0.59 g TOC/g carbon much higher than that reported by Flynn, which was 0.20 mg/mg TOC. The extremely high apparent TOC loading in Flynn's work was attributed to continuous adsorption of slowly biodegraded organics by the carbon particles which were biologically

regenerated many times over the BSRT of the biomass and carbon. Apparent loading, therefore, increases with higher biological solids retention time (BSRT). In this way, the use of PAC would be optimum, until the carbon becomes loaded with completely biorefractory organics. This is a logical explanation. Nevertheless, Crame questioned biological regeneration as an enhancement mechanism, and postulated physical adsorption due to the following reasons:

- the unit with PAC had 50 percent less biomass than the biological control unit as reflected in biomass production rate presented in Table 21.
- the difference in the oxygen uptake rate between the unit with PAC and without PAC was not significant. For instance, the PAC unit had an OUR of 0.12 mg/L-min while the OUR for the unit without PAC was 0.10 mg/L-min.

The author, however, drew his conclusions mainly from the first reason.

It is possible that the greater biomass observed in the PAC units of this investigation was the result of the accumulation of somewhat biodegradation-resistant organics in the pores of the carbon particles, which utlimately resulted in greater colonization of the macropores, greater substrate utilization, and, therefore, greater biomass. However, if this were true, it should be possible to

account for the increased biomass by the increased COD removal. In fact, this cannot be done. For example, the increased biomass concentration in the 280 mg/L PAC unit compared to the control was 230 mg/L. The increased effluent COD removal, however, was only 14 mg/L. Thus, using the influent flow rate, the volume of the reactor, and the sludge age, the increased COD removal was 63 mg per day, but the biomass increase was 271 mg per day. Clearly, the increased COD removal will not by itself, account for the increase in biomass.

The method of obtaining the volatile fraction of the activated carbon may have been too conservative and, therefore, the amount subtrated from the total MLVSS may have been too small. This would have resulted in an MLVSS concentration for the PAC units that was higher that it should have been, based on biomass only. If this were true, however, the increase in MLVSS over control should have been a function of the PAC concentrations, but it wasn't. The increase in the 20 mg/L PAC unit was 209 mg/L, whereas the MLVSS increase in the 160 mg/L PAC unit was only 150 mg/L. Also, the increase in MLVSS in the 20 mg/L PAC unit was only a little less than the increase in the 280 mg/L PAC unit, which increased by 230 mg/L. The inconsistency between the 20 mg/L PAC unit and the other two PAC units is obvious, nevertheless, inaccurate determination of the activated carbon contribution to MLVSS

is the most likely explanation for the biomass in the 160 mg/L and 280 mg/L PAC units that could not be accounted for. The increased in the 20 mg/L PAC unit is too large for such an explanation, but the cause is unknown.

The biological response data for the experimental units is summarized in Table 19, and it shows that the responses were consistent with a real increase in MLVSS in the PAC units. Because the MLVSS concentrations in the PAC units were larger than those in the control units, the control units had higher apparent specific substrate utilization rates than the PAC units, even though the total substrate removals in the PAC units were greater.

Plots of effluent COD and specific oxygen utilization rates with specific substrate utilization rate, given in Figure 36, indicate that the responses of the various units were related to the specific substrate utilization in the units, regardless of the PAC concentrations, which implies that a significant fraction of the apparent MLVSS increase was real.

Biokinetic Constant

The growth kinetic model [5] is presented here to explain the observed yield coefficient obtained in this study.

$$(dX/dt) = (dX/dt)_T - (dX/dt)_E \qquad [41]$$

Table 19. Biological Response Data from Units.

Unit	MLVSS mg/L	COD Removed mg/day	Specific Substrate Utilization Rate, day^{-1}	Specific Oxygen Utilization Rate, day^{-1}
20 mg/L PAC	1220	3210	0.689	0.24
Control	1020	3190	0.819	0.28
160 mg/L PAC	1340	3450	0.674	0.16
Control	1190	3430	0.755	0.18
280 mg/L PAC	1340	2780	0.543	0.139
Control	1110	2760	0.652	0.142

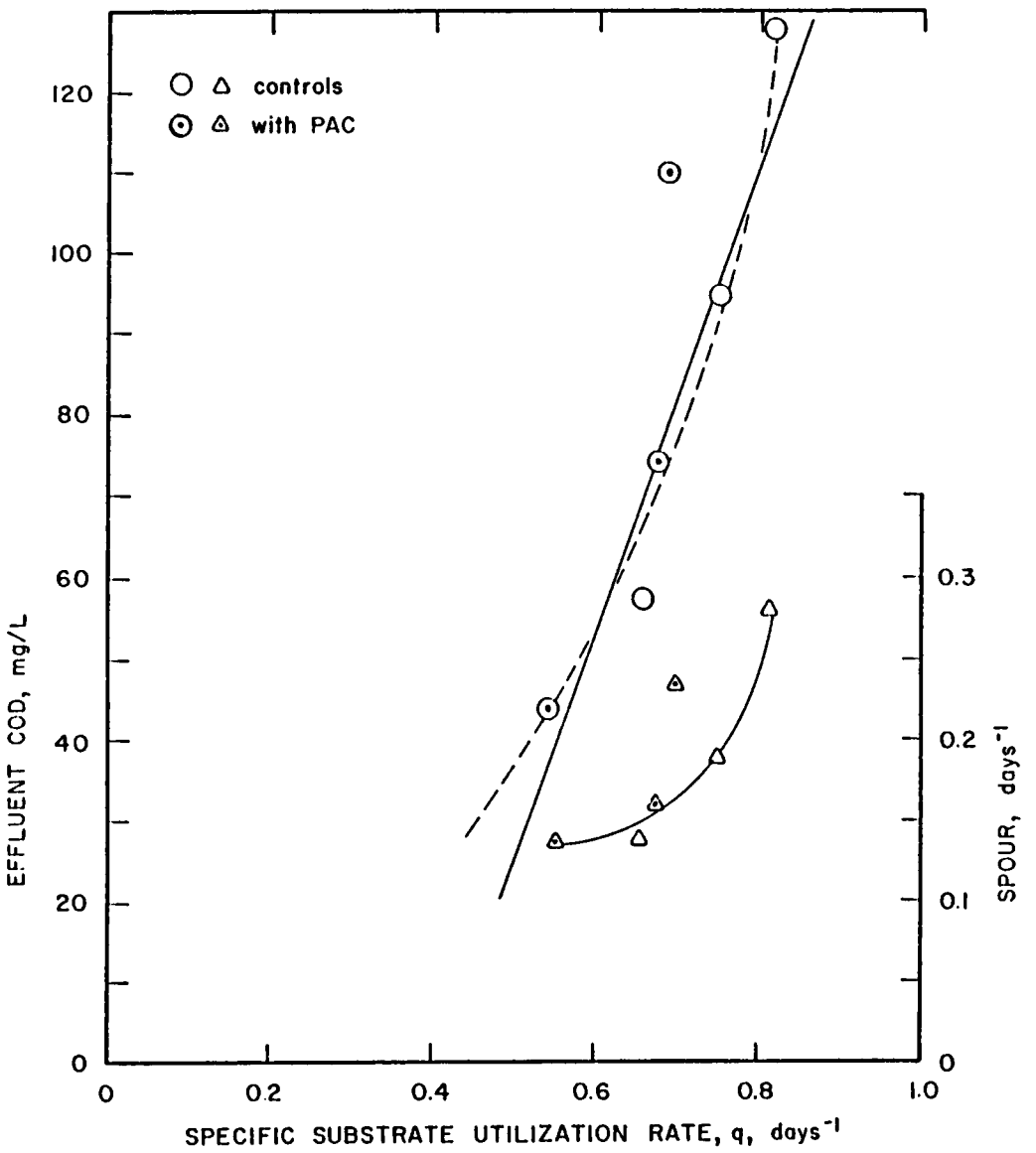


Figure 36. Correlation of System Responses with apparent substrate utilization rate.

$$(dX/dt)_T = Y_T(ds/dt) \quad [42]$$

$$(dX/dt)_E = K_dX \quad [43]$$

where Y_T is the Growth Yield factor, ds/dt is the substrate consumed for growth. K_d is the decay coefficient and represents the biomass destroyed by endogenous respiration. Substituting Equation [42] and [43] in [41], the equation becomes

$$(dX/dt) = Y_T(ds/dt) - K_dX \quad [44]$$

As a simplification, the biomass production rate is related to observed yield coefficient as

$$(dX/dt) = Y_{obs}\ (ds/dt) \quad [45]$$

Benefield and Randall [5] indicate that Equation [44] and [45] are essentially the same, and that the difference is that Equation [45] represents total biomass after biomass lost to endogenous respiration has been subtracted. This is logical, and therefore, will be used to explain the findings of this research. In addition, Equations [44] and [45] will be the basis of comparison with the results of other investigators.

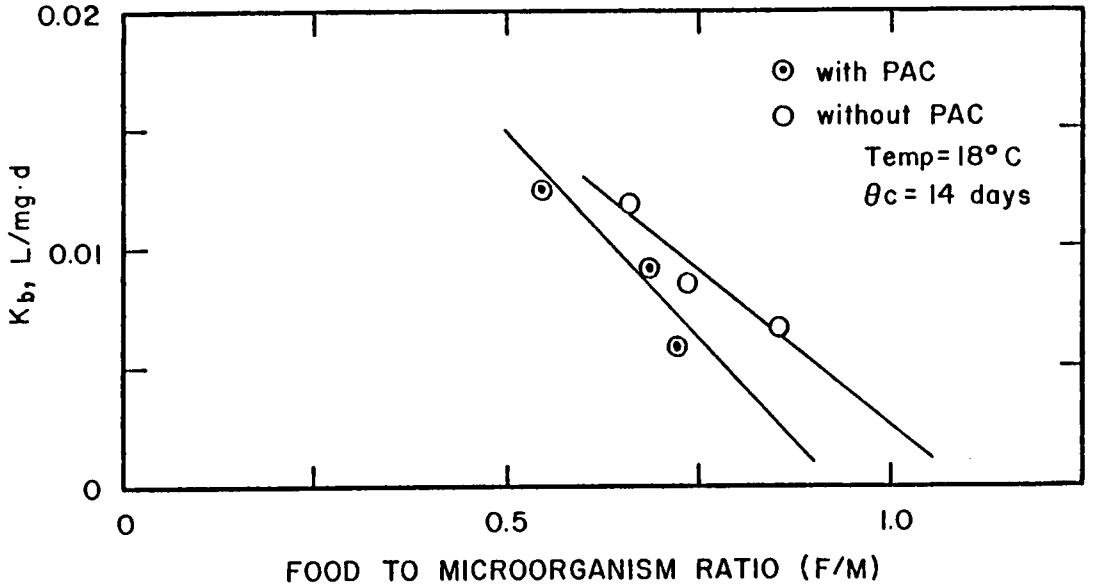
Figure 37 presents the effects of PAC on the first order kinetic constant (K_b). Higher organic loading corresponded to a higher specific substrate utilization rate with a decrease in the first order kinetic parameter. Both the control and PAC units showed this trend.

For each carbon run, the first order kinetic constant increased with lower values of specific substrate utilization rate, and F/M when compared with the control unit. The decrease in the specific sustrate utilization rate and F/M was due to higher biomass exhibited by the PAC units.

Apparently, the results of the first order kinetic constant (K_b) indicates more microbial activities as reflected in better effluent substrate removal achieved by the units during this study.

A closer examination of Figure 37 and Table 16 indicates that the kinetic constant of 20 mg/L PAC was slightly lower than the control units. This observation can be attributed to excessively high biomass level shown by thePACC unit as has already been explained.

Table 16 suggests that the microbial decay coefficient was not specifically determined in this study because the observed yield coefficient was used. Nevertheless, Equations [44] and [45] are sufficient to explain their roles in the bioreactors. Table 16 showed that higher observed cell yield was determined for each equilibrium



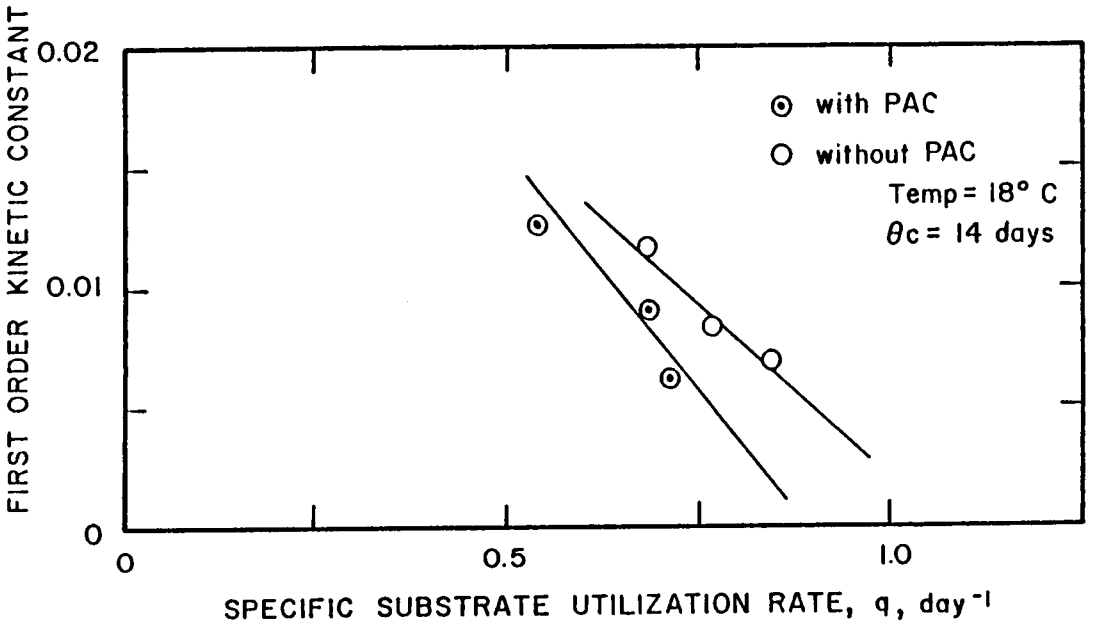


Figure 37. PAC effects on the first order kinetic constant, K_b.

carbon dosage when compared with their control units. The observed yield coefficient is directly related to growth yield coefficient by the following equation.

$$Y_{obs} = Y_T/(1 + K_d\ \theta_c) \qquad [46]$$

It is imperative to point out that Equation [46] is related to Equations [44] and [45], because it was derived from those equations. It is evident from Equation [46] that a high observed yield coefficient corresponds to a high total cell yield coefficient. Thus, endogenous decay coefficient decreased in this experimentfor the PAC units. In other words, a smaller fraction of the produced biomass was lost to endogenous respiration for energy maintenance. On the other hand, the control units exhibited a higher fraction of endogenous decay as reflected in the consistently lower values of mixed liquor volatile suspended solids (MLVSS) as compared to the PAC units. Of course, part of the increased yield in the PAC units was because of greater COD removal, but it is possible the control units also had higher cellular decay rates.

A comparison of the kinetic parameters determined in this investigation with the results of other investigators is presented in Table 20.

Specchia and Gianetto's [68] kinetic parameters appear to be different from the results of this study. Table 20

Table 20. A comparison of the biokinetic constant found in this study with the results of other investigations.

Parameter	PAC Dose (mg/L)	PAC Unit	Control Unit	Researcher	Temperature °C	Reference
Y_T [a]	800	0.48	0.67	Specchia & Gianetto	-	68
K_d	800	0.018	0.043	Specchia & Gianetto	-	68
Y_{obs} [e]	20	0.104	0.0869	This research	18	This research
Y_{obs} [e]	160	0.106	0.0944	This research	18	This research
Y_{obs} [e]	280	0.131	0.109	This research	18	This research
K_b [c]	280	0.0127	0.0115	This research	18	This research
K_b [c]	160	0.00912	0.00807	This research	18	This research
K_b [c]	20	0.00624	0.00643	This research	18	This research
K_b [c]	800	0.000046	0.00032	Specchia & Gianetto	-	68
Y_{obs} [+]	2500	0.08	0.16	Crame	-	14

a = kg MLSS/kg BOD_5

c = L/mgd

e = $\frac{\text{mg active biomass produced}}{\text{mg of COD removed}}$

+ = $\frac{\text{lb MLVSS produced}}{\text{lb COD removed}}$

- = Not reported in the literature

shows that their growth yield and microbial decay coefficients decreased with the addition of powdered activated carbon to the activated sludge units. This is logical unless the inert material added as activated carbon is subtraced from the MLVSS used in determination of the coefficients, and the addition of PAC did not stimulate greater growth through imporved sustrate removal. However, their data were collected over an unsteady state run, and the units were not operated in parallel. Further, the temperature of the test was not reported. These factors may have influenced their results, but the extent of the effect cannot be determined. However, a better comparison would be with the observed cell yield coefficient which is a function of the sludge age. Unfortunately, they did not report the operating sludge age. Nevertheless, the first order kinetic substrate removal coefficient determiend by them quite agrees with the results of this investigation.

DeWalle et al. [17] reported that the MLVSS concentration, when corrected for PAC, decreased and attributed the decrease to an increase in endogenous respiration. This is possible, but the method by which MLVSS was determined is questionable. In the test, there were two equilibrium carbon dosages, and it was assumed that virgin PAC loses 79 percent of its weight on volatilization. The MLVSS was thus corrected on mere observations of volatility of virgin carbon. The

determination could have been performed at the equilibrium carbon concentrations investigated for more reliable results. In addition, temperature of the test was not reported.

Crame [14] reported a decrease in observed yield coefficient upon addition of PAC to his experimental unit, but an increase in substrate removal. The observed cell yield coefficient could have been decreased by the activated carbon if it were not properly accounted for. The author did not report the temperature of the test, but the units with and without PAC were operated in parallel. The interesting aspect of the author's investigation is the conclusion that physical adsoprtion was the means of enhanced substrate removal. The author would have postulated bioactivity and bioregeneration as the mechanisms of substrate removal if the observed yield coefficient had been greater than that of the control unit.

This research noted an increase in COD removal plus increase in the observed yield coefficient, and the oxygen uptake rate with the addition of PAC to activated sludge. The equilibrium MLVSS concentration was also greater in to PAC units, which would be expected, but the increase was greater than what could be explained on the basis of improved COD removal. It is possible that COD removal was enhanced because slowly biodegradable organics were adsorbed by the activated carbon, causing them to remain in

the activated sludge system for much longer than the hydraulic detention time, which gave the microorganisms sufficient time to metabolize them.

Economic Carbon Dose

The highest percent COD removal occurred in the 280 mg/L PAC unit, and, therefore, the reader may draw the conclusion that the most economical PAC dose would be 280 mg/L. However, Tables 11, 12, and 14 indicate that the various carbon dosages were subjected to different organic loadings, and therefore, the operating food to microorganism (F/M) ratios need to be defined for each of the equilibrium carbon concentrations.

The food to microorganism (F/M) ratio is the mass rate of substrate entering into the aeration vessel divided by the total mass of microbes in the aeration vessel. Mathematically, F/M is represented as

$$F/M = QS_o/XV \qquad [47]$$

where

Q = is the influent volumetric flow rate, liters/day

S_o = average influent substrate as measured by COD, mg/L

X = microbes under the aeration vessel, mg/L

V = volume of the aeration basin, liters.

The averages of the parameters shown in Tables 11, 12 and 14 at different carbon dosages were used to compute the F/M ratio. Table 21 summarizes the percent improved COD removal and F/M at various carbon dosages employed in the investigation. Plots of percent improvement in COD and enhanced substrate removal in terms of concentration are presented in Figure 35.

The graphs and Table 21 indicate that the carbon dose of 280 mg/L had the lowest F/M ratio with the highest percentage removal improvement, but lowest in terms of milligrams per liter of the COD removed. However, the effluent COD concentration was considerably lower. However, this carbon dose exhibited higher variability in the data collected based on the high value of percent coefficient of variance computed as evidence in the table, compared to the 20 mg/L PAC run.

Table 20 and Figure 35 seemingly indicate that data collected for carbon dosages at 160 mg/L are better based on the highest amount of substrate removed in mg/L plus the fact that the system was subjected to a higher organic loading as evidence by the F/M. However, the standard deviation and the coefficient of variance cast doubt on this view. Furthermore, a look at the carbon dose 20 mg/L indicates the highest organic loading with the lowest standard deviation, and coefficient of variance. It should be recalled that during the period of the run the system

Table 21. COD removals by PAC concentrations at various F/M.

Parameters	280 mg/L	160 mg/L	20 mg/L
Effluent COD concentration	43	74	110
% COD removal improvement	24	20	15
Improved COD removal, mg/L	14	20	18
STD, %	15	20	8
CV, %	64	100	55
F/M	0.55[c] 0.69[d]	0.69[c] 0.78[d]	0.71[c] 0.86[d]

CV - Coefficient of Variance = STD/Mean

F/M - mg COD Loading/mg MLVSS

c - Data for bioreactor A d - Data for bioreactor B

was consistently subjected to real COD loading of constant value. Nevertheless, the average COD loading during the trial run of 280 mg/L was less than that at 20 mg/L. For example, at 280 gm/L PAC, the average COD loading was 2820 mg/L while at 20 mg/L PAC it was 3320 mg/L.

Considering costs also, 20 mg/L appears to be the most economical dose based on the fact that 160 mg/L only had 2 mg/L of COD better removal regardless of the higher F:M exhibited by 20 mg/L PAC unit. The cost of procurring 160 mg/L PAC may be prohibitive as compared to only 20 mg/L PAC. Based on the fact that the same grade and particle size were used in the investigation, 160 mg/L PAC would cost about 8 times the cost of 20 mg/L to achieve a better reults. Furthermore, the improved COD removal can be offset by changing an operational parameter which is BSRT. Increasing BSRT would improve the effluent quality with more process stability.

Appendix Table I-3, indicate better settling properties by PAC concentration of 280 mg/L unit. Therefore, selection of the most economical dose must consider settling properties also.

Zone Settling Velocity (ZSV) and Sludge Volume Index (SVI)

Figures 15, 19, and 22 imply that a indicate correlation exist between zone settling velocity (ZSV) and sludge volume index (SVI). Figures 15 and 19 exhibits such

a pattern consistently over the data points presented while Figure 23 shows a less consistent pattern.

At the beginning of this study, two measuring cylinders of different heights were used. The heights of the cylinders were 14.7 inches and 13.7 inches. It was anticipated that Unit A would have higher mixed liquor suspended solids concentrations which was true through out the investigation and the larger cylinder was designated for that unit. However, the measuring cylinder for bioreactor A was broken at the end of the second experiment (i.e., the end of 160 mg/L PAC trial run), and during the 20 mg/L PAC trial, the cylinder for Unit B was also used for Unit A.

It was noted that, on some occasions, the SVI and/or ZSV of Unit B were found to be better that the SVI and ZSV for bioreactor A. This appeared to be inconsistent, and temperature differences could not be used to explain the inconsistencies exhibited during this period because the temperature of the sludges were the same and the tests were performed under similar conditions. Nevertheless, considerable correlation between the two parameters was found.

To further elucidate the correlation that existed between SVI and ZSV in this study, plot of ZSV against SVI determined for bioreactor A with carbon doses of 160 mg/L and 280 mg/L, is depicted in Figure 38. In the figure, the

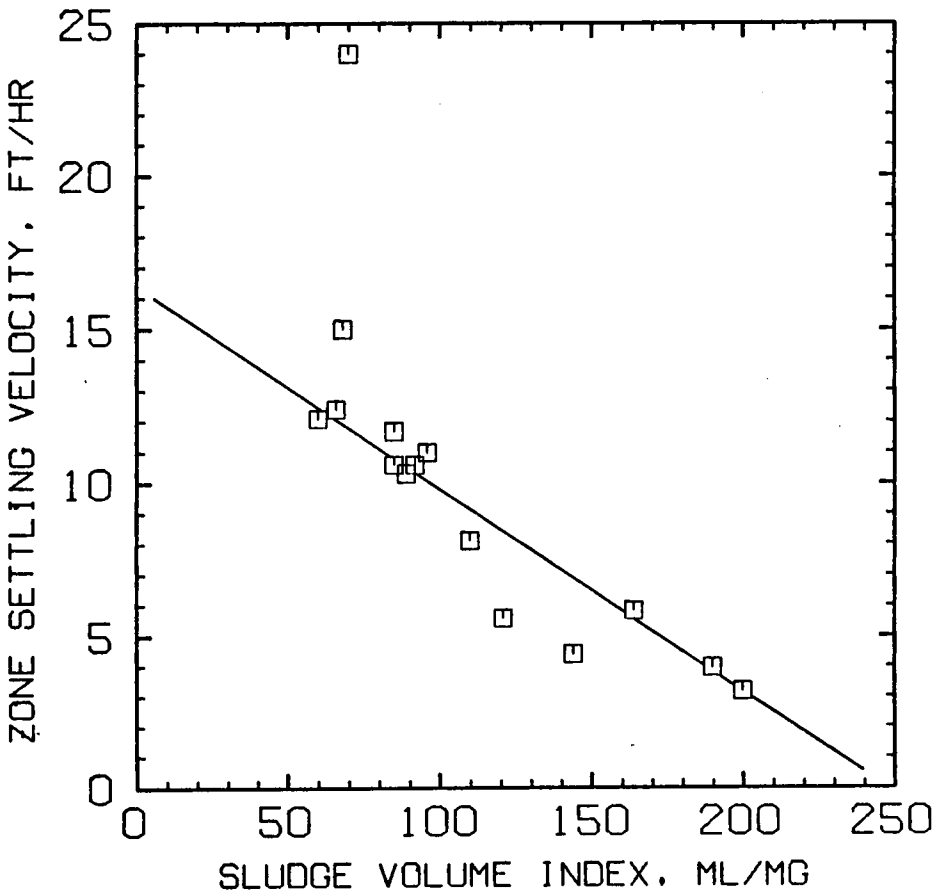


Figure 38. Relationship between ZSV and SVI.

best line of fit was drawn. The slope of the line is negative, indicating an inverse relationship between these parameters, which is mathematically correct. Dick and Vesiland [46] discouraged the use of SVI to measure the settling characteristic of a sludge but encouraged the use of ZSV to quantify the settleability of sludges and its use in research application. These authors also suggested that SVI not be used to compare two different sludges. The two sludges were dissimilar in nature but showed a correlation between ZSV and SVI.

If a significant correlation could be established between SVI and ZSV, then SVI could be used as a monitoring tool and in research applications,as well as ZSV. The results of this study indicate that sufficient correlation exists.

Sezin [62] has also shown a consistent relationship between ZSV and SVI using domestic, partially domestic and industrial sludges. He found that increasing ZSV correlates with decreasing SVI.

The addition of PAC to the activated sludge clearly improved the settleability of the sludge. The ZSV was greater and the SVI lower for each PAC unit compared to its control unit. The greatest improvement occurred in the 280 mg/L unit, but it and its control also had the lowest ZSV values and the highest SVI values observed during the study. SVI improvement showed a better correlation with

PAC dose than did ZSV improvement. The correlation was not linear, but SVI did improve more as the PAC concentration increased. By contrast, the 20 mg/L PAC unit had a greater improvement compared to its control than did the 160 mg/L PAC unit.

Appendix E, Tables E-1 and E-2 indicates that powdered activated carbon did not significantly reduce the effluent suspended solids of the units as would be expected with improved settleability. This raises questions concerning the floc formation characteristics of the microorganisms in the activated sludge. When the experimental investigation was begun, a question to be resolved was whether the microorganisms could produce enough biopolymer for successful flocculation. Nitrogen was added to assist biopolymer formation. The answer was that the sludge produced enough biopolymer [51] based on the results of Kajornatuyudh [23]. In spite of these results, it seems clear that PAC addition added weight to the flocs and improved settleability. However, this apparently worsened the effluent suspended solids concentration becasue the smaller particles separated from the settling blanket. Thus, as shown in Figure 39, as the ZSV increased, the effluent suspended solids increased. This effect has been observed at the Celco plant. It is possible to control the effluent suspended solids at the plant with polymer addition.

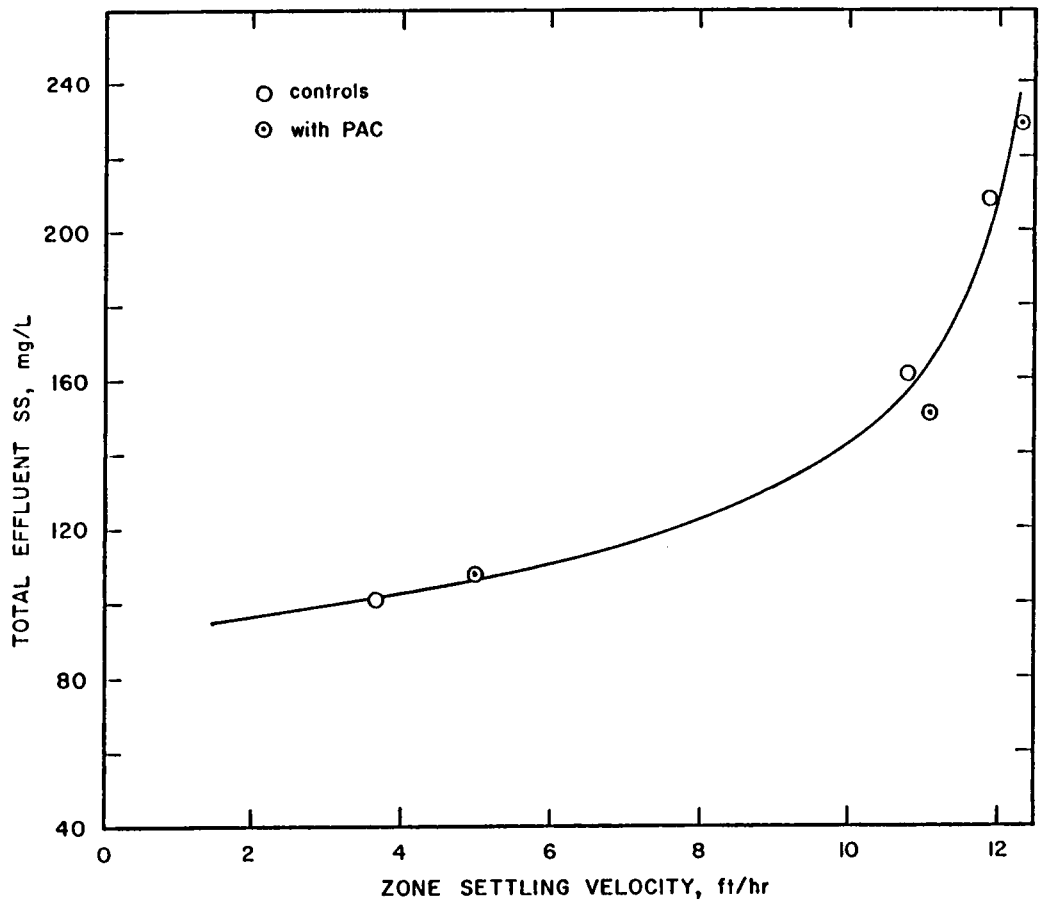


Figure 39. The effect of zone settling velocity on the effluent suspended solids concentration.

Influent Wastewater pH and COD and Aeration pH

A correlation was established between the influent wastewater pH and the influent COD (High COD corresponds to low pH and vice versa).

In the acid recovery and acid manufacturing sections, the waste discharged contains a lot of acetate such as ethyl acetate, methyl acetate, magnesium and sodium acetate. These compounds can only exist as acetate under a high pH. Thus, the low pH indicates that these compounds are dissociated. Taking sodium acetate as an example, the governing reactions can be represented as

$$CH_3COONa \rightarrow CH_3COO^- + Na^+ \qquad [48]$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad [49]$$

$$CH_3COO^- + H^+ \rightarrow CH_3COOH \qquad [50]$$

Any of the compounds cited above follows the example reactions shown above. Thus, the decreasing pH was due to more acetic acid going into the wastewater treatment.

A study of Appendix E indicates that the influent wastewater pH fluctuated around 4.4 to 4.9. However, the aeration pH fluctuated around 7.5 without pH adjustment through chemical addition. The change from a low pH to a

high pH in the aeration vessel was caused by a variety of biochemical reactions, and induced chemical reactions taking place simultaneously in the reactors.

The activated sludge biochemical process can be represented in a simple mathematical form [6].

$$\text{Wastewater} + \text{Microorganims} + \text{Air} = \text{Sludge} + CO_2 + H_2O \qquad [51]$$

The above equation is a biologically mediated reaction. The carbon dioxide produced reacts with the caustic alkalinity resulting in a higher pH as evidenced in the following equations.

$$CO_2 + OH^- \longrightarrow HCO_3^- \qquad [52]$$

$$HCO_3^- + H_2O \longrightarrow H_2CO_3 \qquad [53]$$

The bicarbonate produced acts as a buffer, thus requiring no chemical addition to buffer the system.

Chapter VI

PROBABLE AREAS OF FURTHER RESEARCH

Several problems exist with the treatment of cellulose acetate manufacturing wastewater. This investigation has, hopefully, helped to clarify some of the aspects of the problem. Nevertheless, more investigations need to be conducted to answer all of the confusing questions. Therefore, this chapter will discuss the potential areas for further study.

Nitrogen addition apparently solved the jelly formation problem observed in the clarifier unit of two laboratory-scale activated sludge processes. In order to conclusively demonstrate that nitrogen deficiency is the factor that caused the jelly, jelly formation must be stimulated under laboratory conditions. Kajornatuyudh [29] has attempted such an experiment but did not succeed. This indicates that nitrogen deficiency is not the only factor involved, but is probably a necessary condition.

Another approach would be to feed the wastewater without nitrogen addition and subject the reactors to various temperatures (30°C, 35°C, 40°C and 45°C). In addition, feed the wastewater nitrogen based on the biomass production and vary the temperatures as indicated above. If these experiments also fail to form jelly, raise the pH to 8.4 and run the reactors as earlier stated. The

Dissolved Oxygen (DO) level may fluctuate around 2 to 4 mg/L in all of the reactors. The responsible microorganism should be identified by an expert if jelly formation is successfully stimulated.

Another potential causative agent of jelly formation may be acetic acid, based on the fact that this compound contributes most to the high organic loadings often associated with the treatment plant. The sludge generated by cellulose acetate wastewater may be studied using synthetic wastewater. Add to the synthetic wastewater varying concentrations of sodium acetate, and maintain the pH at 8.4. If this fails, the experiment may be repeated at higher temperatures ($30^{o}C$, $35^{o}C$). Again, the dissolved oxygen (DO) should be maintained at 2.0 to 4.0 mg/L in the trials. Acetone and ethanol may also be tried under operating conditions similar to the acetic acid experiments.

An experiment that is worth trying is the determination of the amount and constituents of biopolymer produced by activated sludge microorganisms treating cellular acetate wastewater. If the amount produced is determined to be insufficient, then organic polymer addition could be employed. Polymer screening investigations may be performed to establish the effective synthetic polymers.

Finally, experiments may be carried out using 20 mg/L PAC at various biological solids retention times (20, 25, and 30 days), and, also, a unified approach to the determination of MLVSS in a PACT system be investigated.

Chapter VII

SUMMARY AND CONCLUSIONS

Two laboratory-scale, continuous flow, activated sludge reactors were operated in parallel to investigate the effects of powdered activated carbon (PAC) on the performance of activated sludge systems treating cellulose acetate manufacturing wastewater. One reactor was operated as a control which the other was operated with three different equilibrium PAC concentrations of 20, 160, and 280 mg/L. All systems were operated at a biological solids retention time of fourteen days.

All three of the PAC units had improved performance compared to the control units. Greater amounts of biomass grew in the PAC units, they removed more COD, produced lower effluent COD concentrations, and had improved settleability. The effluent suspended solids (SS) concentrations from the PAC units were usually higher, however, because the primary factor affecting the effluent SS was the zone settling velocity (ZSV) of the activated sludge. The higher the ZSV, the higher the effluent SS. Since PAC improved the settleability, which increased the ZSV, the effluent SS concentrations were generally higher than those of the control. The PAC reactors also used more oxygen than the control units, even though the specific oxygen uptake rates (SPOUR) of the control activated

sludges were usually higher. This was because the PAC reactors contained more biomass and removed more COD than the control reactors.

The measured biomass increases in the PAC reactors could not be adequately explained by the additional COD removed by these systems. Furthermore, even though the method used to correct for the activated carbon fraction of the mixed liquor volatile suspended solids (MLVSS) concentration probably underestimated it, the total biomass increase in the 20 mg/L PAC reactor could nto be accounted for by PAC addition either. Thus, a significant amount of the biomass increase in the PAC units could not be accounted for, even though increased COD removal was partially responsible.

The formation of jelly in activated sludge, which a type of sludge bulking that is an unusual phenomenon, occurred in the activated sludge reactors during the early part of this investigation. The addition of nitrogen to the wastewater apparently solved the problem and resulted in the elimination of jelly, but related efforts to stimulate jelly formation by inducing nitrogen deficiency were unsuccessful.

The findings of this investigation have led to the following conclusions with respect to the objectives of this investigation:

1. Most of the organics in cellulose acetate manufacturing wastewater are poorly adsorbable by activated carbon.
2. Jelly formation in the activated sludge was apparently stopped and subsequently prevented by the addition of nitrogen to the wastewater. Nitrogen addition also appeared to improve sludge settleability.
3. The presence of 280 mg/L of PAC significantly moderated the effects of an organic shock loading episode that caused filamentous growth in the activated sludge and high effluent suspended solids. The average effluent SS with PAC was 162 mg/L with a range of 51 to 625 mg/L, whereas the average without PAC was 157 mg/L with a range of 51 to 125 mg/L.
4. PAC addition to activated sludge improved the removal of organic substrate compared to a control operated at the same sludge age, for PAC concentrations 20, 160, and 280 mg/L. The improvements did not appear to be closely related to the PAC concentration in the system. The apparent mechanism of improved COD removal was the stimulation of greater biomass production.
5. The addition of PAC to the activated sludge also increased the first order kinetic constant with respect to substrate concentration.
6. The addition of PAC to the activated sludge improved settleability as measured by both ZSV and SVI. However, the improved settleability resulted in higher

effluent SS concentrations because the primary factor affecting the effluent SS was the ZSV. The higher the ZSV, the higher the effluent SS.

7. All of the activated sludge systems generally accomplished complete removal of the specific organic compounds in the wastewater, such as acetone, acetic acid, and mesityl oxide, whether the systems contained PAC or not.
8. Toxic effects of mesityl oxide could not be measured during the investigation.

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APPENDICES

APPENDIX A. Mathematical Modelling of Activated Sludge Process

A continuous growth of biological flocs with good settling characteristics indicates that the activated sludge is performing well [73]. The growth of the flocs is accompanied by organic substrate utilization. An understanding of how this works requires the knowledge of microbial kinetic modelling. A typical completely mixed activated sludge is depicted in Appendix Figure A-1.

A material balance for biomass around the reactor gives

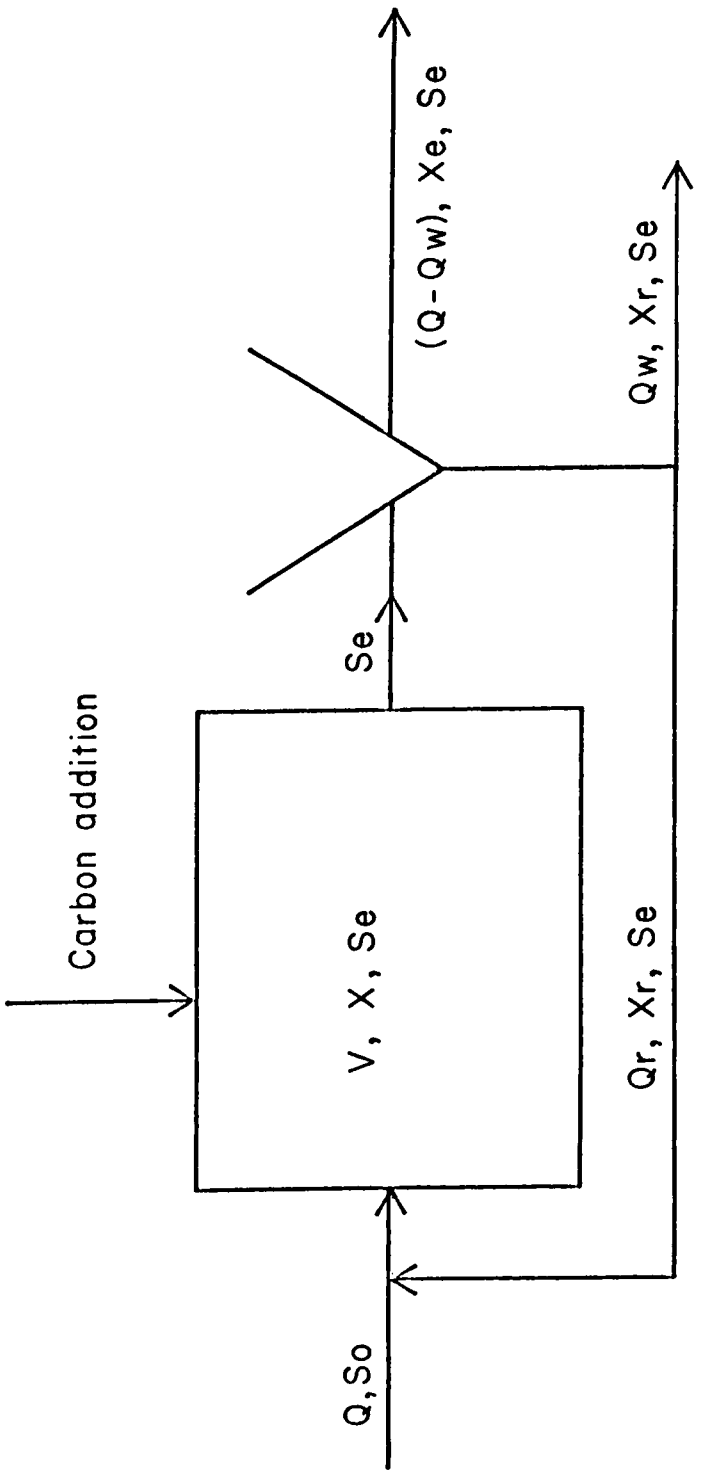
$$\left[\begin{array}{c}\text{Rate of microorganism}\\ \text{concentration of}\\ \text{reactor}\end{array}\right] = \left[\begin{array}{c}\text{Rate of microorganism}\\ \text{growth in the}\\ \text{reactor}\end{array}\right] - \left[\begin{array}{c}\text{Rate of microorganism}\\ \text{outflow from the}\\ \text{reactor}\end{array}\right] \qquad \text{A-1}$$

$$\frac{dX}{dt}\,V = \frac{dX}{dt}\,V - [Q_W X + (Q-Q_W)X_e] \qquad \text{A-2}$$

From Equation [ ], the above equation A-2 becomes

$$\frac{dX}{dt}\,V = \frac{dX}{dt}\,V - \frac{XV}{\theta_c} \qquad \text{A-3}$$

$$\frac{dX}{}\,V = [Y_T \frac{ds}{dt}_u - K_d X]V - \frac{WV}{\theta_c} \qquad \text{A-4}$$



Appendix Figure A-1. The Activated Sludge Process (after Benefield and Randall)[5]

At steady state dX/dt = 0, Equation A-4 becomes

$$1/\theta_c = Y_T \frac{(ds/dt)_u}{X} - K_d \qquad \text{A-5}$$

Substituting with Monod 's equation for substrate utilization and solving the equation, Equation A-5 becomes

$$S_e = \frac{k_s (1+k_d\theta_c)}{\theta_c(Y_T k - k_d) - 1} \qquad \text{A-6}$$

Similarly, material balance for substrate around the reactor can be expressed as

$$(ds/dt)V = QS_o + Q_R S_e - (ds/dt)V - (Q + Q_R)S_e \qquad \text{A-7}$$

At steady state, Equation A-7 reduces to

$$\left(\frac{ds}{dt}\right)_u = \frac{Q\ (S_o - S_e)}{V_a} \qquad \text{A-8}$$

Dividing Equation A-8 by X, Equation A-8 becomes

$$\frac{(ds/dt)_u}{X} = \frac{Q(S_o - S_e)}{XV_a} \qquad \text{A-9}$$

Making appropriate substitution s, Equation A-9 becomes

$$X = \frac{Y(S_o - S_e)}{(1+k_d\theta_c)} \qquad \frac{\theta_c}{\theta} \qquad \text{A-10}$$

A material balance for a conservative substance and at steady state is represented as

$$\frac{QC_o}{VC_1} - \frac{(Q - WS)\ E_e + WS\ C_w}{VC_1} = 0 \qquad \text{A-11}$$

where

C_1 = mixed liquor carbon concentration, mass volume^{-1}

C_e = concentration of effluent carbon, mass volume^{-1}

C_w = concentration of carbon wasted, mass volume $^{-1}$

V = volume of aeration basin

C_o = feed carbon concentration

Making the assumptions that $C_1/X = K$, $C_e/X_e = K$, and $C_w/X = k$ (i.e.,PAC ratio to biomass is the same in the effluent, wastage and mixed liquor) Equation A-11 becomes

$$\frac{QC_o}{VC_1} = \frac{(Q - WS)\ X_e + WS\ X}{VX} \qquad \text{A-12}$$

Recalling that the right hand side of Equation A-11 is inverse of the right hand side of Equation 21, thus, the equation reduces to

$$\frac{QC_o}{VC_1} = \frac{1}{\theta_c} \qquad \text{A-13}$$

$$C_1 = \frac{Q}{V} C_o \quad c = C_o \frac{\theta_c}{\theta} \qquad \text{A-14}$$

Interestingly, Equation A-14 can represent the inert biological solids in the reactor. Thus, inert biological solids will be present in a large amount in the reactor at longer BSRT. However, the effluent discharged does not vary with BSRT and the volume of the reactor. Therefore, in Equation A-14 $\theta_c = 1$, and V = 1. The amount of discharge then becomes X_1Q. Where $X_1 = C_o$, the influent inert solids.

Appendix B. PAC Addition, Wasting and the Replacement for Bioreactor A.

Date 1984	Days	PAC Wasted, mg	Amount Added, mg	Net PAC, mg
8/3	1	0	330	330
8/4	2	24	354	660
8/5	3	47	377	990
8/6	4	71	401	1320
8/7	5	94	424	1650
8/8	6	118	448	1980
8/9	7	141	471	2310
8/10	8	165	495	2640
8/11	9	189	519	2970
8/12	10	212	542	3300
8/13	11	236	566	3630
8/14	12	259	589	3960
8/15	13	283	613	4290
8/16[a]	14	306	636	4620
8/17	15	330	330	4620
8/18	16	330	330	4620
8/19	17	330	330	4620
8/20	18	330	330	4620
8/21	19	330	330	4620
8/22	20	330	330	4620
8/23	21	330	330	4620
8/24	22	330	330	4620
8/25	23	330	330	4620
8/26	24	330	330	4620
8/27	25	330	330	4620
8/28	26	330	330	4620
8/29	27	330	330	4620
8/30	28	330	330	4620
8/31	29	330	330	4620
9/1	30	330	330	4620
9/2	31	330	330	4620
9/3	32	330	330	4620
9/4[b]	33	0	0	4620
9/5	34	330	0	4290
9/6	35	306	0	3984
9/7	36	285	0	3699
9/8	37	264	0	3435
9/9	38	245	0	3190
9/10	39	228	0	2962
9/11	40	212	0	2750
9/12[c]	41	196	86	2640
9/13	42	189	189	2640
9/14	43	189	189	2640

Appendix B. PAC Addition, Wasting and the Replacement for Bioreactor A (cont.).

Date 1984	Days	PAC Wasted, mg	Amount Added, mg	Net PAC, mg
9/15	44	189	189	2640
9/16	45	189	189	2640
9/17	46	189	189	2640
9/18	47	189	189	2640
9/19	48	189	189	2640
9/20	49	189	189	2640
9/21	50	189	189	2640
9/22	51	189	189	2640
9/23	52	189	189	2640
9/24	53	189	189	2640
9/25	54	189	189	2640
9/26	55	189	189	2640
9/27	56	189	189	2640
9/28	57	189	189	2640
9/29	58	189	189	2640
9/30	59	189	189	2640
10/1	60	189	189	2640
10/2	61	189	189	2640
10/3	62	189	189	2640
10/4	63	189	189	2640
10/5	64	189	189	2640
10/6	65	189	189	2640
10/7	66	0	0	2640
10/8	67	189	189	2640
10/9	68	189	189	2640
10/10	69	189	189	2640
10/11	70	189	189	2640
10/12	71	189	189	2640
10/13	72	0	0	2640
10/14[d]	73	0	0	2640
10/15	74	89	0	2451
10/16	75	175	0	2276
10/17	76	163	0	2113
10/18	77	151	0	1962
10/19	78	140	0	1822
10/20	79	130	0	1692
10/21	80	0	0	1692
10/22	81	155	0	1537
10/23	82	110	0	1427
10/24	83	102	0	1325
10/25	84	95	0	1230
10/26	85	88	0	1142

Appendix B. PAC Addition, Wasting and the Replacement for Bioreactor A (cont.).

Date 1984	Days	PAC Wasted, mg	Amount Added, mg	Net PAC, mg
10/27	86	82	0	1060
10/28	87	76	0	984
10/29	88	70	0	914
10/30	89	65	0	849
10/31	90	61	0	788
11/1	91	56	0	732
11/2	92	57	0	675
11/3	93	48	0	627
11/4	94	45	0	582
11/5	95	42	0	540
11/6	96	39	0	501
11/7	97	36	0	465
11/8	98	33	0	432
11/9	99	31	0	401
11/10	100	29	0	372
11/11	101	27	0	345
11/12	102	25	0	320
11/13[e]	103	23	33	330
11/14	104	24	24	330
11/15	105	24	24	330
11/16	106	24	24	330
11/17	107	24	24	330
11/18	108	24	24	330
11/19	109	0	0	330
11/20	110	24	24	330
11/21	111	24	24	330
11/22	112	24	24	330
11/23	113	24	24	330
11/24	114	24	24	330
11/25	115	24	24	330
11/26	116	24	24	330
11/27	117	24	24	330
11/28	118	24	24	330
11/29	119	24	24	330
11/30	120	0	0	330

a The start of equilibrium carbon concentration of 280 mg/L.
b End of equilibrium carbon concentration of 280 mg/L.
b-c The period of wasting without carbon replacement to reduce PAC concentration to the required level.
c New carbon concentration at 160 mg/L was established.
c-d The time equilibrium carbon concentration of 160 mg/L was run to reach another steady state.
d-e Wasting period without carbon replacement to establish another desired equilibrium carbon concentration.
e The start of carbon run of 20 mg/L.

APPENDIX C - EQUILIBRIUM TIME STUDIES

Table C-1. Adsorption Rate Study on Sample Collected Near Clarifier No. 1.

Time	pH Values 6.3	7.0
1 minute	304	284
1.03 hr	307	216
1.60 hr	288	290
2.10 hr	304	300
2.60 hr	284	293
4.06 hr	263	276
6.60 hr	264	278
8.80 hr	269	255
24 hr	237	220

Initial Concentration = 339
Values shown are in mg/L as TOC.

Table C-2. The TOC Concentration taken at Various Time for Sample Collected from the Effluent of the Equalization Basin.

Time	pH Values 4.7	7.0
1 minute	512	555
30 minutes	511	483
45 minutes	497	503
1 hour	578	566
1.5 hr	585	553
2 hours	504	504
4 hours	552	540
5 hours	501	491
7 hours	537	531
12 hours	537	510
24 hours	494	472

Table C-3. Concentration of TOC remaining for Adsorption Isotherm Studies Equilibrated at 12 hours, Temperature 23 ± 1.5°C.

Flask No.	Carbon Dosage	TOC Remaining, mg/L	
		Nuchar WV-W Ce	Celco Carbon
BOA	0.0	502	608
1	15.0	441	573
2	22.5	424	591
3	30.0	433	565
4	45.0	441	551
5	60.0	453	522
6	75.0	434	545
7	90.0	442	555
8	120.0	444	546
9	150.0	436	553
10	300.0	416	516

Volume of wastewater used = 150 ml.

Table C-4. TOC Remaining for Adsorption Isotherm Studies Equilibrated at 24 hours, Temperature 23 ± 1.5°C

Flask No.	Carbon Dosage	TOC Remaining, mg/L	
		Nuchar WV-W Ce	Celco Carbon
BOA	0.0	502	608
1	15.0	476	585
2	22.5	471	578
3	30.0	469	565
4	45.0	441	542
5	60.0	463	525
6	75.0	443	596
7	90.0	436	546
8	120.0	425	495
9	150.0	425	530
10	300.0	395	425

Volume of Wastewater Used = 150 ml.
BOA = Blank Sample (Control)

Table C-5. Data for the plot of Freundlich Isotherm Equilibrated at 12 hours.

Celco Carbon		Nuchar WV-W	
X/M (mg/mg)	Ce (mg/L)	X/M (mg/mg)	Ce (mg/L)
0.35	573	0.61	441
0.11	521	0.52	424
0.22	565	0.35	433
0.19	551	0.20	441
0.22	522	0.12	453
0.13	545	0.14	434
0.088	555	0.10	442
0.078	546	0.070	444
0.055	553	0.066	436
0.045	516	0.043	416

Table C-6. Data Showing Freundlich Model Plot at Equilibration of 24 hours.

Celco Carbon		Nuchar WV-W	
X/M (mg/mg)	Ce (mg/L)	X/M (mg/mg)	Ce (mg/L)
0.23	585	0.26	476
0.20	578	0.21	471
0.22	565	0.17	469
0.22	542	0.20	441
0.21	525	0.10	463
0.10	546	0.12	443
0.14	495	0.11	436
0.08	530	0.10	425
0.06	495	0.08	425
		0.05	395

Table C-7. Langmiur Data Points for 12 Hours

Celco Carbon		Nuchar WV-W	
1/(X/M)	1/Ce	1/(X/M)	1/Ce
2.86	1.75×10^{-3}	1.64	2.27×10^{-3}
9.09	1.69×10^{-3}	1.92	2.36×10^{-3}
4.55	1.77×10^{-3}	2.86	2.31×10^{-3}
5.26	1.82×10^{-3}	5.00	2.27×10^{-3}
4.55	1.92×10^{-3}	8.33	2.21×10^{-3}
7.69	1.84×10^{-3}	7.14	2.30×10^{-3}
11.40	1.80×10^{-3}	10.0	2.26×10^{-3}
12.8	1.83×10^{-3}	14.3	2.25×10^{-3}
18.2	1.81×10^{-3}	15.2	2.29×10^{-3}
21.7	1.94×10^{-3}	23.3	2.40×10^{-3}

Table C-8. Langmiur Data Points for 24 Hours

Celco Carbon		Nuchar WV-W	
1/(X/M)	1/Ce	1/(X/M)	1/Ce
4.35	1.71×10^{-3}	3.85	2.1×10^{-3}
5.00	1.73×10^{-3}	4.76	2.12×10^{-3}
4.55	1.77×10^{-3}	5.88	2.13×10^{-3}
4.55	1.85×10^{-3}	5.00	2.27×10^{-3}
4.76	1.91×10^{-3}	10.00	2.16×10^{-3}
10.00	1.83×10^{-3}	8.33	2.26×10^{-3}
7.14	2.02×10^{-3}	9.09	2.29×10^{-3}
12.50	1.89×10^{-3}	10.00	2.35×10^{-3}
16.67	2.02×10^{-3}	12.50	2.35×10^{-3}
		20.00	2.53×10^{-3}

Table C-9.

Carbon Dosage (mg)	Percent TOC Removed			
	Celco Carbon		Nuchar WV-W	
	12 hours	24 hours	12 hours	24 hours
15.0	5.8	3.78	12.2	5.20
22.50	2.8	4.93	15.5	6.20
30.0	7.1	7.07	13.7	6.57
45.0	9.4	10.2	12.2	12.20
60.0	14.1	13.7	9.8	7.77
75.0	10.4		13.5	11.80
90.0	8.7	10.20	12.0	13.10
120.0	10.2	18.6	11.6	15.30
150.0	9.1	12.8	13.1	15.30
300.0	15.1	18.6	17.1	21.30
0.0	0.0	0.0	0.0	0.0

Appendix D - Computational Procedures for the plots of adsorption isotherm

For example, from Table C-3 of Appendix C, using the data of flask No.s (BOA) and 1, the following results were obtained.

Celco carbon

Flask No. BOA $\frac{X}{M} = \left[\frac{608 - 608 \text{ mg/L}}{0.00 \text{ mg}}\right].15 \text{ L} = 0$

Flask No. 1 $\frac{X}{M} = \left[\frac{608 - 573 \text{ mg/L}}{15 \text{ mg}}\right]95 \text{ L} = 0.35$

$\frac{1}{X/M} = 2.86 \qquad \frac{1}{C_e} = 1.75 \times 10^{-3} \text{ L/mg}$

TOC removed in percent $\frac{502 - 441}{502} 100 = 12.2 \text{ percent}$

Nuchar WV-W

Flask No. BOA $\frac{X}{M} = \left[\frac{502 - 502 \text{ mg/L}}{0.00}\right]0.15 \text{ L} = 0$

Flask No. 1 $\frac{X}{M} = \left[\frac{502 - 441 \text{ mg/L}}{15 \text{ mg}}\right] 0.15 \text{ L} = 0.61$

$\frac{1}{X/M} = \frac{1}{.61} = 1.64 \text{ (mg/mg)}$

$\frac{1}{C_e} = \frac{1}{441} = 2.27 \times 10^{-3} \text{ L/mg}$

TOC removed in percent $\frac{608 - 573}{608} 100 = 5.8 \text{ percent}$

Appendix E - Table E-1. Reactor A - Operational Parameters.

	Days	pH*	pH Inf.	pH Effl.	COD Inf.	COD Effl.	TOC Inf.	TOC Effl.	ZVS ft/hr	SVI ml/gm	DO	Temp. (°C)	O_2 Uptake Rate mg/L-hr	R_r day^{-1}	MLSS	MLVSS	TSS
	1																
	2	8.0	4.4	8.1	3820	70	714	34.5		474					2080	1680	208
	3																
	4	7.8							0.29	423	6.3	19			2340	1840	265
	5	7.9	4.5	8.0	4430	87	775	34.0			6.5	19			2480	1840	233
	6	8.1							0.32	387	7.0				2560		355
	7	7.9									6.0		10.2	0.14*	2080	1770	263
	8	7.8									5.1	18			2110		88
	9	7.8	4.6	8.2	4510	134	792	48.5			4.8	18.5	10.9	0.14*	2260	1840	198
	10	7.6									5.2	19			1780		168
	11	8.0									5.7	18.5			1760	1420	165
	12	8.0							1.25	245	7.0	20			2120	1720	185
	13	8.1									6.7	18			1750	1500	155
b_1	14	7.9	5.0	8.0	2440	60	506	19.5			5.5	18	9.0	0.15	1740	1480	150
	15								4.40	144					1800	1480	100
	16																
	17														2010		170
	18	8.0	4.9	8.0	2360	45.8	530	14.2			6.2	17.5	9.2	0.15	1830	1470	94
	19								8.11	110					1810		84
	20														1630	1380	87
	21	7.9	4.4	8.0	4090	34.7	866	14.3			5.0	18	7.4	0.14	1455	1315	74
	22								5.84	164					1460		63
	23																
	24	7.9	4.4	8.0	4550	33	880	24.3			6.5	17.5	8.24	0.16	1515	1260	70
	25	7.8		8.1					3.98	190	5.4	17.8			1500	1365	106
	26														1615	1365	131
	27	8.0	5.1	8.1	2070	37.5	541	17.2			6.9	18	6.67	0.12	1550	1380	122
	28								3.18	200					1425		164
	29														1520		113
	30	7.9	4.8	7.9	2240	31	582	14.3			7.0	17.8	6.34	0.11	1420	1245	133

Appendix E - Table E-1. Reactor A - Operational Parameters (cont.).

	Days	pH*	pH Inf.	pH Effl.	COD Inf.	COD Effl.	TOC Inf.	TOC Effl.	ZVS ft/hr	SVI ml/gm	DO	Temp. (°C)	O_2 Uptake Rate mg/L-hr	R_{T-1} day^{-1}	MLSS	MLVSS	TSS
	61														1395	1218	80
	62	7.7	5.0	7.9	3060	73			15.0	68	5.5	18.8	7.1	0.150	1400	1173	73
	63																
	64								24	70			9.5	0.170	1565	1415	125
	65	7.8	4.6	7.9	4670	64					4.3				1818	1623	115
	66																
	67									73			15	0.220	1908	1655	108
	68																
	69																
	70																
	71	7.4	4.5	7.8	4550	89					6.0	18.3			1830	1588	143
b_4	72														1930	1705	210
	101																
	102	7.4									7.0	18.5			1650	1420	360
b_5	103	7.1									6.5	18.5			1320	1130	355
	104	7.1								79.5	5.7	18.5			1510	1265	360
	105																
	106														1325		205
	107				2860	532					3.3	19			1280	1100	430
	108	7.5								61.9	7.3	18			1535	1245	520
	109	7.4	4.4	7.2	3790	137			11.5	76.4	7.5	18	13.5	0.25	1510	1360	400
	110	7.4									7.6	18.2			1430	1235	218
	111	7.7	4.5	7.7	3320	106			13		7.7	18	13.2	0.22	1555	1470	180
	112								15.9	91.2	7.4	17.5	13.3	0.24	1645	1395	85
	113	7.6	4.4	7.8	4040	93									1585		88
	114	7.6							11.70	93	7.7	18	12.4	0.23	1510	1355	75
	115		4.9	7.7	2820	96						18.5			1400		95
	116	7.5							11.0	106	7.1	18.5	13.7	0.30	1275	1120	85
	117																
	118	7.4							11.1	100	7.9		9.91	0.22	1305	1115	90
	119		4.8	7.6	2620	120											
b_6	120																

b_1-b_2 Data collected for carbon run of 280 mg/L.

b_3-b_4 Data collected for carbon run of 160 mg/L.

b_5-b_6 Data collected for carbon run of 20 mg/L.

* Not at equilibrium carbon concentration of 280 mg/L and, therefore was corrected for PAC.

Appendix E - Table E-1. Reactor A - Operational Parameters (cont.).

	Days	pH*	pH Inf.	pH Effl.	COD Inf.	COD Effl.	TOC Inf.	TOC Effl.	ZVS ft/hr	SVI ml/gm	DO	Temp. (°C)	O_2 Uptake Rate mg/L-hr	R_r day^{-1}	MLSS	MLVSS	TSS
	31																
	32																
	33	8.1	5.1	8.2	2020	57	548	24.20	10.3	89	6.4	18			1350		96
b_2	34								11.7	85							
	35														1360		101
	36														1190		81
	37														1375		74
	38																
	39														1405		76
	40														1345		63
b_3	41														1355		72
	42														1490		96
	43	8.0	4.7	8.0	3050	50.4	685	17.6	11.0	96	6.5	18			1405	1190	93
	44														1455	1310	137
	45														1375		141
	46	8.0															
	47	7.9	4.6	7.8	3320	46	633	18.9	5.6	121	5.9	18	4.7	0.098	1410	1200	213
	48										5.8	18.5			1395		160
	49										5.5	18.5	8.5	0.170	1400	1230	170
	50	7.9													1425		170
	51		4.6	7.8	3610	80	638	24	10.6	92	6.8	18.3	7.3	0.150	1415		228
	52														1408		250
	53	7.7															
	54	7.8	4.7	7.8	3143	88	748	19.4	10.6	85	5.6	18.2			1420		183
	55														1420	1285	135
	56												0.0	0.190	1490	1320	163
	57	7.7	4.9	7.8	2790	101	628	22	12.4	66	6.9	18.3			1440		130
	58																
	59														1540	1328	220
	60	7.5							12.1	60	6.2	18.5	7.7	0.140	1505	1348	65

Appendix E - Table E-2. Reactor B - Operational Parameters

	Days	pH*	pH Inf.	pH Effl.	COD Inf.	COD Effl.	TOC Inf.	TOC Effl.	ZVS ft/hr	SVI ml/gm	DO	Temp. (°C)	O_2 Uptake Rate mg/L-hr	R_r day^{-1}	MLSS	MLVSS	TSS
	1																
	2	8.1	4.4	8.1	3820	85	714	38		500					1940	1560	360
	3																
	4	8.0							.76	427	8.2	17			2110	1600	350
	5	8.2	4.5	8.2	440	89	775	36.1			7.2	18			2330	1730	518
	6	8.2							.85	334	7.8				2050		930
	7	7.8									5.8		11.1	0.20	1660	1350	370
	8	8.1									7.0	18.5			1280	1190	153
	9	7.9	4.6	8.2	4510	179	792	65.2			6.4	19	10.50	0.18	1620	1400	260
	10	7.8									6.9	18			1670		135
	11	8.1									7.8	18			1630	1370	158
	12	8.2							1.17	285	7.7	18			1840	1650	170
	13	8.0									6.3	17.5			1480	1240	150
a_1	14	8.0	5.0	8.1	2440	76	526	24.1			6.1	18	6.50	0.14	1360	1140	145
	15								4.70	182					1430	1180	65
	16																
	17														1720		163
	18	8.0	4.9		2360	65.4	530	20			6.5	17.8	7.04	0.14	1400	1180	87
	19								5.11	169					1420		66
	20														1400	1180	65
	21	8.0	4.4		4090	48.3	866	18.2			6.2	17.5	6.6	0.14	1280	1095	63
	22								3.86	240					1165		70
	23																
	24	7.7	4.4	8.0	4550	50	880	24.4			6.0	17.5	8.14	0.19	1260	1060	78
	25	7.9		8.1					2.62	272	6.5	18			1250	1090	106
	26														1250	1070	112
	27	8.0	5.1	8.2	2070	63	541	22.3			7.8	18	5.5	0.12	1295	1095	116
	28								3.03	386					1190		185
	29														1165		93
	30	7.9	4.8	8.0	2240	42	582	17.5			7.6	17.5	4.71	0.11	1130	995	112
	31																
	32								3.15	214					1120		114
	33	8.2	5.1	8.3	2020	53	548	23.5			6.4	17.5					
a_2	34								3.50	235					1000		99
	35														900		75
	36														1090		108
	37																
	38														1050		88
	39														1105		51
	40														1120		79
a_3	41														1210		92
	42														1150	1010	168

Appendix E - Table E-2. Reactor B - Operational Parameters (cont.).

	Days	pH*	pH Inf.	pH Effl.	COD Inf.	COD Effl.	TOC Inf.	TOC Effl.	ZVS ft/hr	SVI ml/gm	DO	Temp. (°C)	O_2 Uptake Rate mg/L-hr	R_{r} day^{-1}	MLSS	MLVSS	TSS
	43	7.8	4.7	8.0	3050	71	685	19.7	3.33	157					1275	1075	155
	44														1180		143
	45																
	46	7.8							4.72	137	6.4	17.8	6.0	0.15	1170	965	210
	47	7.8	4.6	8.1	3820	83.0	633	19.3			6.4	18			1090		200
	48										4.8	18.5	8.1	0.20	1170	975	183
	49														1215		240
	50	7.8							10.1	104					1253		210
	51		4.6	7.8	3610	149	638	33.2			7.3	18	5.6	0.13	1200	1005	193
	52																
	53	7.7							10.8	86					1165		98
	54		4.7	7.8	3140	84	748	21.5			6.3	18			1215	1110	95
	55												8.5	0.19	1258	1098	135
	56								11.8	90					1218		128
	57	7.7	4.9	7.9	2790	100	628	22.3			7.2	18					
	58														1430	1248	198
	59																
	60	7.6							11.5	90	6.3	18.5	11	0.25	1220	1068	68
	61														1160		118
	62	7.8	5.0	8.0	3060	88			13.2	76	6.3	18.5	7.7	0.17	1308	1093	83
	63																
	64								21.4	79					1483	1223	150
	65	7.8	4.6	8.1	4670	85						18.3	9.8	0.16	1500	1300	123
	66																
	67									76			11.0	0.20	1580	1353	168
	68																
	69																
	70														1720	1525	208
	71	7.5	4.5	7.8	4550	90					5.0	18.3			1815	1583	260
a_4	72																
	101																
	102	7.2									6.8	18.2			1260	1000	220
a_5	103	7.1									6.7	18.2			1390	1140	135
	104	7.1								93	6.0	18.2			1240	960	210
	105																
	106																
	107				2860	47					6.4	18.0			1010	820	235

Appendix E - Table E-2. Reactor B - Operational Parameters (cont.).

	Days	pH*	pH Inf.	pH Effl.	COD Inf.	COD Effl.	TOC Inf.	TOC Effl.	ZVS ft/hr	SVI ml/gm	DO	Temp. (°C)	O_2 Uptake Rate mg/L-hr	R_r day^{-1}	MLSS	MLVSS	TSS
	108	6.6								78	6.2	18.0			1285	1060	410
	109	7.0	4.4	6.8	3790	140			12.0	96	6.7	18.0	12,2	0.29	1150	1000	280
	110	7.1									6.7	18.2			1350	1160	88
	111	7.5	4.5	7.5	3020	125			11.1		6.0	18	9.5	0.20	1370	1130	175
	112								11.5	90	6.8	18	10.3	0.24	1220	1020	90
	113	7.2	4.4	7.6	4040	114					6.9	18			1190		120
	114	7.2							12.2	108	7.2	18	12.5	0.35	1070	870	135
	115		4.9	7.2	2820	113									1170		125
	116	7.0							12.2	103	6.4	17.5	14.3	0.35	1115	985	625
	117																
	118	6.6							12.2	103	6.7		9.78	0.23	1160	1020	90
	119		4.8	9.7	2620	149											
a_6	120																

a_1 - a_2 Data collected for the control unit during the carbon run of 280 mg/L.

a_3 - a_4 Data collected for the control unit during the carbon run of 160 mg/L

a_5 - a_6 Data collected for the control unit during the carbon run of 20 mg/L.

Table F-1. Improved COD, Increase in OUR and their Percent Improvements for Trial Run of 280 mg/L.

Days	Increased COD Removal (mg/L)	Percent COD Improve-ment	Increased TOC Removal (mg/L)	Percent TOC Improve-ment	Increased OUR (mg/L-hr)	Percent Increase in OUR
14	16	21	4.6	19.1	2.5	39
18	19	29	5.8	29.0	2.16	31
21	13	27	3.9	21.4	0.80	12
24	17	34	0.1	0.41	-0.20	- 2
27	25	40	5.1	22.90	1.17	21
30	11	26	3.2	18.30	1.53	33
33	- 4	- 8	0.7	3.00	-	-

Note: The negative sign indicates that Unit B had a better reading on that day.

- No data collected.

Table F-2. Improved COD, Increase in OUR for Their Respective days.

Days	Increased COD Removal mg/L	Percent Improvement	Increased OUR mg/L	Percent Increase in OUR
43	21	30	+	+
46	+	+	-1.30	-22
47	37	45	+	+
48	+	+	0.40	5
51	69	46	1.70	30
54	-4	-5	+	+
55	+	+	1.50	18
57	-1	-1	+	+
60			-3.30	-30
62	15	17	-.60	-8
64	+		b	+
65	21	25	+	b
67			4	36
71	1	1	+	+
Average	20.0	20.0	0.34	4.14

Negative Sign indicates that Unit B had a better reading on that day.

+ Data were not taken.

b Omitted because reading of the other unit was taken.

Table F-3. Improved COD OUR for their Respective Days

Days	Increased COD Removal mg/L	Percent Improvement in COD	Increased OUR mg/L-hr	Percent Increase in OUR
107	-385+	-263+	C	C
109	3	2	1.3	11
111	19	15	3.7	39
112	C	C	3.0	29
113	21	23	C	C
114	C	C	-.10	-.8
115	17	15	C	C
116	C	C	-.60	C
118	C	C	.13	1.0
119	29	20	C	C
Average	18	15	1.24	12.5

- Unit B had a better reading on that day.

C Data were not taken.

+ Data were not included in computing the average values.

APPENDIX G - Statistical Analysis

Determination of Correlation Factor Between COD and TOC.

Using the table of

$$\sum_{i=1}^{n} X_i = 35,683 \qquad n = 12$$

$$\sum_{i=1}^{n} X_i^2 = 113,356,249$$

$$\sum_{i=1}^{n} y_i = 7805$$

$$\bar{x} = \sum_{i=1}^{n} \frac{x_i}{n} = 2970$$

$$\sum_{i=1}^{n} y_i^2 = 5244487$$

$$\bar{Y} = \sum_{i=1}^{n} \frac{Y_i}{n} = 650$$

$$\sum_{i=1}^{n} xy = 24,207,764$$

$$S_{xx} = n \sum_{i=1}^{n} x_i^2 - \sum_{i=1}^{n} x_i^2 = 86,998,449$$

$$Syy = n \sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} y_i\right)^2 = 2,015,819$$

$$S_{xy} = n \sum_{i=1}^{n} x_i u_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i = 11,987,353$$

Required equation : $TOC = bCOD + a$.....

where $a = \bar{Y} - b\bar{x}$..... $b = S_{xy}/S_{xx} = 0.138$

Substituting b in the equation

$a = 240$

$TOC = 0.138\ COD + 240$

$$r = \frac{S_{xy}}{\left[(S_{xx})(S_{yy})\right]^{1/2}} = 0.91$$

Correlation between pH and COD.

$$\sum_{i=1}^{n} y_i = 107.8 \qquad \sum_{i}^{n} x_i^2 = 276,313,549$$

$$\sum_{i=1}^{n} x_i = 77,313 \qquad \sum_{i}^{n} y_i^2 = 506.50$$

$$n = 23$$

$$\sum_{i}^{n} x_i y_i = 358,579.10$$

$$S_{xx} = 23(276,313,549) - (77,313)^2 = 377,911,658$$

$$S_{yy} = 23(506.50) - (107.8)^2 = 28.66$$

$$S_{xy} = 23(358,519.10) - (107.8)(77,313) = -88,402$$

$$r = \frac{S_{xy}}{[(S_{xx})(S_{yy})]^{1/2}}$$

$$\boxed{r = -0.85}$$

Table H-1. The Influent and Effluent Concentrations of Solvents and Acid for Reactor A at Carbon Run of 280 mg/L.

Days	Methanol (mg/L) Inf.	Eff.	Ethanol (mg/L) Inf.	Eff.	Acetone (mg/L) Inf.	Eff.	Methyl Cyanide (mg/L) Inf.	Eff.	Acid (mg/L) Inf.	Eff.
* 2	10	0	403	0	23	0	43	0	-	-
* 9	10	0	606	0	81	0	100	0	-	-
15	0	0	124	0	48	0	28	0	-	-
21	0	0	118	0	38	0	20	0	770	0
24	0	0	152	0	50	0	26	0	850	0
27	6	0	68	0	37	0	9	0	220	0
30	0	0	110	0	55	0	32	0	200	0

* The first two days indicated on the table are at different carbon concentrations (20 mg/L and 160 mg/L).
- No data collected.

Table H-2. The Influent and Effluent Concentrations of Solvents and Acid for Control Bioreactor R_B during the Carbon Run of 280 mg/L.

Days	Methanol (mg/L) Inf.	Eff.	Ethanol (mg/L) Inf.	Eff.	Acetone (mg/L) Inf.	Eff.	Methyl Cyanide (mg/L) Inf.	Eff.	Acid (mg/L) Inf.	Eff.
* 2	10	0	403	0	23	0	43	0	0	0
* 9	10	0	606	0	81	3	100	0	0	0
15	0	0	124	0	48	0	28	0	0	0
21	0	0	118	0	38	0	20	0	770	0
24	0	0	152	0	50	0	26	0	850	0
27	6	0	68	0	37	0	9	0	220	0
30	0	0	110	0	55	0	32	0	200	0

* The first two days indicated on the table are at different carbon concentrations (20 mg/L and 160 mg/L).

Table H-3. The Influent and Effluent Concentration of Solvents and Acid for Bioreactor A carbon run of 160 mg/L.

Days	Methanol (mg/L) Inf.	Eff.	Ethanol (mg/L) Inf.	Eff.	Acetone (mg/L) Inf.	Eff.	Methyl Cyanide (mg/L) Inf.	Eff.	Acid (mg/L) Inf.	Eff.
46	0	0	110	0	70	0	50	0	300	0
50	0	0	160	0	70	0	50	0	190	0
54	0	0	148	0	42	0	39	0	500	0
58	1	0	86	0	26	0	21	0	300	0
62	5	0	100	0	26	0	25	0	200	0
65	0	0	100		13	0	20	0	200	0
71	10		130		190		20		620	0

Note: Reactors A and B had the same influent and effluents characteristics of solvents and acids on the days indicated above.

Table II-4. Influent and Effluent Concentrations for both Reactors for Carbon Run of 20 mg/L

Days	Influent (Acids) (mg/L)	R_A Effluent (mg/L)	R_B Effluent (mg/L)
113	700	0	0
117	640	0	0
119	240	0	0

Table II-5. Influent and Effluent MeO during the Trial Run of PAC of 280 mg/L.

Days	Influent (mg/L)	R_A Effluent (mg/L)	R_B Effluent (mg/L)
2	0.5	0.7	0.6
9	0.7	0.3	0.2
15	0.5	0.3	0.2
21	0.2	0.1	0.1
24	0.2	0.1	0.2
27	0.3	0.2	0.2
30	0.2	0.2	0.2

Table H-6. Influent and Effluent MeO during the Trial Run of PAC of 160 mg/L.

Days	Influent (mg/L)	R_A Effluent (mg/L)	R_B Effluent (mg/L)
46	0.5	0.3	0.4
50	0.3	0.2	0.2
54	0.1	0.1	0.1
58	0.1	0.1	0.1
62	0.1	0.1	0.1
71	0.2	<0.1	<0.1

Table H-7. Influent and Effluent MeO during the Trial Run of PAC of 20 mg/L.

Days	Influent (mg/L)	R_A Effluent (mg/L)	R_B Effluent (mg/L)
113	0.20	0.1	0.1
117	0.10	0.1	0.1
119	0.10	0.1	0.1

Appendix I

Table I-1. PAC Blank Runs

Equilibrium PAC mg/L	MLVSS mg/L
20	33
160	33
280	35

Table I-2. Sample Calculations on Biokinetic Constant for 20 mg/L PAC Run.

$$R_A/q = \frac{Q(S_o - S_e)}{XV} = \frac{4.32(3318 - 110)}{(16.5)\ (1224)} = 0.686$$

$$K_b = \frac{0.686}{110} = 0.0062 \text{ 1/mg-day}$$

$$Y_{obs} = \frac{1/14}{0.686} = 0.104$$

$$Y_{obs} = 0.104 \quad \frac{\text{mg of active biomass product}}{\text{mg of COD consumed}}$$

$$R_B/q = \frac{4.32\ (3318 - 128)}{(16.5)\ (1015)} = 0.823$$

(Control Unit)

$$K_b = \frac{0.823}{128} = 0.0064 \text{ L/mg-day}$$

$$Y_{obs} = \frac{0.0714}{0.823} = 0.0868$$

APPENDIX J. Summary of the Important Parameters

	MLVSS	COD	Eff COD	Eff SS	OUR	R_r	ZSV	SVI	q, day^{-1}
20 mg/L PAC	1220	3210	110	228	12.7	0.29	12.4	87	0.689
Control	1020	3190	131	209	11.4	0.28	11.9	96	0.819
160 mg/L PAC	1340	3450	74	150	8.7	0.16	11.1	81	0.674
Control	1190	3430	94	161	8.5	0.18	10.8	99	0.755
280 mg/L PAC	1340	2780	43	107	7.8	0.14	5.0	150	0.543
Control	1110	2760	57	100	6.5	0.14	3.7	242	0.652

More biomass in the PAC units.
Higher specific substrate utilization rate in the control units, difference was greatest in 20 mg/L PAC run
Lower effluent COD from PAC units
Effluent SS were mixed, but not very different
OUR was higher in PAC units, but only because of greater biomass
R_r was greater in the control units because of higher specific substrate utilization rate
Settling properties of the sludges were always better in the PAC units, and the difference was greatest at the 280 mg/L concentration

Net Effects of PAC

Greater biomass in units and lower effluent COD
Improved sludge settleability

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