TREATABILITY OF CRUDE DESALTER WASTEWATER FROM A REFINERY BY AN AERATED SUBMERGED BIOLOGICAL FILTER

By

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Bachelor of Science

Oklahoma State University

Stillwater, Oklahoma

1989

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
July, 1991

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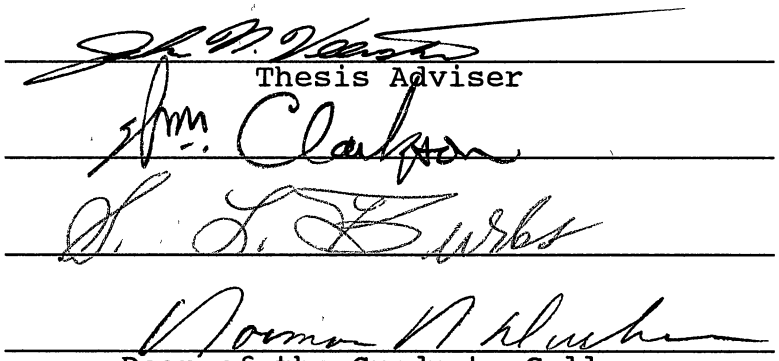
Thesis Approved:



Thesis Adviser

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ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my major advisor, Dr. John N. Veenstra, for his patience, guidance, encouragement, and advise throughout my graduate program. I am very thankful to Dr. William Clarkson and Dr. S. L. Burks for their guidance and for serving as a member of my committee. I am also very thankful to Dr. Burks and Dr. Veenstra for funding my research.

Many sincere thanks go to Don Spoonemore for his help in maintaining the research equipment at Environmental Engineering Research Laboratory. I would also like to thank Elaine Stebler, Hildreth Overcache, and Lisa Robinson for their help in performing bioassays at Water Quality Research Laboratory.

I am also very grateful to my fiance, Wade Anderson, for his patience, understanding, help, and moral support during my graduate program, research, and all other times.

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CHAPTER I

TREATABILITY OF CRUDE DESALTER WASTEWATER FROM A REFINERY BY AN AERATED SUBMERGED BIOLOGICAL FILTER

RaDawn Nicole Martinez

ABSTRACT: The biological kinetic coefficients of a laboratory scale Aerated Submerged Biological Filter (ASBF) which reduced the toxicity of Crude Desalter wastewater were determined by analyzing the data in the Germain kinetic model. The organic removal vs. organic loading graph for the ASBF data indicated that the data was first order or linear. Thus, the first order Germain model was used to determine the kinetic coefficients. The kinetic coefficients were then used to determine the volume, surface area of media, and effluent concentrations of full size ASBF to treat Crude Desalter wastewater at a petroleum refinery. During the study, the ASBF was run at organic loading rates from 3.5 g COD/m^2*day to 13.7 g COD/m^2*day with COD removal efficiency in the range of 57.9% to 88.8% and increased toxicity removal, influent LC50 of 57.47% to effluent LC50 of 100%.

KEYWORDS: ASBF, biological kinetics, Crude Desalter, toxicity, LC50, Ceriodaphnia dubia, fathead minnow.

INTRODUCTION

The 1987 Amendments of the Federal Water Pollution Control Act produced emphasis on the toxic effects of effluents discharged into aquatic environments. The amendments state that "...it is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited" (Burkhard, 1989). In the United States, the water pollution control effort has progressed from controlling "traditional" pollutants (oxygen demanding and eutrophying materials) to controlling pollutants that adversely impact water quality, aquatic life, and human life through toxic effects. Industries and refineries have sufficiently reduced and controlled traditional pollutants (BOD 30 mg/L and suspended solids 30 mg/L). Now they must focus on reducing the amount of pollutants that are toxic to aquatic and human life.

A coalition of Oklahoma refineries is conducting cooperative Toxicity Identification Evaluations (TIE) and Toxicity Reduction Evaluations (TRE) to comply with the toxicity regulations and discharge permits. TREs are performed to determine measures needed to maintain toxicity at acceptable levels. An integral part of the TRE is the

TIE, whose goal is to identify quickly and cheaply the constituents causing toxicity (Burkhard, 1989). The methods used in the cooperative TRE to reduce toxicity of petroleum refinery process wastewater include the following: (1) solvent extraction, (2) adsorption by activated carbon, (3) chemical oxidation, and (4) biological oxidation. The TIE employed by the coalition include fractionation, aeration, filtration and passage through a C_{18} column (a solid nonpolar adsorbent similar to activated carbon in adsorption properties) of influent and effluent samples to determine the toxic fraction of the wastewaters and also to determine the effectiveness of the unit operation. The effectiveness of the TRE methods and TIE methods were measured by the acutely lethal response of Daphnia (Ceriodaphnia dubia) and Fathead minnows (Pimephales promelas) in a 48 hour static exposure (Burks, 1990).

Of all the methods employed in the TRE, biological oxidation has been successful in reducing the toxicity of Crude Desalter wastewater, one of the most toxic and variable refinery process wastewater streams. The Crude Desalter wastewater contains hydrocarbons, the toxic component of oil. The toxic properties of crude oils appear to be related to the amount of hydrocarbons present (Burks, 1982). Thus, the more hydrocarbons in the Crude Desalter wastewater the more toxic it is.

The desalting of crude oil is a primary process in a

refinery because crude oil entering a refinery contains small amounts of emulsified brine, free oils, ammonia, phenol, suspended solids, and hydrocarbons. The emulsified brine in the crude oil may range from 0.1 to 2.0 volume percent and the brine may contain up to 25 weight percent salt (mostly sodium chloride) (Beychok, 1967). The salt content of the brine in the crude oil ranges from 10 to 250 lb per 1000 barrels. A salt content of 20 lb per 1000 bbls is considered a maximum that can be tolerated in crude oil, but desalting operations are generally aimed at a much lower value (Bland and Davidson, 1967). A high salt content can not be tolerated because inorganic salts, particularly chlorides, break down during processing and cause serious corrosion and fouling of equipment. (Bland and Davidson, 1967).

Three general approaches have been developed to remove the salt from crude oil: mechanical, chemical, and electrical, all shown in Figure 1 (Bland and Davidson, 1967). Brine suspensions are removed by heating oil to 250-300^{o}F under pressure, 50 to 250 psig, and mixing the oil with wash water, about 5 volume percent of the crude oil, to assist the desalting process.

The desalting wash water is the Crude Desalter wastewater containing high concentrations of salt, oil, BOD, COD, emulsions, hydrocarbons, and other water soluble materials. In a refinery, the desalter effluents often

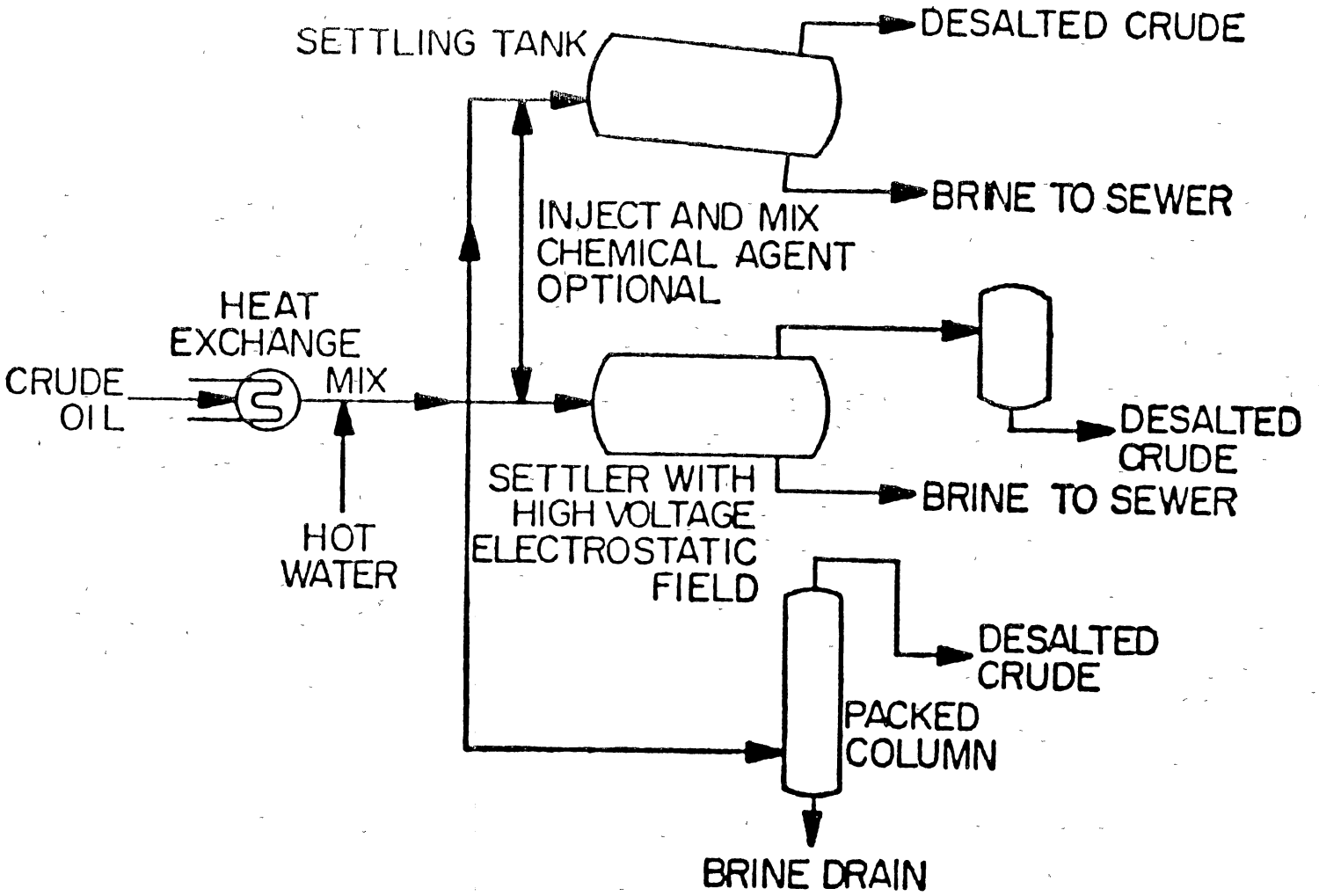

Figure 1. Schematic of Crude Desalter Approaches (Source: Bland and Davidson, 1967)

contribute a significant portion of the total refinery BOD (Beychok, 1967). In addition Crude Desalter wastewater is usually composed of high levels of non-polar organic contaminants which are lethal to aquatic organisms (Burks and Wagner, 1983). Figure 2 shows the percentage of compounds identified in Crude Desalter and other unit process wastewaters (Burks and Wagner, 1989). In addition, fractionation of Crude Desalter wastewater indicated that low molecular weight organics are biodegradable. However, some of the heavier organics, such as those present in influent and effluent samples of Crude Desalter wastewater, are more refractory to degradation and thus become the candidate causative agent for chronic toxicity in biotreated wastewater (Burks, 1990). Thus, the Crude Desalter wastewater is toxic because it contains contaminants removed from the crude oil.

The Crude Desalter wastewater is as variable as the crude oil used in a refinery. Besides variation in crude oil type, the variation of wastewaters is produced by a combination of process operation, chemical addition, plant age, and plant maintenance. Thus, the composition of Crude Desalter wastewater can vary from day to day, year to year, and source to source.

An Aerated Submerged Biological Filter (ASBF) was the bench scale biological unit used in the TRE to successfully reduce the toxicity of Crude Desalter wastewater. The 48

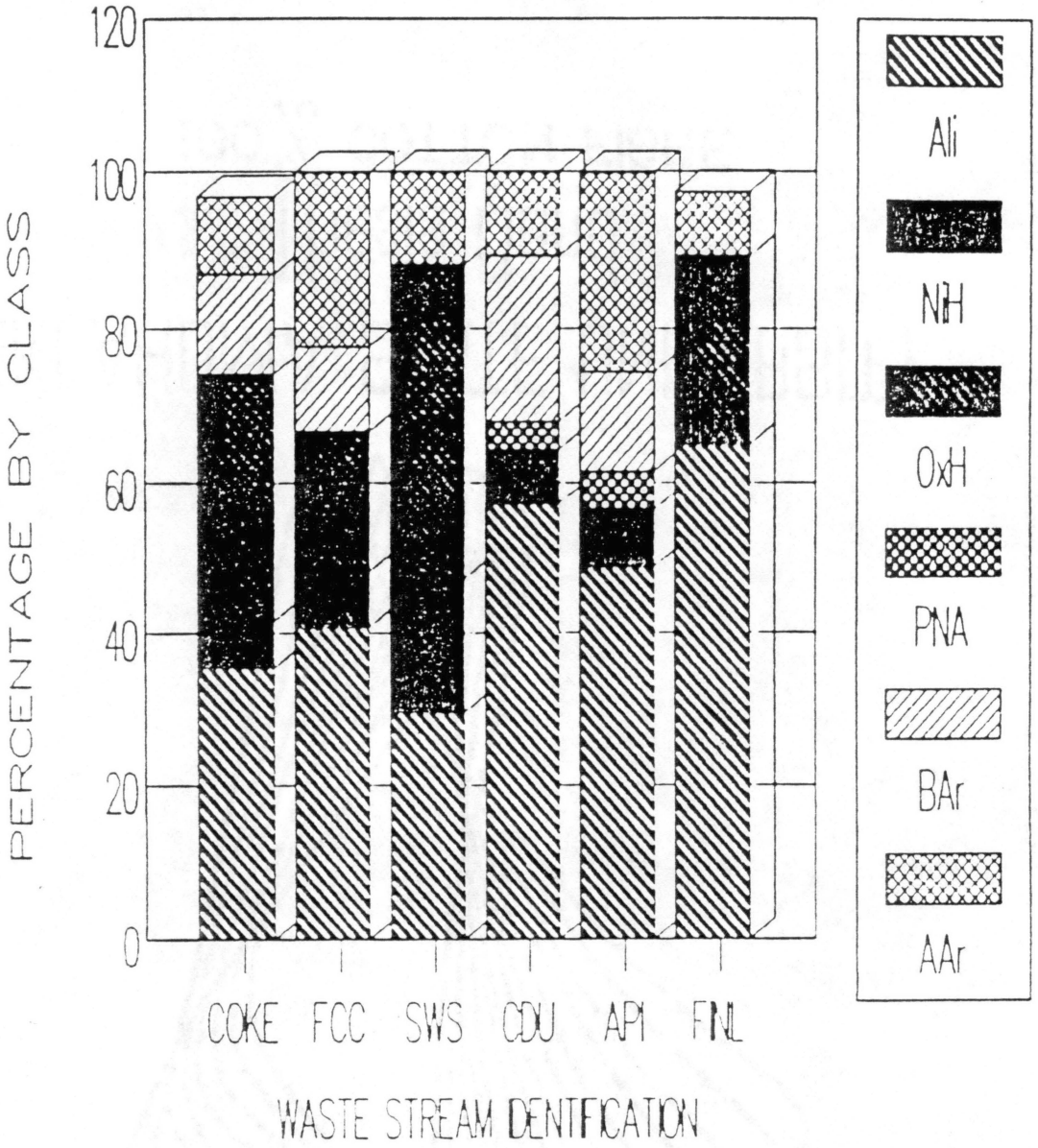

Figure 2. Classes of Organic Compounds in Oil Refinery Waste waters. (Source: Burks and Wagner, 1989)

Ali = Aliphatics, NiH = nitrogen heterocyclics, OxH = oxygenated hydrocarbons, PNA = polynuclear aromatics, BAr = bicyclic aromatics, AAr = alkyl aromatics.
CDU = Crude Desalter Unit , Coke = Coking Unit FCC = Fluid Catalytic Cracker, SWS = Sour Water Stripper, API = API Oil Separator, FNL = Final Effluent.

hour acute toxicity tests showed that the effluent from the ASBF (loaded at 7 and 10.5 gm COD/m^2*d) contained a less lethal toxicant concentration than the influent for Daphnia and fathead minnows (Poesponegoro, 1990). The Chemical Oxygen Demand (COD) removal efficiency of the ASBF increased from 57.9% at 3.5 gm COD/m^2*d to 88.8% at 7 gm COD/m^2*d and 88.7% at 10.5 gm COD/m^2*d (Poesponegoro, 1990).

The success of the ASBF in reducing toxicity of process wastewaters makes the ASBF a good candidate for kinetic analysis to provide parameters for scale-up. The appropriate coefficients determined from kinetic analysis can be used to design a full scale ASBF for installation in a refinery waste treatment system. The kinetic coefficients can be used to determine the design parameters of reactor size, media surface area, and effluent concentrations. The kinetic analysis for the ASBF consisted of substituting the laboratory data in the first order Germain kinetic model previously used to describe growth and substrate utilization in fixed-film reactors.

MATERIALS AND METHODS

The previously operated laboratory scale ASBF responsible for reducing the toxicity of Crude Desalter wastewater was used to determine the kinetic coefficients. The initial 3 runs (COD loadings 3.5, 7.0, and 10.5 g

COD/m^2*d) were conducted to prove that the ASBF reduced the toxicity of the Crude Desalter wastewater (Poesponegoro, 1990). The final 3 runs (COD loadings 4.5, 9.6, 13.7 g COD/m^2*d) were conducted in this study to collect more data to determine the kinetic coefficients of the ASBF. The hydraulic residence times (HRT) corresponding to each of the final 3 runs were 6.3 hrs at 13.7 g COD/m^2*d, 11.4 hrs at 9.6 g COD/m^2*d, and 11.6 hrs at 4.5 g COD/m^2*d.

The ASBF reactor is a hybrid of fixed film and activated sludge biological reactors. The ASBF used in this study was a plexiglass unit with a cross section of 24.1 cm x 24.0 cm, 22.8 cm depth, and an empty bed reactor volume of 10.16 liters. The reactor contained fixed plastic media, similar to biological towers, for microorganisms to attach to a specific surface area of 138 m^2/m^3 and a porosity of 98.7%. The microorganisms are also suspended in the liquid, encompassing the media, similar to activated sludge. Air diffusers were positioned on the bottom of the reactor at angles under a perforated plate located 1 cm above the bottom of the reactor. Compressed air at an average rate of two L/min was introduced through four 10 cm long air diffusers to provide air to maintain an aerobic environment for the microorganisms and to provide adequate mixing of the waste and microorganisms. Figure 3 is a schematic of the ASBF unit.

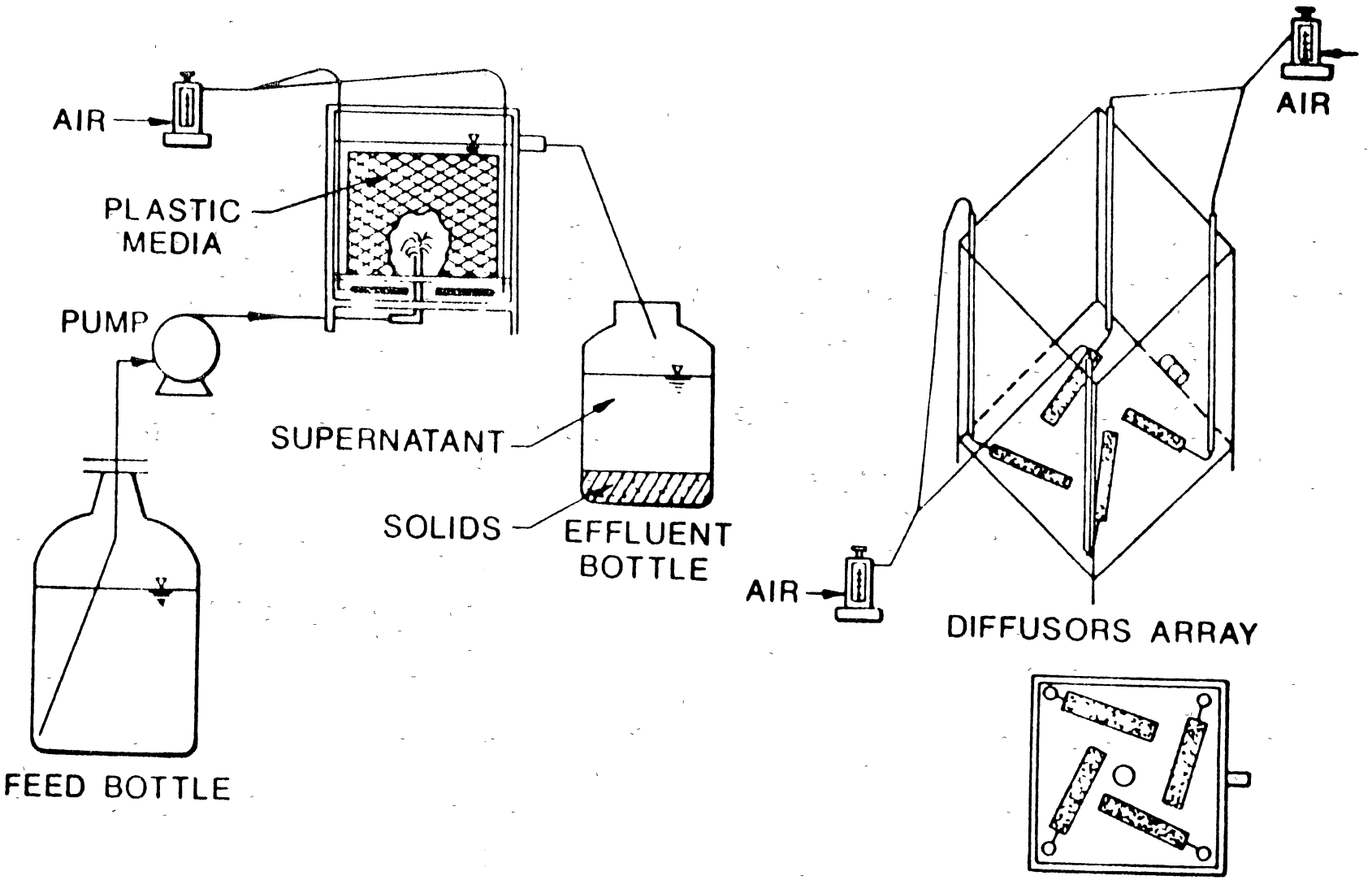

Figure 3. Schematic of ASBF

The ASBF was initially seeded with organisms taken from a Sour Water Stripper wastewater lagoon from a refinery in Oklahoma to develop the biological film on the media of the ASBF. Since the organisms were taken from a SWS wastewater lagoon, the biological film had to be developed by first using only Sour Water Stripper wastewater as a feed solution. To acclimate the biofilm to Crude Desalter wastewater the feed solution was changed to a mixture of Crude Desalter and Sour Water Stripper wastewater. The amount of Crude Desalter in the mixture increased gradually until the entire feed solution was Crude Desalter wastewater.

During the study, the Crude Desalter wastewater used as the influent for the ASBF was collected from a refinery in Oklahoma, delivered to the university about once a month, and stored in 55 gallon teflon lined drums. The nutrients, phosphates as KH_2PO_4 and nitrogen as KNO_3, needed for microorganism growth were added to the Crude Desalter influent solution in amounts to adjust the BOD:N:P ratio to 100:5:1. A Masterflex pump model 7016-20 (Masterflex Company) was used to pump the influent from a 25 liter glass feed bottle through hard plastic feed lines to the ASBF at a measured flow rate. Soft plastic feed lines were not used because of potential problems with the toxicity testing. The effluent from the ASBF was collected by gravity in a plastic collection bottle. Characteristics of the influent

Crude Desalter wastewater are shown in Table 1.

TABLE 1

INFLUENT CRUDE DESALTER WASTEWATER CHARACTERISTICS

PARAMETER		MEAN	SD*	N*	RANGE	
COD	mg/L	813.5	497.5	60		
BOD_5	mg/L	166.4	30.3	11		
NH_3 - N	mg/L	10.5	3.7	10		
ORG. - N	mg/L	1.1	0.4	10		
SULFIDE	mg/L	0.14	0.1	27		
CHLORIDE	mg/L	2287.8	1016.7	41		
ALKALINITY	mg/L	284.6	317.4	28		
pH	SU			65	6.5	8.4

* SD = standard deviation of the mean
* N = number of samples

The ASBF was run as a continuous flow system. The tracer study performed by Poesponegoro (1990) confirmed that the ASBF was a completely mixed system. Data were collected only during steady state conditions for at least two weeks. Steady state was established by several successive low effluent COD readings and approximately 10% variation in effluent COD. In loadings 13.7 and 9.6 g COD/m^2*d, the variation in effluent COD was 12% and in loading 4.5 g COD/m^2*d the variation was 10%. The effluent COD (at steady state) versus time of the final 3 runs is presented in Figure 4. Figure 5 shows the effluent COD (at steady state) vs. time for the entire study, initial 3 runs and final 3 runs. The initial 3 runs performed by Poesponegoro ended on

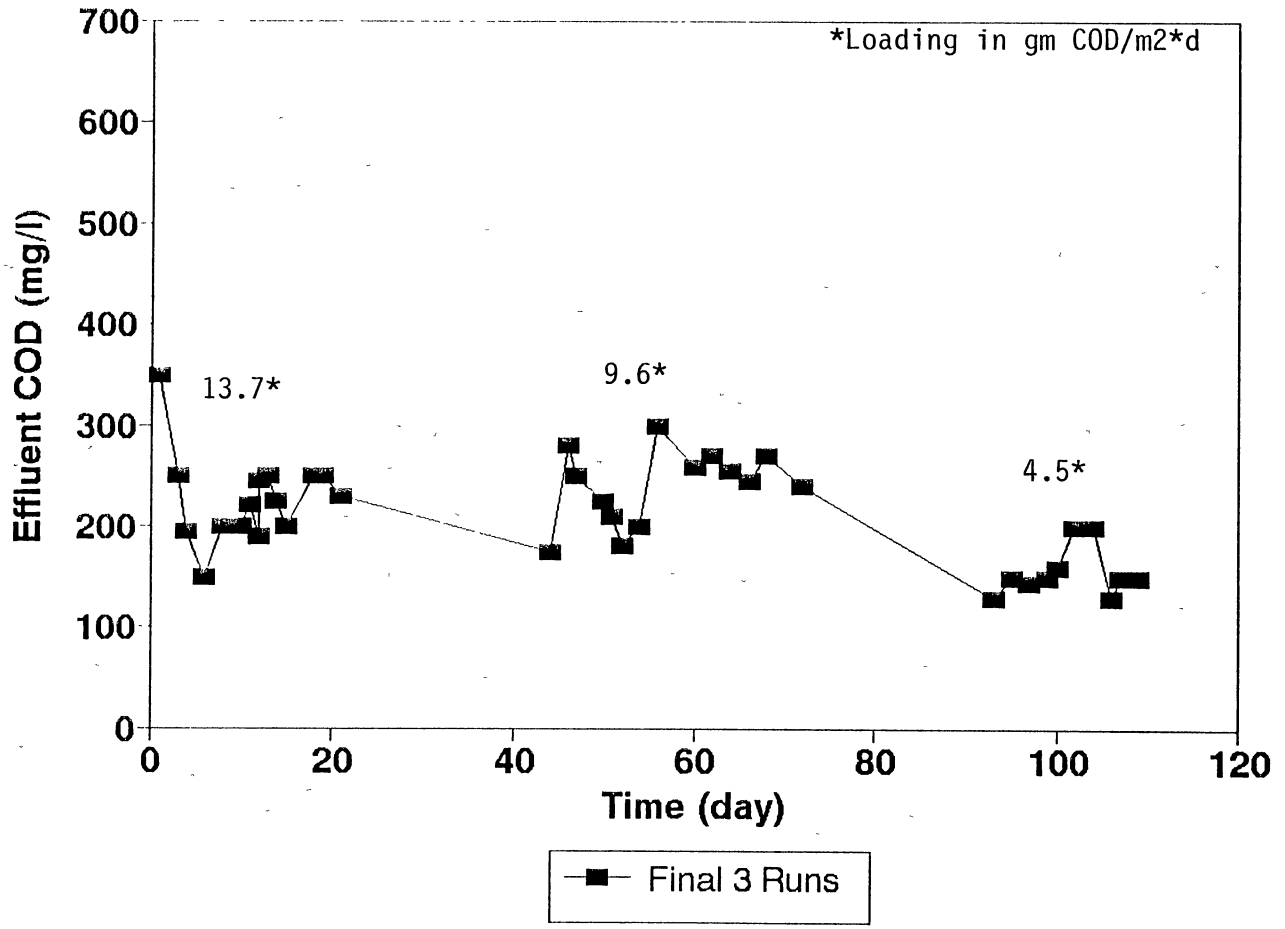

Figure 4. Effluent COD vs. Time of ASBF Final 3 Runs

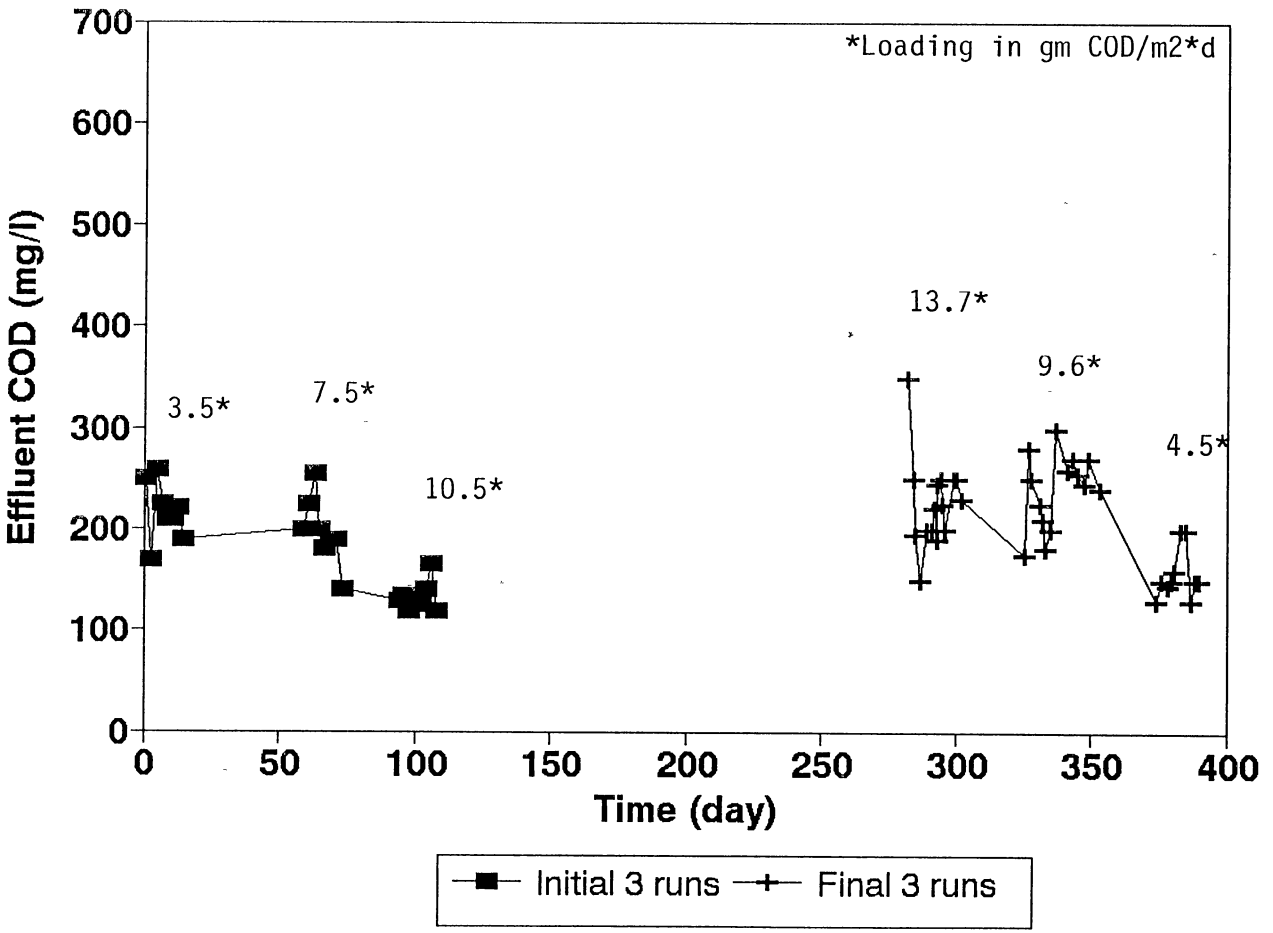

Figure 5. Overall Effluent COD vs. Time of ASBF

approximately day 110. The ASBF was put on feeding maintenance only during the summer corresponding to days 110 through 220 as presented by the gap in Figure 5. Before the final 3 runs were conducted, the loading of the ASBF was raised in increments from the maintenance loading of 5.0 gm COD/m^2*d to the 13.7 gm COD/m^2*d loading for the first run of the final 3 runs. The final 3 runs were performed from days 282 through 390. This sequence of operations is shown in Figure 5.

The ASBF has been successful in treating refinery wastewater because it incorporates advantageous traits of both the fixed film biological towers and suspended growth activated sludge. In common with the activated sludge treatment, the ASBF has the operational advantage of detention time control which enables the contact and aeration time required for the biological treatment of the process wastewater to be controlled (Bach, 1937). The fully submerged characteristic of the ASBF, similar to the activated sludge, helps prevent filter clogging, odor problems caused by anaerobic conditions, and film drying problems of the fixed-film media.

Similar to trickling filters, the ASBF has a long cell residence time which eliminates sludge recycle problems and low operating food-to-microorganisms (F/M) ratio which permits the reactor to withstand hydraulic and organic surges more effectively (Antonie, 1976). Another advantage

of the media plates is their reaction with the diffused air to provide sufficient oxygen to maintain an aerobic condition and to promote more efficient oxygen transfer. As the fine air bubbles strike against the rough obstructive surfaces of the media, the rising air is delayed causing a higher concentration of oxygen in the water (Bach, 1937). The turbulence created by the rising diffused air also allows good contact between the substrate and microorganisms and controls the overgrowth of the biofilm by removing excess solids from the biofilm through shear forces. Opposite of both trickling filters and activated sludge, the ASBF requires less head for its operation and less reactor volume for treatment (Rusten, 1984; Bach, 1937).

An Aerated Submerged Fixed-Film Bioreactor (ASFF) similar to the ASBF with advantageous traits of fixed-film and suspended growth systems has been shown to successfully remove phenol on the order of 99% (Hamoda, 1987). But unlike the Crude Desalter wastewater used in the ASBF, the phenolic waste was a synthetic mixture made in the lab, not derived from the refinery. Therefore, the phenolic waste was not as variable or difficult to treat as Crude Desalter wastewater from a refinery. The ASFF has also successfully reduced the COD (80%) of both pretreated refinery wastewater and synthetic waste with toxic organics such as phenol and nitrobenzene to simulate a hazardous refinery effluent (Hamoda, 1987). The synthetic waste and pretreated refinery

effluent are similar to effluent taken directly from the refinery unit except that the constituents of a unit waste such as Crude Desalter waste are more variable, more concentrated and more diversified.

EXPERIMENTAL PROCEDURES

To determine the kinetics of the ASBF, the unit was operated at room temperature (19-25^{o}C) utilizing six different COD (organic) loading rates (3.5, 4.5, 7.0, 9.6, 10.5 and 13.7 gm COD/m^2*d). The loading rates were obtained by varying the flowrate, instead of the COD concentration of the influent. The COD concentration of the influent waste was unpredictable and varied with refinery operations. Almost all of the Crude Desalter wastewater samples used in the research were collected from crude desalter unit #1 in the refinery. The last sample came from Crude Desalter unit #2 because a fire at the refinery inactivated unit #1. The last sample of Crude Desalter wastewater from Crude Desalter unit #2 used for the 4.5 g COD/m^2*d COD loading had a weaker COD than the previous samples. During all the loadings, settleable solids were wasted from the bottom of the ASBF every other day to avoid excessive solids accumulation.

CHARACTERIZATION TESTS

The Crude Desalter wastewater collected from the refinery was analyzed prior to introduction to the ASBF and during steady state runs. The experimental procedure of the steady state runs included several chemical tests conducted to characterize the wastewater, establish the operation efficiency of the reactor, and determine correlations with toxicity. Flowrate, DO (Dissolved Oxygen), and pH were analyzed every day. COD (Chemical Oxygen Demand), chloride, and solids were analyzed every other day. Other parameters such as toxicity, BOD_5 (Biochemical Oxygen Demand), soluble metal, alkalinity, ammonia nitrogen ($N\text{-}NH_3$), organic nitrogen (N-organic) and sludge chloride (after sludge digestion) were analyzed twice during each loading rate. The sulfide concentration was analyzed at least four times during each organic loading. The samples for these analytical tests were collected for approximately 2 weeks during each loading rate when the reactor reached steady state.

ANALYTICAL METHODS

An Orion Research Oxygen electrode model 97-08-00 was used to determine dissolved oxygen at the bottom of the ASBF. The pH of the influent and effluent was measured by a

pH meter model Accument type 900 from Fisher Scientific which was standardized at pH 7.0 and 4.0 before using. Chemical methods developed by the Hach Chemical Company in Water Analysis Handbook (HACH, 1982) were used to determine COD, sulfide, chloride, and alkalinity of the samples. Chloride tests were performed on the influent, effluent, and digested sludge to track the salt concentration through the ASBF reactor. BOD_5, solids, ammonia nitrogen, organic nitrogen, sludge settling test, and sludge digestion were conducted according to Standard Methods for the Examination of Water and Wastewater (1989). Metal analysis on the influent, effluent, and digested sludge was conducted at the Soil, Water, and Forage Testing Laboratory in the Agronomy Department, Oklahoma State University. For metal analysis the samples were filtered through Whatman no. 42 filter paper and then concentrated nitric acid (HNO_3) was added to the filtrate to maintain the pH < 2. In addition the samples were stored at 4°C prior to analysis. The samples were analyzed for the following soluble metals: calcium (Ca), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), sodium (Na), selenium (Se), and zinc (Zn) using an Inductively Coupled Plasma Emission Spectroscopy (ICAP).

TOXICITY TESTS

Acute static toxicity tests or bioassays were conducted on influent and effluent samples to determine if the ASBF reactor reduced or removed toxic components of the waste. The acute static toxicity test is a short-term method for estimating the concentration (LC50) of the toxicant that causes death to 50% of the test populations of Ceriodaphnia dubia and fathead minnow (Pimephales promelas). The various sample concentrations for the toxicity test were made by diluting the samples to differing concentrations (1%, 10%, 30%, 50%, 75%, and 100%) with reconstituted very hard water. The larger the percentage the larger amount of sample present in the dilution. Very hard reconstituted water was used as the dilution water because the test organisms were cultured in very hard water (USEPA, 1985). Therefore, the dilution water itself was not toxic to the test organisms. Further more it was determined that the hardness of the dilution water and samples were comparable. The dilution water was passed through a Photronix RGW-5 (Reagent Grade Water) system then rehardened with $CaSO_4$ (240 mg/L), $MgSO_4$ (240 mg/L), $NaHCO_3$ (384 mg/L), and KCl (16 mg/L) (EPA, 1985). A blank using only 100% dilution water was also run to insure no mortality resulted from exposure to dilution water itself.

A large LC50 indicates the test organism is not

affected (killed) until it is exposed to larger amounts of sample. Thus, the greater the LC50, the less toxic the sample. The acute static toxicity tests or bioassays were performed on the influent and effluent samples twice during each loading rate to account for waste variation. Prior to all acute toxicity tests, the Crude Desalter influent and effluent were centrifuged for 45 min at 2400 rpm in a Roy-Red Centrifuge to remove the suspended solids. The decanted liquid was used for the acute toxicity tests.

In conjunction with the normal toxicity tests, additional toxicant removal tests were performed on part of the influent and effluent samples to determine the fraction of the waste causing the toxic effects. Part of the centrifuged decanted influent and effluent liquid was run through a BakerBond Octadecyl C_{18} column. The C_{18} column is similar to activated carbon in adsorption properties and removes nonpolar organics. After removal of the nonpolar organics by the C_{18} column, acute static toxicity tests were performed on the influent and effluent samples to determine if the nonpolar organics caused the toxicity of the waste.

In order to prove that the toxic components of the waste were not eliminated by volatilization, the influent was aerated in the absence of all microorganisms. The entire reactor was emptied and cleaned of all traces of microorganisms. The cleaned reactor was used to aerate the waste under the previous operating conditions. After ten

hours of only aeration, samples were collected. There was minimal microorganism growth in the ASBF after aeration. The aerated samples were also centrifuged before acute toxicity and C_{18} removal tests were conducted on the samples for comparison with similar tests conducted on the ASBF treated samples.

The LC50 of all the acute toxicity tests were calculated by using an EPA computer program, LC50.BAS, (EMSLSTAT, 1987). The acute toxicity test results and all of the other test results are presented and discussed in the following chapter.

KINETIC ANALYSIS

A literature review of biological kinetics has yielded the following models. The characteristics of the ASBF helped determine which models would be considered in the kinetic analysis. The ASBF has fixed media similar to a biotower with some suspended solids. The solids data of the ASBF indicated that the major portion of the microorganisms were attached to the fixed media. The total fixed biomass determined at the end of the study (after 4.5 g COD/m^2*d loading) was 60.9 grams. The fixed biomass in the ASBF was stratified with the largest amount of biomass on bottom and the least amount of biomass on top. Only one value of fixed biomass was determined because it was impractical to empty

the ASBF after each loading to determine the fixed biomass. Unlike the ASFF used by Hamoda et al (1989) to treat synthetic carbonaceous waste, the ASBF could not be purged and started again after each loading due to the long acclimation period of the microorganisms to the petroleum refinery wastewater. The average suspended solids in the ASBF at the 4.5 g COD/m^2*d loading was 445 mg/L or 4.44 grams total mass in the 10.16 L reactor. Therefore the percentage ratio of TSS in the liquid to the TSS on the media is only 7% on a mass basis. Thus, the small amount of biomass contributed by suspended solids is negligible when compared to the amount contributed by the attached biomass. In the ASFF treating a soluble synthetic carbonaceous wastewater, Hamoda et al (1989) reported only 5.4 % of the total biomass was suspended. In the kinetic analysis of the ASFF, the suspended solids were considered negligible and system kinetics were modeled by a fixed-film model. Thus, with the low suspended to fixed biomass ratio (7%) of the ASBF, the solids data indicate that the kinetic models best suited for analyzing the ASBF data are fixed-film models such as those describing the substrate utilization in Trickling Filters (TF), Biological Towers (BT), and Rotating Biological Contactors (RBC).

As fixed-film reactors such as TFs and RBCs have gained wide acceptance and use in treatment of municipal and industrial wastewaters, many diverse kinetic models used to

describe the substrate utilization in the reactors have been developed. The mathematical models which describe the growth and substrate utilization in the fixed-film reactors are more applicable for describing the ASBF kinetics than empirical based models such as those developed by Stack (1957), Galler and Gotass (1964), Schulze (1960), and Fairall (1956). Since empirical models describe specific wastes (such as municipal instead of industrial) and specific reactors (not combined reactor types such as the ASBF), they are not appropriate in describing the kinetics of the ASBF.

The mathematical kinetic models considered to describe the growth and substrate utilization of the ASBF are simplified models which do not explicitly account for mass transfer. The models are presented in Table 2.

TABLE 2

KINETIC MODELS TO DESCRIBE SUBSTRATE UTILIZATION KINETICS OF ASBF REACTORS

KORNEGAY AND ANDREWS (1968)	dS/dtA = (P Se)/(Km + Se)
ECKENFELDER (1980)	dS/dtA = Ke * Se
KINCANNON AND STOVER (SUBSTRATE) (1980)	dS/dtA = [Um (FSi/A)] / [KB + (FSi/A)]
KINCANNON AND STOVER (SOLIDS) (1980)	F(Xe-Xo)/A = Yt*F(Si-Se)/A -kd
GERMAIN (1966)	Le/Lo = exp [-kD/(Q^n)]

In 1966, Germain developed a first order kinetic model to describe the substrate utilization in a trickling filter. The kinetic model is based on the concept that the rate of substrate removal is a function of the substrate concentration of the wastewater, the adsorption capacity of the biological growth, and liquid residence time (Germain, 1966). The biological growth which is controlled primarily by food availability will increase as the organic loading increases until a maximum effective thickness is reached. The kinetic formula for remaining substrate in the trickling filter is given as follows:

$$Le/Lo = \exp [-k*D/(Q^n)]$$

where:
- Le = substrate remaining, (mg/L)
- Lo = influent substrate concentration, (mg/L)
- k = rate coefficient or treatability factor
- D = depth of filter, (cm)
- Q = hydraulic dosage rate, ($L/min/m^2$)
- n = exponent of Q, (0.5 for plastic media)

The exponent of n for specific media was determined experimentally by Germain (1966). The treatability factor can be determined from the slope of the Le/Lo vs. D/(Q^0.5) plot. The kinetic coefficient, k, can then be used to determine the effect of depth on required volume of media for a specific Le/Lo ratio and flowrate, Q (L/min).

An early fixed-film mathematical model which describes Monod type substrate utilization was developed by Kornegay and Andrews (1968). The model was based on the following assumptions: 1. Complete mixing is achieved in the liquid phase. 2. Substrate utilization due to suspended biomass

is negligible. 3. A saturation function which incorporates the effects of diffusion and growth rate describes the substrate removal (Kornegay and Andrews, 1968). The following mathematical model based on these assumptions was developed to describe substrate utilization in a annular reactor or tricking filter:

$$dS/dtA = [P * Se/(Ks + Se)]$$

where: Se = effluent substrate concentration, (mg/L)
Ks = saturation constant, (mg/L)
P = capacity constant, (gm/day)
dS/dtA = substrate utilization rate, (gm/day)

The experimental data obtained from the Kornegay and Andrews experiment used in conjunction with the mathematical model indicated that the depth of biofilm, 70 um, was independent of hydraulic or organic loading and dissolved oxygen concentrations and that the concentration of organisms in the biological film, 95 mg/cm^3, was constant.

The Kincannon and Stover kinetic model based on total organic loading was first introduced in the early 1970's. This early organic loading kinetic concept used a graphical solution approach (Kincannon and Gaudy, 1978). The model is based on the assumption that organic loading, not the hydraulic loading or influent concentration, controls the removal of organic matter (Kincannon, 1982). This organic loading concept was supported by Kincannon's research on biological towers (Kincannon, 1982) and Stover's research with RBC's (Stover and Kincannon, 1982). The authors state that the kinetic model is derived from the mono-molecular

theory and is given as follows:

$$dS/dtA = [Umax * (FSi/A)] / [KB + (FSi/A)]$$

where: Umax = maximum specific substrate removal rate, ($gm/day/m^2$)
KB = proportionality constant, ($gm/day/m^2$)
Si = influent substrate concentration, (gm/L)
F = flowrate of substrate, (L/day)
A = area of media, (m^2)

To determine the coefficients, a Lineweaver-Burk plot 1/ [F(Si-Se)/A] vs. 1/ [FSi/A] was constructed to linearize the data. The y-intercept is equal to 1/Umax and the slope is equal to KB/Umax. Kincannon and Stover (1982) developed a design methodology for biological towers and RCBs using the organic loading kinetic model.

Kincannon and Stover also developed a model for determining the growth and solids production of a fixed-film system. The equation for determining the kinetic coefficients for growth and solids production is given as follows:

$$F(Xe-Xo)/A = [Yt*F(Si-Se)/A] - kd$$

where: F = flow rate, (L/day)
Xe = concentration of VSS leaving
Xo = concentration of VSS entering
Yt = true yield, (gm VSS/gm COD)
kd = decay coefficient, ($gm/day/m^2$)

The kinetic model for RBCs presented by Eckenfelder (1980) was based on the multiple zero order organic removal concept. The assumptions for the model include: the organic removal rate in each stage is proportional to the concentration of organic matter remaining in that stage; mass transport of oxygen and substrate are not explicitly

included; and the organic removal by suspended microorganisms is negligible. The kinetic model is given as follows:

$$dS/dtA = Ke * Se$$

where Se = substrate concentration, (mg/L)

Ke = Eckenfelder's removal constant, $(kg/day/m^2)/(mg/L)$

ds/dtA = substrate utilization, $(gm/day/m^2)$

The Eckenfelder model offers the simplicity of only having one constant.

Assuming a completely mixed, steady-state reactor, a mass balance was done on the reactor to expand the Eckenfelder model as follows:

$$Se = So/(1 + KA/Q)$$

where Se = effluent concentration, (mg/L)
So = influent concentration, (mg/L)
A = Area of media, (m^2)
Q = flowrate of substrate, (m^3/d)
K = proportionality constant, $(gm/day/m^2)/(mg/L)$

The proportionality constant, K, is the proportionality constant between the removal rate and the concentration remaining (Eckenfelder, 1980). K also incorporates the properties of the biofilm (Eckenfelder, 1980). K can be obtained from the slope of the plot Q/A(So-Si) versus Si.

CHAPTER II

RESULTS, DISCUSSION AND CONCLUSIONS

The results of the characterization tests, toxicity tests, and kinetic analysis are discussed in the following chapter. The performance of the ASBF over the entire study (initial 3 runs and final 3 runs) can be seen in Figures 6 through 14. Each loading yielded unique results showing a different performance at each loading rate.

CHARACTERIZATION TESTS

Figure 6 shows the variation of influent and effluent COD for each loading during the entire study. The average effluent COD concentration at steady state of the overall study was 202 +/- 49.8 mg COD/L. With respect to the highly variable influent (225 to 2080 mg/l COD), the effluent concentration was practically constant at 200 mg/l COD. A detailed view of the COD concentrations at steady state in the final 3 runs is presented in Figure 7. The influent COD concentrations in the final 3 runs were not as high as the influent concentrations in the initial 3 runs. Effluent

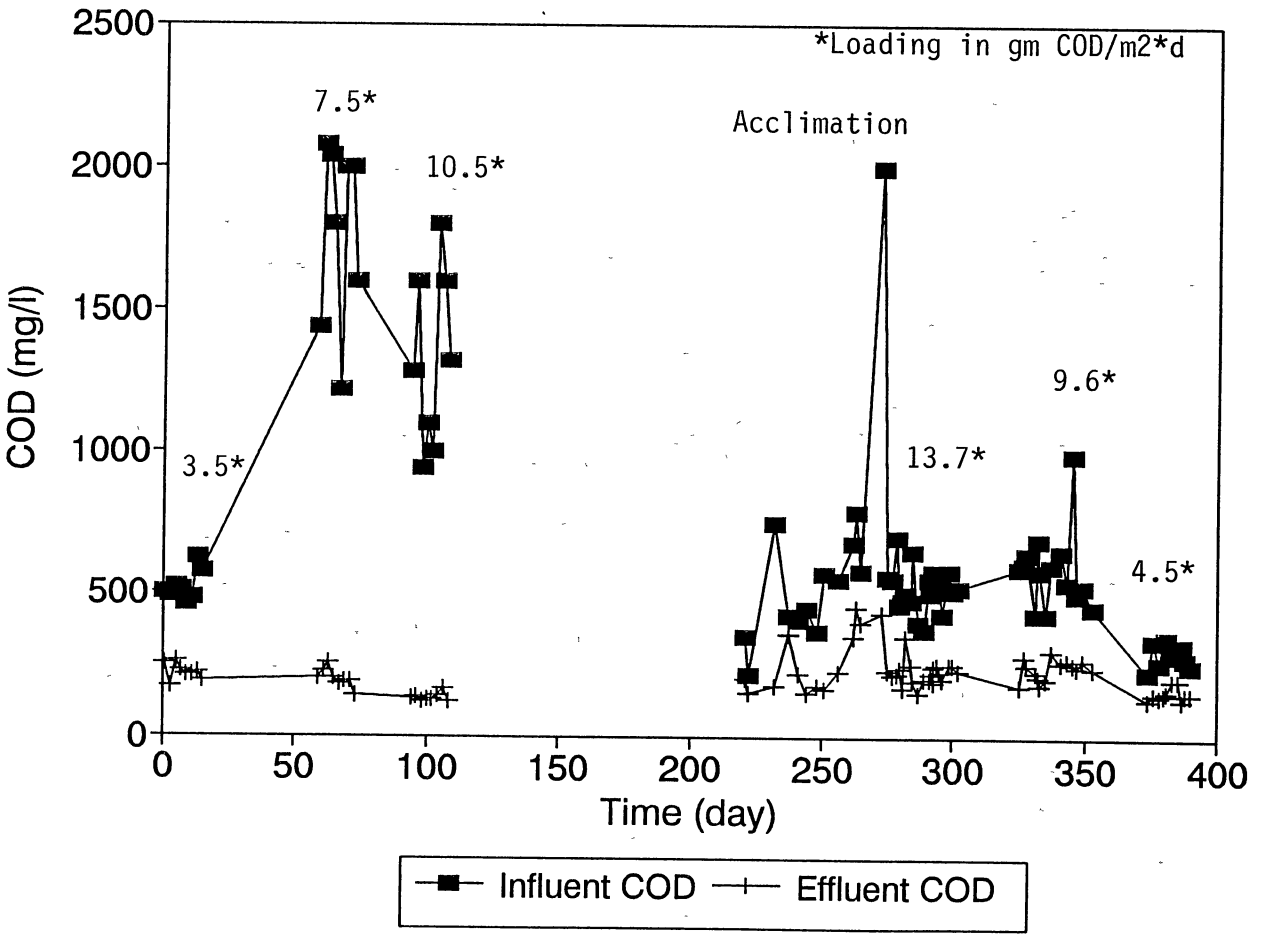

Figure 6. Overall COD vs. Time for ASBF

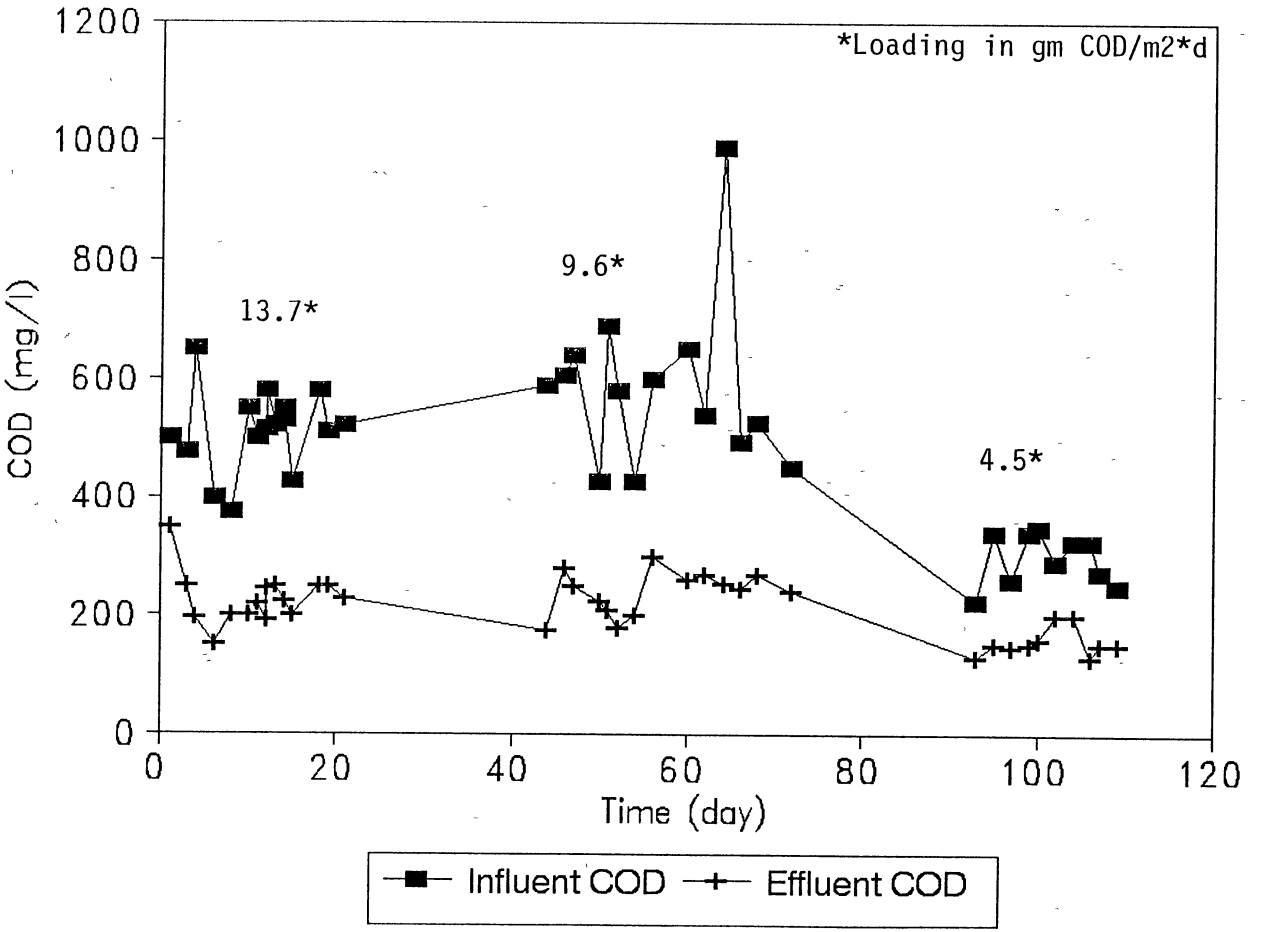

Figure 7. COD vs. Time of ASBF Final 3 Runs

concentrations of the final 3 runs were comparable to the effluent concentrations of the initial 3 runs with a 10% variation. The lowest achievable effluent COD of both runs seems to be 200 mg/L COD, regardless of the influent concentration. This suggests that all the biodegradable matter was utilized leaving only the refractory portion (200 mg/L COD). The base effluent COD (200 mg/L COD) is shown in both Figures 6 and 7. Thus, the low base effluent COD and the low influent COD in the final 3 runs are the reasons for the lower COD removal in the runs as shown in Figure 8. Figure 8 shows the average percent COD removal in each run which was determined by averaging the removal during each run. Each of the six different runs corresponded to different organic loading rates. Because the only value of effluent COD that can be achieved regardless of the influent COD is the base effluent COD of 200 mg/L, the percent removal of total COD is not particularly informative. Near 100 percent conversion of biodegradable COD is indicated at all loadings tested.

The percent COD removal in the 13.7 g COD/m^2*day loading appeared low compared to the percent COD removal at 7.5 and 10.5 g COD/m^2*day loadings due to the less variable influent COD and the base effluent COD of the loading. The 13.7 COD loading also had a low HRT as a result of the low COD influent concentrations, the high flowrates, and large amounts of waste needed to reach the COD loading. The low

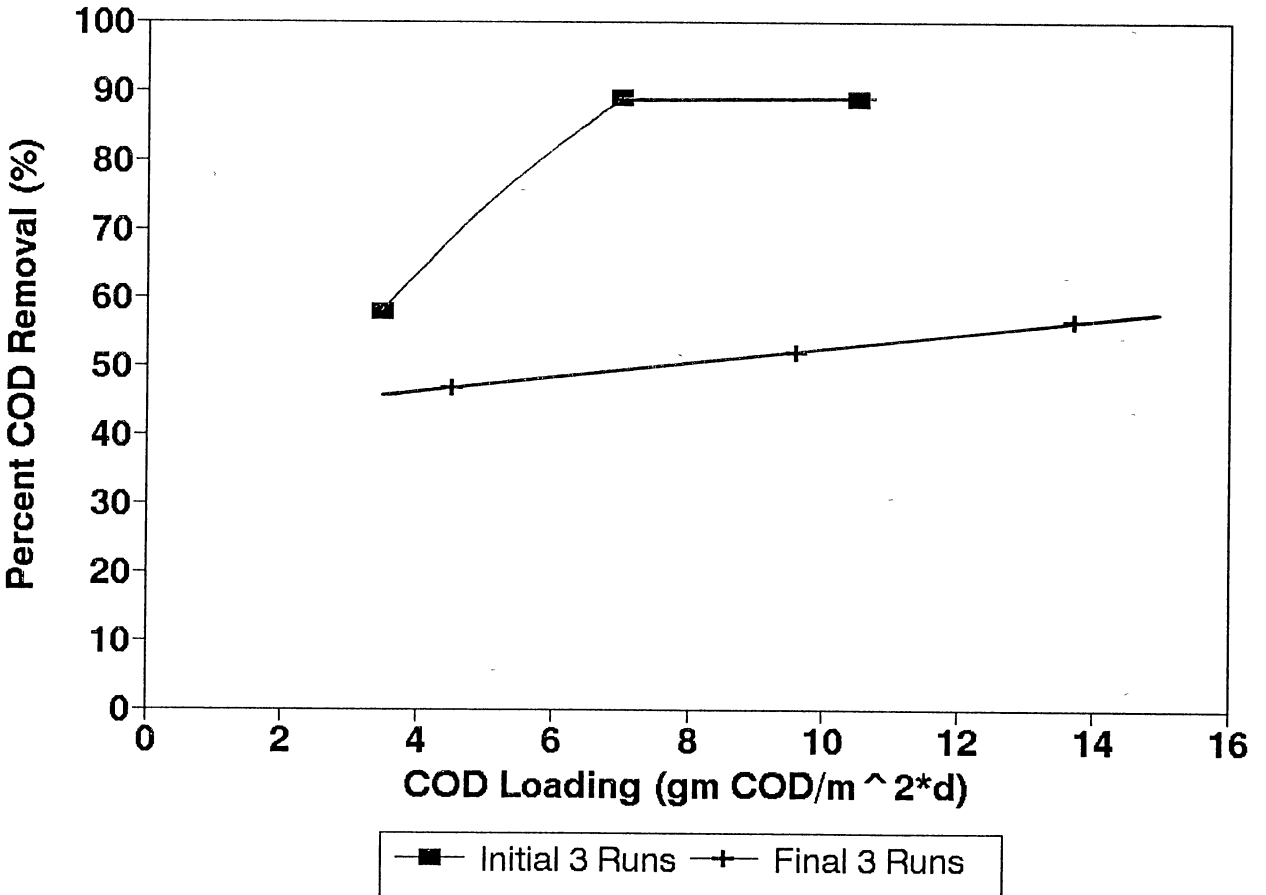

Figure 8. Percent COD Removal vs. COD Loading

HRT (6.3 hrs) caused suspended solids to be washed out with the effluent. During this high loading the average effluent solids concentration was 42.8 mg VSS/L with average waste sludge solids concentration of 573.6 mg VSS/L and average suspended solids concentration inside the ASBF of 282.0 mg VSS/L. Even with a low HRT, solids washout, and low influent concentrations the same low effluent concentration was achieved as in all the other loadings.

In spite of the extraneous circumstances that occurred during the 9.6 g COD/m^2*d loading the same low effluent COD concentration was achieved. At the beginning of the run, the airflow to the ASBF was accidently turned off for over 12 hours. Next, the electricity and heat in the building in which the ASBF was located were turned off for 24 hours for maintenance reasons. Finally, the ASBF was put on feeding only maintenance for 3 days during Christmas break. Thus, the ASBF is very stable and rigorous given the fact that even under extraneous circumstances the low base effluent was still produced.

The solids data of the 9.6 gm COD loading show the microorganisms in the ASBF were dying, sloughing off the media and being suspended in the liquid until wasting. The average effluent solids concentration was 59.0 mg VSS/L, average waste sludge solids concentration was 1091.8 mg VSS/L, and the average solids concentration inside the unit was 189.2 mg VSS/L. Thus, there was a larger amount of

solids in the effluent and the waste sludge in the 9.6 g COD/m^2*d loading than in the 13.7 g COD/m^2*d loading. This suggests the microorganisms did not have enough substrate to survive at the lower loading.

Even though the Crude Desalter wastewater used in the 4.5 g COD/m^2*d loading came from unit #2 instead of unit #1, the same low base effluent COD was achieved. The Crude Desalter wastewater from unit #2 was weaker, in terms of COD, than the waste from unit #1, but it did not to impact the effluent COD concentration. Also, the percent COD removal in the 4.5 g COD/m^2*d was within the allowable 10% variation from the percent COD removal in the 3.5 g COD/m^2*d loading because the influent COD concentrations of the loadings were similar.

During the 4.5 g COD/m^2*d loading, the trend of microorganisms dying, sloughing off the media, and being suspended in the liquid continued. Thus, at this loading as in the 9.6 g COD/m^2*d loading, the substrate concentration was not high enough for the microorganisms to survive. The solids data indicated the dead organisms that were suspended in the liquid settled to the bottom when the air was turned off and appeared in the waste sludge. The average effluent solids concentration was 13.2 mg/L, and average waste sludge solids concentration was 1382.2 mg/L with the average solids concentration inside the unit of 372.2 mg/L.

The mass of VSS in the effluent and waste sludge along with the suspended solids (VSS mg/L) inside the ASBF for the final 3 runs are shown in Figure 9. The washout of the effluent mass at the high loading and the increase in suspended solids and waste sludge mass with decreased loading rate are presented.

The effect of organic loading on COD removal efficiency are shown on Figure 10. Upon first inspection, the removal efficiency appears to be independent of the loading. This independent phenomenon is possible because even at low HRT or different influent concentrations the same effluent concentration was achieved. In addition, the position of the 3.5 g COD/m^2*d loading points in Figure 10 indicates that the biofilm may have been immature and the unit may not have been at steady state. The biofilm could still have been growing which is indicated by the increasing COD removal efficiency during the 3.5 g COD/m^2*d loading. Figure 10 also shows two distinct phases in the data corresponding to the initial 3 runs and the final 3 runs. These distinct phases are also present in Figure 8. The phases seem to be due to the variation in influent COD concentrations between the initial 3 runs and final 3 runs. The different influent COD concentrations coupled with the base effluent COD concentration causes the difference in percent COD removal.

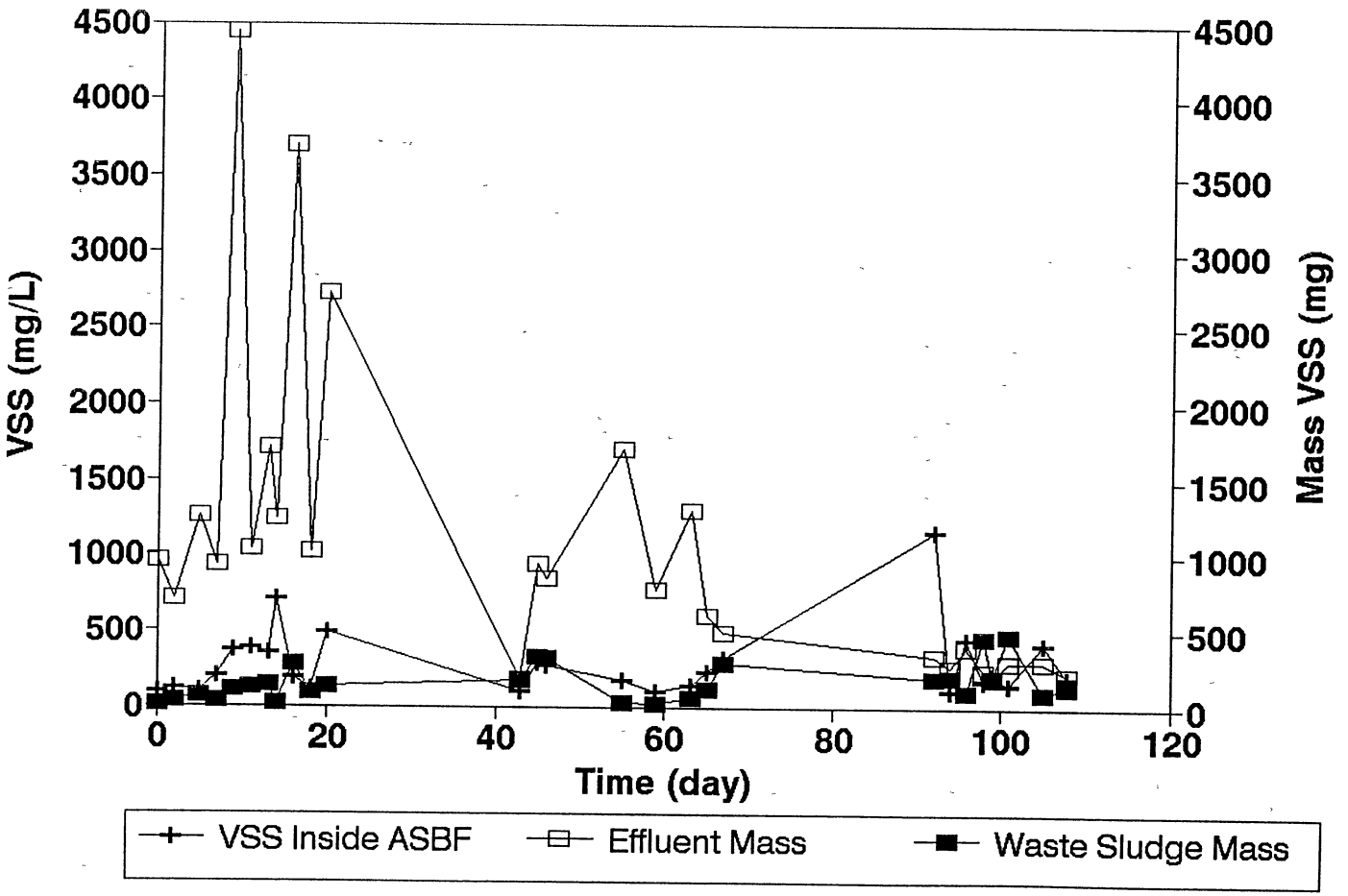

Figure 9. Mass of Waste and Effluent Solids and VSS Inside ASBF for Final 3 Runs

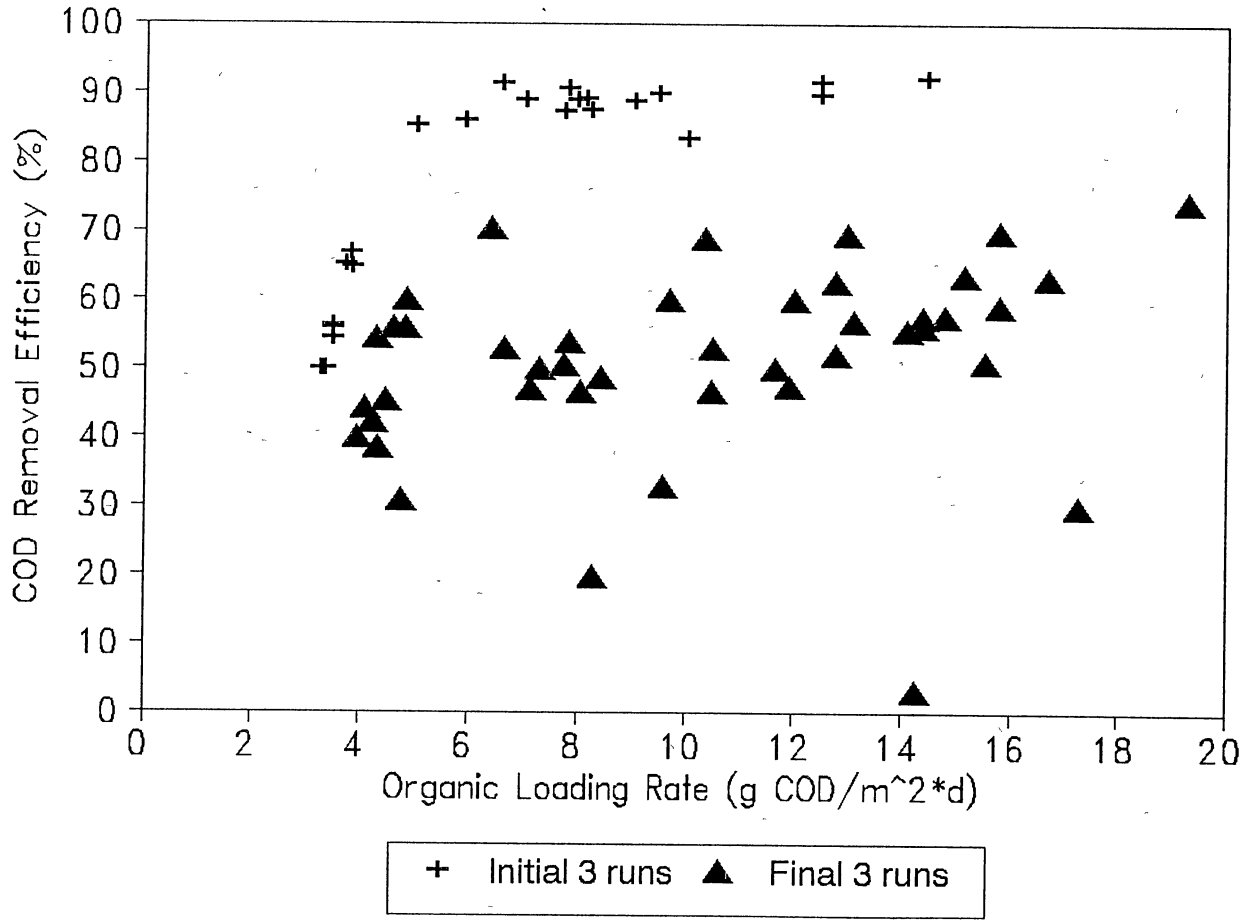

Figure 10. Effects of Organic Loading on COD Removal Efficiency

Other than COD removal rate, the other characterization tests show the performance of the ASBF for the final 3 loadings. The BOD concentrations of the influent and effluent are presented in Figure 11. The average BOD removal of the final 3 runs was 87.3% and the average effluent BOD was 18.6 mg/l. As expected, BOD removal in the ASBF was higher than the COD removal, due to the refractory components in the waste which do not create an oxygen demand in the BOD test but do create an oxygen demand in the COD test. The low effluent BOD concentrations indicate that most of the biodegradable portion of the waste is consumed. The high BOD removal is an excellent feature of the ASBF and makes it an excellent candidate for a petroleum refinery process treatment system which is discharged directly into the receiving stream. The ASBF can be used as a pretreatment unit for process wastewater entering the refinery established treatment system as long as all the pretreatment systems are combined to raise the BOD concentration. Typically, refinery final treatment systems include activated sludge units or biotower and polishing ponds to treat all the combined effluent stream before they enter the receiving stream. Therefore, if the BOD concentration put into the final treatment system is too low to support biological growth, the organisms in the final treatment system may die.

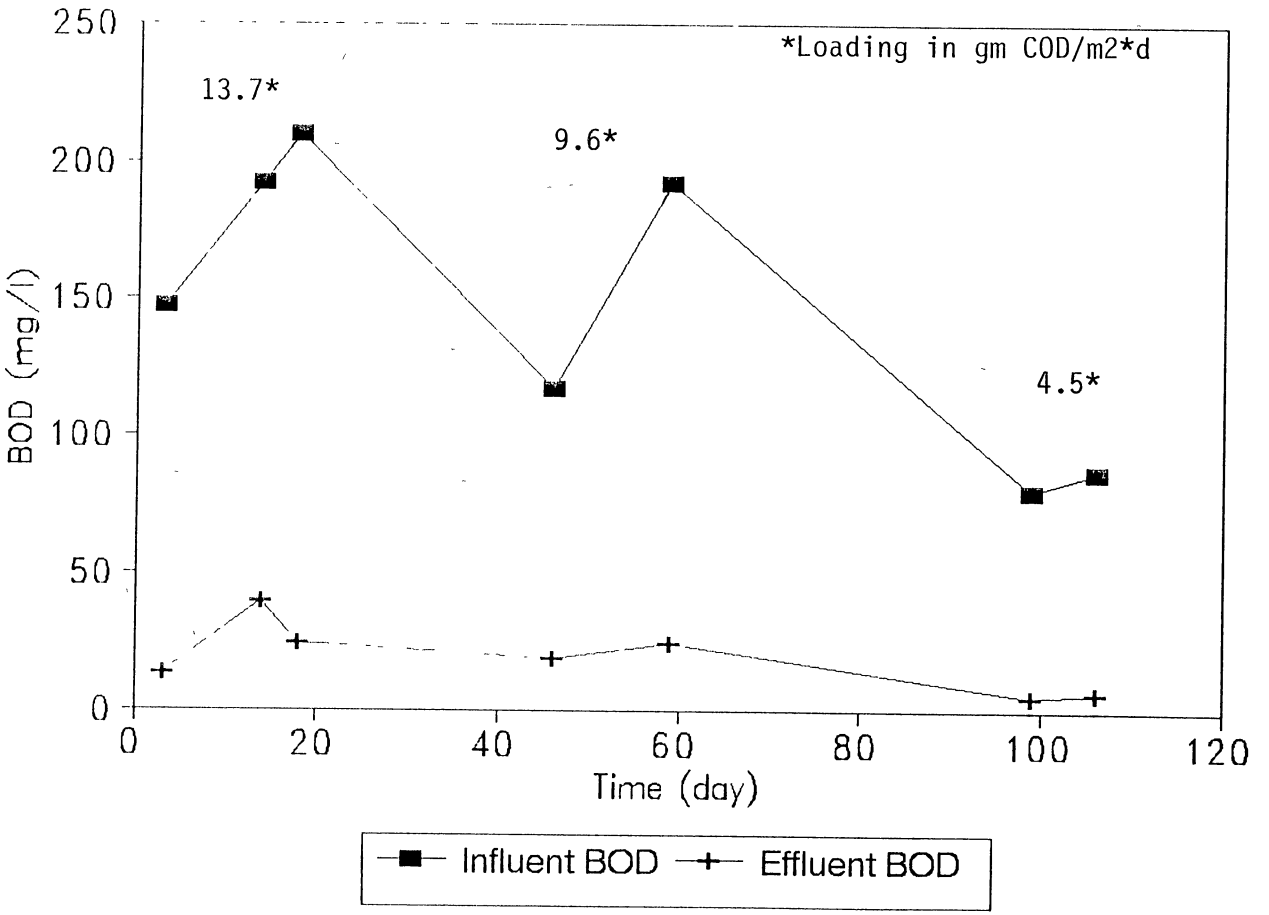

Figure 11. BOD Concentrations of ASBF Final 3 Runs

The chloride characterization test was conducted to monitor the toxic effects of the high salt content in the Crude Desalter wastewater. Figure 12 shows the variation in the chloride concentration in the influent and effluent of the final 3 runs, while Figure 13 shows the chloride concentrations of the sludge corresponding to the final 3 runs. The chloride concentration of the sludge was determined to track the chloride concentration through the ASBF. The variation in the influent chloride concentration can be attributed to differences in crude oil and unit process performance in the refinery. The chloride concentration in the influent and effluent was approximately the same while the sludge concentration was noticeably higher (in the thousands) than both. The high sludge concentrations could be due to the chlorides adsorbing to the sludge.

The chloride concentration in the influent and effluent were definitely not high enough to produce toxic effects in the microorganisms in the ASBF. The toxic chloride concentration for freshwater microorganisms is 15,000 mg/L which was not exceeded in the influent or effluent concentrations (Kincannon, 1966). The high chloride concentrations in the influent, effluent, and sludge are large enough to produce toxic effects in aquatic organisms in the receiving streams. The chloride concentrations were higher than the toxic levels for both Ceriodaphnia and

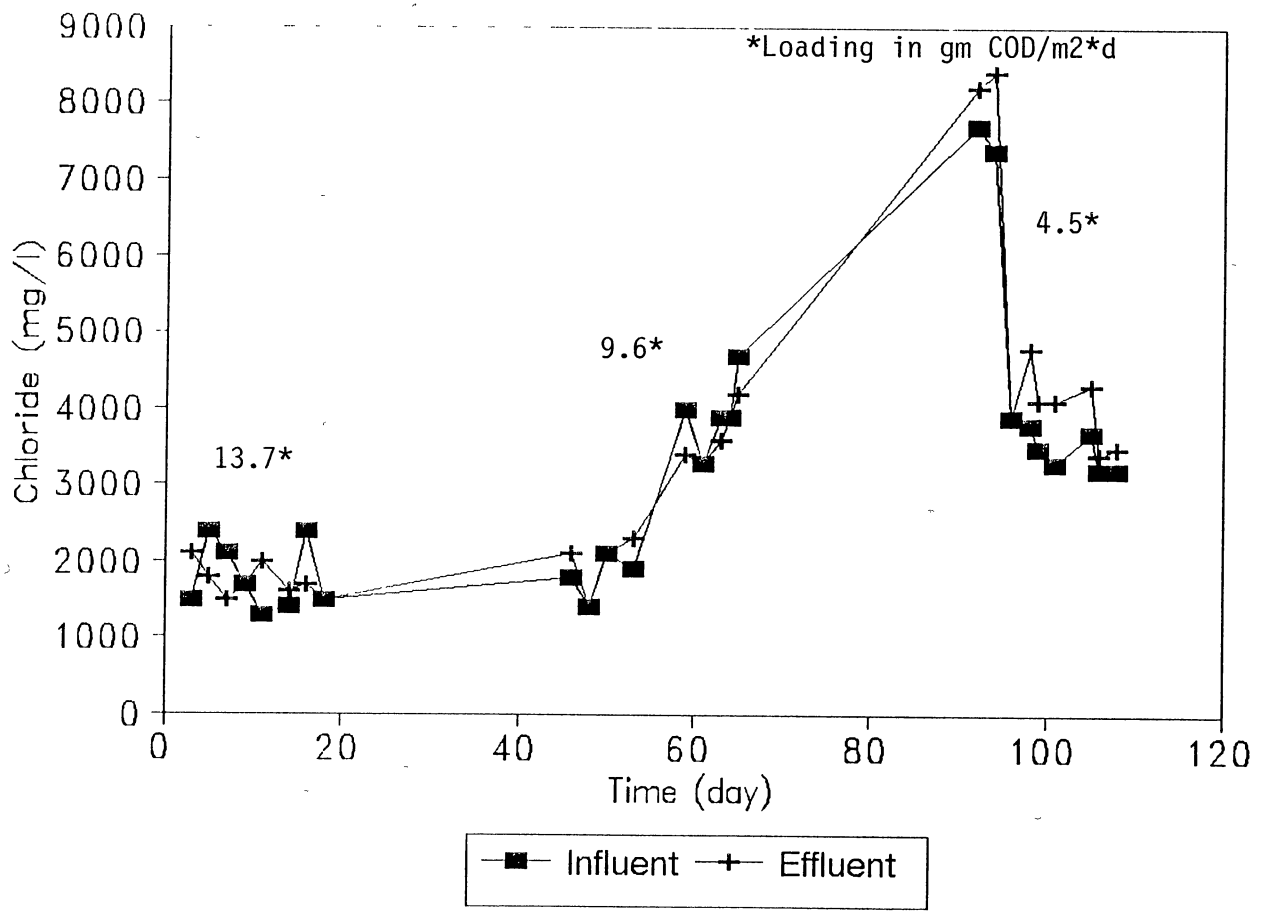

Figure 12. Chloride Concentrations of ASBF Final 3 Runs

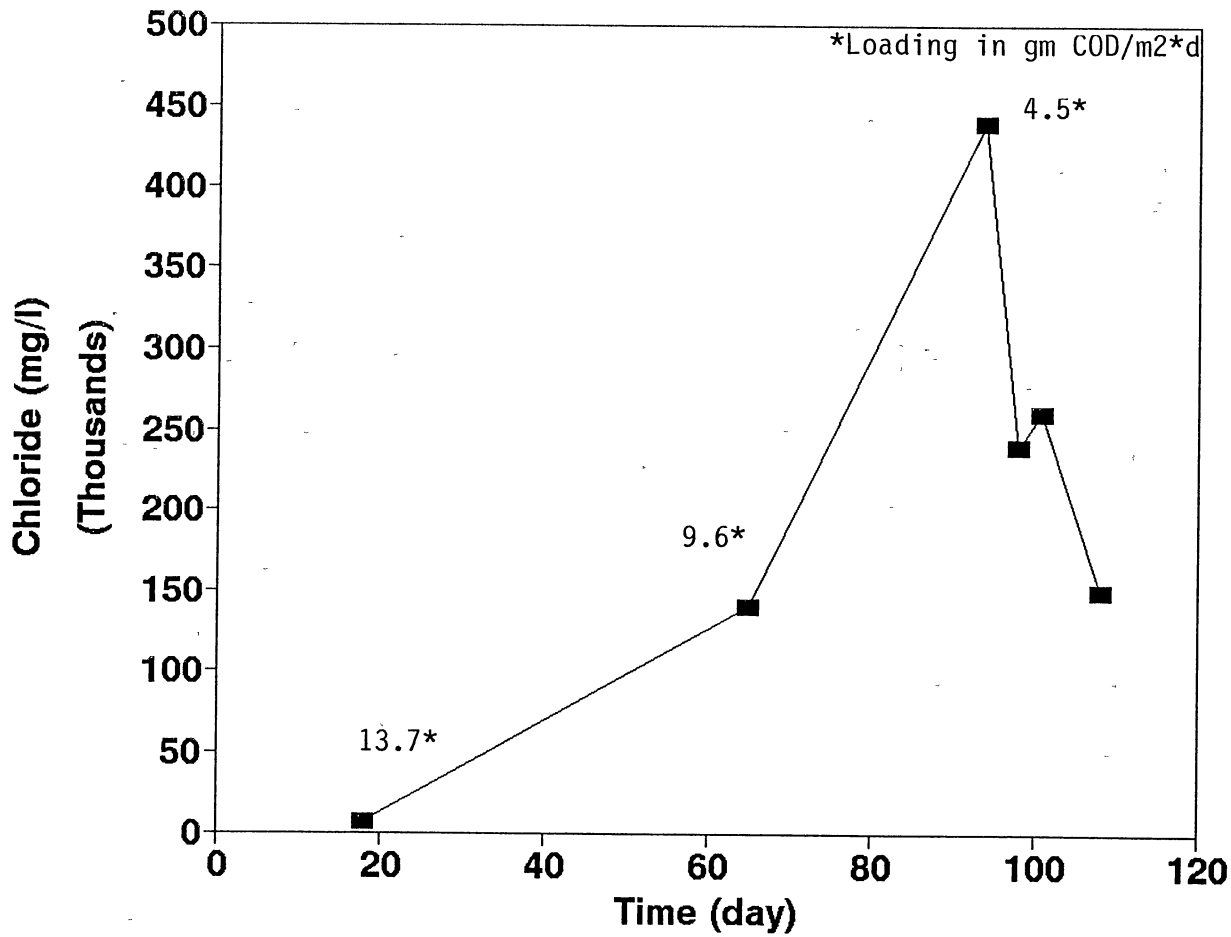

Figure 13. Sludge Chloride Concentrations of ASBF Final 3 Runs

fathead minnows which are reference species for receiving stream toxicity. Sodium chloride is the reference toxicant for Ceriodaphnia. The toxic level of chlorides for Ceriodaphnia ranges from 5000 mg/L to 2500 mg/L at 24 hours and from 5000 mg/L to 1000 mg/L at 48 hours (Stebler, 1991). Fathead minnows are more tolerant to chlorides. The toxic level for fathead minnows ranges from 15,000 mg/L to 10,000 mg/L at 24 hours and from 10,000 mg/L to 5000 mg/L at 48 hours (Stebler, 1991). The extremely high chloride concentrations in the sludge may create disposal problems. The results of the toxicity tests will be presented later in the toxicity section.

The ammonia and organic nitrogen content of the influent and effluent were also monitored to determine a correlation with toxicity. The ammonia nitrogen concentration in the influent and effluent was very low as compared to the ammonia concentration of the Sour Water Stripper wastewater treated by Ramaswamy (1991). The ASBF reduced the ammonia concentration of the influent. The ammonia in the influent could have been converted to organic nitrogen by the microorganisms in the ASBF which is illustrated by the lower ammonia concentration and higher organic nitrogen concentrations of the effluent. The ammonia nitrogen could have also been converted to nitrate or nitrite. It is not known whether nitrification occurred since the nitrate and nitrite concentrations of the samples

were not determined. The ammonia nitrogen and organic nitrogen concentrations are presented in Figure 14.

The most toxic component of nitrogen is unionized ammonia nitrogen. With known pH, temperature, and ammonia nitrogen concentration of a sample, the percent of unionized ammonia can be determined from Table C1 (Emerson, 1975) and Figure C1 in Appendix C. Table 3 summarizes the unionized ammonia concentrations for the entire study. The unionized ammonia content of the Crude Desalter wastewater was not high enough to cause toxic effects to test organisms. The unionized ammonia concentration which caused toxic effects to Ceriodaphnia is 2.5 mg/L which was an order of magnitude larger than the unionized ammonia concentrations of the Crude Desalter wastewater. The ammonia toxicity results are summarized in Appendix C. As compared to the ammonia toxicity caused by Sour Water Stripper wastewater (Ramaswamy, 1991), the ammonia toxicity of the Crude Desalter is negligible.

The sludge settling test which was conducted at the end of each of the final 3 runs was performed to determine the settleability of the sludge for disposal after scale-up. The sludge volume index of each loading was determined from the sludge settling plots. The SVIs were compared with the reference SVI (150) for diffused air activated sludge reactor which indicates well settling sludges (Reynolds, 1982). The high SVIs of the ASBF indicated it did not

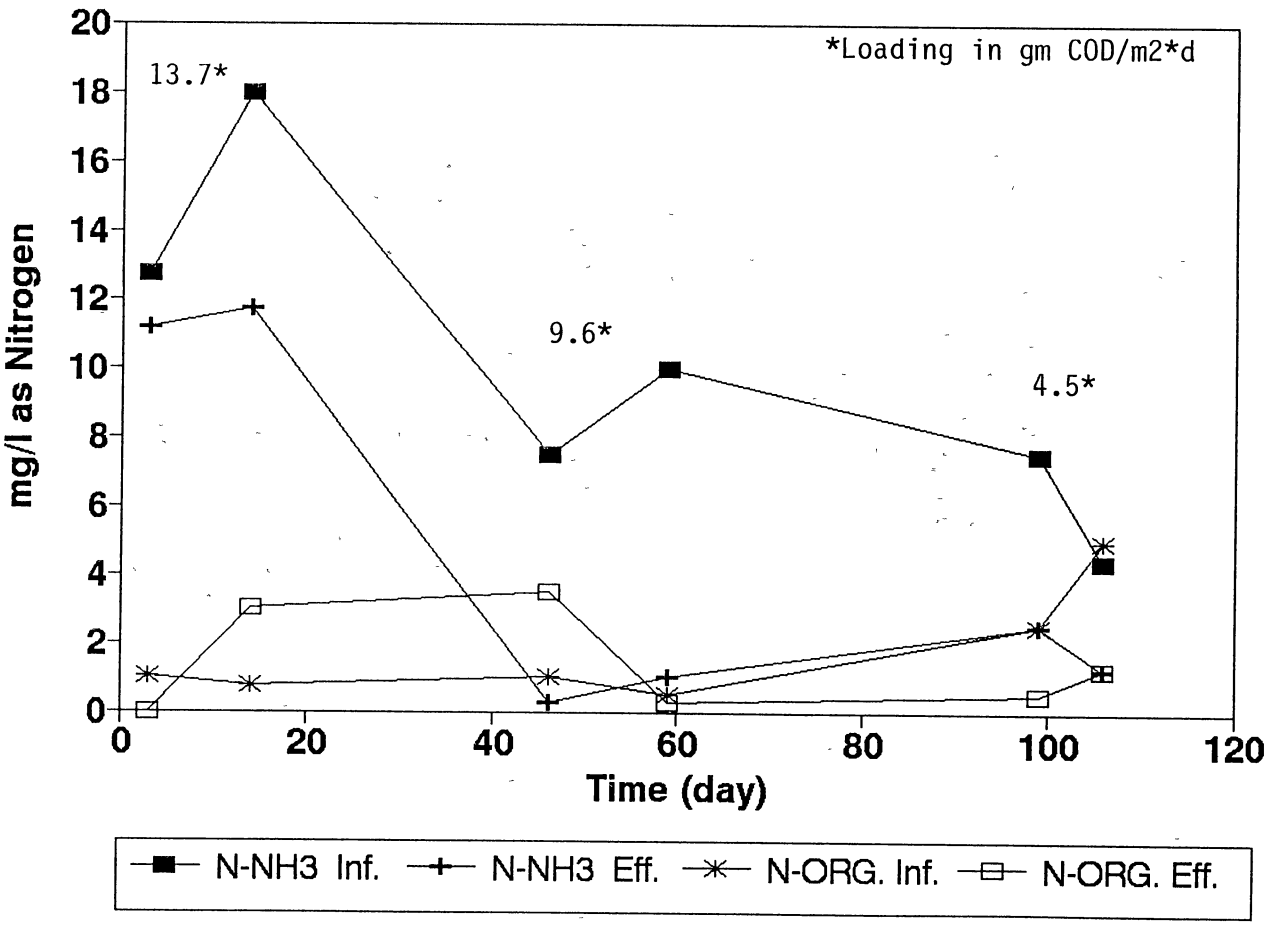

Figure 14. Nitrogen Concentrations of ASBF Final 3 Runs

TABLE 3

PERCENT UNIONIZED AMMONIA AT 22°C

LOADING gm/m^2*d		pH SU	PERCENT UNIONIZED AMMONIA	AMMONIA mg/L	UNIONIZED AMMONIA mg/L
3.5	Influent	7.0	0.457	8.25	0.04
	Effluent	6.0	0.0459	6.25	0.00
	Influent	7.1	0.62	15.6	0.10
	Effluent	6.0	0.0459	4.88	0.00
4.5	Influent	7.0	0.457	7.5	0.03
	Effluent	6.9	0.39	2.5	0.01
	Influent	6.5	0.145	4.4	0.01
	Effluent	6.9	0.39	1.25	0.01
7.0	Influent	7.1	0.62	6.5	0.04
	Effluent	6.45	0.13	0.15	0.00
	Influent	7.1	0.62	9.25	0.06
	Effluent	6.75	0.25	0.18	0.00
9.6	Influent	6.5	0.145	7.5	0.01
	Effluent	6.0	0.0459	0.25	0.00
	Influent	6.9	0.39	10.0	0.04
	Effluent	7.2	0.85	1.0	0.01
10.5	Influent	7.2	0.85	8.5	0.07
	Effluent	7.0	0.457	0.29	0.00
	Influent	7.2	0.85	9.0	0.08
	Effluent	7.0	0.457	0.63	0.00
13.7	Influent	7.5	1.43	12.75	0.18
	Effluent	7.3	0.95	11.18	0.11
	Influent	7.3	0.95	18.0	0.17
	Effluent	7.1	0.62	11.75	0.07

[SOURCE: Emerson et al. 1975]

produce a well settling sludge. This is most likely due to the type of microorganisms in the ASBF which may be filamentous and resist settling. Therefore, chemical coagulants can be added to the ASBF sludge to increase its settleability. The sludge settling for the final 3 runs is shown in Figure 15. The reason for the different pattern in the sludge settling of the 9.6 g COD/m^2*d is unknown. Table 4 contains the SVI and ZSV for the loadings.

TABLE 4

SLUDGE VOLUME INDEX AND ZONE SETTLING VELOCITY

Loading (gm/m^2*day)	SVI	ZSV (m/hr.)	TSS (mg/L)
4.5	1956	0.36	2100
9.6	2145	0.71	420
13.7	314	0.23	460

The experimental performance data of the final 3 runs are presented in Appendix A. The other characterization tests (Sulfide, Alkalinity, DO, pH, and Solids) are summarized in the figures in Appendix B.

TOXICITY TESTS

The results of the two toxicity tests for each of the final 3 runs are summarized on Tables 5 and 6 and illustrated in Figures 16 - 22. The results of the 24 hour bioassays on the Ceriodaphnia test population indicated that

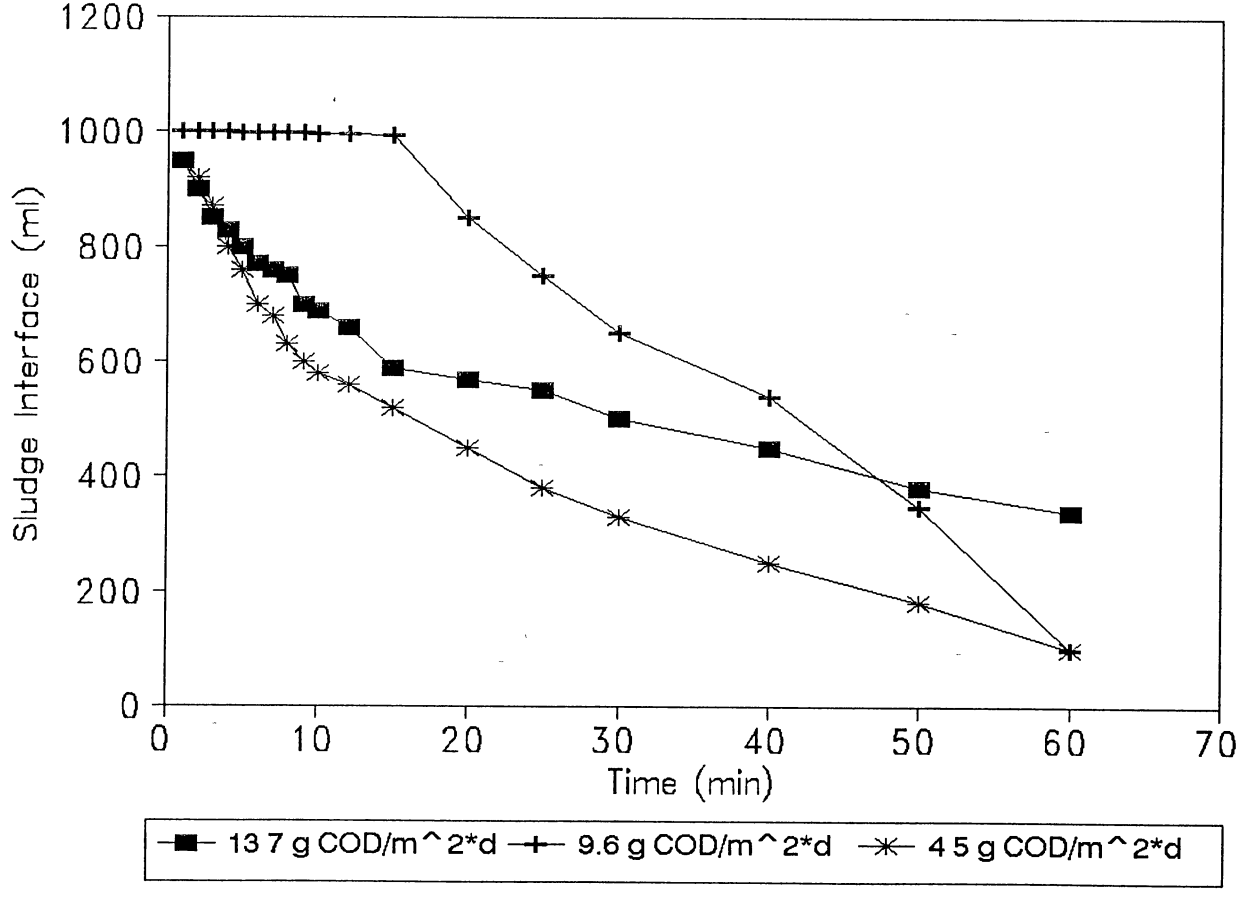

Figure 15. Sludge Settling of ASBF Final 3 Runs

as the organic loading rate increased the reduction in toxicity increased. The fathead minnow test population 24 hour bioassay results (LC50 = 100%) did not indicate that the samples were toxic. But, the 48 hour bioassay results (lower LC50s) for the fathead minnows indicated that the samples were more toxic than at 24 hours. In general, the 48 hour bioassay LC50's, which are lower than the 24 hour LC50's, as shown in Tables 5 and 6 indicate that the influent and effluent Crude Desalter wastewater toxicity was more chronic than acute.

All the toxicity results indicate the ASBF reduced the toxicity of the influent or increased the LC50 for both test populations. The only exception is in the Ceriodaphnia population at 4.5 g COD/m^2*d which could be correlated with the high chloride concentration of the samples and Crude Desalter wastewater being from unit #2. The chloride concentration of approximately 8000 mg/L in the influent and effluent samples was higher than the toxic level for Ceriodaphnia (5000 mg/L to 1000 mg/L) (Stebler, 1991). The fathead minnows were not affected by the chloride concentrations because they were as large as the toxic levels of 15,000 mg/l to 10,000 mg/L (Stebler, 1991). The results of the C18 column toxicity tests at 4.5 g COD/m^2*d for Ceriodaphnia also indicate the toxicity was caused by the chlorides. The C18 column did not significantly improve the toxicity of the samples due to the fact that the C18

column could not remove the chlorides. The chloride concentrations of the influent and effluent are shown in Figure 12. Another alternative is that the ASBF did not remove the toxic organic components at the low COD loading.

Besides determining if the ASBF reduced the toxicity of the Crude Desalter wastewater, the objective of toxicity testing was to determine the toxic component of the Crude Desalter wastewater. For all but one of the toxicity tests (4.5 g COD/m^2*d), passing the samples through the C18 column to remove nonpolar organics increased the LC50 (decreased the toxicity) of the samples for both test populations. Therefore, these results indicate that one of the toxic components of Crude Desalter wastewater is nonpolar organics. Further research is needed to determine the specific organics. The toxicity data on the chloride concentrations indicated chlorides are also toxic components of Crude Desalter wastewater. The ammonia data did not show any correlation between ammonia and toxicity.

The aeration toxicity test (Figure 22) with the Ceriodaphnia test population confirmed the belief that the ASBF, not just aeration, removed the toxic component. In both test populations the effluent was more toxic at 48 hours than at 24 hours, indicating that aeration did not remove the toxic component of the wastewater. In addition, the Ceriodaphnia test population was more sensitive to the aerated waste than the waste treated by the ASBF at higher

loadings. Thus, the toxicity tests demonstrated that the ASBF, not aeration, reduced the toxicity of Crude Desalter wastewater and that organics and chlorides are two of the toxic components of Crude Desalter wastewater.

TABLE 5

TOXICITY MEASUREMENTS FOR FATHEAD MINNOWS

		Bioassay 1				Bioassay 2			
Loading gm/m^2*d		24 hr LC50	TU*	48 hr LC50	TU*	24 hr LC50	TU*	48 hr LC50	TU*
4.5	Influent	100	1.00	100	1.00	100	1.00	91.17	1.10
	Effluent	100	1.00	99.45	1.01	100	1.00	100	1.00
	Infl. + C18	100	1.00			100	1.00		
	Eff. + C18	100	1.00			100	1.00		
9.6	Influent	57.47	1.74	33.20	3.01	86.60	1.15	57.47	1.74
	Effluent	100	1.00	86.60	1.15	100	1.00	100	1.00
	Infl. + C18	100	1.00			100	1.00		
	Eff. + C18	100	1.00			100	1.00		
13.7	Influent	78.81	1.27	70.71	1.41	45.18	2.21	30.00	3.33
	Effluent	100	1.00	100	1.00	54.77	1.83	50.00	2.00
	Infl. + C18	100	1.00			100	1.00		
	Eff. + C18	100	1.00			100	1.00		
3.8 Aeration	Influent	100	1.00	100	1.00				
	Effluent	100	1.00	79.41	1.26				
	Infl. + C18	100	1.00						
	Eff. + C18	100	1.00						

*TU = Toxicity Units (100/LC50)

TABLE 6

TOXICITY MEASUREMENTS FOR CERIODAPHNIA

		Bioassay 1				Bioassay 2			
Loading gm/m^2*d		24 hr LC50	TU*	48 hr LC50	TU*	24 hr LC50	TU*	48 hr LC50	TU*
4.5	Influent	45.18	2.21	14.23	7.03	65.25	1.53	38.73	2.58
	Effluent	45.18	2.21	38.73	2.58	61.24	1.63	54.19	1.85
	Infl. + C18	75.00	1.33			69.20	1.45		
	Eff. + C18	75.00	1.33			61.24	1.63		
9.6	Influent	57.47	1.74	30.00	3.33	57.47	1.74	41.95	2.38
	Effluent	100	1.00	86.60	1.15	61.24	1.63	61.24	1.63
	Infl. + C18	86.60	1.15			79.41	1.26		
	Eff. + C18	100	1.00			86.60	1.15		
13.7	Influent	100	1.00	70.71	1.41	69.20	1.45	57.47	1.74
	Effluent	100	1.00	100	1.00	100	1.00	75.00	1.33
	Infl. + C18	100	1.00			100	1.00		
	Eff. + C18	100	1.00			100	1.00		
3.8 Aeration	Influent	57.47	1.74	10.00	10.00				
	Effluent	61.24	1.63	45.18	2.21				
	Infl. + C18	65.25	1.53						
	Eff. + C18	65.25	1.53						

*TU = Toxicity Units (100/LC50)

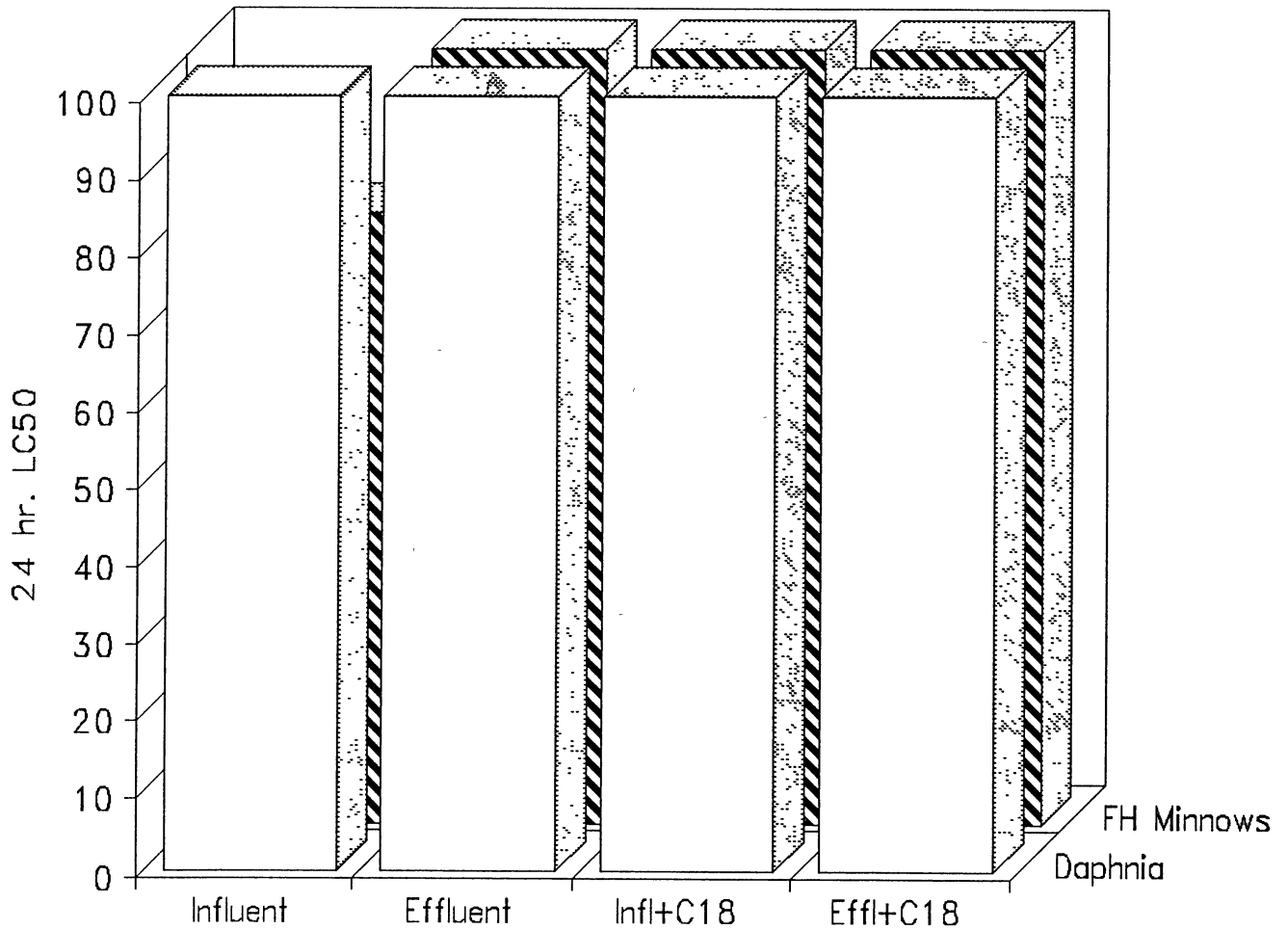

Figure 16. Crude Desalter Bioassay # 1 at 13.7 g COD/m2*d

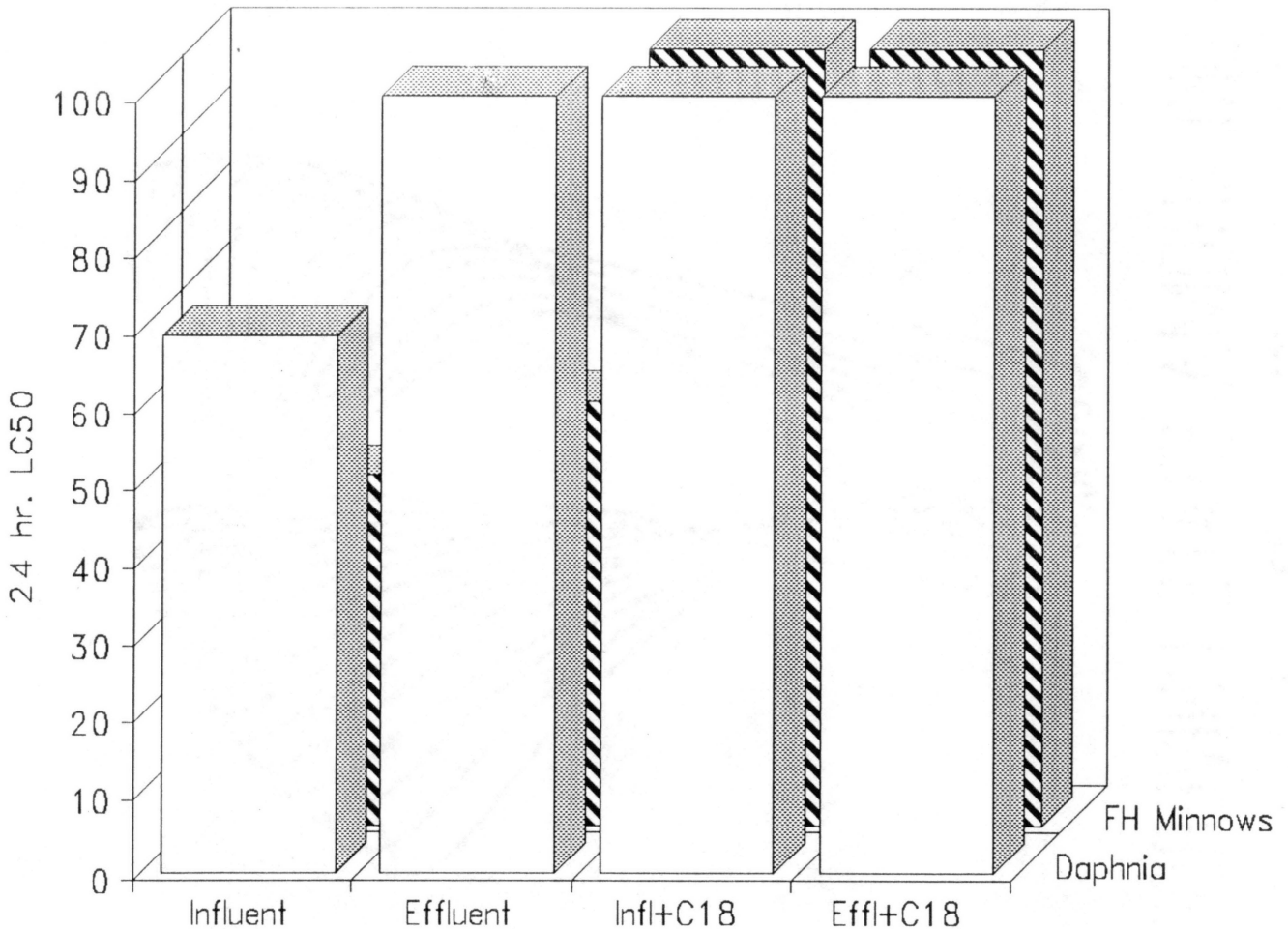

Figure 17. Crude Desalter Bioassay # 2 at 13.7 g COD/m2*d

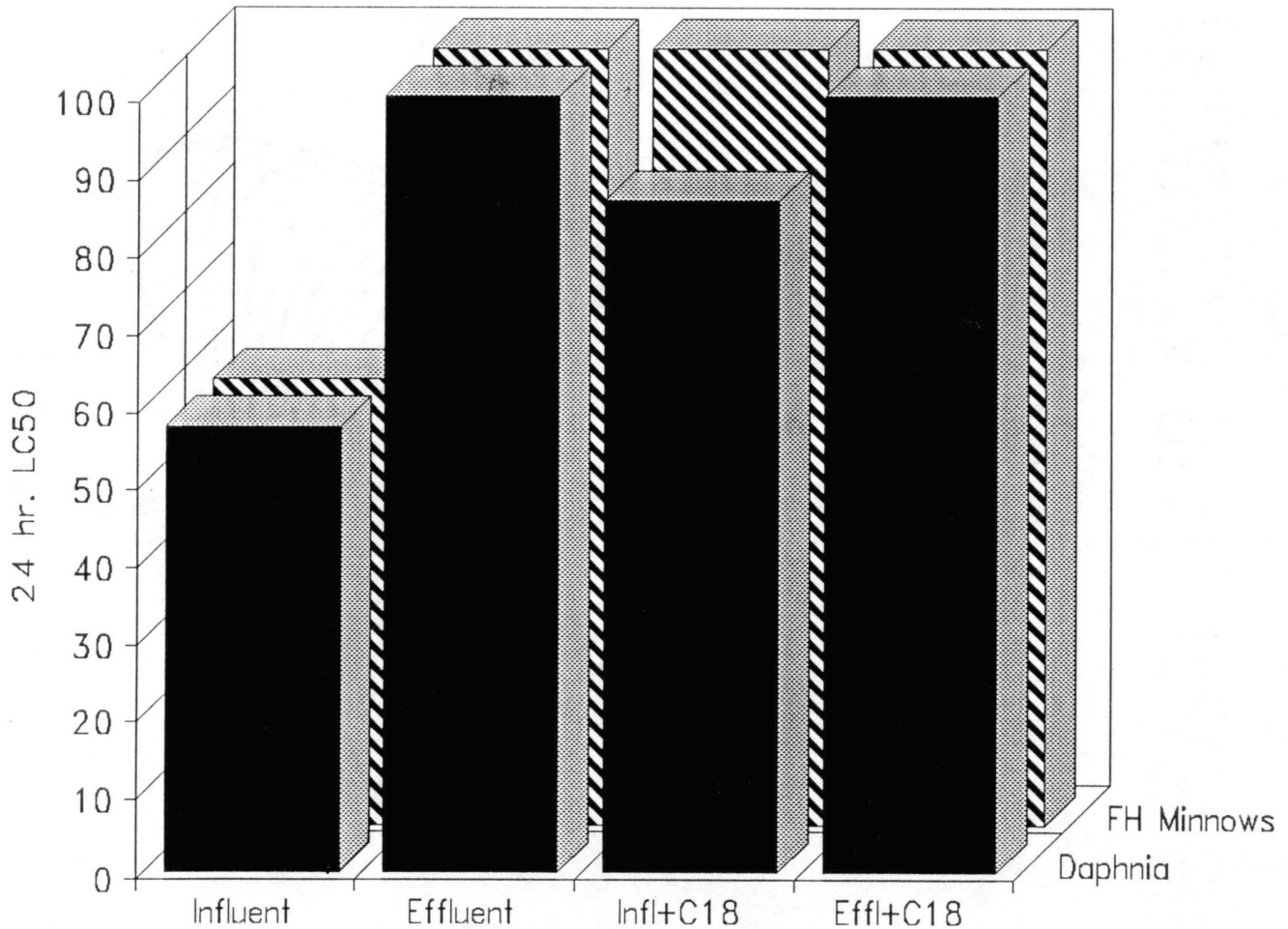

Figure 18. Crude Desalter Bioassay # 1 at 9.6 g COD/m2*d

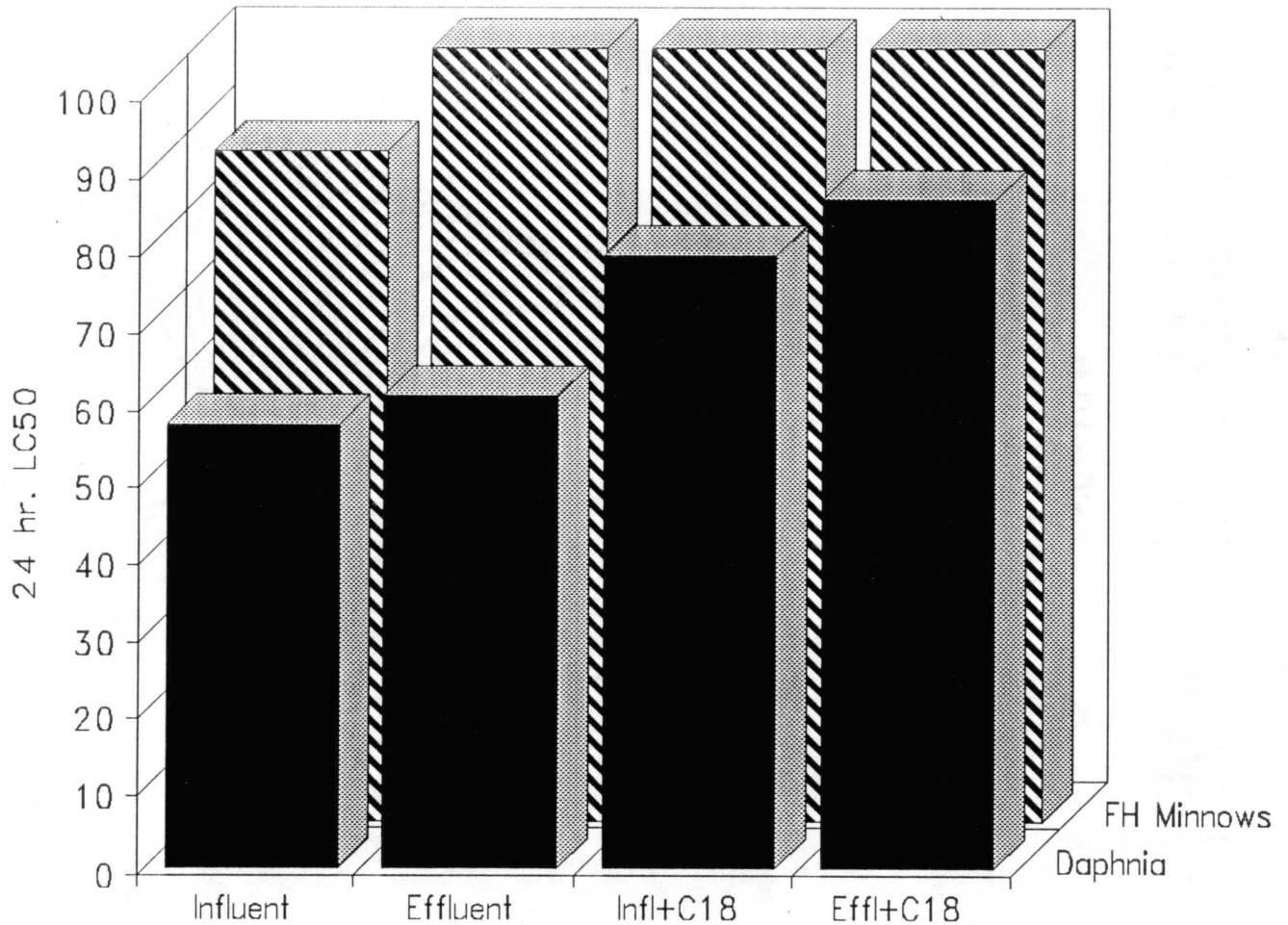

Figure 19. Crude Desalter Bioassay # 2 at
9.6 g COD/m2*d

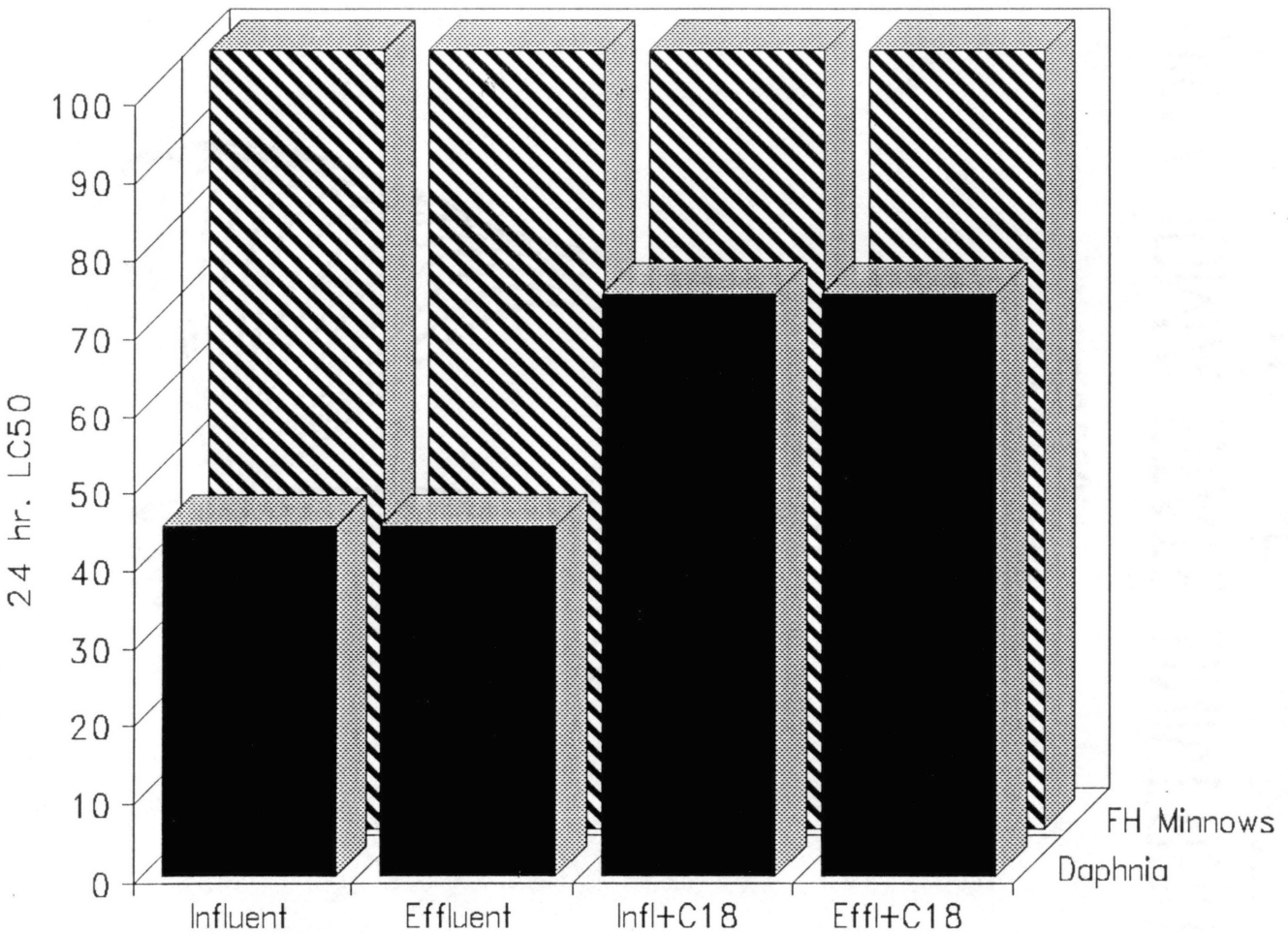

Figure 20. Crude Desalter Bioassay #1 at 4.5 g COD/m2*d

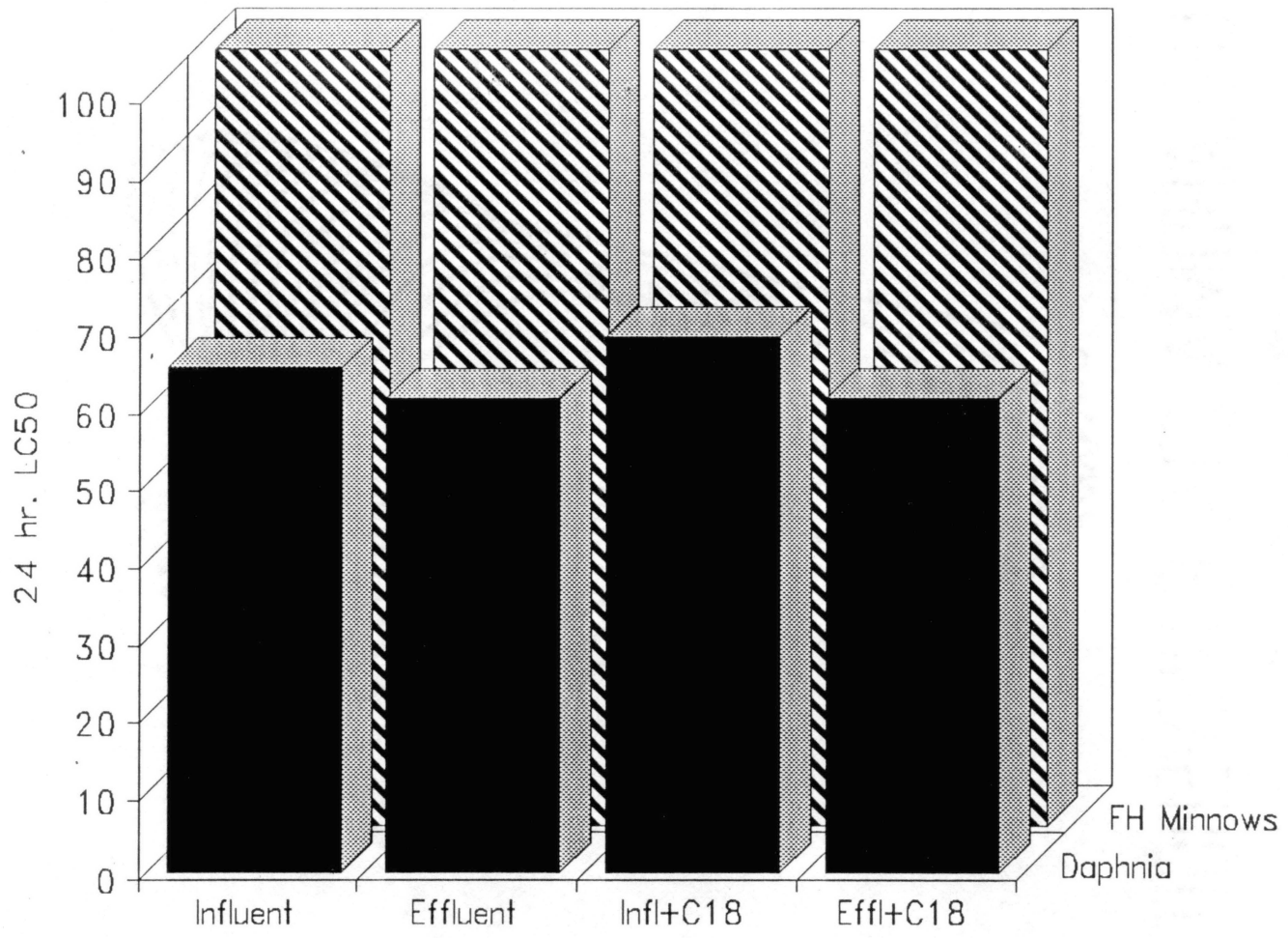

Figure 21. Crude Desalter Bioassay #2 at 4.5 g COD/m2*d

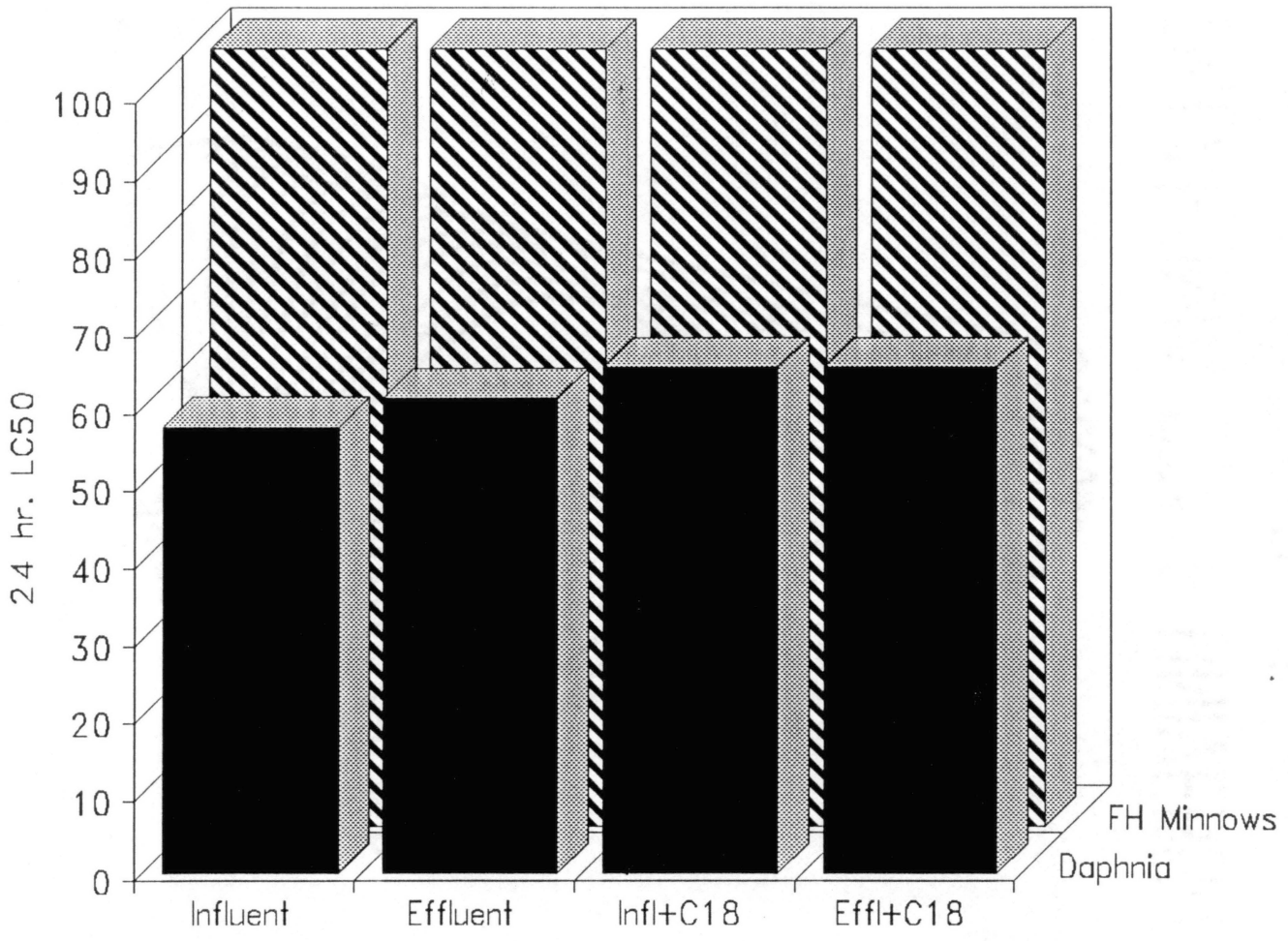

Figure 22. Crude Desalter Bioassay #1 for
Aeration at 3.8 g COD/m2*d

KINETIC ANALYSIS

The kinetic analysis was performed by analyzing the data from the initial 3 runs and the final 3 runs in the appropriate kinetic model and performing a linear regression on the model. The COD, solids, flowrate data, and physical parameters (volume and area) of the ASBF were used in the kinetic models.

All the kinetic models except the Germain model are Monod type kinetic models based on the concept that substrate utilization (organic removal) is a function of substrate concentration (organic loading) or specific loading and varies from first to zero order as loading increases. Figure 23 shows a plot of organic removal versus organic loading for the ASBF. Over the range of the ASBF experiment, the removal appears to be linearly related to the organic loading. It was impossible to run the ASBF at higher loading rates, due to the large amount of waste that would be required coupled with the fact only a limited supply of waste was shipped to the laboratory. Higher loadings would be needed to determine if the plot flattened out, to the point where removal was independent of loading (similar to zero order kinetics).

Figure 23 also shows different trends for the initial 3 runs and final 3 runs as illustrated by the two different lines. This difference could be attributed to variable

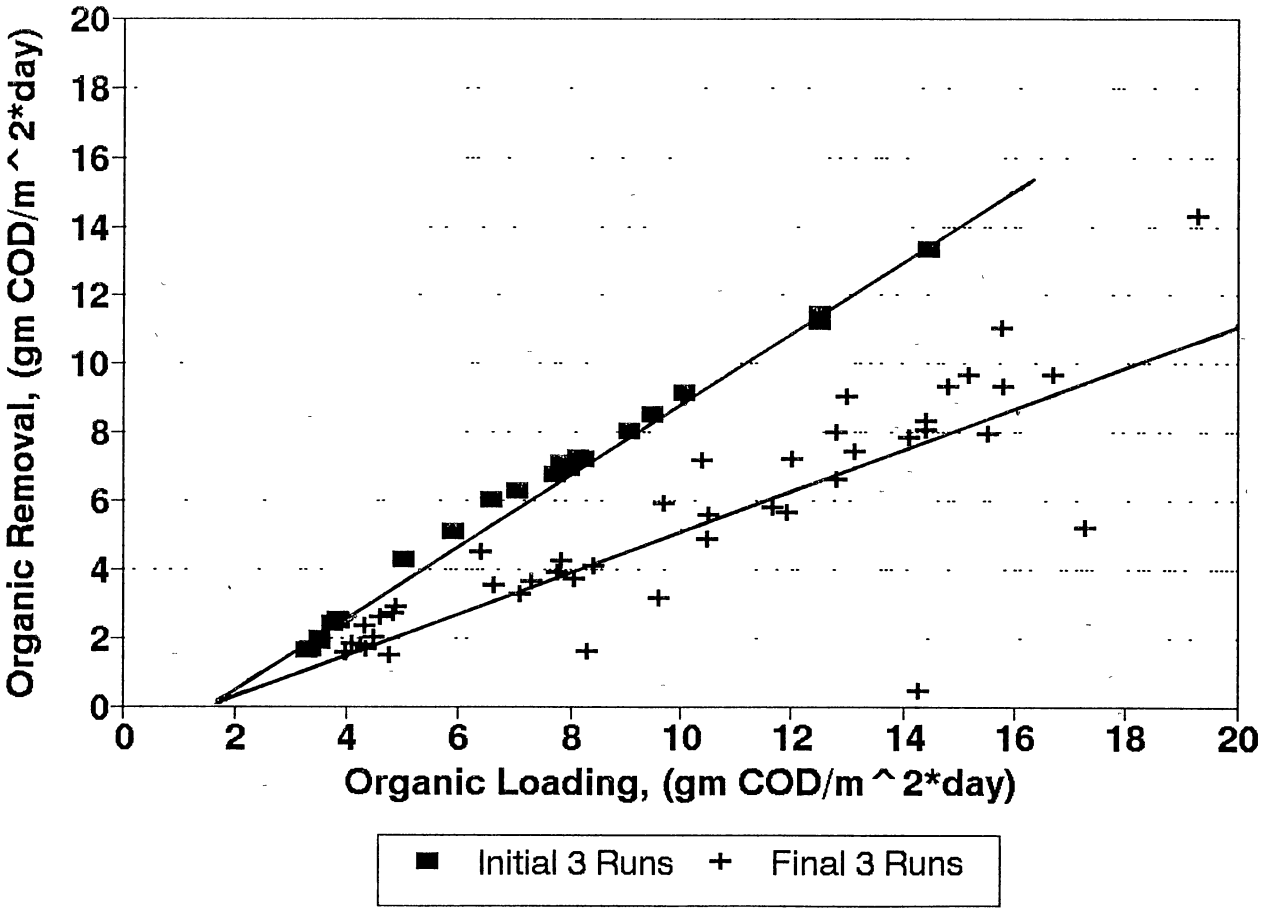

Figure 23. Organic Removal vs. Organic Loading for ASBF

influent waste characteristics caused by changes in the refinery process and variable effluent waste characteristics caused by operating conditions and biofilm of the ASBF. For the initial 3 runs, the ASBF was loaded from lowest to highest loading. Thus, as discussed previously, the biofilm at the first loading (3.5 g COD/m^2*d) was not mature which would give the trend seen for the initial 3 runs in Figure 23. The loadings of the ASBF for final 3 runs were in the reverse direction from highest to lowest. This reverse loading caused the biofilm in the ASBF to die creating more solids (VSS mg/L) in the waste sludge, effluent and inside the unit as the loadings decreased. The loss of active biomass as shown by the increase in solids could cause the different trends between the initial and final 3 runs. The lower organic removal in the final 3 runs may also be caused by the loss of active biomass.

Since the linear relationship of the ASBF data was seen in Figure 23, the Monod type models (Eckenfelder, Kornegay and Andrews, and Kincannon and Stover) were discarded from the analysis. The ASBF data were only in the first order range and did not reach the zero order kinetic range. Therefore, the first order model, the Germain model, was used to analyze the ASBF data. The Germain model of the ASBF data is shown in Figure 24. Two distinct phases corresponding to the initial 3 runs and final 3 runs are also noticeable in Figure 24. A linear regression was

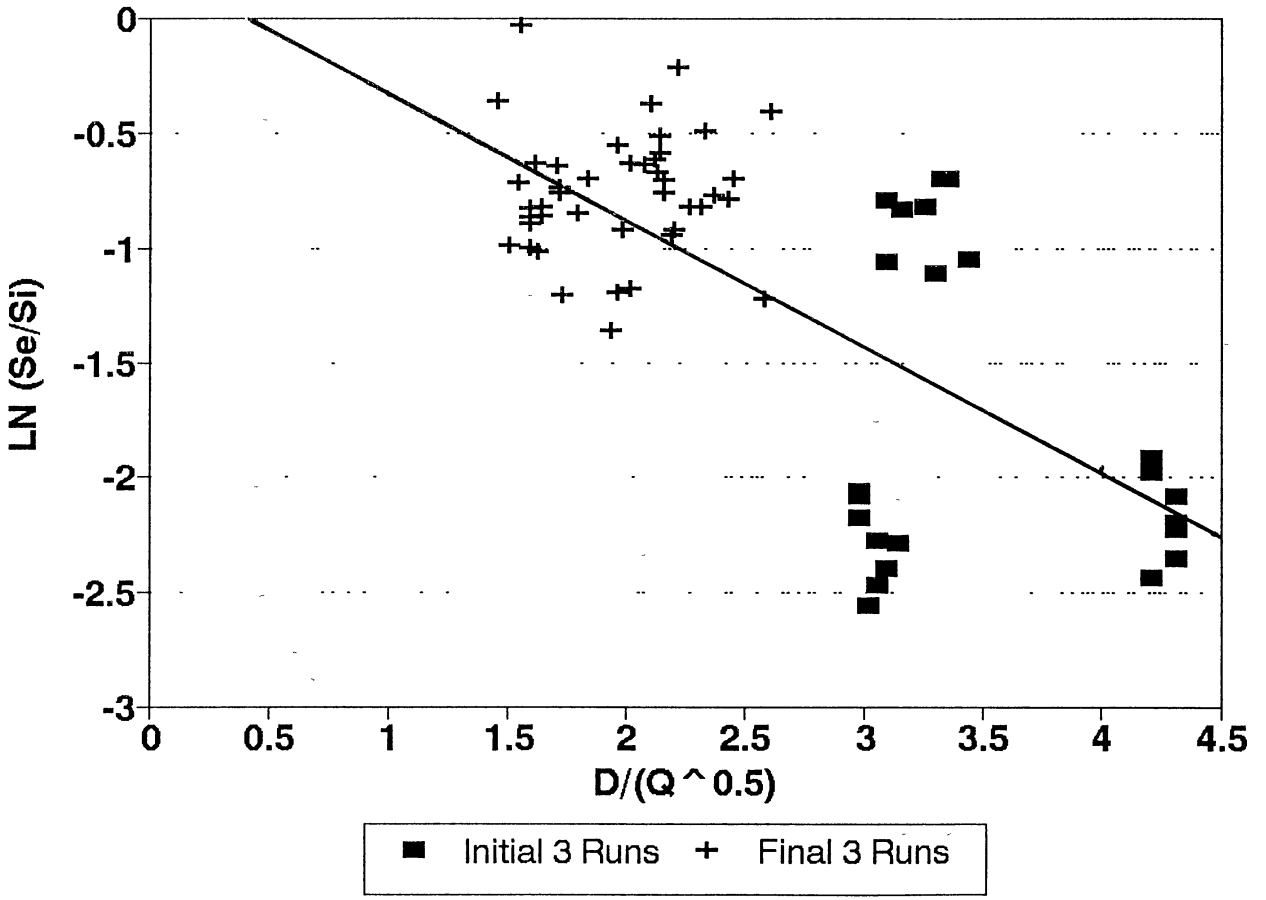

Figure 24. Germain Model for ASBF

performed on the composite of both phases. The treatability factor (k) of the Germain model corresponding the composite was determined from the slopes of the linear regression line shown in Figure 24. The treatability factor and correlation coefficients of the composite data are presented in Table 7.

TABLE 7
GERMAIN KINETIC COEFFICIENTS FOR ASBF

COEFFICIENTS	COMPOSITE DATA
k	0.552
n	0.5
r	0.71

To determine the parameters of full-size ASBF reactors, the different coefficients were applied to example waste stream data from a refinery. The following assumptions were also made to determine the parameters of the ASBFs: (1) the fraction of COD remaining or the Le/Lo ratio in terms of mg/L COD was 200/852; (2) the crude desalter process unit in the refinery had a flowrate of 378.5 L/min (100 gpm); (3) the depth of the ASBF unit was 3.1 m or 2.4 m (respectively 10 ft. or 8 ft.) and (4) the specific area of the media was 138 m^2/m^3. The Le/Lo ratio of 200/852 was chosen arbitrarily from the base effluent and average influent COD concentrations of the entire six runs. The crude desalter process unit flowrate of 378.5 L/min was determined from refinery operations by refinery personnel. The depths of

3.1 m and 2.4 m were assumed due to the fact that the wastewater must be pumped into the unit and overcome hydrostatic pressure. The air needed for the ASBF must also be pumped against the hydrostatic pressure. The hydrostatic pressure associated with these depths can be easily overcome, although pumping the wastewater and air through a higher tower would increase the cost tremendously. The media specific surface area of 138 m^2/m^3 was assumed equal to the surface area of the media used in the study to determine the treatability factors.

The ASBF parameters determined from the composite k of 0.552 and depth of 3.1 m were: volume of 844.8 m^3, surface area of 272.5 m^2 and HRT of 3.7 hrs. With a depth of 2.4 m and the composite k of 0.552, the volume was 1091.2 m^3, the surface area was 454.7 m^2 and the HRT was 4.8 hrs.

The kinetic coefficients obtained from the model may not be 100% accurate due to the variability of the industrial wastewater. But, sound performance data obtained from the bench-scale study can be used to run a full-scale reactor. For example, at a given loading rate, the effluent concentration of the full-scale unit can be estimated from the bench-scale data, not necessarily from the kinetic model.

CONCLUSIONS

In conclusion, the kinetics for the ASBF reactor, which reduced the toxicity of Crude Desalter wastewater, were modeled by the first order Germain model. The size of the ASBF to be used as a process treatment unit in a refinery was determined with the kinetic coefficients and the following assumptions: (1) Le/Lo ratio of 200/852 in terms of mg COD/L; (2) the crude desalter process unit in the refinery had a flowrate of 378.5 L/min (100 gpm); (3) the depth of the ASBF unit was 3.1 m or 2.4 m and (4) the specific area of the media was 138 m^2/m^3. The parameters of the ASBF corresponding to the different kinetic coefficients are as follows: (1) with k = 0.552 and depth = 3.1 m, the volume was 844.8 m^3, surface area was 272.52 m^2, and HRT was 3.7 hrs; and (2) with k = 0.552 and depth = 2.4 m, the volume was 1091.2 m^3, surface area was 454.7 m^2, and HRT was 4.8 hrs. The volume of 1091.2 m^3 and surface area of 454.7 m^2 gave more a reasonable hydraulic loading rate and detention time.

In general, the acute toxicity removal produced by the ASBF will be on the order of 100%. Even though the acute toxicity of the waste treated by the ASBF will be reduced the chronic toxicity of the waste may not be reduced. The 48 hour bioassay results indicated the Crude Desalter wastewater has chronic toxicity tendencies. In the future,

chronic toxicity tests need to be conducted on the Crude Desalter wastewater to confirm its chronic toxicity tendencies. The results indicated that at chloride concentration higher than 5000 mg/l toxicity will occur. Thus, the chloride concentration of the Crude Desalter wastewater must be monitored to prevent chloride toxicity in the receiving stream. The large chloride concentration in the sludge may create some waste disposal problems. The results from the C_{18} column toxicity tests point to nonpolar organics as another potential source of toxicant along with chlorides. A more detailed analysis of the organics in correlation with toxicity needs to be conducted to confirm this and to identify the specific organics causing the toxicity. Ammonia was shown not to be the toxic component of the Crude Desalter wastewater.

The COD removal from the ASBF was in the range of 50% to 89% with BOD removal of approximately 88%. The additional treatment needed in conjunction with the ASBF will be coagulation of the sludge to improve settling. Since the ASBF did not seem to be stressed during the study, the unit needs to be run at higher loadings in the future to determine the stress point of the unit. Additional research should include developing a kinetic model which incorporates toxicity units. The model is needed since the regulations emphasize toxicity instead of BOD or COD concentrations. This will be a difficult challenge because the composition

of the process wastes such as Crude Desalter and Sour Water Stripper vary with process operation. The variation in waste causes a variation in the toxic constituents of the waste. There is still much research to be done for further understanding of biological kinetics and the toxic components of industrial wastewaters.

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APPENDIXES

APPENDIX A

EXPERIMENTAL DATA PERFORMANCE OF ASBF

Loading : 13.7 g COD/m 2*d
Test Began : October 29, 1990
Test Ended : November 18, 1990

DATE	Flowrate ml/min	COD Loading g COD/m 2*d	Influent COD mg/l	Effluent COD mg/l
10 29-90	30.6	17.28	500	350
10-31-90	24.4	11.92	475	250
11 1-90	23.6	15.78	650	195
11-3-90	21.2	12.8	400	150
11-5 90	27.2	10.49	375	200
11-7-90	26.8	15.16	550	200
11 8-90	28	14.4	500	220
11-9-90	28	14.8	515	190
11-9-90	28	16.7	580	245
11-10-90	24	12.8	520	250
11 11 90	28	17.8	550	225
11-11 90	26.4	14.4	530	225
11 12 90	24	10.5	425	300
1 -90	29.2	14.27	475	460
11 15 90	22	13.12	580	250
11-16 90	29.6	15.53	510	250
11-18 90	26.4	14.12	520	230

Loading : 13.7 g COD/m 2*d
Test Began : October 29, 1990
Test Ended : November 18, 1990

DATE	% COD Removal	DO	Influent pH	Effluent pH
10-29-90	70	4.2	8.2	6.6
10-31-90	47.37	3.6	7.7	7.4
11-1-90	70	3.4	7.5	7.3
11-3-90	62.9	4.1	7.4	7.3
11-5-90	46.67	5.3	7.4	7.3
11-7-90	63.6	5.6	8.2	7.6
11-8-90	50	5.7	8.4	6.9
11-9-90	57.7	6	8.1	7.1
11-9-90	63.1	5.7	7.1	7.4
11-10-90	51.9	5.4	7.2	7.1
11-11-90	59	5.6	7.1	6.9
11-11-90	57.5	5.9	7.2	7.1
11-12-90	57.9	5	7.3	7.1
11-14-90	0	5.4	7.4	--
11-15-90	56.9	3.1	7.1	7.2
11-16-90	51	3.7	7.3	6.9
11-18-90	55.7	6.3	7	7.3

Loading : 13.7 g COD/m 2*d
Test Began : October 29, 1990
Test Ended : November 18, 1990

DATE	Influent Temp. (C)	Effluent Temp. (C)	Influent TSS mg/l	Influent VSS mg/l
10-29-90	25	23	36	16
10-31-90	25	23	70	22
11-1-90	25	23	12	2
11-3-90	24	22	52	20
11-5-90	23	21	36	18
11-7-90	21	21.5	80	44
11-8-90	22	22		
11-9-90	21.6	22.5	60	36
11-9-90	22.5	22		
11-10-90	24	21		
11-11-90	22	22		
11-13-90	23.5	22	52	24
11-14-90	23.5	22	45	15
11-14-90	24.5	22.7	30	14
11-15-90	24.5	23.5	26	22
11-16-90	24	23.5	40	18
11-18-90	23.5	22.4	30	16

Loading : 13.7 g COD/m 2*d
Test Began : October 29, 1990
Test Ended : November 18, 1990

DATE	Effluent TSS mg/l	Effluent VSS mg/l	TSS INSIDE MG/L	VSS INSIDE MG/L
10-29-90	32	20	152	96
10-31-90	34	20	180	120
11-1 90	16		84	
11-2-90	40	28	164	100
11-5-90	48	24	317	200
11-7-90	180	115	580	370
11-8-90				
11-9-90	48	26	600	790
11-9-90				
11-10-90				
11-11-90				
11 11-90	90	15	530	350
11-12-90	80	26	1000	710
11-14-90	128	38	340	190
11-15-90	30	16	344	248
11-16-90	48	24	192	120
11-18-90	120	72	940	490

Loading : 13.7 g COD/m 2*d
Test Began : October 29, 1990
Test Ended : November 18, 1990

DATE	Waste TSS mg/l	Waste VSS mg/l	Influent BOD5 mg/l	Effluent BOD5 mg/l
10-29-90	248	168		
10-31-90	336	244		
11-1-90	84		147	13.2
11-3-90	940	640		
11-5-90	460	285		
11-7-90	1100	740		
11-8-90				
11-9-90	1100	640		
11-10-90				
11-11-90				
11-11-90				
11-11-90	1200	720		
11-12-90	168	112	192	29.3
11-14-90	1290	1400		
11-15-90				
11-16-90	1050	650	210	24
11-18-90	1280	700		

Loading : 13.7 g COD/m 2*d
Test Began : October 29, 1990
Test Ended : November 18, 1990

DATE	Influent Sulfide mg/l	Effluent Sulfide mg/l	Influent Chloride mg/l
10-29-90			
10-31-90			
11-1-90	0.31	0.0375	1500
11-3-90			2400
11-5-90			2100
11-7-90	0.33	0.05	1700
11-8-90			
11-9-90			1300
11-9-90			
11-10-90			
11-11-90			
11 11 90			
11-12-90	0.15	0.06	1400
11-14-90			2400
11-15-90			
11-16-90	0.21	0.028	1500
11-18-90			

Loading : 13.7 g COD/m 2*d
Test Began : October 29, 1990
Test Ended : November 18, 1990

DATE	Effluent Chloride mg/l	Influent Alkalinity mg/l	Effluent Alkalinity mg/l
10-29-90			
10-31-90			
11-1-90	2100	33	23
11-3-90	1800		
11-5-90	1500		
11-7-90	1700	110	60
11-8-90			
11-9-90	2000		
11-9-90			
11-10-90			
11-11-90			
11-14-90			
11-17-90	1600	110	90
11-17-90	1700		
11-15-90			
11-16-90	1500	101	88
11-18-90			

Loading : 13.7 g COD/m 2*d
Test Began : October 29, 1990
Test Ended : November 18, 1990

DATE	Influent N-NH3 mg/l	Effluent N-NH3 mg/l	Influent N-org mg/l	Effluent N-org mg/l
10-29-90				
10-31-90				
11-1-90	12.75	11.13	1	0
11-3-90				
11-5-90				
11-7-90				
11-8-90				
11-9-90				
11-9-90				
11-10-90				
11-11-90				
11-11-90				
11-12-90	12	11.75	0.75	0
11-14-90				
11-15-90				
11-16-90				
11-18-90				

Loading : 9.6 g COD/m^2*d
Test Began : December 11, 1990
Test Ended : January 8, 1991

DATE	Flowrate ml/min	COD Loading g COD/m^2*d	Influent COD mg/l	Effluent COD mg/l
12-11-90	10.6	6.4	590	175
12-13-90	12.6	7.84	605	280
12-14-90	14.8	9.7	640	250
12-16-90	10.4	9.6	900	600
12-17-90	16.4	7.1	425	225
12-18-90	18.4	13	690	210
12-19-90	17.4	10.38	580	180
12-21-90	15.2	6.64	425	200
12-23-90	11.8	7.28	600	300
12-26-90	14.1	8.29	560	450
12-27-90	18	12.03	650	260
12-29-90	21	11.66	540	270
12-31-90	19	19.3	990	255
1-2-91	19.2	7.74	495	245
1-4-91	15.6	8.42	525	270
1-8-91	17.4	8.05	450	240

Loading : 9.6 g COD/m^2*d
Test Began : December 11, 1990
Test Ended : January 8, 1991

DATE	% COD Removal	DO	Influent pH	Effluent pH
12-11-90	70.3	5.2	7.2	7.6
12-13-90	53.7	6.2	6.9	7.4
12-14-90	60	6.8	6.5	5.4
12-16-90	33	7	7.1	6.8
12-17-90	47	6.4	7.2	7.4
12-18-90	69.5	5.2	6.8	7.4
12-19-90	68.9	5.9	7.7	7.1
12-21-90	52.9	5.8	7.2	7.3
12-23-90	50	3.6	6.5	7.0
12-26-90	19.64	6.2	7.3	7.4
12-27-90	60	5.2	6.9	7.2
12-29-90	50	5.5	6.6	7.1
12-31-90	74.2	4.4	6.9	7.7
1-2-91	50.5	5.6	6.65	7.2
1-4-91	48.6	5.9	6.7	7.3
1-8-91	46.67	6.3	-	7.7

Loading : 9.6 g COD/m 2*d
Test Began : December 11, 1990
Test Ended : January 8, 1991

DATE	Influent Temp. (C)	Effluent Temp. (C)	Influent TSS mg/l	Influent VSS mg/l
12-11-90	21	21.8	60	44
12-13-90	22.5	22.1	60	60
12-14-90	21	21.5	52	36
12-16-90	23	21.9	92	97
12-17-90	22	21.5	22	22
12-18-90	22	21.8		
12-19-90	22	21.5		
12-21-90	19	21.2	90	40
12-23-90	16	20.3	66	34
12-26-90	20	22		
12-27-90	21	21.8	84	50
12-29-90	20	21.8		
12-31-90	18.5	20.8	356	224
1-2-91	22	21.6	96	40
1-4-91	19.3	21.5	40	21
1-6-91	20	21.2		

Loading : 9.6 g COD/m 2*d
Test Began : December 11, 1990
Test Ended : January 8, 1991

DATE	Effluent TSS mg/l	Effluent VSS mg/l	TSS INSIDE MG/L	VSS INSIDE MG/L
12-11-90	28	12	200	100
12-13-90	66	52	412	288
12-14-90	68	40	440	270
12-16-90	220	164	250	200
12-17-90	38	34	56	56
12-18-90				
12-19-90				
12-21-90	268	120		
12-23-90	185	100	288	176
12-26-90				
12-27-90	52	20	580	98
12-29-90				
12-31-90	65	47.5	200	144
1-2-91	56	28	360	232
1-4-91	39	22	516	328
1-8-91				

Loading : 9.6 g BOD/m 2*d
Test Began : December 11, 1990
Test Ended : January 8, 1991

DATE	Waste TSS mg/l	Waste VSS mg/l	Influent BOD5 mg/l	Effluent BOD5 mg/l
12-11-90	1280	860		
12-13-90	2560	1060		
12-14-90	2700	1620	117	18.6
12-16-90				
12-17-90				
12-18-90				
12-19-90				
12-21-90	4560	3040		
12-23-90	2320	142		
12-26-90				
12-27-90	1520	94	192	24
12-29-90				
12-31-90	470	340		
1-2-91	990	610		
1-4-91	2210	1460		
1-8-91				

Loading : 9.6 g COD/m 2*d
Test Began : December 11, 1990
Test Ended : January 8, 1991

DATE	Influent Sulfide mg/l	Effluent Sulfide mg/l	Influent Chloride mg/l
12-11-90			
12-13-90			
12-14-90	0.3	0.06	1800
12-16-90			1100
12-17-90			
12-18-90			2100
12-19-90			
12-21-90			1900
12-23-90			
12-26-90			
12-27-90	0.095	0.033	4000
12-29-90			3700
12-31-90	20	0.065	2900
1-2-91	0.2	0.03	4700
1-4-91			
1-8-91			

Loading : 9.6 g COD/m^2*d
Test Began : December 11, 1990
Test Ended : January 8, 1991

DATE	Effluent Chloride mg/l	Influent Alkalinity mg/l	Effluent Alkalinity mg/l
12-11-90			
12-13-90			
12-14-90	2100	200	50
12-16-90	1400		
12-17-90			
12-18-90	2100		
12-19-90			
12-21-90	2300		
12-22-90			
12-26-90			
12-27-90	3400	130	110
12-28-90	3300	75	65
12-31-90	2600	70	70
1-4-91	4200	100	70
1-7-91			
1-8-91			

Loading : 9.6 g COD/m 2*d
Test Began : December 11, 1990
Test Ended : January 8, 1991

DATE	Influent N-NH3 mg/l	Effluent N-NH3 mg/l	Influent N-org mg/l	Effluent N-org mg/l
12-11-90				
12-13-90				
12-14-90	7.5	0.25	1	3.5
12-16-90				
12-17-90				
12-18-90				
12-19-90				
12-21-90				
12-23-90				
12-26-90				
12-27-90	10	1	0.5	0.25
12-29-90				
12-31-90				
1-2-91				
1-4-91				
1-8-91				

Loading : 4.5 g COD/m 2*d
Test Began : January 29, 1991
Test Ended : February 14, 1991

DATE	Flowrate ml/min	COD Loading g COD/m 2*d	Influent COD mg/l	Effluent COD mg/l
1-29-91	18.4	4.25	225	130
1-31-91	13.8	4.83	340	150
2-2-91	15.4	4.11	260	145
2-4-91	13.2	4.62	340	150
2-6-91	12	4.32	350	160
2-7-91	16	4.77	290	200
2-9-91	13	4.35	325	200
2-11-91	14.6	4.88	325	130
2-13-91	15.3	4.47	275	150
2-14-91	15.4	3.96	250	150

Loading : 4.5 g COD/m 2*d
Test Began : January 29, 1991
Test Ended : February 11, 1991

DATE	% COD Removal	DO	Influent pH	Effluent pH
1-29-91	42.2	7.6	7	7.0
1-31-91	55.88	7.1	6.8	7.1
2-2-91	44.23	6.7	6.8	7.1
2-4-91	55.88	6.7	6.5	6.5
2-5-91	54.29	6.6	7	6.9
2-7-91	21	6.5	6.7	6.6
2-9-91	38.5	6.4	6.6	6.4
2-11-91	60	6.4	6.8	6.7
2-12-91	47.45	6.4	6.5	6.9
2-14-91	40	6.4	6.8	7

Loading : 4.5 g COD/m 2*d
Test Began : January 29, 1991
Test Ended : February 14, 1991

DATE	Influent Temp. (C)	Effluent Temp. (C)	Influent TSS mg/l	Influent VSS mg/l
1-30-91	19	21.2	30	13
1-31-91	18.8	21.2	27	20
2-2-91	20	21.4	34	15
2-4-91	21.3	21.9	27	13
2-5-91	22.1	22	38	18
2-7-91	21	21.5	40	19
2-9-91	20.7	20.9		
2-11-91	19.9	21.3	48	19
2-12-91	21.8	21.4	22	13
2-14-91	21.3	21.5	24	15

Loading : 4.5 g COD/m 2*d
Test Began : January 29, 1991
Test Ended : February 14, 1991

DATE	Effluent TSS mg/l	Effluent VSS mg/l	TSS INSIDE MG/L	VSS INSIDE MG/L
1-29-91	28	13	1880	1160
1-31-91	28	13	196	112
2-2-91	27	18	760	450
2-4-91	27	13	788	172
2-5-91	19	11	224	216
2-7-91	28	13	264	152
2-9-91				
2-11-91	27	14	720	424
2-13-91	24	14	780	460
2-14-91	16	10	328	204

Loading : 4.5 g COD/m^2*d
Test Began : January 29, 1991
Test Ended : February 14, 1991

DATE	Waste TSS mg/l	Waste VSS mg/l	Influent BOD5 mg/l	Effluent BOD5 mg/l
1-29-91	1500	940		
1-31-91	1780	1020		
2-2-91	820	500		
2-4-91	3860	2300		
2-5-91	2340	980	80	4.8
2-7-91	4080	2400		
2-9-91				
2-11-91	900	480		
2-12-91	95320	3140	97	6.6
2-14-91	1120	680		

Loading : 4.5 g COD/m 2*d
Test Began : January 29, 1991
Test Ended : February 14, 1991

DATE	Influent Sulfide mg/l	Effluent Sulfide mg/l	Influent Chloride mg/l
1-29-91			7700
1-31-91			7400
2-2-91			3900
2-4-91	0.025	0.001	3800
2-5-91	0.045	0.01	3500
2-7-91			3300
2-9-91			
2-11-91	0.035	0.001	3700
2-12-91	0.03	0.0005	3200
2-14-91			3200

Loading : 4.5 g COD/m^2*d
Test Began : January 29, 1991
Test Ended : February 14, 1991

DATE	Effluent Chloride mg/l	Influent Alkalinity mg/l	Effluent Alkalinity mg/l
1-29-91	8200		
1-31-91	8400		
2-2-91	8900		
2-4-91	4800	50	50
2-5-91	4100	60	40
2-7-91	4100		
2-9-91			
2-11-91	4300	60	10
2-12-91	3400	70	70
2-14-91	3500		

Loading : 4.5 g COD/m 2*d
Test Began : January 29, 1991
Test Ended : February 14, 1991

DATE	Influent N-NH3 mg/l	Effluent N-NH3 mg/l	Influent N-org mg/l	Effluent N-org mg/l
1-29-91				
1-31-91				
2-2-91				
2-4-91				
2-5-91	7.5	2.5	2.5	0.5
2-7-91				
2-9-91				
2-11-91				
2-12-91	4.375	1.25	5	1.25
2-14-91				

APPENDIX B

GRAPHICAL REPRESENTATION OF

ASBF PERFORMANCE DATA

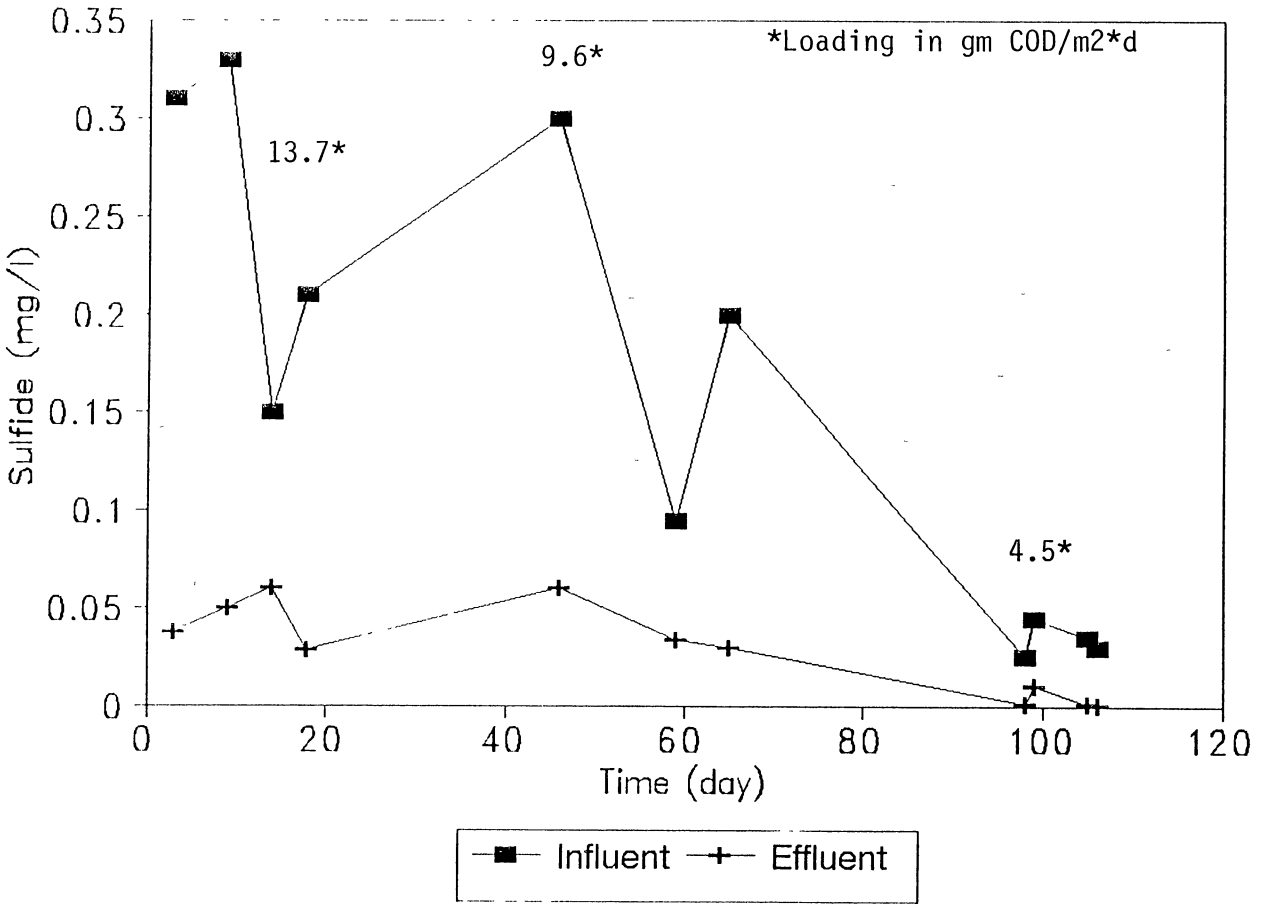

Figure B1. Sulfide Concentrations of ASBF Final 3 Runs

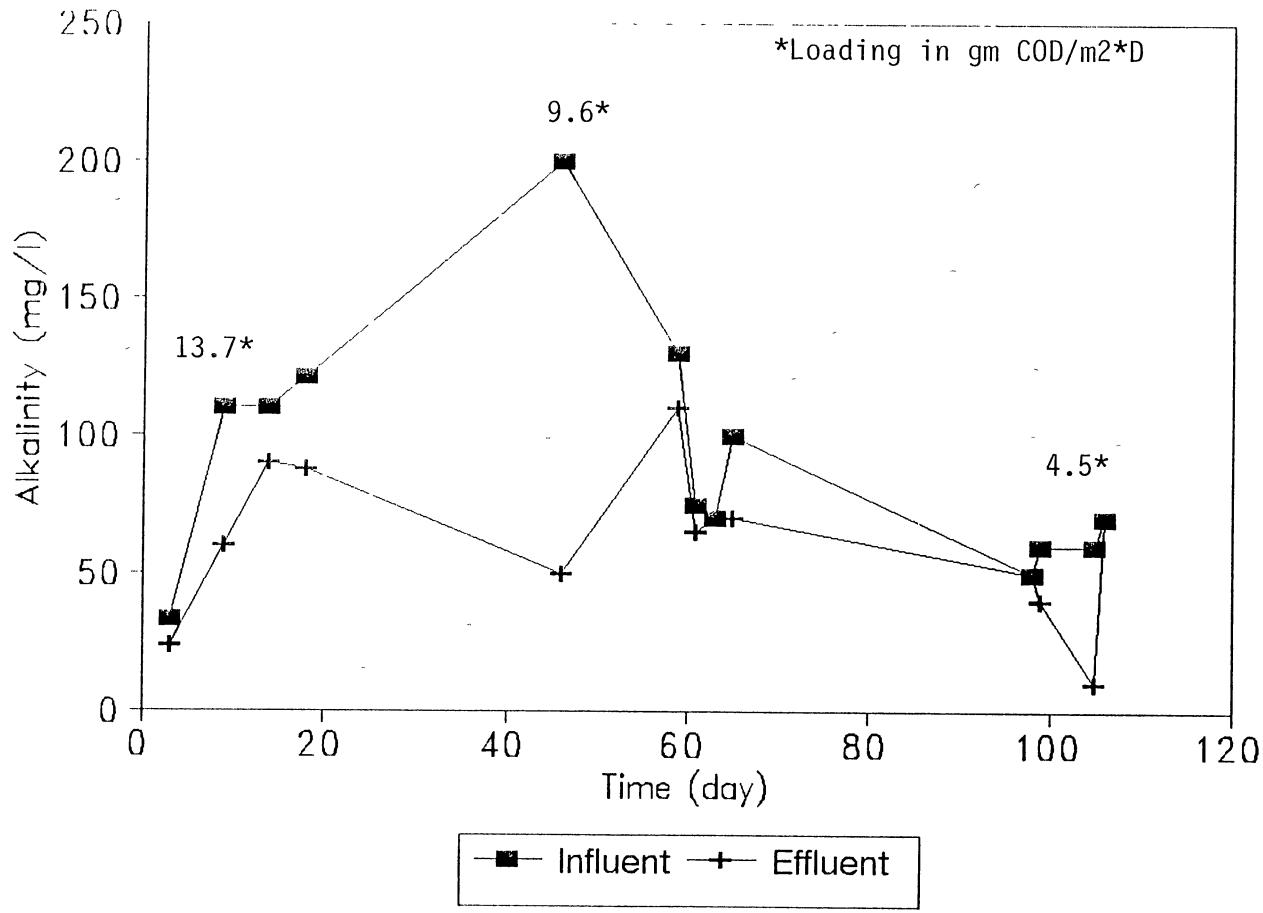

Figure B2. Alkalinity of ASBF Final 3 Runs

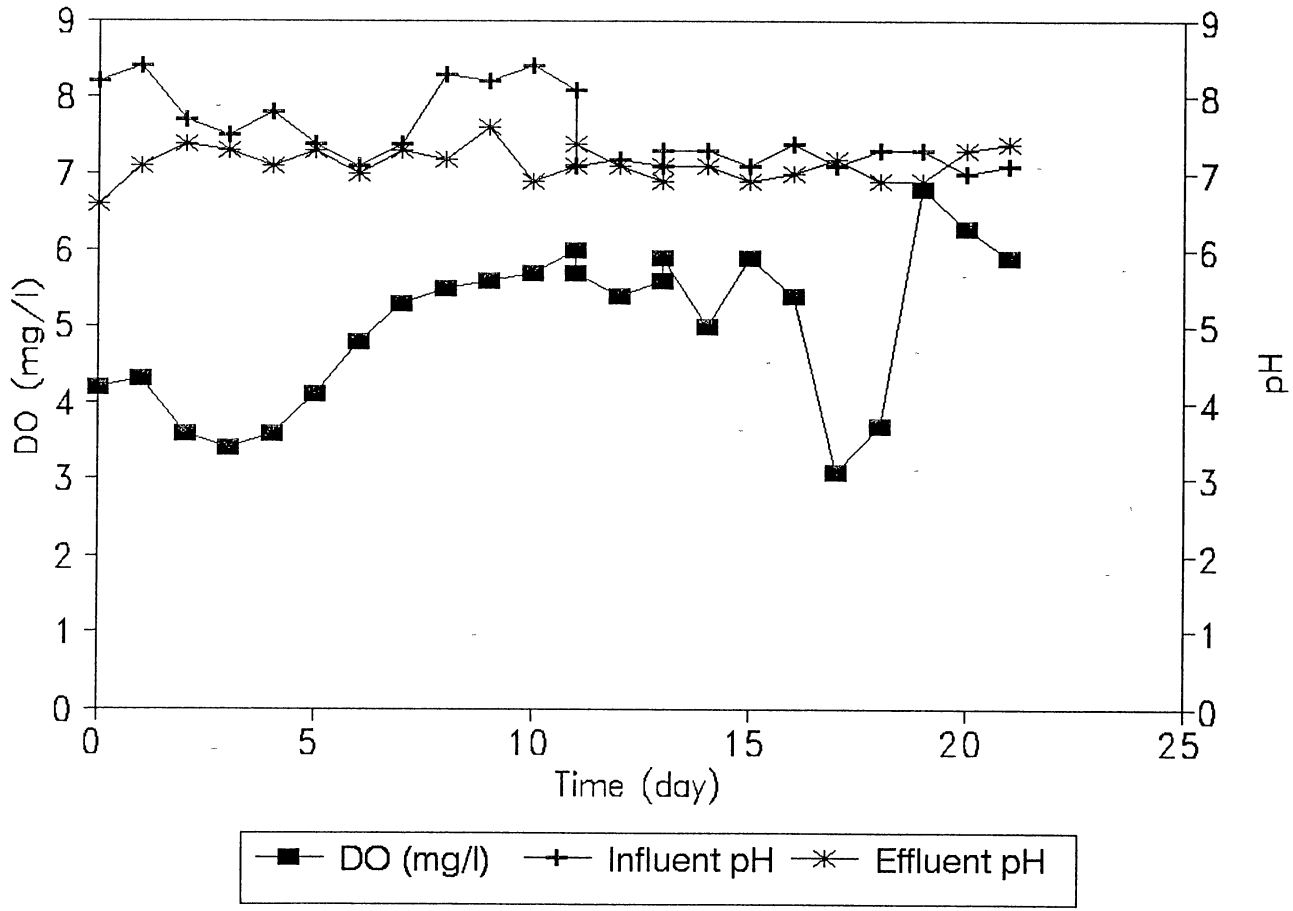

Figure B3. DO and pH Readings at Loading 13.7 gm COD/m2*d

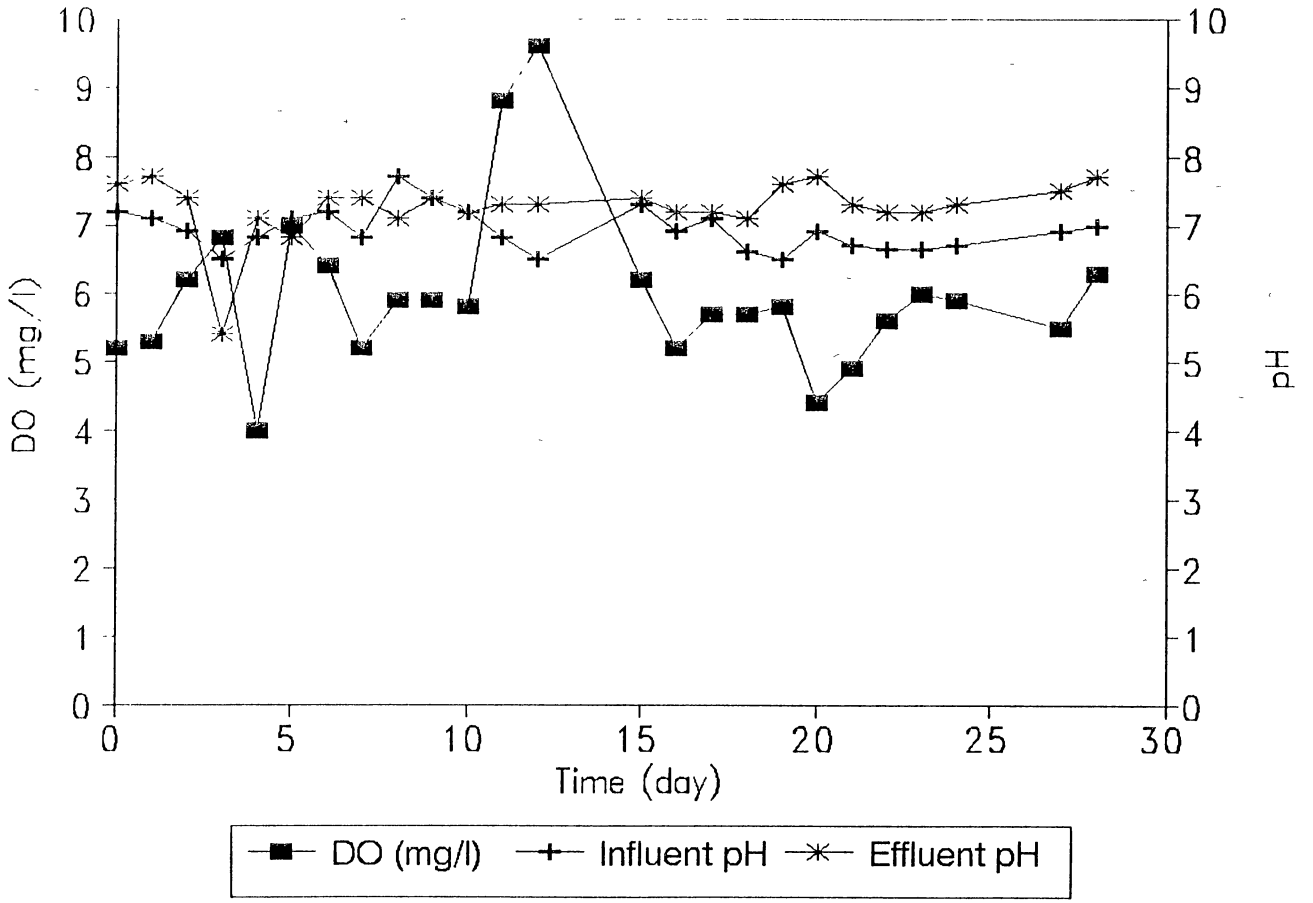

Figure B4. DO and pH Reading at Loading 9.6 gm COD/m2*d

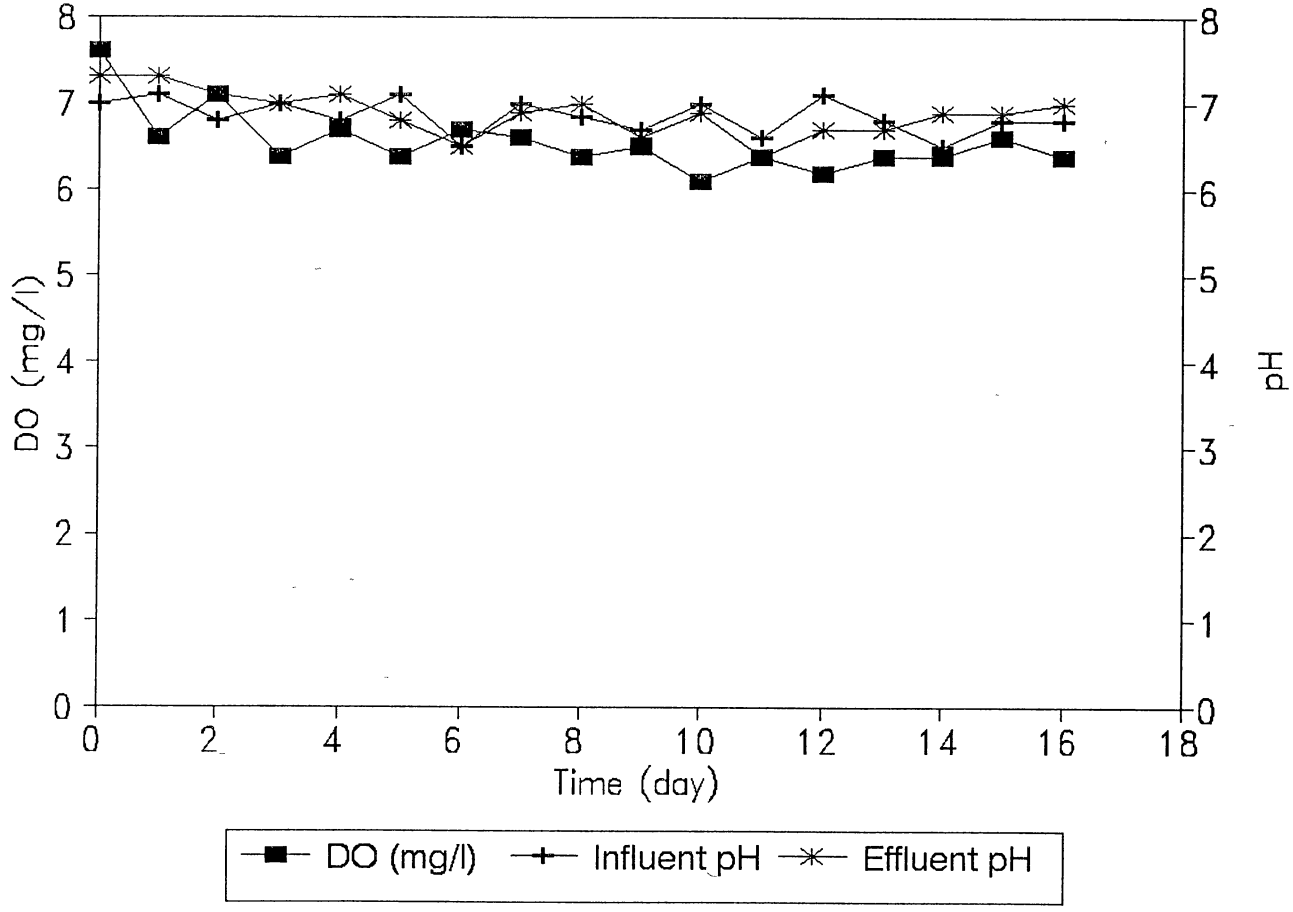

Figure B5. DO and pH Readings at Loading 4.5 gm COD/m2*d

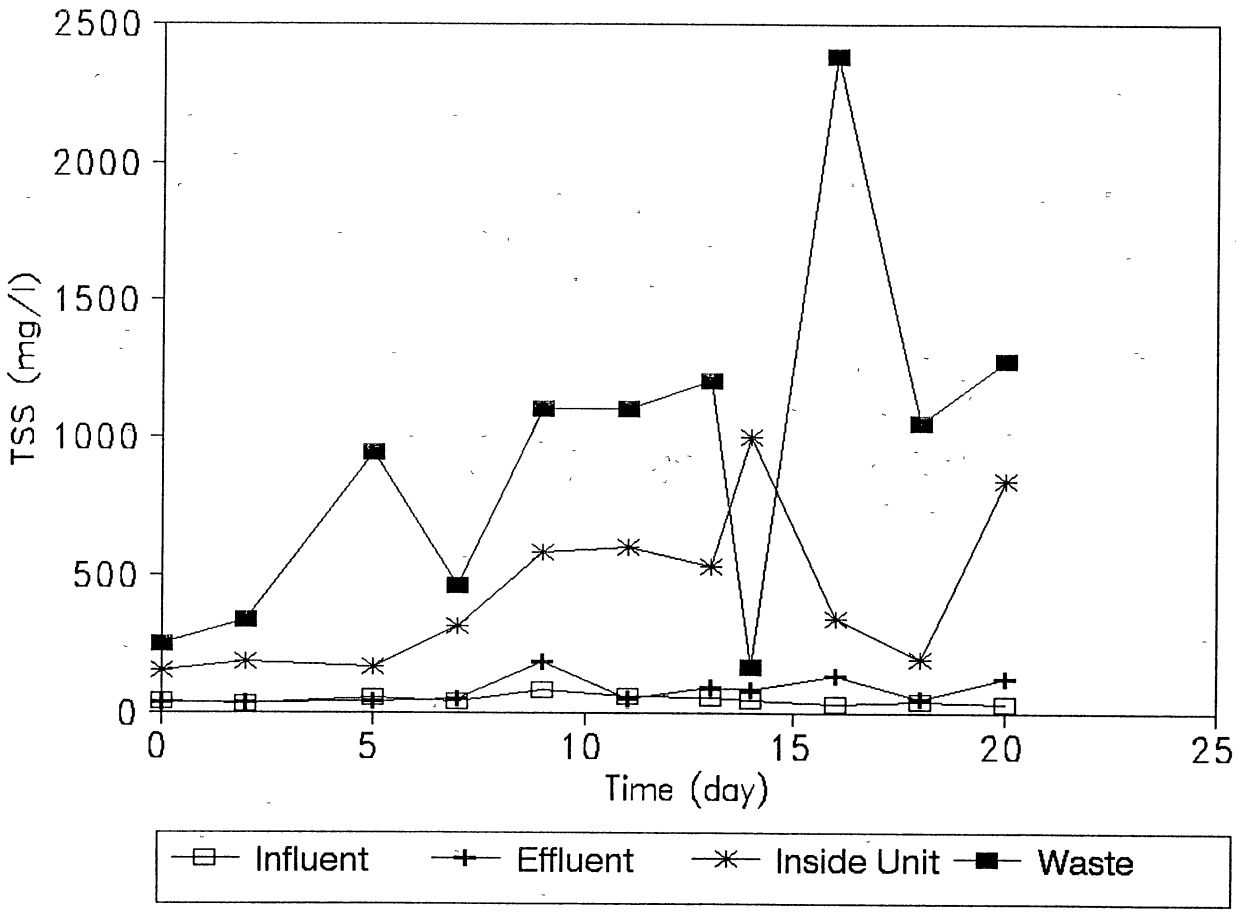

Figure B6. TSS Concentrations at Loading 13.7 gm COD/m2*d

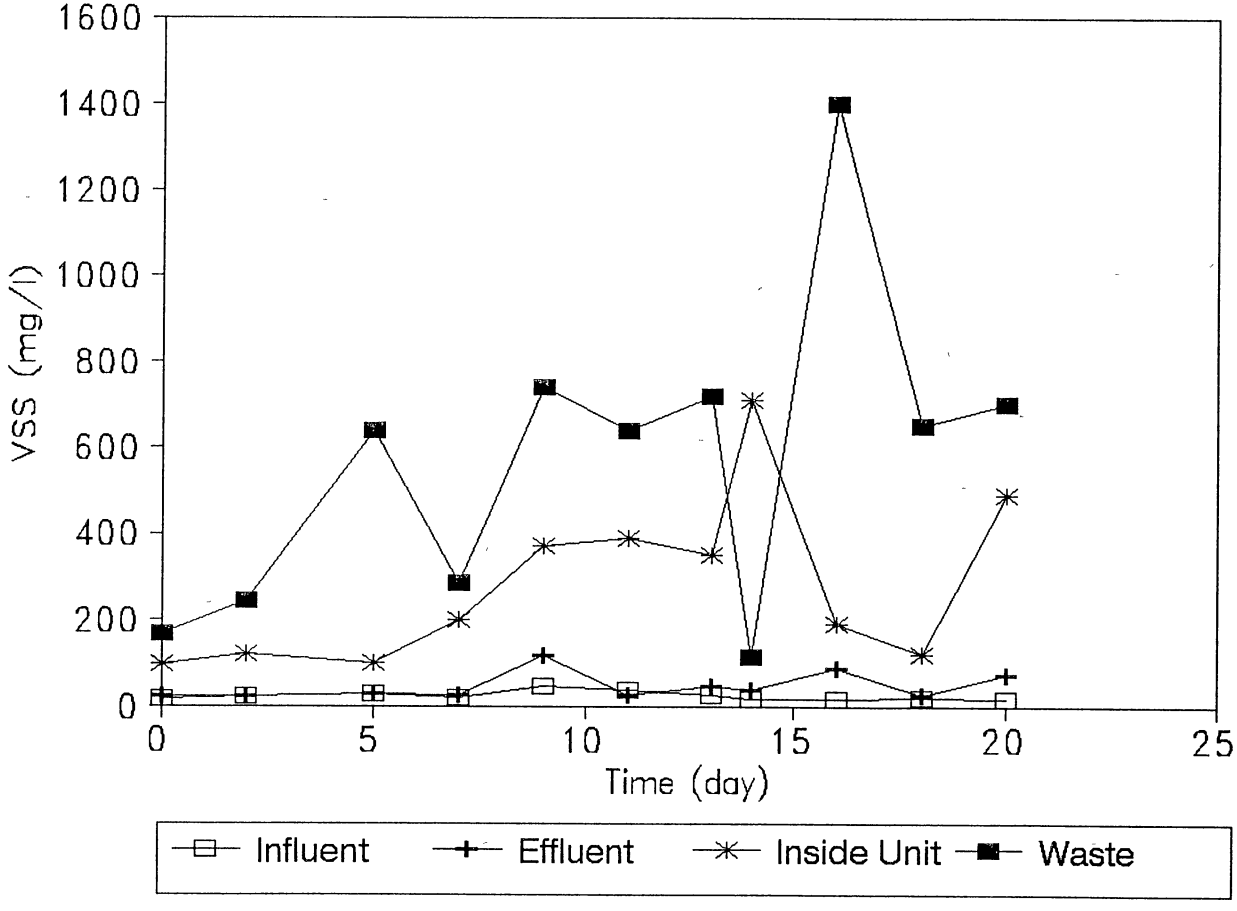

Figure B7. VSS Concentrations at Loading 13.7 gm COD/m2*d

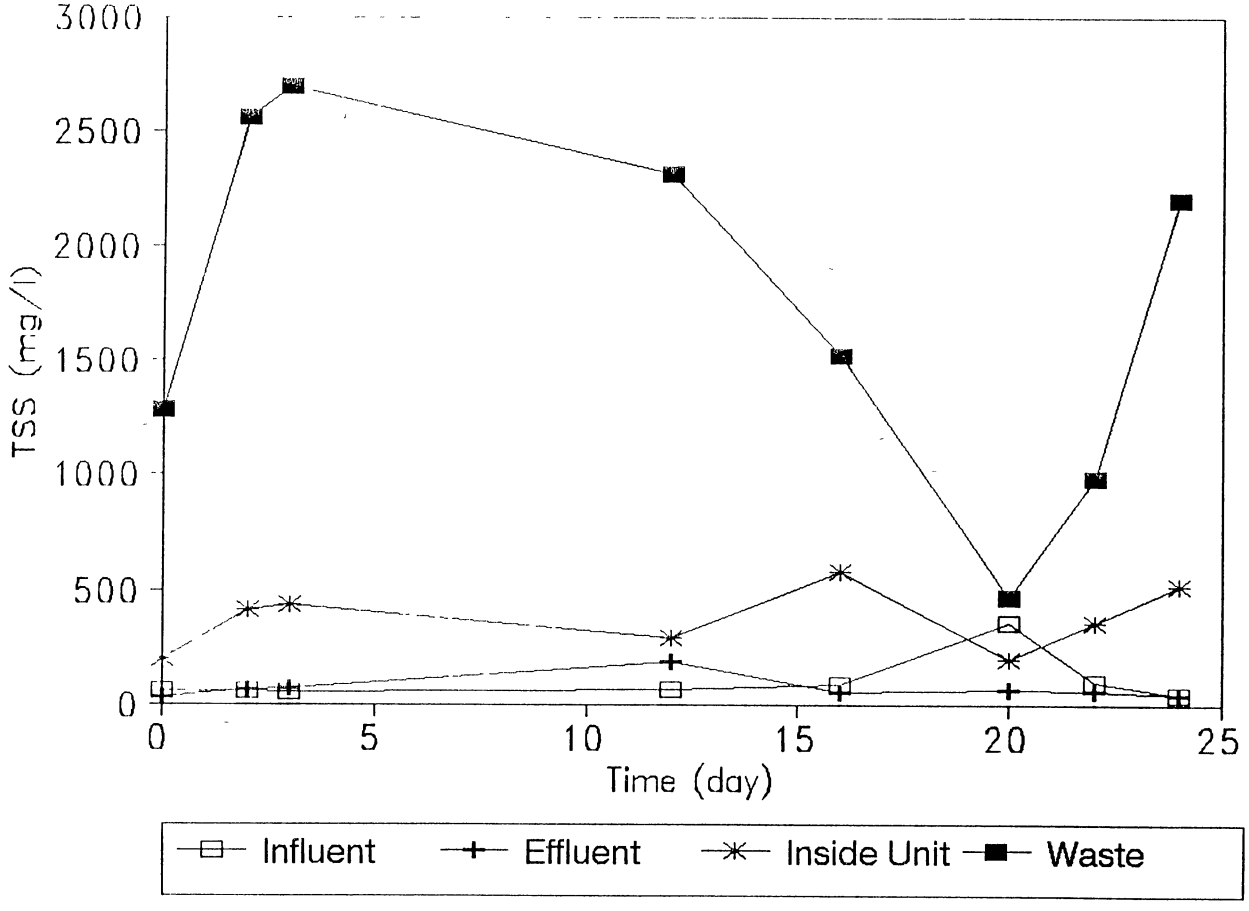

Figure B8. TSS Concentrations at Loading 9.6 gm COD/m2*d

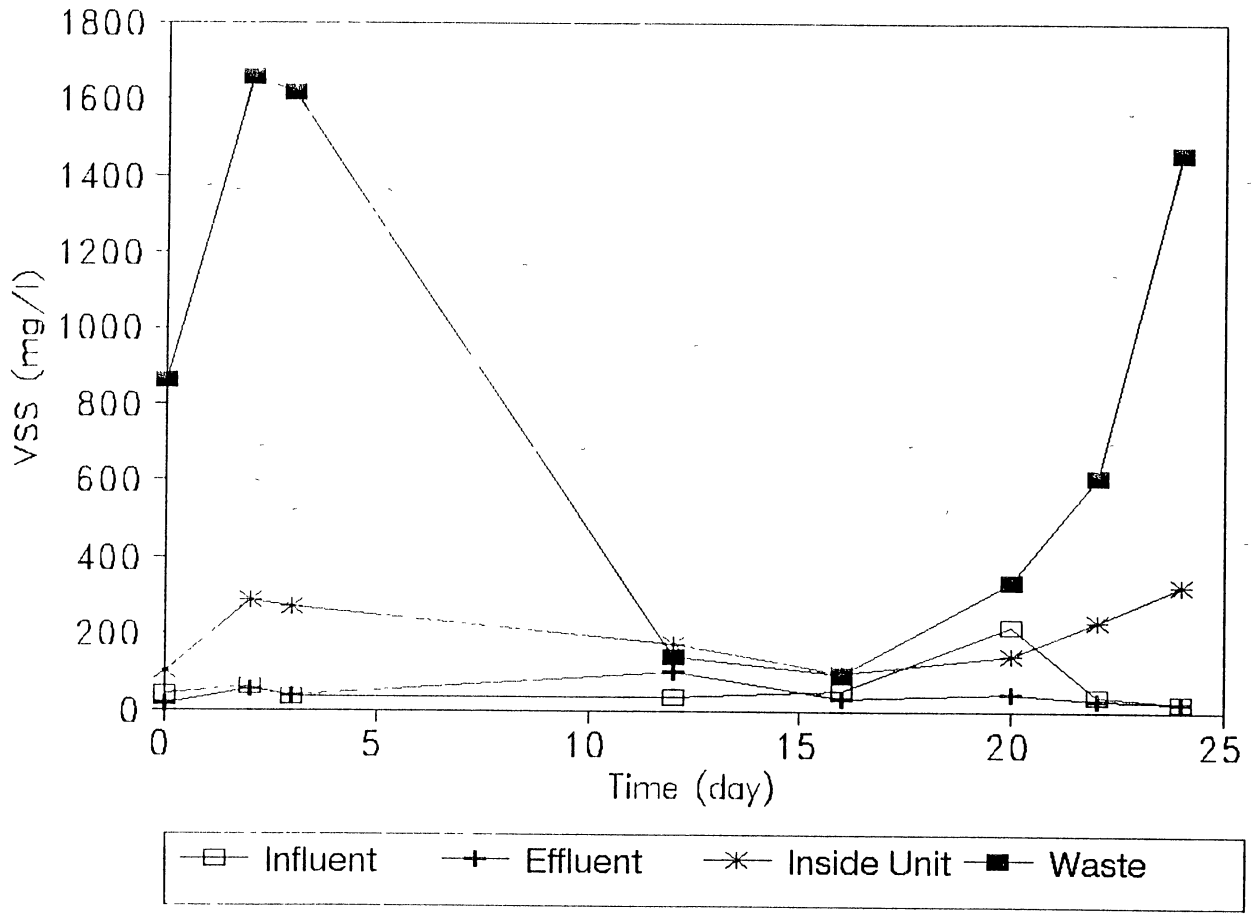

Figure B9. VSS Concentrations at Loading 9.6 gm COD/m2*d

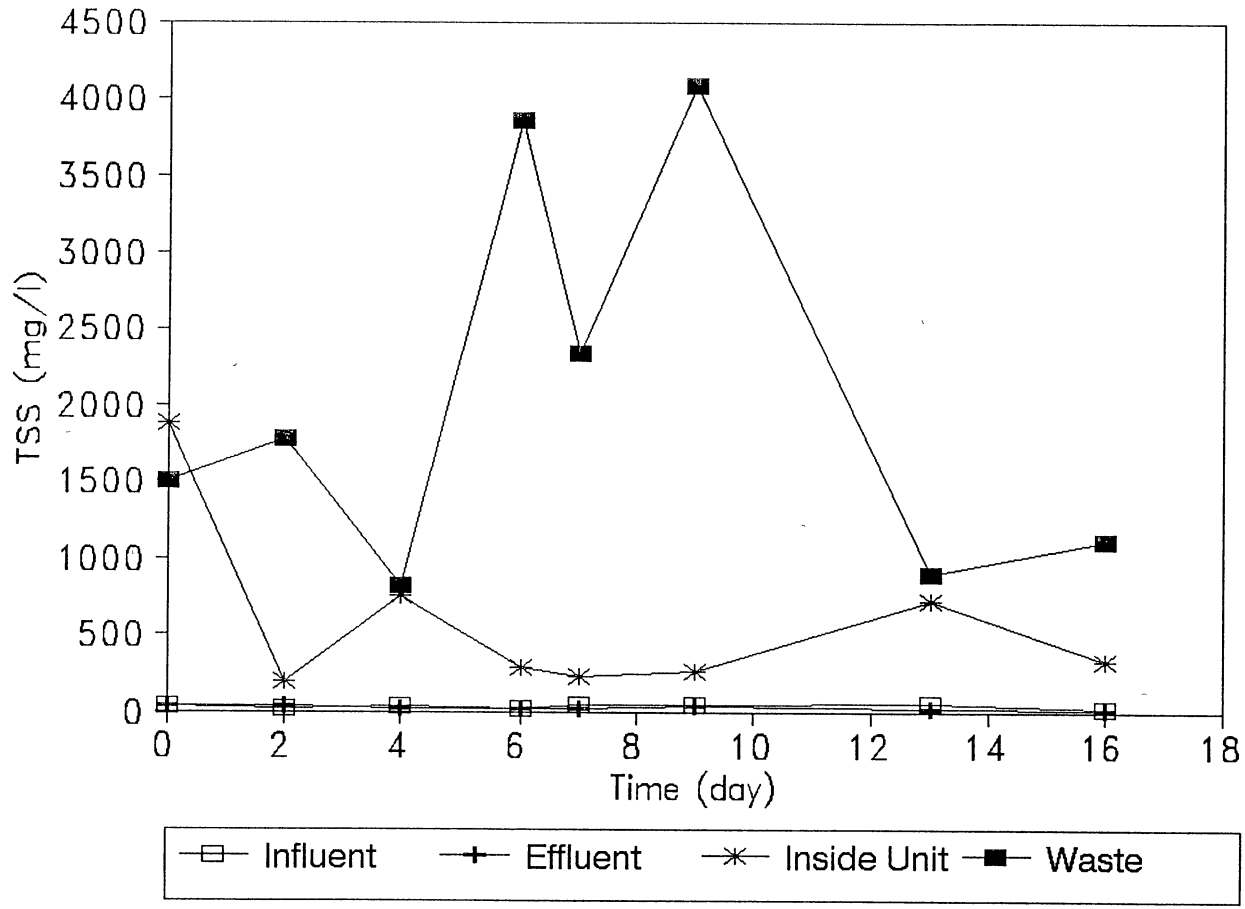

Figure B10. TSS Concentrations at Loading 4.5 gm COD/m2*d

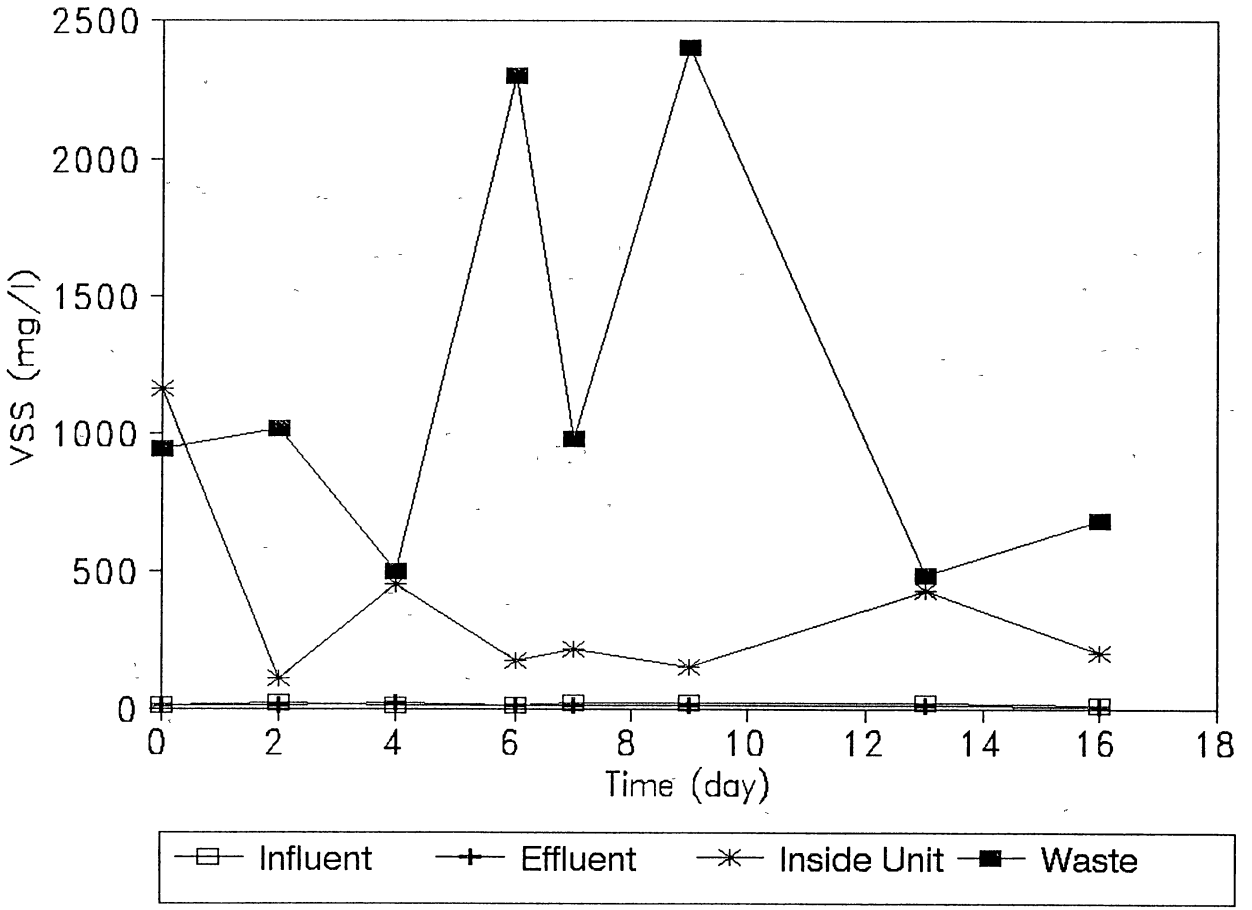

Figure B11. VSS Concentrations at Loading 4.5 gm COD/m2*d

APPENDIX C

UNIONIZED AMMONIA DATA

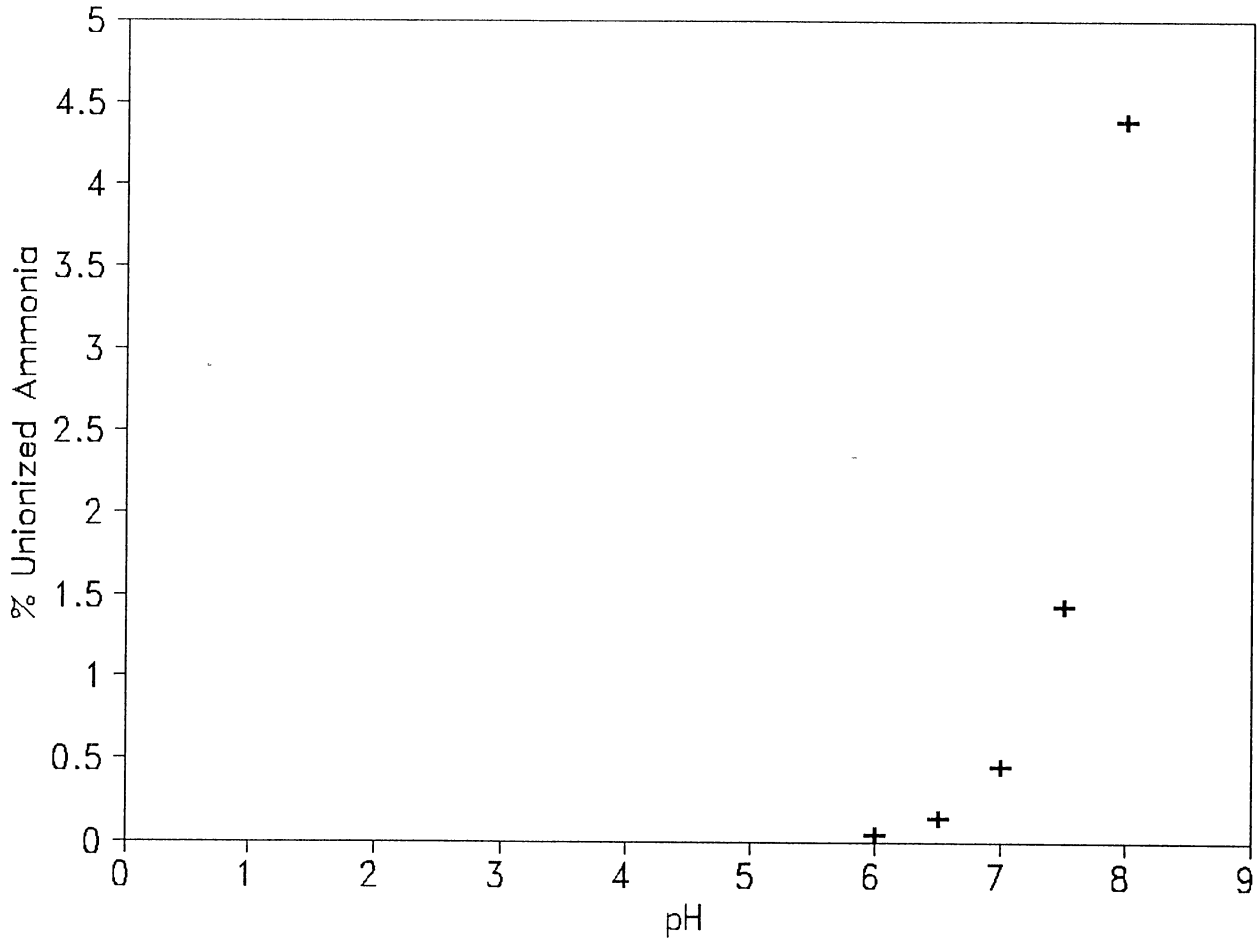

Figure C1. Percent Unionized Ammonia vs. pH

TABLE C1

PERCENT NH_3 IN AQUEOUS AMMONIA SOLUTIONS FOR 0-30 C AND pH 6-10

Temp. (C)	pH								
	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
0	.00827	.0261	.0826	.261	.820	2.55	7.64	20.7	45.3
1	.00899	.0284	.0898	.284	.891	2.77	8.25	22.1	47.3
2	.00977	.0309	.0977	.308	.968	3.00	8.90	23.6	49.4
3	.0106	.0336	.106	.335	1.05	3.25	9.60	25.1	51.5
4	.0115	.0364	.115	.363	1.14	3.52	10.3	26.7	53.5
5	.0125	.0395	.125	.394	1.23	3.80	11.1	28.3	55.6
6	.0136	.0429	.135	.427	1.34	4.11	11.9	30.0	57.6
7	.0147	.0464	.147	.462	1.45	4.44	12.8	31.7	59.5
8	.0159	.0503	.159	.501	1.57	4.79	13.7	33.5	61.4
9	.0172	.0544	.172	.542	1.69	5.16	14.7	35.3	63.3
10	.0186	.0589	.186	.586	1.83	5.56	15.7	37.1	65.1
11	.0201	.0637	.201	.633	1.97	5.99	16.8	38.9	66.8
12	.0218	.0688	.217	.684	2.13	6.44	17.9	40.8	68.5
13	.0235	.0743	.235	.738	2.30	6.92	19.0	42.6	70.2
14	.0254	.0802	.253	.796	2.48	7.43	20.2	44.5	71.7
15	.0274	.0865	.273	.859	2.67	7.97	21.5	46.4	73.3
16	.0295	.0933	.294	.925	2.87	8.54	22.8	48.3	74.7
17	.0318	.101	.317	.996	3.08	9.14	24.1	50.2	76.1
18	.0343	.108	.342	1.07	3.31	9.78	25.5	52.0	77.4
19	.0369	.117	.368	1.15	3.56	10.5	27.0	53.9	78.7
20	.0397	.125	.396	1.24	3.82	11.2	28.4	55.7	79.9
21	.0427	.135	.425	1.33	4.10	11.9	29.9	57.5	81.0
22	.0459	.145	.457	1.43	4.39	12.7	31.5	59.2	82.1
23	.0493	.156	.491	1.54	4.70	13.5	33.0	60.9	83.2
24	.0530	.167	.527	1.65	5.03	14.4	34.6	62.6	84.1
25	.0569	.180	.566	1.77	5.38	15.3	36.3	64.3	85.1
26	.0610	.193	.607	1.89	5.75	16.2	37.9	65.9	85.9
27	.0654	.207	.651	2.03	6.15	17.2	39.6	67.4	86.8
28	.0701	.221	.697	2.17	6.56	18.2	41.2	68.9	87.5
29	.0752	.237	.747	2.32	7.00	19.2	42.9	70.4	88.3
30	.0805	.254	.799	2.48	7.46	20.3	44.6	71.8	89.0

[From Emerson et al. 1975; reproduced with permission from the Journal of the Fisheries Research Board of Canada.]

TABLE C1

AMMONIA TOXICITY MEASUREMENTS

		Bioassay 1	Bioassay 2
Loading gm/m^2*d		Ammonia Toxicity*	Ammonia Toxicity*
4.5	Influent	0.01	0.00
	Effluent	0.00	0.00
9.6	Influent	0.00	0.02
	Effluent	0.00	0.00
13.7	Influent	0.07	0.07
	Effluent	0.04	0.03

* Ammonia Toxicity = $\frac{\text{Measured Unionized Ammonia}}{\text{Standard Unionized Ammonia}}$

* Standard Unionized Ammonia = 2.5 mg/l for Cerio daphnia

VITA

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