REDUCING TOXICITY OF A PETROLEUM REFINERY PROCESS WASTEWATER WITH AN AERATED SUBMERGED BIOLOGICAL FILTER

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#### REDUCING TOXICITY OF A PETROLEUM REFINERY

### PROCESS WASTEWATER WITH AN AERATED

SUBMERGED BIOLOGICAL FILTER

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Abstract-The ability of an Aerated Submerged Biological Filter (ASBF) to reduce toxicity of sour water from an oil refinery sour water stripping unit was evaluated at three organic loading rates. Influent and effluent acute toxicity was tested by performing static 24-hour bioassays with seven percent-by-volume based dilutions using **Ceriodaphnia dubia** and fathead minnows (Pimephales promelas) as test organisms. Lethal concentrations that produced 50% mortality of test organisms ( $IC_{50}$ ) over 24 hours were calculated for influent and effluent to determine if ASBF treatment reduced toxicity. Treatment with the ASBF increased the  $IC_{50}$  of the wastewater at all three loading rates. Selected conventional parameters, as well as  $NH_3$  and sulfides, showed no observable correlations with acute toxicity.

Key Words-aerated submerged biological filter, sour water, LC<sub>50</sub>, bioassay, Ceriodaphnia dubia, fathead minnow, organic loading

### INTRODUCTION

In the past, industrial wastewater discharges have usually been required to meet only technology-based discharge limitations for 5-day biochemical oxygen demand (BOD<sub>5</sub>) and suspended solids. However, due to the mandate by Congress in the Water Quality Act of 1987, renewed attention is being placed on water quality. As a result, the U.S. Environmental Protection Agency and delegated National Pollution Discharge Elimination System (NPDES) States are adding and revising effluent limitations in NPDES permits to include water quality-based effluent limitations according to procedures in the EPA Permit Writers Guide to Water Quality-based Permitting for Toxicity Pollutants (EPA, 1987). Therefore, NPDES permits now contain effluent limitations based on technological capability, State water quality standards, and final effluent toxicity limitations implementing the "no toxic discharge in toxic amounts" language of the Clean Water Act. The oil refining industry seldom had trouble meeting traditional standards in the past but anticipated some difficulty in meeting new toxicity standards. As a result, a joint project of the Oil Refiners Waste Control Council, Oklahoma State University Water Quality Research Lab, and School of Civil Engineering was undertaken to evaluate abilities of several treatment alternatives to reduce toxicity of various refinery wastewater streams (Burks and Wagner et al., 1989). A major portion of toxicity in these waste streams may be attributed to high concentrations of base neutral, methylene chloride extractable,

nonpolar organic contaminants (Burks and Wagner, 1984; Reece and Burks, 1985; and Smith, 1987). Untreated stripped sour water from this oil refinery is a complex mixture of organic compounds (Burks and Wagner, 1984). Aliphatic hydrocarbons compose approximately 48% of the organics found in the wastewater stream, followed by oxygenated hydrocarbons at 25%, nitrogen heterocyclics at 20%, and alkyl aromatics at 7%. Results of a Phase II Toxicity Identification Evaluation (TIE) procedure using **Ceriodaphnia dubia** in a static 48-hour bioassay indicated acutely lethal contaminants were either nonpolar organics, weakly basic organics, or a combination of these fractions (Burks and Wagner, 1984).

Activated sludge and/or combined powdered activated carbon-activated sludge units are effective in reducing the discharge of biodegradable organics in refinery wastewaters to acceptable Best Practicable Treatment (BPT) or even Best Available Treatment Economically Achievable (BATEA) levels (DeJohn and Adams, 1975; Rizzo, 1976; Stenstrom and Grieves, 1977). However, little has been done in terms of evaluation for treatment of oil refinery wastewaters to the level of eliminating discharge of toxic contaminants in toxic amounts as measured by bioassays (Wong and Maroney, 1989).

Specifically, this research centered around evaluating the ability of an Aerated Submerged Biological Filter (ASBF) to reduce acute toxicity of process wastewater from a sour water stripper unit. The ASBF was the biological system of choice for several reasons. It incorporates the best features of both fixed-film and completely-mixed activated sludge units allowing instantaneous dilution of concentrated influents and maintenance of a high bacterial concentration (Hamoda and

Abd-El-Bary, 1987; Gonzalez, 1984; Rusten, 1984; Huang, 1982). This translates into a compact unit providing more intensive treatment than conventional biological treatment systems. Also, operation is comparatively simple relative to other biological systems because there are no moving parts and neither effluent recirculation nor sludge recycling is required for efficient operation. In addition, the ASBF can handle refinery effluents as well as shock loads of solvents and high strength phenolic wastes that commonly occur in oil refineries (Hamoda and Al-Haddad, 1987; Hamoda, Al-Haddad, and Abd-El-Bary, 1987; Bartoldi et al., 1987).

Acute toxicity reduction was measured with static 24-hour bioassays using **Ceriodaphnia dubia** and fathead minnows on unit influent and effluent. The ASBF was operated at three organic loading rates during the course of the experiment to determine system limits. Also, several conventional influent and effluent parameters were measured to help maintain steady-state conditions in the unit and check for observable correlations with acute toxicity. These parameters were flowrate, pH, Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Fixed Solids (FS), Chemical Oxygen Demand (COD), 5-day Soluble Biochemical Oxygen Demand (SBOD<sub>5</sub>), Total Kjeldahl Nitrogen (TKN), ammonia, sulfides, and phenols.

### EXPERIMENTAL DESIGN

A layout of the bench scale system used in this project is shown in Figure 1. The ASBF had a total empty bed reactor volume of 0.0127 m<sup>3</sup>. The media had a specific surface area of  $137 \text{ m}^2/\text{m}^3$ 



Figure 1. Schematic of the ASBF

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and was contained in 0.0096  $m^3$  giving a total media surface area in the unit of 1.32  $m^2$ . Additionally, the media occupied 0.0003  $m^3$  of the total empty bed reactor volume leaving a void volume of 0.0124  $m^3$ and a porosity of 97.6% in the unit.

The ASBF, shown in Figure 1, was an upflow unit. Influent from 26.5 liter reservoir bottles entered through a feed line in the center of the unit bottom. The media rested on a highly perforated plastic false bottom underneath which four four-inch long air diffusers were concentrically arranged to provide uniform air flow. The diffusers supplied 0.28  $m^3/hr$  of air to the system creating a completely mixed system. In such a system the concentration of influent substrate is uniform throughout the reactor (Grady and Lim, 1980). Aerobic conditions were also maintained in the unit by the air diffusers. Analyses and bioassays were made on grab samples. Influent samples were taken directly from feed bottles and effluent samples from a teflon spigot at the point where effluent drained from the unit. Soft plastic tubing has been suspected of leaching plasticizers which cause problems in bioassay tests so its use was avoided.

A dilute-in study was performed to insure completely mixed conditions would exist in the reactor. Theoretically, influent substrate in a completely mixed reactor is instantaneously diluted to a uniform concentration throughout the unit and is equal to the effluent concentration (Grady and Lim, 1980). The unit was filled with clear water and then a feed solution with a known dye concentration,  $(C_0)$ , was pumped into it. Air flow rate into the unit was maintained at a constant rate. In a completely mixed system, the effluent

concentration of dye at any time  $(C_t)$  can be calculated from the equation:

$$C_{+} = C_{0}(1 - e^{-Dt})$$

where D is the dilution factor or dilution rate and equals the flow (F) into the reactor divided by reactor volume (V), D = F/V (Grady and Lim, 1980). If completely mixed conditions exist within the reactor, the effluent dye concentration will gradually increase over time until it reaches influent concentration. Figure 2 shows predicted theoretical values and actual results of the tracer study.

The ASBF was operated based upon total organic loading rate rather than hydraulic loading rate since Kincannon and Stover (1984) and Hamoda and Abd-El-Bary (1987) demonstrated this to be the best operational parameter. Three organic loading rates were used in an effort to determine system limits. The first run was performed at an organic loading rate of 12.9 g COD/m<sup>2</sup> · day with a hydraulic residence time of 31.3 hrs. The second run was performed at an organic loading rate of 19.8 g COD/m<sup>2</sup> · day with a hydraulic residence time of 16.5 hrs and the third run at an organic loading rate of 32.0 g COD/m<sup>2</sup> · day with a hydraulic residence time of 12.4 hrs.

The unit was seeded with microorganisms from an aerated lagoon at the same oil refinery which provided the stripped sour water. The lagoon receives a waste stream coming directly from the sour water stripper. Due to this and because the lagoon has been in operation for over twenty years, no acclimation of microorganisms was needed. In addition, microorganisms were supplied nutrients in the form of  $KH_2PO_4$  and  $KNO_3$  according to a  $SBOD_5:N:P$  ratio of 100:5:1 in order to enhance growth conditions (Sawyer, 1956).



Figure 2. Theoretical versus actual results of dilute-in study performed on ASBF.

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Soluble Biochemical Oxygen Demand (SBOD<sub>5</sub>), Total Suspended Solids (TSS), Fixed Solids (FS), Volatile Suspended Solids (VSS), ammonia and Total Kjeldahl Nitrogen (TKN) were determined using the procedures outlined in <u>Standard Methods for the Examination of Water and</u> <u>Wastewater</u> (1976). Chemical Oxygen Demand (COD), sulfides, and phenols were measured using techniques described in the <u>Hach Water</u> <u>Analysis Handbook</u> (1982). A grab sample was taken each week of a run and analyzed for selected cations. Soluble metal concentrations were determined using Inductively Coupled Plasma Emission Spectroscopy (ICAP).

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Bioassays were performed with Ceriodaphnia dubia and fathead minnows and interpreted according to procedures outlined in "Methods for Measuring the Acute Toxicity of Effluent to Freshwater and Marine Organisms" (USEPA, 1985). A set of bioassays was performed each week during the two week sampling period. The  $LC_{50}s$  of bioassays performed during the first week with Ceriodaphnia and fathead minnows are designated as C1 (Ceriodaphnia, 1st week) and M1 (minnows, 1st week), respectively, in graphs. Those performed the second week are designated as C2 and M2. Bioassays were set up using seven cups for Ceriodaphnia and seven bowls for fathead minnows. Each container represented a different dilution factor. Dilutions started with 1% influent and effluent and went to 100% influent and effluent. Dilution water used in bioassays was classified as very hard (USEPA, 1985). Water used for dilutions was passed through a Photronix RGW-5 (Reagent Grade Water) system equivalent to the MILLIPORE MILLI- $Q^R$  system then rehardened with calcium sulfate (240 mg/l), magnesium sulfate (240 mg/l), sodium bicarbonate (384 mg/l), and potassium chloride

(16 mg/l) (USEPA, 1985). A blank set using only dilution water was also run to insure no mortality resulted from exposure to dilution water itself.

Ceriodaphnia were taken from groups cultured in very hard reconstituted water. Each cup contained five or six Ceriodaphnia and each bowl five or six fathead minnows. Mortality rate was monitored by counting surviving organisms at set time intervals over a 24-hour period. A series of dilutions was used to provide finer resolution of toxicity reduction occurring during tests.

A log-normal plot of percent wastewater volume versus percent of organisms surviving after 24 hours was used to calculate the  $LC_{50}$ . The  $LC_{50}$  is the lethal concentration (or in this case dilution) of sample that kills 50% of the test organisms over a set time interval. The 24-hour test period was selected to eliminate problems associated with low DO stress over time and because most acute toxic effects of oil refinery wastewater are exerted within the first 12 hours of a test (Matthews and Meyers, 1976). If the ASBF was unable to reduce acute toxicity, then further chronic testing would be unnecessary.

### RESULTS

Average concentrations of selected cations in untreated influent (prior to nutrient addition) are shown in Table 1. Physical-chemical characteristics of untreated influent stripped sour water are summarized in Table 2. Table 2 shows that while the refinery sour water stripping unit reduces sulfides to negligible levels, other contaminants, such as ammonia and COD, remain well over concentrations

				/	,			
Ca	Cr	Cu	Fe	K	Mg	Na	Se	Zn
1.0179	.0130	.0189	1.323	.0176	.1491	67.07	*	.0380

Table 1. Mean concentration (ppm) of selected cations in sour water (prior to nutrient addition).

\* - below detection limits

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Parameter	Mean	Minimum	Maximum
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		5.65	10.10
COD	1.753	1.350	2.360
SBOD	1,348	633	2,040
NH <sub>3</sub>	46.7	24.3	72.5
Sulfides	0.047	0.000	0.148
Phenols	240	174	327

Table 2. Means and ranges of values for physical-chemical characteristics of raw stripped sour water over the course of the entire experiment.\*

\*Values expressed in mg/l unless otherwise noted; pH is in SU.

toxic to aquatic life (USEPA, 1986). The complex nature of the waste stream makes it virtually impossible to trace reduction of any single compound through the ASBF. Gross measurements, such as reduction in COD, are basically the only useful parameters in attempting to determine the treatment ability of the ASBF in terms of organics removed.

A preliminary air stripping study was run. Stripped sour water was pumped through the unit with air diffusers operating and no biological growth on the media to determine if stripping of volatile compounds would cause a reduction in toxicity. A bioassay using only Ceriodaphnia dubia was performed with unit influent and effluent. Data from this bioassay are presented in Table 11 of the appendix.

Treatment success was assessed by determining the change in influent and effluent 24 hr  $LC_{50}$ s. Results are presented in Figure 9 along with results at the first loading rate. Surprisingly, air stripping significantly decreased the  $LC_{50}$ . This is in opposition to data obtained by Burks and Wagner (1984) and Matthews and Meyers (1976) that indicated much of the acute toxicity in oil refinery wastewaters is due to volatile contaminants. This decrease could possibly be attributed to contamination in the air supply system. The air supply was subsequently filtered through an activated carbon cartridge.

Prior to the start of each run, the ASBF was allowed to reach steady-state. Steady-state was operationally defined as having COD removal efficiency vary 10% or less for a week prior to the start of data collection. Wasting of solids was also performed as needed to maintain steady-state conditions in the unit. Data were collected for a two week period. Tables and figures in this paper present only data

collected during two week sampling periods. Data for entire runs, which include acclimation periods, are listed in the appendix.

The first run was performed at an average flow rate of 9.5 l/day giving a hydraulic retention time of 31.4 hrs and an average loading rate of 12.9 g  $COD/m^2$  · day. Physical-chemical data for the first run are listed in Table 12 of the appendix.

The ASBF neutralized or reduced all monitored parameters except ammonia. Figure 3 shows ASBF influent and effluent pH levels during the two week sampling period. Influent pH varied considerably from 5.65 to 10.10. Effluent pH remained around 7.75 during the sampling period.

Figure 4 depicts dissolved oxygen levels in the reactor bottom. Dissolved oxygen was monitored to assure anoxic conditions did not occur in the reactor bottom. Near the end of the sampling period dissolved oxygen levels dropped below below 2 mg/l. A corresponding gradual decrease in COD removal efficiency occurred until the DO level again rose above 2 mg/l (Figures 4 and 5). Also, a slight sudden increase in the loading rate corresponded exactly with the small sudden drop in COD removal efficiency at the end of the sampling period (Figure 5).

Maximum variability in COD removal efficiency was 14% for the data collection period. Removals of COD and SBOD<sub>5</sub> were 90% during the sampling period while phenols were reduced by 98%. Sulfides were negligible in both influent and effluent. Ammonia was increased by approximately 35 mg/l in the effluent.

Influent and effluent solids were also monitored. Figures 6, 7, and 8 show trends of TSS, VSS, and FS respectively in influent and



of 12.9 g COD/m2 \* day.



Figure 4. Dissolved oxygen concentration in bottom of ASBF for loading of 12.9 g COD/m2 \* day.



Figure 5. Loading rate (g COD/m2 \* day) and percent COD removal versus time for first run.



Figure 6. Total suspended solids concentration at loading of 12.9 g COD/m2 \* day.



loading of 12.9 g COD/m2 \* day.



effluent during the first sampling period. It appears from comparisons of these three figures the sudden rise and fall in effluent VSS near the end of the first sampling period was probably due to expiration and subsequent wash-out of bacteria caused by the earlier drop of DO levels in the reactor bottom.

A set of bioassays, using **Ceriodaphnia dubia** and fathead minnows, was performed each week of a sampling period. Bioassays denoted C1 and M1 in the Figures 9, 16, and 23 were performed during the first week of a sampling period and C2 and M2 the second week. Both species were used to determine if samples were more toxic to one than the other.

Physical-chemical characteristics of sour water used in the bioassays are shown in Table 3. Concentrations of selected cations in the ASBF influent and effluent (after nutrient addition) for the first and second weeks of this samping period are shown in Tables 4 and 5.

Bioassays showed the  $LC_{50}$  was increased after treatment by the ASBF in all cases (Figure 9). However, the increase in  $LC_{50}$  was greater for the first bioassay (Cl=Ceriodaphnia,Ml=minnows) than for the second. Also, the increase in the  $LC_{50}$  was greater for Ceriodaphnia than for fathead minnows in both cases. Examination of Table 3 shows no particular correlation of toxicity with any one parameter although both influent and effluent COD and SBOD<sub>5</sub> were higher during the second set of assays. Survival data for the bioassays are shown in Tables 13, 14, 15, and 16 of the appendix.

The second evaluation of toxicity reduction was performed at an average flow rate of 18 l/day giving a hydraulic retention time of 16.5 hrs and an average organic loading rate of 19.8 g  $COD/m^2$  · day.

Parameter	I-1	E-1	I-2	E-2	
рН	6.45	7.75	6.65	7.85	
COD	1,700	200	1,840	235	
SBOD5	633	42	1,524	107	
NH <sub>3</sub>	50.0	84.0	53.1	84.4	
Sulfides	?	?	0.101	0.071	
Phenols	,		300.0	5.70	

Table 3. Influent and effluent physical-chemical characteristics of stripped sour water used in bioassays at loading of 12.9 g  $COD/m^2 * day$ .

I - influent, E - effluent

1 - assay performed during week 1 of test run.

2 - assay performed during week 2 of test run.
\*Values expressed in mg/l unless otherwise noted; pH is in SU.
? - Below detection limits

Na	Ca	Mg	K	Fe	Zn	Cu	Cr	Se
Influent 58.02	: 4.853	.7904	6.162	.1476	.1772	.0076	*	*
Effluent 60.20	5.615	.6897	281.3	.1283	.0282	*	*	.2098

Table 4. Concentration (ppm) of selected cations in ASBF influent and effluent during first week of loading at 12.9 g  $COD/m^2 * day$ .

\* - below detection limits

Table 5.	Concen influe at 12.	tration ent and 9 g COD	(ppm) effluen /m <sup>2</sup> * d	of sele t durin ay.	cted ca g secon	tions in dweek (	n ASBF of loa	ding
Na	Ca	Mg	K	Fe	Zn	Cu	Cr	Se
Influent 62.57	: 6.708	1.262	29.40	.1057	.6756	.2019	*	*
Effluent 58.63	7.058	1.115	206.9	.1634	.1061	.0076	*	.2157

\* - below detection limits

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water at loading of 12.9 g COD/m2 \* day.

Physical-chemical data for the second run are listed in Table 17 of the appendix.

Once again the ASBF reduced all monitored parameters except ammonia. Influent pH varied between 6.55 and 6.90 for the run (Figure 10). Effluent pH was slightly more alkaline than at the first organic loading rate, remaining close to 8.00. Dissolved oxygen levels in the reactor bottom remained well above 2 mg/l (Figure 11).

Loading rate and COD removal efficiency for the second run are illustrated in Figure 12. Maximum variability in COD removal efficiency was 8% during the sampling period, although COD removal efficiency declined to an average of 82% compared to 90% at the first loading rate. Decline in SBOD<sub>5</sub> removal was much less with 88% being removed on the average versus 90% at the first loading rate. Sulfide levels were again negligible in influent and effluent. Phenol removal efficiency remained, as in the first loading rate, at 98%. Ammonia levels were once again increased in the effluent.

Influent and effluent solids levels for the second loading rate are illustrated in Figures 13, 14, and 15. Total suspended solids content of the effluent was quite high at the beginning of the run (Figure 13). Comparison of Figures 13 and 15 shows this to be due to a high influent fixed solids concentration. The high fixed solids concentration of the influent was probably related to the age of water samples being treated. Stripped sour water was stored in 55-gallon teflon-lined drums and fixed solids concentrations tended to increase after a certain storage period. There was a transition from an old to a fresh batch of sour water at the beginning of the second run hence the high fixed solids concentration in the influent at the start. For





ASBF for loading of 19.8 g COD/m2 \* day.


Figure 12. Loading rate (g COD/m2 \* day) and percent COD removal versus time for second run.



Figure 13. Total suspended solids concentration at loading of 19.8 g COD/m2 \* day.

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this particular run, COD removal efficiency appeared to roughly correspond with VSS concentrations in the effluent.

Physical-chemical characteristics of the sour water used in the bioassays are listed in Table 6. Table 7 lists concentrations of selected cations in the influent and effluent during the second run. It should be noted that the influent SBOD<sub>5</sub> value in Table 6 exceeds the COD and therefore is probably incorrect. SBODs were performed with bacteria from a separate batch culture maintained in the lab therefore some SBOD<sub>5</sub> values that are either a large percentage of or greater than the COD may be unreliable since, at times, batch reactor growth conditions may not have been the same as growth conditions in the ASBF. Bioassay results are depicted in Figure 16. Survival data from bicassays are given in Tables 18, 19, 20, and 21 of the appendix.

Comparison of wastewater characteristics in Table 6 again shows no particular correlation with results shown in Figure 16. However, the ASBF continued to reduce effluent toxicity (i.e. increased  $IC_{50}$ ) in all cases. The effluent  $IC_{50}$  for minnows was only slightly higher than that of the influent in both sets of bioassays. Conversely, the effluent  $IC_{50}$  for **Ceriodaphnia** in the first bioassay (C1) was tripled compared to that of the influent and almost doubled for the second bioassay (C2).

The final test run was performed at an average flowrate of 24.0 l/day giving a hydraulic residence time of 12.4 hrs and an average organic loading rate of  $32.0 \text{ g COD/m}^2$  · day. Table 22 in the appendix contains physical-chemical data for the third sampling period.

Treatment with the ASBF again reduced all monitored parameters including ammonia. Reductions were, as expected, somewhat less than

Parameter	I-1	<b>E-1</b>	I-2	E-2
рН	6.65	8.09	6.50	8.05
COD	1,550	135	1,500	330
SBOD5			1,635	206
NH <sub>3</sub>	54.0	72.0	47.0	55.0
Sulfides			0.132	0.092
Phenols	174.0	3.0		

Table 6. Influent and effluent physical-chemical characteristics of stripped sour water used in bioassays at loading of 19.8 g COD/m<sup>2</sup> \* day.

I - influent, E - effluent

1 - assay performed during week 1 of test run.

2 - assay performed during week 2 of test run. \*Values expressed in mg/l unless otherwise noted; pH is in SU.

Concentration (ppm) of selected cations in ASBF
influent and effluent at loading of
19.8 g COD/m <sup>2</sup> * day.

Ca	Cr	Cu	Fe	K	Mg	Na	Se	Zn
Influent .9102	.0089	.0167	.0919	73.90	.0687	28.82	.0085	.0549
Effluent .8578	.0089	.0025	1.060	182.4	.1246	29.71	.2986	.0206

,ª 1

\* - below detection limits



those for the first two runs since the unit appeared to be operating close to its maximum organic loading capacity. Influent pH varied between 9.00 and 9.41 while effluent pH ran between 7.60 and 8.45 (Figure 17). Dissolved oxygen levels in the reactor bottom remained above 3.5 mg/l (Figure 18). An increase in organic loading rate of 3 g  $COD/m^2$  · day between day 5 and day 8 corresponded with an appoximate 30% drop in %COD removal (Figure 19). During the two previous sampling periods such small loading rate fluctuations did not correspond with any proportionally large drops in %COD removal. As a result, there was a maximum variance of 41% in %COD removal over the sampling period.

Average reductions of 49% in COD and 64% in SBOD<sub>5</sub> resulted from treatment with the ASBF. Again, sulfides were negligible in both influent and effluent while 90% removal of phenols was maintained. Ammonia levels were substantially lower in the influent and actually decreased by about 2 to 4 mg/l after passage through the ASBF.

Solids data are presented in Figures 20, 21, and 22. Effluent TSS content was high at the beginning of the run due to large amounts of VSS in the effluent (Figures 20 and 21). A possible explanation for this can be seen in a comparison of Figures 18 and 21. This comparison shows that effluent VSS content follows an inverse trend seen in DO levels in the reactor bottom. Since DO levels never fell below 3.5 mg/l during the run, this suggests a relatively higher DO concentration is required in the unit to maintain healthy bacterial respiration at this high loading rate and prevent wash-out.

Physical-chemical characteristics of wastewater used in the bioassays are given in Table 8. Concentrations of selected influent





Figure 18. Dissolved oxygen concentration in bottom of ASBF for loading of 32.0 g COD/m2 \* day.





Figure 20. Total suspended solids concentration at loading of 32.0 g COD/m2 \* day.



loading of 32.0 g COD/m2 \* day.



r			1	
Parameter	<b>I–1</b>	<b>E-1</b>	I-2	E-2
pH	9.30	8.30	9.30	8.40
COD	1,880	1,190	2,020	1,120
SBOD5		- 		
NH3	24.3	20.0	25.5	23.9
Sulfides	0.0	0.0	0.0	0.0
Phenols				
		,		

Table 8. Influent and effluent physical-chemical characteristics of stripped sour water used in bioassays at loading of  $32.0 \text{ g COD/m}^2 * \text{day.}^*$ 

I - influent, E - effluent

1 - assay performed during week 1 of test run. 2 - assay performed during week 2 of test run. \*Values expressed in mg/l unless otherwise noted; pH is in SU.

and effluent cations during the first and second weeks of the sampling period are shown in Tables 9 and 10. Results of the bioassays are shown in Figure 23. Survival data for bioassays are presented in Tables 23, 24, 25, and 26 of the appendix. As Figure 23 shows, even with the system operating close to its maximum organic loading capacity, the 24-hour  $IC_{50}$  was increased in all cases by ASBF treatment. For both sets of bioassays, however, the increase was greater for fathead minnows than for **Ceriodaphnia** unlike the first two sampling periods. The increase in  $IC_{50}$  was obviously also much greater for the first set of bioassays (C1, M1) run during the final loading rate since the  $IC_{50}$  of this set was at least tripled for both types of test organisms. Examination of Table 8 again shows no obvious correspondences with toxicity changes seen in the waste stream although ammonia, which tends to be more toxic to fish, was slightly lower in the effluent used to perform the first set of bioassays.

#### CONCLUSIONS

The main thrust of this research project was to evaluate with biological assays the ability of the ASBF to reduce acute toxicity of a process wastewater from a sour water stripping unit. There appeared to be no observable correlation between toxicity and any monitored parameters. However, more extensive chemical analysis and comparisons would be necessary to establish statistically valid correlations. Undoubtedly, at lower dilutions the high ammonia concentrations must impart some toxicity to both the influents and effluents tested in this experiment. Comparison of calculated 24 hr  $IC_{50}$  ammonia

							r	
Ca	Cr	Cu	Fe	K	Mg	Na	Se	Zn
Influent .6838	.0089	.0302	.7701	19.20	*	149.5	•5825	.0137
Effluent .8645	*	*	1.968	119.0	*	152.5	.0199	.0538

Table 9. Concentration (ppm) of selected cations in ASBF influent and effluent during first week of loading at 32.0 g  $COD/m^2 * day$ .

\* - below detection limits

	loadir	ng at 3	2.0 g C	$OD/m^2 * c$	day.	¥		
		·	···· · · · · · · · ·	، م				
Ca	Cr	Cu	Fe	К	Mg	Na	Se	Zn
Influent .4297	*	× 、	.1488	120.1	*	149.6	.5347	*
Effluent .5671	*	*	.4557	114.9	*	153.3	*	*

Table 10. Concentration (ppm) of selected cations in ASBF influent and effluent during second week of loading at 32.0 g  $COD/m^2 * day$ .

\* - below detection limits

3



concentrations in the influents and effluents tested with values found in the literature (Mount and Anderson-Carnahan, 1989) and through personal communications (Stebler, 1990) for Ceriodaphnia and fathead minnows shows no correspondence. However, refinery wastewaters contain such complex mixtures of organic and inorganic compounds that ammonia may not be the prinicipal toxicant in the waste stream. Ammonia may, for instance, be acting synergistically with other toxicants in the wastewater stream such as non-polar organics. As noted earlier, TIE results indicated non-polar organics seem to be the primary cause of toxicity. This would tend to explain why no obvious connections were seen between the physical-chemical data and toxicity levels.

A satisfactory explanation for increased effluent ammonia levels during the first and second loading rates was not found. The ASBF appears, however, to be reducing wastewater toxicity in all cases. It should be kept in mind that wastewaters coming directly off a process unit are treated in this experiment. Process wastewaters such as those used in this research have CODs and BODs that are at least two to three times greater than those of municipal wastewater. Therefore the absence of huge decreases in toxicity should not necessarily be taken as a sign of poor reactor performance. The ASBF has potential in terms of both economics and treatment ability due to its compact size, ease of operation relative to other biological systems, and demonstrated ability to remove waste stream toxicity.

#### REFERENCES

- Bartoldi, A.J., Hillard, G.E., and Blair, J.E. (1987) Utilizing High Rate Fixed-Film Biological Technology to Control Upset Conditions in Refinery Wastewater Treatment Systems. Proc. 42nd Ind. Waste Conf., Purdue Univ., West Layfayette, IN, 85-92.
- Burks, S.L. and Wagner, J. (1984) Characterization and Treatment of Aqueous Wastes and Residue from Petroleum Refineries. EPA-600/52-83-089.
- Burks, S.L., Wagner, J., and Oil Refiners Waste Control Council. (1989) Proposal for Cooperative Toxicity Identification Evaluation and Toxicity Reduction Evaluation of Oil Refinery Wastewaters. Oklahoma State University Water Quality Research Lab, Oklahoma State University, Stillwater, OK, 31 pp.
- DeJohn, P.B., and Adams, A.D. (1975) Treatment of Oil Refinery Wastewaters with Granular and Powdered Activated Carbon. Proc. Ind. Waste Conf., Purdue Univ., West Layfayette, IN, 1640-1657.
- Gonzalez, Reinaldo. (1984) Evaluation of an Aerated Submerged Biological Filter in the Treatment of Alcohol Wastewater. M.S. Thesis. Oklahoma State University, Stillwater, OK. 49 pp.
- Grady, C.P., and Lim, H.C. (1980) Biological Wastewater Treatment, Theory and Applications. Pollution Engineering and Technology/12, Marcel Dekker, Inc., New York.

Hach Water Analysis Handbook. (1982) Hach Company.

- Hamoda, M.F. and Al-Haddad, A.A. (1987) Investigation of Petroleum Refinery Effluent Treatment in an Aerobic Fixed-Film Biological System. J. Inst. Wat. Environ. Manage. 1, 239-246.
- Hamoda, M.F. and Abd-El-Bary, M.F. (1987) Operating Characteristics of the Aerated Submerged Fixed-Film (ASFF) Bioreactor. Wat. Res. 21, 939-947.
- Hamoda, M.F., Al-Haddad, A.A., and Abd-El-Bary, M.F. (1987) Treatment of Phenolic Wastes in an Aerated Submerged Fixed-Film (ASFF) Bioreactor. J. Biotech. 5, 279-292.
- Huang, C.S. (1982) The Air Force Experience in Fixed-Film Biological Processes. Proc. 1st Intern. Conf. on Fixed-Film Biol. Processes. 3, 1777-1789.

- Kincannon, D.F., and Stover, E.L. (1984) Biological Treatability Data Analysis of Industrial Wastewaters. Proc. 39th Ind. Waste Conf., Purdue Univ., West Layfayette, IN.
- Matthews, J.E. and Myers, L.H. (1976) Acute Toxic Effects of Petroleum Refinery Wastewaters on Redear Sunfish. EPA-600/2-76-241.
- Mount, D.I. and Anderson-Carnahan, L.A. (1988) Methods for Aquatic Toxicity Identification Evaluations: Phase II Toxicity Identification Procedures. EPA/600/3-88/035.
- Reece, C.H. and Burks, S.L. (1985) Isolation and Chemical Characterization of Petroleum Refinery Wastewater Fractions Acutely Lethal To Daphnia magna. Aquatic Toxicology and Hazard Assessment; 7th Symposium, 319-332.
- Rizzo, J.A. (1976) Case History: Use of Powdered Activated Carbon in an Activated Sludge System. Proceedings of the Open Forum on Management of Petroleum Refinery Wastewaters, 359-367.
- Rusten, B. (1984) Wastewater Treatment with Aerated Submerged Biological Filters. J. Wat. Poll. Cont. Fed. 56, 424-431.
- Sawyer, C.N. (1956) Bacterial Nutrition and Synthesis. <u>Biological</u> <u>Treatment of Sewage and Industrial Wastes</u>. Vol.1, Reinhold, New York.
- Smith, G.J. (1987) Correlation Between Trace Contaminant Mixtures in Complex Effluents and Structure of Benthic Macroinvertebrates. Ph.D. thesis, Oklahoma State University, Stillwater, OK, 219 pp.
- <u>Standard Methods for the Examination of Water and Wastewater</u>. (1976) American Public Health Assoc., American Wat. Works Assoc., and Wat. Poll. Cont. Fed., 14th Edition.
- Stebler, E. (1990) Personal Communication. Water Quality Research Lab, Oklahoma State University, Stillwater, OK.
- Stenstrom, M.K., and Grieves, C.G. (1977) Enhancement of Oil Refinery Activated Sludge by Addition of Powdered Activated Carbon. Proc. 32nd Ind. Waste Conf., Purdue Univ., West Layfayette, IN, 23 pp.
- U.S. Environmental Protection Agency. (1985) Methods of Measuring the Acute Toxicity of Effluent to Freshwater and Marine Organisms. EPA 600/85-013. Washington, D.C.
- U.S. Environmental Protection Agency. (1986) Quality Criteria for Water Regulations and Standards. EPA 440/5-86-001. Washington, D.C.
- U.S. Environmental Protection Agency. (1987) Permit Writer's Guide to Water Quality-based Permitting for Toxicity Pollutants. EPA 440/4-87-005.

Wong, J.M. and Maroney, P.M. (1989) Pilot Plant Comparison of Extended Aeration and Pact<sup>R</sup> for Toxicity Reduction in Refinery Wastewater. Proc. 44th Ind. Waste Conf., Purdue Univ., West Layfayette, IN. . . .

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### APPENDIX

Conc. of Waste		No. of Test		]	No. Cer	iodaphn	ia alive	e at
(% by vol.)	~	Animals	3 hrs	10 hrs	21 hrs	27 hrs	34 hrs	48 hrs
Controls	INFL	5	4	4	4	4	4 .	4
(0%)	EFFL	5	5	5	5	ຸ 5	5	5
1%	INFL	5	5	5	- 5	5	<sup>°</sup> 5	5
	EFFL	5.	5	5	5	5	5	5
3%	INFL	5	5	5	5	5	4	4
	EFFL	5	5	5	5	5	5	1
10%	INFL	5	5	5	5	0	0	
	EFFL	6	6	6	6	3	2	0
30%	INFL	5	5	4	3	3	1	1
	EFFL	5	2	2	2	0	` <b></b>	
100%	INFL	5	0					
	EFFL	5	0					

# Table 11. Raw data for bioassay performed during air stripping study with Ceriodaphnia.

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рН	COD (mg/l)	%COD REDUCED	TSS (mg/l)	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/l)	NH3 (mg/l)	TKN (mg/l)	PO4 (mg/l)	SULFIDES (mg/l)	PHENOLS (mg/l)
INFL EFFL	10-11-89	6.40		10.10 8.55	2140 1920	10.2	2.5	1.5	1.0	1068 810	25.0 10.0			250	260
INFL EFFL	10-2 <b>3-89</b>	6 <b>.9</b> 0		8.30 7.60	1900 620	67.3	2.5 47.0	1.5 2.0	1.0 45.0		25.0 10.0	3.5 12.5		-	
INFL EFFL	10-31-89	6.70	X	9.30 8.10	2100 880	58.1		r.		-		-		-	
INFL EFFL	11-06-89	8.30			1920 1440	25.0				,					
INFL Effl	11-9-89	6.80		10.00 8.00	1840 1420	22.8							、		
INFL EFFL	11-13-89	7.10			1960 1160	40.8									
INFL EFFL	11-16-89	7.00	4.20	9.95 7.75	1820 1204	33.8				1068			0.09		
INFL EFFL	11-20-89	7.75	3.80	10.05 7.95	1900 640	66.3	6.5 9.5	3.5 0.5	3.0 9.0						

~

Table 12. Raw physical-chemical data collected at loading rate of 12.9 g COD/m2 \* day.

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рH	COD (mg/l)	%COD REDUCED	TSS (mg∕l)́	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/ŀ)	NH3 (mg/l)	TKN (mg/l)	PO4 (mg/l)	SULFIDES (mg/l)	PHENOLS (mg/l)
INFL	11-23-89			~ ~ ~	2020	70.6	3.0 -	3.0	0.0			- 1	, ,	*	-
EFFL					592	`	18.5	.3.0	15.5					-	-
INFL	12-01-89		د م		1780	78.6						-			
EFFL					-380 -	•					~		-		
INFL	12-04-89	5.20		9.55	<b>1980</b> .	72.7	32.0	10.5	21.5				-		
EFFL	~			7.80	540	-	14.5	3.0	11.5	-	~	2°	-	-	
INFI	12-07-89	4.80		9,50	1900	71.5	13.0	6.0	7.0				-	- 1	
EFFL				8.00	540		16.0	6.0	10.0	· •	-				
INFI	12-12-89	7 50		9 65	1760	64 7	10 0	5.0	5.0	د.	-	,			
EFFL	12 12 O7	1.50		8.10	620	0411	24.0	9.0	15.0			2			
INFI	12-21-80				1800	85 6		-		1688	38 5	30.0	0 04		
EFFL	12 21 07		v	,	260	0,10				1000		^	0104		
TNEI	01-03-00	7 30	2 05	5 75	1540	87 N	20 N	5.0	24 0						
EFFL	01 03 70	,	<b>L.</b> /J	7.60	200	0,10	29.0	4.0	25.0						-
TNEI	01-0/-90	6 20	6 20	5 45											
EFFL	01-04-70	0.20	0.20	7.60											

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рН	COD (mg/l)	%COD REDUCED	TSS (mg/l)	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/l)	NH3 (mg/l)	TKN (mg/l)	PO4 (mg/l)	SULFIDES (mg/l)	PHENOLS (mg/l)
INFL EFFL	01-05-90	5.60	4.30	6.30 7.75	2360 220	90.7	13.0 12.0	3.0 1.0	10.0 11.0	-					
INFL EFFL	01-06-90	6.85	3.20	6.40 7.75			, ,				- ,			e e	x
INFL EFFL	01-07-90	6.23	2.60	6.10 7.85	1960 204	89.6	29.0 44.0	6.0 2.0	23.0 42.0	633 - 42				0.000 - 0.000	<i>.</i>
INFL EFFL	01-08-90	8.00	3.65	6.70 7.85											
INFL EFFL	01-09-90	7.14	2.10	6.45 7.75	1700 200	88.2	19.0 38.0	4.0 5.0	15.0 33.0		50.0 84.0	64.5 2.5.	ι	0.000 0.000	
INFL EFFL	01-10-90	4.65	2.25	6.85 7.80						n_ ~		~	-	Ŧ	
INFL EFFL	01-11-90	7.00	2.60	6.60 7.75	2300 160	93.0	6.0 133.0	2.0 11.0	4.0 122.0	-	x			-	
INFL EFFL	01-12-90	6.40	4.60	6.65 7.75	-			-							

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рН	COD (mg/l)	%COD REDUCED	TSS (mg/l)	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/l)	NH3 (mg/l)	TKN (mg/l)	PO4 (mg/l)	SULFIDES (mg/l)	PHENOLS (mg/l)
INFL EFFL	01-13-90	7.60	3.40	6.75 7.85	1780 205	88.5	4.0 84.0	3.0 7.0	1.0 77.0		·			-	
INFL EFFL	01-14-90	6.60	2.70	6.55 7.65					-						
INFL EFFL	01-15-90	6.00	3.25	6.35 7.90	1600 220	86.3	14.0 38.0	2.0 3.0	12.0 35.0			* e			
INFL EFFL	01-16-90	7.00	3.60	6.60 7.85											
INFL EFFL	01-17-90	7.20	2.60	6.40 7.75	1640 155	90.6	13.0 19.0	1.0 4.0	12.0 15.0					<u>۔</u>	
INFL EFFL	01-18-90	5.30	2.00	6.70 7.85								-			
INFL EFFL	01-19-90	5.26	2.10	6.40 7.80	2000 185	90.8	16.0 50.0	5.0 5.0	11.0 45.0						
INFL EFFL	01-21-90	6.35	0.80	6.45 7.80	1620 175	89.2	54.0 47.0	17.0 5.0	37.0 42.0						

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рH	COD (mg/l)	%COD REDUCED	TSS (mg/l)	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/l)	NH3 (mg/l)	TKN (mg/l)	PO4 (mg/l)	SULFIDES (mg/l)	PHENOLS (mg/l)
INFL	01-22-90	6.33	2.80	6.30				-							~
EFFL				7.65									-		
INFL	01-23-90	4.40	1.50	6.65	1840	87.2	27.0	5.0	22.0		53.1	7.8	0.101	300.0	
EFFL	ı	,		7.85	235		368.0	26.0	342.0		84.4	1.6	0.071	5.7	
INFL	01-24-90	7.69	2.10	6.75						1524					
EFFL	-			7.80						106	-			~	
INFL	01-25-90	9.90		6.55	1620	79.9	33.0	6.0	27.0				-		
EFFL				7.70	325		137.0	11.0	126.0					~ 1	
INFL	01-26-90	7.00	2.18	6.65											
EFFL				7.70											
INFL	01-29-90	5.40	0.55	6.35	1760	87.2	24.0	8.0	16.0						
EFFL				7.70	225		118.0	12.0	106.0			-			
INFL	01-31-90	6.63	2.50	6.60	1720	85.8	11.0	1.0	10.0						
EFFL				7.80	245		54.0	4.0	50.0						
INFL	02-02-90	7.60	2.30	6.85	1740	87.1					72.5			252.0	
EFFL				7.85	225						86.3			3.6	

Conc. of Waste	x	No. of Test	No. fathead minnows alive at										
(% by vol.)		Animals	2 hrs	4 hrs	7 hrs	10 hrs	20 hrs	24 hrs	35 hrs	48 hrs			
Controls	INFL	5	5	5	5	5	5	5	5	5			
(0%)	EFFL	5	5	5	5	5	5	5	, 5	5			
1%	INFL	5	5	5	5	5	- 5	5	5	5			
	EFFL	5	- 5	5	5	5	.5	5	5	5			
3%	INFL	5	5	5	5	5	5	5	5	5			
	ELLT	C.	S	5	<b>Э</b>	4	4	4	4	4			
10%	INFL	5	5	5	3	2	2	2	2	2			
-	EFFL	5	5	5	5	5	5	4	3	3			
30%	INFL	5	5	3	0								
	$\mathbf{EFFL}$	5	5	4	0								
50%	INFL	5	0										
	$\mathbf{EFFL}$	5	5	0									
100%	INFL	5	0										
	EFFL	5	0										

### Table 13. Raw data for first bioassay performed with fathead minnows at loading rate of 12.9 g COD/m2 \* day.

Conc. of Waste		No. of Test			No. Ce	eriodaph	nia aliv	re at		
(% by vol.)		Animals	2 hrs	4 hrs	7 hrs	10 hrs	20 hrs	24 hrs	35 hrs	48 hrs
Controls	INFL	5	. 5	5	5	5	5	5	5	5
(0%)	EFFL	5	5	5	5	5	5	5	5	5
1%	INFL	5	5	5	5	5	5	5	3	2
_ •	EFFL	5	5	5	5	5	5	5	5	5
3%	INFL	5	5	5	5	5	0			
	EFFL	5	5	5	5	5	5	5	5	5
10%	INFL	5	5	5	5	2	0			
	EFFL 2	5	5	5	5	5	5	5	5	5
30%	INFL	5	3	0			^ <b></b>			
	EFFL	5	5	5	5	3	0			
50%	INFL	5	0							
	EFFL	5	5	2	2	0				
100%	INFL	5	0							
	EFFL	5	0							

### Table 14. Raw data for first bioassay performed with Ceriodaphnia at loading rate of 12.9 g COD/m2 \* day.

Conc. of Waste		No. of Test	No. fathead minnows alive at										
(% by vol.)		Animals	1 hrs	2 hrs	4 hrs	8 hrs	20 hrs	24 hrs	48 hrs				
Controls	INFL	5	5	5	5	5	5	5	5				
(0%)	EFFL	5	5	5	5	5	5	-5	5				
1%	INFL	5	5	5	5	5	5	5	4				
	EFFL	5	5	5	4	4	4	4	4				
3%	INFL	5	5	4	4	4	4	3	2				
	EFFL	5	5	4	4	4	4	4	4				
10%	INFL	5	5	5	4	1	1	1	0				
	EFFL	5	5	5	5	2	1	0					
30%	INFL	5	5	0									
	EFFL	5	5	1	0								
50%	INFL	5	1	0									
	EFFL	5	0										
100%	INFL	5	0	^									
	EFFL	5	0										

# Table 15. Raw data for second bioassay performed with fathead minnows at loading rate of 12.9 g COD/m2 \* day.

Conc. of Waste		No. of Test	No. Ceriodaphnia alive at										
(% by vol.)		Animals	1 hrs	2 hrs	4 hrs	8 hrs	20 hrs	24 hrs	48 hrs				
Controls	INFL	5	5	5	5	5	5	5	5				
(0%)	EFFL	5	5	5	5	5	5	5	5				
1%	INFL	5	5	5	5	5	- 5	5	3				
	ELLT	5	5	5	5	5	5	5	· 4				
3%	INFL EFFL	5 5	5 5	5 5	5 5	5 5	5 5	5 5	3 5				
10%	INFL	5	5	5	5	5	2	2	0				
	EFFL	4	4	4	4	4	2	2	0				
30%	INFL	5	3	2	0								
	БГГГ	4	2	2	T	T	U						
50%	INFL												
	EFFL								<b>6400</b> 6600				
100%	INFL												
	EFFL												

Table 16.	Raw data for second bioassay performed with Ce	eriodaphnia
	at loading rate of 12.9 g COD/m2 * day.	

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рH	COD (mg/l)	%COD REDUCED	TSS (mg/l)	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/l)	NH3 (mg/l)	TKN (mg/l)	PO4 (mg/l)	SULFIDES (mg/l)	PHENOLS (mg/l)
INFL	02-13-90	13.40		8.85	2440	65.4				-					
EFFL				7.90	845							-			
INFL	02-14-90	12.70		8.95	2500	53.6		~		2535					
EFFL				7.80	1160										
INFL	02-16-90	15.10	3.10	8.95	2400	64.6				-	,				
EFFL				7.80	850										
INFL	02-18-90	13.00	1.10	8.55	2150	53.5						9.5	0.095	<b>N</b>	
EFFL				8.00	1000										
INFL	02-20-90	11.80	0.40	9.07	2750	55.6									
EFFL				8.00	1220										
INFL	02-26-90	11.20	0.25	8.50	2350	62.6									
EFFL				8.05	880										
INFL	03-01-90	12.00	2.20	9.60	2700	44.8									
EFFL				8.50	1490										
INFL	03-05-90	12.80	2.60	9.59	2750	44.7									
EFFL				8.50	1520										

Table 17. Raw physical-chemical data collected at loading rate of 19.8 g COD/m2 \* day.
## Table 17 (Continued)

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рН	COD (mg/l)	%COD REDUCED	TSS (mg/l)	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/l-)	NH3 (mg/l)	TKN (mg/l)	PO4 (mg/l)	SULFIDES (mg/l)	PHENOLS (mg/l)	`
												*		. *		-
INFL	03-07-90		~		2500	44.0		-	- /							
EFFL			1		1400			2						~		
INFL	03-12-90			-	2500	50.4	-									
EFFL	-				1240		ł									-
INFL	03-16-90				2400	56.7			د ب ب		ref.		~	4		
EFFL		~		-	1040	-										
INFL	03-18-90	I			2700	64.4									ma	
EFFL		-			960							-				
INFL	03-21-90			, 	2700	70.3				1235				<i>t</i> `		
EFFL					800						~			-		
INFL	03-28-90				1600	80.6			**		47.3	5.3	0.020			
EFFL					310							•				
INFL	03-30-90				1350	80.7										
EFFL				,	260											
INFL	04-01-90				1650	85.5										
EFFL	-				240				~							

Table 17 (Continued)

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рН	COD (mg/l)	%COD REDUCED	TSS (mg/l)	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/l)	NH3 (mg/l)	TKN (mg/l)	PO4 (mg/l)	SULFIDES (mg/l)	PHENOLS (mg/l)
INFL EFFL	04-02-90	11.10	4.80	6.65 8.09	1550 135	82.6	421.0 537.0	419.0 424.0	2.0 113.0		54.6 71.6	1.5 0.3			
INFL Effl	04-04-90	13.20	4.65	6.90 7.85	1450 270	81.4	4.0 130.0	3.0 20.0	1.0 110.0						174.0 3.0
INFL EFFL	04-06-90	11.30	5.40	6.70 8.00	1350 210	84.4	2.0 200.0	1.0 <b>30.</b> 0	1.0 170.0			-		x	-
INFL Effl	04-08-90	14.50	5.00	6.55 8.05	1490 304	79.6	15.0 160.0	4.0 20.0	11.0 140.0	1170 127			Y	0.148 0.050	
INFL EFFL	04-10-90	11.00	6.20	6.50 8.05	1500 330	78.0	3.0 100.0	2.0 20.0	1.0 80.0		47.0 54.6	0.3 0.1		0.132 0.092	216.0 0.6
INFL EFFL	04-12-90	13.90	5.75	6.60 8.00	1490 330	77.0	20.0 70.0	4.0 20.0	16.0 50.0	1635 206					

Conc. of Waste		No. of Test			No. fat	head mi	nnows al	ive at
(% by vol.)		Animals	1 hrs	2 hrs	4 hrs	8 hrs	24 hrs	48 hrs
Controls	INFL	5	5	5	5	5	5	5
(0%)	EFFL	5	5	5	5	5	5	5
1%	INFL	5	5	5	5	5	5	4
	EFFL	5	5	5	5	5	5	5
3%	INFL	5	5	5	5	5	5	5
	EFFL	5	5	5	5	5	5	5
10%	INFL	5	5	5	5	3	3	2
	EFFL	5	5	5	5	5	5	5
30%	INFL	5	5	5	0			
	EFFL	5	5	4	3	3	0	
50%	INFL	5	5	0				
	EFFL	5	5	4	1	0		
100%	INFL	5	0					
	EFFL	5	0					
		18-18-19-19-19-19-19-19-19-19-19-19-19-19-19-						

Table 18. Raw data for first bioassay performed with fathead minnows at leading of 19.8 g COD/m2 \* day.

Conc. of Waste		No. of Test			No. Cer	iodaphn	ia alive	e at
(% by vol.)		Animals	1 hrs	2 hrs	4 hrs	8 hrs	24 hrs	48 hrs
Controls	TNFT.	5	5	· 5	5	 5	5	5
(0%)	EFFL	-5 	5	5	5	5	5	5
18	TNFT.	5	5	5	5	5	5	5
<b>±</b> 0	EFFL	5	5	5	5	5	5	5
3%	INFL	5	5	5	5	5	5	3
	EFFL	5	5	5	5	5	5	5
10%	INFL	5	5	5	5	5	2	1
-	EFFL	5	5	5	5	5	5	5
30%	INFL	5	5	3	2	0		
	EFFL	5	5	5	5	5	3	2
50%	INFL	6	0					
	EFFL	6	3	3	3	2	0	
100%	INFL	6	0					
	EFFL	5	0					

Table 19. Raw data for first bioassay performed with Ceriodaphnia at loading rate of 19.8 g COD/m2 \* day.

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Conc. of Waste		No. of Test			No. fat	head mi	nnows al	ive at
(% by vol.)		Animals	1 hrs	2 hrs	4 hrs	8 hrs	24 hrs	48 hrs
Controls	INFL	5	5	5	5	5	5	5
(0%)	EFFL	5	5 <sup>°</sup>	5	5	5	5	5
1%	INFL EFFL	5 5	5 5	5 5	5 5	5 5	5 5	5 5
3%	INFL EFFL	5 5	5 5	5 5	5 <sup>-</sup> 5	5 5	5 5	5 5
10%	INFL EFFL	5 5	5 5	5 5	5 5	5 5	4 5	3 5
30%	INFL EFFL	5 5	5 5	5 5	5 5	0 5	 . 0	
50%	INFL EFFL	5 5	5 4	5 4	2 3	0 0		
100%	INFL EFFL	5 5	2 0	1 	0 			

# Table 20. Raw data for second bioassay performed with fathead minnows at loading rate of 19.8 g COD/m2 \* day.

Conc. of Waste		No. of Test		· ~	No. Cer	iodaphn	ia alive	at
(% by vol.)		Animals	1 hrs	2 hrs	4 hrs	8 hrs	24 hrs	48 hrs
Controls	INFL	5	5	5	5	5	5	5
(0%)	EFFL	5	5	5	5	5	5	4
1%	INFL	5	5	-5	. 5	5	5	5
	EFFL	5	5	5		5	5	5
3%	INFL	5	5	5	5	5	3	1
	EFFL	5	5	5	5	5	5	5
10%	INFL	6	6	6	6	4	4	0
	EFFL	5	5	5	5	5	5	5
30%	INFL	5	5	5	4	2	0	
	EFFL	5	5	5	5	5	2	1
50%	INFL EFFL	5 5	0 5	<u></u> 5	 4	 2	2	
100%	INFL EFFL	5 5	0 0		 			

Table 21. Raw data for second bioassay performed with Ceriodaphnia at loading rate of 19.8 g COD/m2 \* day.

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рН	COD (mg/l)	%COD REDUCED	TSS (mg/l)	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/l)	NH3 (mg/l)	TKN (mg/l)	PO4 (mg/l)	SULFIDES (mg/l)	PHENOLS (mg/l)
INFL EFFL	05-01-90	14.20		~ ~	1660 1580	4.8				1566					
INFL Effl	05-03-90	16.80		*	1620 720	55.6	-		*						-
INFL EFFL	05-06-90	17.50		u	1600 602	64.7	, 7 , 7	•		~ ~ *				-	٥
INFL EFFL	05-08-90	18.10	-		1760 620	64.7				* 4		~	-		
INFL EFFL	05-15-90	16.30		7.15 7.80	1700 800	52.9						-		1	
INFL Effl	05-19-90	<b>.</b> 16.00			1560 700	55.1						-			
INFL EFFL	05-22-90	16.80	3.81	6.85 7.99	1620 950	41.3	41.0 53.0	13.0 6.0	28.0 47.0		52.5 45.0		× .		-
INFL EFFL	05-24-90			ŧ	1740 860	50.0									

Table 22.Raw physical-chemical data collected at<br/>loading rate of 32.0 g COD/m2 \* day.

## Table 22 (Continued)

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рĤ	COD (mg/l)	%COD REDUCED	TSS (mg/l)	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/l)	NH3 (mg/l)	TKN (mg/l)	PO4 _ (mg/l)	SULFIDES (mg/l)	PHENOLS (mg/l)
TNFI	05-27-90				1760	40.9				960	22.0	- 6.3		8	,
EFFL	05 21 70	×	-		1040	4017	-				2210	. 013			
INFL	05-28-90	~			<b>1760</b> <sup>*</sup>	42.1	а Ч					I		-	
EFFL			-		1020	-	-	•					2		
INFL	05-30-90	x.		-	1620	39.5		-				, <b>`</b> ,	1.5	2	
EFFL					980					-	~	-	-		
INFL	06-01-90				1800	55.0	ŵ		80		,		0.114		-
EFFL		~`			810					ι, υ					
INFL	06-03-90				1760	53.9						-			
EFFL					810										
INFL	06-05-90				1620	58.0						2			
EFFL					000	L							÷		
INFL	06-06-90	17.40	4.80	9.41	1720	62.2	23.0	7.0	16.0				a		183.0
EFFL				,0 <b>.</b> 02	UCO		52.0	0.0	44.U			-			0.9
INFL	06-08-90	17.40	3.80	9.00	1780	55.2	27.0	9.0	18.0					0.000	
EFFL				7.99	798		127.0	11.0	116.0					0.023	-

-

Table 22 (Continued)

	DATE	FLOWRATE (ml/min)	D.O. (mg/l)	рH	COD (mg/l)	%COD REDUCED	TSS (mg/l)	FS (mg/l)	VSS (mg/l)	SBOD5 (mg/l)	NH3 (mg/l)	TKN (mg/l)	PO4 (mg/l)	SULFIDES (mg/l)	PHENOL'S (mg/l)
INFL EFFL	06-11-90	17.90	3.60	9,30 7.60	1800 880	51.1	38.0 232.0	14.0 34.0	24.0 198.0		v				
INFL EFFL	06-13-90	18.60	4.80	9.30 8.30	1880 1190	36.7	16.0 98.0	8.0 10.0	8.0 88.0		24.0 20.0	6.6 24.8	• •	0.000 0.000	
INFL EFFL	06-15-90	17.20	6.20	9.20 8.45	1780 998	43.9	10.0 50.0	8.0 4.0	2.0 46.0	-	-				
INFL EFFL	06-17-90	15.70	5.60	9.10 8.20	1596 810	49.3	20.0 48.0	6.0 6.0	14.0 42.0						
INFL EFFL	06-19-90	<b>15.00</b>	5.80	9.15 8.25	1940 990	48.9	46.0 50.0	10.0 12.0	36.0 38.0	1086 542				0.000 0.000	
INFL EFFL	06-21-90	15.40	6.60	9.30 8.40	2020 1120	44.5	14.0 56.0	10.0 8.0	4.0 48.0		25.5 23.9	6.2 4.3		0.000 0.000	
INFL EFFL	06-23-90	15.90	6.20	9.29 8.30	1920 820	57.2	16.0 36.0	12.0 6.0	4.0 30.0	2040 413			-		327.0 63.0

Conc. of Waste		No. of Test			No. fat	head mi	nnows al	ive at	
(% by vol.)		Animals	1 hŕs	2 hrs	4 hrs	8 hrs	12 hrs	24 hrs	48 hrs
Controls	INFL	6	6	6	6	6	6	6	6
(0%)	EFFL	6	6	6	6	6	6	6	6
1%	INFL	6	6	6	. 6	6	6	6	6
	EFFL	6	6	6	6	6	6	6	6
3%	INFL	6	6	6	6	6	6	6	6
	EFFL	6	6	6	6	6	6	6	6
10%	INFL	6	6	6	1	1	0		
	EFFL	6	6	6	6	6	6	6	6
30%	INFL	6	6	2	0				
	EFFL	6	6	6	3	0			
50%	INFL	6	4	0					
	EFFL	6	6	2	0				
100%	INFL	6	0						
	EFFL	6	2	0					
									····

Table 23. Raw data for first bioassay performed with fathead minnows at loading rate of 32.0 g COD/m2 \* day.

Conc. of Waste		No. of			No. Cer	iodaphn	ia alive	e at	
(% by vol.)		Animals	1 hrs	2 hrs	4 hrs	8 hrs	12 hrs	24 hrs	48 hrs
Controls	INFL	6	6	6	6	6	6	6	6
(0%)	EFFL	6	_ 6	·6	6	6	6	6	6
1%	INFL	5	5	5	5	- 5	5	5	4
	EFFL	-6	6	6	6	6 -	6	6	6
3%	INFL	7	7	7	7	7	7	4	0
	EFFL	5	5	5	5	5	5,	5	3
10%	INFL	6	<sup>°</sup> 6	6	6	6	6	1	0
	EFFL	6	6	6	6	6	6	6	5
30%	INFL	5	5	5	3	3	3	3	2
	EFFL	6	6	5	5	5	5	4	0
50%	INFL	7	5	2	1	0			
	EFFL	. 6	1	1	1	0			
100%	INFL	7	0						
	EFFL	6	0						

Table 24. Raw data for first bioassay performed with Ceriodaphnia at loading rate of 32.0 g COD/m2 \* day.

Conc. of Waste		No. of Test			No. fat	head mi	nnows al	ive at	
(% by vol.)		Animals	1 hrs	2 hrs	4 hrs	8 hrs	12 hrs	24 hrs	48 hrs
Controls	INFL	6	6	6	6	6	6	6	6
(0%)	EFFL	6	6	6	6	6	6	6	6
1%	INFL	6	6	6	6	6	6	6	6
	EFFL	6 *	6	J* <b>6</b>	. 6	6	6	6	6
3%	INFL	6	6	6	6	6	6	5	5
	EFFL	6	6	6	6	6	6	6	6
10%	INFL	6	6	6	6	3	1	0	
	EFFL	6	6	6	6	5	5	3	2
30%	INFL	6	6	0					
	EFFL	6	6	2	0				
50%	INFL	6	1	0					
	EFFL	6	5	0					
100%	INFL	6	0						
	EFFL	6	0				<del>-</del> -		

# Table 25. Raw data for second bioassay performed with fathead minnows at loading rate of 32.0 g COD/m2 \* day.

Conc. of Waste		No. of Test	No. Ceriodaphnia alive at						
(% by vol.)		Animals	1 hrs	2 hrs	4 hrs	8 hrs	12 hrs	24 hrs	s 48 hrs
Controls	INFL	6	- 6	6	6	6	6	6	6
(0%)	EFFL	6	6	6	6	6	6	, 6	6
1%	INFL	6	- 6	6	. 6	6	6	<sup>•</sup> 6	4
	EFFL	• 6	6	6	6	6	6	6	6
3% -	INFL	6	6	6	6	6	6	5	0
	EFFL	6	6	6	6	. 6	<sup>-</sup> 5	3	3
10%	INFL	6	6	6	6	6	6	1	0
	EFFL	6	6	6	6	6	6	5	5
30%	INFL	6	6	6	6	6	6	0	
	EFFL	6	6	5	5	5	5	5	1
50%	INFL	6	3	0					
	EFFL	5	5	0					
100%	INFL	6	0						
	EFFL	6	0						

Table 26. Raw data for second bioassay performed with Ceriodaphnia at loading rate of 32.0 g COD/m2 \* day.

Table 27.	Concentrations (ppm) of selected cations in sour water
	(prior to nutrient addition) over the entire course of
	the experiment.

Ca	Cr	Cu	Fe	к	Mg	Na	Se	Zn
.5773	.0130	.0101	.2630	.0176	.0687	28.93	*	.0549
.7233	*	.02,76	.2558	*	.0861	88.30	*	*
1.753	*	*	.8045	*	.2924	83.99	*	.0211

,

\* - below detection limits

#### VITA

### Craig Graham Carroll

#### Candidate for the Degree of

#### Master of Science

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