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TREATMENT OF HIGH SULFITE REFINERY WASTEWATER BY CONVENTIONAL ACTIVATED SLUDGE

Reinaldo A. González, Ph.D.(1)
Project Manager, Burns & McDonnell. Chemical Engineer from the Universidad del Zulia, Venezuela, MS and Ph.D. Degrees in Environmental Engineering from Oklahoma State University. He has worked for the Instituto Nacional de Obras Sanitarias and Petroquímica de Venezuela in Venezuela and for THE STOVER GROUP and Burns & McDonnell (present) in the U.S.
Enos L. Stover, Ph.D., P.E., DEE
President, THE STOVER GROUP

(1) 9400 Ward Parkway, Kansas City, Missouri 64114
Phone: (816) 822-3185, Fax: (816) 822-3414, E-mail: rgonzal@burnsmcd.com

SUMMARY

A clean fuels project at a U.S. refinery included the addition of a gasoline desulfurization unit that generates SO_2 offgas. The offgas will be scrubbed in a caustic scrubber before released to the atmosphere. The SO_2 will primarily be converted to Na_2SO_3 (sodium sulfite) and to a lesser extent to $NaHSO_3$ (sodium bilsulfite) and $NaSO_4$ (sodium sulfate). The scrubber blowdown will require treatment to oxidize the sulfites to sulfate. Two options have been identified to treat the scrubber blowdown: (1) Oxidation in the Refinery's activated sludge wastewater treatment plant and (2) Oxidation in a new air oxidizing system. A preliminary evaluation of (1) indicated that the existing activated sludge system would be capable of treating the scrubber blowdown with minimal impact on its hydraulic and treatment capacity. However, there were some concerns regarding its implementation because of potential inhibitory effects, non-compliance with Whole Effluent Toxicity (WET) test, and incomplete oxidation of sulfites to sulfate in the activated sludge system. In order to address these concerns, a bench-scale simulation of the activated sludge system was operated for six weeks while being fed with wastewater from the Refinery. Results of the study are presented herein.

KEY WORDS

Sulfites, activated sludge, treatability, toxicity, inhibition

INTRODUCTION

The Clean Fuels project at the Refinery included the addition of a gasoline desulfurization unit that utilized a technology that generates SO_2 offgas that will be scrubbed in a caustic scrubber before release to the atmosphere. The SO_2 will primarily be converted to Na_2SO_3 (sodium sulfite) and to a lesser extent to $NaHSO_3$ (sodium bilsulfite) and $NaSO_4$ (sodium sulfate). The scrubber blowdown will be approximately 20 gpm and will require treatment to oxidize the sulfites to sulfate. Two options have been identified to treat the scrubber blowdown:

- Option 1: Oxidation in the existing activated sludge wastewater treatment plant
- Option 2: Oxidation in a new oxidizing system

A preliminary evaluation of Option 1 indicated that the existing activated sludge system would be capable to treat the scrubber blowdown with minimal impact on its hydraulic capacity. Also, the total air required for biological oxidation, nitrification, and oxidation of the sulfites to sulfates can be provided by the existing system by operating the two existing blowers. However, there were the following concerns regarding the implementation of Option 1:

- Potential inhibitory effects on the activated sludge biomass by the presence of high concentration of sulfites.
- Non-compliance with the final effluent permit limits including Whole Effluent Toxicity (WET) requirements.
- Incomplete oxidation of sulfites to sulfate in the activated sludge system.

In order to address these concerns, a bench-scale simulation of the activated sludge system was performed. A bench-scale activated sludge reactor was operated for six weeks while being fed with wastewater from the Refinery. The wastewater feeds were spiked with sodium sulfite and sodium bisulfite to obtain concentrations of 1,333 mg/L and 600 mg/L, respectively. The study methodology, test results, and conclusions of this investigative program are presented in this report.

TREATABILITY STUDY METHODOLOGY

Twenty-four hour composite samples of API separator effluent were collected at the Refinery and sent to THE STOVER GROUP's laboratory for use as feed in a mesophilic activated sludge system. The purpose of this study was to simulate the treatment performance capabilities of the biological activated sludge system for treatment of the process effluent containing the added sulfite.

The study used a bench-scale, complete mix, continuous flow activated sludge system. The system consisted of a plexiglas internal recycle reactor with a 3.01 liter aeration reactor volume and a 1.33 liter settling compartment (clarifier) volume. Feed was pumped from a mixed feed tank to the aeration reactor, and the effluent flowed by gravity from the settling compartment to an effluent collection tank. The influent flow was calibrated and regulated at the desired flow rate using a peristaltic pump and timer switch. Compressed air from an aquarium pump passing through a diffuser air stone was used to supply oxygen to the microbial population as well as to mix the reactor contents. An adjustable plexiglas baffle was positioned to keep the clarifier sludge from compacting too tightly inside the baffle opening but at the same time, to allow efficient sludge settling and recycle.

This study was performed at THE STOVER GROUP's laboratory. The investigative approach for this study was to use the refinery (spiked sulfite) wastewater as the feed to the activated sludge reactor. The volume fed to the activated sludge reactor was three liters per day. The reactor was initially started with biological acclimated seed sludge (return activated sludge) from the refinery.

Refinery API effluent was shipped two to three times per week to the laboratory. These wastewater samples were characterized for the parameters listed in Table 1. All the wastewater samples contained adequate nutrients (nitrogen and phosphorus) for biological treatment, such that nutrients were not added to the wastewaters prior to feeding to the activated sludge system. The wastewater samples were spiked with gradually increasing doses of sodium sulfite (Na_2SO_3) and sodium bisulfite ($NaHSO_3$), until the desired study levels were achieved. Around two weeks time period was used to acclimate and stabilize the reactor, while the sulfite doses were increased to the desired study levels. After reaching the desired operating conditions, each wastewater sample was spiked with 40 ml of 10% Na_2SO_3 and 18 ml of 10% $NaHSO_3$ stock solutions per 3.0 liters of feed (1,333 mg/L Na_2SO_3 and 600 mg/L $NaHSO_3$). The acidity from the $NaHSO_3$ additions required alkalinity (NaOH) additions to the wastewater feeds in order to maintain acceptable pH levels in the activated sludge reactor mixed liquor. The spiked wastewater samples were fed to the bench-scale activated sludge reactor at conditions to simulate expected full-scale operations (Temperature = 36 ^{o}C, D.O. = 5.4 mg/L, MLSS = 3,000 mg/L, and F/M = 0.35).

The reactor contents were monitored daily for pH, temperature, and D.O. along with waste biomass volume, and feed volume (amount fed), as well as the effluent volume and pH. Dissolved oxygen uptake rates and microscopic (microbiological) analyses were performed three times per week. Settling tests were performed toward the end of the study to determine settling characteristics. Samples were taken of the mixed liquor and treated effluent for analysis to monitor loading rates and treatment performance. These samples were analyzed for the key operational/performance parameters. The parameters analyzed are presented in

Table 1. Toward the end of the study, composite effluent samples were collected for WET testing.

TREATABILITY STUDY RESULTS

The characterization results of the twelve (12) refinery API effluent samples utilized for this treatability study are presented in Table 2. The test results indicate that all these samples exhibited consistent wastewater characteristics. A summary of the bench-scale reactor average operating conditions during the stabilized data collection period is presented in Table 3. A comparison of the bench-scale operating conditions to the full-scale operating conditions in Table 3 shows that both systems were operated under very similar conditions. The D.O. uptake rate in the bench-scale system was approximately two times higher than the full-scale D.O. uptake rate due to the oxidation of the spiked sulfites. Operation and performance trend plots for this study are presented in Figures 1 through 8. Figure 1 presents the reactor MLSS and MLVSS during the study period. Figure 2 presents the F/M operating conditions in terms of both COD and BOD. Figure 3 presents the influent and effluent COD concentrations, and Figure 4 presents the influent and effluent BOD concentrations during the study period. Figure 5 presents the treatment performance of the system in terms of both total COD and total BOD. As can be observed in Figure 5, the treatment performance of the system was excellent throughout the study period.

Table 4 presents the treated effluent quality from this study after the stabilized operations data collection period. During this period, the average total COD and total BOD removals were around 86 percent and 98 percent, respectively. A high degree of nitrification was achieved in the bench-scale system with an average effluent nitrate-nitrogen concentration greater than 50 mg/L achieved during the data collection period. The average effluent tCOD and tBOD were 145 mg/L and 7.5 mg/L, respectively. The effluent sCOD concentrations observed during the study were affected by both the significant evaporation rate (due to the aeration and high water temperatures) and the mixed liquor volatile solids concentrations. When the MLVSS decreased below the target operating conditions, due to overwasting of biomass, the effluent sCOD increased. When the MLVSS were allowed to increase back up to the target operating conditions, the effluent sCOD decreased accordingly. The relationship of reactor MLVSS and effluent soluble COD are presented in Figure 6. The average evaporation rate (effluent compared to influent) during the study was around 25 percent. Therefore, the effluent COD concentrations measured during the study were around 25 percent higher due to evaporation.

Figures 7 and 8 present the influent and effluent TDS and sulfate relationships, respectively. The effluent TDS and sulfate concentrations increased significantly over the influent concentrations due to the additions of Na_2SO_3 and $NaHSO_3$ and the significant evaporation rate in the system, as previously discussed. The TDS concentrations were also increased by the additional alkalinity requirement to neutralize the acidity of the spiked $NaHSO_3$ additions. Between 6.0 to 10.0 milliliters of 1.0 N-NaOH were required per feed to neutralize the $NaHSO_3$ acidity. All the sulfites and sulfides in the influent along with the Na_2SO_3 and $NaHSO_3$ added to the influent feeds to the system were oxidized to sulfates. The influent and final effluent sulfate concentrations were around 700 mg/L and 3,500 mg/L, respectively. Therefore, the system effluent sulfate concentrations were around five times higher than the influent sulfate concentrations during the stabilized data collection period. A sulfur mass balance was also performed around the system. Both the influent and effluent sulfate, sulfite, and sulfide concentrations were converted to sulfur concentrations such that the mass balance was calculated in terms of sulfur. With one exception, during the data collection period the sulfur mass balance (influent sulfur compared to effluent sulfur) closed within 10 percent or less.

Results of the mixed liquor settling test are presented in Figure 9. The initial MLSS concentration used for this settling test was 2,980 mg/L. As can be observed in Figure 9, the mixed liquor exhibited excellent settling characteristics. The reactor mixed liquor maintained excellent settling characteristics throughout the entire study period. Periodic microscopic analyses were performed on the refinery mixed liquor throughout the study period. The mixed liquor from the refinery typically contained small to medium filamentous diffuse floc characteristics. It contained a significant amount of *Sphaerotilus natans* filamentous bacteria (predominant filament). It also contained *N. limicola* and Type 0041 filamentous bacteria.

Higher life forms typically observed included stalked ciliates, crawling ciliates, and swimming ciliates. Microscopic analyses of the treatability reactor mixed liquor were performed three times per week during the study period. The mixed liquor from the treatability reactor typically contained small to medium tight and compact floc characteristics. It contained significantly less filamentous bacteria than the refinery mixed liquor. The same types of filamentous bacteria were observed as in the refinery mixed liquor (*Sphaerotilus natans*, *N. limicola*, and Type 0041) with the *Sphaerotilus natans* being the predominant filament. Higher life forms were similar to the refinery mixed liquor with stalked ciliates, crawling ciliates, swimming ciliates, and rotifers routinely observed.

CONCLUSIONS

The bench-scale activated sludge simulation treatability study of the refinery wastewater spiked with sulfite accomplished the following objectives:

- Evaluation of potential inhibitory impacts of sulfite spiked wastewater on activated sludge biomass
- Impacts on Whole Effluent Toxicity tests
- Oxidation of sulfites to sulfates

The refinery wastewater contained excess nutrients (nitrogen and phosphorus) above the requirements for biological treatment. No carbonaceous BOD removal or nitrification inhibitory impacts of the sulfite spiked wastewaters were observed in the activated sludge process. However, both the effluent soluble COD values obtained and nitrification appeared to be sensitive to the MLVSS concentration. When the MLVSS dropped below about 2,000 mg/L, the effluent soluble COD and ammonia-nitrogen concentrations increased. When the MLVSS was increased above 2,000 mg/L, effluent soluble COD concentrations around 110 mg/L were achieved, along with complete nitrification and effluent ammonia-nitrogen concentrations around 1.0 mg/L or less. When allowing for the 25% evaporation rate through the system, this effluent soluble COD value would be around 80 mg/L. The effluent tBOD remained very good throughout the study period with an average value around 7.5 mg/L.

The biomass characteristics remained excellent throughout the study period. Excellent settling characteristics were observed throughout the study period. The microbiological characteristics (bacteria and higher life forms) also remained excellent throughout the study period. Routine microscopic analyses of the full-scale refinery mixed liquor and the bench-scale system mixed liquor were performed throughout the study period for comparison. The same types of higher life forms and filamentous bacteria were consistently observed in both systems. However, the bench-scale system consistently maintained better floc characteristics and significantly less filamentous bacteria. The bench-scale floc characteristics were tighter and more compact than the full-scale floc, which was more diffuse in nature. *Sphaerotilus natans* was the predominant filament in both systems; however, significantly less filamentous bacteria were observed in the bench-scale system mixed liquor. It appears that the high influent sulfite concentrations help control the filamentous bacteria without any negative impacts on the higher life forms along with an overall positive impact on the biomass flocculation characteristics.

After stabilized operating conditions were achieved, chronic Whole Effluent Toxicity (WET) tests were performed with *Mysidopsis bahia* and *Menidia beryllina*. The treated effluent from the sulfite spiked wastewater treatability system successfully passed the WET tests. The sulfites spiked into the wastewater were completely oxidized to sulfates in the bench-scale reactor. The treated effluent contained non-detected levels of sulfites and sulfides. A sulfur mass balance around the system closed to within about 10 percent or less. The acidity from the $NaHSO_3$ additions to the wastewater required additional alkalinity (NaOH) additions.

In summary, no negative impacts of the treatability of the sulfite spiked refinery wastewater were observed. However, both the effluent soluble COD and nitrification appeared to be negatively impacted with MLVSS concentrations below about 2,000 mg/L. When the MLVSS concentrations were above 2,000 mg/L consistent effluent quality was achieved, including complete nitrification. The bench-scale effluent quality successfully passed a WET test. The sulfite spiked wastewater provided positive impacts on the microbiological characteristics of the activated sludge biomass. The acidity produced by the addition of the $NaHSO_3$ to the refinery wastewater required additional alkalinity demands (NaOH) for biological treatment.

Table 1. Analytical Laboratory Monitoring Program

Influent	Reactor	Effluent	
		Acclimation Period	Data Collection Period
pH	TSS	pH	pH
tCOD	VSS	tCOD	tCOD
$tBOD_5$		sCOD	sCOD
tTOC		TSS	$tBOD_5$
TSS		NH_3-N	tTOC
TDS		NO_3-N	TSS
Anions		PO_4-P	TDS
Cations		Sulfur Salts	Anions
TKN		Sulfates	Cations
T-P		Sulfites	TKN
Sulfur Salts		Sulfides	T-P
Sulfates			Sulfur Salts
Sulfites			Sulfates
Sulfides			Sulfites
			Sulfides

Table 2. **Process Wastewater (Refinery API Separator Effluent) Characteristics**

Parameter	Concentrations (mg/L)	
	Average	Range
pH (su)	N/A	10.26 – 10.96
tCOD	666	400 – 764
$tBOD_5$	242	155 – 338
tTOC	181	97 – 210
TSS	92	47 – 135
TDS	2478	2210 – 2780
TKN	47.23	16.80 – 85.10
T-P	3.03	0.78 – 7.40
PO_4-P	0.40	0.11 – 0.63
Sulfate	704	626 – 846
Sulfite	7.57	0.48 – 14.30
Sulfide	6.2	1.0 – 15.2
Flouride	2.73	1.48 – 3.73
Chloride	488	361 – 607
Nitrate-N	1.73	0.13 – 4.26
Nitrite-N	0.71	0.30 – 0.99
Bromide	2.20	1.59 – 3.21
Lithium	<0.1	<0.1
Sodium	850	689 – 1610
Ammonium	15.73	3.90 – 42.80
Potassium	14.23	6.88 – 23.90
Magnesium	4.10	2.50 – 5.20
Calcium	39.0	16.1 – 69.4

Table 3. Reactor Operating Conditions During Stabilized Data Collection Period And Refinery Average Operating Conditions

Parameter	Bench-Scale Average Values	Full-Scale Average Values
pH (s.u.)	6.90 – 7.38	No Data
Temp (^{0}C)	30	36
MLSS (mg/L)	2,987	2,977
MLVSS (mg/L)	2,126	2,300
COD F/M	0.35	0.35
BOD F/M	0.13	---
HRT (Days)	1.0	1.0
D.O. (mg/L)	5.17	5.40
D.O. Uptake (mg/L/hour)	21.0	11.5

Table 4. Treated Effluent Characteristics

Parameter	Concentrations (mg/L)	
	Average	Range
pH (su)	---	6.80 – 7.54
tCOD	145	76 – 201
sCOD	129	75 –192
tBOD$_5$	7.5	4.4 – 12.5
tTOC	39.2	25.6 – 52.5
TSS	31	2 – 60
TDS	6173	5650 – 6540
TKN	15.6	2.2 – 45.1
T-P	3.3	0.1 – 6.6
PO$_4$-P	3.2	0.8 – 6.1
Sulfate	3469	3240 – 3720
Sulfite	<1.0	<1.0
Sulfide	<1.0	<1.0
Flouride	<0.05	<0.05
Chloride	643	504 – 744
Nitrate-N	51	40 – 64
Nitrite-N	<0.01	<0.01
Bromide	2.84	2.08 – 4.22
Lithium	<0.1	<0.1
Sodium	2131	1980 – 2290
Ammonium	6.7	<2.5 – 9.0
Potassium	17.2	9.3 – 24.5
Magnesium	9.84	7.35 – 15.0
Calcium	56.9	37.4 – 80.9

Figure 1. Reactor MLSS and MLVSS During Study Period

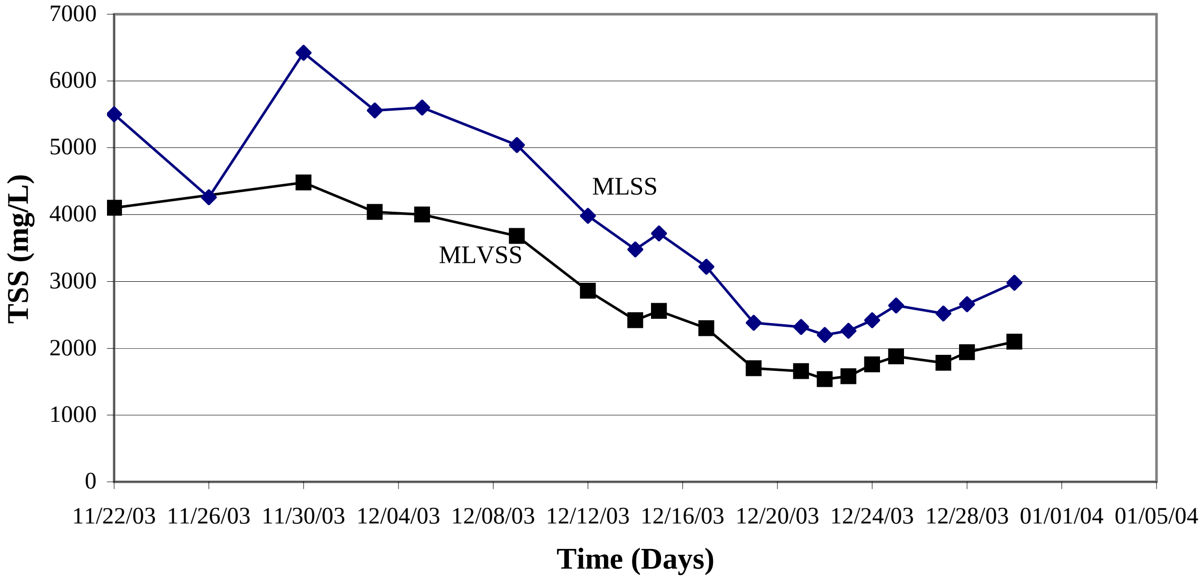

Figure 2. COD and BOD F/M Operating Conditions During Study Period

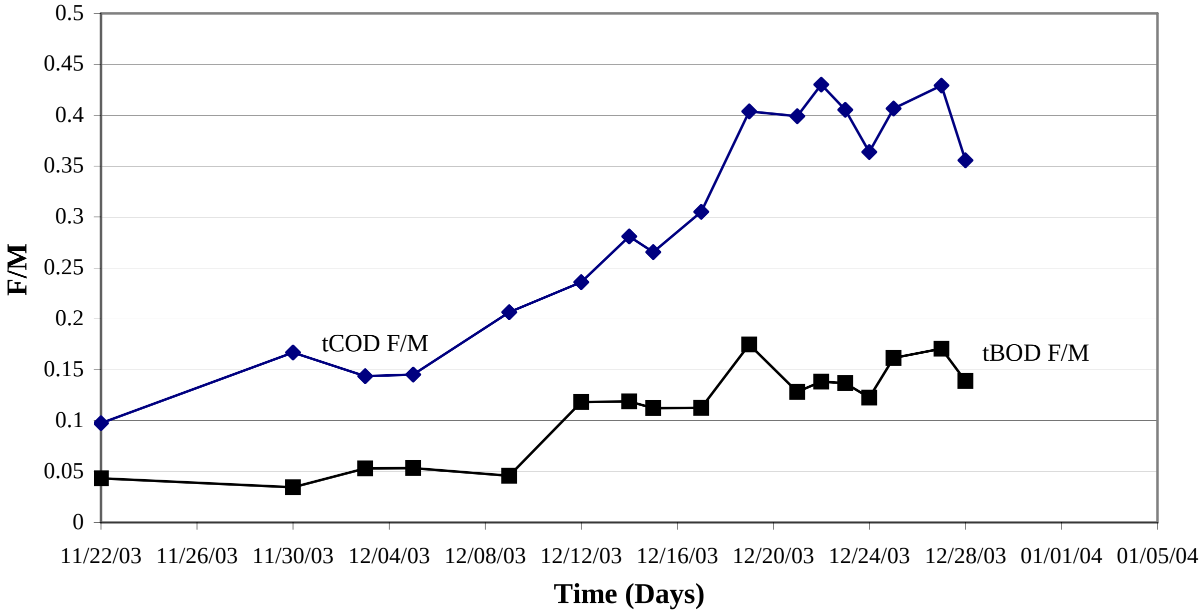

Figure 3. Influent and Effluent COD During Study Period

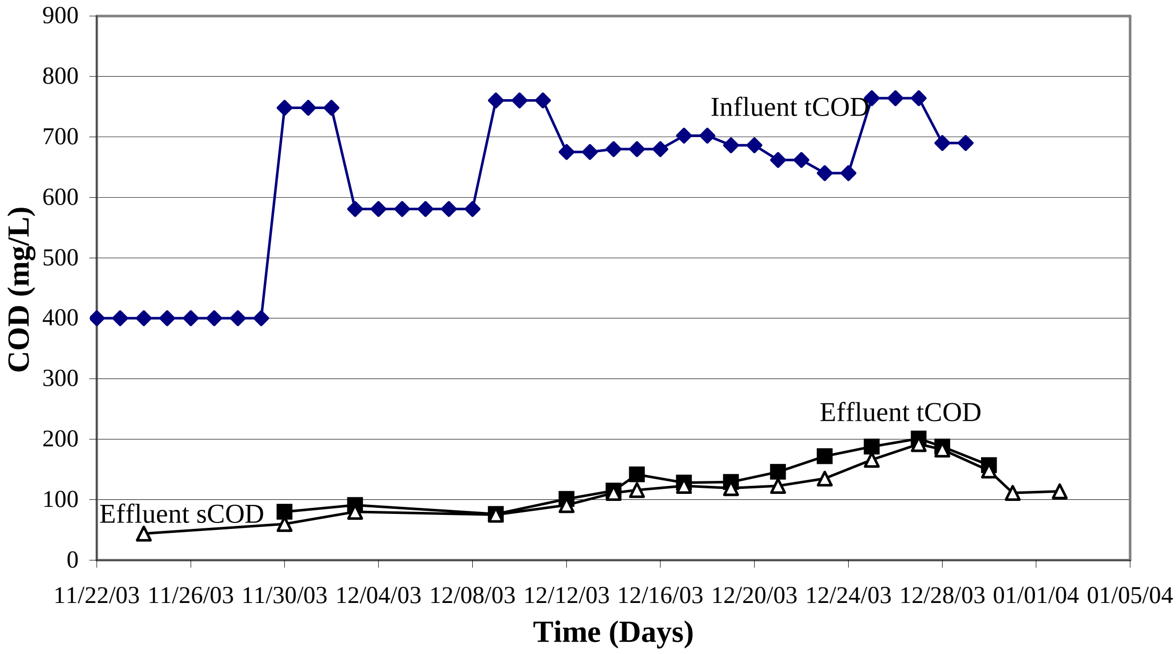

Figure 4. Influent and Effluent BOD During Study Period

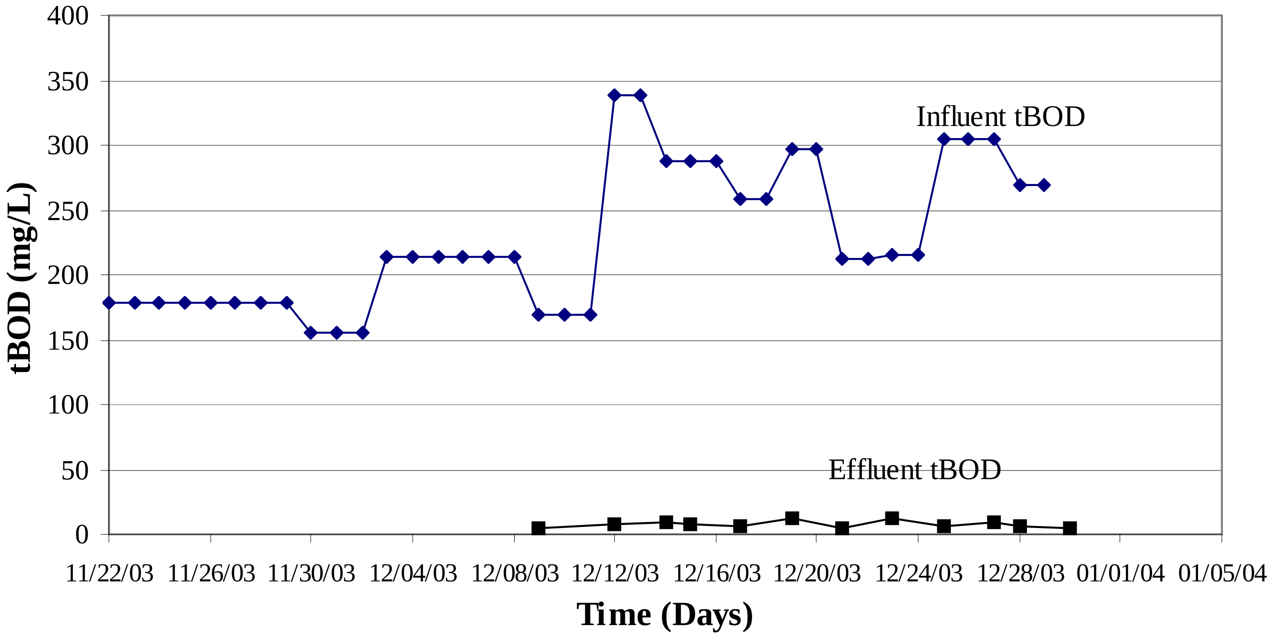

Figure 5. Treatment Performance in Terms of COD and BOD

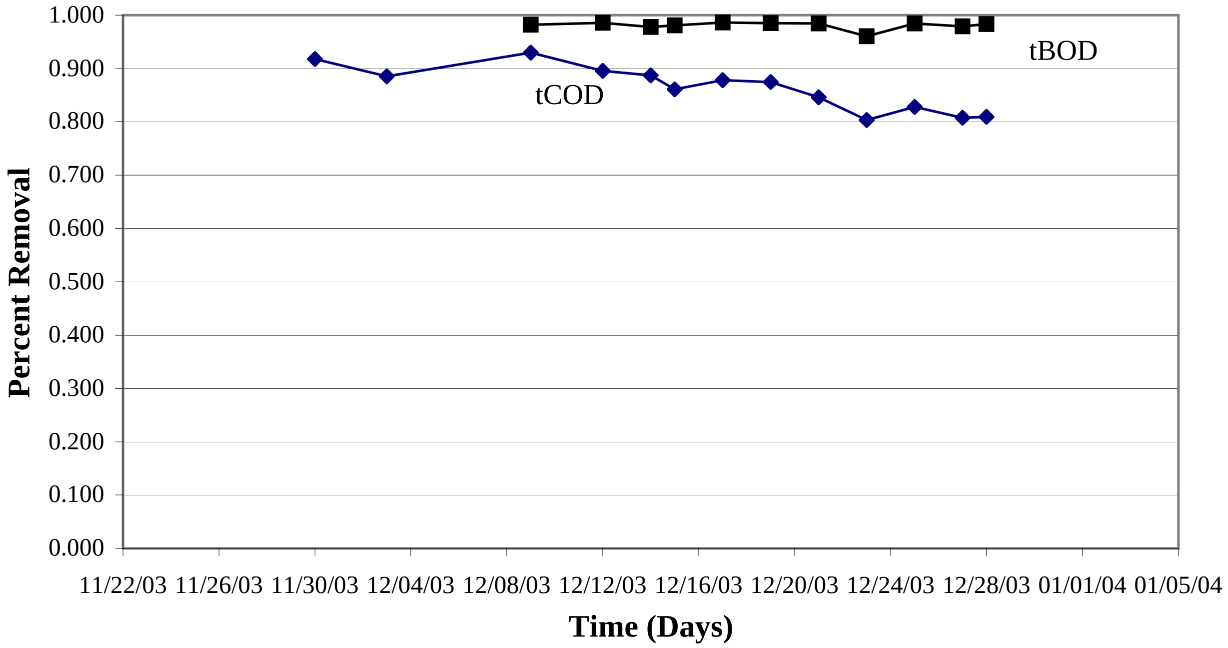

Figure 6. Reactor MLVSS and Effluent Soluble COD During Study Period

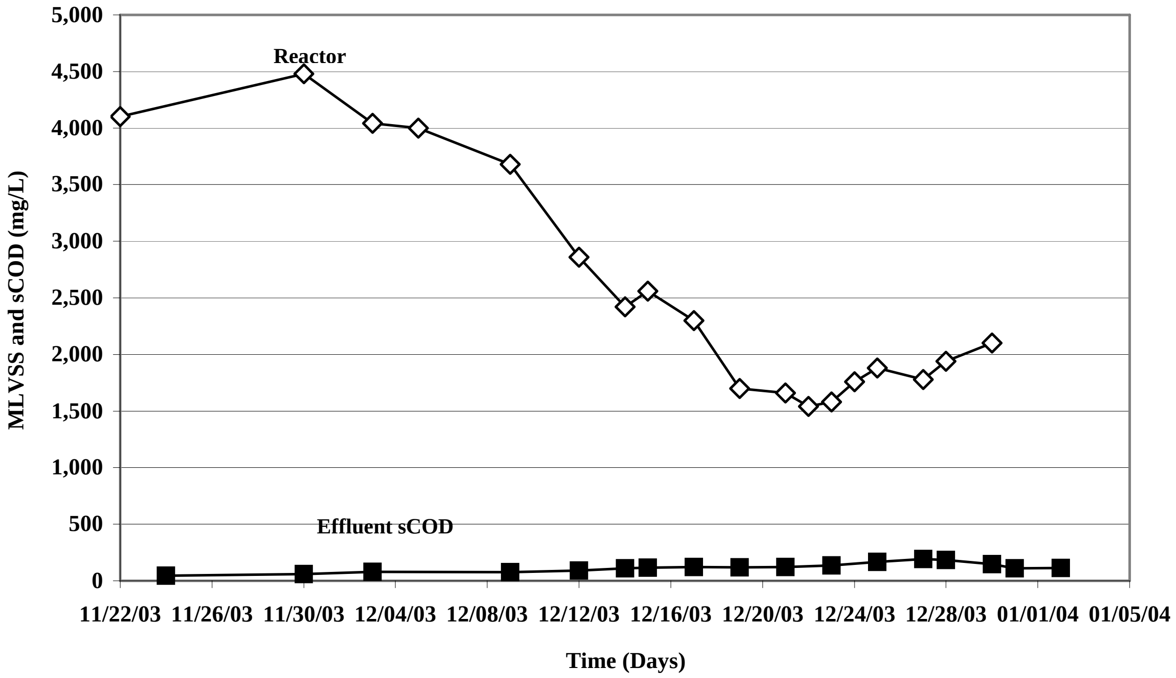

Figure 7. Influent and Effluent TDS During Study Period

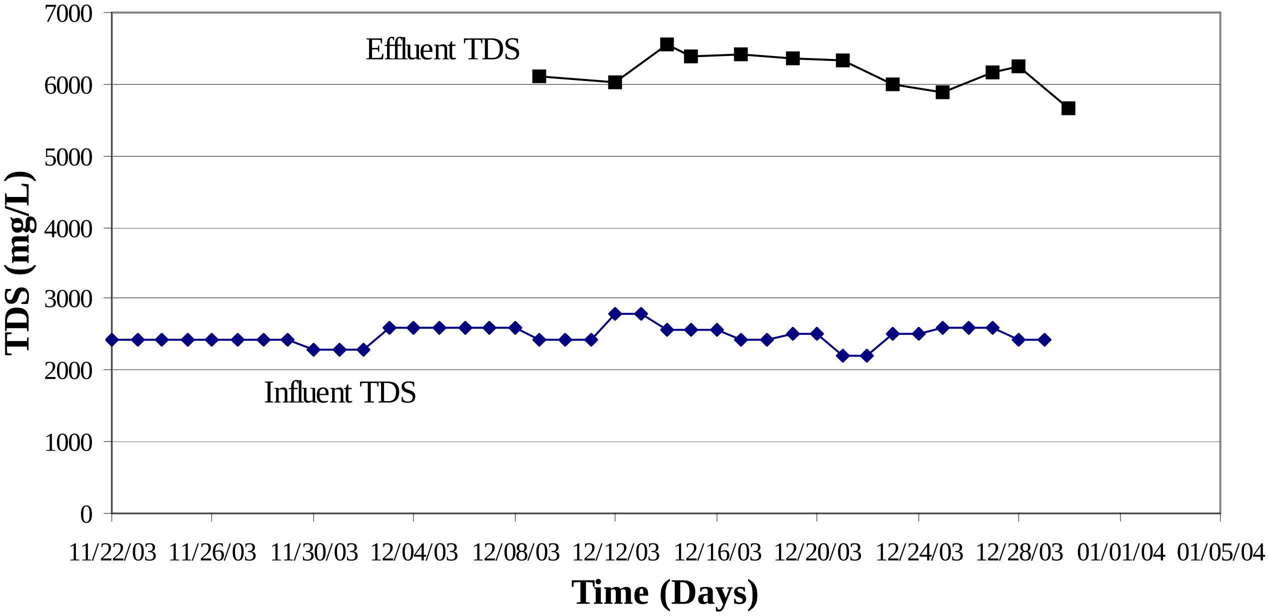

Figure 8. Influent and Effluent Sulfate During Study Period

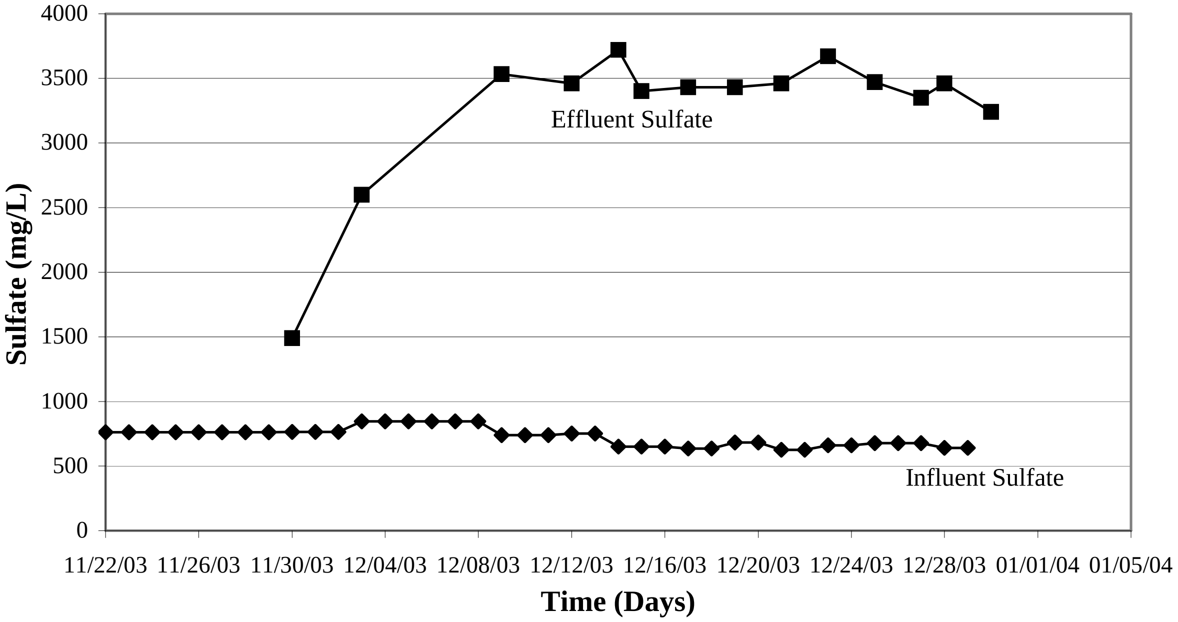

Figure 9. Settling Test