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Bench-Scale Evaluation of the Activated Sludge Process for Treatment of a High-Strength Chemical Plant Wastewater

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Introduction

This paper describes an investigation to determine whether the activated sludge (AS) process could be used for the treatment of wastewater at the Union Carbide Coporation (UCC) plant in Seadrift, Texas. This plant presently utilizes a waste stabilization pond (WSP) system for treatment of the wastewater. The treatment system consists of an in-plant primary WSP and two off-plant WSPs (secondary and tertiary WSPs), run in series. The total hydraulic detention time of the WSP system is approximately 150 days.

Several laboratory-based treatability studies have been conducted to evaluate the performace of the WSP system and the degradability of specific chemical compounds.[1-3] From an additional study,[4] it was determined that the WSP system was stressed and occasionally operating near the limit of its treatment capacity. The existing primary WSP plays an important role in the overall treatmemt system, because it not only functions as a pH and organic-strength equalization basin, but also serves as a"preconditioning" basin by fermenting high strength organic wastes to volatile organic acids for subsequent degradation in the secondary WSP.[4] However, in view of pending-RCRA legislation concerning the "proposed organic toxicity characteristics limits" (40 CFR Part 261: Federal Register, July, 1988), it is possible that the primary WSP will have to be abandoned in favor of alternative treatment options. Therefore the main purpose of this study was to perform activated sludge treatability evaluations for the development of an alternative to the existing primary WSP treatment system. In addition, another purpose was to determine the degradability of bis (2-chloroethyl)ether (Chlorex or CX) and benzene (BZ) in the activated sludge process. The presence of these two chemicals in the wastewater of the plant prompted the question of whether they could be degraded in an activated sludge system.

Materials and Methods

1. Apparatus

Bench-scale, complete mixing, continuous flow activated sludge systems, as shown in Fig. 1, were used in this study. The reactor was a 4-L plexiglass unit with an aeration chamber (3 L) and a clarifier (1 L) separated by an adjustable baffle, which provided continuous sludge recirculation. Wastewater feed was pumped from feed tanks to the aeration chambers and treated effluent-flowed by gravity from settling compartments to effluent collection bottles. The feed flow rates were regulated to provide continuous flows and desired hydraulic retention times (HRT) by using variable-speed peristaltic pumps. Air was supplied by dry diaphragm oilless aerators to each unit through

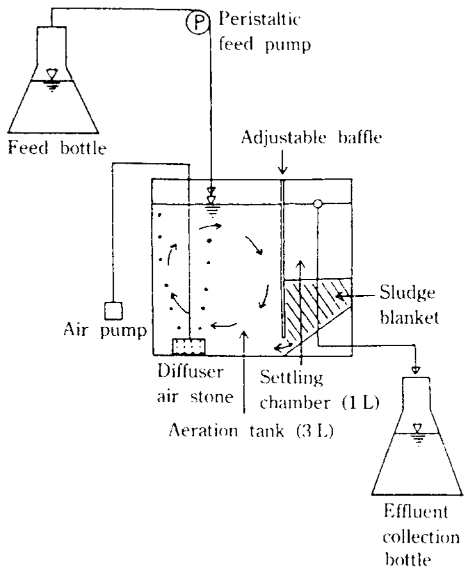

Fig. 1. Schematic diagram of bench-scale activated sludge unit with internal cell recycle.

porous air stone diffusers to generate fine bubbles, to achieve complete mixing, and to maintain dissolved oxygen (DO) levels of at least 2 mg/L.

2. Acclimation

Prior to the beginning of this study, sludge was obtained from a local municipal wastewater treatment plant and from the bottom sediment of the primary WSP at the UCC plant. In order to acclimate and culture the sludge, it was aerated and fed regularly with glucose and glutamic acid, wastewater from the UCC plant, and inorganic nutrients, adopted from Standard Methods, 16th ed.,[3] for approximately 3 months.

3. Operation

Each reactor was operated separately, according to the controlled conditions of the study design as shown in Table 1, and fed daily on a continuous flow basis with the wastewater shipped from the UCC plant. The wastewaters from two shipments each week were composited for feeding and analysis to represent the actual wastewater in the plant as closely as possible and, to some extent, to mimic the effects of equalization.

In the first phase of the study (Phase I), for a period of 7 weeks, 3 units were operated with different wastewater feed flows, without intentionally wasting sludge, to determine an appropriate HRT (Table 1). At the end of this phase, the appropriate HRT was determined to be 2 days.

The second phase of the study (Phase II) was

Table 1. Outline of trealability study design

Operating conditions	Duration	Unit A	Unit B	Unit C	Unit D
HRT-lst run (Phase IA)	4 wks	HRT ld.	HRT 4d.	HRT 8.	–
-2nd run (Phase IB)	3 wks	HRT 2d.	HRT 6d.	HRT 12d.	
SRT(Phase II)	4 wks	HRT 2d. SRT 4d.	HRT 2d. SRT 8d.	HRT 2d. SRT 16d.	HRT 2d. No sludge wasting
CX/BZ Spikes (Phase IIIA)	5 wks	Control HRT 2d. SRT 20d.	Low CX/BZ HRT 2d. SRT 20d.	High CX/BZ HRT 2d. SRT 20d.	– – –
P Addition (Phase IV)	5 wks	Control HRT 2d. SRT 20d.	P added HRT 2d. SRT 20d.	– – –	– – –
CX/BZ Spikes -Repeat run (Phase IIIB)	3 wks	Low CX/BZ HRT 2d. SRT 20d.	High CX/BZ HRT 2d. SRT 20d.	–	– – –

Note : HRT=Hydraulic Retention Time, SRT=Sludge Retention Time, CX=Chlorex, BZ=Benzene, P=Phosphorus.

Table 2. Analyses schedule and methods

Parameter	Feed	Effluent	Reactor	Method
TOC	W	W	–	STD Methods[a] (505A)
COD	W	W	–	Hach[b] (Reactor Digestion)
BOD_5	W	W	–	STD Methods[a] (507)
CX and BZ	W	W	–	GC Analysis
TSS	W	W	W	STD Methods[a] (209C)
VSS	W	W	W	STD Methods[a] (209D)
NH_3-N	W	W	–	STD Methods[a] (213A)
NO_3-N	W	W	–	Hach[b] (Cadmium Reduction)
o-PO_4	W	W	–	Hach[b] (Ascorbic Acid)
SOUR	–	–	W	STD Methods[a] (213A)
SVI	–	–	W	STD Methods[a] (213C)
Alkalinity	W	W	–	STD Methods[a] (403)
pH	TW	TW	TW	STD Methods[a] (423)
DO	TW	–	TW(AN)	STD Methods[a] (421F)
Conductivity	TW	TW	TW	STD Methods[a] (205)

Note : W = Weekly, TW = Twice weekly, AN = As needed, -denotes no measurement
[a]*Standard Methods*, 16th ed. (1985)[9]
[b]Hach Company (1984)[11]

to determine a suitable sludge retention time (SRT) with a fixed HRT of 2 days (Table 1). The method of calculating the SRT was based on the volume of mixed liquor remaining in the tank divided by the volume of mixed liquor wasted each day.[6,7]

After the appropriate HRT and SRT was determined, measured doses of CX and BZ were spiked in the feed that was fed to reactors. For a period of 5 weeks, 3 units were operated during this phase of the study (Phase IIIA): a control unit (not spiked with CX and BZ); a unit spiked with low concentrations of CX and BZ (10 mg/L CX and 50 mg/L BZ); and a unit spiked with high concentrations of CX and BZ (50 mg/L CX and 500 mg/L BZ). Because the capillary column used in the GC analysis failed, the CX and BZ degradation experiment was repeated during the last phase of the study (Phase IIIB). Two units were operated at this time, one unit with a CX and BZ spiking level of 10 mg/L and 50 mg/L (low CX/BZ unit) and the other unit with a CX and BZ spiking level of 50 mg/L and 500 mg/L (high CX/BZ unit).

To determine whether a nutrient supplement could enhance the performance of the activated sludge process, phosphorus (KH_2PO_4) was added to the feeds to make a COD : P ratio of 100 : 1 for a period of five weeks[10] (Phase IV). Adding nitrogen was not considered because the wastewater usually contained high levels of NH_3-N. Two units, one control and one phosphorus-added unit, were operated during this phase.

4. Analytical Methods

A variety of chemical, biological, and physical analyses were routinely conducted each week on feed, effluent, and mixed liquor samples. The analyses, and the methods used are summarized in Table 2.

During the study phase of CX and BZ degradation, CX and BZ were analyzed by direct aqueous injection into a linear temperature programmed gas chromatographic (GC) analyzer (Perkin-Elmer Mode 910) that was equipped with a flame ionizing detector (FID) and a polyethylene glycol coated mega-bore capillary column.

Results and Discussion

1. Wastewater Characteristics

Characteristics of the wastewater, measured weekly, are summarized in Table 3. The wastewater contained high concentrations of organic mate-

Table 3. Wastewater characteristics

Parameter	Median	Mean	Range	S.D.
TOC (mg/L)[a]	2313	2433	977～8678	1268
COD (mg/L)[a]	8127	9024	3356～36574	5309
BOD_5 (mg/l)[a]	3639	4047	920～10083	2156
Flow (MGD)[a]	1.12	1.10	0.20～1.70	0.35
Organic loading				
(kg BOD_5/day)[a]	1767	1926	290～5228	1158
(lbs BOD_5/day)	3901	4252	640～11540	2556
TSS (mg/L)[b]	15	19	2～56	15
VSS (mg/L)[b]	11	14	1～40	10
NH_3-N (mg/L)[b]	70.9	92.4	18.0～215.7	56.9
NO_3-N (mg/L)[b]	1.3	3.1	0.2～22.7	5.2
P-PO_4 (mg/L)[b]	1.00	26.95	0.03～610.00	121.60
pH[b]	8.7	8.6	6.3～10.2	1.2
Conductivity (μmhos/cm)[b]	1350	1724	900～3400	732
Alkalinity (mg/L)[b]	430	563	140～1640	420
Benzene (mg/L)[c]	187	231	115～619	153
Chlorex (mg/L)[c]	N.D.	N.D.	N.D.	N.D.

Note : [a]UCC data for the period 1/4/89～12/27/89.
[b]Data of composite sample during this study (9/18/89～3/5/90).
[c]8 weeks' data (12/5/89～1/4/90 and 2/12/90～3/5/90), N.D.=not detected.

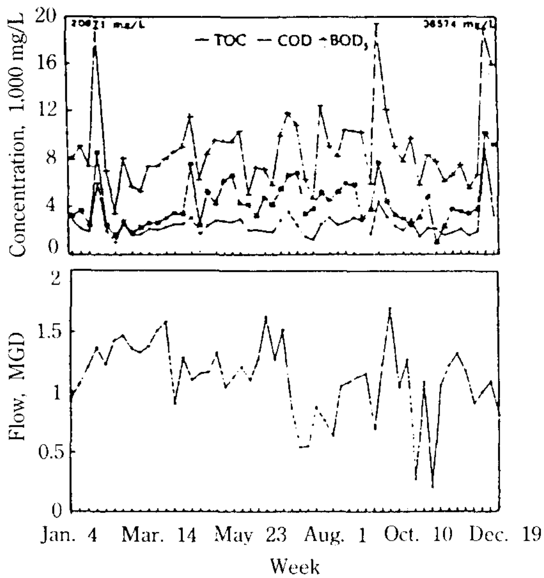

Fig. 2. Chronological variation of waste flows and organic strength (1989 UCC data).

rials with an average TOC of 2,433 mg/L, BOD_5 of 4,047 mg/L, and COD of 9,024 mg/L for the one-year period. Chronological plots of wastewater flow and organic strength over the year period, as shown in Fig. 2, show high degree of fluctuation from week to week. The average BOD_5/COD ratio of raw wastewater, calculated from a linear regression, was 0.4214 and the BOD_5/TOC ratio was 1.6908.

2. Determination of HRT (Phase IA and IB)

The average performance data of each unit with different HRTs during Phases IA and IB are summarized in Table 4. The reduction in organic concentrations was significant at most of the HRTs applied, except at the HRT of 1 day, resulting in an average BOD_5 reduction greater than 80%. The lowest average effluent BOD_5 obtained during this period was 5 mg/L, which corresponded to an effluent COD concentration of 116 mg/L. Organic loading (F/M) averaged from 0.079 to 1 g of BOD_5/g MLVSS/day in a range of the HRTs applied. Apparently, the HRT 1-day unit revealed poor performance in organic removal. This was mainly due to high organic loading, which resulted in an upset condition, and due to the growth of filamentous microorganisms.

The average sludge volume index (SVI) results, shown in Table 4, demonstrated quite acceptable settleability and compaction for units operated at

Table 4. Performance Summary of Activated Sludge Treatment (Phase IA and IB : HRT Determination)

Operational Parameter	Phase IA			Phase IB		
	HRT 1d	HRT 4d	HRT 8d	HRT 2d	HRT 6d	HRT 12d
COD (mg/L)						
Feed	8167	8167	8167	7697	7697	7697
Effluent	4867	1837	1126	653	143	116
% Removal	40.4	77.5	86.2	91.5	98.1	98.5
COD Loading (F/M) (g COD/g MLVSS/d)	1.980	0.499	0.434	0.566	0.227	0.158
Removal Rate (g COD/g MLVSS/d)	0.800	0.387	0.375	0.518	0.222	0.156
BOD_5 (mg/L)						
Feed	4123	4123	4123	3840	3840	3840
Effluent	2123	815	433	242	12	5
% Removal	48.5	80.2	89.5	93.7	99.7	99.9
BOD_5 Loading (F/M) (g BOD_5/g MLVSS/d)	1.000	0.252	0.219	0.283	0.113	0.079
Removal Rate (g BOD_5/g MLVSS/d)	0.485	0.202	0.196	0.265	0.113	0.079
MLVSS (mg/L)	4125	4089	2350	6795	5660	4052
Effluent TSS (mg/L)	12~275	17~76	13~120	9~320	29~354	25~70
SVI (mL/g)	114.8	52.5	102.3	129.0	97.4	70.6
O_2 Uptake Rate (g O_2/g MLVSS/d)	1.36	0.65	0.50	0.40	0.13	0.09
pH (Aeration Tank)	7.2~8.5	7.3~8.7	7.7~8.7	7.4~8.7	7.9~8.5	8.1~8.6

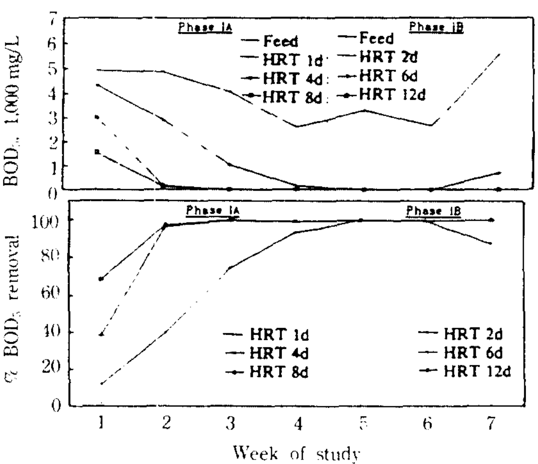

Fig. 3. Influent and effuent BOD_5, and removal efficiency in acativated sludge units during the study phase of HRT determination.

all HRTs applied. The pH in the aeration tank was between 7.2 to 8.7 for all units and within bacterial tolerance for maintaining proper growth. The optimum pH in a biological treatment process is usually between 6.5 and 8.5, while most discharge permits require pH levels between 6.0 and 9.0.[12] The oxygen uptake rate was also presented in Table 4 to allow comparisons of the relative bacterial activity with respect to organic loading.

Fig. 3 shows the weekly measured BOD_5 of the influent and effluent, and the removal efficiency in activated sludge units operated at different HRTs from week 1 to week 7. The effluent quality during this period ranged from 4 mg/L at the HRT of 12 days during week 7, to 4,350 mg/L at the HRT of 1 day during week 1, correponding to BOD_5 removals of more than 99% and 12%. The effuent quality in the first week indicated poor performances for all units, shown by more than 1,500 mg/L of effluent BOD_5 concentration. This was probably due to the unstable conditions of the system, caused by the lack of sludge acclimation and high organic loadings resulting from not enough buildup of solids in the system. After 2 weeks of operation, excellent effluent quality (e.g., <30 mg/L BOD_5) was achieved for all units

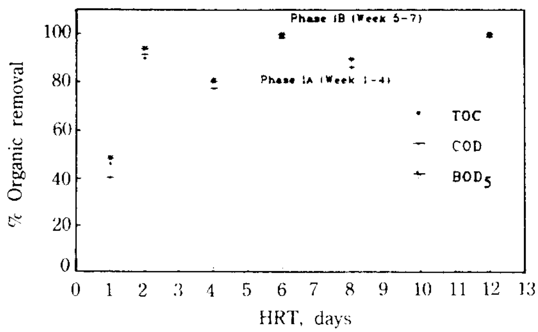

Fig. 4. Effect of HRT on organic removal.

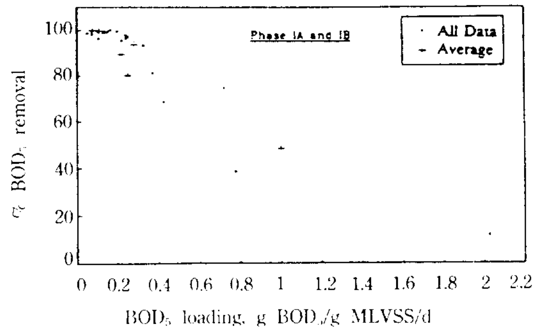

Fig. 5. Effect of organic loading on % BOD_5 removal.

operated at HRTs greater than 4 days. Even at an HRT of 2 days, effluent BOD_5 was maintained at 15~20 mg/L when influent BOD_5 was 2,000~3,000 mg/L during weeks 5 and 6. In general, the organic removal efficiency increased with increased HRT at a constant influent concentration, as shown in Fig. 3. Performance of the system tended to increase due in part to more acclimation and buildup of sludge in the system, resulting in lower organic loading and increase in sludge age. After the second week, the BOD_5 removal at HRTs of 4 and 8 days was consistently above 90%. Also in Phase IB, the BOD_5 was removed by more than 90% at HRTs of 2, 6, and 12 days.

Fig 4 shows the relationships between average % removals for BOD_5, COD and TOC, and HRTs. The average % organic removals of Phase IA are not directly comparable to those of Phase IB since the influent organic concentration is different and the data of Phase IA contains the poor performance-data for the first week. The average removal efficiency increased with increased HRT within the same study period. These results also suggested that there was no additional benefit derived by operating the activated sludge unit with an HRT greater than 2 days if more than 90% removal efficiency was desired. However, due to variation in the influent organic concentrations, it is more meaningful to present the performance data with respect to the organic loading for the interpretation of removal characteristics. The effect of organic loading on the removal efficiency, as BOD_5, is demonstrated in Fig. 5. Generally, the removal efficiency decreased as the organic loading rate increased. The data points showing more than 90% organic removal were distributed around organic loading values less than 0.4 g BOD_5/g MLVSS/day, shown in Fig. 5, and less than 0.8 g COD/g MLVSS/day. These data suggested the selection of moderately low loading rates of 0.4 g BOD_5/g MLVSS/day or 0.8 g COD/g MLVSS/day to achieve more than 90% organic removal.

3. Determination of SRT (Phase II)

The purpose of this phase was to determine an appropriate SRT at a fixed HRT during the activated sludge process. Three units were operated at SRTs of 4, 8, and 16 days and one unit was operated without any intentional sludge wasting. Each unit was operated at a HRT of 2 days with 5,300 mg/L start-up MLVSS concentration in each aeration tank.

The average performance data of each unit with different SRTs are summarized in Table 5. The average influent BOD_5 and COD concentrations during this period of the study were 2,724 mg/L and 6,538 mg/L, respectively. The average organic loading rates (F/M) were 0.192~0.620 g BOD_5/g MLVSS/day and 0.448~1.448 g COD/g MLVSS/day. The average organic loading tended to decrease as the SRT increased, as shown in Table 5, because of the increase of MLVSS concentration with an increased SRT. The average % organic removal increased as the SRT increased. The average effluent BOD_5 concentration ranged from 31 mg/L to 847 mg/L, with BOD_5 reductions from 69% to 99% for the units with SRTs of 4 days and with no sludge wasting. The unit operated

Table 5. Performance summary of activated sludge treatment (Phase II: SRT Determination with Fixed HRT of 2 Days)

Operational parameter	SRT 4d	SRT 8d	SRT 16d	No sludge wasting
COD (mg/L)				
Feed	6538	6538	6538	6538
Effluent	2276	584	357	198
% Removal	64.2	90.8	94.4	96.9
COD Loading (F/M) (g COD/g MLVSS/d)	1.448	0.636	0.585	0.448
Removal Rate (g COD/g MLVSS/d)	0.930	0.577	0.552	0.435
BOD_5 (mg/L)				
Feed	2724	2724	2724	2724
Effluent	847	216	115	31
% Removal	68.9	92.1	95.8	98.9
BOD_5 Loading (F/M) (g BOD_5/g MLVSS/d)	0.620	0.272	0.251	0.192
Removal Rate (g BOD_5/g MLVSS/d)	0.428	0.251	0.240	0.190
MLVSS (mg/L)	2196	5000	5437	7089
Effluent TSS (mg/L)	23~171	18~117	18~1075	11~1615
SVI (mL/g)	158.4	124.5	106.2	113.8
O_2 Uptake Rate (g O_2/g MLVSS/d)	1.84	0.50	0.22	0.20
pH (Aeration Tank)	6.7~8.1	7.6~8.1	7.5~8.1	7.5~8.1

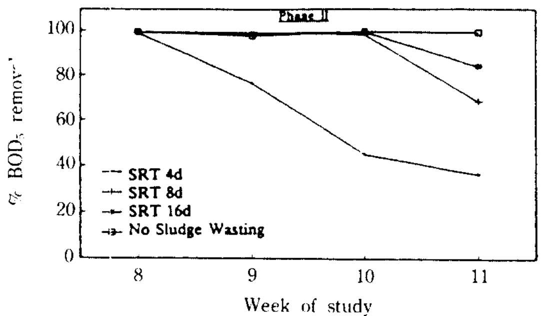

Fig. 6. BOD_5 removal efficiency in activated sludge units during the study phase of SRT determination.

with no intentional sludge wasting demonstrated the best performance, with an average BOD removal of 99% and good sludge settleability under low organic loading at the HRT of 2 days. The average SVI values showed good settleability for the units with SRTs of greater than 8 days, but showed a slightly higher average for the unit with the SRT of 4 days. The average oxygen uptake rate tended to decrease as the organic removal rate decreased with increasing SRT.

Organic loadings during this period of operation were between 0.12 to 0.34 g BOD_5/g MLVSS/day and 0.29 to 0.88 g COD/g MLVSS/day for all the units operated with the SRTs of over 8 days. The 4-day SRT unit showed progressively increasing organic loadings resulting from higher washout rate than sludge reproduction in the system. During the last week, the system became completely upset due to extremely high organic loading. The BOD_5 removal efficiencies for the units having SRTs of 8 days or more, shown in Fig. 6, were achieved by 96% to more than 99% during the first 3 weeks. But the removal efficencies of the 4-day SRT unit decreased over the weeks, showing only a 40% BOD removal during week 11. The units with the SRT of 8 and 16 days showed signs of instability in the system by losing solids in the effluents. The organic removal efficiencies decreased considerably during the last week.

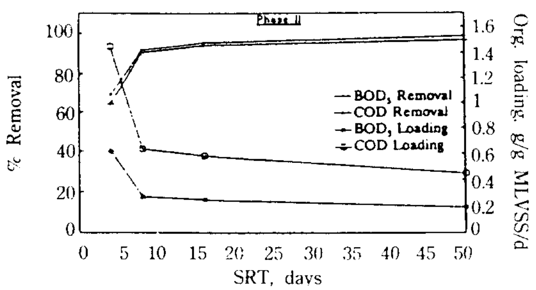

Fig. 7. Effect of SRT on organic removal and organic loading.

Fig. 7 shows the relationships between the SRT and the average % removal, and between the SRT and the average organic loading. As the SRT applied in this study increased, the BOD or COD removal efficiencies increased because more sludge was retained in the system, which resulted in decreasing organic loading.

During this phase, the unit operated with no intentional sludge wasting showed the best performance overall but showed an excessive accumulation of sludge in the system over time. At the end of this phase, it was decided that SRT of around 20 days would be appropriate to maintain a steady MLVSS level and to achieve a high removal efficency.

4. Treatability of chlorex and benzene (Phase IIIA and IIIB)

During Phases IIIA and IIIB, different concentrations of CX and BZ were spiked to the feed of each unit, which was operated at a fixed HRT of 2 days and an SRT of 20 days. The average values of the performance data for each of these activated sludge units, spiked with different CX and BZ concentrations, are summarized in Table 6.

During the first 5 weeks of this study phase (Phase IIIA), the overall performance of the system was poor. This was due mainly to the high organic concentrations of the feed, which resulted in upset conditions of the system. The performance of each unit during Phase IIIA did not show any significant differences between each unit, but during Phase IIIB, the unit spiked with lower concentrations of CX and BZ generally showed better performance. That may have been caused by high concentrations of CX and BZ being inhibitory or toxic to microorganisms. The average influent concentration during this phase was over 15,000 mg/L of COD and 9,000 mg/L of BOD_5, corresponding to average organic loading rates of 2 g of COD/g MLVSS/day and 1.2 g of BOD_5/g MLVSS/day for each unit. Effluent quality was poor, with the average BOD_5 ranging from 4,000 to 4,600 mg/L during the first part of the phase and 920 to 1,700 mg/L during the second part. BOD_5 removal efficiency averaged from 47% to 82%.

Although the overall performances of the system were poor during this phase, sludge settling was not impaired, as shown by the average SVI values between 109 and 168 mL/g. The results of the oxygen uptake rates indicated relatively low and inefficient microbial activity in Phase IIIA as compared to Phase IIIB, resulting in less organic reduction.

Generally, CX and BZ were removed to a great extent despite the upset operating conditions during this period. On the average, BZ was removed from 72% to 86% at the influent BZ concentrations of 171 to 540 mg/L, while CX was removed from 63% at the influent concentration of 10 mg/L, and 37% to 65% at 50 mg/L (Table 6).

Fig. 8 shows the CX concentrations in the feed and effluent, and the % removal of CX during an 8-week period. At a spiked CX concentration of 10 mg/L, the removal of CX averaged 67%, with a range from 30% to 87%, and 6% to 87% of CX was removed at 50 mg/L of influent CX level. However, the removal efficiencies varied from week to week. Any trends or correlations with other operating parameters, such as feed organic loadings and spiked concentrations of CX and BZ, were not observed in weekly removal efficiencies of CX and BZ. Usually, the % CX removal was less at 50 mg/L of influent CX level, especially during weeks 22 through 24. In a previous study which utilized the same wastewater source, Monsen[3] (1985) reported CX removal of 68% at 10 mg/L of CX level during the treatment in the lab model primary WSP, while Davis *et al.*[4] (1987) reported only 30% removal of CX at 10 mg/L level in the lab model primary WSP. Hannah *et al.*[13]

Table 6. Performance Summary of Activated Sludge Treatment (Phases IIIA and IIIB: Chlorex and Benzene Treatability)

Operational parameter	Phase IIIA			Phase IIIB	
	Control	Low CX/BZ	High CX/BZ	Low CX/BZ	High CX/BZ
Benzene (mg/L)					
Feed	171	171	234	331	540
Effluent	47	47	44	46	95
% Removal	72.8	72.4	81.3	86.1	82.4
Chlorex (mg/L)					
Feed	0	10	50	10	50
Effluent	0	3.5	17.7	3.7	31.7
% Removal	---	65	64.6	63	36.6
COD (mg/L)					
Feed	15013	15025	15268	11511	12204
Effluent	9431	9165	8035	2399	4345
% Removal	37.2	39.0	47.4	79.2	64.4
COD Loading (F/M) (g COD/g MLVSS/d)	2.087	1.962	2.106	0.954	1.236
Removal Rate (g COD/g MLVSS/d)	0.776	0.765	0.998	0.755	0.796
BOD_5 (mg/L)					
Feed	8725	8737	8980	5020	5713
Effluent	4428	4630	3977	923	1698
% Removal	49.3	47.0	55.7	81.6	70.3
BOD_5 Loading (F/M) (g BOD_5/g MLVSS/d)	1.213	1.141	1.239	0.416	0.579
Removal Rate (g BOD_5/g MLVSS/d)	0.597	0.536	0.690	0.339	0.407
MLVSS (mg/L)	3598	3829	3625	6035	4935
Effluent TSS (mg/L)	72~770	117~720	60~3417	98~2700	69~3580
SVI (mL/g)	168.2	147.9	168.3	115.6	108.7
O_2 Uptake Rate (g O_2/g MLVSS/d)	0.57	0.53	0.52	1.96	1.96
pH (Aeration Tank)	6.0~9.0	5.8~8.9	7.5~8.8	6.2~8.3	4.8~85

(1988) reported CX removal of 64% in an activated sludge system and 31% in the trickling filter system with the suggestion that CX could be removed by air-stripping. In their previous work[14] (1986), they observed 80% of CX removal in the activated sludge process. Their studies also showed a wide variation in % CX removal with standard deviations of 31% and 38%. The average CX removal result in this study generally agreed with Monsen's study, showing around 63% to 65% removal of CX at a 10 mg/L spiking level. This result also agreed with the CX removal in the work done by Hannah *et al.*[13]

Fig. 9 shows the weekly measurement of influent and effluent BZ concentration and removal efficiency during this phase. Effluent BZ concentration ranged from 2 mg/L to 134 mg/L for the unit without BZ spiking and from 2 mg/L to 278 mg/L for the unit with 500 mg/L of BZ spiking. The percent BZ removal between each unit did not show any significant differences. The overall average BZ removal was 74% with a wide variation from 30% to 99%. However, since the BZ removal result includes data collected mostly during upset conditions, it may not represent maximum removal. The BZ removal could be much higher if the activated sludge units were operated under stable operating conditions. Benzene has

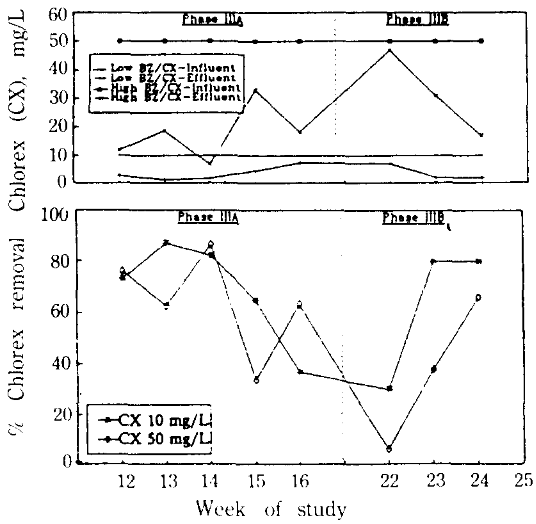

Fig. 8. Influent and effluent Chlorex concentration, and % removal in activated sludge units during the study plase of CX and BZ treatability.

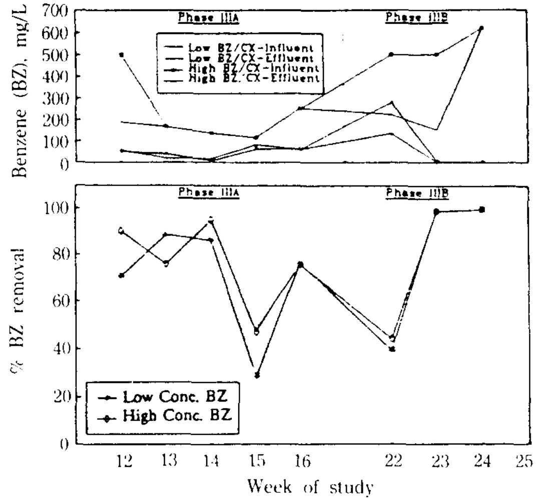

Fig. 9. Influent and effluent benzene concentration, and % removal in activated sludge units during the study phase of CX and BZ treatability.

been classified as a volatile organic and known to be removed more by air-stripping than by biodegradation. While Chorex is a semivolatile organic and is removed by both biodegradation and stripping in the activated sludge system. But unlike BZ, not many studies have been done on the treatability of CX in treatment systems. Many studies have reported that the BZ removal of more than 90% could be achieved in the activated sludge process at various influent BZ concentrations.[15] Eckenfelder[16] (1988) classified benzene as an organic compound that exhibits 5% to 50% removal by air-stripping and a total removal rate of greater than 95%. Stover and Kincannon[17] (1981) reported more than 99% removal of benzene at an influent concentration of 153 mg/L in a bench-scale complete-mixing activated sludge process, and 15% removal by air-stripping.

5. Nutrient Requirement

The objective of this phase of the study was to determine the effect of phosphorus on operational efficiency of the activated sludge process. Two activated sludge units were operated in parallel with an HRT of 2 days and an SRT of 20 days. One unit was supplemented with phosphorus with the COD : P ratio of 100 : 1 and the other unit was operated as a control unit for a comparison.

A summary of the pertinent performance parameters for the two units is shown in Table 7. The average influent organic concentration was higher than usual, with 5,011 mg/L for BOD_5 during this period. The biomass concentration in the aeration tank was maintained as high as 4,560 mg/L and 6,077 mg/L as MLVSS in the control and phosphorus-added units, which resulted in average orgainc loadings of 0.549 g BOD_5/g MLVSS/day and 0.412 g BOD_5/g MLVSS/day, respectively. In general, the phosphorus-added unit showed better performance with respect to organic strength removal and sludge settleability. On the average, BOD_5 was removed by 83% in the phosphorus-added unit while the control unit achieved 71% removal. The average O_2 uptake rate was more than 2 times higher in the phosphorus-added unit, indicating more microbial activity despite lower organic loading. The average SVI data indicated generally good settling characteristics for the phosphorus-added unit but poor settling for the control unit at the HRT of 2 days. The pH in the aeration basin was in the normal range

Table 7. Performance summary of activated sludge treatment(Phase IV : Phosphorus supplement with HRT of 2 days and SRT of 20 days)

Operational Parameter	Control	P Addition
COD (mg/L)		
Feed	10129	10129
Effluent	4184	2015
% Removal	58.7	80.1
COD Loading (F/M) (g COD/g MLVSS/d)	1.111	0.833
Removal Rate (g COD/g MLVSS/d)	0.652	0.668
BOD_5 (mg/L)		
Feed	5011	5011
Effluent	1443	877
% Removal	71.2	82.5
BOD_5 Loading (F/M) (g BOD_5/g MLVSS/d)	0.549	0.412
Removal Rate (g BOD_5/g MLVSS/d)	0.391	0.340
MLVSS (mg/L)	4560	6077
Effluent TSS (mg/L)	31~726	9~1820
SVI (mL/g)	226.0	142.0
O_2 Uptake Rate (g O_2/g MLVSS/d)	0.29	0.63
o-PO_4 (mg/L)		
Feed	1.0	101.3
Effluent	9.5	87.8
NH_3-N (mg/L)		
Feed	73.1	73.1
Effluent	125.7	126.3
NO_3-N (mg/L)		
Feed	5.3	5.3
Effluent	6.9	15.5
pH (Aeration Tank)	5.0~8.7	5.9~8.4

most of the time but was out of the normal range during the last week.

Fig. 10 shows the weekly profiles of BOD_5 and COD in the influent and effiuent and also compares the organic removal efficiencies of the two activated sludge units during this period. For the first three weeks, when the units received the optimum range of influent organic concentration, the organic removal in both units was usually more than 90% without showing any significant differences in performance between the two units. During weeks 20 and 21, when the influent organic concentrations were high (e.g., 18,691 mg/L of

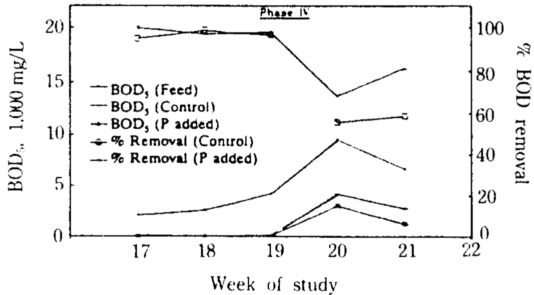

Fig. 10. Influent and effuent BOD_5 and removal efficiency in activated sludge units during the study phase of P supplement.

COD), the control unit exhibited signs of bulking by showing poor performance, poor settling sludge, and turbid effuent. The phosphorus-added unit also showed a tendency for bulking, but showed much better performance and sludge settling. Organic removals as BOD_5 during this period was around 50% to 60% for the control unit and 70% to 80% for the phosphorus-added unit. It indicates that greater utilization of the organic substrate for the synthesis of bacterial cells occurs with phosphorus supplementation. Probably, phosphorus addition may increase the assimilative capacity of microorganisms to utilize more organic materials. During this period, any dramatic change in the oxygen uptake rate was not observed in the control unit despite the high organic loading, while the phosphorus-added unit revealed a great increase of oxygen uptake rate from 6.3 to 96.6 mg O_2/g MLVSS/hour.

It has been known that many industrial wastewaters are deficient in nitrogen and/or phosphorus. The wastewater from UCC is usually deficient in phosphorus. Various researchers have suggested an optimum level of nutrients required for the efficient removal of organic matter by the activated sludge process. Generally, the BOD_5 : N : P ratio of approximately 100 : 5 : 1 has been widely accepted as providing a balanced growth media for the activated sludge process.[8, 18~20)]

6. Removal Rate Kinetics

A number of mathematical expressions have been used to describe the biological process kinet-

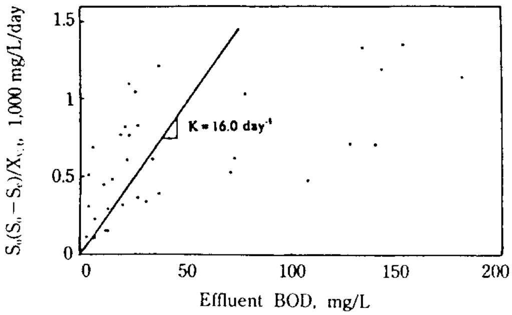

Fig. 11. Determination of BOD_5 removal rate coefficient using data under successful system for activated sludge treatability.

ics. According to Eckenfelder's kinetic model, the removal of organic constituents in the activated sludge process has been described by a correlation which relates the removal rate of BOD to the effluent BOD concentration as follows (Eq. 1) :[12)]

$$U = \frac{S_o - S_e}{X_v t} = kS_e \qquad (1)$$

or

$$\frac{S_o - S_e}{X_v t} = K\frac{S_e}{S_o} \qquad (2)$$

where:

S_o = Influent BOD concerntration, mg/L
S_e = Effluent BOD concentration, mg/L
X_v = MLVSS concentration, mg/L
t = Hydraulic retention time (HRT), days
k or K = BOD removal rate coefficient, L/mg/day, or day^{-1}

The reaction coefficient, k, has been found to be temperature-dependent and needs to be corrected for temperature. If the influent concentration varies significantly, the relationship is expressed more accurately by relating the BOD removal rate to the fraction of BOD remaining (Eq. 2).

By plotting the substrate removal rates against the effluent BOD concentrations or the fractions of the BOD remaining in the effluent, according to Equations 1 or 2, the overall BOD removal rate constant "k or K" can be determined as a slope of the regression line. Since the plot of all data showed considerable data scatter, it was not possible to determine the rate coefficients by linearizing the relationships graphically. Consequently, only data under the successful systems, which received BOD_5 loadings of less than 0.4 g/g MLVSS/day and achieved more than 90% BOD_5 removal, were used to graphically obtain the removal rate coefficient, as shown in Fig. 11. Since the influent BOD varied considerably, Equation 2 was considered to be more applicable. However, the plot shown in Fig. 11 still did not clearly exhibit a linear relationship. It is, in part, due to the applicability of the equation only when the effluent BOD_5 is relatively low and also to the difficulty in separating the effects of solids on reaction kinetics. Thus, the "K" value was calculated by determining the slope of a linear regression line forced through the orgin, using only the data for effluent BOD_5 of less than 100 mg/L, which revealed a linear portion in Fig. 11. These data show that the BOD removal rate coefficient, K, was 16 day^{-1} at room temperature of approximately 22℃. Therefore, this "K" value can represent a removal rate coefficient obtainable under the best performance systems.

The substrate removal rate constants were also calculated for each activated sludge unit on a weekly basis and the results were summarized in Table 8. For the successful systems which received BOD_5 loadings of less than 0.4 g/g MLVSS/day and achieved more than 90% BOC_5 removal, the "k" values were observed to vary from 0.0013 to 0.0605 L/mg/day with an average of 0.0107 L/mg/day and the "K" values from 4.4 to 145.7 day^{-1} with an average of 34.2 day^{-1}.

7. Oxygen Requirement

During the organic removal process in the biological system, oxygen is utilized to provide energy for the synthesis of new cell material and for the basic cell maintenance. The total oxygen required can be estimated from following relationships:[7,12)]

$$R_r = a'S_r + b'X_v \qquad (3)$$

or

$$\frac{R_r}{X_v} = \frac{a'S_r}{X_v} + b' \qquad (4)$$

Table 8. Summary of weekly determined BOD rate coefficients

	% Removal	BOD_5 Loading (g/g MLVSS/d)	k (L/mg/day)	K (day^{-1})
BOD_5 loading> 0.4 or <90% Removal				
Maximum	90.7	7.54	0.00175	7.2
Minimum	11.8	0.25	0.00004	0.2
Average	58.1	1.40	0.00037	2.0
BOD_5 loading< 0.4 or >90% Removal				
Maximum	99.9	0.36	0.0605	145.7
Minimum	93.1	0.05	0.0013	4.4
Average	98.4	0.21	0.0107	34.2

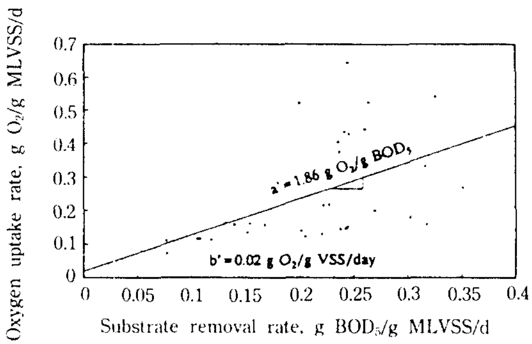

Fig. 12. Determination of oxygen utilization coefficients based on BOD_5 data under successful system for activated sludge treatability.

where:

R_r = Total O_2 utilization, g O_2/day

a' = O_2 utilization coefficient for synthesis, g O_2 utilized/g organics removed

S_r = Organic (BOD) removed ($S_o - S_e$), g/day

b' = Oxygen utilization coefficient for endogenous respiration, g O_2/g VSS in the aeration basin/day

X_v = Average VSS concentration in aeration basin, mg/L

By plotting R_r/X_v vs. S_r/X_v, a', the assimilative O_2 utilization coefficient can be estimated from the slope and b', the endogenous O_2 utilization coefficient, from the intercept of the plot.

For the same reason mentioned for the BOD removal rate coefficient, only the data obtained during the periods of good performance were used to calculate the coefficients, as shown in Fig. 12. The slope of the line gives the value of a' (g O_2/g BOD removed), which is the oxygen consumed to utilize substrates for energy. The intercept represents the value of b' (g O_2/g MLVSS/day), which is the oxygen consumed by endogenous respiration where the source comes from lysing of dead cells. The data illustrated in Fig. 12 showed, according to the relationship given in Equation 3, the O_2 utilization coefficients, a' and b', were 1.86 g O_2/g BOD removed and 0.02 g O_2/g MLVSS/day, respectively.

8. Sludge Production

The model used in this study for the sludge production was the relationship described from the Monod equation in which SRT is related to the specific substrate utilization by means of cell yield and cell decay coefficients, as follows:[12,22)]

$$\mu = \frac{1}{\theta_c} = aU - b = a\frac{S_r}{X_v t} - b \qquad (5)$$

where:

μ = Net specific growth rate, change of microbial concentration per unit time per unit microbial concentration, $time^{-1}$

θ_c = Sludge retention time (SRT) or sludge age, days

U = Specific substrate utilization rate, g BOD/g MLVSS/day

a = cell yield coefficient, g VSS/g BOD removed

b = endogenous or decay coefficient, day^{-1}

S_r = Organic (BOD) removed ($S_o - S_e$), mg/L

X_v = MLVSS concentration, mg/L

t = Hydraulic retention time (HRT), days

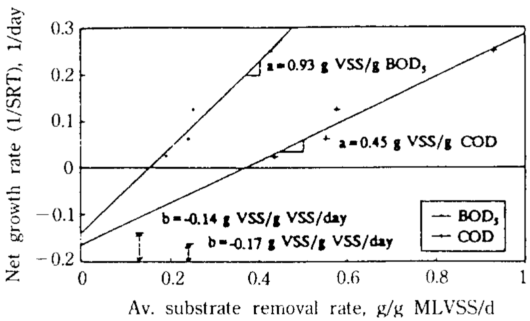

Fig. 13. Determination of yield and decay coefficients using average data during the study phase of STR determination for activated sludge treatability.

This equation implies that the production of biological sludge is directly proportional to the quantity of organic matter removed. The net sludge growth is the sum of sludge generated from the removal of organic matters and the decrease in sludge mass due to endogenous respiration of the microorganisms.

Since the sludge measurement was conducted on a weekly basis under different operating conditions, accurately estimating sludge production by keeping track of changes in sludge balance on a daily basis was not possible. The data obtained from the operating period of SRT determination was used to calculate values of sludge prodcution coefficients because during this period the reactors were operated with varying SRTs and were at relatively steady states with good performances.

A plot of the net growth rate against the specific substrate utilization rate for the data obtained during the study phase of SRT determination is shown in Fig. 13. The slope of a best fit linear regression line indicates a yield coefficient "a" of 0.92 g MLVSS/g BOD_5 removed or 0.45 g MLVSS/g COD removed. From the intercept of the line, an endogenous decay rate "b" was determined to be 0.14 g MLVSS destroyed/g MLVSS per day for BOD_5 data or 0.17 for COD data.

Conclusions and Recommendations

The results of this bench-scale treatability study demonstrated that activated sludge treatment would be an effective process for organic removal in the wastewater from the UCC plant. Generally, the activated sludge system showed stability under a large variation of organic loadings and operating conditions. From the performance data of bench-scale activated sludge treatment of the wastewater, the following conclusions were derived:

- Wastewater characteristics were highly variable with respect to organic concentrations and waste flows. The average BOD_5 was 4,047 mg/L and COD 9,024 mg/L with about 10-fold differences during a one-year period. The average flow was 1.1 MGD with a range of 0.2 to 1.7 MGD. The wastewater was usually deficient in phosphorus.
- The appropriate mode of operation was extended aeration with a long HRT and low organic loading.
- More than 90% of organic removal, along with good sludge settleability, as shown by an SVI of less than 150 mL/g, was achieved at organic loadings of less than 0.8 g COD/g MLVSS /day or less than 0.4 g BOD_5/g MLVSS/day.
- A HRT of greater than 2 days was desired to achieve more than a 90% organic removal and an appropriate organic loading rate in the system.
- Generally, the performance of the system increased with increased SRT. At least 20 days of SRT were required to maintain a steady operation with constant MLVSS levels and to achieve a high level of organic removal with good settling characteristics.
- The supplementation of phosphorus to a COD : P ratio of 100 : 1 enhanced the overall performance of the activated sludge system, resulting in more organic removal and better sludge settleability, especially during the period of stress loading when the system received greater than 0.8 g COD or 0.4 g BOD_5/g MLVSS/day.
- The activated sludge process achieved an average Chlorex removal of 67% and 54% at influent concentrations of 10 and 50 mg/L, while benzene was removed by 74%, on the average, at a range of influent concentrations

Table 9. Summary of activated sludge parameters

Parameter	Value
BOD Reaction Rate Coefficients,	
k (L/mg/day)	0.017
K (day^{-1})	16.0
Yield Coefficient,	
a (g MLVSS/g BOD_5)	0.93
Decay Coefficient,	
b (g VSS/g VSS/day)	0.17
Assimilative O_2 Utilization Coefficient,	
a' (g O_2/g BOD_5)	1.86
Endogenous O_2 Utilization Coefficient,	
b' (g O_2/g VSS/day)	0.02

between 171 and 540 mg/L. The data are inadequate for determining the removal mechanism; however, air-stripping could be significant and should be further studied.

Some of the necessary coefficients for establishing basic design criteria were obtained. The results are summarized in Table 9.

As a result of this study, it is recommended that an activated sludge system be employed for treatment of the UCC wastewater. Equalization would be required prior to the activated sludge system to smooth the organic loading rate and to reduce the concentrations of inhibitory or toxic substances in the raw wastewater.

These conclusions are based on a bench-scale study. It would be risky to use data generated from bench-scale laboratory systems directly for process design due to the limitation in the size of equipment and flow rates used in bench-scale systems. Results from the bench-scale study may instead provide some general guidance for the design and operation of a full-scale system. Extrapolation of results to full scale should be made only with supporting data from pilot plant or larger scale studies.

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