Supplementary Report

MASTER

Additional Work on the Project

Study of the Treatability of Wastewater
From a Coal Gasification Plant

This Report Covers the
Period of the Extension

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School of Public and Allied Health
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Chapter 1

Additional Information on Biological Reaction Kinetics

As discussed in the Final Report, considerable effort was devoted to gathering information on the biological reaction kinetics of the treatment of the coal gasification wastewater in laboratory scale activated sludge units. With the extension of time, additional data were gathered, with renewed attempts to control conditions. In particular, attempts were made to control cell detention at selected levels by chemical precipitation of the biological effluent, with return of the appropriate portion of solids to the aeration tank. Results were:

- a. Basic data for estimating parameters of biological reaction kinetics (unit 1 in all cases):

Five-day Detention Attempted

<u>Date</u>	<u>Trial</u>	<u>Cell Detention (O_c, days)</u>	<u>Influent BOD (S_o,mg/l)</u>	<u>Effluent BOD (S,mg/l)</u>	<u>MLVSS (X, mg/l)</u>	<u>Hydraulic Detention (O, days)</u>
8/4/80	15	4.2	485	248	788	0.99
8/5/80	16	3.7	220	88	728	1.04
8/6/80	17	2.1	455	238	736	0.82
8/7/80	18	0.9	430	288	756	0.78
8/8/80	19	2.4	195	78	748	0.77
		$\bar{x} = 2.7$				

Ten-day Detention Attempted

8/27/80	20	6.2	235	68	920	1.15
8/28/80	21	13.7	255	88	892	1.60
8/29/80	22	11.6	185	90	693	0.94
		$\bar{x} = 10.5$				

Fifteen-day Detention Attempted

9/3/80	23	10.9	230	20	612	1.21
9/4/80	24	8.7	125	23	873	1.12
9/5/80	25	9.3	130	43	1272	0.97
		$\bar{x} = 9.6$				

Twenty-five-day Detention Attempted

9/10/80	26	14.9	307	134	1170	1.07
9/11/80	27	9.6	230	113	1400	1.01
9/12/80	28	28.8	237	141	2210	0.99
		$\bar{x} = 17.8$				

b. Processed data for calculating K_s and k in the equation:

$$\frac{X\theta}{S_0 - S} = \frac{K_s}{k} \left(\frac{1}{S} \right) + \frac{1}{k} :$$

<u>Trial</u>	<u>$y = \frac{X\theta}{S_0 - S}$</u>	<u>$x = \frac{1}{S}$</u>
15	3.29	0.00403
16	5.74	0.01136
17	2.78	0.00420
18	4.15	0.00347
19	4.92	0.01282
20	6.34	0.01471
21	8.55	0.01136
22	6.86	0.01111
23	3.58	0.05000
24	9.59	0.04348
25	14.18	0.02326
26	7.24	0.00746
27	12.09	0.00885
28	22.80	0.00709

Linear regression yielded the equation:

$$\frac{X\theta}{S_0 - S} = -9.187 \left(\frac{1}{S} \right) + 8.148$$

The K_s was found to be -1.13, and k was determined as 0.12. The correlation coefficient was found to be 0.02, which has very low significance.

c. Processed data for calculating Y and k_d in the equation:

$$\frac{1}{\theta_c} = Y \frac{S_0 - S}{X\theta} - k_d$$

<u>Trial</u>	<u>$y = \frac{1}{\theta_c}$</u>	<u>$x = \frac{S_0 - S}{X\theta}$</u>
15	0.238	0.304
16	0.270	0.174
17	0.476	0.360
18	1.111	0.241
19	0.417	0.203
20	0.161	0.158
21	0.073	0.117
22	0.086	0.146
23	0.092	0.284
24	0.115	0.104
25	0.108	0.071
26	0.067	0.138
27	0.104	0.083
28	0.035	0.044

Linear regression yielded the equation:

$$\frac{1}{\theta_c} = 1.506 \frac{S_0 - S}{X\theta} - 0.0217$$

Thus, k_d was found to be 0.0217, and Y was determined as 1.51. The correlation coefficient was 0.499, which is significant at more than the 90% confidence level.

Separating the data for Unit 1 and Unit 2 did not improve the correlation. In further analyses, all data were included, except the first data, which were assembled from existing information. Those may be regarded as the most significant data developed in the study of the biological reaction kinetics:

<u>Equation</u>	<u>Correlation Coefficient</u>	<u>Values of Constants</u>
$\frac{X\theta}{S_o - S} = -83.44 \left(\frac{1}{S}\right) + 11.42$	0.25 (significant at over 80% confidence level)	$K_s = -7.306$ $k = 0.08757$
$\frac{1}{\theta_c} = 0.9988 \frac{S_o - S}{X\theta} + 0.01328$	0.47 (significant at over 99% confidence level)	$k_d = -0.01328$ $Y = 0.9988$

These data are graphed in Figures 1 and 2.

TO 39.31

FIGURE 1

LINEAR REGRESSION FOR DETERMINING K_A AND k

FIGURE 2

LINEAR REGRESSION
FOR DETERMINING
Y AND k_d

Chapter 2

Additional Information on Chemical Precipitation of Biological Effluent

Through the experimentation that was carried out in this project to determine the feasibility of solids removal by chemical coagulants, it was found that ferric chloride was the most effective of the coagulants tried. This chapter summarizes the effects of the coagulants tested, and, through discussion, tries to analyze their effects on this wastewater.

The first coagulant to be tested was alum. After numerous jar tests, it was found that, at pH 6.0, alum had its greatest effectiveness in this wastewater. As Figure 3 shows, this coagulant was not effective in removing the solids present in the wastewater to any great extent. Only 25% of the solids was removed, even at a 1,000 mg/l dose of alum.

Next, ferric (III) chloride was utilized in jar test analyses to determine if it was an effective coagulant in this wastewater. Using doses ranging from 50 to 250 mg/l in 50 mg/l increments, it was found that, at a 250 mg/l dose, an average of 71% of the suspended solids was removed. Because ferric chloride is a proton donor, the pH of the system was dropped to approximately 3.6 by its addition. The purpose of this was to determine if the coagulation characteristics of ferric chloride were due to the pH of the system. As Figure 4 illustrates, the pH of the system was important. At a pH of 4.0, the 250 mg/l ferric chloride dose was most effective. Lime or Ca(OH)_2 was used to adjust the pH of the ferric chloride dosed system. The use of Ca(OH)_2 also had the advantage of increasing the alkalinity of the system. To determine if it was just pH adjustment and not an increase in alkalinity that caused the solids to more readily coagulate, NaOH and H_2SO_4 also were used to adjust the pH.

Since optimum pH had been found for the system, experiments were undertaken in which a series of lower doses of ferric chloride was used to see if the dosage

Figure 3. Alum precipitation with pH adjusted to 6.0, suspended solids vs. alum dose

Figure 4. The effects of pH change using Ca(OH)_2 at an optimum FeCl_3 dose of 250 mg/l, NFR and VNFR vs. pH.

could be lowered and adequate results obtained for solids removal.

As Figures 5 and 6 show, when a system adjusted to pH 4.0 was compared to an unadjusted system, the adjustment of pH was significant in removing the solids present in the wastewater. As Figures 5 and 6 also show, at the 250 mg/l the maximum solids removal was obtained in both the adjusted and unadjusted systems.

Because optimum ferric chloride and pH for the system had been determined, further experimentation was conducted in which the solids of the system were increased to determine if an increase in particle contact would increase the removal of solids from the system. Bentonite clay was added to a series of jar tests in doses of 8 mg/l, 80 mg/l, and 160 mg/l. These doses would provide a 0.1 times, a 1.0 times, and 2.0 times increase over the average amount of solids found in this wastewater. As Figure 7 illustrates, at the 8.0 mg/l Bentonite addition, the removal of solids was increased by approximately 20%. At all other doses, only an increase was observed for both suspended solids and volatile suspended solids. Because the addition of Bentonite to increase solids was found to only remove a small portion of solids over those removed by the 250 mg/l ferric chloride dose, solids addition was not deemed significant in this study.

The last coagulants to be utilized in this study were polyelectrolytes produced by the Allied Colloid Corporation. The polymers from their 700 series consisted of a nonionic polymer, an anionic polymer, and three cationic polymers, which were medium high and very high in their cationic configuration. Each polymer was applied to jar tests in doses of 0.1 mg/l, 1.0 mg/l, and 10.0 mg/l. Of all the polymers tested, as Figures 8, 9, 10, 11, and 12 illustrate, only the nonionic polymer showed effectiveness. Due to these findings, it was determined by the experimenter that polymers which were tested in this study would be poorly effective in removing the suspended solids present in this wastewater.

Figure 5. A comparison of pH adjustment to pH 4.0 and unadjusted FeCl₃ concentration from 50 mg/l to 250 mg/l, NFR vs. FeCl₃ concentration.

Figure 6. A comparison of pH adjustment to pH 4.0 and unadjusted FeCl₃ concentrations from 50 mg/l to 250 mg/l, VNFR vs. FeCl₃ concentration.

Figure 7. Use of Bentonite clay to increase the solids content in a 250 mg/l dose of FeCl_3 with pH adjusted to 4.0, with 1.0 N H_2SO_4 , NFR and VNFR vs. Bentonite clay.

Figure 8. Percol 720, nonionic polymer, NFR and VNFR vs. polymer concentration.

Figure 9. Percol 726, high anionic polymer, NFR and VNFR vs. polymer concentration.

Figure 10. Percol 722, medium cationic polymer, NFR and VNFR vs. polymer concentration.

Figure 11. Percol 776, high cationic polymer, NFR and VNFR vs. polymer concentration.

Figure 12. Percol 744, very high cationic polymer, NFR and VNFR vs. polymer concentration.

Two polymers were chosen to be used along with the ferric chloride to determine if they would be effective as coagulant aids. Because it was somewhat effective in removing solids, the nonionic polymer was chosen for use in this phase of experimentation. Along with the nonionic polymer, the anionic polymer was also chosen. The anionic polymer was chosen because it was found in literature that anionic polymers could be effective coagulant aids when utilized in the presence of cations. As Figures 13, 14, and 15 show, the addition of these polymers as coagulant aids did not increase the effectiveness of the ferric chloride in reducing the solids present in this wastewater.

Finally, to determine if the jar test analysis was accurate in finding the proper coagulant dose, larger scale experiments were performed in which one week's generation of wastewater effluent was precipitated using the 250 mg/l dose of ferric chloride and adjusting the wastewater to pH 4.0. To insure that the results were accurate and representative of the ability of the ferric chloride to remove the solids present in the wastewater, this experiment was performed on four separate occasions. The amount of wastewater precipitated averaged approximately 50 liters for each one-week collection. As can be observed from the data summarized in Table 1, the 250 mg/l ferric chloride dose was effective in removing the solids suspended in this wastewater. By using the 250 mg/l dose of ferric chloride, a maximum value of 66.2% was obtained for removal of turbidity, 94.9% for removal of suspended solids, and a maximum of 97.1% for volatile suspended solids. From the data obtained in this phase of experimentation, it was found that the jar test analysis was accurate in determining the ability of the ferric chloride to remove the suspended solids found in this wastewater.

Discussion

Based on observations made during this study, ferric chloride was the most effective chemical coagulant used in the experimentation. Although 250 mg/l is

Figure 13. FeCl_3 with addition of 1.0 mg/l Percol 720, nonionic polymer, NFR and VNFR vs. FeCl_3 concentration.

Figure 14. FeCl_3 dose without polymer addition as a coagulant aid, NFR and VNFR vs. FeCl_3 concentration.

Figure 15. The effects of a 1.0 mg/l dose of Percol 726, high anionic polymer, as a coagulant aid, on FeCl_3 doses, NFR and VNFR vs. FeCl_3 concentration.

TABLE 1
Precipitation With Ferric Chloride

	<u>Turbidity FTUs</u>			<u>NRF^a mg/l</u>			<u>VNFR^b mg/l</u>		
	Raw	Precipitate	% Removal	Raw	Precipitate	% Removal	Raw	Precipitate	% Removal
Trial 1	48	20	58.3	142	7.3	94.9	106	3.0	97.1
Trial 2	48	27	43.8	75	9.3	87.6	55	4.3	92.2
Trial 3	58	28	51.7	77	4.9	93.6	52	2.3	95.6
Trial 4	65	22	66.2	45	7.3	83.7	33	4.9	85.2
Mean	54.3	24.3	55	84.8	7.2	89.9	61.5	3.6	92.5
SD ^c	8.3	3.8	9.5	40.9	1.8	5.2	31.2	1.2	5.3

^aNFR = Non-filterable residue

^bVNFR = Volatile non-filterable residue

^cSD = Standard deviation

a relatively high dose of coagulant, it is not an excessively high dose, and was only one quarter the dose required for the alum to be only somewhat effective. As for the mode of destabilization which ferric chloride followed to flocculate the colloidal particles, one may only theorize. From the use of such a high dose of ferric chloride, it is known that an insoluble precipitate is formed in such quantity that the colloidal particles would be enmeshed in this precipitate and settle out. At pH 4.0, which was the optimum pH for the system, FeOH^{++} is the dominant iron species. It was observed in literature that the presence of this species in the presence of colloidal particles may also produce destabilization due to adsorption and particle neutralization. In this mode of destabilization, the FeOH^{+2} species is readily adsorbed on the surface of the colloidal particles. When the plus 2 cation is adsorbed, it effectively neutralizes the net negative charge present on particles, thus allowing van-der-waals forces of attraction to bring the particles together, coagulate with other particles, and settle out. The experimenter believed that the removal of solids was brought about by both particle neutralization and enmeshment in an insoluble precipitate.

The reasons why the polymers were ineffective as coagulants were not exactly known by the experimenter. From literature, it was found that when colloidal particles are in the presence of certain organic acids and polymers were used for coagulation, the polymers first reacted with the organic acids and then with the colloidal particles. Due to their reactions with the organic acids, the polymers must be dosed at unusually high levels to produce destabilization by inter-particle bridging. When the dose of the high cationic polymer was increased to the 30 and 40 mg/l levels, there was still no destabilization of the colloids observed. Because coal gasification wastewater is high in organic molecules and compounds, the polymers could have reacted with these organic

molecules even at the high 30 to 40 mg/l levels, thus leaving no polymer, or insufficient polymer to destabilize the colloids present in the wastewater. Thus, the ineffectiveness of the polymers as coagulant aids may also be explainable. If carbon adsorption is to be used to remove the organic compounds that are present in this wastewater, then some means of solids removal should be used so that the activated carbon can be used to its fullest potential.

Because this was only initial study of the removal of solids from coal gasification wastewater, it is not suggested by the author that chemical precipitation can provide adequate solids removal easily and at a modest cost. If further studies are conducted, they should center on ferric chloride as a primary flocculant.

Chapter 3

Additional Information on Tertiary Treatment by Granular Activated Carbon Columns

Introduction

Bench scale upflow activated carbon column studies have been conducted to determine the feasibility of treating a biologically oxidized coal gasification wastewater by carbon adsorption. Total organic carbon (TOC) was chosen as the primary parameter for evaluating the efficiency of treatment. Generally, a minimum contact time of 45-60 minutes was required to achieve a continuous removal efficiency of 80% and an effluent TOC of 35 mg/l or less.

Although additional factors may require further investigation, this study has demonstrated that carbon adsorption is a viable treatment alternative for this wastewater in that an effluent of discharge quality may be obtained.

Materials and Methods

A) Column Assembly

The column apparatus, as illustrated in Figure 16, consisted of a 50 l Plexiglas filling reservoir from which wastewater flowed, by gravity, to a 22 l Plexiglas equalization tank. An overflow channel from the equalization tank maintained a constant liquid level in the tank. Valves were used to control the rate of liquid flow but required frequent adjustment due to sedimentation of solids present.

From the equalization tank, wastewater was siphoned into a 0.3 l Plexiglas aquarium filter housing, subsequently entering the influent channel of the first column. Screw clamps were used to maintain a constant flow rate of 20 ml/min (0.32 gal/hr).

A series of six Pyrex columns was constructed for carbon treatment. Each column had an inside diameter of 8.9 cm and a length of 45.7 cm. Large rubber stoppers with holes bored for fitting glass tubing were used to close either end of each column. Flexible tubing arranged at the effluent channel enabled insertion of a plastic tube which was fitted for sampling.

Once through the last column the treated wastewater flowed through a rotameter into a 500 ml graduated cylinder. The rate of liquid flow was determined via timed volumetric collection of the effluent. The rotameter served only to assure a constant flow rate once the desired flow rate had been obtained.

B) Column Preparation

Prior to filling the columns with carbon, the liquid volume of the columns and associated tubing was determined (13.6 l). Into each column, 122.4g (300 ml)* of washed and dried carbon were placed. The

*Note: $\text{Wt. Carbon/column} = \text{Carbon Volume} \times (\text{Apparent density}) \times (\text{Pore Volume})$
Apparent density = 0.48
Pore Volume = 0.85

Figure 16
Column Assembly

liquid volume was again determined (11.8 l). Therefore, the throughput volume was estimated at 12 l (2% error) for simplicity.

Using washed, dried, and sieved carbon (Calgon Filtrasorb-300), each column was packed with 122.4 g of prepared carbon and sealed. To prevent the formation of air pockets during operation, the packed columns were initially charged with tap water, "spiked" with 40 mg/l HgCl_2 (bacteriostat) and 40 mg/l $\text{Na}_2\text{S}_2\text{O}_3$ (O_2 removal). After charging in this manner, the columns were left dormant for 24 hours.

C) Column Operation and Sampling

During the initial stages of operation, the columns were operated continuously for 24 hours by contacting with equal portion mixtures of effluent from biological units I and II. After 50 l had been passed through each column, operation proceeded in 12 hour intervals using effluent from biological reactor II only. Generally, the columns were operated at a liquid flow rate of 20 ml/min for 1 hour, 40 minutes, stopped 20 minutes for sampling, and then restarted. During sampling, approximately 5 ml of effluent were withdrawn (from each column) into 10 ml glass vials.

D) Sample Pretreatment and Analysis

Each 5 ml sample was treated with 2 drops of 50% HCl and sparged with nitrogen gas for 2 minutes to remove any inorganic carbon present. Each sample was then filtered using glass fiber filters to remove solids (carbon fines).

All TOC analyses were performed on a Beckman Model 915-B Total Organic Carbon Analyzer. Injections of 20 ml were performed in duplicate for each analysis. Medical grade O_2 at a flow rate of 200 cc/min served as the carrier gas. Generally, the TOC Analyzer was calibrated every 6 hours of column operation using seven standards (200, 150, 100, 75, 50, 25, and 10 mg/l TOC) and a water blank. A least squares degree 2 polynomial was fitted to the calibration data. The fit obtained was very good with an absolute residual of less than 2 mg/l TOC over the entire calibration range.

E) Adsorption Isotherms

Additional adsorption isotherm testing was conducted on the waste sample. As in previous isotherms, 200 ml of waste sample were contacted with increasing amounts of pulverized (<325 mesh) activated carbon for 3 hours in sealed 300 ml Wheaton BOD bottles. After agitation, the samples were removed, purged of CO_2 , filtered, and analyzed for equilibrium TOC.

A total of four runs were made, each with 7 carbon-containing samples and 1 control.

F) Volatile Organic Carbon

Since volatile organic carbon may be lost in the acid sparging procedure, samples were taken to estimate the VOC. Three sample series were taken at 12 l intervals.

Results and Discussion

A) Column Data

TOC data obtained during column operation are given in Table 2. A total of 212 l of wastewater was applied to the six columns. Due to the initial 12 l tap water charge, a subtractive 2 l per column displacement value has been incorporated in the tabulation of Table 2. Additional data recorded during column operation included:

	$\bar{x}$	N	s.d.
Flow Rate	20 ml/min	114	< 1
Temperature	23°C	114	2.3
pH	6.8 - 7.1	-	-

Plots of TOC versus volume throughput are presented in Figures 17 through 23. The curves obtained have the s-shaped configuration encountered in similar column studies. A data scatter is evident in the plots.

Data points representing the first 20 l of operation appear to have less scatter. For this reason, the scatter is assumed to be primarily due to column shutdown of 12 hours or more. Instrument malfunctions were responsible for a 3½ week shut-down at an influent volume of 60 l. A similar 2-week incident occurred at an influent volume of 110 l. The influent data represented in Figure 17 were used to calculate a mean influent TOC.

	$\bar{x}$	N	s.d.
Influent TOC	149 mg/l	114	13

Limits of 25, 30, 35, and 40 mg/l TOC were chosen as breakpoints for allowable discharges. The volumes treated were read from the plots at each breakpoint for each column. From these values the carbon exhaustion rates were calculated. Table 3 gives the data and calculations for the 25 mg/l TOC breakpoint. Exhaustion rates for the 30, 35, and 40 mg/l breakpoints were determined similarly.

TABLE 3

Exhaustion Rates for 25 mg/l TOC Breakpoint

Contact Time (min.)	Wt. Carbon (grams)	Volume Treated (l)	Exhaustion Rate lb Carbon/1000 gal. wastewater
15	122.4	-	-
30	244.8	14	146
45	367.2	25	123
60	489.6	40	102
75	612.0	62	82
90	734.4	77	79

Table 2
Carbon Column Data
TOC Effluent

Vol Through (1)	(mg/l)						
	IN	A	B	C	D	E	F
0	103	26	23	14	13	16	15
0.5	129	31	24	29	19	23	-
1.0	131	36	20	17	18	18	34
1.5	130	40	15	13	-	-	-
2.0	128	37	23	25	11	13	18
2.5	-	-	-	-	-	-	-
3.0	133	47	22	14	9.3	11	16
3.5	-	-	19	22	-	-	-
4.0	131	51	-	-	-	8	14
4.5	-	-	-	-	-	-	-
5.0	128	47	18	-	8	9	19
5.5	-	-	-	11	-	-	-
6.0	-	-	-	-	9	9	-
6.5	131	41	17	-	-	-	-
7.0	-	-	-	11	9	9	-
7.5	-	-	-	-	-	-	-
8.0	125	42	-	13	9	-	-
8.5	-	-	-	-	-	-	-
9.0	-	43	24	14	-	-	19
9.5	131	-	-	-	-	-	-
10.0	-	46	21	14	13	12	-
10.5	-	-	-	-	-	-	-
11.0	-	54	23	14	-	-	17
11.5	113	-	-	-	-	-	-
12.0	-	49	23	-	8	15	-
13	148	52	-	14	-	-	-
14	140	51	28	-	13	15	13
15	-	47	26	14	-	-	28
16	134	64	-	-	14	10	23
17	-	56	28	21	-	10	30
18	146	61	-	-	14	12	10
19	-	61	36	-	10	14	14
20	130	66	-	22	12	12	-
21	-	67	-	15	15	12	9
22	141	-	40	16	16	-	31
23	-	-	21	20	19	12	13
24	137	79	22	23	-	19	11
25	-	43	26	25	16	14	10
26	135	46	39	-	15	15	19
27	124	52	44	29	17	17	12
28	130	71	-	22	22	19	-
29	118	71	44	30	19	19	15
30	146	-	33	30	30	-	-
31	141	81	18	31	24	20	20
32	-	63	50	35	-	-	-
33	150	78	46	35	24	-	15
34	117	89	51	36	-	-	15
35	162	75	56	41	-	22	20

Table 2 (cont'd)

Vol Through (1)	(mg/l)						
	IN	A	B	C	D	E	F
36	-	87	58	-	-	21	17
37	146	98	63	42	31	21	19
38	152	94	-	-	33	23	20
39	144	89	62	45	33	22	-
40	155	-	-	47	32	20	20
41	157	105	61	45	26	-	22
42	-	-	66	42	24	23	20
43	-	97	62	36	-	25	-
44	-	99	62	32	29	24	26
45	159	105	49	35	33	-	26
46	157	-	46	40	32	34	25
47	-	75	52	42	-	29	24
48	-	83	55	48	41	31	23
49	147	91	63	-	43	37	-
50	150	91	67	51	40	31	19
51	160	99	-	58	42	-	-
52	158	111	67	54	40	22	17
53	160	-	78	52	-	-	-
54	-	96	72	54	23	18	17
55	-	90	74	-	-	-	-
56	132	104	81	29	24	15	14
57	151	114	-	-	-	-	-
58	158	106	40	27	19	17	16
59	161	-	-	-	-	-	-
60	161	66	39	29	21	18	21
61	-	-	-	-	-	-	-
62	172	88	55	36	29	27	16
64	148	95	65	40	33	23	22
66	158	103	68	48	29	28	24
68	158	103	77	45	40	32	15
70	169	114	69	61	48	26	22
72	172	104	79	67	38	34	27
74	157	119	87	57	50	31	25
76	162	122	83	61	46	27	24
78	174	112	88	61	34	28	27
80	154	124	82	57	42	34	33
82	165	105	83	57	44	38	33
84	153	115	81	66	51	39	31
86	169	119	90	64	53	41	30
88	167	121	79	64	53	36	32
90	174	109	86	70	48	36	-
92	150	114	94	63	49	-	29
94	155	118	83	59	-	37	34
96	150	118	81	-	46	39	37
98	148	122	-	59	44	44	-
100	154	-	82	61	54	-	22
102	-	113	87	72	-	27	13
104	148	113	85	-	34	19	6
106	145	119	-	42	26	11	21
108	159	-	67	42	21	28	30

Table 2 (cont'd)

Vol Through (1)	(mg/l)						
	IN	A	B	C	D	E	F
110	-	116	72	42	49	40	44
112	149	107	69	67	51	51	35
114	140	97	88	68	65	43	33
116	124	116	92	81	60	52	38
118	149	118	99	76	57	46	45
120	141	131	100	74	59	53	41
122	160	129	100	80	65	56	37
124	157	129	100	89	69	45	38
126	157	122	105	82	58	53	43
128	158	131	107	76	64	47	41
130	160	127	93	81	67	49	44
132	152	123	95	81	62	50	47
134	136	118	98	81	60	55	35
136	162	129	100	81	69	49	41
138	158	129	102	81	65	52	49
140	153	126	100	78	69	52	41
142	162	127	95	82	61	53	42
144	161	120	99	79	68	54	48
146	149	127	95	74	57	61	48
148	165	122	102	87	68	52	41
150	148	125	104	85	52	56	48
152	146	131	104	75	66	58	-
154	161	127	101	82	67	54	51
156	150	127	100	82	69	60	45
158	150	131	103	84	72	58	51
160	163	131	100	85	77	65	-
162	153	133	104	91	74	-	31
164	151	129	111	89	-	45	-
166	155	128	105	-	54	-	42
168	148	129	-	69	-	51	43
170	158	-	86	-	58	43	41
172	-	119	-	78	60	51	-
174	145	-	97	78	65	-	40
176	-	125	101	83	-	49	43
178	152	130	100	-	65	49	51
180	150	132	-	80	58	53	51
182	150	-	108	83	72	57	64
184	-	130	112	87	72	67	-
186	147	130	107	92	83	-	42
188	149	126	109	89	-	59	50
190	147	134	112	-	70	55	50
192	146	134	-	82	64	64	61
194	149	-	107	86	73	67	70
196	-	138	107	82	82	68	63
198	151	126	115	99	81	67	59
200	151	138	113	96	80	64	65

Figure 17. Plot of TOC vs. Throughput
For Influent

Figure 20. Plot of TOC vs. Throughput

For Column C

Figure 21. Plot of TOC vs. Throughput

For Column D

Figure 22. Plot of TOC vs. Throughput

For Column E

Figure 23. Plot of TOC vs. Throughput
For Column F

Figure 24 represents a plot of the exhaustion rates versus the superficial contact time. Above a contact time of 60 minutes, the plots appear linear, indicating no significant gain in adsorptive capacity. Therefore, for this system, operated at a flow rate of 20 ml/min, it appears that a 45-60 minute contact time at a carbon exhaustion rate of 86 lb. Carbon/1000 gal. wastewater will produce an effluent with a TOC of 35 mg/l or less.

B) Adsorption Isotherms

The adsorption isotherm data are presented in Table 4. In Figure 25, a linear plot of the adsorptive capacity (mg TOC/g Carbon) versus equilibrium TOC is presented. Generally, the plots represent the sections of interest in actual column operation. A dramatic increase in adsorptive capacity was observed above an equilibrium TOC of 120 mg/l. Similar plots with solutions generally yield an asymptotic approach to a constant adsorptive capacity. It is thought that, in this case, a contaminant fraction is responsible for a large carbon coverage. The species having a high adsorptive potential are preferentially adsorbed. As more surface area becomes available, species with lower potentials are linearly adsorbed. This point is graphically illustrated in Figure 26 which is the Freundlich plot of the data. Below an equilibrium TOC of 100 mg/l, the data appear to follow the Freundlich model.

$$\text{Log} \left(\frac{\text{mg TOC}}{\text{g Carbon}} \right) = 0.870 \text{ Log } (\text{TOC}_{\text{eq}}) - 0.069$$

$$N = 17$$

$$r^2 = 0.97$$

The equilibrium TOC's of the two sections of the plot in Figure 26 may be compared by coefficients of variation. Below an equilibrium TOC of 100 mg/l, the coefficient of variation is 57%, while above 100 mg/l TOC_{eq} , the coefficient of variation is only 12%.

The Freundlich portion of the curve predicts that, for an influent TOC of 149 mg/l, the minimum carbon exhaustion rate is 19 lbs carbon/1000 gal. of wastewater (as shown in Figure 24).

C) Volatile Organic Carbon

Table 5 presents the VOC data obtained by subtracting the acid-sparge TOC from the difference TOC ($\text{TC} - \text{IC} = \text{TOC}$). The inorganic carbon and VOC concentrations were:

	$\bar{x}$	N	s.d.
Inorganic Carbon	15	21	2.4
VOC	15	21	7.0

Too few samples were taken to permit an interpretation of VOC except that the VOC may represent up to 10% of the total TOC.

Figure 24

Plot of Exhaustion Rate vs. Superficial Contact Time

Table 4
Adsorption Isotherm Data

Run No.	Sample No.	Wt. Carbon (grams)	TOC _{eq} (mg/l)	Ads. Cap. (<u>mg TOC</u> <u>g carbon</u>)
I.	C	-	176	-
	1	0.05	152	98
	2	0.10	144	65
	3	0.25	120	45
	4	0.50	90	34
	5	1.00	61	23
	6	2.50	25	12
	7	5.48	10	6
II.	C	-	185	-
	1	0.01	167	188
	2	0.02	162	128
	3	0.05	151	100
	4	0.10	136	79
	5	0.25	111	52
	6	0.50	84	37
	7	1.00	56	24
III.	C	-	175	-
	1	0.05	136	153
	2	0.10	115	118
	3	0.25	104	57
	4	0.50	65	44
	5	1.00	41	27
	6	2.50	18	13
	7	4.90	12	7
IV.	C	-	177	-
	1	0.01	154	463
	2	0.02	146	260
	3	0.05	-	-
	4	0.10	122	110
	5	0.25	99	62
	6	0.50	85	37
	7	0.33	106	43

Figure 25. Linear Plot of Adsorptive Capacity vs. Equilibrium TOC.

Figure 26

Freundlich Plot of Adsorptive Capacity
vs. Equilibrium TOC

Table 5
Volatile Organic Carbon Data

Sample No.	Acid Sparge TOC (mg/l)	TC (mg/l)	IC (mg/l)	TC-IC (mg/l)	VOC (mg/l)
124 IN	153	182	24	159	6
124 A	132	160	17	144	12
124 B	90	108	17	92	2
124 C	70	85	14	70	1
124 D	53	82	14	68	15
124 E	41	75	14	61	20
124 F	37	67	14	52	16
130 IN	146	182	17	165	20
130 A	136	158	17	141	5
130 B	101	128	17	112	10
130 C	76	105	14	91	15
130 D	63	103	17	86	23
130 E	51	89	14	75	24
130 F	39	76	17	60	21
136 IN	148	179	12	167	19
136 A	139	160	12	148	10
136 B	111	136	14	122	12
136 C	95	120	14	106	11
136 D	73	111	14	96	23
136 E	60	95	14	80	21
136 F	55	87	14	73	17

Conclusion

This study has shown that, under the specified conditions, a contact time of 45-60 minutes and a carbon exhaustion rate of 86 lb Carbon/100 gal. wastewater produce an effluent with a TOC of 35 mg/l or less. The Freundlich isotherm model predicted a minimum carbon exhaustion rate of 19 lb. Carbon/1000 gal. wastewater. In actual operation, the minimum obtained was 56 lb. Carbon/1000 gal. wastewater. Inorganic carbon concentrations were quite stable at 15 mg/l. VOC values ranged from less than 1 mg/l to 24 mg/l, with a mean VOC of 15 mg/l.

Additional factors requiring further investigation include reactivation of the spent carbon, changes in liquid flow rates, and determination of additional physical and chemical parameters.

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