

PETROLEUM REFINING PHENOLIC WASTEWATERS

by

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INTRODUCTION

The phenolics content of petroleum refining wastewater has been a concern of both regulatory agencies and refiners for some time. This is primarily due to toxicity to aquatic organisms and the characteristically high oxygen demand that phenolics can and do impose on receiving streams. In addition, there is the taste and odor problem caused when very low concentrations of phenolics are present in potable water supplies. This is particularly true when waters containing phenolics are disinfected with chlorine. The resulting chlorophenolics produce a very noticeable taste and odor problem.

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This paper presents major sources of phenolics in petroleum refining wastewater; also, consideration is given to the amounts of phenolics produced by refiners which must either be controlled or treated before discharge. Additionally, it reviews the problems in analyzing for phenolics content; and finally, presents an examination of the treatment methodology for these wastewaters.

Methods of Analysis for Phenolics

Phenols are defined as hydroxy derivatives of benzene and its condensed nuclei.

The EPA manual (Methods of Chemical Analysis for Water and Wastes 1971) recommends that Standard Methods for the Examination of Water and Wastewater or "ASTM Method D-1873-70" be used for analysis of samples for phenolics. In these procedures, samples obtained in the field for analysis of phenols are fixed by the addition of copper sulfate and phosphoric acid. Even with the preservatives the sample must still be kept iced and the analysis must be done within 24 hours.

There are numerous test methods available to assess phenolic concentration in a waste stream. "Standard Methods" lists a Gas Chromatographic procedure and the 4-Aminoantipyrine procedure. In addition, the derivative electron capture detector method and an ultra violet bathochrome shift method are scheduled for round robin testing. Some water pollution laboratories make use of the Technicon Auto Analyzer system and report good results. By far, the most common method is the 4-Aminoantipyrine test.

In this test procedure, phenols react with 4-Aminoantipyrine at a pH of 10.0 ± 0.2 in the presence of potassium-ferricyanide to form a colored antipyrine dye. The light absorbance of this dye is measured by use of a spectrophotometer at 460 m μ wavelength. The absorbance relates directly to the amount of phenol which is present in the sample.

Phenol decomposing bacteria, oxidizing and reducing substances, and alkaline pH cause interference in the testing for phenol. By using the fixing reagents mentioned earlier and by distillation of the sample, most interferences can be eliminated. Further extraction of the distillate by chloroform can concentrate the phenol so that very low values can be detected colorimetrically. Presumably, the 4-Aminoantipyrine method does not measure parasubstituted phenols in which the substitution is an alkyl, aryl, nitro, benzoyl, nitroso or aldehyde group. It has also been reported that triaryl phosphates are positive interferences in the 4-Aminoantipyrine test. Unfortunately, color response of the 4-Aminoantipyrine test is not the same for all phenolic compounds. Because phenolic wastes usually contain a variety of phenols, it is not feasible to determine the exact quantity of phenols in a sample. For this reason pure phenol is selected as the standard for the test and all results are expressed or reported as phenol.

Because of the obvious deficiencies of the 4-Aminoantipyrine test, EPA has assigned certain laboratories to continue evaluation of other testing procedures for phenolics.

Sources of Phenolics From Refining

The majority of phenols present in refinery wastewater originate from the catalytic cracking process. The reaction products from the cat cracker contain steam and the subsequent main fractionator uses stripping steam. Thus the main fractionator overhead reflux drum produces sour, foul condensate containing ammonia, light hydrocarbons, hydrogen sulfide, cyanide, and of course phenols. Caustic treatment of cracked gasoline removes sulfur compounds (mercaptans and thiophenols) and phenolic compounds. Hence, spent caustics are another source of phenol.

Thermal cracking also produces a similar foul condensate. Thermal cracking processes include visbreakers, delayed coking, and steam crackers which produce ethylene, propylene, and petrochemicals. Similarly hydrocrackers may also produce phenolic wastewaters.

Another possible source of phenolics is loss of phenol used as a solvent in extraction processes such as the Duo-Sol process.

EPA/API Survey of Refinery Raw Waste Loads

In 1972 the American Petroleum Institute and the Environmental Protection Agency cooperated in a study whose primary purpose was to evaluate the amounts and constituents of raw aqueous wastes that were generated by the refining industry. Raw wastes were defined to be those wastes which have received no treatment other than gravity separation. Another objective of the study was the evaluation of treatment

efficiencies of activated sludge units handling refinery wastewaters. The goal of the study was to produce a "real life" data base for this industry.

API contacted every known refinery in the United States and solicited their cooperation for the study. Each refinery was requested to sample and analyze each of the raw waste streams in the refinery. Results of the analyses were then reported on a uniform questionnaire; 135 questionnaires were received and accepted for use in the study. These 135 refineries represented approximately 85 percent of the nation's crude refinery capacity.

The survey results pertaining to phenolics in raw wastewaters are presented in Table 1. The amounts of phenolics produced by each class of refinery surveyed is listed according to the API refinery classification system utilized in the study. Each class is defined by the following:

<u>Refinery Class</u>	<u>Processes</u>
A	Crude Distillation
B	Cracking
C	Cracking and petrochemicals
D	Cracking and lubes
E	Cracking, lubes, and petrochemicals

Generally, as the refinery class goes from A through E, the complexity of the refinery increases.

The effect of refinery classification on phenolics production is quite apparent from Table 1. Class A refineries (no cracking) produce only

TABLE 1
REFINERY PHENOLICS RAW WASTE LOAD SURVEY

<u>Class</u>	<u>No. of Refineries</u>	<u>Total Crude Capacity</u>	<u>Median pounds Phenolics per 1000 BBL Crude</u>	<u>pounds Phenolics/day</u>
A	13	204,900	0.03	1,809
B	71	3,448,900	1.54	16,620
C	27	3,416,830	4.02	27,668
D	11	1,068,450	2.18	4,317
E	13	3,354,470	2.67	18,430
Total	135	11,493,550	-	68,844

0.03 lbs of phenolics per 1000 BBL refined. Whereas classes B through E (with cracking) produce much higher levels of phenolics (1.54--4.02 lbs/1000BBL). As Table 1 indicates, the refineries surveyed (with 85% of the nation's crude capacity) produce about 69,000 lbs of phenolics per day which are contained in their raw wastewaters.

In order to validate the study's results, 10% of the surveyed refineries were selected at random. EPA representatives visited the refineries to observe the sampling and to obtain "split samples" which were preserved and returned to the Robert S. Kerr Environmental Research Laboratory for analysis. The refinery laboratory or the consulting laboratory for the refinery also analyzed the split samples.

The results of this split sampling are shown in Table 2. As can be seen, there are considerable differences between some of the measurements made by EPA and API on the same split sample. However, a statistical analysis of the results (student's T test) indicates the average difference between the results obtained by two laboratories is not significant. Since "average" data were to be used in the EPA/API study, the results were considered acceptable. These results brought about concern for those cases where a limited number of samples might be analyzed and compared, such as could occur in an environmental enforcement action. The most apparent reason for this analytical difference was analyst deviation from the EPA methodology.

Following the EPA/API study, an inquiry was received from the Oklahoma Petroleum Refiners Waste Control Council (OPRWCC) expressing

TABLE 2 120

EPA/API SPLIT SAMPLING RESULTS FOR PHENOLICS

<u>EPA</u>	<u>API</u>	<u>DIFFERENCE</u>	<u>% DIFFERENCE</u>
0.01	0	.01	100.0
1.6	1.5	.1	6.3
0.01	0.02	-.01	-100.0
2.3	0.02	2.28	99.1
0.01	0.1	-.09	-900.0
0.9	0.1	.80	88.9
140.0	115.0	25.0	11.9
0.01	0.0	.01	100.0
4.6	4.7	-.1	- 2.2
7.6	7.7	-.1	- 1.3
0.01	0.004	.006	160.0
0.01	0.013	-.003	- 30.0
0.02	0.023	-.003	- 15.0
0.01	0.05	-.04	-400.0
2.90	3.5	-.6	- 20.7
0.01	0.0017	-.0083	- 83.0
4.55	0.3330	4.217	92.7
0.01	0.	.01	100.0
0.01	0.0037	.0063	63.0
0.39	0.32	.07	18.0
2.2	2.2	.00	.0
0.01	0.	.01	100.0
2.46	1.9	.56	22.8
12.2	5.9	6.3	51.6
3.1	2.5	.6	19.4
0.01	0.0	.01	100.0
410.0	115.0	295.0	72.0
0.1	0.038	.062	62.0
0.06	0.016	.044	73.3
64	26.7	37.3	58.3
0.52	0.412	.108	20.8
0.6	0.441	.158	26.3
0.01	0.0	.01	100.0
0.48	0.6	-.12	- 25.0
0.48	0.063	0.417	86.9
0.01	0.027	-.017	-170.0
8.2	6.1	2.1	25.6
0.001	0.015	-.014	-1400.0
0.01	0.01	0.0	0.0
0.02	0.02	0.0	0.0
500.0	600.0	-100.0	- 20
1.4	0.97	.43	30.7
13.8	1.51	12.3	89.1
3.6	0.025	3.585	99.6
2.2	2.3	-.1	- 4.5
525.0	280.0	245.0	46.7
14500.0	2400.0	12100.0	83.4
4.5	0.1	4.49	99.8
0.4	0.01	.39	97.3
0.4	0.255	.145	36.3
13.1	0.295	12.805	97.7
0.6	0.49	.11	18.3
2.5	0.94	1.56	62.4
0.01	0.0	.01	100.0
0.01	0.0	.01	100.0
0.01	0.0	.01	100.0
0.43	0.4	.03	7.0
5.4	5.3	.1	1.9
0.65	1.0	-.35	- 53.8
0.52	0.5	.02	3.8
0.52	0.5	.02	3.8
62.0	67.0	-5.0	- 8.1
0.38	0.4	-.02	- 5.3
0.38	0.4	-.02	- 5.3
0.03	0.0	.03	100.0
0.01	0.14	-.13	-1300.0
0.01	0.0	.01	100.0
31.0	32.0	-1.0	- 3.2
3.2	0.1	3.1	96.9

Average Difference 183.36
 σ Difference 1,456.47
 N 69
 T 1.047

their concern over analytical variances experienced in analyzing industrial wastewater samples. This organization, composed of 11 refinery members has employed a self-reporting system for wastewater discharge analyses since 1955. Each month, the individual refineries report analytical data to the Oklahoma State Corporation Commission.

To attain the major and ancillary objectives of a study to define intra and interlaboratory repeatability and reproducibility, a steering committee including one EPA, one State, and three refinery representatives was formed. Formation of the study plan was the responsibility of the committee while the liaison and project direction were responsibilities of RSKERL personnel.

Participant selection from the Council was voluntary, with the agreement that any refiner who volunteered would, of necessity, have to participate in the total program. Eight of the eleven member refineries agreed to participate in the project. Those refineries who did not choose to participate represent refineries which either contract the analysis of their wastewater samples or could not participate due to internal restrictions. Refinery size of the participants varied from 12,000 to 112,000 barrels of crude per calendar day. The size distribution of the participating refineries is shown below:

CAPACITY OF PARTICIPANTS

<u>Refinery</u>	<u>Thousand Barrels/Calendar Day</u>
A	12.0
B	25.0
C	28.5
D	29.5
E	48.5
F	51.0
G	87.0
H	112.0

Size variance of the participants is an important factor since the population (industrial participants) involved in the study should represent a spectrum from small to large. Refinery size also reflects laboratory capabilities for wastewater analyses since the analytical staff size is dependent on refinery size.

Two Oklahoma State agencies, which are currently involved in analyzing industrial wastewaters, requested participation in the program. These State agencies were the Oklahoma State Health Department, whose responsibilities include analyses of petroleum refinery wastewater for the Oklahoma Corporation Commission (Oklahoma's Pollution Control Enforcement Agency for industrial discharges) and the Zoology Department of Oklahoma State University (OSU). The Zoology Department has performed bio-assays on petroleum refinery wastewaters since 1956 and regularly analyzes refinery wastewaters.

EPA laboratories participating in the study were the Robert S. Kerr Environmental Research Laboratory at Ada and the Methods Development

and Quality Assurance Research Laboratory located in Cincinnati, Ohio. MDQARL participation was primarily that of a referee laboratory while RKSERL duties included project liaison, sampling, intralaboratory analyses, data analyses, and report preparation.

The research program developed by the steering committee called for a two-phase study. In the first phase, a uniform sample of refinery wastewater would be obtained. The participating laboratories would handle the analysis in a routine fashion. Following the first phase, each analyst or his representative attended a seminar in which the analytical procedures were discussed. The purpose of the seminar was to achieve uniformity in analytical techniques. After the seminar, another set of samples would be analyzed to measure the effect of instruction.

Wastewater for the first phase was obtained from a final clarifier effluent at a petroleum refinery. The water had been biologically treated and represented all the wastewater sources in the refinery with the exception of sanitary sewage.

Wastewater for the second phase was obtained from the discharge of the API separator. This water was not biologically treated.

The sampling method used for the study involved pumping the water into a 35 gallon drum which had an inert inner liner. Calculated amounts of preservatives were added to the sample and an electric stirrer was used to mix the sample thoroughly. After five minutes

of mixing, replicate samples were withdrawn through a valve located near the bottom of the barrel into previously numbered one-quart plastic or glass containers. The numbered containers were filled at random. The samples were then placed into ice chests to assist in sample preservation.

To insure uniformity of starting time, the participants were instructed to begin analysis at 10:00 a.m. (CDT). Since the samples were obtained about 16 hours previous, the samples could be air delivered to MDQARL, Cincinnati, Ohio.

The phenolic analytical results of the study are presented in Tables 3 and 4. As can be seen, there is a very noticeable improvement in the coefficient of variation (standard deviation divided by the mean) for the results after the seminar. This is demonstrated graphically in Figure 1. Plotted are the standard deviations from this study versus the concentrations of phenolics. Also indicated on this plot are a range of standard deviations that can normally be expected. This range is based on results reported in the literature on analytical procedures. As can be seen, before the seminar, the standard deviation for the interlaboratory results is well above the normal range. After the instruction seminar, the standard deviation is brought down within the normal range. This indicates that instruction in proper analytical technique is essential to obtaining optimal analytical results.

TABLE 3

PHENOL ANALYTICAL METHOD EVALUATION

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Phase I

(Results obtained before Instruction)

Intralaboratory Evaluation:

----- µg/l -----		
<u>Lab No.</u>	<u>Phenol</u>	<u>Duplicate</u>
01	15.0	11.3
01	14.4	11.3
01	9.7	10.2
01	14.0	11.2
01	13.9	11.7
01	13.9	9.8
01	13.5	10.8
Average Phenol		= 12.2 µg/l
Standard Deviation		= 1.8 µg/l

Interlaboratory Evaluation:

----- µg/l -----		
<u>Lab No.</u>	<u>Phenol</u>	<u>Duplicate</u>
02	14.0	15.0
05	24.0	21.9
08	3.3	4.0
10	20.0	17.0
11	29.0	29.0
13	4.0	4.0
16	15.6	20.7
17	12.5	3.8
20	12.0	13.0
Average Phenol		= 15.2 µg/l
Standard Deviation		= 8.1 µg/l

Combined Evaluation:

Average Phenol = 13.9 µg/l
 Standard Deviation = 6.3 µg/l
 Coefficient of Variations = 45.3%

TABLE 4
PHENOLICS ANALYTICAL METHOD EVALUATION

Phase II
(Results obtained after Instruction)

Intralaboratory Evaluation:

<u>Lab No.</u>	----- µg/l -----	
	<u>Phenolics</u>	<u>Duplicate</u>
01	5480	5367
01	5470	5500
01	5480	5150
01	5320	5367
01	5320	5283
01	5070	4800
	Average Phenolics = 5300.6 µg/l	
	Standard Deviation = 206.5 µg/l	

Interlaboratory Evaluation:

<u>Lab No.</u>	----- µg/l -----	
	<u>Phenolics</u>	<u>Duplicate</u>
02	6338	6088
05	6600	6720
08	6600	5000
10	4250	4400
11	6150	6200
16	5400	5500
17	5100	5200
20	6080	6550
	Average Phenolics = 5761.0 µg/l	
	Standard Deviation = 795.8 µg/l	

Combined Evaluation:

Average Phenolics = 5563.7 µg/l
Standard Deviation = 650.4 µg/l
Coefficient of Variation = 11.7%

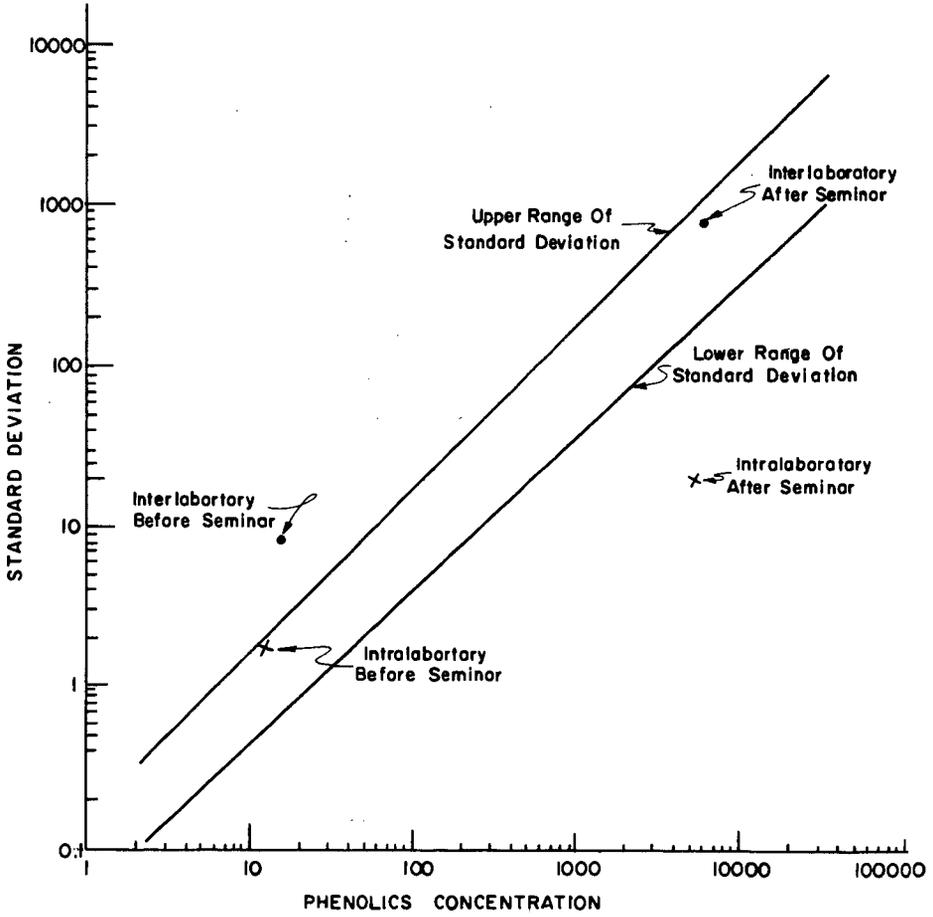


FIGURE 1 - PHENOLICS ANALYTICAL VARIABILITY

Treatment Efficiency Study

Another part of the EPA/API study was to evaluate the pollutant removal capability of activated sludge units which treat refinery wastewaters. Six existing full-scale refinery waste treatment systems were selected for this study. Each activated sludge unit was sampled for a two-week period. Grab samples were taken every two hours and composited for 24-hour periods. Influent to the treatment system (normally from the API separator) and the effluent (normally from the final clarifier) were studied to determine the amount of each pollutant removed.

The refinery treatment systems selected for this study were of sound design and operated in an effective manner. Another criterion in the selection was location. Selection was made so that the distribution would approximately follow the density or distribution of the entire refining industry. The refineries selected had capacities ranging from 35,000 to 117,600 BPD. Two of the refineries were class C, the other three were class B.

Refinery No. 9973 is a 56,000 barrel per day, class B, refinery located in the midwest. A flow diagram of the refinery wastewater treatment is shown in Figure 2. Refinery process wastewater from the API separator is held in an equalization basin with a retention time of about 7 1/2 hours. The wastes then flow into an activated sludge unit with 12 hours detention time in the aeration basin. On the average, this

REFINERY NO. 9973

Class B

Refinery Capacity = 56,000 BPD

Location Midwest



129

Median Influent Phenolics = 11.0 mg/L
Median Effluent Phenolics = 0.01 mg/L
Median Phenolics Removal = 99.9%

FIGURE 2

Activated Sludge Treatment Efficiency Study

(S) denotes sample point

unit handled wastewater with 11 mg/L of phenolics and reduced it to less than 0.01 mg/L for a typical removal of over 99.9%. A graphical presentation of the daily results is presented in Figure 3. Note that there is some variation in influent concentration. However, for the most part, this variation is small. As a result, the effluent concentration is relatively constant and the removals are quite good on a day-to-day basis. However, one sample (the 12th day) showed a substantial increase in phenolics for no apparent reason.

Refinery No. 2115 is an 88,000 BPD, class B refinery located in the northwest. The oily refinery wastewaters from the API separator are discharged to a primary clarifier, then to a trickling filter, and finally to an activated sludge unit with a detention time of 2.7 hours in the aeration basin. A diagram of the refining wastewater treatment system is shown in Figure 4. For this treatment system, samples were collected following the API separator, the trickling filter, and final clarifier. During the sampling period the median influent to the treatment system was 10.45 mg/L. The trickling filter reduced this to 0.99 mg/L. Finally the activated sludge reduced the phenolics to 0.35 mg/L for a total removal of 99.6%. Figure 5 shows the daily results of the sampling. As can be seen, the final concentration of the activated sludge unit responds very sensitively to the concentration from the trickling filter. Note that between the second and third day into the study, a small increase in phenolics from the trickling filter resulted in a very sharp increase in the discharge from the

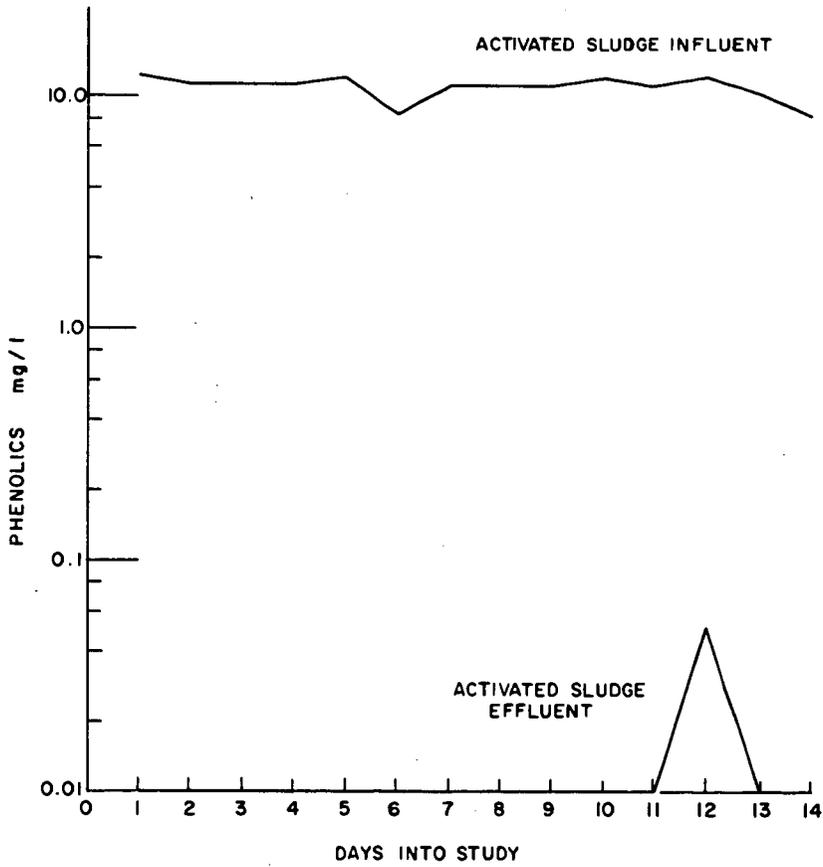


FIGURE 3 - TREATMENT EFFICIENCY STUDY RESULTS
REFINERY NO. 9973

REFINERY NO. 2115

Class B
Refinery Capacity 88,000 BPD

Location Northwest



132

Median Influent Phenolics = 10.45 mg/L
Median Trickling Filter Phenolics Effluent = 0.99 (90.5% removal)
Median Effluent Phenolics = 0.035 mg/L
Median Phenolics Removal = 99.6%

FIGURE 4

Activated Sludge Treatment Efficiency Study

(S) denotes sample point

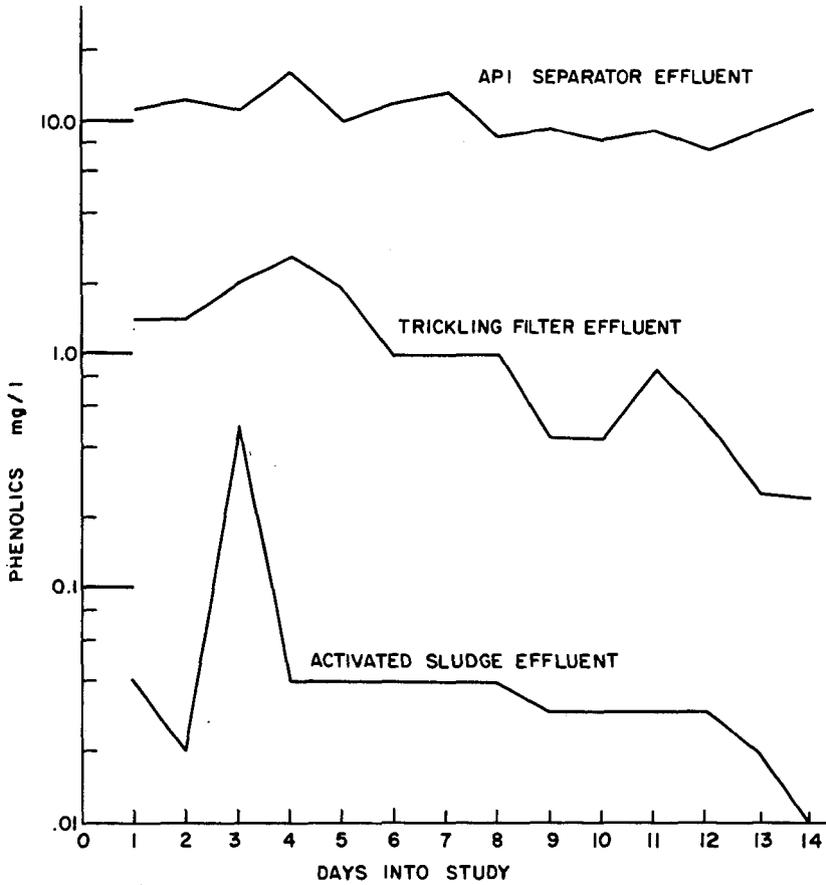


FIGURE 5 - TREATMENT EFFICIENCY STUDY RESULTS
REFINERY NO. 2115

activated sludge system. On the other hand, at about 11 days into the study the trickling filter showed a fair increase in concentration whereas the activated sludge indicated no change. The major difference between these two situations is that the first increase ("upset") occurring 2 days into the study resulted in a 2.5 mg/L concentration going into the activated sludge. Whereas the second "upset" resulted in a concentration of only 0.85 mg/L. Thus, it appears reasonable to expect that the effect of an "upset" is related not only to the relative change in concentration, but is also highly dependent upon the maximum concentration of the upset.

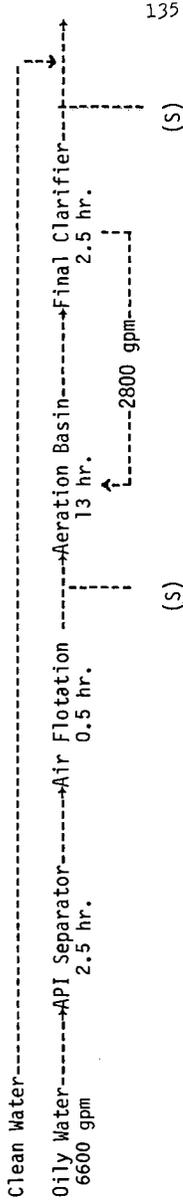
Refinery No. 0288 is an 117,600 BPD, class C refinery located in the midwest. The refinery's oily wastewater from the API separator is treated by air flotation and then treated by an activated sludge system whose aeration basin has a 13-hour detention time. A diagram of the refinery wastewater treatment system is shown in Figure 6. In the study of this refinery, samples were obtained from the air flotation unit and the final clarifier effluents. The median phenolics concentration of the wastewater sent to the activated sludge unit was 2.5 mg/L. The median effluent from the activated sludge unit was 0.01 mg/L, for a median removal for phenolics of 99.4%. Figure 7 shows the daily concentration during the study. In the first week of the study the feed concentration increased very significantly twice (3rd and 5th days). As expected, the effluent from the activated sludge also increased in response to the feed concentration. In the second week, there was a slight increase in feed concentration, however, the effluent from the final clarifier did not indicate

REFINERY NO. 0288

Class C

Refinery Capacity, 117,600 BPD

Location Midwest



Median Influent Phenolics = 2.5 mg/L
Median Effluent Phenolics = 0.01 mg/L
Median Phenolics Removal = 99.4%

FIGURE 6

Activated Sludge Treatment Efficiency Study

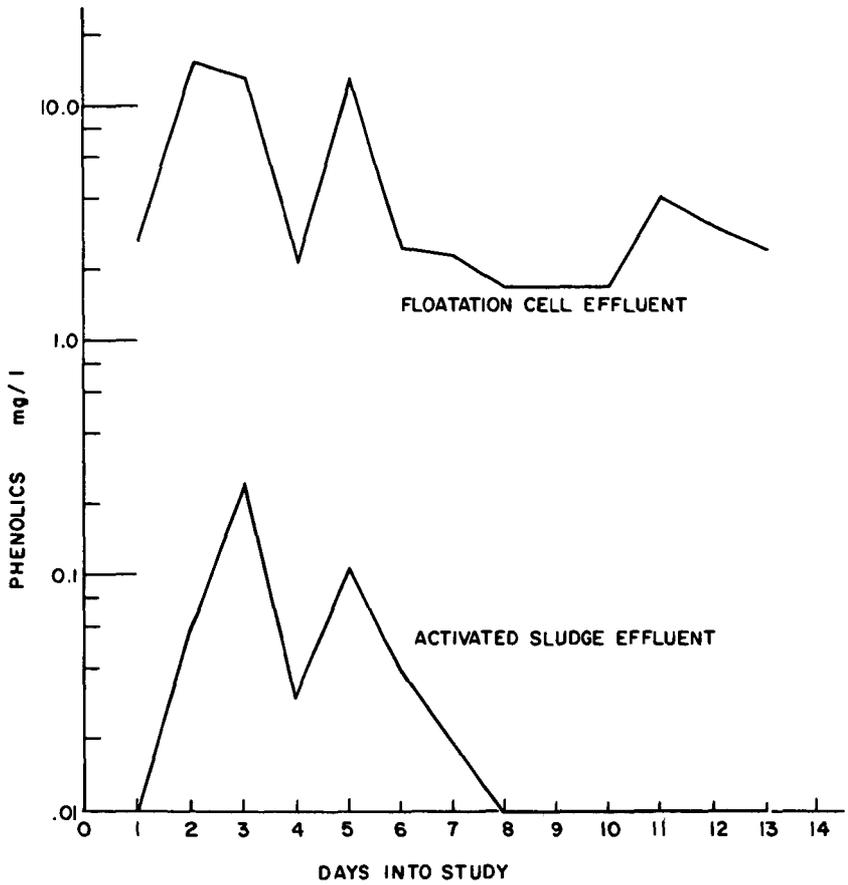


FIGURE 7 - TREATMENT EFFICIENCY STUDY RESULTS
REFINERY NO. 0288

any effect. Apparently, the feed concentrations were not high enough to adversely effect the performance of the treatment system.

Refinery No. 6512 is a 90,000 BPD, class C refinery, located in the southwest. All of the wastewater from the refinery flows through an API separator to an equalization basin. From there, the water is treated by chemical coagulation and then by an activated sludge treatment system which has a total detention time of 12 hours. A diagram of this waste treatment facility is shown in Figure 8. From the equalization basin the median phenolics concentration is 0.61 mg/L. The effluent from the activated sludge is about 0.01 mg/L for 97.6% removal of phenolics. Figure 9 shows the daily concentration from this study. During the first week, there were two periods in which the phenolics in the effluent were running higher than normal (3rd and 5th days). These periods generally correspond to periods when the feed concentration was higher than normal. During the second week, a very high effluent concentration was noted at the 11th day, although the feed concentration remained fairly level. There is no apparent explanation for this "upset." It was also noted that during this period the sulfide content of the activated sludge effluent was abnormally high.

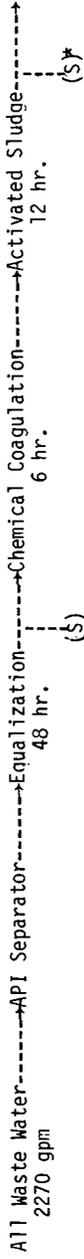
Refinery No. 6693 is a 35,000 BPD, class B refinery located in the southwest. All of the refinery wastewater flows through an API separator to an activated sludge unit whose aeration basin has a 48-hour detention time. Figure 10 contains a diagram of the refinery

REFINERY NO. 6512

Class C

Refinery Capacity 90,000

Location Southwest



Median Influent Phenolics = 0.61
Median Effluent Phenolics = 0.01
Median Phenolics Removal = 97.6%

138

*Sample was taken of clarified effluent from combined aeration-clarifier unit.

FIGURE 8

Activated Sludge Treatment Efficiency Study

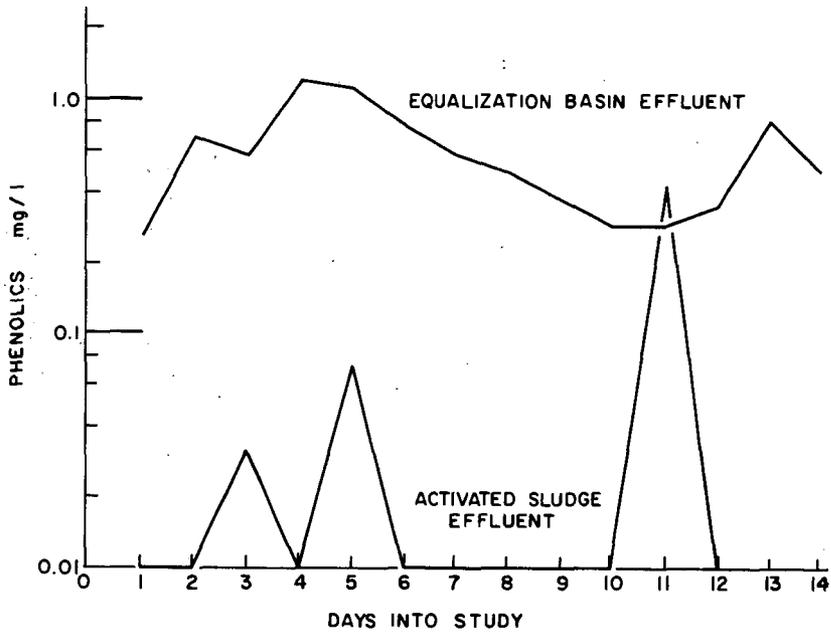


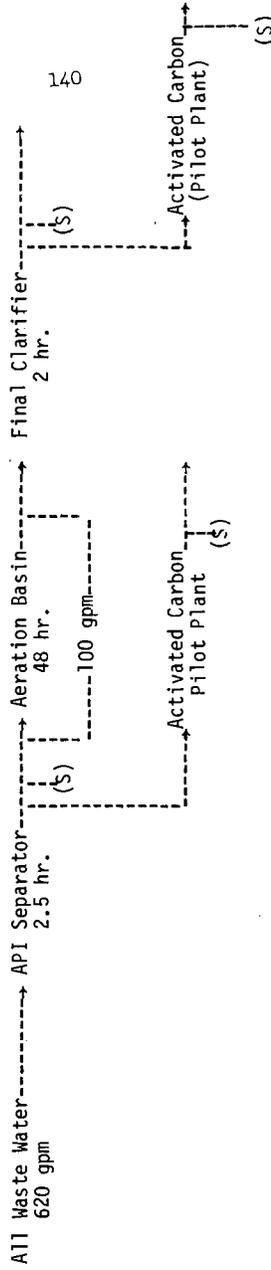
FIGURE 9 - TREATMENT EFFICIENCY STUDY RESULTS
REFINERY NO. 6512

REFINERY NO. 6693

Class B

Refinery Capacity 35,000 BPD

Location Southwest



Median Influent Phenolics = 3.38 mg/L
Median Biotreatment Effluent Phenolics = 0.013 mg/L (99.6% removal)
Median Carbon Treatment Effluent Phenolics = 0.003 mg/L (99.91% removal)
Median Bio-Carbon Treatment Effluent Phenolics = 0.001 mg/L (99.97% removal)

FIGURE 10

Activated Sludge and Activated Carbon
Treatment Efficiency Study

(S) denotes sample
point

wastewater treatment system. For this treatment system, samples were collected at the API separator effluent and the final clarifier effluent. As an additional study, this treatment system was chosen for an evaluation of activated carbon treatment of refinery wastewater. Sample streams from the API separator and final clarifier were sent to an activated carbon pilot plant.

In the first pilot plant, activated carbon was the sole treatment process for the API separator effluent (i.e., secondary). In the second pilot plant, a biologically treated effluent from a final clarifier was "polished" using the activated carbon adsorption process (i.e., tertiary). Two complete pilot plants were installed and operated simultaneously.

Figure 11 is a flow diagram of the pilot activated carbon treatment systems. The wastewater to be treated first flows through a dual-media filter constructed of a 4" pipe. This filter consisted of an 18" layer of sand over pea gravel, topped with a 6" layer of anthrafilt. The purpose of the dual-media filtration pretreatment was to reduce the suspended solids and oil content to an acceptable level. Pretreatment for oil and suspended solids removal is a necessity in the handling of refinery wastewater with activated carbon since excess solids or oil will plug off the column prematurely.

After pretreatment, the wastewater entered a "Calgon" activated carbon pilot plant. This pilot plant was set up so that the wastewater flowed down three of the 5" ID columns. The first column contained

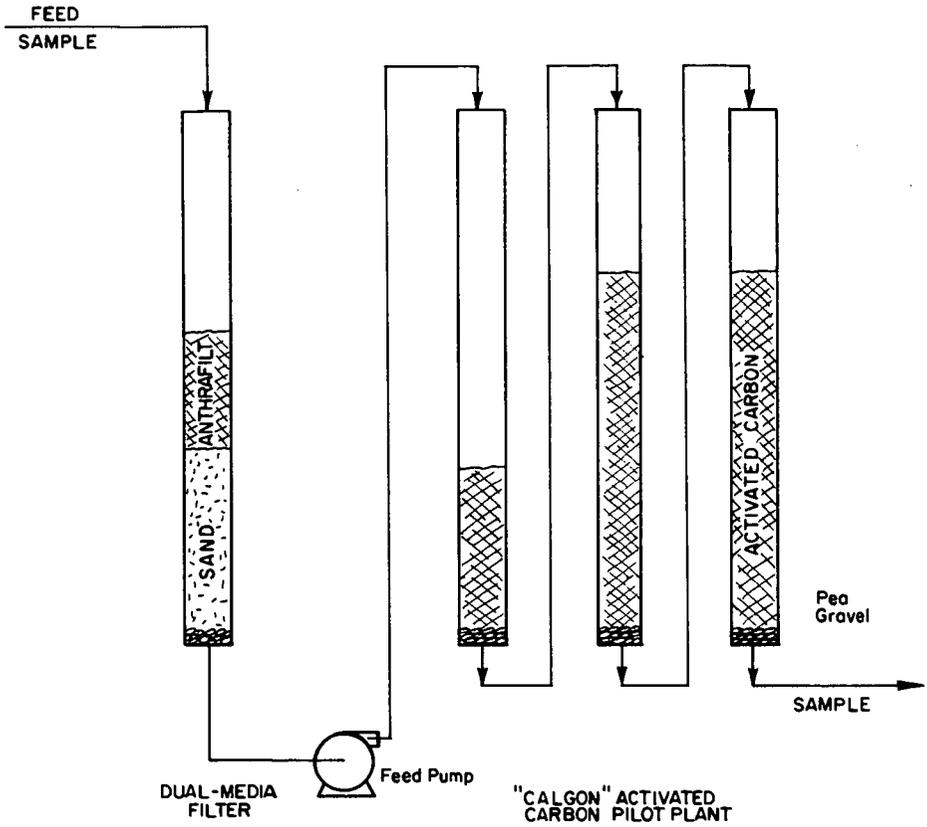


FIGURE II - ACTIVATED CARBON PILOT PLANT FLOW DIAGRAM

an 18" layer of granular activated carbon while the remaining columns had a 36" layer of carbon.

The flow rate through each pilot plant was adjusted to about 1/4 gpm. During the operation of the pilot plant, samples of the API separator effluent, biological treatment effluent, and both pilot plants' effluents were taken every two hours. These samples were composited and preserved according to recommended EPA methods. Twenty-four hour composite samples were analyzed daily for a spectrum of water pollution control parameters using EPA analytical methodology and analytical quality control techniques.

The dual-media filter and carbon columns were backwashed whenever the pressure in the first column exceeded 20 psi.

The median phenolics content of the API separator effluent was 3.38 mg/L. The activated sludge effluent contained a median 0.013 mg/L for a 99.6% removal. The activated carbon treatment system treating API separator effluent had a median 0.003 mg/L effluent concentration for a 99.91% removal. The activated carbon system following biological treatment had an effluent concentration of 0.001 mg/L for a 99.97% removal.

Figure 12 is a graphical presentation of the API separator effluent and the activated sludge effluent. For the most part the influent concentration was fairly free of any sharp increases of phenolics. With the exception of the first 2 or 3 days, the activated sludge effluent was fairly constant. During the last 5 days of the study the feed showed a gradual increase in concentration. However, there was no apparent effect on the effluent.

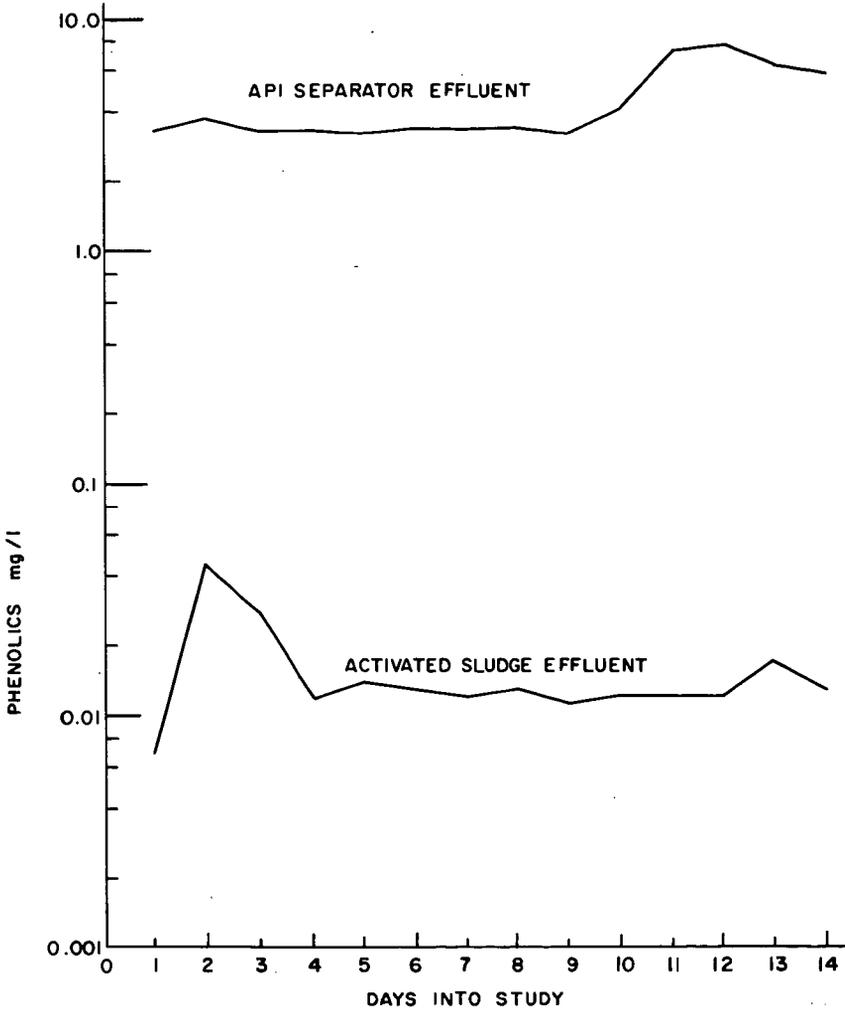


FIGURE 12 - ACTIVATED SLUDGE TREATMENT EFFICIENCY
STUDY - REFINERY NO. 6693

Figure 13 is a graphical presentation of the daily phenolics content of the API separator effluent and the activated carbon effluent. During the 5th day into the study the carbon effluent showed a tremendous increase in phenolics. At about the same time a shift in the column feed pH from 6 to 9 was noted. During the remainder of the study, the pH remained on the alkaline side. It is very likely that a slug of caustic went through the column causing the carbon to release any adsorbed phenolics. This occurs under alkaline conditions because phenol shifts to the phenate form which is more water soluble and difficult to absorb. After the initial "upset" the column effluent showed a continuous increase in concentration to the point where at the end of the study the column effluent was approaching the feed concentration. This continuing increase was probably due to the fact that the column was operating under alkaline conditions, and its capacity for phenolics adsorption was significantly reduced. The increased phenolics content at the end of the study was probably attributable to column exhaustion (breakthrough).

Figure 14 contains a graphical presentation of the effluent of the activated carbon pilot plant which followed biological treatment. The activated sludge produced an effluent whose pH was consistently less than 7 (5 to 7). As a result of pH level being consistently below 7, the phenolic content from the carbon columns remained fairly constant at a very low level.

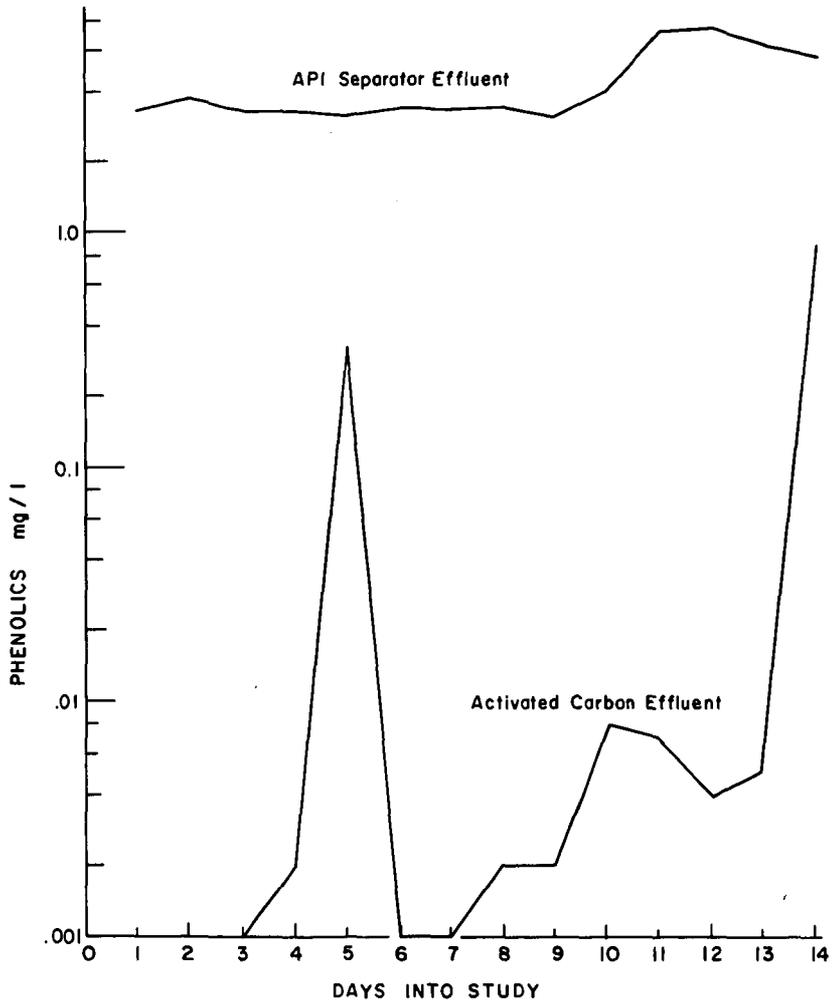


FIGURE 13 - ACTIVATED CARBON TREATMENT EFFICIENCY STUDY - REFINERY NO. 6693

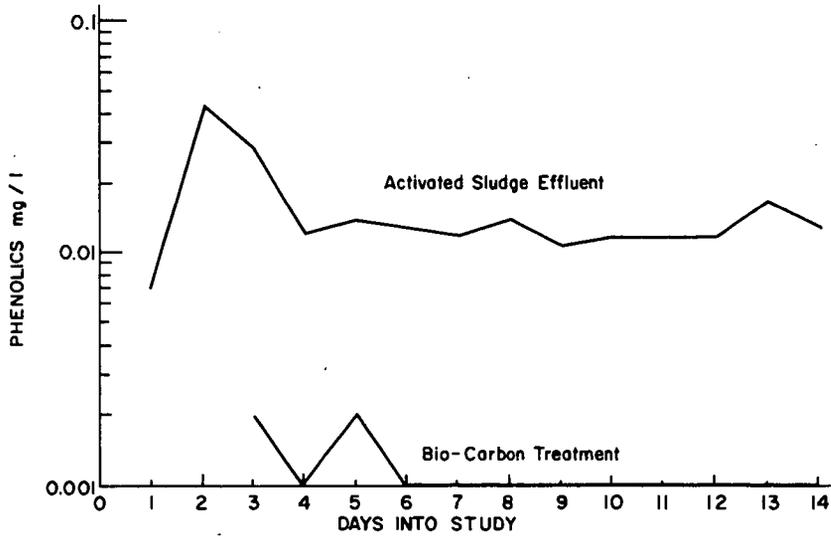


FIGURE 14 — BIO-CARBON TREATMENT EFFICIENCY STUDY
REFINERY NO. 6693

SUMMARY

1. Analytical variability of refinery wastewater data, as analyzed EPA methodology, was improved after a seminar on analytical procedures.

2. Both biological and activated carbon treatment systems showed high capacity for the removal of phenolics.

3. Biological systems appear to "upset" easily with changes in phenolics concentration. At times biological systems will "upset" with no apparent cause.

4. Activated carbon systems can provide excellent treatment capability if the hydrogen ion concentration of the waste streams is controlled. It is particularly important to avoid caustic conditions in the activated carbon columns.

This report has been reviewed by the Office of Research and Development, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.