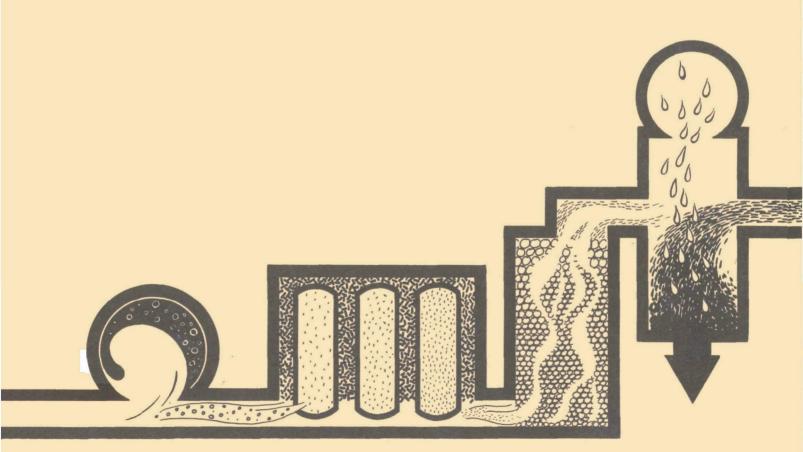


Improving Granular Carbon Treatment



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IMPROVING GRANULAR CARBON TREATMENT

bу

FMC Corporation Princeton, New Jersey 08540

for the

ENVIRONMENTAL PROTECTION AGENCY

Project #17020 GDN Contract #14-12-901

July 1971

EPA Review Notice

This report has been reviewed by the 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.

ABSTRACT

The magnitude and effects of biological activity in expanded carbon beds used for direct clarification/adsorption treatment of wastewater were investigated. Major aspects of the project involved comparisons of the relative effectiveness of aerobic and anaerobic conditions in the expanded-bed systems, and a comparison of the relative treatment effectiveness of expanded carbon beds of high and low sorptive activity under aerobic operating conditions. The use of short polishing columns to remove traces or organics escaping from on-line adsorbers was also evaluated.

The feed, primary effluent from a treatment plant near Trenton, New Jersey, was coagulated with FeCl₃, clarified and filtered. Clarification removed over 60% of the charged total organic carbon (TOC) and 55% of the BOD. The clarified primary effluent was fed to the carbon columns. Carbon activity comparisons with and without addition of oxygen were made in identical series of four columns containing a total of 24 ft of carbon.

TOC removal in activated carbon beds operated constantly with 6 to 10 mg/l of dissolved oxygen dropped from 81% originally to 66% during nine months of operation, and averaged 77.6% for the entire 889,600 gal. (8896 bed volumes) of feed treated. During 3-1/2 months in similarly aerated columns, beds of unactivated coal removed 44.3% of charged TOC, entirely due to biological activity. Activated carbon beds operated without oxygen (anaerobically) removed 66.9% of the TOC, and presented problems of $\rm H_2S$ evolution. Anaerobic conditions should be avoided.

Over the nine-month operating period, combined chemical clarification plus aerobic activated carbon treatment (in 24-ft-deep beds at a 5-gpm/sq ft flow rate) removed 87% of the TOC and over 90% of the BOD. The product had a TOC of 8 mg/l or less, and carbon column operation was continuous except for three short interruptions to cleanse the columns. With inactive coal, combined coagulation and aerobic treatment gave 80% TOC removal and 90% BOD removal. The product averaged about 10 mg/l BOD or TOC. Estimated treatment costs for combined clarification/adsorption treatment at 10 mgd are 20¢/l,000 gal. with activated carbon, and about 18¢/l,000 gal. with the unactivated coal.

Polishing columns were effective in reducing effluent TOC to about 2 mg/l, but to be economically practical regeneration must be very low cost. The best regenerants studied were not effective enough to offer promise for developing an economically practical process embodying this technique for producing an organic-free water.

This report was submitted in fulfillment of Project Number 17020GDN, Contract 14-12-901, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

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SECTION I

CONCLUSIONS

- 1. In continuous, nine-month pilot-scale studies, aerobic expanded-bed activated carbon columns effectively and economically treated a chemically coagulated and clarified primary effluent to produce a high quality effluent.
- 2. Overall organic carbon removal by the combined coagulation and activated carbon treatment averaged almost 87.2% for the entire nine-month period. BOD removal was over 90%.
- 3. Combined coagulation and treatment in the aerobic non-activated coal columns removed over 80% of the organic carbon in primary effluent. BOD removal was over 90%.
- 4. Activated carbon removed 75% of organic carbon in chemically coagulated and clarified primary effluent; non-activated carbon removed about 50% after 2 to 4 weeks when biological activity developed inside the columns.
- 5. In activated carbon beds, more organics were removed with aerobic operation than with anaerobic. Aerobic products retained their clarity but anaerobic products clouded on standing.
- 6. A combined anaerobic-aerobic system was also effective. However, the anaerobic section gave a much poorer organic removal than did the corresponding aerobic section.
- 7. The effectiveness of the expanded-bed adsorbers was enhanced by occasional air scrubbing and backwashing to remove excess biomass and precipitated coagulant from the carbon beds.
- 8. Anaerobic effluents consistently contained 8 to 13 mg/l $\rm H_2S$, but effluents from aerobic columns were essentially free of $\rm H_2S$.
- 9. With only 24-ft-carbon-depth treatment, efficiencies dropped in severely cold weather, probably due, in part, to higher fluid viscosity, lower sorption rates, and a decline in bacterial activity.
- 10. NaOH and 4% $\rm H_2O_2$ were the most active regenerants for partially-spent polishing column carbons. However, neither regenerant restored the original activity of the lightly-loaded carbon.

SECTION II

RECOMMENDATIONS

The following studies should be conducted to develop an economical and effective expanded-bed physico-chemical process:

- 1. Study ways of aerating streams to and between columns to devise a plant-operable system capable of introducing at least 6 mg/l of O_2 into the stream before it enters the succeeding column.
- 2. Determine whether low activity sorbents can be operated more effectively in expanded-bed adsorbers for long periods of time. The use of such materials would offer major cost economies.
- 3. Prepare flow sheet designs and economic evaluations for a demonstration plant of about 1-mgd capacity.

SECTION III

INTRODUCTION

Under the sponsorship of the FWPCA and EPA, the FMC Corporation has been conducting investigations on advanced physico-chemical methods for wastewater treatment for over three years. This work was primarily a study of expanded-bed contacting for effective utilization of granular activated carbon on the treatment of both secondary and primary clarified sewage effluents.

In expanded-bed operation, sewage is passed up through a bed of carbon at a sufficient velocity to expand the bed to at least 115% of the volume of the carbon at rest. Weber had shown the feasibility of using expanded-bed adsorbers to treat secondary effluent. Expanded-bed adsorbers gave essentially the same organic removal as fixed beds of carbon, but the latter required frequent interruptions for backwashing. 2,3,4

The expanded-bed adsorption system was also used to treat primary effluent. With a chemically coagulated and clarified primary effluent feed, the expanded-bed carbon adsorption system produced a clear, high quality effluent. Thus, the combined chemical clarification and adsorption systems removed over 95% of the organics, essentially all suspended solids and turbidity, and over 90% of the phosphates in the primary effluent. Treatment cost for a 10-mgd plant, based on 1969 values, was estimated to be 20¢/1,000 gal. of product water. During four months of steady operation, the expanded-bed treatment system needed little or no cleaning or backwashing and operated with a low and relatively constant feed pressure requirement.

The results not only demonstrated the effectiveness of expanded-bed carbon contacting, but also pointed up the potential advantages of physico-chemical water treatment. A modern well-operated biological treatment plant might reduce suspended solids (SS) by 95% and yield a product with a BOD of 20 mg/l or less. However, such performance is difficult to maintain on a continuous basis. By contrast, the products from the pilot-plant expanded-bed system constantly had a BOD of under 10 mg/l and the performance of this system equalled or exceeded the performance of conventional plants in other characteristics as well.

The growth in the concern for the quality of surface waters has accentuated the search for more efficient methods of treating wastewaters. Conventional biological treatment

plants will be able to meet more stringent demands for better water quality or more effective pollution control only by adding tertiary treatment processes to existing biological plants. Such processes increase sewage treatment costs significantly and require land areas that are becoming increasingly difficult to acquire in developed areas. In addition, the effective operation of such a tertiary treatment system is still dependent upon consistent and efficient operation of the biological secondary treatment process, which is subject to problems arising from changing waste composition, fluctuations in flow, and the presence of materials that are toxic to bacteria.

Physico-chemical processes, on the other hand, produce the desired higher treatment quality at costs approaching those for efficient biological processes, and with smaller land requirements and greater resistance to those upsets that plague biological processes.

During the course of the previous studies, the formation and presence of biological growth on the carbon was noted. The presence of such growth was attributed to the high concentration of adsorbed organic material accumulated on the carbon. There was no evidence that the biological activity hindered the adsorption process. On the contrary, the presence of such activity enhanced the capacity of the system for removal of organics, permitting longer treatment periods before exhaustion of the activated carbon.

To take full potential advantage of this phenomenon, the relative effect of biological activity on the carbon in expanded-bed columns was studied. Although the studies noted above indicated that such activity increased the capacity of carbon for removal of organic matter from clarified primary effluent, no work had been performed or reported to establish its magnitude under varying conditions of The work described here evaluated the effect of operating expanded-bed carbon columns treating primary effluent under conditions which would enhance biological activity in order to assess the relative value of operating a physico-chemical treatment process under such conditions. After the preferred conditions for bacteriological growth were established, they were evaluated with carbons of different sorptive capacities to determine if adsorption on carbon surfaces affected biological activity within a carbon column.

In virtually all carbon treatment processes, there is a leakage of organic compounds through the activated carbon column.³ The exact nature of this leakage is unknown, but it probably is due to dead cell fragments or small highly degraded, polar materials that are adsorbed poorly. Studies

using small, fresh carbon beds as a polishing adsorber showed that this leakage was at a minimum when treated effluent was first passed through fresh carbon, but that it increased to 4 to 5 mg/l in a few days, presumably due to a chromatographic effect in which the more easily adsorbed materials displace those that are adsorbed weakly. The action and potential utilization of the polishing column, as a means of extending the effectiveness of the physico-chemical treatment system, were also examined in this study.

SECTION IV

DESCRIPTION OF PILOT PLANT

A. Pilot Plant Installation

The pilot plant used for the experimental work was the same as that described in the FWQA report of the preceding study on the treatment of secondary effluent in expanded-bed adsorbers. The plant was located at the sewage treatment facility of the Ewing-Lawrence Sewerage Authority (ELSA) near Trenton, New Jersey which serves residential, commercial, and industrial areas within the two townships of Ewing and Lawrence. The sewage consists of about 25% industrial waste and 75% domestic waste. This is a trickling filter plant which includes four circular, primary sedimentation basins.

For this study, primary effluent was taken from one of these basins and siphoned through a 300-ft long, 1.5-in. polyethylene pipe to a pump at the pilot plant site. Primary effluent was used as feed because of the presence in the raw sewage of varying amounts of large solids which would have been difficult to handle in the small lines and valves of the pilot system. The primary basins provide settling for raw sewage plus the liquid from return sludge and the supernatant from the anaerobic sludge digestor.

The experimental apparatus at the pilot plant was set on a poured concrete slab installed next to the ELSA return pump, and controls were located in a 10-ft by 16-ft building constructed on the slab. The carbon adsorbers were internally coated steel pipe columns resting on the slab and supported by an angle iron frame. The filter and other tanks were located on the slab next to the building. Connections between the columns and valves were made with rubber hoses which passed through the building walls.

B. Clarification System

The clarification system consisted of two 55-gal. drums for rapid mix, coagulation, and flocculation followed by an upflow clarifier and dual media filter, as shown in Figure 1. The primary effluent was pumped through a float valve which controlled the level in the rapid mix compartment in the upper part of the first 55-gal. drum. The coagulant, a 30 weightpercent aqueous solution of ferric chloride, was fed by a metering pump into the stream of primary effluent, discharging from a 5/8-in. nozzle into an elbow to impart a circular motion in the

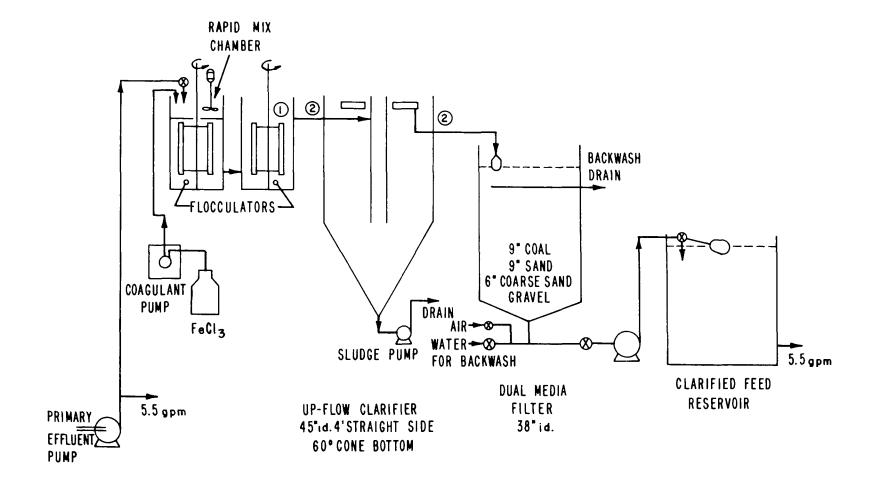


FIGURE 1 - FLOW DIAGRAM OF CLARIFICATION SYSTEM

rapid-mix compartment. A motor driven propeller was used to provide additional rapid mixing. After an average detention time of two minutes at the design flow of 5.5 gpm, the mixture flowed successively into the lower part of the first drum for flocculation with slow mixing, into the bottom of the second drum for further flocculation with slow mixing, and then out at the top and into the clarifier. The slow stirring in both tanks was provided by 24-in. by 2-in. redwood paddles, with the 24-in. dimension in the vertical position, mounted at a 7-in. radius to a vertical shaft driven by a constant speed motor. first flocculation tank was also fitted with three vertical redwood stators, 24-in. by 1.5-in. by 0.5-in. attached to the side of the tank. At 5.5 gpm flow, the detention times were 7 min. in the first flocculation chamber and 9 min. in the second. The motor-driven paddles in these tanks could be operated at various speeds to provide different degrees of mixing.

The up-flow clarifier was designed for this project. It was a 400-gal. capacity, shop fabricated, steel cylindrical tank, 3 ft 9 in. in diameter with a 4-ft high straight section, and a 60° cone bottom. Flocculated water entered a central 8-in. diameter chimney, discharged at a depth of about 4-ft below the surface, then flowed upward to the over-flow trough at the surface. The detention time at 5.5 gpm was approximately one hour. The product water from the clarifier flowed to the dual-media filter, which consisted of 9 in. of anthracite coal (effective size 0.59 mm) over 9 in. of filter sand (effective size 0.62 mm) supported on gravel with a pipe underdrain. Filtered water was pumped to a 250-gal. reservoir to provide feed to the pumps for the carbon column systems.

Sludge was pumped from the clarifier by a positive pressure pump attached to the bottom of the cone and operated by a cycle timer to remove and discard sludge at predetermined intervals. Usually this pump was operated for one minute, three times an hour, to discharge about 15 gal. of sludge per hour.

C. Carbon Adsorption Systems

1. Multi-Bed Adsorbers

The carbon adsorbers were vertical columns constructed of internally coated 10-in.-diameter steel pipes with flanges at each end. The pilot plant had eight such columns which were operated as two parallel systems of four columns each.

The flow diagram for each system is shown in Figure 2. The first two columns in each system were 9-ft steel columns with a l-ft section of ll-in.-i.d. transparent pipe to permit observation of the expanded carbon beds, and to provide a visual check to ensure that carbon was not being washed out of the column. The last two columns in each system were ll ft steel columns. Figure 3 shows a schematic view of the columns with the transparent pipe. The all-steel pipes had identical construction except for the absence of the transparent section. Hose connections were provided at the tops and bottoms of the columns.

Each column was charged with 3.25 cu ft carbon which provided a 6-ft-deep bed of settled carbon. The carbon was supported on a 6-in. layer of gravel and coarse sand over an inverted 5-in.-diameter cone shaped distributor. The two carbons used in this investigation were Pittsburgh Filtrasorb 400 activated carbon, marketed by the Calgon Corporation, Pittsburgh, Pennsylvania, and "Filt-O-Cite" No. 1 filter media, an anthracitic material marketed by the Shamokin Filter Company, Shamokin, Pennsylvania. Both carbons were charged as received. The analyses of these carbons is shown in Table 1.

Feed was supplied to the columns by constant displacement pumps driven by electric motors through variable speed drives. The feed charge rate was 5 gpm/sq ft. Reinforced rubber hose, 5/8-in. i.d., was used for the connecting lines to and between the columns to provide for ease of installation. All flow controls, including in-line valves, pressure gauges, flow meters (water meters), and solenoid sampling valves were mounted on one central operating panel within the pilot building. Stream flows were maintained at constant rate by adjustment of the pump drives. Treated water from the expanded-bed columns was discharged into a drum so that any carbon particles carried out could be collected and returned to the column if necessary. All product water was returned to the sewage treatment plant.

When added to column influents, oxygen was fed into the feed lines just downstream from the column solenoid sampling valves inside the pilot building. The oxygen was bled from high-pressure storage cylinders through calibrated rotameters at rates designed to give oxygen concentrations of 6 to 10 mg/l in column feed lines. Samples were taken from the bottoms of each column to monitor their dissolved oxygen contents.

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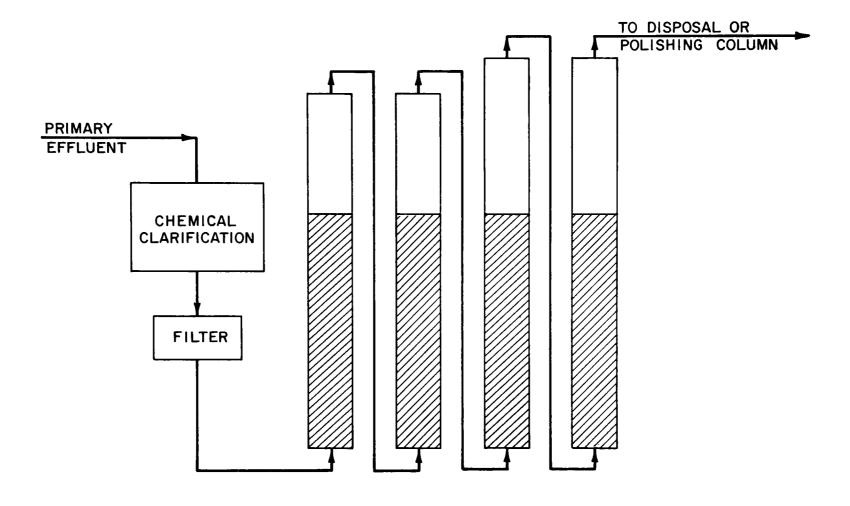


FIGURE 2-FLOW DIAGRAM OF CARBON BED SYSTEM

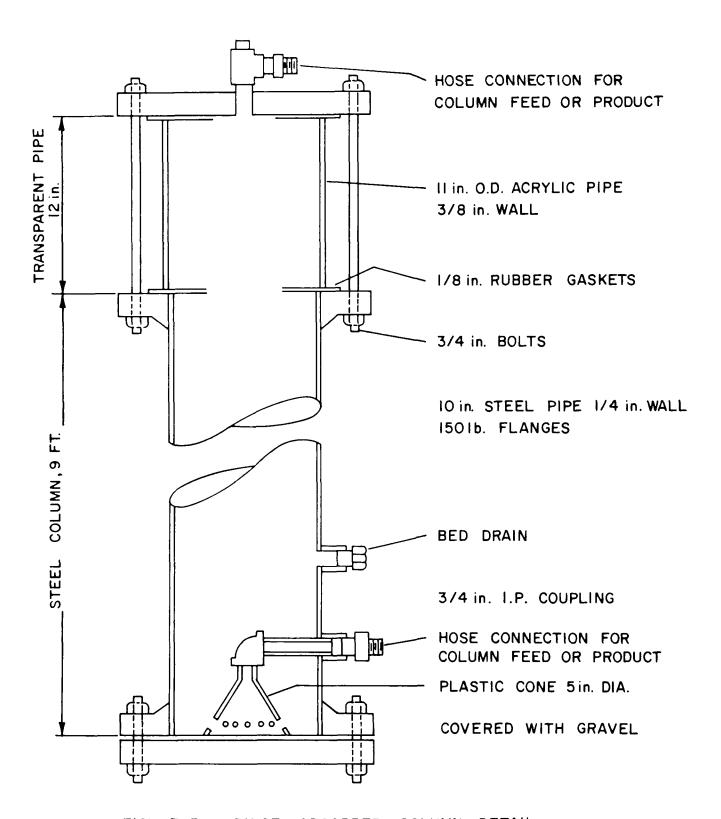


FIGURE 3 - PILOT ADSORBER COLUMN DETAIL

Table 1

MESH SIZE DISTRIBUTION AND PHYSICAL ANALYSES OF ACTIVATED CARBON AND NON-ACTIVATED COAL DERIVATIVE

	Filtras	orb 400 ^a	Filt-O-Cite No. 1b		
Sieve Analysis	Sieve U.S. No.	Retained	Sieve U.S. No.	% Retained	
	16 20 30 40 50 Pan	9.0 42.6 33.0 13.2 2.0 0.2	8 10 16 20 30 Pan	10.8 23.9 54.1 9.6 1.4 0.2	
Density-lb/ft ³					
Bulk		24.6		52.5	
% Moisture		1.2		9.6	
% Volatile Matter		1.0		< 1.0	
% Ash		6.6		19.3	
Iodine No. mg/g		1,270.		150.	

a Purchased from Calgon Corp., Pittsburgh, Pa.

b Purchased from Shamokin Filler Co., Shamokin, Pa.

In the up-flow operations used, the carbon seldom required cleaning. When it did become necessary, however, to dislodge solids trapped in the carbon beds, the most effective procedure consisted of lowering the water level to within a foot of the top of the carbon bed, injecting air into the bottom of the column for 5 to 10 min. and then backflushing with clean water to sweep away the dislodged solids. The sludge resulting from the carbon cleaning operation was collected in a drum so that any activated carbon lost from a column could be returned to that column.

The entire system was designed for essentially automatic operation. A technician visited the plant daily to adjust flows, perform routine maintenance, and take samples for analysis.

2. Polishing Column

The polishing column consisted of a 6-in.-i.d. glass column containing 20 lb of fresh Filtrasorb 400. This amount of carbon formed a 4-ft-long bed in the columns. The column was washed upflow with city water to purge approximately 0.5 lb of dust that rose to the surface before each run. Feed for this column was effluent from the 24-ft columns. During polishing column tests, the column effluent was collected in a clean, polyethylene 5-gal. bottle which served as the reservoir for the polishing column feed. This feed was charged up-flow at 1 gpm, which was the same 5-gpm/sq ft rate used in the large columns.

Regeneration studies on spent carbons for the polishing columns were conducted in the laboratory. The adsorption effectiveness of the treated carbons was evaluated in glass columns having a cross-sectional area of 1 sq in. in beds 18 in. long. Effluent from the 24-ft carbon beds at the pilot plant was collected in clean 5-gal. polyethylene bottles daily and brought to the laboratory. This effluent was passed upflow through the laboratory glass columns at a rate of 1 gpm/sq ft.

D. Product Sampling and Analytical Methods

Composite samples of the primary effluent feed to each carbon column and the product water from each column were collected automatically by timer-controlled solenoid valves which opened at 15-min. intervals to draw 60-ml samples. These samples were composited in 5-gal. polyethylene bottles in an acid medium to maintain stability and prevent deterioration or biological activity over the sampling periods. Spot samples were collected by hand.

Chemical and biochemical analyses were performed at the FMC Chemical Research Center. Analytical determinations on composited samples included TOC, soluble organic carbon (SOC), and suspended solids (SS). BOD, turbidity, dissolved oxygen, pH and all analyses not performed routinely were run on spot samples brought unacidified to the laboratory for immediate analysis.

Suspended solids concentration of the primary effluent and treated water samples was measured by a procedure involving the use of 0.45-micron membrane filters. The membrane filters, which in manufacture are treated with an organic conditioning agent, were washed in distilled water before use to remove this agent. They were then dried in individual desiccators to constant weight. After filtration of a sample, each filter was dried again in the same desiccator and weighed to determine weight gain by retention of suspended solids. The filtrates were collected to provide samples for SOC analyses.

Well-mixed composite samples were analyzed on the Beckman Carbonaceous Analyzer for organic carbon analysis. TOC was determined directly, and SOC on the filtrate from the suspended solids determination.

Dissolved oxygen was determined by a Precision Scientific Company galvanic cell oxygen analyzer. Hydrogen sulfide in aqueous streams was determined by titration with standardized iodine solutions.

BOD of the unacidified spot samples was determined by the dilution procedure described in "Standard Methods". 7

All turbidity determinations were made with a Hach Model 2100 Photoelectric Turbidimeter.

Total phosphate was determined by ASTM Procedure D-515-60T on samples that had been digested to convert all phosphate to the ortho form. 8

Nitrate was determined by ASTM Procedure D-992-52. Ammonia and organic nitrogen were determined by the Kjeldahl Procedure as outlined in "Standard Methods".

SECTION V

OBJECTIVES

The primary objective of this investigation was to study the effects of biological activity in expanded-beds of carbon treating clarified primary effluent. In each phase of the program parallel tests provided direct comparison between tests under different conditions.

The specific objectives of the projects were:

- 1. To compare the relative effectiveness of aerobic and anaerobic conditions.
- 2. To compare the relative effectiveness of aerobic and combined anaerobic-aerobic conditions.
- 3. To compare the behavior of an activated and a non-activated carbon under aerobic conditions.
- 4. To evaluate the concept of using a short bed of fresh activated carbon as a final polishing adsorber to produce an essentially organic-free effluent.
- 5. To determine if a simple, effective technique can be developed to make polishing carbon treatment economical.

SECTION VI

EXPERIMENTAL RESULTS

A. Comparison of Aerobic and Anaerobic Column Activities

The relative effectiveness of aerobic versus anaerobic column operation was studied for two months. Clarified feed was pumped from a common storage vessel to the two sets of columns which had the same geometry and quantity of activated Precautions were taken to minimize splashing in the clarification and filtration vessels so that the feed would pick up a minimum of dissolved oxygen. Usually, this amounted to less than 2 mg/l O_2 (see Table 2). A dissolved oxygen content of 6 to 10 mg/l O_2 was obtained in the aerobic columns by bleeding oxygen into the feed entering the columns. Originally, 0.1 cfh of oxygen was bled into each of the four columns. Later it was found that the desired oxygen content could be maintained by adding the same quantity of oxygen to only the first and third columns. The oxygen did not dissolve completely, as oxygen bubbles were observed in the transparent sections at the top of the columns. At the start of the run these oxygen bubbles entrained tiny particles of carbon to the top of the column. This ceased after a few days.

Clarifying primary effluent with approximately 140 mg/l of ferric chloride in the coagulation-clarification system reduced the TOC by about 50% during this part of the work, as shown in Figure 4. The TOC of the primary effluent averaged about 60 mg/l and the clarified primary effluent showed a TOC of approximately 30 mg/l. Figure 5 shows the reduction in the turbidity of the primary effluent due to clarification. Primary effluents generally had turbidities of between 40 to 50 Jackson Turbidity units (JTU). The clarified effluent generally had turbidities of between 1 and 7 JTU. The only two high values, 11 and 17 JTU respectively, were recorded in periods when the clarifier became septic.

The removal of TOC in the aerobic and anerobic columns is shown in Figures 6 and 7, respectively. The solid line shows the TOC of product leaving the fourth column, and the triangles show the TOC of product leaving the second column.

Effluent from the aerobic column contained less than 8 mg/l, except when approximately 65,000 and 175,000 gal. of effluent feed were passed through the columns. These were the two aforementioned periods in which the clarifier became

Table 2 DISSOLVED OXYGEN CONCENTRATIONS IN AEROBIC AND ANAEROBIC COLUMN STREAMS

Dissolved oxygen, mg/l

			Stream							
Date	Fee	Feed		Aerobic				Anaerobic		
	PE	CPE	A-1	<u>A-2</u>	A-3	A-4	U-1	U-2	U-3	<u>U-4</u>
9/28	3.7	4.8	7.0	4.6	4.5	5.0	3.7	-	_	3.5
9/30	2.1	3.5	7.0	4.9	5.2	5.5	2.6	-	-	1.5
10/2	2.1	2.8	3.8	7.3	9.4	7.7	1.8	-		1.3
10/5	1.4	2.5	8.0	4.3	9.4	12.5	2.8	-	-	1.8
10/7	2.6	2.2	4.1	7.0	12.5	12.7	1.6	-	_	1.4
10/12 a	am 0.3	2.5	5.5	7.2	7.6	8.6	0.7	0.6	0.6	0.3
ŗ	om 0.4	0.4	-	9.5	_	7.0	_	0.9	-	0.8
10/14	0.3	0.6	6.9	11.2	9.9	9.2	0.8	0.6	1.0	0.6
10/16	0.5	0.4	6.6	9.2	5.3	5.6	1.2	0.6	0.5	0.4
10/19	0.8	0.5	5.0	10.3	7.4	9.3	0.7	0.5	0.8	1.1
10/21	0.8	0.5	6.2	10.6	7.2	7.4	1.4	0.7	0.6	1.0
10/23	0.7	0.6	7.2	8.7	7.7	7.0	0.7	0.5	0.7	0.8
10/26	0.5	0.2	5.6	6.9	5.1	3.4	0.5	0.4	0.4	0.4
10/28	0.6	0.5	7.7	12.5	5.0	1.8	0.9	0.6	0.7	0.6
10/30	0.7	0.6	7.0	7.6	3.0	0.5	0.7	0.5	0.6	0.3
11/2	4.2	3.1	7.6	7.6	10.8	10.5	O	peration	on stop	pped

PE - Primary effluent CPE - Clarified primary effluent

A-1, etc. - First aerobic carbon column, etc.

U-1, etc. - First anaerobic carbon column, etc.

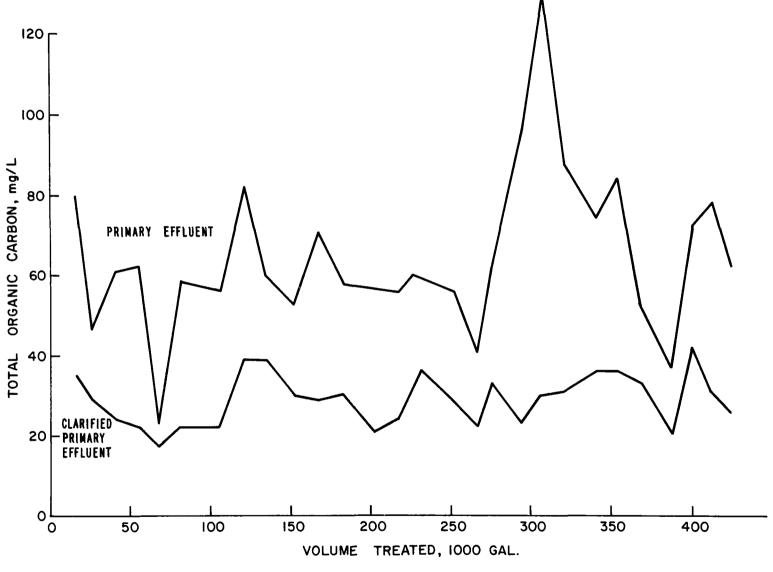


FIGURE 4 — CLARIFICATION OF PRIMARY EFFLUENT WITH 140 ppm FeCl3

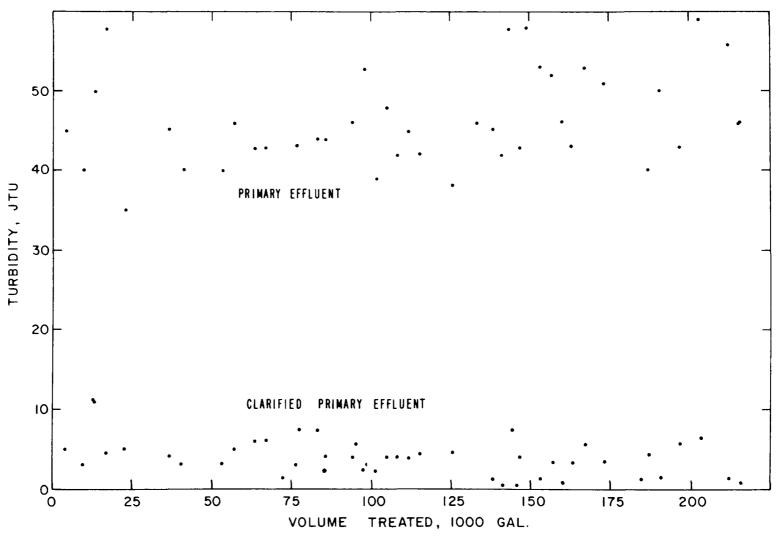


FIGURE 5 — TURBIDITIES OF PRIMARY EFFLUENT AND OF CLARIFIED PRIMARY EFFLUENT

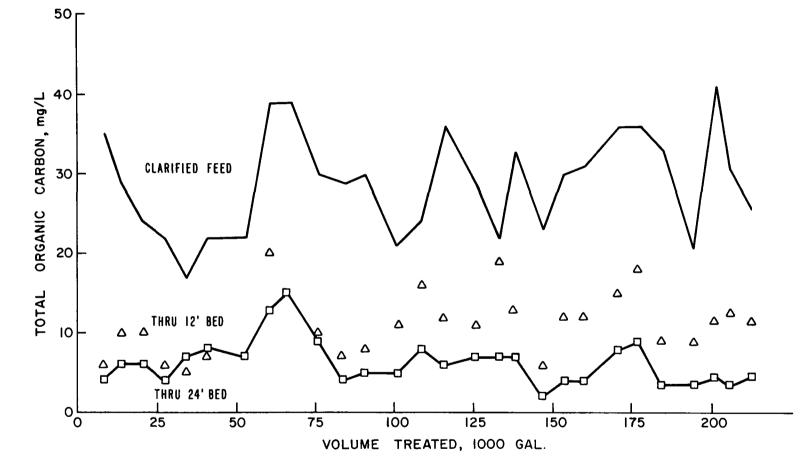


FIGURE 6 - REMOVAL OF TOC WITH OXYGENATED CLARIFIED FEED IN EX-PANDED BEDS OF ACTIVATED CARBON

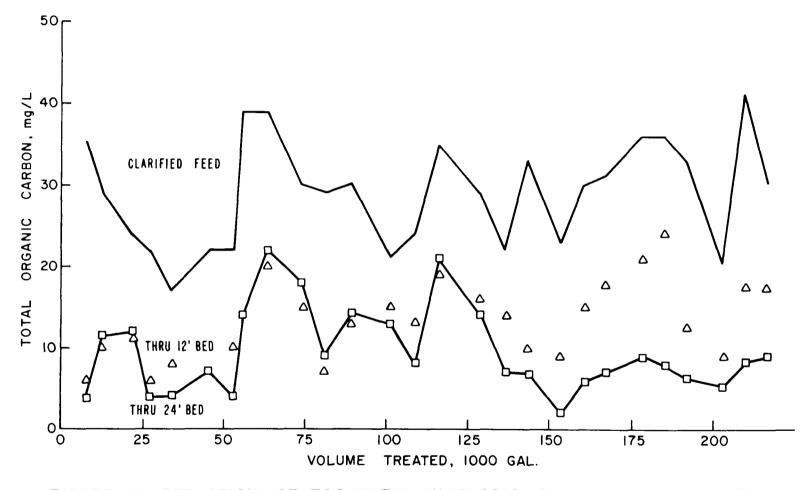


FIGURE 7—REDUCTION OF TOC WITH ANAEROBIC CLARIFIED FEED IN EX-PANDED BEDS OF ACTIVATED CARBON

septic. While the first 50,000 gal. was passed through the column, the 12-ft. column was nearly as effective as the 24-ft column, but the 12-ft column then lost effectiveness and the effluent was definitely inferior to that from the 24-ft columns by the time 100,000 gal. of feed had been treated.

In the anaerobic system, the quality of the effluent was not nearly as consistent as that of the aerobic system. Thus, the TOC of effluent rose after 10,000 to 15,000 gal. of feed had been charged, and when approximately 85,000 to 115,000 gal. were charged, in addition to the two aforementioned periods when the septic conditions were encountered. The occasional higher values with the anaerobic system may be indicative of a more unstable system. It should be noted, however, that despite these occasional high values, the effluent from the anaerobic system had low TOC several times during this study.

A comparison of the data in Figures 6 and 7 shows that when the first 50,000 gal. was passed through the columns containing fresh carbon, the removal of TOC in the aerobic and anaerobic columns was not greatly different. Thereafter, the TOC removal in the aerobic carbon columns was signicantly greater than in the anaerobic columns. Except for two readings, the aerobic column effluent TOC was consistently under 10 mg/l during that period when between 60,000 to 135,000 gal. was charged to the columns, but the TOC of the effluent from the anaerobic columns was under 10 only twice during that period.

After 135,000 gal. had been pumped through both columns, the clarification vessel became septic and the entire system had to be shut down and cleaned thoroughly. Following this cleaning, both the aerobic and anaerobic columns again showed essentially the same degree of TOC reduction until 175,000 gal. had been treated. Thereafter, the TOC of effluent from the anaerobic columns again became significantly higher than those of the aerobic columns and this continued until the end of the run.

The data in Figures 6 and 7 show that the bulk of the TOC was removed in the first 12 ft of the carbon. After 150,000 gal. of feed had been passed through the anaerobic columns, removal of TOC by the first 12 ft dropped markedly. However, both systems still had considerable residual sorptive capacity in the first 12 ft of the respective columns.

The cumulative removal of TOC in the 24-ft aerobic and anaerobic columns during the two-month period studied is presented in Figure 8. The aerobic columns removed 77% of the charged TOC, the anaerobic columns 67%. Both systems removed a larger fraction of the charged TOC after the system had been cleaned and aerated. The cleaning became necessary because the clarification vessel became septic. This probably is a further indication of the harmful effect of septicity in a carbon sorption system. The improved removal of TOC after aeration was not manifested, however, in the first 12-ft beds of carbon. Thus, plots of the amount of TOC removed vs that applied in the 12-ft beds of carbon show no significantly increased rate of sorption of TOC after 32 pounds of TOC had been applied and the system was backwashed and aerated (see Figure 9).

Of the first 50 pounds of TOC charged to both columns, the 12-ft anaerobic columns sorbed 54% as opposed to 62% for the aerobic. This relative difference is virtually the same as the 67% and 77%, respectively, found in the 24-ft beds.

The turbidities of various streams of the carbon treating system are shown in Table 3. Clarification of the primary effluent with 140 mg/l FeCl₃ removed over 90% of the turbidity. Product from the first aerated column usually was more turbid than the clarified primary effluent. Product from the last aerated column was almost always more turbid than product from the unaerated columns, but the latter usually became more turbid on standing. Thus, samples of fresh unaerated product that had turbidities of one or two JTU, showed turbidities of 30 or 40 JTU after standing 24 hours. By contrast, the turbidities of the aerated samples dropped significantly after standing 24 hours and this clarification was accompanied by a settling of grayish solids which were presumed to be bacterial remains removed from the carbon.

Typical hydrogen sulfide contents of carbon-treated streams are shown in Table 4. The clarified primary effluent normally contained up to 4 mg/l of material which reacted with iodine and was reported as $\rm H_2S$ even though no $\rm H_2S$ odor could ever be detected in these streams. Effluents from the second and fourth aerated columns contained approximately 0.5 ppm of material titratable with iodine, as compared with 0.4 ppm for city water. Samples from the second and fourth anaerobic columns consistently contained from 7 to 13 mg/l of $\rm H_2S$ and had a pronounced $\rm H_2S$ odor. After standing at room temperature for 24 hours, samples of this $\rm H_2S$ -containing product contained less than 0.6 mg/l $\rm H_2S$ and never more than a trace of $\rm H_2S$ odor.

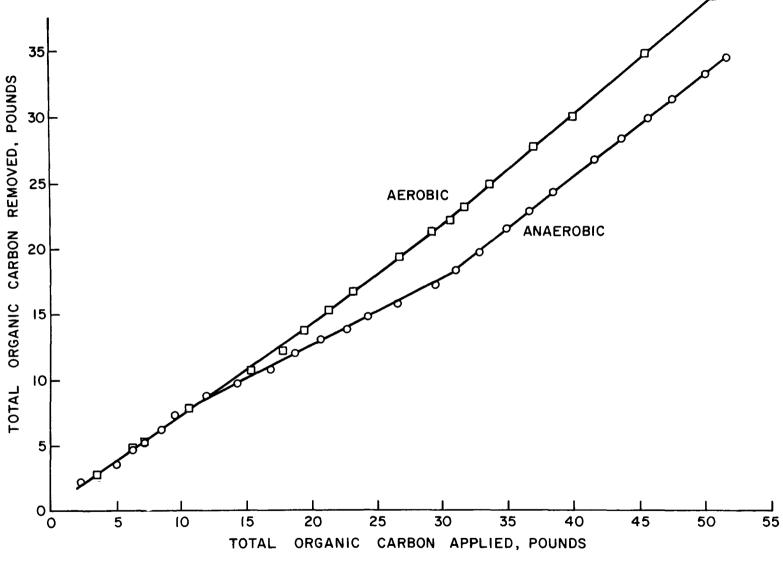


FIGURE 8 — CUMULATIVE REMOVAL OF TOC IN 24FT EXPANDED BEDS OF ACTI-VATED CARBON IN AEROBIC AND ANAEROBIC OPERATIONS

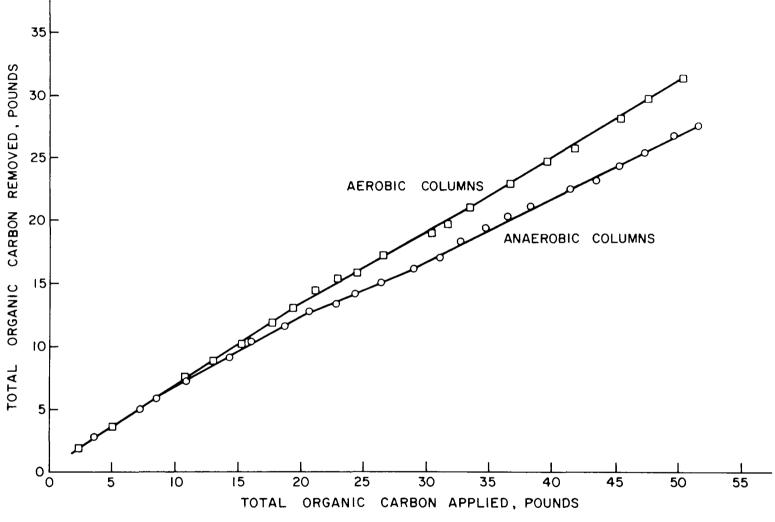


FIGURE 9 — CUMULATIVE REMOVAL OF TOC IN 12 FT EXPANDED BEDS OF ACTIVATED CARBON IN AEROBIC AND ANAEROBIC COLUMNS OPERATIONS

Table 3

TURBIDITIES OF CARBON-TREATED EFFLUENTS

Turbidities, JTU

Date	PE	CPE	A-1	A-4	U-1	U-4
9/2	50	8.0				
9/4	35	5.0				
9/11	40	4.0	3.0	3.0		
9/14	40	4.0	3.0	3.0		
9/21	43	3.2	2.4	2.0	1.5	1.0
9/23	44	7.5	7.5	2.8	2.8	1.5
9/25	48	10	13	6.5	4.0	2.0
9/28	39	4.0	7.0	4	4.0	2.5
9/30	42	4.0	8.0	5.5	6.0	4.0
10/2	42	4.0	15	8.0	5.0	4.0
10/5	38	3.5	15	18	5.0	2.5
10/12	43	3.8	5.8	11	2.3	1.2
10/14	54	1.0	7.3	10.5	1.2	1.2
10/16	46	0.8(32) ^a	7.5	19.0(7.8) ^a	1.3	$1.6(31)^{a}$
10/19	47	6.8	14	29	5.0	4.0
10/21	49 h	3.7(9.0)	13	18(3.5)	1.8	1.5(48)
10/23	42 (7.2) b	1.1(13.0)	10	11(1.8)	0.7	11.3(5.6)
10/26	44	5.0	14	17	4.6	4.8
10/28	43	6.6	22	16	3.2	2.3
10/30	48	6.5	17	19	2.3	1.5

b After settling 72 hours.

PE	Primary Effluent
CPE	Clarified Primary Effluent
A-1	Effluent from first aerated column
A-4	Effluent from 4th aerated column
U-1	Effluent from first anaerobic column
U-4	Effluent from 4th anaerobic column

a Numbers in parenthesis are values obtained in samples kept 24 hours at room temperature.

Table 4

HYDROGEN SULFIDE CONCENTRATIONS IN CARBON-TREATED EFFLUENT STREAMS

H_2S Concentration, mg/1

Date	PE	CPE	<u>A-2</u>	$\underline{A-4}$	<u>U-2</u>	<u>U-4</u>
10/22	2.0	3.1	0.6	0.4	9.2	13.4
10/23	0.9	1.7		0.6		7.9
10/26	1.6	1.7		0.4		7.0
10/28	1.5	3.9	0.7	0.6	9.9	11.9
10/30	2.0	2.0	0.5	0.5	9.9	12.5

No differences were found in the pH of the aerobic and anaerobic products. Virtually all final products from both the aerobic and anaerobic columns had pH of between 6 and 7, and the variations in pH between aerobic and anerobic products taken in the same day rarely exceeded 0.2.

Except for short periods during which the clarifier was down for cleaning, operation of the carbon columns was not interrupted during the entire 2-month aerobic-anaerobic evaluation period during which time 210,000 gal. of feed (2100 bed volumes) were treated. There was no evidence of any pressure build-up inside the columns at any time during this period. This confirmed the anticipated benefit from up-flow, expanded-bed operation.

B. Comparison of Aerobic and Combined Anaerobic-Aerobic Carbon Column Activities

The anaerobic four-carbon column system was operated with two anaerobic and two aerobic columns to determine if this type of operation offered any advantages over a completely aerobic system. The aerobic system was operated as described above without interruption but the combined anaerobic-aerobic operation was started about two weeks after anaerobic operation had been suspended.

In anaerobic-aerobic operation, the first two columns were operated exactly as described above for anaerobic operation, and 0.1 cfm of oxygen was bled into the last two columns. Table 5 shows that this provided sufficient oxygen to generally maintain the desired 6 to 10 mg/l O_2 in the last two columns of the anaerobic-aerobic system. The aerobic system had a higher oxygen level than that shown in Table 2, even though

Table 5 DISSOLVED OXYGEN CONCENTRATIONS IN STREAMS FROM AEROBIC AND ANAEROBIC-AEROBIC COLUMNS

Dissolved oxygen, mg/l

	<u>Fe</u>	ed	Columns							
				Aerob	ic		Ana	erobi	c-Aero	bi c
1970	PE.	CPE	<u>A-1</u>	<u>A-2</u>	<u>A-3</u>	<u>A-4</u>	<u>U-1</u>	<u>U-2</u>	<u>U-3</u>	<u>U-4</u>
11/11 13 16 18 20 23 25 30	1.0 2.0 2.2 2.3 2.0 3.7 0.3 0.1	1.7 1.4 4.2 3.5 1.6 2.8 0.1	12.3 14.5 11.5 13.5 12.0 12.5 12.6 17.5	4.4 10.5 3.0 4.2 7.4 6.2 4.0 4.5	6.0 10.0 10.4 9.6 10.5 14.0	8.0 13.1 10.0 10.4 9.2 10.0 15.0 7.2	1.5 2.2 2.5 2.1 1.6 4.4 1.0	1.0 1.6 1.9 1.4 2.5 0.6 0.8	6.0 16.0 4.3 8.5 4.2 8.1 4.0 2.7	7.5 17.5 8.8 10.5 10.0 11.0 4.1
12/ 2 4 7 9 11 14 16 18 23 29	0.6 0.4 0.4 1.1 0.6 1.4 3.2 3.6 2.8 2.0	0.6 0.4 0.7 0.5 1.4 1.2 2.2 0.7	25.6 19.0 24.0 14.3 15.4 17.0 13.6 13.0 17.0	5.1 3.6 6.6 5.9 11.1 12.0 9.2 10.0 9.0 4.0	17.8 10.0 20.0 7.3 5.7 13.5 8.8 12.0 15.0	15.8 6.6 13.0 7.6 6.0 11.2 7.6 10.5 17.0	2.8 0.6 1.2 0.9 1.7 2.9 2.0 5.8 1.2	1.0 0.6 0.7 0.6 1.4 2.3 2.0 4.0 1.2	4.4 2.6 10.0 4.0 8.4 9.4 4.0 8.0 1.3	6.4 3.7 7.1 4.6 10.0 13.5 4.4 8.4 8.0 1.2
1971 1/4 8 11 13 20 22 25 27 29	1.7 7.2 5.0 3.2 2.4 0.8 4.7 4.6	1.7 2.2 4.0 0.8 0.6 2.9 1.2 0.3 1.7	21.0 11.2 13.0 15.2 15.7 6.6 15.6	9.2 12.5 5.0 8.0 5.8 1.2 2.1 6.3 6.4	26.7 20.0 13.5 17.0 15.2 7.9 14.5	28.6 18.7 14.1 21.0 18.0 18.8 9.5 24.5 16.0	1.1 2.5 4.0 1.0 0.9 1.3 	1.1 2.2 4.0 1.7 1.0 0.7 0.8 1.6 0.8	4.2 4.4 6.7 3.2 1.7 5.8 4.0	6.7 15.6 10.2 8.0 9.7 5.7 6.6 7.9
2/ 1 5	3.0 6.2	1.0 1.2	15.0 9.7	6.5 4.1	21.0 11.7	 11.2	1.5 1.2	0.7 0.9	5.1 3.8	15.2 7.7

oxygen was added at the same rotameter setting. The higher oxygen content could have been due to a lower oxygen consumption by the bacteria during the winter weather and to the greater solubility of oxygen in water at low temperatures. Oxygen solubility is 43.4 mg/l at 20°C (68°F), and 60.7 mg/l at 5°C (41°F), the water temperature that was attained quite often during the winter. The dissolved oxygen content was particularly high in January when temperatures were the lowest. The oxygen rotameter setting was too low to make the critical adjustments with the control valve that would have given 6 to 10 mg/l in cold weather.

The relative removal of TOC by the aerobic and anaerobic-aerobic systems is shown in Figure 10. Except for the two sharp peaks for the anaerobic-aerobic effluent at the 270,000 and 430,000-gal. regions, the effluents from the two systems had essentially the same TOC values. The fact that anaerobic-aerobic activity, unlike anaerobic, was equivalent to aerobic activity constituted additional evidence for the beneficial effects of aerobic carbon column operation.

TOC removal generally was poorer during this evaluation than during the aerobic-anaerobic comparison, as shown in Table 6. Between August 28 and October 30 when the aerobic and anaerobic systems were compared, TOC removal averaged 77.5% through the aerobic columns, and 67% in the anaerobic columns. Between October 31 and November 11, the aerobic columns still removed 78% of the charged TOC, but removals fell steadily from December 1 through February 8, and were significantly lower than during September through November.

The drop in TOC removal was due to at least four factors. These were:

- 1. The much colder weather in winter reduced bacterial activity within the columns.
- 2. Rates of adsorption of organic matter from aqueous phase are decreased at lower temperatures.
- 3. During December, several clarified effluents had TOC of 20 to 22 mg/l as compared with 27 to 35 mg/l that was characteristic of earlier operation. Since the TOC values of column effluents obtained with this weaker feed were not lower than those obtained with the stronger feed, the actual percent of TOC removed by the columns dropped.

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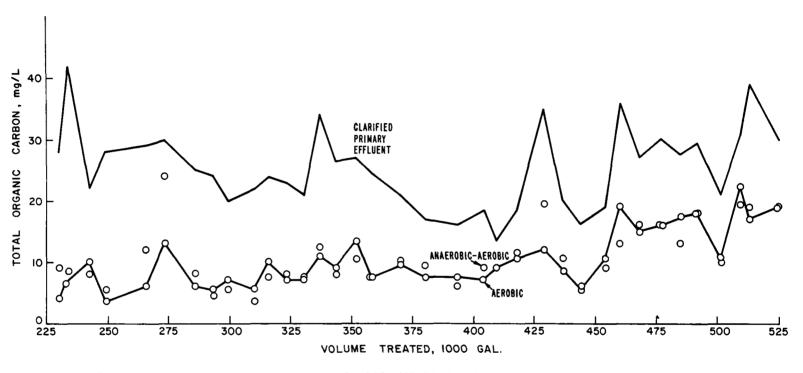


FIGURE IO-REMOVAL OF TOC BY ACTIVATED CARBON IN AEROBIC AND COMBINED ANAEROBIC-AEROBIC OPERATION

Table 6

TOC REMOVED BY CARBON

Column	Aerobic				Anaerobio	<u> </u>	Anaerobic-Aerobic			
	lb TOC	1b TOC	wt% TOC	lb TOC	lb TOC	wt% TOC	1b TOC	1b TOC	wt% TOC	
	Charged	Removed	Removed	Charged	Removed	Removed	Charged	Removed	Removed	
Aug 28-Sep 30	24.6	17.7	72	24.3	14.9	62				
Oct 1-Oct 30	24.6	20.4	83	27.3	19.5	72				
Oct 31-Nov 11	7.6	5.9	78			i				
Nov 12-Nov 30	13.2	9.9	7 5				13.6	8.3	61	
Dec 1-Dec 29	19.7	12.5	6 4				18.1	12.0	66	
Dec 30-Jan 29	21.7	10.8	50				21.9	10.7	51	
Jan 30-Feb 8	7.8	3.5	45				8.7	3.8	44	
Feb 9-Feb 26	11.9	7.9	67							

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4. In both December and January, coincident with the two sharp peaks observed in Figure 10, a marked buildup of solids occurred within the columns. This was manifested by a rise in effluent TOC to 10 mg/l or more, a gradual buildup of pressures within the columns, and the presence of iron hydroxide precipitate in the column effluents. The solids were dislodged from the carbon bed by air scouring and backwashing.

The cleaning of the carbon involved draining the water down to about 1 ft above the top of the bed, blowing a stream of air through the column to scour the carbon, and backwashing with city water at a flow rate of about 10 gpm/sq ft, about double the usual treating rate. The run was then continued in the normal manner.

The cleaning treatment removed considerable iron from the last two columns, but little from the first two. It is believed that some iron used in coagulation entered the columns and was precipitated as ferric hydroxide inside the last two columns.

After the air scouring, the effluent TOC dropped to the 7 to 8 mg/l level that had been obtained before the upset, and the pressure inside the columns dropped significantly. The pressures in the four aerated columns dropped from 22 to 15 psig before washing, to 16 to 9 psig after washing.

During the entire two-week period before the second cleaning in February, the TOC of effluents from both columns averaged about 15 mg/l. The near zero weather was too cold to permit stopping feed flow through the lines to air-scour the columns. During this period much grey material, which was believed to be bacterial remains, was carried from the column. This may have been due to the destruction of a large fraction of the bacterial population due to the severe weather.

After the second cleaning, 7 to 8 mg/l TOC product was again obtained from the aerobic columns and the product quality remained good throughout the balance of February (see Table 6). From February 12 through March 1, TOC removal in the columns averaged 67% of the TOC charged. During this period, the average TOC of the primary effluent was 71 mg/l and the average for the effluent from the carbon column was 9 mg/l, giving an overall TOC removal by the combined coagulation and carbon treatment of 89%, which approached that which was attained when the columns were started in September. During this period, the amount of clarified primary effluent charged to the columns increased from 535,000 to 604,000.

Figures 11 and 12 show the cumulative quantities of TOC removed by the aerobic and anaerobic-aerobic systems. Overall, the two systems removed nearly the same amount of TOC during the test period, (36 vs 34 lb of the 60 lb charged), but the 12-ft anaerobic section was much less effective than the 12-ft aerobic section. Thus, the aerobic 12-ft section removed 25 lb or 42% of the charged TOC, whereas the anaerobic removed only 17 lb or 28%. The relatively good overall activity of the anaerobic-aerobic system was therefore due to the fact that the second 12 ft, which was aerobic, removed 17 lb of TOC as compared to only 11 lb in the last 12 ft of the aerobic system.

Product from the anaerobic-aerobic systems had neither the $\rm H_2S$ odor nor the instability that characterized the product from the all-anaerobic system. Table 7 shows that the $\rm H_2S$ content of the anaerobic-aerobic effluent was not significantly higher than that of the aerobic effluent, despite the pronounced $\rm H_2S$ content of product from the anaerobic sections. On standing 24 hours at room temperature, the anaerobic-aerobic effluents did not develop the haze observed in anaerobic effluents, as described above.

Table 7

H₂S CONCENTRATIONS IN EFFLUENTS FROM AEROBIC AND COMBINED ANAEROBIC-AEROBIC CARBON SYSTEMS

H_2S Concentration, mg/l

	Fe	ed	Columns									
			Aerobic				Anaerobic-Aerobic					
Date	PE	CPE	<u>A-1</u>	<u>A-2</u>	<u>A-3</u>	<u>A-4</u>	<u>U-l</u>	<u>U-2</u>	<u>U-3</u>	<u>U-4</u>		
11/11	3.0	1.4	2.1	1.7	0.5	0.4	9.0	12.1	0.9	0.9		
. 13	1.4	1.0	0.9	0.7	0.7	0.3	5.5	6.9	0.7	0.5		
16	1.0	0.7	0.4	0.7	0.5	0.3	1.2	2.4	0.7	0.5		
18	1.0	0.7		0.9		0.3	3.1	5.2	0.5	0.5		
23	1.2	0.7		0.7		0.5	2.8	4.5	0.5	0.7		
30	1.2	1.0	0.9	0.5	0.7	0.7	4.1	5.8	0.7	0.5		

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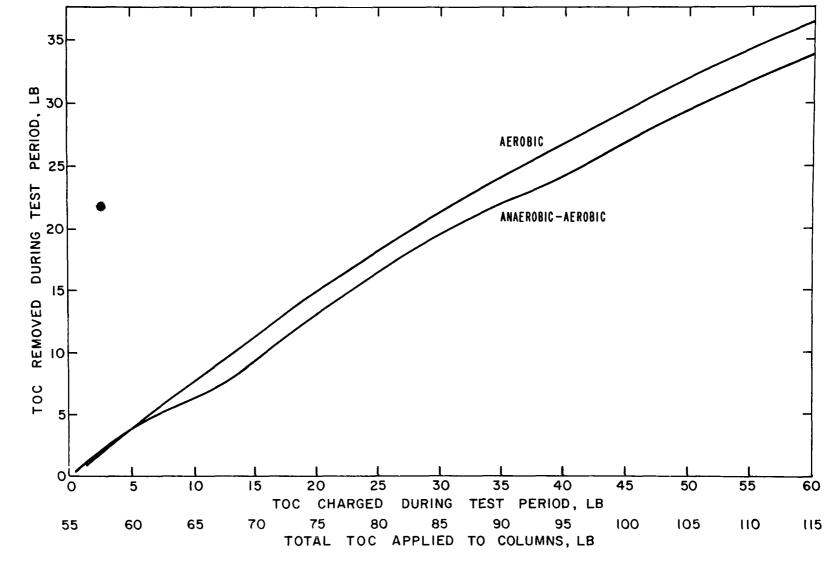


FIGURE II -- CUMULATIVE REMOVAL OF TOC IN 24 FT EXPANDED BEDS OF ACTIVATED CARBON IN AEROBIC AND ANAEROBIC-AEROBIC OPERATIONS

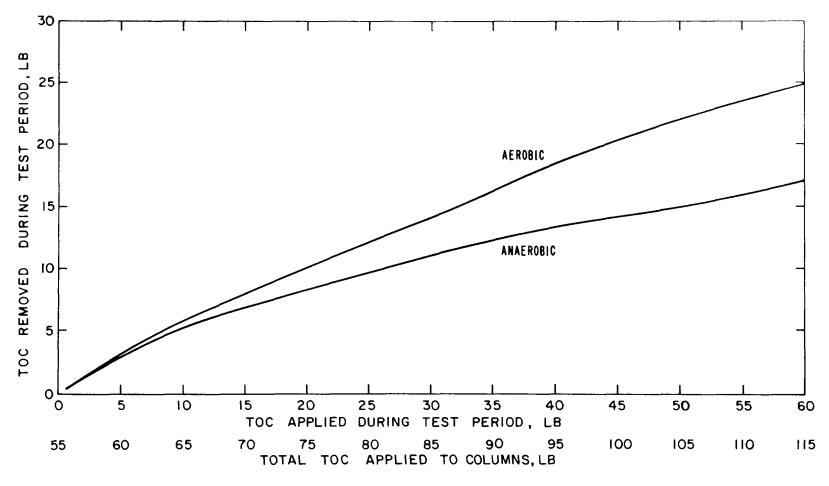


FIGURE 12 — CUMULATIVE REMOVAL OF TOC IN 12 FT EXPANDED BEDS OF ACTIVATED CARBON IN AEROBIC AND ANAEROBIC OPERATION

Comparison of Activated Carbon and Non-Activated Coal Derivative Under Aerobic Conditions

After aerobic bacterial activity had been found to give improved removal of organics from sewage streams by carbon, a study was begun to determine the extent to which properties of the carbon affected bacterial activity within a column. For this study, the active carbon in the anaerobic-aerobic system was replaced with an anthracitic, unactivated filtering material.

The properties of the coal-derived product are compared with those of activated carbon in Table 1. The activated carbon was 16 x 40 mesh, and the coal 8 x 20 mesh. The coal had a packed density of 56.4 lb/cu ft, which was nearly double that of the activated carbon. Presumably because of its coarser size, the higher density coal columns did not give higher back pressures than the carbon in the upflow operations.

The major differences between these two carbons was in their sorptive properties. The iodine numbers of fresh activated carbon and coal, 1270 and 150, respectively, were indicative of the relative adsorptive properties of these two carbons. By operating the two sets of columns aerobically under identical conditions, it was possible to determine the relative organic removal efficiencies of carbons having good and poor adsorption properties. However, at the time when the comparison with the coal was started, the activated carbon column had already treated 535,000 gal. (5,350) volumes of clarified primary effluent in 5.5 months of steady operation.

The coal behaved completely differently from fresh activated carbon in the columns. Unlike the fresh activated carbon which gave products with TOC of 5 mg/l or less for the first 100,000 gal. treated, (see Figure 6) the initial products attained with fresh coal had a TOC of over 20 mg/l, and this dropped rather slowly, perhaps indicating a gradual buildup of sorbed organics and bacteria within the columns (see Figure 13).

As the comparison continued, the performance of the unactivated carbon columns improved and approached that of the partially spent activated carbon columns. The average TOC removal in March through May is shown in Table 8. In the March through May period, TOC removal by the partially spent carbon was higher than the 45 to 50% shown in Table 6 for the December 30 to February 8 period.

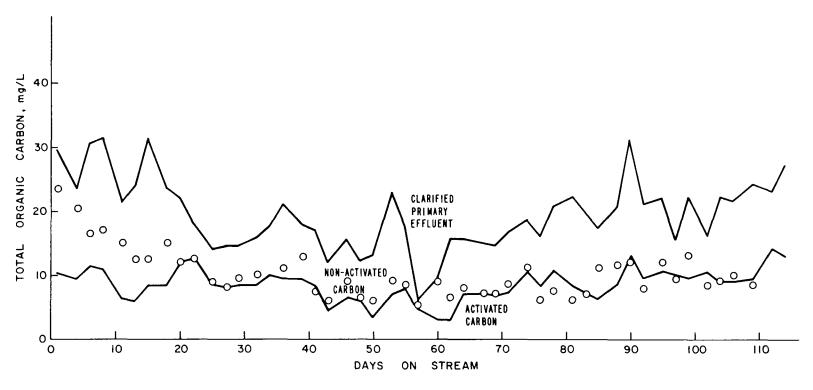


FIGURE 13 — RELATIVE TOC REMOVAL IN NON-ACTIVATED AND PARTIALLY SPENT ACTIVATED CARBON COLUMNS

Table 8

REMOVAL OF TOC WITH NON-ACTIVATED AND SPENT ACTIVATED CARBONS

			TOC of Effl	uents,mg/l	% TOC Removal		
Month	Average TOC of Feed, mg/l	Average TOC of Clarified Feed, mg/l	Non- Activated Carbon	Spent Activated Carbon	Non- Activated Carbon	Spent Activated Carbon	
March	64	16.8	9.5	7.7	43.5	54.3	
April	57	15.5	7.7	6.7	50.4	57.8	
May	74	21.6	11.9	9.7	45.0	54.7	

The carbon column effluents showed the same low (6-7 mg/l) average TOC throughout March and April that had been obtained several months earlier, but these low TOC values probably were due to the low TOC of the column feeds. Whereas, clarified primary effluents normally had a TOC of about 30 mg/l, the TOC averaged about 16 mg/l during much of March and April. The low TOC of the feed lowered the TOC removal efficiency, as was also noted above on page 29.

Late in April, clarified feed in the storage tank developed a haze, and slime appeared on the walls of the vessel. This condition had been observed during hot weather periods in work conducted on previous contracts, but when it occurred in the current study the weather was not hot. During the period in which this unstable feed was charged to the column, the column product had a TOC of almost 10 mg/l, and turbidities of 10 to 15 JTU, compared to the normal 1 to 4 JTU range.

Throughout this study, the filter was backwashed routinely twice a week to prevent the formation of septic growths within the bed. The backwash water normally contained much reddish iron oxide. During this period when the feed appeared to be unstable, the filter backwash contained black material which would normally indicate a septic condition. Septicity did cause poorer TOC removal in the past, and could have accounted for the poor TOC removals during this period. However, unlike other septic conditions, this one could not be corrected by repeated backwashings. The Ewing-Lawrence Sewerage Authority reported abnormal operations at the same time, so that the problem may have been associated with some contaminant in the feed. The only abnormality noted in our feed analyses was a number of high pH values for the primary effluent. This stream normally had a pH between 6.5 and 7.5, but in May readings between 8.0 and 8.8 were common.

The activated carbon columns were backwashed on June 1 to determine whether the activity of the carbon could again be improved. This backwashing brought no improvement in the carbon column activity, and the project was discontinued before another backwash could be attempted.

The relative cumulative TOC removals by the activated and unactivated carbons are shown in Figures 14 and 15. The TOC removals that had been achieved when the activated carbon was fresh are plotted as dotted lines for comparison. The partially spent 24-ft bed of activated carbon, which had already removed 84 lb of TOC when this comparison was started, removed 56% of the charged TOC, during this test period, as

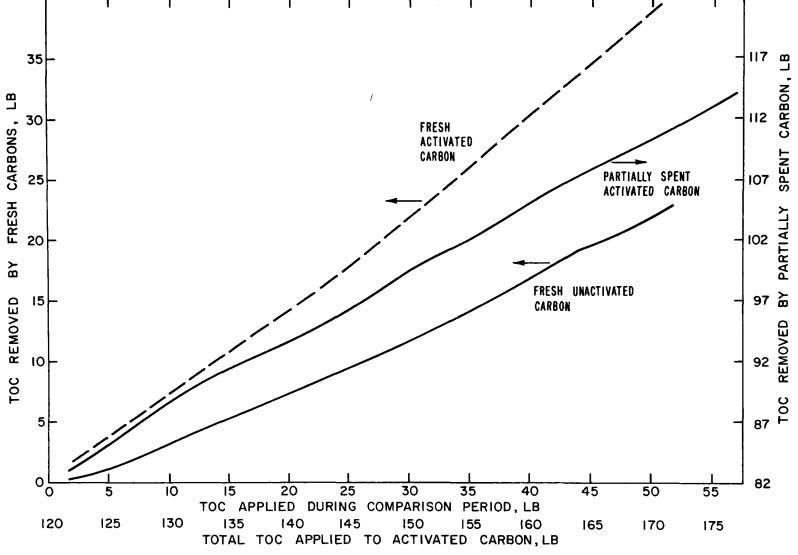


FIGURE 14 — CUMULATIVE REMOVAL OF TOC IN 24FT EXPANDED BEDS OF ACTIVATED AND NON-ACTIVATED CARBONS IN AEROBIC OPERATION

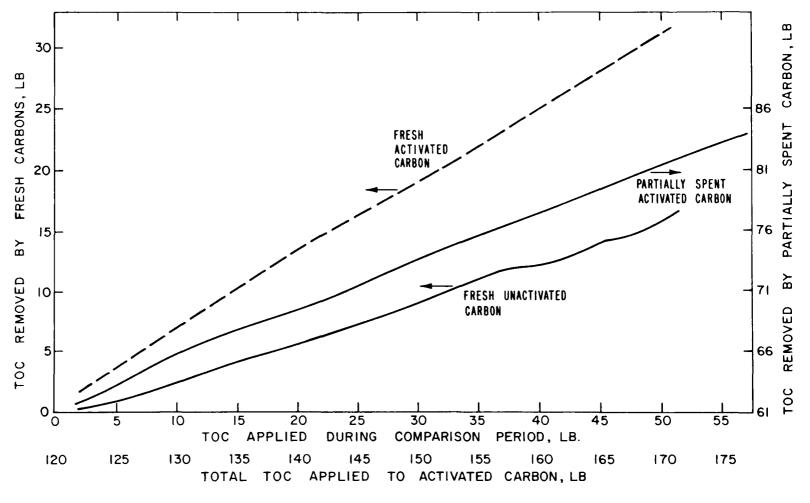


FIGURE 15 — CUMULATIVE REMOVAL OF TOC IN 12 FT EXPANDED BEDS OF ACTI-VATED AND NON-ACTIVATED CARBONS IN AEROBIC OPERATION

compared to 44% for the unactivated material. Fresh activated carbon removed an average of 80% of the first 50 lb of TOC charged, which was double the removal achieved with the unactivated carbon. In 12-ft beds, the fresh activated carbon also removed twice as much TOC as the unactivated carbon, the respective removals being 64 and 32%. The 12-ft sections of spent activated carbon removed 42% of the charged TOC.

The analyses of the spent activated carbon and coal are shown in Table 9. The activated carbon taken at the end of the runs from both the anaerobic-aerobic and the aerobic columns had essentially the same analyses, despite the fact that the aerobic columns had been on-stream almost twice as long as the anaerobic-aerobic columns. Both carbons gained considerable weight during use. After devolatilization at 750°C, weight of the carbon increased from 10 to 20%. This probably was due to accumulated iron salts within the beds. As anticipated, the iodine numbers of the dried and devolatilization carbons dropped 50 and 30%, respectively.

Unlike the activated carbons, the non-activated carbon showed no gain in volatile matter or ash, showed a much smaller gain in weight during use, and showed no drop in iodine number during use. These trends were not associated with differences in on-stream lives, since the non-activated carbon columns were on-stream as long as the anaerobic-aerobic columns.

It is not known why the devolatilized non-activated carbon samples had lower iodine numbers than dried samples. This may be a peculiarity inherent in the iodine number determination for relatively inactive materials.

D. Summary of Carbon Column Operations

The aerobic columns were operated without interruption for nine months during which time 889,607 gal. (8,896 carbon bed volumes) of chemically clarified primary effluent were treated and in which the three comparison runs described above were conducted. Data for the removal of TOC and SOC in these runs are summarized in Table 10. In the three test periods listed, the aerobic activated carbon system removed 90.1, 85.2 and 87.2%, respectively, of the charged TOC, and 81.2, 72.4 and 74.6, respectively, of the charged SOC. Lowest removals of both TOC and SOC occurred during the colder months. For the entire nine-month period, average TOC removal was 87.2%, and average SOC removal was 75.5%.

Table 9

ANALYSES OF SPENT ACTIVATED AND NON-ACTIVATED CARBONS FROM THE PILOT OPERATIONS

Carbon Source			Proxi	.mate An	alysis				Numbers g/g
	Column	Mois- ture	Vola- tile Matter, Wt. % Dry Basis	Ash, Wt.% Dry Basis	Drained Wt., lb.	Dry Wt., lb.	Devola- tized Wt., lb.	Dried	Devola- tized
Pittsburgh Filtrasorb 400		1.3	1.0	6.75		85. ^a		1270	
Anaerobic- Aerobic Activated Carbon	1 2 3 4	41.0 43.2 43.8 46.8	16.0 13.3 15.5 9.2	10.6 12.9 8.8 17.7	232.0 200.7 187.1 188.8	136.1 116.8 107.7 103.0	114.4 96.5 92.0 94.5	450 610 610 740	800 870 850 850
Activated Carbon	2 3 4	43.6 49.7 47.4	14.7 11.7 10.1	11.3 16.1 16.8	219.4 212.4 190.9	126.5 109.8 102.8	109.2 98.0 93.3	490 660 680	750 860 870
Filt-O- Cite #1		9.6	4.1	19.3		154. ^a		150	
Aerated Nor Activated Carbon	1 2 3 4	23.0 23.9 20.6 17.4	5.6 5.8 4.3 4.5	16.5 15.4 18.2 15.3	202.9 233.5 181.6 163.5	158.3 178.0 144.0 135.0	 	155 155 145 155	70 70 70 70

a Weight charged to each column.

Table 10

REMOVAL OF TOC AND SOC FROM PRIMARY EFFLUENT BY CHEMICAL CLARIFICATION AND CARBON TREATMENT

Date System	August 28, 1970 to November 2, 1970 Anaerobic Carbon 217,107 Aerobic Carbon 212,464								
Charge, Gal.		21/,	10 /			212,			
	TOC		sc	C	TOC	·	soc		
	lb.	8	lb.	8	lb.	ક	<u>lb.</u>	- %	
Organics Charged Removed by Clarifi-	118.0		55.0		115.5		53.8		
cation	66.4	56.3	9.4	17.1	65.0	56.2	10.8	20.0	
Removed in Columns	34.5	29.2	30.8	55.9	39.2	33.9	32.9	61.2	
Total Removed	100.9	85.5	40.2	73.0	104.2	90.1	43.7	81.2	
Date System	N Anaerob	ovembe	r 10,	1970 to	Februa	ry 8,	1971		
Charge, Gal.	Anacros	299,		arbon		303,	348		
charge, car.		•				•		_	
	TOC		SO	<u>C</u>	TOC			<u>C</u>	
Organics Charged Removed by Clarifi-	172.2		79.1		174.2		80.0		
cation		63.8			110.8			35.6	
Removed in Columns	34.8	20.2		-	37.7			36.8	
Total Removed	144.7	84.0	56.9	71.9	148.5	85.2	58.0	72.4	
Date	70	Febru erobic		1971 t	o June	6, 197	1		
System Charge, Gal.	A	323,				361,	693		
•	lb. T	OC	lb.	soc	lb. T	oc	<u>lb.</u>	soc	
Organics Charged	178.0		73.7		199.2		82.6		
Removed by Clarifi- cation Removed by Columns Total Removed	126.5 22.8 149.3	71.1 12.8 83.9		37.0 30.7 67.7	141.4 32.3 173.7		30.7 30.9 61.6	37.2 37.4 74.6	

During the nine-month period in which the aerated activated carbon columns were operated, a total of 488.5 lb of TOC was passed through the adsorption system. Clarification removed 317.2 lb or 64.9% of the TOC, and the carbon 109.2 lb or 22.3%. The carbon thus removed 63.6% of that TOC not removed in the clarification step. During this same period, the feed contained 216.4 lb of SOC. Clarification removed 70.1 lb of SOC or 32.5%, and carbon adsorption 93.2 lb or 43.0%. This is equivalent to 64.4% removal of SOC not removed in the coagulation step. One peculiarity in the data in Table 10 is the improvement in clarification efficiency which occurred with time. Since the clarification system and coagulant dosage were not varied during this study, this is probably associated with changes in the nature of the feed.

Table 10 also shows that with fresh carbons the anaerobic carbon system removed 11% less TOC and 9% SOC than the aerobic system. The unactivated carbon removed 44.3 and 48.7%, respectively, of the TOC and SOC not removed by clarification. During this same period the partially spent carbon which had already treated over 515,000 gal. removed 55.9 and 59.6% of the charged TOC and SOC, respectively. By contrast, fresh activated carbon removed 71 and 76% of the charged TOC and SOC, respectively, in treating the first 300,000 gal. of feed pumped through the columns.

E. Regeneration of Polishing Column Carbon

When used in an adsorption system, fresh activated carbon initially removes essentially all dissolved organics; but in a relatively short time, the effluent from the columns contains from 4 to 6 mg/l of TOC. In the earlier carbon contacting studies cited previously, small columns containing l-ft deep beds of fresh activated carbon effectively removed for a period of 24-hours most of the residual TOC that was not removed by 24-ft of partially spent carbon. The organics adsorbed in short carbon beds evidently were adsorbed only weakly and at a slow rate. If removal of these organics and regeneration of the carbon could be achieved easily and inexpensively, the use of a short regenerable polishing column would offer a treatment scheme suitable for those applications which demanded nearly complete removal of organics from water for reuse or recycle.

Since the earlier studies had already demonstrated that polishing columns removed residual traces of dissolved organics, the present work dealt primarily with studies that would establish the weight of material that could be sorbed on the

polishing column carbon before significant breakthrough occurred, and if simple regeneration techniques which would make polishing column operation economically feasible could be developed. The relatively short active on-stream life of polishing columns made the thermal reactivation of the carbon impractical.

Typical operating data are summarized in Tables 11 and 12. As expected, the active life of a polishing column carbon increased as the organic content of the feed decreased. Thus, with feed in Run B averaging less than 7 mg/l TOC, Table 12, the effluent contained less than 2 mg/l TOC after 10,000 gal. had been treated, and was under 3 mg/l after treating 20,000 gal. By contrast, such high quality product was seldom achieved in Run A with feed which almost always had TOC of at least 9.5 mg/l, Table 11.

The spent carbon from the 6-in. glass polishing columns was taken to the laboratory for regeneration studies. The activity of the regenerated material was measured in 24-in. long glass columns having a one-square-inch cross-sectional area. Results were compared with those for fresh activated carbon. The test solution was the final effluent from the carbon columns which had TOC of 7 to 9 mg/l.

Table 13 shows typical removal of TOC from column effluent with fresh activated carbon in the laboratory columns. Initially, virtually all organics were removed by the carbon bed, but a small leakage occurred after only 4 liters were treated, and product TOC increased until the effluent had about the same organic content as the charge. Organic removal in the laboratory column was less than that achieved in the pilot polishing column, possibly due to leakage and channeling in the smaller columns.

The two best regenerants found in this study were sodium hydroxide solution and 4% hydrogen peroxide.

Although sodium hydroxide removal adsorbed organics readily, as evidenced by the immediate buildup of organics in caustic regeneration solutions, it was difficult to wash from the carbon. Thus, the wash water used to flush 300 ml of carbon that had been treated with 12.4 pH caustic still had a yellow color after the 35th wash with 500 ml of cold water.

Table 14 shows results obtained with a carbon that had been regenerated with 11.0 pH NaOH solution. Unlike the fresh carbon, the regenerated carbon never gave an effluent with less than 2.5 mg/l TOC. When the same batch of carbon was regenerated a second time with caustic solution, a minimum TOC of 4 mg/l resulted. The iodine numbers of carbon from the first and second regeneration were 1030 and 1000, respectively, as compared to the original value of 1040.

Table 11

POLISHING COLUMN FIELD STUDY WITH A 4-FOOT BED OF CAL CARBON - RUN A

	Date	Time	Min. Elapsed per Interval	Gal. Charged	Cumulative Gal. Charged	Rate gal./min.	TO Feed	
Started	2/17/71	10:50 AM	4.0	C 0	60	1 2	0 "	r 0
	2/17	11:38 AM	48	60	60	1.3	9.5	5.0
	2/18	9:00 AM	1,282	2,095	2 ,1 55	1.6	9.5	3.5
	2/19 ^a	10:15 AM	1,295	1,609	3,764	1.3	10.0	2.0
	2/20	5:15 AM	1,860	1,298	5,062	0.7	12.5	2.0
	2/22 _h	9:30 AM	2,415	4,178	9,240	1.7	10.0	2.5
	2/23 ^D	10:55 AM	1,645	2,251	11,491	1.4	15.0	5.0
	2/24	9:30 AM	1,355	976	12,467	0.7	10.0	3.5
	2/26	4:45 AM	3,315	5,327	17,794	1.6	13.0	7.5
	2/27	8:50 AM	1,850	1,032	18,826	1.1	8.5	4.0

a Column down 3 hours on 2/19.

NOTE: When the rate deviated from the specified 1.0 gpm rate, the column was operated for a minimum of 30 minutes at the correct rate before sampling for TOC analyses.

b Column down 10 hours on 2/23 due to blocked feed lines.

Table 12

POLISHING COLUMN FIELD STUDY WITH A LOW TOC FEED - RUN B

Date 1971	Time	Min. Elapsed per Interval	Gal. Charged	Cumulative Gal. Charged	Rate Gal./ Min.	TO Feed	
			<u>cur ge u</u>			1004	
3/25	9:30 AM 10:00 AM 11:00 AM 12:00 Noon 2:40 PM 3:40 PM 4:30 PM 7:15 PM 10:30 PM	30 30 60 60 160 50 165	34 33 65 56 205 63 52 197 249	34 67 132 188 393 456 508 705 954	1.1 1.1 0.9 1.3 1.0 1.0	6.0 6.0 6.0 4.8 4.2 3.6 3.6 4.7 5.3	1.8 1.2 0.6 1.2 0.6 0.6 1.2
3/26	8:15 AM 10:15 AM	585 120	687 139	1,641 1,780	1.2 1.15	3.6 3.6	1.8 1.2
	Off for 4.	5 hours					
3/27	7:40 AM 5:11 PM 8:45 PM	1,015 570 215	971 651 226	2,751 3,402 3,628	.95 1.15 1.05	11.5 7.0 6.0	1.2 1.8 2.4
3/28	2:05 AM 12:10 PM 8:35 PM	320 605 505	333 711 443	3,961 4,672 5,115	1.05 1.15 .85	6.5 4.0 11.2	2.4 1.8 3.0
3/29	9:50 AM 8:35 PM	735 705	703 397	5,818 6,215	.95 .55	7.5 5.7	1.2 6.0
3/30	8:18 AM 4:37 PM 9:18 PM	700 500 280	753 383 275	6,968 7,351 7,626	1.05 .75 1.0	4.7 7.1 7.0	0.6 1.2 1.2
3/31	8:20 AM 10:57 AM	660 157	526 156	8,152 8,308	0.8	8.5 7.7	1.2 3.6
	Off for 9	hours					
4/1	7:40 PM	700	1,155	9,463	1.65	7.7	2.4
4/2	9:04 AM 4:20 PM 8:50 PM	804 436 270	1,047 534 331	10,510 11,044 11,375	1.3 1.2 1.2	6.5 8.2 9.0	1.2 1.8 2.4

Table 12 (Cont'd)

POLISHING COLUMN FIELD STUDY WITH A LOW TOC FEED - RUN B

Date 1971	Time	Min. Elapsed per Interval	Gal. Charged	Cumulative Gal. Charged	Rate Gal./ Min.	TO Feed	
17/1	11110	Incervar	Charged	Chargea		1000	<u> </u>
4/3	7:57 AM	667	771	12,146	1.15	8.0	2.4
	4:07 PM	490	525	12,671	1.07	11.2	2.4
	9:05 PM	300	225	12,896	.75	16.5	8.2
4/4	11:58 AM	893	1,023	13,919	1.15	6.0	2.4
	9:10 PM	552	575	14,494	1.05	22.4	12.5
	Off for 35	hours					
4/6	4:07 PM	480	514	15,008	1.05	10.0	3.6
	10:00 PM	353	360	15,368	1.0	12.3	4.2
4/7	8:40 AM	640	538	15,906	0.85	8.2	3.0
	8:03 PM	683	629	16,535	.95	4.7	2.4
4/8	8:20 AM	737	808	17,343	1.1	4.7	1.8
4/9	8:05 AM	1,425	1,121	18,464	0.8	7.0	2.4
	5:00 PM	535	566	19,030	1.05	6.0	3.0
	Off for 3 of	lays					
4/14	8:17 AM	1,440	1,870	20,900	1.3	8.2	3.0
	9:15 PM	780	590	21,490	.75	9.4	4.2
4/15	8:35 AM	680	785	22,275	1.15	10.	3.6
	9:00 PM	745	1,033	23,308	1.4	11.8	8.2
4/16	8:40 AM	700	896	24,204	1.3	8.2	6.0
	9:00 PM	740	900	25,104	1.2	7.0	2.4
4/17	4:50 PM	1,190	1,432	26,536	1.2	7.0	4.7
4/18	12:05 AM	1,155	1,387	27,923	1.2	6.5	5.3
	9:40 PM	575	675	28,598	1.15	7.0	5.3
4/19	8:30 AM	650	760	29,358	1.15	6.0	3.6
	10:30 PM	840	1,125	30,483	1.35	11.8	6.5
4/20	8:30 AM	600	545	31,028	0.9	8.9	4.7
	9:30 PM	780	850	31,878	1.1	7.0	4.2
4/21	8:30 AM	660	714	32,592	1.1	6.5	2.4
	4:14 PM	465	482	33,074	1.05	7.0	4.2
4/22	8:70 AM	965	1,117	34,191	1.15	8.9	4.7
	9:45 PM	805	909	35,100	1.15	9.4	5.3

Table 13

REMOVAL OF TOC FROM ON-LINE COLUMN EFFLUENT WITH FRESH ACTIVATED CARBON IN LABORATORY COLUMN

Volume of 9 TOC Feed Charged, 1.	Cumulative Volume Charged, 1.	TOC of Product
2.5	2.5	< 1.0
1.5	4.0	1.0
1.0	5.0	2.0
1.5	6.5	2.5
1.0	7.5	5.5
1.0	8.5	7.5
1.0	9.5	9.0

Table 14

REMOVAL OF ORGANICS BY POLISHING CARBON REGENERATED WITH 11.0 pH SODIUM HYDROXIDE SOLUTION

First Regeneration		Second Rege	eneration
Cumulative Volume of 9 mg/l TOC Feed Charged, 1	TOC of Product, mg/l	Cumulative Volume of 9 mg/l TOC Feed Charged, l	TOC of Product, mg/l
4 19	2.5 3.0	4 5	4 7
20	4.5	-	-

No way was found to improve the action of NaOH solutions on spent carbon. An 8.0 pH NaOH solution effected no regeneration. Carbon treated with 9.0 pH NaOH solution for 60 min. and then washed in a beaker with running tap water for 30 min. removed only 35% of the charged organics. Repeated washings with hot water did not cut the washing time and gave the same organic removal. Incompletely washed carbon that had been treated with 12.5 pH NaOH solution removed no organics. The same result occurred when the incompletely washed carbon was neutralized with dilute HCl and washed with water until the effluent had a pH of 6.7.

All other basic solutions studied were less effective than sodium hydroxide. Carbon treated with 10% Na₂CO₃ removed a maximum of 50% of the organics, and the Na₂CO₃ was no easier to remove by washing than NaOH. Carbons washed with concentrated ammonia and saturated lime water removed no organics. Carbons treated with KOH solutions of 11 and 12 pH removed less than 50% of the charged organics.

Spent polishing column carbons reacted vigorously with hydrogen peroxide solutions. Spent carbon reacted with 15% by weight $\rm H_2O_2$ and backwashed removed no TOC. Carbon treated with 4% $\rm H_2O_2$ and backwashed for 30 min. with tap water initially gave a product with a TOC of 5.5 mg/l, but then produced 2 l of effluent with 3.5 mg/l TOC and 2 l with 3.0 mg/l TOC as shown in Table 15. It is not known why the first 5 l charged to the column had a relatively high TOC.

Table 15

REMOVAL OF ORGANICS BY POLISHING COLUMN REGENERATED WITH 4% BY WT. H₂O₂

Run No.	I Unacidifie	ed Carbon	II Acid-Treate	-
	Cumulative Volume of 9 mg/l TOC Charged	TOC of Product, mg/l	Cumulative Volume of 9 mg/l TOC Charged	TOC of Product, mg/l
	5 7 9 11	5.5 3.5 3.0 3.0	3 5 6 12	4.5 1.5 2.5 3.5

Part of the reaction between carbon and $\rm H_2O_2$ was attributed to reaction with iron salts that were associated with the carbon. Therefore, a sample of carbon was treated with dilute HCl to dissolve the iron and was washed before being reacted with 4% $\rm H_2O_2$. Following a period of poor TOC removal, this carbon gave the best organics removal obtained in any regeneration study, as shown in Run No.II, in Table 15, but its effective sorptive life was short. Thus, only three liters of product with TOC of 1.5 to 2.5 mg/l were obtained. After the acid- $\rm H_2O_2$ treatment this carbon had an iodine number of 1040, the same as fresh carbon.

Washing repeatedly with hot tap water gave no regeneration of spent carbon. Carbon heated in boiling water for 30 min. reduced the TOC of five liters of feed from 8.5 to 4.5 mg/l, and of an additional four liters to 5.5 mg/l. After blowing steam down a bed of carbon inside the 1-sq.in. column for 5 hours, the carbon reduced the TOC of feed from 12 to 9 mg/l. During the steaming, the TOC of the condensate dropped steadily from 105 mg/l in the first hour to 57 mg/l in the fifth.

Carbon treated with HCl and $\rm H_2SO_4$ removed less than one-third of the charged TOC. Even poorer results were obtained with carbon soaked in one-tenth normal potassium permanganate and ammonium persulphate solutions.

SECTION VII

MISCELLANEOUS ANALYSES

Miscellaneous analyes were run at various times during this study to observe effects resulting from the conditions studied.

Table 16 shows BOD removal accomplished by chemical clarification and treatment in aerobic and anaerobic columns. Except for the January values when the columns were known to be performing poorly, the system including aerobic columns consistently removed about 90% of the BOD and the system including anaerobic columns only slightly less. Table 17 shows that clarification and treatment with partially spent carbon, which had treated over 700,000 gal. (7000 volumes) of sewage when the tests were made, removed 93% or more of the BOD. A system including unactivated carbon gave an average removal of 93%.

The relative stabilities of the various effluent streams are indicated in Table 18 which shows the turbidities of the various streams at the time they were sampled and after being allowed to stand exposed to air for 18 to 30 hours. these data were shown in Table 3. Primary effluents generally become clearer on standing due to settling of the suspended material, but clarified primary effluents became more turbid. Effluents from the aerated columns invariably became clearer on standing, due to settling of grayish solids which were presumably biological remains. effluents from the unaerated columns showed a different behavior before and after the last two columns were made aerobic. When the entire system was anaerobic, the turbidities of samples from the fourth column increased from 1 to as much as 48 JTU on standing. However, after the first two months when the last two carbon columns were run aerobically, the effluents showed no increase in turbidity on standing.

Although 140 mg/l of FeCl₃ were used to clarify the primary effluent, the column effluents contained only about 3 mg/l of iron (Table 19). The concentration of ferrous iron in the water increased as the effluent passed from the second to the fourth column.

Essentially no phosphorus reduction occurred in the columns, as column effluents had about the same phosphorus contents as clarified primary effluent (Table 20). The amount of phosphorus removed in the clarification of the primary effluent

Table 16

BOD REMOVAL IN AERATED AND UNAERATED ACTIVATED CARBON COLUMNS

BOD, mg/l

Sample	10/22/70	10/30/70	11/12/70	12/8/70	1/21/71
Primary Effluent	99	130	113	92	70
Clarified P.E.	44	62	48	35	40
Aerated Carbon Col.2	19.5	16	18	21.5	25
Aerated Carbon Col.4	8.0	13	12.5	11.0	16
& DOD Domotrod	92	90	91	88	77
naerated Carbon (1)					
Col.2	26.5	29	21	27.5	34.5
Unaerated Carbon					
Col.4	14.0		14	10	17
% BOD Removed	86		88	90	76

Table 17

BOD REMOVAL IN SPENT ACTIVATED CARBON AND NON-ACTIVATED CARBON COLUMNS

BOD, mg/1

Sample	3/3/71	4/2/71	4/14/71	4/23/71
Primary Effluent	124	103	68	140
Clarified P.E.	24.5	26	17	26
Aerated Activated				
Carbon, Col.4	4.5	4	5	5
% BOD Removal	97	97	93	96
Aerated Non-Activated				
Carbon, Col.4	4.5	15	4.5	4.5
% BOD Removed	97	86	93	97

Table 18

STABILITIES OF EFFLUENTS FROM AEROBIC AND ANAEROBIC COLUMNS RELATIVE TO TURBIDITIES

	10/1	3/70	10/1	6/71	10/2	3/70	11/1	9/70	2/24	/71
	Initial	30 hrs	Initial	24 hrs	Initial	18 hrs	Initial	30 hrs	Initial	18 hrs
Primary Effluent	-	11.0	0.8	32.0	42.0	7.2	40.0	18.0	46.0	15.0
Clarified Primary Effluent	0.5	11.0	0.8	32.0	1.1	13.0	1.3	16.0	0.4	1.5
Aerated Carbon Column 4	10.5	4.5	19.0	7.8	11.0	1.8	4.8	2.8	6.5	3.0
Unaerated Carbon* Column 4	1.0	48.0	1.6	31.0	1.3	5.6	3.0	3.8	-	_
Unactivated Carbon Column 4									0.5	0.8

All turbidity values in this table are in Jackson Turbidity Units (JTU).

^{*} After 11/10/70, the first two columns were kept anaerobic and the last two columns were kept aerobic.

Table 19

IRON IN COLUMN EFFLUENTS

May 20, 1971

Iron Content, ppm	Fe ⁺²	Total
Effluent		
12-ft Carbon 24-ft Carbon 12-ft Coal 24-ft Coal	0.59 1.69 0.15 2.05	1.25 2.83 2.26 2.64

Table 20
TOTAL PHOSPHORUS OF EFFLUENT STREAMS

Total Phosphorus, mg/l P

	10/15/70	11/24/70	1/20/71	2/2/71	2/4/71
Primary Effluent	9.6	5.1	13.4	>25.0	>20.0
Clarified P.E.	0.7	0	1.7	>17.0	9.5
Aerated Carbon					
12-ft	0.7	0.3	1.7	>17.0	7.8
24-ft	<0.3	0.5	2.3	>17.0	8.5
Anaerobic Carbon					
12 -f t	0.7	0.3	1.8	>17.0	8.8
24-ft	1.0	0	2.2	>17.0	9.5

varied with the phosphorus concentrations in the feed. The concentration of ferric chloride used in the clarification removed virtually all phosphorus from primary effluents having about 5 mg/l P; but as the phosphorus content of the primary effluent increased, the concentration of phosphorus in the clarified primary effluent also increased.

Table 21 shows the effect of carbon treatment on the concentration of nitrogen compounds in effluent streams. Ammonium nitrogen concentrations underwent little change, but organic nitrogen contents dropped as organic compounds were removed by the carbon beds. A small reduction in nitrate concentrations occurred in both the aerobic and anaerobic columns.

Table 21
NITROGEN ANALYSES OF EFFLUENT STREAMS

Nitrogen, mg/l	Ammonium	Organic
<pre>Stream, 10/15/70</pre>		
Primary Effluent	8.6	3.2
Clarified Primary Effluent	8.8	1.7
Aerated - 12-ft Carbon	8.7	1.7
- 24-ft Carbon	10.6	1.2
Anaerobic - 12-ft Carbon	8.4	3.2
- 24-ft Carbon	7.7	1.0

Nitrates as N, mg/l

	10/15/70	1/7/71	2/2/71
Primary Effluent Clarified P.E.	<0.5 <0.5	3.5 5.3	10.0 4.8
Aerated Carbon 12-ft 24-ft	<0.5 <0.5	4.0 2.7	2.5 2.0
Anaerobic Carbon 12-ft	<0.5 <0.5		
24-ft Anaerobic-Aerobic Carbon 12-ft	<0.3	2.0	2.5
24-ft		0.5	2.0

SECTION VIII

DISCUSSION OF RESULTS

A. Effect of Aerobic Conditions Within Carbon Columns

In this study, aerobic conditions inside a carbon column gave better performance than anaerobic conditions. The aerobic columns removed more of the carbonaceous impurities in sewage and produced more stable products. Unlike anaerobic effluents, aerobic effluents contained no hydrogen sulfide. The combined anaerobic-aerobic operation, in which the first one-half of the carbon column system was operated anaerobically and the other aerobically, produced essentially the same organic removal and product quality as the all aerobic system. However, since the activity of the 12-ft anaerobic section was much less than that of the corresponding aerobic section, the effectiveness of the combined anaerobic-aerobic system depended essentially on the effectiveness of the aerobic section, and there was no advantage in operating with the mixed anaerobic-aerobic system.

B. Effect of Carbon Properties on Column Efficiencies

In aerobic columns, the treating effectiveness of fresh activated carbon was much superior to that of unactivated carbon, as the fresh activated carbon columns removed approximately 50% more TOC than the unactivated coal product.

The different behavior of these two types of carbon showed that at least two different mechanisms are involved in carbon treatment. The low organic removal obtained initially with fresh non-activated coal material indicated that very little adsorption occurred on this material and that only gradually did effective biological activity develop on its surfaces. On the other hand, the excellent removal obtained immediately with the activated carbon indicated that this material rapidly adsorbed organics and facilitated rapid development of bacteriological activity within the columns. The high degree of organic removal observed at the beginning of the run with activated carbon was due principally to adsorption. However, the fact that the first 12-ft of this material was able to remove essentially its own weight of organics indicated that some of the material removed by adsorption was subsequently degraded by biologic activity at the carbon surfaces, which in turn freed these surfaces for further adsorption.

C. Comparison of Results from Current and Previous Studies

In the period in which clarified primary effluent was tested in the earlier study, 5 product with 3 to 5 mg/l TOC was obtained consistently during four summer months. Although product from the current study had TOC of 6 to 8 mg/l after a few weeks, these higher values are not indicative of poorer carbon column performance than that experienced previously. On the contrary, overall TOC removal in the columns from August 28 to November 30 averaged 76.9%, compared with 70.4% during the earlier study. Because the TOC of the feed was higher during this study, 70 lb of TOC was charged to the columns in the three months between August 28 and November 30, 1970; whereas only 62.1 lb was charged during the four-month period between April 29 and September 2, 1969 in the previous The improved TOC removal in this study may reflect better control of aerobic conditions within the columns. It may also be that higher concentrations of organics in the feed promote better organics removal in the carbon beds.

D. Cleansing of Carbon in the Columns

During the nine months in which the carbon columns were operating, the carbon was cleansed by air scrubbing and backwashing three times. The air scouring and backwashing probably aided column operation by improving the hydraulic characteristics of the system, and by freeing the adsorptive surfaces of dead, non-active biomass and inorganic precipitate. After long periods of operation ratholing and inefficient contacting probably occurred within the columns, tending to reduce the effectiveness of the carbon treatment. Further, ferric hydroxide that precipitated in the columns likely interfered with flow and/or covered the carbon with a coating which inhibited its sorptive activity. This is supported by the observation that much red ferric hydroxide was recovered from the columns after backwashing.

Cleansing of the carbon improved its effectiveness and increased its useful life. To take full advantage of this finding, columns should be designed so that they can be backwashed and air scoured efficiently. The carbon chosen should have sufficient abrasion resistance to withstand several cleansings. Otherwise, large amounts of fine material produced during the air and water scouring would be carried from the columns.

E. In Situ Biologic Regeneration

One of the most notable findings of this study is the remarkable increase in the effective capacity of activated carbon facilitated by aeration in expanded-bed operation. Carbon has been found to function efficiently as an adsorbent for markedly longer periods than those predicted either by saturation data obtained from measurements of adsorption isotherms or from reports by others of sorption capacities obtained in the treatment of wastewaters in packed-bed adsorption systems. The enhanced effective capacity of the carbon observed in the present studies is, as suggested by Weber, Hopkins, and Bloom, 5,10 in earlier studies of the treatment of wastewaters in expanded-bed adsorbers, apparently attributable to bacterial activity on the surfaces of the carbon. This activity can be tolerated, indeed encouraged, in expanded-bed adsorbers, whereas packed-bed adsorbers tend to clog and foul as a consequence of biological growths. In expanded-bed adsorbers. biological activity can be enhanced by addition of air or oxygen, a treatment which could cause air-binding of packedbed adsorbers.

As noted earlier in this report, maintenance of aerobic conditions in the solution phase passing through adsorbers was determined to enhance the quality of the effluent, both from the point of view of TOC reduction and the prevention of H₂S generation. It was not immediately obvious, however, whether aerobic solution conditions would affect the operating capacity of the carbon. The data obtained in this study indicated that the biological activity within the aerobic columns increased the useful life of the carbon significantly.

The precise mechanisms by which "in situ" biologic regeneration functions to achieve the remarkably effective sorption capacities observed in the current study, are difficult to isolate and characterize. However, some logical deductions can be made from the data observed earlier by Weber et al.^{5,10} and the results of the present pilot investigation.

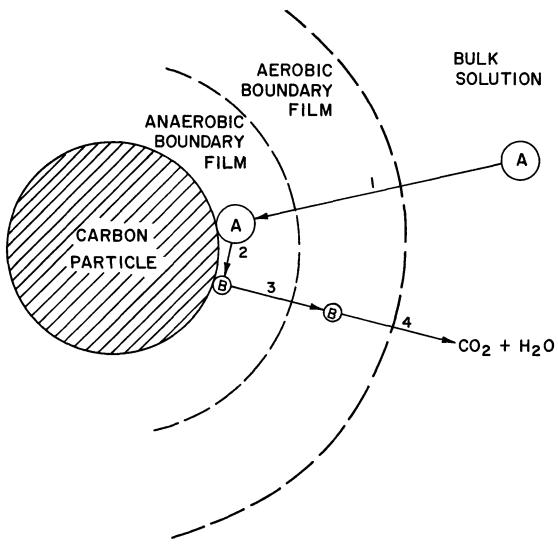
First, the principal separation process operating in these systems is adsorption from solution onto the surfaces of the activated carbon. Evidence of this is the rapidity with which organic matter is removed to a high degree from the aqueous phase, and observations on the lower effectiveness of other solid materials, such as sand and anthracite coal, which have less capacity for adsorption than does

activated carbon. Active adsorbents do not function merely as expanded-bed trickling filters. Once organic material is adsorbed on the carbon, a highly enriched substrate environment is created at the surfaces. This environment fosters the growth of micro-organisms which utilize the organic matter as food source, and, in so doing, free the surface of the carbon for continued function as an adsorbent. This then extends the effective operating life, or apparent capacity, of the carbon.

Adsorbed organic substances can be held at the surface of the carbon for long periods of time. The effective detention time of such materials in the sorption system may be several days or several weeks, rather than the few minutes residence time of the fluid from which they are adsorbed. With this long residence time, micro-organisms on the carbon surface have sufficient time to acclimate to even relatively non-degradable or biologically-resistant materials. Further, and by the same reasoning, because the biologic activity takes place on the carbon surface rather than in the bulk solution and because the substrate is so abundant, the micro-organisms are protected, or buffered, against shock loads of toxic materials and/or wide variations in waste composition.

The microbiologic growth responsible for substrate breakdown at the surface and consequent surface regeneration might be anaerobic. There are several observations which support this supposition. First, there is no evidence of rapid and massive sludge accumulation on the carbon, as would be expected for a completely aerobic system. sludge that does build up does so gradually and in relatively small amounts. Second, the accumulated sludge scoured from the carbon by vigorous agitation contained dark material that could have been an anaerobic residue. Third, even though the introduction of air or oxygen enhances adsorption effectiveness and apparent capacity, the amount of oxygen required is much less than that which would be required for aerobic oxidation of the mass of organic matter extracted from solution and concentrated on the carbon surfaces. Based on the dissolved oxygen analyses of the column feeds, an oxygen mass balance does not support an hypothesis of aerobic regeneration.

One possible explanation of the observed phenomena may be that shown in Figure 16. It is assumed for this explanation that two biologically active films surround each carbon particle. The interior film is anaerobic; the external film is aerobic. Adsorbable molecules pass through the films to the carbon surface. At the surface there is an opportunity



EVENT SEQUENCES: I. DIFFUSION OF LARGE ADSORBING ORGANIC MOLE-CULE (A) TO SURFACE OF CARBON.

- 2. ANAEROBIC DEGRADATION OF LARGE MOLECULE
 (A) TO SMALL MOLECULE (B).
- 3. DIFFUSION OF SMALL NON-ADSORBING ORGANIC MOLECULE (B) AWAY FROM SURFACE OF CARBON.
- 4. AEROBIC DEGRADATION OF SMALL MOLECULE B
 TO CO₂ AND H₂O.

FIGURE 16 — SCHEMATIC INTERPRETATION OF THE MODE OF IN
SITU BIOLOGIC EXTENSION OF ADSORPTION CAPACITY

for anaerobic degradation. The anaerobic degradation will not be complete, however, and low molecular weight degradation products, such as organic acids and alcohols, will form. The low molecular weight degradation products so formed have an inherently low relative energy for adsorption, and thus will back-diffuse from the surface through the external boundary film to the bulk solution. Under anaerobic conditions in the bulk solution there would be no aerobic film and these degradation products would join other materials which were never adsorbed from solution, and pass out in the effluent from the sorbers. If, however, oxygen or air is added to the expanded-beds of carbon, the solution phase as well as the outer layer of the boundary film on the carbon can be maintained in an aerobic state. Aerobic micro-organisms in the outer film could oxidize the outward diffusing products of the anaerobic decomposition. This is consistent with the observation that the effluent from the aerobic adsorbers contains less TOC leakage than does that from the anaerobic adsorbers. The leakage in the aerobic case would be comprised principally only of relatively non-adsorbable organics initially present in the wastewater. This interpretation is, of course, speculative. Considerable further study is required before the effective mechanisms can be unequivocally defined.

F. Polishing Column

The rapid breakthrough of organics in effluents from carbon columns indicated that the carbon quickly became saturated with some fraction of organic matter. One method for achieving a closer approach to an organic-free renovated water would consist of passing effluent from an on-line adsorber through a short polishing column of fresh carbon which is changed or regenerated frequently to remove the residual TOC comprised of weakly adsorbing, easily displaced organic substances. To be practical, this concept requires a low-cost, rapid regeneration.

None of the regeneration studies conducted offered promise for ultimate development of a rapid, simple reactivation system. Sodium hydroxide and $4\%~\mathrm{H_2O_2}$ were the best carbon regenerants found. However, neither restored more than 75% of the original sorption capacity of the spent carbon, and such activity losses could not be tolerated because of the low sorptive efficiency use of the carbon in a polishing operation. In addition, the regenerants were washed from the carbon with such difficulty that in many cases the volume of wash water greatly exceeded the volume of feed treated.

G. Treatment Costs

On the basis of results obtained previously, a physico-chemical wastewater treatment system was proposed. That system, shown in Figures 17 and 18, included coagulation of raw sewage with lime and treatment of the clarified effluent with carbon adsorption units to remove dissolved organics. Lime was the chosen coagulant because it gave good clarification and a rapid-settling sludge. Unlike FeCl3, lime can be recovered from settled sludge by incineration. The organic solids in the sludge would be destroyed in this incineration.

Although the beneficial effects of aeration were only partially realized previously, that process design included open tanks with trough-type overflows at the surface of the contacting basin to induce aeration of the wastewater during treatment, thus ensuring aerobic conditions inside the columns. The 6 to 10 mg/l oxygen concentration used in the current study was selected because this is in the range of the solubility of oxygen in water aerated at ambient temperatures.

The investment and operating costs for a 10-mgd combined coagulation-activated carbon treatment plant, like that shown in Figures 17 and 18, were presented in detail previously. The prices of the individual items in that cost estimate were adjusted to an ENR Index of 1300, which was representative of anticipated prices in 1970. The current estimate is based on an ENR Index of 1400. Nothing in the current study affected clarification costs, but the change in the ENR Index increased capital costs for this section of the treating plant from 1.93 to 2.08 million dollars. This increased clarification treatment operating costs from the 11.6¢/1000 gal. cited previously to 12.5¢/1000 gal.

The current study did make changes in the projected active life of the carbon and in the potential carbon treatment costs. The earlier study had assumed a carbon dosage of 500 lb/million gal. treated. Experience with aerated carbon columns has shown that much longer life can be obtained without sacrificing product quality. Thus, during April when the 340 lb of carbon in the aerated columns had already treated approximately 800,000 gal. of water, the TOC of the product averaged less than 8 mg/l. Almost 90% of the TOC was removed, and over 90% of the BOD was removed in the total treatment system. Actually, the carbon treated 890,000 gal. of water satisfactorily without reactivation. If all the carbon were to be reactivated,

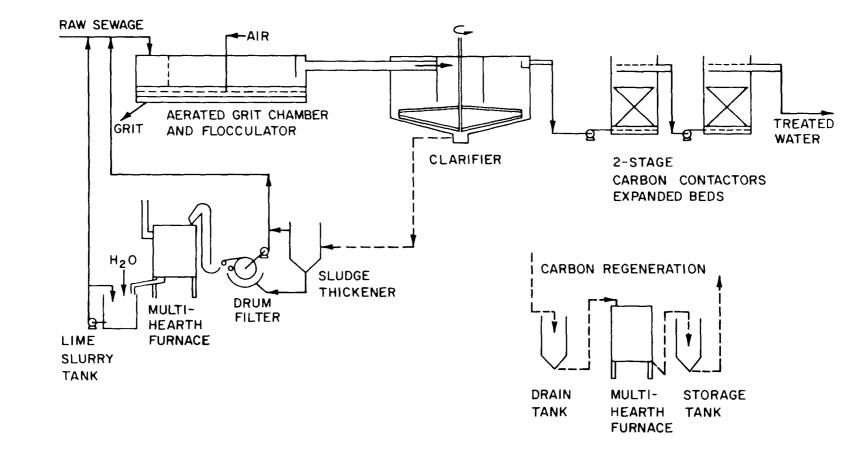


FIGURE 17 — PROPOSED SCHEME OF TREATMENT OF RAW SEWAGE BY CHEMICAL CLARI-FICATION AND ADSORPTION ON ACTIVATED CARBON

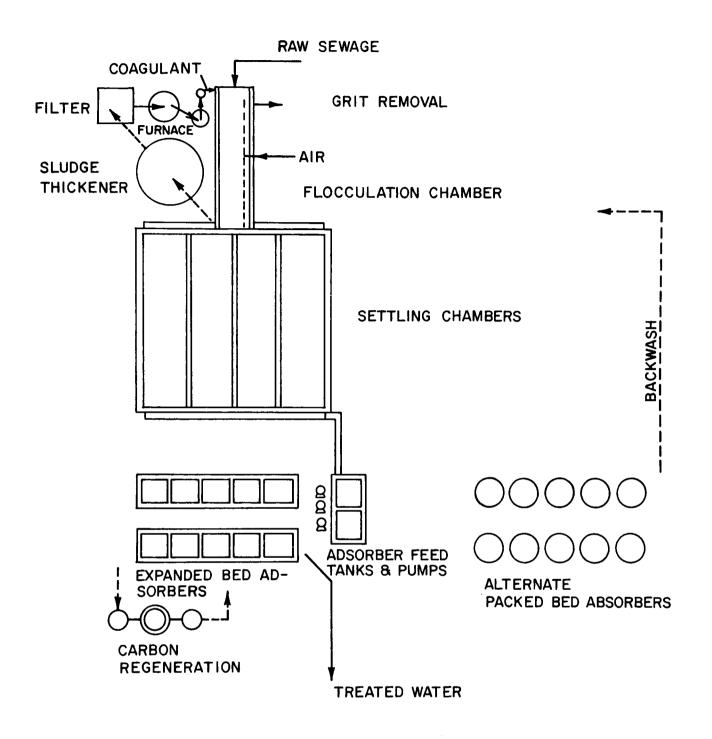


FIGURE 18 - PROPOSED ARRANGEMENT OF PROCESSING UNITS

the dosage would be 380 lb/million gal. In a system of contactors in series, however, only one half or even one quarter of the carbon need be reactivated at one time. If, in this case, part of the carbon had been reactivated, and those contactors placed after the contactors in which the carbon was not reactivated, more acceptable product water could have been obtained. The carbon dosage would then have been less than 380 lb/million gal. It is impossible to obtain an accurate figure for the "steady state" carbon dosage without actually carrying out further operation with reactivation. It can probably be assumed, however, that the dosage would be about 250 lb/million gal. It should be emphasized that this value is for the particular wastewater used in the study. Variations with wastewater from other locations can be expected.

Table 22 shows the estimated capital costs for the carbon-treating systems, and Table 23 shows the estimated operating costs for treating clarified municipal sewage in aerobic carbon beds. The first column of Table 23 is based on the same carbon dosage of 500 lb/million gal. used in the earlier estimate. The second column shows the estimated cost with a projected dosage of 250 lb/million gal. of effluent treated. The savings accruing from the longer treating life of the carbon are reflected in a 50% reduction in the amount of makeup carbon needed and a similar cut in the fuel and power required to regenerate the carbon. A small additional reduction resulting from a smaller regeneration system was not included. The net effect of these economies is to lower the treatment costs for the carbon adsorption treatment by approximately $0.7 \div /1,000$ gal. Based on a $7.6 \div /1,000$ gal. carbon treating cost, total costs for a 10 mgd combined coagulation and treatment with activated carbon are 20.1¢/ 1,000 gal.

Considerably greater economies can be achieved if the quality of product obtained with the unactivated coal product would be acceptable. Based on the experience in this study, a carbon with low sorptivity can produce an effluent with 10 to 12 mg/l TOC and a BOD reduction of approximately 90% when combined with chemical clarification. activated coal material probably would not deteriorate. Therefore, replacement costs were estimated on the basis of a small amount needed to replace fines that formed during cleansing of the bed and that were carried from the reactor. The coal price of \$50 per ton is high, but it is the actual price paid for the sized product purchased in bags for this If unactivated coal is used to treat the sewage stream. the multiple hearth furnace used to regenerate activated carbon would not be needed and certain economies could be made in the piping. This, plus the lower carbon cost, reduces the estimated capital costs to \$978,600, as compared to almost \$1.6 million

Table 22

ESTIMATED CAPITAL COSTS FOR TREATMENT OF CLARIFIED RAW SEWAGE IN ACTIVATED CARBON AND UNACTIVATED COAL

Material Columns

Basis: 10 mgd	Activated Carbon	Unactivated Coal Product	
Equipment Adsorption System Regeneration System	\$ 185,900 139,600 325,500	\$ 185,900 - 185,900	
Piping Adsorption System Regeneration System	209,600 14,500 224,100	209,600	
Total	\$ 549,600	\$ 395,500	
Instrumentation Painting and Insulation Buildings and Structures	26,900 10,700 136,500 \$ 174,100	19,800 7,900 98,900 \$ 126,600	
Physical Costs	\$ 723,700	\$ 522,100	
Engineering Home Office Field Contractors	\$ 126,600 123,000 43,000 \$ 292,600	\$ 91,400 88,800 31,300 \$ 211,500	
Base Cost	\$1,016,300	\$ 733,600	
Contingency, 15% of Base Cost	152,400 \$1,168,700	110,000 \$ 843,600	
Auxiliary Facilities Power Fuel Oil Roads, Walks and Fence	\$ 25,000 20,000 60,000 \$ 105,000	\$- 25,000 - 60,000 \$ 85,000	
Total Plant Cost Carbon Charge	\$1,273,700 288,000 \$1,561,700	\$ 928,600 50,000 \$ 978,600	

Sor	bent	Active (Unactivated Coal Product	
lb/	million gallons treated	500	250	
1.	Operational Labor*	\$ 43,300	\$ 43,300	\$ 43,300
2.	Maintenance Labor, 3% Plant Physical Costs	20,100	20,100	15,800
3.	Maintenance Materials, 2% Plant Physical Costs	13,500	13,500	10,500
4. 5.	Maintenance Supplies, 15% of 2 & 3 Supervision, 15% of 1	5,000 6,500	5,000 6,500	3,900 6,500
6.	Payroll Overhead, 15% of 1 & 2	9,500	9,500	8,900
7. 8.	General Overhead, 30% of 1, 2 & 6 Insurance, 1% of Plant Physical Costs	21,900 7,200	21,900 7,200	20,400 5,700
9.	Carbon Makeup, 5% @ 28¢/lb	27,500	13,750	
10.	Fuel, @ \$0.50/million Btu Power, @ \$0.01/kwh	13,000 13,500	7,000 6,750	6,700
12. 13.	Amortization, 24 yrs @ 6% Coal Makeup, 2% @ \$50/ton	124,200	124,200	77,800 1,000
	Total Treatment Costs Treatment Costs - ¢/1000 gal.	\$305,200 8.36	\$278,700 7.64	\$200,500 5.50

^{* 2} Shift Men + 2 day men @ \$4.00/hr.

for the carbon system. Columns with unactivated carbon or other inert material could probably be operated at a cost of $5.5 \div /1,000$ gal. and the combined coagulation-carbon treatment cost would be about $18 \div /1,000$ gal.

SECTION IX

ACKNOWLEDGMENTS

This report was prepared by Louis D. Friedman, Walter J. Weber, Jr., Ralph Bloom, Jr. and Charles B. Hopkins. Pilot plant operations and physical and chemical analyses were performed by W.H. Behn, E.M. DiPolvere and E.R. Smith.

Dr. Carl A. Brunner of the Environmental Protection Agency was Project Officer.

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SECTION X

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SECTION XI

PUBLICATIONS

Friedman, L.D., Hopkins, C.B., Behn, W.H., and Bloom, R., Jr., "Improving Effectiveness of Adsorption Systems for Sewage Treatment". Presented at the Annual Meeting of the New Jersey Water Pollution Control Association, May 6, 1971, Atlantic City, New Jersey.

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16. Abstract The magnitude and effects of biological activity in expanded carbon beds used for direct clarification/adsorption treatment of wastewater were investigated.						
Primary sewage effluent was coagulated with FeCl ₃ , clarified, filtered and charged to carbon columns. Clarification removed 60% of the total organic carbon (TOC) and 55% of the BOD. Carbon activity comparisons were made in identical series of four columns containing 24 ft of carbon.						
Aerobic conditions achieved by bleeding 6 to 10 mg/l O ₂ into the feed, enhanced activated carbon's activity and prolonged its effectiveness. In a nine-month pilot-scale study, overall TOC removal was 87.2%, BOD removal exceeded 90%, and effluent TOC or BOD averaged 8 to 9 mg/l. Aerobic activated carbon columns removed 14% more TOC than anaerobic, and over 20% more TOC than aerobic coal columns. Products from anaerobic columns contained H ₂ S and clouded on standing; aerobic products did not. Estimated treatment costs for combined clarification/adsorption treatment at 10 mgd are 20¢/1000 gal. with activated carbon and 18¢/1000 gal. with coal, which yields a product with a TOC or BOD of about 12 mg/l.						
17a. Descriptors			_			
*Carbon Treatment, *Clarification, *TOC Removal, BOD Removal, Activated Carbon, Unactivated Carbon, Coal, Aeration, Carbon Regeneration, Costs, Carbon Reactivation.						

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