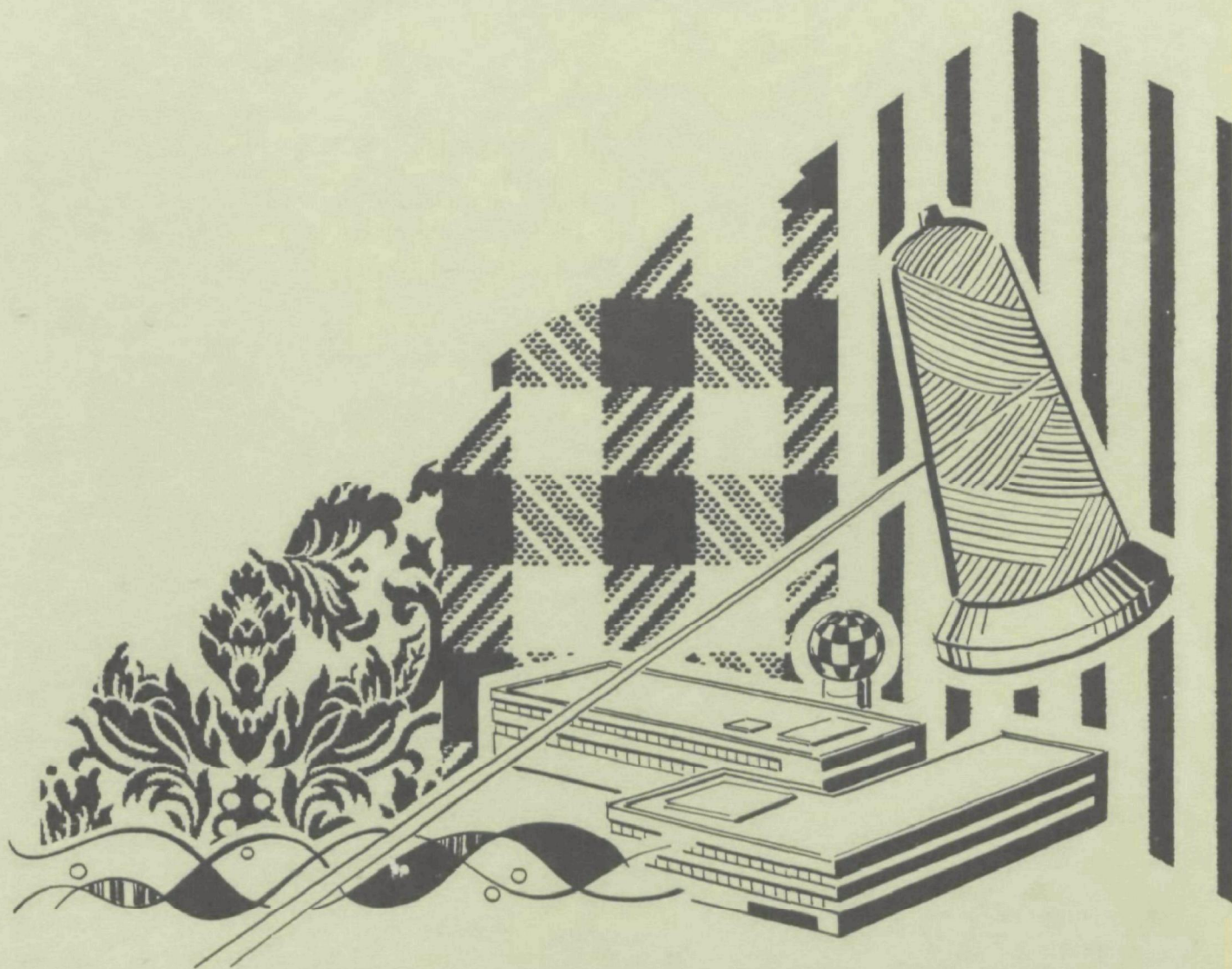




Bio-Regenerated Activated Carbon Treatment of Textile Dye Wastewater



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BIO-REGENERATED ACTIVATED CARBON
TREATMENT OF
TEXTILE DYE WASTEWATER

by

FRAM CORPORATION

East Providence, Rhode Island 02916

on behalf of

C. H. MASLAND & SONS

Carlisle, Pennsylvania 17013

for the

ENVIRONMENTAL PROTECTION AGENCY

Water Quality Office

GRANT PROJECT NO. 12090 DWM

January 1971

EPA Review Notice

This report has been reviewed by the Water Quality Office of the Environmental Protection Agency 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

A novel approach to treating a highly colored textile dyeing waste effluent is described. It comprises the removal by sorption of color bodies and other organic matter on activated carbon granules. Spent carbon granules are then subjected to a virule aerobic biological culture which desorbs and bio-oxidizes the desorbed matter, thereby regenerating the carbon for subsequent new sorption steps.

Laboratory confirmation of the phenomenon is presented. Field testing of the treatment process concept in a 50,000 gpd plant installed at a yarn spinning mill (C. H. Masland & Sons, Wakefield, Rhode Island) is reviewed.

Color removal was virtually complete at two flow rates evaluated: 8.5 gpm/ft² and 15.6 gpm/ft² carbon column bed flow. COD removal was 85% or higher at 8.5 gpm/ft² and only 48% at 15.6 gpm/ft².

It was demonstrated that activated carbon had an adsorption capacity in excess of 1.6 poundsCOD per pound of carbon when the carbon was reactivated only by biological means. The estimated operating cost for decolorizing 1,000,000 gpd is 8.3 cents/1000 gallons not including amortization.

This report was submitted in fulfillment of Grant No. 12090 DWM between the Water Quality Office of the Environmental Protection Agency and C. H. Masland & Sons.

KEY WORDS: Wastewater treatment, industrial wastes, textiles, color, adsorption, activated carbon, costs, total organic carbon

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SECTION I

CONCLUSIONS

1. Exhausted activated carbon can be biologically regenerated, provided that the adsorbate is biodegradable.
2. The textile dye wastes can be easily decolorized by a single pass flow through fixed granular activated carbon beds at an average flux of 12 gpm/ft², provided that the color bodies are receptive to adsorption on the carbon.
3. A continual adsorption-biological regeneration cycle of the activated carbon beds has been achieved over a four month period resulting in a continuous decolorization and organic reduction of a textile dye waste.
4. Economically, the process is well suited for handling complete treatment of small volume textile wastes (up to 75,000 gpd), and for pretreatment (complete color removal and 50% organic removal) of large volume textile wastes prior to discharge to conventional biological waste treatment systems.
5. An effluent profile analysis of the Masland-Wakefield dyehouse waste effluent was made. The average COD was 700 mg/l, BOD 350 mg/l, suspended solids < 40 mg/l and pH range 4.0 - 6.0.
6. Two test periods were operated as "Phase I" and "Phase II". Phase I was conducted from 6/2/69 through 10/6/69. Phase II was conducted from 7/21/70 through 10/23/70. Phase I operation illustrated the need for mechanical alterations, a better performing activated carbon, and the addition of a pH buffering chemical and biological nutrient to perfect the required biological regeneration step. Phase II operation including these alterations and modifications in operating procedures is the basis for the success of this project in meeting the objectives of this demonstration.
7. A 1.0 mgd plant design was developed from the data generated from the Phase II operation. For a 50% COD removal, the estimated construction cost is \$230,000 with an estimated operating cost of 8.3¢/1000 gallons. For a 75% COD removal, the estimated construction cost is \$550,000 with an estimated operating cost of 23.1¢/1000 gallons.

SECTION II

RECOMMENDATIONS

The Masland-Wakefield treatment facility was installed as an experimental pilot plant subject to modifications deemed necessary during its operational study period. Although it could be continued for use as a pretreatment facility providing 50% COD removal prior to discharge into a proposed regional sewer system, it is recommended that the plant be further modified as follows:

- 1) Installation of an equalization basin
- 2) Installation of two parallel activated carbon column units whereby one unit of three columns is on stream while the other unit is on biological regeneration

Such a modification would increase the level of treatment to an effluent suitable for stream discharge.

The complete (over 99%) decolorization demonstrated by the Masland-Wakefield pilot plant study warrants the location and selection of a manufacturing plant discharging a similar colored waste in quantities approaching or exceeding one million gallons per day. The design, construction and operational study of a treatment plant of this concept under a Federal demonstration grant funding is recommended.

SECTION III

INTRODUCTION

Biological treatment of wastewater can be markedly improved by providing a myriad of solid surfaces upon which biological growth is accelerated. The trickling filter and the rotating biological surface process are examples of employment of this extended area principle (1). The increased effect produced by providing considerably greater effective solid surface area in a biological reactor has been noted by I. S. Kugelman (2). Kugelman describes but does not explain an "unexpected" biodegradation taking place in a tertiary granular anthracite filter used to polish a secondary treatment effluent.

It is evident then that proper utilization of an adsorbent with a biological waste treatment process might provide an important step in designing more effective and less expensive waste treatment systems. Studies made along this line by S. S. Blecharczyk, E. L. Shunney and A. E. Perrotti at the Fram Research Laboratories resulted in a further breakthrough in technology - namely, the regeneration of an adsorbent's capacity by biological means. The application of this technique on the waste effluent of a carpet yarn textile mill is the subject of this report.

Conventional color removal methods for handling textile dyeing waste discharges have been: (1) lime coagulation and flocculation; (2) alum coagulation and flocculation; and (3) more recently, activated carbon columns with external thermal regeneration. With the exception of Method 3, only partial success has been achieved. Coagulation-flocculation will adequately handle insoluble and/or dispersed dyestuffs reasonably well. Soluble dyestuffs such as those used in carpet yarn dyeing are not removed by such techniques. Activated carbon with cyclic thermal regeneration is probably the most efficient method for removing color. Its complexity, the relatively high installation cost, operating requirements, and relatively high operating costs dampen its desirability. The fact that regeneration of the activated carbon's color removal characteristics can be accomplished in place by biological means makes the method more attractive than Method 3 where the carbon is regenerated externally.

In order to prove out the efficiency of the technique of biological regeneration of activated carbon as it would apply to color removal, there was a need to develop the technique at an industrial site. It appeared that the most expeditious approach was to apply for a Federal demonstration grant. Such a grant was applied for and awarded.

The grant project objectives were:

To conduct effluent profile analyses; to design, construct, operate, test and evaluate a pilot facility to treat the entire combined plant process and primary treated sanitary wastewater (50,000 gpd) utilizing the Fram Corporation's activated carbon modified activated sludge process; to develop design criteria for a 1.0 to 1.5 mgd plant.

SECTION IV

BIOLOGICAL REGENERATION

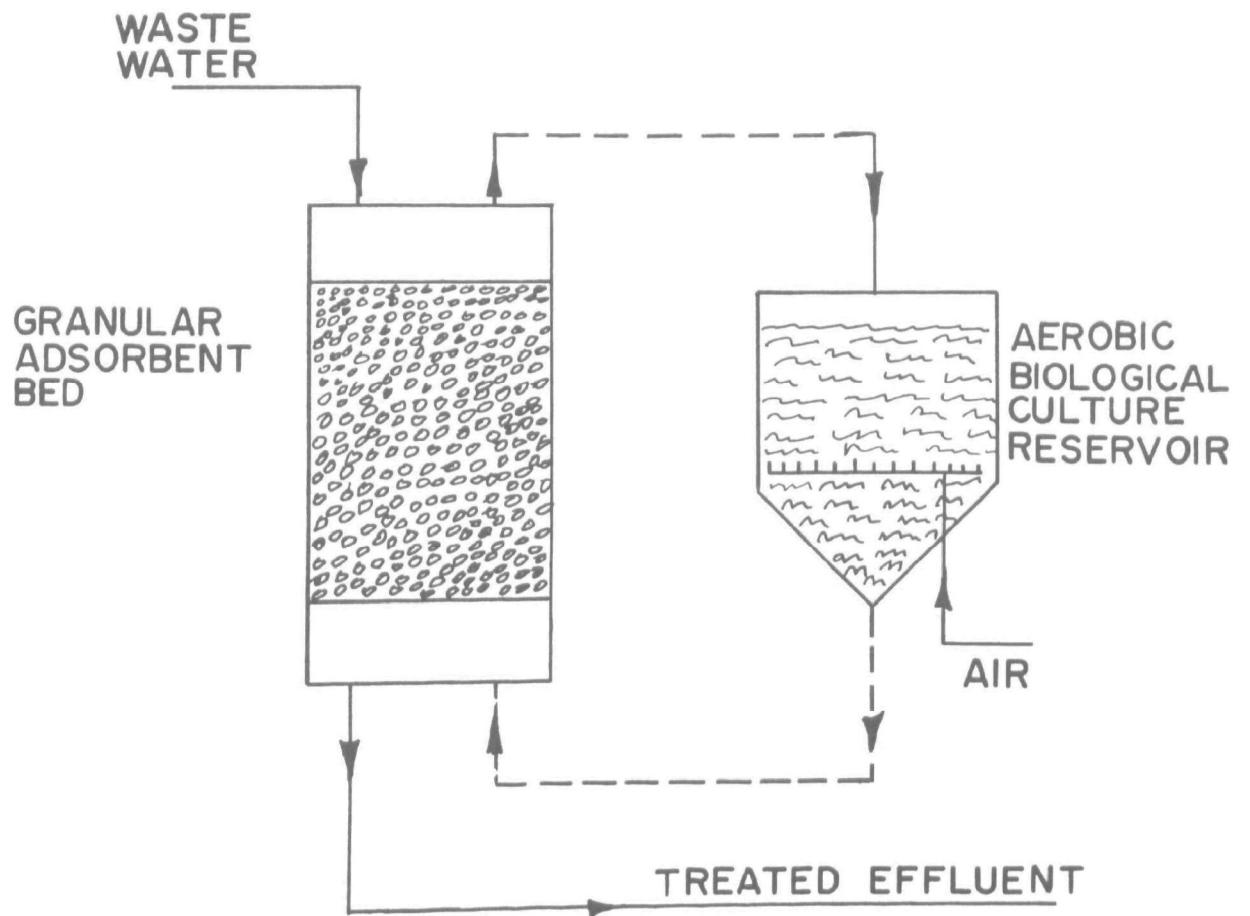
Organic matter contained in wastewater is adsorbed on an adsorbent contained in a fixed bed (Figure 1). Wastewater is fed through the adsorbent in a downflow mode until the adsorption capacity is exhausted. The exhausted adsorbent is regenerated by circulating in an upflow mode a liquid stream containing an aerobic biological culture. The resultant bio-oxidation of the eluted organic matter continues to take place until the adsorbent is reactivated. The reactivated bed is then ready to perform again its adsorption-filtration function on a wastewater stream.

The bio-culture which is acclimated to the wastewater to be treated in many cases receives enough nutrient from the contaminated carbon to maintain itself. When nutrient content is deficient, sufficient nutrient can be added to the bio-culture to maintain the desired bio-chemical activity required to achieve regeneration.

Previous to this demonstration project, two laboratory fixed bed adsorbent columns were in operation on a sorption-biological regeneration repeating cycle for over fifteen months. The same adsorbent removed a quantity of organic matter over 100 times its weight. In this experiment, the adsorbent was contained in packed columns six feet in length and two inches in diameter. Each column was packed with 1200 grams of Witco 718 (12 x 30 mesh) granular activated carbon. The carbon was retained by a perforated sheet with 0.045 inch diameter holes in a staggered fashion and with a 26% open area. Flow rate through the system was maintained at 12 gallons per minute per square foot of cross-sectional area in a downflow mode.

The regeneration cycle was accomplished by recirculating a virulent dispersed bacterial culture in an upflow mode at 10 gpm/ft². The dissolved oxygen in the culture was maintained at a level greater than 2 ppm by bubbling air into it. The source of activated sludge was a municipal secondary treatment plant. The sludge solids in the regeneration liquor did not exceed 1000 mg/l and were generally less than 200 mg

A synthetic wastewater was prepared in accordance with the formula in Table I and its COD (chemical oxygen demand) was 295 mg/l. An average reduction in COD of 51% was maintained for the entire fifteen month period. The variation in COD reduction was 46 - 58%.



SORPTION-REGENERATION PROCESS
FIGURE 1

Table I
Synthetic Waste Formula Used in Original
Bio-regeneration Studies

Starch, Soluble	39.4 mg/l
Glucose	39.4 mg/l
Glycine	21.0 mg/l
Nutrient Broth	31.0 mg/l
Leucine	31.0 mg/l
Glycerine	5.5 mg/l
Octanoic Acid	5.5 mg/l
Oleic Acid	5.5 mg/l
Sodium Acetate	5.5 mg/l
COD of Solution	295 mg/l

SECTION V

FIELD APPLICATION DEVELOPMENT

SITE FOR PILOT PLANT

The carpet yarn fiber dyeing facility of C. H. Masland & Sons, Wakefield, Rhode Island was well suited for field studies of this sorption-biological regeneration treatment process. The waste from the dyehouse was predominantly a clear, heavily colored solution dumped directly into the river downstream of a mill dam. Its quantity, 50,000 gallons per day over a 10 hour dyeing period, was low enough to permit employment of a pilot plant handling the entire effluent. Also, a 10 hour adsorption-filtration phase followed by a 14 hour biological regeneration phase could be maintained without providing an otherwise duplicate system for continual 24 hour service.

PRELIMINARY PROFILE ANALYSIS

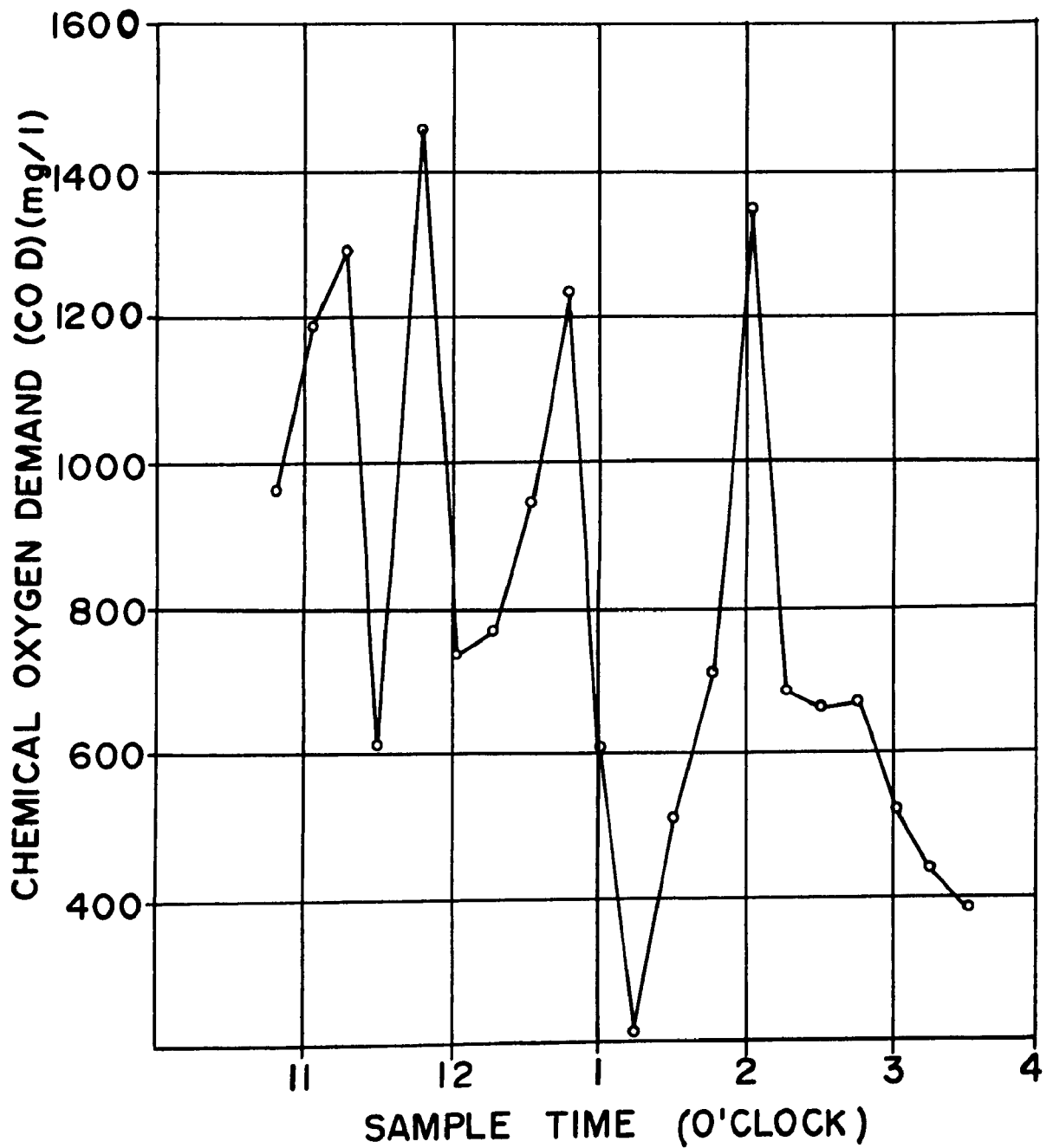
Analyses pertinent to the pollutant waste content of the Masland-Wakefield effluent stream were performed. Figure 2 is a plot of COD (chemical oxygen demand) as a function of time in 15 minute steps over a 4 hour period. A relationship of COD to TOD (total oxygen demand) was established where $COD = 0.98 TOD$; further, $COD = 2.51 BOD_5$ (five day biochemical oxygen demand) and also $COD = 2.54 TOC$ (total organic carbon). See Appendix E for a detailed explanation of these relationships.

For the purpose of clarity, the chemical oxygen demand (COD) parameter will be used in the remainder of the text.

Figure 3 is a plot of color versus time. Tinctorial strength is ten times the absorbance obtained on a colorimeter at a wavelength of 450 millimicrons.

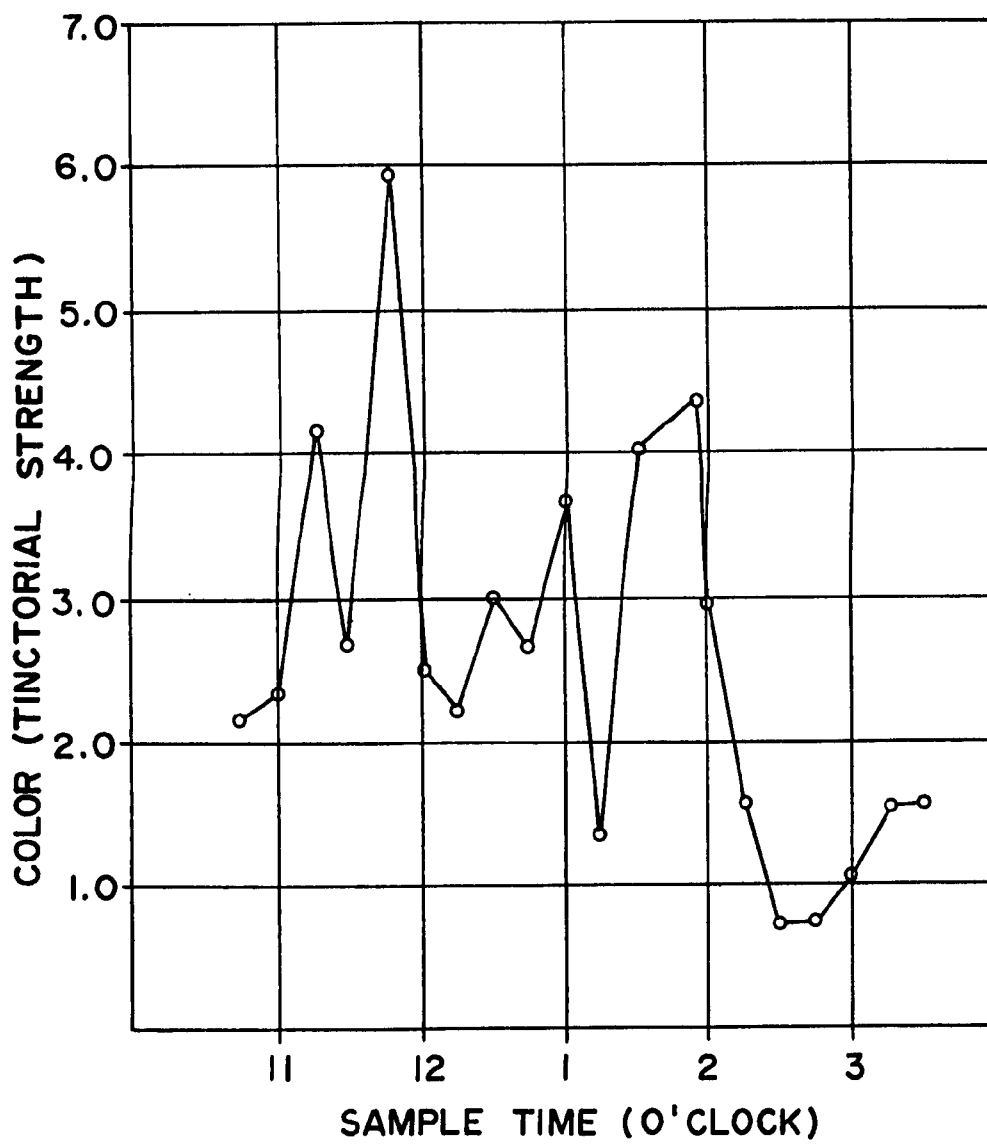
Figure 4 is a plot of BOD versus time. Figure 5 is a plot of suspended solids versus time. The mean values and range for each parameter evaluated are presented in Table II.

The profile data as shown graphically in Figures 2, 3, 4 and 5 and summarized in Table II reveals that the wastewater is predominantly solid-free (suspended solids: 6 - 70 mg/l, mean 27). The contaminants contributing to high coloration (2.5 color units mean, which is comparable in intensity to that of a dark red wine) and a moderate BOD and COD concentration are predominantly soluble in nature and well suited for adsorption column treatment.

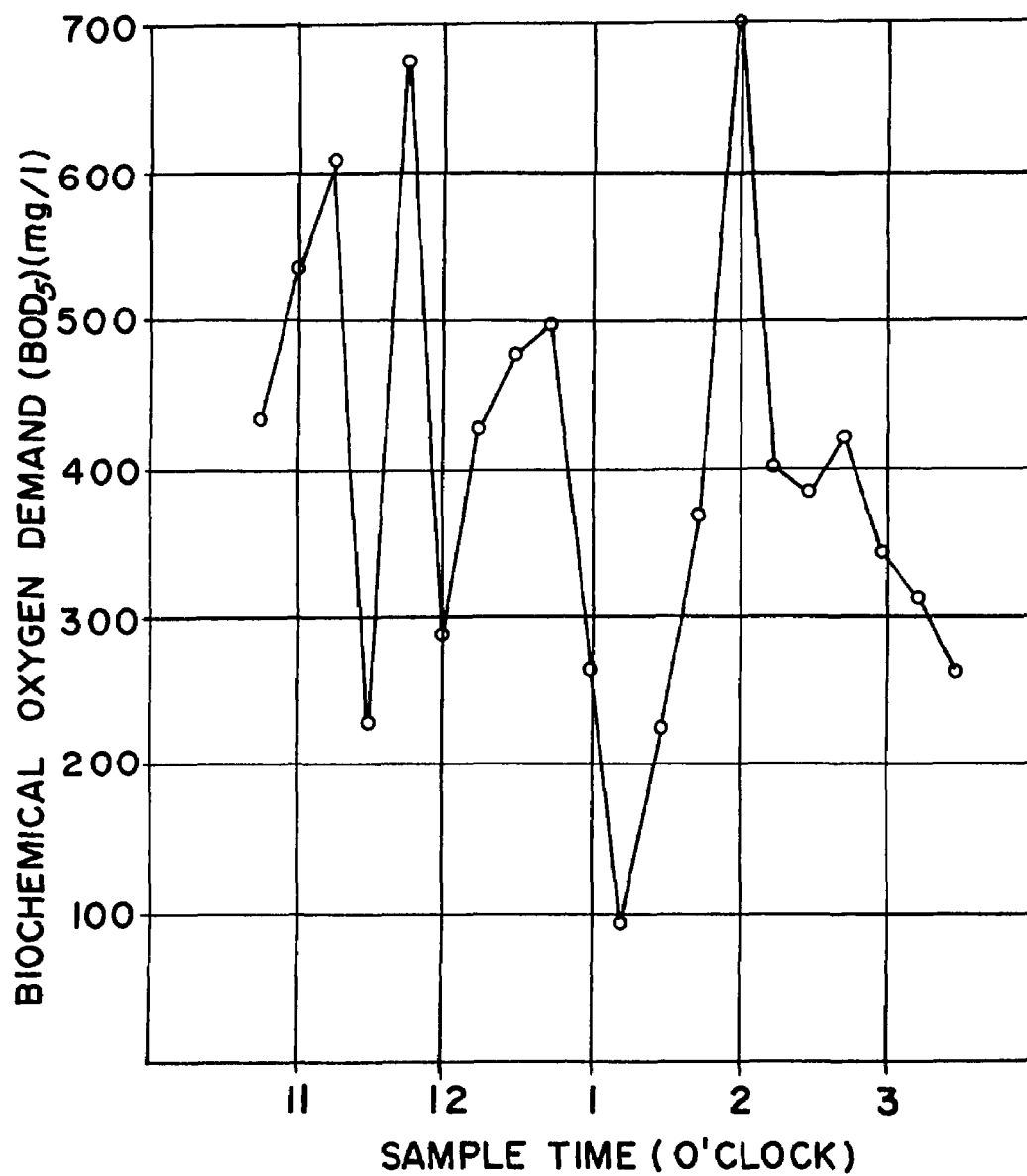


EFFLUENT PROFILE COD vs TIME

FIGURE 2

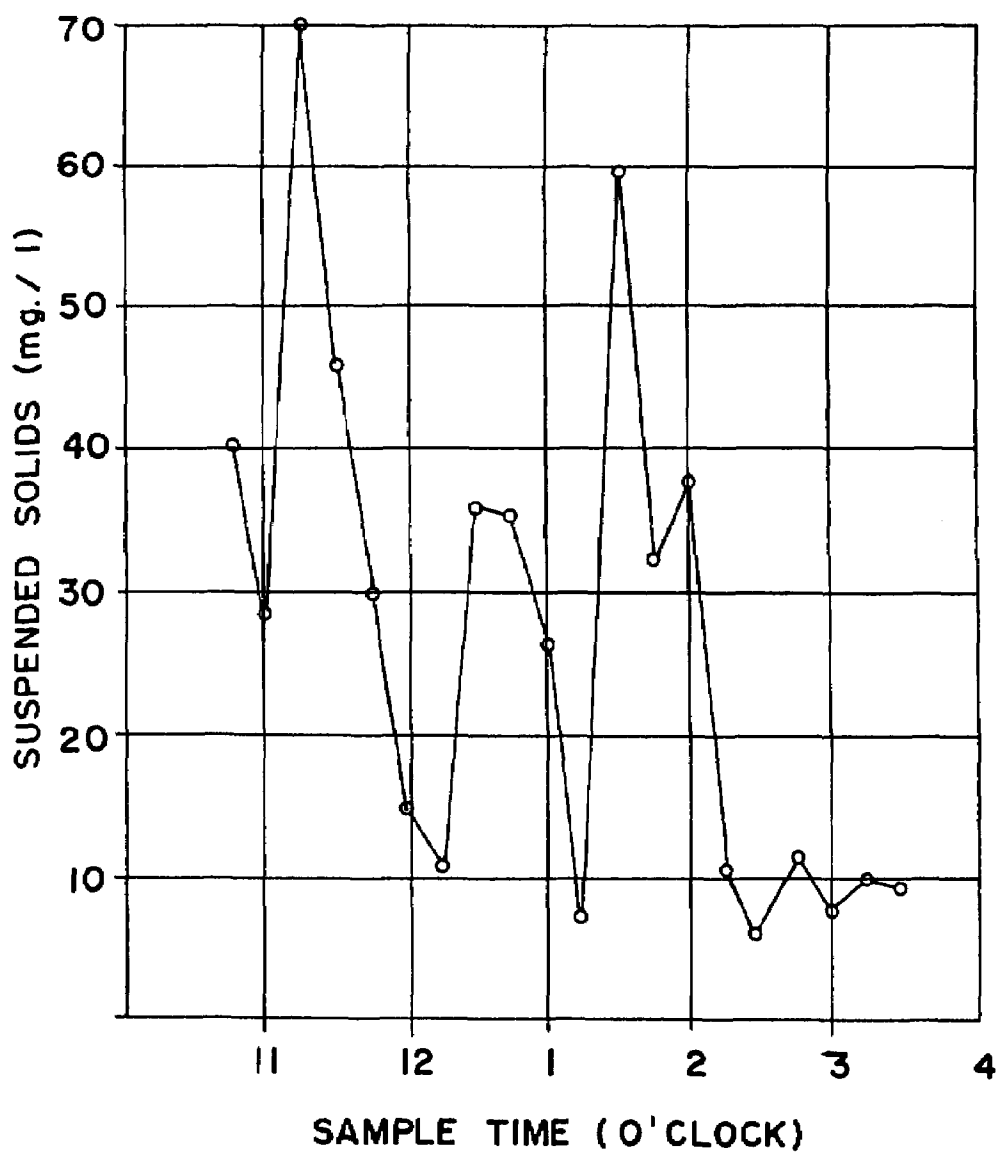


EFFLUENT PROFILE COLOR vs. TIME
FIGURE 3



EFFLUENT PROFILE BOD₅ vs TIME

FIGURE 4



EFFLUENT PROFILE-SUSPENDED SOLIDS vs TIME
FIGURE 5

Table II
Masland Dyehouse Raw Waste Profile

<u>Parameter</u>	<u>Mean</u>	<u>Range</u>
Color - units *	2.5	0.7 - 5.9
pH	4.3	4.0 - 6.0
Temperature- ° F.	110	90 - 124
BOD ₅ (biochemical oxygen demand) mg/l	396	95 - 700
COD (chemical oxygen demand) mg/l	700	305 - 1450
Suspended Solids - mg/l	27	6 - 70

* Tinctorial Strength.

Before designing an adsorption column treatment system for installation at the Masland-Wakefield plant, contamination-regeneration re-cycling tests were performed employing actual Masland dyehouse wastewater of known composition to contaminate. Figure 6 shows the decrease of COD removal as the adsorption capacity of the activated carbon is used up (contamination cycles C1, C2, etc.), with each contamination cycle followed by a bio-regeneration cycle (R1, R2, etc.).

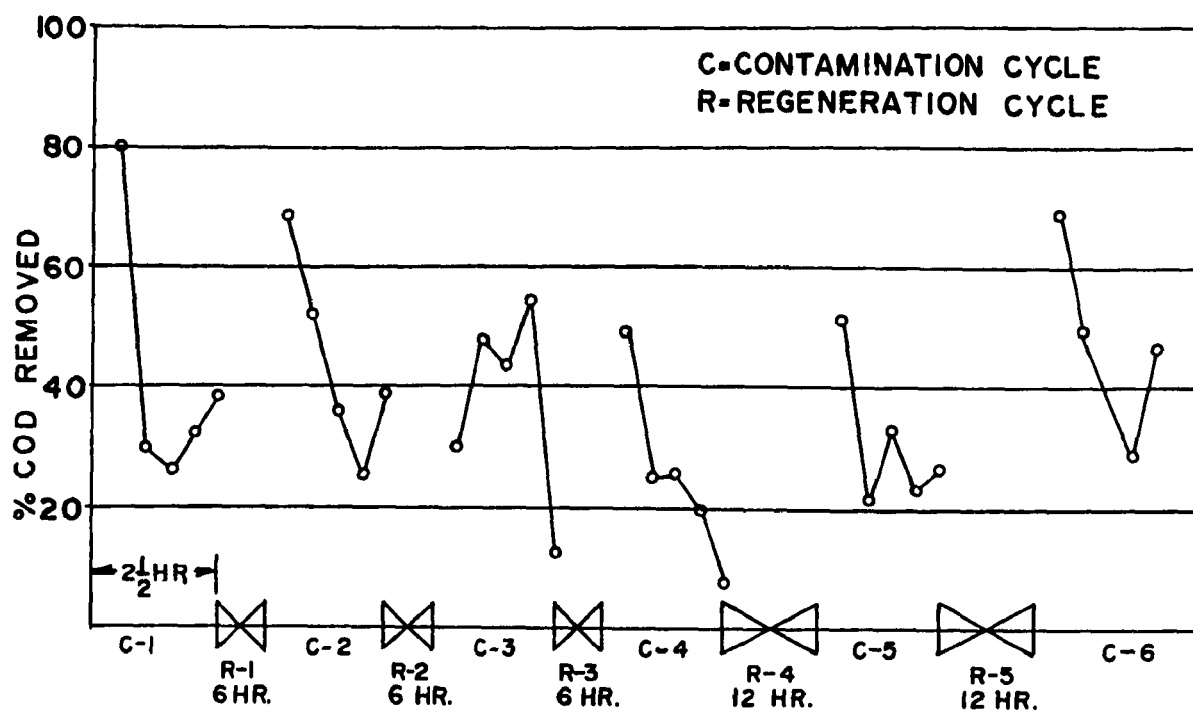
Each contamination cycle (C1, C2, etc.) was 2-1/2 hours in duration at 100 gph through two five-inch diameter columns, each packed with 5000 grams of granular Witco 718 carbon (12 x 30 mesh). Columns were contaminated in the downflow direction in series, and biologically regenerated in the upflow direction in parallel. Hence, during the contamination cycle, the columns were operated in a packed mode and during the regeneration each adsorbent bed was fluidized. Although the natural waste influent varied widely in COD and chemical composition, the COD level was generally above 700 mg/l.

Each plotted point in Figure 6 represents the per cent COD reduction over a 30-minute interval. A gradual decrease in removal efficiency (first plotted point of each test cycle) can be observed during contamination cycles C1 through C4. This was attributed to regeneration times which were too short in duration (6 hours). When the regeneration time was increased to 12 hours (R4 and R5), a corresponding increase in "first point" removal efficiency is then achieved.

Actual contamination experienced on a stated day was a composite from the dyehouse effluent stream resulting from the batch dyeing operations listed in Table III. The spectrum of dyeing formulation chemicals in this test series was widespread.

LABORATORY DESIGN CRITERIA

The Masland-Wakefield effluent averages 700 mg/l COD at a flow of 50,000 gpd. At this level, the treatment plant will remove 300 pounds of COD per day. Three sections of two-inch diameter acrylic plastic columns were each packed with 1,200 grams of Witco 718 12 x 30 mesh activated carbon. A total of 720 liters of composite dyehouse effluent samples was passed through each column in series at one liter per minute. Figure 7 shows the per cent COD removed for each column versus total flow throughput in liters. From these data, it was calculated that 0.076 pounds of COD were removed per pound of carbon at a flow rate of 12 gpm/ft². Based upon a conservative 0.05 pound of COD removal per pound of carbon for a 300 pound COD load per day, 6,000 pounds of carbon would be required.



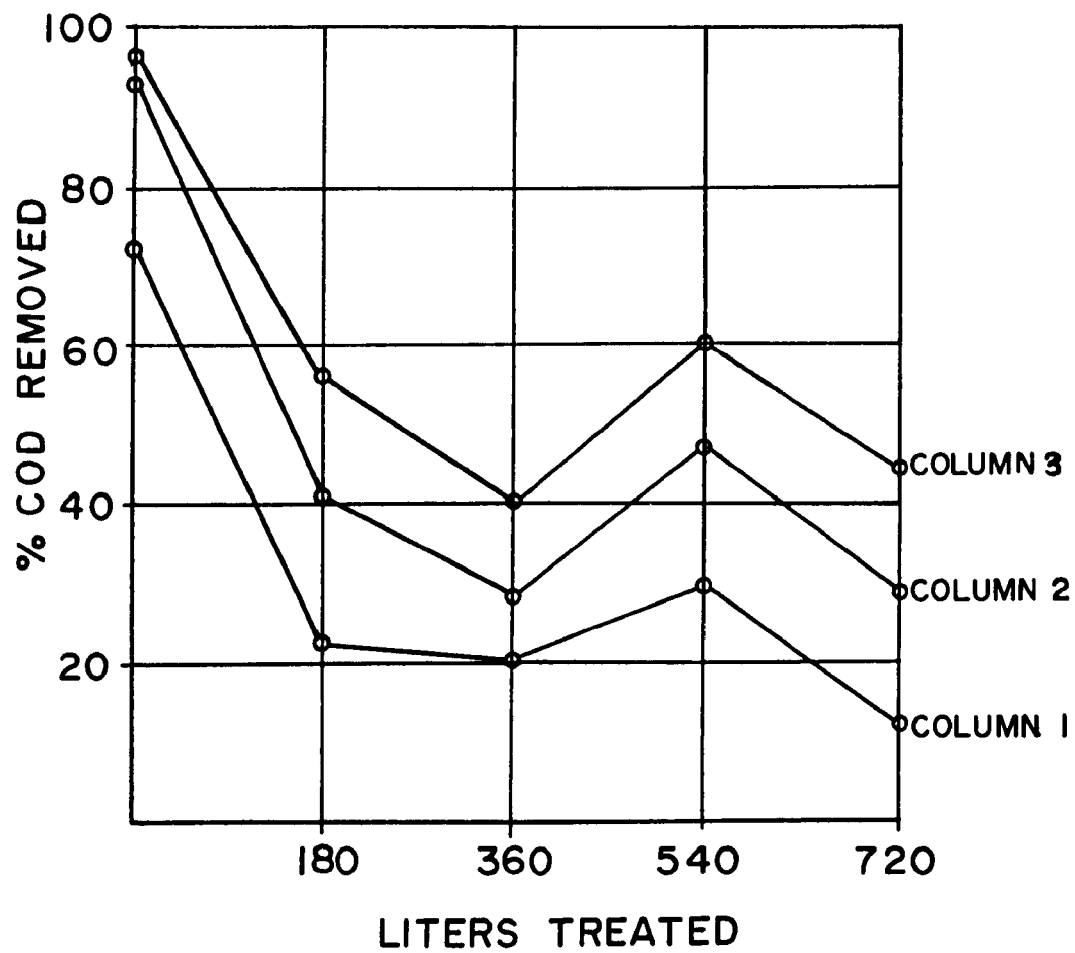
**REGENERATION STUDIES
FIGURE 6**

Table III

COMPONENTS OF WASTE EFFLUENT FOR EACH
CONTAMINATION CYCLE PLOTTED IN FIGURE 6

<u>CYCLE C1: LIGHT RED ACRYLIC</u>		<u>CYCLE C4: RUST WOOL</u>	
Dyes	Calcozine Acrylic Blue HP Cove	Dyes	Lanafast Orange RDL
	Calcozine Acrylic Red B		Lanafast Navy NLF
	Calcozine Acrylic Violet 3R		Lanamid Red 2GL
	Calcozine Acrylic Yellow 3RN		Acetic Acid, 56%
	Astrazon Yellow 7GLL		Emkalana WSDC
	Acetic Acid, 56%		Moth Snub
	Merpel DA		
	Salt		
	Retarder 98		
<u>CYCLE C2: BLUE WOOL</u>		<u>CYCLE C5: GOLD ACRYLIC</u>	
Dyes	Alizarine Light Blue 3F	Dyes	Astrazon Yellow 7GLL
	Xylene Mill Green B		Astrazon Red GTL
	Merpel DA		Astrazon Blue 5GL
	Salt		Acetic Acid, 56%
	Acetic Acid, 56%		Merpel DA
	Moth Snub		Retarder 98
	Sulfuric Acid		Salt
	Erioclarite B		
	Leveling Agent PD		
<u>CYCLE C3: BLACK WOOL</u>		<u>CYCLE C6: GREEN ACRYLIC</u>	
Dye	Omega Chrome Black ALA	Dyes	Sevron Yellow 3RL
	Acetic Acid, 56%		Astrazon Red GTL
	Moth Snub		Astrazon Blue 5GL
	Nabor Blue 2G		
	Acetic Acid		
	Merpel DA		
	Salt		

NOTE: Components which develop color of the wastewater are designated above as "Dyes".
The other components are used for stabilization, leveling, pH control, etc.



PERFORMANCE OF LABORATORY
SCALE ADSORPTION COLUMNS

FIGURE 7

SECTION VI

FIELD STUDIES

DESCRIPTION OF PILOT PLANT

The unit based upon the above discussed design criteria was installed in a service building (Building #4) on a tidal river bank (Figure 8). The dyehouse is across the street. The waste effluent is pumped through a conduit beneath the road bed and through a pipe line located in Building #4 and hence to the tidal estuary outfall.

Figure 9 shows the waste effluent line emerging from the conduit, the bypass line, the pump, and three of the four activated carbon adsorption columns. Figure 10 illustrates the back side of the adsorption columns, the biological culture tank used for regeneration, the air pump which supplies air to the culture tank, and the recirculation pump used during the regeneration cycle. The whole treatment plant occupies only 150 square feet, and is no more than 12 feet high.

The four adsorption columns were 3 feet in diameter by 10 feet high constructed out of mild steel and innerlined with a fiberglass reinforced polyester resin and built to withstand 60 psi. The regeneration reservoir was 5 feet in diameter by 8 feet high constructed out of fiberglass reinforced polyester plastic. It had an open top and a sloping bottom. All piping was 3-inch diameter PVDC plastic. Tank valving comprised penton coated three-way diverter plug valves. Pumps were of an all-iron positive displacement type. The blower was of a rotary lobe design. Other design features of the pilot plant appear in Table IV.

Figure 11 is a schematic flow diagram of the waste treatment system. Solid flow lines trace the flow of the dyehouse waste effluent through the adsorption filter columns during the contamination cycle. Broken flow lines trace the flow of the aerobic biological culture through the columns during the bio-regeneration cycle. The biological culture is prepared from a source of activated sludge and maintained in a dispersed aerobic phase.

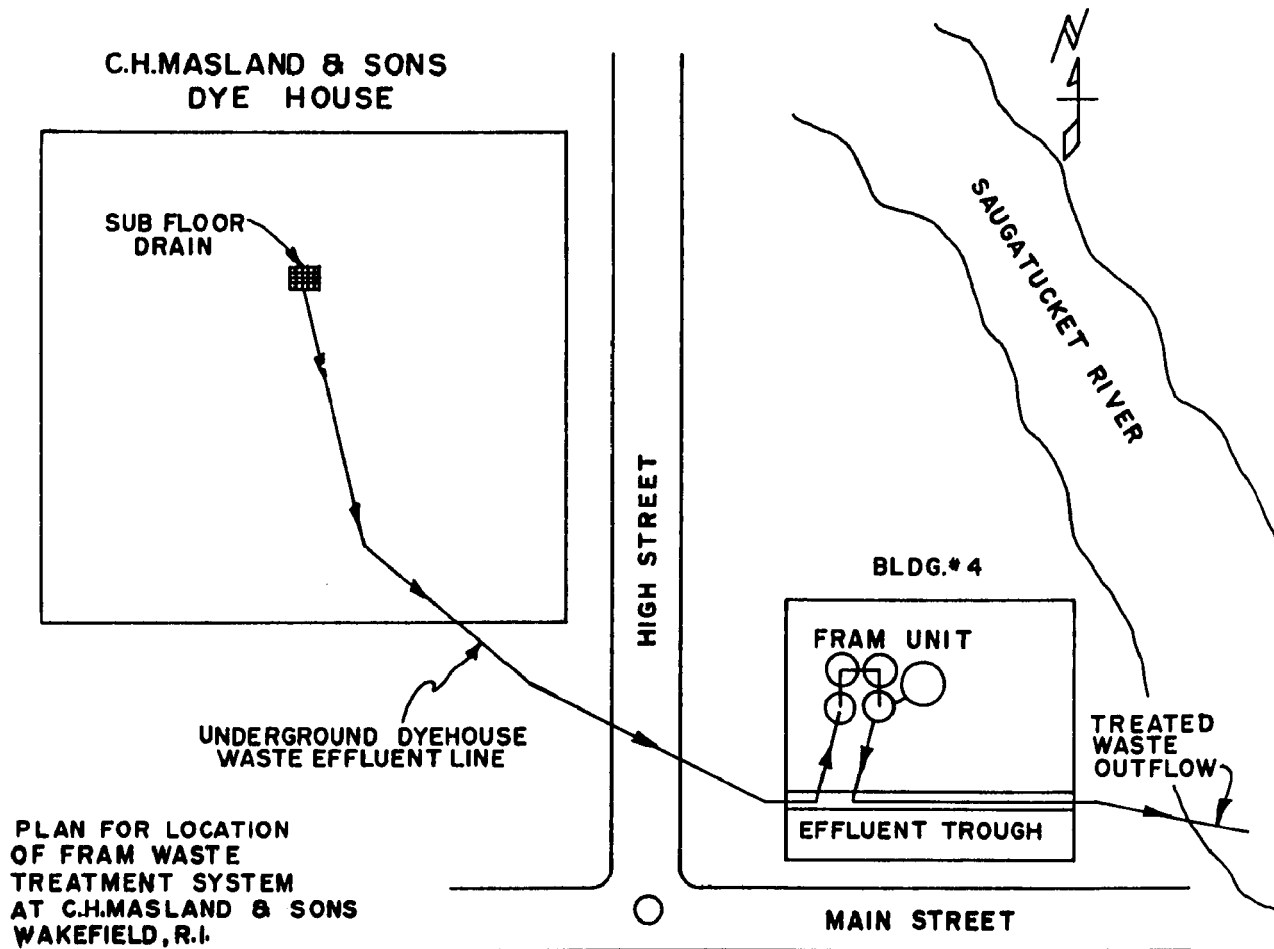


FIGURE 8



Waste Treatment System - C. H. Masland & Sons,
Wakefield, R. I. - Activated Carbon Columns

Figure 9

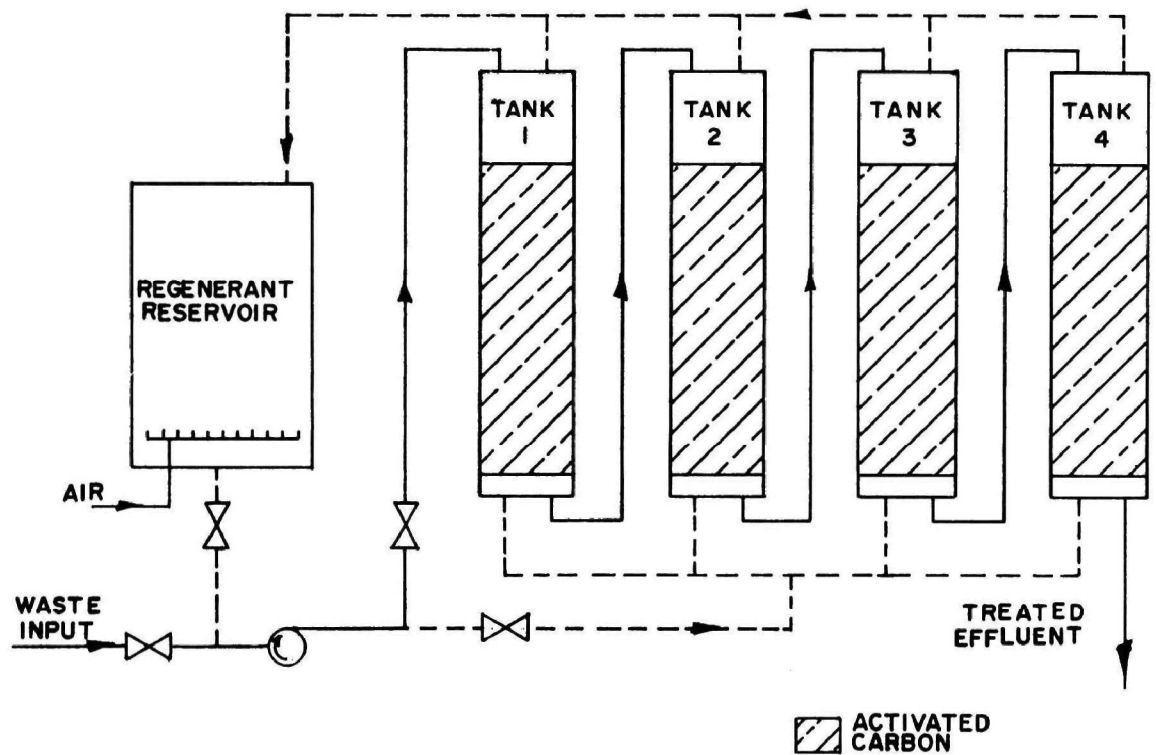


Waste Treatment System - C.H. Masland & Sons,
Wakefield, R. I. - Regenerant Reservoir

Figure 10

Table IV
Pilot Plant Design Features

Activated Carbon	-	Up to 6,000 pounds
Flow Rate	-	Variable to 120 gpm
Carbon Column Flux Rate	-	Up to 17.0 gpm/ft ²
Biological Culture Capacity	-	1,000 gallons
Aeration Capacity	-	40 SCFM



SCHEMATIC FLOW DIAGRAM
FIGURE II

As previously stated, the equipment operates on a batch sequence basis: for 10 hours, the columns are operating on a contamination cycle (adsorption-filtration) during which time the filtered waste effluent flows into the river; for 14 hours, the columns are back-flushed (regeneration cycle) on a recirculation basis with an aerobic biological culture. During the contamination cycle, liquid flow is through each carbon column in series in a downflow mode. During the regeneration cycle, the biological culture flows in a parallel pattern through the columns in an upflow mode.

PHASE I OPERATION

The treatment plant was put on stream to operate without interruption (except downtime during weekends, holidays, and vacation period) for 11 months. Unfortunately, this operation was plagued with several mechanical failures. Originally, the carbon (Witco 718 12 x 30 mesh) was restrained top and bottom in each tank by screening; carbon fines blocked the holes in the screen during several regeneration cycles, and two of the screens ruptured owing to excessive pressures. The top screens were removed. It was found that the carbon bed did not expand sufficiently to pass through the upper outlet port of the vessel. Continued regeneration cycling caused eventual plugging of the bottom screens. This was resolved by placing liquid distributor crosses in the carbon above the bottom screens.

Because the unit was shut down for relatively long periods of time (2 days to 4 weeks for each difficulty), the activated carbon was subjected to an erratic contamination and regeneration operation with the result that the carbon became deactivated to a state in which it could not be reactivated. Hence, it was not possible to attain in practice the degree of adsorption-reactivation demonstrated in the laboratory pilot studies over a sufficient time period to ascertain continued effluent quality criteria and the operational economics of the system.

However, it was shown in this first operational phase that better than 99% decolorization did take place and that COD could be removed at a relatively high level. Table V lists some of these results. During the entire Phase I operation, which extended over an 8-month period, 904,000 gallons of waste effluent were treated, and 3,035 pounds of COD were removed. Even under the adverse operating conditions experienced, this represents eight times the single adsorption capacity of the carbon.

Table V

COD and Color Removal Data: Phase I Operation *

Thousand Gallons Dyehouse Wastewater Treated	Influent COD mg/liter	Effluent COD mg/liter	% COD Removed	Treated Effluent Coloration
48.0	1000	191	80.9	No perceptible color
25.2	917	251	72.2	No perceptible color
42.0	1054	333	68.4	Very slight tinting
12.6	963	269	72.1	No perceptible color
48.0	950	213	77.6	No perceptible color
25.2	988	401	59.4	Very slight tinting.
14.4	747	206	72.4	No perceptible color

* See Appendix A for complete Phase I data.

PILOT PLANT MODIFICATIONS

The cross distributors in the carbon columns caused poor flow distribution through the carbon; also, the bottom screens became plugged with a hard resinlike composite of carbon fines and organic matter. Graded stone appeared to be a better carbon support and a better bioculture liquor diffuser.

The four carbon columns were refitted to take a graded gravel support bed, ranging from 3/4" diameter stone to 10 x 10 mesh gravel in contact with the carbon. Also, the top carbon retaining screens were removed and this made it necessary to decrease the quantity of carbon from 1,500 pounds to 1,000 pounds in each column.

The adsorption affinity of Witco 718 activated carbon for organic matter in the Masland dyehouse effluent had been questioned. Adsorption isotherms were conducted on five commercially available activated carbons (see Appendix B for method of conducting this study and the results). Calgon Filtrasorb 400, Westvaco Nuchar WV-G and Atlas Darco 12 x 20 all had a greater affinity than Witco 718. The choice of Nuchar WV-G was one of availability and apparent better ability to withstand mechanical fragmentation of the carbon granules. Fresh activated carbon of a more active grade (Westvaco Nuchar WV-G Granular 12 x 40 Mesh) replaced the spent carbon of the Phase I operation.

The dyehouse effluent was found to be deficient in nitrogen and hence a sufficiently viable aerobic biological culture could not be maintained for the carbon regeneration. During the contamination (adsorption-filtration) cycle, all dissolved oxygen was removed and some degree of unwanted anaerobic biological activity took place accompanied by a low pH. A desirable pH for an aerobic culture is pH 7. When the bioculture was recirculated through the carbon beds, an acid pH of less than three was initially encountered. This shocked the culture and upset at least three and sometimes all of the 14 hours of regeneration by inhibiting a large proportion of the aerobic micro-organism population. The addition of sodium bicarbonate on the basis of 3 pounds/week appeared to buffer the culture sufficiently to withstand the temporary low pH of the contaminated carbon columns and thereby prevent an unwanted shock effect.

PHASE II OPERATION

During Phase I, the flow rate was maintained at 60 GPM which was 54% of the total dyehouse effluent flow (the remainder was by-passed). However, the entire dyehouse effluent was treated during Phase II.

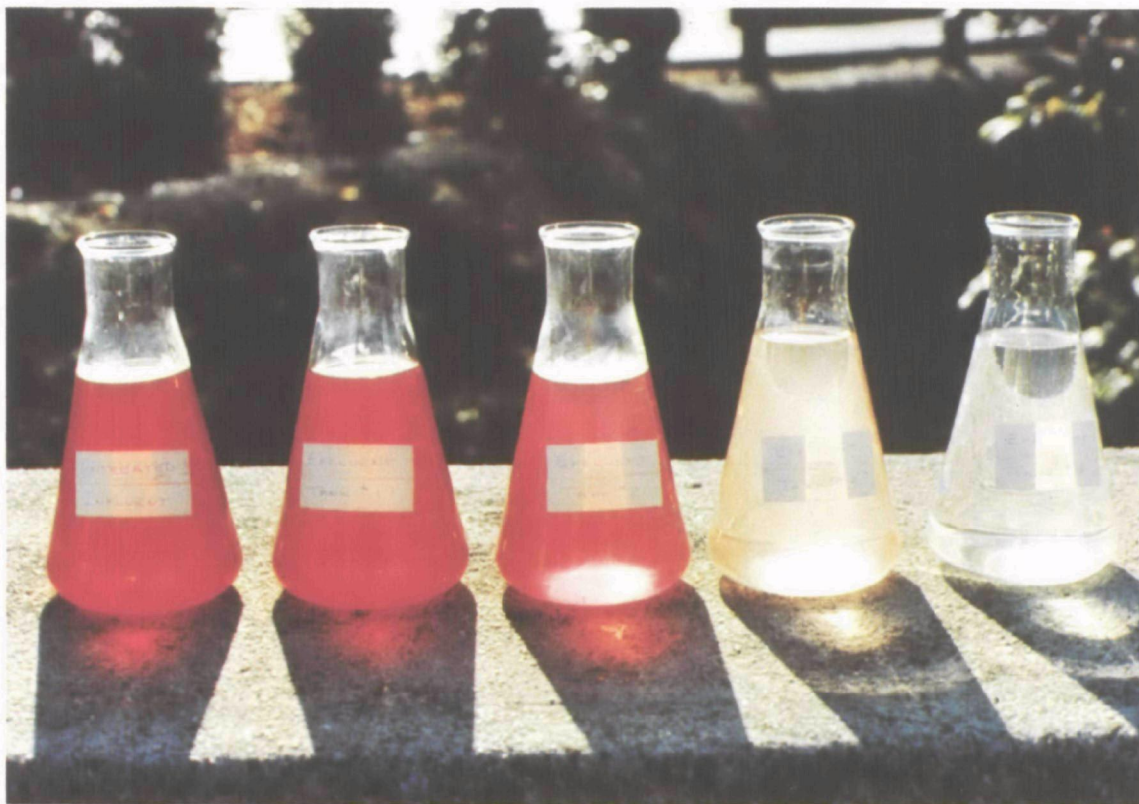
The addition of 5 pounds of available nitrogen per 100 pounds of BOD₅ for Phase II operation was accomplished by the further addition of ammonium chloride on the basis of 1.3 pounds/week. The culture tank was reseeded with an acclimated textile dye waste activated sludge and buffered on a continuing basis with sodium bicarbonate to maintain a 7-8 pH even when the biological liquor contacted the relatively acid residual liquid in the activated carbon tanks.

Phase II was started on July 20, 1970 and was run continuously without shutdown (except for holidays and weekends) for 98 days, with no change or make-up of activated carbon. Daily monitoring of the effluent during the adsorption mode took place through October 23, 1970. All effluent samples were colorless or very faintly tinted. Figure 12 is a picture of effluent samples taken on October 30, 1970. The samples are sequential; starting with the untreated dyehouse effluent discharge on the far left, effluents from Columns 1 through 4 with the colorless effluent of Column 4 as it was being discharged into the Saugatucket River.

Figure 13 is a plot of pounds of COD removed versus gallons of water treated for both Phase I and Phase II operations. Not shown in this graphical presentation is the erratic nature of the Phase I operation and the numerous shutdowns. The Phase II operation was continuous for a 98-day period and discharged a colorless effluent to the Saugatucket River. Undesirable color breakthrough occurred in Phase I at about 600,000 gallons and continued in a deeper coloration up to the end of Phase I. It should also be noted that the flow rate during Phase I was 54% of the total dyehouse discharge. Phase II flow rate was 100% of the dyehouse discharge.

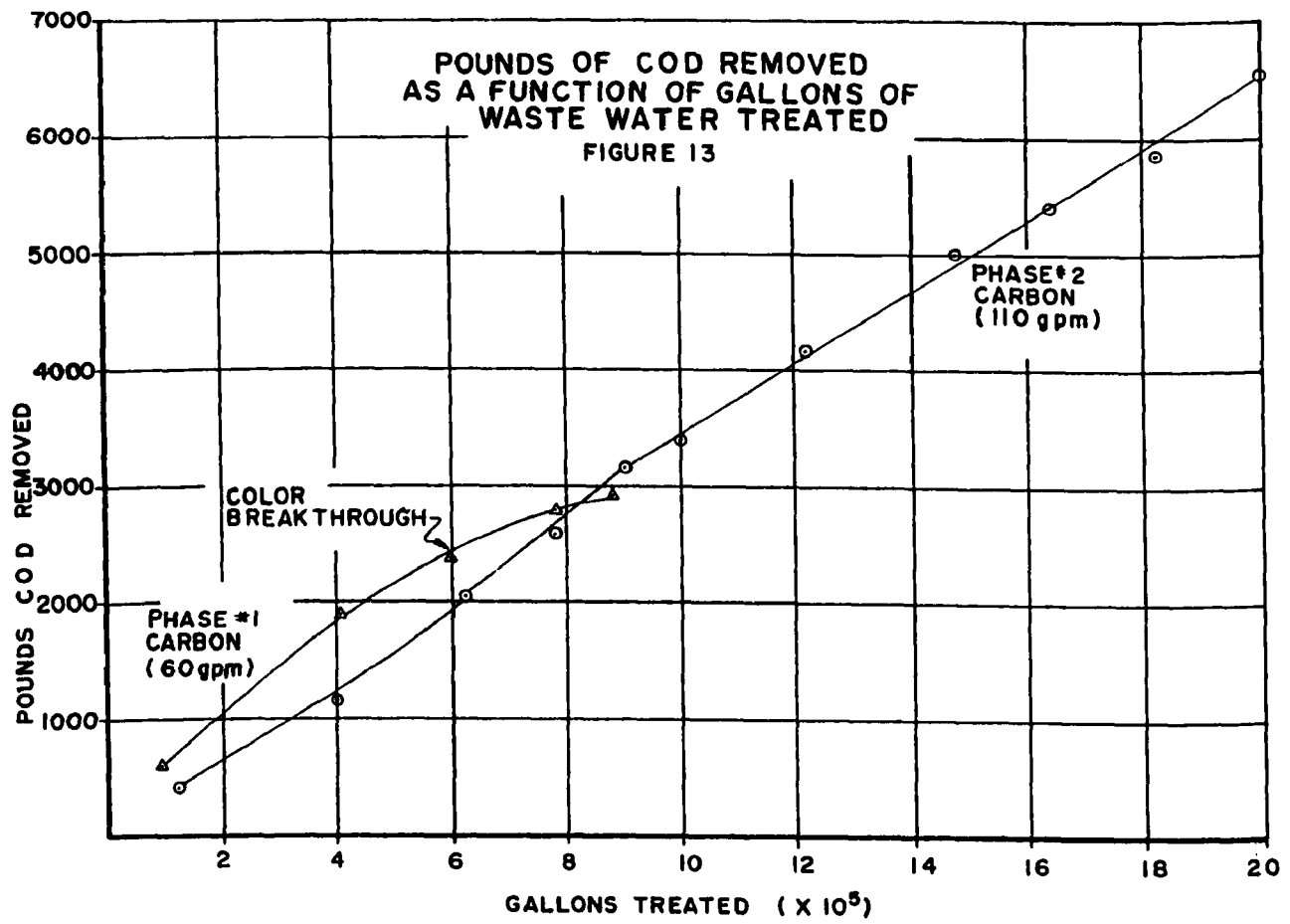
The average results of the Phase II operation in terms of COD, TOC and color are summarized as follows:

	<u>Dyehouse Wastewater Influent</u>	<u>Treatment Plant Effluent</u>	<u>% Reduction</u>
COD - mg/l	550	280	49.0
TOC - mg/l	220	115	47.8
Color	- -	- -	99.5



EFFLUENT SAMPLES - October 30, 1970 -
C. H. Masland-Wakefield Waste Treatment System
Flasks from Left to Right: Influent - Dye House
Discharge, Effluent - Carbon Column No. 1,
Effluent - Column No. 2, Effluent - Column
No. 3, and Effluent - Column No. 4

Figure 12



Color was measured by a visual technique set up for on-site determinations. The influent was diluted with tap water until it matched the color of the effluent. One hundred milliliter graduates were used for color comparison checks. If the treated effluent matched a 100 ml graduate containing only tap water, the per cent reduction was recorded as 100%. For complete data on the Phase II operation, please refer to Appendix C.

SYSTEM CONTROL

Naturally, as with any waste treatment system, there are some important operational factors over which a certain degree of control is needed in order to insure good operation. Consider the system operation in two parts; namely, (1) the treatment cycle and (2) the regeneration cycle:

TREATMENT CYCLE

- (1) FLUX - No higher than 15 gpm/ft² with optimum being 7 gpm/ft²
- (2) EQUALIZATION - For discharges less than 100,000 gallons per day: at least 5 hours equalization with the optimum being one working day. For discharges 1 mgd or over: some equalization desirable, but not essential due to continual mixing of multi-dye vat dumping and rinsing

REGENERATION CYCLE

- (1) BIO-SOLIDS - maintain the settleable solids in the regenerant liquor at less than 10 ml/l, with optimum being 5 ml/l.
- (2) pH - maintain the pH of the regenerant liquor in the range of 6.5 - 8.0.
- (3) NUTRIENTS - Supply 5 lbs. of available nitrogen and one pound of available phosphorus for every 100 pounds of BOD treated by the system.
- (4) DISSOLVED OXYGEN - maintain at least 2 mg/l D. O. in the regenerant liquor, with optimum being saturation (~ 9 mg/l)

SECTION VII

WASTE TREATMENT SYSTEM DESIGN AND ECONOMICS

PROPOSED REDESIGN OF PILOT PLANT AT WAKEFIELD, R. I.

Phase II operation has indicated the following performance parameters heretofore unknown:

- (1) At a system flow rate of 15.6 gpm/ft^2 during the adsorption treatment cycle, 4,000 pounds of Westvaco Nuchar WV-G 12 x 40 mesh activated carbon have a decolorization capacity in excess of 3,000,000 gallons.
- (2) The COD removal efficiency for the same 15.6 gpm/ft^2 flow is 48%; the COD removal efficiency at below 8.5 gpm/ft^2 is in excess of 85% (based on original Phase I data).

There were three problems realized during both the Phase I and Phase II operations:

- (1) The lack of equalization of dyehouse effluent resulted in slugs of dye kettle discharges being carried directly to the carbon columns;
- (2) Batch adsorption operation required handling the full hydraulic load of the dyehouse discharge rather than extending the adsorption phase operation over a longer time period;
- (3) Erratic feeding experienced by the biological culture in the regenerant tank due to 10 hours without feeding and 14 hours in the carbon regeneration cycle.

Two parallel systems of adsorption tanks will permit a more dependable biological culture because of its continuous feeding.

After due consideration of these factors, a redesign of the treatment system along the direction indicated in Figure 14 is proposed:

- (a) The dyehouse effluent should be held in an equalization tank having a capacity of 50,000 gallons.
- (b) The effluent should then pass in series through three 1,200 pound activated carbon columns at a flow rate of 30 to 40 gpm.

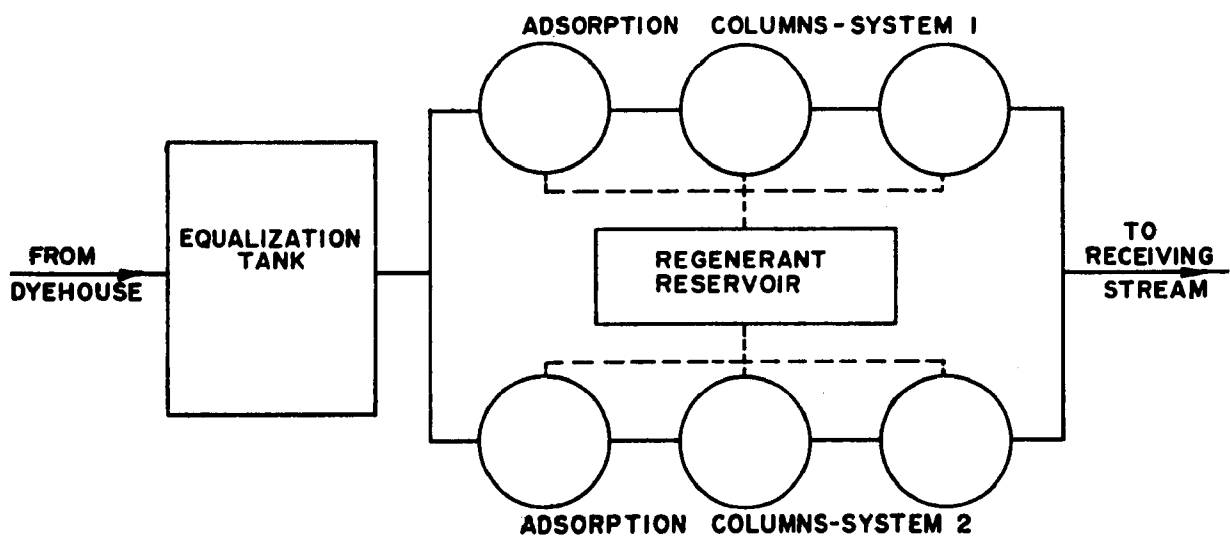


FIGURE 14 SECOND GENERATION SYSTEM

- (c) A second series of activated carbon columns should be undergoing a regeneration cycle while the first series is on stream.
- (d) The two series of columns should then be cycled, accordingly, on stream and on regeneration.
- (e) The biological regenerant tank should be 5,000 gallons in size as opposed to the current 1,000 - 1,200 gallon tank. This would provide greater buffering capacity and faster regeneration cycles.

It has been estimated that the modified plant cost would be \$75,000 with an operating cost per year of \$6,000.00. There is sufficient room in the building where the present treatment system is located to expand the system to the proposed redesign which would occupy 1,000 ft².

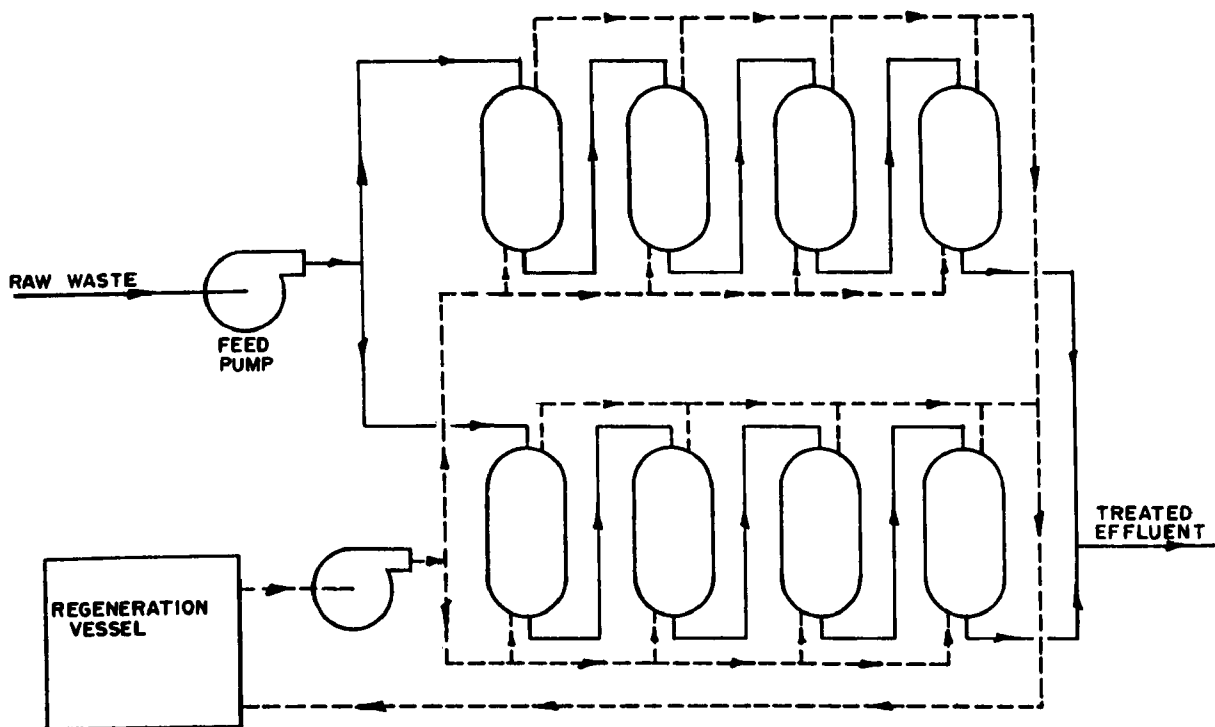
The effluent quality of such a system should be tertiary treatment level with values of:

COD Removal	75 + %
BOD Removal	95 + %
Color Removal	100%
Turbidity	5 Jackson units

PROPOSED 1 MGD TREATMENT PLANT

Based upon kinetics derived from the Phase II operation (see Appendix F), the amount of activated carbon required to remove 50% and 75% COD was calculated for a one million gallon per day plant. Figure 15 is the flow diagram of a proposed 1 mgd plant capable of removing all color and 47 - 53% COD. A plant capable of removing 75% or more COD is considered to be infeasible. Although a 50% COD removal plant would be insufficient for a total waste treatment system, the COD reduction coupled with virtually complete color removal makes the process very attractive as a pretreatment system for a conventional biological waste treatment operation.

As shown in Figure 15, raw waste is pumped through four columns 8 feet in diameter and 16 feet high, each containing 17,500 pounds of carbon. A parallel bank of four columns is on biological regeneration. The biological regeneration vessel is rectangular 25 feet by 25 feet x 10 feet SWD (side water depth). Chemical feeders are provided for feeding nutrient and pH buffers if required for the dye waste to be treated. Equalization is not considered necessary for a pretreatment



PROPOSED 1 MGD SYSTEM
FIGURE 15

plant of this high flow rate and has not been provided. A wet sump is provided, however, to maintain a head for the pump. Flow through the columns during the treatment phase is automatically controlled by demand per the liquid level in the wet sump.

A decolorization system of this kind is best suited for a predominantly soluble colored wastewater where the suspended solids are below 75 mg/l and preferably averaging no higher than 30 mg/l. The COD should be below 1,600 mg/l and should average no higher than 800 mg/l. It is further limited by the ability of the activated carbon to decolorize the waste, and the adsorbed color and other associated organic matter to be biologically oxidized. The techniques for determining these important parameters to ascertain the feasibility of this treatment approach are well discussed and described in this report.

ECONOMICS - 1 MGD PLANT

Listed below are the economics of the 1 mgd plant operating at 50% COD removal and at 75% TOD removal efficiency. The estimated daily power and chemical costs are:

<u>Treatment</u>	<u>Operating Cost</u>
50% COD Removal	\$83/day or 8.3¢/1000 gallons
75% COD Removal	\$231/day or 23.1¢/1000 gallons

The construction cost of a 1 mgd plant is estimated to be:

<u>Treatment</u>	<u>Cost</u>
50% COD Removal	\$230,000
75% COD Removal	\$550,000

When amortization is figured into operating costs (capital recovery 20 years at 8% per annum), the costs become:

<u>Treatment</u>	<u>Operating Cost</u>
50% COD Removal	\$147/day or 14.7¢/1000 gallons

<u>Treatment</u>	<u>Operating Cost</u>
75% COD Removal	\$384/day or 38.4¢/1000 gallons

All these cost estimates include an estimate for replacement or other regeneration of the carbon on the basis of two changes of activated carbon per year.

Because of the particular or peculiar conditions for each industrial location where such a treatment system might be applicable, it is difficult to determine accurately costs of wet sumps, pipe lines, maintenance, labor, and nutrient and/or buffering chemical additions. However, estimates have been included for these costs and, given due consideration, small fluctuations in their magnitude would have little effect on these estimates.

SECTION VIII

ACKNOWLEDGMENTS

Supervision of the Masland pilot plant operation and back-up laboratory work was carried out by Edward L. Shunney of Fram Corporation. He was assisted by Edward Chase and Anthony Perrotti of the Fram staff. The cooperation of Mr. Harold Burkholder, Masland-Wakefield Plant Manager, and his assistants, Walter Redmond and Steven Burdick, is also gratefully acknowledged.

The critical analysis of the biochemical reactions taking place during the first phase operation of the plant was done by Professor Calvin P. C. Poon of the University of Rhode Island. His findings leading to a successful bio-regeneration procedure are greatly appreciated.

The design of the one million gallon per day plant was accomplished by Dr. Allen Molvar, Philip Virgademo and Charles Kertell of the Fram staff. The biological regeneration process is the development of Dr. Stephen Blecharczyk and is the subject of a pending patent application assigned to the Fram Corporation.

The organization, preparation and writing of this report was the work of Clarke Rodman of the Fram Corporation.

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SECTION IX

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SECTION X

APPENDICES

APPENDIX A

FIELD DATA, PHASE I OPERATION

Table VI
MASLAND - WAKEFIELD
Phase I Data
June 26, 1969 thru October 6, 1969

<u>Date</u>	<u>Daily Flow ³ (Gallons x 10)</u>	<u>Total TOC In (mg/l)</u>	<u>Total TOC Out #4 (mg/l)</u>	<u>% Reduction TOC thru #4</u>
6/2	48.0	394	75	80.9
6/4	48.0	374	84	77.5
6/9	42.0	415	131	68.4
6/12	30.0	360	129	64.1
7/18	25.2	361	99	72.5
7/21	14.4	294	81	72.4
7/22	12.6	379	106	72.0
7/23	25.2	389	158	59.3
7/24	28.8	480	260	45.8
7/29	28.8	485	374	22.8
7/30	25.2	410	338	17.5
8/5	25.2	325	150	53.8
8/7	28.8	320	204	36.2
8/8	25.2	355	184	48.1
8/12	25.2	237	103	56.5
8/19	28.8	410	252	38.5
8/20	14.4	372	241	35.2
8/25	18.0	249	140	43.7
8/26	18.0	361	229	36.5
8/27	18.0	257	173	32.6
8/28	18.0	399	299	25.0
8/29	18.0	489	312	36.1
9/3	18.0	380	309	18.6
9/4	18.0	297	207	30.3
9/5	18.0	243	175	27.9
9/8	18.0	316	261	17.4
9/9	18.0	301	167	44.5
9/10	18.0	440	297	32.5
9/11	18.0	401	239	40.3
9/12	18.0	445	359	19.3
9/15	18.0	360	218	39.4
9/17	18.0	273	179	34.4
9/18	18.0	229	138	39.7
9/19	18.0	240	168	30.0
9/25	18.0	280	238	15.0
9/26	18.0	268	200	25.3
9/29	18.0	335	264	21.1
10/1	18.0	365	275	24.6
10/2	18.0	366	308	15.8
10/3	14.4	201	157	21.8
10/6	18.0	571	396	30.6

APPENDIX B

ACTIVATED CARBON

ADSORPTION ISOTHERMS

APPENDIX B

EXPERIMENTAL PROCEDURE

ADSORPTION ISOTHERM DETERMINATION⁽³⁾

- A. Add prescribed amounts of dry activated carbon (eg. 1, 2, 4, 8, 16, --- gms.) to 500 ml Erlenmeyer flasks and record combined weight of each.
- B. Add 400-500 ml distilled water to each flask, stopper, and wet out carbon in a mechanical shaker for one hour.
- C. Decant liquor, including suspended carbon fines. Caution should be exercised to prevent loss of granules. Wash with 400-500 ml distilled water (stirring with a glass rod). Allow granules to settle.
- D. Decant as much liquor as possible without loss of carbon granules⁽¹⁾. Weigh flask containing greatest water residual and adjust all others, including a carbon free control flask, to an equivalent amount.
- E. Immediately after adding 200 ml of contaminant⁽²⁾ (100° F.) to each flask, agitate on mechanical shaker for prescribed time.
- F. Filter liquor from each flask through Whatman #1 filter paper⁽³⁾ and analyze filtrate for TOD.
- G. Prepare a table listing grams of carbon (M), supernatant selected parameter (such as TOD) (C), water residual as determined in Step D in order to calculate total volume of solution in liters (V).

- (1) More than one washing may be needed to remove carbon fines, depending on type of carbon used.
- (2) Contaminant should be filtered initially if sufficient undissolved material is present.
- (3) If fines are present in filtrate, filter through more appropriate material.

H. From the table, calculate "q"

$$q = V \frac{(C_o - C)}{M}$$

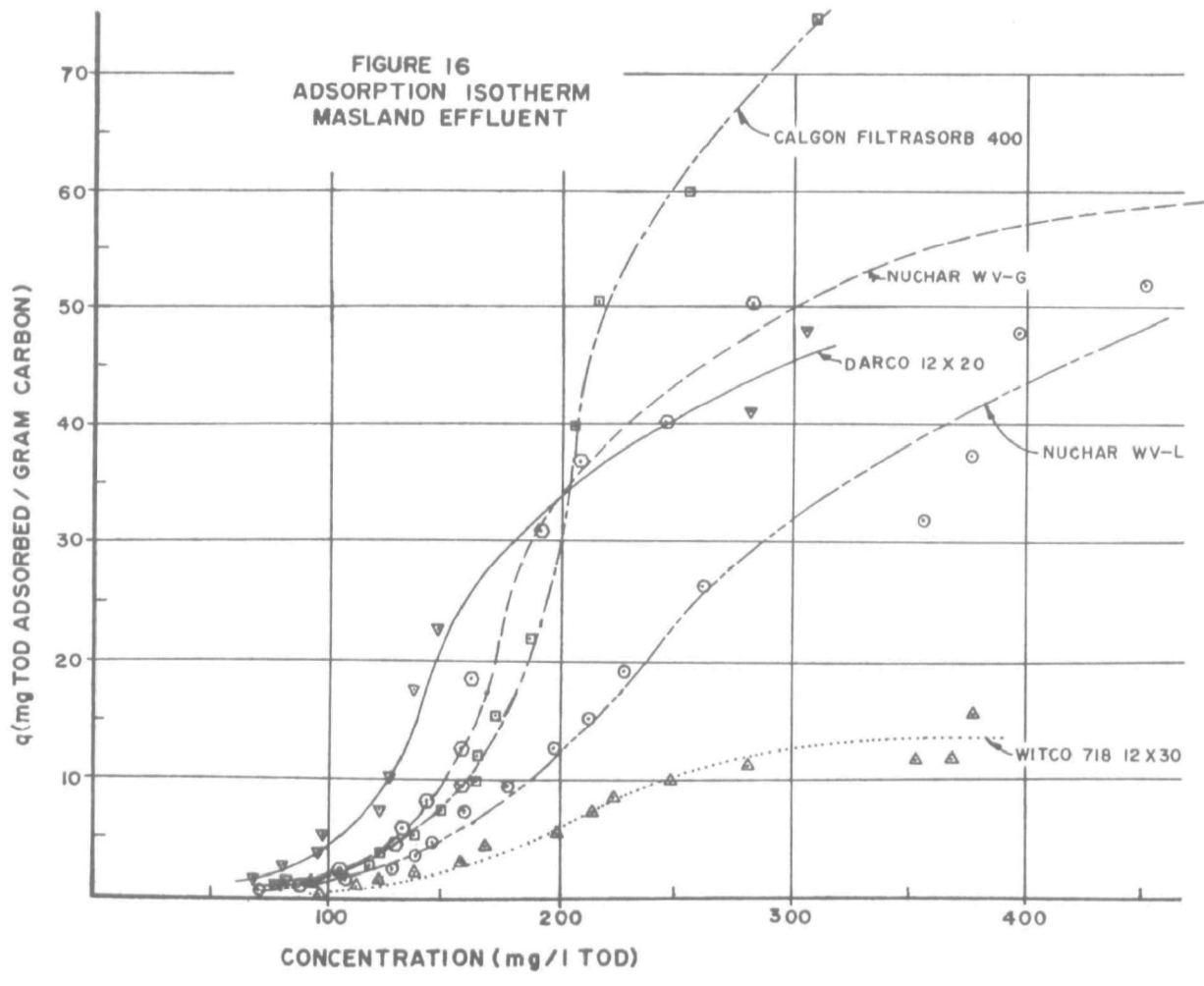
where V = total volume of solution in liters.

C_o = concentration of influent in mg/l of TOD.

C = concentration of supernatant in mg/l of TOD.

M = grams of carbon.

I. Plot "q" versus C (Figure 16).



APPENDIX C

FIELD DATA, PHASE II OPERATION

Table VII
MASLAND - WAKEFIELD
Phase II Data
Week 1

		Tuesday - 7/21		Wednesday - 7/22		Thursday - 7/23		Friday - 7/24	
		A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In		130	325	280	270	180	190	210	225
	Out #1	40	140	130	160	105	145	135	165
	Out #2	30	100	100	130	82	120	100	130
	Out #3	20	92	86	120	78	105	85	115
	Out #4	10	86	62	110	75	90	80	100
% Reduction thru #4		92.3	73.5	77.8	59.2	58.5	52.6	61.9	55.5
Total COD - In		345	945	792	835				
	Out #1	110	363	439	592				
	Out #2	69	297	345	439				
	Out #3	49	246	306	419				
	Out #4	47	180	286	235				
% Reduction thru #4		86.5	81.0	64.0	71.9				
Total BOD - In		118	370	282	350				
	Out #1								
	Out #2	41	84						
	Out #3								
	Out #4	25	57	60	165				
% Reduction thru #4		78.6	84.6	78.7	52.9				
pH - In		5.6	4.9	5.3	4.7	6.4	6.2	5.7	
	Out #1	8.2	7.7	7.2	5.9	6.9	6.4	6.4	
	Out #2	7.7	8.1	8.2	6.9	7.1	6.5	6.9	
	Out #3	7.6	8.1	8.3	7.2	7.3	6.8	7.1	
	Out #4	7.7	8.1	8.3	7.4	7.4	6.9	7.3	
% Color Reduction									
	Thru 1								
	Thru 2								
	Thru 3								
	Thru 4								
Total Daily Flow (Gallons x 10 ³)			9.0		15.5		15.2		14.4

Table VIII
MASLAND - WAKEFIELD
Phase II Data
Week 2

		Monday - 7/27		Tuesday - 7/28		Wednesday - 7/29		Thursday - 7/30		Friday - 7/31	
		A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In		120	122	220	190	200	210	102	140	260	270
	Out #1	52	60	175	142	160	160	73	115	233	241
	Out #2	40	40	132	118	150	130	56	70	190	180
	Out #3	30	35	105	105	150	105	35	42	180	167
	Out #4	25	30	75	95	140	95	30	30	175	160
% Reduction thru #4		79.0	75.5	66.0	50.0	30.0	54.8	70.5	78.5	32.6	40.7
Total COD - In				574	496	519	419				
	Out #1				333	425	374				
	Out #2				278	404	314				
	Out #3				257	380	253				
	Out #4			202	255	380	223				
% Reduction thru #4				65.0	48.5	26.8	46.8				
Total BOD - In				265	235	320	280				
	Out #1										
	Out #2										
	Out #3										
	Out #4			120	128	245	245				
% Reduction thru #4				54.7	45.5	23.4	12.5				
pH - In		4.0	3.9	5.5	5.5	5.4	5.2	5.3	3.9	4.2	4.2
	Out #1	5.5	4.8	5.8	5.7	5.5	5.5	6.0	5.0	4.5	4.3
	Out #2	6.8	6.4	6.1	5.9	5.8	5.7	6.3	6.3	5.0	4.4
	Out #3	7.2	6.9	6.6	6.1	6.2	6.0	6.4	6.1	6.6	4.7
	Out #4	7.3	7.1	6.7	6.4	6.6	6.4	6.5	6.4	6.8	5.9
% Color Reduction											
	Thru 1										
	Thru 2										
	Thru 3										
	Thru 4										
Total Daily Flow (Gallons x 10 ³)			30.9		31.7		41.2		39.6		39.6

Table IX
MASLAND - WAKEFIELD
Phase II Data
Week 3

		Monday - 8/3		Tuesday - 8/4		Wednesday - 8/5		Thursday - 8/6		Friday - 8/7	
		A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In		130	110			220	150	180	190	225	
	Out #1	71	62			95	120	155	185	195	
	Out #2	55	41			75	105	135	160	175	
	Out #3	52	35			60	80	120	145	150	
	Out #4	52	35			60	60	110	130	140	
% Reduction thru #4		60.0	57.7			72.7	60.0	38.9	31.6	37.8	
Total COD - In						411				692	768
	Out #1					178					
	Out #2					126					
	Out #3					99					
	Out #4					85				300	574
% Reduction thru #4						79.3				56.6	25.3
Total BOD - In						165					
	Out #1					76					
	Out #2					56					
	Out #3					48					
	Out #4					44					
% Reduction thru #4						73.4					
pH - In		3.7	3.7			4.1	4.8	5.6	5.3	5.7	6.0
	Out #1	5.8	5.1			4.0	4.9	5.6	5.3	5.9	5.9
	Out #2	6.3	5.8			4.3	4.7	5.6	5.4	6.1	5.9
	Out #3	6.6	6.1			4.6	4.6	5.4	5.4	6.3	5.9
	Out #4	6.7	6.2			5.3	4.8	5.3	5.5	6.3	6.0
% Color Reduction											
	Thru 1							80	70		40
	Thru 2					60	60	90	90	90	90
	Thru 3					90	90	100	100	100	100
	Thru 4					100	100	100	100	100	100
Total Daily Flow (Gallons x 10 ³)			32.4		31.3		39.0		35.2		22.3

Table X
MASLAND - WAKEFIELD
Phase II Data
Week 4

		Tuesday - 8/11		Wednesday - 8/12		Thursday - 8/13		Friday - 8/14	
		A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In		170		240	140	215	250	260	295
	Out #1	120		190	130	150	170	175	190
	Out #2	100		105	90	145	140	160	160
	Out #3	60		75	85	100		145	105
	Out #4	55		70	80	95	120	115	105
% Reduction thru #4		67.5		70.8	42.8	55.9	52.0	55.7	64.4
Total COD - In		648	547			680	610		
	Out #1	532				572			
	Out #2	442				501			
	Out #3	390				455			
	Out #4	347	231			453	378		
% Reduction thru #4		46.5	57.7			33.4	38.1		
Total BOD - In									
	Out #1								
	Out #2								
	Out #3								
	Out #4								
% Reduction thru #4									
pH - In				5.5	5.5	5.2	5.4	5.8	5.9
	Out #1			5.8	5.6	5.2	5.8	6.1	5.9
	Out #2			6.0	5.8	5.4	5.9	6.2	5.9
	Out #3			6.2	5.8	5.8	6.2	6.4	6.2
	Out #4			6.3	5.9	5.9	6.2	6.5	6.4
% Color Reduction									
	Thru 1	60		60	60	40	50	70	40
	Thru 2	60		80	80	90	70	90	80
	Thru 3	90		100	90	100	90	100	100
	Thru 4	100		100	100	100	100	100	100
Total Daily Flow (Gallons x 10 ³)		30.0		31.2		21.6		28.8	

Table XI
MASLAND - WAKEFIELD
Phase II Data
Week 5

		Monday - 8/17		Tuesday - 8/18		Wednesday - 8/19		Thursday - 8/20		Friday - 8/21	
		A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
Total TOC - In		115	120	224	212	153	264	395	333	294	298
	Out #1	50	90	173	160	122	192	370	270	162	251
	Out #2	45	75	155	135	70	180	354	242	151	243
	Out #3	40	60	140	130	65	150	342	223	140	214
	Out #4	35	50	120	118	62	131	250	215	134	196
% Reduction thru #4		69.5	58.4	46.4	44.3	59.5	50.4	36.7	35.5	54.5	34.2
Total COD - In				491	693	644	766				
	Out #1			353		580					
	Out #2			285		499					
	Out #3			244		487					
	Out #4			208	330	479	520				
% Reduction thru #4				57.5	52.4	25.7	32.1				
Total BOD - In						195	325				
	Out #1					155					
	Out #2					150					
	Out #3					118					
	Out #4					93	192				
% Reduction thru #4						52.3	41.0				
pH - In		5.7	5.6	5.9	5.0	6.2	6.1	4.6	5.7	6.2	5.9
	Out #1	6.0	5.8	6.3	5.9	6.7	6.9	4.7	5.9	6.4	6.0
	Out #2	6.1	6.0	6.5	5.9	6.8	6.9	5.2	6.0	6.5	6.0
	Out #3	6.2	6.0	6.7	6.0	6.9	6.9	5.5	6.0	6.5	6.0
	Out #4	6.2	6.0	6.8	6.1	7.0	7.1	5.6	6.0	6.4	6.0
% Color Reduction											
	Thru 1	60	60	50	60	60	80	100	80	90	90
	Thru 2	85	90	80	90	90	90	100	100	100	100
	Thru 3	100	100	90	100	100	100	100	100	100	100
	Thru 4	100	100	100	100	100	100	100	100	100	100
Total Daily Flow (Gallons x 10 ³)			28.8		29.2		22.0		34.4		28.8

Table XII
MASLAND - WAKEFIELD
Phase II Data
Week 6

		Monday - 8/24		Tuesday - 8/25		Wednesday - 8/26		Thursday - 8/27		Friday - 8/28	
		A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
Total TOC - In		250	275	455	410	260	305	285	290	260	270
	Out #1	210		395	385	230		235		230	
	Out #2	195		305	370	195		200		190	
	Out #3	180		280	340	180		190		180	
	Out #4	170	175	245	330	165	145	175	180	160	140
% Reduction thru #4		32.0	40.0	46.	19.5	36.5	52.5	38.6	37.9	38.5	48.2
Total COD - In						612	729				
	Out #1					586					
	Out #2					467					
	Out #3					418					
	Out #4					331	331				
% Reduction thru #4						62.3	54.7				
Total BOD - In						250	320				
	Out #1										
	Out #2										
	Out #3										
	Out #4					160	222				
% Reduction thru #4						36.0	30.6				
pH - In		5.7	5.5	4.9	4.7	5.5		5.6	5.3	5.3	5.4
	Out #1										
	Out #2										
	Out #3										
	Out #4	6.7	5.9	5.4	5.3	5.8		5.8	5.5	5.6	5.6
% Color Reduction											
	Thru #1	80	60	40	40	40		40	50	40	40
	Thru #2	100	80	100	80	60		60	90	60	60
	Thru #3	100	100	100	100	80		80	100	80	80
	Thru #4	100	100	100	100	90		100	100	100	100
Total Daily Flow (Gallons x 10 ³)			32.4		33.6		30.0		33.6		33.6

Table XIII
MASLAND - WAKEFIELD
Phase II Data
Week 7

		Monday - 8/31		Tuesday - 9/1		Wednesday - 9/2		Thursday - 9/3	
		A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In		270	295	290	170	215	405	260	295
	Out #1	190		170		180		220	
	Out #2	165		140		155		200	
	Out #3	140		120		140		180	
	Out #4	125	130	105	100	120	210	145	195
% Reduction thru #4		53.7	56.0	63.9	41.2	44.2	48.2	44.2	34.0
Total COD - In						520	582		
	Out #1					394			
	Out #2					358			
	Out #3					342			
	Out #4					330	434		
% Reduction thru #4						36.5	25.4		
Total BOD - In						195	285		
	Out #1					192			
	Out #2					190			
	Out #3					178			
	Out #4					150	255		
% Reduction thru #4						23.0	10.5		
pH - In		6.3	6.1	4.1	4.6	5.9		4.7	4.3
	Out #1								
	Out #2								
	Out #3								
	Out #4	5.7	5.6	5.0	5.3	5.8		6.3	6.0
% Color Reduction									
	Thru 1	90	90	40	40	40		50	30
	Thru 2	100	100	90	80	80		80	70
	Thru 3	100	100	100	90	90		100	90
	Thru 4	100	100	100	100	100		100	100
Total Daily Flow (gallons x 10 ³)			32.4		32.8		28.8		32.4

Table XIV
MASLAND - WAKEFIELD
Phase II Data
Week 8

		Tuesday - 9/8		Wednesday - 9/9		Thursday - 9/10		Friday - 9/11	
		A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In		150	160	130	210	225	190	230	190
	Out #1	130	150	100	190	150			
	Out #2	115	140	95	170	130			
	Out #3	100	120	80	140	105			
	Out #4	85	105	60	110	90	110	115	115
% Reduction thru #4		43.4	34.4	53.7	47.6	60.0	42.0	50.0	39.5
Total COD - In				269	490				
	Out #1			239					
	Out #2			131					
	Out #3			100					
	Out #4			98	247				
% Reduction thru #4				63.5	29.2				
Total BOD - In				122	235				
	Out #1			80					
	Out #2			72					
	Out #3			62					
	Out #4			56	145				
% Reduction thru #4				54.1	38.3				
pH - In				5.1	5.1	6.4	4.9	4.7	4.9
	Out #1								
	Out #2								
	Out #3								
	Out #4			6.5	6.7	6.7	6.5	6.2	6.2
% Color Reduction									
	Thru 1	60	90	80	70	80	70	80	
	Thru 2	80	100	90	80	90	80	90	
	Thru 3	90	100	100	90	100	100	100	
	Thru 4	100	100	100	100	100	100	100	
Total Daily Flow (Gallons x 10 ³)			27.6		29.2		28.0		27.2

Table XV
MASLAND - WAKEFIELD
Phase II Data
Week 9

		Monday - 9/14		Tuesday - 9/15		Wednesday - 9/16		Thursday 9/17		Friday - 9/18	
		A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In		235	260	315	305	220	260	245	210	205	290
	Out #1										
	Out #2										
	Out #3										
	Out #4	90	185	175	140	145	190	100	105	80	140
% Reduction thru #4		61.7	28.8	44.5	54.1	34.1	27.0	59.2	50.0	61.0	51.8
Total COD - In						451	592				
	Out #1					400					
	Out #2					398					
	Out #3					359					
	Out #4					321	445				
% Reduction thru #4						28.8	24.8				
Total BOD - In						205	232				
	Out #1					178					
	Out #2					172					
	Out #3					152					
	Out #4					130	215				
% Reduction thru #4						36.6	7.3				
pH - In		6.7	5.5	6.6	5.3	4.7	5.2	5.5	5.6	5.7	5.3
	Out #1										
	Out #2										
	Out #3										
	Out #4	6.5	6.0	6.8	5.9	6.4	6.2	6.2	6.1	6.3	5.9
% Color Reduction											
	Thru 1	90	80	90	80	90	90	90	90	80	80
	Thru 2	100	90	100	90	100	100	100	100	80	90
	Thru 3	100	100	100	100	100	100	100	100	90	100
	Thru 4	100	100	100	100	100	100	100	100	100	100
Total Daily Flow (Gallons x 10 ³)			28.8		28.0		28.8		27.2		27.2

Table XVI
MASLAND - WAKEFIELD
Phase II Data
Week 10

		Monday - 9/21	
		A. M.	P. M.
Total TOC - In		150	170
	Out #1	140	
	Out #2	120	
	Out #3	100	
	Out #4	90	90
% Reduction thru #4		40.0	47.0
Total COD - In			
	Out #1		
	Out #2		
	Out #3		
	Out #4		
% Reduction thru #4			
Total BOD - In			
	Out #1		
	Out #2		
	Out #3		
	Out #4		
% Reduction thru #4			
pH - In		6.9	6.7
	Out #1		
	Out #2		
	Out #3		
	Out #4	6.9	6.9
% Color Reduction			
	Thru 1	70	80
	Thru 2	100	100
	Thru 3	100	100
	Thru 4	100	100
Total Daily Flow (Gallons x 10 ³)			24.0

Table XVII
MASLAND - WAKEFIELD
Phase II Data
Week 11

	Wednesday - 9/30		Thursday - 10/1		Friday - 10/2	
	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In	320	195	210	270	290	205
Out #1	300					
Out #2	240					
Out #3	210					
Out #4	185	100	135	190	130	85
% Reduction thru #4	42.2	48.7	35.7	29.6	55.2	58.5
Total COD - In	464	584				
Out #1	408					
Out #2	340					
Out #3	321					
Out #4	284	316				
% Reduction thru #4	38.8	45.9				
Total BOD - In	220	234				
Out #1	200					
Out #2	140					
Out #3	132					
Out #4	105	181				
% Reduction thru #4	52.3	22.6				
pH - In	5.2	5.1	5.4	6.2	6.1	6.5
Out #1						
Out #2						
Out #3						
Out #4	6.7	6.7	6.6	6.3	6.3	6.6
% Color Reduction						
Thru 1	70	70	90	80	70	60
Thru 2	85	90	100	90	80	70
Thru 3	90	100	100	90	100	80
Thru 4	100	100	100	100	100	100
Total Daily Flow (Gallons x 10 ³)		42.9		47.9		44.6

Table XVIII
MASLAND - WAKEFIELD
Phase II Data
Week 12

	Monday - 10/5		Tuesday - 10/6		Wednesday - 10/7		Thursday - 10/8		Friday - 10/9	
	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In	230	180	135	220	215	150	140	150	225	190
Out #1										
Out #2										
Out #3										
Out #4	115	105	65	120	100	85	55	85	90	75
% Reduction thru #4	50.0	41.7	51.8	45.5	53.5	43.3	60.7	43.3	60.0	60.5
Total COD - In					273	441				
Out #1					241					
Out #2					120					
Out #3					101					
Out #4					94	232				
% Reduction thru #4					65.6	47.4				
Total BOD - In					123	227				
Out #1										
Out #2										
Out #3										
Out #4					53	136				
% Reduction thru #4					56.9	40.1				
pH - In	5.4	5.7	6.4	6.1	5.3	6.2	5.3		6.2	5.1
Out #1										
Out #2										
Out #3										
Out #4	6.9	6.1	6.5	6.7	6.2	6.6	6.0	6.1	6.8	6.7
% Color Reduction										
Thru 1	70	90	40	80	75	75	90	75	50	40
Thru 2	80	100	80	80	80	90	90	90	70	60
Thru 3	80	100	90	100	90	100	100	100	100	90
Thru 4	100	100	100	100	100	100	100	100	100	100
Total Daily Flow (Gallons x 10 ³)		38.0		39.0		47.9		38.0		47.9

Table XIX
MASLAND - WAKEFIELD
Phase II Data
Week 13

	Monday - 10/12		Tuesday - 10/13		Wednesday - 10/14		Thursday - 10/15		Friday - 10/16	
	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In	215	150	130	140	210	155	145	210	230	160
Out #1										
Out #2										
Out #3										
Out #4	105	105	75	105	160	100	50	105	115	95
% Reduction thru #4	51.2	30.0	42.3	25.0	23.8	35.5	65.5	50.0	50.0	40.6
Total COD - In					284	452				
Out #1					239					
Out #2					141					
Out #3					94					
Out #4					80	214				
% Reduction thru #4					71.8	52.6				
Total BOD - In					134	218				
Out #1										
Out #2										
Out #3										
Out #4					62	140				
% Reduction thru #4					53.7	35.8				
pH - In	5.5	5.6	6.3	6.0	4.9	6.2	5.4	5.2	6.2	5.4
Out #1										
Out #2										
Out #3										
Out #4	7.0	6.0	6.7	6.2	6.1	6.7	6.0	6.4	6.6	6.3
% Color Reduction										
Thru 1	60	70	70	60	70	70	50	60	50	40
Thru 2	80	100	70	80	80	80	60	70	70	70
Thru 3	90	100	90	90	100	100	90	80	90	80
Thru 4	100	100	100	100	100	100	100	100	90	90
Total Daily Flow (Gallons x 10 ³)		46.2		39.6		42.9		47.9		44.6

Table XX
MASLAND - WAKEFIELD
Phase II Data
Week 14

	Monday - 10/19		Tuesday - 10/20		Wednesday - 10/21		Thursday - 10/22		Friday - 10/23	
	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.	A. M.	P. M.
Total TOC - In	155	190	150	165	240	190	190	290	325	355
Out #1										
Out #2										
Out #3										
Out #4	110	120	95	100	160	105	80	125	130	205
% Reduction thru #4	29.0	36.8	36.7	39.4	33.3	44.7	57.9	56.9	60.0	42.3
Total COD - In					310	362				
Out #1					262					
Out #2					156					
Out #3					120					
Out #4					115	222				
% Reduction thru #4					62.9	38.7				
Total BOD - In					190	246				
Out #1										
Out #2										
Out #3										
Out #4					92	105				
% Reduction thru #4					51.6	57.3				
pH - In	4.2	6.2	6.2	6.4	6.7	6.3	5.2	6.7	4.8	5.3
Out #1										
Out #2										
Out #3										
Out #4	6.4	6.5	6.4	6.5	6.9	7.6	6.1	6.7	6.4	6.8
% Color Reduction										
Thru 1	70	40	70	60	30	80	50	70	40	70
Thru 2	80	50	90	80	60	90	60	80	60	90
Thru 3	100	60	100	100	70	100	90	100	90	100
Thru 4	100	90	100	100	90	100	100	100	90	100
Total Daily Flow (Gallons x 10 ³)		39.6		42.9		42.9		47.9		42.9

APPENDIX D

CHEMICAL REGENERATION STUDIES

APPENDIX D

CHEMICAL REGENERATION STUDIES

When the Witco 718 activated carbon during Phase I operation became non-regenerable biologically, consideration was given to other methods of regeneration in place (4). The most feasible appeared to be the use of a chemical oxidant. Laboratory studies were initiated. Oxidants such as hydrogen peroxide, sodium hypochlorite, potassium persulfate, sodium peroxide, and sodium bromite were evaluated. Potassium persulfate appeared to be the most effective.

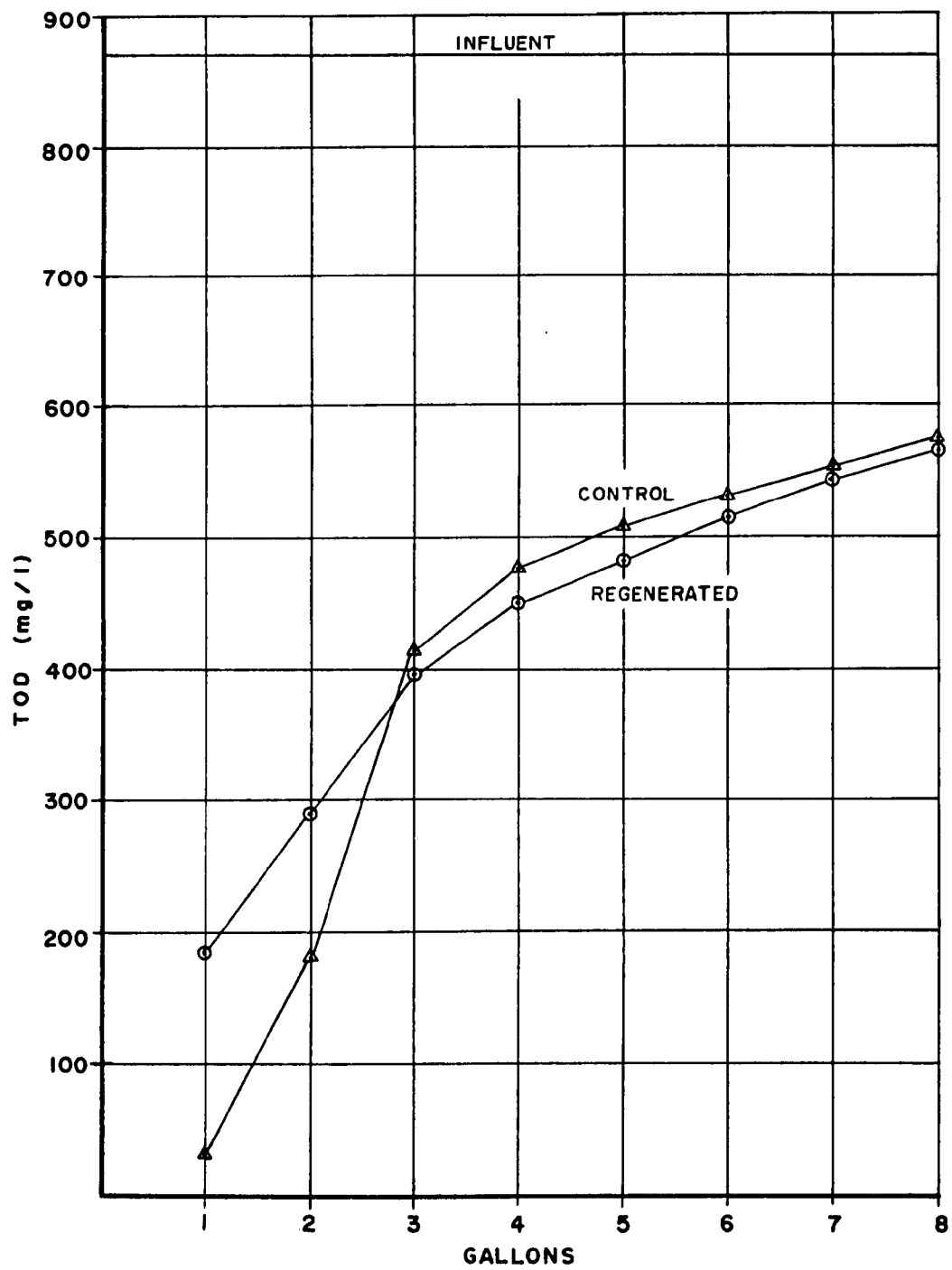
Two 5-inch diameter 3 feet high plexiglass columns were filled with 5,000 grams of exhausted carbon removed from adsorption column No. 1 of the Masland pilot plant. Both columns were washed (upflow in a fluidized bed flow) with equal volumes of tap water. A reservoir containing 5 gallons of 2% regenerant solution was connected to one of the columns and the solution was recirculated upflow through the column for 8 hours at 5 l/min. Both columns were again washed with tap water, drained and actual composite samples of dyehouse waste liquor were pumped through the columns upflow in parallel with each running at 100 mls/min. The total test column effluent from each column was collected in one gallon increments and analyzed for TOD.

Figure 17 is a plot of the effluent TOD in mg/l as the contaminant passed through each test column; one column contained exhausted carbon which had not been subjected to an oxidant and the other contained exhausted carbon which had been contacted with a 2% hydrogen peroxide solution in the manner described above. The same lack of regeneration effect occurred for all the other oxidants with the exception of potassium persulfate. Figure 18 is a similar plot to that of Figure 17 and illustrates that actual regeneration which took place - the column effluent of the $K_2S_2O_8$ when dye waste was passed through was considerably lower in TOD than that for the control column. Figure 19 is a plot of TOD in the effluent after the first repetition of $K_2S_2O_8$ regeneration. Figure 20 is a plot of TOD in the effluent after the third regeneration with $K_2S_2O_8$. Also included in Figure 19 is a plot of the effluent TOD through a third test carbon adsorption column where fresh or "virgin" Witco 718 carbon was used.

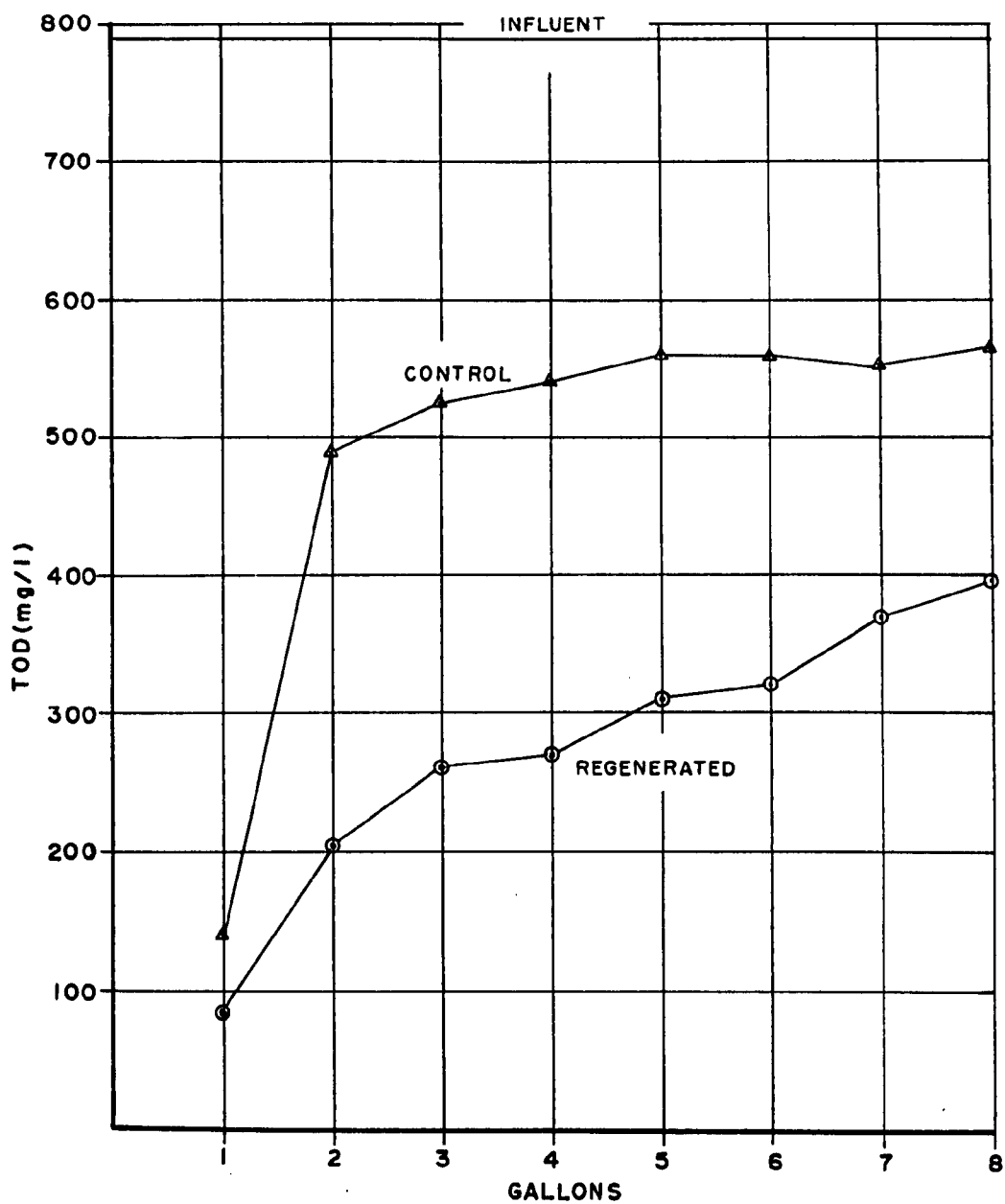
All of the previously discussed $K_2S_2O_8$ regenerations were carried out at $25^\circ C$. When the regeneration temperature was increased to $50^\circ C$., the degree of regeneration was markedly increased as shown in Figure 20. Figure 21 is a similar plot after a second $K_2S_2O_8$ regeneration at $50^\circ C$.

The degree of carbon adsorption recovery by hot $K_2S_2O_8$ ($50^\circ C$.) regeneration was 70 - 80%. It was felt that if this could be accomplished on the four columns of exhausted Witco 718 carbon at the Masland pilot plant installation, the productive life of the carbon could be materially extended. One column was put on such a regeneration cycle. The bronze lining of the recirculating pump was eaten away and the oxidant played havoc with other components of the system.

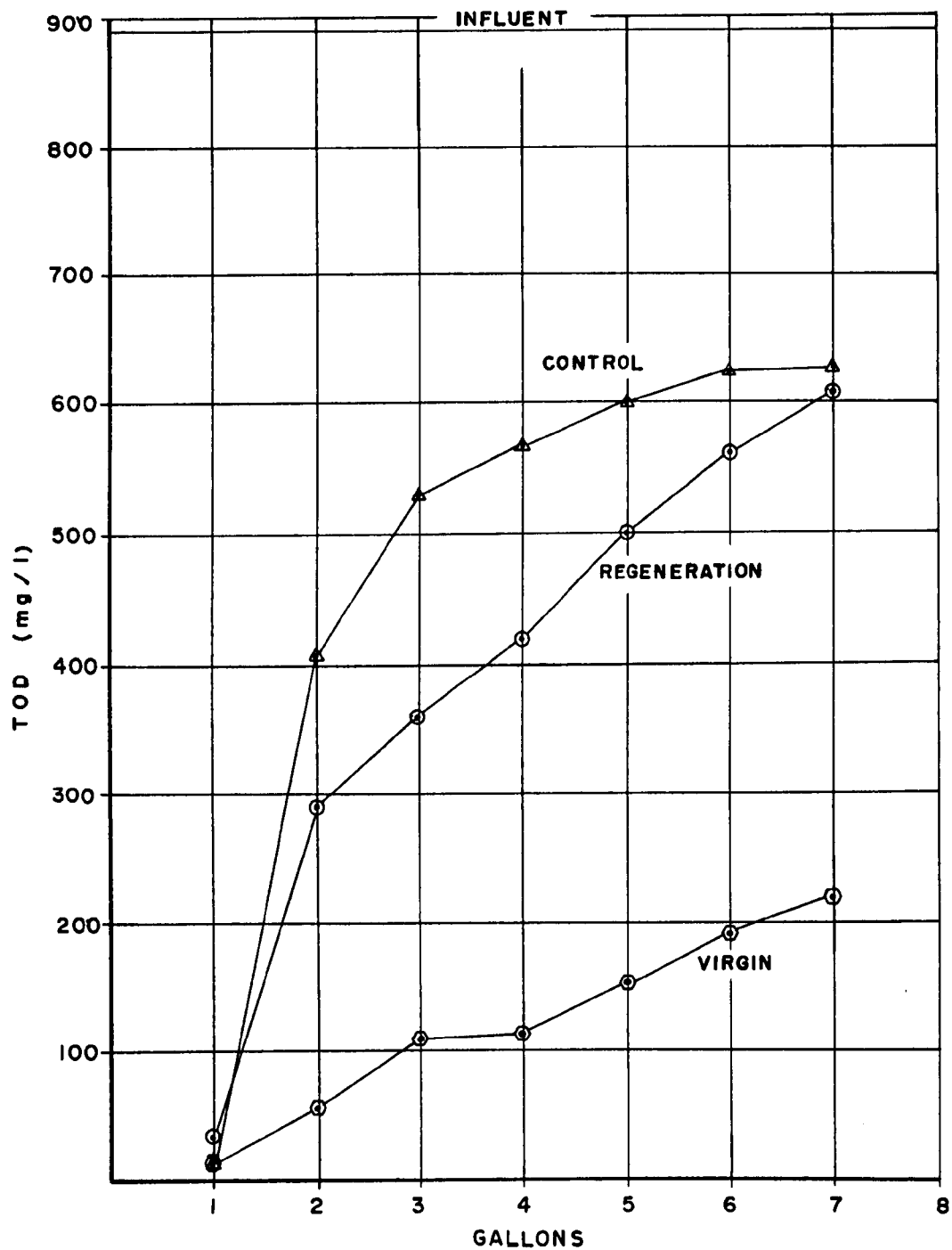
For this reason, no further work was done along these lines in the laboratory or on the pilot plant operation. With materials of construction compatible with $K_2S_2O_8$, chemical regeneration of activated carbon exhausted by the presence of non bio-degradable organic matter can be achieved. The regenerated columns can then be put back in use with bio-regeneration up to the time that color breakthrough is noticed, and then again chemically regenerated.



REMOVAL PROFILE
 H_2O_2 REGENERATION (25°C)
FIGURE 17

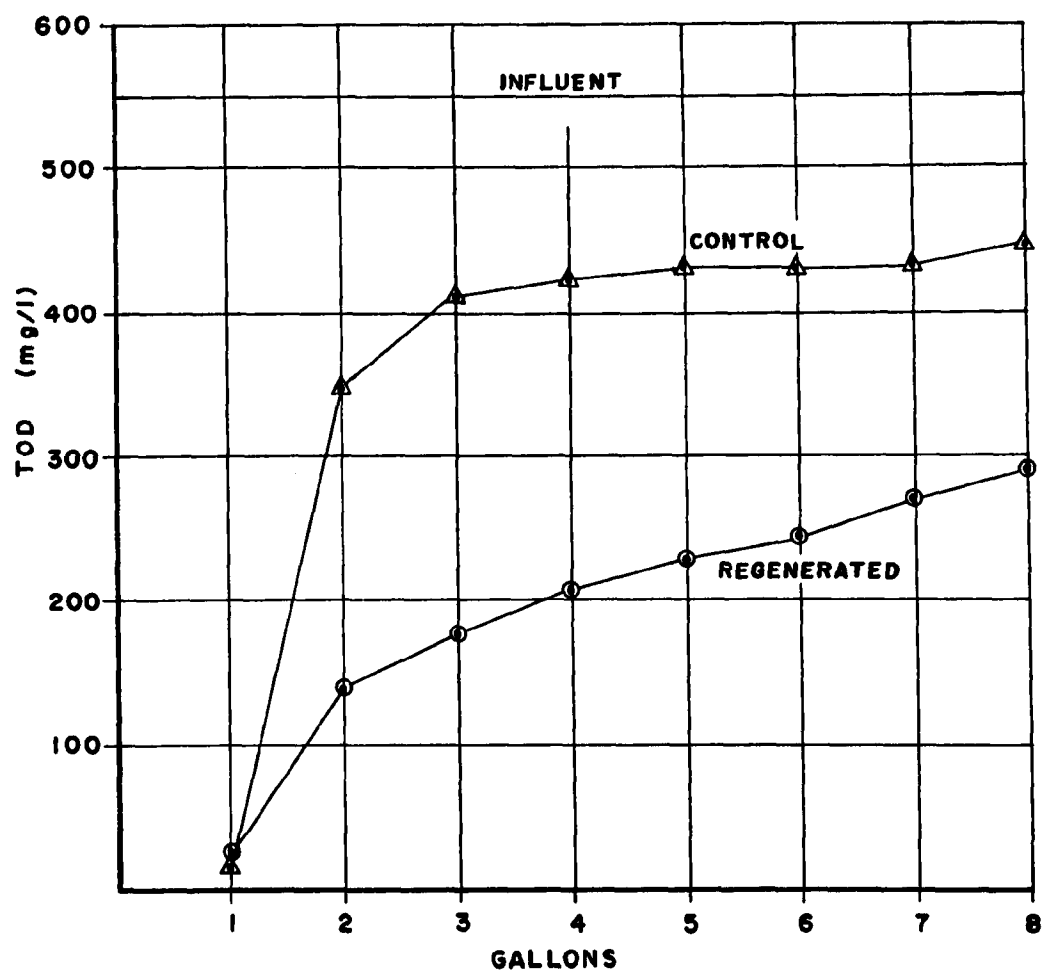


REMOVAL PROFILE
 $K_2S_2O_8$ REGENERATION (25°C)
FIGURE 18

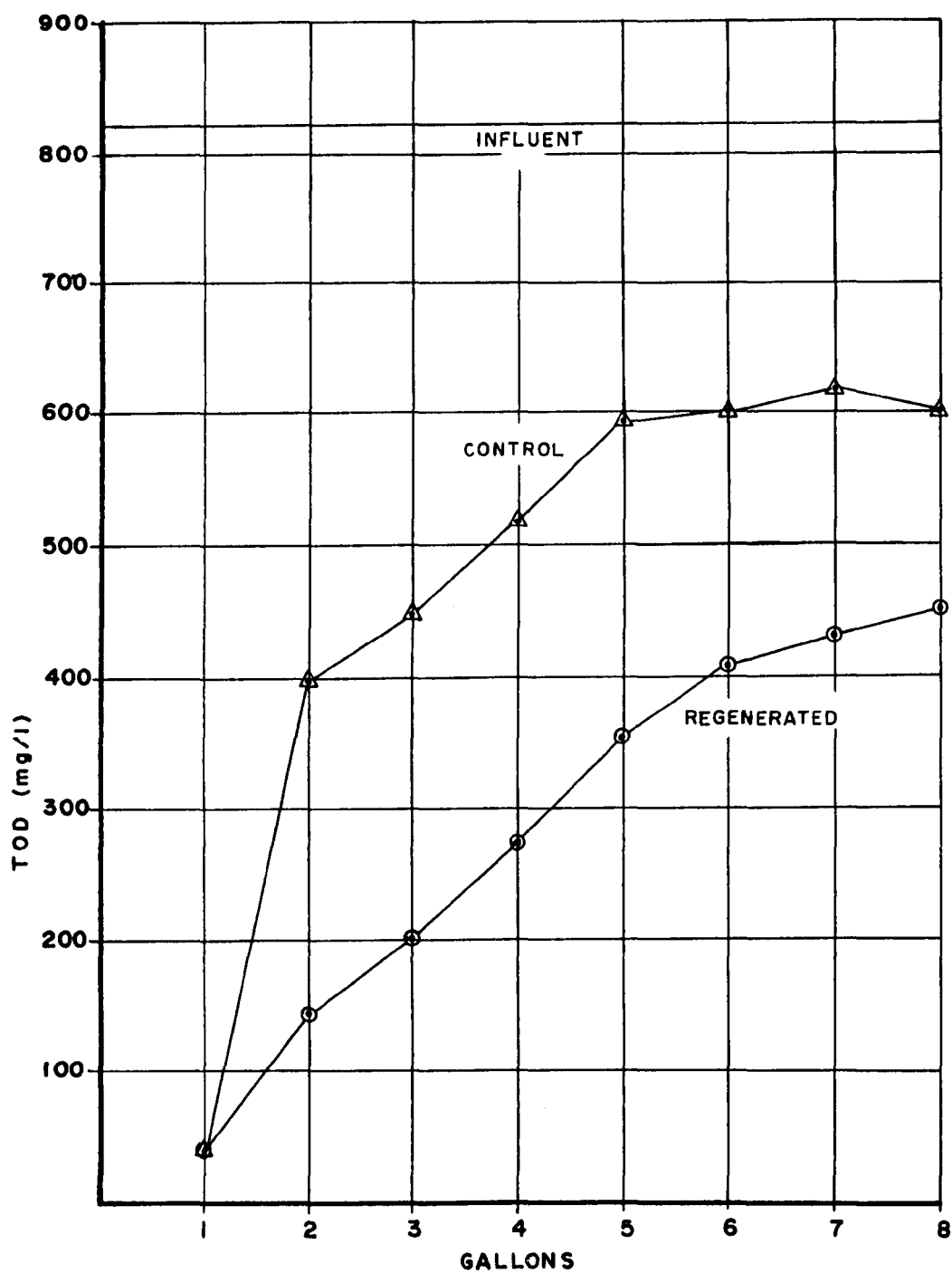


SECOND $K_2S_2O_8$
REGENERATION (25°C)

FIGURE 19



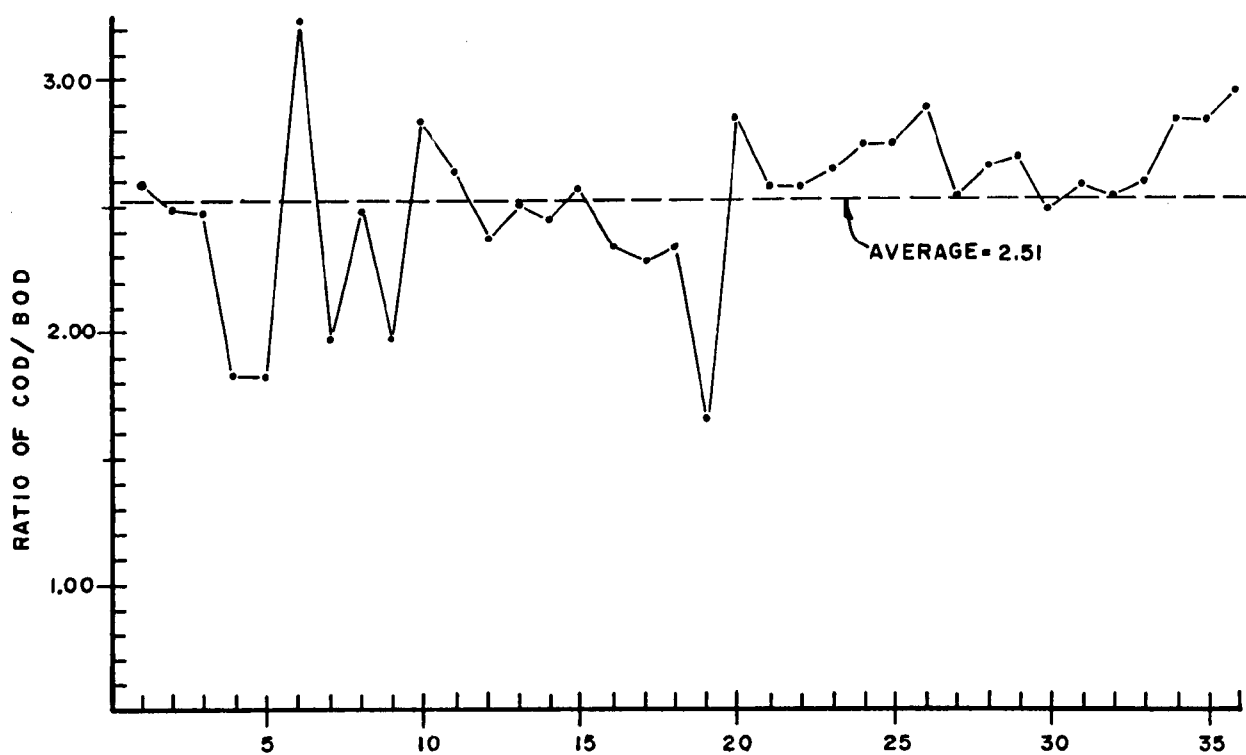
THIRD $K_2S_2O_8$
REGENERATION (50°C)
FIGURE 20



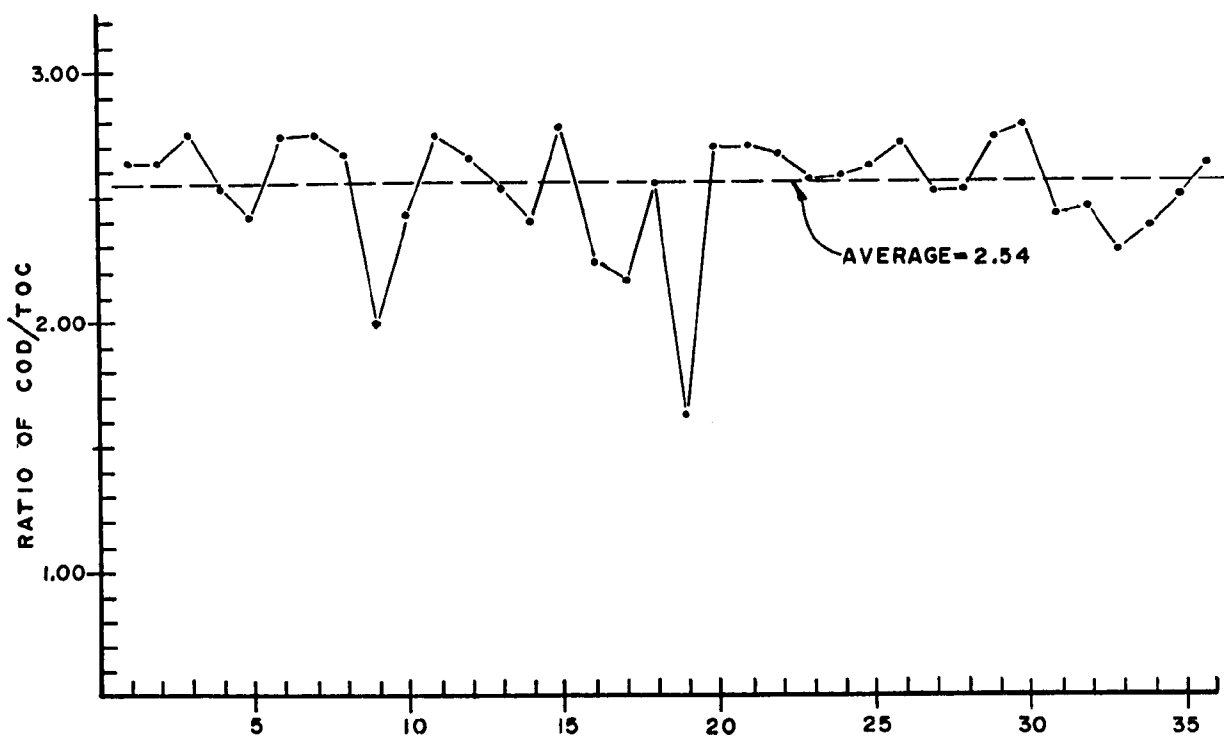
REPEAT OF 50°C
 $K_2S_2O_8$ REGENERATION
FIGURE 21

APPENDIX E

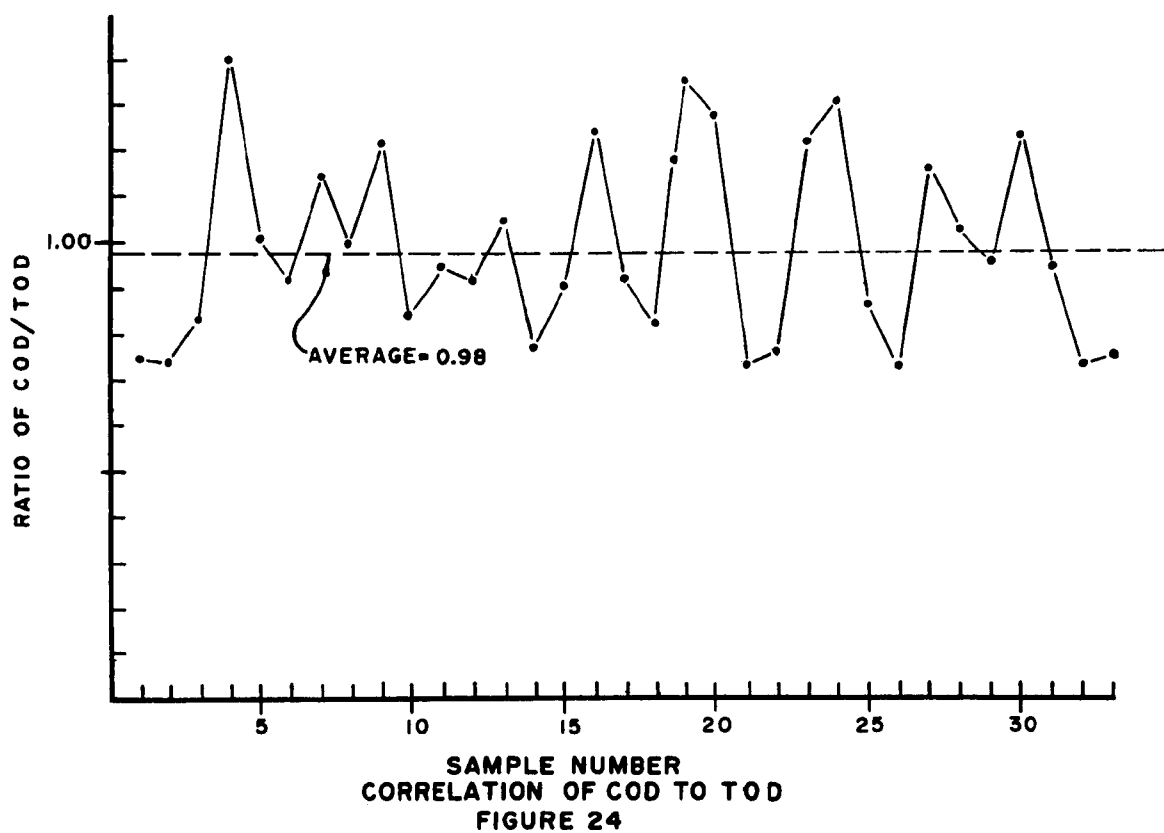
COD, BOD, TOC, TOD RELATIONSHIPS



SAMPLE NUMBER
CORRELATION OF COD TO BOD
FIGURE 22



SAMPLE NUMBER
CORRELATION OF COD TO TOC
FIGURE 23



APPENDIX F

1 MGD DESIGN CRITERIA

The scale-up from the pilot plant data to a 1 mgd plant is accomplished by maintaining dynamic and geometric similarity between the pilot plant and the full sized plant. A theoretical analysis of the kinetics of mass transfer in fixed bed adsorption systems (Chemical Engineering Handbook, Perry, 4th Edition, Section 16) indicates that

$\frac{k V e}{F}$ and $\frac{k \times T}{D}$ are the important similarity groups:

k = overall mass transfer coefficient
 V = ft^3 of activated carbon
 e = fraction of void volume
 F = flow rate
 D = distribution ratio = $\frac{q_{\infty} \rho}{C_o e}$
 ρ = density of activated carbon
 q_{∞} = capacity of activated carbon at influent concentration
 C_o = influent concentration
 G = flux (gpm/ft^2)
 T = time

Since the same activated carbon, mass flux rates, and cycle duration will be used in the 1 mgd plant, k , e and $\frac{k \times T}{D}$ are also equal for the pilot and full scale plant. Therefore, scale-up is approximated through the principle of equal relative residence times (V/F). Analysis of the experimental data indicates the following values:

<u>Per cent Reduction (COD)</u>	<u>V/F (days)</u>	<u>G (gpm/ft²)</u>
50	0.025	12
75	0.076	12

Applying the equal residence time criteria for a 1 mgd plant utilizing Nuchar WV-G activated carbon ($e = .4$, $\rho = 32 \text{ lbs}/\text{ft}^3$), the amounts required are:

<u>Per cent Reduction (COD)</u>	<u>Carbon (lbs.)</u>	<u>G (gpm/ft²)</u>
50	110,000	12
75	330,000	12

Determine Carbon Column Size for 50% COD Removal

Carbon required for 50% COD removal = 110,000 lbs.

$$110,000 \text{ @ } 27 \text{ \#/ft}^3 = 4075 \text{ ft}^3$$

with 50% bed expansion

$$4075 \times 1.5 = 6110 \text{ CF Required}$$

Assume 2 banks of 4 columns each

$$\frac{6110}{8} = 765 \text{ ft}^3 \text{ col.}$$

$$\text{For 8' diameter area} = 50.3 \text{ ft}^2$$

$$\text{Height} = \frac{765}{50.3} = 15.2'$$

Check the surface area for flux

$$\text{Flux} = \frac{694 \text{ gpm}}{50.3} = 13.8 \text{ gpm/ft}^2$$

$$13.8 > 12 \text{ gpm/ft}^2 : \text{ O.K. for flux}$$

Use 8 columns 8' diameter x 16' high

Regeneration Vessel Size

Vol. = 2 x the capacity of columns to be regenerated.

$$\text{Vol.} = 2 \times 4 \times 765 = 6110 \text{ ft}^3$$

Use 25' x 25' x 10' SWD Regeneration Vessel

Determine Carbon Column Size for 75% COD Removal

Carbon required for 75% removal = 330,000 lbs.

$$330,000 \text{ @ } 27 \text{ \#/ft}^3 = 12,200 \text{ ft}^3$$

with 50% bed expansion

$$12,200 \times 1.5 = 18,300 \text{ ft}^3$$

Assume 4 banks of 4 columns

$$\frac{18,300}{16} = 1,145 \text{ ft}^3/\text{col.}$$

$$\text{For 9' diameter, area } 63.5 \text{ ft}^2$$

$$\text{Height} = \frac{1145}{63.5} = 18'$$

Check the surface area for flux

$$\text{Flux} = \frac{694 \text{ gpm}}{63.5 \text{ ft}^2} = 10.9 \text{ gpm/ft}^2$$

$$10.9 \cong 12 \text{ gpm/ft}^2 : \text{ O. K. for flux}$$

Use 16 columns 9' diameter x 18' high

Regeneration Vessel Size

Volume = 2 x capacity of columns to be regenerated

$$V = 2 \times 8 \times 1145 = 18,300 \text{ ft}^3$$

Use 30' x 60' x 10' SWD Regeneration Vessel

1	Accession Number	2	Subject Field & Group 05D	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM	
5	Organization C. H. Masland & Sons Carlisle, Pennsylvania 17013				
6	Title Bio-Regenerated Activated Carbon Treatment of Textile Dye Wastewater				
10	Author(s) Rodman, Clarke A. and Shunney, Edward L.		16	Project Designation EPA-WQO Grant Project 12090 DWM	
			21	Note	
22	Citation				
23	Descriptors (Starred First) * Wastewater Treatment, * industrial wastes,* textiles * Activated Carbon, adsorption, color, costs				
25	Identifiers (Starred First) * Total Organic Carbon				
27	Abstract <p>A novel approach to treating a highly colored textile dyeing waste effluent is described. It comprises the removal by sorption of color bodies and other organic matter on activated carbon granules. Spent carbon granules are then subjected to a virule aerobic biological culture which desorbs and bio-oxidizes the desorbed matter, thereby regenerating the carbon for subsequent new sorption steps.</p> <p>Laboratory confirmation of the phenomenon is presented. Field testing of the treatment process concept in a 50,000 gpd plant installed at a yarn spinning mill (C. H. Masland & Sons, Wakefield, Rhode Island) is reviewed.</p> <p>Color removal was virtually complete at two flow rates evaluated: 8.5 gpm/ft² and 15.6 gpm/ft² carbon column bed flow. COD removal was 85% or higher at 8.5 gpm/ft² and only 48% at 15.6 gpm/ft².</p> <p>It was demonstrated that activated carbon had an adsorption capacity in excess of 1.6 pounds COD per pound of carbon when the carbon was reactivated only by biological means. The estimated operating cost for decolorizing 1,000,000 gpd is 8.3 cents/1000 gallons.</p> <p>This report was submitted in fulfillment of Grant No. 12090 DWM between the Water Quality Office of the Environmental Protection Agency and C. H. Masland & Sons.</p>				
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