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ACTIVATED CARBON TREATMENT OF PHENOLIC PAINT STRIPPING WASTEWATER

Anthony E. Perrotti

Facet Enterprises Industries, Incorporated

Prepared for:

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ACTIVATED CARBON TREATMENT OF PHENOLIC PAINT STRIPPING WASTEWATER

FACET ENTERPRISES INDUSTRIES, INC.
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The use of activated carbon for removal of phenol from wastewater is a well demonstrated and generally accepted treatment method. The Air Force operates a number of facilities for the depainting of aircraft and related equipment and the wastewater generated sometimes contains high concentrations of phenol. A study was conducted to ascertain both the economical and technical practicality of utilizing a granular carbon system for treating large volumes of this type of phenol bearing wastewater. Basically, this work involved two phases. The initial phase was performed in the laboratory and involved an in-depth

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characterization of the wastewater and the evaluation of different activated carbons for treating this wastewater. The second phase was performed on-site at Kelly Air Force Base and involved operating a pilot plant for treating phenol wastewater. The carbon was exhausted five times and thermally regenerated four times. The pilot plant was operated intermittently and was on-site for a period of six months. The technical feasibility of using activated carbon on this specific wastewater was demonstrated and the cost of constructing and operating full size plants was determined.

PREFACE

This report was prepared by Facet Enterprises Industries, Inc., Warwick RI, under contract F08638-74-C-0005. The research was performed under Program Element 64708F, Project 2054.

Inclusive dates of the research were May 1974 through May 1975. The report was submitted 8 August 1975 by the Air Force Civil Engineering project officer, Captain Dean D. Nelson.

This technical report has been reviewed by the information officer and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public including foreign nations.

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This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

To prevent corrosion of metallic surfaces, the Air Force repaints its aircraft and ground equipment approximately every five years. Before this repainting can be accomplished, however, the old paint must be completely removed, leaving only the bare metallic surface. The type of material which is used as a paint stripper is dictated by the type of top coat and primer being removed. Until recently, most Air Force aircraft were painted with an acrylic lacquer top coat over a zinc chromate primer and this system could be removed using non-phenolic type strippers. Now, however, the Air Force utilizes a polyurethane top coat over an epoxy primer. Removal of this type of paint system requires the use of strippers containing relatively large concentrations of phenol (currently 10 percent by weight).

Phenol is an aromatic hydrocarbon defined as a hydroxy derivative of benzene. It is somewhat soluble in water (9 grams per 100 grams of H_2O), and is highly toxic to most types of living organisms. Chlorination of waters containing relatively low concentrations of phenol usually results in the production of chlorophenols which impart an objectionable odor and taste to the water. Because of this, many of the existing or proposed discharge standards limit the concentration of phenol which can be discharged to less than 0.2 milligrams per liter.

At present, the Air Force operates a number of maintenance facilities which are responsible for stripping and repainting of aircraft. Kelly Air Force Base in San Antonio, Texas is one such facility and is responsible for the maintenance of many of the larger type aircraft, including their repainting. Currently, Kelly Air Force Base is using large amounts of phenolic base strippers to depaint aircraft. The wastes from these stripping operations are discharged to an industrial waste treatment facility that uses pretreatment and a trickling filter system which is operated by base personnel. In order to reduce the high concentrations of phenol in this wastewater which might otherwise destroy the bacterial component of the treatment system, large amounts of potassium permanganate are added to oxidize the phenol. This chemical addition is made within the stripping areas before the waste is discharged into the sewer and again at the treatment facility with the following reaction taking place:

$$3\,C_6H_6O + 28\,KMnO_4 + 5\,H_2O \rightarrow 18\,CO_2 + 28\,KOH + 28\,MnO_2$$

Although this approach does reduce the concentration of phenol before it enters the biological system, it has proven to be expensive and impractical for this particular application.

Kelly Air Force Base has been experimenting with allowing the wastewater from the paint stripping facility in Building 375 to be discharged to the sanitary sewer rather than the industrial wastewater system. Domestic sewage at Kelly Air Force Base is treated by the city of San Antonio. To date, the results have been good with no known domestic plant upsets. This solution is probably short-lived, however, as when C-5 aircraft begin to return to Kelly Air Force Base for their second depot level maintenance they will have the polyurethane and epoxy paint system. The removal of this paint on such a large aircraft will greatly increase the phenolic paint stripping wastewater load. To determine a viable future treatment or pretreatment method, activated carbon adsorption together with thermal regeneration was investigated as a method for the treatment of phenolic wastewater including the type generated during aircraft paint stripping operations. The purpose of this study was to incorporate this adsorption concept into an on-site process for the treatment of paint stripping wastewater where high concentrations of phenol are present. This on-site pilot plant was to provide information useful in both assessing the technological and economical practicality of such an approach and allow the necessary scale-up that would not be feasible in a laboratory.

Basically, this study involved two phases. The initial phase was performed in the laboratory and entailed an in-depth characterization of the wastewater and an evaluation of a number of different activated carbons for treating this material. Carbon evaluations were based on both adsorptive isotherms and continuous flow columns. The second phase was conducted on-site at Kelly Air Force Base and involved using the single most effective carbon, as determined in the laboratory in a full scale pilot plant facility.

The wastewater in question resulted at Kelly Air Force Base from the following operation (the same basic stripping procedure is followed at other maintenance facilities). First, a section of the aircraft is sprayed with the viscous paint stripper and this is allowed to remain on the surface until the paint begins to soften and starts to loosen from the metal surface. This initial application of stripper usually includes a brushing operation to insure uniform coverage. Usually, a 20- to 30-minute contact time is sufficient for the stripper to loosen the paint. The next step is to rinse the section using a high pressure stream of water (approximately 40 to 75 gallons of water for every gallon of stripper applied). Depending on the particular structural component being worked on, this entire operation may be repeated several times. The last operation is to wash the section with detergent and rinse with clean water.

From the standpoint of activated carbon treatment, the wastewater at Kelly Air Force Base is further complicated by other operations carried out at the same time and discharged into common drains. Of particular importance is a carbon removing operation. This involves soaking an aircraft section, such as an engine housing, in a large soak tank to remove carbon deposits in tanks that contain an aqueous-alkaline solution of creosote and orthodichlorobenzene. After soaking several hours, a section is removed and rinsed with water. This rinse water, including any full strength solution that drains from the part while removing it from the tank, is inter-mixed with waste from the paint stripping operations.

Additionally, the paint stripper itself also contains components other than phenol, such as methylene chloride and hexavalent chromium. It was anticipated that much of the methylene chloride would evaporate fairly rapidly and, therefore, not present a major problem in terms of increasing the organic loading on the carbon. It is known, however, that activated carbon does remove some heavy metals under certain conditions, including hexavalent chromium. This would be beneficial strictly from a waste treatment standpoint because high concentrations of chromium are detrimental to biological systems and aquatic life in general. However, chromium could build up within the porous carbon structure and might not be removed during the thermal regeneration process. This buildup could also continue to increase with each contamination cycle and eventually blind the porous structure of the carbon to the extent that regeneration would not renew it to a reasonably active level.

Because this wastewater also contains large amounts of suspended solids, primarily undissolved paint particles, the treatment system should include a means of separating these solids from the wastewater prior to activated carbon treatment. These solids would, otherwise, have a tendency to accumulate within the carbon bed, creating pressure drops and channeling problems affecting the efficient use of the carbon. Although operation in an upflow mode reduces the likelihood of plugging, gelatinous solids have a tendency to coat the surface of the carbon granules and to establish a diffusion barrier, i.e., the sorbate cannot enter the carbon's macroporous structure. Because of this, the on-site treatment system at Kelly did encompass an effective means of solids removal.

SECTION II

LABORATORY EVALUATION

Wastewater Collection

Samples of wastewater were collected over a normal workday from the stripping facilities at Kelly Air Force Base (Building 375). Sample collection was conducted at a sump which received the discharges from all the processes taking place within the facility. The processes taking place during the sampling period included depainting with phenolic type stripper, washing, degreasing, and carbon removing. Non-phenolic type stripping material is also used on occasion, but the operations in which this is used were not being performed during the sampling period. Because this wastewater would be subjected to a rigorous laboratory investigation which would provide the basis for the pilot plant design, every effort was made to insure that the samples collected were as representative as possible. To insure that the integrity of the suspended solids (paint chips) was maintained, the collection was accomplished by hand bailing rather than by pump.

Wastewater Analyses

The results of the analyses made on these wastewater samples are shown in Table 1. Analyses other than those of immediate concern were performed to gain some additional insight into the nature of this waste as well as to identify potential problems. The wide variations in the ranges of some contaminants are the result of the particular operations being conducted during the time of sampling.

Surfactant and phosphate levels were greatest during degreasing operations or the final washing of a component following a stripping operation. In general, the organics level (COD or TOC) was greatest during the period when aircraft components were being taken out of the carbon remover soak tanks, which contain creosote and dichlorobenzene in the solution. There is also a correlation between the phenol concentrations and those of the methylene chloride and chromium. This was expected considering all three are components of the same stripper.

It was discovered that most of the suspended solids (paint chips) tended to dissolve when in contact with the wastewater for a long period of time. This is exemplified by the relatively low suspended solids levels found in this material. The negligible difference between the filtered and unfiltered organic type analyses indicates further that essentially all the organics are completely solubilized. A comparison of total and volatile solids shows that most of the solids (previously in the dissolved state) are volatile in nature and, therefore, probably organic.

TABLE 1. PROFILE ANALYSIS OF PHENOLIC TYPE PAINT STRIPPING WASTEWATER

Parameter	Concentration Range
Phenol	1,040 - 4,060 mg/1
pH	8.0 - 8.6
Total Phosphate (as P)	10.0 - 28.0 mg/1
Suspended Solids	107 - 303 mg/1
Volatile Solids	458 - 2,700 mg/1
Total Solids	800 - 3,830 mg/1
COD	9,200 - 36,400 mg/1
COD Filtered (0.45 μ)	7,250 - 35,100 mg/1
Total Chromium	17.5 - 59.5 mg/1
TOC	2,710 - 14,400 mg/1
TOC Filtered (0.45 μ)	2,520 - 13,600 mg/1
Methylene Chloride	75 - 2,000 mg/1
Surfactants	120 - 4,000 mg/1
Oil and Grease	8.40 - 66.3 mg/1

It should be noted here that one of the problems encountered continuously through the laboratory phase of this study was one of wastewater variability. This was especially true when dealing with organic parameters. It appears that much of this resulted from loss through rapid volatilization of components, especially methylene chloride.

Chemical Pretreatment Study

A composited sample of wastewater was subjected to a chemical treatment screening study to determine if suspended solids could be removed and also determine if, at the same time, the level of soluble organics could be reduced through precipitation. It was reasoned that if this could be accomplished in a feasible manner from the point of implementation and economics, it could enhance the on-site treatment process by prolonging the useful life of the carbon.

A number of water treatment chemicals known for their flocculative and precipitative properties were screened by combining them with the waste (References 1, 2). They included alum, lime, ferric chloride, and various types of synthetic polyelectrolytes. The combination of alum and a high molecular weight cationic polyelectrolyte was found to be particularly effective. It removed essentially all the suspended material and also reduced the total organic concentration in the waste by approximately 65 percent. The cost for this type of chemical pretreatment proved to be prohibitive, however, since it was in the range of $12.00 per 1,000 gallons of wastewater treated and still left a solids disposal problem. Based on this work, it was concluded that any pretreatment based on chemical addition would not be economically feasible.

Since it appeared inevitable that any on-site carbon system would have continuous plugging problems and related pressure drip, it was obvious that a physical means of solids separation was necessary (References 2, 3, 4, 5, 6). A mechanical scheme comprised of a series of strainers was devised to accomplish this and a more detailed description of this equipment will be given later in this report.

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1. W. W. Eckenfelder Jr., Water Quality Engineering for Practicing Engineers (New York: Barnes & Noble, Inc., 1970).
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3. "Summary Report Advanced Waste Treatment," U. S. Department of the Interior, Federal Water Pollution Control Administration, Publication WP-20-AWTR-19 (1968).
4. "Process Design Manual for Carbon Adsorption," U. S. Environmental Protection Agency Technology Transfer, October, 1973.
5. "Activated Carbon for Wastewater Treatment," Atlas Chemical Industries, Inc. D-110 (July, 1969).
6. J. W. Hassler, Activated Carbon (New York: Chemical Publishing, 1963).

Carbon Adsorption Isotherms

Batch adsorption experiments were performed using 12 different granular carbons in order to determine which had the greatest capacity in terms of phenol removal. The three most effective carbons would then be subjected to a series of continuous flow column experiments (References 4, 5, 6, 7, 8). Based on these results, one carbon would be selected for use in the on-site pilot plant at Kelly Air Force Base.

All the carbons used during the batch testing were selected on the basis of applicability for aqueous phase treatment, mesh size similarity and cost. Many of these carbons differed as to the base material used in their manufacturing, i.e., petroleum base, coal base, nut shell base, etc (References 6,8). The following activated carbons were selected for the batch adsorption screening study:

1. Calgon® Filtrasorb 300, 8 x 30 mesh
2. Calgon® Filtrasorb 400, 12 x 40 mesh
3. Westvaco Nuchar WV-G, 12 x 40 mesh
4. Westvaco Nuchar WW-W, 8 x 30 mesh
5. Westvaco Nuchar WV-H, 6 x 16 mesh
6. ICI Darco, 12 x 40 mesh
7. ICI Darco, 12 x 20 mesh
8. Witco 718, 12 x 30 mesh
9. Witco 235, 12 x 30 mesh
10. Barnebey Cheney PC, 12 x 30 mesh
11. Norit, 8 x 20 mesh
12. Ionac P-50, 14 x 40 mesh

References
7. "Evaluation of Granular Carbon for Wastewater Treatment," Atlas Chemical Industries, Inc. D-111 (August, 1969).
8. C. L. Mantell, Adsorption (New York and London: McGraw-Hill Book Company, Inc., 1951).

Batch Adsorption Isotherm Procedure

A common procedure for conducting batch isotherms is to use a carbon which has first been pulverized so that 90 percent of it passes through a 325 mesh sieve. The pulverization, in turn, normally reduces the contact time to reach equilibrium to about 30 minutes. In order to maintain a closer correlation between the results of the batch isotherms and what could be expected during a continuous flow column situation, these isotherms were performed using non-pulverized carbon (References 7, 9, 10, 11, 12). This however, necessitates a much longer contact time before equilibrium could be reached. The basic procedure used for setting up each isotherm is as follows:

1. Each carbon tested was first vigorously rinsed with distilled water to wash out as much fine material as possible and then dried at 103°C for several hours before weighing. Since these tests were performed on non-pulverized carbon, it is important to eliminate the inherent fines created during the activation process or packaging of a carbon. If this is not done, those carbons containing more initial fines would have a distinct advantage over those having less fines, i.e., greater exposed surface area per unit weight.

2. 0.5, 1.0, 2.0, 4.0, 6.0, and 10.0 grams of each washed carbon were added to each of six 500-milliliter screw top Erlenmeyer flasks along with 200 milliliters of filtered (1.2-micron rated membrane type glass fiber) composited wastewater.

3. Each set of flasks, along with a control, was placed on a mechanical shaker and periodically monitored for supernatant TOC (which is indicative of both phenol and COD levels in the supernatant) to determine equilibrium time. Since TOC analyses require only 20 microliters of sample, any change in volume was negligible. It was concluded that TOC equilibrium occurred at about 30 hours and, therefore, all isothermal data in this report is based on at least 30 hours contact time.

References

9. "Enhancement of Biological Waste Treatment by Activated Carbon," Chemical Engineering Progress, Vol 69, No 11 (November, 1973) pp 63-64.
10. "Decolorization of Carpet Yarn Wastewater," American Dyestuff Reporter, Vol 60, No 6 (1971) p 32.
11. "Purifying Liquids with Activated Carbon" (Wilmington, Delaware: Atlas Chemical Industries, Inc., Bulletin D-101).
12. R. H. Kroop, "Treatment of Phenolic Aircraft Paint Stripping Wastewater," AFWL-TR-72-181.

4. After reaching equilibrium, each sample was filtered through a 0.45 micron rated milipore filter. This was done because any carbon fines generated during shaking would be small enough to pass larger porosity filters, and fines present during analyses would tend to yield erroneous data, i.e., elevated COD or TOC.

Batch Isotherm Results

The carbon contacted wastewater was then analyzed for phenol, COD and TOC concentration. These results are plotted on logarithmic coordinates with the abscissa (C_f) in units of impurities remaining in the treated wastewater and the ordinate (X/M) in units of impurities adsorbed per unit weight of carbon (References 4, 5, 6, 7).

$$k \quad (X/M)^n = K\left(\frac{(C_o - C_f)\ V}{M}\right)^n = C_f$$

Where:

C_o = initial concentration of impurities in wastewater.

C_f = final concentration of impurities in wastewater.

M = grams of activated carbon used.

V = volume of sample in liters.

X = total impurities removed.

k & n = constants.

Figures 1 through 6 show the isotherms in terms of phenol, COD and TOC. In general, all isotherms appear to follow the Freundlich equation which is expressed as a straight line on a logarithmic plot (References 6, 8). In some cases, the results were not plotted for the higher carbon doses (6.0 or 10 grams) because the contaminant concentration remaining in solution at equilibrium was negligible, indicating that a lesser amount of carbon is adequate.

Basically, adsorption isotherms indicate whether a desired level of contaminant adsorption can be attained by a particular carbon (Reference 7). In addition, isotherms indicate the relative efficiencies of different carbons in the removal of these impurities. Generally, as the initial concentration of these impurities increase, the removal efficiency of a carbon also increases. The isotherms used here were all conducted on the same contaminant and, therefore, a direct comparison of their efficiencies (X/M) can be made relative to the same concentration remaining in solution (C_f).

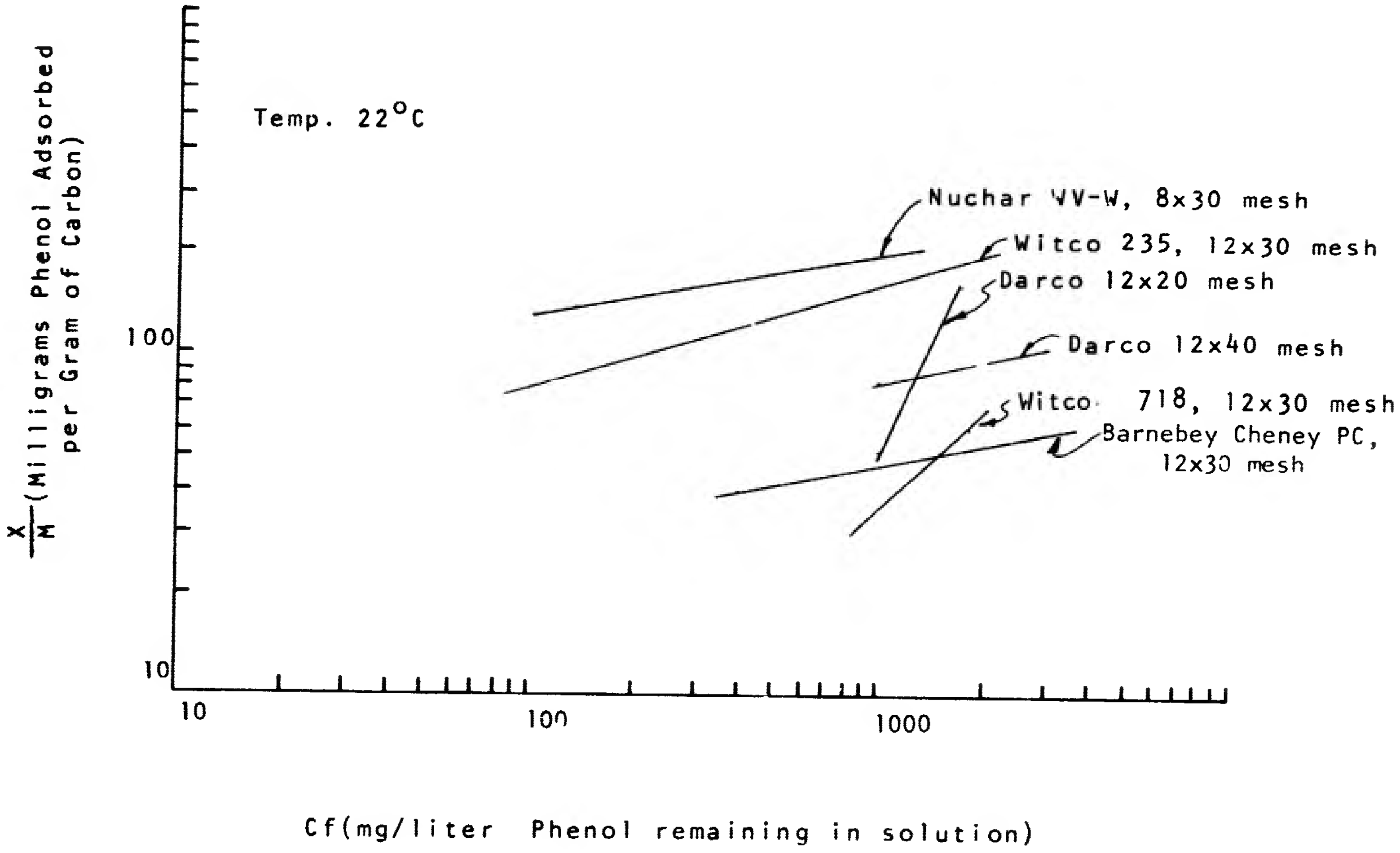

Figure 1. Phenol Adsorption Isotherms

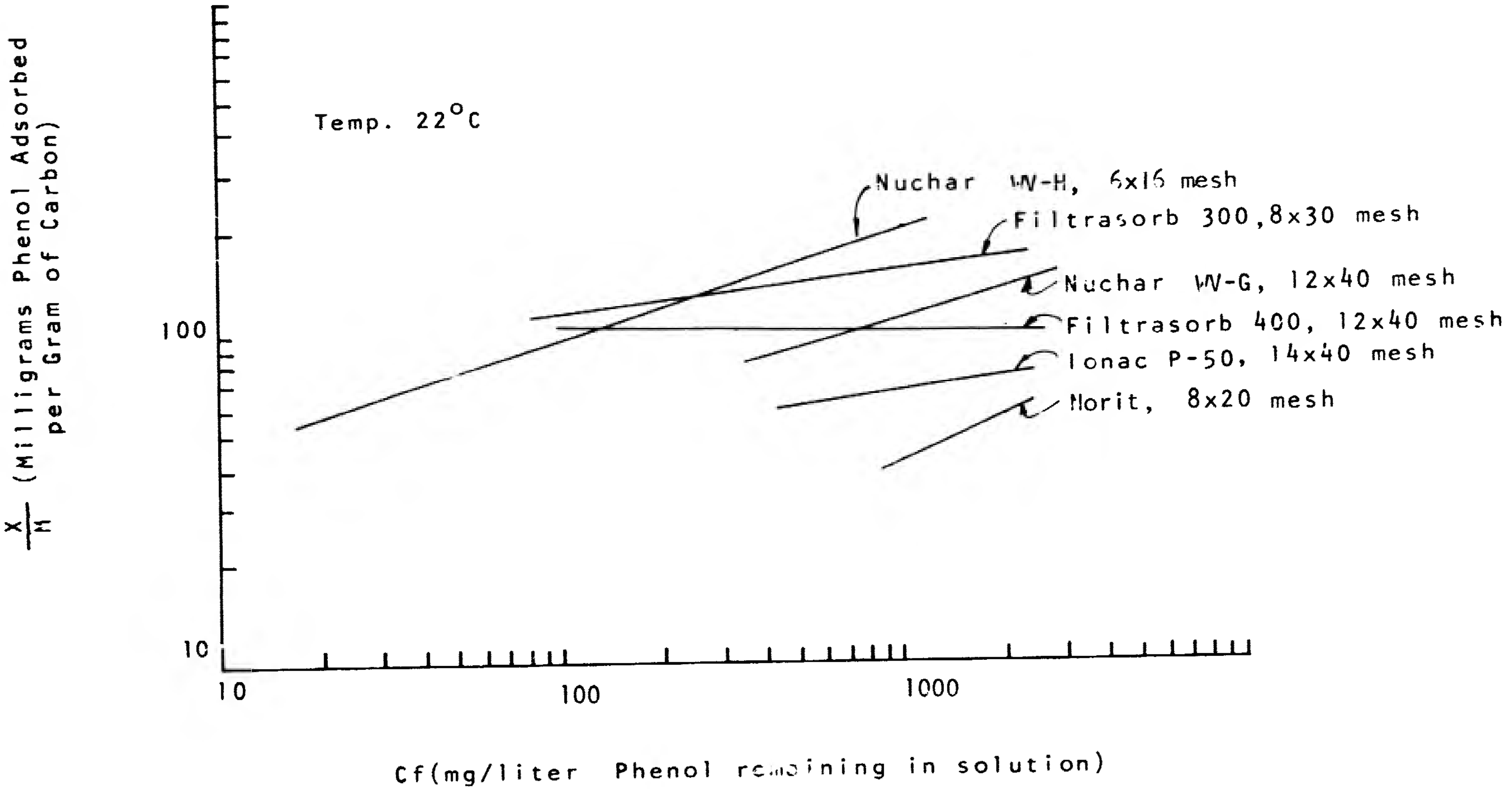

Figure 2. Phenol Adsorption Isotherms

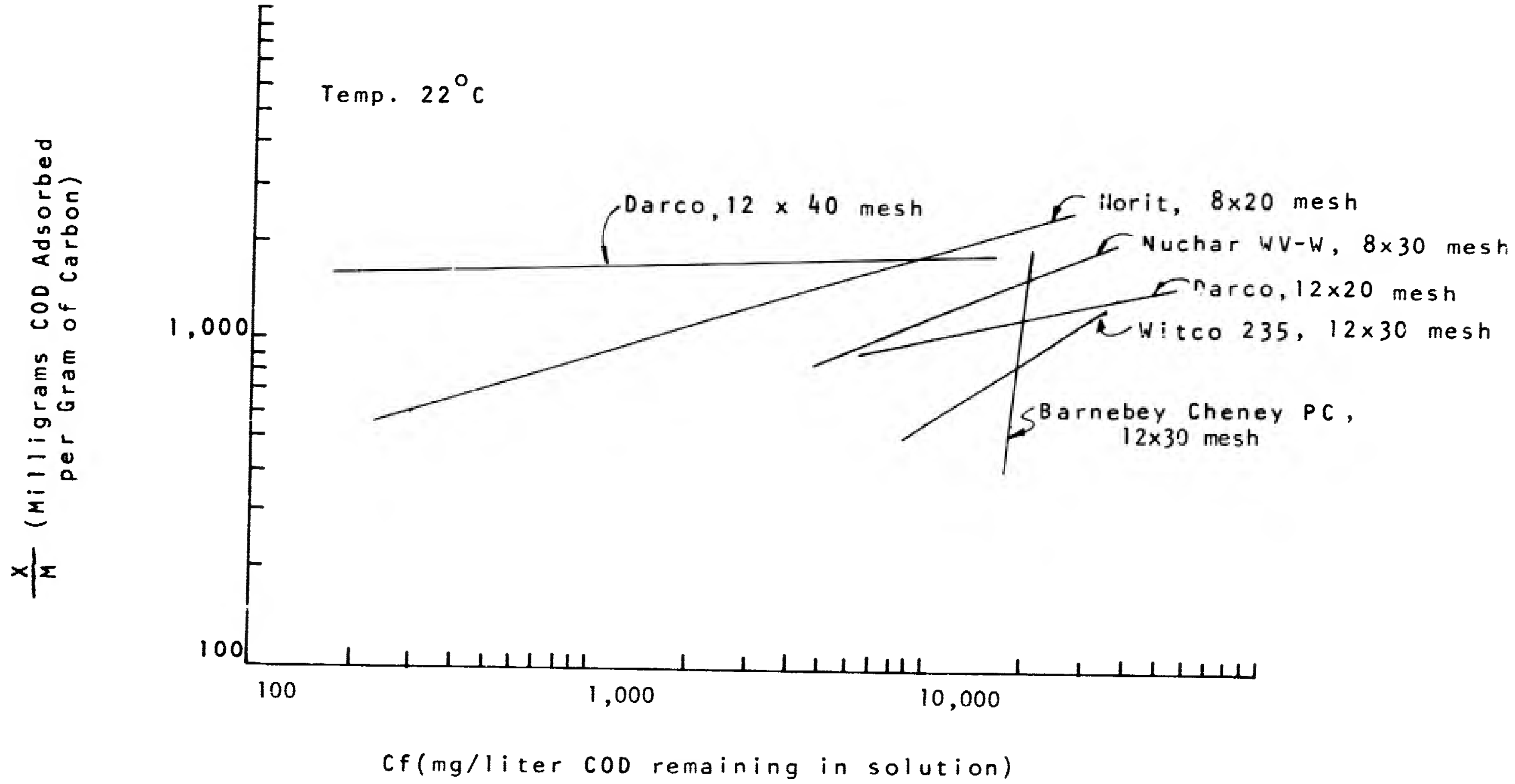

Figure 3. COD Adsorption Isotherms

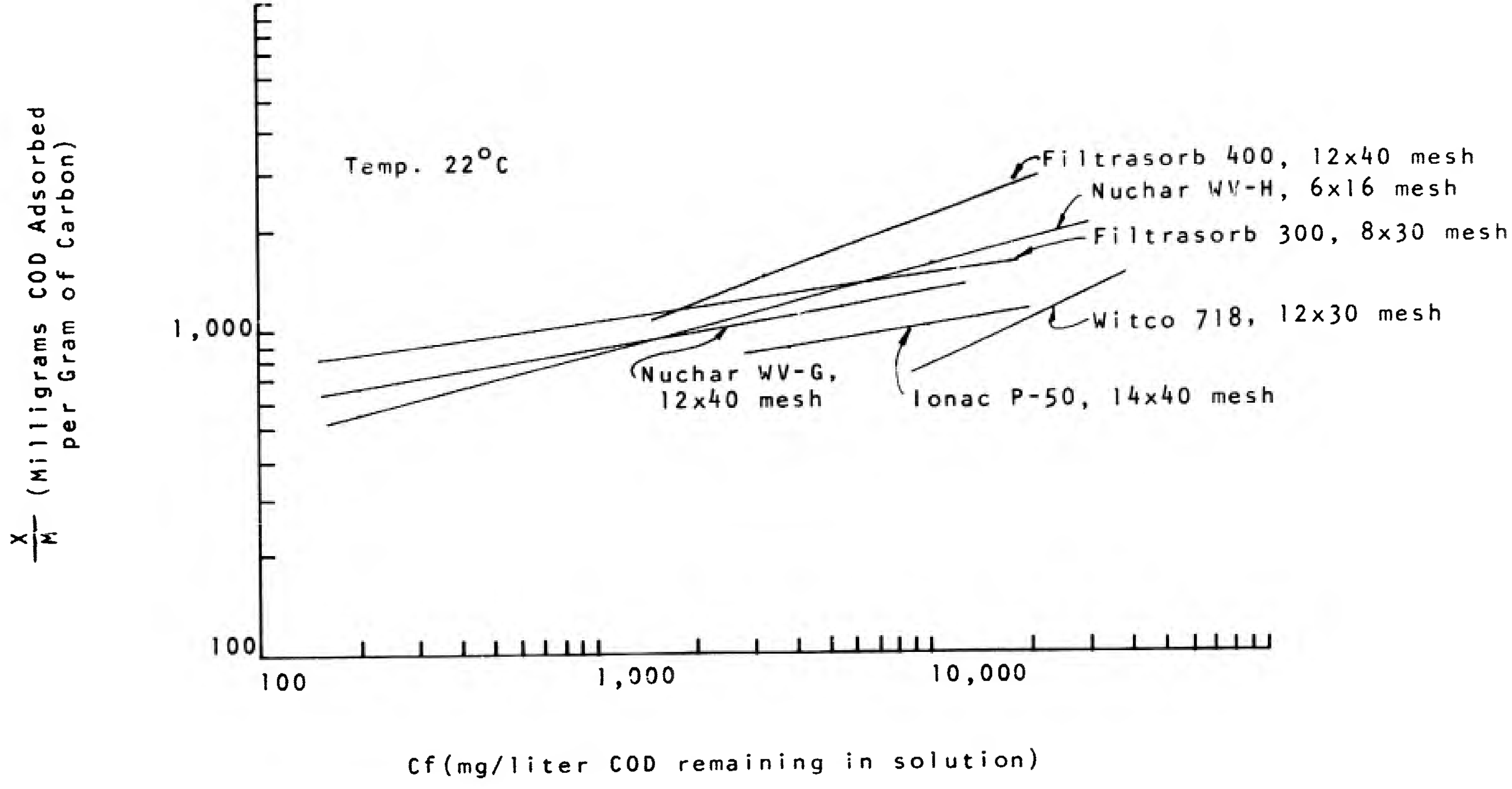

Figure 4. COD Adsorption Isotherms

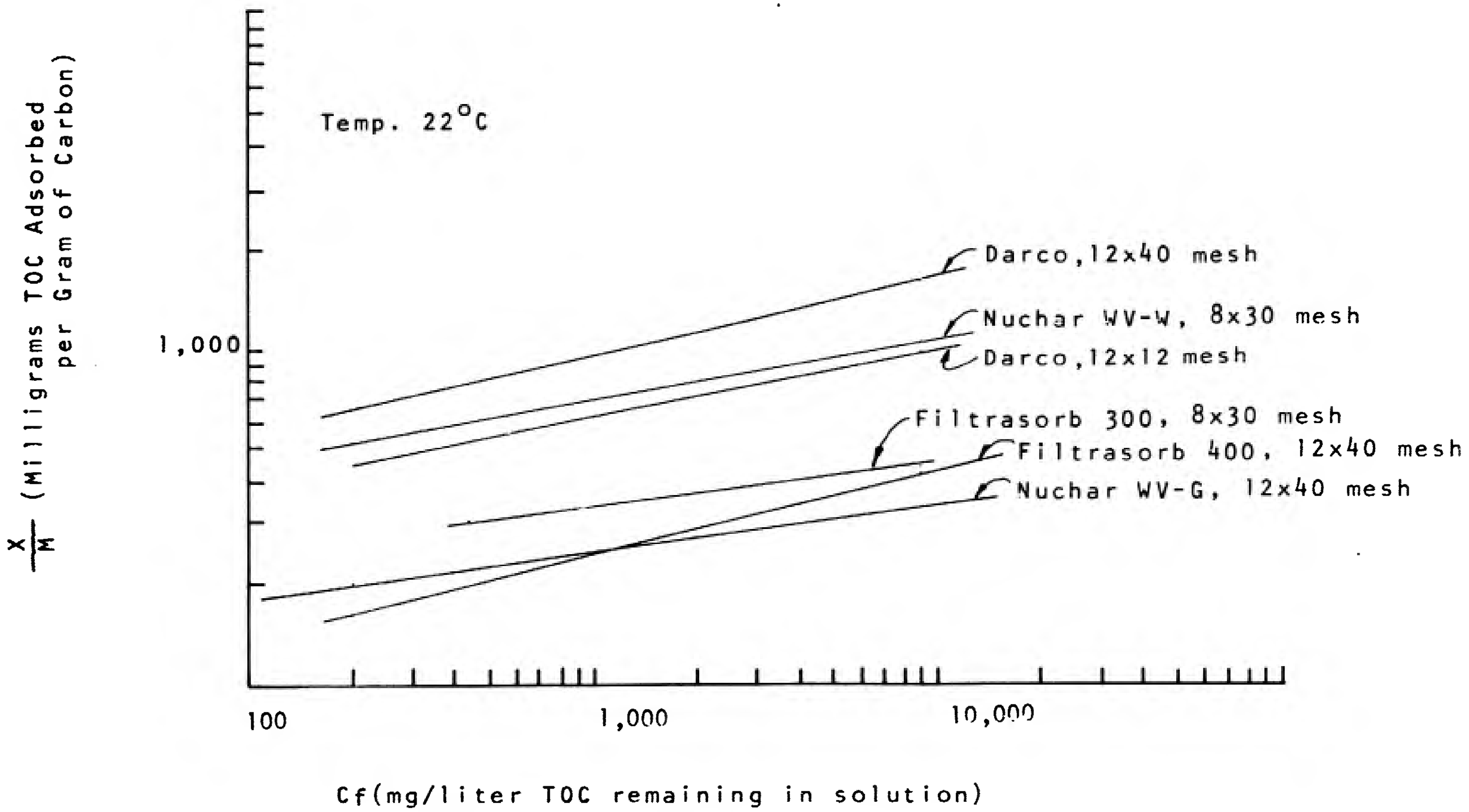

Figure 5. TOC Adsorption Isotherms

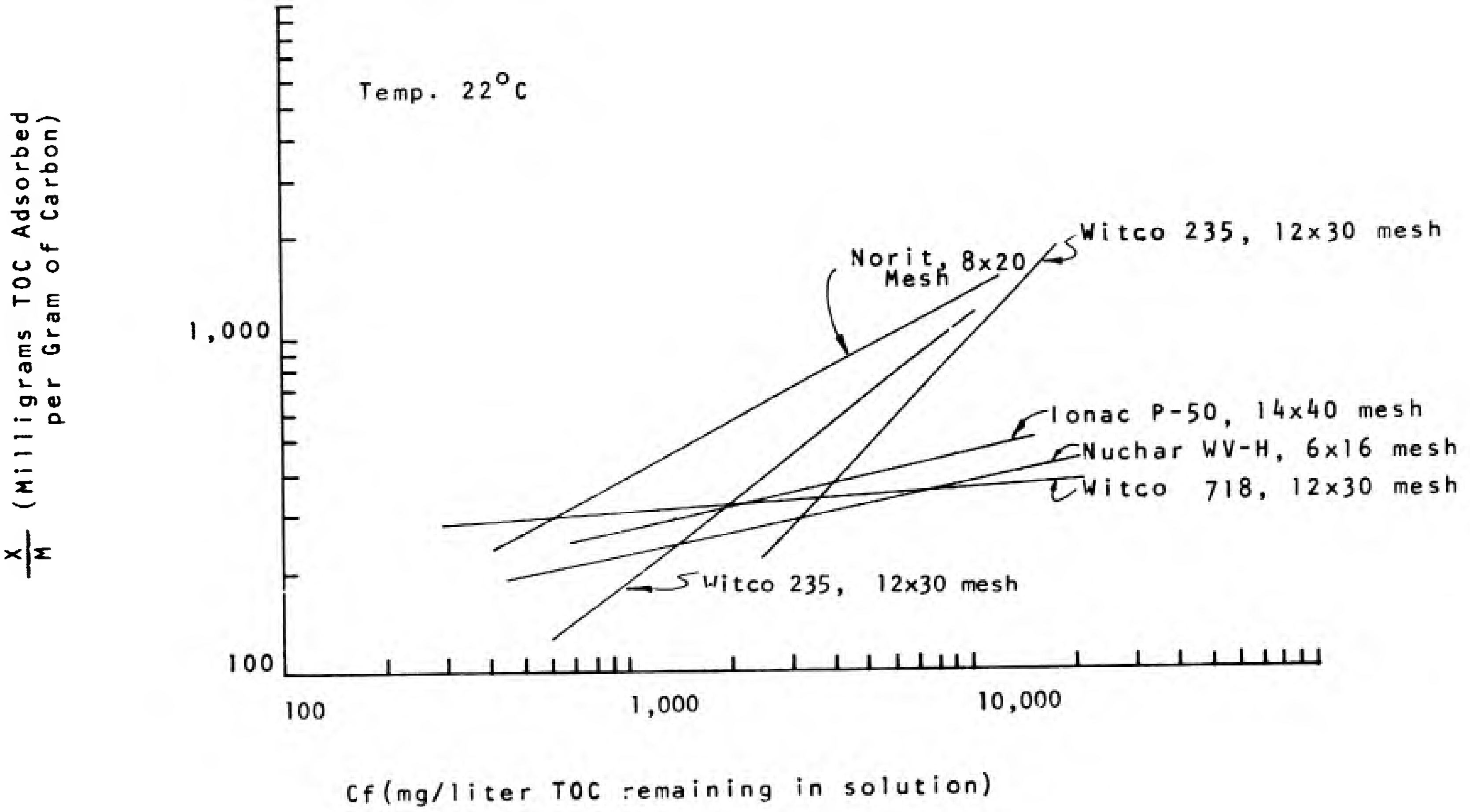

Figure 6. TOC Adsorption Isotherms

When an isotherm has a relatively slight slope and remains at a high level as shown by Nuchar WV-W in Figure 1, it indicates that this carbon has good adsorption characteristics over the entire concentration range. A carbon having a similar slope but at a lower level as shown in Figure 1 by Barnebey-Cheney PC means that this particular carbon has adsorbed proportionately less. If an isotherm has a steep slope as Darco 12 x 20 in Figure 1, it suggests this carbon would provide good adsorption at a high concentration but relatively poor adsorption at low concentrations. It should be pointed out that the preferable carbon may not necessarily be the one showing the greatest adsorption efficiency over the entire range of concentrations tested (References 5, 7). Considerations such as cost, regenerability and friability should also be taken into account.

In terms of phenol removal (Figures 1 and 2) for the 12 test carbons, these results indicate that Nuchar WV-H, Nuchar WV-W and Filtrasorb 300 are the three most effective for this type of wastewater. Nuchar WV-H performed best at the higher concentration ranges but was considerably less effective at lower concentrations. Filtrasorb 300 and Nuchar WV-W both performed in an almost identical manner over the entire range of concentrations tested. At an equilibrium phenol concentration of 250 milligrams per liter (approximately 90 percent removal), the removal efficiencies for each of these three carbons in terms of phenol are: Nuchar WV-H = 0.14 grams per gram carbon; Filtrasorb 300 = 0.13 grams per gram carbon; and Nuchar WV-W = 0.13 grams per gram carbon.

Figures 2, 3, 4 and 5 show the adsorption isotherms for the 12 test carbons in terms of COD and TOC removal. Both of these parameters are indicative of the organic material in this wastewater including phenols. The reason both were used during the initial laboratory phase is that a TOC analysis can be completed in about one to two minutes and requires a relatively small sample volume (20 microliters). COD analysis, on the other hand, requires two to three hours for completion and requires a much larger sample.

The ratio of COD/TOC is a function of the particular material being analyzed. In the case of aircraft paint stripping wastewater, this ratio (COD/TOC) was usually found to be in the area of 2.5 per liter. Because this ratio was fairly stable during all the initial testing, it was determined that TOC could be used as a yardstick for estimating COD levels when it was not practical to analyze directly for this parameter.

These same three carbons (Nuchar WV-H, WV-W and Filtrasorb 300) were also among the most effective for COD and TOC removal. It appears from these results that some of the carbons which showed poor phenol removal performed extremely well in terms of COD and TOC removal. This indicates a greater affinity for the other organics in this relatively complex wastewater. Since phenol removal is the major problem area and the basis of this study, however, the three carbons chosen for continuous column testing were Filtrasorb 300, Nuchar WV-H and Nuchar WV-W.

Continuous Flow Column Experiments

The scheme used to conduct the continuous flow testing is shown in Figure 7. A separate column was operated in this manner for each of the three test carbons. Basically, it involved operating each column at three different flow rates, each time with a fresh charge of virgin carbon.

Column Test No. 1

The first series of carbon column tests was operated at a flow rate of 17 milliliters per minute, i.e., one hour residence time or a hydraulic loading of 0.206 gpm/ft^2. Figures 8 through 13 show the breakthrough curves for each parameter tested. Both Nuchar carbons showed similar phenol breakthrough characteristics and both appeared to be more effective than Filtrasorb 300 under these test conditions. For example, Filtrasorb 300 showed essentially complete instantaneous breakthrough at 35 bed volumes throughput, while both Nuchar carbons were functioning at over 80 percent instantaneous phenol removal at this point. It should be noted that during the latter part of this column test (at a point near complete breakthrough), the effluent phenol concentration in the Filtrasorb column was greater than that of the feed material. This same phenomenon also existed with respect to methylene chloride (Figure 11). It would seem that this resulted from the displacement of elution of adsorbed contaminants as the carbon approached complete exhaustion.

All three types of carbons exhibited similar breakthrough characteristics in terms of COD and TOC removal (Figures 9 and 10). Filtrasorb 300 appeared to be the most effective carbon in removing these parameters during the first 24 bed volumes; beyond this point, however, both Nuchar carbons performed slightly better than the Filtrasorb 300.

Figure 11 shows the methylene chloride breakthrough curves for Column Test No. 1. The performance of each carbon, indicated by the shape of these curves, was very similar to their respective COD and TOC breakthrough characteristics. As noted earlier, the methylene chloride level in the effluent became greater than the influent concentration when the Filtrasorb 300 carbon column approached complete breakthrough. During one sampling period, the methylene chloride in the effluent from this column approached a level approximately three times that of the feed. At 29 bed volumes, however, there was an abrupt decrease in the level of this compound present in the column effluent. This phenomenon may have resulted from a renewed carbon retention capacity immediately after the dumping of a large amount of the previously retained methylene chloride.

Both Nuchar carbons have the same basic shape breakthrough curves with respect to total chromium removal (Figure 12). Both of these carbons were still removing approximately 50 percent of the influent chromium after 30 bed volumes and, based on the slope of their curve, considerably more

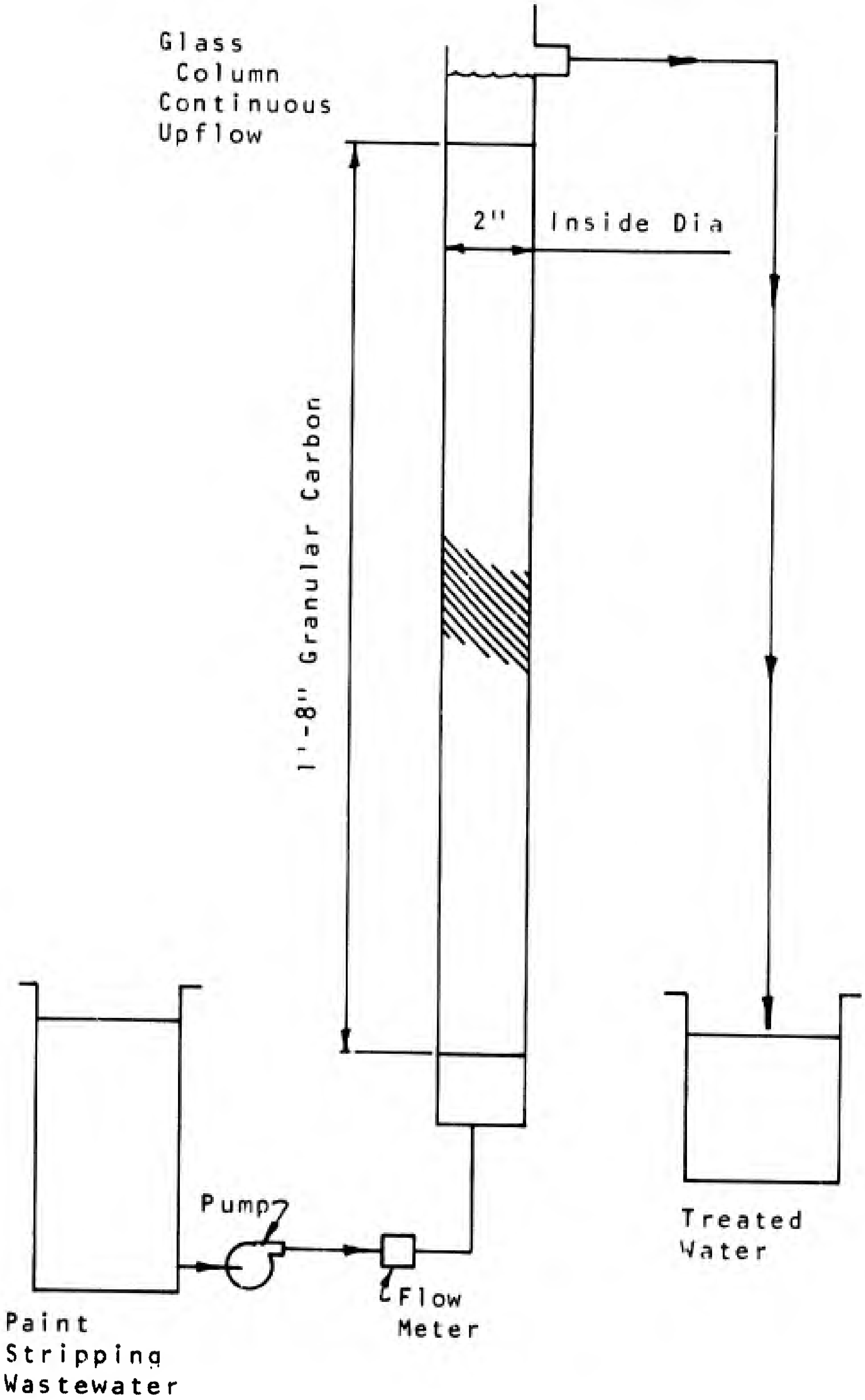

Figure 7. Continuous Flow Carbon Column Laboratory Apparatus

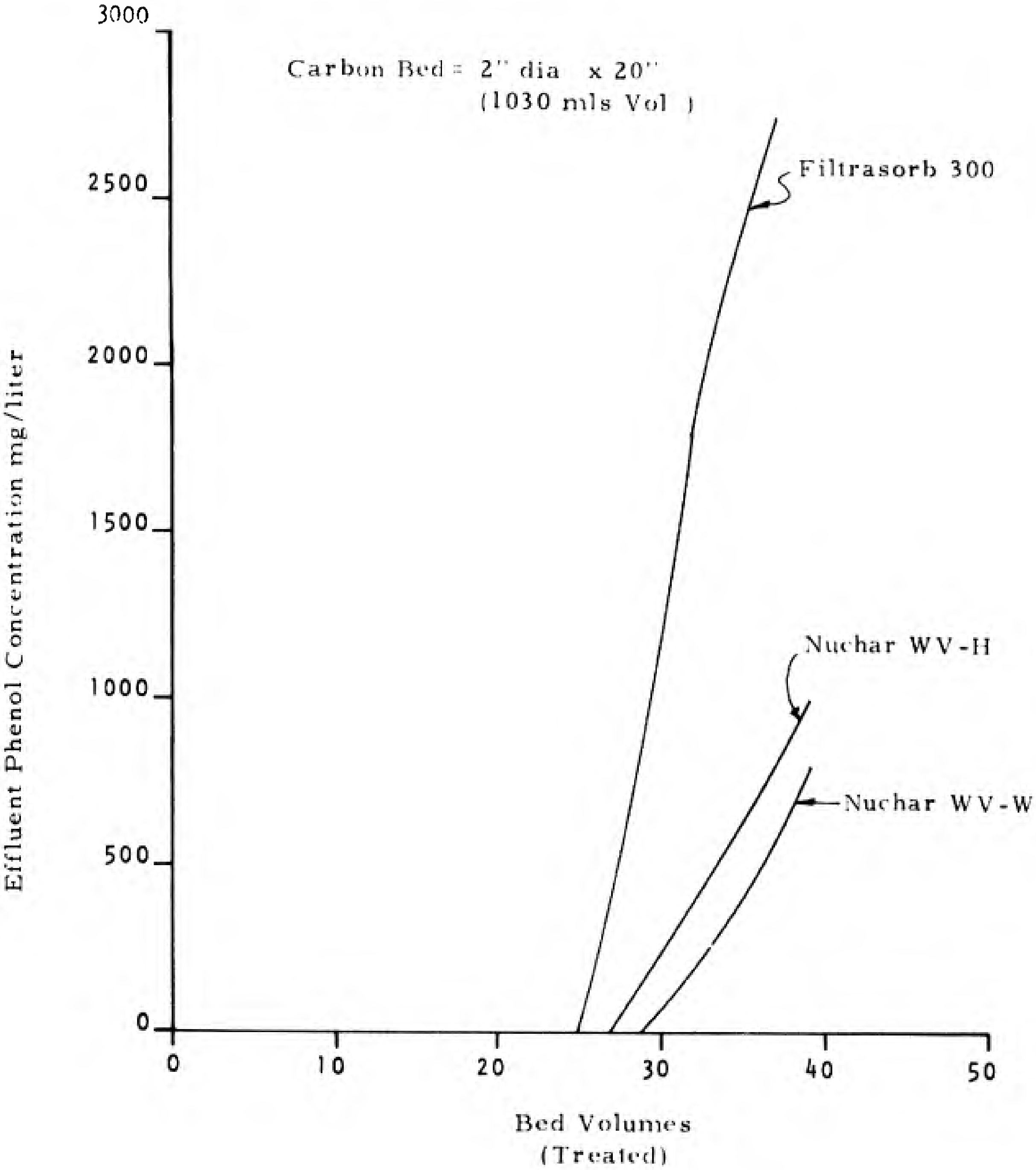

Figure 8. Phenol Breakthrough Curves (Flow Rate 17 Milliliters Per Minute)

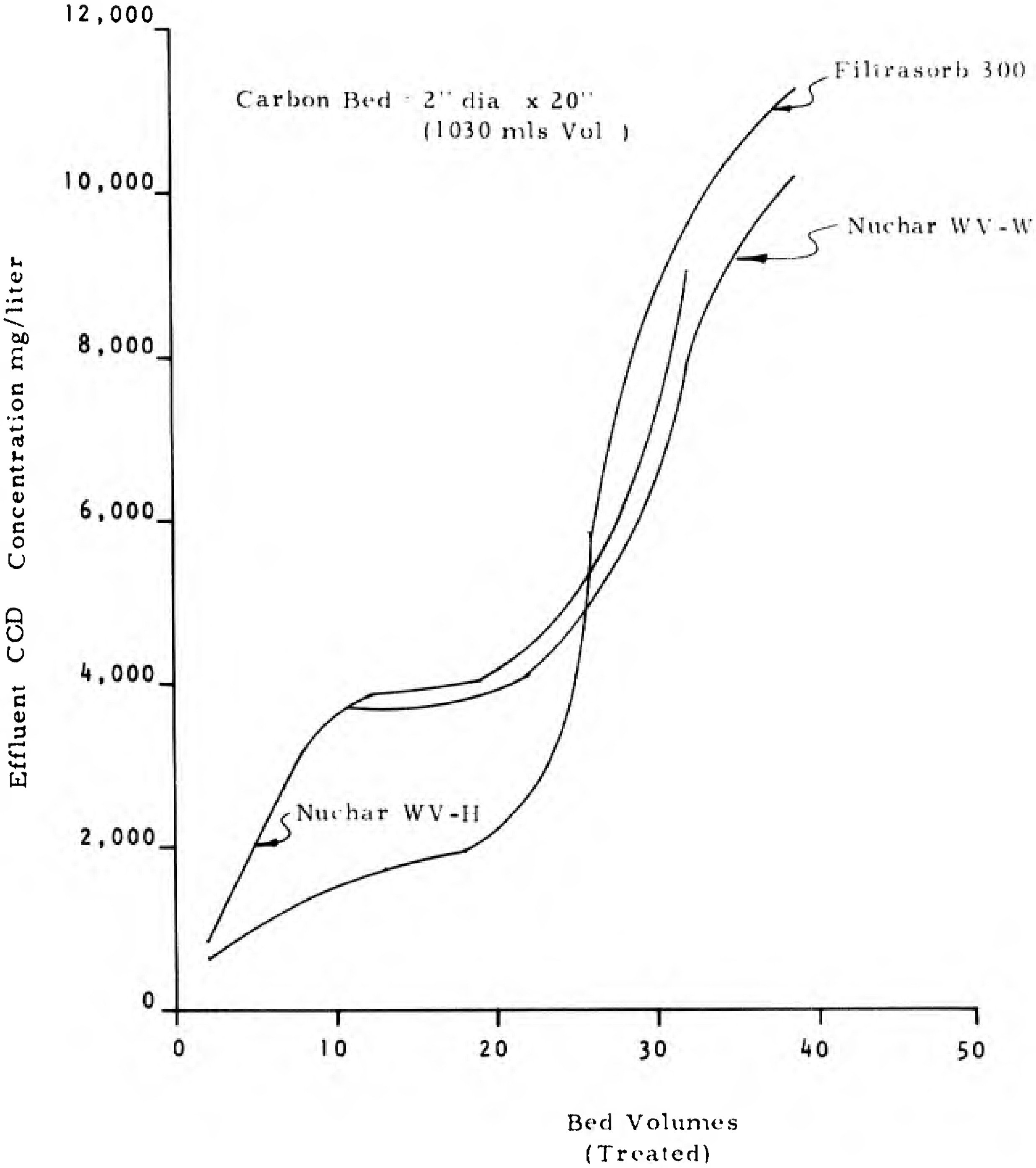

Figure 9. COD Breakthrough Curves (Flow Rate 17 Milliliters Per Minute)

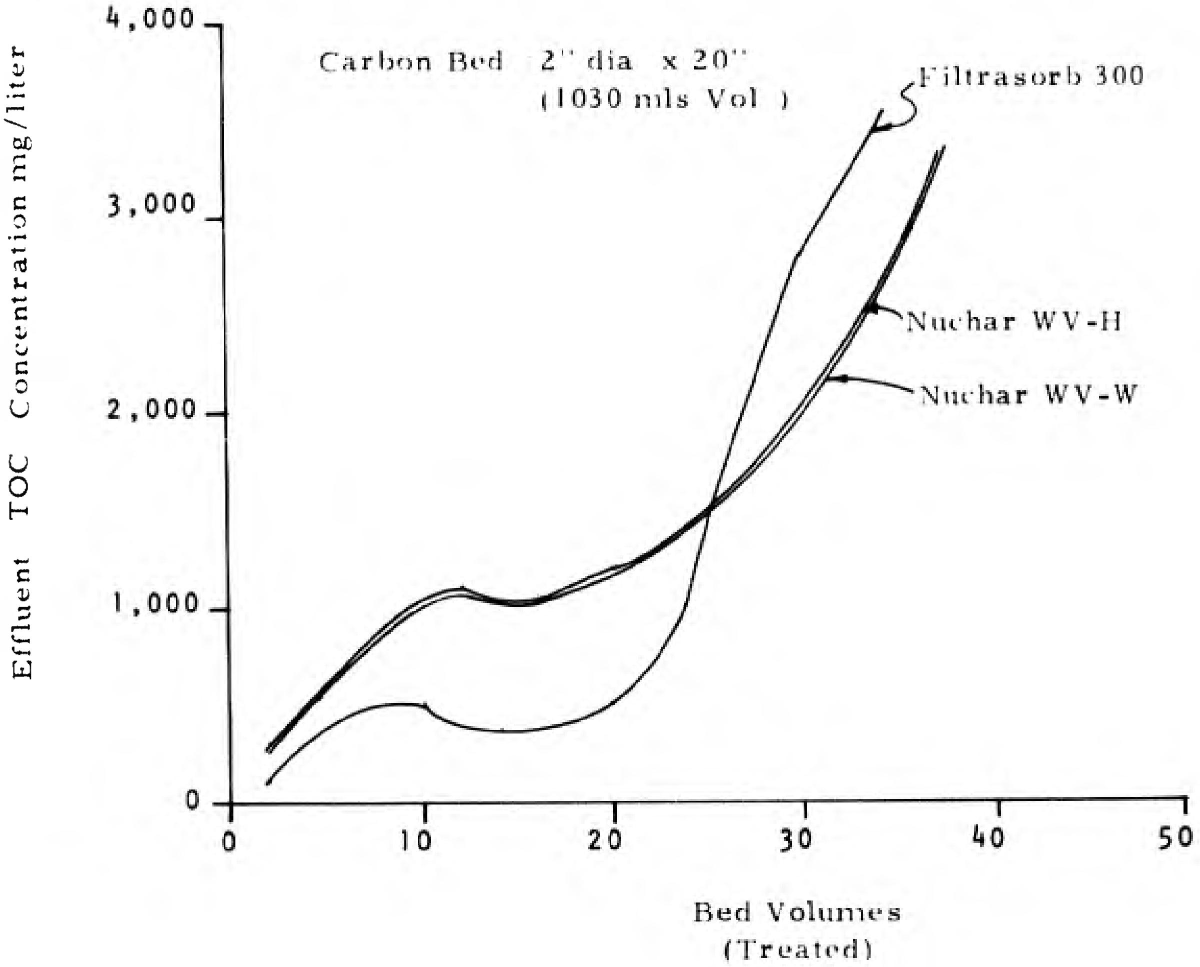

Figure 10. TOC Breakthrough Curves (Flow Rate 17 Milliliters Per Minute)

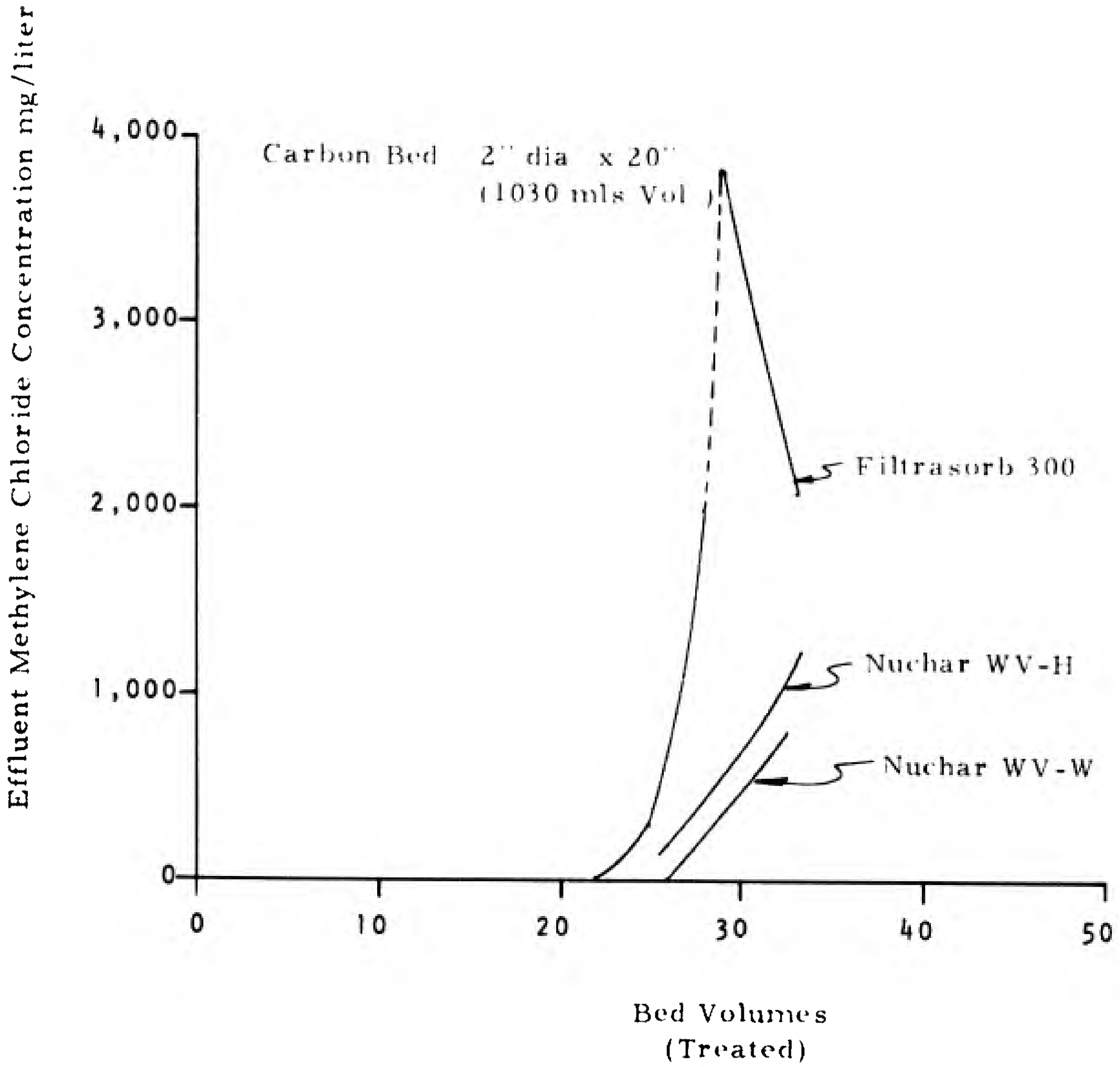

Figure 11. Methylene Chloride Breakthrough Curves
(Flow Rate 17 Milliliters Per Minute)

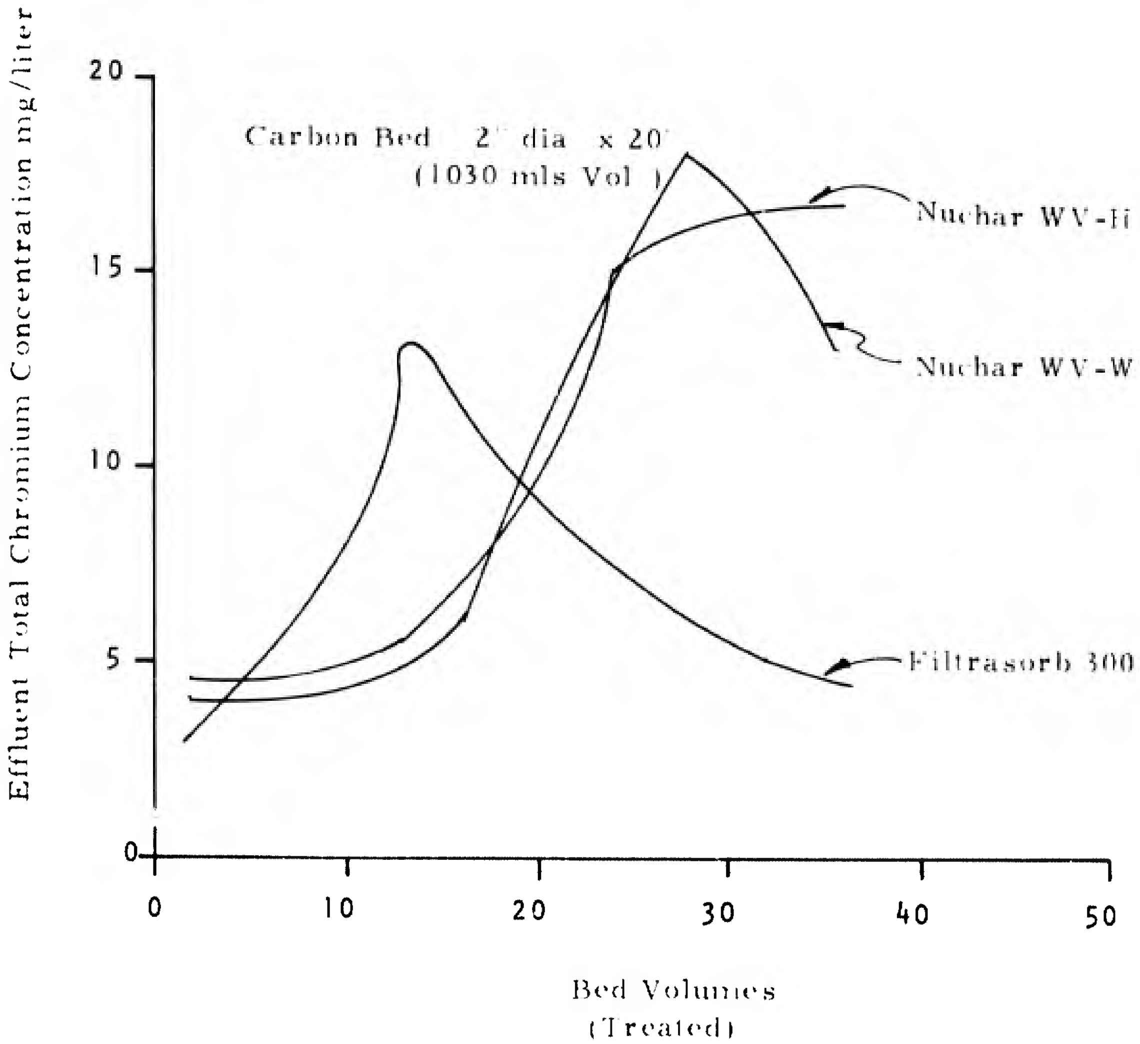

Figure 12. Total Chromium Breakthrough Curves
(Flow Rate 17 Milliliters Per Minute)

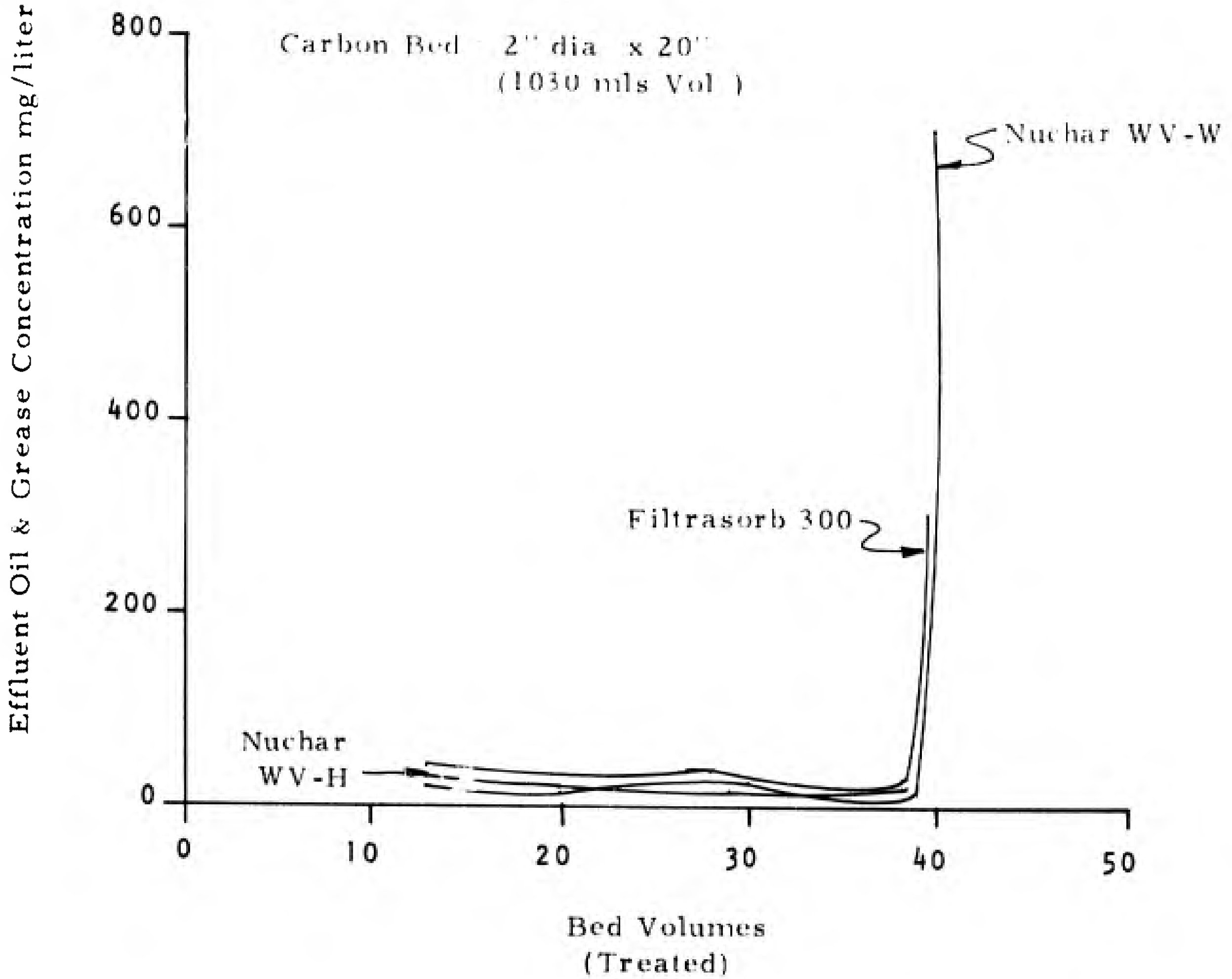

Figure 13. Oil and Grease Breakthrough Curves
(Flow Rate 17 Milliliters Per Minute)

wastewater could have been treated before the chromium breakthrough point was reached. Filtrasorb 300, on the other hand, showed a relatively rapid rate of leakage during the first 18 to 20 bed volumes. After treating 15 bed volumes, however, this system exhibited a sudden renewed capacity for total chromium.

Breakthrough curves for oil and grease are shown in Figure 13. All three carbons performed in a similar manner and all exhibit only a small amount of oil and grease retention throughout the entire contamination run. Between 37 and 39 bed volumes, however, a very rapid increase in effluent oil and grease level occurred for both Nuchar WV-W and Filtrasorb 300 columns. This probably resulted from the sudden dumping of the entrained oil and grease (this component appeared to be poorly adsorbed by the carbon). It is probable that, had the sampling period been extended, Nuchar WV-H would have exhibited a similar increase in effluent oil and grease. The effluent pH from each carbon column was monitored but, in all cases, showed only a negligible difference compared to the influent value. Therefore, this parameter is not graphically represented.

Column Tests No. 2 and No. 3

Using the same apparatus, two additional continuous flow column experiments were performed, each at different flow rates. They were 34 milliliters per minute and 68 milliliters per minute, which represent a 30-minute residence time (hydraulic loading of 0.412 gpm/ft^2) and a 15 minute residence time (hydraulic loading of 1.214 gpm/ft^2), respectively. As before, virgin carbon was used for each test. Figures 14 through 25 show the breakthrough curves for each of these column tests.

It should be noted that, although Filtrasorb 300 is similar in mesh size to both the Nuchar carbons tested, the Filtrasorb column showed a buildup in suspended matter during the latter two column evaluations. In the case of the 34-milliliter-per-minute column test, this solids buildup resulted in a continuous pressure drop and an effluent flow reduction which had to be compensated for by increasing the influent flow rate. In the case of the 68-milliliter-per-minute column test, suspended matter built up within the carbon bed to such an extent that this run had to be discontinued after 22 bed volumes throughput. The net result of these plugging problems rendered the Filtrasorb 300 column data both questionable and incomplete for both the second and third experiments. For this and other reasons, the use of Filtrasorb in the pilot plant study was ruled out. The reason for the performance of this carbon with respect to solids buildup is not known; however, it was felt that the granular shape of this material is slightly more irregular and jagged than either of the Nuchar carbons. This property may make it easy for solids to cling to the carbon granule and, subsequently, accumulate to plug the column.

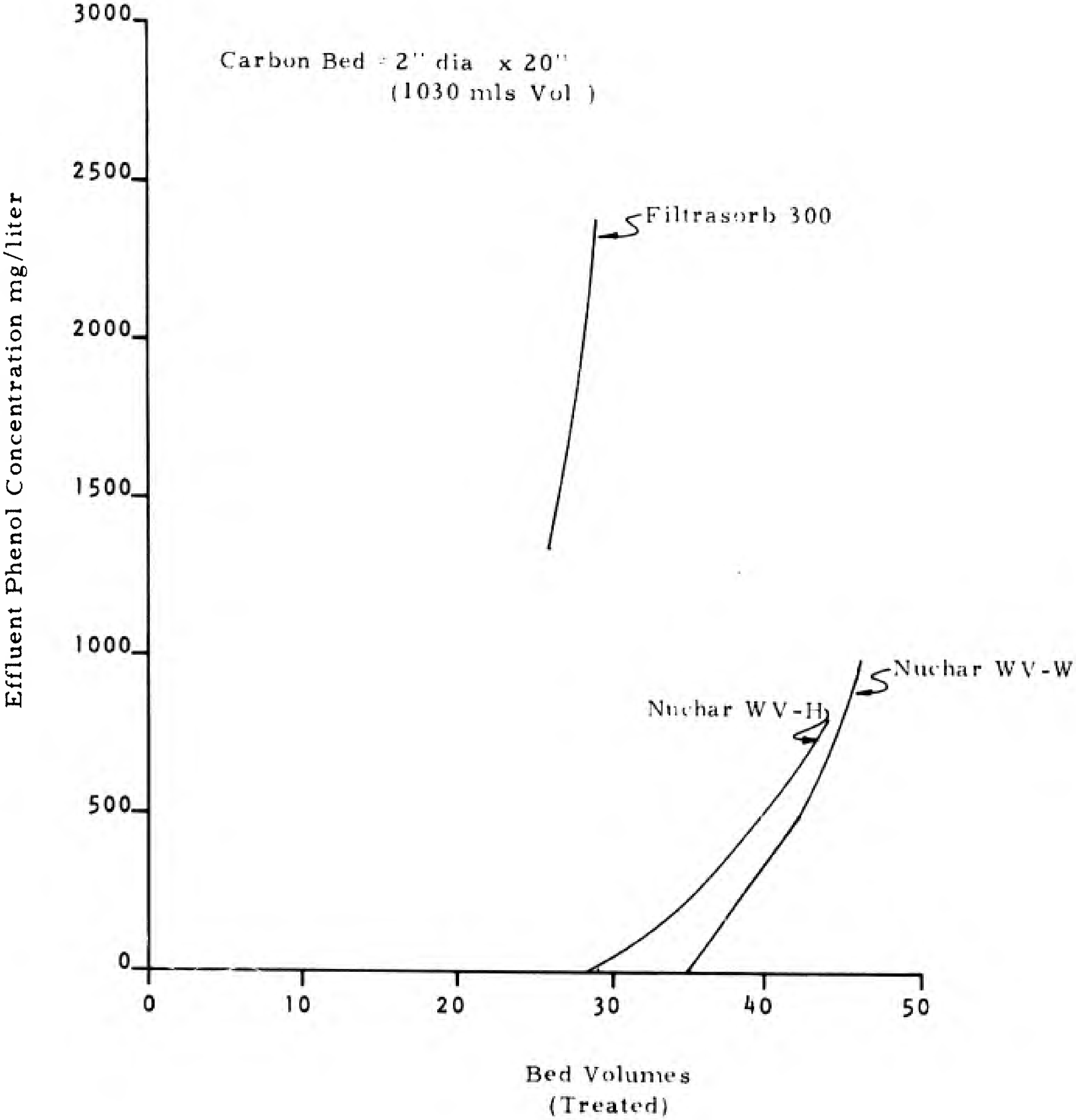

Figure 14. Phenol Breakthrough Curves
(Flow Rate 34 Milliliters Per Minute)

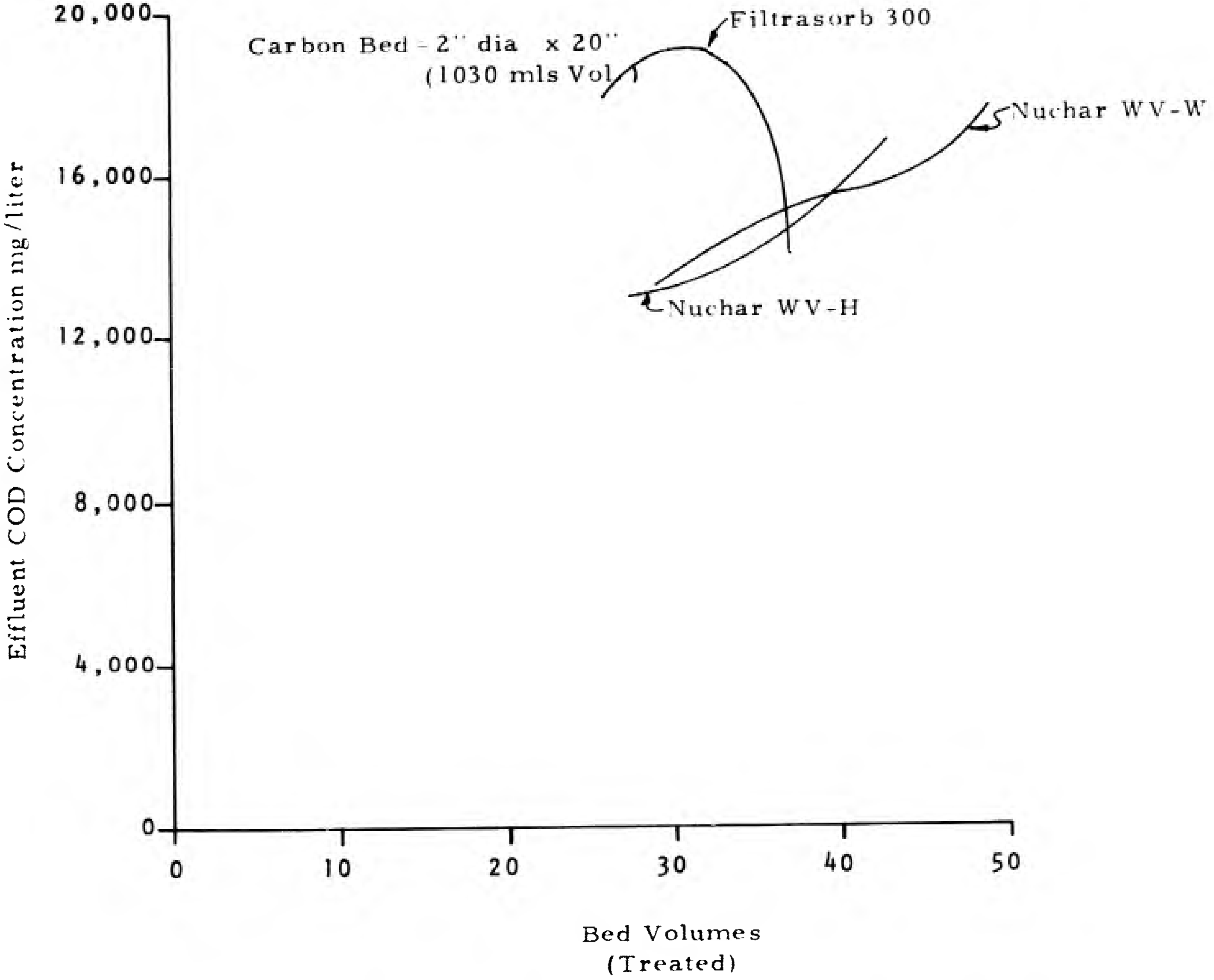

Figure 15. COD Breakthrough Curves (Flow Rate 34 Milliliters Per Minute)

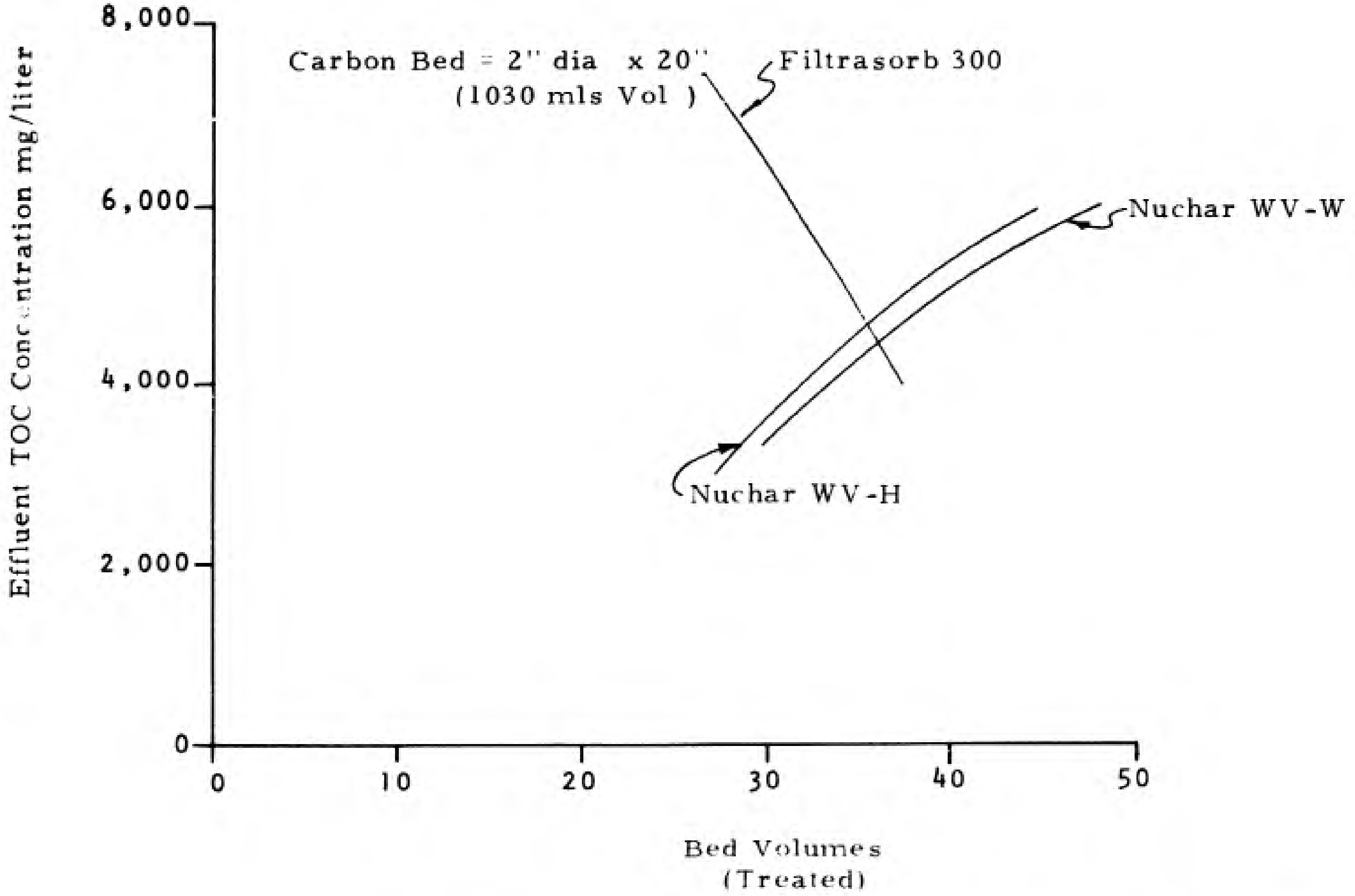

Figure 16. TOC Breakthrough Curves (Flow Rate 34 Milliliters Per Minute)

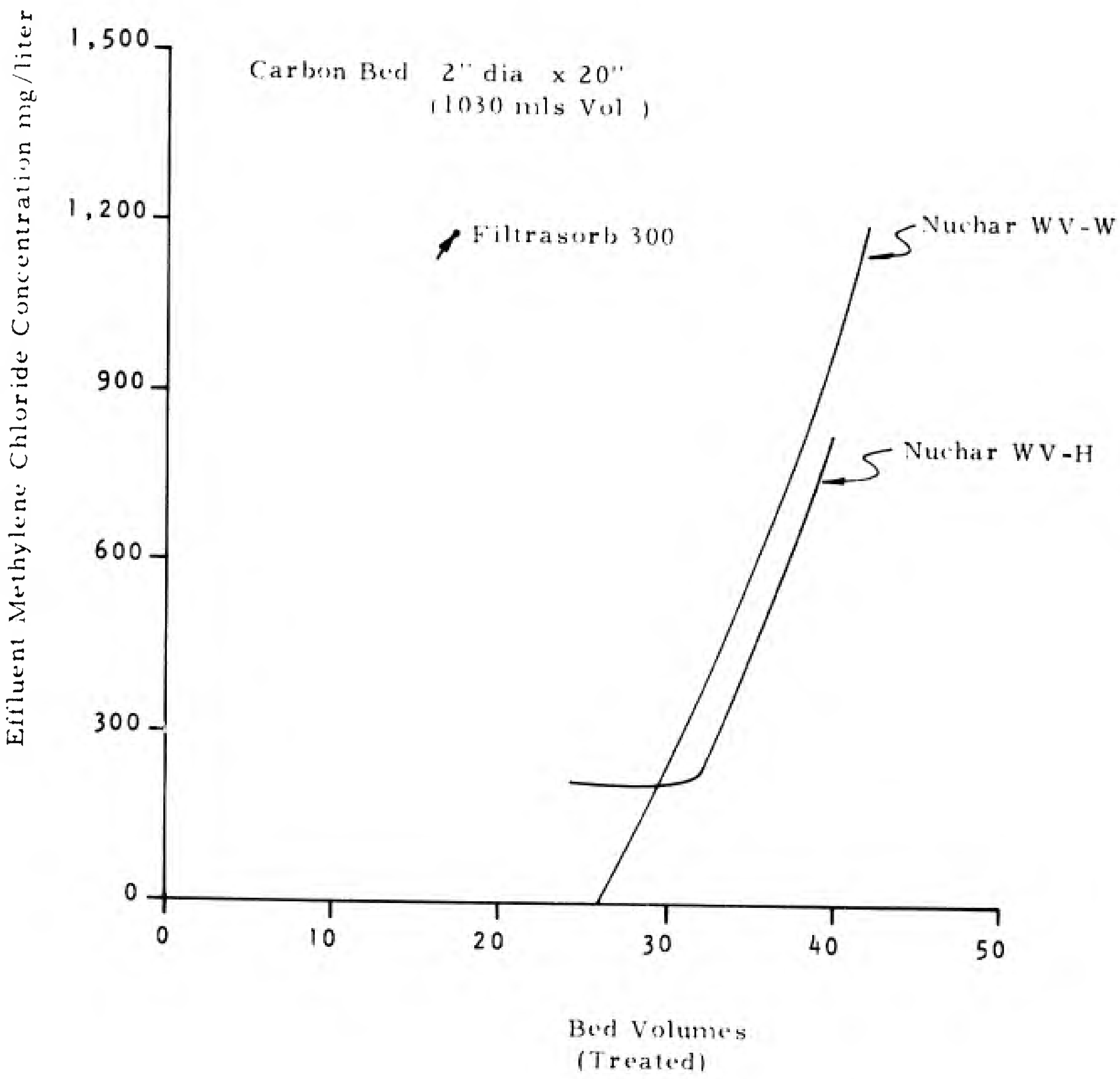

Figure 17. Methylene Chloride Breakthrough Curves
(Flow Rate 34 Milliliters Per Minute)

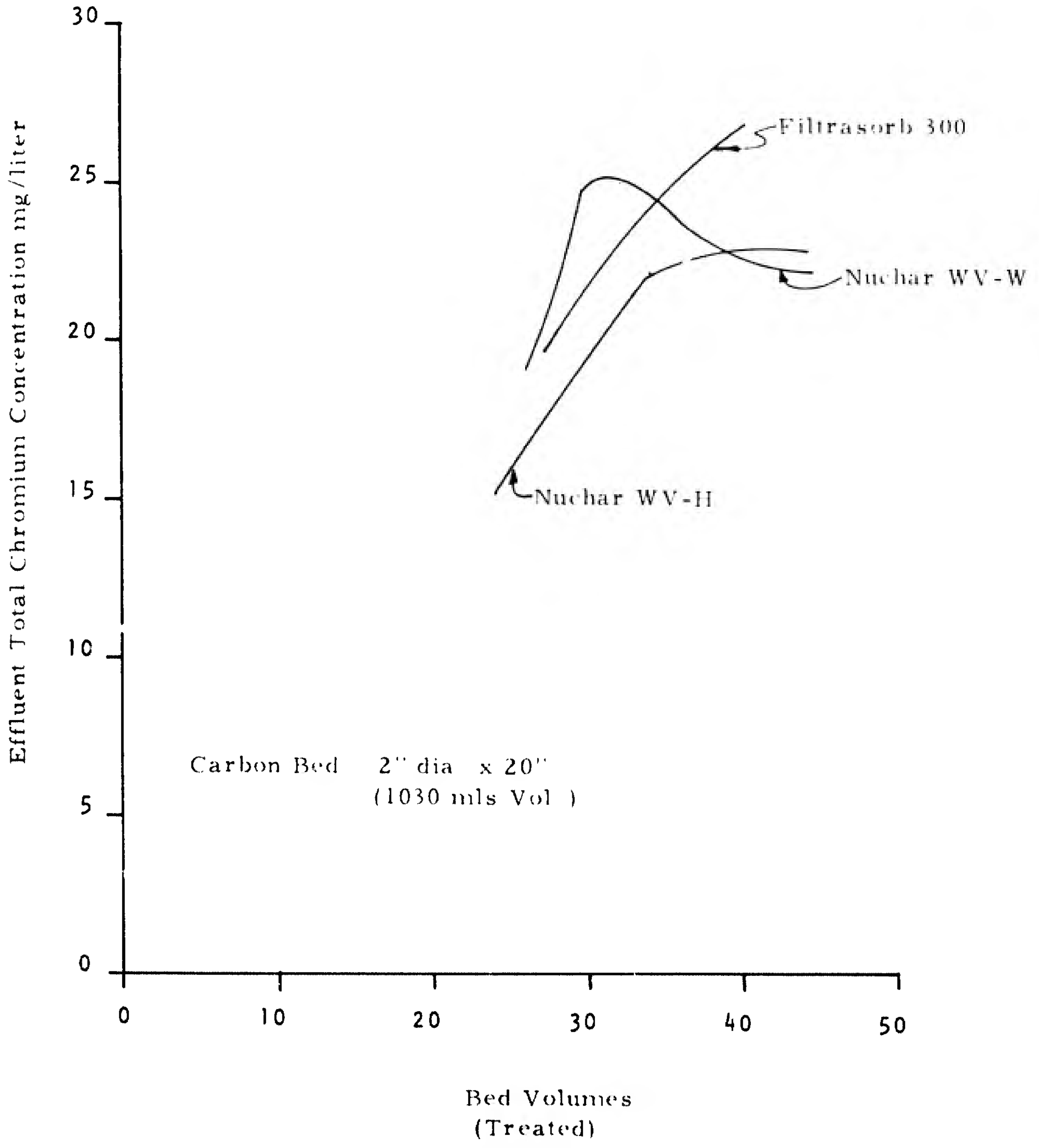

Figure 18. Total Chromium Breakthrough Curves
(Flow Rate 34 Milliliters Per Minute)

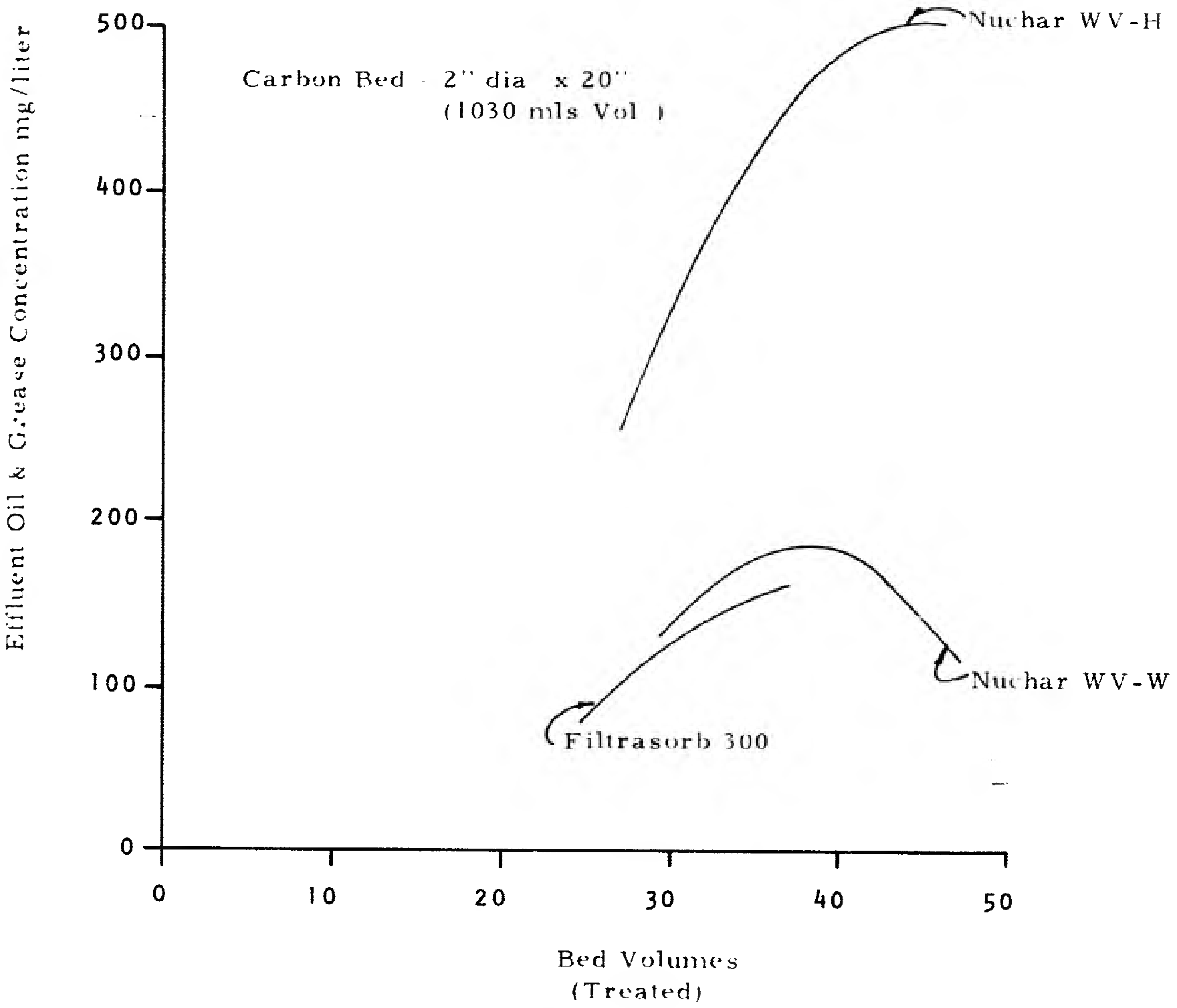

Figure 19. Oil and Grease Breakthrough Curves (Flow Rate 34 Milliliters Per Minute)

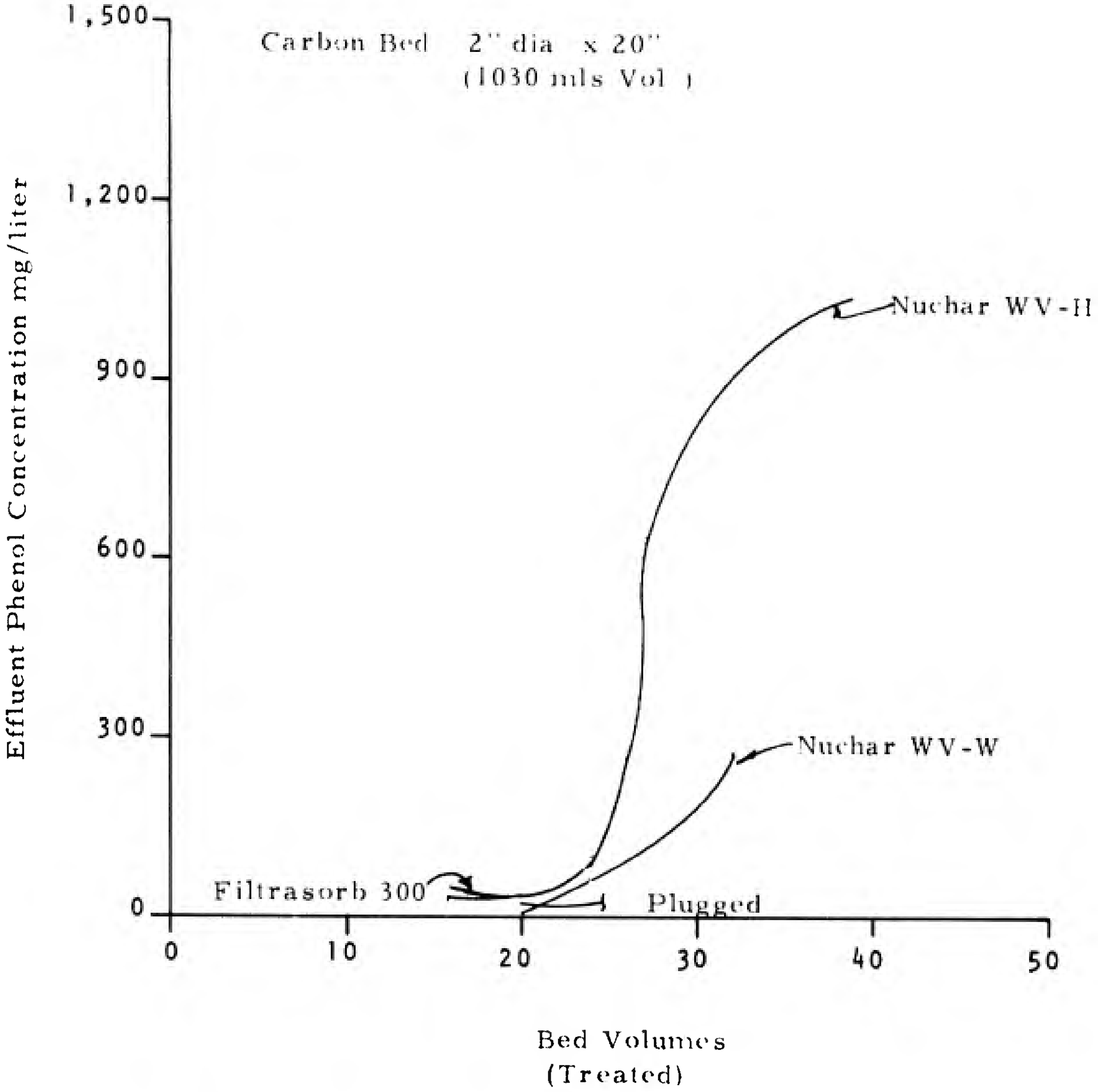

Figure 20. Phenol Breakthrough Curves (Flow Rate 68 Milliliters Per Minute)

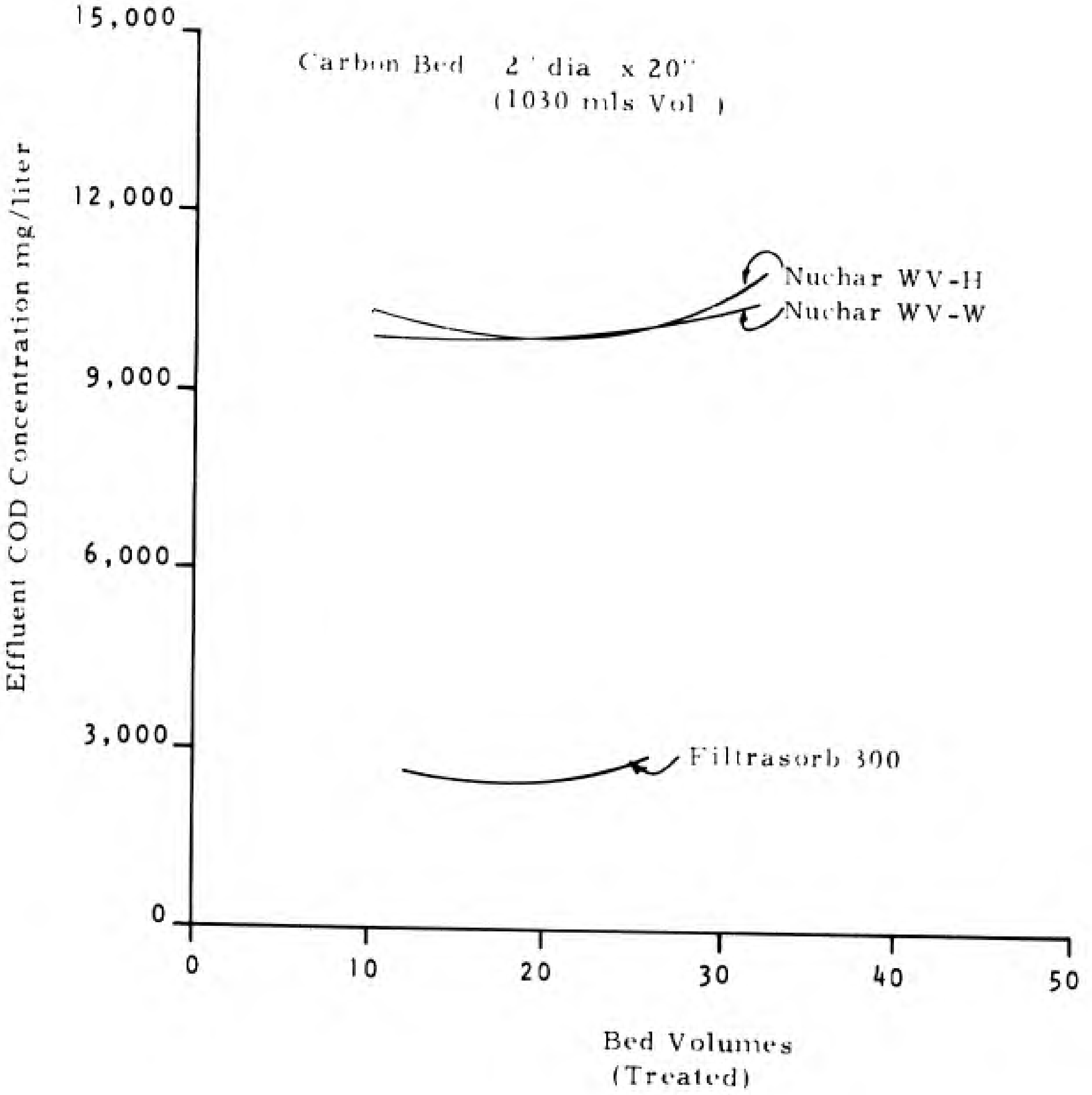

Figure 21. COD Breakthrough Curves (Flow Rate 68 Milliliters Per Minute)

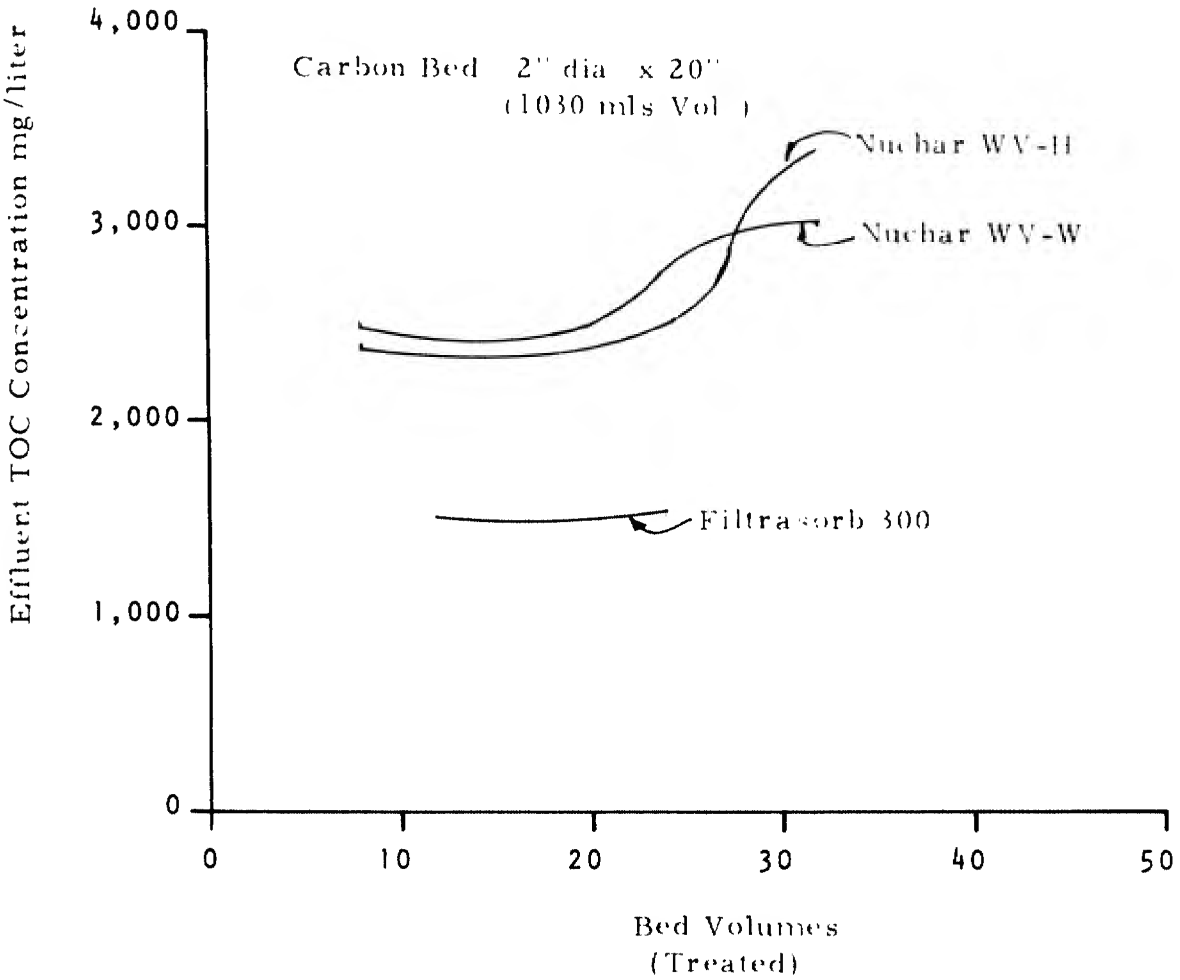

Figure 22. TOC Breakthrough Curves (Flow Rate 68 Milliliters Per Minute)

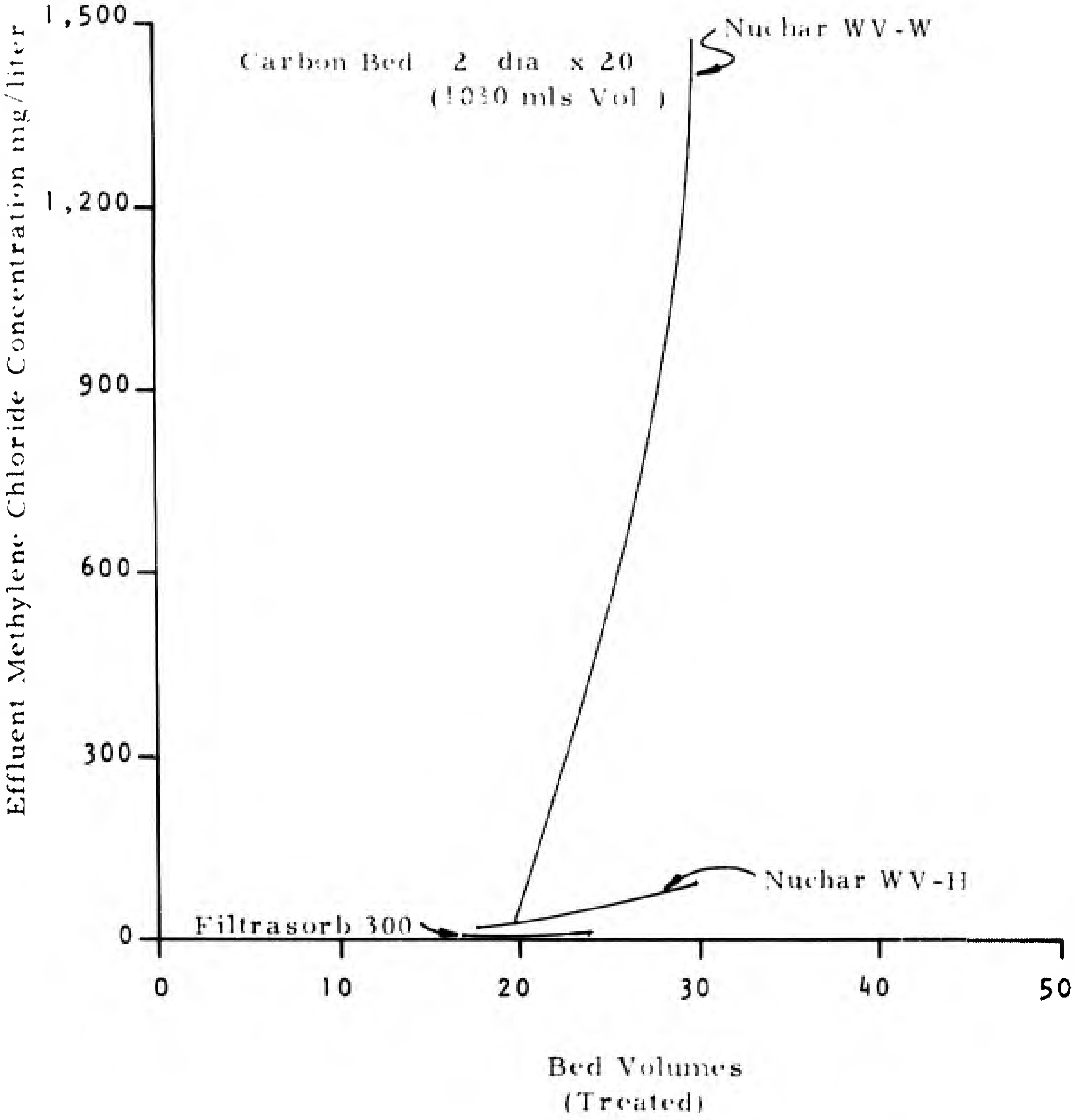

Figure 23. Methylene Chloride Breakthrough Curves
(Flow Rate 68 Milliliters Per Minute)

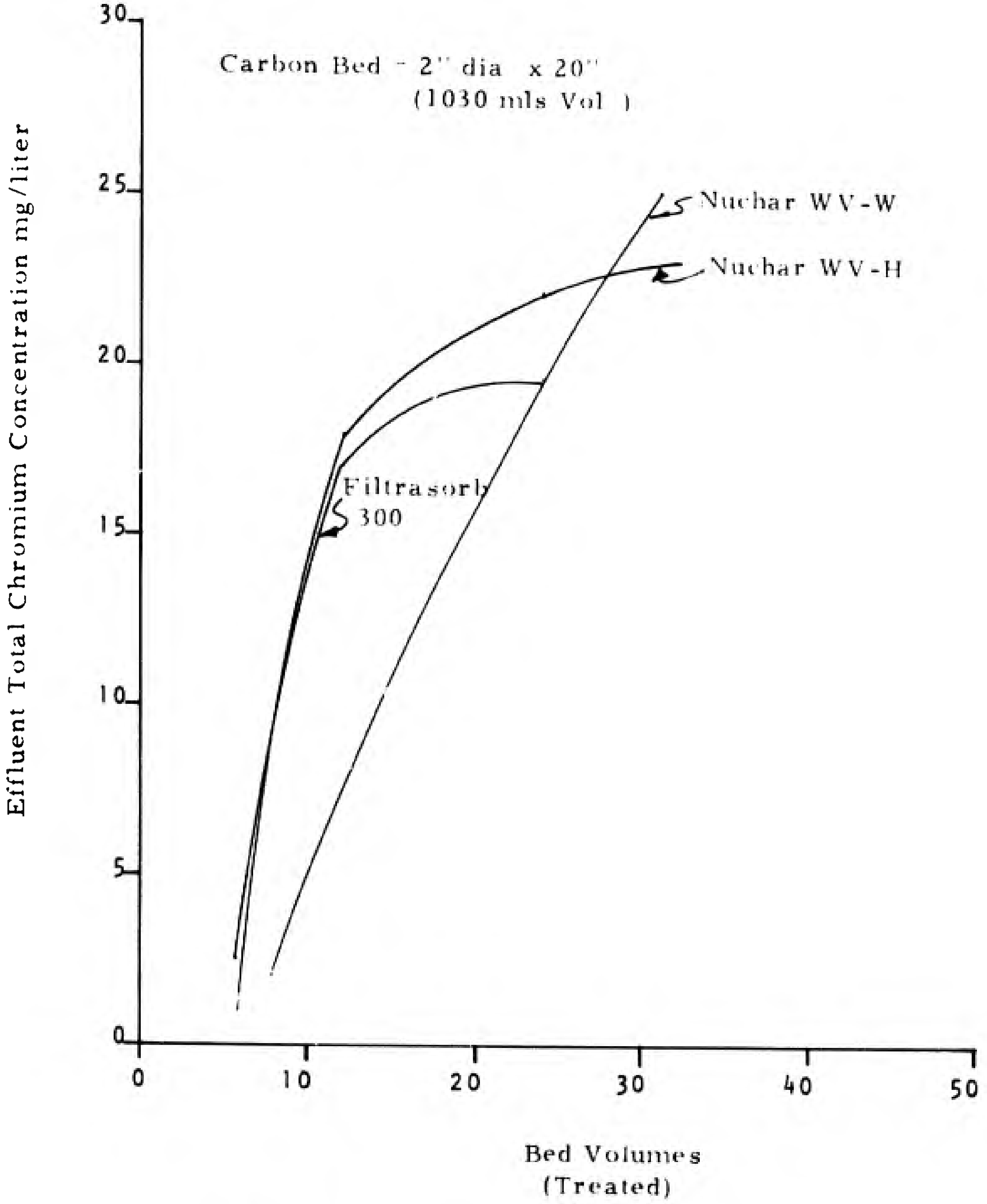

Figure 24. Total Chromium Breakthrough Curves (Flow Rate 68 Milliliters Per Minute)

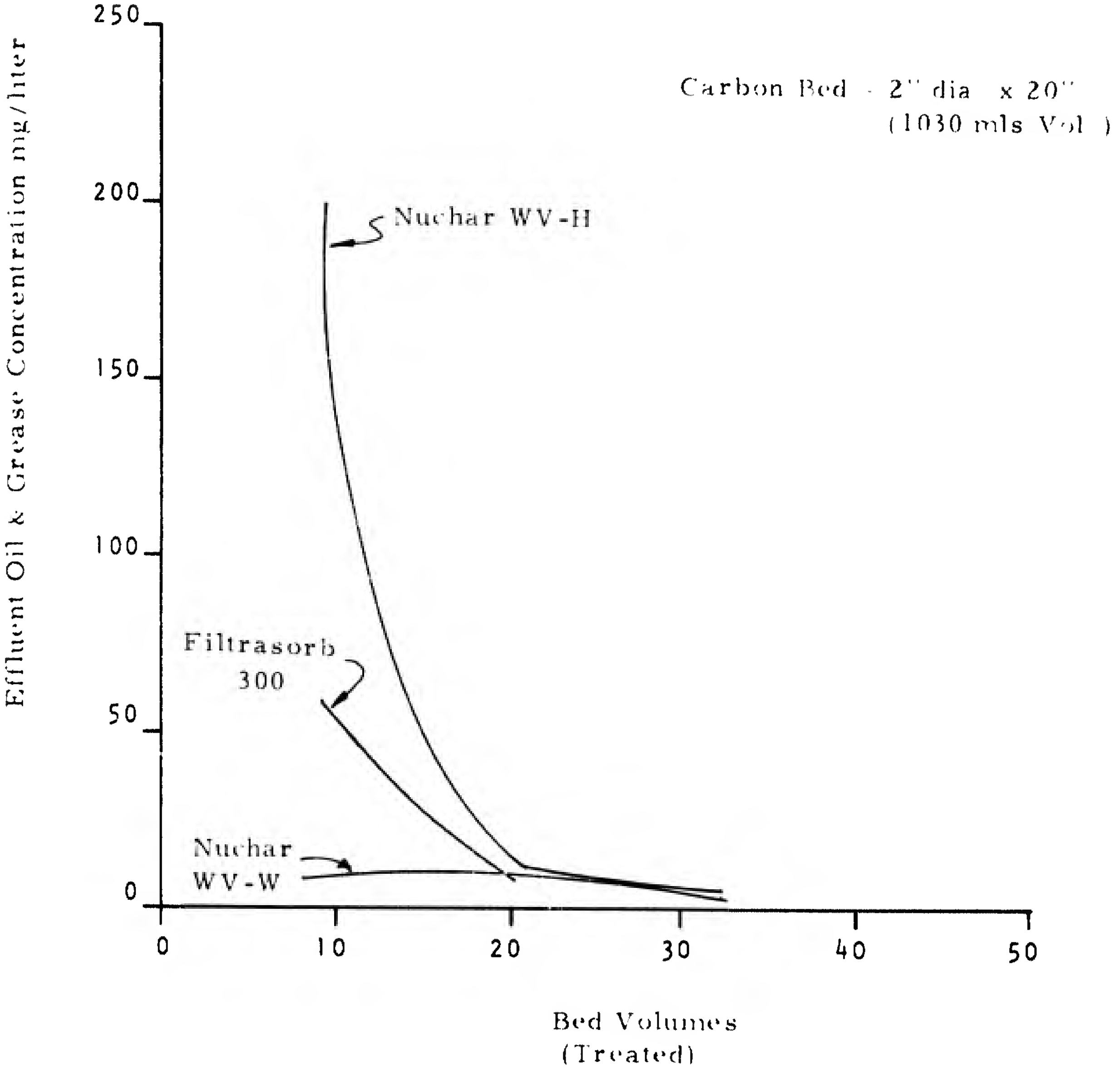

Figure 25. Oil and Grease Breakthrough Curves
(Flow Rate 68 Milliliters Per Minute)

As can be seen in Figure 14, the rate of phenol breakthrough for the Nuchar carbons was not as rapid during the 34-milliliter-per-minute column test as it was during the 17 milliliters per minute column test. For example, the effluent phenol concentration for Nuchar WV-W at 17 milliliters per minute was 1,000 milligrams per liter at 40 bed volumes (by extrapolation), while for the 34 milliliters per minute flow test, 46 bed volumes of waste were treated before the effluent concentration was at that level. This is probably because phenol is less dependent on the residence time than some of the other adsorbable organics in the wastewater. For example, as the flow was increased, some of the other organics were adsorbed less efficiently, as can be seen by the rapid breakthrough for COD and TOC (Figures 15 and 16). At 68 milliliters per minute flow rate (Figure 20), the effluent phenol concentration increased more rapidly relative to throughput than during the previous two runs. It was assumed that this residence time was too short for optimum phenol removal at this concentration. This same reasoning appears to be true in terms of methylene chloride removal (Figure 23).

Total chromium removal was slightly more effective during the first column test (17 milliliters per minute) than during either of the other two tests (34 milliliters per minute and 68 milliliters per minute). Here again, residence time may be an important factor.

The shape of the oil and grease breakthrough curves for both of the latter two column tests might be due to the retention of oil and grease on the carbon particles rather than adsorption. This would result in a periodic dumping after a given capacity was reached.

Column Test No. 4

The results indicate that Nuchar WV-W was the most effective carbon tested in terms of phenol removal. To determine if slightly acid conditions would improve the amount of phenol adsorbed by this material, the pH of the waste was adjusted to 4.9 with H_2SO_4. This wastewater was then passed through a bed of Nuchar WV-W at 17 milliliters per minute in the same manner as before. The breakthrough curves for this experiment are represented in Figures 26 through 31.

It appears from these results that an acid pH had no apparent effect on phenol removal, i.e., the run made at 17 milliliters per minute with no pH adjustment (Figures 8 through 13) show almost identical breakthrough curves for Nuchar WV-W. There was, however, a slight improvement in the degree of COD, TOC and methylene chloride removal at a pH of 4.9. There was also a notable increase in the level of total chromium removed at this lower pH, but this might have resulted from the solubilization of previous undissolved chromium, thereby making it more available for adsorption.

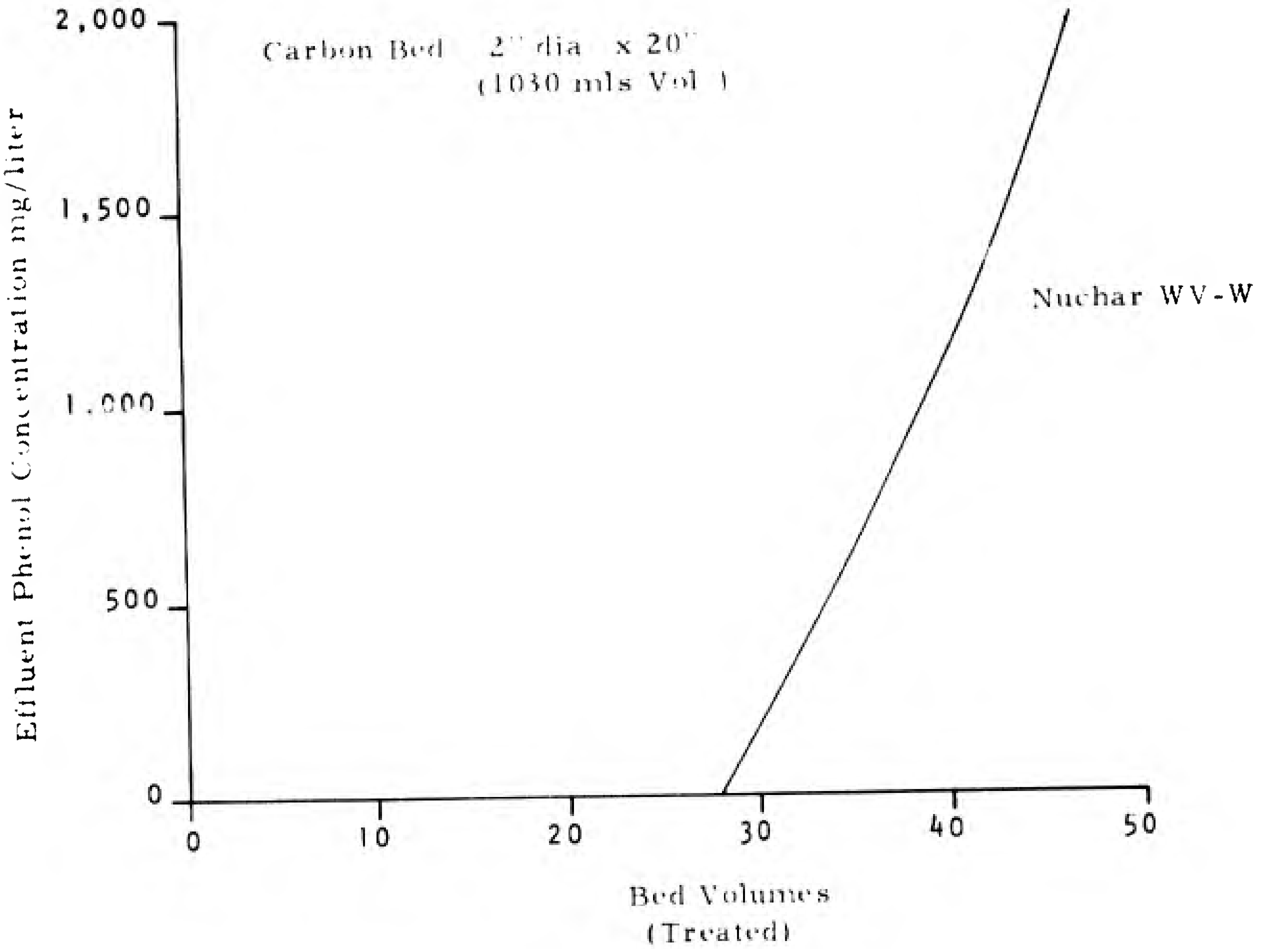

Figure 26. Phenol Breakthrough Curves
(Wastewater pH Adjusted to 4.9 -
Flow Rate 17 Milliliters Per Minute)

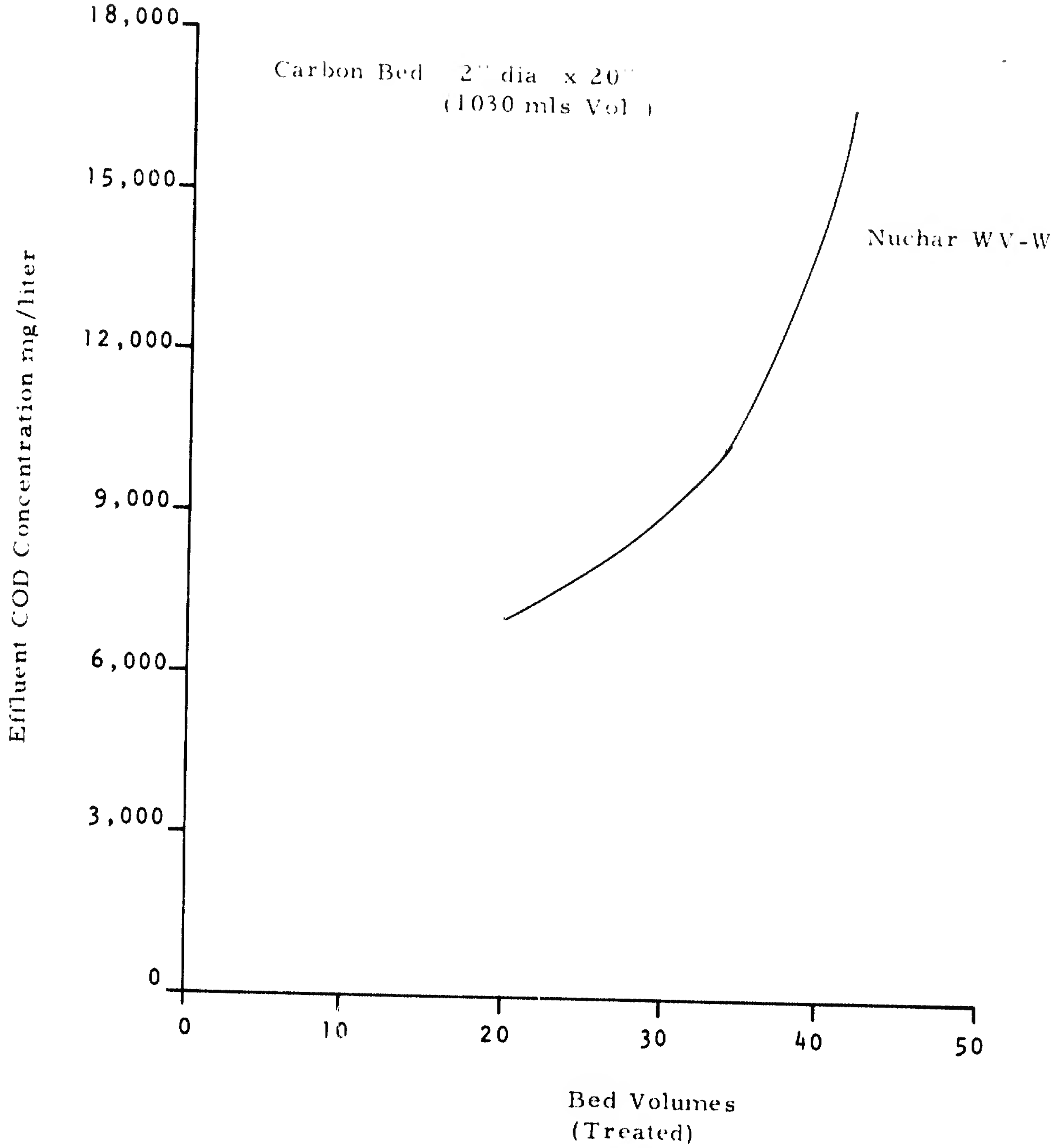

Figure 27. COD Breakthrough Curves
(Wastewater pH Adjusted to 4.9 -
Flow Rate 17 Milliliters Per Minute)

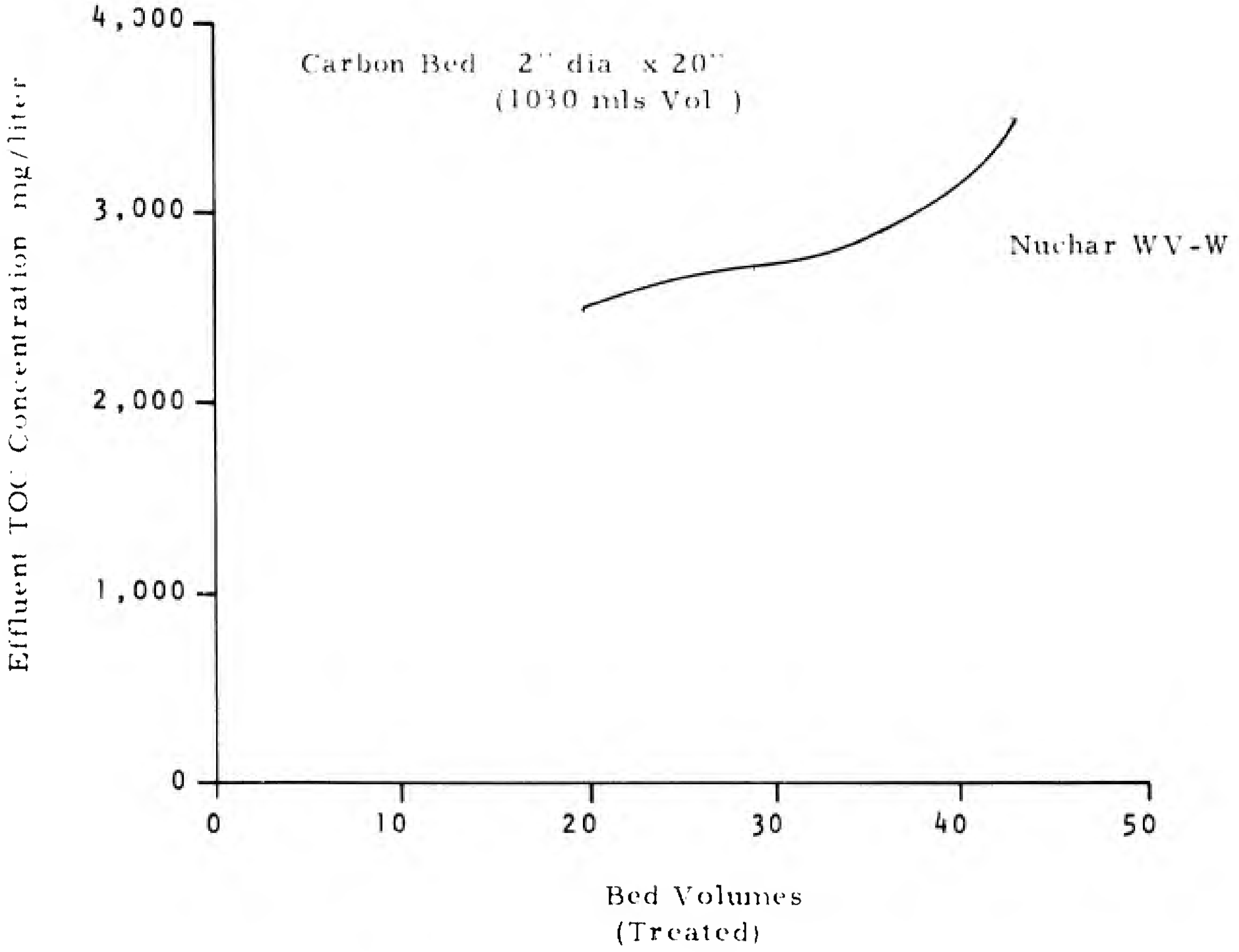

Figure 28. TOC Breakthrough Curves
(Wastewater pH Adjusted to 4.9 -
Flow Rate 17 Milliliters Per Minute)

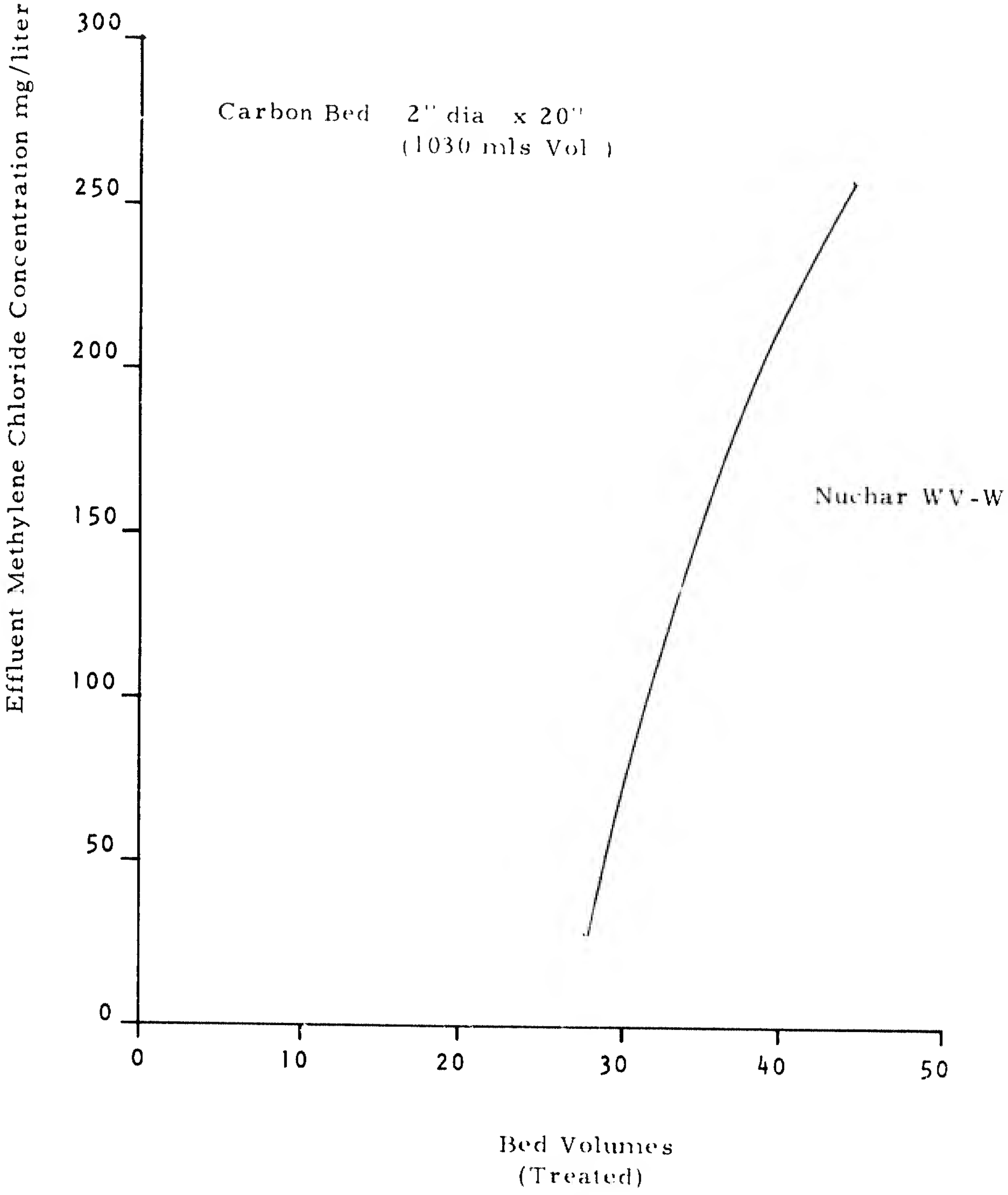

Figure 29. Methylene Chloride Breakthrough Curves
(Wastewater pH Adjusted to 4.9 - Flow Rate 17 Milliliters Per Minute)

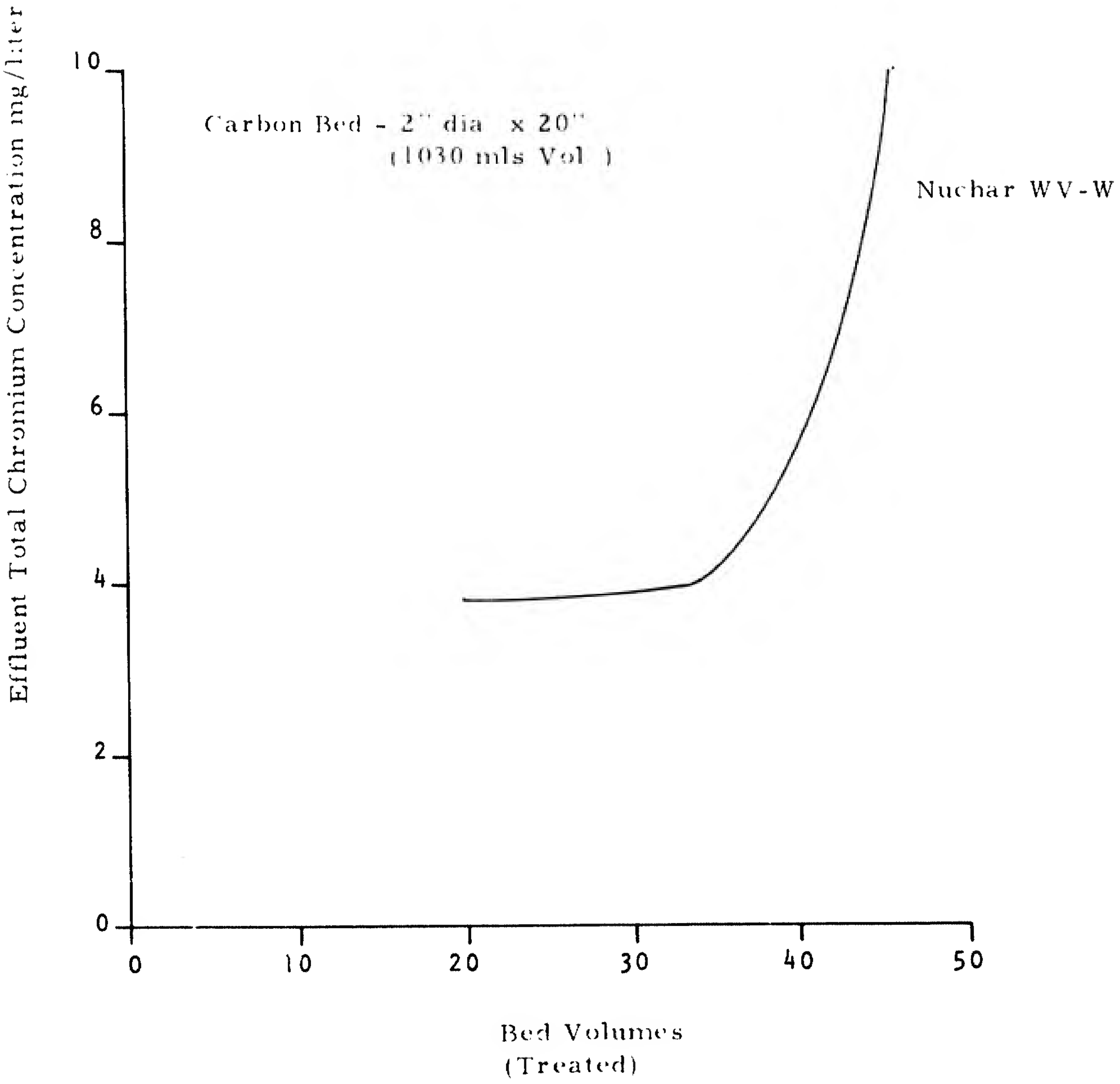

Figure 30. Total Chromium Breakthrough Curves
(Wastewater pH Adjusted to 4.9 - Flow Rate 17 Milliliters Per Minute)

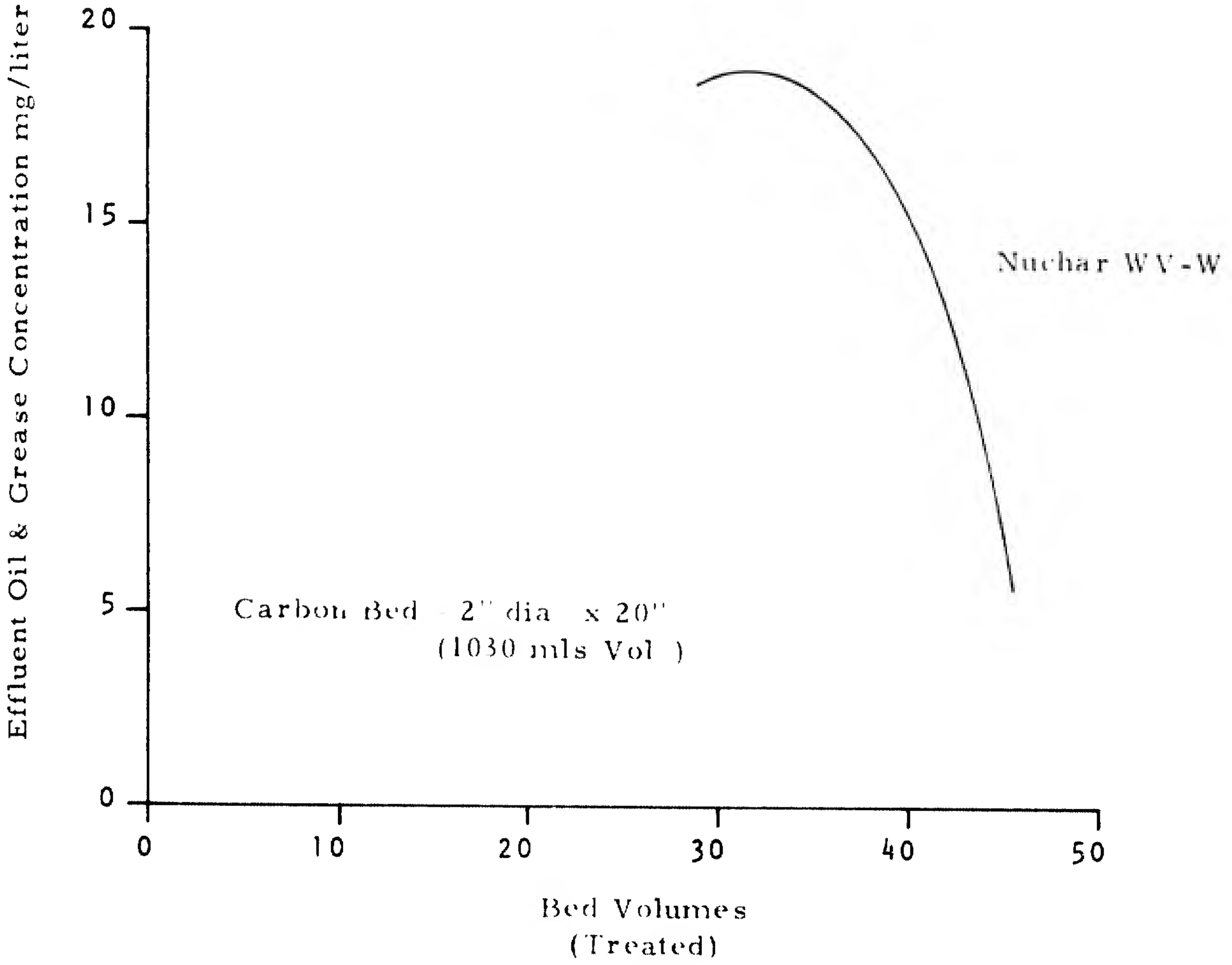

Figure 31. Oil and Grease Breakthrough Curve
(Wastewater pH Adjusted to 4.9 - Flow Rate 17 Milliliters Per Minute)

Carbon Chosen for On-Site Testing

The laboratory results show that, in terms of overall performance, Nuchar WV-W 8 x 30 mesh activated carbon was the best material tested. Accordingly, 133 ft^3 were ordered from the manufacturer, Westvaco of Covington, Virginia, for on-site use.

The properties of Nuchar WV-W are listed in Table 2.

TABLE 2. PROPERTIES OF NUCHAR WV-W GRANULAR CARBON

Iodine Number, Minimum	850
Ash Percent, Maximum	7
Percent Moisture (Packed)	2
Apparent Density (lb/ft^3)	36
Methylene Blue Number	210
Surface Area (m^2/g)	850
Voids in Packed Bed (Percent)	40

SECTION III

ON-SITE TESTING

Equipment and Process Description

The carbon treatment pilot plant was designed to continually treat phenol contaminated wastewater generated during the depainting of aircraft parts. It was located at the south wall of the paint stripping facility, Building 375, Kelly Air Force Base for six months of intermittent field testing. This period ran from 4 September 1974 until the system was turned over to the Air Force on 19 March 1975. The original plan was to operate this pilot plant 16 hours per day, five days per week until carbon exhaustion. However, during the on-site operation this schedule was modified and the system was operated continuously over a 24-hour-per-day period until carbon breakthrough. The basic column design was such that the same residence times could be used during the on-site testing that were used during the laboratory studies.

Figure 32 shows the general floor plan of the paint stripping facility at Kelly Air Force Base and Figures 33 and 34 show aircraft components in the process of being depainted. As noted earlier, the wastewater generated from all the operations taking place within this facility drains into a common trough which runs the length of the stripping area and empties into a pit located at the south wall of the building. From here the waste discharges into a sewer line leading to a trickling filter system. This pit was the source of the wastewater used for the on-site pilot plant operations. A Mobile Laboratory used for conducting various analyses for this on-site phase was located directly outside the building relatively close to the pilot plant location. Figure 35 shows a view of the inside of the Mobile Laboratory and a technician setting up the phenol apparatus.

Figure 36 shows the pit arrangement and modifications which were made to reduce the suspended solids level before the waste entered the carbon bed. The wastewater entering the pit first passed through a square removable basket strainer with 3/4 inch diamond shaped perforations. This removed most of the larger solids and paint chips. A cylindrically shaped unit constructed of 1/4 inch perforated metal was also located in the pit and served to further reduce solids concentration before the wastewater entered the carbon bed. The suction line of the main feed pump (carbon column influent) was located within this cylindrical strainer. This entire scheme was such that if any suspended material passed the first basket strainer, it would either settle out in the pit or be eliminated by the second, finer strainer.

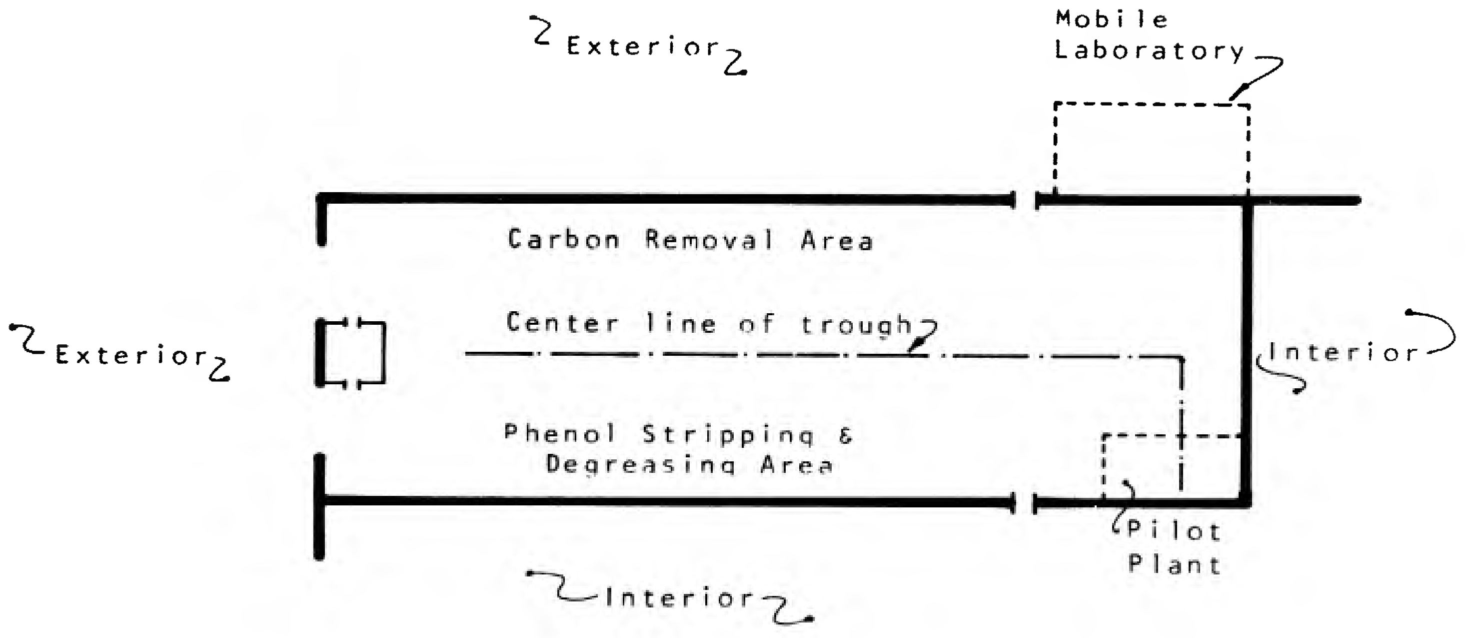

Figure 32. Floor Plan of Paint Stripping Area

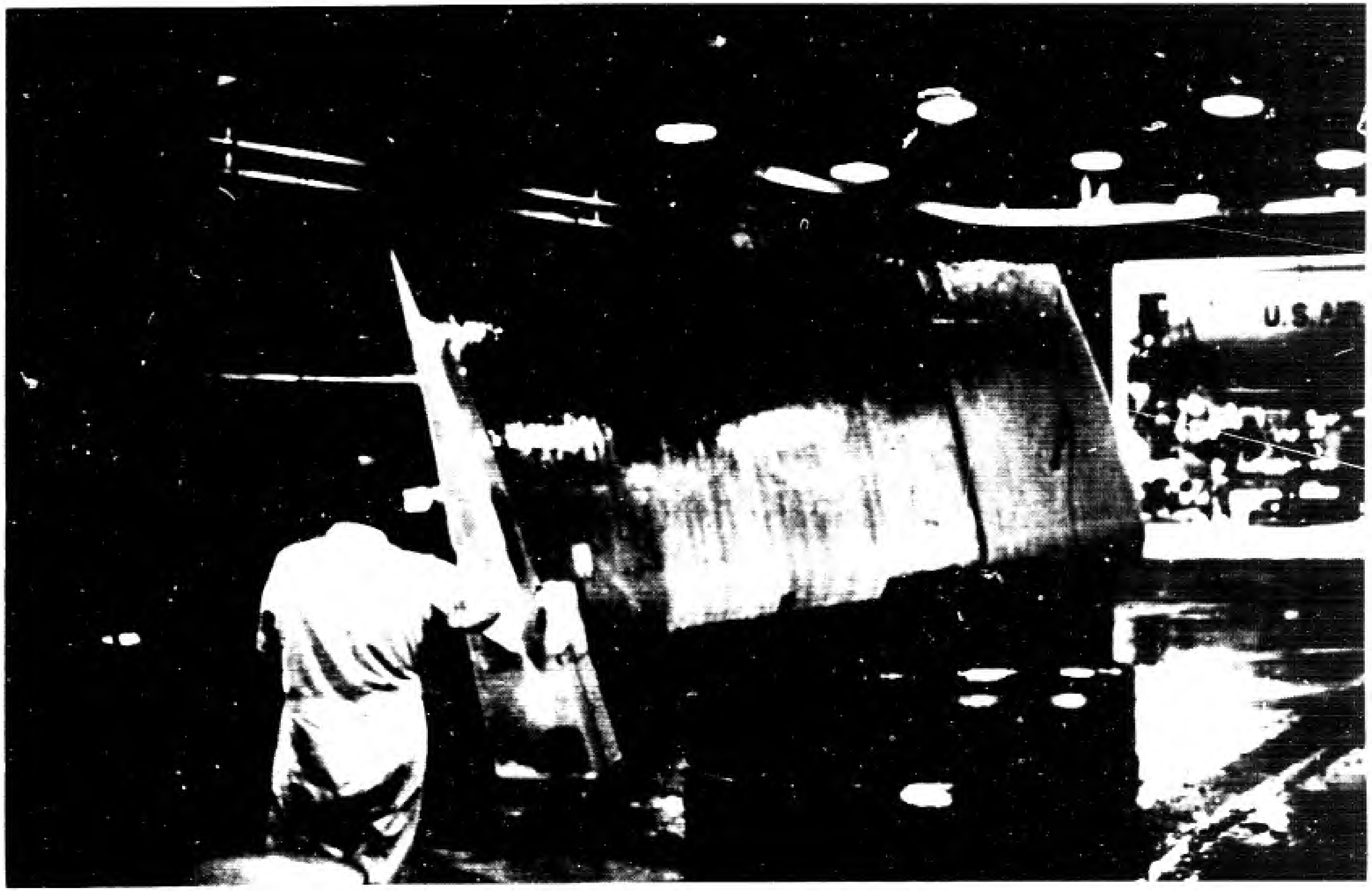

Figure 55. Aircraft Section Being Depainted

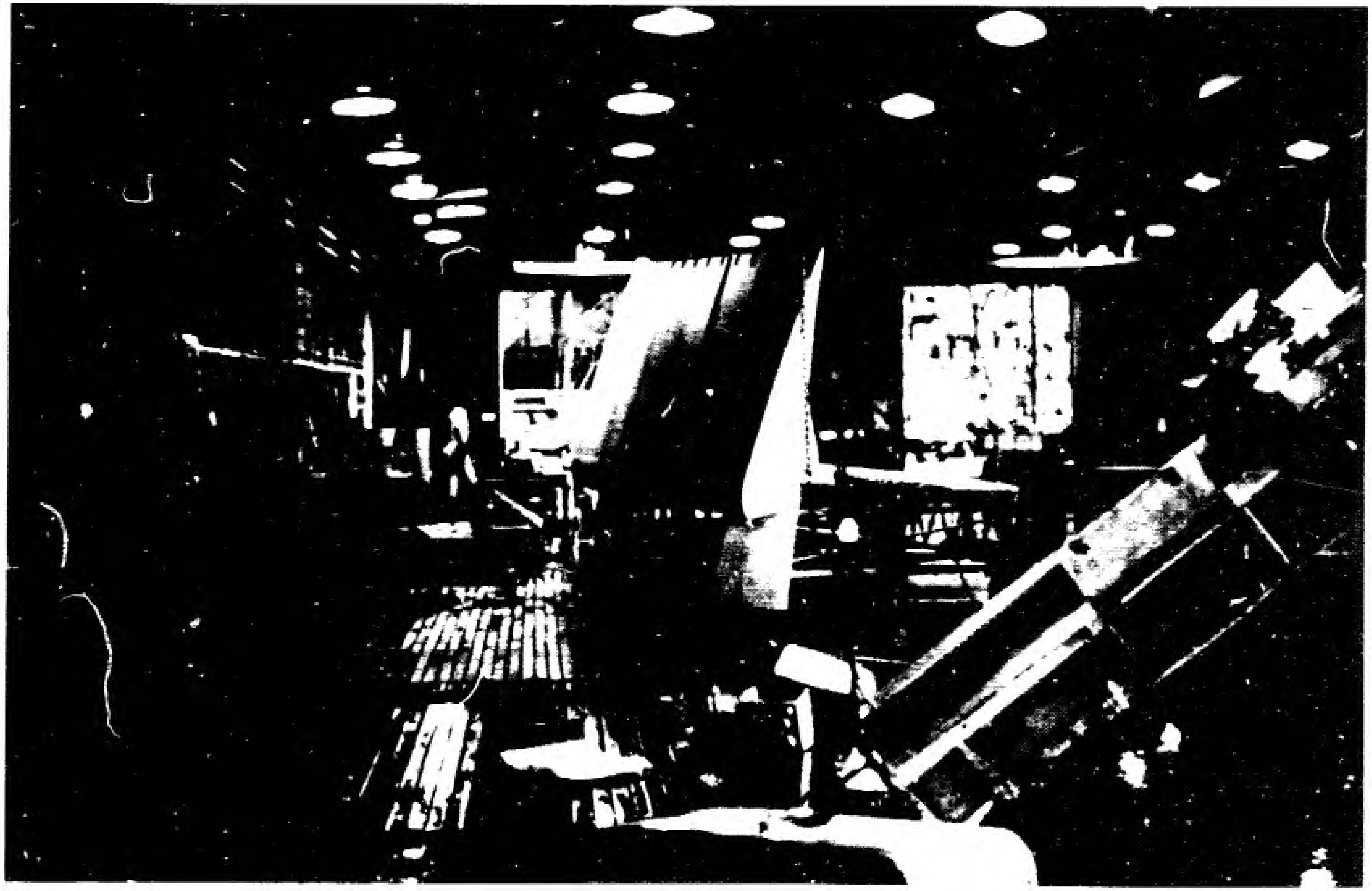

Figure 31. Paint Stripping Facility (Bldg. 375, Kelly AFB)

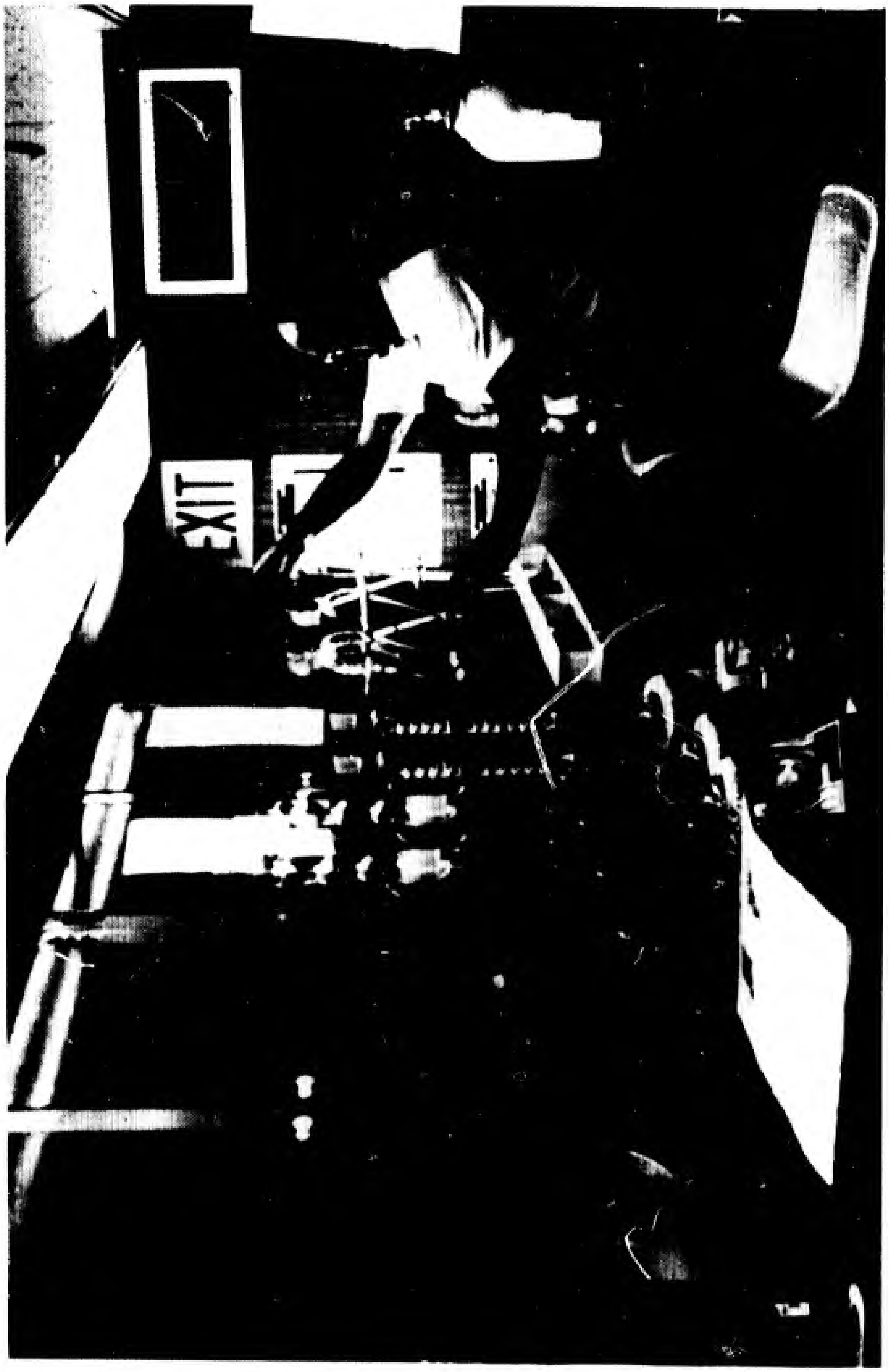

Figure 35. Interior View of Mobile Lab

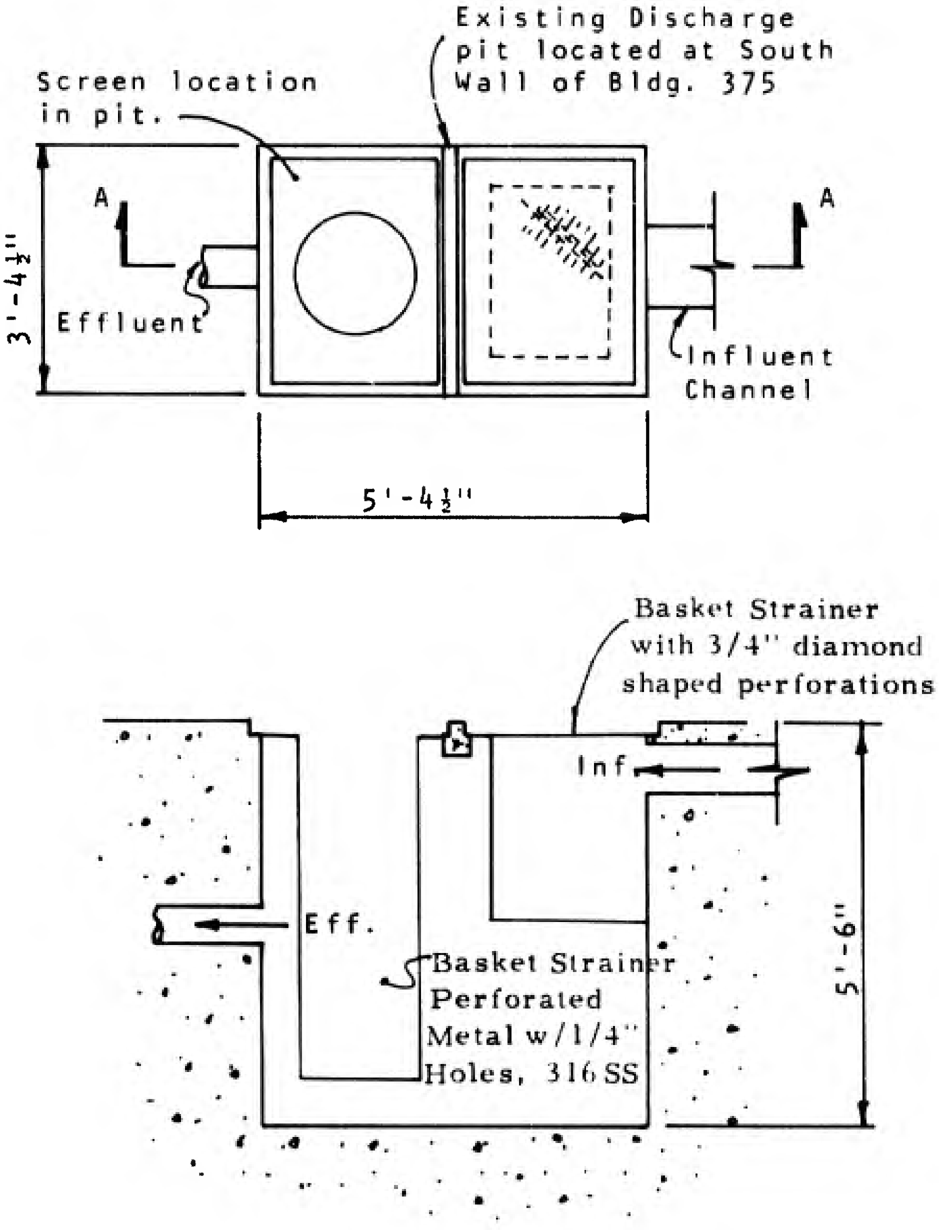

Figure 36. Detail of Discharge Pit

A process schematic of the pilot plant is presented in Figure 37. The wastewater is pumped into a 3,000-gallon-capacity equalization tank by means of a positive displacement pump. From this tank, the wastewater is pumped through a fine in-line basket strainer and flow meter prior to entering the bottom portion of the carbon contactor. Sample ports are located every 12 inches along the carbon bed depth. At the top of the column is an overflow line which empties by gravity into a 50-gallon holding tank. This treated wastewater is then discharged into the industrial sewer line beyond the pit area.

The carbon contactor is filled by adding carbon to the slurry tank and at the same time adding water in a manner rapid enough to keep the material in suspension. This mixture is then pumped into the top of the contactor vessel at a point below an upper carbon retention screen.

After the carbon charge has been exhausted, it is removed by means of a 6-inch drain located at the bottom of the column. The carbon is collected by means of a perforated 30-gallon drain pan which retains the carbon but at the same time allows any water to drain. Figure 38 shows a section of the pilot plant including the contact column, slurry tank, and holding tank.

Description of Components

A more detailed description of the major components of the pilot plant is listed as follows:

Process Pumps

Three similar type pumps were used to operate the pilot plant, i.e., equilization tank feed pump, carbon contactor feed pump and carbon slurry pump. The pumps are pneumatic (because of solvent vapor in the atmosphere within the stripping facility) diaphragm pumps, Model SB1-1/2-A Sandpiper, manufactured by the Warren Pump Company. All metallic parts were furnished in 316 stainless steel with Viton diaphragms and check valves. The pumps have 1-1/2-inch intake and discharge ports and can be operated to 125 psi with a maximum capacity of 90 gallons per minute at 100 psi and 40-foot discharge head.

Equalization Tank

The equilization tank (Figure 39) is a 3,000-gallon, open top, cylindrical vessel of 304 stainless steel. The bottom is conically shaped and has a draw-off valve for removing any settled solids. The feed line is located 18 inches from the top of the vessel and the discharge line is located 1/2 inch above the base of the coned bottom. There is an overflow port located approximately 4 inches below the top of this vessel.

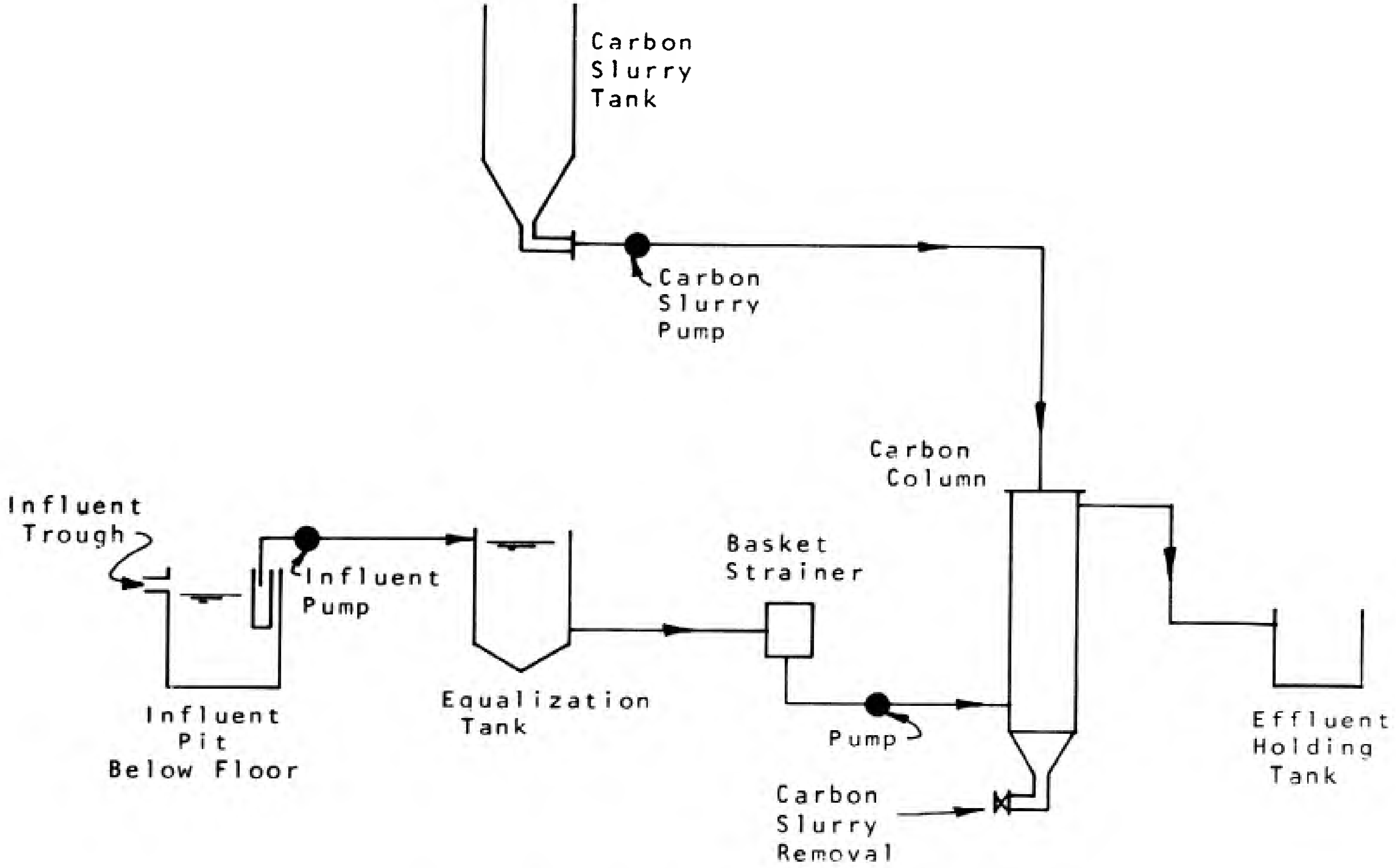

Figure 37. Flow Schematic

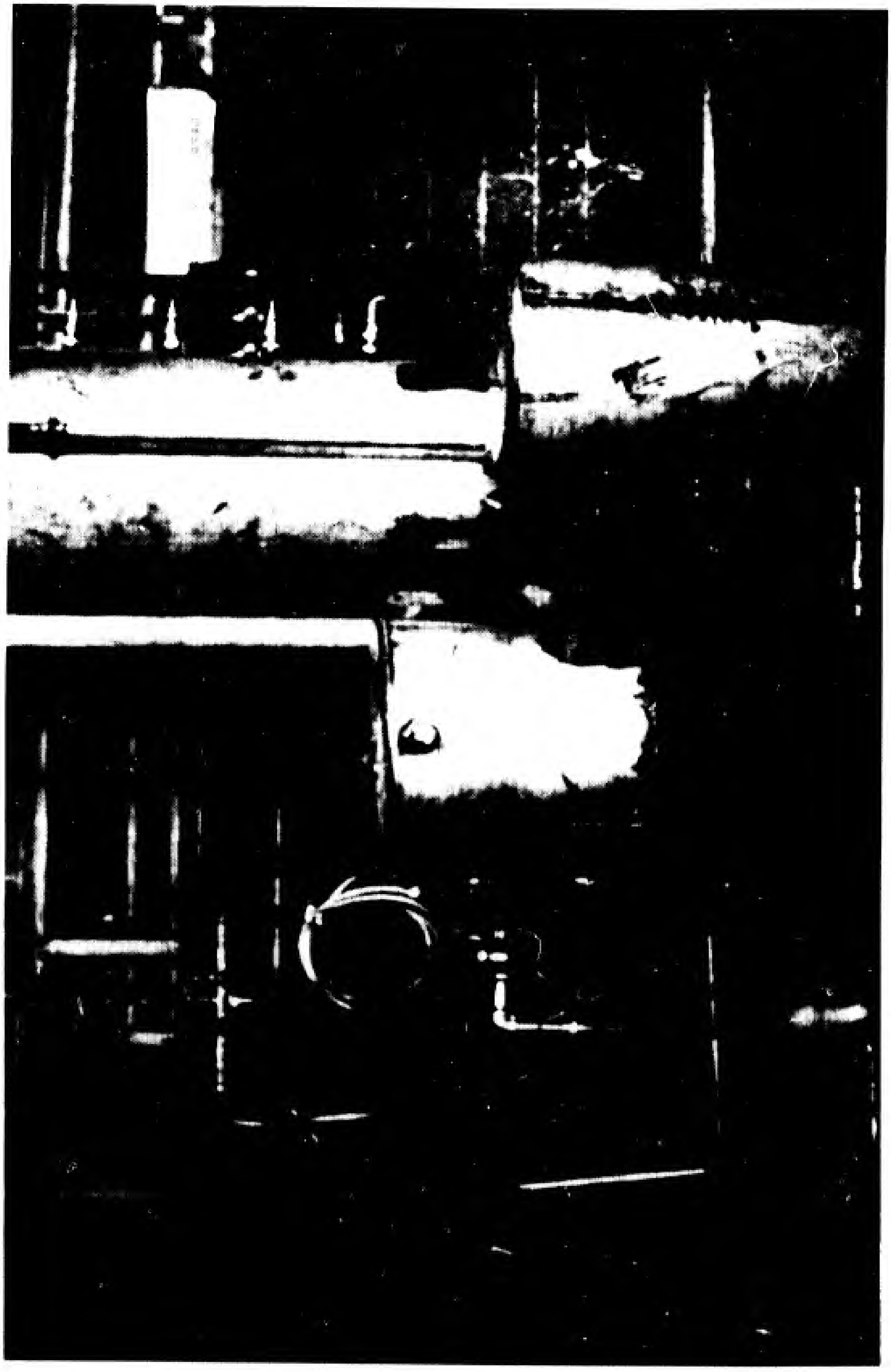

Figure 38. Pilot Plant

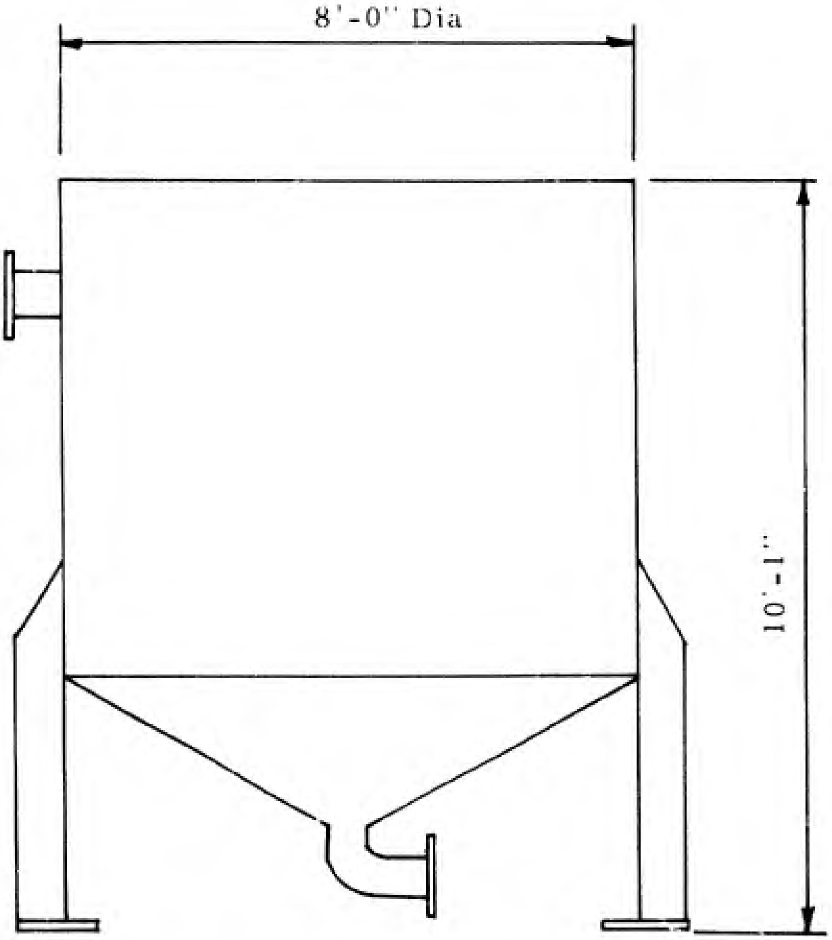

Figure 39. Equalization Tank

Carbon Contactor

The carbon contact column (Figure 40) is constructed of 304 stainless steel and has an overall height of 11 feet 7-1/4 inches and a 26-inch inside diameter. It is designed for continuous upflow operation and contains a carbon retention screen located 31-1/4 inches below the top of the vessel. The waste inlet port is located approximately 24 inches below the base of the vessel's coned bottom and the discharge port is located 18-1/4 inches below the top of the vessel. Carbon is added via the 4-inch slurry line which discharges immediately below the carbon retention screen and is removed via a 6-inch carbon removal line located at the bottom. Sample ports are positioned every 12 inches along that portion of the column which accommodates the carbon bed. A ladder is affixed to the column for easy access.

Holding Tank

The holding tank is a 50-gallon, 304 stainless steel vessel into which the treated effluent from the carbon column flows before discharging by gravity into the sewer line at a point just beyond the pit area.

Carbon Slurry Tank

The carbon slurry tank (Figure 41) is a 50-gallon, open top, 304 stainless steel vessel. Carbon is added to this tank in a batch-wise fashion, while at the same time water is being added via a series of inlet ports located along this tank. The rate of water and carbon addition is adjusted so that a slurry is maintained which can be accommodated by a diaphragm pump.

Drain Pan

The drain pan has a 30-gallon capacity and is used to collect the exhausted carbon as it is being removed from the bottom of the column. It consists of two separate components, one fitting into the other. The inner component is a stainless steel basket of 60 mesh wire screen with reinforced bottom and side. The outer component is a solid stainless steel pan which is just large enough to accommodate the basket. Wet carbon is added to the basket strainer while it is affixed inside the solid pan. The basket is then lifted out and the water allowed to drain from the carbon before it is dumped into a larger container. Handles are provided on each side of both the basket strainer and the solid pan so that two men can adequately lift and transport the unit when filled with carbon.

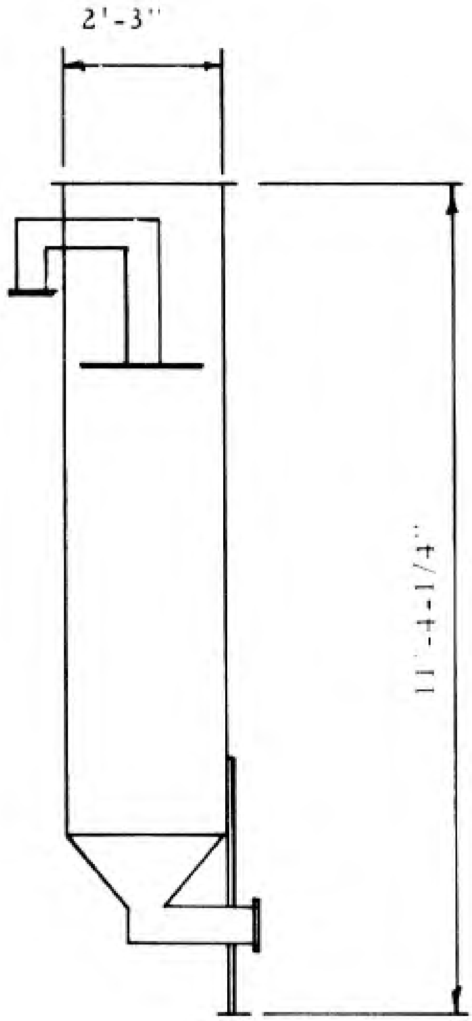

Figure 40. Carbon Contactor

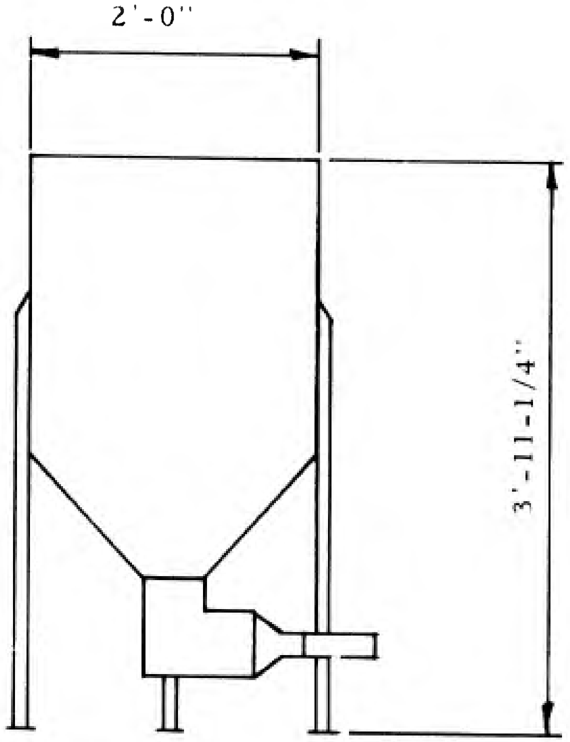

Figure 41. Carbon Slurry

Pipe and Valving

All piping is 304 stainless steel and has either flanged or threaded ends. Valves are stainless steel ball type with Teflon® seals. The carbon contactor contains a 6-inch stainless steel butterfly valve used for carbon removal.

Flow Meter

The flow meter is a positive displacement disc meter with a non-resettable totalizing register. It is a Model BNS-3/4 Inch, manufactured by the Niagara Meter Company. It is fitted with Teflon® gaskets and a "K-lif" disc.

Basket Strainer Assembly

The basket strainer assembly is an in-line pressure vessel designed for bulk removal of suspended solids via a removable cartridge. It is a cylindrically shaped, two sectioned, 304 stainless steel unit, Model B-8-2, manufactured by Facet Enterprises, Inc. The outer shell measures 27 inches high by 8-5/8 inches wide and has a flanged top designed for easy cartridge removal and cleaning. The cartridge (basket strainer) is constructed of 100 x 100 mesh wire screen with a 60 x 60 mesh back-up screen, both stainless steel.

Pilot Plant Objectives

On-site testing involved the contamination of eight charges of activated carbon with paint stripping wastewater. The first four contaminations, each subjected to a different contact time, were performed using virgin carbon. Based on a comparison of those results gathered during the laboratory column testing phase, an optimum flow rate would be selected. This optimal rate would then be used during four more exhaustion cycles using the same charge of carbon. At the termination of each cycle, the exhausted carbon was thermally regenerated. The particular charge of carbon used to determine the optimum flow rate would, in effect, be taken to exhaustion five times and thermally regenerated four times.

The major objectives of the pilot plant phase were to determine:

1. The required contact time to reduce the phenol concentration to a reasonable level.

2. Optimal hydraulic loading.

3. Adsorptive capacity of the carbon.

4. If any pressure drops occurred as a result of solids plugging the carbon bed.

5. Performance of the carbon in removing contaminants other than phenol.

6. Efficiency of thermal regeneration including carbon losses.

Except for total chromium and methylene chloride, all the required analyses were performed on-site in the Mobile Laboratory. The two exceptions were performed at Facet's Laboratory in Rhode Island.

Pilot Plant Operation

The first four virgin carbon exhaustion cycles using Nuchar WV-W 8 x 30 carbon were made with the following operating conditions:

Exhaustion Cycle	Flow Rate	Residence Time	Hydraulic Loading
1	12.50 gpm	15 minutes	3.264 gpm/ft^2
2	6.25 gpm	30 minutes	1.632 gpm/ft^2
3	4.16 gpm	45 minutes	1.086 gpm/ft^2
4	3.13 gpm	60 minutes	0.816 gpm/ft^2

Except for the difference in flow rate, the system was operated in essentially the same manner for all four virgin carbon contamination runs. The equalization tank feed pump was initially operated at a rate two to four times faster than the pump which fed the carbon contactor. This was done until the level of waste was near the capacity of the equalization tank; then both pumps were adjusted to the same rate for the remainder of a contamination run. Since the capacity of the equalization vessel is 3,000 gallons, it provided a holding time of from 4 to 16 hours, depending on the contamination rate, for each of these four runs. Although a 16-hour-per-day contamination cycle was originally proposed, the system was continuously operated (24 hours per day) until 50 to 80 percent of the influent phenol had broken through, i.e., present in the effluent relative to the influent at the time of sampling. Twenty-four-hour continuous operation was preferable to the 16-hour-per-day cycles, because past experience showed that intermittently operating a carbon system until exhaustion is achieved tends to produce gaps in the data. These gaps result because wastewater, allowed to sit quiescently in contact with the carbon for long periods between contamination runs, is being acted on by the carbon over an extremely long residence time. This results in the levels of adsorbable contaminants being significantly reduced so that this waste acts, in effect, as dilution water when the system is operating again.

Because, in this case, the amount of liquid maintained within the carbon bed is significant (approximately 200 gallons), it would require a considerable amount of running time to overcome the effect of this dilution. Another reason for operating the system continuously was that the paint stripping facility is usually in operation for three 8-hour shifts, 24 hours per day so wastewater should always be available.

Influent and effluent samples were collected periodically with the frequency dependent on flow rate and previous effluent values. Influent sampling was accomplished at a point located immediately after the in-line basket strainer, while effluent samples were collected from the contact column discharge line at a point where it enters the wet well. In addition, samples were collected from the access ports, which run vertically (at 12-inch intervals) up the carbon contactor column. This was done to monitor the progress of carbon exhaustion and to anticipate when breakthrough would be most likely to occur. The major parameter used to analyze the samples collected from these vertically located ports was TOC. Since these results were used primarily to anticipate when a given set of influent and effluent samples should be taken, the data obtained from these samples will not be presented as part of this report.

As indicated, all four virgin carbon contaminations were performed under as similar a set of conditions (except flow rate) as could be controlled. On occasion, this required unscheduled modifications. For example, the phenol concentrations were relatively low during Run No. 3. This was because a greater amount of washing and rinsing operations than usual took place during this period, resulting in a more dilute wastewater. To compensate for this, a small amount of straight paint stripper was added directly to the equalization vessel on several occasions during this run. The amount of stripper used for each addition was approximately 3 to 4 gallons per 3,000 gallons of wastewater.

Virgin Carbon Exhaustion Cycles

Figure 42 shows the variability of the wastewater in terms of phenol concentration during each of the four virgin carbon contamination runs. These variations correspond rather closely to the type of operation being performed within the paint stripping facility during the sampling period. Phenol concentrations in the system feed tend to drop during the latter part of each contamination run. In most cases, this corresponds to the complete cessation of phenolic type paint stripping operations and an increase in related activities. The average influent phenols for each of these runs are shown in Table 3.

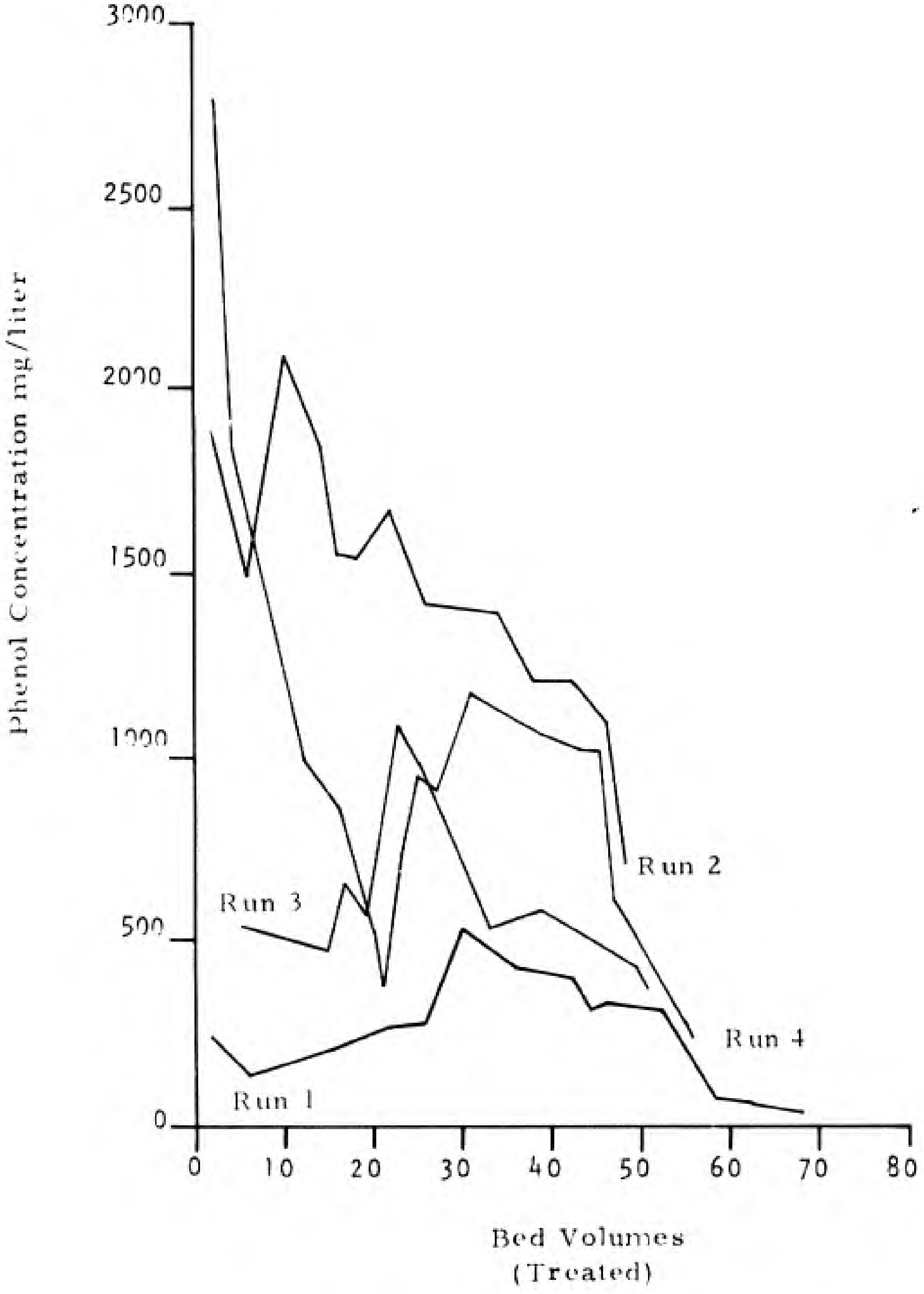

Figure 42. Influent Phenol Concentration (Runs 1 through 4)

TABLE 3. AVERAGE INFLUENT PHENOL CONCENTRATION

Run No. 1	480 mg/1
Run No. 2	1440 mg/1
Run No. 3	500 mg/1
Run No. 4	1040 mg/1

Figure 43 shows the breakthrough curves in terms of phenol removal for each of these four contamination runs. Although Run No. 1 (15 minutes residence time) had the lowest influent phenol concentration, it showed the earliest leakage of phenol in the effluent which was 20 milligrams per liter after only 6 bed volumes. Also during this run, the effluent showed much more susceptibility to any fluctuations in the influent phenol concentrations than were found during any of the other runs. This indicates that some degree of channeling may have occurred at this flow. The other three virgin runs appeared less susceptible to fluctuation in the influent phenol concentrations and, therefore, their respective breakthrough curves were less erratic and more predictable.

Figures 44 and 45 show the influent and effluent TOC concentrations for these four virgin carbon runs. Basically, the same trends developed for this parameter as were found for phenol, i.e., their respective curves have similar shapes for both these parameters.

In some cases, influent TOC values were much greater than could be achieved from the components of the phenolic paint stripping waste alone. Rather, this was because of the increase in related activities such as the carbon removal operation which generates large amounts of wastewater containing high TOC components. These components are non-phenolic and, in the case of carbon remover, are primarily creosote and orthodichlorobenzene. The TOC breakthrough curve for Run No. 4 is more erratic than for other runs and this was probably due to the unusually erratic nature of the influent material. The COD breakthrough results for these virgin carbon contaminations are indicated in Figure 46. All of these curves generally follow the same trends that were noted for TOC. However, they do appear much smoother than their respective TOC counterparts and this is probably because COD sampling intervals were longer than for TOC tending to normalize the curves.

System influent samples were collected downstream of the in-line basket strainer and, therefore, contained relatively little suspended material. Figure 47 shows the breakthrough curves for suspended solids and it appears from these results that essentially none of this material was retained by the carbon. This was expected because the solids which passed through the basket strainer would be small enough to pass through a granular carbon bed operated in an upflow mode.

Oil and grease breakthrough curves are shown in Figure 48. Basically, the carbon showed little affinity for this component of the wastewater. This material appeared to pass the carbon bed with no noticeable buildup or fouling of the carbon. The unusually high oil and grease in the column effluent from Run No. 4 probably resulted in a spill of carbon remover solution which occurred just before this run was initiated.

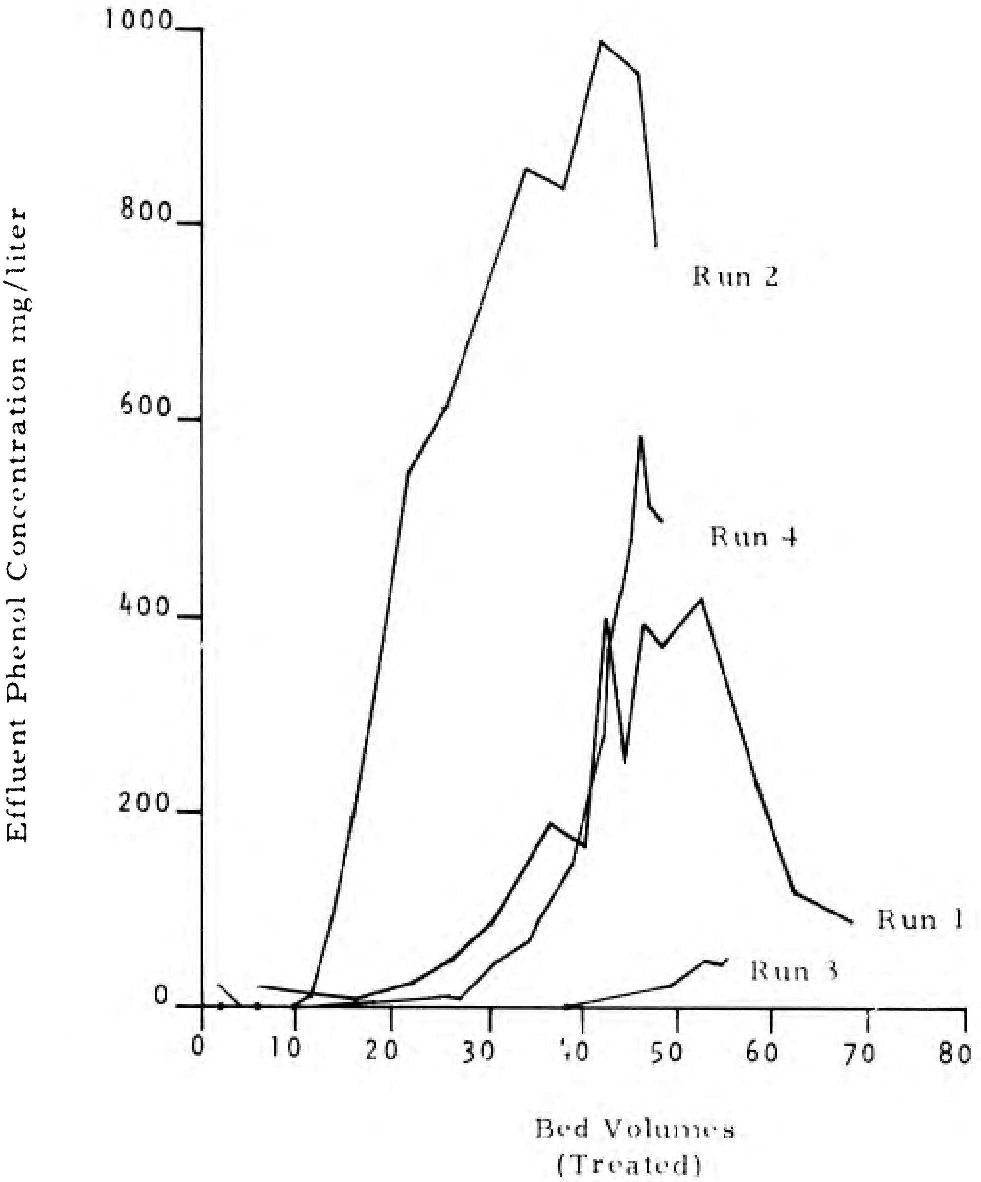

Figure 43. Phenol Breakthrough Curves (Runs 1 through 4)

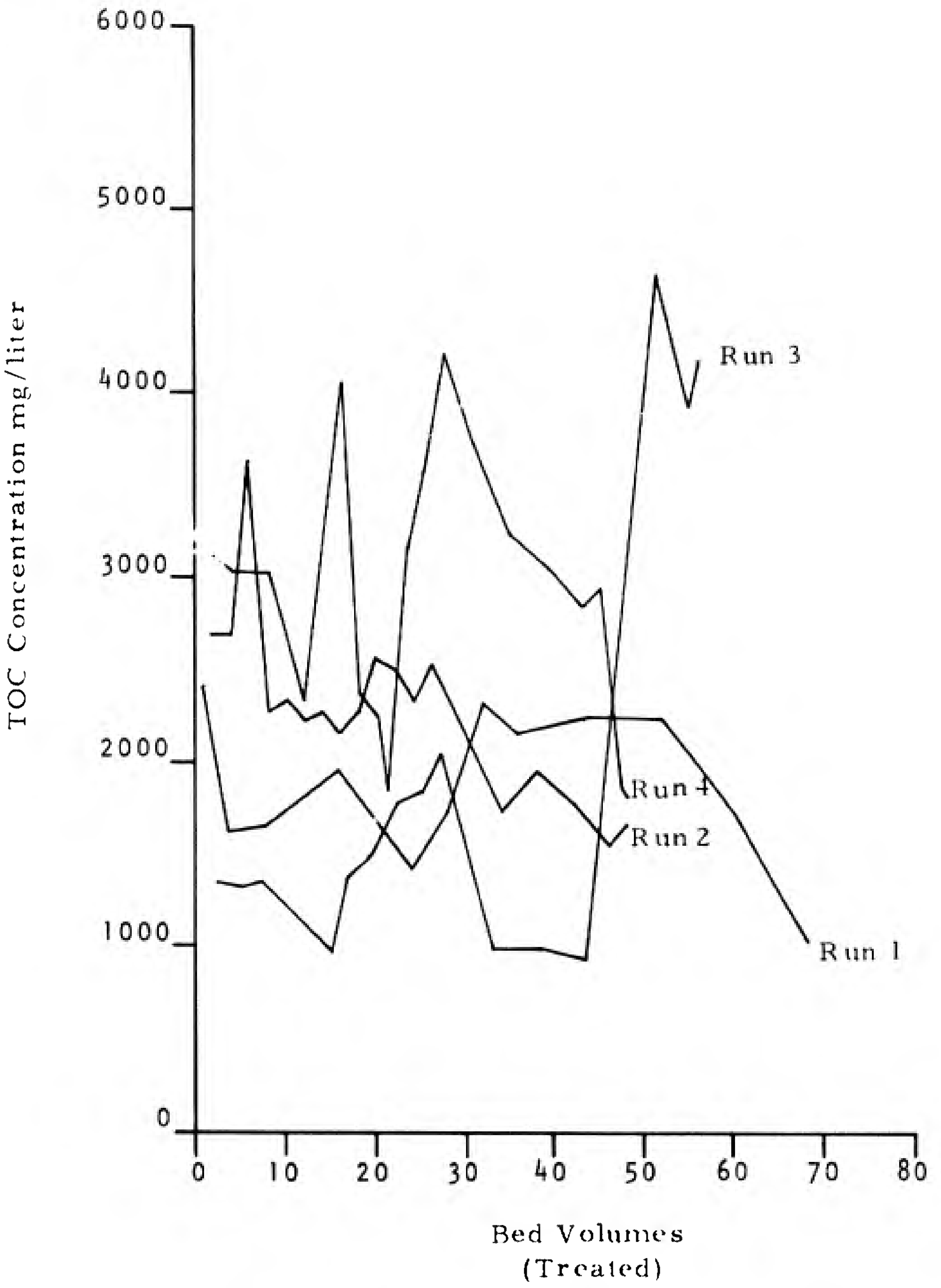

Figure 44. Influent TOC Concentration (Runs 1 through 4)

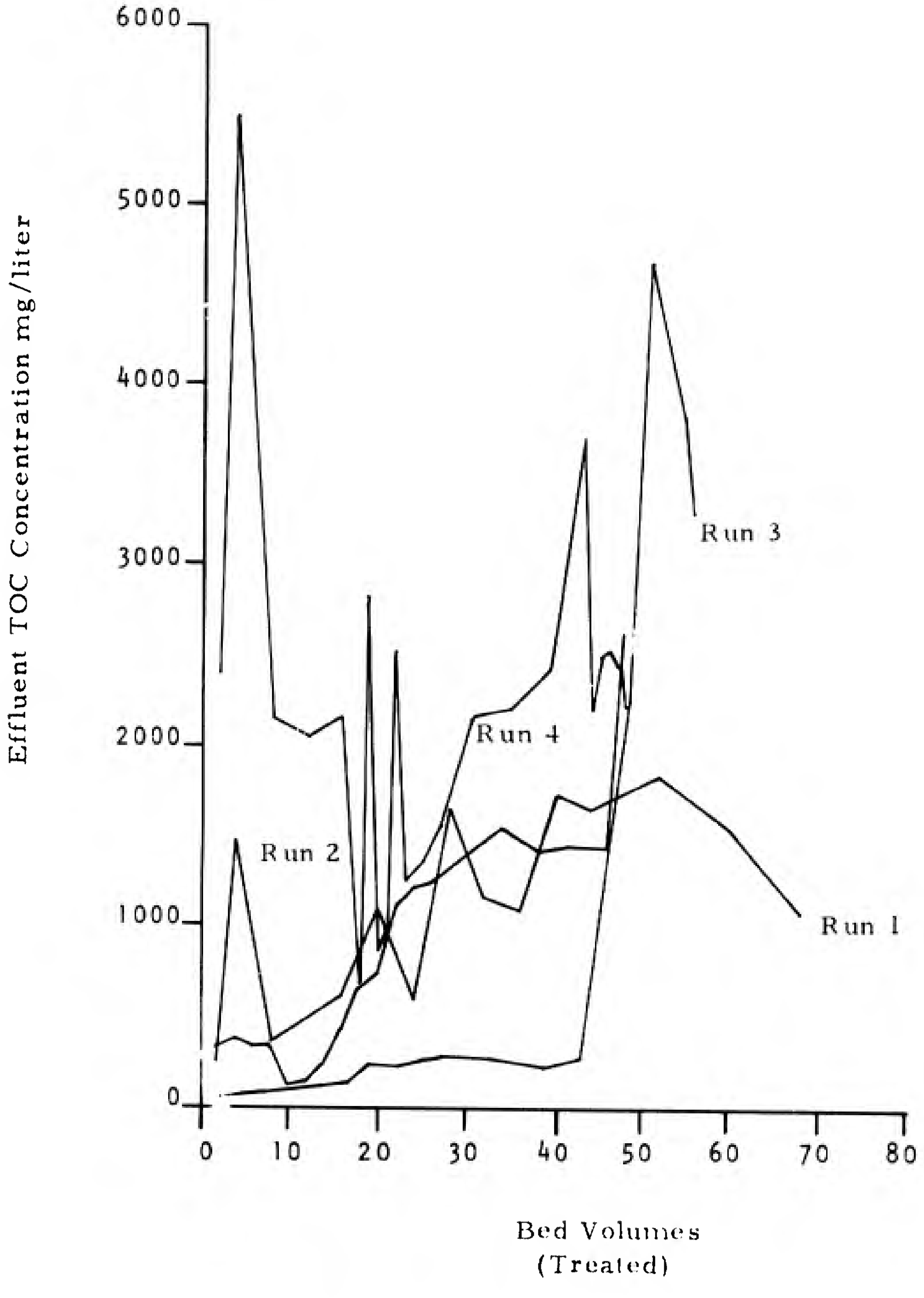

Figure 45. TOC Breakthrough Curves (Runs 1 through 4)

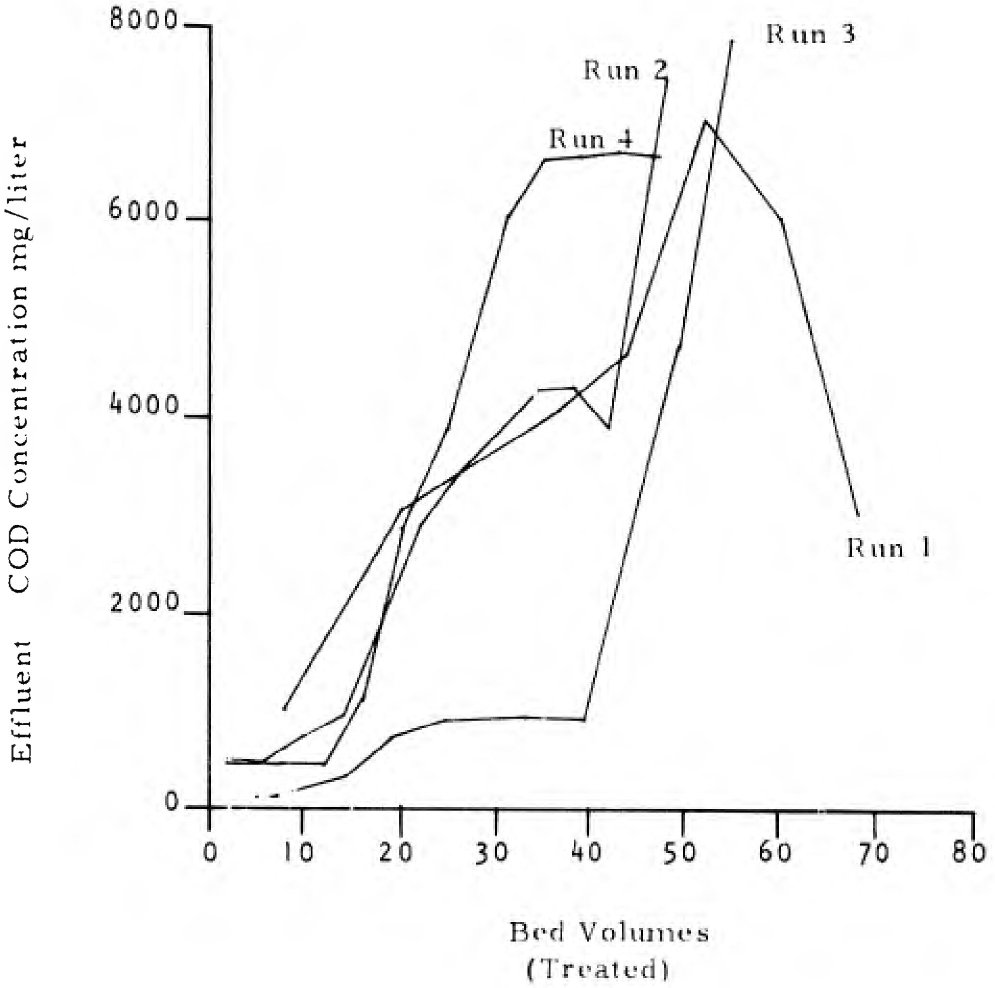

Figure 46. COD Breakthrough Curves (Runs 1 through 4)

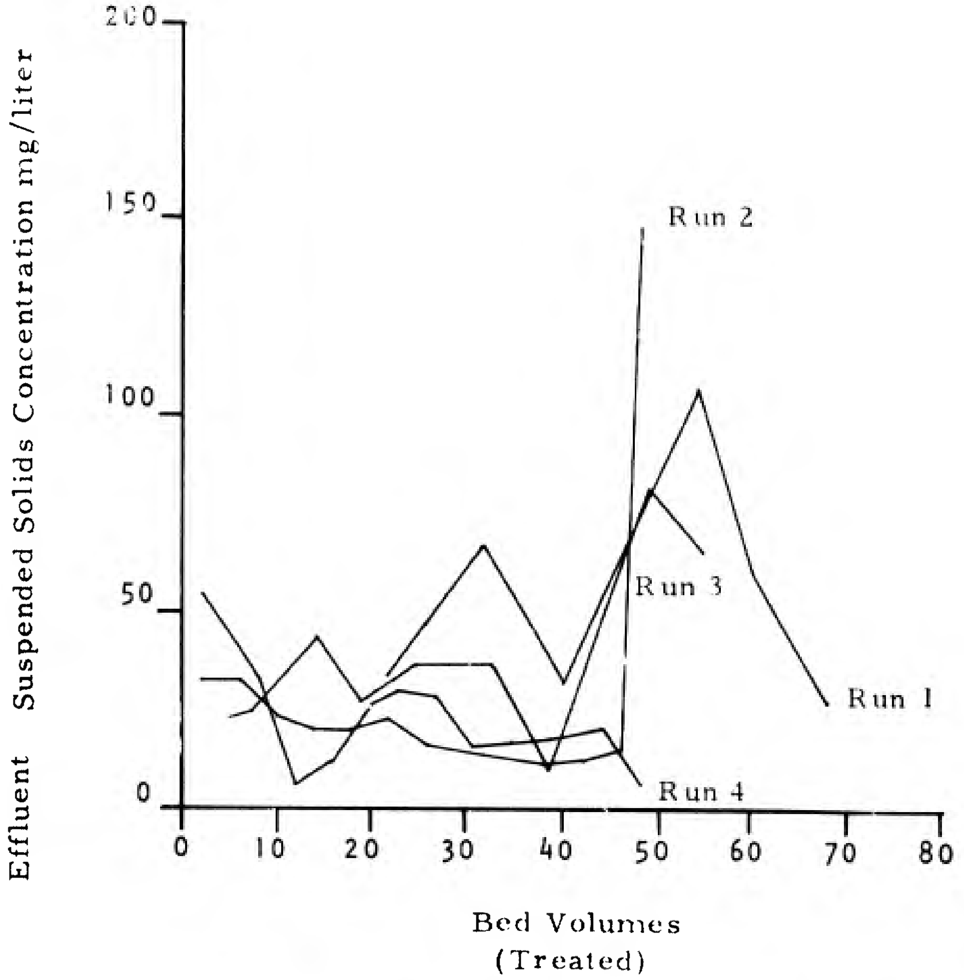

Figure 47. Suspended Solids Breakthrough Curves (Runs 1 through 4)

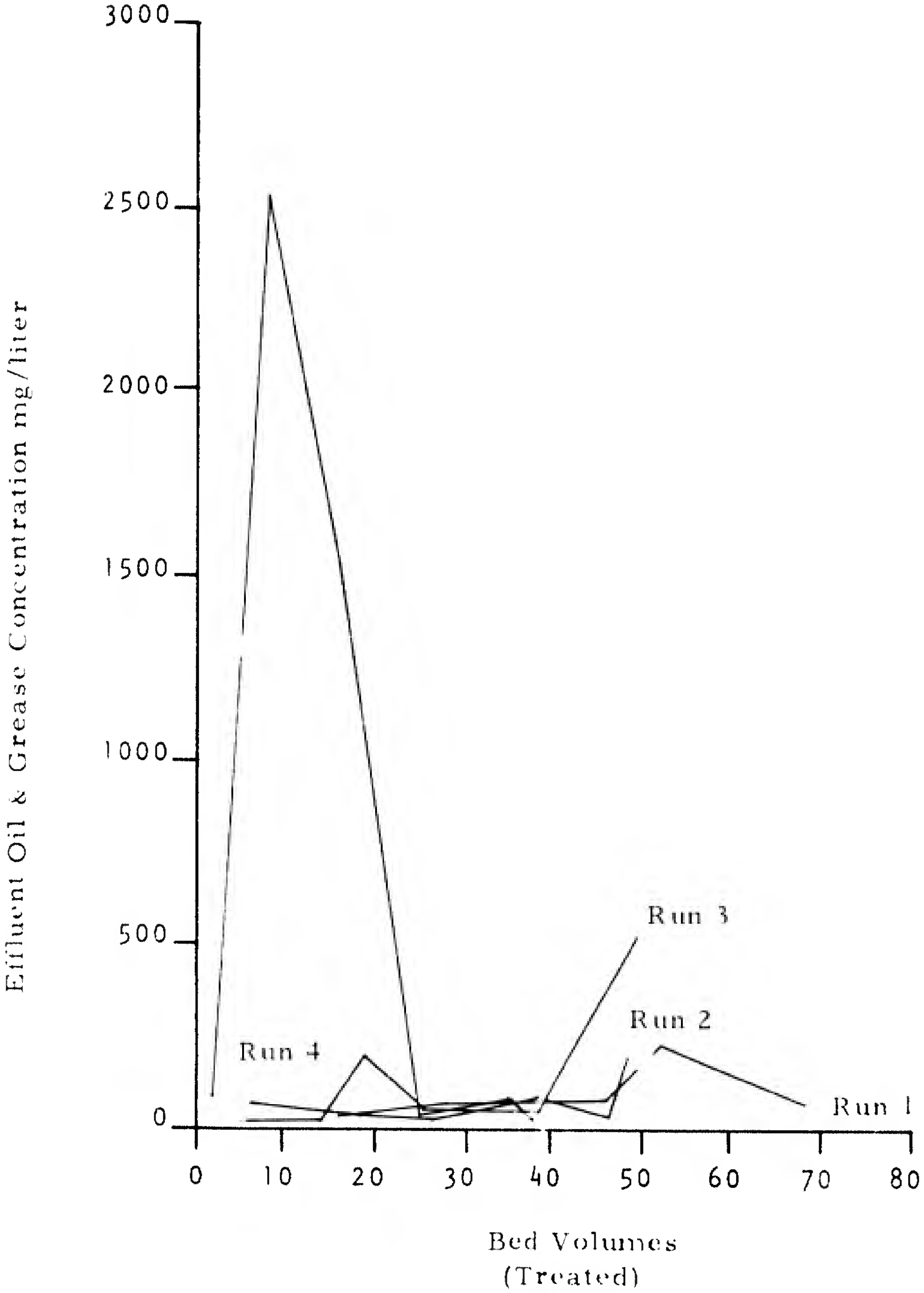

Figure 48. Oil and Grease Breakthrough Curves (Runs 1 through 4)

The breakthrough curves for total chromium are shown in Figure 49. It appears from the results that the activated carbon definitely has an affinity for the chromium component of this wastewater. Because of the fluctuations in the chromium levels of the untreated waste, it is difficult to determine the importance of contact time in removing this component, i.e., no correlation can be made between flow rate and removal.

Figure 50 shows the breakthrough curves in terms of methylene chloride removal for these first four virgin carbon runs. Except for the initially high effluent concentrations in Run No. 3 (probably resulting from some initial channeling or short circuiting through the carbon bed), the removals produced during Runs No. 1 through No. 3 correspond closely to their respective flow rates as well as the average influent concentrations. During Run No. 4, however, the system was operated at the lowest flow rate on one of the lowest average influent concentrations for methylene chloride, yet this run showed the most rapid breakthrough for this parameter. The reason for this is not known. However, it should be pointed out that it is extremely difficult to maintain a representative sample for methylene chloride analyses because of the rapid volatilability of this material.

The performance of each run, in terms of removal efficiencies for phenol and TOC, was calculated, using the influent and effluent concentrations between zero time and time equals 20 percent instantaneous phenol breakthrough. Table 4 shows these results.

The results indicate that the rate of phenol removal is governed primarily by contact time rather than concentration. For example, during Run No. 2, the influent phenol concentration was three times greater than during Run No. 3, yet Run No. 3 (having a longer contact time) showed a better removal efficiency in terms of phenol. This same phenomenon appeared true in terms of TOC removal.

In terms of overall removal efficiency, the carbon removed more phenol at the 20 percent breakthrough point during Run No. 4 than during any of the other virgin runs made. Run No. 3, however, showed the best carbon removal efficiency for phenol when the low influent concentration of this component is considered.

Basically, these results show that the longer residence time tended to give more efficient removals. Because of the economics involved, as well as the size of the pilot plant, a flow of less than 6.25 gallons per minute (30 minutes residence time) was not considered practical. Therefore, the next phase of the study dealing with regenerated carbon would be performed utilizing a 6.25 gallons per minute flow rate.

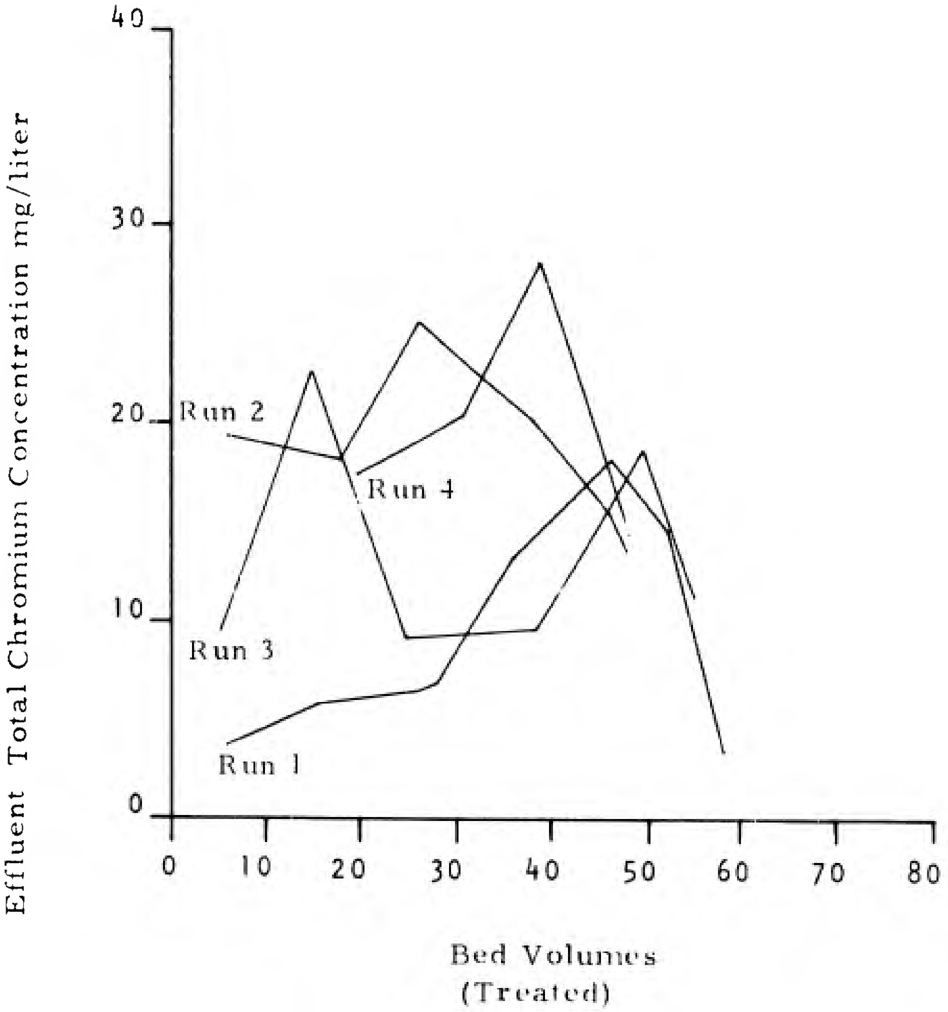

Figure 49. Total Chromium Breakthrough Curves (Runs 1 through 4)

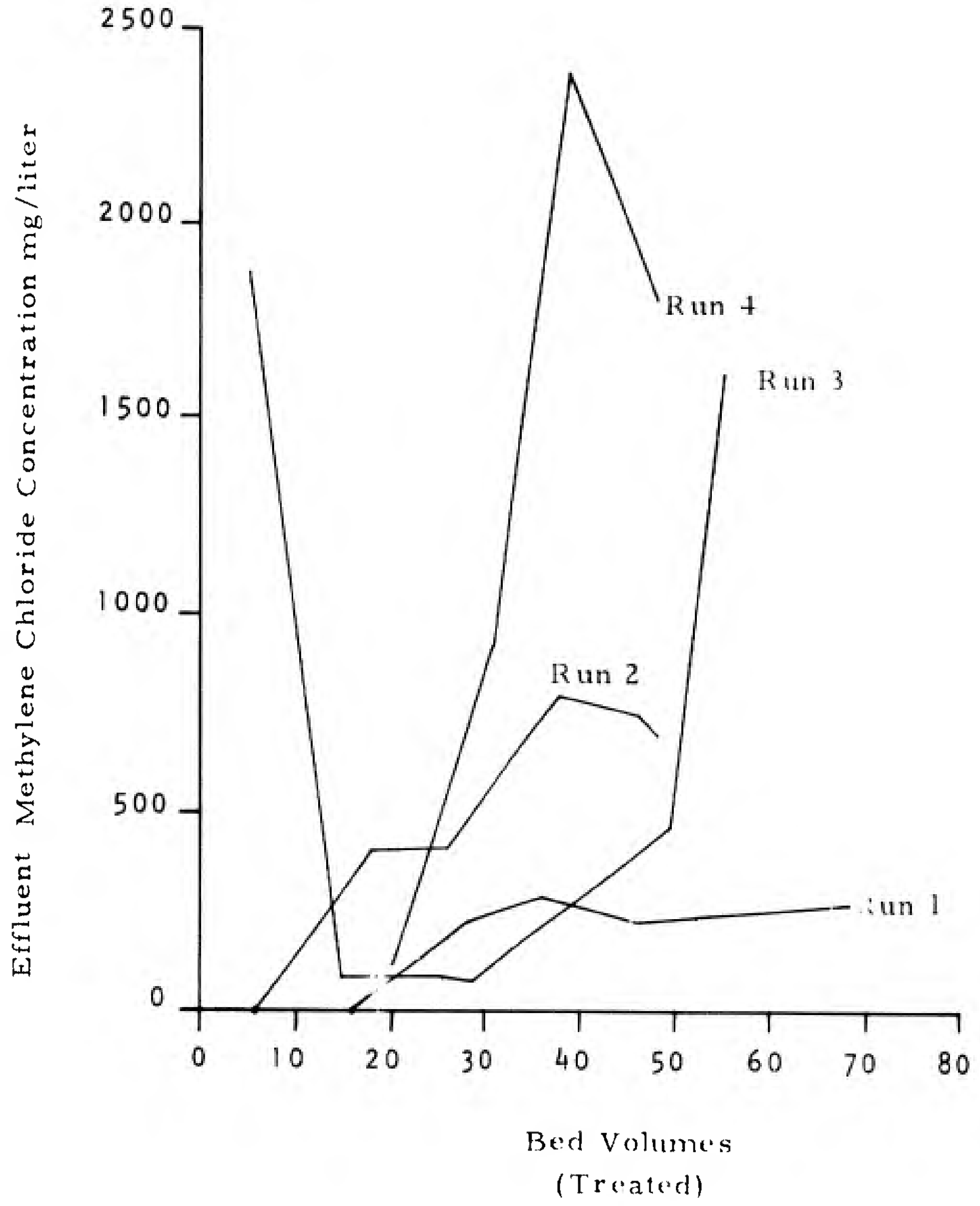

Figure 50. Methylene Chloride Breakthrough Curves (Runs 1 through 4)

TABLE 4. CARBON COLUMN PERFORMANCE BETWEEN TIME = 0
AND TIME = 20 PERCENT INSTANTANEOUS PHENOL BREAKTHROUGH

Run	Residence Time (min)	Bed Volumes Treated	Average Phenol Concentration (mg/l)	Phenol Removal Efficiency (lbs/lb of carbon)	Average TOC Concentration (mg/l)	TOC Removal Efficiency (lbs/lb of carbon)
1	15	36	488	0.0280	1740	0.0593
2	30	18	1580	0.0480	2240	0.0618
3	45	56	524	0.0505	1820	0.1073
4	60	40	1060	0.0710	3000	0.0659

Regenerated Carbon Exhaustion Cycles

The contaminated carbon from the first two runs was thermally regenerated (see Section IV) and, once regenerated, the carbon from one batch (Run No. 1) was stored aside, used only for makeup to compensate for any subsequent regeneration losses. The material from the other batch (Run No. 2) was the primary adsorbent used to fill the contact column and all subsequent contamination-regeneration cycles were performed using this particular batch of carbon.

In all, four more contaminations were made using this batch of carbon so that, including the virgin run, the same carbon was contaminated five times using the same flow rate (6.25 gallons per minute = 30 minutes residence time).

Except for some minor modifications such as the installation of a bypass line to achieve a more homogeneous wastewater within the equalization tank, all contaminations on regenerated carbon were performed in essentially the same manner as with the virgin carbon runs.

Figures 52, 54, 55 and 57 show breakthrough curves for the four runs made on regenerated carbon in terms of phenol, TOC, COD and total chromium (no chromium analyses were performed on the grab samples from Run No. 5). Figures 51, 53 and 56 show the influent concentration for each run in terms of phenol, TOC, and total chromium. pH, suspended solids, oil and grease, and methylene chloride determinations were not performed on influent and effluent grab samples during these later contaminations. This was due to the fact that these constituents, as experienced during the virgin carbon contaminations, either were not affected by carbon treatment or were very unstable.

Although the results for Run No. 5 (first recontamination of regenerated carbon) are represented along with the other runs, they should not be used to make direct performance comparisons. This is because the entire system was inadvertently contaminated with a large amount of potassium permanganate for several hours. The result was the creation of a gelantinous floc in the wastewater which accumulated in the carbon bed as well as the smaller sample lines causing pressure drops and plugging. In addition, it appeared that this contamination affected the ability of the system to remove many constituents of the wastewater (note the premature breakthrough for Run No. 5 in the breakthrough curves at 14 bed volumes). After purging the system of the permanganate contaminated wastewater, a fresh supply of waste was rapidly pumped into the equalization tank and it was passed through the carbon bed. This is reflected by the rapid changes at approximately 18 bed volumes.

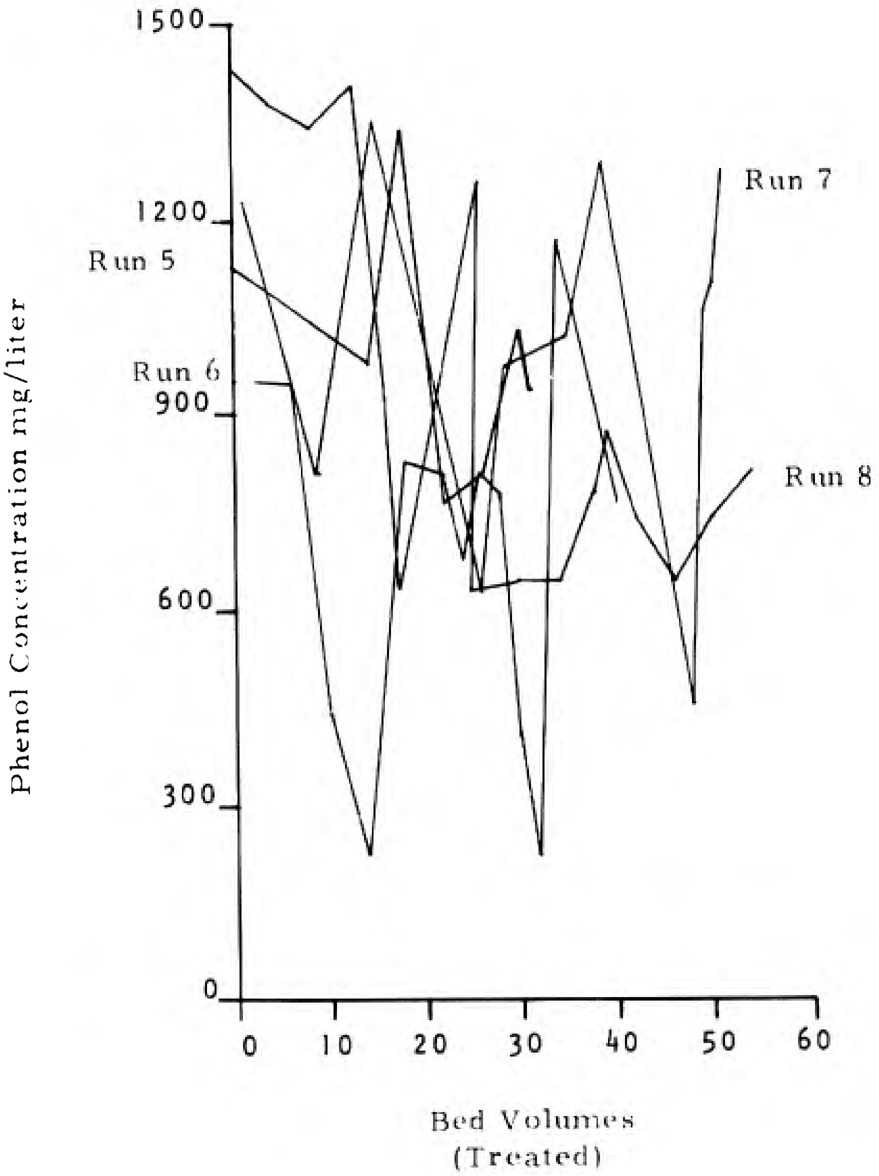

Figure 51. Influent Phenol Concentration (Runs 5 through 8)

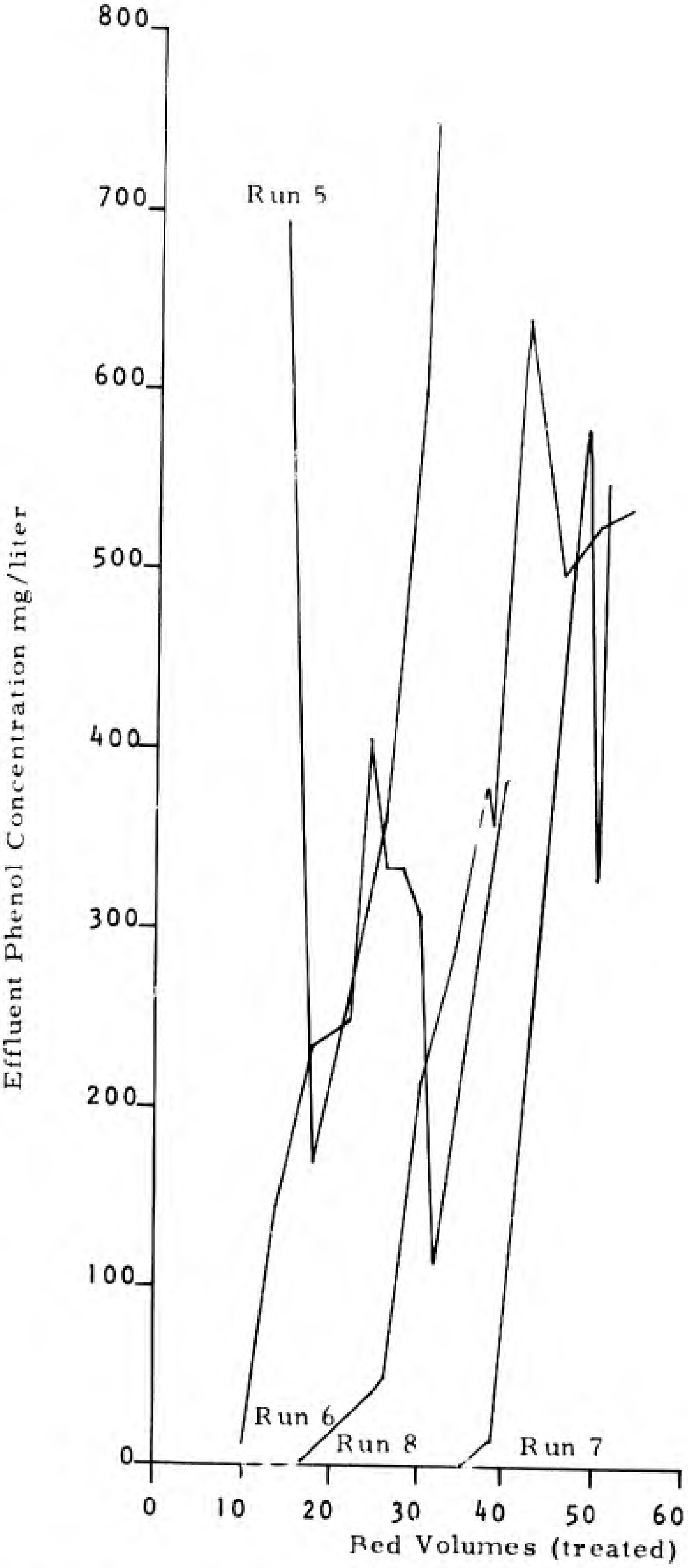

Figure 52. Phenol Breakthrough Curves (Runs 5 through 8)

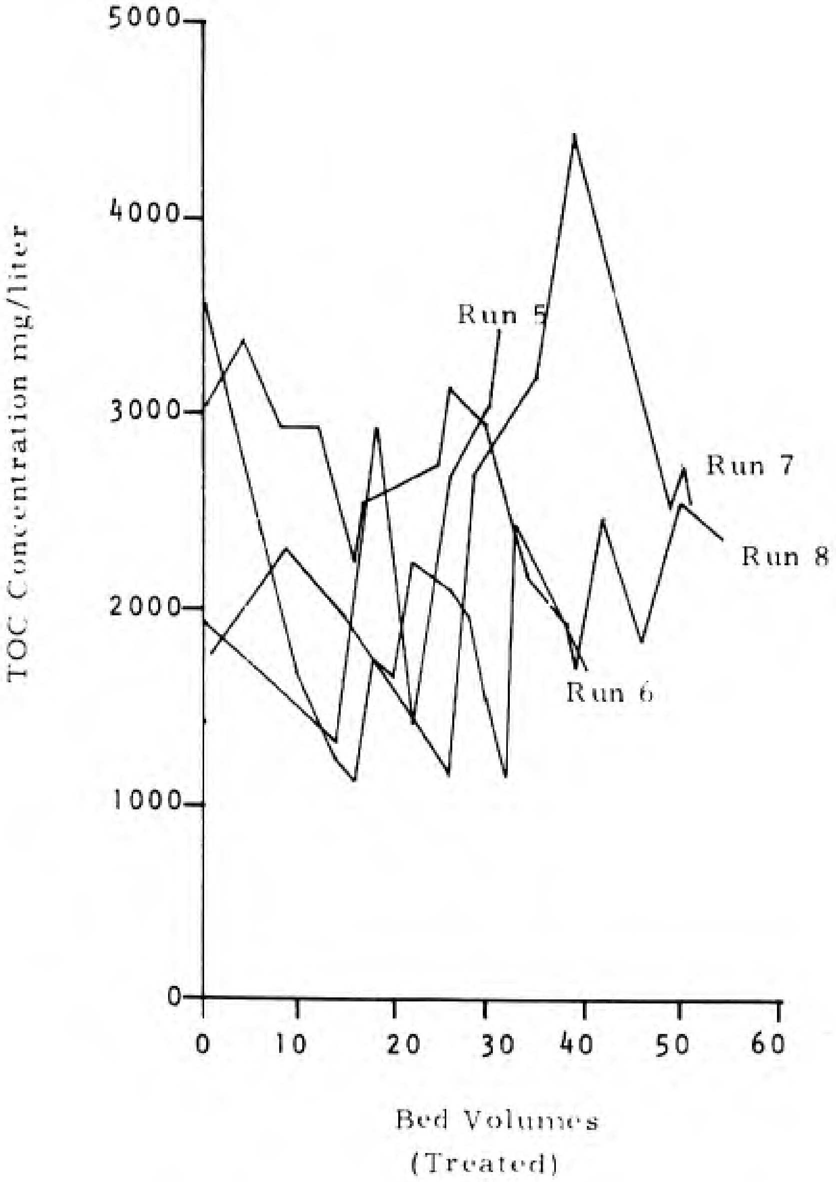

Figure 53. Influent TOC Concentration (Runs 5 through 8)

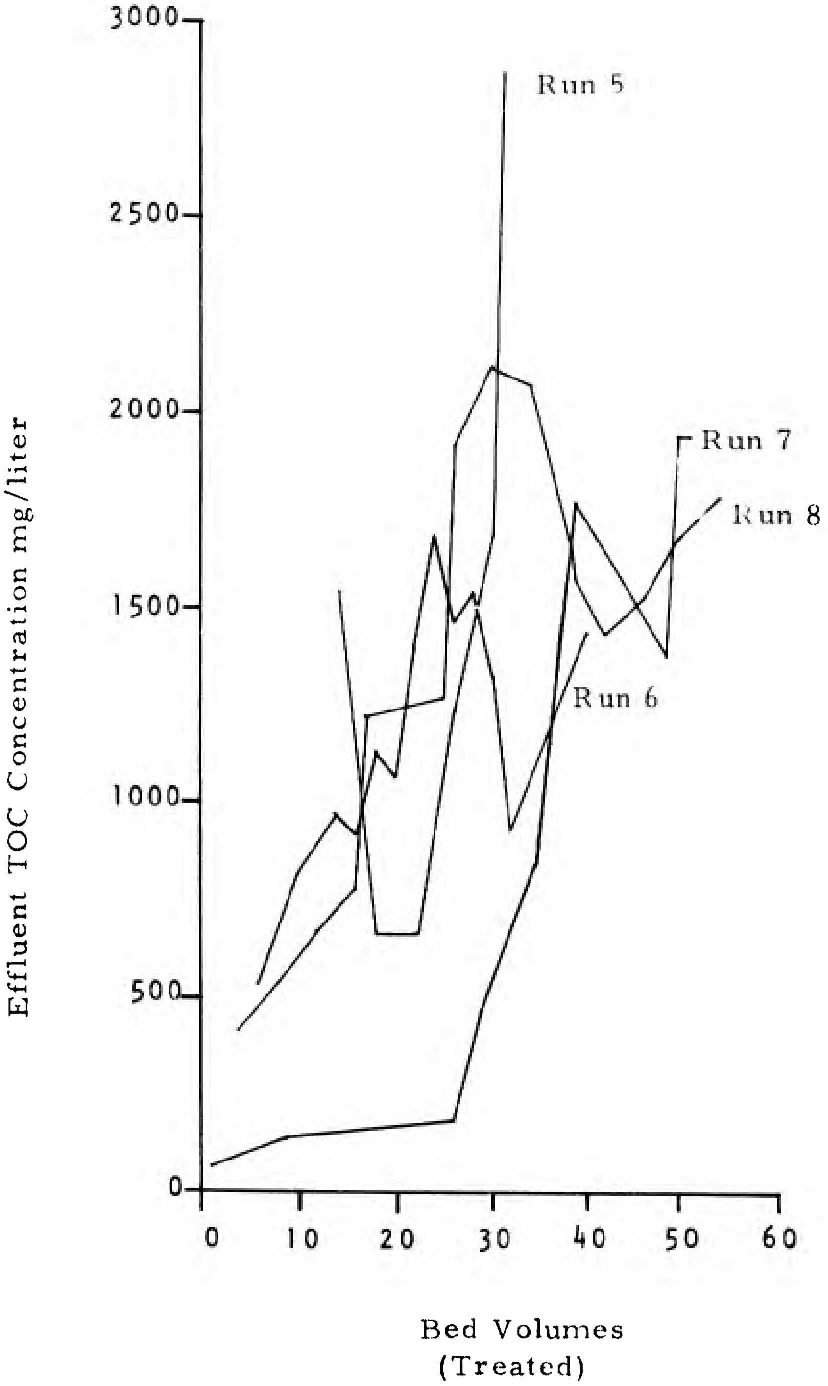

Figure 54. TOC Breakthrough Curves (Runs 5 through 8)

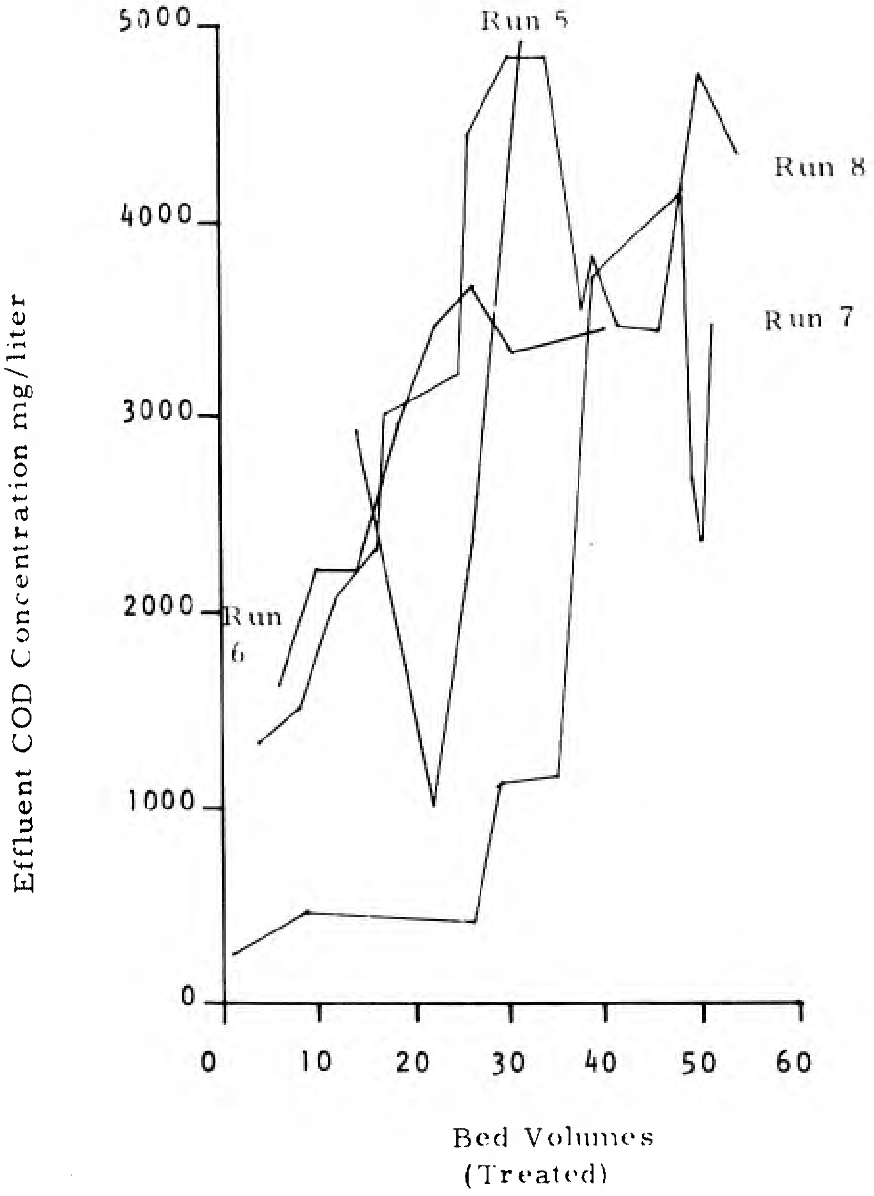

Figure 55. COD Breakthrough Curves (Runs 5 through 8)

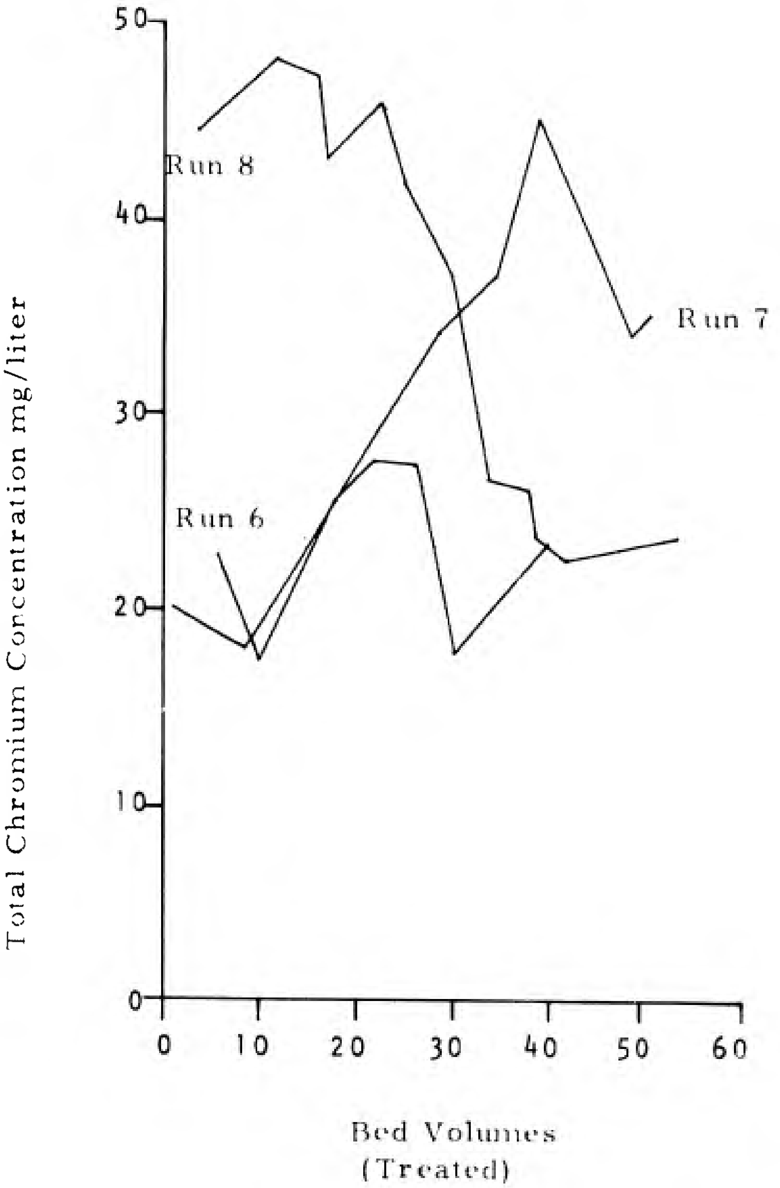

Figure 56. **Influent** Total Chromium Concentration (Runs 6 through 8)

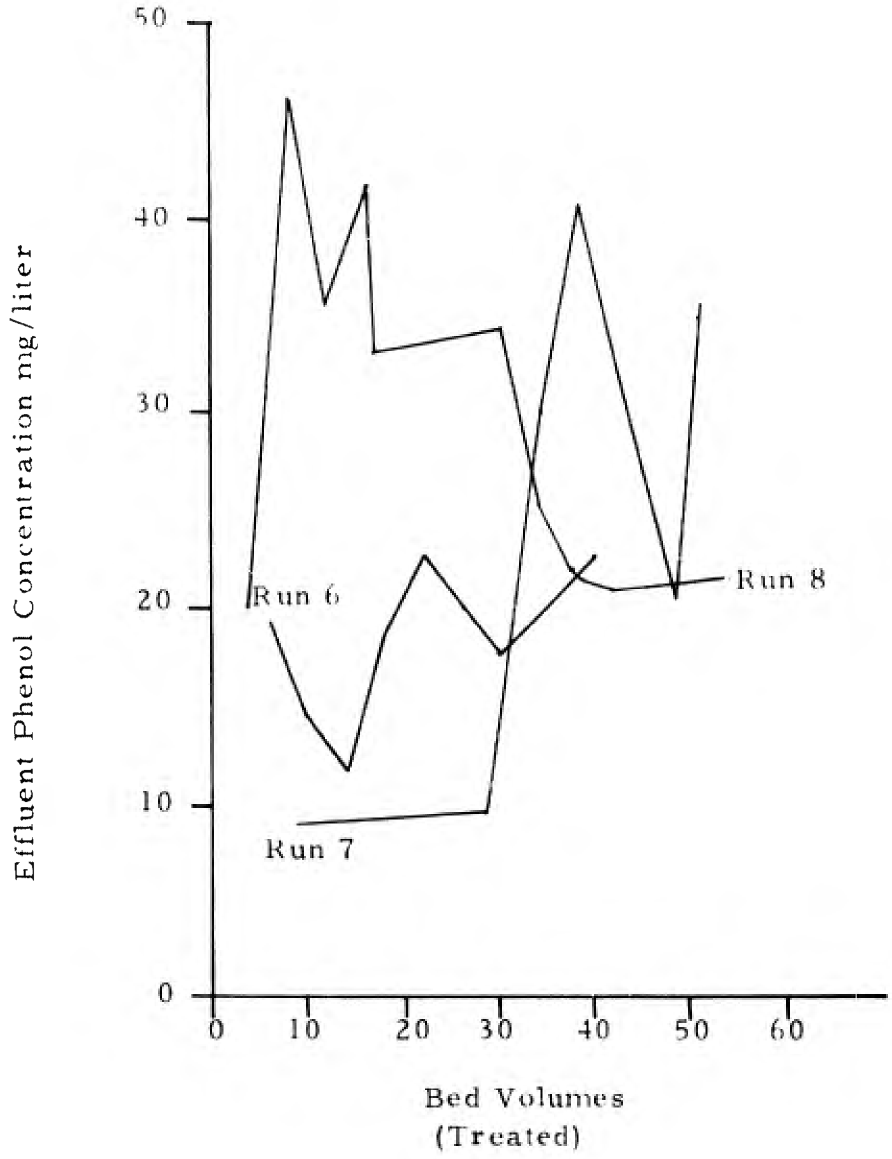

Figure 57. Total Chromium Breakthrough Curves (Runs 6 through 8)

Because of this permanganate contamination, a direct comparison between this run and one using virgin carbon (Run No. 2) operating at the same flow rate could not be made. Therefore, to determine the extent to which this regenerated carbon compared to virgin carbon in terms of phenol removal, equilibrium isotherms were performed. These isotherms were conducted in essentially the same manner as during the laboratory phase, as both carbons were maintained in the granular state. The wastewater used was a dilute solution of the phenolic type stripping material taken directly from a storage drum. The results of these isotherms are shown in Figure 58. It is apparent from these results that both carbons performed in an almost identical manner in terms of phenol removal. Therefore, it can be concluded that the capacity of the carbon for phenol removal had been completely renewed by thermal regeneration.

Influent variability during the four regenerated carbon runs (Figures 51, 53 and 56) was not reflected by changes in the effluent concentrations (except for chromium) until the system approached breakthrough. Once a substantial breakthrough level was achieved, however, any change in the influent level of phenol, TOC and COD is almost immediately reflected in the effluent concentration level. Total chromium as indicated by the breakthrough curves appears to be an exception, being affected by every change in influent levels almost at the onset of each contamination. Although there is definite chromium removal. the results indicate that the kinetics are somewhat different than they are for the other parameters tested.

Figures 59 and 60 graphically show the cumulative percent leakages versus bed volumes treated for phenol and TOC, respectively. This cumulative percent leakage is analagous to the average effluent concentration from the start of contamination through a given bed volume. As indicated, Run No. 5 is not represented because of inconsistencies in the data due to permanganate contamination.

Leakage curves make it possible to predict what the quality of the total effluent would be at any point in a contamination run. This information is useful in designing other activated carbon systems used to treat similar wastes. Also, it serves as a basis for determining the extent to which the carbon has been regenerated. Theoretically, if regeneration is complete, these leakage curves should superimpose. As shown, however, there was considerable difference between each run in terms of phenol and TOC removal. There appears to be a correlation between the number of times the carbon has been regenerated and its performance. Runs No. 7 and No. 8 were performed on wastewater having similar influent concentrations, yet Run No. 8 showed 20 percent leakage of phenol after less than 50 bed volumes, while Run No. 7 treated approximately 60 bed volumes (by extrapolation)

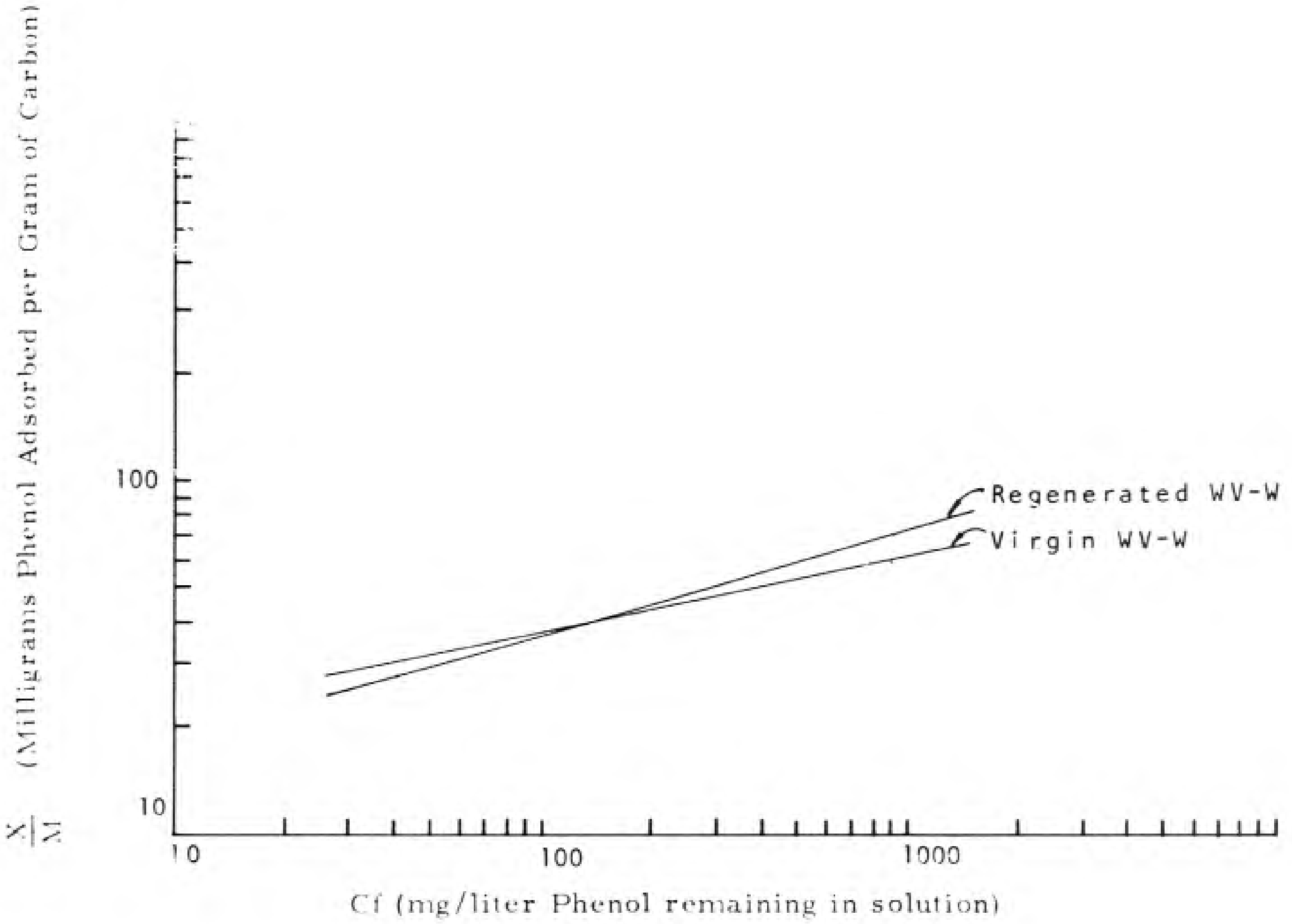

Figure 58. Phenol Adsorption Isotherms (Temperature = 22°C)

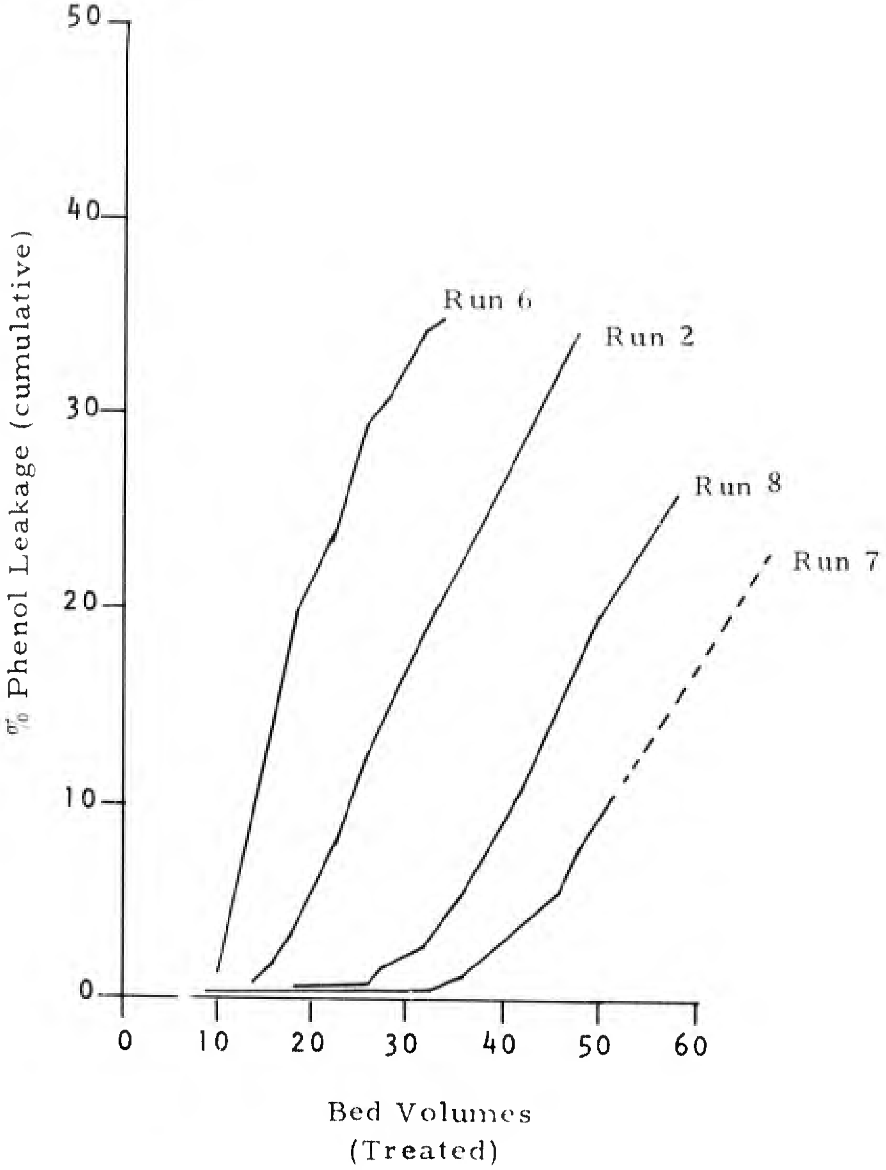

Figure 59. Phenol Leakage Curves

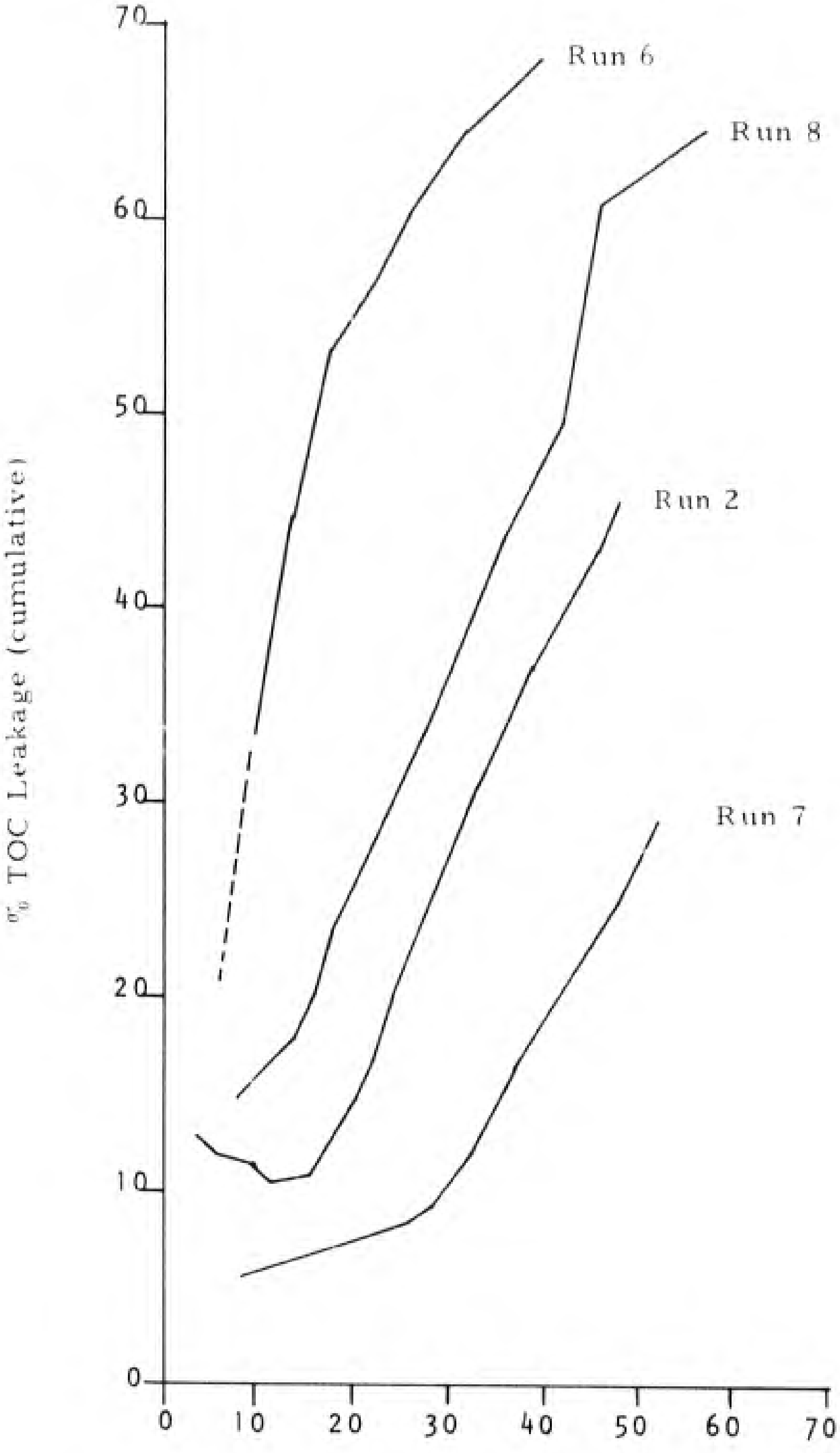

Figure 60. TOC Leakage Curves

before reaching that leakage. In terms of TOC removals, after 22 bed volumes were treated, the leakage rate for Run No. 8 was 30 percent, while during Run No. 7 approximately 50 bed volumes were treated before this level was reached.

Also, the relationship between the average influent concentrations and subsequent removals was not predictable in the case of either phenol or TOC. For example, Run No. 6 has the lowest average influent levels for both phenol and TOC and, based on this, one would expect to find that more bed volumes of this waste could be treated before any substantial leakage occurs, compared to runs where the waste contaminations were greater. This, however, was not the case. Rather, the buildup of each component in the effluent was extremely rapid for both components, i.e., approximately 50 percent TOC breakthrough after treating only 15 bed volumes. Based on these factors, as well as the information generated during the regeneration process, it may be concluded that these ambiguities result primarily from wastewater variability. The reason may be that certain untreated components may inhibit the removal of other components either by directly affecting the mechanism of adsorption or by forming a non-adsorbable complex with components that would normally be removed.

Figure 61 shows removal efficiencies (X/M) for both phenol and TOC that were achieved at various percents (cumulative) phenol leakage for points between 1 and 25 percent. These plots were derived using average values from Runs No. 2, No. 6, No. 7 and No. 8 at three leakage (cumulative) values which were 1, 10 and 25 percent. Run No. 5 was not included for reasons already indicated. As expected, the efficiencies for both parameters increase sharply as the volume of treated waste increases and, therefore, the level of contaminants in the effluent increases. It is well known that the efficiency of any adsorption system will continue to improve until adsorbent reaches saturation or the influent and effluent are at equilibrium. For example, the carbon capacity at 1 percent breakthrough was 0.038 pound of phenol per pound of carbon, while at 25 percent breakthrough, this capacity increased to 0.061 pound per pound. At these same breakthrough points, the capacity of the carbon in terms of TOC increased from 0.066 to 0.099 pound per pound.

The theoretical TOC of phenol is about 77 percent on a weight basis, i.e., each 100 milligrams per liter phenol should yield 77 milligrams per liter TOC. The dotted curve in Figure 61 shows the theoretical efficiency of the portion of TOC contributed by phenol alone. There is a difference of approximately 55 percent between this efficiency curve and the one which represents total wastewater TOC. This means that more than twice as much TOC was removed by the carbon as was contributed by phenol alone or, to state it differently, only half the carbon capacity was utilized by the TOC from the phenolic constituents of the wastewater.

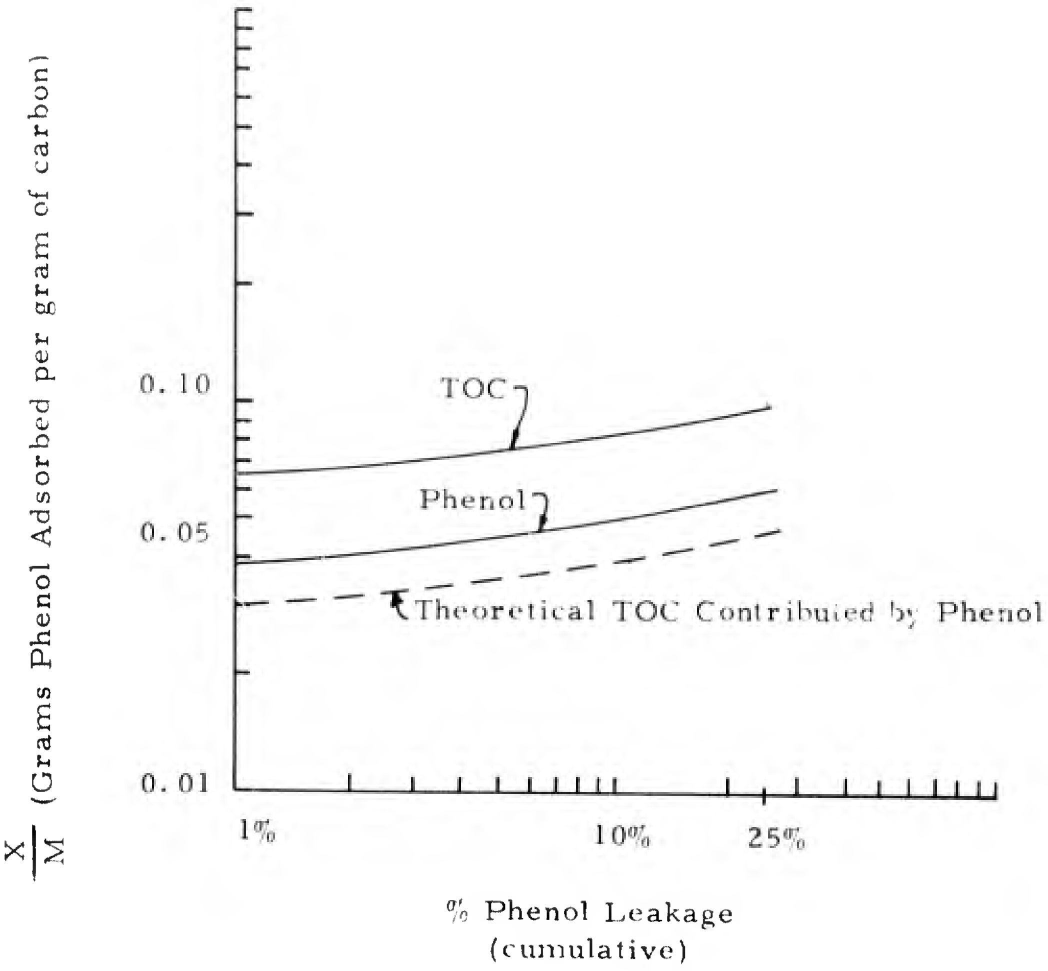

Figure 61. Phenol Removal Efficiency Versus Percent Leakage

It should be re-emphasized that the performance of the system was impossible to predict when influent values were used as a basis of comparison. This is due to the inherent complexity as well as variability of the wastewater. Also, it can be generally concluded that, in terms of removal of the tested parameters, the carbon appeared to have been successfully regenerated.

SECTION IV

ACTIVATED CARBON REGENERATION

The spent carbon to be regenerated was removed from the contact column via the bottom outlet port, drained, packed in 55-gallon drums and shipped to Eimco-BSP Development Laboratory in Brisbane, California. In all, four thermal regeneration cycles were performed on the same charge of carbon.

Equipment

A flow schematic and equipment description was provided by Eimco-BSP and is included in Appendix A.

Procedure

First, the basic process conditions were determined from batch tests using a 13-inch inside diameter single hearth furnace. This had to be done immediately before the first regeneration run was performed because of the uniqueness of any given contaminated carbon, i.e., process conditions may vary with type of carbon, type of adsorbate, degree of regeneration desired, etc.

All subsequent regenerations were performed using the 30-inch inside diameter pilot furnace system. Prior to each feeding, the furnace was bedded down with a similar type carbon which was sacrificed in order to minimize losses in the test batch itself. This beddown procedure was necessary once during each regeneration before the test batch was fed into the furnace. Beddown carbon consumption should be of negligible consequence in a full scale, continuously operated system.

Discussion of Results

Table 5 shows the feed rates and furnace losses for each of the four runs.

As the data indicates, furnace losses on a total weight basis were extremely small once the regeneration process achieved a steady state. Before this point is reached, however, most of the bedded down carbon is destroyed along with a small amount of the test carbon. BSP estimates the carbon burnoff to be about 5 percent (based on ash content) per run but this could probably be reduced in a full scale furnace where better atmospheric control is possible.

TABLE 5. FURNACE FEED RATES AND LOSSES

Run	Feed Rate (wet lbs/hr)	Product Rate (wet lbs/hr)	Furnace Losses - Total Weight Basis (Steady State)
1	110	98	Negligible
2	649	64.8	Negligible
3	136	82	Negligible
4	97	84	Negligible

Iodine numbers are indicative of the carbon's total surface area in terms of its ability to adsorb low molecular weight substances (References 6, 8). This was, therefore, one of the major criteria used in determining the extent to which the regenerated material approached the original activity of virgin carbon. As shown in Appendix A, the average iodine numbers for the regenerated carbon were 709, 820, 787 and 873 for Runs No. 1 through No. 4, respectively, while the iodine number for virgin carbon is 850. These results indicate that, as the regeneration conditions were optimized, the activity of the regenerated carbon in terms of iodine numbers approached and, in one case, surpassed that of virgin carbon.

Table A-2 (Appendix A) shows the furnace operating conditions for each of the first three spent carbon regeneration runs. Except for a feed rate of 150 pounds per hour wet weight, the fourth contamination run was performed using the same operating conditions as Run No. 3. A temperature of approximately 1750°F (1700°F for Run No. 3) was maintained within the bottom three hearths where steam was introduced at a rate of one pound per pound dry carbon. Because newly regenerated carbon oxidizes very rapidly when in contact with air, the carbon was immediately quenched upon leaving the furnace. This quenched material was then fed by screw conveyor to a 55-gallon drum for weighing and shipping. Samples were periodically collected and analyzed for apparent density, moisture, iodine number, and ash content and these results are shown in Table A-3 (Appendix A). The same analyses were performed on the feed materials for each run and these results are shown in Table A-4 (Appendix A).

To determine if there was a buildup in total chromium on the carbon which could not be removed by regeneration, samples of carbon were analyzed using emission spectroscopy. This was accomplished by first ashing the carbon at 550°C and analyzing this ash for total chromium. The results are shown in Table 6.

A screen analysis of the feed and product composites was performed for Run No. 4 to determine if the thermal regeneration process produced any major changes in the particle size range, i.e., primarily in the production of fines.

There appears to be a definite correlation between the removal efficiency exhibited by a given carbon charge and the iodine numbers obtained on that carbon before regeneration. For example, in terms of removal efficiency (Figures 59 and 60) Carbon Contamination No. 7 was the most efficient and this carbon was found to have the lowest iodine numbers before regeneration (Run No. 4) compared to all the other carbon charges.

TABLE 6. TOTAL CHROMIUM RETAINED BY CARBON

Sample	Total Chromium as Cr_2O_3 (by weight in original sample)
Virgin Carbon (WV-L 8 x 30 mesh)	0.004
Run No. 1 Feed (Composite)	0.05
Run No. 1 Product (Composite)	0.12
Run No. 2 Feed (Composite)	0.20
Run No. 2 Product (Composite)	0.17
Run No. 3 Feed (Composite)	0.20
Run No. 3 Product (Composite)	0.25
Run No. 4 Feed (Composite)	0.24
Run No. 4 Product (Composite)	0.16

The ash percentage is important in determining the extent of inorganics building within the carbon, resulting in a reduction in adsorptive ability. Virgin WV-W carbon has a maximum percent ash of 7.0. The percent ash content in the regenerated products for all four runs shows no substantial increase and, therefore, it can be assumed that inorganic buildup will not be a problem in carbon used to treat this type of wastewater (Reference 6).

Apparent density is the weight per unit volume of a carbon including the pores and voids when applied to a packed bed. It is useful in determining if regeneration produced any major change in the size and shape of the carbon granules. The results show that no major change in apparent density was encountered. This is also consistent with the screen analyses shown for Regeneration No. 4 in Table A-5 (Appendix A) (no screen analyses were conducted during the first three regenerations).

As shown in Table 6, there was somewhat more total chromium present in the spent carbon compared to virgin carbon. This residual chromium appears to be the same for the last three regenerations, indicating that there was an initial buildup of this metal during the first two contaminations with no further increase during subsequent regenerations. In addition, it appears that total chromium is not removed during the thermal regeneration process.

In their report, BSP states; "The results of the series of tests demonstrate that regeneration of the spent material is technically feasible and well suited to the multiple hearth furnace. It is recommended that the conditions used for this fourth run be adopted as the operating parameters for the full scale furnace. Basically, this would be a regeneration temperature of 1750°F, steam addition at a rate of 1 pound per pound of dry regenerated carbon and a residence time of 45 minutes. An afterburner is recommended to insure the burning of all the volatile material that is given off. Strong odors of phenol were apparent on the third run when the afterburner was not fired. No such odors were noted during this last run with the afterburner maintained at about 1400°F."

It appears that the conditions used to regenerate the carbon during the last (Run No. 4) cycle were optimum for these carbons. The loading rate (dry basis) used was 3.6 pounds per hour per foot^2 and BSP indicated that in a full scale furnace it would not be unreasonable to expect a loading rate of 4.8 pounds per hour per foot^2 to achieve the same results.

SECTION V

PROCESS DESIGN AND COST ESTIMATES

The degree of paint stripping and related activities now being performed at Kelly Air Force Base varies considerably from one period to another. This has a corresponding effect on the wastewater generated, causing wide fluctuations in flow rates. The average flow rate, however, appears to be in the range of 10 gallons per minute over an average operating day.

It was found during the on-site study that at least a 30-minute residence time was required in order to achieve an acceptable level of treatment in terms of phenol removal. This residence time corresponded to a 6.25-gallon per minute flow rate for the carbon contact column. Therefore, assuming no other major changes, a somewhat larger system would have to be used to treat a 10-gallons per minute average flow in order to maintain the required 30-minute minimum residence time. Figure 62 shows a schematic of the proposed system (References 4, 12). It may be possible to modify the existing pilot plant to accomplish this.

This modified system involves a contact column operated in upflow countercurrent fashion with pulsed-bed carbon addition and removal. This same column design could be used to achieve any desired level of phenol in the effluent, simply by varying the carbon addition rate.

Assuming a 10-gallons per minute average flow rate and an average influent phenol concentration of 920 milligrams per liter, the following method would be used to calculate daily carbon consumption when proposed average effluent concentrations are to be 10 milligrams per liter and 100 milligrams per liter, respectively.

Carbon Consumption

For 10 milligrams per liter average phenol effluent:

Pounds of phenol removed per day = 14,400 gal x 0.00759 lbs/gal = 109.30

Pounds of carbon required per day = 109.30 lbs of phenol removed/day

÷

0.038 carbon efficiency at 10 mg/1*

= 2876

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* See Figure 61.

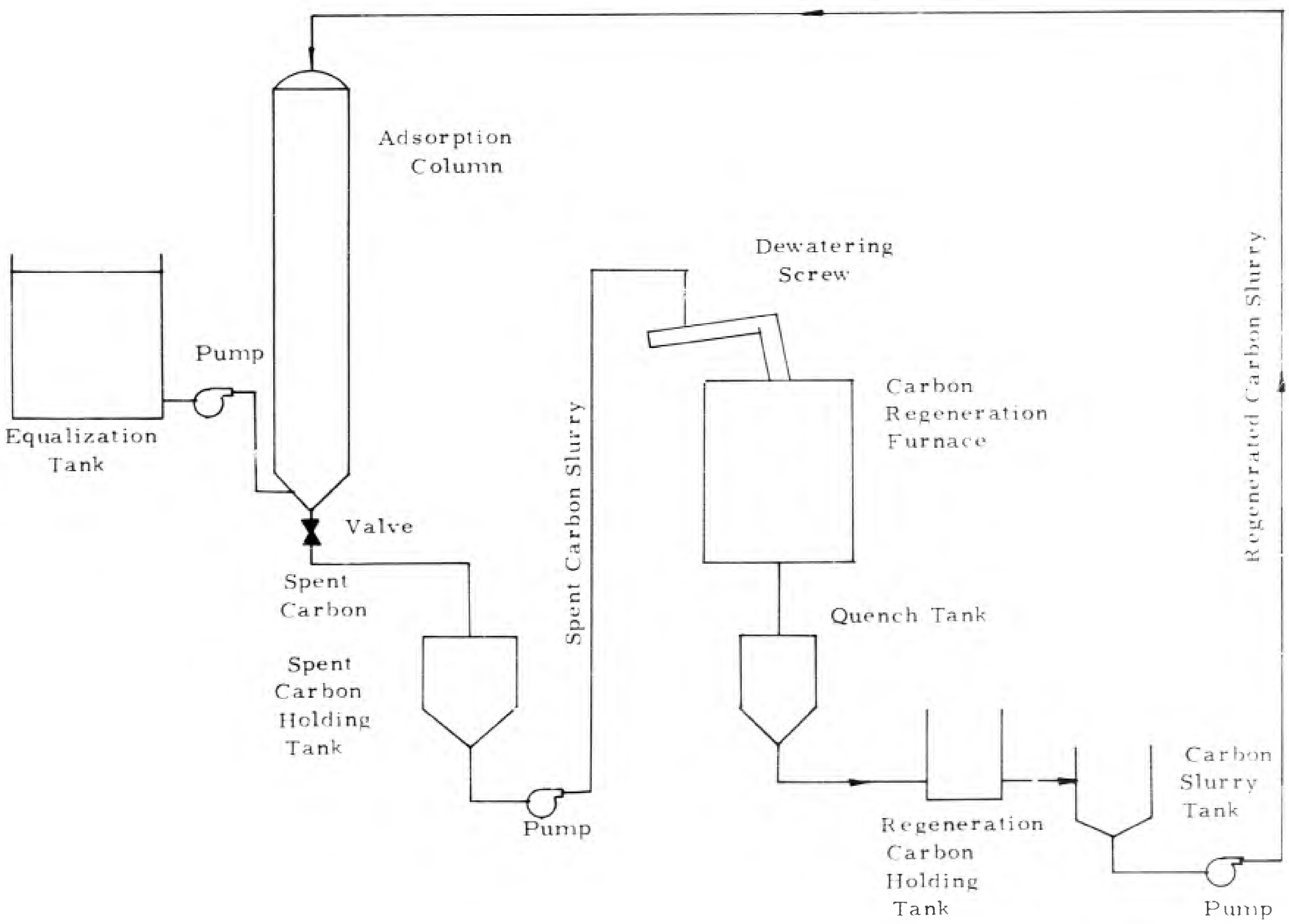

Figure 62. Schematic of Proposed Carbon Treatment System

For 100 milligrams per liter average phenol effluent:

Pounds of phenol removed per day = 14,400 gal x 0.00684 lbs/gal = 98.50

Pounds of carbon required per day = 98.50 lbs of phenol removed/day

÷

0.053 carbon efficiency at 100 mg/l*

= 1858

* See Figure 61.

Generally, it is more economical to use on-site regeneration when carbon usage exceeds 1,000 pounds per day as the current cost of custom regeneration is about $0.26 per pound, plus freight charges. Depending upon the availability of regeneration facilities, it may be economically feasible to use on-site regeneration even if daily usage is less than 1,000 pounds per day, thereby eliminating freighting charges. The system proposed for the treatment of paint stripping wastewater, therefore, encompasses an on-site regeneration facility.

As indicated, the only major difference between the two levels of treatment desired (10 or 100 parts per million average effluent) would be in the carbon usage and, therefore, the regeneration furnace and related equipment would be sized differently for each. Table 7 lists the major equipment and general capital cost estimates. All treatment equipment is fabricated of 304 stainless steel except the equalization tanks which are fabricated of reinforced concrete and include a chemical resistant coating.

The multiple hearth furnaces used on each 10-gallons per minute system would be:

For 10 milligrams per liter average phenol effluent = 30-inch diameter, six-hearth, gas-fired furnace rated at 120 pounds per hour.

For 100 milligrams per liter average phenol effluent = 30-inch diameter, four-hearth, gas-fired furnace rated at 80 pounds per hour.

Table 8 shows the estimated operating costs for this system.

It was assumed that, at some future time, the amount of depainting and related activity might increase at Kelly Air Force Base such that wastewater is generated at five times the current volume. In order to maintain the appropriate residence time of at least 30 minutes, a considerably larger system would have to be constructed. Basically, it would involve a direct

TABLE 7. MAJOR EQUIPMENT AND CAPITAL COST ESTIMATES FOR 10 GALLONS PER MINUTE CARBON TREATEMENT SYSTEM

Item	10 mg/l Average Phenol Effluent	100 mg/l Average Phenol Effluent
Equalization Tank (8 hours capacity)		
Contact Column (200 ft^3 carbon)		
Carbon Storage Tanks (spent and regenerated @ 3-day supply)		
Miscellaneous, including pumps, piping, instruments, etc.	$140, 000	$109, 000
- -		
Regeneration Furnace, including dewatering screen, quench tank, afterburner, controls, etc.	$170, 000	$135, 000
Activated Carbon Inventory For initial column charge and 3-day supply @ $0.38/lb	$3, 800	$2, 500
ESTIMATED TOTAL INSTALLED COSTS	$313, 800	$246, 500

TABLE 8. ESTIMATED OPERATING COSTS FOR

10 GALLONS PER MINUTE CARBON TREATMENT SYSTEM

	10 mg/l Average Phenol Effluent	100 mg/l Average Phenol Effluent
Fuel, power, steam, etc., based on:		
Natural gas @ $1.65/million BTU Electricity @ $0.02/KWH Steam @ $1.80/1,000 lbs	$52.00	$33.00
Maintenance (including carbon regeneration and related activities) @ 2% of capital costs/yr		
Operating Labor @ $6.00/hr	$161.00	$157.00
Carbon Make-up @ $0.38/lb (based on 5% regeneration losses)	$55.00	$35.00
ESTIMATED TOTAL DAILY OPERATING COSTS	$268.00	$225.00

scale-up of the system proposed for the 10 gallons per minute flow. The hydraulic loading on the column, however, should be changed from 1.63 gpm/ft^2 to 3.14 gpm/ft^2 in order to have a contact column of reasonable dimensions. Table 9 shows the capital cost estimates for the major equipment (References 13, 14, 15, 16).

The multiple hearth furnaces used on each 50 gallons per minute system would be:

For 10 milligrams per liter average phenol effluent = 7 ft OD, six-hearth, gas-fired furnace rated at 625 lbs/hr.

For 100 milligrams per liter average phenol effluent = 6 ft OD, six-hearth, gas-fired furnace rated at 425 lbs/hr.

Table 10 shows the daily operating costs for a 50 gallons per minute system.

References

13. C. H. Huether and S. B. Stanton, "Regeneration of Granular Activated Carbon," Westvaco, Chemical Division (1973).
14. R. A. Hutchins, "Thermal Regeneration Costs," <u>Chemical Engineering Progress</u>, Vol 71, No 5 (May, 1975) 80-86.
15. K. I. Himmelstein et al, "In-Place Regeneration of Activated Carbon Used in Industrial Waste Treatment," 75th National Meeting of the AIChE, June 4, 1973.
16. W. G. Schuliger and J. M. MacCrum, "Granular Activated Carbon Reactivation System Design and Operating Conditions," 75th National Meeting of the AIChE, June 5, 1973.

TABLE 9. MAJOR EQUIPMENT AND CAPITAL COST ESTIMATES FOR 50 GALLONS PER MINUTE CARBON TREATMENT SYSTEM

Item	10 mg/l Average Phenol Effluent	100 mg/l Average Phenol Effluent
Equalization Tank (8 hrs capacity)		
Contact Column (200 ft^3 carbon)		
Carbon Storage Tanks (spent and regenerated @ 3-day supply)		
Miscellaneous, including pumps, piping, instruments, etc -	$231,000	$217,000
Regeneration Furnace, including dewatering screen, quench tank, afterburner, controls, etc	$275,000	$210,000
Activated Carbon Inventory For initial column charge and 3-day supply @ $0.38/lb	$19,000	$12,500
ESTIMATED TOTAL INSTALLED COSTS	$525,000	$439,500

TABLE 10. ESTIMATED OPERATING COSTS FOR

50 GALLONS PER MINUTE CARBON TREATMENT SYSTEM

	10 mg/l Average Phenol Effluent	100 mg/l Average Phenol Effluent
Fuel, power, steam, etc., based on:		
Natural gas @ $1.65/million BTU Electricity @ $0.02/KWH Steam @ $1.80/1,000 lbs	$191.00	$111.00
Maintenance (including carbon regeneration and related activities) @ 2% of capital cost/yr		
Operating labor @ $6.00/hr	$172.00	$168.00
Carbon Make-up @ $0.038/lb (based on 5% regeneration losses)	$55.00	$35.00
ESTIMATED TOTAL DAILY OPERATING COSTS	$418.00	$314.00

SECTION VI

CONCLUSIONS

1. Solids removal based on chemical addition does not appear feasible but this can be accomplished by means of properly designed strainers.

2. Of 12 granular carbons tested on phenolic aircraft stripping wastewater Nuchar WV-W 8 x 30 mesh granular activated carbon showed the highest efficiency of phenol removal.

3. The adsorptive capacity of Nuchar WV-W for phenol, based on an adsorption isotherm at a wastewater equilibrium concentration of 250 milligrams per liter phenol, is 0.12 gram of phenol per gram of activated carbon.

4. A minimum contact time of 30 minutes must be used in any activated carbon system to properly treat the phenolic paint stripping wastewater.

5. The concentration of other constituents has a considerable effect on phenol adsorption.

6. No pressure losses were incurred across the contact column during normal operation.

7. At 10 percent average leakage (based on an average of 920 milligrams per liter phenol and 2,000 milligrams per liter TOC), the average removal efficiencies for four runs at 30 minutes residence time were 0.052 gram of phenol per gram of carbon and 0.084 gram of TOC per gram of carbon.

8. Removal efficiencies achieved during the laboratory study were considerably lower during the on-site study.

9. Thermal regeneration of the carbon appeared to be generally effective in restoring and removing the adsorptive activity of the carbon.

10. Although the activated carbon did reduce the level of total chromium in the wastewater, the adsorbed chromium did not affect the thermal regenerability of the carbon.

11. On-site thermal regeneration would be more economical than custom regeneration for the amounts of carbon needed to treat the entire wastewater flow (10 gallons per minute).

12. Activated carbon pretreatment of the paint stripping wastewater will reduce the phenol concentration to an acceptable level.

SECTION VII

RECOMMENDATIONS

1. If an activated carbon system is to be employed to treat primarily the phenolic constituents, every effort should be made to segregate the waste streams so as not to put an unnecessary loading on the carbon.

2. Since activated carbon appears to be a viable treatment method for the removal of phenol, it is suggested that the Air Force consider the installation of a full scale system. This system should be sized to handle a 50 gallons per minute flow which is the expected increase in loading due to the C-5 aircraft.

3. A study should be undertaken to determine the feasibility of in-place chemical regeneration of the activated carbon which has been used to remove phenol.

4. A study should be undertaken to determine the feasibility of adding powdered carbon directly to the wastewater prior to its discharge into a sewer system. This approach might render the phenol less toxic to a bacterial system and also enhance the degradation process.

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APPENDIX A

THERMAL REGENERATION EQUIPMENT AND RESULTS

Description of Equipment

30-Inch-Inside-Diameter Multiple Hearth Furnace

The pilot furnace system used for the continuous test is shown in the accompanying figure.

Feeding System

The material was fed to the furnace by use of the variable speed screw conveyor which was adjusted to deliver the required feed rate.

Furnace

The multiple hearth furnace is a 30-inch-inside-diameter by six-hearth units of approximately 24 square feet of effective hearth area. There are two main burners with proportional gas-air mixers per hearth. A revolving central shaft and attached radial rabble arms sweep the material across each hearth. Alternating in-feed and out-feed material is moved across each hearth as it drops from level to level. All material is processed for the same time regardless of particle size spread. The rabble teeth arrangement compensates for about 25 percent back rabbling (plowback). This increases the material exposure to the furnace gas without decreasing the furnace retention time. This retention time (shaft speed) is controlled by an adjustable sheave on the shaft drive motor and a series of pulleys.

Screw Conveyor

The furnace discharges into the screw conveyor which feeds the product into a drum.

Cyclone

The exhaust gases can exit from either the top or No. 1 hearth or bottom No. 6 hearth. The gases enter the cyclone where solid particles are captured by centrifugal action.

Afterburner

The gases spiralling through the top of the cyclone are sent to the afterburner where remaining volatile materials (if they exist) are burned. The total volume of this afterburner is 3.54 cubic feet.

Wet Impingement Scrubber

After exiting the afterburner, the gases enter the wet scrubber where they pass through an impingement plate prior to the packed section. Water flows countercurrently to the gases and collects the remaining fine particles that escaped the cyclone.

Induced Draft Fan

The gases are induced through the exhaust system and out through the stack by the induced draft fan. A pressure probe connected from either the first hearth or sixth hearth to the ID fan controls the pressure drop in the furnace.

The 30-inch-ID experimental multiple hearth furnace is used to determine the loading rate for sizing purposes and to detect possible problems that may not have been gleaned in the batch furnace test.

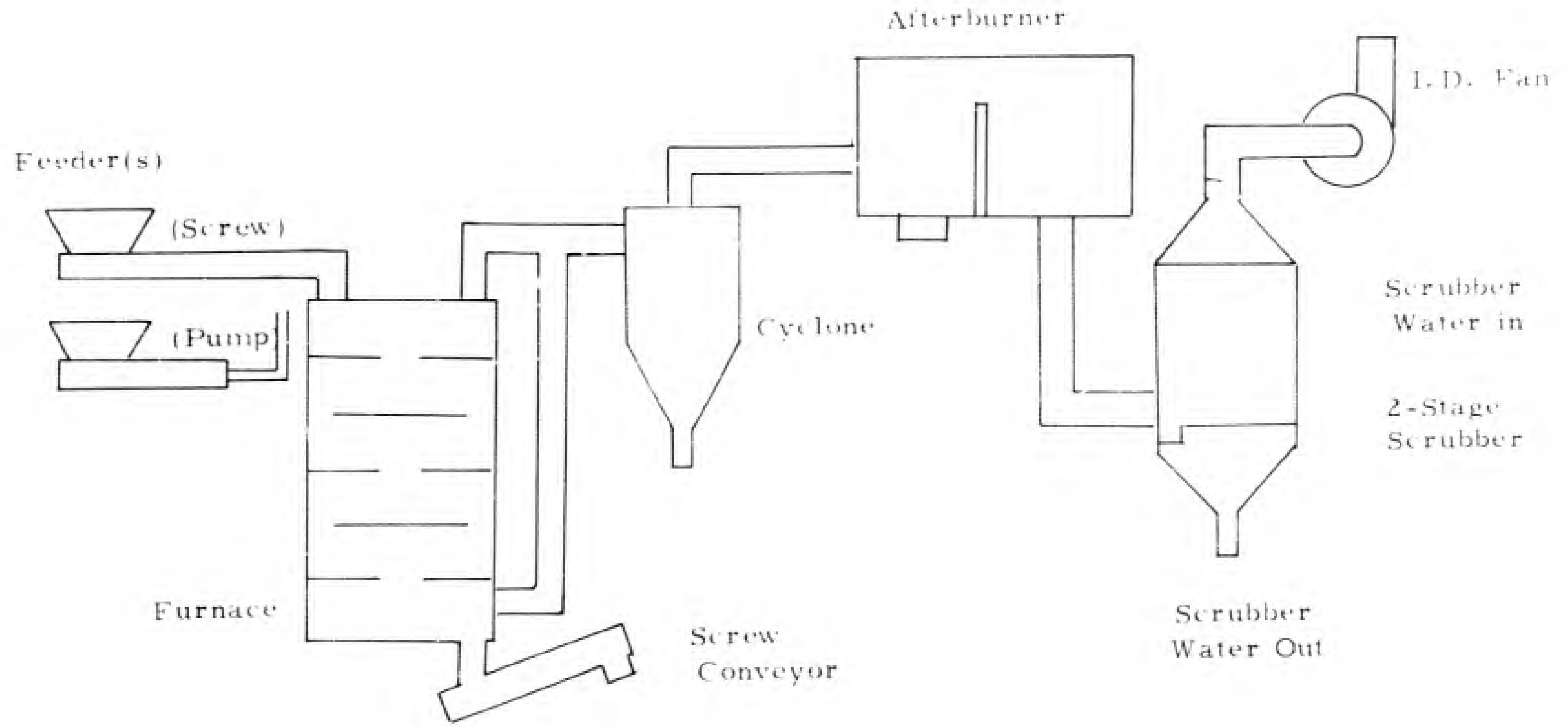

Figure A-1. 30-Inch-Inside-Diameter x 6-Hearth-Unit Pilot Furnace System

TABLE A-1. AVERAGE RESULTS FOR EACH REGENERATION

	H_2O (Percent)	AD (g/ml)	Iodine No.	Ash (Percent)
First	23.0	0.57	709	5.7
Second	48.1	0.56	820	6.2
Third	45.2	0.55	787	7.0
Fourth	40.3	0.54	873.3	7.49

TABLE A-2. FURNACE OPERATING CONDITIONS

	First Regeneration	Second Regeneration	Third Regeneration *
Feed Rate	100 lbs spent carbon per hr	100 lbs spent carbon per hr (wet basis)	200 lbs spent carbon per hr (wet basis)
Retention Time	30 minutes	45 minutes	45 minutes
Burners	Fired on Hearths 4, 5 and 6. Set rich.	Fired on Hearths 4, 5 and 6. Set for 20% excess air.	Fired on Hearths 4, 5 and 6.
Temperatures	Controlled at 1750°F on Hearths 4, 5 and 6.	Controlled at 1750°F on Hearths 4, 5 and 6.	Controlled at 1700°F on Hearths 4, 5 and 6.
After-burner	Fire as required.	Off.	Off.
Draft	Set to 0.0" W.C. on Hearth 6.	Set to 0.01" W.C. on Hearth 1.	Set to 0 on Hearth 1.

* Fourth run regenerations performed under similar conditions.

TABLE A-3. SUMMARY OF REGENERATION RESULTS

FIRST REGENERATION

Time	Total Feed (lbs)	Total Products (lbs)	AD * (g/ml)	Ash (Percent)	H_2O (Percent)	Iodine No.
12:30 PM	190	0	0.64			
1:00 PM	240	30	0.68			
2:30 PM	390	151	0.54			
3:30 PM	500	249	0.58			
4:30 PM	600	328	0.55			783
5:30 PM	700	426	0.54			
6:30 PM	805		0.57	5.61		
7:30 PM	905	654	0.56			
8:30 PM	1025	764	0.56			701
9:30 PM	1125	869	0.54			
10:30 PM	1250	969	0.57			651
11:30 PM	1325	1075	0.56			
12:30 PM	1475	1174	0.55	5.75		782
1:30 AM	1575	1272	0.58			
2:30 AM	1675	1388	0.57		29.0	699
3:30 AM	1775	1477	0.57		20.0	
4:30 AM	1895	1550	0.58		24.1	682
5:30 AM	2015	1634	0.57		17.5	

* Apparent density

TABLE A-3. SUMMARY OF REGENERATION RESULTS (CONTINUED)

SECOND REGENERATION

Time	Total Feed (lbs)	Total Products (lbs)	AD * (g/ml)	Ash (Percent)	H_2O (Percent)	Iodine No.
1:00 PM			-	-	-	-
2:00 PM			-	-	-	-
3:00 PM	124	143	-	6.7	56.5	-
4:00 PM	224	-	0.54	-	-	-
5:00 PM	328	475	0.55	6.1	53.3	861
6:00 PM	432	608	0.55	-	52.8	-
7:00 PM	537	-	0.54	6.0	48.5	875
8:00 PM	648	935	0.55	-	52.7	-
9:00 PM	759	1047	0.55	5.7	43.8	727
10:00 PM	870	1158	0.58	-	36.4	-
11:00 PM	974	1245	0.57	6.4	38.8	809
12:00 AM	1077	1301	0.55	-	50.2	-
1:00 AM	1180	1391	0.56	6.3	-	829
2:00 AM	1373	-	-	-	-	-

* Apparent density

TABLE A-3. SUMMARY OF REGENERATION RESULTS (CONCLUDED)

THIRD REGENERATION

	AD (g/ml)	Iodine No.	H_2O (Percent)	Ash * (Percent)
1:00 Product	0.53	-	54.3	7.0
3:00 Product	0.59	793	46.9	7.0
4:00 Product	0.52	-	41.5	7.4
5:00 Product	0.55	781	38.1	6.7

FOURTH REGENERATION

1:00 PM	0.52	876.4	54.7	7.16
2:00 PM	0.55		38.6	
3:00 PM	0.53	868.2	42.4	
4:00 PM	0.55		0.17	
5:00 PM	0.55	880.5	38.7	
6:00 PM	0.54		42.0	7.82
7:00 PM	0.53	868.2	52.3	
8:00 PM	0.52		53.6	

* Reported on a dry solids basis.

TABLE A-4. ANALYSIS OF COMPOSITE FEED SAMPLES

	First Regeneration	Second Regeneration	Third Regeneration	Fourth Regeneration
Percent Moisture	36.6	38.5	31.9	35.3
Percent Ash	2.8	5.9	6.2	7.5
Apparent Density (g/ml)	0.77	0.59	0.58	0.60
Iodine Number	-	548	534	386

* Average values

TABLE A-5. SCREEN ANALYSIS FOR FOURTH REGENERATION

Feed Composite

Mesh	Percent Retained	Percent Cumulative Retention
10	21.0	21.0
20	59.2	80.2
28	12.9	93.1
42	4.34	97.44
48	0.72	98.16
65	0.49	98.65
-65	1.35	100.00

Product Composite

10	18.7	18.7
20	61.9	80.6
28	14.1	94.7
42	3.73	98.43
48	0.35	98.78
65	0.29	99.07
-65	0.93	100.00

APPENDIX B

ANALYTICAL PROCEDURES

During this study, various quantitative analytical techniques were used to monitor both the untreated and treated wastes. The following is a discussion of those techniques:

Phenol

During the laboratory phase of this project, it became obvious that the number of samples requiring phenol analysis by the technique described in "Standard Methods for the Examination of Water and Wastewater" would consume an inordinately high amount of time. An investigation was undertaken to find an alternative technique which would allow greater speed in determining the phenol content without compromising the accuracy and precision of measurement. Such a technique was found described in "Procedures, Chemical Tests and Glassware for Water and Wastewater Analysis" as published by Hach Chemical Company, Ames, Iowa.

A direct comparison of the "Standard Methods" technique and the "Hach" technique was made and the results were sufficiently comparative to allow the use of the Hach technique throughout the remainder of the project.

Total Organic Carbon

Total organic carbon measurements were made according to the procedure in "Standard Methods for the Examination of Water and Wastewater," 13th edition, p. 257 A Model 915 Total Organic Carbon Analyzer as manufactured by Beckman Instruments, Inc., Fullerton, California, was used.

Total Chromium

Total Chromium was analyzed by the "Atomic Absorption Spectrophotometric Method" in "Standard Methods for the Examination of Water and Wastewater," 13th edition, p. 211. A Model AC2-20 Atomic Absorption Spectrophotometer as manufactured by Bausch & Lomb Co., Rochester, N. Y., was used.

pH

pH was measured via a Model 10 meter as manufactured by Corning Glass Works, Corning, N. Y. The meter was equipped with Corning triple purpose glass and calomel electrodes.

Methylene Chloride

Samples were analyzed directly for methylene chloride content by gas chromatography. The chromatograph was operated with an injection port temperature of 275°C, column oven temperature of 225°C and detector temperature of 230°C. The column used was 6 feet long by 1/8 inch diameter stainless steel with divinyl benzene polymer packing. Aqueous dilutions of known methylene chloride were used to calibrate the peak area. A Model 820 Gas Chromatograph as manufactured by Perkin-Elmer Co., Norwalk, Conn., was used.

Chemical Oxygen Demand

Chemical oxygen demand was measured by the dichromate-reflux method as described in the Environmental Protection Agency manual "Methods for Chemical Analyses of Water and Wastes - 1971," p. 17.

Oil and Grease

Oil and grease measurements were made using the Hexane Soxhlet Extraction technique as described in the EPA manual "Methods for Chemical Analyses of Water and Wastes - 1971," p. 217.

Suspended Solids

Suspended (non-filterable) solids were measured by the technique described on page 278 of "Methods for Chemical Analyses of Water and Wastes - 1971."

LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS

C_6H_6O	Phenol
CO_2	Carbon Dioxide
H_2O	Water
H_2SO_4	Sulfuric Acid
KOH	Potassium Hydroxide
$KMnO_4$	Potassium Permanganate
MnO_2	Manganese Dioxide
AD	Apparent Density
°C	Degrees Centigrade
COD	Chemical Oxygen Demand
°F	Degrees Fahrenheit
g	Grams
GPM/ft^2	Gallons per Minute per Square Foot
hr/day	Hours per Day
ID	Inside Diameter
lb/ft^3	Pounds per Cubic Foot
lbs/hr	Pounds per Hour
μ	Microns
mls	Milliliters
ml/min	Milliliters per Minute

LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS (CONCLUDED)

m^2/g	Square Meters per Gram
mg/l	Milligrams per Liter
OD	Outside Diameter
pH	The negative logarithm of the hydrogenion concentration.
ppm	Parts per million
SS	Stainless Steel
TOC	Total Organic Carbon