1974

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Recommended Citation

Narasimhan, K. A., "Relative performance of two activated carbons in treating pharmaceutical waste." (1974). *Masters Theses*. 3416.
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RELATIVE PERFORMANCE OF TWO ACTIVATED CARBONS IN TREATING PHARMACEUTICAL WASTE

BY

K. A. NARASIMHAN, 1939-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI - ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

IN

CIVIL ENGINEERING

1974

Approved by

Huang (Advisor) Sotirios G. Grigoropoulos

ABSTRACT

This work examined the feasibility of the carbon adsorption system to treat a high organic strength waste (having a COD of 8,100 mg/ℓ) from a pharmaceutical plant, and also compared the relative treatment efficiencies of two different kinds of carbon, Calgon Filtrasorb 400 and Darco S-51, both having the same size ranges.

The overall treatment scheme employed consisted of chemical clarification and activated carbon adsorption. Jar tests were conducted to select a proper type of coagulant and determine an optimum dosage. Batch and column adsorption studies were conducted using both carbons.

Alum was found to be a better coagulant than ferric chloride for the specific waste studied. At a dose of 50 mg/ℓ, the turbidity was reduced from 31 Ju to less than 5 Ju. Batch carbon adsorption studies indicated that the adsorption isotherms were in conformity with the Freundlich model. Column studies indicated that high efficiency organic removal could only be achieved for the initial small volume of the wastewater treated under this particular experimental setup. This was because the pharmaceutical waste had a very high organic concentration and as such, organic leakage through the carbon bed became common unless a very long contact time was provided. Similarly, both NH_3-N and Org-N were removed only in the initial brief operation period. Since the original waste contained no phosphorus, there were no data available concerning the phosphorus removal by carbon adsorption.

This study also demonstrated that the two carbons tested differed in their adsorptive capacities. It was found that the Calgon carbon had nearly twice as much adsorptive capacity as the Darco carbon. On the weight basis, the former could adsorb COD to an extent of 19.9 percent, while the latter could reach only 8.8 percent when the carbon beds were completely exhausted.

ACKNOWLEDGEMENT

The author wishes to express his sincere thanks to his advisor, Dr. Ju-Chang Huang, for his continuous encouragement and guidance during the course of this investigation. Appreciation is also extended to Dr. Sotirios G. Grigoropoulos for his consent to review the thesis material during the period when Dr. Huang was away from campus on another assignment and to serve as a committee member. Thanks are also extended to Dr. Ernst Bolter for his help and service as a committee member.

The author also wishes to thank the Department of Civil Engineering of the University of Missouri - Rolla for providing the facilities which were used during the study.

Special gratitude is also extended to Dr. Huang for his assistance in providing financial assistance for five months in the form of a research assistantship.

This study was supported in part by the United States Department of the Interior, Office of Water Resources Research Annual Allotment Grant (71) A-037-MO.

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I. INTRODUCTION

Beginning with the late 1960's, there has been considerable national concern over the adequacy of water resources in the United States followed by the recognition of the necessity of treating wastewater before discharge. In a recent U.S. Geological Survey publication (1), it was reported that in 1970 the total water use (public supply, rural irrigation, and self-supplied industrial) in this country was 370 bgd (1400 mil cu m/day). This represented a 19 percent increase over the use of 310 bgd (1173 mil cu m/day) in 1965 and amounted to more than 70 percent of the estimated dependable supply in 1980. As a result of the above reported situation, stringent effluent quality requirements have been established, and deliberate reuse of the reclaimed wastewater is being considered in some selected cases. Conventional biological treatment methods are not always able to provide the degree of treatment necessary to meet the required effluent quality and neither are they able to produce water for direct reuse. Consequently, there has been considerable research conducted to develop and test new techniques for more effective removal of a broad spectrum of contaminants.

Since 1960, the Cincinnati Water Research Laboratory (formerly the Robert A. Taft Sanitary Engineering Center) has sponsored a number of research programs to develop and evaluate methods of advanced waste treatment (2). Several processes, including chemical coagulation and clarification, activated carbon adsorption, chemical oxidation, electrodialysis, ion exchange, and reverse osmosis, have been investigated and were found effective in removing suspended solids, soluble organics, and inorganic nutrients. An evaluation of these processes by Bayley and Waggott (3) has indicated that activated carbon adsorption combined with chemical coagulation and clarification was the most economical process in producing effluents of high quality.

The ability of activated carbon to remove organics from water has been long recognized. Tertiary treatment using activated carbon adsorption was proposed in the early 1960's and several studies (4-7) have proven the effectiveness of carbon in producing a high quality effluent. These studies have also indicated, however, that tertiary carbon treatment required additional land area and increased the cost of the overall system. In addition, the capacity of the carbon adsorption system to handle toxic materials and surges in flow and strength could not be fully utilized due to the biological step ahead of tertiary system. Further, the biological system hydrolyzed large organic molecules into smaller ones and produced cell fragments which resisted adsorption. It was, therefore, natural to question the validity of a biological step ahead of the tertiary adsorption operation, especially when activated carbon could completely adsorb all the biodegradable organics. Consequently, over the past 4 or 5 yr, there has been considerable research conducted (6-18) on the technical and economic feasibility of eliminating biological treatment and using physical-chemical processes alone for waste renovation. Activated carbon has been employed in these studies as the major tool in removing organics (removals of up to 98 percent have been reported). Other methods have also been investigated, but were not found as effective (17). For example, a chemical-physical system which employed coagulation and continuous countercurrent filtration through a moving sand bed removed only 87 percent of the influent organic matter.

A major portion of the cost in the physical-chemical treatment scheme is associated with the carbon system which accounts for 61 percent of the capital outlay and a considerable percentage of the operating expenditure because of amortization and carbon replacement (18). Activated carbons are manufactured from different sources, using various activating processes. As a result, the characteristics of various carbons, which are marketed in different particle sizes under a variety of trade names and prices are different. Two different carbons cannot be expected to have the same adsorptive capacity for various kinds of organics. Size also appears to be an important characteristic. Slechta and Culp (7) have reported that the 12 x 40 mesh carbon was more efficient than the 8 x 30 mesh carbon, while Zuckerman and Molof (9) have found that granular carbon was more efficient than powdered carbon. Bishop _et_ _al_. (5), however, using 12 different types of carbon found no definite correlation between the adsorptive capacity of the carbon and its physical parameters such as total surface area, ABS (alkyl benzene sulfonate) No.,* Phenol No.,** or dye (Methylene blue or eosine B) adsorption.*** The adsorption capacity also depends on the initial waste strength. According to Zuckerman and Molof (9), Joyce and Sukenik (19) using ABS found that the equilibrium adsorption capacity increased with increasing solute concentration; however, the rate of increase declined with higher initial concentrations.

Laboratory studies of activated carbon adsorption have been conducted using batch and continuous flow column systems. Although the findings of batch studies have been frequently used to predict column performance, the controlling mechanisms in the two systems are different. According to Weber (20), in a rapidly agitated batch system intraparticle transport processes are rate limiting, but in a column type sorption operation, external transport mechanisms such as boundary layer renewal or film transport govern the rate of adsorption. Biological activity might also have an effect in column operation.

Most physical-chemical studies have been confined

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* Defined as the mg of carbon necessary to reduce ABS from 5.0 to 0.5 mg in one ℓ of solution.

** Defined as the mg of carbon necessary to reduce phenol from 5.0 to 0.5 mg in one ℓ of solution.

*** Defined as the residual concentration of the dye after a specific quantity of the dye (340 mg/ℓ for methylene blue and 45 mg/ℓ for eosine B) has been treated with 1 g/ℓ of carbon for one hr, expressed as mg/ℓ.

to domestic wastewaters. However, according to Klimek (21), industry is the largest user of water in the United States and a major producer of liquid wastes. National projections made in 1968 by the Water Resources Council indicated that for the average manufacturing plant, the water recirculation rate would increase from 2.3 times in 1965 to 6.3 times in 2020 (21). Industrial waste treatment would, therefore, need to employ advanced technologies in order to produce a reusable water. Further, industrial wastes are frequently composed of complex organic compounds and are generally very high in organic strength which in some cases may make biological treatment systems not too effective.

In order to evaluate the applicability of physical-chemical methods in the treatment of industrial wastewaters, a research program has been undertaken at the Environmental Research Center of University of Missouri: Rolla since 1970. Under this program, the treatability of a chemical and a refinery waste has already been evaluated by Huang and Hardie (22-24), and the results indicate that activated carbon system is capable of producing high-quality effluents. The thesis reported herein was conducted to further evaluate the feasibility of using the activated carbon adsorption system to treat a high-strength pharmaceutical waste. Specific objectives of this study were to determine: (a) the relative treatment efficiencies of two activated carbons having the same particle size range but supplied by different manufacturers; (b) the usefulness of batch studies in predicting column performance; and (c) the effect of initial carbon concentration on the adsorption rate and capacity in batch reactors.

The waste* was first characterized using a number of standard determinations. It was then pretreated by chemical coagulation and clarification; jar tests were employed to evaluate the use of two coagulants, alum and ferric chloride, and to determine the optimal chemical dosage and pH. The clarified waste was then used to evaluate the performance of two different carbons (both 12 x 40 mesh), Filtrasorb 400** and Darco S-51*** using batch and column studies. Batch studies included evaluations of the rate of uptake and also equilibrium isotherms. Column investigations were conducted in a packed-bed downflow mode of operation and were used to evaluate the treatment efficiency in terms of reduction in organics and in inorganic nutrients.

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* The waste was obtained from the Hoffman-Taff Pharmaceutical Company, Springfield, MO. This waste had a COD of 8100 mg/ℓ and a TOC of 2400 mg/ℓ.

** A product of Calgon Corporation, Pittsburgh, PA.

*** A product of Atlas Chemical Industries, Inc., Wilmington, DE.

II. REVIEW OF LITERATURE

In order to develop a proper procedure to achieve the objectives of this investigation, a study of previous investigations using the physical-chemical carbon adsorption system was undertaken. During the review of published materials, emphasis was placed on specific aspects, such as the characteristics of the wastewater used, degree of treatment obtained, kind of activated carbon used, mode of operation, residence time and hydraulic loading used, and operational difficulties, if any.

The literature reviewed is presented under the following headings: (a) Activated carbon treatment of municipal wastes, (b) Activated carbon treatment of industrial wastes, and (c) The effect of carbon type and size.

A. ACTIVATED CARBON TREATMENT OF MUNICIPAL WASTES

Weber, et al. (8) undertook a study on the direct application of physical-chemical processes to treat primary effluent. The processes which were used included chemical clarification, filtration, and activated carbon adsorption. Laboratory jar tests were conducted using alum, ferric chloride, lime, and polyelectrolytes. Ferric chloride was found more desirable than alum due to its being less influenced by pH and ease of handling and care, although both coagulants at a dosage of 250 mg/ℓ and supplemented by lime at 250 mg/ℓ produced the same effluent turbidity of 1 Ju. Several anionic and nonionic organic polyelectrolytes were tested in dosages ranging from 0.1 to 5 mg/ℓ, but none was found to be particularly effective as a primary coagulant. However, if they were used as secondary floc strengtheners in combination with iron or alum, some of the polyelectrolytes produced larger floc particles which settled more rapidly than those formed with iron or alum alone. Turbidity removal was generally not improved and the dosage of primary coagulant could not be reduced.

Pilot plant studies were conducted using coagulation (with 170 mg/ℓ ferric chloride), upflow clarification, and dual media filtration as pretreatment prior to carbon adsorption. Carbon adsorption studies were conducted using 4 columns in series, each 10 in. (25.4 cm) in diameter and packed with 85 lb (38.6 kg) of 12 x 40 granular carbon* to provide a settled carbon column height of 6 ft (1.8 m). A flow rate of 5 gpm/sq ft (203.5 ℓ/min/sq m) was used. Parallel studies were conducted using packed bed and expanded-bed modes of operation, with and without the chemical clarification step prior to adsorption, and with a filtration step prior to or following the carbon adsorption step. Continuous operation was maintained for a period of 125 days with complete steps of chemical clarification, filtration, and activated carbon adsorption.

The results of the study indicated no practical difference in performance between the packed bed and expanded-bed

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* Marketed by the Pittsburgh Carbon Company, Pittsburgh, PA, under the trade name Cal-activated Carbon.

modes of operation. Good organic removals were observed even without chemical clarification. A summary of the overall average performance is listed below:

	Primary Effluent	Chemically Clarified Effluent	Final Effluent
BOD, mg/ℓ	50	15	5
TOC, mg/ℓ	55	18	4
Turbidity, Ju	35	7	1
Total-P, mg/ℓ	30	3	2
NH_3-N, mg/ℓ	35	35	34
Org-N, mg/ℓ	8.5	2.5	1

Based on this study, the authors predicted a treatment cost of $0.16/1000 gal ($0.0425/cu m) with this type of treatment, which is less than $0.26/1000 gal ($0.069/cu m) required for a tertiary system, after primary and secondary treatment, to achieve the same degree of treatment. In addition to less cost, they also reported and anticipated reduction in land requirement of up to 75 percent.

Hager and Reilly (10) conducted adsorption isotherm studies on raw wastewaters from 11 municipal plants located principally in western Pennsylvania. Column studies were also conducted on six of the above plants. Column studies indicated less carbon requirements than were predicted by the isotherm data. The authors attributed the improved performance to biological activity within the carbon columns. The authors perdicted the cost of treatment, using the following conditions: Raw wastewater with 200 gm/ℓ BOD, and 250 mg/ℓ SS, plant flow of 10 mgd (37,850 cu m/day), and effluent after physical-chemical treatment with 10-20 mg/ℓ BOD and 5 mg/ℓ SS. Carbon requirements were assumed at 750 lb/mil gal (90 g/cu m) for 90 percent removal and 1000 lb/mil gal (120 g/cu m) for 95 percent BOD removal. Combining operating costs with amortization, the cost was predicted at $0.178/1000 gal ($0.0470/cu m) for an activated sludge process and at $0.179/1000 gal ($0.0475/cu m) for physical-chemical treatment to achieve the same degree of treatment (90 percent removal of BOD). The authors noted that physical-chemical treatment could also deliver 95 percent removal at an additional cost of only $0.007/1000 gal ($0.00186/cu m). The land area requirements for the two plants were found to be 20 acres (8.1 ha) for the biological system and 10 acres (4.05 ha) for the physical-chemical system. The authors concluded that the cost of physical-chemical treatment requiring carbon dosages of 300 to 1000 lb/mil gal (36 to 120 g/cu m) could compare favorably with that of the activated sludge process.

Bishop, *et al*. (11) reported a study of physical-chemical treatment conducted on a weak domestic wastewater at a pilot plant in Washington, DC, operated jointly by the Environmental Protection Agency and the District of Columbia. This automated pilot system consisted of pretreatment with cyclone degritting, two-stage lime precipitation with intermediate recarbonation dual-media filtration, pH control, selective ion exchange, and downflow carbon adsorption. The carbon adsorption system consisted of four downflow columns connected in series. Each column was packed with 840 lb (3780 g) of 8 x 30 mesh granular carbon. The size of the columns and carbon bed heights were not indicated. The hydraulic loading rate was 7 gpm/sq ft (285.2 ℓ/min/sq m) providing a carbon contact time of 27 min. The results of the operation for a period of 6 months indicated good treatment, as summarized below:

	Raw Waste	Effluent
BOD, mg/ℓ	100	5
COD, mg/ℓ	260	12
TOC, mg/ℓ	120	6
Total-P, mg/ℓ	7.5	0.15
Total-N, mg/ℓ	21	4.6

The COD loading on the spent carbon was 0.41 lb/lb carbon (0.41 g/g carbon). Carbon adsorption alone did not remove any nitrogen from the wastewater. Based on the pilot study, the process cost for a proposed 300 mgd (1,135,000 cu m/day) plant size was found to be $0.32/1000 gal ($0.085/cu m).

Villiers (12) has reported the results of a pilot plant study at Lebanon, OH. The process consisted of the following steps: Pretreatment with degritting, upflow lime clarification, pH adjustment to 9.5, filtration through dual-media filters, holding tank, and further treatment with carbon adsorption. There were three carbon contractors, each with 1500 lb (680 kg) of 8 x 30 mesh granular activated carbon, connected in series for an upflow operation. The carbon contractors had a surface loading rate of 2.4 gpm/sq ft (97.7 ℓ/min/sq m) with a residence time of 15.7 min through each column. Each column was 5-ft (1.5-m) deep and had a

27.9-sq ft (2.195-sq m) area. The source of carbon was not indicated. The study was conducted over a period of 53 consecutive days with a total through-put volume of 2.3 mil gal (8,703 cu m). The overall performance of the pilot plant study is presented below:

	Raw Waste-Water	Effluent After Lime Precipitation and Dual-Media Filtration	Effluent After Granular Carbon Adsorption
BOD, mg/ℓ	98	19	6
COD, mg/ℓ			
Total	257	60	29
Soluble	69	56	19
TOC, mg/ℓ			
Total	87	24	9
Soluble	36	23	8
SS, mg/ℓ	110	7	2
Total-P, mg/ℓ	8	2	2
Turbidity, Ju	54	5	4

Operational difficulties were attributed to the carbon columns becoming anaerobic. Pure oxygen injection eliminated this difficulty. The studies indicated that the carbon requirement was 300 lb/mil gal (36 g/cu m). The estimated cost for a single stage lime clarification and carbon treatment system similar to the one studied was found to be at \$0.12/1000 gal (\$0.0318/cu m) for a plant size of 100 mgd (378,500 cu m/day). The author discussed the possibility of upgrading treatment efficiency in older plants by converting from biological treatment to carbon treatment. Conversion could conceivably be achieved by converting the aeration tanks to gravity flow carbon contactors. This would eliminate the new construction and pumping costs, and consequently would reduce the capital and operating costs.

Friedman, et al. (13) conducted a pilot plant study at Trenton, NJ. The waste treated at this plant was 25 percent industrial and 75 percent domestic and the feed for this study was primary effluent. The pretreatment consisted of coagulation-clarification with ferric chloride in a 30 percent (by weight) aqueous solution at a rate of 140 mg/ℓ and dual media filtration. The carbon adsorbers were 10 and 11-ft (3.05 and 3.35-m) tall, vertical, internally coated 10-in. (25.4-cm) diam steel pipes. Each column contained 85 lb (38.59 kg) of 10 x 40 mesh carbon* which provided a 6-ft (1.83-m) deep bed of settled carbon. Four columns, or 24 ft (7.32 m) of carbon, were used to treat the clarified effluent. The carbon was supported on a 6-in. (15.24-cm) layer of gravel and coarse sand over an inverted 5-in. (12.7-cm) diam cone shaped distributor. All columns were operated in an upflow manner with a superficial velocity of approximately 0.1 ft/sec (3.048 cm/sec). In order to maintain an aerobic atmosphere of 6 to 10 mg/ℓ dissolved oxygen within the column, sufficient oxygen was introduced into the individual columns. Continuous operation was maintained for a period of 9 months. Analytical data on various stages of treatment were not reported in the paper. The average TOC removal by clarification was 63.6 percent and the removal by adsorption was 23.9 percent. The effluent TOC averaged 8.3 mg/ℓ. The BOD reduction averaged 92 percent. When the primary effluent

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* Pittsburg Filtrasorb activated carbon.

contained less than 20 mg/ℓ of Total-P, the product water contained less than 1.5 mg/ℓ of Total-P. Spot samples showed that column effluents contained only 1 mg/ℓ Org-N and less than 3 mg/ℓ NO_3-N. As part of the study, the relative performance of aerobic as well as anaerobic columns was evaluated. The cumulative TOC removal by anaerobic columns was found to be less than that by aerobic columns. Product water from anaerobic columns had always a pronounced hydrogen sulfide odor and contained from 6 to 14 mg/ℓ of H_2S as compared to less than 0.5 mg/ℓ of H_2S for aerobic effluents. Studies were also made using anthracite coal in the columns. Coal was found much less effective than activated carbon under either aerobic or anaerobic conditions showing that adsorption was an important factor in column performance. Cost analysis for a 10 mgd (37,850 cu m/day) plant indicated a cost of $0.20/1000 gal ($0.053/cu m) to achieve an effluent quality of less than 10 mg/l TOC or BOD.

Peck (14) reported the results of a study using physical-chemical treatment. Pilot plant studies were conducted at the town of Hamburg, NY. The city had a peculiar problem: Large infiltration and storm waters in sewers produced a very weak sewage, which had an average BOD of 70 mg/ℓ and a SS content of less than 60 mg/ℓ. Treatment methods, including the activated sludge process, were unsuccessful because the consistently weak waste strength could not support the biological life in the aeration tanks and resulted in the system going into the endogenous respiration phase. The treatment scheme included chemical clarification and activated carbon adsorption. Pickling liquor from the nearby Bethlehem Steel Plant, containing considerable amounts of ferrous chloride, was used for chemical clarification. For the study, a 5-gpm (0.316-ℓ/sec) Infilco Densator unit was used for chemical mixing, flocculation, and clarification. Basically, this unit is a high-density solids contact unit, which has been used primarily for water treatment. Various chemical dosages were used to provide a Fe/P ratio of 2/1 for accommodating the variation in influent phosphorus concentration. Along with the pilot study, bench scale tests were conducted with ferric chloride and activated carbon. In the pilot plant, varying chemical and powdered carbon dosages were applied. The method of carbon treatment was not indicated; it appears, however, that activated carbon in required dosages was fed as a carbon slurry along with ferric chloride. The results of the study can be summarized as indicated below:

Carbon dosage, mg/ℓ	Influent BOD, mg/ℓ	Effluent BOD, mg/ℓ
80	62.8	16
90	32.25	7.6

The effluent phosphorus was less than 1 mg/ℓ. In general, activated carbon could remove approximately 50 percent of the soluble BOD.

Flynn and Thompson (15) reported the results of a pilot plant study conducted for the City of Niagara Falls, NY. The city is highly industrialized and the pH of the wastewater ranged from 2 to 11; consequently, a physical-chemical method incorporating chemical precipitation of phosphates, flocculation and clarification, and activated carbon adsorption was included in the pilot plant study. An attempt was made to evaluate the relative effectiveness of clarification with chemical coagulation and sedimentation, over clarification with air floatation. Lime at a dosage of 90 mg/ℓ was added to raise the pH to 11.2 to 11.4. Lime produced good clarification and also precipitated phosphates. Polyelectrolyte at a dosage of 0.25 mg/ℓ was equally effective; but whenever the wastewater pH was below 6.0, lime had to be added to keep the pH at high values. The carbon columns were 6 ft (1.8 m) in length with an inside diam of 5 in. (12.7-cm). Each column was charged with 18 lb (8.2 kg) of granular activated carbon. A total contact period of 30 min was provided through the columns which were connected in series. Arrangements were provided to operate sets of columns in an upflow or downflow mode. The studies indicated the feasibility of treating the Niagara Falls wastewater using the physical-chemical method. Removals of COD and SS were good throughout the study period, and up to 75 percent reduction in phosphate was observed. Organic phosphorus was not removed either by chemical clarification or by carbon adsorption. The carbon requirement was found to be 250 lb/mil gal (30 g/cu m). Diffused air floatation was not found to be more effective than chemical clarification. The authors used the pilot plant findings to develop design parameters for a 48 mgd (180,200 cu m/day) plant for the city of Niagara Falls.

Atkins, et al.(16) reported the results of a pilot plant study at Owosso, MI, which was undertaken in order to evaluate the treatment of Owosso wastewater and the feasibility of using chlorination followed by dechlorination with activated carbon for the removal of NH_3-N. The pilot plant consisted of chemical coagulation with lime at pH of 8.8 to 9.4, sedimentation, straining using a Kinney unit, deep-bed filtration, activated carbon adsorption, chlorination, and dechlorination by activated carbon columns. The carbon columns were made of 12-in (30.04-cm) diam pipes. The first stage carbon adsorption had three units in series with a total bed height of 12 ft (3.6 m). The flow through the columns was at 6 gpm/sq/ft (244.2 l/min/sq m). The carbon used was Calgon Filtrasorb 400*. The second stage columns had two units in series providing a total bed height of 8 ft (2.4 m). The following overall removals were obtained:

Parameter	Removal, %
BOD	94-96
SS	90
Phosphorus	80 or better
NH_3-N	85 or better
Org-N	90

The total cost of treatment was prediced at $0.36/1000 gal (0.09/1000 cu m) for a 6-mgd (22.710-cu m/day) flow.

Zuckerman and Molof (9) conducted batch and column studies using primary effluents from several sewage treatment plants. Batch studies were conducted using 100 mℓ

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* A product of Calgon Corporation, Pittsburg, PA.

serum bottles, while column studies were conducted using three columns each of 1.5 x 30 in. (3.8 x 76.2 cm) containing 12 x 40 mesh West Virginia-W granular carbon packed to a bed height of 25 in. (63.5 cm). There was no mention about the flow rate or residence time. The main objective of the study was to examine the effect of the molecular weight of the constituents of wastewater on the treatment efficiency by both biological and carbon adsorption processes. Liquid chromotographic column studies were conducted in order to determine molecular weight. The authors found that with respect to molecular weight, the domestic wastewater contained two fractions of organics, one with a molecular weight greater than 1200 and the other with molecular weight less than 400. The biological process as well as the adsorption process removed only that portion of the organics having a molecular weight of less than 400; consequently, chemical hydrolysis was attempted by raising the pH to a value above 11.5 with the aid of lime. It was found that the treatment scheme with the incorporation of chemical hydrolysis could remove essentially all organics and produce a clear effluent. Column studies were conducted with raw wastewater and activated sludge effluent with and without chemical hydrolysis pretreatment. The results of the study are presented on the following page:

	COD/ mg/ℓ			
	Column Influent		Column Effluent	
Waste Stream	Without Chemical Pretreatment	With Chemical Pretreatment	Without Chemical Pretreatment	With Chemical Pretreatment
Raw Wastewater	65	57	9.1	2.0
Step aeration activated sludge effluent	26	21	15.5	4.4
Modified aeration activated sludge effluent	34	28	17.5	5.0

Based on their studies, the authors suggested a treatment scheme consisting of: (a) solids separation with chemical coagulation using lime to elevate the pH to 11.5, (b) hydrolysis in a special reaction chamber, (c) neutralization with sulfuric acid or carbon dioxide, (d) sand filtration, and (e) activated carbon adsorption. The authors have predicted a total operating cost of \$0.143/ 1000 gal (\$0.038/cu m).

B. ACTIVATED CARBON TREATMENT OF INDUSTRIAL WASTEWATER

Hardie (22) and Huang and Hardie (23,24) undertook a study to evaluate the feasibility of using activated carbon to treat two types of industrial wastewaters. The wastes used were a chemical waste (COD of 2900 mg/ℓ and a refinery waste (COD of 296 mg/ℓ). The treatment scheme included chemical coagulation and activated carbon adsorption for the refinery waste and only activated carbon adsorption for the chemical waste. For the refinery waste, jar tests indicated that both alum and ferric chloride had almost identical effectiveness in the removal of turbidity. At a dosage of 250 mg/ℓ, ferric chloride reduced turbidity from 70 to about 1 Ju. Coagulation was also effective in removing COD and TOC from the refinery waste. Phosphorus removal was also observed, while ammonia removal was very poor. The results of the study are summarized below:

Characteristics	Original Waste	Coagulated Waste
COD, mg/ℓ	296	75
TOC, mg/ℓ	74	20
SS, mg/ℓ	154	11
Turbidity, Ju	94	3
Phosphorus, mg/ℓ as P		
Ortho	0.7	0.2
Total	0.7	0.2
Nitrogen, mg/ℓ as N		
NH_3	12.9	12.4
Total	13.5	13.0

Carbon adsorption studies were conducted in batch and column modes. Batch studies evaluated the rate of uptake and equilibrium adsorption. Both wastes had adsorption isotherms in conformity with Freundlich isotherm models. Column studies as well as batch studies indicated the effectiveness of carbon adsorption system for the treatment of both the industrial wastewaters. Exceptionally high quality effluents with TOC less than 2 mg/ℓ were obtained after the carbon adsorption treatment. In the treatment of chemical wastewater, both upflow and downflow column studies were conducted. The removal efficiency was only slightly better for the downflow operation than for the upflow operation.

C. THE EFFECT OF CARBON TYPE AND SIZE

Bishop, *et al.* (5) undertook a study to evaluate the performance difference between different types of carbons. Twelve powdered activated carbons were used in this evaluation which consisted of batch studies using trickling filter effluents. The effluents were analyzed for TOC, phenol No.* ABS No.,** and dye adsorption on methylene blue or eosine B.*** A series of tests were made to obtain better reliability. Tests were also made to evaluate the ability of the activated carbon to remove colloidal fractions. The results of the study indicated a marked difference between carbons in their ability to remove organic matter. Surface area could not be correlated with the ability of the carbon in removing organics. The phenol No., which has been used for many years as a purchasing specification for water-treating carbons, was found to have very poor correlation with the ability of the carbon to remove general organic matter. As the carbons differ in their adsorptive capacity for a given substance and they show highly specific interactions with various substances, the authors suggested the use of the carbons under full scale field conditions in

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* Defined as the mg of carbon necessary to reduce phenol from 5.0 to 0.5 mg in one liter.

** Defined as the mg of carbon necessary to reduce ABS from 5.0 to 0.5 mg in one liter.

*** Defined as the residual concentration of the dye after a specific quantity of the dye (340 mg/ℓ for methylene blue and 45 mg/ℓ for eosine B) had been treated with 1 g/ℓ of carbon for 1 hr, expressed as mg/ℓ.

order to determine the efficiency of each carbon.

In the study by Zuckerman and Molof (9), it was mentioned that three types of carbon were used during the study, West Virginia Pulp and Paper Company's 12 x 40 mesh WV-W granular carbon, Pittsburgh Activated Carbon Company's 12 x 40 mesh SGL granular carbon, and Nuchar 190N powdered carbon were used. It was not reported whether there was any performance difference when two granular carbons were used on the same wastewater. It was only reported that granular carbon had better performance than powdered carbon.

III. EQUIPMENT, MATERIALS, ANALYTICAL DETERMINATIONS, AND EXPERIMENTAL PROCEDURE

A. EQUIPMENT

The equipment used in this research study is described below.

1. Batch Studies

a. Wrist Action Shaker

In order to keep the samples thoroughly mixed with activated carbon during the batch studies, a wrist action shaker* was used. Up to 12 samples could be mounted on this instrument and shaken continuously for a preset period of time.

b. Magnetic Stirrers

Several jumbo-size magnetic stirrers** were also used in the batch studies. These stirrers were used in order to keep samples thoroughly mixed with activated carbon in relatively large reactors, such as 4-ℓ bottles.

2. Column Studies

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* Supplied by Burrell Corporation, Pittsburgh, PA.
** Supplied by Fischer Scientific Company, St. Louis, MO.

a. Sigma Motor Pump

For pumping samples through carbon columns, a sigma motor pump* was used. A variable speed reducer mounted on the pump unit could be used to adjust the flow rate from 0 to 125 mℓ/min. Higher flow rate could be obtained through a combination of two or more feed lines at the influent end.

b. Carbon Columns

Several carbon columns were used in this study. A typical column is shown schematically in Figure 1. The column was constructed from a 4-ft (1.22-m) section of plexiglas tube with an ID of 1-1/2 in. (3.8 cm) and OD of 1-3/4 in. (4.4 cm). Each column contained 13 sampling ports spaced at 3-in. (7.62-cm) intervals starting 6 in. (15.28 cm) from the top. Each sampling port consisted of a 2-in. (5.08-cm) section of 1/4-in. (0.626-cm) diameter, acrylic plexiglas tap, which was packed with 1-mm glass beads and closed off at both ends with stainless steel screens to minimize carbon losses during sampling. The taps were also inserted 1/4 in. (0.626 cm) into the plexiglas column to eliminate the possibility of withdrawing the short circuiting fluid which might have slided down along

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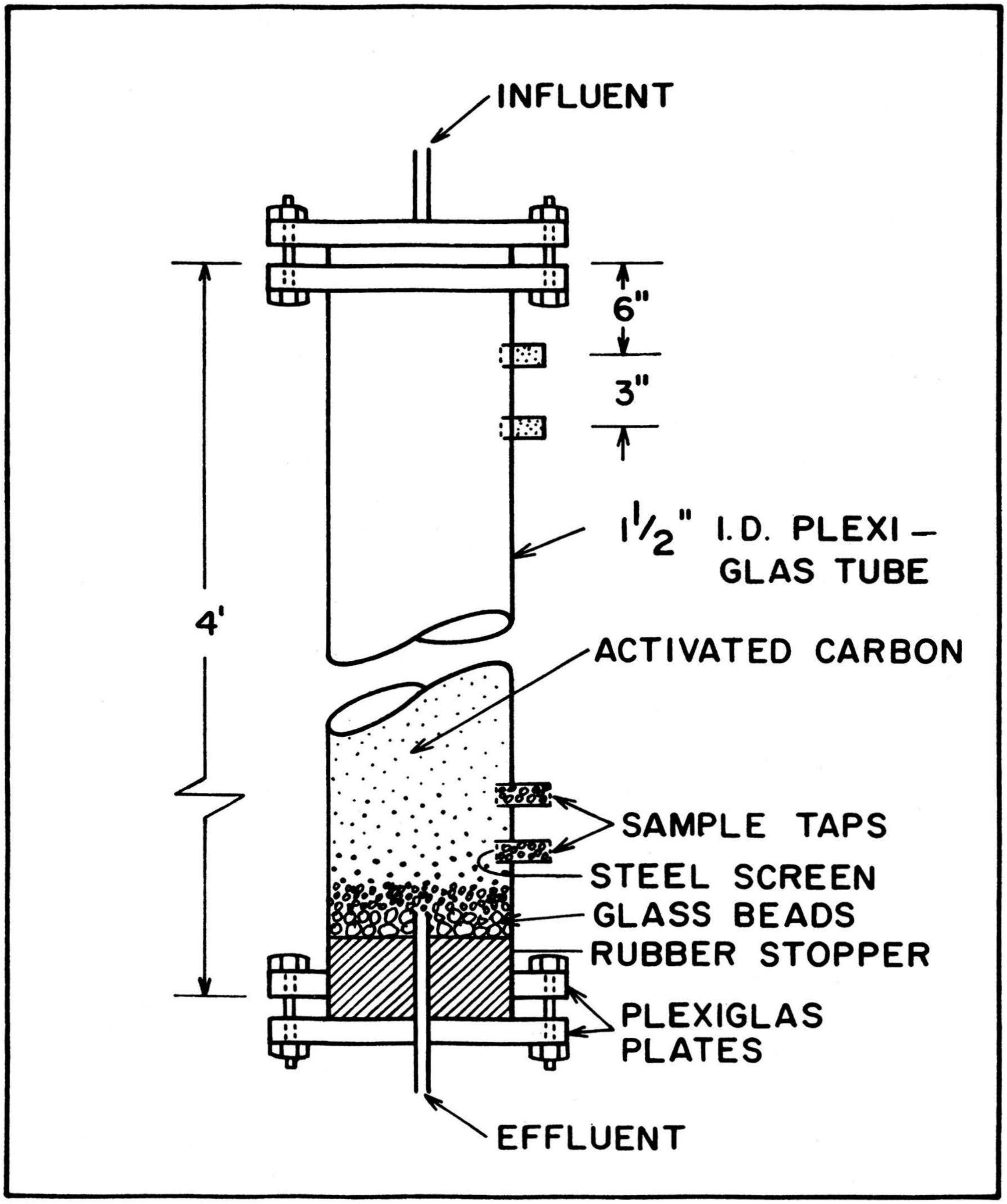
* Model T-8, Manufactured by Sigma Motors, Middleport, NY.



1 in. = 2.54 cm;
1 ft = 0.3048m

Figure 1. Schematic Diagram of a Typical Activated Carbon Column Used in This Study

the inner wall of the column. Rubber tubings were connected to the sampling ports and were closed with pinch clamps. Rubber stoppers were used to seal both ends of the column and kept securely in place by plexiglas plates bolted together. Glass tubes were inserted into the rubber stoppers to serve as inlets and outlets from the column.

B. MATERIALS

1. Waste Sample

The waste sample used in this study was obtained from Hoffman-Taff, Springfield, MO. It was first collected in several epoxy-lined, 55-gal (208.2-ℓ) drums and then brought to the laboratory where it was stored in a walk-in refrigerator maintained at a temperature of 4°C. Samples were drawn from these drums for the experiments whenever needed.

2. Activated Carbons

Two types of granular activated carbons were used in this study: Calgon Filtrasorb 400* and Darco S-51**. The two carbons were of the same size range of 12 x 40 mesh and their properties are compared in Table I.

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* A product of the Calgon Corporation, Pittsburgh, PA.

** A product of the Atlas Chemical Industries, Inc., Wilmington, DE.

TABLE I. PROPERTIES OF THE TWO ACTIVATED CARBONS USED IN THIS STUDY

Physical Properties	Atlas Darco S-51	Calgon Filtrasorb 400
Surface Area, Sq m/g	600-650	1000-1200
Apparent Density, g/mℓ	0.34	0.44
Density, backwashed and drained (kg/cu m)	384	400
Real Density, g/mℓ	-	2.1
Particle Density, g/mℓ	0.67	1.3-1.4
Effective Size, mm	-	0.55-0.65
Uniformity Coefficient	-	1.9 or less
Pore Volume, mℓ/g	0.98	0.94
Mean Particle Diameter, mm	1.05	0.9-1.1
Specifications (US Standard Series)		
Sieve Size		
Larger than No. 8 max %	-	-
Larger than No. 12 max %	5	5
Smaller than No. 30 max %	-	-
Smaller than No. 40 max %	5	5
Ash, %	-	8.5
Moisture as packed, max %	-	2

C. ANALYTICAL DETERMINATIONS

During waste characterization, the following analyses were performed: SS and VSS, turbidity, pH, COD, TOC, Total-P and Ortho-P, NH_3-N and Org-N.

During the treatment study COD and TOC were the major parameters employed to determine the treatment efficiency. The above analyses were performed, unless otherwise noted, according to the procedures outlined in "Standard Methods" (25); the methods employed are summarized in this section.

1. Solids

To determine suspended (nonfilterable) and dissolved (filterable) solids (25, p. 244), a 30-mℓ gooch crucible with a single fiberglass filter was used for filtering a desirable sample volume. The drying temperature used was 103°C. Filterable fixed and volatile solids were determined by igniting the sample at 600°C in a preheated furnace.

2. Chemical Oxygen Demand

The COD tests were conducted to determine the organic strength of the wastewater. This parameter was measured by determining the amount of oxygen required to convert the organic matter in the wastewater into carbon dioxide and water through a wet combustion process using the dichromate reflux method (25, p. 510). A suitably diluted

20-mℓ sample mixed with 0.4 g mercuric sulfate, 10 mℓ 0.25 N potassium dichromate, and 30-ml sulfuric acid with silver nitrate was refluxed for 2 hr. The COD was calculated from the amount of potassium dichromate consumed in oxidizing the organics in the sample.

3. Total Organic Carbon

Total organic carbon determinations were made using a carbonaceous analyzer*. The procedure adopted was that outlined by the Beckman Instruments Bulletin No. 7000-17. The carbonaceous analyzer was first set into proper operating conditions with regard to furnace temperature, pure oxygen flow rate, and proper gain selection. A calibration curve was next prepared by injecting known amounts of acetic acid. Then an appropriate volume of suitably diluted sample was acidified with concentrated hydrochloric acid carbon dioxide free to a pH around 2, and pure CO_2-free nitrogen gas was bubbled through the sample for a minimum period of 5 min in order to drive away inorganic carbon. A 20-mℓ liquid sample was then injected into the furnace. The TOC values were obtained by comparing the peak heights registered on the recorder provided with the instrument.

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* A product of Beckman Instrument Co., Fullerton, CA.

4. Phosphorus Determinations

Both Total-P and Ortho-P determinations were made following the procedure introduced by Jankovic, et al. (26)

To determine Ortho-P, a mixed reagent consisting of 120 mℓ 5N sulfuric acid, 37.5 mℓ ascorbic acid and 12.5 mℓ potassium antimonyl tartrate was prepared prior to every batch of analysis. Eight mℓ of the mixed reagent was first placed in a 50-mℓ nessler tube and enough sample was added to bring the volume to the mark. The contents were mixed and allowed to stand for 10 min for color development. Percentage transmittance was measured by using a spectrophotometer*. A test for optimum transmittance wave length for the waste sample used in this study indicated that a wave length of 710 mμ was the best to use. A calibration curve was then prepared by measuring the percentage transmittance with known amount of Ortho-P. The amount of phosphate (ortho) present in the sample was obtained by interpolating the measured percentage transmittance against the standard curve.

For Total-P determination, 40 mℓ sample was mixed with 2.0 mℓ 5N sulfuric acid and 1.0 g potassium persulfate, and refluxed for 15 min. The mixture was cooled and the steps necessary for Ortho-P determinations were performed.

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* Perkin-Elmer Model No. 139, UV-V15 spectrophotometer, manufactured by Hitachi, Ltd., Tokyo, Japan.

5. Nitrogen Determinations

The procedure outlined in the Standard Methods (25, p. 187) for NH_3-N and total Kjeldahl-N was employed for nitrogen analysis.

For NH_3-N determinations, a 50-mℓ sample was used. The sample was placed in an 800 mℓ Kjeldahl flask. The pH of the sample was neutralized to 7.0. Then 0.25 mℓ of 0.5 M phosphate buffer solution was added to the sample to maintain the pH of the sample at 7.0 during subsequent distillation. The sample was then diluted to 400 mℓ with ammonia-free water. After dilution the sample was distilled using the distillation apparatus. The distillate was collected in a flask containing 50 mℓ indicating boric acid solution until about 200 mℓ volume had been obtained. The content of the flask was back titrated with 0.02 N sulfuric acid to determine the NH_3-N content.

Organic nitrogen determinations were made by using the residue in the NH_3-N determination. A 50-mℓ volume of sulfuric acid - mercuric sulfate - potassium sulfate was added to the residue, and the mixture was digested for 20 to 30 min until the solution became colorless. It was then cooled, and 300 mℓ of ammonia-free water was added. To this, a sodium hydroxide - sodium thiosulfate solution was added until the solution became alkaline as determined by using phenolphthalein as indicator. The remaining procedure was similar to that in the NH_3-N determination.

The Total Kjeldahl-N was then obtained by adding NH_3-N and Org-N values.

6. pH Determinations

The pH of the waste samples was measured using a pH meter* and adopting the procedure outlined by the supplier of the meter.

7. Turbidity Determinations

A laboratory turbidimeter** was used for turbidity determinations. The procedure as outlined in the instrument manufacturer's manual was followed for these determinations.

D. EXPERIMENTAL PROCEDURE

1. Waste Characterization

In order to obtain complete information regarding the general characteristics of the wastewater, waste characterization was done as the first step of this research study. This would provide information to determine the necessary physical-chemical treatment requirement. No attempt was made to identify the individual chemical components in the wastewater during the waste

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* A product of the Beckman Instruments Inc., Fullerton, CA.

** A product of Hach Chemical Company, Ames, IA.

characterization. Measurements were limited to suspended and dissolved solids, volatile and fixed solids, turbidity, pH, COD, TOC, Total-P and Ortho-P, NH_3-N and Total Kjeldahl-N. The measurements of the above parameters were repeated until reliable values were obtained.

As a result of characterization, it was found that although the wastewater had a very low SS content, the turbidity was as high as 31 Ju (a detail tabulation of waste characteristics is presented on Page 41), indicating the presence of a significant amount of colloidal and other fine particles. Since particulate organics will not be effectively adsorbed on activated carbon, the physical-chemical treatment considered for the pharmaceutical waste consisted of two stages: Chemical clarification and activated carbon adsorption.

2. Chemical Clarification

Standard jar tests were conducted to evaluate the relative performance of alum [$Al_2(SO_4)_3 18H_2O$)] and ferric chloride ($FeCl_3 3H_2O$) in clarifying the waste and to estimate the optimum dosage and pH. In order to determine the optimum coagulant dosage, 600 mℓ of waste sample was placed in each of six 1-ℓ beakers. The beakers were positioned under the stirrers of a multi-unit stirrer*. Each coagulant, in solution, in dosage of 25, 50, 75, 100,

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* A product of Phipps-Bird, Inc., Richmond, VA.

125, and 150 mg/ℓ was added to each of the six beakers, flash mixed for 30 sec at 100 rpm and then flocculated for 30 min at 35 rpm. The samples were allowed to settle for 1 hr. The clarified samples were then siphoned off into clean containers for further analysis of turbidity to determine the coagulation efficiency.

After obtaining the optimum dosage, the jar tests were repeated with the initial pH adjusted to 4, 5, 6, 7, 8, and 9 to obtain the optimum pH. This study indicated that alum was a better coagulant than ferric chloride. At a dosage of 100 mg/ℓ with the initial pH adjusted to 8.0, alum produced rapidly settling strong flocs and clarified the waste to a turbidity of about 1 Ju.

Large scale chemical clarification of the waste sample for further experimental work was done in a 20-ℓ pyrex glass bottle. After adjusting the pH and adding the coagulant, the sample was flash mixed for 4 min and flocculated for 15 min, using a stirrer*. The settling time was 1 hr.

3. Activated Carbon Adsorption Studies

a. Batch Studies

Batch studies were conducted in two stages. The first stage was the rate of uptake study and the

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* Fisher Dyna-Mix Stirrer, a product of the Fisher Scientific Company, St. Louis, MO.

second was the equilibrium study.

The rate study was conducted in five 4-ℓ wide-mouth pyrex bottles. Jumbo-size magnetic stirrers were used for thorough mixing of the samples. In order to dissipate any heat generated by the magnetic stirrers, the bottles were mounted on wooden wedges so that there was free air circulation around the bottles. A volume of 3 ℓ of chemically clarified sample was placed in each of the five bottles. The experiment was started by adding 25, 50, and 100 g/ℓ of Calgon carbon into the first three bottles and 25 and 50 g/ℓ of Darco carbon in the other two bottles. During the test, a 20-mℓ sample was withdrawn frequently at the end of 1/2, 1, 2, 3, 5, 8, 12, 18, 24, 30, and 39 hr, after allowing the mixture to settle for 2 min. The samples were filtered through fiberglass filters and were stored for further analysis. The TOC measurement was rapid and thus was used to provide information as to whether the reaction had reached an equilibrium state.

After completing the rate of uptake study, equilibrium studies were undertaken. A total of 10 flasks, each 250-mℓ capacity, were used for this study. In each flask, 125 mℓ of waste sample was added. Then an accurately weighed dosage of 0, 6.25, 12.5, 25, 50, 100, 150, 200, 300, and 500 g/ℓ of activated carbon was added into the flasks. Two sets of runs were made.

The first was with Calgon carbon and the second was with Darco carbon. After adding the carbon, the flasks were mounted on the wrist-action shaker and agitated continuously for 24 hr. After this period, the equilibrium concentrations of remaining organics were measured.

An additional equilibrium study was conducted with the initial pH adjusted to 3.0, 8.0, and 11.4, and with dosages of 50 and 200 g/ℓ of each carbon. The test was again conducted for 24 hr and the final organic concentrations as well as the final pH were measured.

b. Column Studies

Several columns were used which were connected in series to obtain any desired effective bed depth. Each column was packed with 408 g of activated carbon. Prior to packing, the carbon was soaked in deionized water for a period of 24 hr, and was periodically stirred. At the end of this period, the water was drained off and fresh deionized water was added. Stirring was continued for another 12 hr. Then again fresh water was added. At the end of the next 12 hr, the carbons in slurry form were ready for packing. During packing glass beads were first loaded into the column up to about 4-in. (10.16-cm) high. Then the carbon was loaded in slurry form up to a height of

3-ft (0.9-m).

Previous investigations (8,22) had indicated no significant difference in performance by fluidized or packed, upflow or downflow modes of operation; consequently, it was decided to use packed bed downflow mode of operation. Since the wastewater did not contain appreciable amounts of suspended and colloidal material, it was expected that the filtering effect would not clog the carbon columns which were connected in series in order to provide downflow packed bed operation. A sigma motor pump was used to pump the wastewater through the columns. The arrangement of columns and the pump is schematically shown in Figure 2. After making the connections, a volume of 20 ℓ of deionized water was pumped through the columns before the start of the experiment.

The first column study was undertaken with the Calgon carbon. For this experiment, three columns were connected in series. The flow rate was adjusted to 2 gpm/sq ft (81.4 ℓ/min/sq m) which corresponded to 116 mℓ/min through the 1.5-in,(3.8-cm) ID columns. After starting the experiment, samples were drawn at 1/2, 1, 1-1/2, 2, 3, 4, 5, 7, 10, 12, 14, 16, and 24 hr from sampling ports at 1, 2, 3, 4, 5, 6, 7, 8, and 9-ft (0.3, 0.6, 0.9, 1.2, 1.5, 1.8, 2.1, 2.4, and 2.7-m) column bed depths. The samples were stored in

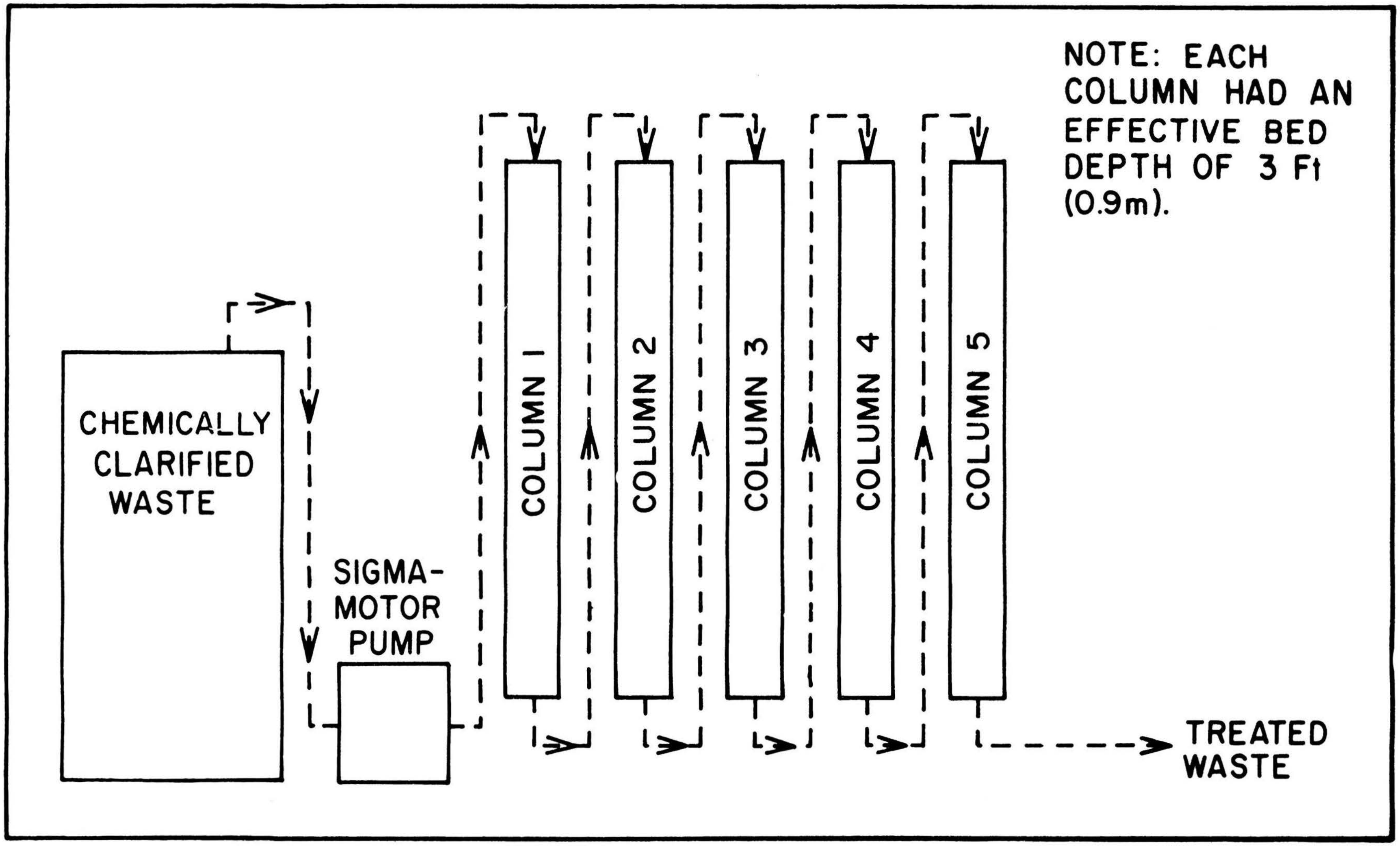

Figure 2. Schematic Diagram of the Experimental Set-Up

refrigerators and analyzed as early as possible. At the end of 24 hr, the column was thoroughly exhausted as verified by the TOC measurement.

For the study with the Darco carbon, an effective column height of 15 ft (4.57 m) was provided by connecting 5 columns in series. This was due to the observations in the study with the Calgon carbon. The residence time provided in the Calgon carbon study could not produce an effluent of high quality. Thus, it was decided to increase the column depth. When five columns were connected in series, the sigma motor pump, due to limitations in its capacity, could not deliver a flow rate of 2 gpm/sq ft (81.4 ℓ/min/sq m). So a flow rate of 1.5 gpm/sq ft (61.35 ℓ/min/sq m) was used in this study. After the start of the experiment, samples were drawn at 1/6, 1/3, 1/2, 3/4, 1, 1-1/2, 2, 3, 5, 8, 12, 16, 20, and 24-hr period from each sampling port at a 1-ft (0.3-m) depth interval. At the end of the 24-hr period, the columns were completely exhausted as indicated by TOC measurements.

IV. RESULTS AND DISCUSSION

The feasibility of using physical-chemical processes for the treatment of a high organic strength pharmaceutical waste and the relative performance of two different kinds of granular-activated carbon were carefully evaluated in this research study. The experimental results are discussed in this chapter.

A. WASTE CHARACTERIZATION

As indicated in the previous chapter, no attempt was made to identify the individual chemical components of the waste. The waste collected in each of the four drums was analyzed individually in order to determine whether there was any variation in character from drum to drum. The characteristics of the waste in the four drums are presented in Table II.

As seen from the table, the wastewater from the plant had indicated a nearly uniform character. It had a very high organic strength with a COD of around 8,000 mg/ℓ and a TOC of 2,400 mg/ℓ. There was only a small amount of SS, indicating that the organic strength was mainly due to dissolved and colloidal organics. The waste did not have a specific color except that it appeared cloudy due to colloidal matter which caused a turbidity of 31 Ju. It had a slight odor, typical of a pharmaceutical product. The TDS content of the waste was around 2,800 mg/ℓ, and

TABLE II. CHARACTERISTICS OF THE PHARMACEUTICAL WASTEWATER

Characteristics	Drum No.			
	1	2	3	4
pH	6.8	6.8	6.9	6.8
COD, mg/ℓ	8,180	8,020	8,220	7,980
TOC, mg/ℓ	2,460	2,380	2,360	2,500
Turbidity, Ju	31	31	32	31
Solids, mg/ℓ				
Suspended (Nonfilterable)	35	34	33	34
Dissolved (Filterable)	2,865	2,786	2,727	2,846
Filterable Fixed	1,185	1,184	1,188	1,180
Filterable Volatile	1,680	1,602	1,539	1,666
Phosphorus, mg/ℓ as P				
Ortho	0	0	0	0
Total	0	0	0	0
Nitrogen, mg/ℓ as N				
Ammonia	117	116	119	116
Organic	16	17	13	18

the fraction of the VS was about 60 percent. The pH of the sample was near neutrality with a value of 6.8. The waste was completely devoid of phosphorus (both Total-P and Ortho-P). Nitrogen was present with values of about 16 mg/ℓ as Org-N and 117 mg/ℓ as NH_3-N.

The characteristics in Table II would indicate that if this waste were to be treated by conventional biological processes, large quantities of phosphorus and nitrogen would need to be supplemented in order to satisfy the needs of microorganisms.

B. CHEMICAL CLARIFICATION

The pharmaceutical waste had a turbidity of 31 Ju because of the presence of a considerable amount of colloidal solids. In an activated carbon adsorption system, the colloidal organics will not be effectively removed by the adsorption process. Although partial removal may be effected by the mechanism of straining in the interparticle spaces, this will normally result in column-clogging and shorter runs due to pressure build-up, thus requiring frequent backwash. So a chemical clarification step became a necessity.

Standard jar tests were conducted to evaluate the relative performance of two coagulants, alum and ferric chloride, and to determine the optimum dosage and pH. When the jar tests were first done without pH adjustment, the coagulation was not effective since there was no floc formation for either type of coagulant. When the pH was raised to a value above 8, both coagulants produced rapidly settling strong flocs. Tests were conducted with both coagulants administered separately, each with dosages ranging from 25 to 150 mg/ℓ, after adjusting the pH to 9.0. Reductions of turbidity and variations in pH in the clarified effluent at different coagulant doses are shown in Figure 3.

In general, alum appeared to be a better coagulant than ferric chloride for this particular waste. Both coagulants were able to clarify the waste to a final turbidity of less than 5 Ju even at a dosage as low as 50 mg/ℓ; however, only alum, at a dosage of 100 mg/ℓ or more, could produce rapidly settling strong flocs and clarified the waste to a turbidity of 1 Ju. Both coagulants had a tendency of depressing the pH of the final effluent.

In order to determine the optimum pH, jar tests were conducted with the initial pH adjusted to values ranging from 5 to 10. Alum was then used as coagulant at the optimum dosage of 150 mg/ℓ. The observed results are presented in Figure 4. As seen from this figure, pH above 8 seemed to be able to reduce the turbidity to a value around 1 Ju. Therefore, it was deemed necessary to adjust the initial pH to a value of at least 8.0 to effect good coagulation and clarification. At such a pH, an alum dosage of as low as 25 mg/ℓ was able to clarify the waste

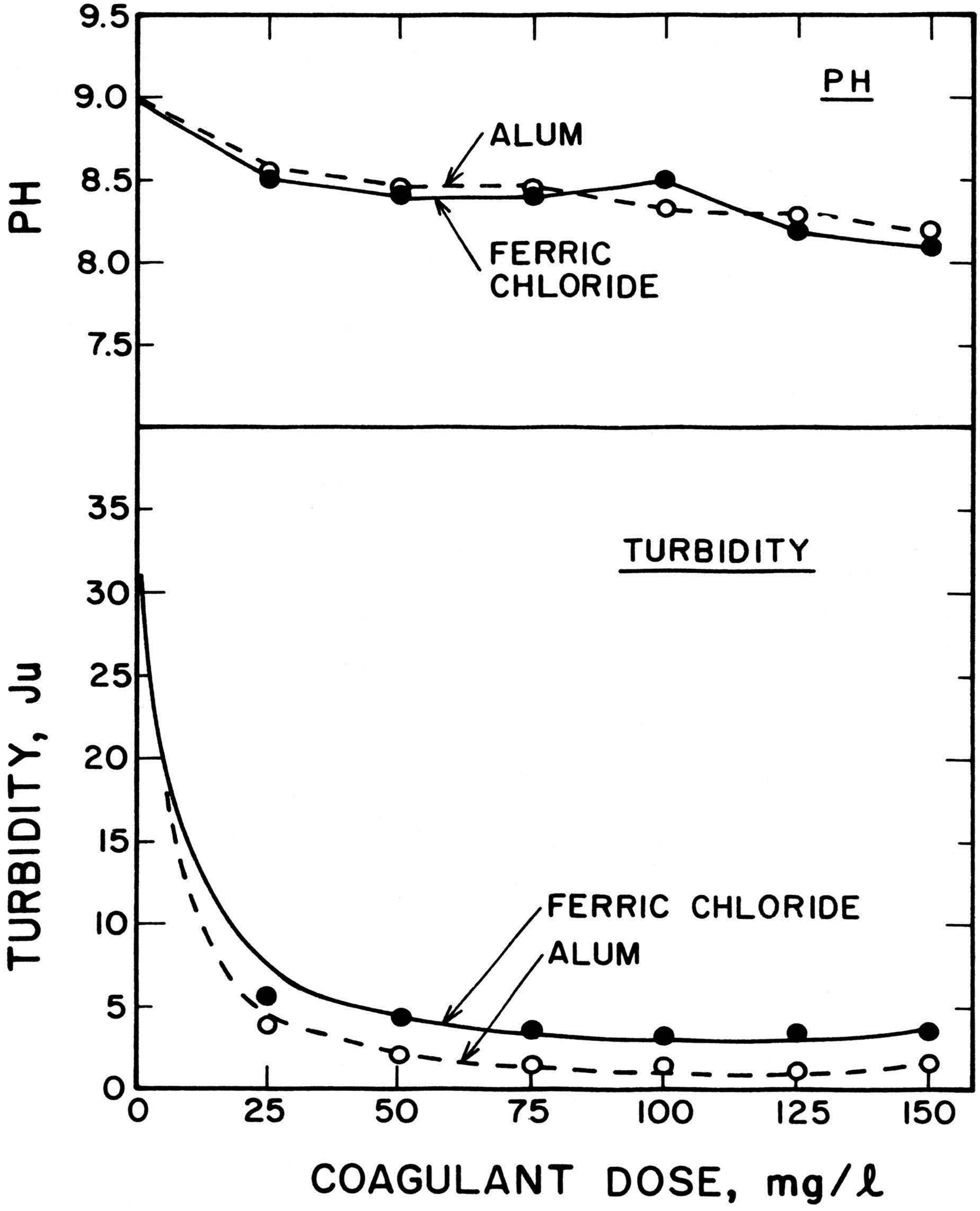

Figure 3. Effect of Chemical Coagulation

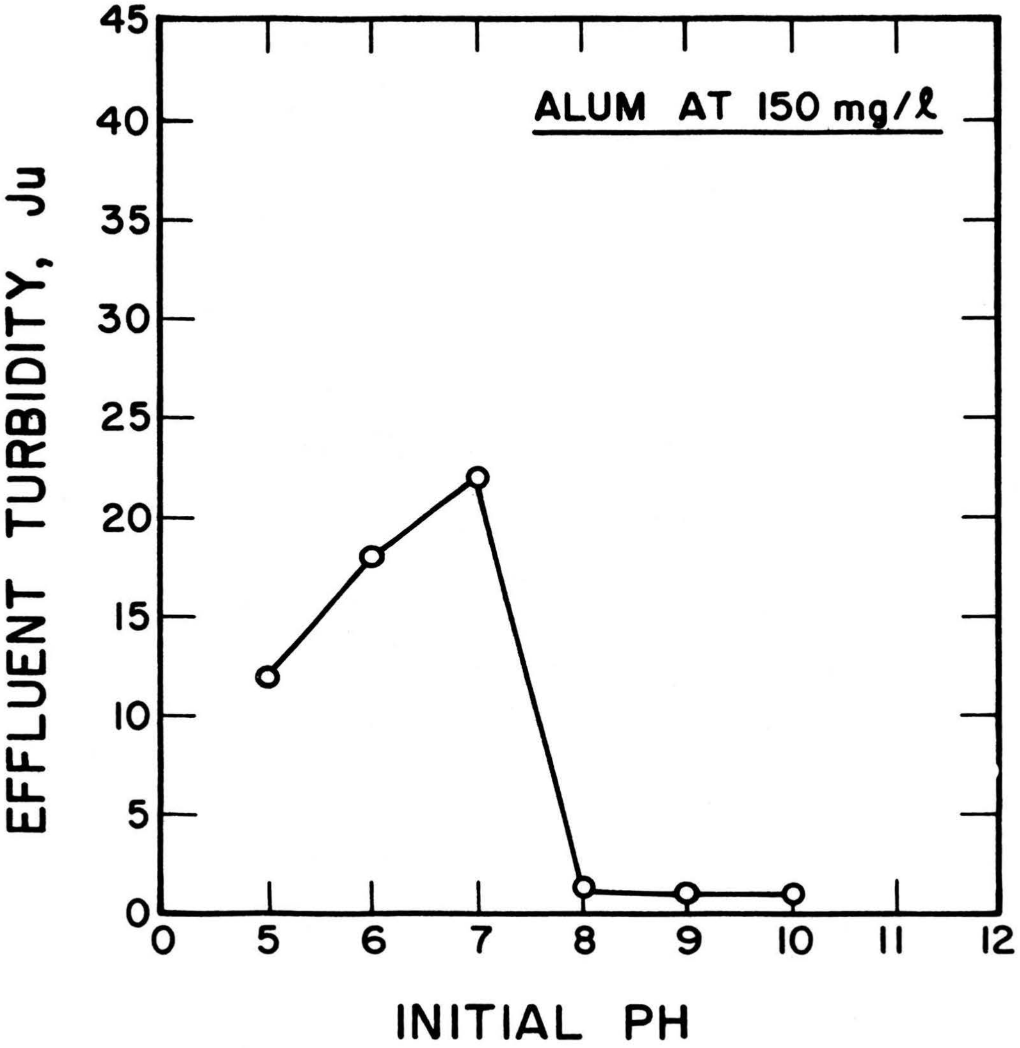

Figure 4. Effect of Initial pH on Alum Coagulation

to a turbidity of less than 5 Ju. In the design of the full-scale facilities for treating this waste, a dosage of 50 mg/ℓ would be recommended for clarifying the waste so that the length of filter run could be extended. Since the present bench-scale research work was intended to provide a longer filter run with as much reduction of turbidity as could practically be achieved in the influent feed, alum at a dose of 150 mg/ℓ was used for clarifying the waste.

The characteristics of the wastewater after chemical clarification are presented in Table III. Even though chemical clarification was very effective in removing turbidity, there was only a 6 percent reduction in COD. In a similar study by Hardie (22) on a refinery waste, it was found that chemical clarification was very effective in the removal of turbidity as well as organic matter. The disagreement in results is mainly due to the fact that the refinery waste had a considerable fraction of SS that contributed to the original waste strength, whereas in the pharmaceutical waste, the organic strength was mainly due to dissolved organics which were not subjected to reduction by chemical clarification. However, chemical coagulation did effect a significant reduction in Org-N, although the reduction in NH_3-N was not prounced. These findings are in agreement with those reported by Weber, et al. (8) who indicated that chemical coagulation was effective in removing Org-N but was ineffective in removing NH_3-N.

TABLE III. CHARACTERISTICS OF THE RAW AND COAGULATED* PHARMACEUTICAL WASTE

Characteristic	Raw Waste	Coagulated Waste
pH	6.8	7.3
COD, mg/ℓ	8,100	7,600
TOC, mg/ℓ	2,400	2,340
Turbidity, Ju	31	1.0
Solids, mg/ℓ		
Suspended (non-filterable)	34	6
Dissolved (filterable)	2,806	2,890
Filterable Fixed	1,184	1,260
Filterable Volatile	1,622	1,630
Nitrogen, mg/ℓ as N		
Ammonia	117	114
Organic	16	11

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* The waste was coagulated using alum at a dosage of 150 mg/ℓ following initial pH adjustment to 7.5 using lime.

C. ADSORPTION STUDIES

1. Batch Studies

a. Rate Study

The results of the rate study are presented in Table IV and Figure 5. The effluent concentrations of COD and TOC at various times for various carbon dosages are presented in Table IV. The five curves in Figure 5 are for the COD and TOC remaining in solution with respect to time after adsorption by 25, 50, and 100 g/ℓ of Calgon carbon and 25 and 50 g/ℓ of Darco carbon. The curves indicate the dependency of removal efficiency upon the carbon dosage. When the carbon dosage was increased, higher removals of TOC or COD were obtained. An important result of this study could be noticed in that the two carbons differed very much in their adsorptive capacities. The traces of COD and TOC for 25 g/ℓ of Calgon carbon practically coincide with those for 50 g/ℓ of Darco carbon. This would indicate that twice as much of the Darco carbon would be required to treat this particular waste to the same removal efficiency. The reason for such a drastic difference in performance may be due to the fact that activated carbons are manufactured from different sources with different activating agents and different processes, producing materials of varying surface area,

TABLE IV. RELATIVE RATES OF ADSORPTION BETWEEN CALGON AND DARCO CARBONS

Reaction Time	Type of Activated Carbon									
	Calgon						Darco			
	Carbon Dose, g/ℓ									
	25		50		100		25		50	
	Effluent Concentration, mg/ℓ									
Hour	COD	TOC	COD	TOC	COD	TOC	COD	TOC	COD	TOC
0	7,600	2,300	7,600	2,300	7,600	2,300	7,600	2,300	7,600	2,300
1	5,680	1,340	4,930	1,170	4,020	760	5,520	1,680	6,030	1,940
2	5,200	1,620	4,640	1,400	4,060	1,210	5,750	1,820	5,200	1,640
3	5,180	1,420	4,600	1,360	4,020	1,110	5,830	1,800	5,120	1,550
5	4,820	1,530	4,440	1,350	3,930	1,130	5,740	1,730	4,960	1,460
8	4,880	1,490	4,240	1,220	3,740	1,090	5,620	1,730	4,830	1,510
12	4,680	1,470	4,130	1,260	3,820	1,110	5,440	1,720	4,680	1,440
18	4,790	1,460	3,970	1,240	3,850	1,000	5,420	1,690	4,790	1,490
24	4,320	1,290	3,850	1,090	3,350	970	4,950	1,510	4,170	1,300
30	4,210	1,265	3,590	1,065	3,390	955	4,980	1,510	4,280	1,220
39	4,140	1,260	3,545	1,070	3,350	950	4,920	1,505	4,170	1,275

NOTE: The experiment was conducted at a constant temperature of 75°F (24°C).

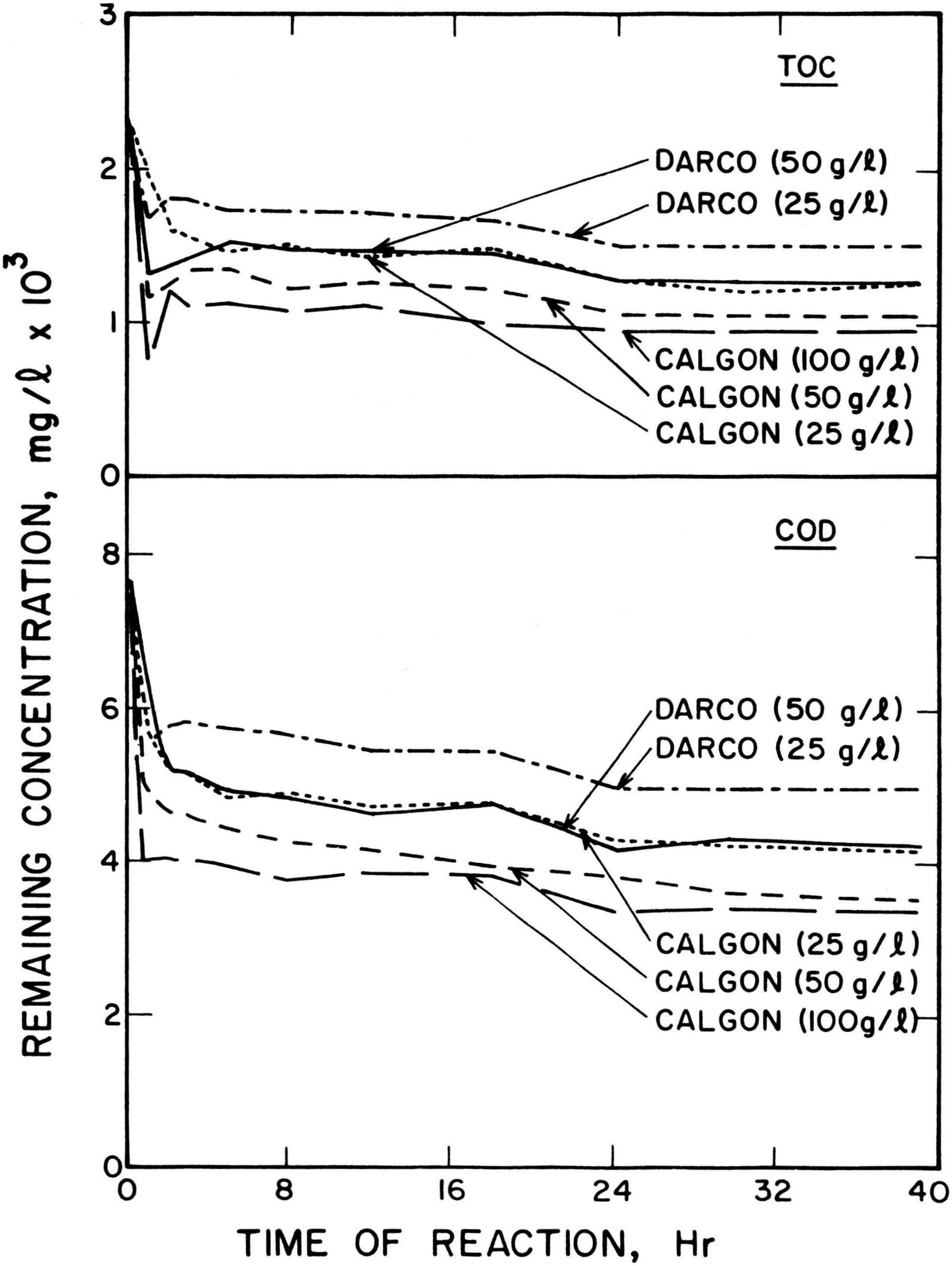

Figure 5. Relative Rates of Adsorption Between Calgon and Darco Carbons

density, and specific volume. Therefore, a particular carbon which is manufactured under certain conditions and best suited for a given waste of a specific composition may not be the best carbon for a different waste of some other origin and composition. This result clearly indicates the necessity of conducting pilot plant studies with different carbons on a given waste before selecting a carbon type and designing treatment facilities using activated carbon adsorption system; hopefully, in the future additional data may be made available which would enable the selection of carbon type by merely knowing the individual components of a complex wastewater. Figure 5 also indicates that an equilibrium adsorption stage was reached after a period of 24 hr, and longer adsorption periods effected no further reductions.

b. Equilibrium Study

The results of the equilibrium study are presented in Table V and Figure 6. Perhaps the best way to evaluate the relative COD and TOC removal efficiencies by different activated carbons at an equilibrium state is to compare their relative adsorption isotherms. As will be seen in Figure 6, the equilibrium data for each carbon conform fairly well with the Freundlich isotherm which has the following mathematical relationship (23):

TABLE V. EQUILIBRIAL ADSORPTION OF CALGON AND DARCO CARBONS

Carbon Dose g/ℓ	Type of Activated Carbon									
	Calgon					Darco				
	Equilibrial Concentration mg/ℓ		$\frac{X^*}{\overline{M}}$ mg/ℓ		Final pH	Equilibrial Concentration mg/ℓ		$\frac{X^*}{\overline{M}}$ mg/ℓ		Final pH
	COD	TOC	COD	TOC		COD	TOC	COD	TOC	
0.0	7,600	2,330	-	-	8.2	7,560	2,350	-	-	8.2
6.25	6,320	1,968	204.8	57.9	7.9	6,820	2,160	118.4	30.4	7.8
12.5	5,620	1,805	158.4	42.0	8.0	6,520	2,040	83.2	24.8	7.8
25	4,920	1,555	107.2	31.0	8.2	5,540	1,780	80.8	24.3	7.8
50	4,180	1,325	68.4	20.1	8.6	4,960	1,530	53.0	16.4	7.8
100	3,840	1,087	37.6	13.4	8.7	4,150	1,240	34.1	11.1	7.8
150	3,410	1,000	27.9	8.8	8.7	3.760	1,130	25.3	8.1	7.8
200	3,180	902	22.1	7.1	8.6	3,490	1,040	20.3	6.5	7.8
300	2,710	795	16.3	5.1	8.5	2,980	890	15.3	4.9	7.8
500	2,060	610	11.0	3.4	8.3	2,520	695	10.8	3.3	7.8

*X = COD or TOC removed after 24 hr at a temperature of 75°F (24°C), mg/ℓ.
M = Weight of carbon, g/ℓ.

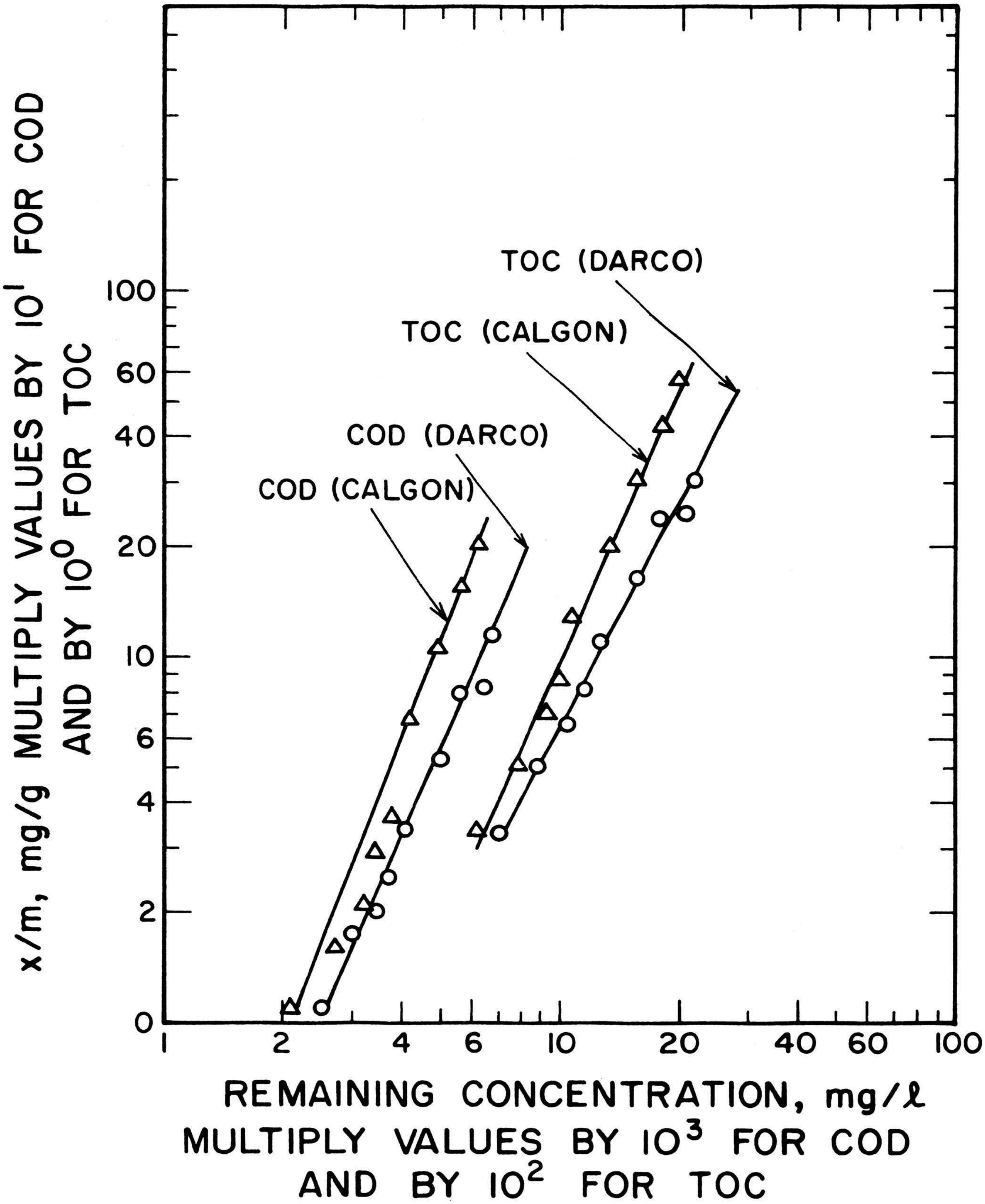

Figure 6. Freundlich Adsorption Isotherms for the Pharmaceutical Waste and Different Activated Carbons

$$\frac{X}{M} = KC^{1/n} \qquad \text{(Eq. 1)}$$

in which X = the amount of COD or TOC removed at the equilibrium state

M = the weight of carbon used

C = the concentration of COD or TOC remaining at an equilibrium state

K and n = experimental constants for the Freundlich isotherm

The Freundlich isotherm shown in Equation (1) can be rewritten into the following linear form:

$$\text{Log } \frac{X}{M} = \log K + \frac{1}{n} \log C \qquad \text{(Eq. 2)}$$

If the plot of $\frac{X}{M}$ versus C on log-log paper could be linearized, then it could be stated that the adsorption relationship conforms to the Freundlich model. As seen in Figure 6, the experimental data obtained in the equilibrium study fit fairly well into a straight line on the log-log plot, indicating that the equilibrium removals of COD and TOC by both carbons were in accord with the Freundlich isotherm. These data further show that the isotherms for COD and TOC were almost parallel to each other for both carbons; also that the Calgon carbon effected better removal of COD and TOC than did the Darco carbon. For example, at an equilibrium solute concentration of 5,000 mg/ℓ, the adsorbed COD/carbon ratios were found to be 106 and 52 for the Calgon carbon and Darco carbon, respectively. This clearly indicates the better quality of Calgon carbon for this particular waste.

It had been indicated by Zuckerman and Molof (9) that chemical hydrolysis of higher molecular weight organics (by raising the pH to a value of 11.4) could result in better organic removals. In order to study the effect of initial pH on the adsorption capacity, tests were conducted with the initial pH adjusted to 3, 8, and 11.4, and the results are shown in Table VI. An evaluation of these data indicate that pH adjustment did not alter the performance characteristics of the two carbons. These data are clearly in contradiction to those reported by Zuckerman and Molof (9), but it is not known why this contradiction exists.

2. Column Studies

Batch studies are relatively easier to operate in the laboratory and they provide basic information in predicting column performance. As the future full-scale field operations will be most likely conducted in columnar fashion, column studies were undertaken. Column operation offers the advantages of: Not requiring subsequent carbon separation; higher removals in equilibrium with the

TABLE VI. EFFECT OF pH ON EQUILIBRIAL ADSORPTION

		Type of Activated Carbon					
		Calgon			Darco		
		Equilibrium Concentration mg/ℓ			Equilibrium Concentration mg/ℓ		
Carbon Dose g/ℓ	Initial pH	COD	TOC	Final pH	COD	TOC	Final pH
50	3.0	4,120	1,360	6.8	4,350	1,390	5.3
200		3,080	940	8.5	3,280	950	7.4
50	8.0	4,270	1,450	8.1	4,620	1,440	7.7
200		3,160	960	9.0	3,510	1,020	7.7
50	11.4	4,560	1,520	10.2	4,840	1,580	8.1
200		3,190	980	10.2	3,260	908	8.6

NOTE: Equilibrium time of reaction was 24 hr, and temperature was 75°F (24°C).

influent concentrations rather than the effluent concentrations; and greater flexibility in operation. Two separate studies were conducted, one using Calgon carbon and the other using Darco carbon.

a. Study with Calgon Carbon

For this study an effective bed height of 9 ft (2.75 m) was provided. Three columns, each of 3 ft (0.9 m) bed height, were connected in series using rubber tubing. Only downflow operation was provided as the previous study by Hardie (22) had indicated no difference in performance in either the upflow or downflow-mode of operation. Also in the previous study, it was noticed that upflow operation had some operational difficulties in the laboratory, such as the separation of the carbon packing within the column. It was, therefore, decided to use only downflow-mode of operation. The pumping rate was selected to provide a flow of 2 gpm/sq ft (81.4 ℓ/min/sq m). This corresponded to a flow rate of 116 mℓ/min through the 1-1/2-in. (3.8-cm) ID carbon column.

During the study, the chemically clarified waste was stored in a polyethylene tank. As the clarified waste had a turbidity of 1 Ju only, mixing of the waste prior to pumping was not considered necessary.

The results of this study are given in Table VII and Figure 7 which present the COD and TOC concentrations determined in samples obtained at three different column depths [3 ft (0.91-m), 6 ft (1.83-m), and 9 ft (2.75-m) (the column effluent)] after varying volumes of waste had been treated. The carbon in the first 3 ft (0.91-m) of bed reached near exhaustion after a volume of 83 ℓ had been passed through; however, the entire 9-ft (2.75-m) column continued to adsorb additional organics until a total volume of 165 ℓ was passed through. Adsorption through the total bed depth of 9 ft (2.75-m) with a contact time of 10.8 min was able to produce a removal efficiency of 91 percent (on the basis of COD removal) only in the first 3.5 ℓ of waste. Thereafter, break-through occurred and the quality of the effluent deteriorated, although as was indicated earlier, the COD concentration in the effluent did not become the same as that in the influent until a total volume of 165 ℓ had been treated. The TOC curves (Figure 7) are similar to the COD curves. The TOC break-through also occurred after a waste volume of 3.5 ℓ had been passed through, and TOC removal continued until a total volume of 165 ℓ had been treated.

The COD and TOC profiles presented in Figure 8 give some identification regarding the degree of

TABLE VII. COLUMN ADSORPTION STUDY - CALGON CARBON COLUMN

Volume of Waste Treated ℓ	Column Depth					
	3 ft (0.91 m)		6 ft (1.83 m)		9 ft (2.75 m)	
	Effluent Concentration, mg/ℓ					
	COD	TOC	COD	TOC	COD	TOC
3.45	4,640	1,426	2,090	972	695	196
6.9	4,640	1,600	4,530	1,492	3,960	1,340
10.35	4,780	1,620	4,220	1,556	4,940	1,408
13.8	5,140	1,688	4,460	1,558	5,010	1,440
20.7	5,540	1,820	4,560	1,600	5,360	1,460
34.5	6,200	1,930	4,920	1,680	5,050	1,576
48.4	6,840	2,070	5,600	1,792	5,010	1,600
82.8	7,490	2,120	6,400	2,040	5,930	1,860
110.4	7,680	2,200	7,120	2,180	6,450	1,900
165.6	6,680	2,300	7,680	2,240	7,490	2,200

NOTE: Column Dia = 1.5 in. (3.75 cm).
Flow Rate = 2 gpm/sq ft (81.4 ℓ/min/sq m).
Influent concentration (coagulated waste): COD = 7,600 mg/ℓ
TOC = 2,340 mg/ℓ

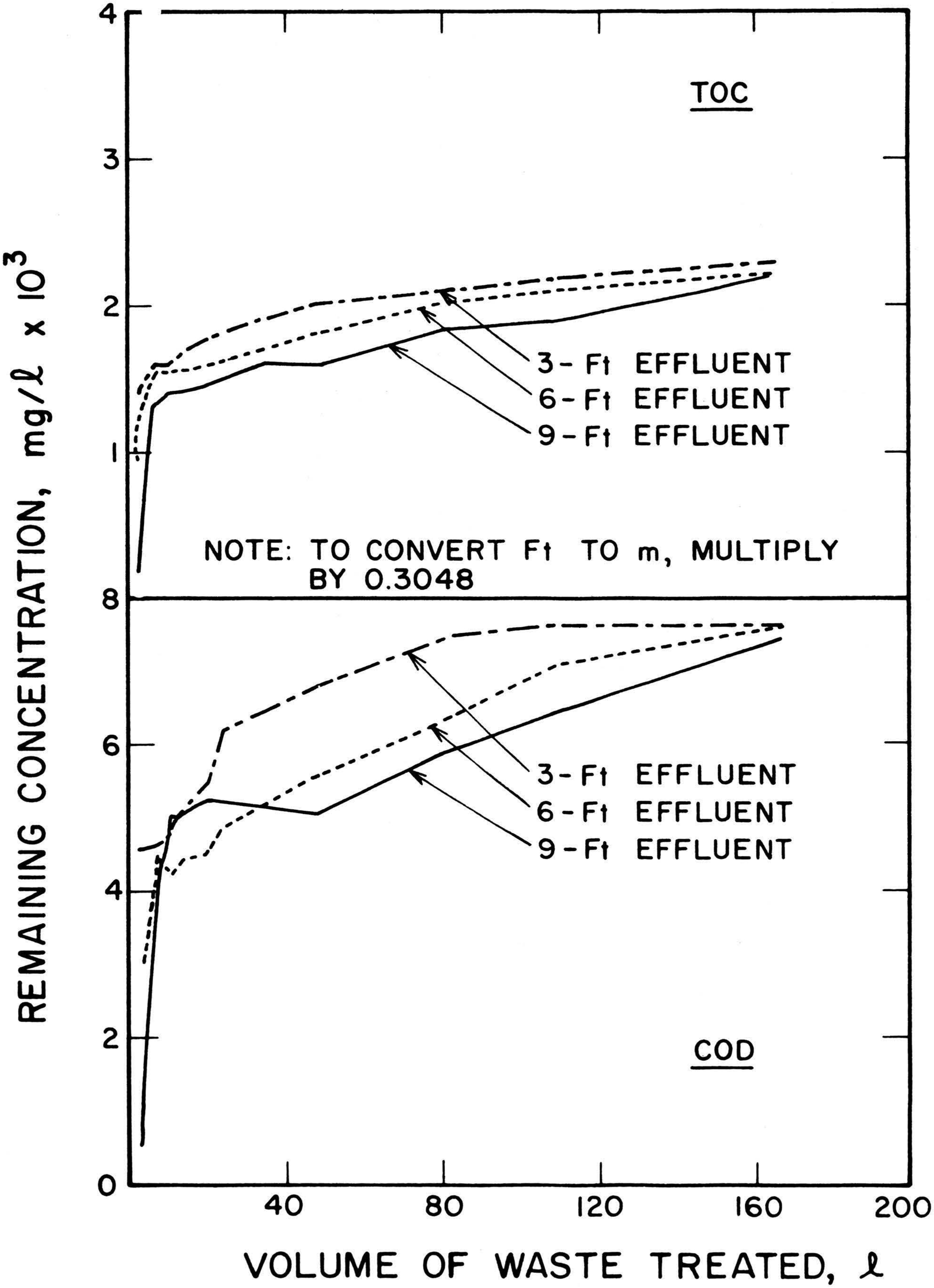

Figure 7. Performance of Calgon Column

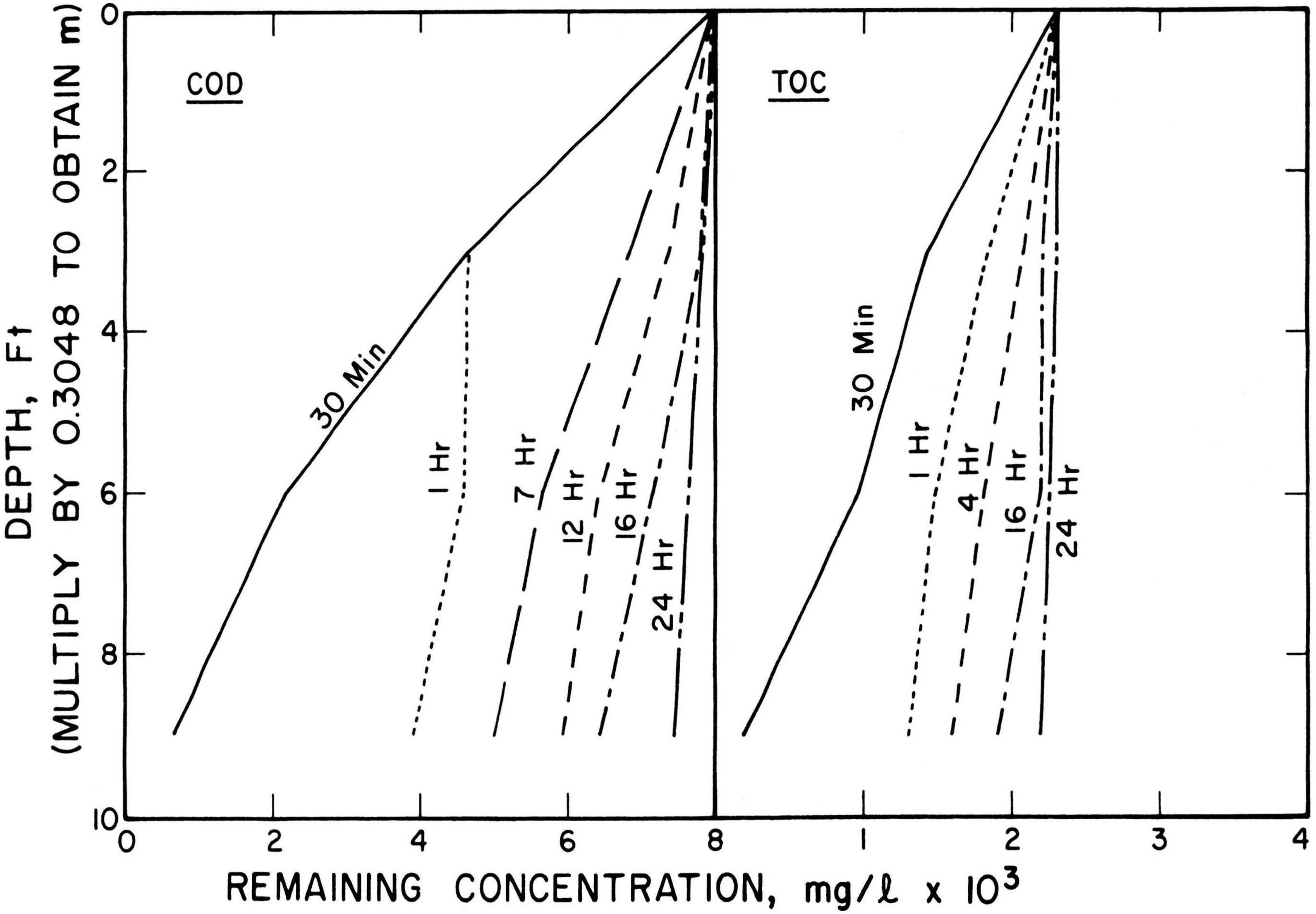

Figure 8. Profiles of COD and TOC Removal by the Calgon Carbon Column

carbon exhaustion which had been attained at different depths and after different periods of treatment.

b. Study With Darco Carbon

During the column studies with the Calgon carbon, the results indicated that a bed height of 9 ft (2.75 m) was not sufficient enough to provide a good adsorption for this high organic strength waste. The contact time of 10.8 min in the 9-ft (2.75-m) column, corresponding to a flow rate of 2 gpm/sq ft (81.4 (81.4 ℓ/min/sq m), seemed to be insufficient. Further, during the batch studies it was observed that the Darco carbon had less adsorptive capacity than the Calgon material. So it was decided to provide a total bed height of 15 ft (4.56 m) for the Darco carbon in the subsequent column study. In addition, a flow rate of 1.5 gpm/sq ft (61.1 ℓ/min/sq m) was selected, partly due to the limitations of sigma motor pump and partly due to the decision to increase the bed contact time. The pump was adjusted to a flow rate of 87 mℓ/min through the column providing a total contact time of 24.0 min for the 15-ft (4.56-m) bed depth.

Five columns were connected in series. The clarified waste was stored in polyethylene drums. The test was started and samples were drawn at shorter time intervals at the beginning of the study. The samples were acidified, stored in a refrigerator, and analyzed subsequently.

The amounts of COD and TOC remaining in the effluent as a function of volume treated are presented in Table VIII and Figure 9. Both COD and TOC removals were exceptionally good for the first 5 ℓ of effluent. The COD was removed from the original value of 7,600 mg/ℓ to less than 80 mg/ℓ, while TOC was removed from an original value of 2,350 mg/ℓ to less than 20 mg/ℓ. The 15-ft (4.56-m) column came to near exhaustion after a total quantity of 85 ℓ was passed through; after that, there was only slight removal until the 15-ft (4.56-m) column had been exhausted completely at a total treated volume of 122 ℓ.

The COD and TOC profiles presented in Figure 10 provide some indication of the degree of the carbon exhaustion which had been attained at the different bed depths following various periods of treatment.

During the study, the pH of the samples which were drawn at different bed heights at different time intervals were measured and the results are plotted in Figure 11 as a function of the waste volume treated. It is interesting to note that the pH profiles are almost similar to the COD profiles and the stabilization of the pH value seemed to indicate that the carbon in the column was approaching the exhaustion level.

TABLE VIII. COLUMN ADSORPTION STUDY - DARCO CARBON COLUMN

Volume of Waste Treated ℓ	Column Depth									
	3 ft (0.91 m)		6 ft (1.83 m)		9 ft (2.75 m)		12 ft (3.6 m)		15 ft (4.57 m)	
	Effluent Concentration, mg/ℓ									
	COD	TOC	COD	TOC	COD	TOC	COD	TOC	COD	TOC
0.86	1,375	408	232	12.0	232	10.0	244	14.0	84.0	9.0
1.72	3,740	855	336	28.0	160	9.0	244	10.0	76.0	9.0
2.58	4,720	1,015	1,495	403	204	33.0	96	5.0	92.0	10.0
3.88	5,000	1,840	4,260	1,600	2,050	960	248	43.0	76.0	6.0
5.17	5,460	2,000	4,020	1,760	3,880	1,600	844	1,520	118	22.0
7.75	5,920	1,920	4,900	1,760	4,690	1,760	4,540	1,660	2,300	1,340
10.34	6,300	2,080	5,130	1,800	4,780	1,720	4,810	1,700	4,310	1,660
15.51	6,960	2,200	5,870	2,000	4,970	1,880	5,010	1,840	4,890	1,800
25.85	7,160	2,280	6,650	2,080	6,100	2,040	5,600	1,920	4,810	2,040
41.36	7,460	2,320	7,160	2,320	6,700	2,200	6,220	2,080	5,910	2,080
62.04	7,380	2,320	7,340	2,320	7,140	2,320	6,720	2,200	6,200	2,320

TABLE VIII. COLUMN ADSORPTION STUDY - DARCO CARBON COLUMN (Continued)

Volume of Waste Treated ℓ	Column Depth									
	3 ft (0.91 m)		6 ft (1.83 m)		9 ft (2.75 m)		12 ft (3.6 m)		15 ft (4.57 m)	
	Effluent Concentration, mg/ℓ									
	COD	TOC	COD	TOC	COD	TOC	COD	TOC	COD	TOC
82.72	7,180	2,320	7,180	2,320	7,260	2,320	7,140	2,320	6,750	2,320
103.40	7,600	2,320	7,510	2,320	7,450	2,320	7,400	2,320	7,400	2,320
122.08	7,510	2,360	7,510	2,400	7,400	2,400	7,520	2,320	7,520	2,320

NOTE: Column dia = 1.5 in. (3.75 cm).
Flow Rate = 1.5 gpm/sq ft (61.4 ℓ/min/sq m).
Influent concentration (coagulated waste): COD = 7,600 mg/ℓ.
TOC = 2,340 mg/ℓ.

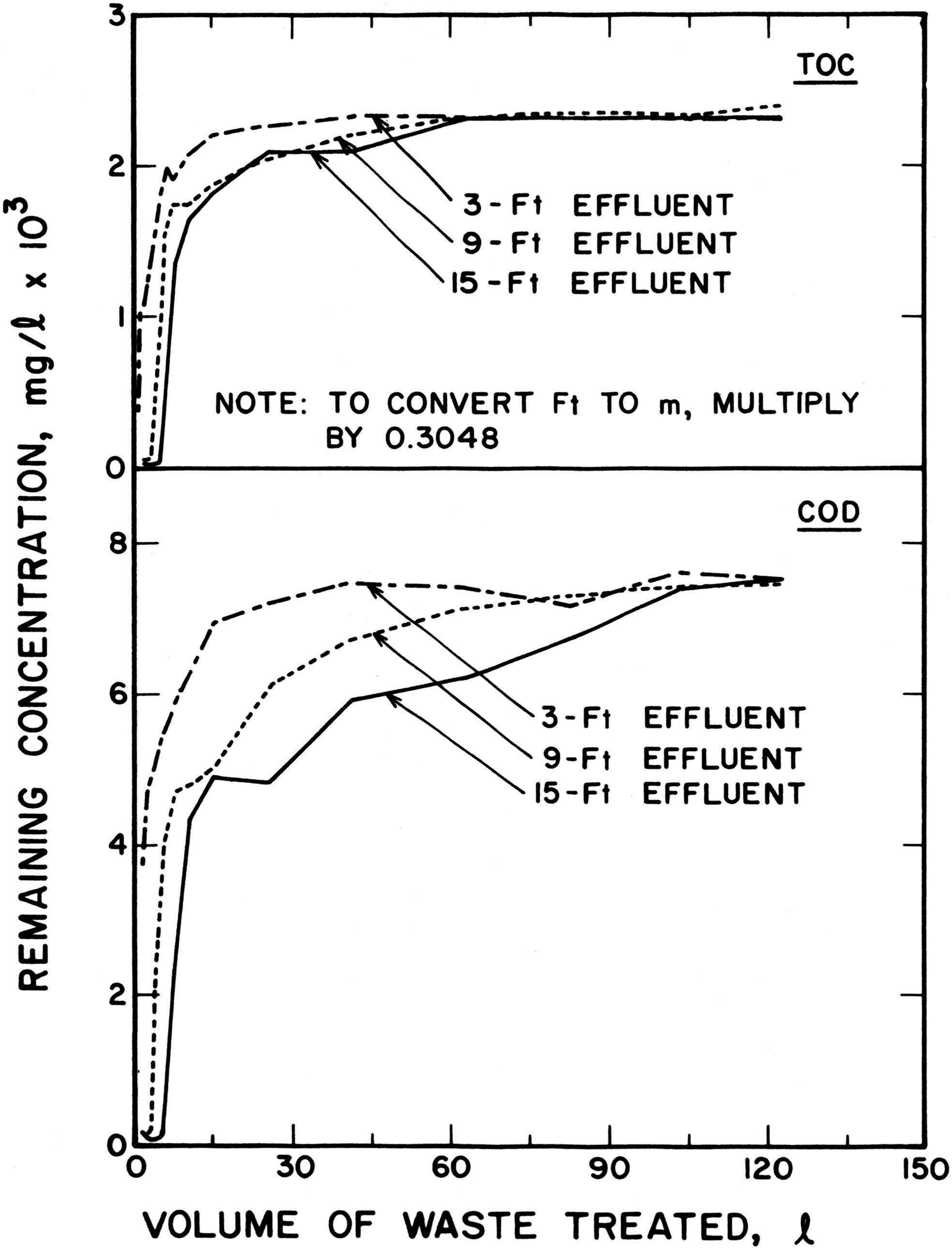

Figure 9. Performance of Darco-Carbon Column

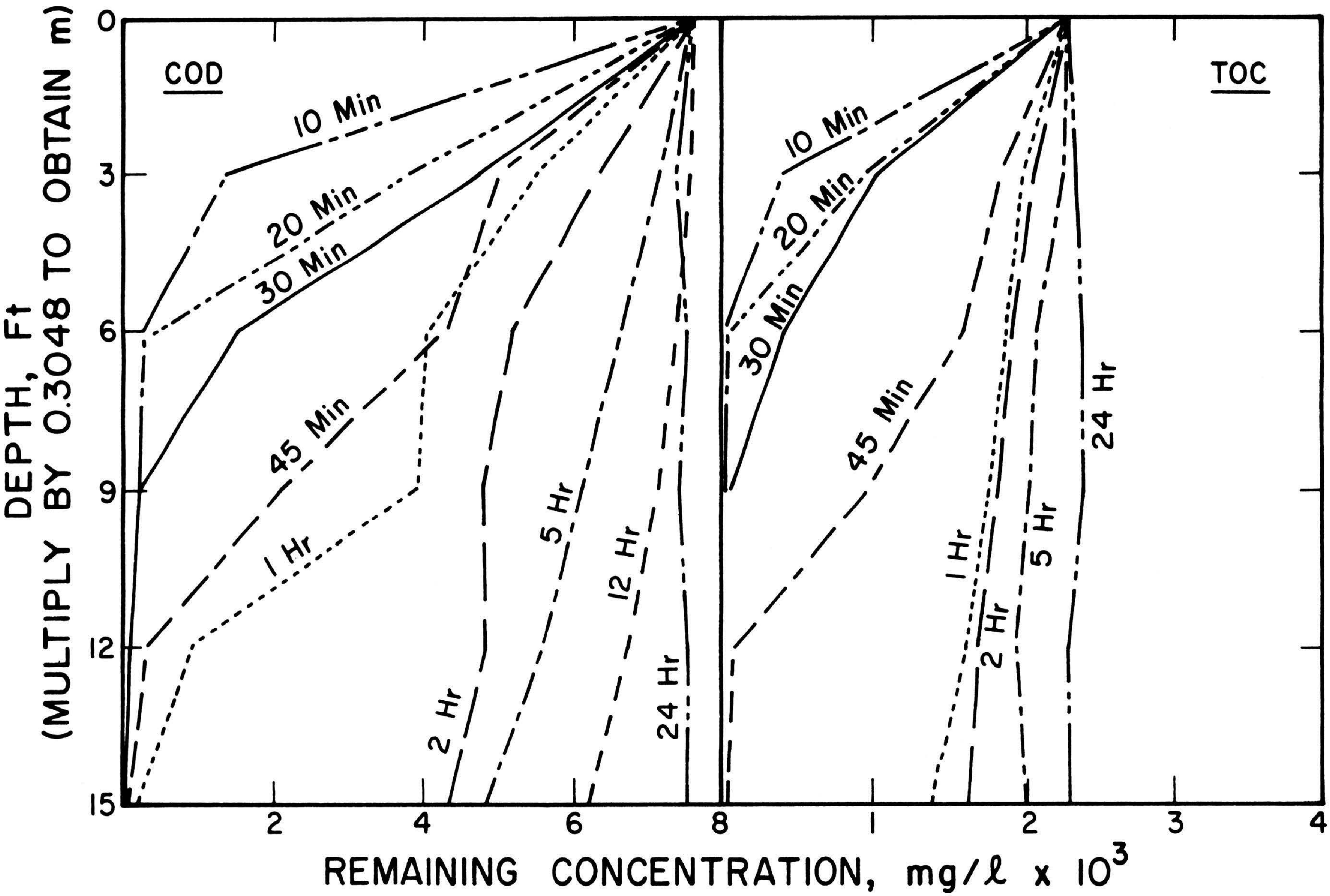

Figure 10. Profiles of COD and TOC Removal by the Darco Carbon Column

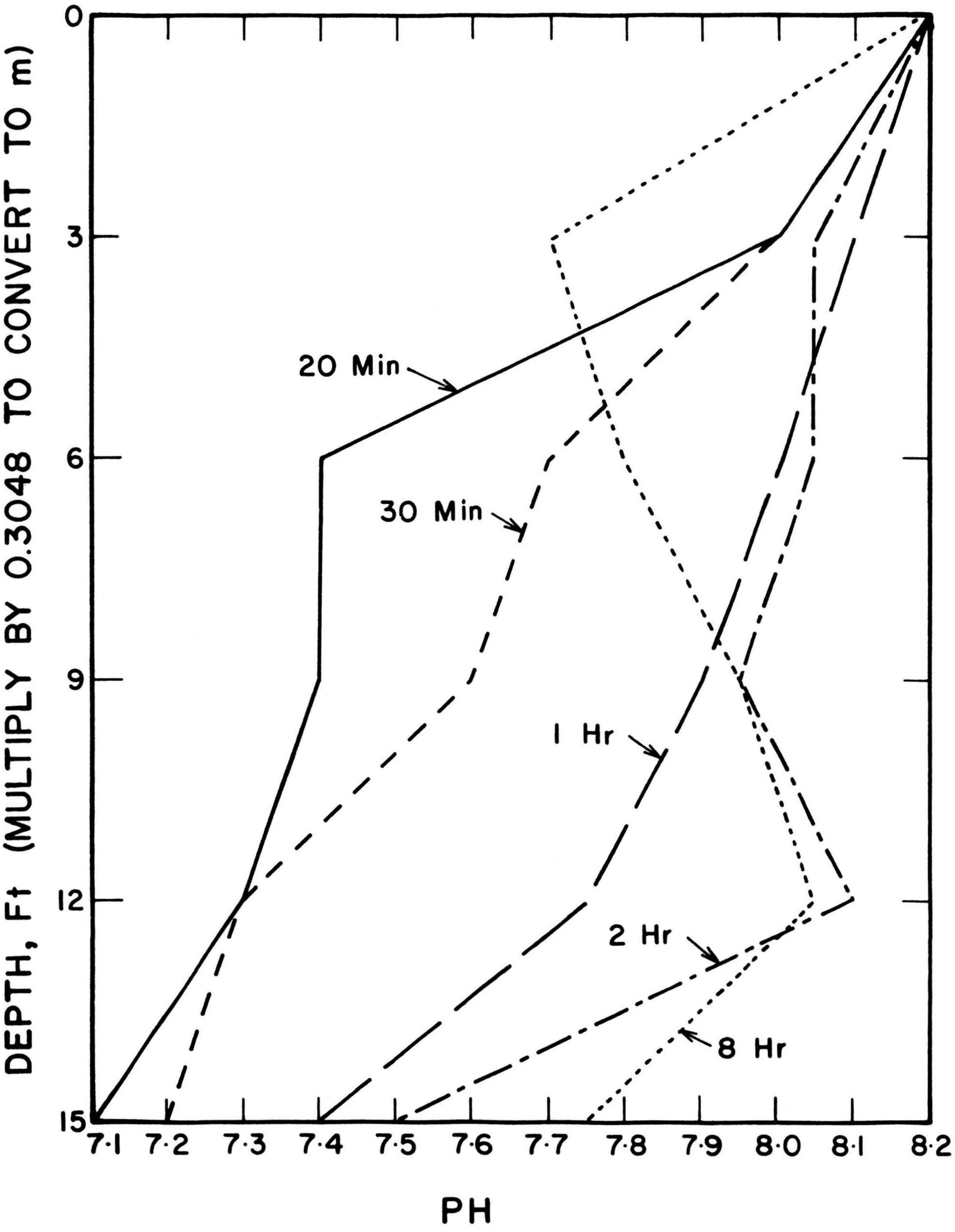

Figure 11. pH Variation in the Darco Carbon Column Effluent

The samples were also analyzed for the presence of NH_3-N and Org-N, and the results are presented in Table IX. Ammonia nitrogen was removed completely in the first 4 ℓ of the waste treated, and additional removals were noticed until approximately 10 ℓ of the waste had been passed through the column. On the other hand, the removal of Org-N was fairly consistent, amounting to 50 to 60 percent throughout the total treated volume of 122 ℓ. These results are in conformity with those reported by Weber, *et al*. (8) who found that Org-N could be removed by carbon adsorption, while ammonia nitrogen removals were not.

3. Comparison of the Performance of the Two Carbons

The results of the batch study indicated that the Calgon carbon had better capacity than the Darco carbon for treating this pharmaceutical waste. Similar results were also noticed during the column study. Figure 12 is presented to enable a comparison of the performance by both types of carbons; it shows the two traces for the COD remaining in the wastewater from the 9-ft (2.75-m) effluents as a function of waste volume treated. Even though more contact time was provided in the Darco column (14.4 min as compared to 10.8 min in the Calgon column), the quality of wastewater effluent from the same 9-ft (2.75-m) bed heights indicates that the Calgon had a better removal efficiency.

TABLE IX. REMOVAL OF NITROGEN BY CHEMICAL COAGULATION AND CARBON ADSORPTION

Type of Sample	Nitrogen Concentration mg/ℓ as N	
	NH_3	Org
Raw Waste	117.0	16.4
Chemically Clarified Waste	114.0	11.2
Carbon Column Effluent* after treating the indicated volume of waste in ℓ		
1.72	0.0	6.0
3.88	0.0	7.0
5.17	49.6	5.8
10.34	121.0	5.6
15.51	117.0	6.3
25.85	112.0	5.6
51.70	110.0	7.3
77.50	112.8	8.0
122.00	113.2	8.0

* From a 15-ft (4.57-m) Darco carbon bed depth.

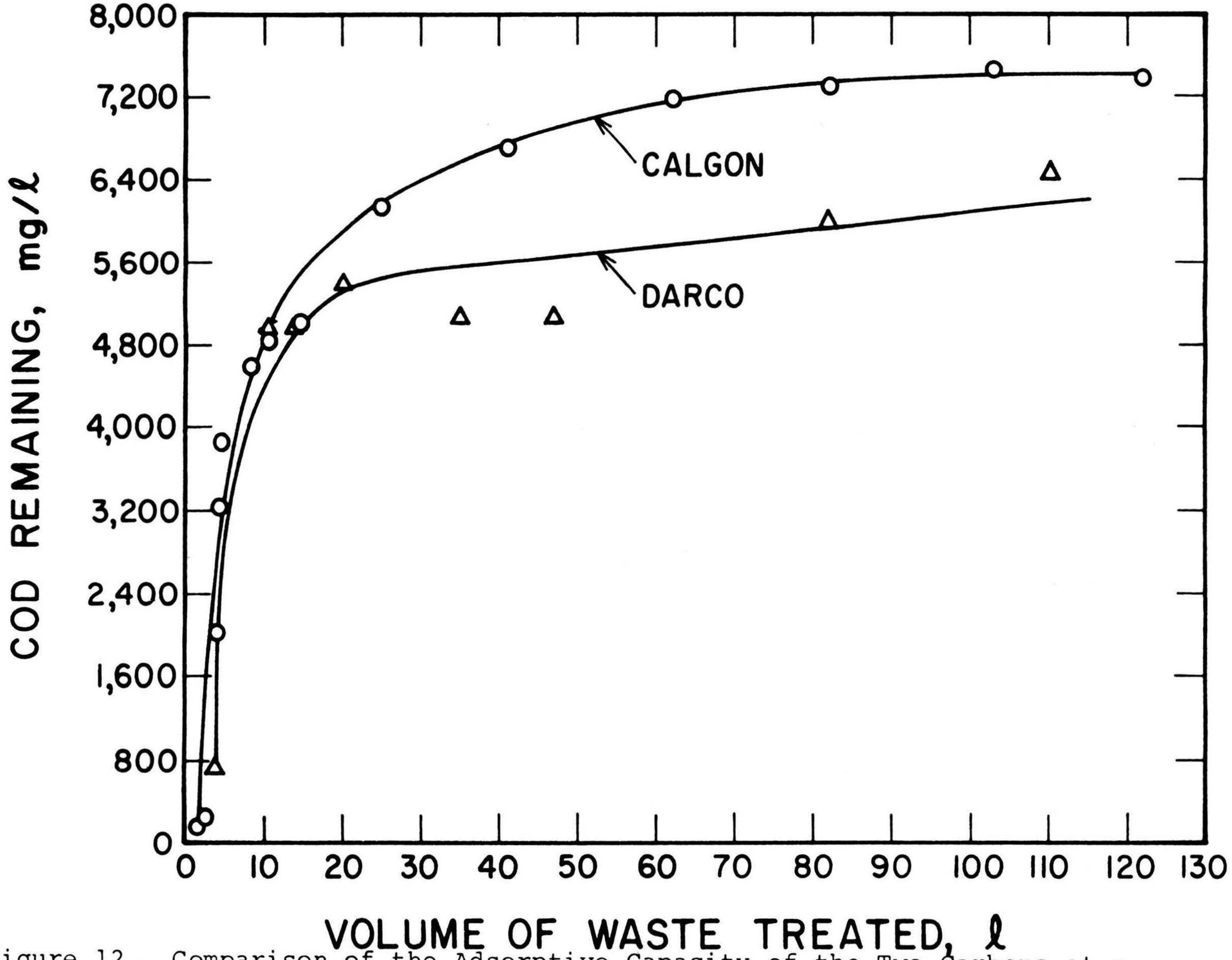

Figure 12. Comparison of the Adsorptive Capacity of the Two Carbons at a 9-ft (2.75-m) Column Depth

Batch studies had also indicated that the rates of uptake by Calgon at 25 mg/ℓ and Darco at 50 mg/ℓ were almost identical. In other words, for the same uptake rate the dose of Darco carbon needed was twice as high as Calgon.

The adsorptive capacity of the two carbons is compared in Figure 13. The cumulative COD removal by a 9-ft (2.75-m) column until the carbons had been completely exhausted were calculated; this depth corresponds to a total quantity of carbon of approximately 1,224 g. The Calgon carbon adsorbed a total of 240 g of COD, while the Darco carbon adsorbed only 108 g of COD. These correspond to an adsorptive capacity of nearly 19.9 percent by weight for Calgon carbon and only 8.8 percent for Darco's. Weber *et al.* (8) has reported a 27 percent carbon adsorption by weight for domestic waste. Of course, it is understandable that the adsorptive capacity of any carbon depends greatly on the nature of organics contained in the waste.

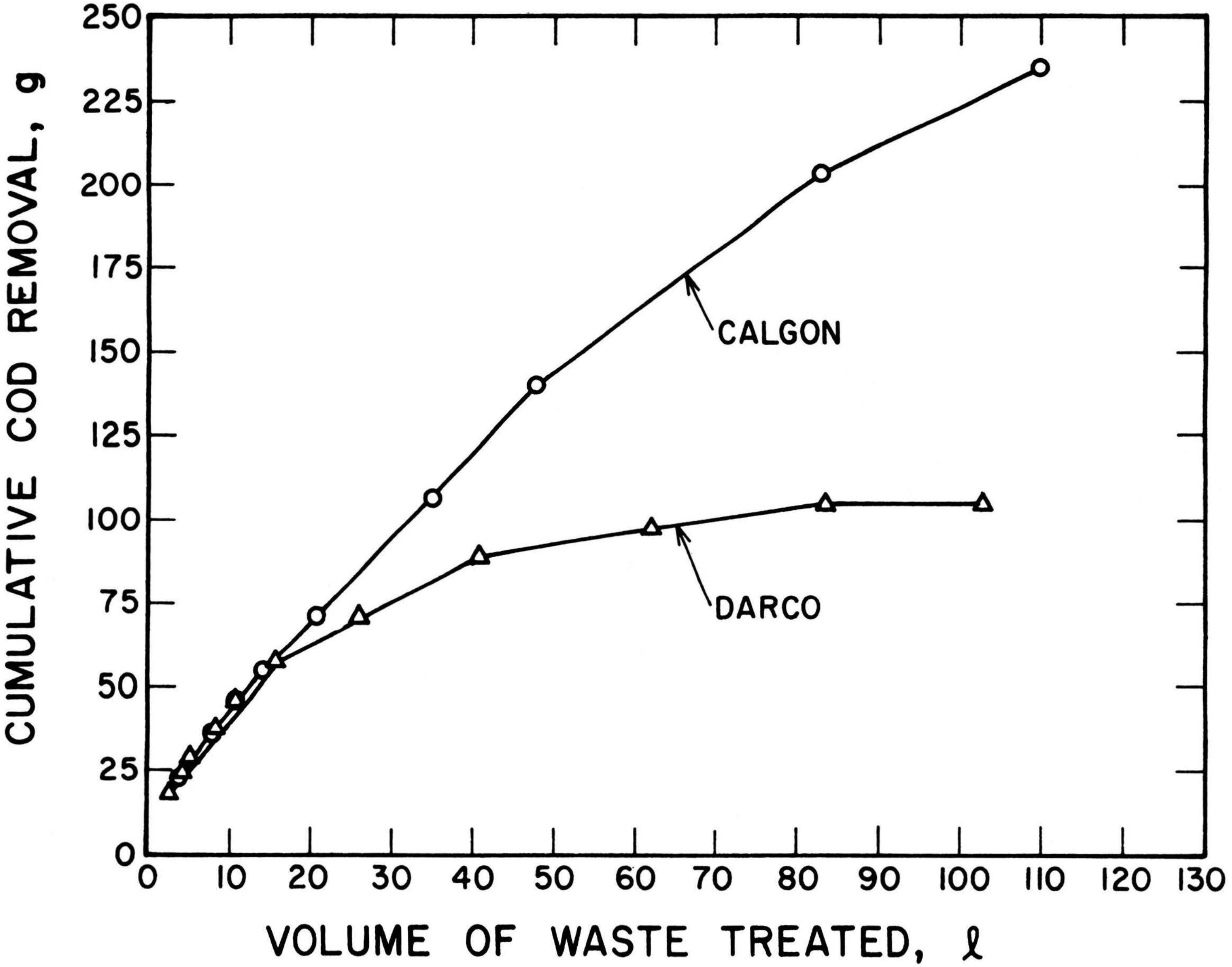

Figure 13. Comparison of the Adsorptive Capacity of the Two Carbons at a 9-ft (2.75-m) Column Depth

V. CONCLUSIONS

Based on the findings of this research, the following conclusions can be made:

1. Physical-chemical treatment by activated carbon adsorption could be successfully applied for treating the pharmaceutical waste employed in this study.
2. Irrespective of initial concentration of organics, the activated carbon treatment system, following a chemical pretreatment, was able to yield an overall efficiency of up to 91 percent for the particular pharmaceutical waste studied. However, this efficiency could only be maintained for the initial very small volume of the wastewater treated.
3. Alum was found to be a better coagulant than ferric chloride for the chemical pretreatment of this waste; it was also found that proper pH adjustment was necessary for efficient chemical clarification of the waste.
4. Chemical pretreatment did not effect significant reductions in COD, since in this waste the organics were mostly in the dissolved form.
5. Batch studies on activated carbon adsorption indicated that the adsorption isotherms were in conformity with the Freundlich equation.
6. Chemical hydrolysis of the waste by pretreatment with alkali or acid did not have a significant influence on the carbon adsorption efficiency.

7. Carbon column studies indicated that the residence time of the liquid waste within the columns had a considerable impact on the adsorption efficiency.
8. The findings of the column studies were not in conformity with the results predicted by batch studies, at least for this particular waste.
9. Ammonia nitrogen removals were observed by treatment with activated carbon adsorption.
10. There was a significant difference in performance between the two different carbons used in this study. Calgon Filtrasorb 400 and Darco S-51, at least when they were used for treating this particular waste.

BIBLIOGRAPHY

1. Murray, C. R., and Reeves, E. B., "Estimated Use of Water in the United States in 1970," U.S. Geological Survey Circular No. 676 (1972).

2. "Summary Report of Advanced Waste Treatment Research Program - 1964 to 1967," Robert A. Taft Sanitary Engineering Center, FWPCA Publication WP-20-AWTR-19 (1968).

3. Bayley, R. W., and Waggott, A., "Some Recent Advances in Water Reclamation," Journal of the Institute of Water Pollution Control, 71, 1, 45 (1972).

4. Joyce, R. S., Allen, J. B., and Sukenik, V. A., "Treatment of Municipal Wastewaters by Packed Activated Carbon Beds," Journal of Water Pollution Control Federation, 38, 813 (1966).

5. Bishop, D. F., Marshall, L. S., O'Farrell, T. P., Dean, R. B., O'Conner, B., Dobbs, R. A., Griggs, S. H., and Villiers, R. H., "Studies on Activated Carbon Treatment," Journal of Water Pollution Control Federation, 39, 188 (1967).

6. Parkhurst, J. D., Dryden, F. D., McDermott, G. N., and English, J., "Pomana Activated Carbon Pilot Plant," Journal of Water Pollution Control Federation, 39, R70 (1967).

7. Slechta, A. F., and Culp, G. L., "Water Reclamation Studies at the South Tahoe Public Utility District," Journal of Water Pollution Control Federation, 39, 787 (1967).

8. Weber, W. J., Jr., Hopkins, C. B., and Bloom, R., Jr., "Physico Chemical Treatment of Wastewater," Journal of Water Pollution Control Federation, 42, 83 (1970).

9. Zuckerman, M., and Molof, A. H., "High Quality Reuse Water by Chemical-Physical Wastewater Treatment," Journal of Water Pollution Control Federation, 42, 437 (1970).

10. Hager, D. G., and Reily, P. B., "Clarification-Adsorption in the Treatment of Municipal & Industrial Wastewater," Journal of Water Pollution Control Federation, 42, 794 (1970).

11. Bishop, D. F., O'Farrell, T. P., and Stamburg, J. B., "Physical-Chemical Treatment of Municipal Wastewater," *Journal of Water Pollution Control Federation*, *44*, 361 (1972).

12. Villiers, R. V., "Single Stage Process Checks Out," *Water & Wastes Engineering*, *9*, 1, 32 (1972).

13. Friedman, L. D., Bloom, R., Jr., and Weber, W. J., Jr., "Think Physico-Chemical," *Water & Wastes Engineering*, *9*, 9, 67 (1972).

14. Peck, K., "Physical-Chemical Beats Biological for Weak Sewage," *Water & Wastes Engineering*, *8*, 11, 30 (1971).

15. Flynn, F. X., and Thompson, J. C., "Physical-Chemical Treatment Plant for Combined Municipal-Industrial Wastewater at Niagara Falls, New York," Presented at the 27th Purdue Industrial Waste Conference, May 2-4, 1972.

16. Atkins, P. F., Jr., Scherger, D. A., and Barnes, R. A., "Ammonia Removal in a Physical-Chemical Wastewater Treatment Process," Presented at the 27th Purdue Industrial Waste Conference, May 2-4, 1972.

17. Libby, D. V., Bell, G. R., and Wirsig, O. A., "Chemical-Physical Treatment of Municipal Wastewater Using Continuous Countercurrent Filtration," *Journal of Water Pollution Control Federation*, *44*, 574 (1972).

18. "Process Design Manual for Carbon Adsorption," Environmental Protection Agency Technology Transfer (1971).

19. Joyce, R. S., and Sukenik, V. A., "Feasibility of Granular Activated Carbon Adsorption for Wastewater Renovation." AWTR-10, U.S. Public Health Service,
R Cincinnati, OH (1964).

20. Weber, W. J., Jr., "Discussion on High Quality Reuse Water by Chemical-Physical Wastewater Treatment," *Journal of Water Pollution Control Federation*, *42*, 456 (1970).

21. Klimek, J. C., "Forecasting Industrial Water Requirements in Manufacturing," *Water Resources Bulletin*, *8*, 561 (1972).

22. Hardie, M. G., "Advanced Waste Treatment of Industrial Wastewaters by Physicochemical Processes," M.S. Thesis, University of Missouri - Rolla (1971).

23. Huang, J. C., and Hardie, M. G., "Water Reclamation by Physicochemical Treatment of Wastewater," Water Resources Bulletin, 7, 148 (1971).

24. Huang, J. C., and Hardie, M. G., "Treatment of Refinery Waste by Physicochemical Processes," Journal of the Sanitary Engineering Division, ASCE, 97, 467 (1971).

25. "Standard Methods for the Examination of Water and Wastewater," 12th Edition, American Public Health Association, New York, NY (1965).

26. Jankovic, S. G., Mitchell, D. T., and Buzzell, J. C., Jr., "Measurement of Phosphorus in Wastewater," Water and Sewage Works, 114, 471 (1967).

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