

---

Masters Theses

Student Theses and Dissertations

---

1971

## Advanced waste treatment of industrial waste waters by physicochemical processes

Michael Gay Hardie

Follow this and additional works at: [https://scholarsmine.mst.edu/masters\\_theses](https://scholarsmine.mst.edu/masters_theses)



Part of the [Civil Engineering Commons](#)

Department:

---

### Recommended Citation

Hardie, Michael Gay, "Advanced waste treatment of industrial waste waters by physicochemical processes" (1971). *Masters Theses*. 7228.

[https://scholarsmine.mst.edu/masters\\_theses/7228](https://scholarsmine.mst.edu/masters_theses/7228)

This thesis is brought to you by Scholars' Mine, a service of the Missouri S&T Library and Learning Resources. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact [scholarsmine@mst.edu](mailto:scholarsmine@mst.edu).

166

ADVANCED WASTE TREATMENT OF INDUSTRIAL WASTEWATERS  
BY PHYSICOCHEMICAL PROCESSES

BY

MICHAEL GAY HARDIE, 1940-

---

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 of

MASTER OF SCIENCE IN CIVIL ENGINEERING

1971

T2571  
98 pages  
c.1

Approved by

James H. Hurling (Advisor) Bobby L. Wilson  
Wood S. Hale

194205

## ABSTRACT

The primary objective of this investigation was to determine the general applicability of using physicochemical processes for treating different types of industrial wastes. Emphasis was placed on the evaluation of the treatment efficiency and the performance difficulties encountered in the treatment of each waste.

Two types of waste were studied, one a high strength acidic industrial chemical waste and the other a petroleum refinery waste. The physicochemical system utilized included chemical coagulation and clarification plus activated carbon adsorption. Parallel operations of fixed-bed and expanded-bed carbon adsorbers were conducted. Treatment efficiencies were evaluated in terms of the removals of chemical oxygen demand, total organic carbon, turbidity, and inorganic nutrients.

Because of the low suspended solids level contained in the acidic chemical waste, carbon adsorption was the only treatment needed for this waste. It was found that soluble organics were effectively removed from the chemical waste by carbon adsorption. Initial pH adjustments for the chemical waste to 3.2, 7.0, and 11.4 did not significantly affect the COD removal efficiency. Turbidity and nitrogen (total kjeldahl and ammonia-N) were removed to some extent by carbon adsorbers, while phosphorus (total and ortho-P) was totally unaffected.

Treatment of the refinery waste used a combination of iron coagulation at a dosage of 250 mg/l as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 3 ft carbon column adsorption. Exceptionally high water quality having a TOC of less than 3 mg/l and turbidity of less than 1 JTU was obtained. However, small quantities of organic leakage were observed consistently in all

the carbon adsorber effluents. The nature of the nonadsorbable organic material was not established. Orthophosphate removal was effected by chemical coagulation while nitrogen (ammonia and organic-N) was not. Carbon adsorbers were not found to remove any of the inorganic nutrients from the refinery waste.



## ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to his advisor, Dr. Ju-Chang Huang, for his constant counsel and encouragement during the course of this investigation. Appreciation is also extended to Dr. Bobby G. Wixson and Dr. Nord L. Gale for their help and service as committee members. Thanks are also extended to Dr. S.G. Grigoropoulos for his aid in obtaining the Federal Water Quality Administration Traineeship which made the graduate study available to the author.

The author also wishes to thank the Civil Engineering Department of the University of Missouri-Rolla for providing the facilities which were used during the study. Gratitude is also extended to the faculty and fellow students of the Civil Engineering Department for their suggestions and assistance in the investigation.

Special acknowledgment is due Mr. Edward Sullivan of the American Oil Company, Wood River Refinery, Wood River, Illinois, for his cooperation in supplying waste samples for this investigation and also in providing information which was of value in the preparation of this thesis.

Special thanks are also due the author's wife, Madonna, whose overall support and understanding were invaluable during the investigation.

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. The author was supported by Training Grants 5T1-WP-86-04 and 5T2-WP-86-05 from the Federal Water Quality Administration.

## TABLE OF CONTENTS

	Page
ABSTRACT .....	ii
ACKNOWLEDGMENTS .....	iv
LIST OF FIGURES .....	vii
LIST OF TABLES .....	ix
I. INTRODUCTION .....	1
A. Objective .....	4
B. Scope .....	4
II. REVIEW OF LITERATURE .....	6
A. Feasibility of Granular Activated Carbon Adsorption for Renovating Secondary Effluents .....	6
B. Comparison of Packed-Bed and Expanded-Bed Activated Carbon Adsorption Systems .....	10
C. Direct Use of Physicochemical Treatment System for Renovating Primary Effluents .....	12
III. EXPERIMENTAL EQUIPMENT, MATERIALS, AND METHODS .....	17
A. Equipment .....	17
1. Carbonaceous Analyzer .....	17
2. pH Meter .....	17
3. Turbidimeter .....	17
4. Walk-In Refrigerator .....	17
5. Analytical Balance .....	21
6. Drying Oven .....	21
7. Multi-Unit Stirrer .....	21
8. Stirrer .....	21
9. Sigma Motor Pump .....	21
10. Jumbo Magnetic Stirrer .....	28
11. Wrist Action Shaker .....	28
12. Spectrophotometer .....	28
B. Materials .....	28
1. Waste Samples .....	28
2. Activated Carbon .....	32
C. Methods .....	32
1. Waste Characterization .....	32
a. Chemical Oxygen Demand .....	33
b. Total Organic Carbon .....	33
c. Suspended Solids .....	35
d. Phosphorus Determinations .....	35
e. Nitrogen Determinations .....	36
2. Establishment of Treatment Scheme .....	38
a. Chemical Coagulation and Clarification .....	38
b. Carbon Adsorption Studies .....	39

	Page
IV. RESULTS AND DISCUSSION.....	43
A. High Strength Acidic Chemical Waste.....	43
1. Waste Characterization.....	43
2. Coagulation and Clarification.....	45
3. Activated Carbon Adsorption.....	45
a. Batch Studies.....	45
b. Equilibrium Studies.....	46
c. Column Studies.....	50
B. Petroleum Refinery Waste.....	66
1. Waste Characterization.....	66
2. Coagulation and Clarification.....	68
3. Activated Carbon Adsorption.....	72
a. Batch Studies.....	72
b. Equilibrium Studies.....	72
c. Column Studies.....	75
V. SUMMARY AND CONCLUSIONS.....	81
VI. RECOMMENDATIONS FOR FUTURE STUDIES.....	84
BIBLIOGRAPHY.....	85
VITA.....	87

## LIST OF FIGURES

Figure	Page
1 Proposed Clarification-Adsorption Process for Wastewater Treatment [after Weber <u>et al.</u> (1)] .....	16 *
2 Carbonaceous Analyzer .....	18
3 pH Meter .....	19
4 Turbidimeter .....	20
5 Walk-In Refrigerator .....	22
6 Analytical Balance .....	23
7 Drying Oven .....	24
8 Multi-Unit Stirrer .....	25
9 Stirrer .....	26
10 Sigma Motor Pump .....	27
11 Jumbo Magnetic Stirrer .....	29
12 Wrist Action Shaker .....	30
13 Spectrophotometer .....	31
14 Chemical Oxygen Demand (COD) Reflux Apparatus .....	34
15 Schematic Diagram of the Adsorption Column .....	41
16 Rate of COD Removal from the Chemical Waste .....	47
17 Freundlich Adsorption Isotherm for the Chemical Waste with Various pH Adjustments .....	51
18 COD Remaining at Different Depths and in the Effluent of the Fixed-Bed Adsorber .....	53
19 COD Remaining at Different Depths and in the Effluent of the Expanded-Bed Adsorber .....	55
20 Comparison of COD Removals Between Fixed-Bed and Expanded-Bed Adsorbers .....	56
21 Cumulative COD Removals Between Fixed-Bed and Expanded-Bed Adsorbers .....	57

Figure		Page
22	Profile of COD Remaining in Fixed-Bed Adsorber.....	59
23	Profile of COD Remaining in Expanded-Bed Adsorber.....	60
24	Removal of Turbidity by Fixed-Bed and Expanded-Bed Adsorbers.....	61
25	Removal of Inorganic Nutrients by Fixed-Bed Adsorber.....	63
26	Removal of Inorganic Nutrients by Expanded-Bed Adsorber.....	64
27	Variation of pH in the Effluent of Fixed-Bed Adsorber.....	65
28	Removal of Turbidity and Change in pH by Chemical Coagu- lation.....	69
29	Rate of COD Removal from the Clarified Refinery Waste.....	73
30	Freundlich Isotherms for the TOC and COD Adsorptions from the Clarified Refinery Waste.....	74
31	TOC and COD Remaining at Different Depths and in the Column Effluents of the Fixed-Bed Adsorber.....	76
32	TOC and COD Remaining at Different Depths and in the Column Effluents of the Expanded-Bed Adsorber.....	78
33	Removal of Inorganic Nutrients in the Fixed-Bed Adsorber....	79

## LIST OF TABLES

Table		Page
1	Major Characteristics of the Chemical Waste.....	44
2	Equilibrium Adsorption of the Chemical Waste with Various Initial pH Adjustments.....	49
3	Major Characteristics of the Refinery Waste.....	67
4	Major Characteristics of the Original and the Coagulated Refinery Waste.....	71

## I. INTRODUCTION

Since his beginning man has considered water to be in sufficient abundance and able to sustain his misuse and waste of it. It is only recently that the people in the United States have fully realized that this supposedly limitless supply is dwindling and that steps must be taken if the present standard of "water living" in this country is to be maintained. It has been estimated that by the year 2000 the fixed natural water resources here in the United States will no longer be adequate to supply the needs of a rapidly expanding municipal and industrial society. Efforts must be undertaken now to prevent our economic and social growths from being restricted by a reduced supply of this most important natural resource, water.

The consequences of the past misuse and disregard for water have first been felt in our large metropolitan areas where the majority of our population and industrial complexes are located. The addition of wastes, both urban and industrial, from these areas into existing waterways has created serious water pollution problems and also increased the depreciation of our water supply; and if this situation is not corrected it will deprive us of its use in the future.

Therefore the one-time use of water has become a luxury which we can no longer afford. An alternative must be provided and that alternative is to provide more effective control of water pollution or ultimately to renovate wastewater for direct reuse. The need for water reuse brings with it a demand for new advanced technologies for waste treatment. This is primarily because our present day use of conventional "primary" plus "secondary" processes of wastewater renovation does not provide sufficient degrees of treatment to produce

high quality reusable effluents. The advanced treatment technologies must not only be developed but must also be placed into actual practice.

Some European countries have already practiced water reuse for some time, but in the United States, it has only been with the increasing public outcry against pollution in recent years that considerable research interests have been focused on the development of urgently needed advanced waste treatment technologies. The ultimate objectives of these new developments will be to alleviate the nation's increasing water pollution problem and also to renovate wastewater for deliberate reuse.

The study of advanced waste treatment techniques was first undertaken by the Robert A. Taft Engineering Center in 1960. Since that time a large number of potential waste treatment techniques have been screened and those showing greater promise have been subjected to further rigorous investigations. A number of those methods such as chemical coagulation and clarification, carbon adsorption, chemical oxidation, electrodialysis, ion exchange, and reverse osmosis, etc., have proved effective in the removal of suspended solids, soluble organics, and inorganics, including algal nutrients. It is plainly seen that the majority of the above treatment methods belong to the so-called "physicochemical" treatment processes.

A leading facet of this new advanced waste treatment technology using physicochemical techniques has been the implementation of activated carbon adsorption for the removal of organics. This technology has undergone intensive study, but still has remained primarily as a step to provide "final treatment" for wastewaters which have previously been subjected to conventional secondary biological treatment. The



reason for this idea stems from the fact that many sanitary engineers label "advanced" treatment as a "tertiary" step which, of course, would be expected to follow a secondary treatment stage.

If the biological process is included in the waste treatment scheme, the overall treatment efficiency will be largely dependent upon the performance of that process. Unfortunately, the biological treatment system is difficult to control and is easily susceptible to failure by a number of factors such as overloading with waste, deficient oxygen supply, and undesirable waste characteristics, etc. The construction and operation of biological systems can be costly, too. Furthermore, the use of activated carbon adsorption in conjunction with secondary biological treatment has not proved a satisfactory treatment approach. For example, organic leakage occurs which is composed partially of nonadsorbable cell fragments produced during the secondary biological treatment stage and partially of small organic molecules which have been extensively hydrolyzed within the biological treatment system. Therefore, perhaps a better approach would be to eliminate the biological system from the waste treatment scheme. The resulting system would employ only physicochemical processes.

In an effort to eliminate the aforementioned problems, Weber and his associates (1) attempted a new approach which employed only physicochemical processes without a biological intermediate system to treat a waste complex composed of 25 percent industrial waste and 75 percent domestic wastewater. The new treatment scheme consists of the conventional primary treatment in conjunction with chemical coagulation and clarification, filtration, and activated carbon adsorption. The data which Weber et al. obtained revealed that exceptionally high

removals of chemical oxygen demand (COD), total organic carbon (TOC), and suspended solids (SS) were achieved. Phosphate and organic nitrogen removals were obtained through chemical coagulation while nitrates were reduced to some degree within the activated carbon columns as a result of biological activity. Costs estimated at 16 and 11 cents per 1,000 gal, respectively, were obtained for the physicochemical treatment versus the conventional primary-secondary biological method, but adding tertiary treatment to the secondary biological effluents in order to obtain the equivalent degree of treatment as the new approach could run costs as high as 25 cents per 1,000 gal. Since advantages in both efficiency and economy of treatment were obtained using the new approach as reported in that study, additional work is required to gain further information regarding the general applicability of this new approach to the treatment of various types of wastewater having different constituents and characteristics.

#### A. Objectives

The objective of this investigation was to determine the general applicability of using physicochemical processes for treating selected types of industrial wastes. Emphasis was placed on the evaluation of treatment efficiency and performance difficulties encountered in the treatment of each waste.

#### B. Scope

Two types of industrial waste were studied, one a high strength acidic industrial chemical waste and the other a petroleum refinery waste.

In the study of each waste the first step was the characterization of the individual wastes. Included in the characterization

were the measurements of pH, chemical oxygen demand (COD), total organic carbon (TOC), suspended solids, turbidity, phosphorus (both ortho and total), and nitrogen (both ammonia and total). Completion of the waste characterization allowed the establishment of a proper waste treatment scheme. In general the scheme would include chemical coagulation and clarification, filtration, and activated carbon adsorption. However, if it was found that the suspended solids content in the chemically clarified waste was not too high, the filtration step was eliminated.

Two coagulants, alum and ferric chloride, were evaluated. Standard jar tests were conducted to compare their relative efficiencies on the waste and also obtain the optimum dosage for the treatment before carbon adsorption.

Both batch and column studies were conducted for the carbon adsorption. Batch tests were used to evaluate the adsorption rates and capacity at equilibrium. Column studies were operated in two different modes, fixed-bed (downflow) and expanded-bed (upflow), in order to determine if there were differences in the treatment efficiencies and operational difficulties.

Evaluations of the treatment efficiency were based on the reductions of suspended solids, turbidity, organic material, and inorganic nutrients (phosphorus and nitrogen). Careful observations were taken to see if there were any performance difficulties encountered in each stage of treatment.

## II. REVIEW OF LITERATURE

The objective of this literature review was to study previous investigations pertaining to the use of physicochemical processes in the treatment of wastewater. Limited references were available that dealt with the use of physicochemical processes for direct renovation of raw wastewater or primary effluents. However references were available concerning the use of activated carbon adsorption for the treatment of conventional secondary effluents.

The literature presented herein is divided into three areas:

a) feasibility of granular activated carbon adsorption for renovating secondary effluents, b) comparison of packed-bed and expanded-bed activated carbon adsorption systems, and c) direct use of physicochemical treatment systems for renovating primary effluents.

### A. Feasibility of Granular Activated Carbon Adsorption for Renovating Secondary Effluents

Present conventional wastewater treatment methods do not provide for removals of all the soluble organics that are present in raw wastewater. Some wastewaters, even after biological treatment, may still contain as much as 50 to 150 mg/l of organic materials. In an attempt to find a solution to this problem Joyce and Sukenik (2) undertook research studies to establish the feasibility and economics of removing organic matter from secondary effluents by granular activated carbon adsorption in a column operation process. Prior to that study it was already known that activated carbon would adsorb organic matter from wastewater effluents, but it had not been determined if this could be done economically.

Initially Joyce and Sukenik chose an aqueous solution of alkylbenzenesulfonate (ABS) for the first phase of their study. Since they were also interested in studying the regeneration of the spent carbon, they felt that ABS would represent a typical refractory organic which might interfere with the regeneration. It was observed by Joyce and Sukenik that granular activated carbon used in a continuous column operation process was able to reduce ABS in an aqueous solution to negligible amounts. For example, virgin carbon removed ABS from a 10 ppm aqueous solution to a 0.5 ppm breakpoint with a dosage of 0.5 lb per 1,000 gal, at a flow rate of 2.5 gal per min per sq ft of cross-sectional bed area. Subsequent tests made at higher flow rates indicated that carbon dosage was primarily a function of residence time of water within the carbon bed and that a dosage of 0.5 lb per 1,000 gal could be obtained at flow rates as high as 10 gpm/sq ft provided the activated carbon beds were sufficiently deep.

The column utilized by Joyce and Sukenik consisted of 1-in. diameter Pyrex pipe sections. Flange caps were connected to the top and bottom of each section and a piece of 50 mesh stainless steel wire screen, held in place by gaskets, was used to support the carbon bed. Polyethylene tubing was used for connections between columns and from the pumps to the columns.

Joyce and Sukenik went on to study the treatment of secondary effluent containing approximately 50 ppm COD and 5 ppm ABS with granular activated carbon in a countercurrent column operation. The treatment produced effluents having COD values of from 12 to 20 ppm and ABS concentrations well under 0.5 ppm. Based on these results

they estimated the cost of carbon treatment would run from 6 to 8 cents per 1,000 gal of secondary effluents.

It was felt by Joyce and Sukenik that if the unadsorbable COD in the effluent was attributed by soluble organic matter, perhaps an increase in residence time in the carbon column might allow for higher removal. This question led them to another study (3) to determine if an increased contact time in the carbon bed, as effected by a reduction in flow rate, would improve the degree of COD removal. The results indicated that treatment of a secondary effluent with 72 ppm COD and 3.8 ppm ABS in a granular carbon bed of 20 ft deep, at a flow rate of 4 gpm/sq ft reduced the COD to an average of 18.5 ppm and ABS to well below 0.5 ppm. The estimated amount of activated carbon required to accomplish this degree of purification was approximately .75 lb per 1,000 gal of secondary effluent treated. The residual COD level of 18.5 ppm obtained during the second study was no better than the 12 to 20 ppm concentrations obtained in their previous study (2) at a high flow rate of 10 gpm/sq ft at the same bed depth. Filtration tests showed that the residual COD present was not due to suspended matter. They felt perhaps the residual COD was due to some colloidal organics which were difficult to adsorb.

Additional studies consisting of flocculation with alum followed by settling of the secondary effluent, prior to the activated carbon adsorption, increased the adsorption capacity. This resulted in much lower COD residual than those obtained with the unflocculated effluent.

After completion of the above studies Joyce and Sukenik ran a single test using primary wastewater effluent (3). The primary

effluent was passed through a sand filter and then treated in a granular activated carbon bed 20 ft deep. The average concentrations of the contaminants after sand filtration were 5.6 ppm ABS, 236 ppm COD, and 154 ppm BOD. Activated carbon treatment reduced the values to 0.2 ppm ABS, 91 ppm COD, and 67 ppm BOD. Filtration tests showed that a considerable amount of the residual COD present in the carbon column could be accounted for by the suspended solids which passed through the carbon bed.

There are several large scale studies of activated carbon treatment of wastewaters presently being made in the United States. The largest of these studies are at South Lake Tahoe (4) and Pomona (5), California, where packed-bed carbon contacting systems are being utilized. A packed-bed system is also being used in Nassau County, New York (6), where adsorption on granular activated carbon is one of a series of processes being used to treat secondary sewage effluent to produce water of satisfactory quality for recharging ground water aquifers. Additional studies are also being conducted at smaller plants (4).

For over 14 months secondary effluent has been applied directly to a four-stage granular activated carbon adsorption column in Pomona, California (5). There have been a number of significant conclusions resulting from the overall studies:

1. Downflow, backwashable, granular activated carbon adsorbers can remove successfully 10 mg/l of suspended solids found in activated sludge plant effluents.

2. Pretreatment of the secondary effluent not only appears unnecessary but would cost more than the savings which could be credited to it.

3. Removal efficiency of dissolved COD is greater than anticipated, amounting to 55 lb/100 lb of carbon or an average of almost 78 percent dissolved COD removal for one year of operation.

4. Active biological flora established within carbon beds contributes significantly to the total reduction of organic matter by the column.

5. The addition of a readily available organic food supplement to the column feed water increases proportionately the column's denitrification capacity.

6. The total cost of carbon adsorption treatment is estimated at about 8 cents/1,000 gal for a 10-MGD plant.

B. Comparison of Packed-Bed and Expanded-Bed Activated Carbon Adsorption Systems

Packed activated carbon beds are useful for the treatment of liquids that contain little or no suspended solids, and can be expected to operate effectively for extended periods without clogging or excessive pressure loss. However, the presence of suspended solids presents problems in the packed beds because they clog the beds and increase the head loss. Expanded-bed adsorbers offer certain advantages over packed-bed adsorbers for solutions which contain suspended solids; because by passing the solution to be treated upward through the bed of activated carbon the plugging and increasing head loss problems can be eliminated. Through these advantages effective operation is possible; in addition, smaller particle sizes for the activated carbon can be utilized thus increasing adsorption rates.

After extensive laboratory studies to provide the required information to design a pilot plant, Hopkins, Weber, and Bloom (6)



conducted field studies to evaluate the performance of expanded-bed and packed-bed adsorbers. In these studies the two modes of operation were compared in parallel operation using biologically treated secondary sewage effluent from a trickling filter plant. Included in the studies were the secondary effluent without any additional treatment as well as the clarified secondary effluents. Clarification methods applied to the secondary effluent included chemical coagulation, dual media filtration, and the two combined.

The entire study was made using a flow rate of 5 gpm/sq ft. The activated carbon columns were 6-in. or 10-in. in diameter with depths of 12 or 24 ft. Commercial carbon ranging in size from 12 x 40 mesh for the packed-bed to 20 x 40 mesh for the expanded-bed was utilized.

The packed-bed and expanded-bed adsorption columns both gave essentially equivalent effectiveness of removal of the soluble organics present in the effluents. The suspended solids remaining after the pretreatment were partially removed in the packed-bed adsorption columns, but as expected led to clogging and head loss problems. Frequent cleaning of the beds with air agitation and backwashing was required to eliminate the problem. The expanded-bed adsorbers also removed some of the suspended solids, but to a lesser extent than the packed-bed adsorber. The accompanying head loss buildup was eliminated. The suspended solids removed in the expanded-bed adsorber tended to surround the individual particles of carbon in a relatively uniform film. The film had the appearance of biological slime; these films might have functioned to trap some of the smaller suspended solids from the wastewater moving through the beds.

The results of these experiments by Hopkins, Weber, and Bloom (6) indicated that in expanded-bed adsorbers the same degree of organic removal can be provided from secondary sewage effluent as the packed-bed adsorbers can. The expanded-bed adsorbers had less down time, lower operating pressures, and lower cleaning costs. They should provide treatment at a cost several percent below that of packed-bed techniques.

### C. Direct Use of Physicochemical Treatment System for Renovating Primary Effluents

Weber, Hopkins, and Bloom (1) have proposed a new treatment approach for activated carbon adsorption which represents a major divergence from the traditional concept of "tertiary" treatment. They attempted the direct application of physicochemical processes for the treatment of a primary effluent. The processes as developed include chemical coagulation and clarification, filtration, and adsorption on activated carbon.

Initially laboratory studies were performed and the results indicated that high levels of organic removal could be obtained by direct treatment of primary wastewaters with physicochemical processes (1). Due to the success of the laboratory studies a pilot plant for field testing of the physicochemical processes was constructed and operated at a trickling filter plant.

The wastewater from the plant was comprised of approximately 25 percent industrial waste and 75 percent domestic sewage. Average daily flows were 9.0 MGD. Primary effluent was piped by gravity from the primary sedimentation basins to the pilot plant site. The feed rates were closely controlled at 5.5 gpm to the rapid mix chamber.

Upon entering the rapid mix chamber the waste was mixed thoroughly with ferric chloride dosed at 250 mg/l. Rapid mixing for 2 min was followed by flocculation for a period of 15 min. Clarification was carried out in an up-flow clarifier maintaining a 1-hr detention time at the 5.5 gpm flow rate. The chemically clarified waste was then filtered through a dual-media (anthracite coal and sand) gravity filter. Filtered effluent was then fed to a bank of 8 activated carbon columns. The columns were constructed of 10-in. diameter steel pipe coated with epoxy paint. Four of the columns were 9 ft tall and were used for packed-bed operation, the remaining columns were packed to a depth of 12 ft and were used for expanded-bed operation. Each column contained 85 lb of 12 x 40 mesh granular activated carbon, which provided a 6 ft deep bed of settled activated carbon. Constant displacement pumps were used to supply controlled feed streams to the columns. Analytical determinations included TOC, SOC (soluble organic carbon), BOD, suspended solids, turbidity, phosphates, and nitrates.

Their investigations were divided into several phases. The initial phase was a detailed study of the chemical clarification of the waste sample utilizing the standard jar test. The results showed good coagulation of the primary effluent was obtained with an iron dosage of approximately 250 mg/l as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , or with about 250 mg/l of Alum as  $\text{Al}_2\text{O}_3 \cdot 18\text{H}_2\text{O}$ , or with about 300 mg/l of lime. These dosages of coagulant reduced the turbidity of the primary effluent from about 30 to 40 JTU (Jackson Candle Turbidity Unit) to about 1 to 2 JTU. The chemical clarification stage was very effective in removing suspended matter. In addition to providing a high degree of

clarification for the wastewater, this stage also accomplished a very effective removal of phosphorus. Phosphorus was removed from an average value of about 30 mg/l to approximately 2 to 3 mg/l in the clarified water.

Under the second phase of the study, the effectiveness of treating primary effluent by activated carbon alone was evaluated. The third phase was a long term study of complete physicochemical treatment systems (consisting of chemical coagulation, filtration, and adsorption on activated carbon) for renovating the primary effluent. TOC and BOD removals of 95 to 97 percent, respectively, were maintained throughout the study. The effluent produced by the physicochemical process was essentially free of suspended solids and contained 5.0 mg/l or less of TOC and BOD, compared with average TOC and BOD values of about 30 to 35 mg/l for the same wastewater when treated conventionally. Periodic analyses were made for ammonia, organic nitrogen, and nitrate in the product water from the physicochemical system. Neither coagulation nor carbon adsorption affected the concentration of ammonia, which ranged from 20 to 50 mg/l in the primary effluent. The organic nitrogen was reduced by both chemical clarification and carbon adsorption from a concentration of 7 to 10 mg/l in the primary effluent to 2 to 3 mg/l by chemical clarification and to about 1 mg/l by carbon adsorption. The nitrates were affected only slightly by chemical clarification, but were reduced to an average of less than 0.5 mg/l during the adsorption process. Weber *et al.* felt that this observed reduction in nitrate was due to biological activity within the carbon adsorbers.

Based on the results of the study a physicochemical wastewater treatment plant design was suggested by Weber et al. (Figure 1). Preliminary cost estimates, based on published cost figures derived from statistical analyses on actual plants (1), indicated that this high degree of treatment by physicochemical processes could be achieved at a reasonable cost. The cost was estimated to be about 16 cents per 1,000 gal.

Following the work conducted by Weber et al. (1) Zuckerman and Molof (7) reported additional research on the chemical-physical treatment of wastewater. The objective of the Zuckerman and Molof study was to investigate the adsorption rate and capacity of activated carbon for organic material of various molecular size ranges in wastewater.

Zuckerman and Molof proposed a so-called "Z-M" process which was similar to the coagulation-adsorption system described by Rizzo and Schade (8), Hager (9), and Weber et al. (1). The process consisted of the following treatment steps: 1) solids separation by chemical coagulation with lime plus elevation of pH to 11.5; 2) reaction chamber to allow hydrolysis to occur; 3) neutralization of the waste with  $H_2SO_4$  or  $CO_2$ ; 4) sand filtration; and 5) activated carbon adsorption. The most significant difference in the proposed system was that the waste was first raised to a very high pH prior to treatment and maintained there for an extended period of time before further treatment. The objective of raising the pH to 11.5 was to accomplish conversion of high molecular weight organic compounds to low molecular weight ones to enhance their adsorption on activated carbon.

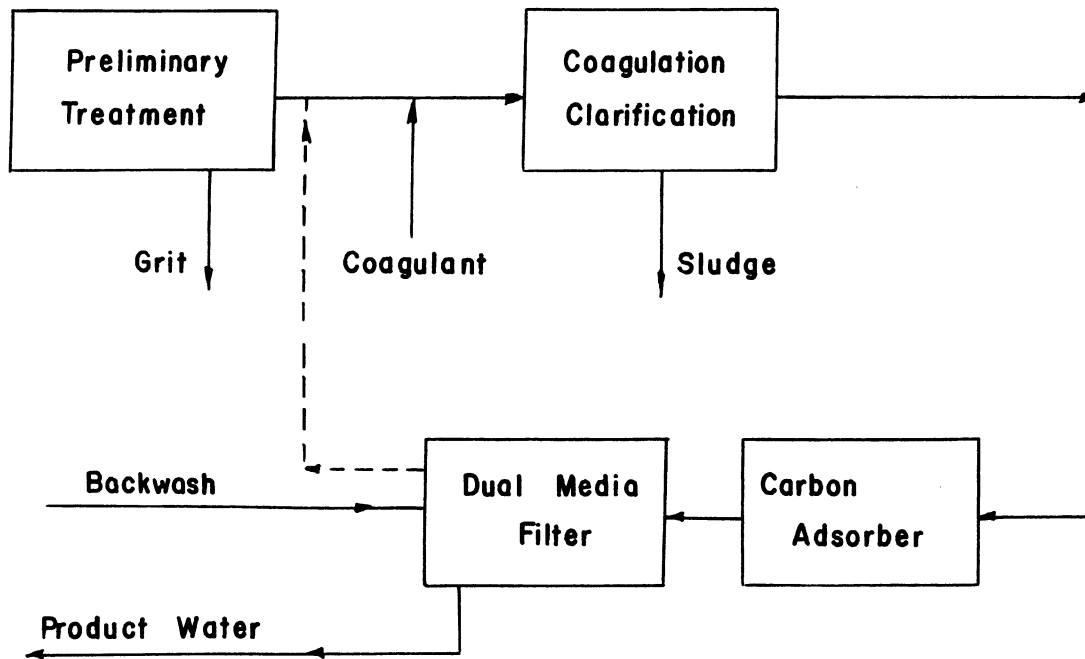


Figure 1. Proposed Clarification-Adsorption Process for Wastewater Treatment  
 [after Weber et al. (1)]

## III. EXPERIMENTAL EQUIPMENT, MATERIALS, AND METHODS

A. Equipment

The laboratory equipment employed during this study are the following pieces of equipment:

1. Carbonaceous Analyzer
2. pH Meter
3. Turbidimeter
4. Walk-In Refrigerator
5. Analytical Balance
6. Drying Oven
7. Multi-Unit Stirrer
8. Stirrer
9. Sigma Motor Pump
10. Jumbo Magnetic Stirrers
11. Wrist Action Shaker
12. Spectrophotometer

A brief description of each of the above is included below.

1. Carbonaceous Analyzer

The carbonaceous analyzer utilized for Total Organic Carbon (TOC) determinations was a Beckman Carbonaceous Analyzer No. 137879, a product of Beckman Instruments, Inc., 2500 Harbor Boulevard, Fullerton, California 92631. (Figure 2).

2. pH Meter

The pH of waste samples was determined by use of a Beckman Zeromatic pH meter, Model 96, as manufactured by Beckman Instruments, Inc., Fullerton, California 92631. (Figure 3).

3. Turbidimeter

Turbidity determinations on waste samples were made using a Hach Laboratory Turbidimeter Model 1860, manufactured by the Hach Chemical Company, Box 907, Ames, Iowa. (Figure 4).

4. Walk-In Refrigerator

A Labline, Model 704, Incubator, a product of Labline Instruments, Inc., 15th and Bloomingdale Avenue, Melrose Park, Illinois 60160,



Figure 2. Carbonaceous Analyzer





Figure 3. pH Meter



Figure 4. Turbidimeter

was utilized for storage of samples prior to analysis. The unit was maintained at 10 degrees Centigrade. (Figure 5).

#### 5. Analytical Balance

A Sartorius Analytical Balance, Model 1503, as distributed by Brinkman Instrument Company, 115 Cutter Mill Road, Great Neck, New York 11020, was used for gravimetric analysis of suspended solids concentration. (Figure 6).

#### 6. Drying Oven

During the determination of suspended solids, samples were dried in a Precision Scientific Company Thelco drying oven, Model 16. (Figure 7).

#### 7. Multi-Unit Stirrer

Standard Jar Tests for coagulation studies were run using a Phipps-Bird Multi-Unit Stirrer as manufactured by Phipps-Bird, Inc., Richmond, Virginia. (Figure 8).

#### 8. Stirrer

Mixing of waste samples in the Polyethylene tank during the carbon adsorption study was accomplished by use of a Fisher Dyna-Mix Stirrer, Model 43, a product of the Fisher Scientific Company, 1241 Ambassador Boulevard, St. Louis, Missouri 63113. The mixer has an adjustable operating range of from 0 to 6,000 rpm. (Figure 9).

#### 9. Sigma Motor Pump

The flow rate for the carbon column adsorption study was controlled by a Sigma Motor Pump, Model T-8, manufactured by Sigma Motor, Middleport, New York. (Figure 10). The pump is operable in ranges of flow from 0 to 125 ml/min. A variable speed reducer contained on the pump unit allows control over flows in this range. Increases in



Figure 5. Walk-In Refrigerator

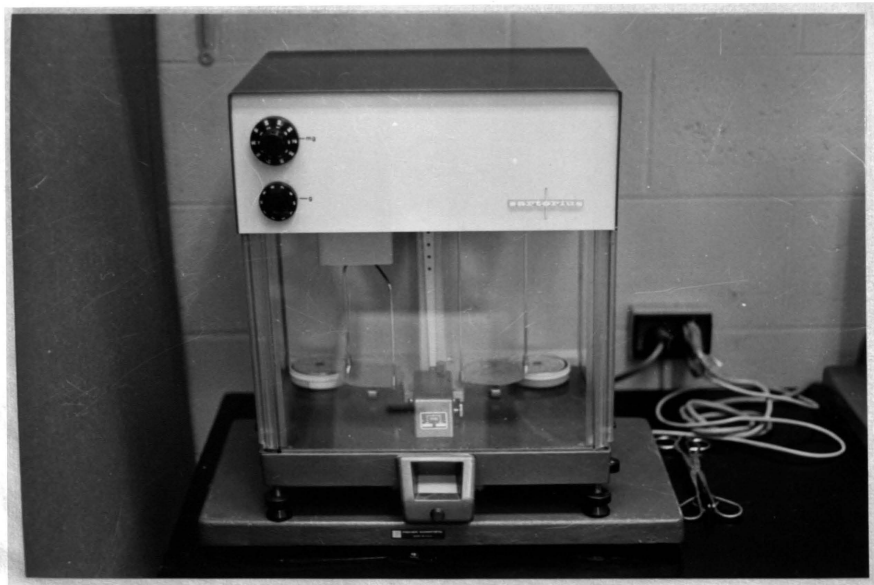


Figure 6. Analytical Balance



Figure 7. Drying Oven

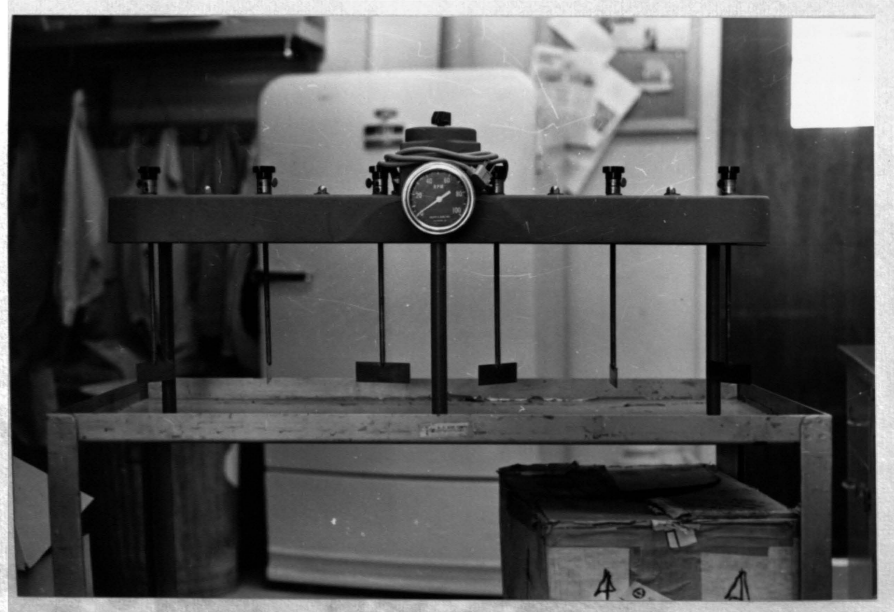


Figure 8. Multi-Unit Stirrer



Figure 9. Stirrer



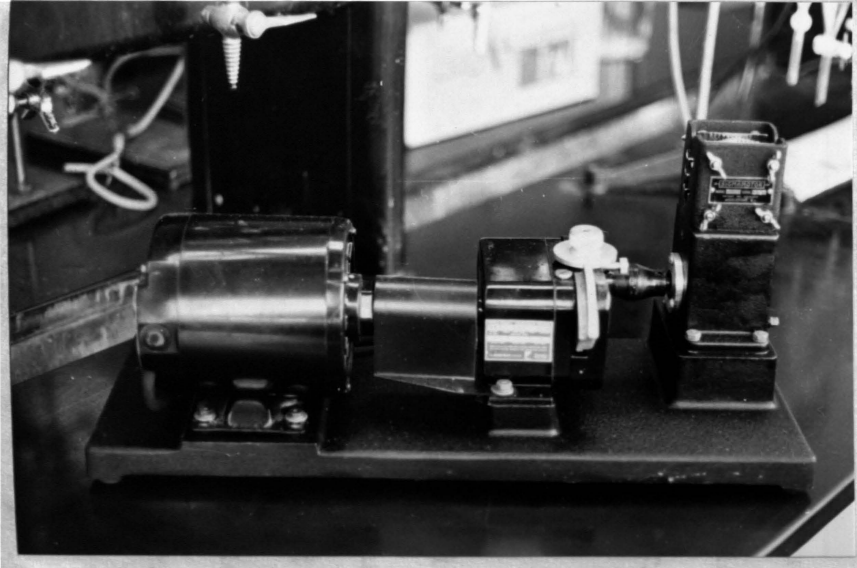


Figure 10. Sigma Motor Pump

flow rate can be obtained through a combination of two or more feed lines in the influent end.

#### 10. Jumbo Magnetic Stirrers

Batch activated carbon adsorption studies for evaluating adsorption rate were undertaken utilizing Jumbo Magnetic Stirrers manufactured by Fisher Scientific Company, 1241 Ambassador Boulevard, St. Louis, Missouri 63113. (Figure 11).

#### 11. Wrist Action Shaker

Batch activated carbon adsorption studies for evaluating adsorption capacity at equilibrium were made using a Wrist Action Shaker, a product of the Burrell Corporation, Pittsburgh, Pennsylvania. (Figure 12).

#### 12. Spectrophotometer

In determinations of total phosphorus and orthophosphate concentrations, a Model 139 UV-VIS Hitachi Perkin Elmer Spectrophotometer was employed to measure the light absorbed and thus determine the phosphorus concentrations present in the samples.

The Hitachi Perkin Elmer Spectrophotometer is an analytical instrument designed for spectroscopic studies of radiant energy emitted at a specific wavelength ranging from the UV to near the IR region. It is manufactured by Hitachi, Ltd., Tokyo, Japan. (Figure 13).

### B. Materials

#### 1. Waste Samples

Two types of industrial waste were employed in this study. One was a high strength industrial chemical waste and the other was a petroleum refinery waste.



Figure 11. Jumbo Magnetic Stirrer

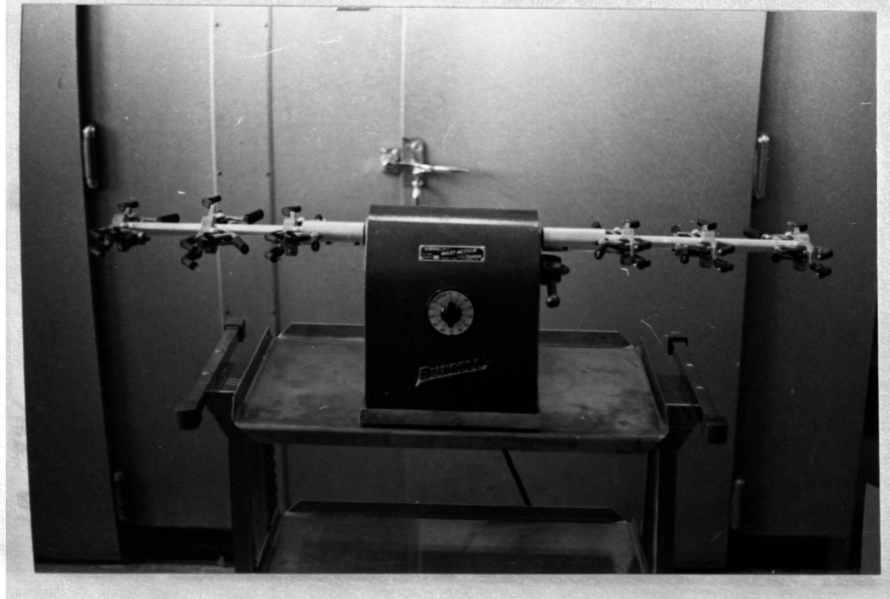


Figure 12. Wrist Action Shaker

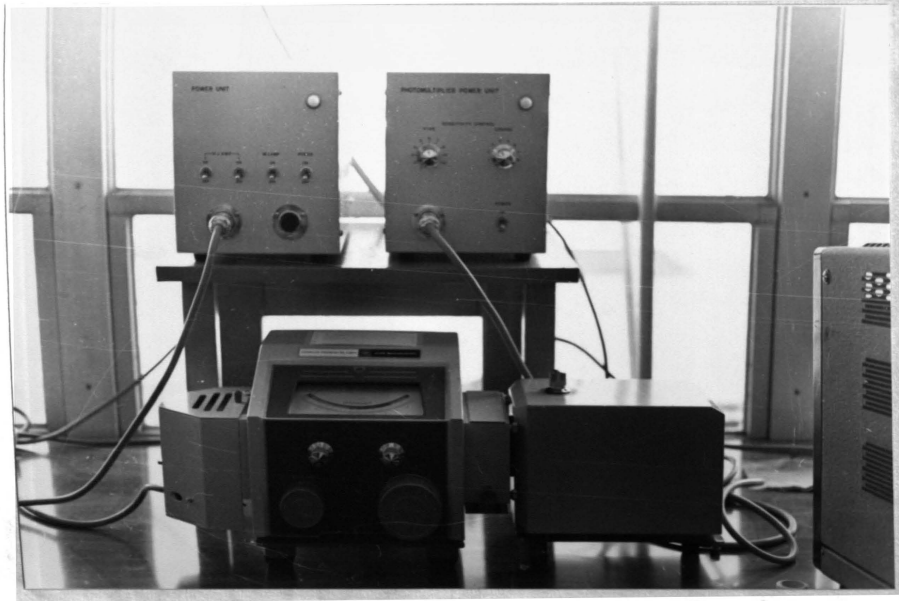


Figure 13. Spectrophotometer

The high strength industrial chemical waste was obtained from a large industrial chemical complex. Composite waste samples were taken from the plant's combined wastewater stream over a two-day period. The waste samples were stored in several 55-gal drums which were epoxy lined to guard against the low pH of the waste.

The refinery waste was obtained from the American Oil Company, Wood River Refinery Plant, Illinois. The samples were also stored in 55-gal drums but without the epoxy linings after being collected from the main sewer line entering the primary API separator basins.

After the samples of each waste were collected, they were shipped back to the laboratory immediately and were stored in the walk-in cooler at 40° F.

## 2. Activated Carbon

The activated carbon selected for this study was Calgon Filtrasorb 400, a product of Calgon Corporation, Pittsburgh, Pennsylvania. The activated carbon was in granular form and has a mesh size ranging between 12 and 40.

## C. Methods

### 1. Waste Characterization

Waste characterizations were performed as the first step of this investigation to obtain information regarding the general characteristics of the waste samples and to establish a required treatment scheme using physicochemical processes. The determinations that were made in characterizing the samples were chemical oxygen demand (COD), total organic carbon (TOC), total phosphorus and orthophosphate, total and ammonia nitrogen, suspended solids, turbidity, and pH. Analytical methods utilized for the above determinations were as

follows:

a. Chemical Oxygen Demand

The chemical oxygen demand test was employed to provide a measurement of the organic strength present in the original wastewater and also in the effluent obtained after the activated carbon adsorption treatment. COD is determined by measuring the amount of chemical oxygen required to convert the organic matter present in the sample to carbon dioxide and water.

The COD apparatus consisted of 11 reflux assemblies, each consisting of a 300 ml round bottom flask with a ground glass neck attached to a reflux condenser. (Figure 14).

The dichromate reflux method as outlined in Standard Methods (10, p.510) was used for the determination. A mixture containing .4 g mercuric sulfate, 10.0 ml .250N potassium dichromate, 20.0 ml sample, 30 ml sulfuric acid with silver sulfate added, and a number of glass beads was refluxed for a period of 2 hr. It was then cooled and diluted to approximately 140 ml with distilled water. The remaining potassium dichromate was then titrated with .10N ferrous ammonia sulfate using a ferroin indicator. A reagent blank containing distilled water in place of the sample was also run.

b. Total Organic Carbon

Total organic carbon determinations were made using the Beckman Carbonaceous Analyzer No. 137879 following the procedures outlined in the Beckman Instruments Bulletin No. 7000-17. The procedure generally incorporates the following steps: an appropriate volume of thoroughly mixed sample was acidified with concentrated hydrochloric acid to a pH of around 2. After acidification



Figure 14. Chemical Oxygen Demand (COD) Reflux Apparatus



pure CO<sub>2</sub>-free nitrogen gas was bubbled through the sample for a minimum of 5 min to strip off all dissolved CO<sub>2</sub> gas. Upon acidification and purging with nitrogen gas a 20 ul sample was injected into the combustion tube of the carbonaceous analyzer. The carbon content of the sample was determined by the measurement of the resultant peak which was observed on the recorder chart. A standard calibration curve was made with acetic acid to determine the carbon content of the sample from the peak indicated on the recorder chart.

c. Suspended Solids

Suspended solids were measured by the procedure outlined in Standard Methods (10, p.245) for filterable residue. The filtering apparatus used for this determination consisted of a Gooch crucible, 30 ml capacity, fiber glass filter pad, filter flask, and a rubber hose. A single fiber glass filter was placed in the Gooch crucible, dried for 1 hr at 103° C, cooled in a desiccator, and weighed. A suitable sample volume was taken by means of a pipet and filtered under suction. The crucible was then dried for 1 hr at 103° C, cooled in a desiccator, and weighed. The increase in weight represented the suspended solids present in the sample.

d. Phosphorus Determinations

Both total phosphorus and orthophosphate determinations were measured by the procedure introduced by Jankovic, Mitchell, and Buzzel, Jr. (11). The determinations were used to measure the concentration of phosphorus present in the original industrial wastes, and to determine the amount removed by the chemical coagulation and clarification, and also carbon adsorption.

An appropriate volume of sample, approximately 50 ml, plus 8 ml of a mixed reagent were placed into a 50 ml Nessler tube. The mixed reagent consisted of mixing thoroughly 125 ml of 5N H<sub>2</sub>SO<sub>4</sub> and 37.5 ml of ascorbic acid solution and 12.5 ml of potassium antimonyl tartrate solution. The mixed reagent was prepared newly for each day's determinations in the proper amount required. After placing the sample and mixed reagent in the 50 ml Nessler tubes and shaking the contents, the tubes were allowed to stand for a minimum of 10 min to allow color development. After color development the samples were observed using a Perkin Elmer spectrophotometer at 710 mμ. Phosphorus contents were determined by comparing the light absorption against a calibration curve prepared using standard phosphate solutions.

Total phosphorus determinations followed the same procedure as those for orthophosphate except that the determinations were preceded by the following steps: Ten ml of sample were placed in a 125 ml Erlenmeyer flask. Added to the sample was 2.0 ml of 5N H<sub>2</sub>SO<sub>4</sub> and 1.0 g of potassium persulfate. This solution was then diluted with 30 ml of distilled water and refluxed for 15 min. It was then cooled and diluted to 500 ml with distilled water. The steps for the orthophosphate test were then repeated.

e. Nitrogen Determinations

The nitrogen determinations were used to determine the concentrations of nitrogen, both ammonia and total kjeldahl, present in the original waste sample and those remaining after chemical coagulation and clarification, and carbon adsorption treatment. The procedures utilized were those outlined in Standard Methods for ammonia and total organic nitrogen (10, p.187).

In the ammonia nitrogen determinations an appropriate volume of sample was placed in an 800 ml kjeldahl flask. The pH of the sample was neutralized to 7.0. Then .25 ml of .5M phosphate buffer solution was added to the sample. The addition of the buffer solution was to enable the pH of the sample to remain at 7.0 during the subsequent distillation process. The sample was then diluted to 400 ml with ammonia-free water. After dilution the sample was distilled. The distillate obtained from the sample (approximately 200 ml) was collected in a 250 ml flask which contained 50 ml of indicating boric acid solution,  $H_3BO_3$ . Upon collection of the distillate it was back titrated with standard sulfuric acid titrant to determine the amount of ammonia nitrogen present. The calculation is shown below:

$$\text{mg/l ammonia nitrogen} = \frac{\text{ml } H_2SO_4 \text{ titrant} \times .28 \times 1,000}{\text{ml of sample}}$$

Total kjeldahl nitrogen determinations utilized the residue from the ammonia nitrogen determinations. To this residue was added 50 ml of sulfuric acid-mercuric sulfate-potassium sulfate solution. This mixture was then digested for 20 to 30 min, after which the solution would become clear in color. This solution was then cooled and 300 ml of ammonia-free water was added. Sodium hydroxide-sodium thiosulfate, using phenolphthalein as an indicator, was then added until the solution became alkaline. The remaining procedure paralleled that for the determination of ammonia nitrogen. The amount of organic nitrogen present is calculated as follows:

$$\text{mg/l organic N} = \frac{(A-B) (280)}{C}$$

where A = ml  $H_2SO_4$  used for sample

B = ml  $H_2SO_4$  used for blank

C = ml sample

## 2. Establishment of Treatment Scheme

After the waste characterization study was completed, a careful establishment of a treatment scheme for each industrial waste was attempted. The physicochemical treatment processes considered initially in this study generally consisted of a three stage treatment, chemical coagulation and clarification, filtration, and activated carbon adsorption. Due to the low level of suspended solids present in the original chemical waste and in the chemically clarified petroleum refinery waste, the filtration step was eliminated. The resulting physicochemical treatment processes utilized in the study consisted of chemical coagulation and clarification and activated carbon adsorption.

### a. Chemical Coagulation and Clarification

A chemical coagulation and clarification study was undertaken to evaluate the relative coagulation efficiencies between the use of alum  $Al_2(SO_4)_3 \cdot 18H_2O$  and ferric chloride as coagulants. The general purpose of the chemical coagulation was to remove suspended solids, turbidity, color, and taste and odor producing substances. Orthophosphate removal has also been reported with chemical coagulation.

The procedure utilized for the coagulation study was that used for the standard jar test. To start the test, 600 ml of waste sample was placed in each of 6 one-l beakers. The beakers were then placed under a multi-unit stirrer. A desired amount of coagulant prepared in solution form with 2 percent strength was added to each sample while it was being stirred vigorously. The sample with the coagulant

dose added was then flash mixed for 10 sec at 100 rpm. After flash mixing the samples were flocculated for between 20 and 30 min at 35 rpm and then allowed to settle for 1 hr. After settling, the clarified supernatant was siphoned off into a clean container for analysis. Analysis of each sample included pH, turbidity, and suspended solids. The removals of COD, TOC, phosphorus, and nitrogen by coagulation at the optimum dosage were also determined.

Coagulation and clarification of the waste samples prior to activated carbon adsorption was done in a 20 l Pyrex glass bottle using the optimum dosage of coagulant as determined in the jar test. The sample plus coagulant was flash mixed for 4 min, flocculated for 15 min, and allowed to settle for 1 hr. After settling, the supernatant was drawn off and used for influent to the activated carbon adsorption columns.

b. Carbon Adsorption Studies

Both batch and column activated carbon adsorption studies were employed in this study. The batch studies were undertaken because they are relatively easy to operate in the laboratory, and they provide basic information which is of value in predicting column operation, and in explaining column performance data. Column operations received more attention in this study because it is felt that, in future full scale field installations, column type operations will be most likely preferred than the batch process. Column operation offers the advantages of not requiring subsequent carbon separation, higher removals in equilibrium with the influent concentrations rather than the effluent concentrations, plus a greater flexibility of operation.

### Batch Studies

Batch studies were conducted on the two wastes to evaluate the adsorption rate and capacity by activated carbon. The studies were divided into two segments, rate uptake and equilibrium studies. The rate uptake study was performed in several 4-l widemouth Pyrex bottles arranged on magnetic stirrers in order to provide complete mixing of the test solutions. The bottles were placed on wooden support blocks on the stirrers. This enabled air to circulate freely around the bottles during the runs and reduce any heat build-up caused by the stirrers. A small fan provided a constant flow of air to dissipate all the heat generated. Samples were taken at the following time intervals: 5, 15, 30 min and 1, 2, 3, 5, 8 hr, and went on as necessary until equilibrium was reached. Samples were taken generally at 3-hr intervals after the first 5-hr time period had been reached.

The equilibrium studies were performed using a series of 250 ml flasks. To each flask was added 150 ml of waste sample, either clarified refinery waste or the original chemical waste, and a varied amount of carbon. The flasks were agitated by a wrist action shaker for a sufficient period of time (as determined in the rate study) in order to allow the adsorption reaction to reach equilibrium. After equilibrium was reached, the COD of all the samples was determined.

### Column Studies

Several activated carbon adsorption columns were constructed for this study. Each consisted of a 4-ft section of acrylic plexiglas tube; a typical column is shown schematically in Figure 15. The column was 1-3/4 in. outside diameter and 1-1/2 in. inside diameter. Each contained 13 sampling ports, which were spaced at 3-in. intervals

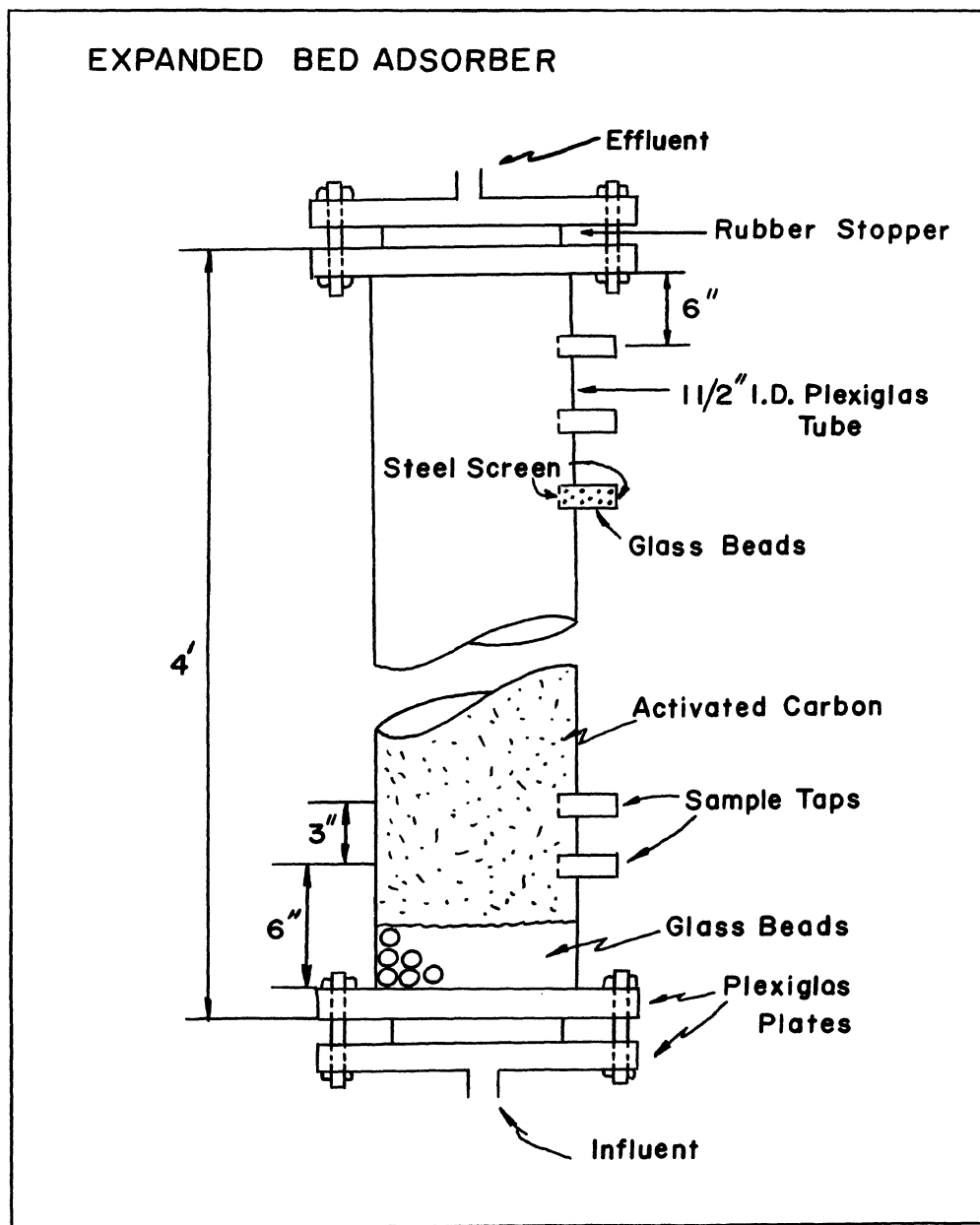


Figure 15. Schematic Diagram of the Adsorption Column

beginning 6-in. from the top and ending 6-in. from the bottom. Each sampling port consisted of a 2-in. section of 1/4 in. diameter acrylic plexiglas tap which was packed with 1 mm glass beads and closed off at both ends with a small piece of stainless steel screening to minimize carbon losses during sampling periods. The taps were also inserted 1/4 in. into the plexiglas column to eliminate the possibility of "picking up" the short circuiting fluid which might occur by sliding down along the inner wall of the column. A 3-in. latex rubber tubing was placed over the exposed end of the sampling tap and was clamped off with a pinch clamp when samples were not being taken. Rubber stoppers were used to seal the ends of the columns. To enable the stoppers to remain firmly seated during column operation and subsequent pressure build-up, two acrylic plexiglas plates were bolted at each end of the column to secure the stoppers in place. Samples were obtained from the sampling ports periodically as scheduled until the columns had been exhausted in their adsorption capacity.



#### IV. RESULTS AND DISCUSSION

The feasibility of using physicochemical processes on the two selected industrial wastes was carefully examined during this research. The experimental data obtained are presented below.

##### A. High Strength Acidic Chemical Waste

###### 1. Waste Characterization

After three drums of the chemical waste sample were obtained from the industrial plant and brought back to the laboratory, the first step was to carry out the waste characterization study to determine the make-up of the chemical waste being studied. There was no attempt made to identify each individual chemical component in the waste. However, the general characteristics of the waste as determined are shown in Table 1.

As shown in Table 1 the characteristics of the chemical waste varied from drum to drum to some extent. This variation was probably due to a shift in the industrial operations which took place during the two day sampling period. In general the waste was highly acidic in nature, with a pH ranging from 2.1 to 3.2. The organic strength of the waste was very high, with the chemical oxygen demand (COD) levels being between 2300 and 3270 mg/l. Ninety-seven percent of this high organic strength, measured by COD, proved to be soluble in nature. There were no significant quantities of suspended solids present in the waste, but turbidity showed values of between 13 and 33 Jackson Turbidity Units (JTU). Although not shown in the table, the waste appeared to have a claret wine color except for the third drum which had a golden color. The high strength industrial waste contained only relatively small amounts of inorganic nutrients such

TABLE 1. Major Characteristics of the Chemical Waste

Characteristics	Drum Number		
	1	2	3
pH	3.2	2.4	2.1
COD (mg/l)	3100	2300	3270
Soluble COD (mg/l)	3000	2220	3140
SS (mg/l)	0.128	0.084	0.076
Turbidity (JTU)	33	13	15
Phosphorus (mg/l as P)			
Total	6.5	2.5	2.0
Ortho	1.05	1.25	0.85
Nitrogen (mg/l as N)			
Total	1.22	0.89	0.58
Ammonia	1.12	0.19	0.38

as phosphorus and nitrogen. If the waste were to be treated by biological processes, significant quantities of phosphorus and nitrogen would have to be supplemented in order to satisfy the needs of the microorganisms.

## 2. Coagulation and Clarification

Due to the extremely low level of suspended solids, ranging from .076 to .128 mg/l, chemical coagulation and clarification were deemed unnecessary prior to activated carbon adsorption.

## 3. Activated Carbon Adsorption

Both batch and column activated carbon adsorption studies were employed in this investigation. The batch studies were undertaken because they are relatively easy to perform in the laboratory, and yet they provide basic information which is of value in predicting column operation and in explaining column performance data. Column operations received more attention during this study because it is felt that future full scale field installations will most likely be of the column type rather than the batch type process. Column operations offer the advantages of not requiring subsequent carbon separation steps, higher removals in equilibrium with the influent concentration rather than the effluent concentration, plus a greater flexibility of operation.

### a. Batch Studies

Batch studies were conducted on the waste to evaluate the adsorption rate and capacity of the waste on activated carbon. The studies were divided into two segments, i.e. rate of uptake and equilibrium studies.

The uptake rate studies were performed in several 4-l widemouth Pyrex bottles arranged with magnetic stirrers in order to provide complete mixing for the test solutions. The bottles were placed on wooden blocks which were placed on the magnetic stirrers. The use of the wooden blocks enabled air to circulate freely under the Pyrex bottles during the test runs and reduce any heat build-up caused by the stirrers. A small fan provided a constant flow of air to dissipate all the heat generated.

For each test, 3 l of the chemical waste was placed into each bottle, to which was then added an appropriate, accurately weighed amount of activated carbon. The test solutions were constantly stirred and samples of about 50 ml were taken at frequent intervals until determinations of COD indicated an equilibrium state had been reached.

The rate of COD removal from the chemical waste in the batch system is shown in Figure 16. At the activated carbon dosages of 0.5 and 5.0 g/l, the rates of uptake were about the same and states of equilibrium were essentially reached within a period of 12 hr. It was observed during the test that removal of COD was generally accompanied by corresponding degrees of color removal from the waste.

#### b. Equilibrium Studies

Equilibrium studies were performed using a series of 250-ml flasks. To each 250-ml flask was added 150 ml of waste and a varied amount of activated carbon. The flasks were agitated by use of a wrist action shaker for a sufficient period of time (as determined in the rate study) in order to allow the adsorption reaction to

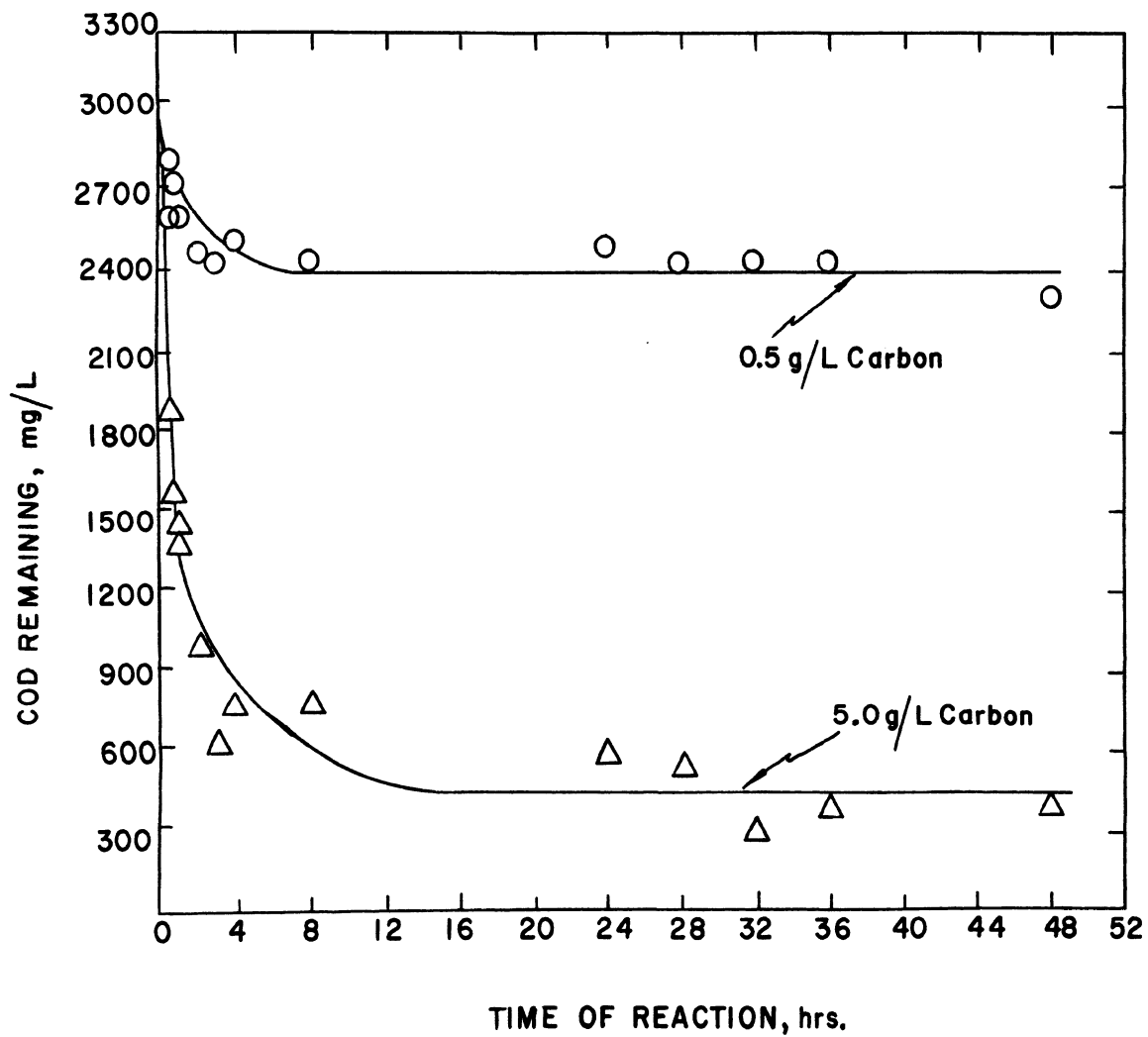


Figure 16. Rate of COD Removal from the Chemical Waste

reach equilibrium. Table 2 shows the data obtained from the equilibrium study of the chemical waste.

Three separate equilibrium tests were conducted. The first test was performed with the original chemical waste without any initial pH adjustment; the second test was made on the waste with the initial pH adjusted to 7.0 while the third test was made with the pH adjusted to 11.4. These tests were designed to determine if the initial pH adjustment provided for the acidic chemical waste would result in any change in the COD removal efficiency. A reaction period of 40 hr was allowed for each equilibrium test in order to ensure that the equilibrium state was reached before the test was terminated.

In tests No. 1 and No. 2 of Table 2, a higher carbon dosage appeared to result in a greater increase in the pH of the test solution after the adsorption equilibrium was reached. However, the pH increase in test No. 3, which had an initial pH of 11.4, was not significant; presumably the initial pH of the test solution was too high to be raised by the carbon.

Perhaps the best way to evaluate the relative COD removal efficiencies of the three test systems of Table 2 at the equilibrium state is to compare their adsorption isotherms. As will be seen in Figure 17, the equilibrium data of each system conform fairly well to the Freundlich adsorption isotherm, which has

$$x/m = KC^{1/n} \quad (1)$$

in which  $x$  = the amount of COD removed at an equilibrium state,  $m$  = weight of carbon,  $C$  = concentration of COD remaining at an equilibrium state, and  $K$  and  $n$  = experimental constants for the

TABLE 2. Equilibrium Adsorption of the Chemical Waste  
with Various Initial pH Adjustments

Carbon Dosages g/l	Test No. 1*		Test No. 2**		Test No. 3***	
	pH	COD, mg/l	pH	COD, mg/l	pH	COD, mg/l
0	3.2	3270	7.0	3270	11.4	3270
0.25	3.2	2960	8.0	2890	11.5	2850
0.75	4.0	2580	8.0	2580	11.5	2510
2.5	4.0	1710	8.6	2080	11.6	2080
10	4.2	456	8.4	1050	11.6	836
30	6.1	304	10.0	341	11.5	304
70	7.2	304	9.7	190	11.4	268

\*No initial pH adjustment; initial pH - 3.2

\*\*Initial pH adjusted to 7.0

\*\*\*Initial pH adjusted to 11.4

Freundlich adsorption isotherm. The Freundlich isotherm shown in Equation (1) can be rewritten

$$\log x/m = \log K + 1/n \log C \quad (2)$$

If the adsorption relationship conforms to the Freundlich model, the plot of  $x/m$  versus  $C$  on log-log paper should be linearized. As the experimental data shown in Table 2 can be fitted fairly well (Figure 17) into a straightline relationship of Equation (2), the equilibrium removals of COD from the chemical waste at various initial pH levels are in reasonable accord with the Freundlich isotherm. From Figure 17, if equilibrium COD levels were below 1600 mg/l, generally more COD was removed per unit weight of activated carbon from the original acidic chemical waste than from the neutralized and alkalized wastes. These findings are not in agreement with the data reported by Zuckerman and Molof (7) who indicated that chemical hydrolysis of sewage organic molecules at pH of 11.4 or above would result in a more effective organic removal by activated carbon adsorption. Perhaps the organic molecules which were present in this industrial waste sample were completely different in nature from those which are commonly found in domestic wastewater and therefore could not be hydrolyzed at the pH of 11.4.

### c. Column Studies

Two different modes of operation were employed during the columnar carbon adsorption studies, fixed-bed (or downflow pumping) and expanded-bed or fluidized-bed (upflow pumping). The use of parallel modes of operation allowed comparison of the treatment efficiencies and performance characteristics between the two methods of carbon adsorption.



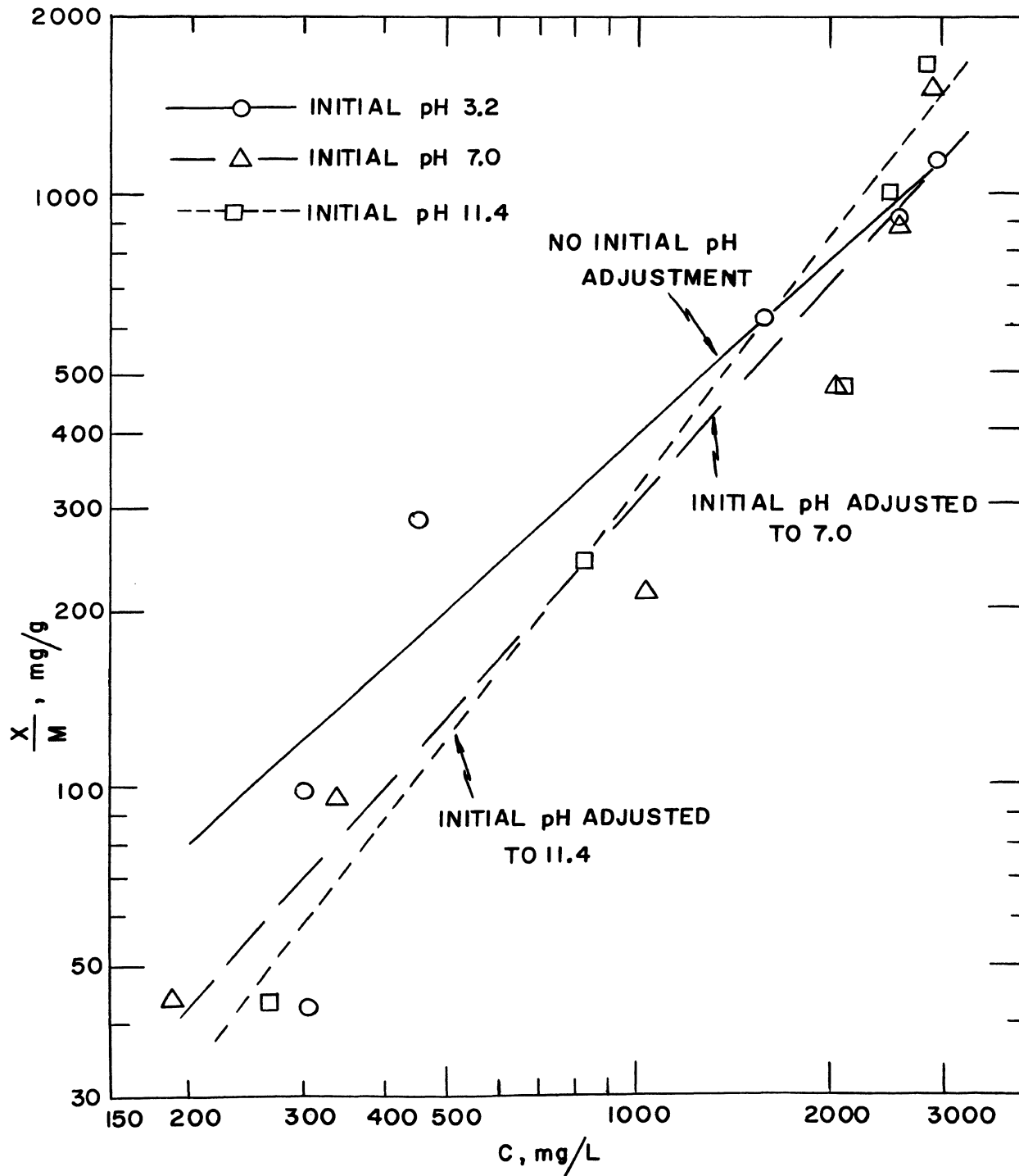


Figure 17. Freundlich Adsorption Isotherm for the Chemical Waste with Various pH Adjustments

The waste samples used during the column studies were stored in a 15 gal polyethylene tank in which a stirrer was attached to provide constant mixing of the sample throughout the test run. The chemical waste samples used were evenly blended waste mixtures from the three drums shown in Table 1. A flow rate of 2 gpm/sq ft was used throughout the study for each activated carbon column. This was equivalent to a pumping rate of 116 ml/min through the 1-1/2 in. ID carbon columns.

The COD remaining in the wastewater samples from the different taps as well as from the column effluent of the fixed-bed adsorber are presented in Figure 18 as functions of the waste volume treated. The uppermost trace in this figure represents the COD remaining in the samples taken from the tap located 6-in. below the carbon bed surface. After approximately 7 l of the waste had been passed through the adsorber the COD in the 6-in. tap effluent increased sharply, which was a sign of the COD breakthrough at that tap. When the treated volume was increased to 20 l, the COD breakthroughs were found in the 12- and 18-in. tap effluents. The last two taps at 24- and 30-in. showed only a slight, if any, COD increase when approximately 60 l of the waste was pumped through. Although in this adsorber the COD breakthrough occurred relatively fast, the complete exhaustion of the carbon within the adsorber, i.e., the effluent having the same COD as the influent, was not found until approximately 170 l of the waste had been passed through the columns.

It is difficult to understand why the column effluent very often had higher COD levels than the corresponding 30-in. tap effluent, which was taken at a point 6-in. above the bottom of the carbon adsorber. One possible reason could be that some influent waste fluid

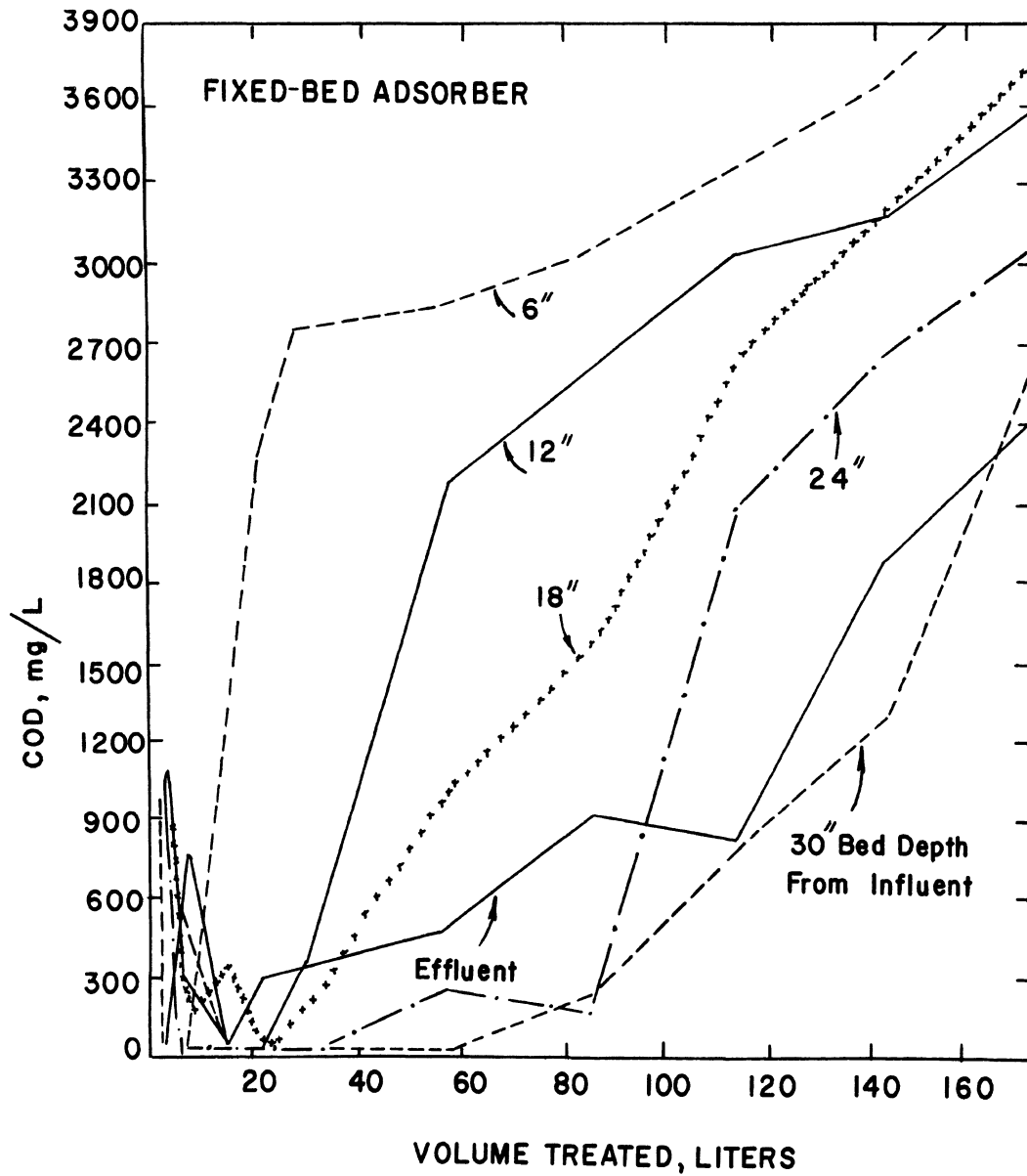


Figure 18. COD Remaining at Different Depths and in the Effluent of the Fixed-Bed Adsorber

might "slip" down directly along the immediate inner wall of the plexi-glas tube and reach the effluent without having much contact with the activated carbon; this phenomenon is commonly referred to as "short circuiting." Since each sample tap was inserted 1/4-in. into the main column, the "pick up" of the short circuiting influent fluid during sampling would seem to have been unlikely.

Similar to Figure 18, a plot for the expanded-bed adsorber is shown in Figure 19. In this figure the COD breakthrough for the 6-in. tap occurred within a very short period of operation, while for the other taps 20 to 30 l of wastewater was needed before sharp increases of COD were observed. As in the fixed-bed operation, continuous COD elutions from all sampling taps were relatively slow even after the breakthroughs seemed to have occurred; approximately 160 l of wastewater was needed to completely exhaust the adsorber.

In order to compare the relative treatment efficiencies between the fixed-bed and expanded-bed adsorbers, the COD remaining in the 18- and 30-in. tap effluents as functions of the treated volume of waste are contrasted in Figure 20. From this figure it becomes apparent that the COD removal efficiencies were not significantly different in the 18-in. taps of the two adsorbers. However, at the 30-in. taps, the fixed-bed adsorber was able to produce superior effluents over the expanded-bed adsorber.

A further comparison of treatment efficiencies can be made on the two adsorbers by plotting the cumulative amount of COD removed in each adsorber to any depth within the column after the adsorber was completely exhausted versus the corresponding cumulative weight of the carbon contained in the bed, as shown in Figure 21. From this

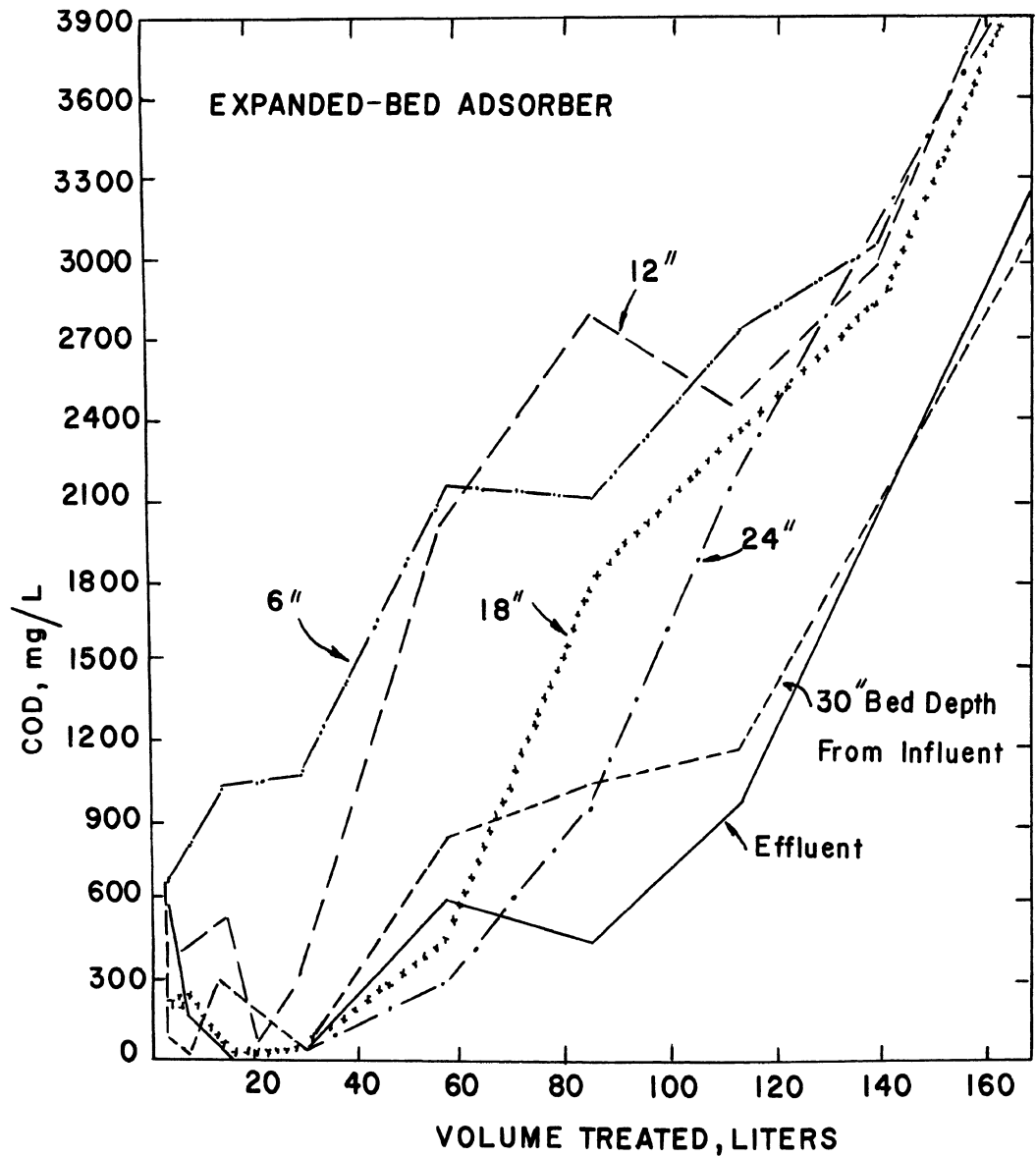


Figure 19. COD Remaining at Different Depths and in the Effluent of the Expanded-Bed Adsorber

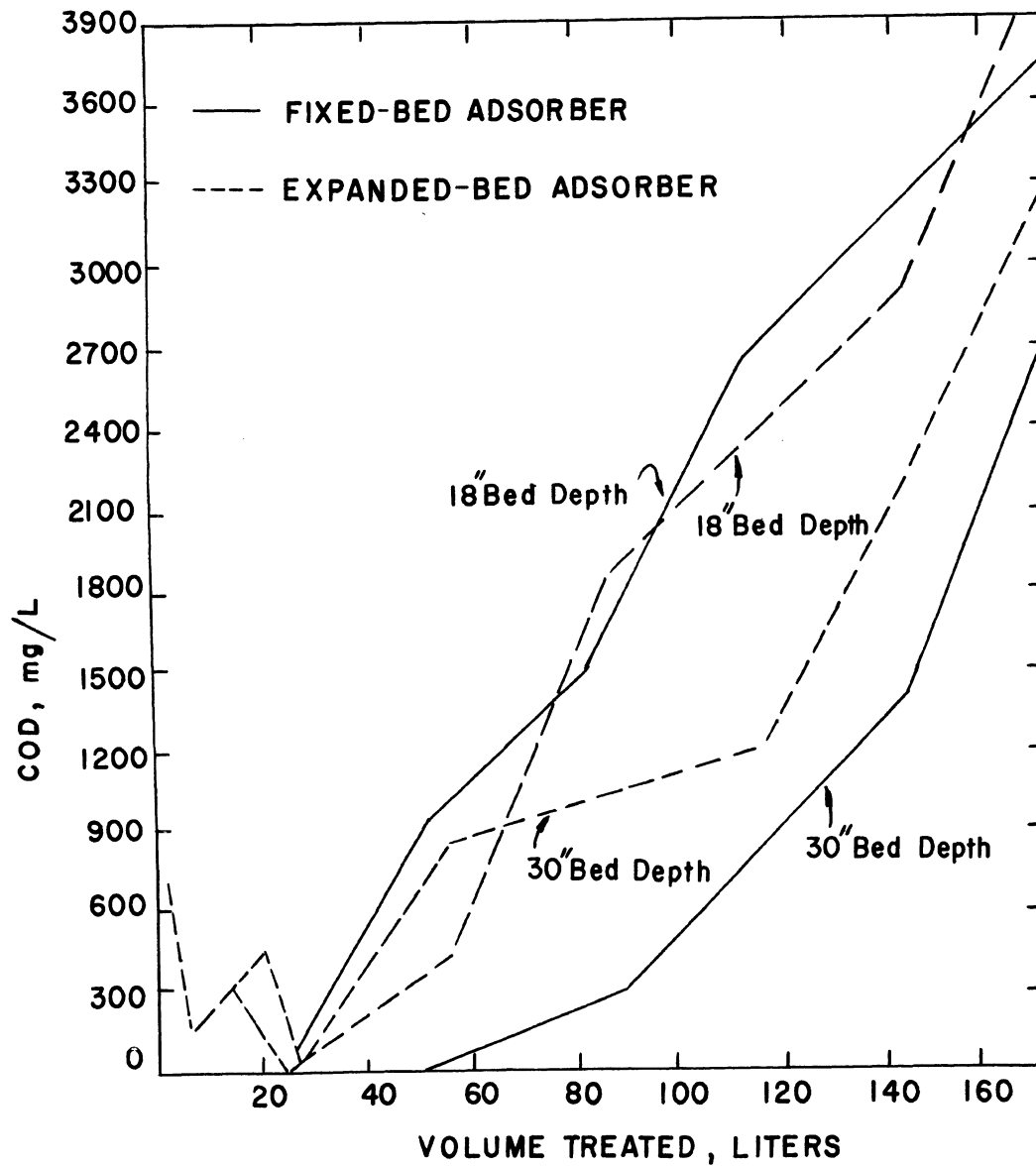


Figure 20. Comparison of COD Removals Between Fixed-Bed and Expanded-Bed Adsorbers

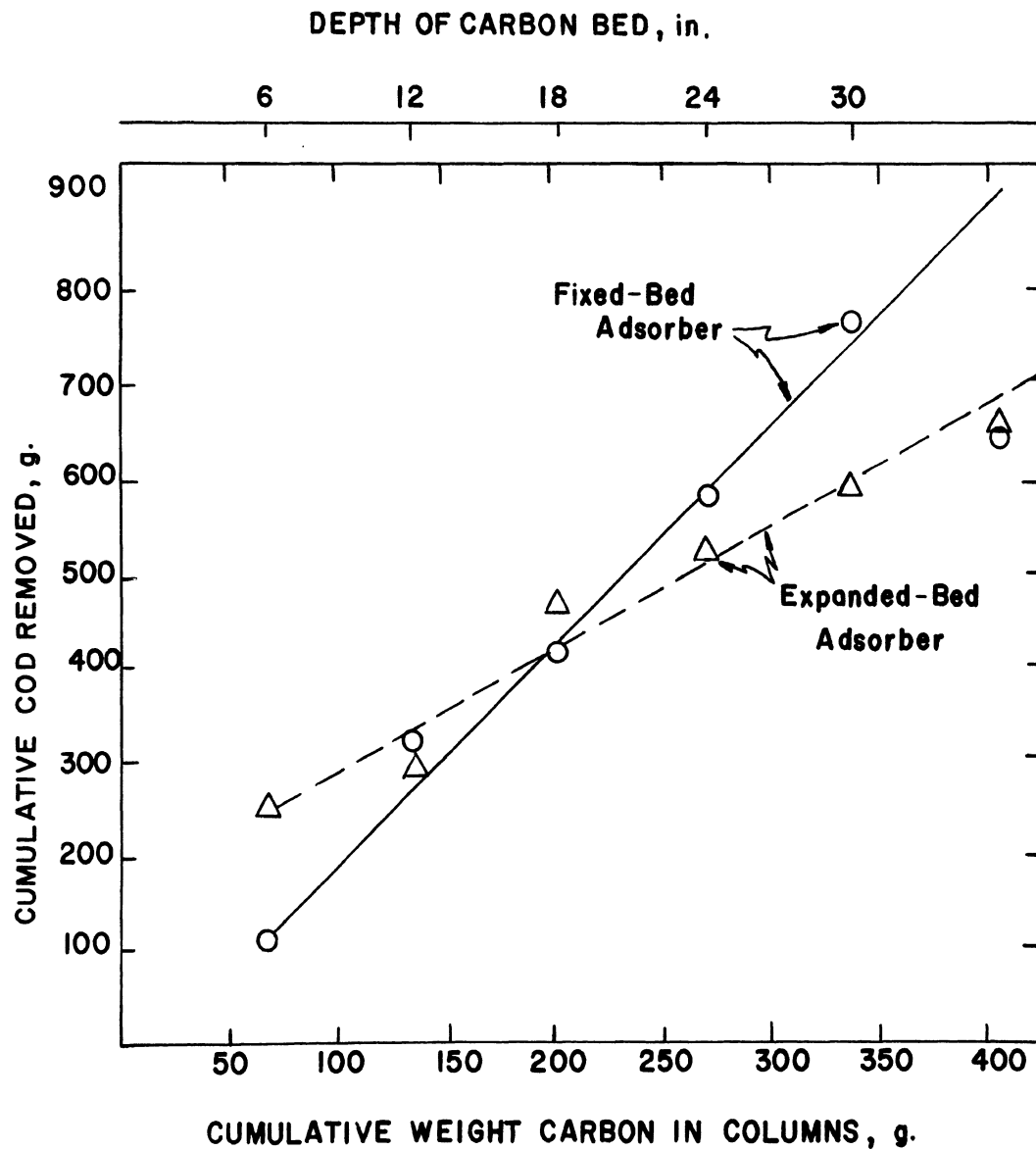


Figure 21. Cumulative COD Removals Between Fixed-Bed and Expanded-Bed Adsorbers

figure, at a bed depth of shorter than 18-in. the cumulative COD removal was smaller in the fixed-bed than in the expanded-bed adsorber. When the bed depth was longer than 18-in., the reverse was true. At a depth of 18-in. there was no substantial differences in the cumulative COD removal between the two adsorbers. Of course, the observation is still preliminary and is only expressed for this particular chemical waste and carbon adsorber. The findings should not be considered as a generality.

The COD profiles of the two adsorbers as functions of the waste volume treated are shown in Figures 22 and 23. The profiles give some indication regarding the degree of the carbon exhaustion which had been attained at any bed depth and at any moment of treatment. In general, for the first 80 l of wastewater treated, the COD profiles of the fixed-bed adsorber were steeper than those of the expanded-bed. This implies that a better effluent quality would be expected from the fixed-bed adsorber.

The turbidity of the effluents from the two adsorbers was constantly monitored throughout the test and the results are shown in Figure 24. The average turbidity present in the influent wastewater was approximately 20 JTU. As shown in the figure, the fixed-bed adsorber continuously yielded effluents of lower turbidity than the expanded-bed adsorber, which often produced an effluent having turbidity even greater than the influent value, 20 JTU. This was because some of the suspended solids which were first trapped within the carbon adsorber could suddenly be flushed out from the column by the upward hydraulic action. In interpreting the turbidity data, however, it is significant to note that before the COD breakthroughs



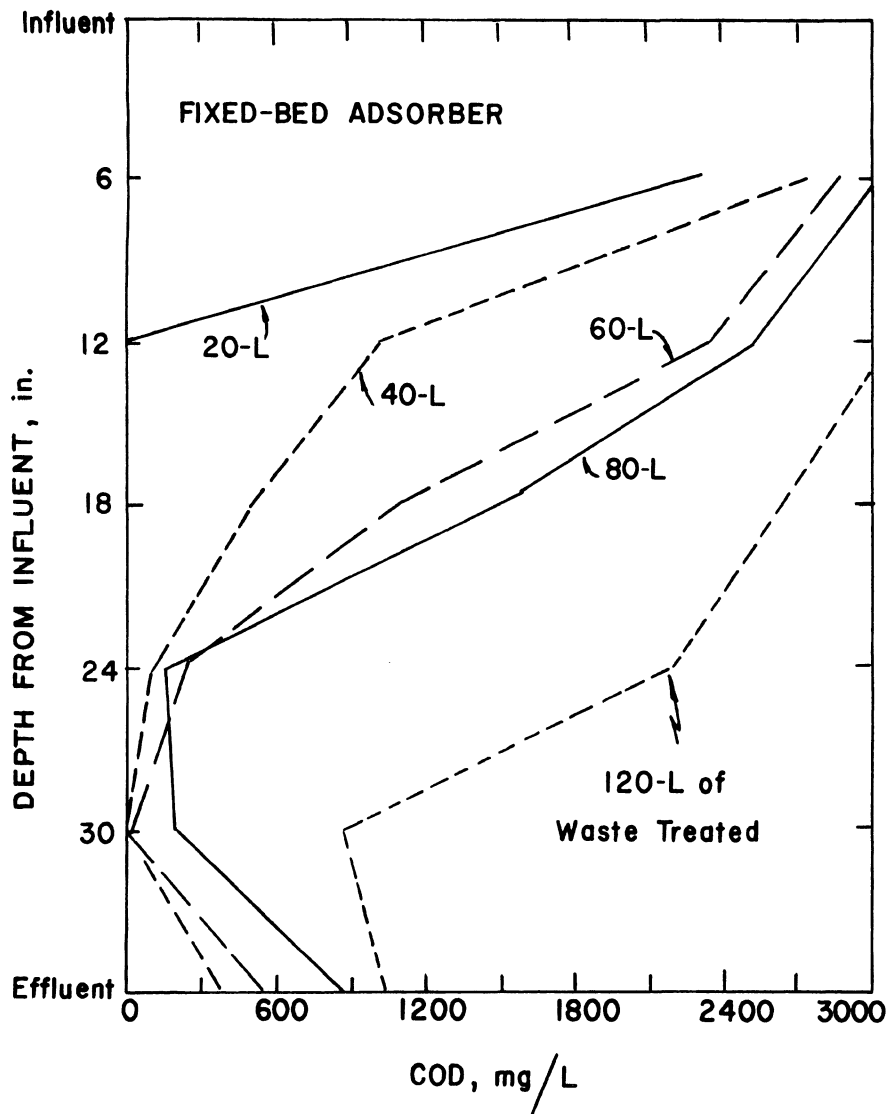


Figure 22. Profile of COD Remaining in Fixed-Bed Adsorber

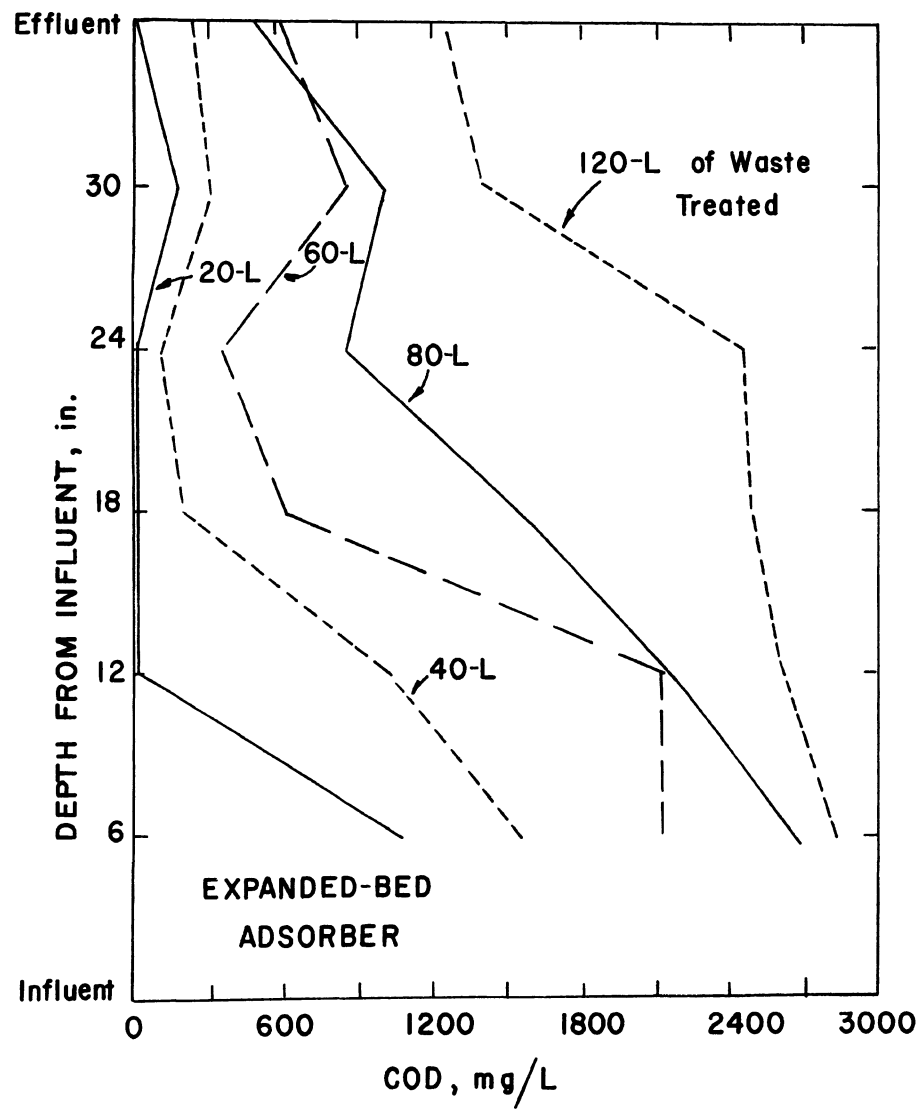


Figure 23. Profile of COD Remaining in Expanded-Bed Adsorber

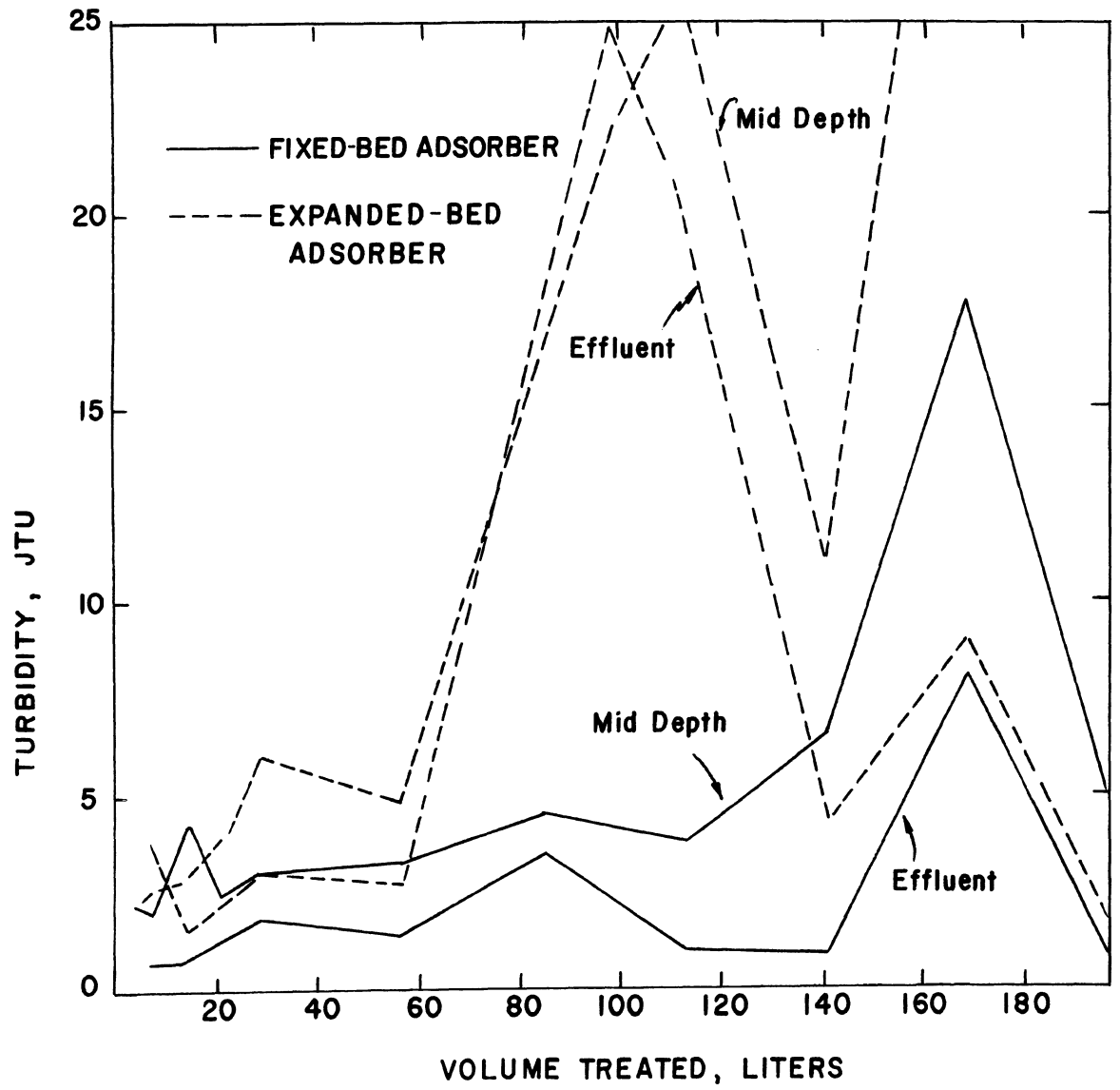


Figure 24. Removal of Turbidity by Fixed-Bed and Expanded-Bed Adsorbers

occurred in the column effluents, turbidities were generally less than 5 JTU, which in many instances is good enough to meet reuse applications.

The removal of inorganic nutrients, including phosphorus and nitrogen, by the carbon adsorbers was also studied in this investigation and the results are presented in Figures 25 and 26. As anticipated, both carbon adsorbers were not effective at all in the removal of total phosphorus and orthophosphate, but total kjeldahl and ammonia nitrogen were removed to some extent by both adsorbers. In general, the two nitrogen forms were removed in increasing amounts as the period of carbon operation was extended. Whether or not the removal of nitrogen was accomplished by biological action was not established in this study. Yet it is worthy to compare this data with the data reported by Weber *et al.* (1), who indicated that no ammonia nitrogen was significantly removed by carbon adsorption, yet organic nitrogen and nitrates were removed by carbon adsorption to some extent, probably as a result of biological activity in the carbon columns.

The pH of the column effluents was also determined constantly. The pH variations observed in the fixed-bed adsorber are shown in Figure 27. In general, the pH of the mid-depth tap and the column effluents remained relatively unchanged as compared to the influent pH of 2.6, except for the first 30 min of operation at which time the pH of the column effluent appeared to be somewhat higher than the influent value. The observed initial rises in the effluent pH seem to agree with the data presented in Table 2, which indicated that in the batch equilibrium tests, higher final pH's were observed at the

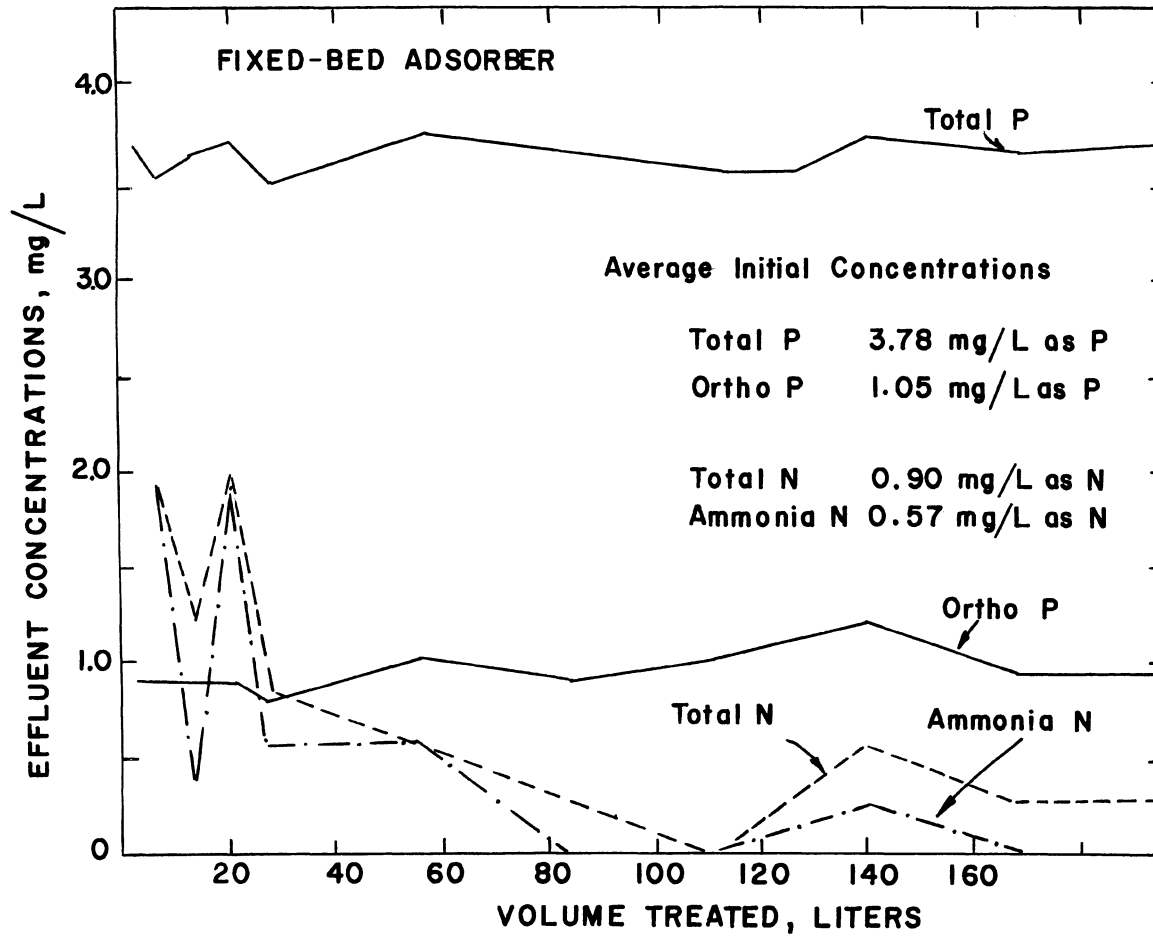


Figure 25. Removal of Inorganic Nutrients by Fixed-Bed Adsorber

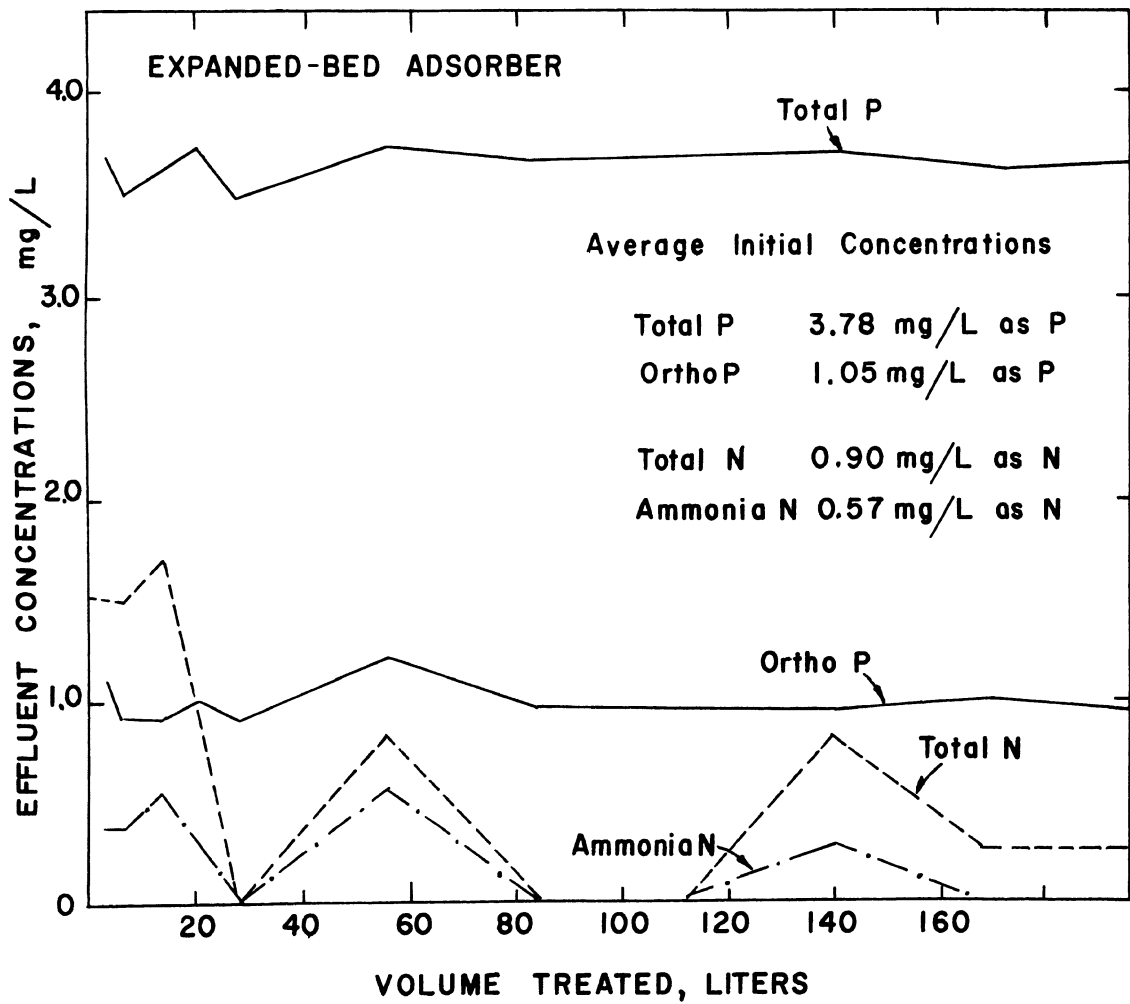


Figure 26. Removal of Inorganic Nutrients by Expanded-Bed Adsorber

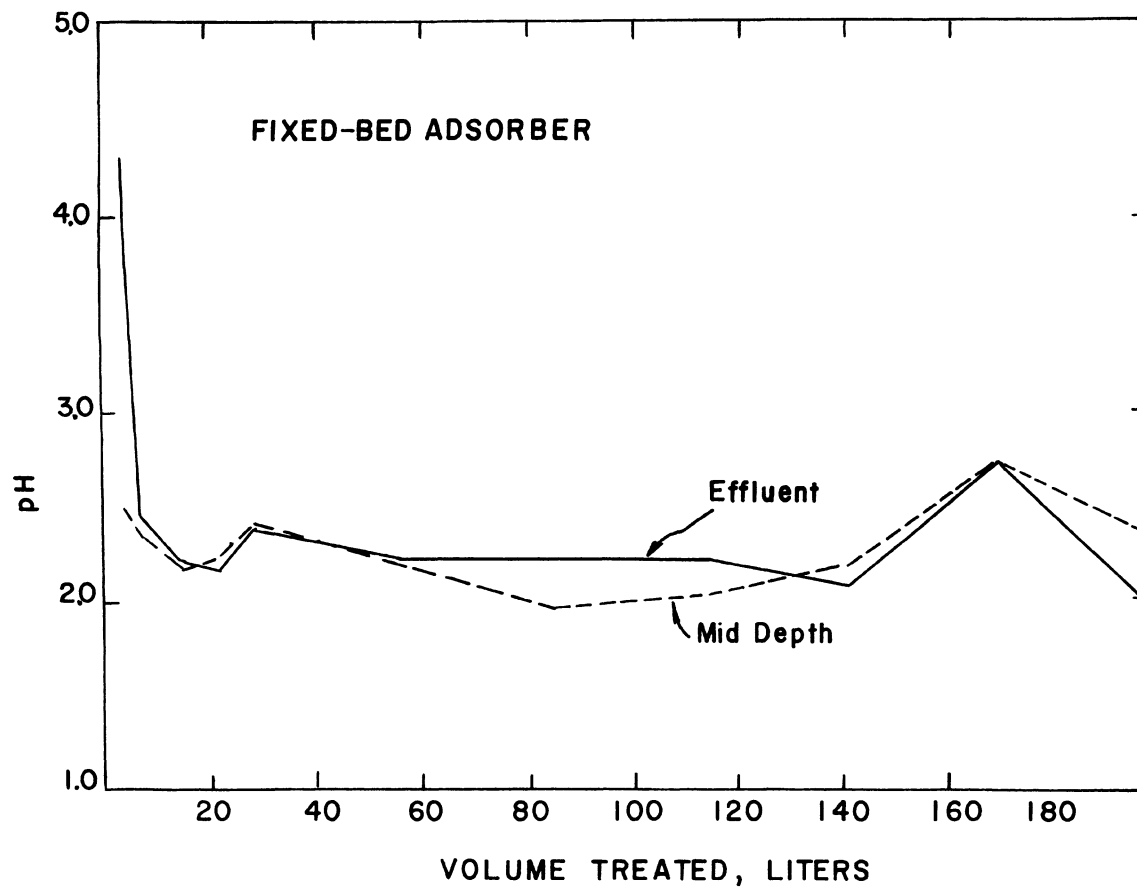


Figure 27. Variation of pH in the Effluent of Fixed-Bed Adsorber

higher carbon dosages. The variations of the effluent pH for the expanded-bed adsorber generally followed the same pattern as noted for the fixed-bed column.

In addition to the certain performance variations which have been mentioned above for the two carbon adsorbers, other operation difficulties were also noted. Specifically, the fixed-bed adsorber clogging problems began to occur after 140 l of wastewater was treated. In order to bring the column back into operation a brief backwash was provided for the column. Although the clogging problems were not encountered in the expanded-bed adsorber, carbon separation or formation of a "gap" within the column occurred from time to time during operation. In general, after a hairlike crack developed in the carbon bed, the crack gradually increased in size until a gap of approximately 1-1/2 in. wide was formed; at that time the upper level of carbon granules would suddenly collapse. After a brief period of tumbling and bubbling, the carbon granules repacked themselves and the gap disappeared. The occurrence of the gap was probably not a problem associated with the carbon packing; it might have been caused by the pulsating action of the sigma motor pump which does not provide a continuous homogeneous flow rate.

## B. Petroleum Refinery Waste

### 1. Waste Characterization

As in the characterization of the chemical waste no attempt was made to identify each individual component in the refinery waste. The major characteristics of the refinery waste are shown in Table 3. As shown in the table, the waste is slightly alkaline in nature, with a pH of 9.0. Chemical oxygen demand (COD) and total organic carbon



TABLE 3. Major Characteristics of the Refinery Waste

---

pH	9.0
COD, mg/l	296
TOC, mg/l	74
SS, mg/l	154
Turbidity, JTU	94
Phosphorus, mg/l as P	
Ortho	0.7
Total	0.7
Nitrogen, mg/l as N	
Ammonia	12.9
Total	13.5

---

(TOC) of the waste were around 296 and 74 mg/l, respectively, which are slightly less than the strength of regular domestic sewage. The waste is relatively high in suspended solids and turbidity and appeared to have an amber color. The concentrations of total phosphorus and total nitrogen were 0.7 and 13.5 mg/l as P and N, respectively. The former was present exclusively in the form of orthophosphate while the latter was predominantly in the form of ammonia nitrogen. These levels of inorganic nutrients are relatively low as compared to those present in sewage. As with the chemical waste, if the refinery waste were to be treated by biological processes it would have to have certain quantities of phosphorus and nitrogen supplemented to satisfy the biological need.

## 2. Coagulation and Clarification

Because of the high turbidity and suspended solids levels contained in the refinery waste, it was necessary to provide coagulation and clarification before the waste was subjected to subsequent activated carbon adsorption treatment. Laboratory tests were conducted to evaluate the relative coagulation efficiencies between the use of alum  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and ferric chloride as coagulants.

Standard jar tests were performed to compare the relative coagulation efficiencies between alum and ferric chloride. Each coagulant was added in solution form (2 percent strength) and dosages were varied from 25 to 300 mg/l. Reductions of turbidity and variations of pH in the clarified waste at different coagulant levels are shown in Figure 28. In general, alum and iron coagulants had almost identical effectiveness in the removal of turbidity for the refinery waste. At a dosage of 100 mg/l, turbidity was reduced from about 70 to 10 JTU.

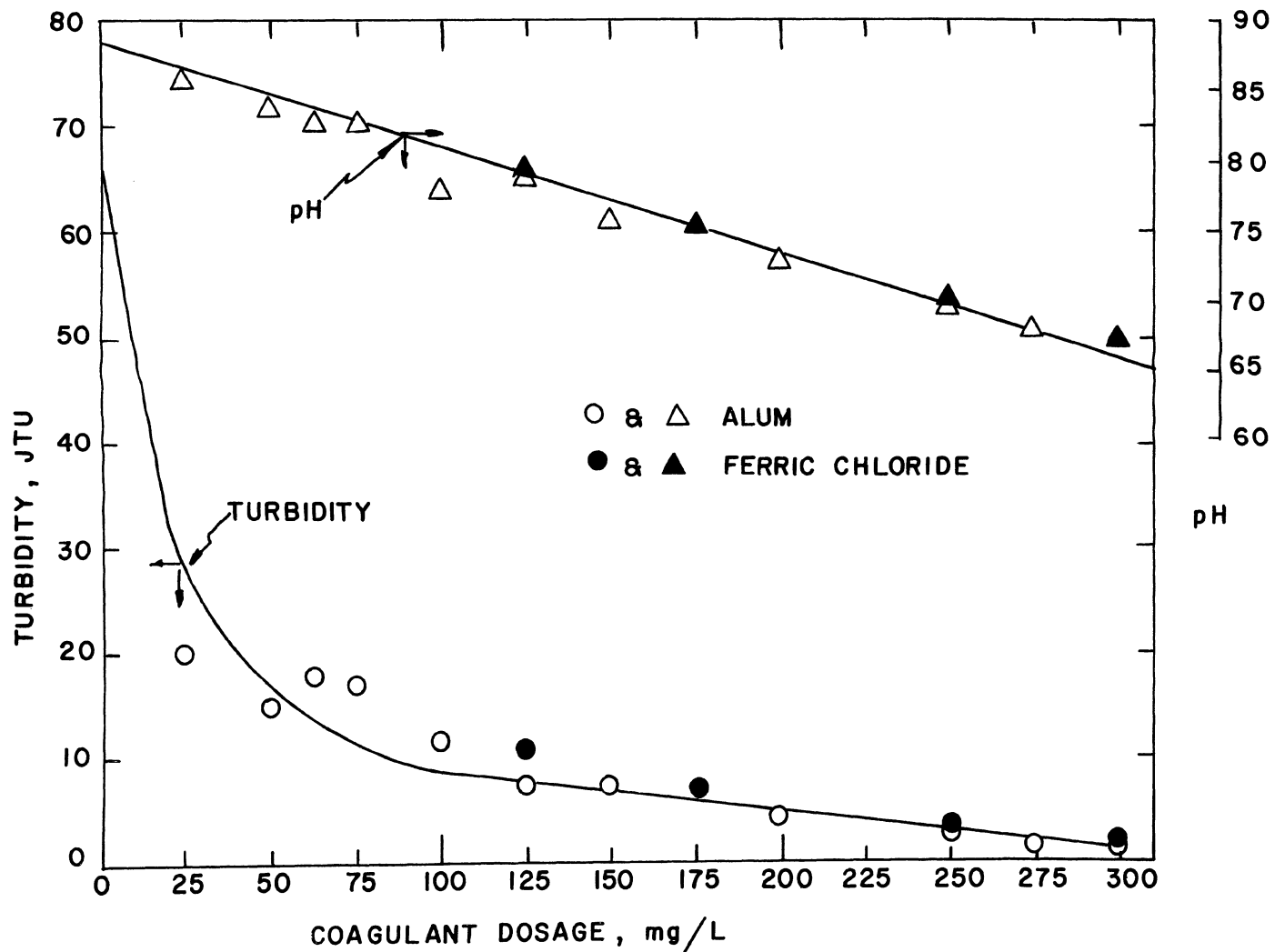


Figure 28. Removal of Turbidity and Change in pH by Chemical Coagulation

With dosages increased to 250 mg/l or more, both coagulants produced rapidly settling flocs and good clarifications were constantly obtained; turbidity of the clarified waste was reduced to 3 JTU or less. It is also significant to note that the final pH of the clarified waste was increasingly lowered by the addition of increasing dosages of both coagulants. However, the refinery waste had sufficient alkalinity to maintain a proper pH for good coagulation even at dosages as high as 300 mg/l. Ferric chloride was selected as the coagulant to be used prior to subjecting the waste to activated carbon adsorption treatment.

The iron dosage for coagulation was 250 mg/l, which was considered the optimum in this study and able to produce a clarified waste having sufficiently low turbidity for subsequent carbon adsorption. The other waste qualities of the coagulated waste are shown in Table 4. In addition to the removal of suspended solids and turbidity, significant amounts of organic matter were also removed. For example, COD was reduced from 296 to 75 mg/l, while TOC was reduced from 74 to 20 mg/l after coagulation. Effective removal was also obtained for orthophosphate, which was reduced from an original level of 0.7 mg/l to about 0.2 mg/l. However, removals of ammonia and total nitrogen were hardly effected by iron coagulation. These observations substantiate the findings reported by Weber et al. (1) who indicated the phosphate was effectively removed by chemical coagulation while ammonia nitrogen was not. Although the removal of organic nitrogen by coagulation was observed by Weber et al., the concentration of organic nitrogen present in the refinery waste

TABLE 4. Major Characteristics of the Original  
and the Coagulated Refinery Waste

<u>Characteristics</u>	<u>Original Waste</u>	<u>Coagulated Waste</u>
pH	9.0	7.0
COD, mg/l	296	75
TOC, mg/l	74	20
SS, mg/l	154	11
Turbidity, JTU	94	3
Phosphorus, mg/l as P		
Ortho	0.7	0.2
Total	0.7	0.2
Nitrogen, mg/l as N		
Ammonia	12.9	12.4
Total	13.5	13.0

was too low, approximately 0.6 mg/l, to allow a conclusive examination regarding the removability of organic nitrogen by coagulation.

### 3. Activated Carbon Adsorption

#### a. Batch Studies

The rate of COD removal from the chemically clarified refinery waste in a batch system is shown in Figure 29. At the carbon dosages of 1.0 and 5.0 g/l, the rates of uptake were the same and the states of equilibrium were essentially reached within a period of 4 hr. It is significant to note that a higher carbon dosage of 5.0 g/l did not appear to remove any more COD than the lower dosage of 1.0 g/l. This indicated that at the higher carbon level, the quantity of organic matter present in the waste becomes a limiting factor for adsorption. In addition, the waste may also have certain quantities of nonadsorbable organic materials.

#### b. Equilibrium Studies

In the equilibrium adsorption tests it was found that any carbon dosage higher than 1.0 g/l did not increase the COD removal efficiency. However, with the carbon concentrations being equal to or less than 1.0 g/l, the equilibrium adsorptions of COD and TOC generally conform fairly well to the Freundlich adsorption isotherm, as shown in Figure 30. The TOC adsorption isotherm has a steeper slope and appears to fit better the straight-line relationship than the COD isotherm. Perhaps this is due to the fact that TOC measures primarily soluble organic matter (because little suspended solids could be easily picked up by the extremely small tip opening of the sampling syringe) while COD may be contributed by various amounts of suspended

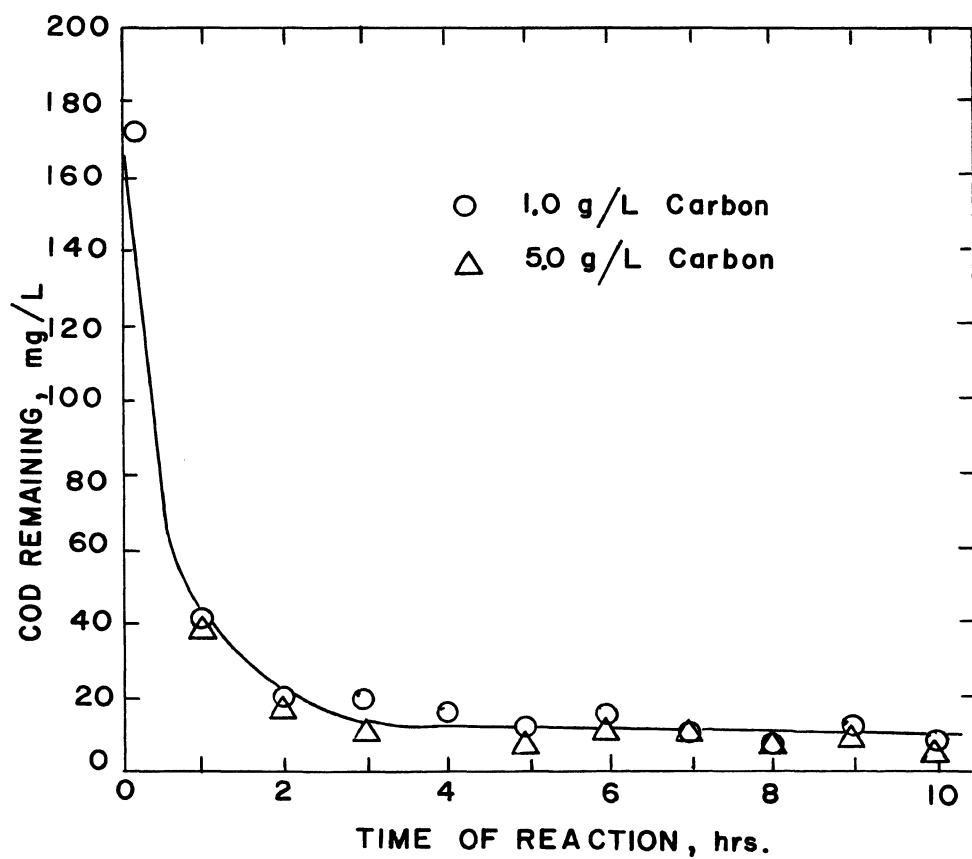


Figure 29. Rate of COD Removal from the Clarified Refinery Waste

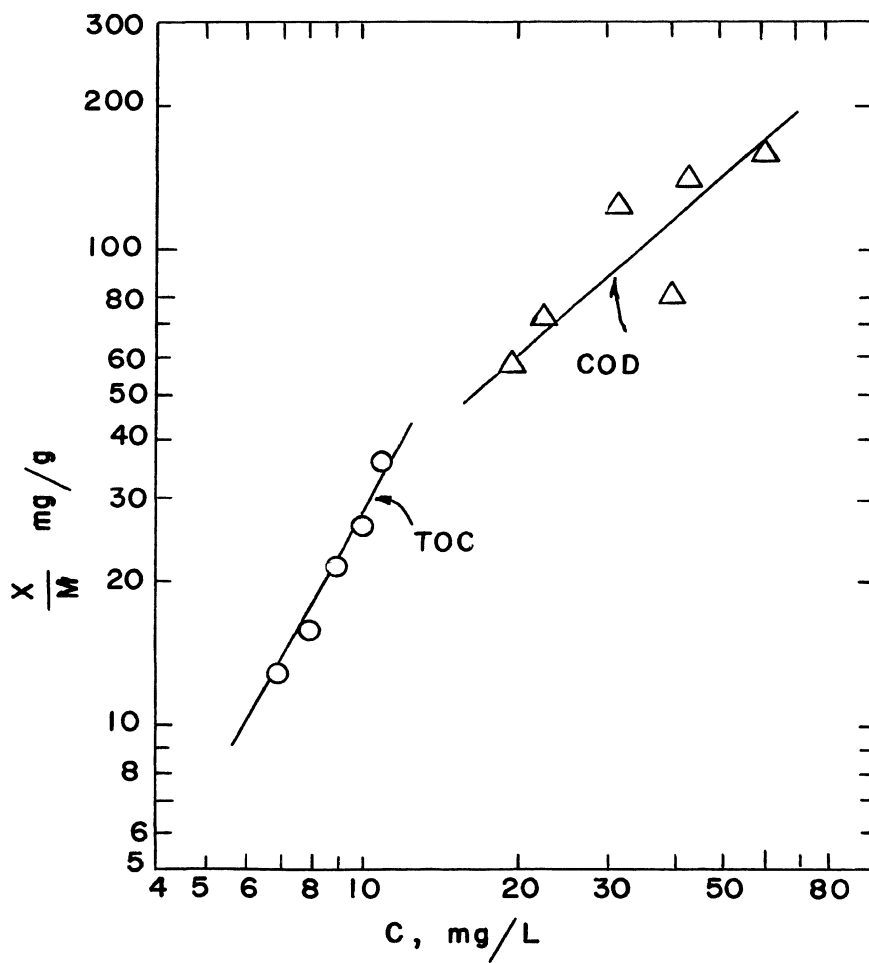


Figure 30. Freundlich Isotherms for the TOC and COD Adsorptions from the Clarified Refinery Waste



organic solids which, of course, are less effectively removed by carbon adsorption and also frequently introduce erratic experimental results.

From the adsorption isotherm it can be predicted that when the final effluent organic concentration is in equilibrium with the influent level (COD of 75 mg/l and TOC of 20 mg/l), each g of activated carbon would adsorb about 0.2 g of COD and 0.11 g of TOC.

c. Column Studies

Parallel fixed-bed and expanded-bed activated carbon adsorbers were operated at the same time for the treatment of the refinery waste.

The TOC, turbidity, and pH of the refinery wastewater sample taken from different taps (located at 6-in., 12-in., 18-in., 24-in., and 30-in. bed depths from the influent) as well as from the column effluent were continuously monitored throughout the test. In addition, COD, phosphorus, and nitrogen remaining in each column effluent were also determined constantly. The TOC and COD remaining in the wastewater samples from the column effluents of the two independent fixed-bed adsorbers are shown in Figure 31 as functions of the waste volume treated. In this study, a volume of 280 l of clarified refinery wastewater was pumped through each fixed-bed adsorber. As shown in Figure 31, TOC of the 12-in. tap effluents were consistently less than 4 mg/l in the two adsorbers for the first 200 l of wastewater treated. After that, one of the two adsorbers started to have TOC breakthrough while the other still continued to yield high quality effluent. Although the 24-in. tap and the column effluent consistently produced high quality water,

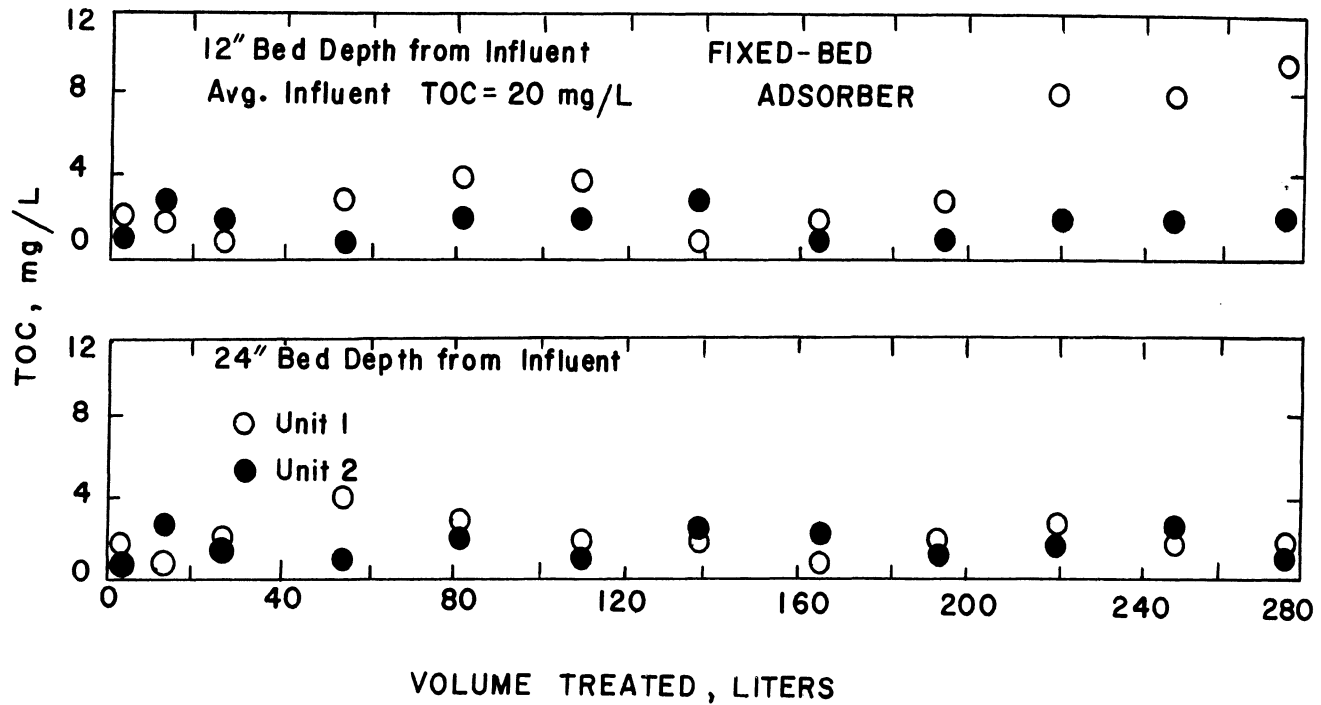
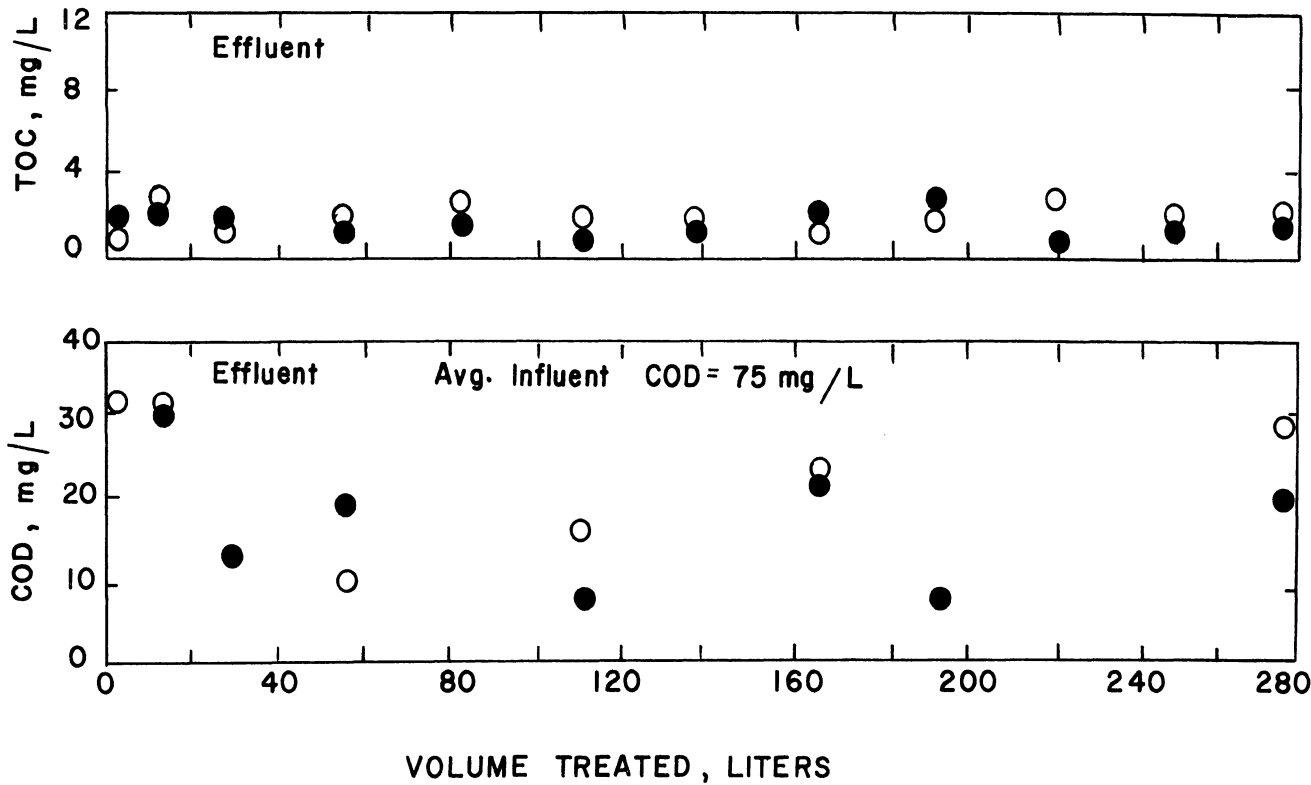


Figure 31. TOC and COD Remaining at Different Depths and in the Column Effluents of the Fixed-Bed Adsorber



the TOC of the effluent was never removed completely and a residual value ranging from 1 to 3 mg/l was observed throughout the study. Similarly, although the COD of the column effluent was low, the values fluctuated between 10 and 30 mg/l. All of these findings seem to indicate that there were present in the refinery waste some organic materials which were not subjected to carbon adsorption effectively. Unfortunately, the nature of this organic leakage was not established in this study.

Similar to Figure 31, a plot of treatment efficiency for the expanded-bed adsorber is shown in Figure 32. In general, there were no significant differences in the TOC and COD removal efficiencies between the fixed-bed and expanded-bed adsorbers, except in the latter, both independent units had TOC breakthroughs at their 12-in. taps after 200 l of wastewater were passed through the columns. Like the fixed-bed adsorbers, the TOC of the expanded-bed adsorber effluent varied from 1 to 3 mg/l and the COD fluctuated from between 10 and 30 mg/l, both indicating the presence of nonadsorbable organic matter in the refinery waste.

The turbidities of the effluents from all the carbon adsorption columns remained consistently less than 1 JTU throughout the test, while the pH of the effluents remained close to the neutral value.

In this study with the refinery waste, ammonia and total nitrogen were totally unaffected by carbon adsorption. Typical results are shown in Figure 33 for the fixed-bed adsorber. However, in the previous study on the high strength acidic chemical waste, it was found that both total kjeldahl and ammonia nitrogen were removed to some extent, especially as the period of carbon adsorption was extended.

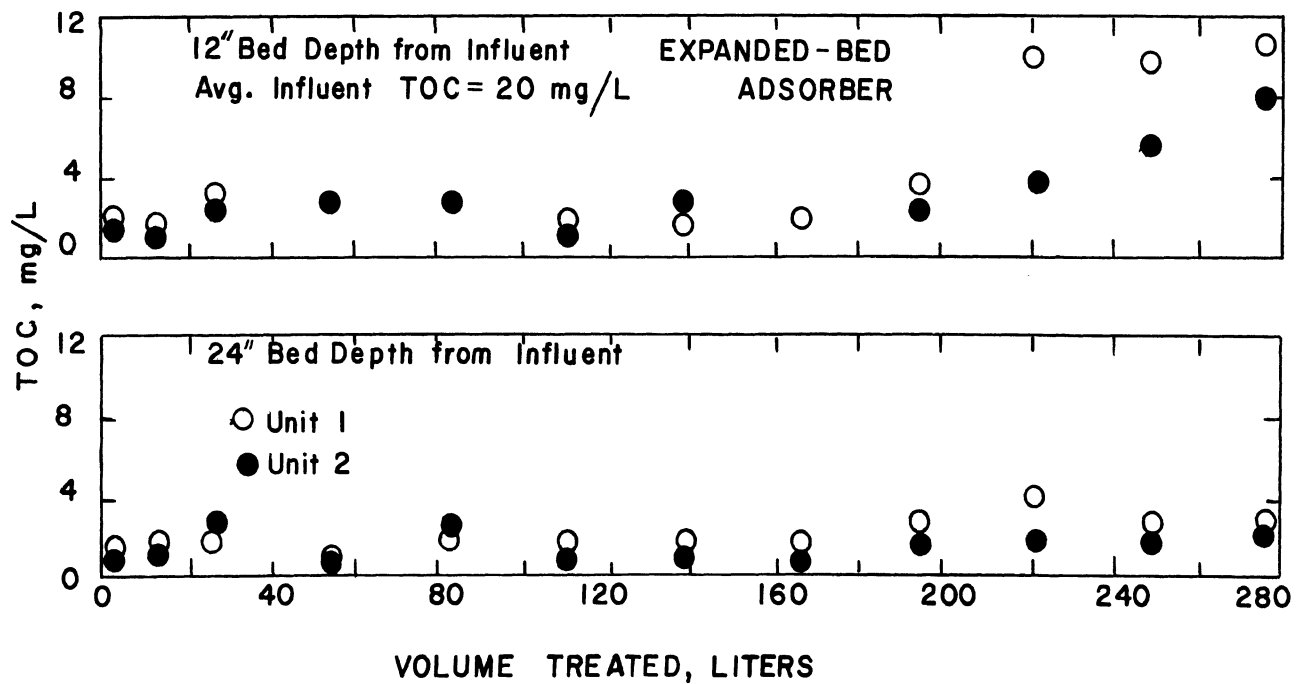
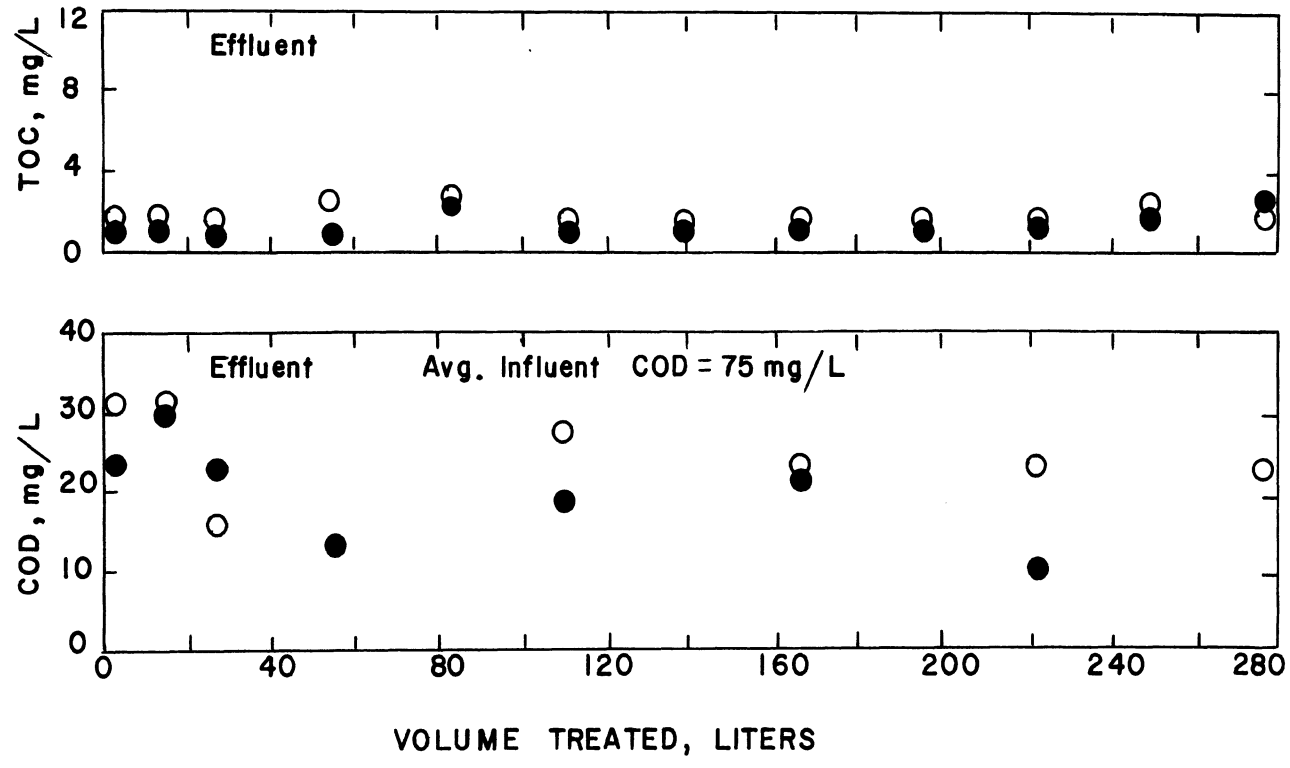


Figure 32. TOC and COD Remaining at Different Depths and in the Column Effluents of the Expanded-Bed Adsorber



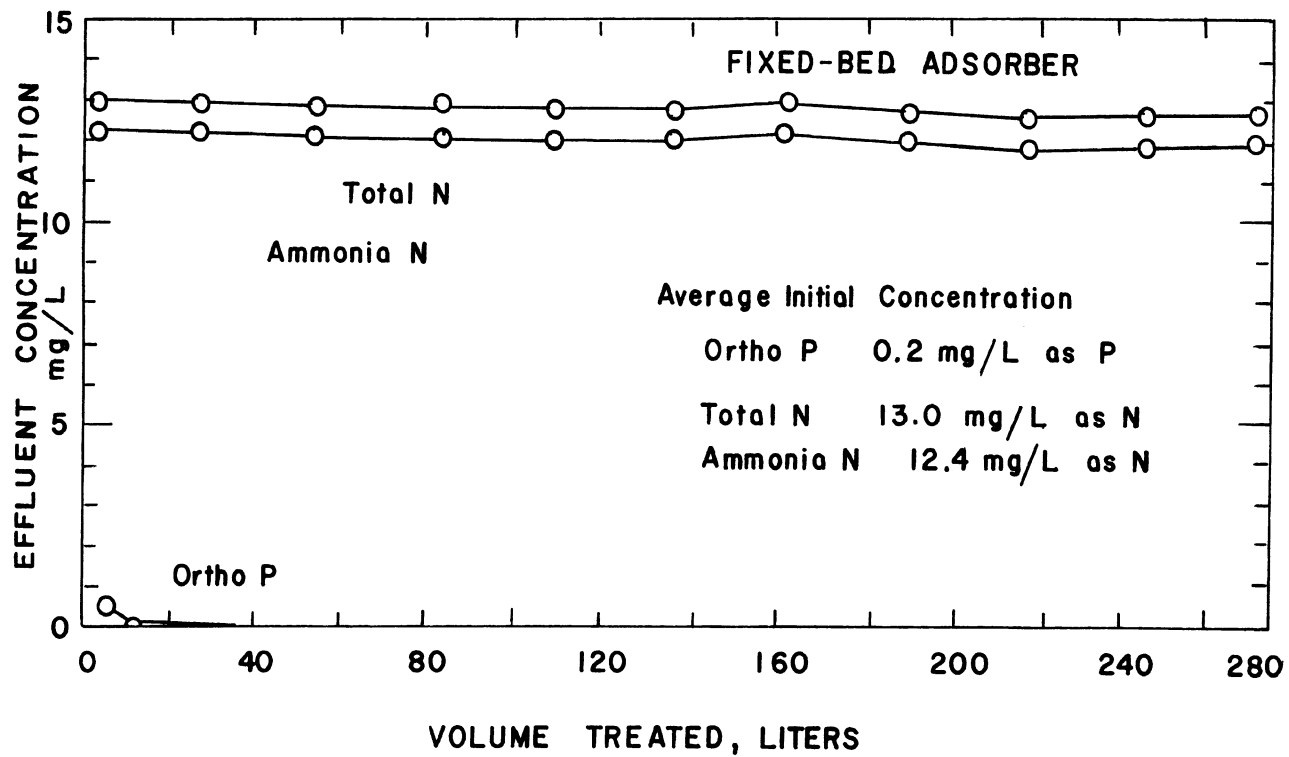


Figure 33. Removal of Inorganic Nutrients in the Fixed-Bed Adsorber

Weber et al. (1) also indicated that although ammonia nitrogen was not removed by carbon adsorption, organic nitrogen was removed to some degree, probably as a result of biological activity in the activated carbon columns. In general, it is believed that neither ammonia nitrogen nor organic nitrogen can be removed by carbon adsorption per se if there is no biological activity within the column.

The coagulated refinery waste had an extremely low orthophosphate content, being only 0.2 mg/l. After 14 l of the clarified refinery wastewater were pumped through the column, the effluents appeared consistently to have a zero phosphorus value. However, due to the extremely low phosphorus concentration present in the clarified waste and the sensitivity limitations of the analytical method, it is difficult to conclude whether the phosphorus removal observed in the study is significant or not. Weber et al. (1) have indicated that carbon adsorbers are not effective in the removal of orthophosphate and total phosphorus.

Although there were no substantial differences in the treatment efficiencies between the fixed-bed and the expanded-bed adsorbers, certain variations regarding operational difficulties were noted, some similar to those experienced in the study of the chemical waste. In general, clogging problems developed occasionally in the fixed-bed adsorbers. In order to bring the columns back into operation, a brief backwash was provided the column. Although clogging problems were not encountered in the expanded-bed adsorber, carbon separation or formation of a "gap" within the column occurred. This gap phenomenon was similar to that previously observed during the chemical waste study.



## V. SUMMARY AND CONCLUSIONS

During the past 10 years the application of carbon adsorption and other associated physicochemical processes, i.e., chemical clarification and filtration, etc., was primarily limited to conventional secondary effluents as a means of providing a tertiary step of treatment. However, some difficulties were experienced concerning the complete removal of organic materials from secondary effluents by carbon adsorption (1). The nature of this leakage is not exactly known but it may be nonadsorbable cell fragments which have been produced and small organic molecules which have been hydrolyzed extensively during biological treatment. Because of this suspicion, Weber et al. (1) initiated a new approach of applying physicochemical processes directly to primary effluents rather than to secondary effluents with the hope that the above difficulties could be eliminated and a high degree of waste treatment could be achieved economically without any biological involvement. This study was undertaken along the lines of this new approach to determine if the direct use of physicochemical methods could treat different types of industrial wastewaters successfully.

The results obtained in this study generally substantiate those found by Weber et al. (1) and reflect chemical processes consisting of chemical coagulation and clarification and activated carbon adsorption, can provide effective treatment when applied directly to the two selected industrial wastes without the incorporation of any biological process. The chemical coagulation and clarification provide effective removal of the suspended solids and turbidity present in the primary effluent. In addition, the removal of phosphate is

also effected. The adsorption on activated carbon provides effective removal of the soluble organics present in the clarified wastewaters. The treatment approach eliminates the effect of toxic substances which may be present in many industrial wastewaters and can adversely affect biological treatment processes.

The physicochemical treatment system can also provide flexibility to accommodate changes in design due to growth and changing effluent standards. It can also reclaim wastewaters for direct reuse and thus help to meet the challenge of the demand for increasing quantities of water that otherwise will soon be limited by our natural supply. Based on the findings of this research the following conclusions can be made:

1. For the acidic industrial chemical waste employed in this study, no chemical clarification was necessary because of its low suspended solids content. Treatment by activated carbon adsorption was very effective in removing organic matter and color from the chemical waste.

2. Physicochemical treatment of the refinery waste using a combination of iron coagulation at a dosage of 250 mg/l as  $\text{Fe}_3 \cdot 6\text{H}_2\text{O}$  and 3 ft carbon column adsorption provided a high degree of treatment; the effluent quality had a TOC of less than 3 mg/l and a turbidity of less than 1 JTU.

3. No substantial differences in the treatment efficiencies between the fixed-bed and the expanded-bed adsorbers were noted during the treatment of the two industrial wastes, but certain operational difficulties were noted. In general, clogging problems developed occasionally in the fixed-bed adsorbers, which were not encountered

in the expanded-bed adsorbers. On the other hand, carbon separation or formation of a gap within the expanded-bed columns occurred from time to time during their operation.

4. Initial pH adjustments for the industrial chemical waste to 3.2, 7.0, and 11.4 did not significantly affect the COD removal efficiency during activated carbon adsorption.

5. Slight removals of turbidity and nitrogen (total kjeldahl and ammonia-N) from the chemical waste were obtained by activated carbon adsorption, while phosphorus (total- and ortho-P) were totally unaffected.

6. For the refinery waste, ammonia and total nitrogens were totally unaffected by activated carbon adsorption. Orthophosphate removal of this waste was effected by the chemical coagulation and clarification step.

7. Small quantities of organic leakage (TOC of less than 3 mg/l and COD of less than 30 mg/l) were observed consistently in all the carbon effluents during the treatment of the refinery waste. The cause of this organic leakage was perhaps due to the presence of certain organic materials, but their nature was not established.

## VI. RECOMMENDATIONS FOR FUTURE STUDIES

From the findings and experience obtained in this study, the following recommendations are made for future investigations.

1. Continue this study to evaluate the direct use of physicochemical processes of an additional number of industrial wastes which have varied strengths and characteristics. This should give further insight into the general applicability of these processes to industrial waste treatment.

2. Investigate the improvement of effluent qualities if an additional filtration step is provided either prior to or following activated carbon adsorption.

3. Since in the treatment of the refinery waste in this study small quantities of organic leakage were observed consistently in the carbon column effluent, future studies should investigate the nature of this leakage. It should be determined if the leakage was due to the presence of nonadsorbable organic matter or operational faults.

4. Develop an additional unit process which can be incorporated into the physicochemical treatment scheme to improve the removal of inorganic nutrients both effectively and economically.

5. Make a detailed cost analysis to compare the relative treatment economy between the direct physicochemical approach and the conventional physical-biological-chemical method for various sizes of plants.

6. Evaluate the feasibility of developing an effective and economic method for the direct in-column activated carbon regeneration.

## BIBLIOGRAPHY

1. Weber, W. J., Jr., Hopkins, C. B., and Bloom, R., Jr., "Physicochemical Treatment of Wastewater," Journal Water Pollution Control Federation, 42, p. 83, (1970).
2. Joyce, R. S., and Sukenik, V. A., Feasibility of Granular Activated-Carbon Adsorption for Wastewater Renovation, FWPCA Publication No. AWTR-10, R. A. Taft Water Resources Center, U.S. Department of Health, Education, and Welfare, 32 pp, (1964).
3. Joyce, R. S., and Sukenik, V. A., Feasibility of Granular Activated-Carbon Adsorption for Wastewater Renovation, FWPCA Publication No. AWTR-15, R. A. Taft Water Resources Center, U.S. Department of Health, Education, and Welfare, 38 pp, (1965).
4. Stenburg, R. L., Convey, J. J., and Swanson, C. L., "New Approaches to Wastewater Treatment," Journal of the Sanitary Engineering Division, ASCE, 94, p. 1121, (1968).
5. Parkhurst, J. D., Dryden, F. D., McDermott, G. N., and English, J., "Pomona Activated Carbon Pilot Plant," Journal Water Pollution Control Federation, 39, p. R70, (1967).
6. Hopkins, C. B., Weber, W. J., Jr., and Bloom, R., Jr., A Comparison of Expanded-Bed and Packed-Bed Adsorption Systems, "Advanced Waste Treatment Research," FWPCA Publication No. TWRC-2, R. A. Taft Water Resources Center, U.S. Department of Interior, Cincinnati, Ohio, 74 pp, (1968).
7. Zuckerman, M. M., and Molof, A. H., "High Quality Reuse Water by Chemical-Physical Wastewater Treatment," Journal Water Pollution Control Federation, 42, p. 437, (1970).
8. Rizzo, J. L., and Schade, R. E., "Secondary Treatment with Granular Activated Carbon," Water and Sewage Works, 116, p. 307, (1969).
9. Hager, D. G., "Adsorption-Filtration in the Treatment of Municipal and Industrial Wastewater," Paper presented at 42nd Annual Conference, Water Pollution Control Federation, Dallas, Texas (Oct. 5-10, 1969).
10. "Standard Methods for the Examination of Water and Wastewater," 12th Ed., American Public Health Assn., New York, N.Y., (1965).
11. Jankovic, S. G., Mitchell, D. T., and Buzzell, J. C., Jr., "Measurement of Phosphorus in Wastewater," Water and Sewage Works, 114, p. 471, (1967).

12. Sawyer, C. N., Chemistry for Sanitary Engineers, McGraw Hill, New York, (1960).
13. Eckenfelder, W. W., Jr., Industrial Water Pollution Control, McGraw Hill, New York, (1966).
14. Juhola, A. J., and Tepper, F., Regeneration of Spent Granular Activated Carbon, "Advanced Waste Treatment Research," FWPCA Publication No. TWRC-7, R. A. Taft Water Resources Center, U.S. Department of Interior, Cincinnati, Ohio, 91 pp, (1969).

## VITA

Michael G. Hardie was born May 11, 1940, in New York City, New York. He received his elementary and secondary educations in several places including Washington, D.C., New York, and Tokyo, Japan. He received the degree of Bachelor of Science in Civil Engineering from the University of Missouri-Rolla in August 1967.

Following graduation from the University he accepted employment with Rex Chainbelt, Inc., Milwaukee, Wisconsin, where he worked in both the research and application engineering sections of the Process Equipment Division. He enrolled as a graduate student at the University of Missouri-Rolla in February 1968 under a Federal Water Quality Administration traineeship.

He is a member of the American Society of Civil Engineers, American Water Works Association, and Water Pollution Control Federation.

He was married to Miss Madonna Krekel on June 19, 1965.