ADSORPTION ON ACTIVATED FLYASH

BY

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ABSTRACT

An experimental study was undertaken to compare the adsorptive characteristics of activated carbon, flyash, and activated flyash. Due to the contradictory evidence available in the literature, emphasis was placed on the effect of acid activation on the physical properties of the adsorbent. The experiment consisted of two parts; batch isotherm studies, and continuous column operations. An artificial sewage composed of a mixture of deionized water and beef broth was used as the adsorbate. This solution was prepared daily and exerted a COD of 225 ± 30 mg/l. Flyash activation was found to increase the degree of adsorption indirectly rather than directly, by altering ash properties. Acid activation neutralized ash pH, reduced ash COD by 73%, lowered leachable solids by 50 to 70% and effectively hindered desorption. Within the limits of its adsorptive capacity activated ash exhibited characteristics similar to those of activated carbon, however the carbon adsorbed 67.2 times more COD than an equal volume of activated ash.

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TABLE OF CONTENTS

Page

Appendix

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The amount of water available for utilization remains essentially constant. Increasing population and technology have greatly increased the need for potable water. This need may eventually exceed existing supplies of water. Restricting the use of water is not feasible, therefore an alternate solution must be found. The most practicable solution would be that of reusing the available water. Water reuse is not a new concept, it has gained widespread acceptance in industry and has been practiced by municipalities in time of drought.

Water can not be immediately reused, it must first be cleansed of impurities, the degree of purification depending on the intended reuse. Present primary and secondary treatment methods will not achieve the degree of purity needed for drinking water. Tertiary treatment processes are required to remove refractory contaminants. Among the existing advanced wastewater treatment methods activated carbon adsorption shows promise of becoming the most valuable. Activated carbon, in granular or powdered form, will effectively remove all contaminants normally found in wastewaters.(21) For most applications it is not economically practicable to discard carbon after it becomes saturated with impurities. The carbon must be regenerated in furnaces, thereby significantly increasing the cost of operation. The added cost of regeneration excludes carbon adsorption from many possible applications.

This problem has led to a continuing search for a new low cost adsorbent which could be used once and then discarded. Among the many materials tested, flyash emerges as the most promising adsorbent from both technological and economic standpoints. Waste and carry-over ash from the thermal processing of fuel exhibit certain adsorptive characteristics.(24) The conditions under which incomplete combustion occurs are favorable for the activation of carbonaceous material. While the adsorptive capacities of these waste substances are naturally much lower than those of activated carbon, their large availability and low cost will allow the use of much larger amounts of adsorbent to accomplish the same purpose. After saturation these wastes can be ecomomically replaced and discarded.

Flyash is the powdered residue of burning coal and oil. Law forbids the discharge of flyash into the atmosphere. It must be collected and ultimately disposed. The electric power industry produces more than 20,000,000 tons of this waste annualy. Attempts have been made to find a marketable use for flyash, to ease the cost of disposal. Flyash has been used in landfill, concrete blocks, and as an aggregate in road surfacing. Recently a process has been developed to separate iron from flyash.(6) Aside from the marketable iron, new uses have been discovered for the ironless flyash. The ash quality is improved so that it can be substituted for shale in cement manufacture. The high silica content of the ash can be used to produce cenospheres, which can be added to plastics to make them heat resistant. These and various other applications of flyash account for only one sixth of the flyash produced in the United States.(20) The remainder must be disposed of at high cost to industry.

Preliminary testing has indicated the feasibility of using flyash in wastewater treatment. Logic dictates the desirability of this twofold solution. The problem of flyash disposal may provide the answer to the problem of wastewater purification. Further investigations have discovered that activation of flyash greatly enhances the adsorptive nature of the ash. This paper will attempt to compare the adsorption characteristics of activated carbon with those of flyash and determine the effect of activation on the same flyash.

THEORY

A. Activation Theory

The formation of activated carbon may best be understood if it is first considered to occur in two stages, carbonization and activation. During the first stage, the carbonaceous starting material undergoes a pyrolytic decomposition removing most of the non-carbon elements, such as oxygen and hydrogen. Freed elementary carbon atoms are arranged into organized crystallographic formations. These formations resemble the structure of graphite and are therefore known as elementary graphitic crystallites. Graphite is composed of layers of pure carbon atoms ordered in regular hexagons. These layers or planes are arranged in parallel with respect to a common perpendicular axis. (Figure One) The crystallites formed during carbonization are less perfectly ordered than those of graphite, resulting in the occurence of a large number of free interstices. Tarry deposits of amorphous or non-organized carbon fill these spaces and the surface of the crystallites. The amount of non-organized carbon formed is dependent on both the temperature of carbonization and the nature of the starting material. The final product of this pyrolysis has a very low adsorptive capacity.

In the second stage, activation, the clogged spaces are cleared of non-organized carbon. In addition some carbon of the elementary crystallites is also removed. These freed spaces or pores have a large internal surface area, which is responsible for the high adsorptive capacity of the carbon. In this two stage procedure, known as physical activation, gaseous substances such as steam or air are the usual activating agents.

The two steps of carbonization and activation are combined in a process called chemical activation. Chemicals which inhibit the formation of tar are added to the initial material before carbonization. The most common activating agents used are zinc chloride, potassium sulphide and sulfuric acid. These two methods can also be used in combination to manufacture carbons for special applications.

Flyash is not a product of pyrolysis but rather a byproduct of combustion occuring in the presence of air, resulting in the formation of many metallic oxides. However, a large amount of fixed carbon is distributed throughout the ash.(20) Flyash also has a very large external and internal surface area. Waste from incomplete combustion always possesses a certain adsorptive capacity, which can be improved by suitable treatment.(24) Flyash may be activated in much the same sense as carbon using an activating agent such as hydrochloric or sulfuric acid. The acid will partially neutralize the metallic oxides and other substances formed during combustion thus freeing active sites for adsorption.(20)

B. Surface Chemistry

Adsorption is a surface phenomenon; Therefore, any adsorptive investigation must first consider surface chemistry. The properties of the surface layer can best be illustrated by the simple case of a water droplet deposited on a flat surface. Intermolecular cohesive forces attract the surface molecules of the drop into the drop body. The molecules of the solid surface also exert an attractive force on the water molecules. The cohesive forces of the drop are stronger than the adhesive forces of the solid, resulting in water molecules being pulled away from the solid surface thus minimizing the surface area of the droplet. The surface tension of the drop is the force on the liquid surface which opposes the expansion of the surface area. It is equal to the amount of work needed to overcome the intermolecular cohesive forces. To increase the surface area of the drop the intramolecular bonds of the liquid must first be broken then reformed with molecules of the solid phase.

Soluble materials can alter the interfacial, or surface tension of a liquid. These substances can either raise or lower the surface tension. The effect of raising the surface tension will be small since the solute will be forced out of the surface layer into the body of the liquid. Substances which lower the surface tension, such as detergents, cause spreading of the surface area. These surface active substances migrate to the boundary area and reduce the amount of work required to enlarge the surface area. The reduction will be proportional to the amount of solute or substance at the surface. The solute will be forced to the boundary layer since the solvent molecules have a greater attractive force for each other than for the solute molecules. Any substance, dissolved in a liquid, which lowers the surface tension of that liquid will be collected at the boundary of that liquid. This phenomenon is termed adsorption. The well known Gibbs equation relates the adsorption on a surface to the change in surface tension.

C. Attractive Forces

Many substances which do not lower the surface tension of water can be readily adsorbed from solution.(10) While the mechanism just described clearly does not explain all situations it is an important factor in adsorption, which can be said to be the result of many factors. It has long been recognized that adsorption can involve mutual affinities between a given solvent-solute-solid system. One of the most important of these is the degree of solubility of the solute. The greater the affinity of the solute for the solvent, the smaller the amount of solute that will be adsorbed. In an aqueous solution, substances which have an affinity for the solvent are termed hydrophylic. Hydrophobic or water disliking substances are more likely to be adsorbed. Molecules which contain both hydrophylic and hydrophobic groups will become oriented at the interface, the hydrophylic portion being adsorbed and the hydrophobic portion remaining in solution.

Another important factor is the affinity of the solute for the solid. In the case of physical adsorption, the solute molecules are unchanged and weakly held to the solid by van der waals forces. The solute molecule is not fixed to a specific site on the solid but has translational freedom. When electrons are shared or exchanged between the solute and solid molecules a much stronger chemical bond is created. In this, chemical adsorption, the solute molecule is fixed to a specific location on the solid. A certain activation energy is often required for chemical adsorption. Generally, physical adsorption predominates at lower temperatures

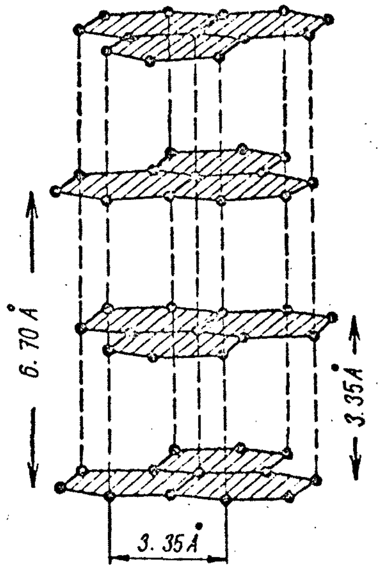


Figure One
Structure of Graphite (24)

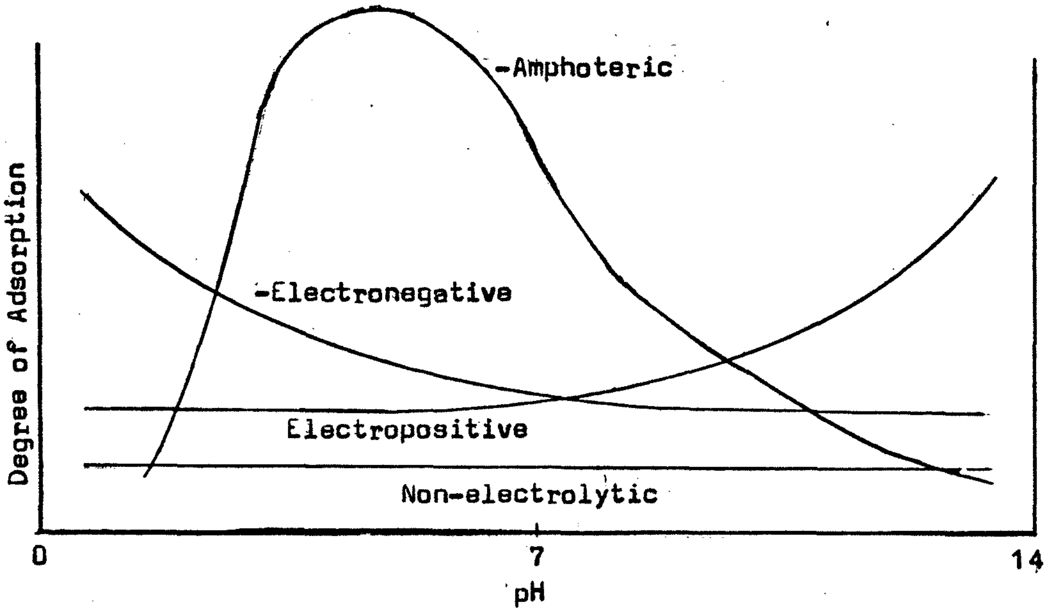


Figure Two
Influence of pH on adsorption of solutions of various electrical properties. (15)

because of the higher energy needed for chemical adsorption. It is often difficult to distinguish between physical and chemical adsorption, since chemisorption is preceded by physical adsorption and two dimensional diffusion over the solid surface.(4) Adsorption is often a product of all the mechanisms previously mentioned. A large amount of research has been conducted in this area.(24)

D. pH Influence

Factors which affect the affinities just described have a considerable effect on adsorption. In these studies the most important of these factors was found to be the hydrogen ion concentration or pH of the system. Figure two shows a generalized chart of adsorption efficiency as a function of solution pH. Solutes are classified by their electrical properties. The adsorption of nonelectrolytic substances such as sugar is not affected by pH, while electronegative and electropositive materials, are highly pH dependent. Amphoteric substances such as colloids and proteins represent a special group in that they may act as both acids and bases. They are adsorbed most effectively at their isoelectric point, where they show neither basic or acidic properties. One explanation of this behavior is that pH will effect the solubility of the solute in solution. In the case of amphoteric substances the isoelectric point is also the point of minimum solubility. Studies(15) have also linked the pH effects with functional groups formed on the carbon surface during activation.(30)

E. Influence of Surface Area

The extent of adsorption is proportional to the specific surface area of the adsorbent. Specific surface area is defined as that portion of the total surface available for adsorption. The actual proportional relationship will be dependent on the mechanism of adsorption. The slowest step in this mechanism will control the rate of adsorption. The adsorption rate should exhibit a monotonic increase with some function of the inverse of particle diameter. "Rate of adsorption by particles of a fixed size should vary approximately linearly with dosage of adsorbent over a range of dosages that do not result in great changes in solute concentration."(24)

F. Isotherm Equations

A very large number of adsorption theories and their corresponding equations exist at this time. They are readily available in the literature and no attempt will be made to describe or summarize these equations. Only those theories which will lead to a better understanding of carbon-flyash adsorption will be discussed.

Adsorption of a solute onto a solid will continue until a dynamic equilbrium exists between the solute concentrated on the solid and the solute remaining in solution. It may be a function of solute concentration, solute nature, solvent nature or any number of factors including outside interferences. The most commonly employed representation of the equilbrium states of a system is the adsorption isotherm. It expresses the variations in adsorption with solute concentration in a system at constant temperature. The adsorption isotherm is a useful tool which enables the calculation of: adsorbing area, pore size and distribution, magnitudes of heats of adsorption, and adsorbent-adsorbate affinities. All adsorption isotherm equations are semi-empirical in that their constants must be experimentally determined for each system.

Langmuir developed a simplified model of adsorption in which he considered the solid of an adsorbent to be composed of a number of sites, each of which could adsorb one molecule. He further assumed each space to have identical attractive powers and to be free of interferences by solute molecules already adsorbed on neighboring sites. Maximum adsorptive capacity would correspond to a monolayer of solute molecules. The isotherm equation is:

$$\frac{X}{M} = \frac{abc}{1 + bc} \tag{1}$$

Where

$\frac{x}{m}$ = amount adsorbed per unit weight of adsorbent

a,b = empirical constants

c = equilbrium concentration of adsorbate

This equation can be rewritten:

$$\frac{C}{X/M} = \frac{1}{ab} + \frac{1}{a}C \tag{2}$$

This form of the equation is plotted as shown by Figure Three.

Brunauer, Emmet, and Teller adapted the Langmuir equation for multilayer adsorption. For adsorption from solution the BET equation can be written in linearzed form.

$$\frac{C}{(C_S - C)\frac{X}{M}} = \frac{1}{B\frac{X1}{M}} + \frac{B-1}{B\frac{X1}{M}} \quad \frac{C}{C_S} \tag{3}$$

Where

C_S = saturation concentration of solute

$\frac{X^1}{M}$ = amount adsorbed per unit of adsorbent to form a complete monolayer or the adsorbent surface

B = empirical constant

The graphical representation of the BET equation is shown in Figure Four.

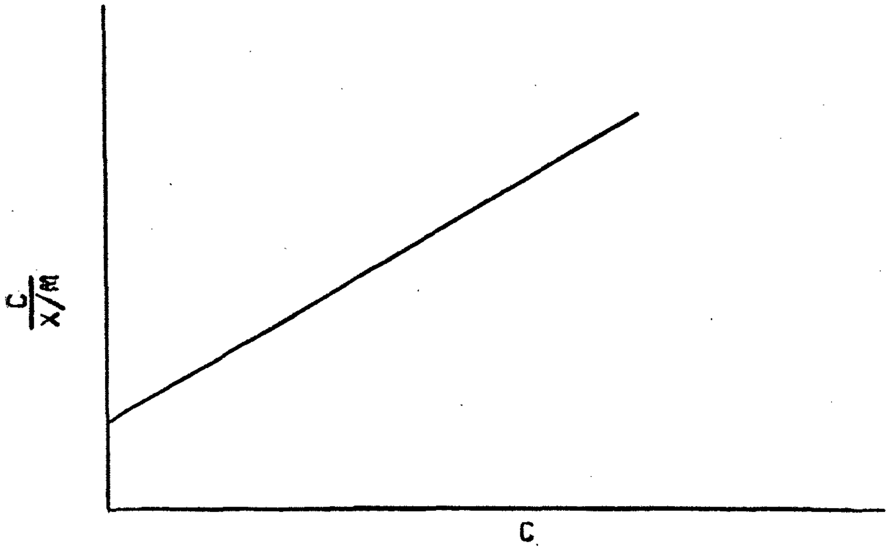


Figure Three
Plot of Langmuir Equation

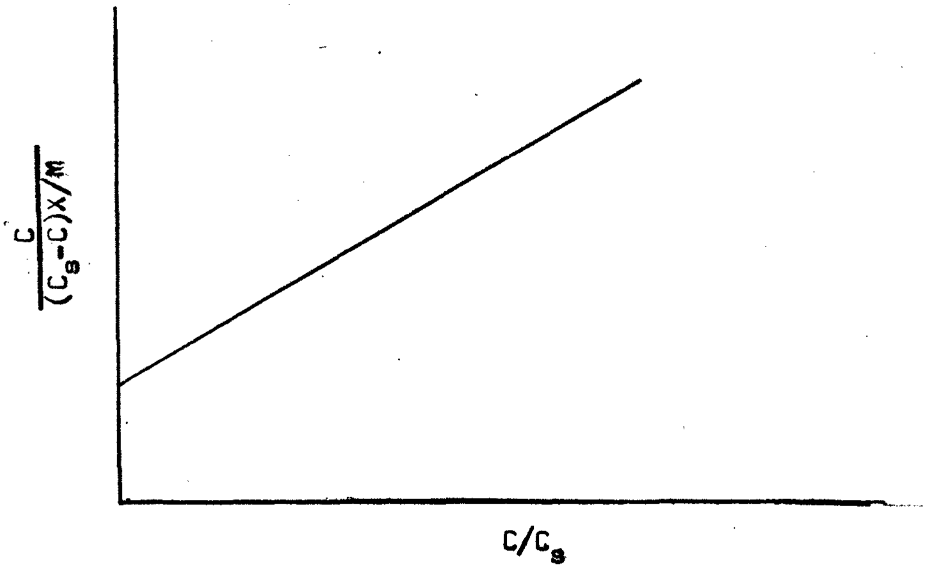


Figure Four
Plot of BET Equation

The Freundlich equation, derived from empirical considerations is the most widely used adsorption equation in wastewater treatment. It may be derived by assuming a heterogeneous surface with adsorption on each class of sites that obey the Langmuir equation.(15) At moderate concentrations the Freudlich equation generally agrees with that of Langmuir. Since adsorption is assumed to increase indefinitely with concentration, the equation is unsatisfactory at high concentrations. The equation is written:

$$\frac{X}{M} = KC^{1/n} \tag{4}$$

Where

K, n = empirical constants

The Freundlich equation is commonly written in linear form and plotted as in Figure Five.

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C \tag{5}$$

This form of the Freundlich equation is used for carbon isotherm tests. The intercept, K, is a measure of the adsorption capacity, while the slope, 1/n, defines the effect of concentration of adsorbate on adsorption.

An equation analogous to that of Freundlich has been developed by Mancy.(14) The mathmatical form of the equation remains the same but the parameters have been modified

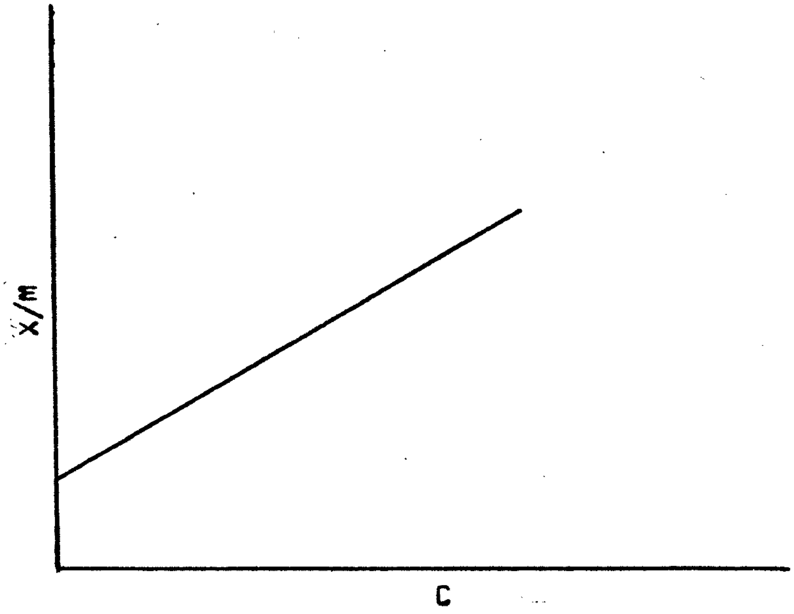


Figure Five
Plot of Freundlich Equation

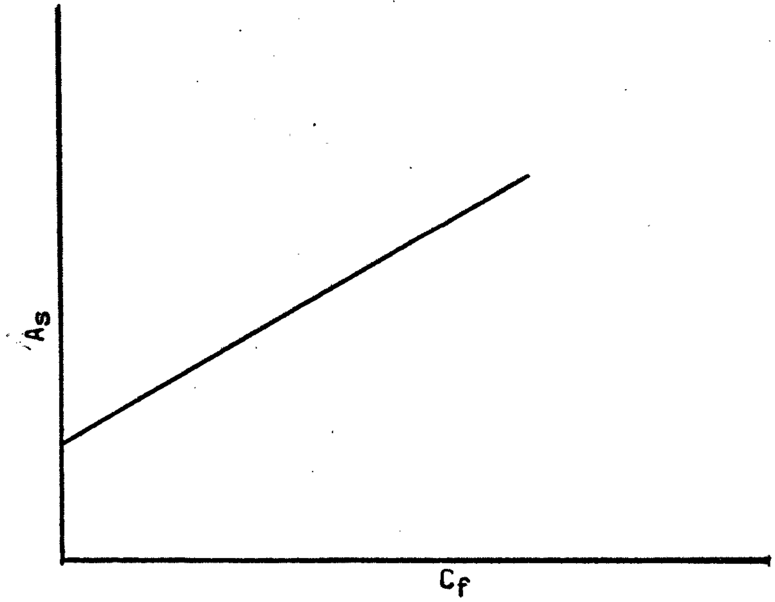


Figure Six
Plot of Mancy Equation

to accommodate flyash adsorption, which has a much lower capacity.

$$As = K\ C_f^n \qquad (6)$$

Where A_s = percent adsorbate removed

C_f = adsorbent concentration

K,n = empirical constants

The Mancy equation can be linearlized in the same manner as the Freundlich equation. A plot of this form is illustrated by Figure Six.

$$\log A_x = n \log C_f + \log K \qquad (7)$$

The slope of the plotted equation is a direct measure of the effect of ash concentration on removal of adsorbate. The intercept, K, is dependent on the extent of adsorbate removal for a given flyash.(14)

G. Continuous Adsorption Systems

The equations mentioned are applicable for the batch operations involved in the determination of adsorption isotherm. Continuous adsorption characteristics will be dependent on the contacting system chosen; however, the basic principles examplified by a fixed bed downflow column are equally pertinent to the other contact systems. In the fixed bed downflow system the adsorbate is passed through a stationary bed of adsorbent. This process is non-steady state since an increasing amount of solute is removed from the adsorbate during the operating cycle.

Figure Seven represents the concentration gradient or profile developed by the column effluent. This profile is called an adsorption wave.(29) As the solution passes into the bed rapid adsorption occurs in the top bed layer in equilbrium with the influent concentration. As solution continues to flow, the adsorption zone in equilbrium with the influent begins to move down the bed. At time (b) in the diagram the effluent concentration is still small but half of the bed is saturated. As the adsorption zone reaches the bottom of the bed, (c), the effluent concentration rises substantially for the first time. The system can now be said to have reached the break point. The adsorption zone will continue to fall until it passes through the bed bottom. As shown in (d) the effluent concentration will rise quickly until it is equal to the influent concentration. This portion of the graph (between (c) and (d)) is termed the break-through curve.

For the majority of adsorption systems used in wastewater treatment the break through curve will exhibit a characteristic S shape.(6) Many factors may cause deviations from the characteristic curve. The most common of these being: pH, solute concentration, flow rate, adsorption mechanism, and particle size.

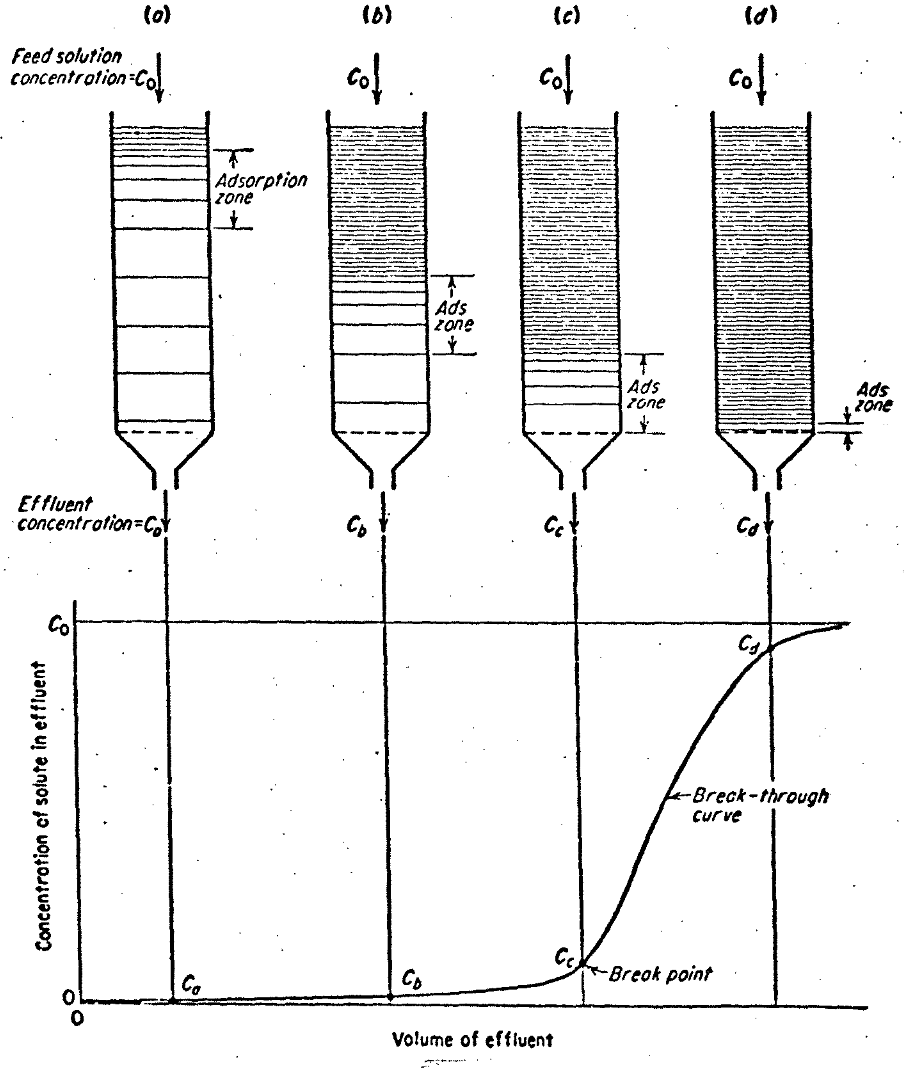


Figure Seven

The Adsorption Wave (29)

The critical bed depth is defined as the depth needed to just prevent penetration of the column bed by the adsorption zone at the time of initial contact. If the critical depth is greater than the actual bed depth the effluent concentration will rise sharply with initial operation until it equals the influent concentration. In general the time needed to reach the breakpoint will decrease with: increasing particle size, increasing pH, decreasing bed depth, increasing flow rate, and increasing influent concentration.

LITERATURE REVIEW

The search for adsorbents which could serve as cheap substitutes for activated carbon originated in the early sixties. At that time the adsorptive powers of carbon had long been well established, but an economic regenerative process was yet to be found. It was not until 1969 that the U.S. Public Health Service recognized activated carbon adsorption as an economically acceptable tertiary treatment method.(21) Therefore, it was necessary to find a cheaper adsorbent, preferably one which could be discarded after it become saturated.

The Advanced Waste Treatment Research Program (AWTR), initiated by the U.S. Public Health Service, investigated the possible use of many substances as adsorbents. An AWTR Summary Report(27) published in April of 1965 placed emphasis on the suitability of waste materials as adsorbents. Preliminary adsorption studies were conducted on coal fired flyash, ashes from sewage sludge incineration, and an activated aluminum oxide. Results indicated that the ashes possessed a low adsorptive capacity. These tests were followed by continuous column operations using an adsorbate rich in both COD and ABS. (Alkyl Benzene Sulfonate) Flyash was found to be a fairly good adsorbent producing reductions of 17 to 83%. Only a negligable amount of COD was contributed by the flyash. It was also recognized that the effectiveness of flyash as an adsorbent increases with the carbon content of the ash. Similar tests performed on other materials such as lignite, pretreated coals, Michigan peat, and steel mill slag found them unsuitable as adsorbents.

The U.S. Bureau of Mines conducted batch experiments on the adsorptive powers of various coals and flyashes at the same time as the AWTR Program. Their report(12), published in July of the same year, was in complete agreement with the findings of AWTR. Results of the coal isotherms were impossible to correlate but it was determined that pretreatment of coal had little positive effect on adsorption. The adsorptive nature of flyash was confirmed, removals of 17 to 83% being reported. Secondary effluent from a municipal treatment plant was used as an adsorbate. Flyash dosages ranged from 500 to 8,000 mg/l. Flyash effectiveness was again found to be dependent on ash carbon content. The untreated flyash, obtained from commercial power plants, added very small amounts of COD to the adsorbate.

Additional batch tests were performed on untreated flyash by the Philadelphia Water Department in 1967.(18) Final effluent from a municipal waste treatment facility was used as the adsorbate. The Philadelphia Electric

Company supplied all the flyash, which had a carbon content of 7.25%. The effect of flyash addition on COD, BOD, and suspended solids was evaluated. Ash concentrations ranged from 250 to 3,000 mg/l. Flyash was found to add appreciable amounts of COD and suspended solids to the effluent. No BOD addition was attributal to the flyash. After correction for control samples, flyash was reported to remove very little COD or BOD, the highest removal being 6% at a dosage of 450 mg/l. The suspended solids level was increased by any addition of flyash. It was concluded that very little COD could be removed by the addition of flyash.

A series of papers and graduate theses were prepared on flyash adsorption in a combined effort by the University of Cincinnati and the Cincinnati Gas and Electric Company. The two most pertinent articles of this series will be briefly outlined.

The first article(5) was a two part investigation into the parameters controlling COD Adsorption on flyash. Secondary effluent was again used as the adsorbate. The first part of the investigation consisted of batch testing to determine the effect of mixing time, initial COD, and flyash dosage on adsorption. These three parameters were logarithmically related with the removal of COD. These relationships can be expressed and plotted in forms similar to those of the Freudlich equation. The major part of COD removal occured during the first ten minutes of mixing: any extension of contact time resulted in insignificant COD removal. It was also determined that addition of a small amount of activated carbon greatly enhanced the adsorptive capacity of flyash. The second part of the study, a continuous flow pilot plant, was very poorly defined in the literature. The author, however, concluded that this study "demonstrated the applicability of flyash in a continuous flow system".

The second relevant article from Cincinnati(14) examined the adsorption kinectics of flyash using ABS as an adsorbate, Isotherm studies were conducted on five different types of flyash, the amount of adsorption increasing with the ash carbon content. As stated in the preceding article, adsorption occured rapidly upon initial contact then continued at considerably slower rates. A logarithmic relationship (see theory) was developed between percent removal of ABS and flyash dosage. This relationship combined with a similar relationship for contact time is the Mancy equation. (By making contact time a constant the Mancy equation reduces to the form used in this paper) Flyash efficiency, measured as the amount of COD adsorbed per unit weight of ash, was investigated over a large range of flyash concentrations. Efficiency was found to decrease quickly with increasing ash concentration. No attmept was made to compare the adsorptive capacity of the ash with other adsorbents.

In April of 1962, the Environmental Protection Agency working in unison with Canton Textile Mills initiated a feasibility study into the possible use of on-site flyash to remove dye from plant effluent water.(22) The flyash, from coal-fired boilers, had an unusually high carbon content of 46% by weight. Preliminary isotherm tests indicated that the ash possessed the ability to remove color. Attempts at continuous column operation in upflow, downflow, gravity feed, and pressurized systems were all unsuccessful, due to hydraulic problems. These failures were all attributal to clogging caused by the small particle size of flyash. Batch slurry contact processes proved successful removing 50% of the effluent color. Unfortunately, the amount of ash available at the plant was insufficient to provide complete color removal on a continuous basis. Studies evaluating the use of flyash as a coagulant aid on sludge were also highly successful.

Much of the investigation into flyash utilization as an adsorbent has occured outside of the United States.

This is especially true of industrial waste treatment. In Germany, flyash adsorption was successfully used to recover phenol from a power plant effluent.(13) Flyash was mixed with the waste liquid then lagooned, resulting in a 94% phenol reduction from an original concentration of 4,500 mg/1. Even India(1) has recently examined the effectiveness of ash adsorption. A relationship was developed for the design of flyash columns for detergent removal in a continuous fixed bed system. It was concluded that bed depth, adsorbate concentration, and flow rate have a marked effect on removal efficency.

The most exhaustive study on flyash adsorption was conducted in Prague using TNT as an adsorbate.(25) Two types of flyash were used: generator ash having a carbon content of 14.51% and furnace ash with a 9.31% carbon content. The influence of pH on adsorption was recognized, a factor overlooked in all American flyash literature. At an optimum pH of 6.8, generator ash adsorbed .801% of its weight in TNT from a solution containing 100 mg/1 of TNT. Furnace ash adsorbed .754% of TNT under the same conditions. Elution studies determined that very little TNT was desorbed from the ash, only .3% in the worst instance. Furnace ash was also used in a continuous trickling filter system. During a year of operation, 90% of all TNT passed into the filter was removed. A volume of effluent one hundred times greater in weight than the flyash was treated during this time. The total amount of TNT removed from the waste was far greater than the adsorptive capacity of the ash as indicated by isotherm tests. This is a common occurence in activated carbon adsorption studies.(3)

There has been very little literature published on flyash activation and its subsequent effect on adsorption. In the available literature two opposing views, both backed by experimental data, were discovered. Phosphate adsorption studies(7) on untreated and activated flyash were performed by the Chemical Engineering Department of Northwestern University. The flyash, obtained from Commonwealth Edison Company, was activated at various concentrations of either sodium hydroxide, nitric acid, or hydrochlonic acid. Maximum adsorption was attained with untreated flyash. It was reported that any attempt at treating flyash resulted in a decrease in the amount of phosphate adsorbed. The actual method of activation was unreported and no attempt was made to determine the effect of pH on the system. All data was plotted according to the Freundlich equation and at times proved highly erratic.

Dr. Donald Othmer, in a paper presented before the American Institute of Chemical Engineers(20), drew quite contradictory conclusions on the effect of ash activation. He advocated a simple total sewage treatment method which combined adsorption, coagulation and sedimentation into one continuous process. In this system flyash would be used to adsorb all impurities, then be precipated out of solution with the aid of polyelectrolytes. The flyash would first be acid treated to neutralize the metallic oxides present on the ash. This treated flyash, Othmer claims, is much more effective in removing phosphates, BOD, COD, and refractory materials from wastewater. Flyash is also a proven sludge conditioner, therefore the sludge produced by this process will have a lower water content than conventional sludge. This process has already been tried on several types of industrial and domestic wastewaters. The entire process can be completed in 15 to 30 minutes. An industrial waste containing a COD of 625 mg/l, phosphate level of 15.8 mg/l and turbidity of 115 Jackson units was reduced to contaminant levels of 9.4 mg/l, .05 mg/l, and 1 Jackson unit respectively. Similar treatment of a municipal waste resulted in a COD reduction of 98% phosphate removal of 97%, and a turbidity decrease of 99%. The cost and treatment efficiency of this method are far superior to conventional processes.

As mentioned in the Othmer article, flyash has long been known to posses excellent sludge conditioning properties.(28) Although sludge conditioning is itself not relevant to this review it may provide the solution to the problem of ultimate flyash disposal. The city of Cedar Rapids, Iowa conducted tests on the use of various additives to dewater sludge from their municipal treatment plant.(8) It was found that flyash, produced by a local power station, performed satisfactorily without the addition of any chemicals. Flyash was used on a one to one ratio with digested sludge. "Flyash itself is an excellent soil conditioner. It contains many trace elements which accelerate plant growth and has fertilizer value when mixed with sewage sludge". The final dewatered sludge and flyash mixture has been used as a fertilizer on city parks and golf courses. The savings to the city in both fertilizer and sludge disposal costs has been considerable.

EXPERIMENTAL

A. Purpose of the Investigation

Comparative tests were conducted on activated carbon, flyash, and activated flyash to determine their respective adsorptive characteristics.

B. Experimental Plan

Before initiation of the main body of experimentation, it was necessary to conduct several preliminary studies. The first group of these studies investigated the suitability and necessary dosage of several adsorbates. After chosing an adsorbate, the physical properties of each adsorbent were evaluated. Finally, the relative dosage of each adsorbent needed to achieve a measurable COD removal was determined.

Batch isotherm tests were performed on activated carbon, flyash, and activated flyash using the data obtained from the preliminary studies. An additional series of adsorption isotherms were made to examine the influence of pH on adsorption.

Adsorbent performance was evaluated on the basis of the isotherm results. It was then determined which adsorbents would be used in continuous column operation. Literature research had revealed a history of hydraulic problems connected with attempts at flyash column operation. A supply of sized bottom ash was prepared to be used in the event of a development of these hydraulic problems. This plan was later amended to include elution studies on all adsorbents, since column data suggested the possibility of desorption.

C. Materials

I. Adsorbate. An artificial sewage composed of a mixture of Campbell's Beef Broth and deionized water was used as the adsorbate. This was found to be an ideal solution to the problems of biological decay and uniformity of concentration. A case of soup, produced from the same bathc, was obtained and used to prepare fresh adsorbate each experimental day. A soup concentration of five milliliters of soup per liter of mixture was used throughout all experimentation. Appendix A lists the composition of this adsorbate, determined both experimentally and by information supplied by Campbell Soup Company.(19) At the dosage used, this soup mixture was found to exert a COD of 225 ± 30 mg/l and a total solids concentration of 310 ± 30 mg/l. A large amount of chlorides (46 mg/l), attributal to the heavy seasoning of soup, were found to be present in the adsorbate. Since chloride ions interfere with COD determination, it was necessary to use an inhibiting agent in the analysis.

Appendix A also contains composition data of a "typical" domestic sewage as envisioned by Metcalf and Eddy.(17) By comparison of these effluents it can easily be recognized that beef broth, in diluted form, closely resembles municipal sewage.

From the Campbell literature it was ascertained that the adsorbate was rich in protein (135 mg/l), which is amphoteric in nature. In the theory section of this paper the adsorption of amphoteric substances was reported to vary with pH of solution. This fact was recognized and experimentally confirmed. (Figure Ten) The influence of pH on adsorption was an important factor in this investigation.

II. Activated Carbon. Comercially available Calgon Filtrasorb 400 was used for all carbon experiments. This adsorbent has a carbon content of 91.5% and a mean particle diameter of .9 to 1.1 millimeters. The surface area of Filtrasorb 400 is reported to vary between 1000 to 1200 m2/g.(23) Appendix B lists the physical properties of all adsorbents. In addition to isotherm and column studies, carbon was also the adsorbent in the tests which determined pH influence. Carbon was dryed at 100°C for a minimum of two hours before being used.

III. Flyash and Bottom Ash. A large supply of flyash and bottom ash was simultaneously obtained from the Hudson Generating Plant of the Public Service Gas and Electric Company in Jersey City, New Jersey. At the time of sampling the Hudson station was operating on a combination coal-oil fuel mixture. This fact most probably accounts for the comparatively low carbon content of the ash. (3.31% flyash, 2.89% bottom ash) Appendix B lists the physical properties of flyash, activated flyash, and activated bottom ash. The pH of flyash as received was slightly higher (10 versus 9.8) than that of the carbon. The COD and leachable solids content of raw flyash are very high. Appendix B also contains a sieve analysis of both flyash and bottom ash. Flyash particles are extremely small in diameter, 82.6% passing through a U.S. number 200 sieve. (74 microns) No attempt was made to size particles below this diameter. The surface area of flyash was also not determined, however literature values were reported to range from 3,310 to 6420 cm^2/g.(14)

The composition of flyash will obviously be dependent on the type of fuel used and the degree of combustion developed in the furnace. Although economic considerations prevented an anaylsis of flyash composition, many such analyses are available in the literature. (8) (18) Appendix C reproduces five flyash analyses from typical generating stations. While flyash composition varies, the similarity of content is apparent. A more complete analysis is also included to illustrate that flyash contains several trace elements beneficial for plant growth.

All ashes, including those treated, were dryed at 100°C for a minimum of two hours before being used. It should also be noted that untreated flyash exhibited evidence on the presence of nitrites which are known to interfere in COD determination. Sulfamic acid was used in all COD tests to eliminate this interference.

D. Apparatus

I. Analytical.

1. Analytical Balance, Voland Model 220R
2. Laboratory Oven, Grieve Corporation Model LW200C
3. Furnace, Thermolyne Type 1400
4. Dessicator, Calcium Chloride
5. pH meter, Corning Model 12
6. Demineralizer, Crystalab Model DI-3
7. U.S. Standard Sieves
8. Glassware and hardware as described in *Standard Methods*(26)

II. Isotherm.

1. Shaker, Burrell Wrist Action, Model 75-775
2. Glassware and hardware as described in *Advanced Wastewater Treatment*(3)

III. Continuous Column. These numbers refer to items in Figure Eight.

1. Mixer, Lightnin Model CV4
2. Mixing tank, 50 gallon stainless steel
3. Pump, Eastern Industries Model M41150
4. Reservoir, 5 gallon expoxied chemical can equipped with sightglass
5. Mixer, T-Line Stirrer Model W105
6. Rotometer, Fisher and Porter, two models used (Appendix D)
7. Column, plexiglass (Figure Nine)
8. Effluent sample tap
9. Tank drain valve
10. Rotometer control valve
11. Pump control valve

E. Methods of Procedure

I. Analytical Procedures.

1. Chemical Oxygern Demand, Standard Methods(26) test 220 (Both mercuric sulfate and sulfamic acid were added to eliminate interferences)
2. Total Solids, Standard Methods(26) test 148A
3. Chloride, Mecuric Nitrate method, Hach Water Handbook (Standard Methods test 240)
4. Nitrate, Diazotization mentod, Hach Water Handbook (Standard Methods test 240)

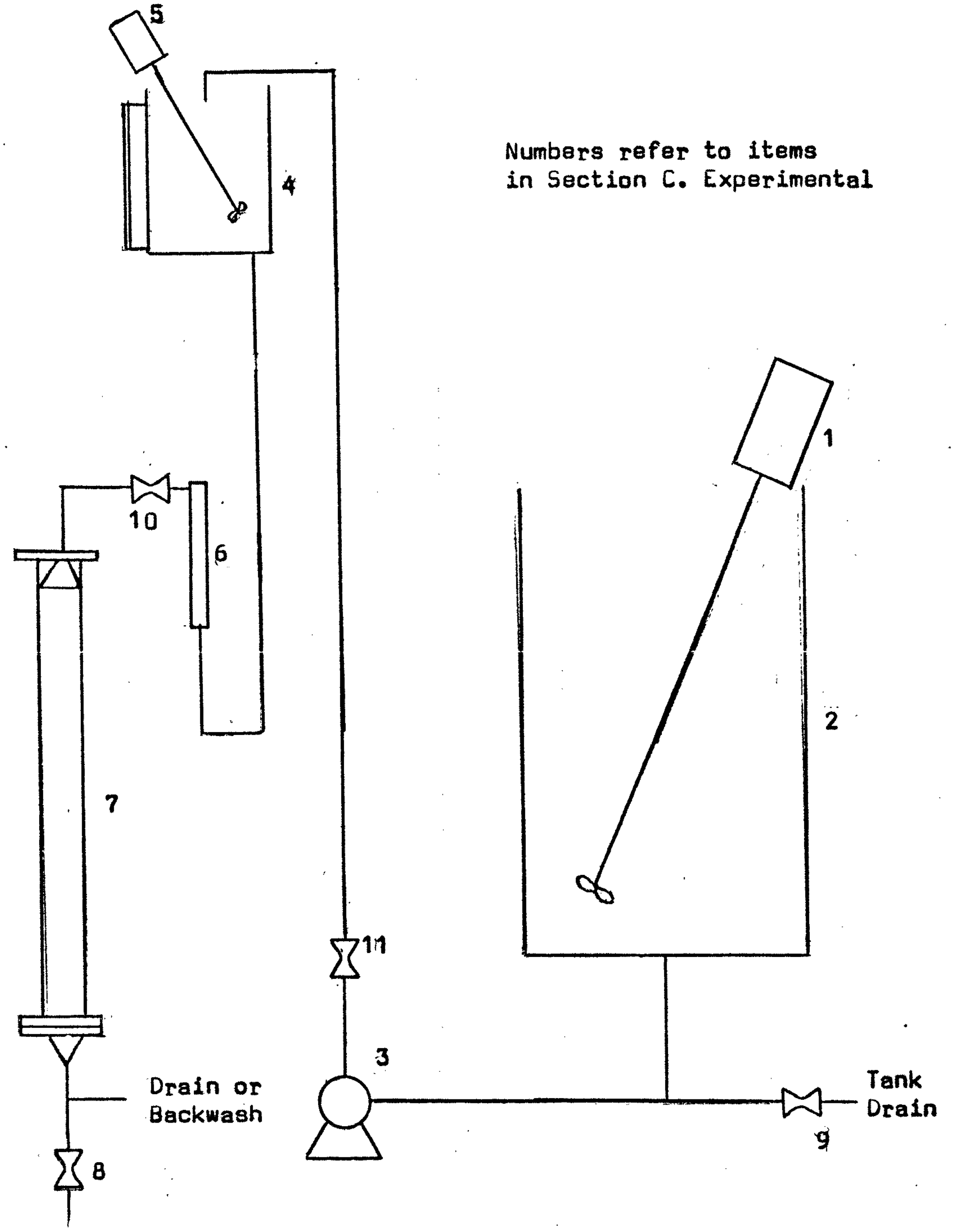


Figure Eight

Continuous Adsorption System

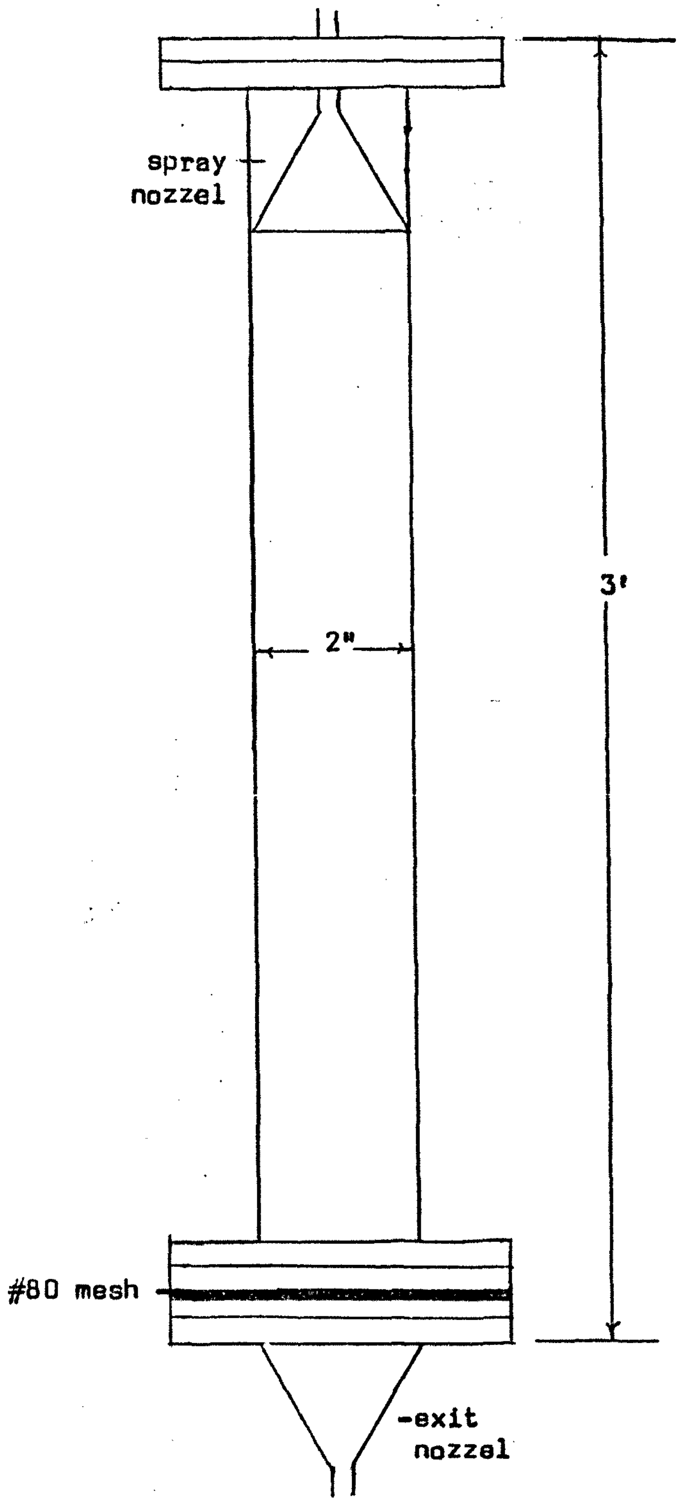


Figure Nine

Column Detail

5. Apparant Density, Advanced Wastewater Treatment(3)
6. Sieve Analysis, Particle Size: Measurement, Interpretation, and Application(11)
7. pH, liquids, Standard Methods(26) test 221
8. pH, adsorbents, Carbon and Graphite Handbook(16) test 151
9. Carbon Content, American Society for Testing Material Standards Part 3, 1955

II. Sample Preservation. COD samples were preserved according to section 200B of Standard Methods(26) All other tests were performed at the time of sampling.

III. Adsorbate Preparation.

1. batch - Five milliliters of soup measured by pipet, were prepared with deionized water in a one liter volumetric flask daily.
2. Continuous - The mixing tank was filled to a predetermined depth with tap water. A graduated cylinder was used to deposit the exact amount of soup needed to obtain the batch concentration.

IV. Activation Procedure.

1. Flyash - Approximately thirty milliliters of

flyash were added to two hundred milliliters of deionized water. This mixture was then placed inside of a laboratory hood. (Caution: H_2S gas is released by flyash during activation) After the careful addition of fifty milliliters of concentrated sulfuric acid, the solution was slowly stirred for one hour. At that time the mixture was allowed to settle. The subsequent flyash slurry was then repeatedly washed with deionized water until the solution pH was lowered to six units. The slurry was dryed overnight at 100°.

2. Bottom ash - The activation of bottom ash was identical to that of flyash with the exception of washing. The larger particle bottom ash was retained and rinsed on a sieve rather than being washed in a slurry.

V. Isotherm Procedure:

Advanced Wastewater Treatment(3)

VI. Continuous Column Operation. Dry adsorbent was loaded through the top of the column. After acheiving the desired bed depth, the column was first fluidized, then allowed to drain resettling the bed. A predetermined amount of adsorbate was prepared in the mixing tank and pumped into the reservoir at regular intervals. The reservoir level was never allowed to drop below five liters. The rotometer control valve was used to maintain a constant flowrate into the bed. Effluent samples were taken from the sample tap periodically. After determining their pH, these samples were preserved for COD analysis. Solid samples were also taken at larger intervals. An adsorbate sample was taken from the mixing tank both before and after the run. At the completion of each run the system was thoroughly flushed with tap water. Carbon and flyash runs were identical with the exceptions of flowrates and sampling times. These are recorded on the data sheet of each run.

VII. Elution Studies. This procedure closely followed that of the isotherm studies. A correction factor was experimentally determined to account for adsorbate carryover on the filter paper.

DATA

Table I.

pH Influence on Adsorption

Sample	Adsorbent Conc.	pH_i	pH_f	C_f	% Rem.
52	0	5.7	5.7	216	-
53	1,000	5.7	6.9	138	36.1
54	1,000	3.0	2.7	156	27.8
55	1,000	4.5	5.8	142	34.3
56	1,000	9.5	8.5	156	27.8
57	1,000	9.0	7.5	144	33.3
58	1,000	8.0	7.0	140	35.2
59	1,000	10.0	9.2	160	25.9
60	0	5.3	5.3	220	-
66	1,000	10.8	10.3	168	23.6
67	1,000	11.5	11.0	171	22.3

Temperature = 23.5°C

Activated Carbon used as adsorbent

Table II.

Activated Carbon Isotherms

Run IC-1

Sample	Carbon Conc.	C_f	X	X/M	$\frac{C}{X/M}$	% Rem.
32	0	198.0	-	-	-	-
33	1,000	126.0	72.0	.072	1,750	36.4
34	2,000	81.8	116.2	.058	1,410	58.7
35	3,000	59.0	138.9	.046	1,283	70.2
36	4,000	47.3	150.7	.037	1,255	76.1
37	5,000	34.7	163.3	.033	1,061	82.5

Run IC-2

Sample	Carbon Conc.	C_f	X	X/M	$\frac{C}{X/M}$	% Rem.	pH
60	0	220.0	-	-	-	-	5.3
61	1,000	141.0	79.0	.079	1,785	35.9	5.8
62	2,000	98.0	122.0	.061	1,607	55.4	6.7
63	3,000	80.0	140.0	.047	1,713	63.6	7.0
64	4,000	70.0	150.0	.038	1,867	68.2	7.2
65	5,000	65.0	155.0	.031	2,097	70.5	7.6

Run IC-3

Sample	Carbon Conc.	C_f	X	X/M	$\frac{C}{X/M}$	% Rem.
21	0	235.2	-	-	-	-
22	1,000	149.6	85.6	.086	1,740	36.4
23	2,000	110.0	125.2	.063	1,746	53.2
24	3,000	78.0	157.2	.052	1,500	66.8
25	4,000	68.0	167.2	.042	1,619	71.1
26	5,000	54.0	181.2	.036	1,500	77.0

Table III.

Untreated Flyash Isotherms

Run IF-1

Sample	Ash Conc.	C_f	X	X/M	$\frac{C}{X/M}$	%Rem.	pH
40	0	225.7	-	-	-	-	6.0
41	10,000	222.7	3.0	3.00x10^{-4}	7.42x10^{5}	1.33	8.6
42	30,000	214.7	11.0	3.67x10^{-4}	5.85x10^{5}	4.87	9.2
43	50,000	204.8	20.9	4.18x10^{-4}	4.90x10^{5}	9.26	9.4
44	70,000	194.8	30.9	4.40x10^{-4}	4.40x10^{5}	13.69	9.6
45	100,000	178.9	46.8	4.68x10^{-4}	3.82x10^{5}	20.70	9.8

Percent COD Removal Corrected to a pH of 6.0

Sample	% Rem.
40	-
41	7.83
42	13.37
43	18.16
44	23.19
45	30.60

Run IF-2

Sample	Ash Conc.	C_f	X	X/M	$\frac{C}{X/M}$	%Rem.
103	0	203.8	-	-	-	-
104	10,000	200.8	3.04	3.04x10^{-4}	6.60x10^{5}	1.49
105	30,000	192.1	11.76	3.92x10^{-4}	4.90x10^{5}	5.77
106	50,000	184.2	19.60	3.92x10^{-4}	4.70x10^{5}	9.62
107	70,000	176.4	27.47	3.92x10^{-4}	4.50x10^{5}	13.46
108	100,000	164.0	39.84	3.98x10^{-4}	4.10x10^{5}	19.54

Table IV.

Treated Flyash Isotherms

Run IT-1

Sample	Ash Conc.	C_f	X	X/M	$\frac{C}{X/M}$	%Rem.	pH
46	0	221.8	-	-	-	-	6.4
47	10,000	217.7	4.1	4.1×10^{-4}	5.3×10^{5}	1.85	6.4
48	30,000	205.6	16.2	5.4×10^{-4}	3.8×10^{5}	7.30	6.4
49	50,000	195.6	26.2	5.3×10^{-4}	3.7×10^{5}	11.80	6.4
50	70,000	171.4	50.4	7.2×10^{-4}	2.4×10^{5}	22.70	6.0
51	100,000	155.2	66.8	6.7×10^{-4}	2.3×10^{5}	30.03	6.1

Run IT-2

Sample	Ash Conc.	C_f	X	X/M	$\frac{C}{X/M}$	%Rem.
75	0	224.6	-	-	-	-
76	10,000	220.0	4.6	4.6×10^{-4}	4.8×10^{5}	2.02
77	30,000	208.0	16.6	5.5×10^{-4}	3.8×10^{5}	7.37
78	50,000	187.6	37.0	7.4×10^{-4}	2.5×10^{5}	16.46
79	70,000	174.0	50.6	7.2×10^{-4}	2.4×10^{5}	22.50
80	100,000	153.7	70.9	7.1×10^{-4}	2.2×10^{5}	31.55

Run IT-3

Sample	Ash Conc.	C_f	X	X/M	$\frac{C}{X/M}$	%Rem.
68	0	223.1	-	-	-	-
69	5,000	219.1	4.0	8.0×10^{-4}	2.7×10^{5}	1.80
70	10,000	217.1	6.0	6.0×10^{-4}	3.6×10^{5}	2.70
71	20,000	213.1	10.0	5.0×10^{-4}	4.0×10^{5}	4.50
72	30,000	207.2	15.9	5.3×10^{-4}	3.9×10^{5}	7.13
73	40,000	197.2	25.9	6.5×10^{-4}	3.1×10^{5}	11.60

Table V.

Column Test Activated Carbon - CC-1

bed depth = 1 foot

flow = 10%
= 5.2 ml/sec.

Sample	Time	Volume	C_f	pH	Solids	COD_{ap}	COD_{ad}
1	10:25	-	213.0	6.5**	405	-	-
2	10:25	1.560	70.0	8.0*		332.3	223.0
3	10:41	6.552	91.4			1395.6	829.8
4	10:57	11.544	108.9		280	2458.9	1349.2
5	11:13	16.536	116.7	7.0*		3522.2	1829.8
6	11:29	21.528	130.3	7.0*		4585.5	2242.4
7	11:45	26.520	127.4			5648.8	2719.6
8	12:01	31.512	132.0	6.8*		6712.1	3123.9
9	12:17	36.504	131.3			7775.4	3531.8
10	12:33	41.496	138.5		182	8838.7	3903.7
11	12:49	46.488	137.2	6.8**		9901.9	4282.1
12	1:05	51.480	138.6			10965.2	4653.5
13	1:21	56.472	159.5			12028.5	4920.6
14	1:37	61.464	158.7			13091.8	5191.4
15	1:53	66.456	158.7		165	14155.1	5462.2
16	2:09	71.448	160.7	6.5**		15218.4	5723.2
17	2:25	76.440	169.2			16281.7	5941.6
18	2:41	81.432	166.6			17345.0	6173.2
19	2:57	86.424	175.0			18408.3	6362.9
20	3:13	91.416	176.0			19471.6	6547.5
21	3:29	96.408	176.0			20534.9	6732.3
22	3:45	101.400	181.0		255	21598.2	6892.0
23	Tank Sample		218.0	6.5**	-	-	-

* pH paper used

** pH meter used

Table VI.

Column Test Activated Carbon - CC-2

bed depth = 10.5 inches

flow = 10%
= 5.1 ml/sec.

Sample	Time	Volume	Cf	pH	Solids
24	Tank Sample		216.0	6.0	321
25	10:20	1.560	69.4	10.0	269
26	10:36	6.552	99.2	9.8	
27	10:52	11.544	115.1	9.7	
28	11:08	16.536	131.0	9.5	
29	11:24	21.528	136.1	9.2	201
30	11:40	26.520	239.0	9.0	
31	11:56	31.512	142.8	8.8	
32	12:12	36.504	144.8	8.7	
33	12:28	41.496	140.5	8.3	
34	12:44	46.488	156.7	8.2	
35	1:00	51.480	155.0	8.0	
36	1:16	56.472	158.0	7.9	228
37	1:32	61.464	158.0	7.8	
38	1:48	66.456	162.0	7.7	
39	2:04	71.448	165.7	7.6	
40	2:20	76.440	164.0	7.5	
41	2:36	81.432	165.0	7.5	
42	2:52	86.424	168.0	7.5	
43	3:08	91.416	164.0	7.5	
44	3:24	96.408	172.0	7.5	210
45	3:40	101.400	172.0	7.4	
46	3:56	106.392	167.5	7.4	
47	4:12	111.384	175.5	7.0	
48	4:28	116.376	180.0	7.0	293
49	Tank Sample		228.0	7.0	

Table VII.

Column Test Treated Bottom Ash - TC-1

bed depth = 1 foot

flow = 8%
= 4.16 ml/sec.

pH_{flyash} = 7.0

rotometer #1

Sample	Time	Volume	C_f	pH	Solids
71	Tank Sample		203.1	6.7	377
72	12:17	.4992	85.2		
73	12:19	.9984	190.0	6.5	205
74	12:21	1.4976	214.0		
75	12:23	1.9968	225.0		
76	12:25	2.4960	225.0	6.8	327
77	12:27	2.9952	217.4		
78	12:29	3.4944	228.6		
79	12:31	3.9936	221.3	6.7	369
80	12:33	4.4928	227.2		
81	12:35	4.9920	213.4		
82	12:37	5.4912	213.4		
83	12:39	5.9904	224.5	6.7	286
84	12:41	6.4896	240.0		
85	12:43	6.9888	217.4		
86	12:45	7.4880	217.4		
87	12:47	7.9872	217.4		
88	12:49	8.4864	209.5	6.8	367
89	12:51	8.9856	217.4		
90	12:53	9.4848	209.5		
91	12:55	9.9840	203.5		
92	12:57	10.4832	207.5	7.0	428

Table VIII.

Column Test Treated Bottomash - TC-2

bed depth = 12 inches

flow = 14%
= 2.1 ml/sec.

rotometer #2

Sample	Time	Volume	C_f	pH	Solids	COD_{ap}	COD_{ad}
101	Tank Sample		217.0	6.0	377	-	-
102	10:01	.126	0	6.0		27.34	27.34
103	:02	.252	56.4	6.0	196	54.68	47.58
104	:03	.378	101.5	6.0		82.03	62.13
105	:04	.504	138.0	6.0		109.37	72.08
106	:05	.630	146.6	6.0	213	136.71	80.95
107	:06	.756	164.0	6.0		164.05	87.63
108	:07	.882	172.0	6.0		191.39	93.30
109	:08	1.008	176.0	6.0		218.74	98.47
110	:09	1.134	186.0	6.0	263	246.08	102.38
111	:10	1.260	186.0	6.0		273.42	106.29
112	:11	1.386	195.0	6.0		300.76	109.06
113	:12	1.512	202.0	6.0	282	328.10	110.95
114	:13	1.638	204.0	6.0		355.45	112.59
115	:14	1.764	204.0	6.0		382.79	114.23
116	:15	1.890	206.0	6.0		410.13	115.62
117	:16	2.016	216.0	6.0	326	437.47	115.75

Table IX.

Elution Studies

Sample	Adsorbent	Adsorbent Conc.	C_o	C_f	COD Adsorbed
118	Blank	-	-	204.5	-
119	Carbon	200	204.5	85.3	119.2
120	Carbon	400	204.5	56.2	148.3
121	Act. Ash	50,000	204.5	164.0	40.5
122	Act. Ash	70,000	204.5	154.0	50.5
123	Ash	70,000	204.5	170.5	34.0
97	Ash	50,000	214.3	186.5	27.8

Sample	Elute Conc.	Corrected Conc.	% Loss	2nd Elute Conc.
118	31.00	-	-	0
119	34.88	3.88	3.26	0
120	40.70	9.70	6.54	2
121	29.07	-	0	0
122	29.07	-	0	0
123	54.26	23.26	68.40	0
97	35.87	15.87	57.10	0

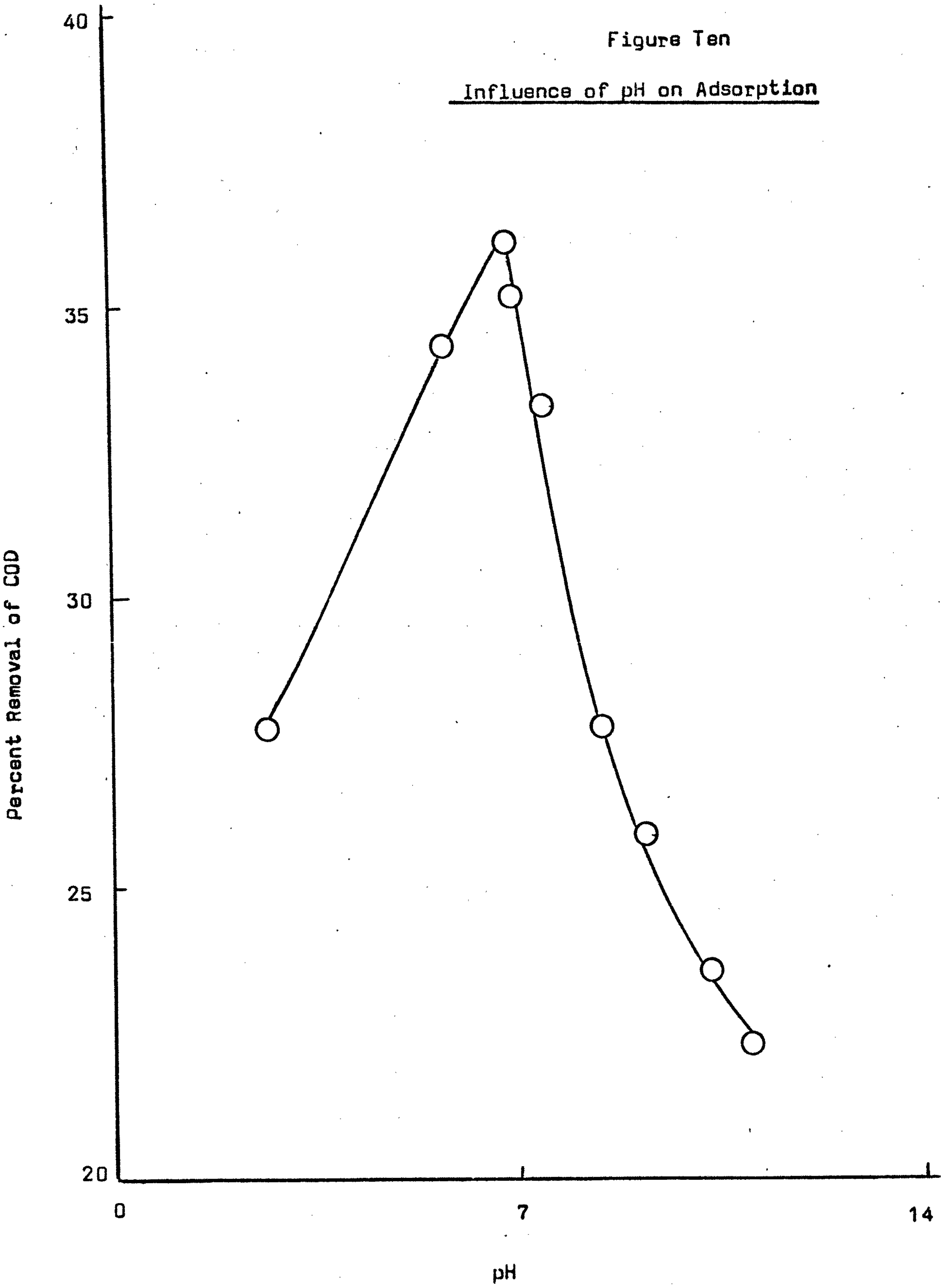


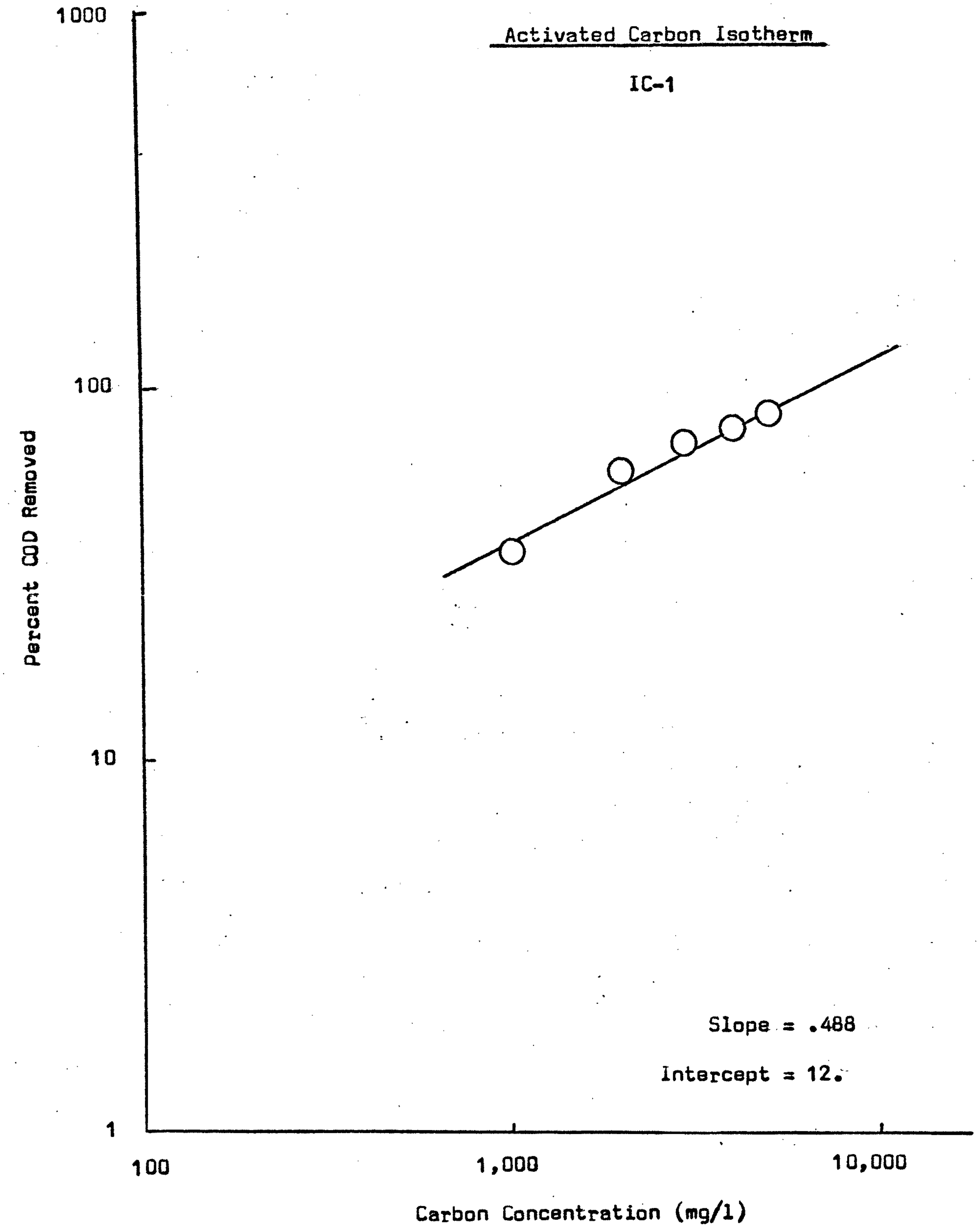
Figure Ten

Influence of pH on Adsorption

Figure Eleven

Activated Carbon Isotherm

IC-1



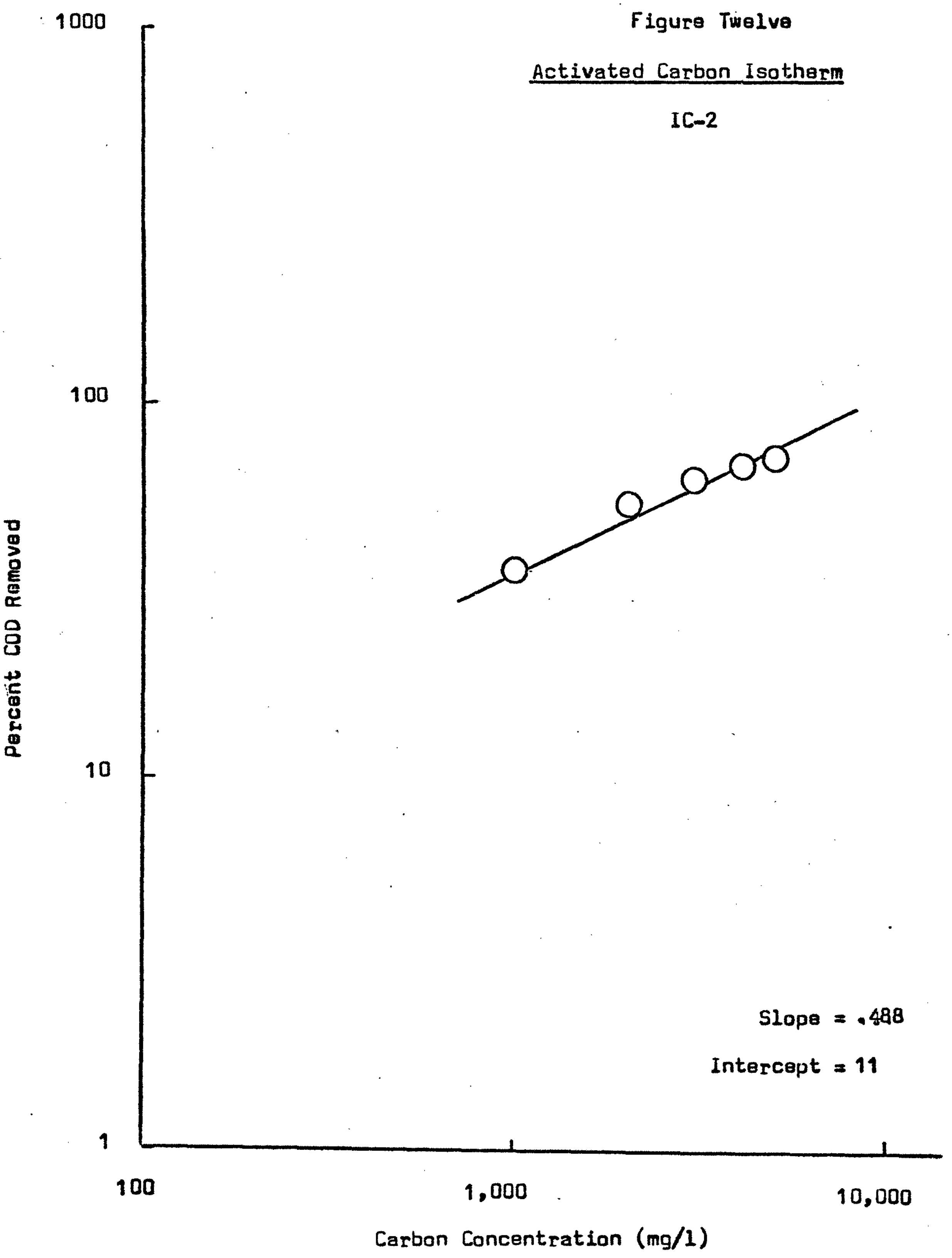


Figure Twelve

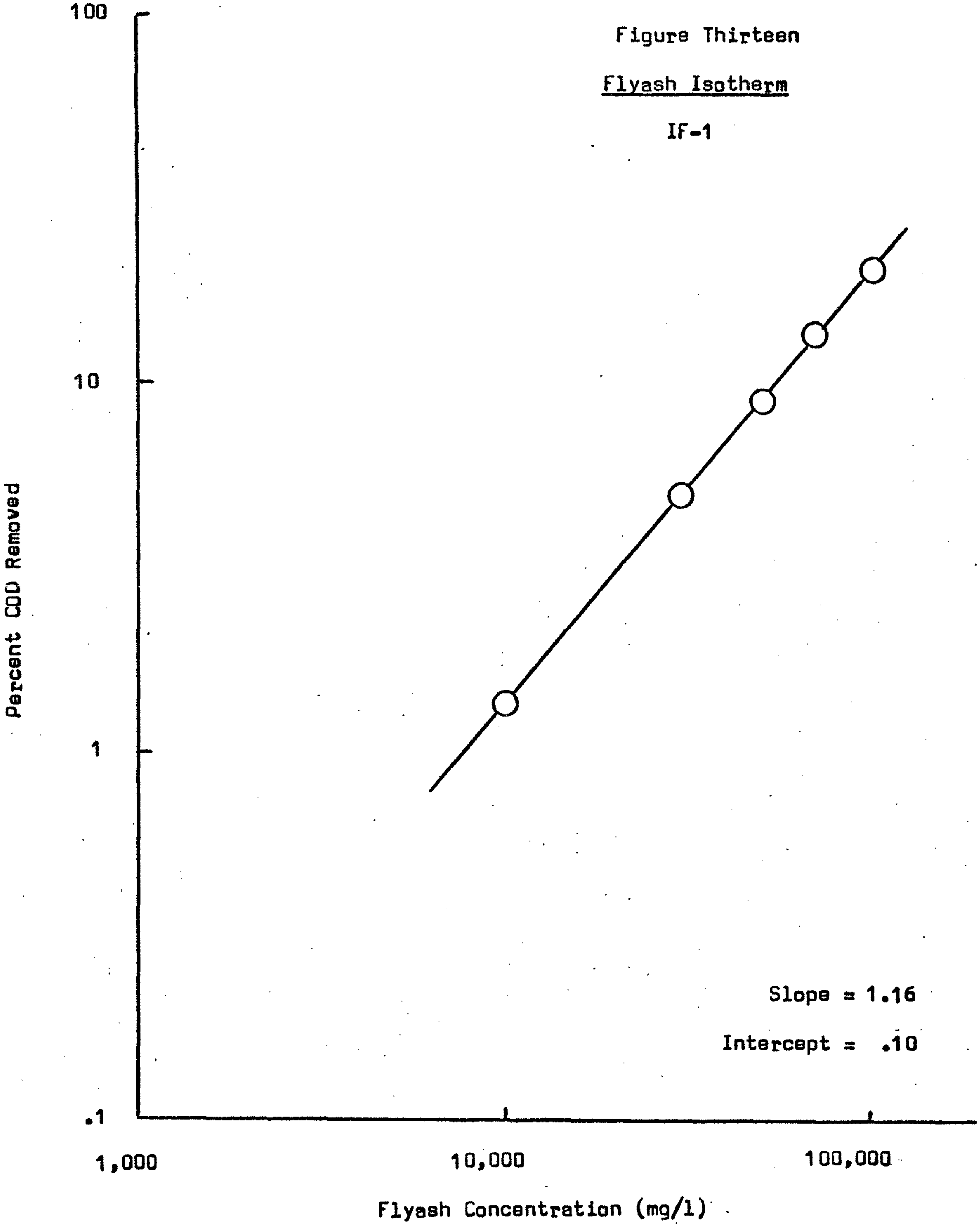
Activated Carbon Isotherm

IC-2

Figure Thirteen

Flyash Isotherm

IF-1



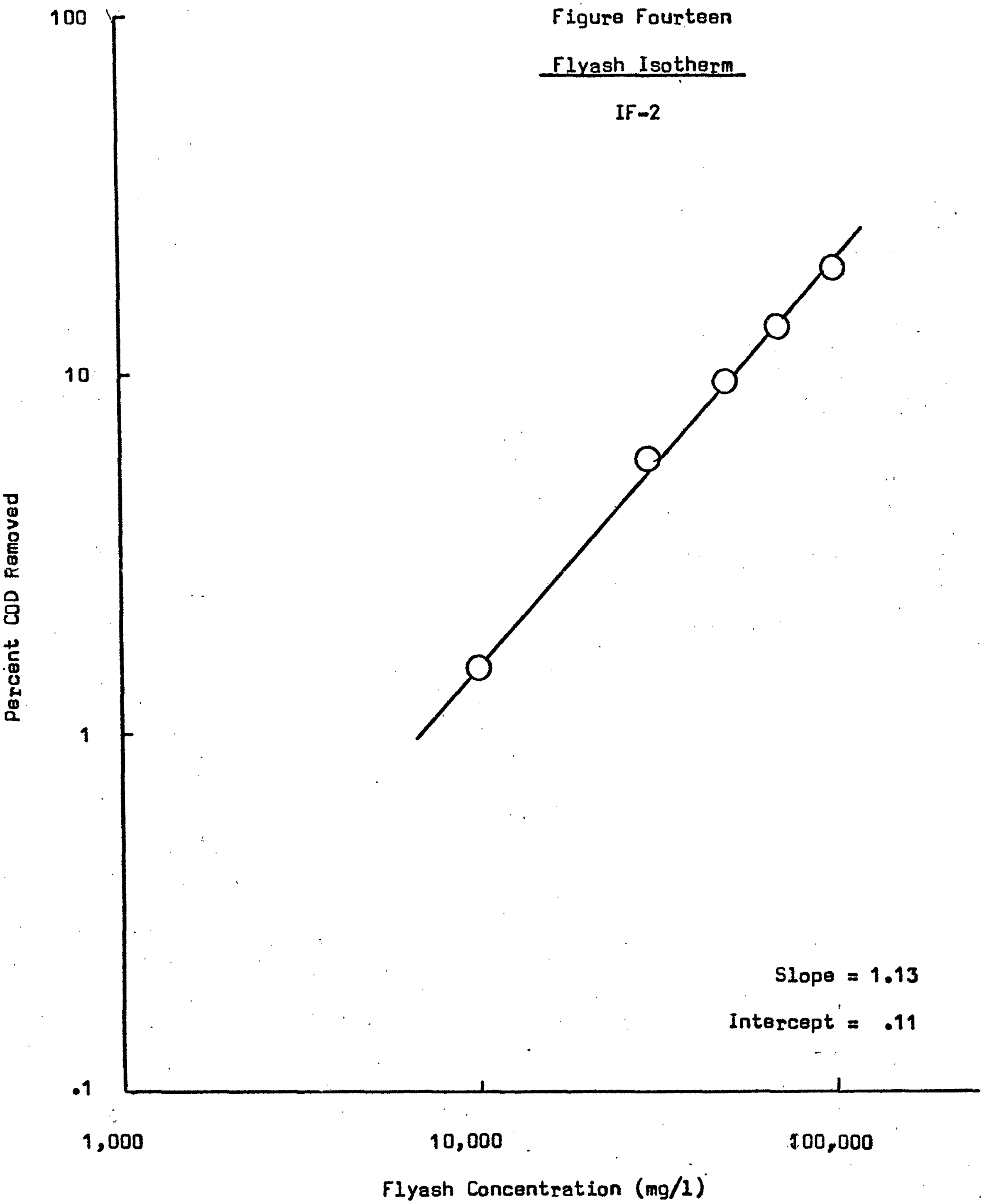


Figure Fourteen

Flyash Isotherm

IF-2

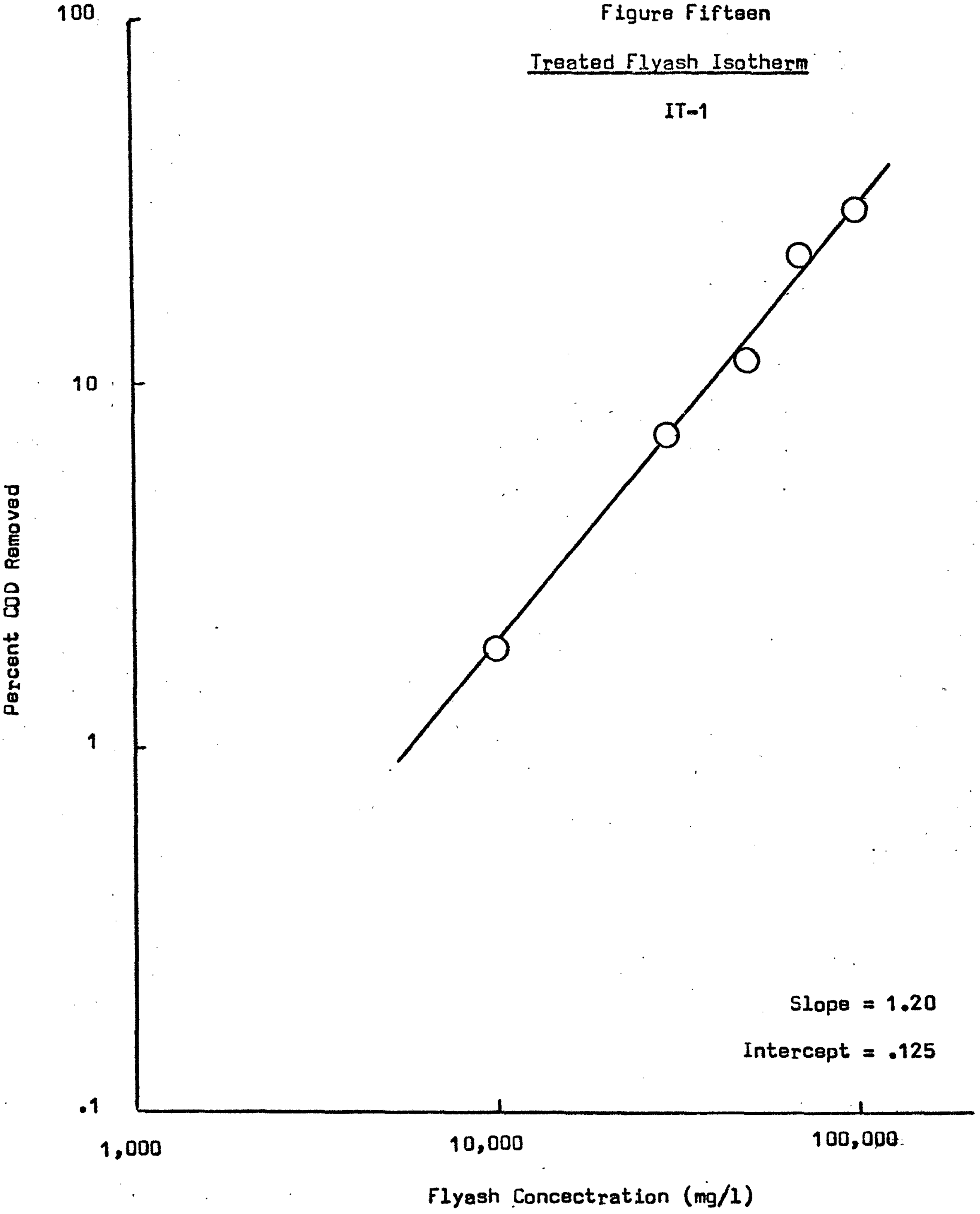
Slope = 1.13

Intercept = .11

Figure Fifteen

Treated Flyash Isotherm

IT-1



Slope = 1.20

Intercept = .125

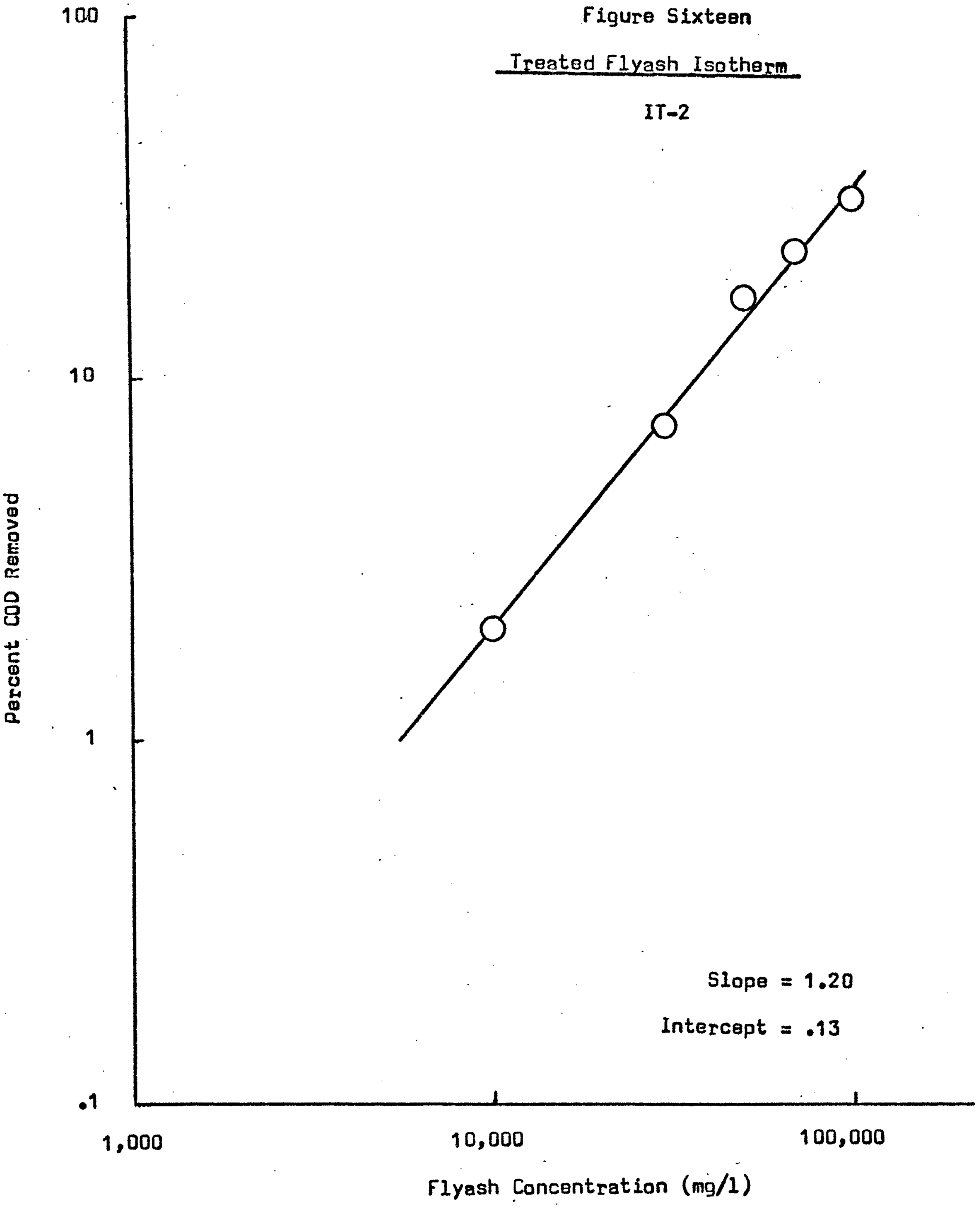
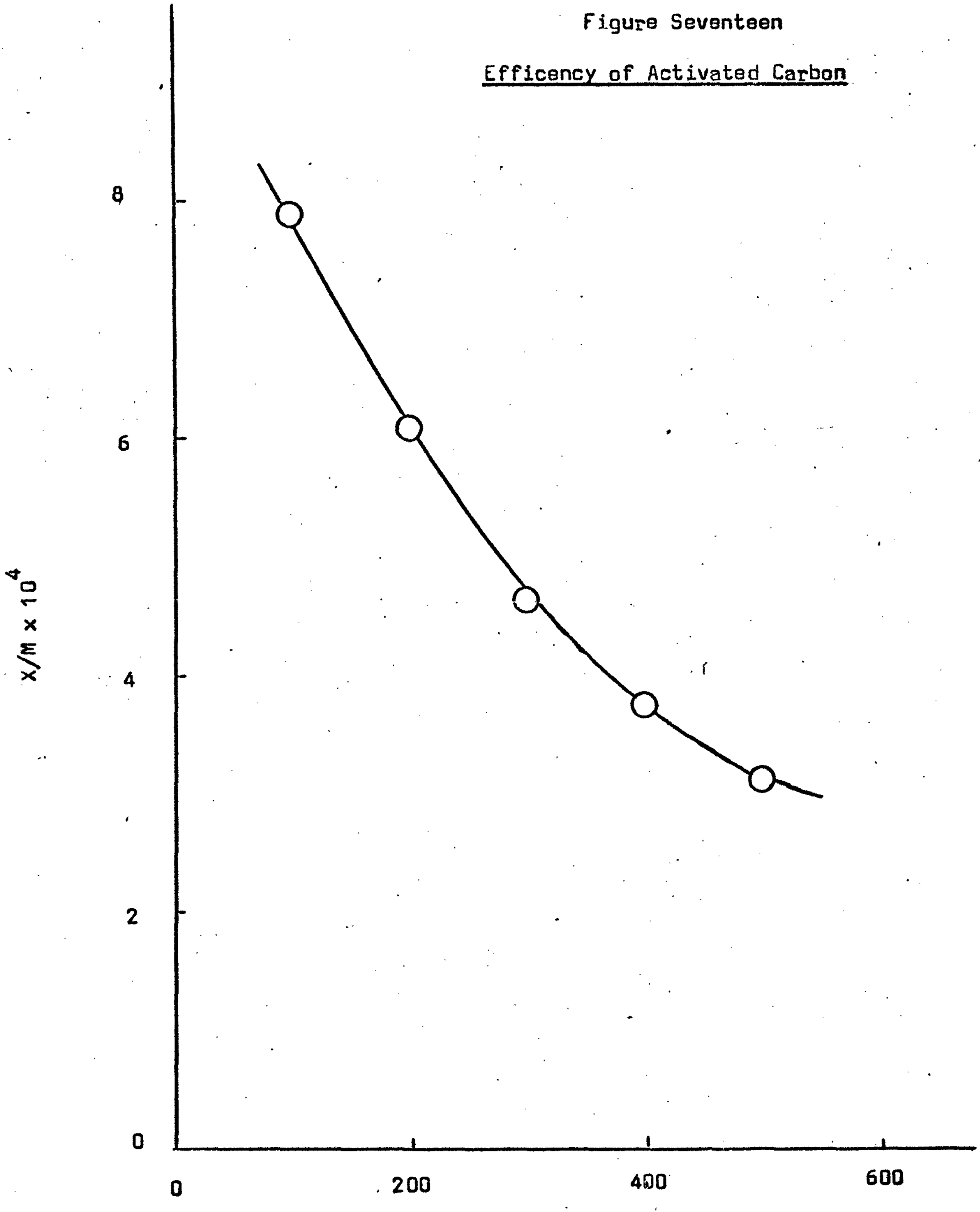


Figure Sixteen
Treated Flyash Isotherm
IT-2
100
10
1
.1
Percent COD Removed
1,000
10,000
100,000
Flyash Concentration (mg/l)
Slope = 1.20
Intercept = .13

Figure Seventeen

Efficency of Activated Carbon



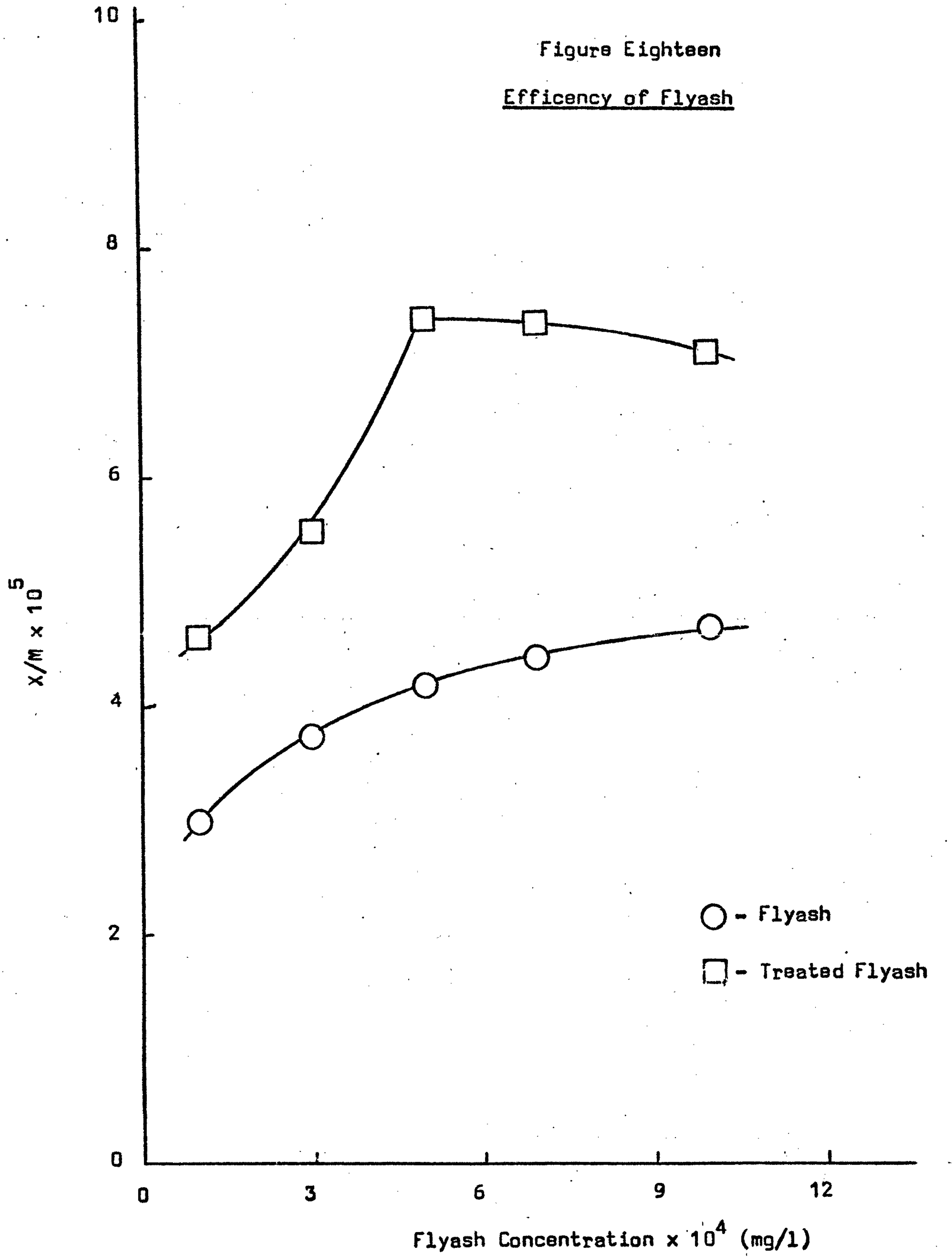


Figure Eighteen

Efficency of Flyash

Figure Nineteen

Isotherm Plot

Runs: IT-2, IF-2, IC-1

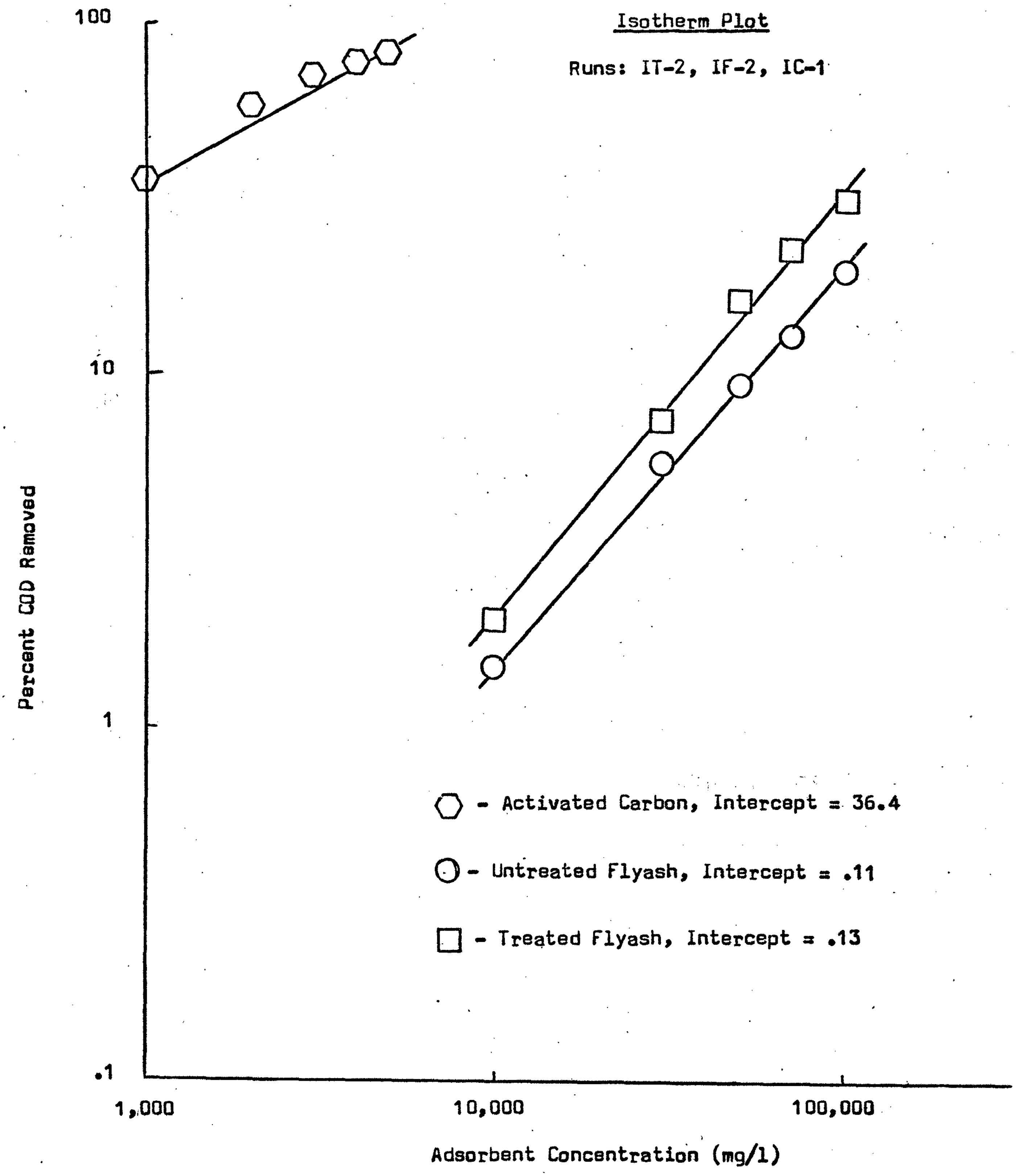
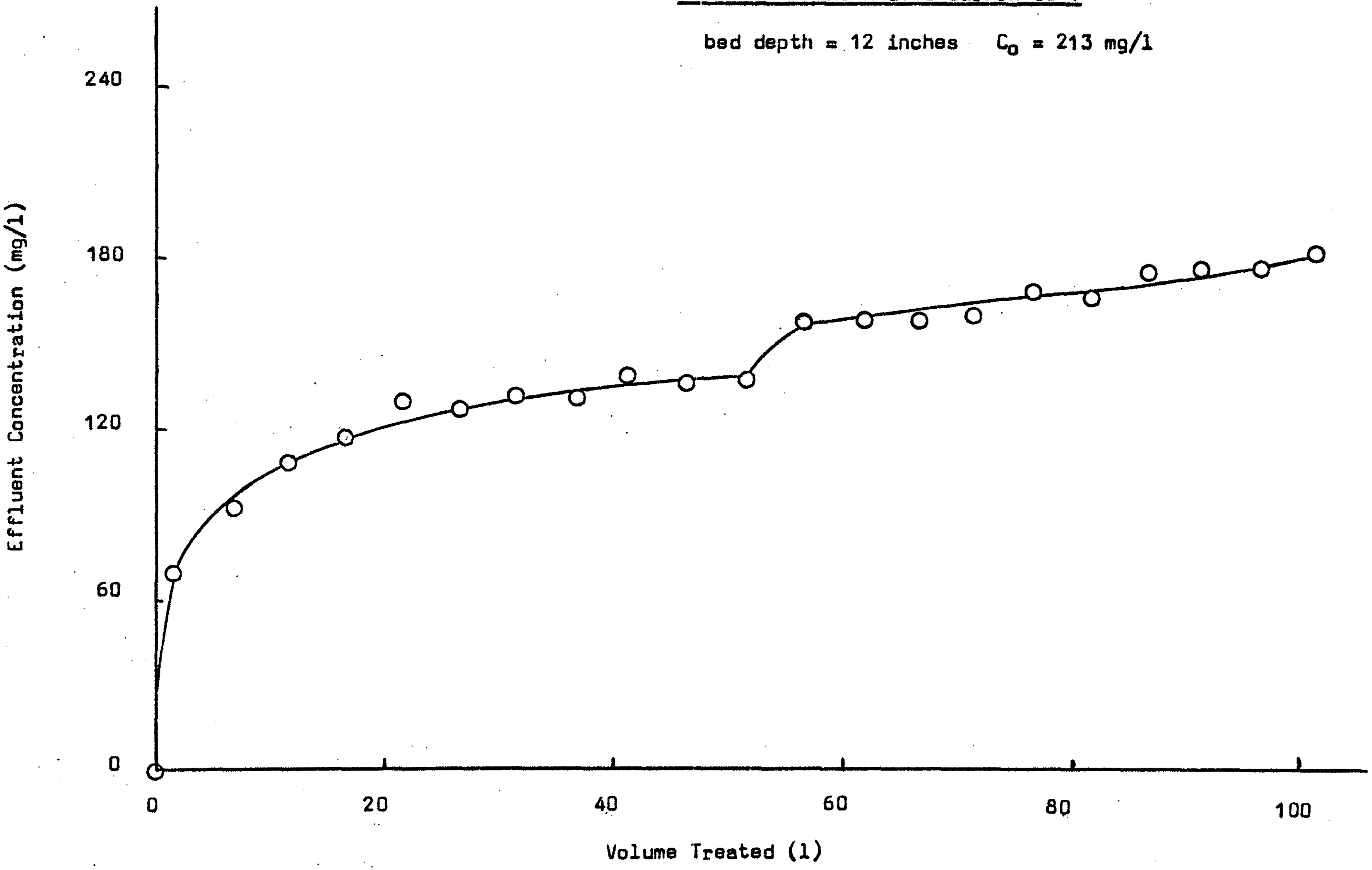


Figure Twenty

Column Test Activated Carbon CC-1

bed depth = 12 inches C_o = 213 mg/l



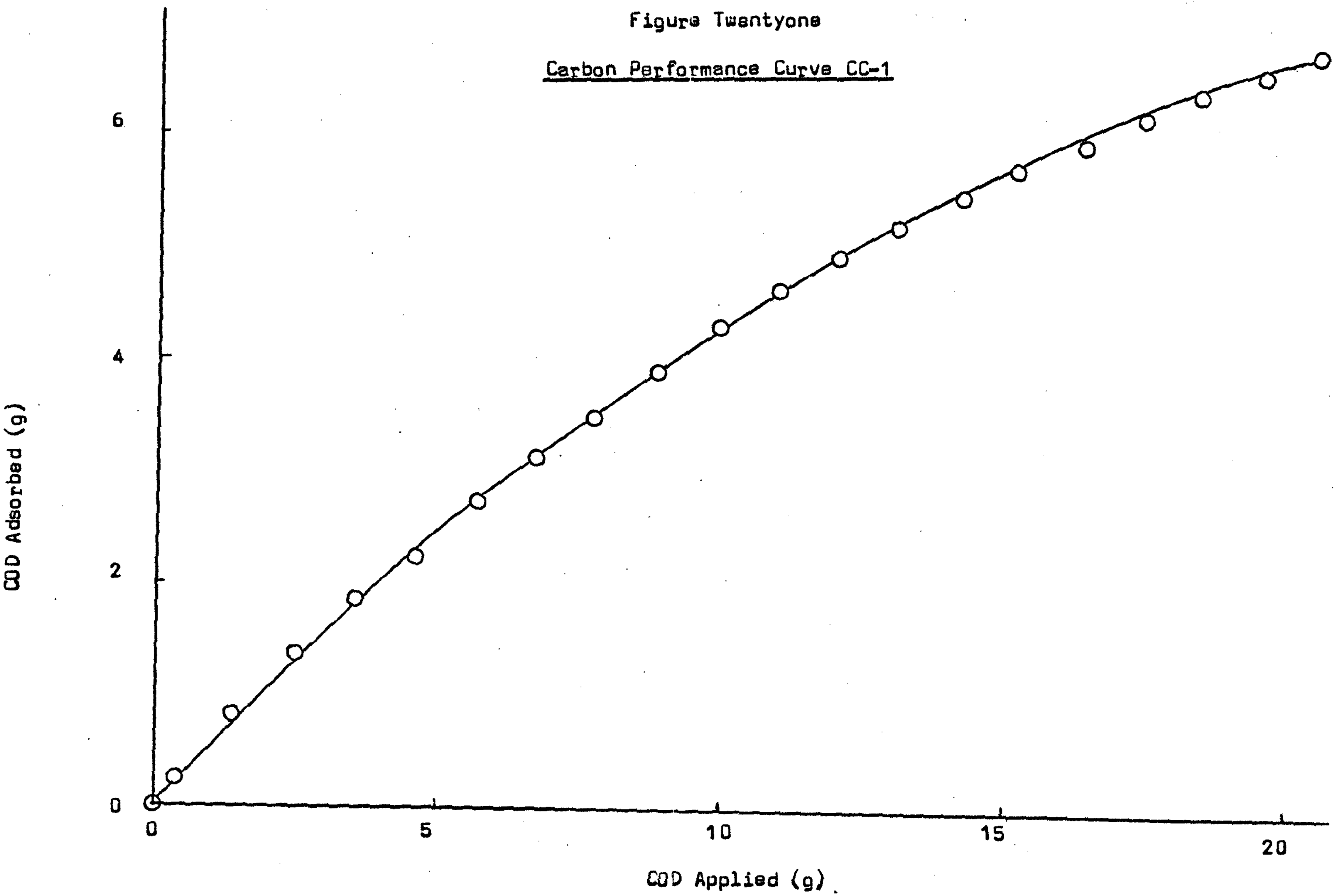


Figure Twentyone

Carbon Performance Curve CC-1

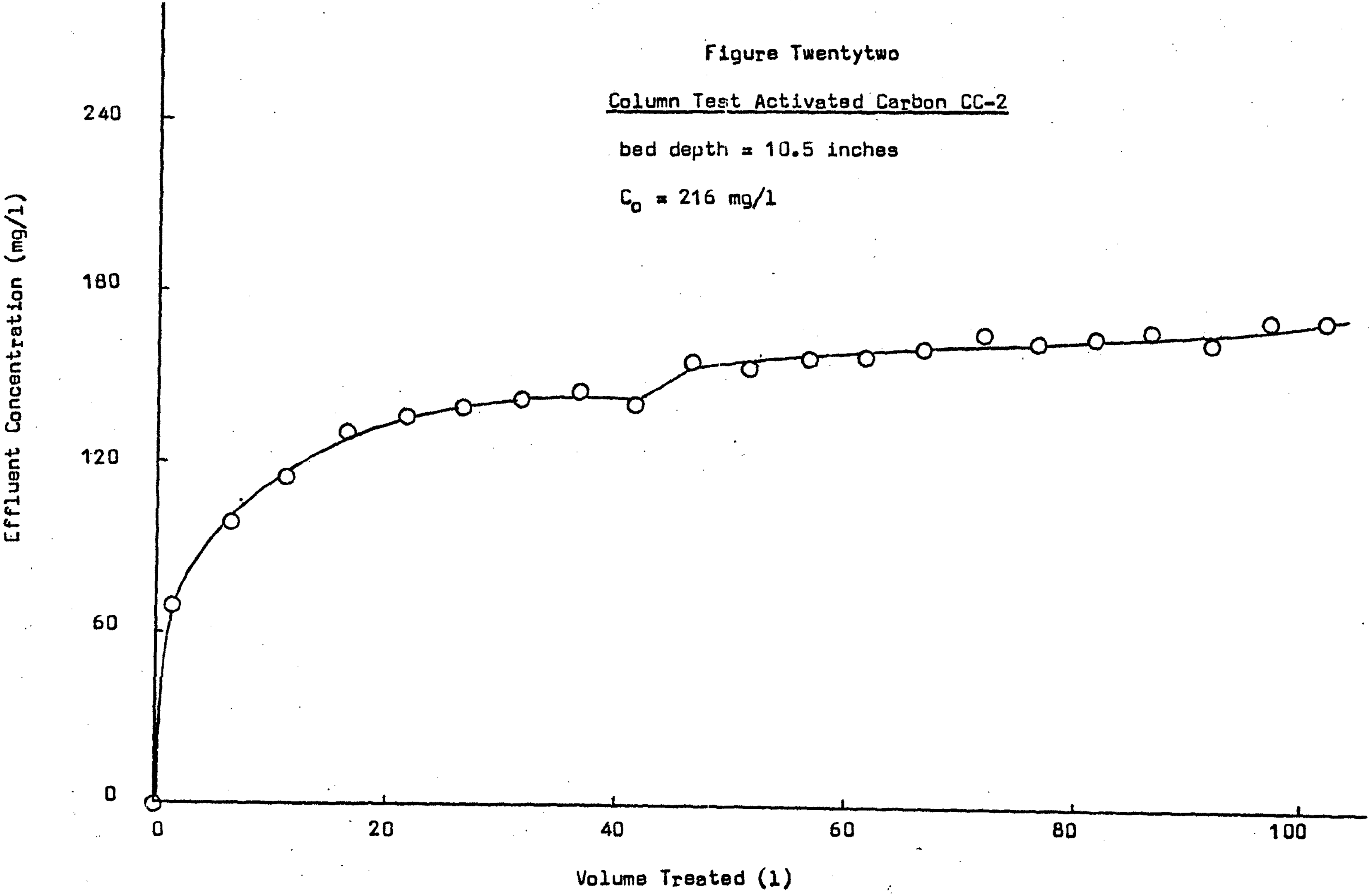


Figure Twentytwo

Column Test Activated Carbon CC-2

bed depth = 10.5 inches

C_o = 216 mg/l

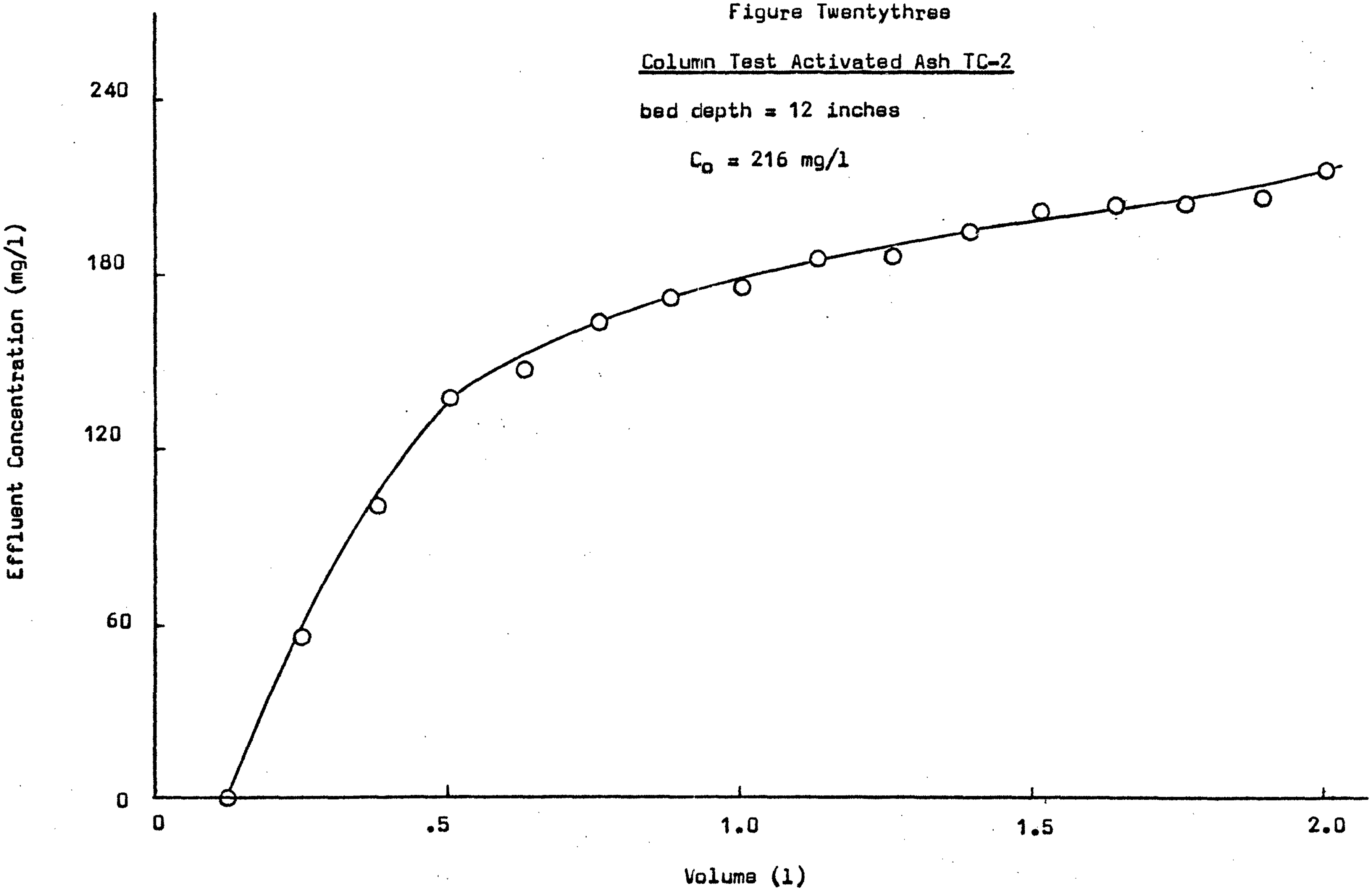


Figure Twentythree

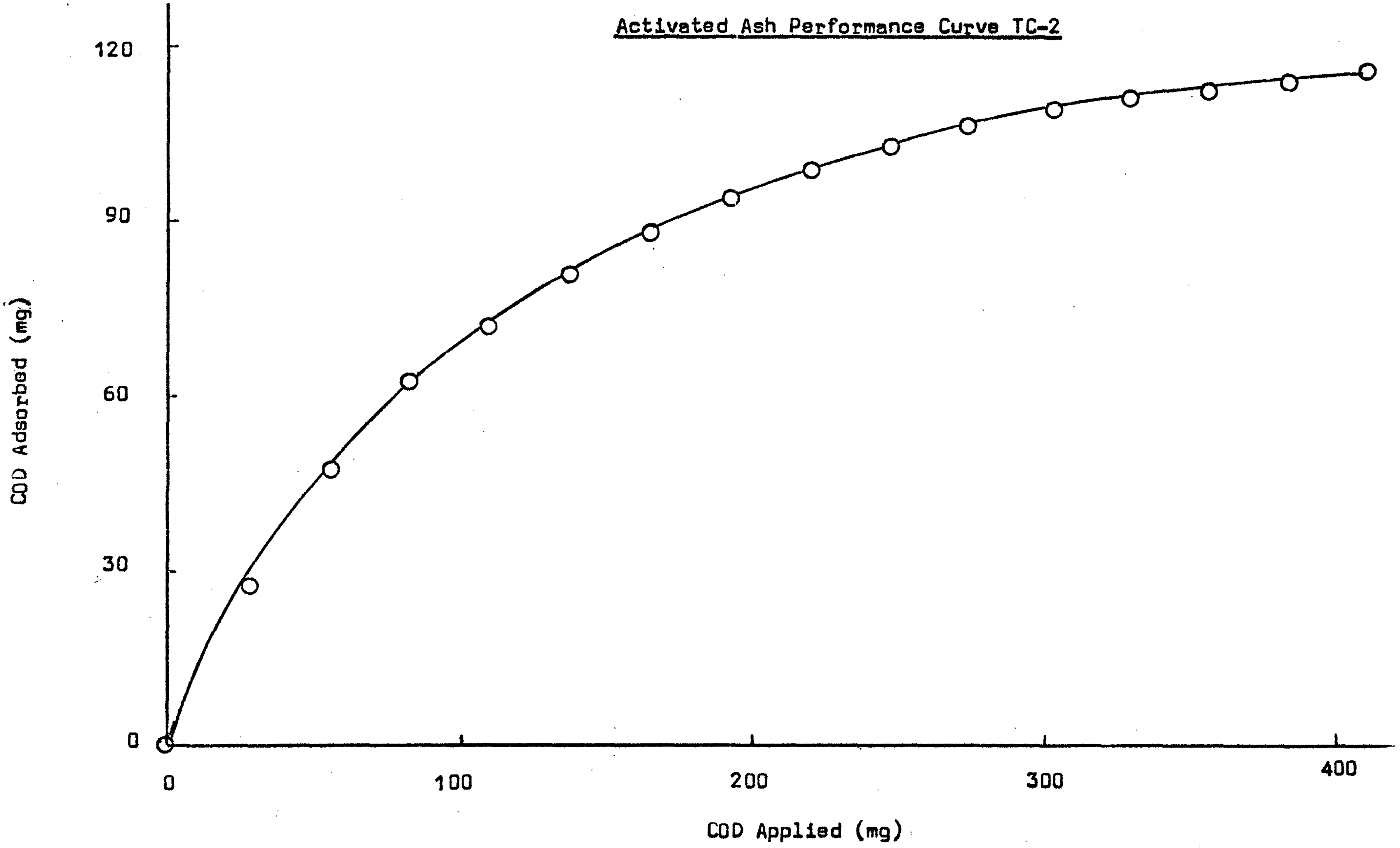
Column Test Activated Ash TC-2

bed depth = 12 inches

C_o = 216 mg/l

Figure Twentyfour

Activated Ash Performance Curve TC-2



DISCUSSION OF RESULTS

A. pH Influence on Adsorption

The adsorbate used in this study was found to be amphoteric, thus the degree of adsorption varied with solution pH. It is therefore first necessary to examine these variations before further investigations may be discussed.

Tests were conducted, varying pH for a constant adsorbate concentration and carbon dosage. The results, expressed as percent COD removal, were plotted as a function of equilibrium pH. (Figure 10) This graph was found to follow the generalized curve of Figure 2. It was found that adsorption increased with increasingg pH, reaching a maximum value at 6.9. Any further increase in pH resulted in decreasing adsorption. Since all adsorbents used in this study were originally basic, experimental emphasis was placed on the higher pH values. These values will be important to further discussions.

B. Isotherm Evaluation

Isotherm studies were conducted to provide a basis for comparison of the adsorptive properties of activated carbon, flyash, and activated flyash. In order for these comparisons to be effective, it was necessary to use an equation which would be adequate to equally depict all the isotherms developed. Initially, this presented a problem since the traditional Freundlich and Langmuir equations are best represented over a large range of adsorbate equilibrium concentrations not practiable with the lower adsorptive powers of flyash. It was found that, due to the small differences in equilibrium concentrations obtained with flyash, small mistakes in laboratory analysis would produce large distortions in the plots of these equations. Examination of isotherm data, presented in the parameters of the traditional equations, illustrates the small range of these values. (Tables II - IV) The BET equation was equally unsuitable since the molecular weight of the adsorbate was not determined. These problems were overcome through the use of the Mancy equation, which while analogous to that of Freundlich, has the parameters of percent COD removed and adsorbent concentration. These parameters present equally well the larger COD removals of carbon and the much smaller removals attained with flyash. This equation was developed at the University of Cincinnati and has been successfully used there in several investigations.(14,5)

As mentioned in the theory section, the slope of the Mancy equation is a direct measure of the effect of adsorbent concentration on the removal of adsorbate. Activated carbon was found to have a slope of .488 or roughly one half. The percent removal of COD may be said to be proportional to the square root of the carbon concentration. The untreated flyash isotherms were found to have an average slope of 1.15, while those corresponding to activated flyash were only slightly higher, 1.20. On the basis of this data, it can readily be seen that an increase in dosage of either type of flyash will have a much greater effect on COD removal than a corresponding increase in carbon dosage. For example, doubling the carbon dosage will roughly enhance the removal by an increment of one half. Doubling the flyash will more than double the percent COD removed.

Due to the fact that adsorption is largely system dependent, it is not practicable to numerically compare the experimental results with literature values. It is possible, however, to report experimental trends in each instance. During the isotherm tests conducted at the University of Cincinnati(5,14), it was found that carbon isotherms always had a steeper slope than flyash isotherms. As mentioned in the preceeding paragraph, the opposite result was observed in this investigation.

At this point it is of interest to compare the efficiency of the adsorbents. Efficiency is determined by plotting the COD adsorbed per unit weight of adsorbent, X/M, as a function of adsorbent concentration. Figure 17 represents the efficiency of activated carbon isotherm

IC-2. For this adsorbent the efficiency decreases rapidly with increasing carbon concentration. Figure 18, a similar plot of flyash efficiency, exhibits increasing efficiency with increasing flyash concentration. This result is in direct contrast to flyash efficiency plots developed by Mancy.(14) The same reasoning which previously prevented the application of the Freundlich equation is still valid in this instance. (Flyash $\frac{x}{m}$ values are not reliable due to the small concentrations involved) However, the trend of flyash to increase in efficiency with increasing flyash dosage is undeniable. The extent of this increasing trend was not determined in this study but it appears to decrease at higher flyash dosages. It should also be noted that the efficiency of the activated flyash was always greater than that of the untreated flyash.

A comparison of the slopes of the Mancy equation would be misleading if the importance of the intercept, k, were overlooked. The intercept is an indicator of the adsorptive capacity of the adsorbent. The absolute value of k will be determined by the scales chosen for the isotherm plot, therefore, the more significant comparative values will be used throughout this discussion. In Figure 19 an isotherm of each adsorbent is plotted on the same scale. The value of k was found to be 36.4, .13

and .11 for activated carbon, activated flyash and flyash respectively. It is obvious that carbon is greatly superior in adsorptive capacity to either type of flyash, a fact never disputed in this paper. Based on this data carbon adsorbed over 37 times as much adsorbate as either type of flyash. It is also apparent that the isotherms developed for activated and unactivated flyash are nearly parallel, the only difference being their adsorptive capacity which was 15% higher for activated flyash.

Since pH was discovered to have a large effect on adsorption in this system, records were made of equilibrium pH. (Table II - IV) The basic nature of the carbon and flyash lowered the acidic pH of the soup solution. Due to the greater adsorptive powers and consequently much lower dosages of carbon the effect of pH change was insignificant, changing the removal by only three percentage points on Figure Ten. Conversely, the greater dosage needed for flyash resulted in a pH change of 3.8 units. Referring to Figure 10 again the change in percent removal attributal to pH influence is 9.9 at maximum flyash concentration. Considering the low removals of flyash this pH effect is highly significant. The pH of untreated flyash is equal to 10, while that of acid activated flyash was adjusted to 6.0. Thus, the pH of the activated flyash isotherm remained essentially constant. In Table III the removal values for flyash were corrected for pH influence. Comparison of these values with those of the activated flyash reveals conformity at the higher flyash dosages but a large discrepancy at lower levels. The probable cause of this disagreement is the fact that untreated flyash exerts a COD four times in excess of that attributal to activated flyash. The change of properties caused by activation will be examined later in this discussion. At this point it appears that the activation of flyash does not significantly improve adsorption directly but rather indirectly in that it neutralizes the pH effect.

C. Continuous Column Studies

The batch isotherm studies provide important data but any valid adsorbent comparison must include a continuous adsorption system. Only in this manner can dynamic removal performance and actual adsorption capacity be effectively evaluated. The simplest possible system, a fixed bed downflow column, was chosen. Two runs were made with activated carbon at depths of 12 and 10.5 inches and a flow rate of 5.2 ml/sec. Samples were taken every 5 liters and the total volume treated was 101.4 and 116.4 liters respectively. An adsorption wave or plot of effluent concentration as a function of volume passed, was consturcted for each run. (Figures 20 and 22)

Owing to the similarities exhibited by the isotherm tests it was decided to omit column tests on untreated flyash and proceed directly with activated flyash. Hydraulic problems, caused by the small particle size of flyash, prevented column operation. This problem was previously reported in the literature by Pollock,(22) therefore contigency provisions were made in the original experimental plan. A large amount of clinkers or bottom ash, created in the same firing as the experimental flyash, were obtained from the Public Service generating station. This bottom ash, similar in composition to flyash, was pulverized through the use of a stone mill. All particles which passed through a U.S. Number 40 sieve but were retained by a Number 50 sieve were collected and acid activated. (420-297μ) Three column tests were made with activated bottom ash. The first two runs were inclusive since the flow rate proved too high, exhausting the adsorptive powers of the ash after only two samples were taken. After installation of a new rotometer and new sampling intervals, the final run proved successful. It must be kept in mind that by changing the flowrate and particle size of the ash the adsorption characteristics of the system were also modified. These changes do not adversely affect the scope of this investigation which was only intended to investigate the feasibility of ash adsorbents.

The results of the activated bottom ash run, TC-2, were also plotted in an adsorption wave. (Figure 23) Approximately two liters of adsorbate were passed through a 12 inch column at a flowrate of 2.1 ml/sec, samples being taken at one minute intervals. The shape of the ash adsorption wave was similar to those produced by activated carbon. The carbon plots were identical having a rapid initial rise then a slower climb reaching an inflection point at an effluent concentration of 140 mg/l. At this point the concentration jumped to 158/mg/l and then very gradually rose to 180 mg/l. In the ash run the effluent concentration also rose rapidly to a valve slightly higher than 140 mg/l, after which it gradually increased until it became equal to the influent concentration. The inflection point was much less pronounced in this run. All runs failed to exhibit the characteristic shape of an adsorption wave. During the carbon runs this deviation was attributed to the pH fluctuation, however the subsequent ash run at constant pH also exhibited similar deviations. The actual cause is probably a combination of the factors listed in the theory section and is irrelevant to this study.

Performance curves(2) or graphs of adsorbed COD as a function of COD applied were plotted for a carbon and ash run. (Figures 21 and 24) The similarity of both curves indicates common adsorptive characteristics as did the adsorption waves. During carbon run CC-1, 6,892 mg of COD were adsorbed from an applied total of 21,598 mg. This is equal to an overall removal of 31.9%. Consideration must be given to the fact that the column was kept in operation until the effluent concentration equaled 180 mg/l. If operation had been suspended sooner a higher removal percentage would have been accomplished. For the same range of concentration on ash 41.6% or 102.4 mg of COD were removed from an applied load of 246 mg. Once again it must be remembered that a total of 101 liters were treated by the carbon while only 1.13 liters were passed through the ash. For equal volumes of adsorbent, carbon was found to adsorb 67.3 times more COD than activated ash.

Total solids levels were monitored at regular intervals during all runs. The reasoning for these tests were twofold; (1) solid removal is a measure of adsorption; (2) the adsorbent can add additional solids to the adsorbate. In the carbon run 30% of the solids were initially removed, increasing to a high of 59% and finally decreasing to 37% removal at the conclusion of the run. The ash run had a higher initial solid removal of 48% but thereafter slowly decreased to 30% at the final acceptable effluent concentration.

TC-1, the first column test on activated flyash, was continued after the adsorptive capacity of the ash was saturated. From the results of this run (Table VII) it is apparent that some elution or desorption had occurred. (the effluent concentration being higher at times than the initial concentration) Elution studies were conducted on all adsorbents to compare the degree of desorption. Table IX is a summary of these tests. The method used in this experiment (see Experimental) necessitated the use of a common correction factor, thereby making all results inexact or only approximate. It was determined that, at the concentrations investigated, untreated ash lost between 57 to 68% of adsorbed COD, while the amount lost by treated ash was negligable. Activated carbon was found to desorb between 4 to 10% of adsorbed COD. The adsorbent concentrations were representative of those used in the isotherms.

D. Effect of Activation on Adsorbent Properties

Appendix A lists the properties of all adsorbents including those of activated and untreated flyash. Activation was found to slightly lower the apparent density of flyash, probably due to the loss of fines during the washing. Surprisingly, the carbon content of the ash was found to increase from 3.31% to 3.86% after activation. Early literature reported high solid and COD loading attributable to the flyash itself.(18) This is confirmed by Appendix A, however it was also determined that acid activation reduced ash COD by 73% and ash solid levels by 50 to 70%. It is also interesting to note that at equal concentrations these parameters are slightly higher for activated carbon than for activated flyash. This fact is not readily apparent since the much greater adsorptive powers of carbon allow the application of comparatively small adsorbent dosages.

The beneficial effect of acid activation on effluent quality as evidenced by this study is in complete agreement with investigations undertaken by Othmer.(20) Experiments at Northwestern(7) in which acid activation of flyash was found to have little effect on effluent quality are in disagreement with the findings of this study. (See Literature Review)

CONCLUSIONS

Comparative tests on the adsorptive characteristics of activated carbon, flyash, and activated flyash for a given adsorbate lead to the following conclusions:

1. Activation of flyash does not directly increase adsorption. It does increase adsorption indirectly by: neutralizing ash pH, reducing ash COD by 73%, lowering leachable ash solids by 50 to 70%, and hindering desorption.

2. Activated carbon was found to adsorb 67.2 times more COD than activated flyash. Within the limits of its adsorptive capacity, activated ash was found to have characteristics similar to those of activated carbon.

RECOMMENDATIONS

1. This study should be enlarged to include a pilot plant using activated flyash to adsorb a municipal secondary effluent.
2. Prefiltering of the adsorbate to allow a distinction to be made between filtrable COD and non-filtrable COD.
3. A study to investigate the possible use of the saturated flyash sludge as a plant fertilizer.
4. A study to investigate the suitability of flyash as an adsorbent for hazardous wastes.

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APPENDIX A.

TABLE A-1

Adsorbate Analysis

Component	Beef Broth	Domestic Sewage*
(mg/l)	(5 mill/liter)	(weak)
Protein	135.0	105.0
Carbohydrates	101.0	87.5
Fats	33.8	17.5
Chlorides	46.0**	30.0
Total Solids	310 ± 30**	350.0
COD	225 ± 30**	250.0
pH	6.5 ± .5**	-
Nitrates	0	0

* Wastewater Engineering (17), P. 231

** Experimentally determined, all other values from Nutrition (19)

APPENDIX B.

TABLE B-1
Adsorbent Tests

Carbon Content

Adsorbent	% Carbon
Flyash	3.31
Act. Flyash	3.86
Bottom Ash	2.89
Carbon	91.50

Apparent Density

Adsorbent	Density (gm/cm$_3$)
Flyash	1.277
Act. Flyash	1.250
Sized Bottom Ash	.931
Carbon	.446

COD

Adsorbent	Adsorbent Conc.	C_f
Flyash	50,000	14.85
Act. Flyash	50,000	3.97
Act. Carbon	50,000	8.91

Total Solids

Adsorbent	Adsorbent Conc.	Solid Conc. (mg/l)
Flyash	10,000	200
Flyash	50,000	1,300
Act. Flyash	10,000	62
Act. Flyash	50,000	500
Powder Carbon	1,000	10
Powder Carbon	10,000	110
Granular Carbon	1,000	4
Granular Carbon	10,000	69

pH

Adsorbent	pH
Flyash	10.0
Carbon	9.8
Act. Flyash	6.0

Nitrite (Presence of trace Amts.)

Adsorbent	Prescence
Flyash	Yes
Carbon	No
Act. Flyash	No

APPENDIX B.

TABLE B-2

Flyash Sieve Analysis

Sieve No.	Sieve Opening (mm)	% Finer Than
10	2.000	99.96
40	.420	99.33
60	.250	97.36
100	.149	91.13
140	.104	88.55
200	.074	81.63

Bottom Ash Sieve Analysis

Sieve No.	Sieve Opening (mm)	% Finer Than
4	4.760	71.83
10	2.000	49.91
20	.841	24.91
40	.420	14.27
60	.250	9.00
100	.149	4.70
200	.074	1.67

APPENDIX C.

TABLE C-1

Flyash Analysis*

Component	Site Investigated Baltimore Md.	 Hagerstown Md.	 Newark N.J.	 Philadelphia Pa.
SiO_2 (%)	45.06	44.42	45.42	40.32
Fe_2O_3 (%)	15.60	12.62	11.54	13.39
FeO (%)	0.72	3.65	3.74	3.95
Al_2O_3 (%)	34.76	27.62	29.62	32.92
CaO (%)	0.37	3.10	1.93	2.34
MgO (%)	0.37	1.27	0.94	0.74
Carbon (%)	4.17	6.05	4.81	5.79
Sp. Gravity	2.29	2.24	2.36	2.30

Cedar Rapids, Flyash Analysis**

Component	Percentage
P_2O_5	0.25
SiO_2	37.40
Fe_2O_3	20.99
Al_2O_3	20.45
TiO_2	1.01
CaO	8.54
MgO	1.33
SO_3	8.16
K_2O_3	1.56
Na_2O	0.17

* Manual of Flyash as Related to its Proper Use in Concrete (18)

** Flyash as a Filter Aid (8)

Appendix D

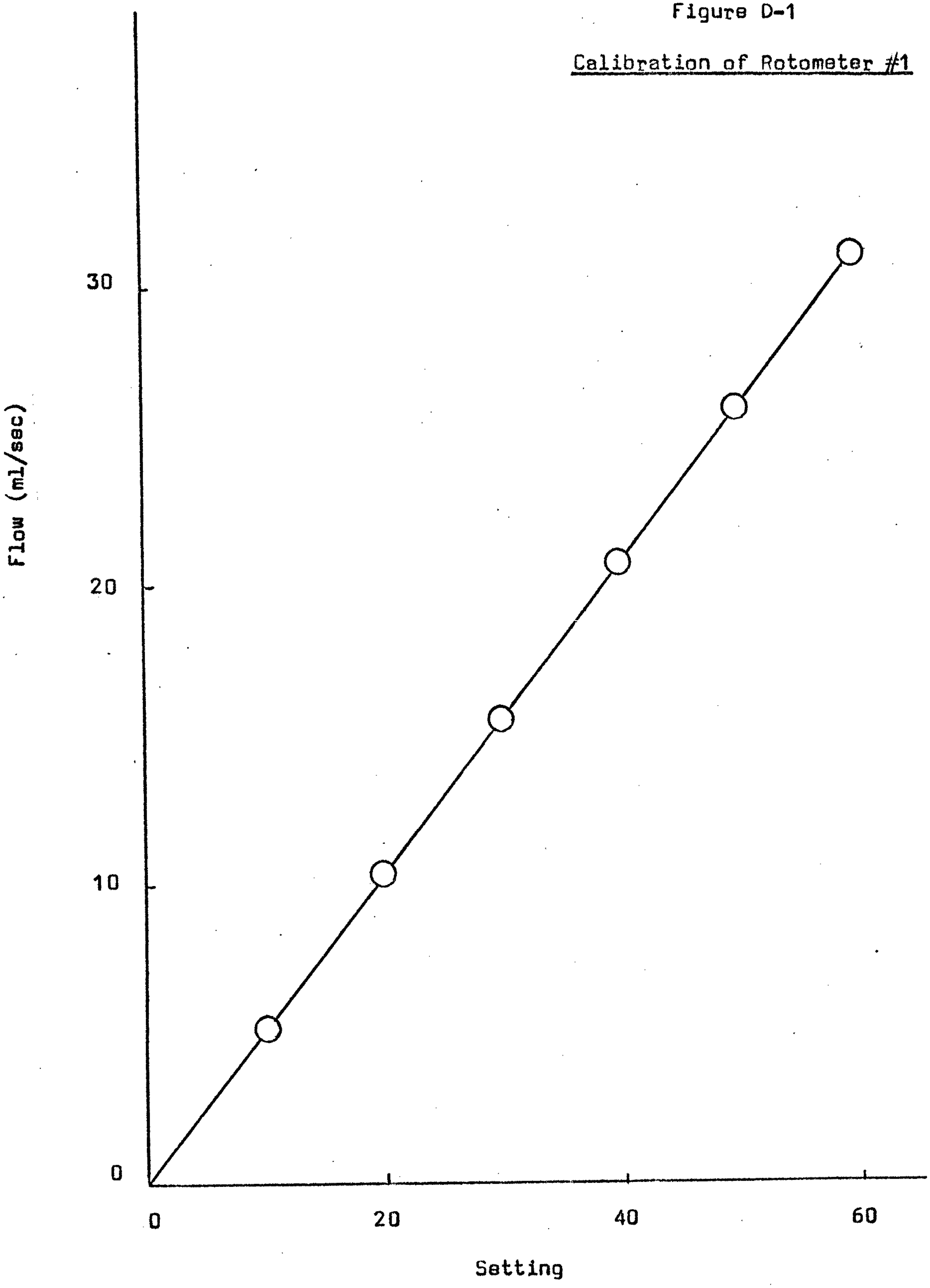

Figure D-1

Calibration of Rotometer #1

Figure D-2

Calibration of Rotometer #2