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HUMIC SUBSTANCES REMOVAL BY ACTIVATED CARBON

by

Michael C.-Y. Lee

and

Vernon L. Snoeyink
Department of Civil Engineering
University of Illinois
at Urbana-Champaign

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UNIVERSITY OF ILLINOIS
WATER RESOURCES CENTER
2535 Hydrosystems Laboratory
Urbana, Illinois 61801

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NOTATION

C	Liquid-phase concentration	M/L ³
C ₀	Initial bulk concentration	M/L ³
C _e	Equilibrium concentration in solution	M/L ³
C _s	Liquid-phase concentration adjacent to the particle surface	M/L ³
D	Diameter of the particle	L
D ₀	Dosage of carbon	M/L ³
D _g	Solute distribution parameter, $\frac{\rho_s q_e (1-\epsilon)}{\epsilon C_0}$	
D _l	Free liquid diffusion coefficient	L ² /t
D _s	Surface diffusion coefficient	L ² /t
F	F-distribution	
K	Freundlich isotherm constant	M/M
k _f	Film transfer coefficient	L/t
k _{fc}	Column film transfer coefficient	L/t
n	Number of data points	
1/n	Freundlich isotherm constant	
p	Number of parameters	
q	Solid-phase concentration	M/M
q _e	Equilibrium surface concentration	M/M
R	Adsorbent radius	L
Re	Reynolds number, $\frac{\rho_l V_s D}{\epsilon \mu_l}$	
r	Radial coordinate	L
Sc	Schmidt number, $\frac{\mu_l}{\rho_l D_l}$	

Sh	Sherwood number, $\frac{k_f R(1-\epsilon)}{\epsilon D_g D_s}$	
S(θ)	Allowable variance	
S($\hat{\theta}$)	Minimum of variance	
t	Time	t
v	Interstitial velocity	L/t
V _s	Superficial velocity	L/t
z	Longitudinal adsorption bed coordinate	L
ϵ	Fraction of volumetric space unoccupied by the adsorbent or void fraction	
μ_ℓ	Viscosity of the fluid	ML/t
ρ_a	Adsorbent density which includes pore volume	M/L ³
ρ_ℓ	Density of the fluid	M/L ³
ρ_s	Adsorbent density	M/L ³

ABSTRACT

Humic substances are a major concern to the water treatment industry because they can cause odor and color problems and are potentially toxic and/or carcinogenic. A commercial humic acid and a fulvic acid extracted from peat were used to evaluate the removal of humic substances by various activated carbons. Different analytical methods were investigated to measure the concentration of humic substances and their chloroform formation potential. Total organic carbon measurement and ultraviolet/visible absorbance correlate well with the chloroform formation potential of humic substances. Evidence was found that pore size distribution was the most important physical characteristic of activated carbon for adsorption of humic substances. Pore volumes of activated carbon in pores between 100 and 500 Å radius were correlated with adsorption capacity. A decrease of pH in solution, lower molecular weight fractions of humic substances, smaller carbon particles, and presence of soluble alum were found to increase the carbon adsorption. Chemical pretreatment with alum increased the absorption capacity of carbon almost three-fold. This increase of adsorption capacity is probably because of the removal of weakly- or non-adsorbable humic substances by alum coagulation. The presence of soluble alum in the solution also enhances the adsorbability of humic substances. The application of a developed mathematical model to predict the performance of the carbon bed for the adsorption of humic substances was successful. Model parameter estimation techniques and model verification were evaluated and the applicability of the model was verified. In general, this model is sensitive to values of adsorption capacity of activated carbon and the surface diffusion coefficient of humic substances inside the adsorbent particle. The surface diffusion coefficient was also correlated with the adsorption capacity. The higher the adsorption capacity, the lower the diffusion coefficient. Based on the model predictions, the empty bed contact time of the carbon bed and the influent concentrations were the two most important factors in designing a carbon bed for humic substances removal.

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coagulation-sedimentation

1. INTRODUCTION

Aqueous organic matter is currently a major concern to the water treatment industry. Recent studies have shown that, in addition to compounds that cause color and odor, there are potentially toxic and/or carcinogenic compounds present in water supplies. The USEPA (1978) has proposed the establishment of a maximum contaminant level (MCL) for total trihalomethanes in drinking water and the requirement of granular activated carbon (GAC) treatment for the removal of industrially-derived organic contaminants. Many fundamental questions remain concerning the application of GAC for this purpose, especially because GAC has rarely been used for the treatment of water supplies in this way.

Studies have shown that the predominant type of organic matter present in water is humic substances. According to Schnitzer and Khan (1972), these materials result from decay processes and microbiological activity in soil and water. The presence of humic substances not only poses an aesthetic nuisance (color), but also presents a health hazard when chlorinated. Humic substances react readily with chlorine to yield haloforms (predominantly chloroform) when raw water and drinking water are chlorinated (Rook, 1974; Symons et al., 1975). Humic substances also interfere with activated carbon used in the removal of specific organics of concern. Humic substances may associate with pesticides, phthalates, nitrogen-containing organic compounds, and heavy metals to form complexes (Schnitzer and Khan, 1972; Stevenson, 1979).

In order to solve the problem posed by haloform formation from humic substances, three major approaches have been studied. The first is the reduction of haloform concentrations after their formation, using processes such as adsorption on powdered or granular activated carbon, ozonation, and aeration. The second approach is the prevention of haloform formation by using disinfectants

other than chlorine, such as ozone, chlorine dioxide, and chloramines. The last approach, the removal of humic substances before chlorination, involves using processes such as coagulation-sedimentation-filtration, and adsorption on powdered and granular activated carbon. The last approach was studied in this research.

Coagulation-sedimentation is conventionally operated to remove substances causing turbidity, color, and hardness in water supplies. Likewise, coagulation-sedimentation can remove organics, both particulate and soluble, from water. Granular activated carbon (GAC) adsorption is primarily used to remove dissolved organic substances. Since many organic compounds, including the slightly soluble pesticides, polynuclear aromatic hydrocarbons, phenols, and other aromatic compounds generally present in trace concentrations are very strongly adsorbed, whereas humic substances are less strongly adsorbed (Symons et al., 1975; McCreary and Snoeyink, 1976), the removal of humic substances will likely control regeneration frequency.

The use of coagulation before activated carbon adsorption is an important process. Coagulation can remove some organic matter, but the extent of removal by coagulation may be insufficient in some cases. Following water clarification, activated carbon treatment is required to reduce the organic content of some water supplies to a desirably low level. Optimum coagulation should reduce the loading of organic matter to the carbon, thereby reducing the frequency of carbon regeneration. It is therefore necessary to consider how the coagulation process influences the ability of activated carbon to remove organics.

The objective of this study was to evaluate the important characteristics of activated carbon for the adsorption of humic substances from water, and to show the importance of the chemical and physical parameters involved in this

adsorption process. The effect of chemical coagulation before carbon adsorption for removal of humic substances was also investigated, because most water treatment plants that use activated carbon also use coagulation. Emphasis was also given to finding an easy-to-measure parameter to indicate the chloroform formation potential of humic substances in water. Using data determined in the laboratory investigation, a verified mathematical model was applied to determine the breakthrough curves for the humic substances removal by carbon beds. The model predictions provide additional information about the performance of carbon adsorbers without the need for experimental studies.

2. REVIEW OF LITERATURE ON THE REMOVAL OF HUMIC SUBSTANCES BY COAGULATION AND ADSORPTION

Humic substances in water are most frequently removed by the coagulation and adsorption processes. Metal salts and polyelectrolytes are used as coagulants in the coagulation process, while powdered carbon, granular carbon, and resins can be used as adsorbents for the adsorption process. Coagulation with metal salts and GAC adsorption, which are the primary interests of this research, are discussed in this section.

2.1 Coagulation

Humic substances, which constitute the major organic fractions of natural water, can be removed by the chemical coagulation process. Both Kavanaugh (1978) and Semmens et al. (1979) have reviewed in detail the characteristics of coagulation in conjunction with sedimentation and filtration. They reported that the types of organic matter and coagulant, the dosage of coagulant, and pH of the solution are important factors in the removal of organic matter by the chemical coagulation process. The extent of removal depends on the type of organic matter present in the water. As reviewed by Kavanaugh (1978), the removal percentages for humic acid were between 60% and 90%. Removals of between 10% and 60% have been reported for fulvic acid, which is considered a predominant constituent of humic substances in natural water. Removal percentages of the natural organic matter in water are somewhat similar to those obtained with fulvic acid. Results of a pilot-scale study of Ohio River water treatment showed that 60% of the nonpurgeable total organic carbon (NPTOC) was removed, whereas approximately 30% of NPTOC was removed in 63 water treatment plants surveyed in the National Organics Reconnaissance Survey for Halogenated Organics (NORS). In the Federal Republic of Germany, 25% to 40% removal of

dissolved organic carbon (DOC) from surface waters of the Rhine River and of several Alpine lakes was reported.

Selective removal of haloform precursors by coagulation is also of interest. Table 1 presents the results of the percent of reduction in terms of total organic carbon (TOC) and chloroform formation potential (CFP) from several researchers. The reduction percentages for haloform precursors from natural waters and peat fulvic acid were higher than reduction percentages for TOC. On the other hand, a substantial amount of TOC of peat humic acid was removed, but the removal of haloform precursors was not as great as the removal of TOC. However, the selective removal of haloform precursors by coagulation does not occur everywhere. Kavanaugh (1978) did not observe this selective removal by coagulation in the study of surface water in California. He reported a linear relationship between the concentrations of TOC and haloform formation potential for this source of water after coagulation with alum and ferric chloride. Kavanaugh's data indicated that there was no selective removal of haloform precursors by coagulation.

2.2 Carbon Adsorption

The removal of humic substances from water by activated carbon adsorption has been of interest to many researchers recently. Several factors may affect the performance of a carbon bed for adsorbing humic substances in water. In general, the type of humic substances, the characteristics of the carbon, and the pretreatment processes are the most important factors.

2.2.1 Effect of Types of Humic Substances

McCreary and Snoeyink (1979) studied the effect of types of humic substances on the adsorption by activated carbon from both leaf and soil extracts, from well water, and from a commercially available humic acid.

Table 1. Reduction Percentages for Total Organic Carbon (TOC) and Chloroform Formation Potential (CFP) by Coagulation Process

Sample	Reduction, %		Reference
	TOC	CFP	
Natural Water	40	60	Young and Singer (1977)
Natural Water	34	61	Oliver and Lawrence (1979)
Peat Fulvic Acid	22	70	Babcock and Singer (1979)
Peat Humic Acid	86	70	Babcock and Singer (1979)

They found that the adsorption properties of the humic substances from different sources varied widely. The need for on-site pilot studies to determine adsorbability of humic substances for a particular location was emphasized in their work. Other research involving the study of humic substances removal by activated carbon was carried out by the group under the leadership of Professor Weber at the University of Michigan. Commercially available humic acid from the Aldrich Chemical Company was the only source of humic acid in their studies. Consequently, their conclusions are drawn from the use of only one type of material.

Other factors found to be important include the phosphate concentration of the buffer solution and the pH of the solution. McCreary and Snoeyink (1979) found that a higher phosphate concentration in a water sample yielded a higher adsorption capacity for carbon. The pH effect was also noticed by Weber et al. (1978) and McCreary and Snoeyink (1979). A decrease of pH in solution rendered humic substances less soluble and more readily adsorbed on activated carbon.

However, this group of researchers used different analytical techniques to determine humic substances. Weber et al. (1978) used ultraviolet absorbance with a wavelength of 250 nm, while Snoeyink et al. (1977) and McCreary and Snoeyink (1979) used fluorescence intensity with an excitation wavelength of 365 nm and an emission wavelength of 415 nm. According to Snoeyink et al. (1977), the adsorption characteristics of the humic substances are also dependent on the method of analysis used to quantify them. They found that the species that fluoresce the most, and adsorb the best are the fractions with a lower molecular weight, whereas ultraviolet adsorbing species do not adsorb as well as the fluorescing species. Because there is no analytical method that can directly measure the concentration of humic substances in water, an analytical method

must be carefully selected in the study of humic substances removal by activated carbon.

2.2.2 Effect of Types of Carbon

Five characteristics of carbon are important in the adsorption of organic molecules from solution. Zogorski (1975) reviewed several articles in the literature and suggested that these factors are (1) particle size, (2) surface area, (3) chemisorbed oxygen, (4) hardness and uniformity, and (5) pore structure. These adsorptive characteristics of carbon depend upon the source material of the carbon and the activation process.

For humic substances removal from water, little information is available concerning the importance of the characteristics of carbon. In the study of commercial humic acid adsorption by carbon, Weber et al. (1977) tested four different carbons and selected F-400 carbon for their study. F-400 carbon was chosen because it had better adsorption rates and capacities and had more resistance to abrasion than the other carbons. Snoeyink et al. (1977) used two bituminous carbons, F-200 and F-400, to evaluate the adsorbability of commercial humic acid from water. The F-400 carbon, which has a larger average pore size and more surface area than F-200, showed a much higher capacity for humic acid in the isotherm tests. In another study of Snoeyink et al. (1978), five different activated carbons were studied. It was found that the F-400 carbon performed slightly better than the WV-G carbon, and that the lignite carbon HD-4000 had a capacity very close to that of the F-400 and WV-G carbons. The F-200 and WV-W carbons did not adsorb as well as the other three carbons. In the study of the effect of particle size of carbon on the adsorption of humic substances in water, Weber et al. (1978) found that the rate of adsorption of commercial humic acid was inversely related to the particle size.

On the adsorption of organic matter in natural water, Sontheimer and Maier (1972) carried out an extensive evaluation of ten different activated carbons to determine their adsorbability of organic matter from the River Rhine. This river is highly polluted, and 42% of its organic content is humic substances (Rook, 1974). Sontheimer and Maier found that neither the phenol number nor the Brunauer-Emmett-Teller (BET) surface area could provide an indication of carbon effectiveness for organic removal from the Rhine. It is of interest to know whether similar results will be obtained in the study of humic substances.

2.2.3 Performance of Pilot- and Full-Scale Carbon Beds

A pilot plant for eliminating haloform precursors has been evaluated by the USEPA (1975). This pilot plant was equipped with a 30 inch GAC filter operated at 2 gpm/ft² to treat raw Ohio River water. It was shown that measurable amounts of chloroform were being detected after chlorination of the effluent after 3 to 4 weeks of operation. For a 50% haloform formation potential breakthrough, the lifetime for the GAC filter was only 10 weeks. It is obvious that the adsorption capacity of granular activated carbon is limited.

The performance of a full-scale GAC bed in the actual plant operation has been reported. Wilson (1960) investigated the removal of fulvic acids from water by a carbon bed. Hydrogen peroxide was added to this water before carbon adsorption for the purpose of oxidizing the fulvic acids. Wilson found that, for a 50% breakthrough of ≈ 2 mg/l of fulvic acid, the service time for the carbon bed was 3 months at a flow rate of 3 gpm/ft². The removal efficiency decreased very rapidly, from an initial 100% to about 20%. He suggested that the pore exclusion of the organic molecules might cause this sharp decrease of adsorption. These large organic molecules could be excluded, because the average pore size of the carbon was smaller than the size of organic molecules.

In the National Organics Reconnaissance Survey for Halogenated Organics, Symons and coworkers (1975) also evaluated the effectiveness of GAC as a combination filtration-adsorption medium to treat surface water and chlorinated raw water in eight water treatment plants. They found that the average nonvolatile TOC removal was not much higher than 30% for those carbon beds that had been in service for several months. Fresh lignite-based and coal-based replacement activated carbons in different plants showed a marked improvement in efficiency. The results of three studies of water treatment plants were reported in the Interim Treatment Guide (1978). It was found that the removal of trihalomethane precursors by adsorption on GAC was variable and site specific. It was also reported that longer empty bed contact time and lower influent trihalomethane formation potential increased the lifetime of a carbon bed.

2.3 Coagulation Followed by Adsorption

The above literature review illustrates the limited effectiveness of the coagulation and carbon adsorption processes for the removal of humic substances and organic matter from natural water. The humic substances that cause haloform formation can be removed in some cases by a properly operated coagulation-sedimentation-filtration process. However, the removal efficiency of organic matter from natural water is generally lower. Fresh GAC removes humic substances effectively just after starting but becomes less effective after a few months. Operating the water treatment process to remove as much organic matter as possible by coagulation and then using carbon adsorption should result in a lower overall treatment cost than if the coagulation process is not optimized for organic removal.

Sontheimer and Maier (1972) evaluated the adsorbability of organic matter from Rhine River water by GAC after clarification with aluminum sulfate and ferric chloride. This water was bank filtered and directly passed into the GAC without prior ozonation. They found better adsorption when aluminum sulfate was used as the coagulant. Unfortunately, there was no control sample in their study; consequently, no comparison of the adsorption capacity can be made before and after aluminum sulfate coagulation. However, for the bank filtrate followed by ozonation before GAC, the coagulation using both aluminum sulfate and ferric chloride significantly increased the adsorbability of these organics for carbon. Similarly, the adsorption capacity of the organics in the samples coagulated with aluminum sulfate was higher than for those in samples coagulated with ferric chloride. Nevertheless, Sontheimer and Maier did not evaluate how the adsorption capacity will change for the organic matter not removed by coagulation.

The coagulation process can also reduce the adsorption capacity of carbon for some organic molecules. Kavanagh (1977) presented data for tannic acid removal using a combination of iron coagulation and carbon adsorption. It was found that coagulation with iron retarded the adsorption of tannic acid by carbon. He suggested that pore blockage was the main reason for the slow and poor uptake.

In pilot plant systems, different effects of precoagulation on carbon adsorption have been reported in the Interim Treatment Guide (1978). Love et al. (1976) found the GAC bed was only initially effective for removing coagulated, settled, undisinfected Ohio River water. On the other hand, a similar study of the Merrimac River carried out by Sylvia (1978) at the Lawrence Experiment Station in Lawrence, MA, showed different results. The Merrimac River received considerable industrial contamination in the area upstream from the study site.

Haloform precursors in this river were only slightly reduced through coagulation and the settling processes. However, these treated organics were effectively removed for a long period of time by granular activated carbon adsorption.

2.4 Summary

The literature review of the removal of humic substances and other organic matter from water indicates that each different source of humic substances behaves differently. Coagulation may effectively remove some of the organic matter, but the extent of removal depends greatly upon the type of humic substances. An activated carbon bed may remove haloform precursors well initially, but the removal efficiency decreases sharply shortly after start-up. The performance of coagulation followed by adsorption also varies with the location. In some cases, coagulation before adsorption may result in improving carbon adsorption efficiency. Therefore, there is a need for on-site pilot studies for each individual water source. The research reported in this thesis is oriented toward making such pilot tests more economical and effective. The approach which is developed enables one to use simple bench-scale experiments and a mathematical model to predict the results of pilot tests. Based on these predictions, the pilot plant can be designed and operated to verify the model. Consequently, the data obtained from the pilot plant study should enable the design of a more effective full-scale water treatment plant.

3. SCOPE OF STUDY

The scope of the study was established to achieve the objective given in Section 1. Activated carbon adsorption of commercial humic and fulvic acid extracted from peat was studied in the present work. Commercial humic acid was selected so that the results from this study can be compared with previous works of Snoeyink *et al.* (1977 and 1978). Peat fulvic acid was selected because: (1) fulvic acid is a predominant organic in natural water, and (2) little carbon adsorption research using peat fulvic acid is available.

Different types of commercially available granular activated carbons were used to make the results more practical for the water treatment industry. These activated carbons were made from various raw materials and provide a range of values for parameters such as surface area, total pore volume, and pore size distribution. Thus the importance of these characteristics of activated carbon relative to the adsorption of humic substances can be evaluated.

Adsorption isotherm studies were conducted to evaluate the effect of pH, particle size of carbons, the molecular weight of the humic substances, as well as adsorption following coagulation was studied. The effect of soluble alum on adsorption was also determined.

The kinetics of adsorption of humic substances were evaluated as a function of activated carbon particle size and the molecular weight of the humic substances. The effect of coagulation with alum before adsorption on the rate of adsorption was also investigated. The mass transfer coefficients obtained from these batch kinetic tests were then used in the mathematical model to predict the performance of activated carbon in columns.

A mathematical model was used to simulate the breakthrough curves for humic substances removal by a carbon bed. Column experiments with different humic substances, along with various hydraulic loading, were subsequently conducted to verify the model predictions. Predictions of the performance of different activated carbon beds with humic substances with and without coagulation were made. Moreover, the effects of the different influent concentration and empty bed contact time on the behavior of the carbon bed were also predicted.

4. MATERIALS AND METHODS

4.1 Materials

4.1.1 Humic Substances

Humic substances from different sources were prepared for this study. These sources included a commercially available humic acid (Pfaltz and Bauer, Inc., Stanford, CT) and humic and fulvic acids extracted from podzol soil (Spodosol) and peat (Histosol). To further purify the commercial humic acid, it was dissolved in 1.5% NaOH, centrifuged, acidified to pH 1 with HCl to precipitate the humic acid, washed to remove chloride, and then freeze-dried. The podzol soil, which was obtained from an area south of Bellaire, Michigan, was on top of B horizon at a depth of between 12 and 22 inches in a zone defined as HIRM. The soil is poorly drained and sandy with a strongly cemented, reddish-brown subsoil. The peat was obtained from the Houghton muck farm of Michigan State University at East Lansing. This abandoned plot is a well decomposed field that has not been fertilized for about 10 years. The peat sample, located on the Oa1 zone at a depth of up to 9 inches is described as a black sapric material with about 5% fiber and with a trace-rubbed, weak coarse subangular blocky structure. The soil is neutral, with an abrupt smooth boundary. The fibers were taken out by screening prior to the extraction. The extraction of humic materials from podzol soil and peat followed the procedure outlined by Snoeyink *et al.* (1977), but with some modifications suggested by Dr. Stevenson, Department of Agronomy, University of Illinois. Figure 1 gives the details of the extraction procedure. The humic acids in the podzol soil and peat were extracted with 0.1 M $K_4P_2O_7$ and were recovered by precipitation with HCl. Following centrifugation, the residue was washed free of acid and was freeze-dried. The fulvic acids were recovered after

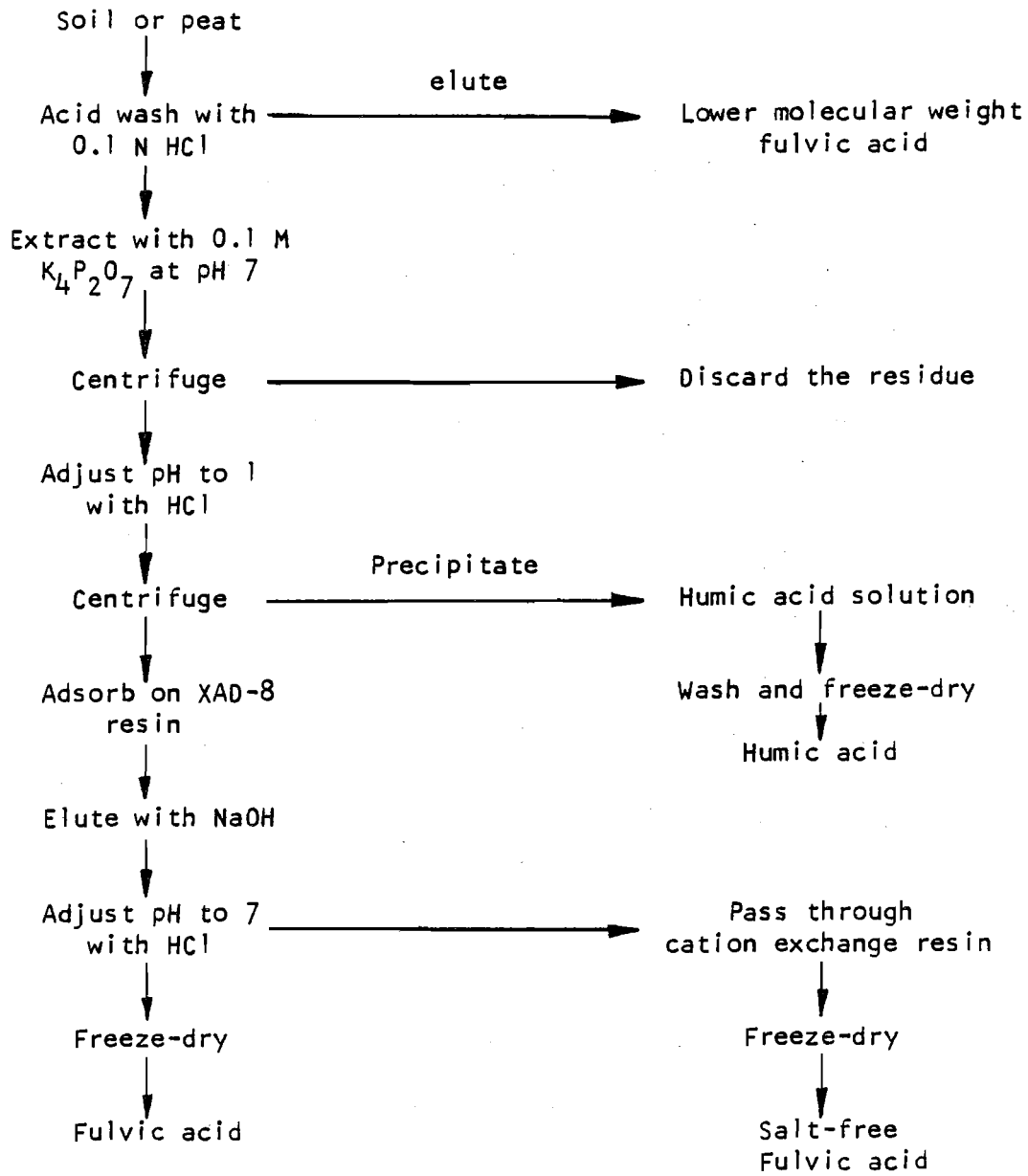


Figure 1. The Extraction Procedures of Soil and Peat.

removal of humic acids from the extracts, and the supernatant was passed through an Amberlite XAD-8 resin (Rohm and Haas, Philadelphia, PA) and then eluted with NaOH. This solution was neutralized with dilute HCl to pH 7 and then split for different treatment processes. Part of the solution was desalted on a cation exchange resin (Dowex 50, 200-400 mesh, The Dow Chemical Co., Midland, MI), and freeze-dried to yield a salt-free fulvic acid. The other part of the solution was freeze-dried only.

Infrared spectra of the commercial humic acid and peat humic and fulvic acids are given in Figure 2. By comparing the infrared spectra of the commercial humic acid and peat humic acid, one can see that peat humic acid can be the major constituent of this commercial humic acid because the infrared spectra are similar. Based on the classification of Stevenson and Goh (1971), the commercial and peat humic acids can be classified as Type I humic substances, while the peat fulvic acid belongs to Type II humic substances. According to Stevenson (1979) and Schnitzer and Khan (1972), the major assignments of absorption bands for these humic substances are given in Table 2. The humic and fulvic acids have similar spectra. The main difference is the absorption intensity of the 1740 cm^{-1} band: fulvic acid is considerably stronger than humic acid because of the presence of more COOH groups (Stevenson, 1979). Spectra of the peat fulvic acids showed strong absorption at 1370 cm^{-1} as well as at 840 cm^{-1} . Since inorganic nitrate absorbs in these regions (Bellamy, 1959), it is suggested that nitrate (present as a contaminant) is responsible for absorption at these frequencies. The source of the inorganic nitrate is unknown but may have been extracted from the peat.

A pronounced difference between the infrared spectra of curve C and D in Figure 2 was observed. Both curves C and D are spectra of peat fulvic acid: curve C was obtained from peat fulvic acid without cation exchange resin

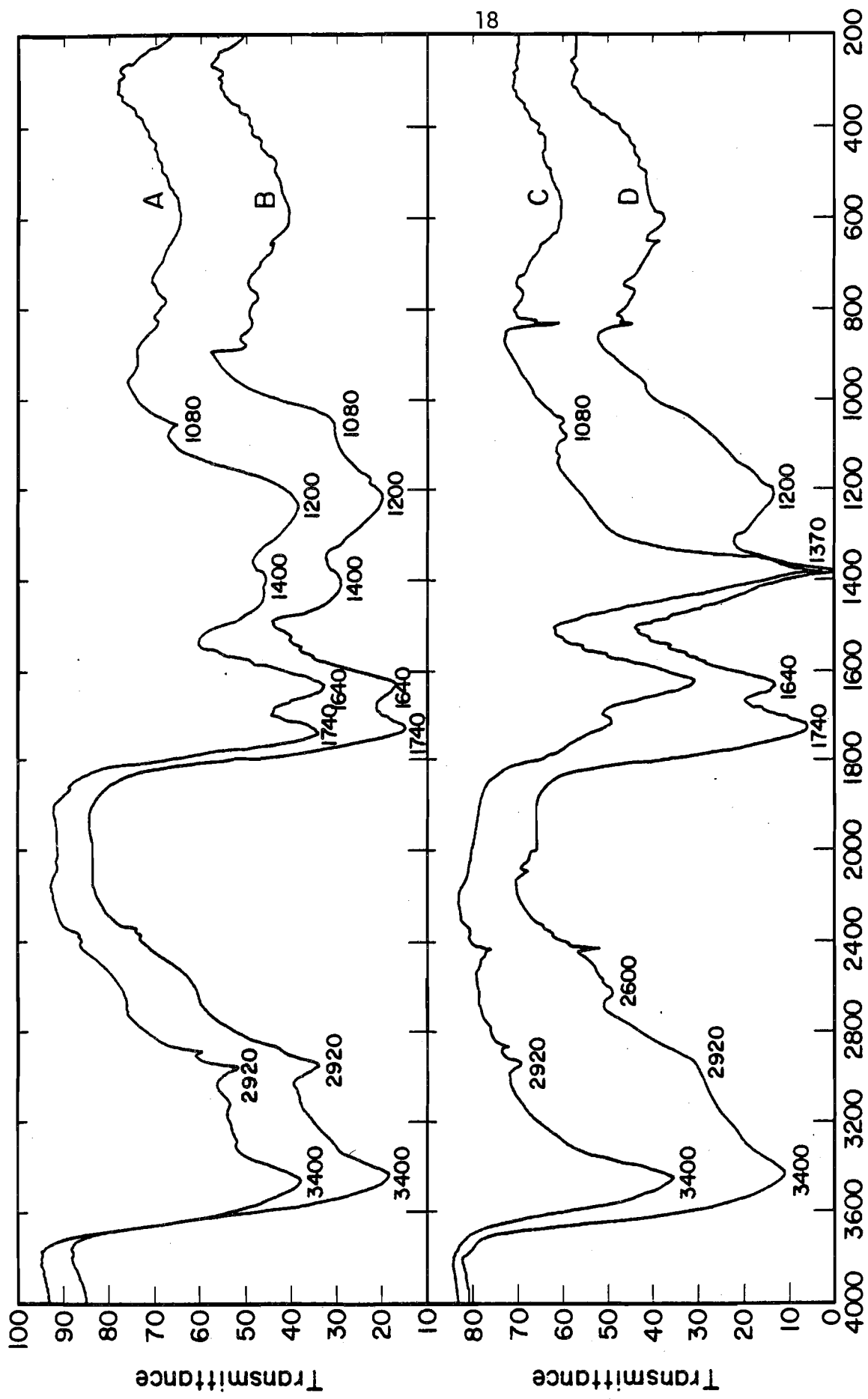


Figure 2. Infrared Spectra of Humic and Fulvic Acids. A. Humic Acid from Pfaltz and Bauer; B. Michigan Peat Humic Acid; C. Michigan Peat Fulvic Acid with Ion Exchange Resin Treatment; D. Michigan Peat Fulvic Acid without Ion Exchange Resin Treatment.

Table 2. Assignments of Absorption Bands for Humic Substances

Wave number, cm^{-1}	Assignment
3400	O-H stretching (H_2O , COOH)
2920	Aliphatic C-H stretching (carbohydrates)
2600	O-H stretching of COOH
1720-1740	C=O stretching of COOH and ketones
1640	Aromatic C=C, strongly H-bonded C=O of conjugated ketones (quinones)
1400	OH deformation and C-stretching of phenolic OH, C-H deformation of CH_2 and CH_3 groups, COO^- antisymmetric stretching
1200	C-O stretching and OH deformation of COOH, C-O stretching of aryl ethers
1170-950	C-O stretching of polysaccharide or polysaccharide-like substance
570-600	Iron

treatment, whereas peat fulvic acid in curve D was subjected to cation exchange resin treatment. The cation exchange resin removed all the salts (mainly Na and K) and converted this peat fulvic acid to the H form, therefore providing a higher adsorption band at 1740 cm^{-1} . The application of the cation exchange resin seemed to recover salt-free peat fulvic acid. However, this peat fulvic acid with cation exchange resin treatment was found to produce a low pH solution when dissolved in water. Therefore, pH adjustment with NaOH was necessary to bring this solution to neutral or desired pH values. The addition of NaOH will not only introduce more Na ions to the solution, but will also possibly convert this fulvic acid to Na fulvic acid, which was the product without cation exchange resin treatment. It was therefore decided to use the peat fulvic acid without cation exchange resin treatment for this entire research.

The elemental analysis of the humic and fulvic acids is given in Table 3. The values agree with previous research indicating that fulvic acids generally have lower carbon but higher oxygen contents than humic acids. The range of the carbon and oxygen contents for peat humic substance is higher than for soil humic substance. The iron content of humic acids was found to be higher than the fulvic acids. This finding is in agreement with the results of Babcock and Singer (1979). However, it was also noticed that the iron contents for humic and fulvic acids were both higher than for their samples. The aluminum content is in the range of 0.02 to 0.11% for all samples.

To obtain different molecular weight fractions of humic substances, an Amicon stirred cell (Amicon Co., Lexington, MA) was used. The Amicon Diaflo Filters of UM2, UM10, and XM50 were used with molecular weight cut-offs of 1,000, 10,000, and 50,000, respectively. The concentration of each molecular weight fraction was measured by TOC.

Table 3. Elemental Content of Humic and Fulvic Acids (Percent, Dry Weight)

Element	Commercial humic acid	Peat		Soil	
		Humic acid	Fulvic acid	Humic acid	Fulvic acid
C	46.32	44.53	42.18	38.04	35.78
H	3.37	4.05	3.62	4.53	3.29
O	31.38	41.97	44.51	34.19	38.67
N	0.57	2.57	2.85	2.84	2.67
S	2.94	1.33	0.47	0.83	0.87
Fe	0.37-0.48	0.56	0.37-0.42	0.42	0.06
Al	0.08	0.09	0.10-0.11	0.08	0.02
Ash	15.41	5.55	5.90	19.57	18.72

Humic substance solutions for adsorption studies were prepared from a stock solution. Stock solutions were prepared by weighing appropriate amounts of the freeze-dried humic substances and dissolved them in adequate volumes of deionized distilled water. The fulvic acid dissolved more easily in water than humic acid, but only a couple of pellets of NaOH was necessary to dissolve the humic acid. All the stock solutions were stored in a refrigerated chamber at a constant temperature of 5°C. Stock solutions were warmed up to room temperature and diluted with appropriate amounts of deionized distilled water before each experiment. A suitable amount of the phosphate buffer in the form of sodium phosphate dibasic anhydrous (Na_2HPO_4) was introduced into the solution and maintained at 10^{-3}M concentration. The pH of the solution was then adjusted with NaOH and HCl. In most cases, the pH was maintained at 6 unless stated otherwise.

For the studies of alum coagulation followed by adsorption, peat fulvic acid solution from a stock solution was diluted with deionized distilled water to a concentration of 70 mg/l as TOC. Coagulation was done by adding 50 mg/l of alum from a stock solution to a peat fulvic acid solution and adjusting the pH to 6. A standard jar test was then carried out for the coagulation experiment. The supernatant aliquots were filtered through 0.45 μm Millipore HA filter paper (Millipore Co., Bedford, MA). This solution was then diluted with deionized distilled water to a desired TOC value for adsorption studies.

4.1.2 Coagulant

Alum is the most popular coagulant used for water treatment. Although it has been contended that ferric sulfate has advantages over aluminum sulfate for removal of color substances from water (Singley et al., 1965), the latter coagulant is widely and successfully used. In this research, aluminum sulfate

(Analytical grade, Mallinckrodt, Inc., St. Louis, MO) was used as the only coagulant.

4.1.3 Activated Carbons

In order to better understand the adsorption phenomena of the humic substances, several different activated carbons were selected for this study. Activated carbons made from a variety of raw materials such as bituminous coal, lignite, petroleum residue, and wood have different properties. Table 4 gives the surface area and pore volume of these activated carbons. The BET nitrogen surface area ranged between 575 and 1422 m²/g, the pore surface area measured by mercury intrusions from 20 psia to 60,000 psia was between 99 and 778 m²/g. No correlation was found between BET and pore surface area. The WV-B and WV-DC carbons both had a large pore volume and a higher surface area. The HD-3000 carbon had a large pore volume with a smaller surface area, and thus had a large quantity of macropores. The F-400, WV-G, and WV-L carbons had a moderate pore volume and a moderate surface area. The WV-W, WV-H, and Witcarb carbons were the opposite of the HD-3000 carbons: they had a large surface area but a small pore volume indicating a large volume of micropores.

The pore volume for Hg and total is also given in Table 4. The volume of mercury displacement at a maximum pressure of 60,000 psia gives the macropore volumes; the volume filled by nitrogen gives the micropore volumes. By adding the successive volume increments measured by mercury penetration to the pore volume occupied by nitrogen, the pore size distribution and total pore volume may be obtained. The total pore volume (pores < 10⁵ Å radius) ranged between 0.599 and 1.865 cc/g. Figures 3 and 4 give the pore size distributions of these carbons. These analyses were provided by Carborundum Company (Niagara Falls, NY). Figure 3 presents the pore size distribution for the various carbons. Three types of pore size distribution among these carbons

Table 4. Surface Area and Pore Volume of Selected Activated Carbons*

Activated carbon	Manufacturer	Raw material	Surface area, m ² /g		Pore volume, cc/g	
			BET	Pore	Hg	Total
F-400 (< 14)	Calgon Corp.	Bituminous coal	1,228	366	0.625	1.108
F-400 (20 x 30)	Calgon Corp.	Bituminous coal	1,075	309	0.643	1.071
F-400 (40 x 60)	Calgon Corp.	Bituminous coal	1,155	433	0.847	1.235
HD-3000 (20 x 40)	ICI America Inc.	Lignite coal	575	99	0.787	0.975
Witcarb-940 (14 x 20)	Witco Chemical Corp.	Petroleum-based coke	950	106	0.208	0.599
WV-B (20 x 35)	Westvaco	Bituminous coal	1,422	778	1.290	1.865
WV-DC (20 x 35)	Westvaco	Wood-based coal	1,115	621	1.230	1.764
WV-G (20 x 40)	Westvaco	Bituminous coal	1,020	238	0.398	0.814
WV-H (8 x 16)	Westvaco	Bituminous coal	910	133	0.251	0.610
WV-L (20 x 30)	Westvaco	Bituminous coal	976	188	0.420	0.818
WV-W (20 x 40)	Westvaco	Bituminous coal	861	154	0.281	0.612

* Data of surface area and pore size distribution were analyzed by Carborundum Company (Niagara Falls, NY).

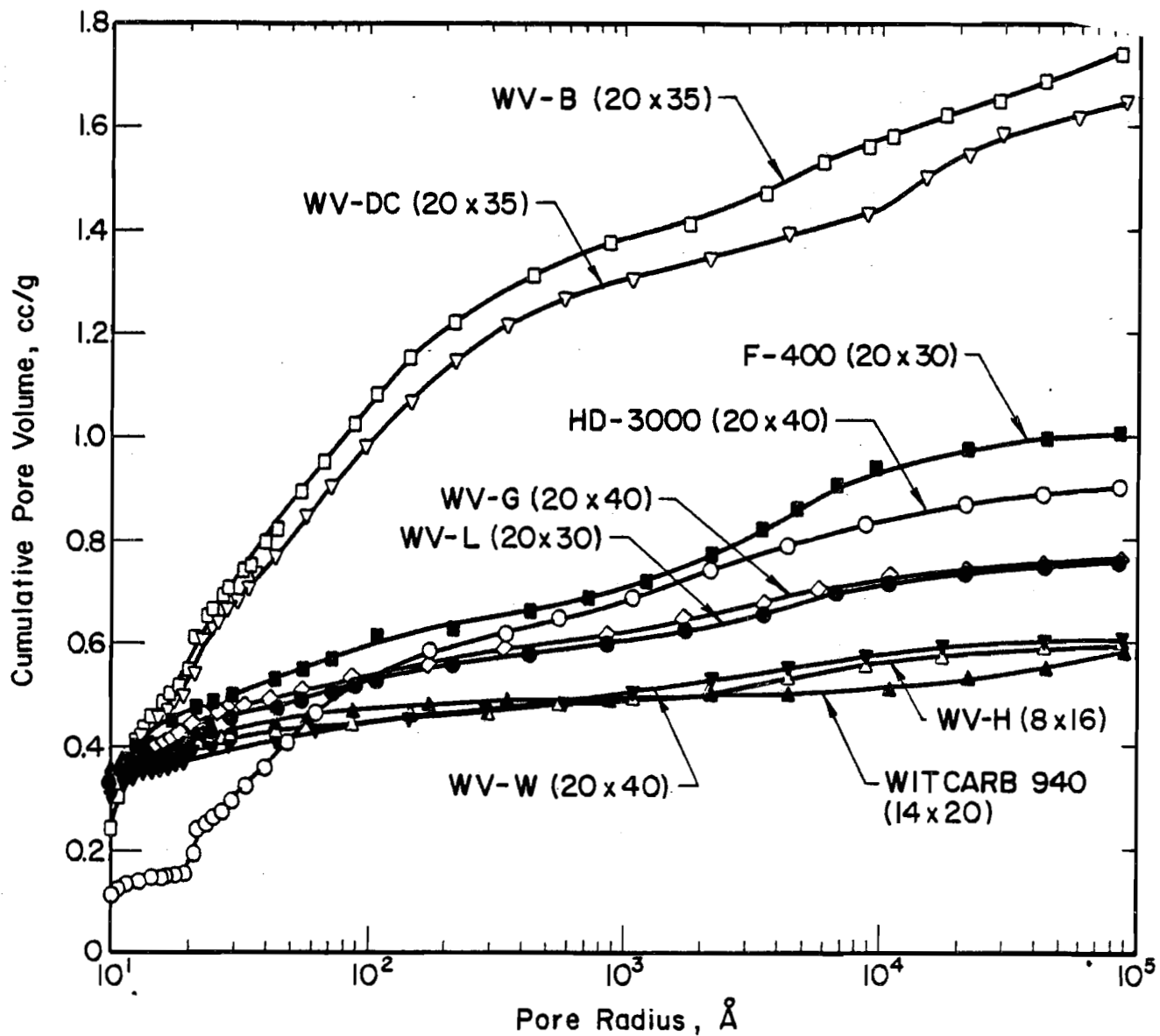


Figure 3. Pore Size Distributions for Different Activated Carbons.

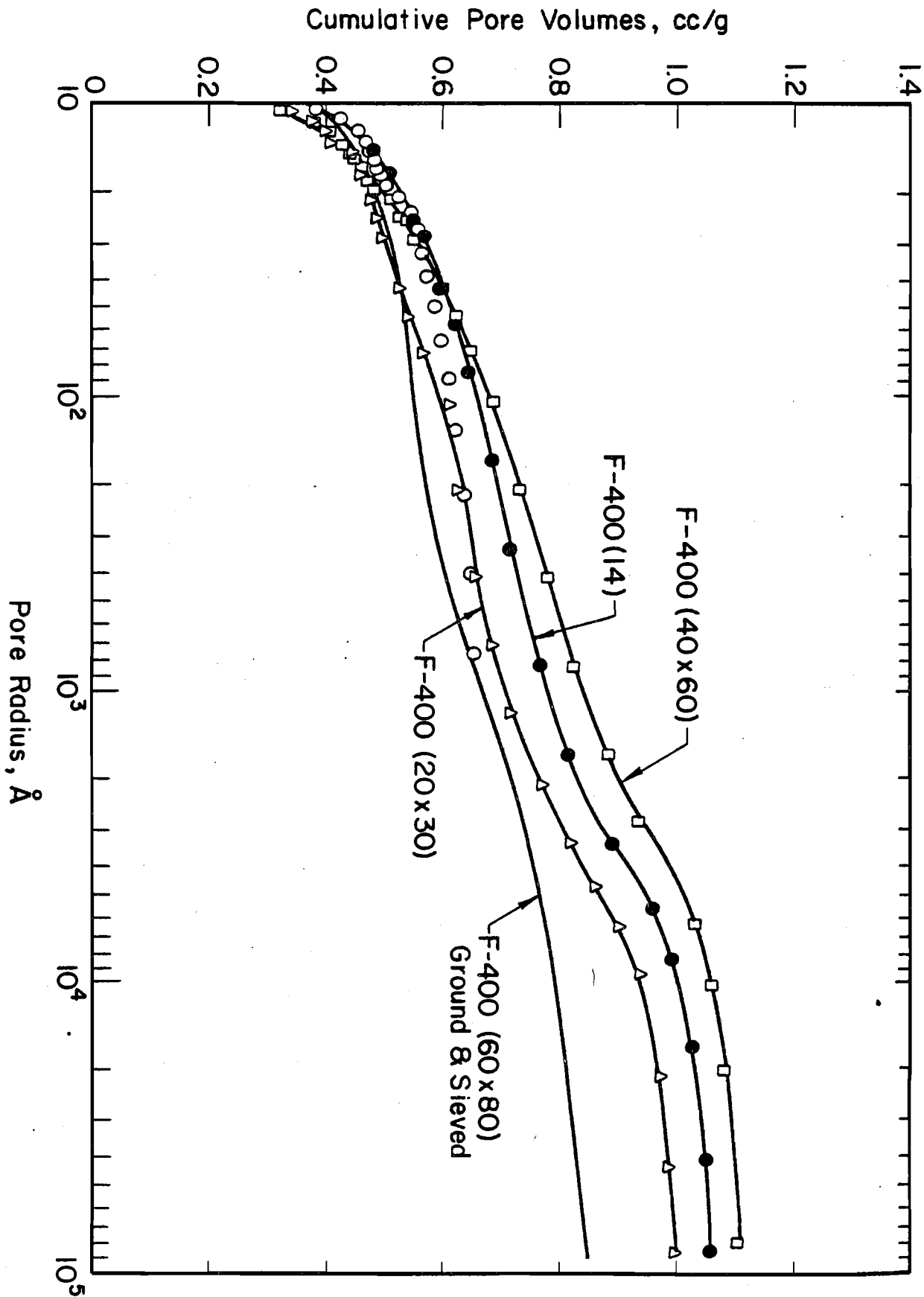


Figure 4. Pore Size Distributions for Different Particle Sizes of F-400 Activated Carbon.

were observed. According to the classification of Dubinin (1966), pores with radii larger than $1,000 \text{ \AA}$ are macropores, pore radii smaller than 20 \AA are micropores, and pores between 20 \AA and $1,000 \text{ \AA}$ are transitional pores. The WV-B, WV-DC, and HD-3000 carbons had predominantly macropores. The F-400, WV-G, and WV-L were carbons with a wide spectrum of pore sizes but predominantly transitional pores; and the WV-H, WV-W, and Witcarb carbons had predominantly micropores. The nature of the raw material, the impurities in it, and the activation processes will provide activated carbons with different pore size distributions. Figure 4 shows the pore size distributions of carbons with different particle sizes. It is likely that no significant difference of pore size distribution is presented among these different particle sizes. The ground and sieved F-400 (60 x 80) provides a slightly lower pore volume compared with that of carbons of other sizes.

Most of the carbons were sieved to yield a particle size of 20 x 40 mesh, which represented the most abundant particle size of the commercially available carbons. The Witcarb and WV-H have larger grained carbons; therefore, mesh sizes of 14 x 20 and 8 x 16 were selected. The carbons were then washed with deionized water to remove fines and impurities and rinsed with deionized distilled water, followed by drying at 110°C overnight to evaporate all the moisture and volatile organics.

Granular activated carbon (GAC) was used for the batch rate and column experiments, whereas powdered GAC was used for the isotherm studies. The powdered GAC was prepared by pulverizing granular carbons for 3 minutes, using a Tekmar mill (Tekmar Co., Cincinnati, OH). The powdered carbon in the isotherm samples was removed by filtering with a $0.45 \mu\text{m}$ Millipore HA filter paper, followed by centrifuging at 7,500 rpm for 20 minutes to remove

carbon fines less than 0.45 μm . Several types of filter papers were tested and the 0.45 μm Millipore HA filter paper was chosen. This type of filter paper was able to remove carbon fines and did not cause interference for analysis of humic substances.

4.2 Analytical Methods

Samples for infrared spectra were prepared using the KBr pellet method. The procedures for this method are described well in the Perkin-Elmer (Perkin-Elmer Co., Norwalk, CT) bulletin. Freeze-dried humic substances were dried in a vacuum oven at 40°C overnight, approximately 1 mg of the sample was ground with 300 mg of KBr powder, and this mixture was then pressed at an elevated pressure into a small disc. Precautions as given by Stevenson (1979) were also taken to eliminate moisture interference. This KBr disc was then analyzed using a Beckman Model 260 double-beam spectrophotometer (Beckman Instruments, Inc., Fullerton, CA).

The fluorescence measurements were taken using a Turner model 110 fluorometer with an excitation wavelength of 365 nm, and an emission wavelength of 415 nm using a 1 cm light path (Turner Associates, Palo Alto, CA). Fluorescence scans were obtained with a Perkin-Elmer model 204 scanning spectrofluorometer. UV/Vis absorbance measurements were made using a Beckman Acta III spectrophotometer. The wavelengths for quantitative analysis of the humic and fulvic acids were 420 nm and 300 nm, respectively. The total organic carbons were measured by a Dohrmann DC 50/54 TOC Analyzer (Envirotech Co., Santa Clara, CA). Aluminum was determined using a Perkin-Elmer model 370 atomic absorption spectrophotometer.

A modified liquid-liquid extraction method for the analysis of chloroform concentration was developed for this research. This analytical technique was

found to be accurate and reproducible at a detection limit of 10 $\mu\text{g}/\text{l}$. It has been used by several other researchers in the Department of Civil Engineering at the University of Illinois, and has been shown to be precise and fast. The details of this analytical method are given in Appendix A.

4.3 Experimental Techniques

4.3.1 Coagulation Experiments

Standard jar tests were used for the coagulation experiments. The optimum conditions for coagulation were investigated. The samples were mixed rapidly at 100 rpm for 5 min followed by a slow mix at 30 rpm for 20 min on a jar test machine. The samples were allowed to stand overnight, after which time supernatant aliquots were filtered through 0.45 μm Millipore HA filter paper and analyzed for TOC. Results of this preliminary study indicated that the optimum pH for the coagulation of commercial humic acid was between 5 to 6, while a much wider range of pH values between 5 to 8 was found for peat fulvic acid. At pH 6, the optimum dosages of alum for 5 mg/l of commercial humic acid and of peat fulvic acid are 50 mg/l and 20 mg/l, respectively. Similar results for the optimum pH for alum coagulation were reported by Kavanaugh (1978) and Semmens et al. (1979).

4.3.2 Adsorption Isotherm Experiments

The adsorption isotherm tests used well established techniques. These tests consisted of mixing known concentrations of humic substance solution and weighted amounts of selected powdered GAC. The sample bottles were placed on a rotary shaker, which provided excellent mixing at a rotation speed of about 25 rpm. After the samples reached equilibrium, they were filtered with a 0.45 μm Millipore filter and the filtrate was analyzed. The time to reach

equilibrium is given in Section 6.2.

4.3.3 Batch Rate Experiments

Batch rate tests were conducted in a 4-liter reactor. A variac-controlled stirrer operated at approximately 1,200 rpm provided good mixing conditions. The power input to the stirrer was as large as possible without causing vortexing or carbon particle breakup. The initial concentration of the humic substances and concentrations at different time intervals after addition of known amounts of granular activated carbon to the reactor were measured. A time interval was used that would provide sufficient data for the determination of film transfer and surface diffusion coefficients by the batch reactor model.

4.3.4 Column Experiments

The column tests used a laboratory-scale glass column that contained known amounts of GAC of uniform size. The particle size was the same as that used in the batch rate tests. To avoid wall effects, a careful selection of column diameter was chosen. Preliminary study of the selection of column diameter for a particle size of 20 x 40 mesh indicated that wall effects were observed when the column diameter was 1.0 cm. The selection of a 3.0 cm column diameter was satisfactory for avoiding wall effects. The flow rate and the bed length of the carbon column were also investigated. A combination of 0.78 gpm/ft² flow rate and 24.0 cm bed length gave a good breakthrough curve. This hydraulic loading was equal to 7.5 min empty bed contact time (EBCT). The column was operated in an upflow packed-bed mode. The humic substance solution was stored in a 45-liter glass carboy and then applied to the column at a constant flow rate of 0.78 gpm/ft². The effluent from the column was analyzed to establish a breakthrough curve.

5. MODELING

Adsorption of dissolved organic substances from dilute aqueous solutions by a porous adsorbent such as activated carbon involves several sequential and parallel transport and reaction phenomena. These steps are: the transport of the adsorbate through a liquid boundary layer surrounding the exterior of the adsorbent, the diffusion of the adsorbate within the pores of the adsorbent, and the adsorption of the solute on the interior surfaces of the pore and capillary spaces of the adsorbent.

A model incorporating mathematical descriptions of the following phenomena, as reported by Crittenden and Weber (1978a), was used in this study: (1) film transfer resistance to mass transfer (i.e., the linear driving force); (2) local adsorption equilibrium adjacent to the carbon surface; (3) surface diffusion as the predominant intraparticle mass transfer process (predicated on comparative analysis of parallel mechanisms for pore solute flux). An illustration of the model mechanisms is presented in Figure 5. Crittenden and Weber verified their model by comparing the predicted breakthrough curves of experimental data of adsorbates that had different controlling mass transfer resistances. Furthermore, they showed that the controlling mass transfer resistances can be determined from the Sherwood number. A Sherwood number greater than 50 indicates that surface diffusion resistance is controlling the rate of adsorption. On the other hand, a Sherwood number less than 1 indicates that film transfer resistance is controlling the rate of adsorption.

Although humic substances are considered as a heterogeneous mixture of molecules, they range in molecular weight from several hundred to perhaps more than 300,000. Humic substances were treated as a single solute in the model.

MODEL MECHANISMS

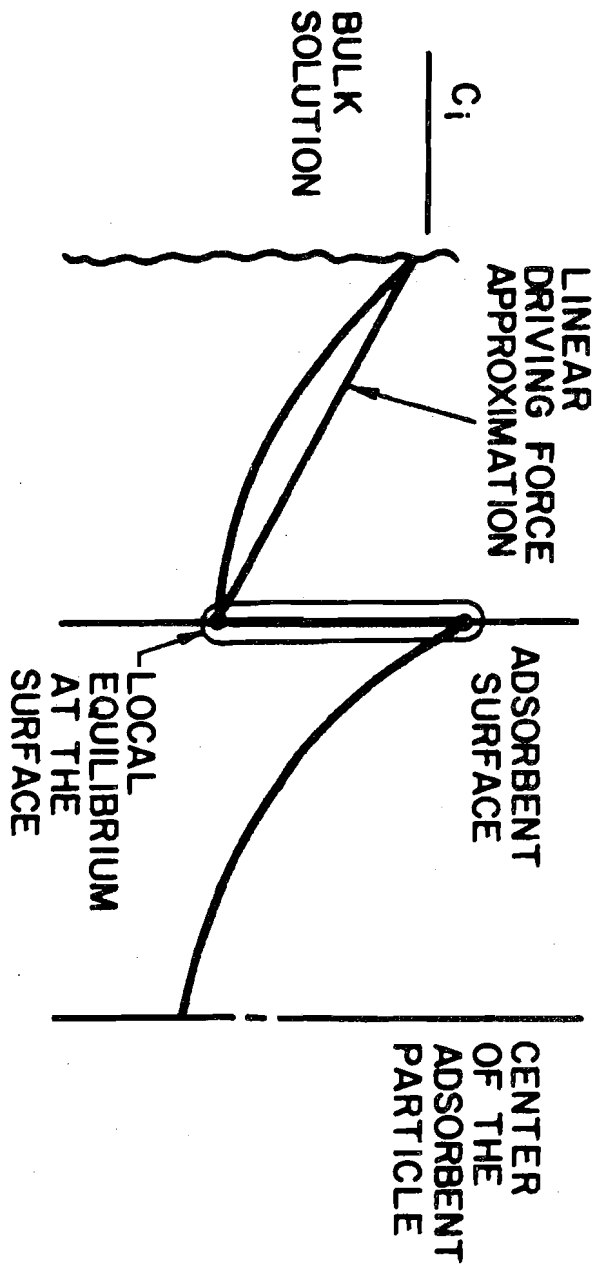


Figure 5. An Illustration of the Model Mechanisms of Dissolved Organics from Dilute Aqueous Solutions Adsorbed by Activated Carbon.

5.1 Batch Reactor Model

Development of the batch reactor model was based on the framework of the column model developed by Crittenden and Weber (1978a,b). The mathematic equations involved in this model are presented here. A mass balance on the liquid-phase is given by this equation:

$$\frac{dC}{dt} = \frac{-3 k_f D_o}{(1 - D_o/\rho_a) \rho_a R} (C - C_s) \quad (1)$$

in which, C = liquid-phase concentration (M/L^3)

C_s = liquid-phase concentration adjacent to the particle surface (M/L^3)

D_o = dosage of carbon (M/L^3)

k_f = film transfer coefficient (L/t)

R = adsorbent radius (L)

t = time (t)

ρ_a = adsorbent density that includes pore volume (M/L^3)

The initial condition for the liquid-phase material balance is:

$$C = C_o \text{ at } t = 0 \quad (2)$$

in which, C_o = initial bulk concentration (M/L^3).

The solid-phase material balance for the mass transport within the adsorbent particle is:

$$\frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) = \frac{\partial q}{\partial t} \quad (3)$$

in which, D_s = surface diffusion coefficient (L^2/t)
 q = solid-phase concentration (M/M)
 r = radial coordinate (L)

The boundary conditions necessary for the solution of equation 3 are:

$$\frac{\partial q}{\partial r} = 0 \text{ at } t \geq 0 \text{ and } r = 0 \quad (4)$$

$$\frac{k_f R^2}{\rho_a} (C - C_s) = \frac{\partial}{\partial t} \int_0^R q r^2 dr \text{ at } t \geq 0 \quad (5)$$

Equation 5 states that the rate of mass transfer through the surface film is equal to the rate of change of the average surface concentration inside the particle. The initial condition for the solid-phase material balance is:

$$q = 0 \text{ at } t = 0 \text{ and for } 0 \leq r \leq R \quad (6)$$

To complete the solution of the model, the Freundlich adsorption equation is used to couple equations 1 and 3.

5.2 Column Model

The model developed by Crittenden and Weber (1978a,b) was used in this study. Model equations that result from a solid-phase material balance in a fixed bed and its respective boundary and initial conditions are the same as those for the batch reactor model. The liquid-phase material balance is presented as,

$$v \frac{\partial C}{\partial z} - \frac{3 k_f (1-\epsilon)}{\epsilon \rho_a R} (C - C_s) = \frac{\partial C}{\partial t} \quad (7)$$

in which, v = interstitial velocity (L/t)
 z = longitudinal adsorption bed coordinate (L)

ϵ = fraction of volumetric space unoccupied by the adsorbent or void fraction

The boundary condition necessary for the solution of equation 7 is:

$$C = C_0(t) \text{ at } t \geq 0 \text{ and } z = 0 \quad (8)$$

The initial condition is given as,

$$C = 0 \text{ for } \frac{tv}{L} < z \leq L \quad (9)$$

The Freundlich adsorption isotherm is used to couple the solid-phase and fixed-bed mass balance equations 3 and 7.

5.3 Orthogonal Collocation and Finite Difference Methods

Differential equations involved in the models were solved by Crittenden and Weber (1978a,b) using a finite difference technique. Finite difference techniques convert these differential equations to algebraic equations that are solved on a computer. The finite difference techniques are discussed by Mathews and Weber (1976) and Crittenden (1976). The disadvantage of this technique is the model's lack of stability. An optimized combination of numbers of time, radius, and bed steps has to be selected by trial-and-error for each different column analysis. It is quite difficult to obtain such a combination for these three parameters.

Orthogonal collocation has been shown to be more efficient and accurate than the finite difference techniques (Finalyson, 1972; Crittenden et al., 1979). Thacker and Crittenden (personal communication) applied the techniques of orthogonal collocation to solve the model equations in batch and column adsorbers. In this method, the axial and radial derivatives are approximated by specified trial

functions having coefficients adjusted so that the substitution of the trial function into the differential equations results in zero error at specified grid or collocation points. Orthogonal collocation was compared with analytical solutions to check its accuracy and stability, and excellent comparisons were obtained. Therefore, both batch reactor and column models were solved using orthogonal collocation.

5.4 Parameter Estimation

The adsorption isotherm constants, surface diffusion coefficient, and column film transfer coefficient must be determined independently of column experiments. The column model can only be verified by comparing model predictions with experimental data.

5.4.1 Isotherm Constants

The Freundlich isotherm equation is generally used for heterogeneous surface systems such as activated carbon. The equation is as follows:

$$q_e = KC_e^{1/n} \quad (10)$$

in which, C_e = equilibrium concentration in solution

K = Freundlich constant which relates to adsorption capacity

$1/n$ = Freundlich constant which relates to adsorption intensity

q_e = equilibrium surface concentration

By taking the logarithmic form of equation 10, one arrives at a straight line with a slope of $1/n$ and an intercept of K at $C_e = 1$. The slope and intercept of this adsorption isotherm were estimated by linear regression.

5.4.2 Surface Diffusion Coefficient

Surface diffusion coefficient was determined using batch reactor studies. Experimental concentration-time data were compared with model predictions, and the best statistical fit was used to determine the mass transfer parameters.

Although film transfer and surface diffusion coefficients were obtained simultaneously from batch reactor data by a model developed by Mathews and Weber (1976), it is quite difficult and expensive to apply a model with two unknown parameters. DiGiano (1969) and Letterman (1974) had noticed that the rate of solute uptake is controlled by film diffusion in the initial stages and by particle diffusion in the latter stages. Assuming the surface concentration was negligible for the initial period, equation 1 can be rearranged and integrated to give the following equation:

$$\ln \left(\frac{C_0}{C} \right) = \frac{3 k_f D_0}{R \rho_a} t \quad (11)$$

The value of k_f can be estimated by plotting $\ln \left(\frac{C_0}{C} \right)$ versus t . Strictly speaking, this equation is valid only at time $t=0$, where the surface concentration is zero. Mathews and Weber (1976) investigated the effect of intraparticle diffusion on the initial adsorption rate. For a lower value of the film transfer coefficient (5×10^{-3} cm/sec), initial rates are not significantly affected by diffusion within the particle. However, for a large value of film transfer coefficients (1.5×10^{-1} cm/sec), the use of initial rate data beyond the first few minutes would result in large errors in computing values for k_f .

A batch rate study using commercial humic acid solution with F-400 (60 x 80) activated carbon in a 15-l reactor was conducted to determine the film transfer and surface diffusion coefficients. The linear relationship for a plot of $\ln \left(\frac{C_0}{C} \right)$ versus t holds up to a period of 2 hours. The estimation of the film transfer

coefficient from the initial rate data gives a value of 6.14×10^{-5} cm/sec. The film transfer coefficient determined using the batch model was 6.5×10^{-5} cm/sec. By comparing the film transfer coefficient obtained from the initial slope method and the batch model, the value determined by plotting $\ln \left(\frac{C}{C_0} \right)$ versus t is acceptable.

The film transfer and surface diffusion coefficients were determined to be 6.5×10^{-5} cm/sec and 6.0×10^{-12} cm²/sec for this batch reactor model. Weber *et al.* (1978) studied the adsorption of commercial humic acid from the Aldrich Chemical Co., Inc. (Milwaukee, WI) and obtained values for k_f and D_s of 1.3×10^{-4} cm/sec and 3.2×10^{-11} cm²/sec, respectively. Since the value of film transfer coefficients can be varied with the conditions of mixing, no comparison of this value is made. However, the discrepancy between the values of surface diffusion coefficient may be due to the fact that their batch rate data were collected for only 12 hours, which may not be a sufficiently long duration to accurately estimate the surface diffusion coefficient.

5.4.3 Statistical Analysis of Batch Surface Diffusion Coefficient

An evaluation of the accuracy of surface diffusion coefficients was needed for the column predictions. This evaluation was conducted by using a confidence interval concept, as given by Draper and Smith (1966). The following equation was used to indicate the data scatter associated with the batch reactor model.

$$S(\theta) = S(\hat{\theta}) \left\{ 1 + \frac{p}{n-p} F(p, n-p, (1-\alpha)) \right\} \quad (12)$$

In which, F = F distribution with p and $n-p$ degrees of freedom

n = number of data points

P = number of parameters

$S(\theta)$ = allowable variance

$S(\hat{\theta})$ = minimum of variance

Figure 6 displays the sample deviation with different values of the film transfer and surface diffusion coefficients in the batch reactor model by fitting data obtained from commercial humic acid and WV-G carbon. The square root of the sum of the difference between actual and predicted data divided by the number of data points gives the sample deviation. The minimum sample deviation occurs at the point where the value of k_f and D_s is 1.50×10^{-3} cm/sec and 2.10×10^{-11} cm²/sec, respectively. The minimum sample deviation is 0.0231; the 90%, 95%, and 99% confidence regions are presented in Figure 6. Values of different sample deviations of 0.03 and 0.04 are also given in this figure. The shape of these contours indicates that the value of k_f is not determined as accurately as D_s . This can be explained by examining the value of the Sherwood number: range of the Sherwood number is from 99 to 1744. Such a high Sherwood number indicates that surface diffusion resistance is a predominant factor in adsorbing humic substances. However, the shape of these contours can be open or closed ellipses depending on the experimental data. With 95% confidence, the D_s can vary from 1.75×10^{-11} to 2.55×10^{-11} cm²/sec in this case.

5.4.4 Column Film Transfer Coefficient

The film transfer coefficient was determined using a correlation developed by Williamson et al. (1963). This correlation was found to be satisfactory in the predictions of carbon adsorption of phenol, p-bromophenol, p-toluene sulfonate, and dodecyl benzene sulfonate, as reported by Crittenden and Weber (1978a,b). The correlation equation is as follows:

$$\frac{k_{fc}}{V_s} S_c^{0.58} = 2.40 Re^{-0.66} \quad (0.08 < Re < 125) \quad (13)$$

$$Sc = \frac{\mu_l}{\rho_l D_l} \quad (14)$$

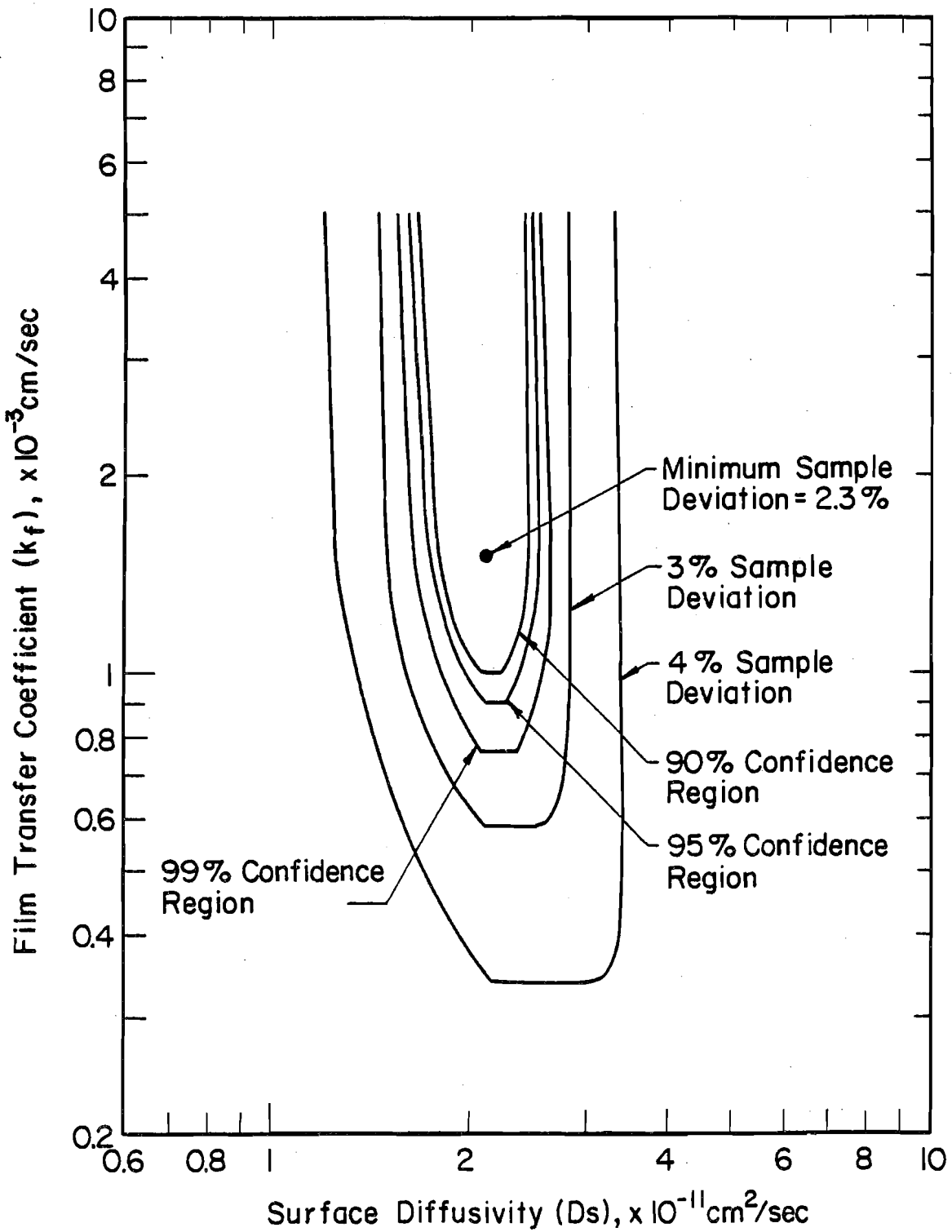


Figure 6. The Contour Lines of Sample Deviation with Respect to Different Values of D_s , k_f , and Confidence Region.

$$\text{Re} = \frac{\rho_l D V_s}{\epsilon \mu_l} \quad (15)$$

in which, D = diameter of the particle

D_l = liquid diffusivity

k_{fc} = film transfer coefficient of the column

Re = Reynold's number

Sc = Schmidt number

V_s = superficial velocity

μ_l = liquid viscosity

ρ_l = density of liquid

This correlation equation requires an estimate of the free liquid diffusivity of humic substances. Since no information was available in the literature on the free liquid diffusivity of humic substances, an estimate of this value was made.

Several methods were used to calculate the free liquid diffusivity:

(1) Arbuckle, 1978; (2) Wilke and Chang, 1955; (3) Polson, 1950. The estimated free liquid diffusivities from the above three correlations were introduced to the Williamson correlation to determine the column film transfer coefficient. For a typical column experiment of commercial humic acid adsorbed by F-400 (60 x 80) carbon, the average particle diameter is 0.021 cm, the flow rate is 4.6 ml/min, and the column diameter is 1.0 cm. The porosity of the column is calculated as 0.41, the superficial velocity as 9.762×10^{-2} cm/sec, and the Reynold's number as 0.558. Therefore, the corresponding values of column film transfer coefficients for the above three methods were 1.163×10^{-3} , 3.170×10^{-4} , and 1.479×10^{-3} cm/sec. The column film transfer coefficient determined by the best fit of model prediction to experimental data was 1.0×10^{-3} cm/sec. Both values of the column film transfer coefficients calculated from Arbuckle's and Polson's methods are

close to the value determined from the model analysis. Consequently, the estimation of humic substance liquid diffusivity by the Arbuckle's and Polson's methods are adequate for use in this study.

6. RESULTS AND DISCUSSION

6.1 Evaluation of Different Analytical Methods to Indicate the Chloroform Formation Potential of Humic Substances

Fluorescence intensity, ultraviolet/visible (UV/Vis) absorption and total organic carbon (TOC) are the three parameters most often used to determine the concentration of humic substances in water. Since humic substances are precursors of trihalomethanes, these three analytical methods were correlated with the chloroform formation potential (CFP) of humic substances. The suitability of using these analytical methods in the studies of alum coagulation and carbon adsorption of humic substances in water was also examined.

6.1.1 Comparison of Fluorescence Intensity and Ultraviolet/Visible Absorption with Total Organic Carbon Measurements

Table 5 presents a correlation of TOC with fluorescence intensity of a commercial humic acid solution before and after carbon adsorption. Fluorescence intensities were measured using an excitation wavelength of 365 nm, an emission wavelength of 415 nm, and a path of 1 cm, as described by McCreary and Snoeyink (1979). As shown in Table 5, preferential adsorption of humic acid species that fluoresce occurred when activated carbon was introduced into the solution. The fluorescence intensity per mg/l TOC was significantly less for the solution equilibrated with carbon than for the solution that was not dosed with carbon. Figure 7 shows the fluorescence spectra of humic acid solution before and after carbon treatment. These fluorescence scans were obtained by exciting the samples at 365 nm and scanning the emission wavelengths from 300 to 700 nm. As this figure shows, the fluorescence emission peak shifted when carbon was added to the humic acid solution. This shift may be caused by the preferential absorption

Table 5. Correlation of TOC with Fluorescence Intensity of Commercial Humic Acid Solution

Sample*	TOC, mg/l	Fluorescence intensity	Fluorescence intensity per mg/l TOC
A	5.037	442	87.75
B	3.417	110	32.19
C	3.400	300	88.24

* Samples A and C were commercial humic acid solutions without carbon adsorption, sample B was obtained by equilibrating 10 mg of activated carbon F-400 with 100 ml of sample A, and sample C was diluted from sample A to the same TOC of sample B.

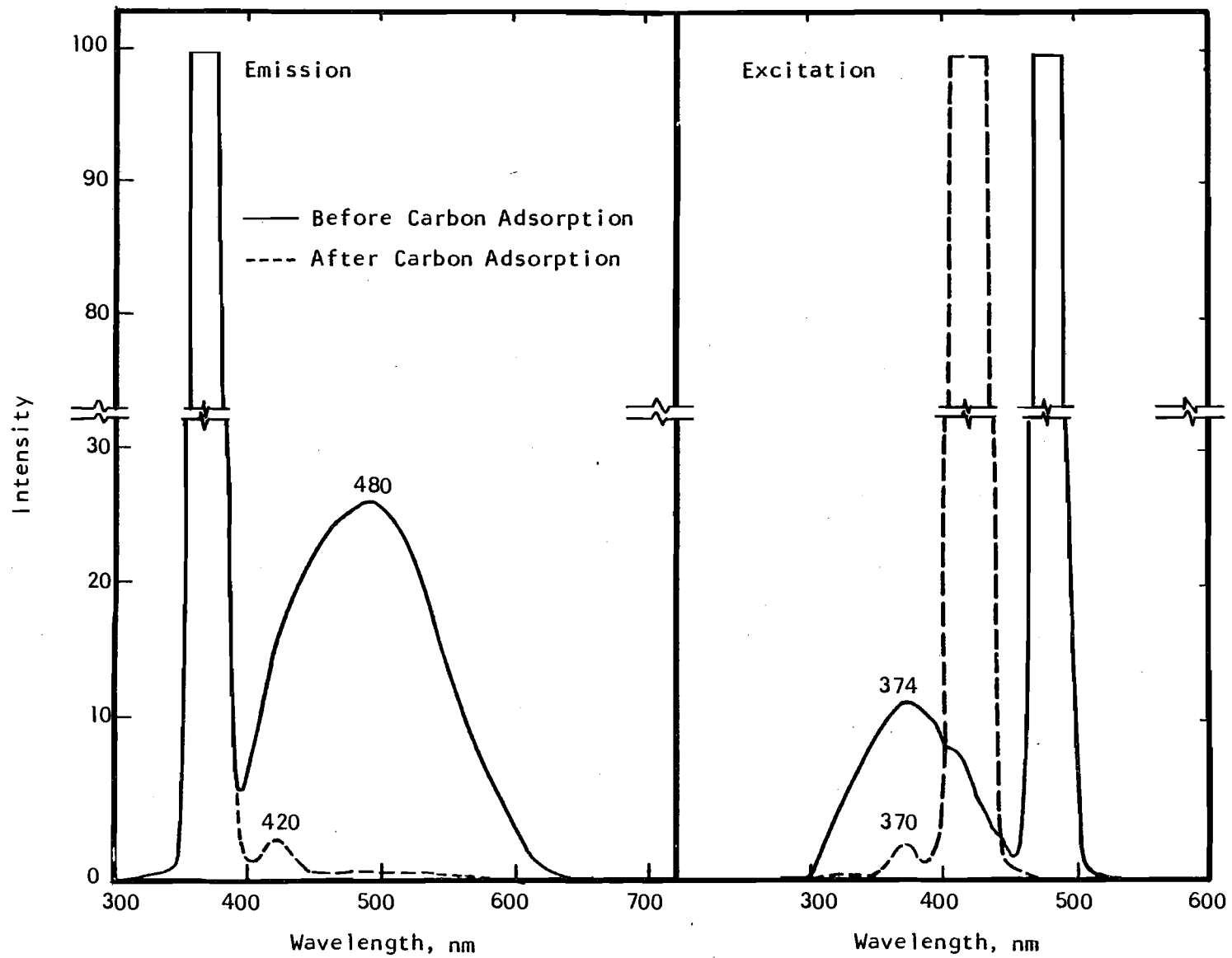


Figure 7. Fluorescence Spectra of a Commercial Humic Acid before and after Carbon Adsorption.

of fractions of humic acid that fluoresce.

There was a very good correlation of UV or Vis light absorbance with TOC, as shown in Figure 8. Line B was obtained from peat fulvic acid solution dosed with different amounts of alum. The other lines are plots of different humic substances after passage through different activated carbon beds. The specific wavelength for commercial humic acid was 420 nm, whereas it was 330 nm for peat fulvic acid and peat fulvic acid remaining after coagulation with alum. The correlation coefficient for these linear regression analyses varied from 0.994 to 0.999, which indicated a good linear relationship between UV or Vis light absorbance and TOC. Since samples for this correlation were analyzed after alum coagulation and/or adsorption, there is probably no preferential coagulation or adsorption of fractions of humic substances that absorb UV or Vis light.

6.1.2 Total Organic Carbon and Chloroform Formation Potential

The data from the NORS study by Symons et al. (1975) indicate that chloroform is the major component of the trihalomethanes found at water treatment plants. Since only chloroform was formed when the humic substances used in this study were chlorinated (no Br^- or I^- was present), an extensive investigation of the relationship between TOC and CFP was conducted. To evaluate the suitability of these analyses for the carbon adsorption studies, different humic substances were dosed with various amounts of F-400 carbon. The carbon was removed by filtering with 0.45 μm Millipore filter paper; the water samples were then analyzed for both TOC and CFP. The CFP was obtained by chlorination with 10 mg/l free chlorine as Cl_2 for 48 hours at a constant temperature of 20°C and a pH of 6.

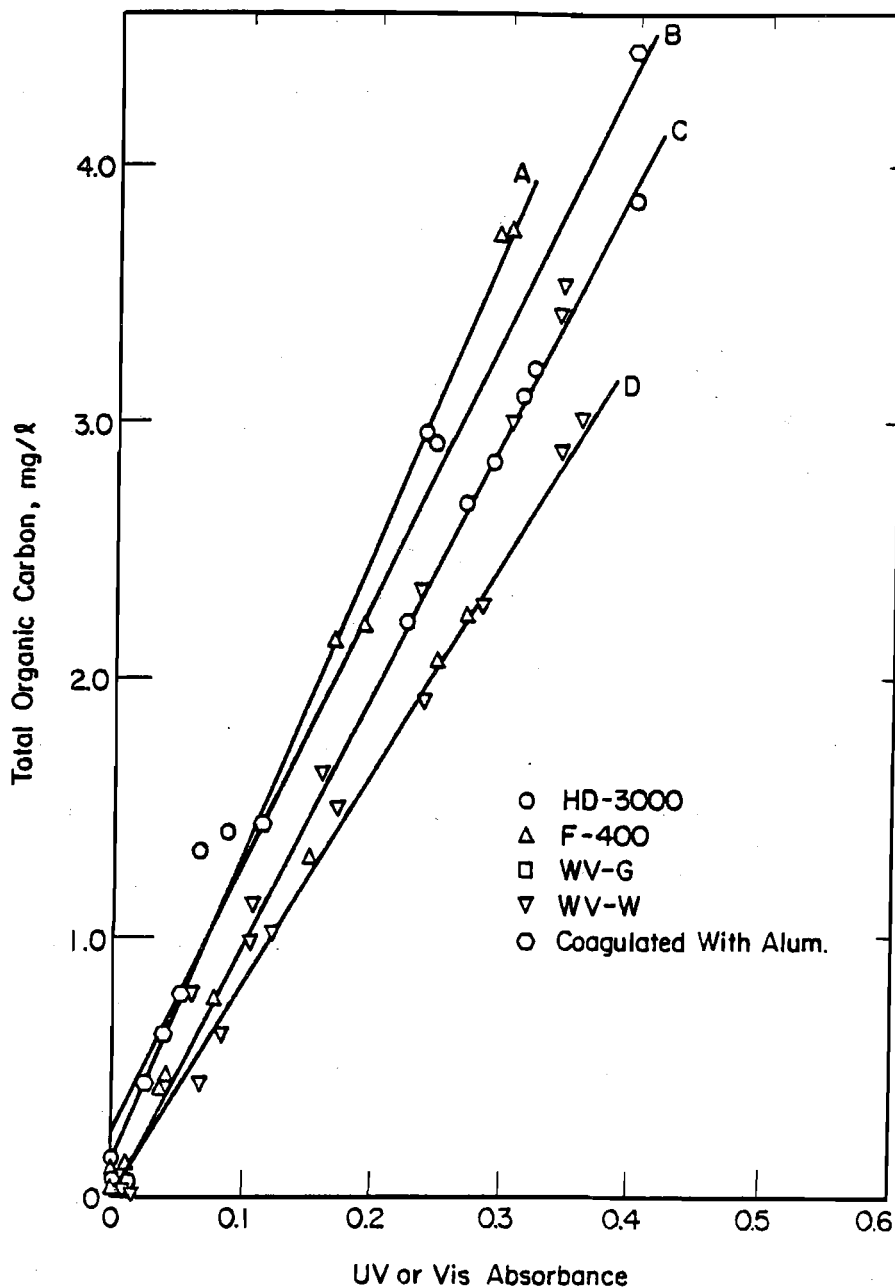


Figure 8. The Correlation of UV or Vis Absorbance with TOC Measurement. A. Humic Acid from Pfaltz and Bauer with Carbon Adsorption; B. Peat Fulvic Acid with Alum Coagulation; C. Peat Fulvic Acid with Carbon Adsorption; D. Peat Fulvic Acid after Coagulation with Alum and Followed by Carbon Adsorption ($\lambda = 330$ and 420 nm for Fulvic and Humic Acids, Respectively).

As shown in Figure 9, the CFP of commercial humic acid, peat fulvic acid, and peat fulvic acid remaining after coagulation with alum increased linearly with TOC. This linear relationship also exists for peat humic acid as reported by Babcock and Singer (1979), and for the organics in water samples taken throughout the country (Symons et al., 1975).

The chloroform yield per mg TOC was estimated from the slope of the line in Figure 9; the results are tabulated in Table 6. The commercial humic acid from Pfaltz and Bauer had the highest chloroform yield, whereas peat fulvic acid remaining after coagulation with alum had the lowest chloroform yield. The chloroform yield data of Snoeyink et al. (1977), which were estimated using the same procedure, are also presented in Table 6. A similar chloroform yield of commercial humic acid was obtained in both studies, although different treatments of commercial humic acid were used. Humic acid remaining after carbon treatment was used in this study, whereas humic acid without carbon treatment was used in the Snoeyink study. By comparing the chloroform yields of peat fulvic acid before and after alum coagulation in Table 6, we found a lower chloroform yield of the peat fulvic acid fraction remaining after coagulation. Similar results with peat fulvic acid were calculated from the data of Babcock and Singer (1979). They also reported that a reduction in yield was found for peat humic acid. It thus appears that alum coagulation selectively removes fractions of humic substances that have the greatest potential for chloroform formation.

6.2 Adsorption Equilibrium Studies

6.2.1 Preliminary Studies

One of the problems associated with the study of humic substance adsorption by activated carbon is the slow equilibration. In an initial

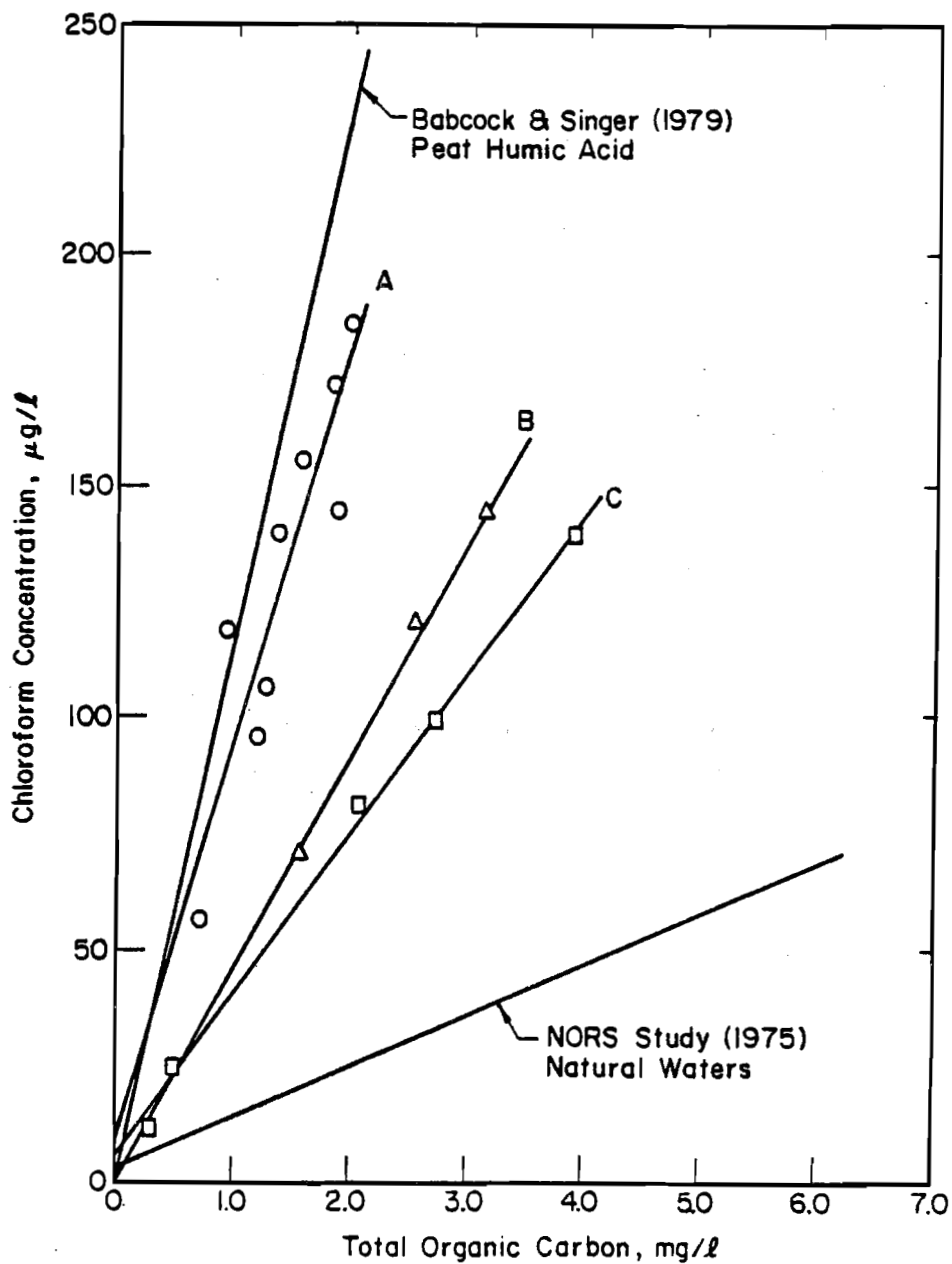


Figure 9. The Correlation between Total Organic Carbon and Chloroform Formation Potential for Various Humic Substances.
 A. Humic Acid from Pfaltz and Bauer; B. Peat Fulvic Acid;
 C. Peat Fulvic Acid Remaining after Coagulation with Alum.

Table 6. Chloroform Formation Potential of
Different Sources of Humic Substances

Humic substance	Yield of chloroform* mg CmCl_3 /mg TOC, %		
	A	B	C
Commercial humic acid	8.50	8.40	NA
Peat fulvic acid	4.67	NA	3.85
Peat fulvic acid remaining after coagulation with alum	3.58	NA	1.28

* Data in column A were obtained in this study, data in column B were reported by Snoeyink *et al.* (1977) for 96 hours reaction time at pH 7, data in column C were calculated from the results of Babcock and Singer (1979) for 48 hours reaction time at pH 6.5.

NA indicates data are not available.

study, the TOC concentration of humic substances in contact with activated carbon was monitored over a long period of time. This study was conducted using commercial humic acid solution with selected GACs. The percentage of concentration remaining as a function of time is shown in Figure 10.

Apparently at least two months are required to reach equilibrium. The diffusion of such large and heterogeneous organic molecules into the smaller pores of carbon is very slow. Several problems are caused by this slow adsorption process, including the time required for each experiment, and abrasion of the carbon particle when agitated in the reaction bottle for such a long period of time. The carbon fines that are generated will interfere with the analysis of humic substances.

It is generally agreed that decreasing the size of the carbon particles enhances the rate of uptake of organics in water. A study was therefore conducted to evaluate the adsorption of commercial humic acid on powdered GAC. Selected GACs were pulverized and were used for the time-dependent studies. Figure 11 shows the percentage TOC of humic substances remaining in solution with respect to time. The time required for commercial humic acid to equilibrate with all the selected powdered GACs was only 5 days compared with 60 days for GAC. Isotherm studies were then conducted using GAC and powdered GAC to determine whether pulverization affects its adsorption capacity. Figure 12 shows the commercial humic acid isotherm data. No significant difference between F-400 GAC and powdered GAC was observed. However, the adsorption data for WV-H carbon indicated a possible slight difference. Because of the results of the comparison between GAC and powdered GAC, powdered GAC was used for all isotherms.

No attempt was made to eliminate biological growth from the adsorption test systems. This entire study was conducted under nonsterile conditions.

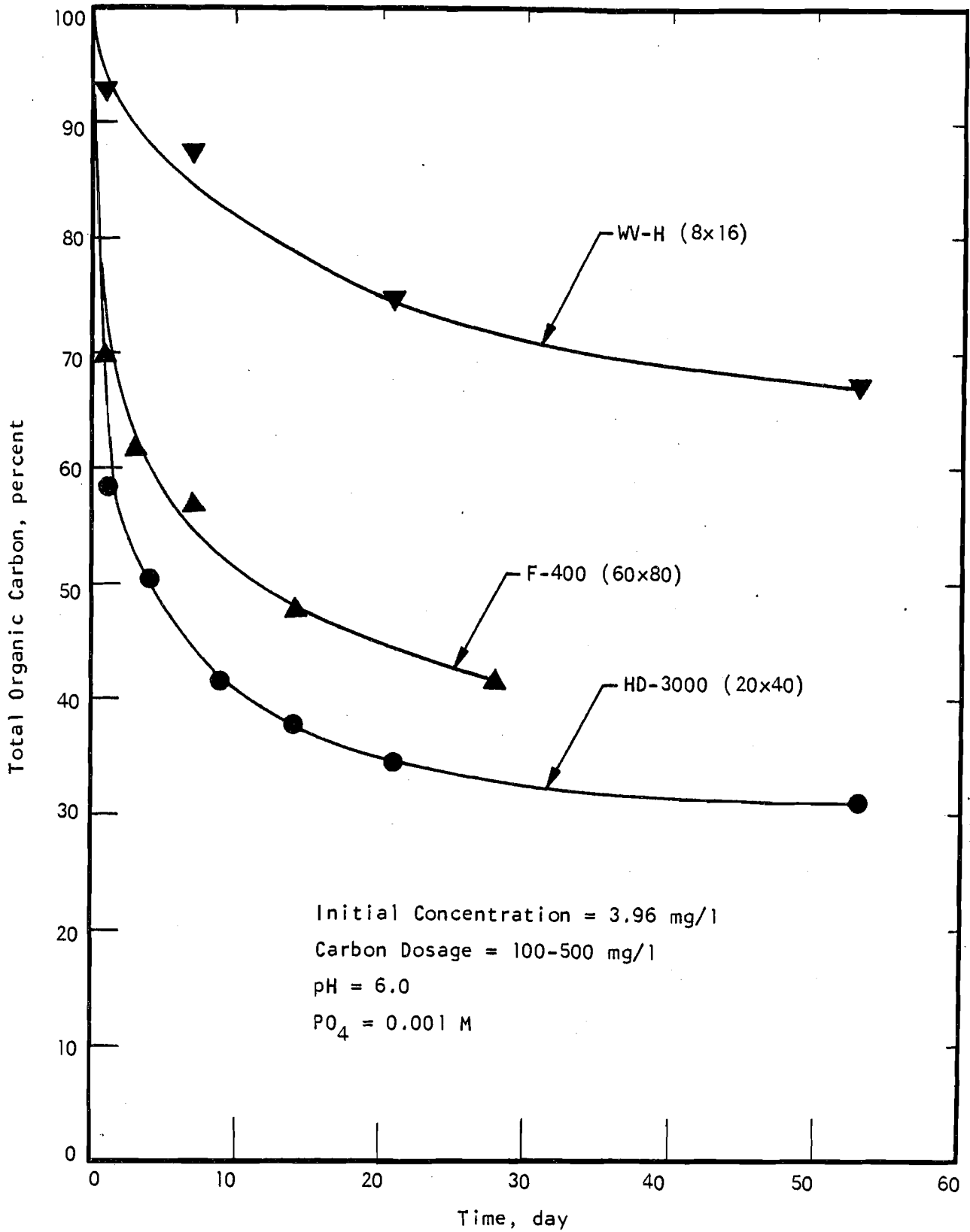


Figure 10. Percentage of TOC Removal of Commercial Humic Acid Adsorbed by GACs.

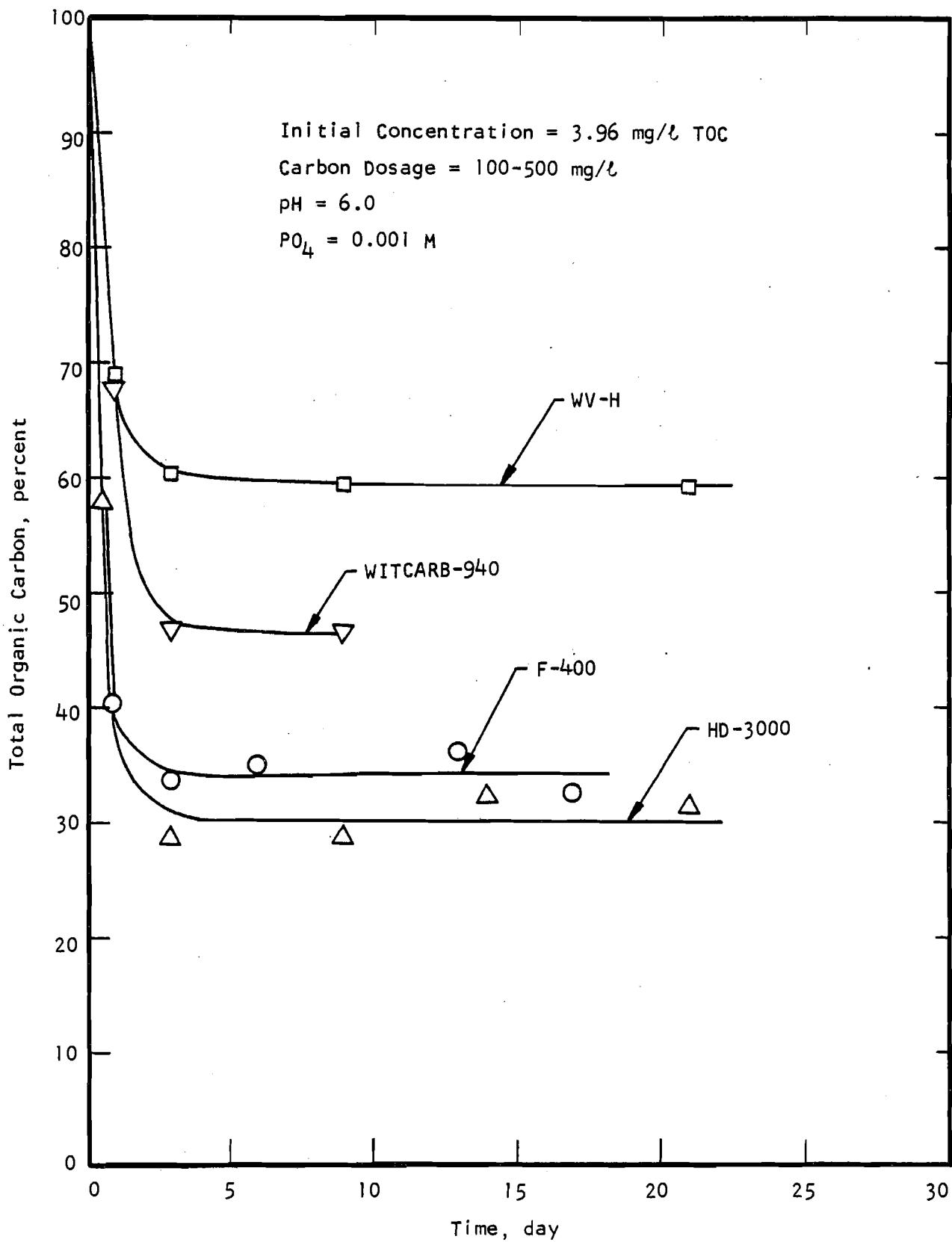


Figure 11. Percentage of TOC Removal of Commercial Humic Acid Adsorbed by Powdered GACs.

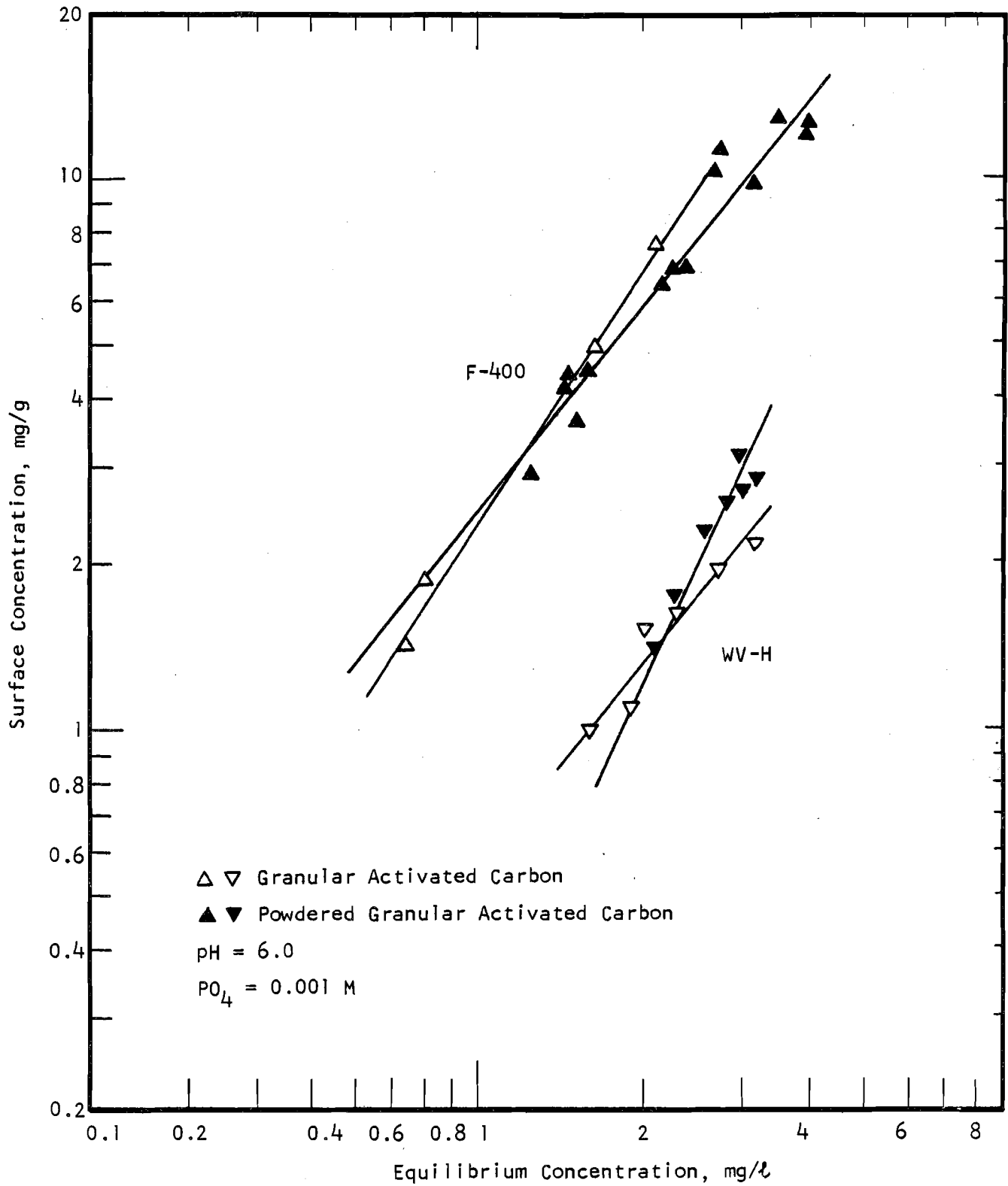


Figure 12. Isotherms for Commercial Humic Acid on GAC and Powdered GAC.

The results of the Standard Plate Count test (35°C, 48 hours; see Standard Methods, 1975) indicate that microorganisms were in the isotherm test bottles. To evaluate whether the organisms present had a significant effect on the adsorption of humic substances in the test solutions, a study of the adsorption of commercial humic acid by powdered F-400 GAC at different equilibrium times was conducted. Both samples showed the presence of bacteria. Data from both isotherm experiments are presented in Figure 13. The adsorption isotherm drawn from the combination of both sets of data had a correlation coefficient of 0.980, which suggests that there was no significant difference between these two experiments. Significant amounts of biodegradation would have yielded an isotherm showing a much greater capacity for the carbon equilibrated for 3 weeks compared with that equilibrated for 1 week. In addition, adsorption data for powdered GAC equilibrated for 1 week coincides with data for GAC equilibrated for 2 months, as shown in Figure 12.

Another important factor in determining the adsorption isotherm of humic substances is the reproducibility of the data. The experiments were repeated four times to evaluate this. These isotherms were conducted using commercial humic acid and WV-H activated carbon. The isotherm obtained by combining all the data is presented in Figure 14. Linear regression analysis yielded a correlation coefficient of 0.977, which indicated good reproducibility.

6.2.2 Effect of Pore Size Distribution of Carbon

Selected carbons with different pore size distributions were evaluated for their adsorption capacity for humic substances. These carbons included some with higher volume ratio of macropore/micropore, WV-B, WV-DC, and HD-3000; some with lower volume ratio of macropore/micropore, WV-W, WV-H, and Witcarb-940;

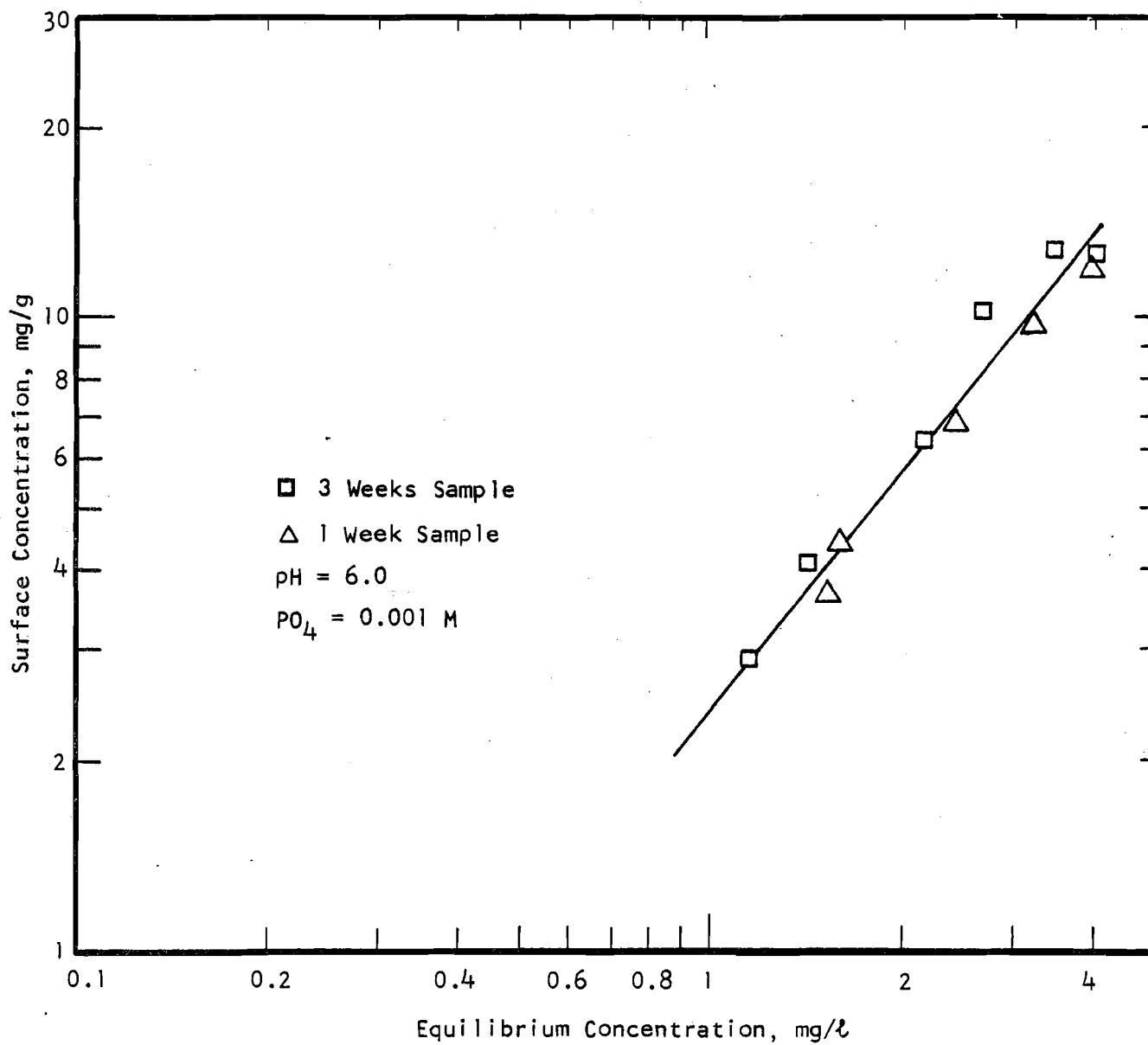


Figure 13. Isotherm for Commercial Humic Acid Adsorbed by Powdered GAC F-400 with Different Equilibration Times.

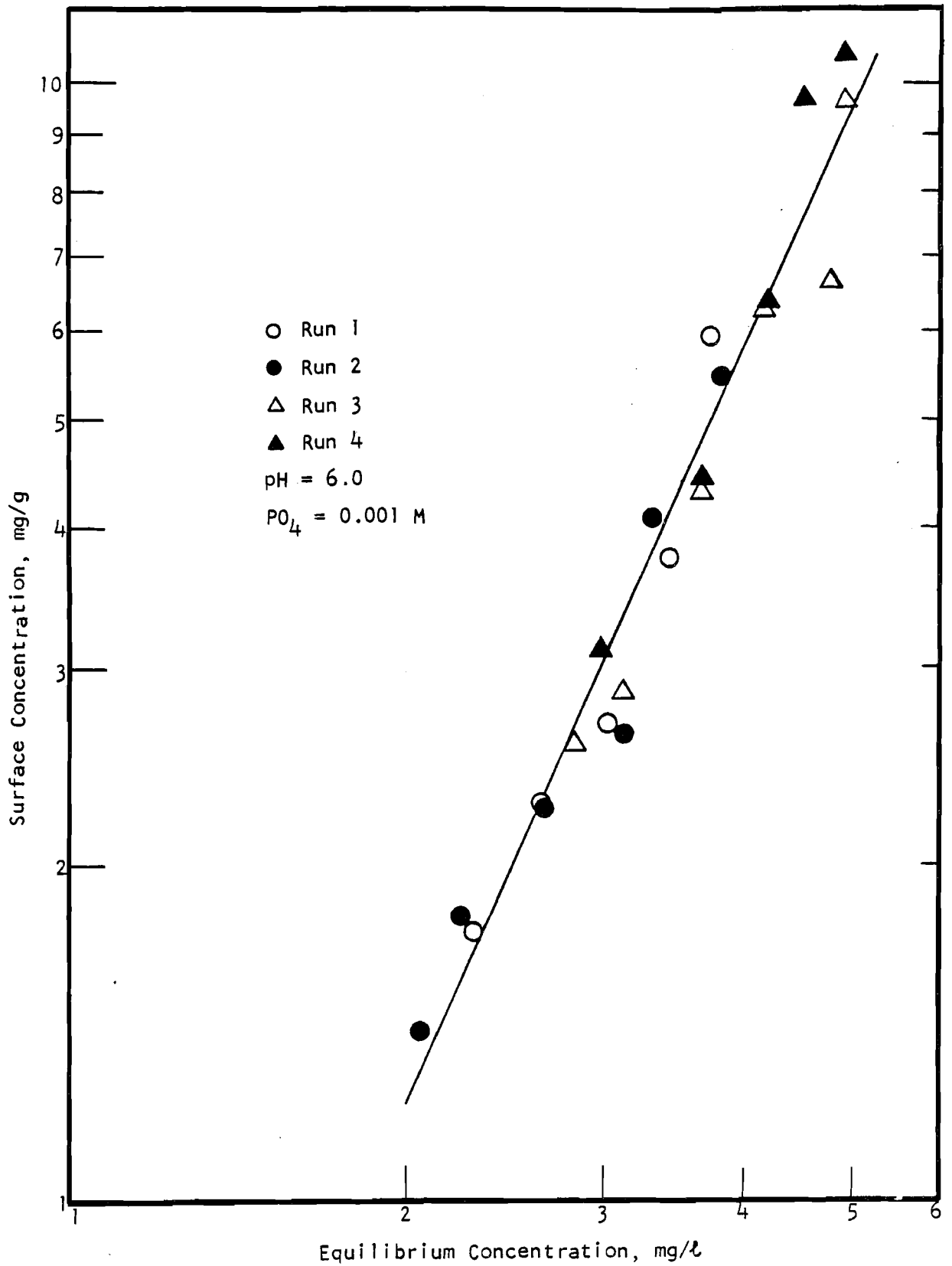


Figure 14. Reproducibility of Isotherm for Commercial Humic Acid Adsorbed by Powdered GAC WV-H.

and carbons with a wide spectrum of pore sizes, F-400, WV-G, and WV-L. Commercially available humic acid and peat fulvic acid were used as different types of humic substances. Since humic substance is a heterogeneous mixture, different molecular weight fractions of peat fulvic acid were also examined. A correlation of adsorption capacity of humic substances to volume of pores of a given size was then made. In addition, the effect of alum coagulation pretreatment on carbon adsorption of peat fulvic acid was investigated.

a. Type of Humic Substances and Type of Carbon

The adsorption isotherms for two different humic substances adsorbed by different activated carbons are presented in Figures 15 and 16. Figure 15 gives the adsorption isotherms for commercial humic acid. Freundlich isotherm constants for these data, nitrogen surface area and total pore volume of selected carbons are presented in Table 7. The adsorption isotherms all have a slope greater than one. This steeper slope indicates that adsorption is better at high concentrations than at low concentrations. This finding is consistent with the heterogeneity of the humic material. WV-B carbon has the highest capacity for commercial humic acid, followed by WV-DC and HD-3000 carbons. The carbons with the smaller pores, WV-W, WV-H, and Witcarb-940, have the lowest capacity. WV-L and WV-G with almost identical pore size distribution have a very similar adsorption isotherm. The sequence for the surface concentration, from highest to lowest, evaluated at an equilibrium concentration of 1.0 mg/l of TOC, is as follows: (1) WV-B, (2) HD-3000, (3) WV-DC, (4) WV-G, (5) F-400, (6) WV-L, (7) WV-W, (8) Witcarb-940, (9) WV-H, and (10) F-200.

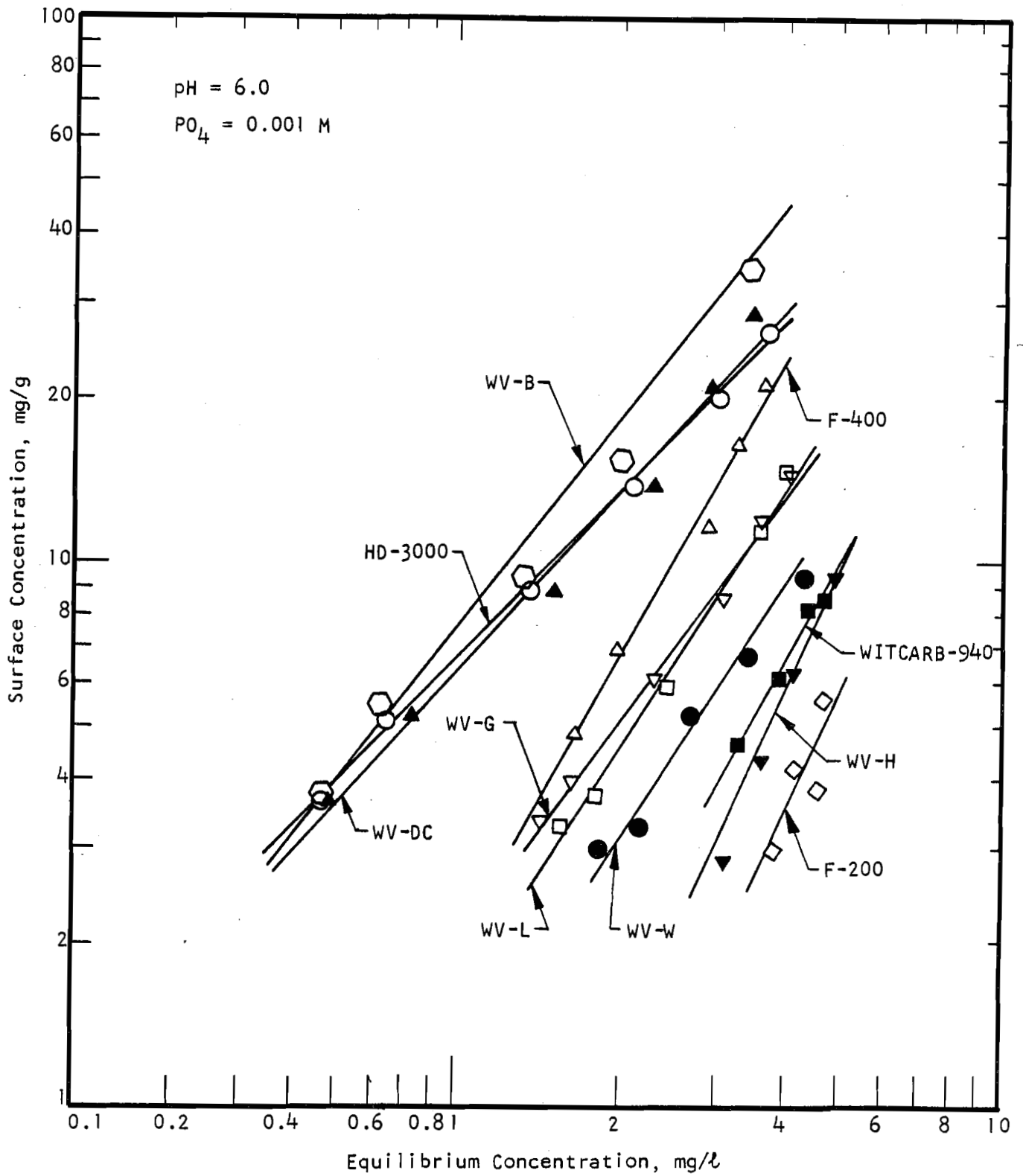


Figure 15. Adsorption Isotherms for Commercial Humic Acid.

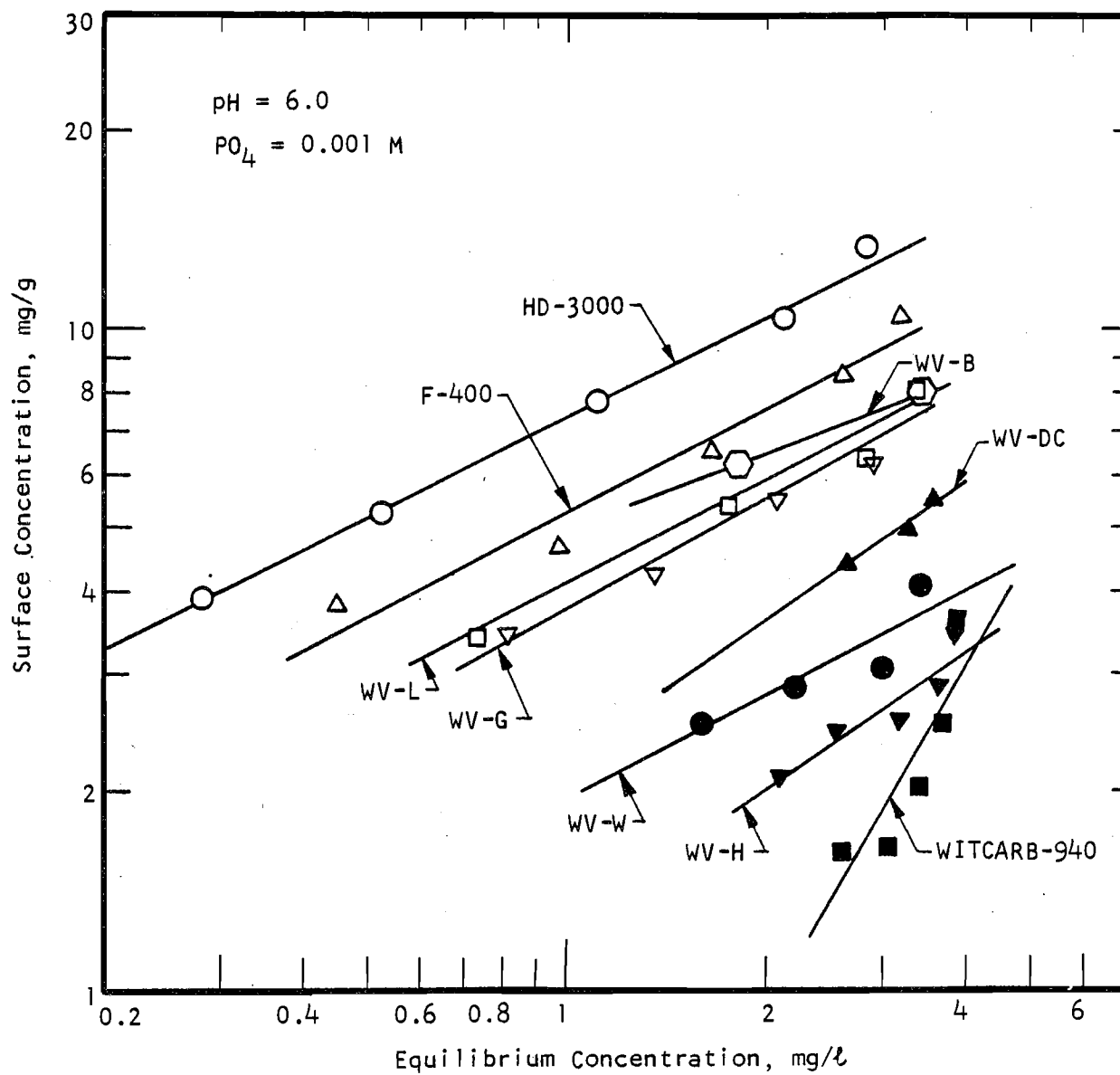


Figure 16. Adsorption Isotherms for Peat Fulvic Acid.

Table 7. Nitrogen Surface Area and Total Pore Volume of Selected Carbons and Freundlich Adsorption Constants for Commercial Humic Acid

Activated carbon	Nitrogen surface area, m ² /g	Total pore volume,* cc/g	Freundlich constant		Correlation coefficient, r ²
			K	1/n	
WV-B (20 x 35)	1,422	1.865	7.668	1.281	0.973
WV-DC (20 x 35)	1,115	1.764	6.258	1.117	0.991
HD-3000 (20 x 40)	575	0.975	6.617	1.022	0.998
WV-G (20 x 40)	1,020	0.814	1.982	1.374	0.997
F-400 (20 x 30)	1,075	1.071	1.905	1.818	0.993
WV-L (20 x 30)	976	0.818	1.507	1.592	0.995
WV-W (20 x 40)	861	0.612	1.098	1.524	0.972
Witcarb-940 (14 x 20)	950	0.599	0.527	1.817	0.994
F-200 (60 x 80)	850-900	0.660	0.176	2.155	0.987
WV-H (8 x 16)	910	0.610	0.260	2.235	0.977

* Volume of pores less than 10⁵ Å radius.

By comparing the values of total pore volume ($< 10^5 \text{ \AA}$ radius), as given in Table 7, with the capacity at 1 mg/l TOC, it can be seen that the carbons with the larger pore volume have the higher capacities for commercial humic acid. However, no satisfactory correlation can be found when the capacity data are compared with the surface areas of the carbons. The HD-3000 carbon has the least surface area, $575 \text{ m}^2/\text{g}$, but its capacity for commercial humic acid is considerably higher than nearly all the other carbons. WV-B has the largest total pore volume and surface area, and it shows the best performance. It is evident that the nitrogen surface area of carbon cannot give a satisfactory measure of adsorption capacity of large molecules such as humic acid.

Figure 16 presents the isotherms for peat fulvic acid. The adsorption isotherms for all the carbons had a smaller slope than the slopes of the commercial humic acid isotherms. All the carbons except the Witcarb-940 carbon had a higher adsorption capacity over the entire range of concentration. The sequence of the adsorption capacity at an equilibrium concentration of 1.0 mg/l of TOC was slightly different from that for the commercial humic acid: (1) HD-3000, (2) F-400, (3) WV-B, (4) WV-L, (5) WV-G, (6) WV-DC, (7) WV-W, (8) WV-H, and (9) Witcarb-940.

It was surprising to note that the adsorption capacity of the WV-B carbon was less than the F-400 carbon, and the adsorption capacity of WV-DC was less than the WV-L and WV-G carbons. The WV-B and WV-DC carbons have very large pore volumes and surface areas, and their capacity for peat fulvic and humic acids should be higher than those of the other carbons. A careful examination of the nature of WV-B and WV-DC carbons shows that they have a different surface chemistry. When these carbons are introduced

into deionized distilled water, the pH values of the solution decrease. When the other carbons were similarly tested, the pH of the deionized distilled water increased. Thus WV-B and WV-DC carbon absorb hydroxide ions and are classified as L-carbons, while the other carbons adsorb acid and are called H-carbons (Steenberg, 1944). The adsorption of less fulvic acid by the L-carbons may be attributable to the higher acidity of fulvic acid as compared with humic acid (Stevenson, 1979), but further research is needed to establish this. Despite the results obtained by the WV-B and WV-DC carbons, the same trends of increased adsorption capacity with increased total pore volume were observed for peat fulvic acid.

Four experiments were conducted to determine the influence of the size of the activated carbon particle on the adsorption of commercial humic acid. In these experiments the initial concentration of the humic acid solution, dosage of F-400 carbon, and pH (= 6) were kept constant while the carbon size was varied from <14 to 60 x 80 mesh size. These carbons were pulverized and used in this study. The results of these experiments are presented in Figure 17. As shown, the particle size of the carbon significantly influenced the amount of commercial humic acid adsorbed. The adsorption capacity, evaluated at an equilibrium concentration of 1.0 mg/l TOC, was higher for the smaller particle size (40 x 60 mesh) than for the larger particle sizes (20 x 30 mesh and < 14 mesh). The 60 x 80 mesh could not be obtained by sieving the 12 x 40 mesh size, as could the other fractions, so the GAC as received from the manufacturer was ground in a blender and sieved to provide a 60 x 80 mesh fraction. It is possible that this fraction may have had a combination of highly activated small particles and less activated large particles. The adsorption isotherm of this 60 x 80 mesh carbon (shown in Figure 17) indicates that it

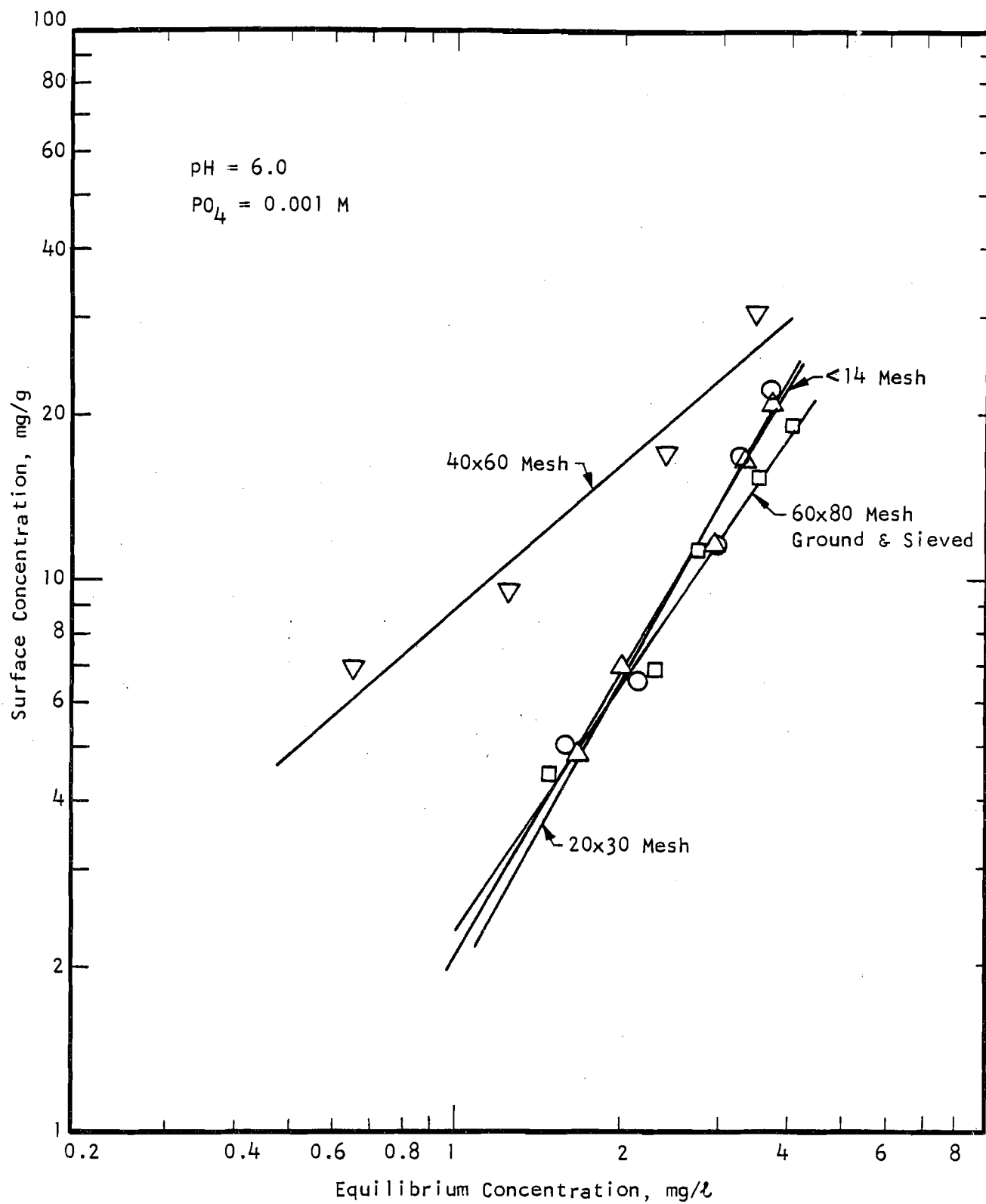


Figure 17. Isotherms for Commercial Humic Acid Adsorbed by Various Particle Sizes of Carbon F-400.

provides an adsorption capacity similar to the other meshes of 20 x 30 and < 14 fractions. However, the fraction of 60 x 80 carbon particles may have a much higher adsorption capacity if a different crushing procedure were to be used.

b. Different pH

The adsorption isotherms of peat fulvic and commercial humic acids at several pH values are presented in Figures 18 and 19. The HD-3000 and WV-H carbons were selected because these two carbons represent the extreme characteristics of surface area and pore size distribution. The adsorption capacity of HD-3000 and WV-H for peat fulvic acid increased as pH decreased. Similar results were found for commercial humic acid. These observations of peat fulvic acid and commercial humic acid are similar to the results obtained by Snoeyink et al. (1977 and 1978) and Weber et al. (1978).

When the results obtained by Snoeyink et al. and those from this study were combined, the increased adsorption capacity of carbon at decreased pH was found to be true for different sources of humic substance over a pH range of 3.0 to 11.0. These different humic substances include commercial humic acid, peat and soil fulvic acid, and organic matter in well water from the Department of Civil Engineering at the University of Illinois.

A steady increase in the extent of adsorption with decreasing pH value was found for fulvic acid solutions. This is evident in the case of soil fulvic acid adsorbed by F-400 carbon as reported by Snoeyink et al. (1977) and peat fulvic acid adsorbed by HD-3000 and WV-H carbons in this study. However, in the study of commercial humic acid, as shown in

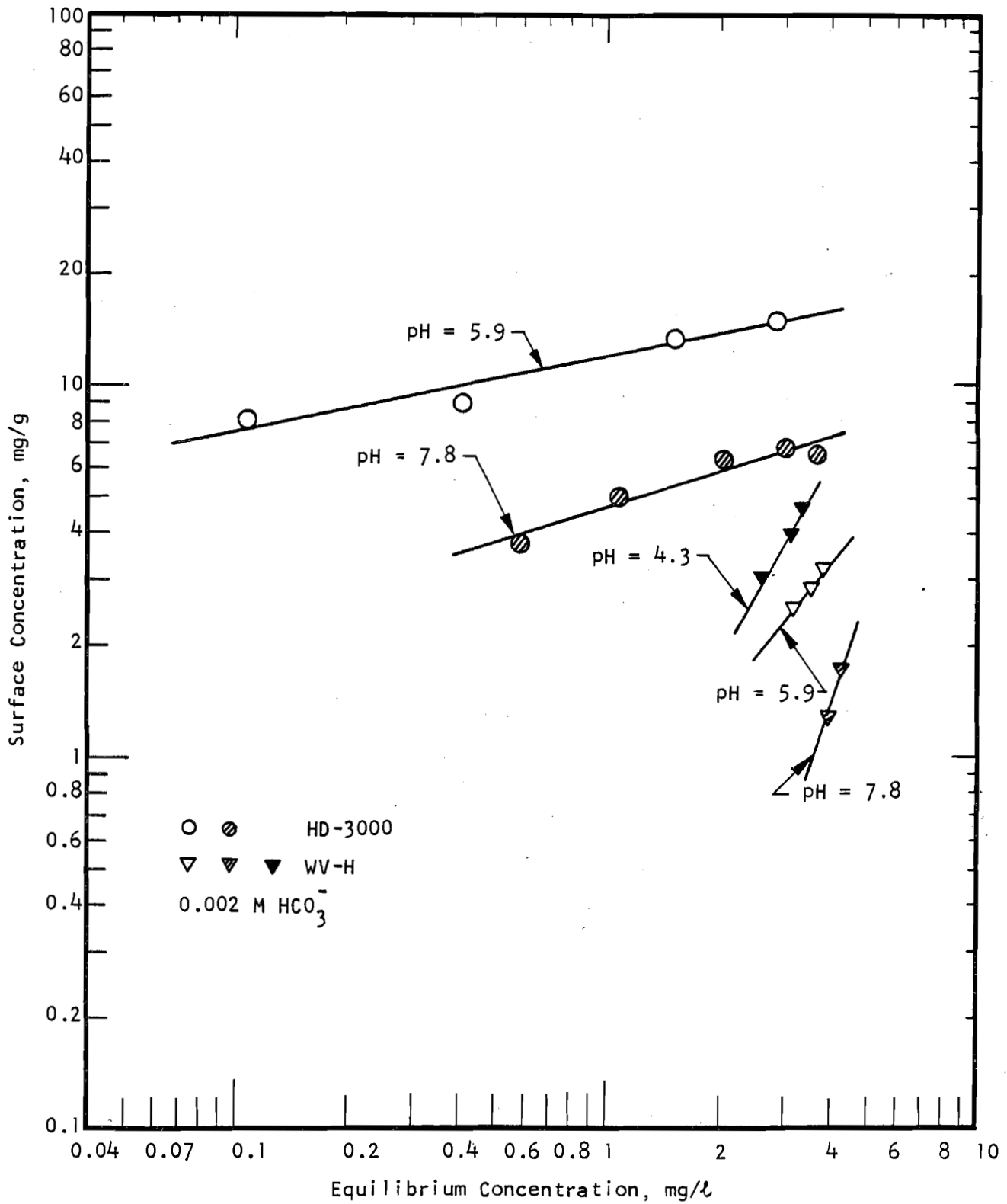


Figure 18. Effects of pH on the Adsorption of Peat Fulvic Acid by Different Activated Carbons.

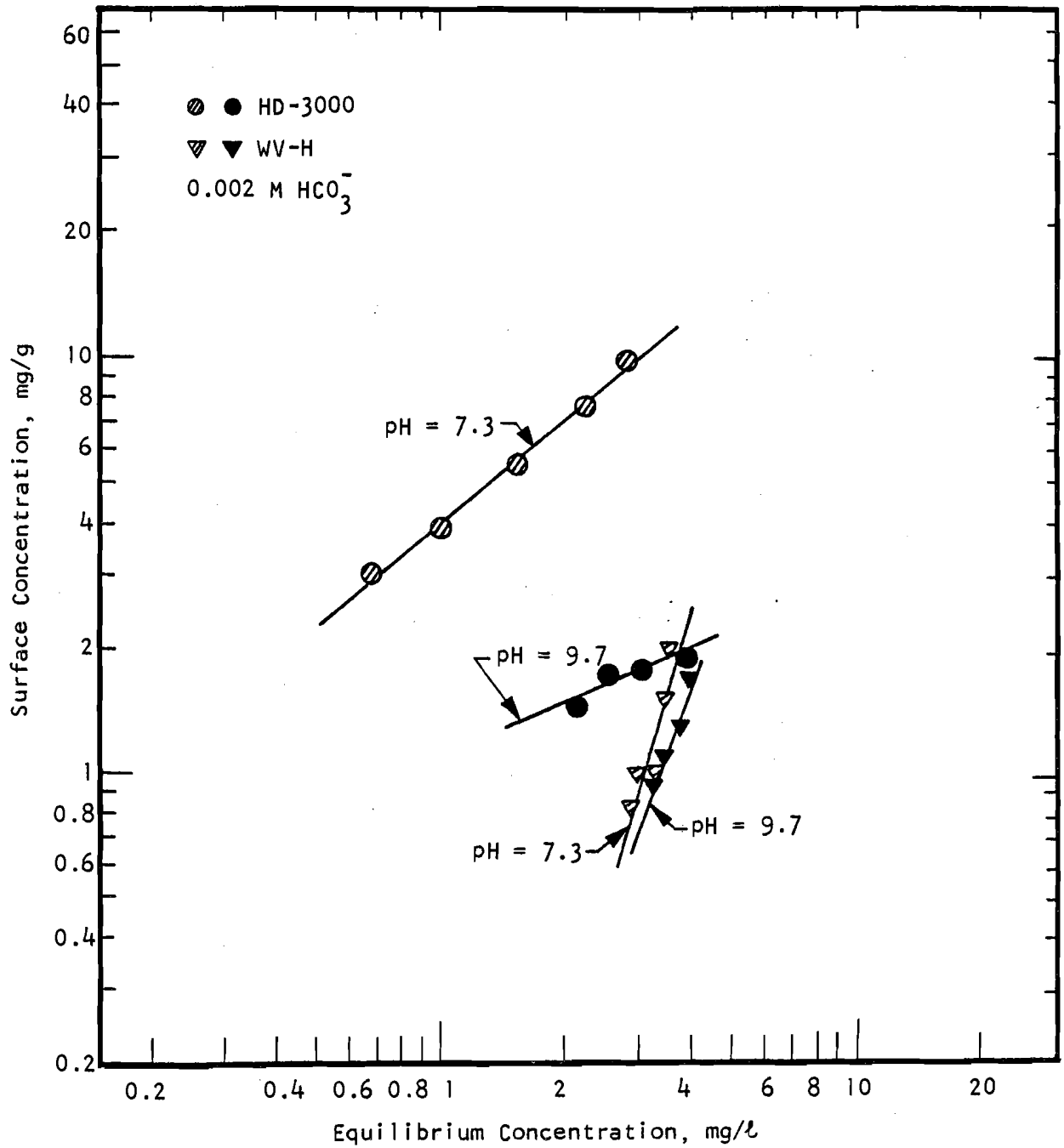


Figure 19. Effects of pH on the Adsorption of Commercial Humic Acid by Different Activated Carbons.

Figure 19, the gradual increase of adsorption with decreasing pH was only observed for the HD-3000 carbon. No difference was noted between isotherms of WV-H carbon at pH 7.3 and 9.7. In their study with F-400 carbon, Snoeyink et al. (1978) indicated no significant difference between the isotherms at pH 3.0 and 7.0, but a significant difference was found between the isotherms at pH 7.0 and 10.8.

A possible explanation for the different pH effects on the adsorption of humic acids is related to the molecular size of humic acid at different pH values and the pore size distributions of carbon. At an acidic pH value, humic acid is protonated and more hydrophobic. However, it aggregates at a lower pH. The formation of aggregates of humic acid at a lower pH value of 3.0 was observed when the solution was filtered with a 0.45 μm Millipore filter paper. A large fraction of humic acid molecules was retained on the paper. At an alkaline pH value, the humic acid is dissociated and less hydrophobic. No aggregation was observed for a high pH value of 9.7. The observation of aggregate formation at a lower pH value is of interest when one examines the effect of pore size distribution of carbon on the adsorption of humic acid. For the HD-3000 carbon, the increase of molecular size of humic acid at a low pH did not alter the steady increase of its adsorption capacity with decreasing pH. This large-pore carbon was still able to adsorb the larger microaggregates of humic acid at an acidic pH. However, for the F-400 carbon, the effect of the increased particle size of humic acid at a lower pH was more pronounced. This carbon with its wide spectrum of pore sizes does not provide pores large enough for the larger molecular size of humic acid when it has a lower pH value. Therefore, its isotherms at pH 3.0 and 7.0 had insignificant differences in adsorption capacity.

The small-pore WV-H carbon essentially does not have adequate pores for humic acid; therefore, a change in pH values showed no effect on the adsorption capacity of the WV-H carbon.

c. Different Molecular Weight Fractions of Humic Substances

The isotherms for different molecular weight fractions of peat fulvic acid are presented in Figures 20 and 21. Figure 20 shows the adsorption isotherms for a fraction of less than 1,000 molecular weight, while Figure 21 shows the isotherms for a fraction of more than 50,000 molecular weight. As illustrated in Figures 20 and 21, the higher molecular weight fraction was less adsorbed than the lower fraction. Similar results were observed for leaf fulvic acid by Snoeyink *et al.* (1977) and for soil humic substances by McCreary and Snoeyink (1979).

The capacity of different activated carbons for the molecular weight fractions depended upon pore size. The lower molecular weight fraction was adsorbed better than the higher fraction by the F-400 activated carbon because it has more surface area in pores accessible to this fraction.

As shown in Figure 3, the Witcarb-940 carbon has more of its surface area in pores with a radius of less than 100 \AA than the WV-H carbon has. Because the Witcarb-940 carbon adsorbed more of this lower molecular weight fraction than did the WV-H carbon, it appears that pores with a radius of less than 100 \AA are available to this fraction even though these carbons have approximately the same total pore volume and surface area.

The higher molecular weight fraction was adsorbed better by HD-3000 than by F-400. This finding is consistent with the larger amount of surface area in pores accessible to this fraction by HD-3000. However, pore size

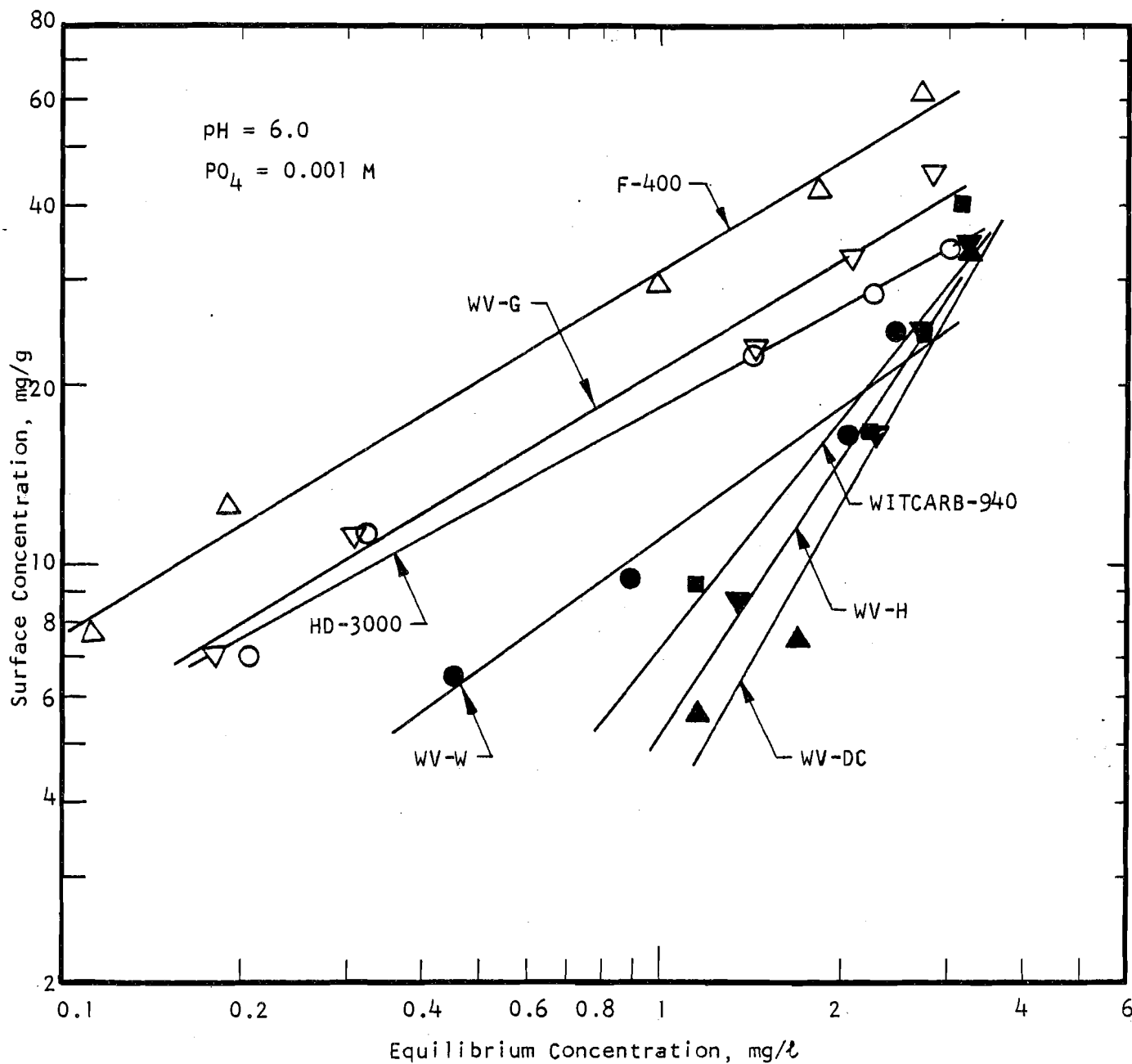


Figure 20. Adsorption Isotherm for Lower Molecular Weight Fraction (< 1,000 MW) of Peat Fulvic Acid.

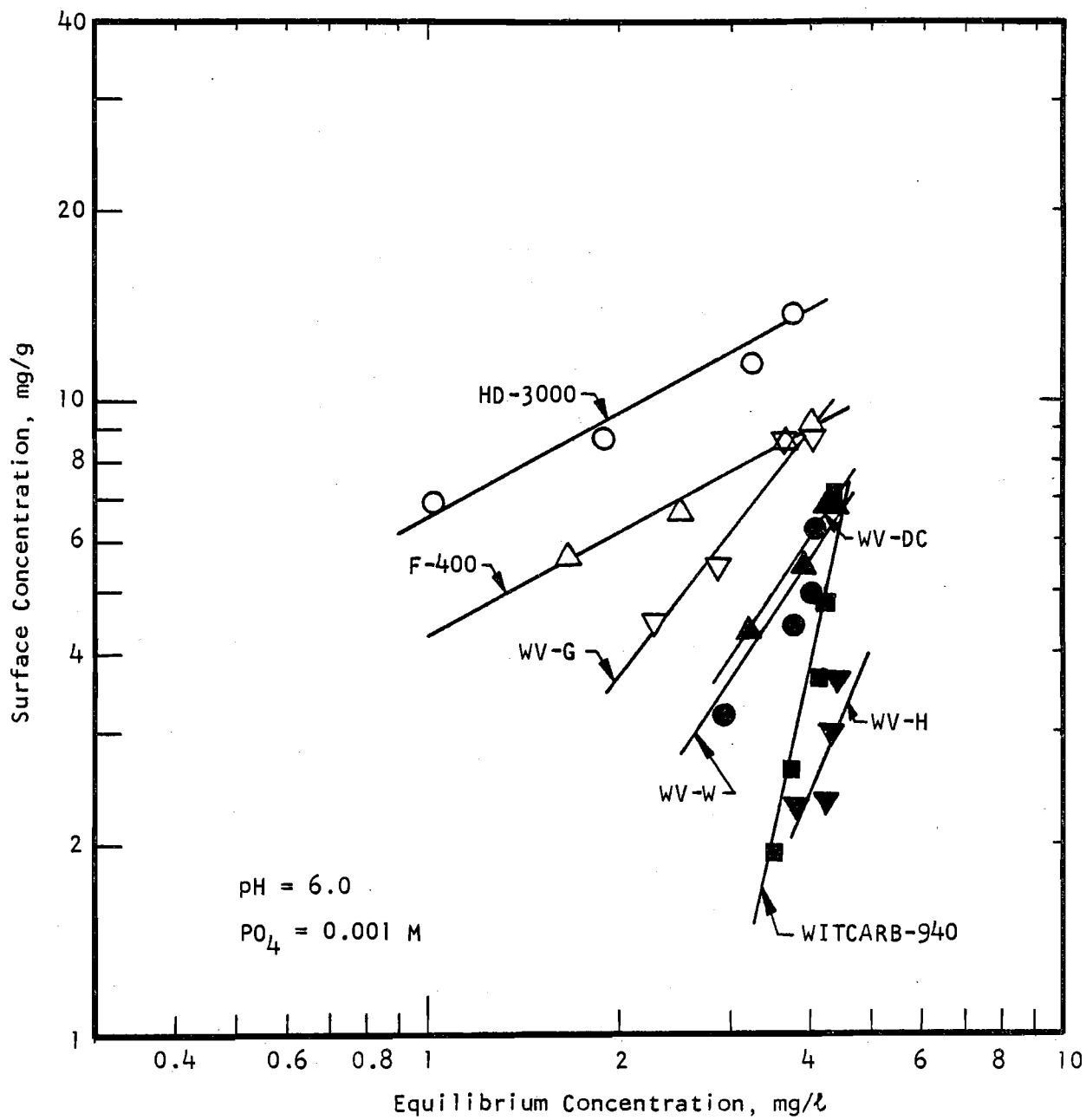


Figure 21. Adsorption Isotherms for Higher Molecular Weight Fraction (> 50,000 MW) of Peat Fulvic Acid.

comparisons alone do not allow one to predict capacity because WV-DC with its very large volume of large pores (see Figure 3) did not absorb this fraction better than the HD-3000. This situation is possibly due to the fact that WV-DC carbon is an L-carbon, which adsorbs hydroxide ions, while HD-3000 is an H-carbon, which adsorbs hydrogen ions.

Isotherms for the higher molecular weight peat fulvic acid adsorbed by F-400 and WV-G carbons also show the importance of pore size distribution. As shown in Figure 3, the F-400 carbon has more of its surface area available in larger pores ($> 100 \text{ \AA}$ radius) than the WV-G carbon, although both of these carbons have surface areas in excess of $1,000 \text{ m}^2/\text{g}$, as given in Table 5. This comparison indicates that the pore size distribution for pores larger than 100 \AA are probably the specific sites for adsorption of these higher molecular weight fractions.

It is also of interest to compare the adsorption isotherms of the HD-3000 carbon with unfractionated, lower and higher molecular weight peat fulvic acids, shown in Figure 22. The adsorption capacity of the lower molecular weight fraction was much higher than that of the others. There is no significant difference of adsorption capacity between the unfractionated and higher molecular weight peat fulvic acids. As illustrated in Table 8, only 9% of the fulvic acid is larger than 50,000 molecular weight, whereas 39 percent is less than 1,000 molecular weight. The presence of small amounts of the higher molecular weight fraction controls the adsorption capacity of the unfractionated peat fulvic acid by the HD-3000 carbon. This finding can be explained either by the pore blockage phenomenon or by the association of the lower fraction with the larger fraction in the

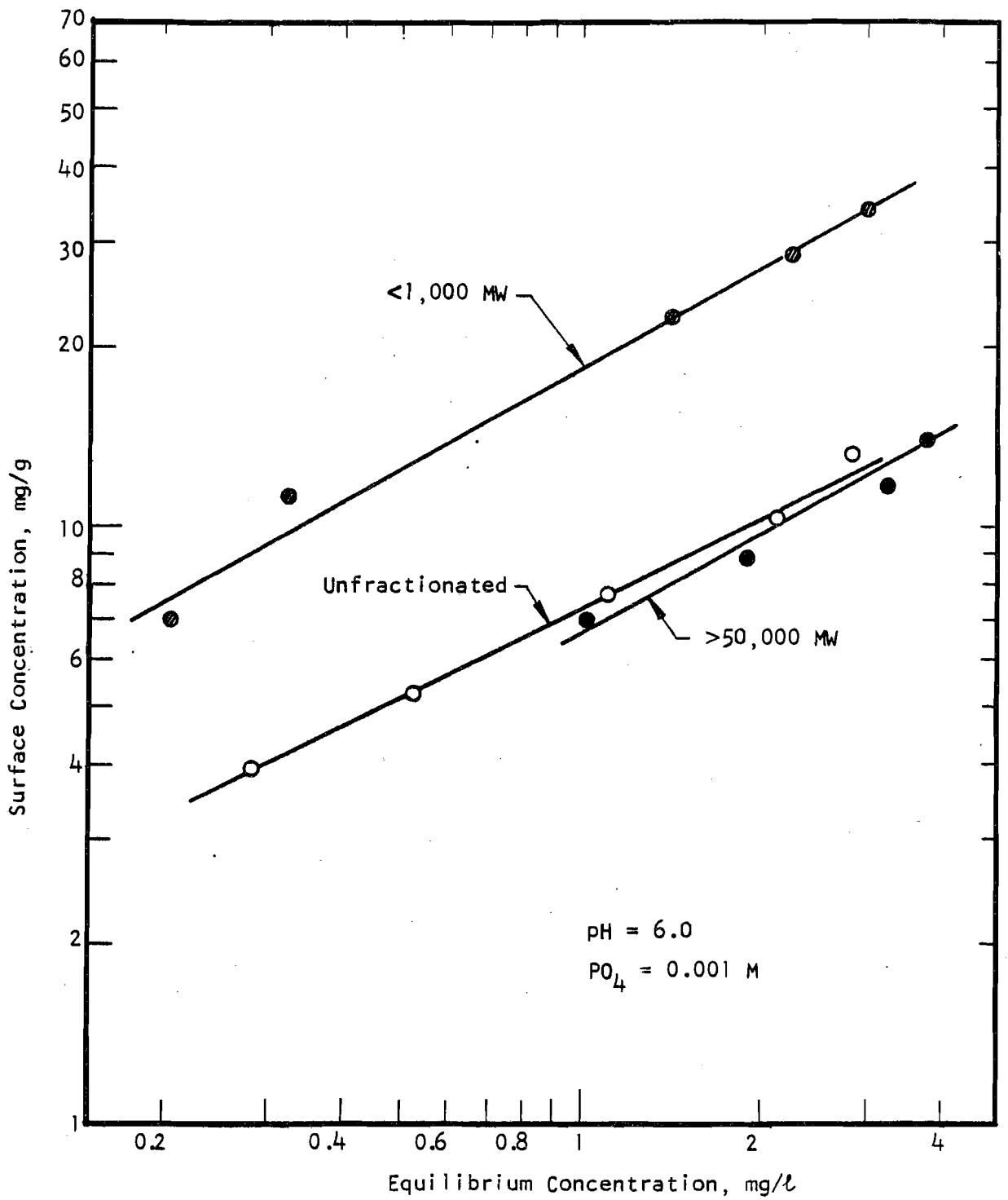


Figure 22. Isotherms for Different Molecular Weight Fractions and Unfractionated Peat Fulvic Acid Adsorbed by HD-3000 Carbon.

Table 8. Molecular Weight Fractionation
of Peat Fulvic Acid

Molecular weight	Percent
> 50,000	9
10,000-50,000	42
1,000-10,000	11
< 1,000	39

unfractionated mixture. Although the HD-3000 carbon has pore surface area accessible to the lower molecular weight fraction as shown in Figure 22, these pores may be blocked by the larger molecular weight fraction that occupied macropores of the carbon. However, the association of the lower fraction with the larger fraction in the unfractionated mixture is probably a better explanation.

The lower molecular weight fraction may result from the breaking of hydrogen bond between the structure of humic substance by the process of molecular fractionation under a pressure of 50 psi of nitrogen. Although this lower molecular weight fraction can be adsorbed by carbon much better than the other fractions, this fraction can associate with the larger fraction in the unfractionated mixture. A similar phenomenon has been observed when humic substances are separated by gel filtration (Stevenson, personal communication). Therefore, the adsorption capacity of unfractionated peat fulvic acid and the higher molecular weight fraction are similar.

d. Correlation with Adsorption Capacity

Results of the above studies qualitatively indicate that the adsorption of humic substances from water depends on the pore size distribution of carbon, and that the adsorption was not related to the total nitrogen surface area of carbon but to the surface area in pores accessible to the adsorbate. Further analyses of the data were then conducted to obtain a better indication of the pore sizes of importance for each type of adsorbate. Juhola (1977) has correlated the iodine number with the total surface area of the carbon and the molasses number with the surface area of the pores

larger than 28 \AA diameter. The iodine number is the amount of iodine adsorbed in mg/g of carbon from a standard KI-I₂ solution when the final equilibrium concentration is 0.02 N. The molasses number is the decolorizing capacity of the test carbon relative to the decolorizing capacity of a standard carbon. By a similar approach, the pore volume within a certain range of pore radii was plotted as a function of the adsorption constant K for each humic substance, where K is the capacity at an equilibrium concentration of 1 mg/l. This procedure was repeated for different ranges of pore radii until a statistically significant straight line was obtained. As shown in Figure 23, the adsorption constants of commercial humic acid, peat fulvic acid (unfractionated), and peat fulvic acid (> 50,000 MW) correlated well with the pore volume between pore radii of 100 \AA and 500 \AA . The adsorption constant of peat fulvic acid (< 1,000 MW) correlated well with the pore volume in pore radii less than 70 \AA and did not correlate with the pore volume between pore radii of 100 \AA and 500 \AA . The correlation coefficients for the fits shown in Figure 23 were 0.972 to 0.998. None of the adsorption constants correlated with the surface area of carbons.

These plots of the correlation of pore volume within a certain range of pore radii for different activated carbons with adsorption constant K suggest that it was the portion of the pore volume between 100 \AA to 500 \AA that was involved in the absorption of commercial humic acid, peat fulvic acid, and the higher molecular weight fraction (> 50,000 MW) of peat fulvic acid. The adsorption sites for the lower molecular weight fraction (< 1,000 MW) of peat fulvic acid were located where the pore volume of pore radii were less than 70 \AA .

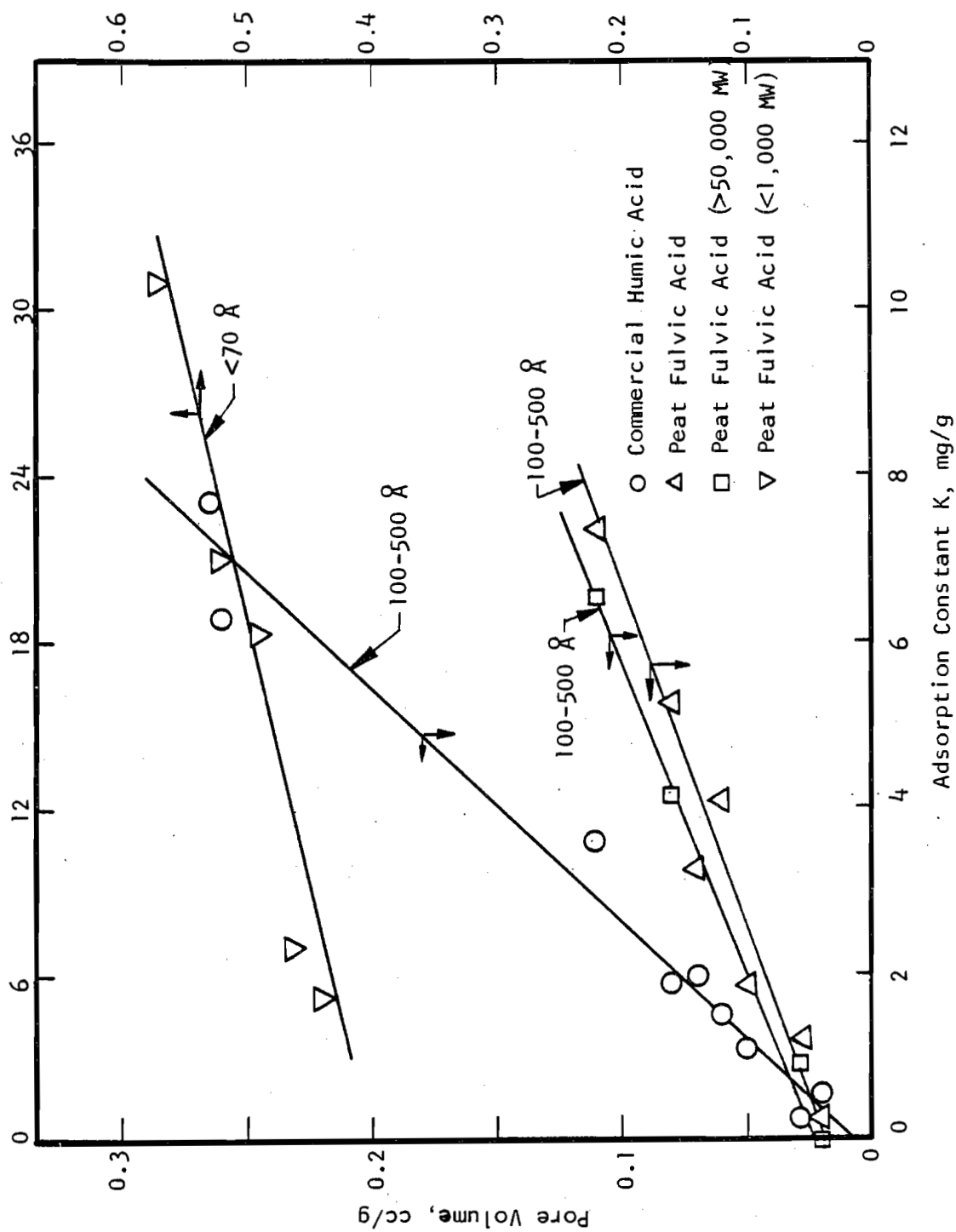


Figure 23. Adsorption Constant of Humic Substances as a Function of Pore Volume within a Certain Range of Pore Radii of Carbon.

6.2.3 Alum Coagulation Followed by Adsorption

Preliminary studies on the coagulation of commercial humic and peat fulvic acids with alum indicated that 98% of these two humic substances were removed at the optimum conditions. The optimum conditions were found at a pH value of 6.0 and an alum dosage of 50 mg/l and 20 mg/l for humic and fulvic acids at an initial concentration of 5 mg/l TOC.

To study the alum coagulation followed by carbon adsorption, peat fulvic acid solution from a stock solution was diluted with deionized distilled water to a concentration of 70 mg/l as TOC. Coagulation was conducted by adding 50 mg/l of alum from a stock solution to the solution and adjusting the pH to 6.0. The samples were allowed to stand overnight. Approximately 57 mg/l of fulvic acid remained in solution after coagulation, providing a stock solution of coagulated fulvic acid for use in subsequent experiments.

The adsorption isotherms of peat fulvic acid remaining after coagulation with alum are presented in Figure 24. Removal of this fulvic acid by carbon was significantly higher than the fulvic acid without alum pretreatment. When the results of peat fulvic acid before and after alum coagulation were compared, as shown in Figures 16 and 24, the capacity of activated carbon for peat fulvic acid had nearly tripled after alum coagulation. Similar results of increased adsorption capacity after alum coagulation were observed by Sontheimer and Maier (1972) and Scheidtmann *et al.* (1973). In their studies, the Rhine River water was bank-filtered, ozonated, coagulated, and followed by carbon adsorption. Although different organic matter was present in their studies, results obtained from both studies indicate that alum pretreatment can enhance the adsorbability of organics by carbon or remove nonadsorbable organics.

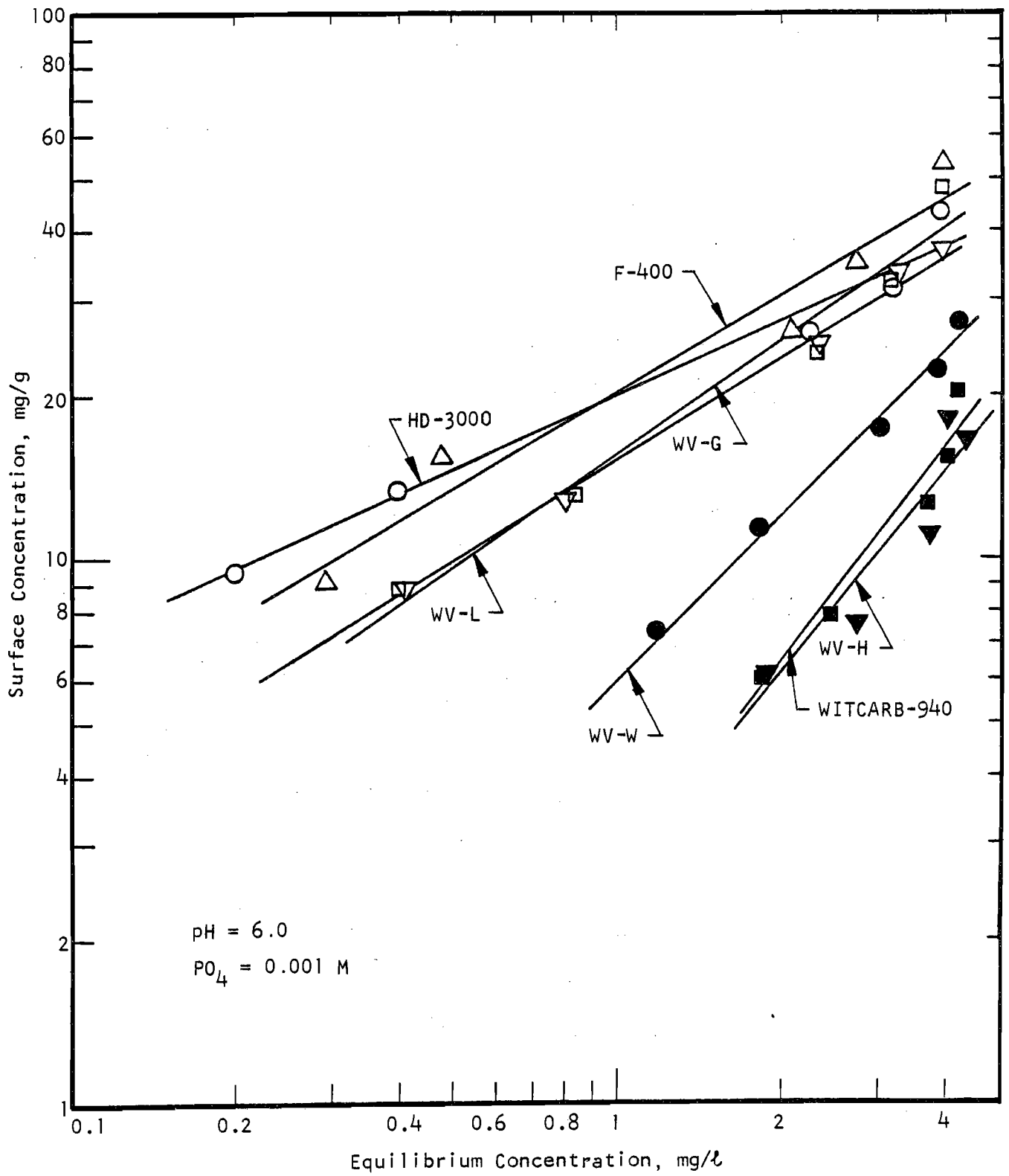


Figure 24. Adsorption Isotherms for Peat Fulvic Acid Remaining after Coagulation with Alum.

Since approximately 450 $\mu\text{g}/\ell$ of aluminum was detected by atomic absorption spectrophotometric analysis of the solution of peat fulvic acid remaining after coagulation with alum, it is of interest to evaluate the effect of the presence of soluble aluminum on adsorption. The soluble aluminum is the aluminum remaining in the solution after filtering with 0.45 μm Millipore filter paper. A sample of peat fulvic acid from the stock solution was diluted to the desired TOC value of 5.0 mg/ℓ . Alum (70 $\mu\text{g}/\ell$ Al) was then added to this solution. Adsorption isotherms for this solution with different activated carbons are given in Figure 25. The order of adsorption capacity for different carbons was the same as the order followed for peat fulvic acid remaining after coagulation with alum. Table 9 gives a summary of the Freundlich constants for peat fulvic acid with various concentrations of soluble aluminum. The concentration of aluminum in solution remaining after coagulation with alum, with alum added, and the control were 450 $\mu\text{g}/\ell$, 70 $\mu\text{g}/\ell$ and 0.11 $\mu\text{g}/\ell$, respectively. In all cases except WV-H carbon, the Freundlich constant K increased as aluminum concentration increased. The adsorption capacity of WV-H decreased when soluble alum was added to the solution, but it increased in the case of peat fulvic acid remaining after coagulation.

To determine whether any portion of the capacity for fulvic acid remaining after coagulation could be attributed to removal of weakly adsorbed species by coagulation, 450 $\mu\text{g}/\ell$ Al was added to a fulvic acid solution. The HD-3000 isotherm was then determined. This isotherm was essentially the same as for fulvic acid with 70 $\mu\text{g}/\ell$ Al added, and significantly less than (approximately 35 percent) the isotherm for fulvic acid remaining after coagulation containing 450 $\mu\text{g}/\ell$ Al. These results show that alum coagulation removes

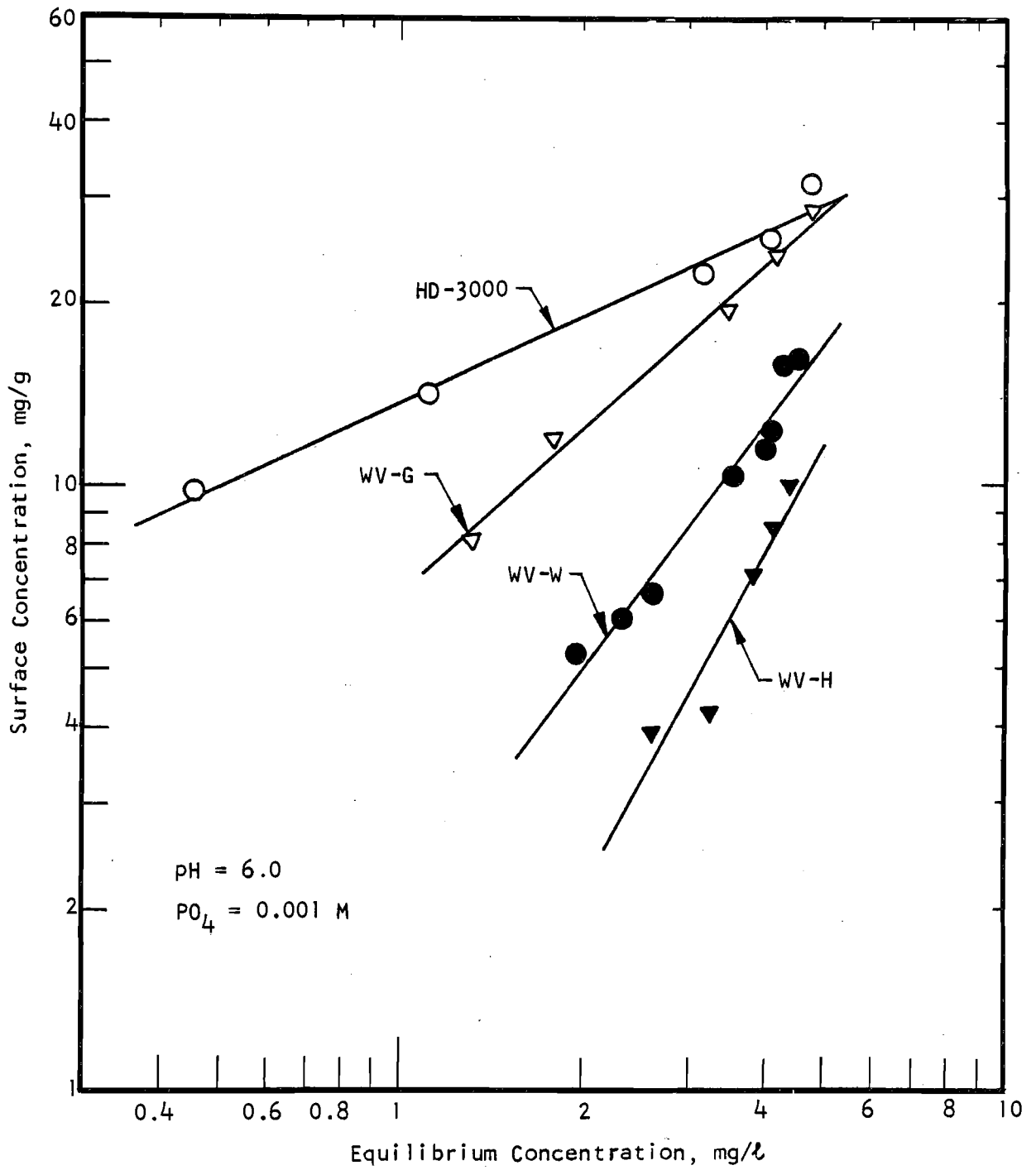


Figure 25. Adsorption Isotherms for Peat Fulvic Acid after Addition of 70 µg/l Soluble Al.

Table 9. Freundlich Constants of Peat Fulvic Acid with Various Concentrations of Soluble Aluminum

Adsorbent	Peat fulvic acid					
	Coagulated with alum, 453 $\mu\text{g}/\ell$ of Al		Alum added, 70 $\mu\text{g}/\ell$ of Al		Control, 0.11 $\mu\text{g}/\ell$ of Al	
	K*	1/n	K*	1/n	K*	1/n
HD-3000	20.00	0.451	13.75	0.466	7.37	0.516
WV-G	15.12	0.624	6.54	0.919	3.29	0.565
WV-W	5.91	1.006	2.00	1.322	1.91	0.532
WV-H	2.54	1.254	0.56	1.892	1.23	0.696

* K is the adsorption capacity at an equilibrium concentration of 1 mg/l.

some of the weakly- or non-adsorbable organic substances from fulvic acid solution.

Attempts were made to pinpoint a reasonable explanation for the increase in adsorption capacity when soluble Al is added to fulvic acid solution. One explanation is that the molecular size of peat fulvic acid decreases when soluble alum is present; another is that the affinity of peat fulvic acid for the carbon increases when soluble alum is introduced. Molecular weight fractionation was used to evaluate the molecular size distribution. Table 10 gives the results of molecular weight fractionation of peat fulvic acid, peat fulvic acid remaining after coagulation with alum, and peat fulvic acid containing soluble alum. The molecular weight of peat fulvic acid became larger after coagulation with alum, and after soluble alum was added. No significant difference was observed in the molecular weight fractionations between peat fulvic acid after coagulation with alum and with fulvic acid and after soluble alum was added. The results of this molecular weight fractionation make it quite evident that the chemical change of the humic substances was the main reason for the enhancement of their adsorbability by carbon. The results were similar to those from the study of pH effect on the adsorption of acid. The fulvic acid molecule becomes larger owing to aggregation of molecules as reported by Black and Christman (1963). Higher adsorption capacity at low pH was found in the present study and by McCreary and Snoeyink (1979).

6.3 Adsorption Kinetic Studies

The uptake of humic substances by four different activated carbons was measured under similar experimental conditions. The HD-3000, F-400, WV-G, and WV-W were used as the adsorbents for this study. The F-400 particle size

Table 10. Molecular Weight Fractionation of Peat Fulvic Acids (Percent, TOC)

Molecular weight	Peat fulvic acid	Peat fulvic acid remaining after coagulation with alum	Peat fulvic acid added with soluble alum
> 50,000	9	33	33
10,000-50,000	42	40	49
< 10,000	50	27	18

was 20 x 30 U.S. Standard Mesh, and the others were 20 x 40 U.S. Standard Mesh. Other characteristics of the adsorbents and adsorbates were also evaluated, including different sources of humic substances, carbon particle sizes, different molecular weight fractions, and humic substance remaining after coagulation with alum.

6.3.1 Type of Humic Substances and Type of Carbon

Peat fulvic acid adsorption kinetic data are shown in Figure 26. HD-3000 and F-400 carbons adsorbed slightly faster than WV-G and WV-W. The adsorption capacity of HD-3000 and F-400 was also slightly higher than the capacity of WV-G and WV-W, as shown by the results of the adsorption isotherm study. The continuous curves in Figure 26 represent the best fit of the batch reactor model. In the study of commercial humic acid, the order in the rate of uptake by the F-400, HD-3000, WV-G, and WV-W carbons was the same as the order observed for peat fulvic acid. TOC removal for peat fulvic acid was only 20% to 30%. These percentages were slightly less than those for commercial humic acid, which had 30% to 40% removal. In addition, the difference in the uptake of peat fulvic acid by various carbons was not as great as the difference in the uptake of commercial humic acid.

The effects of the carbon particle size on the adsorption kinetics of commercial humic acid are shown in Figure 27. Two different particle sizes of F-400, 20 x 30 mesh and 40 x 60 mesh, were used. The rate of adsorption of humic acid increased as the size of the carbon decreased. Similar results were reported by Weber *et al.* (1978). As shown in Figure 4, the 40 x 60 mesh carbon had a larger pore volume in pores with radii of 20 to 1,000 Å than the 20 x 30 mesh carbon. The 40 x 60 mesh carbon also had a higher capacity, as shown in Figure 17. Both factors could contribute to the faster rate of humic

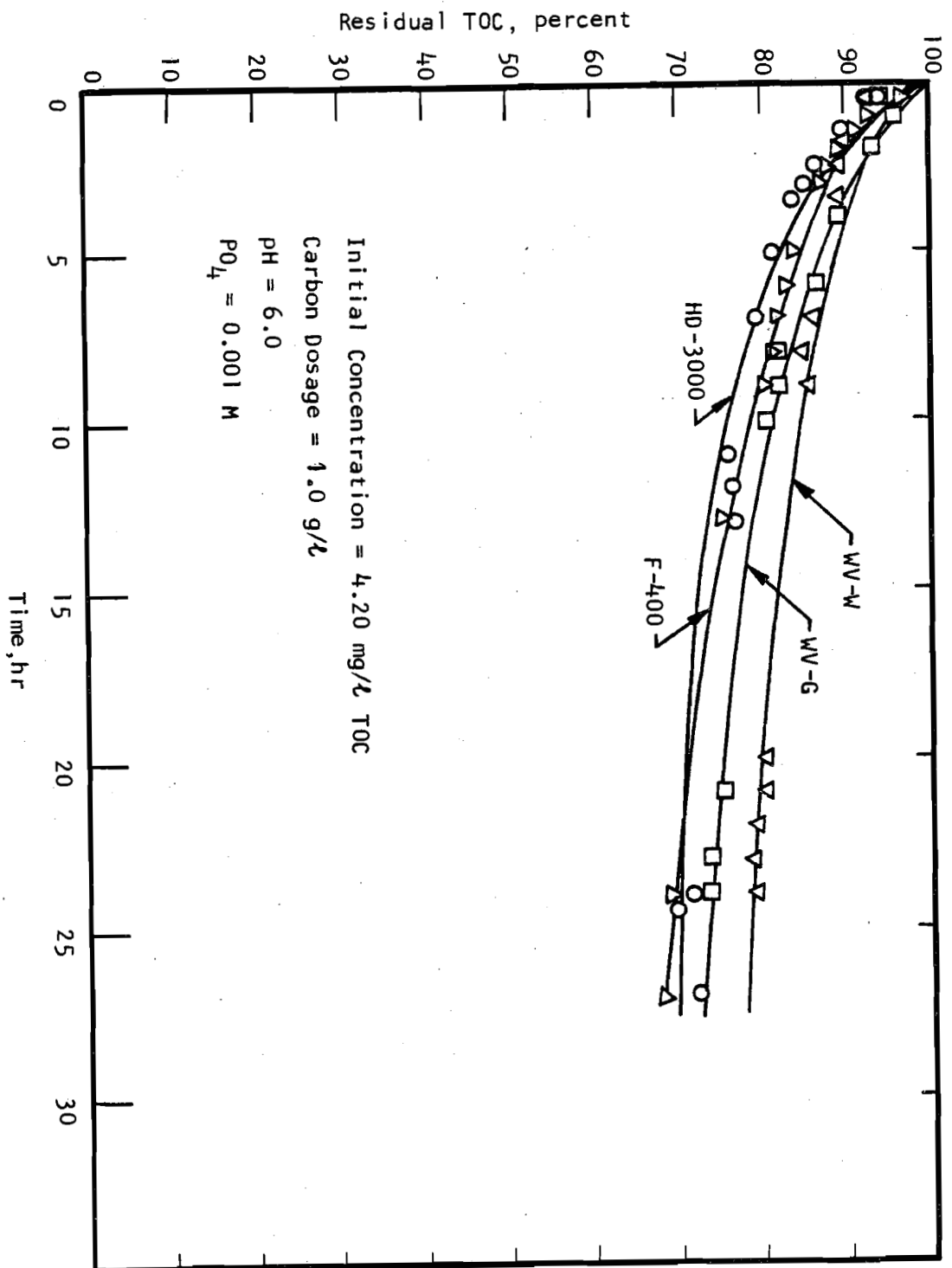


Figure 26. The Rate of Adsorption of Peat Fulvic Acid.

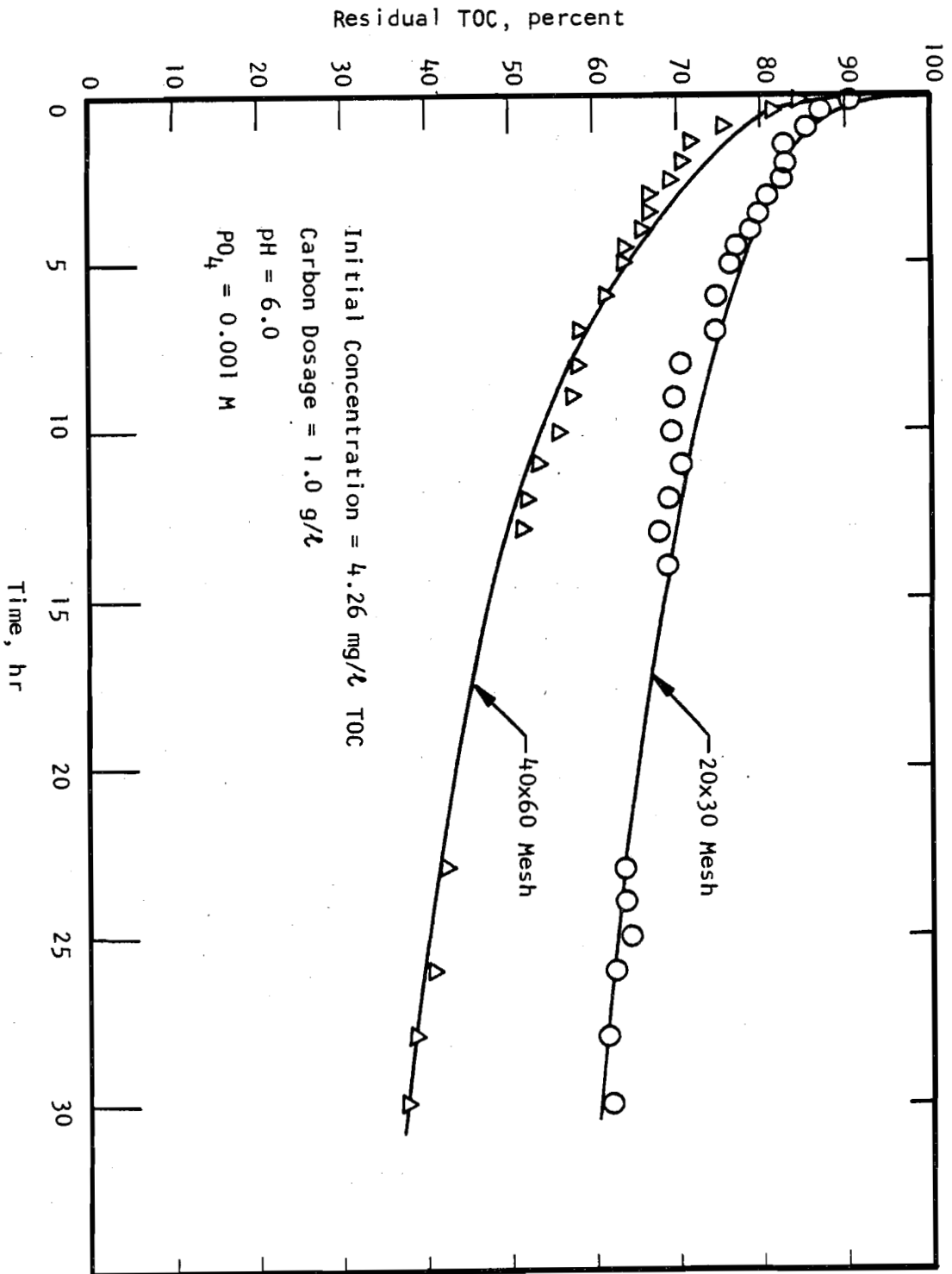


Figure 27. Effects of Carbon Particle Size on the Rate of Adsorption of Commercial Humic Acid by F-400 Carbon.

acid uptake by the smaller particle size. The two continuous curves in Figure 27 represent the best fit of the mathematical model to the experimental data. This batch reactor model describes the rate of humic acid uptake by F-400 with different particle sizes.

6.3.2 Different Molecular Weight Fractions of Humic Substances

Significant differences in the rate of uptake of different molecular weight fractions of peat fulvic acids ($< 1,000$ and $> 50,000$ MW) were observed and are presented in Figures 28 and 29. The uptake rate of the lower molecular weight fraction was much higher than the rate for the higher fraction. The residual TOC for the lower fraction was from 10% to 30% of the initial concentration of 4.03 mg/l TOC, while for the higher fraction the residual TOC was in the range of 60% to 80% of 4.58 mg/l initial TOC concentration. In both cases, the order of the rate of uptake of these two molecular weight fractions by different activated carbons was similar. The F-400 carbon performed the best, followed by WV-G and HD-3000. The WV-W carbon adsorbed much more slowly and adsorbed less than the other carbons. The continuous curves in Figures 28 and 29 are the best fits of the mathematical model.

Results of the above experiments are interesting when one compares them with the uptake of unfractionated peat fulvic acid. The rate of adsorption of the unfractionated material was similar to the rate of the higher molecular weight fraction. As illustrated in Table 8, only 9% of the fulvic acid is larger than 50,000 molecular weight, whereas 39% is less than 1,000 molecular weight. It can be seen that the presence of small amounts of the higher molecular weight fraction controls the rate of uptake of unfractionated peat fulvic acid by activated carbon.

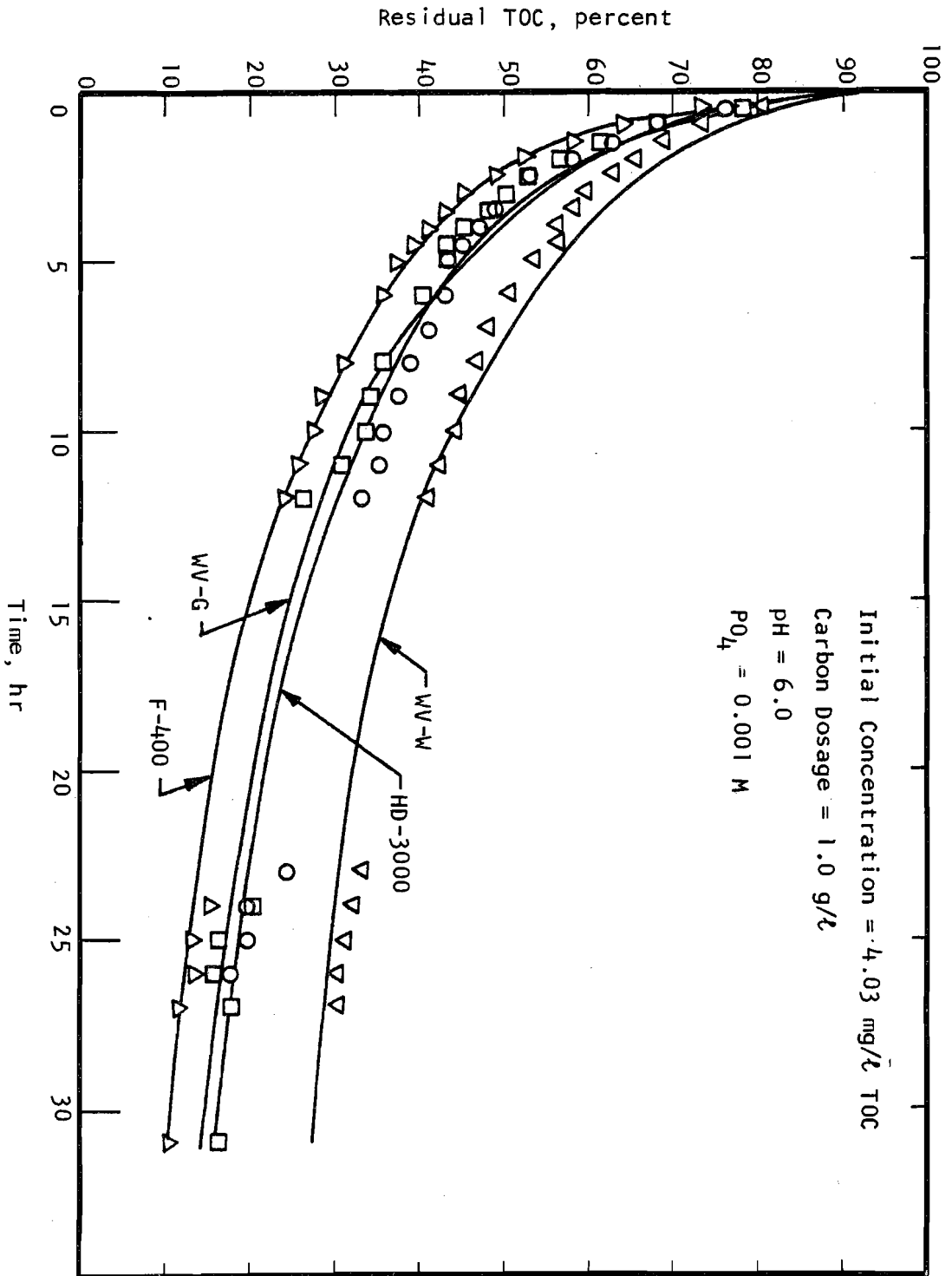


Figure 28. Rate of Adsorption of Lower Molecular Weight Fraction (< 1,000 MW) of Peat Fulvic Acid.

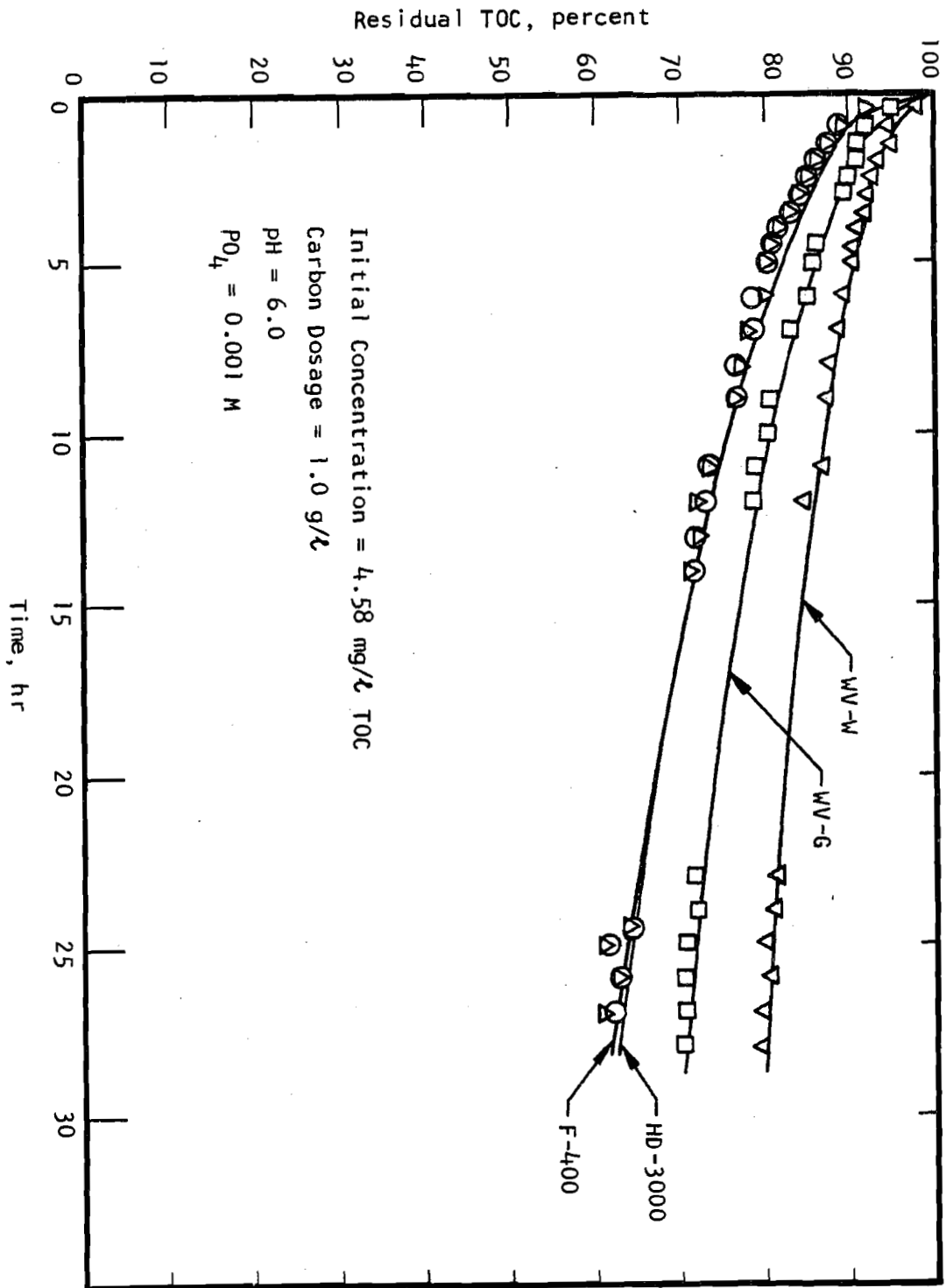


Figure 29. Rate of Adsorption of Higher Molecular Weight Fraction (> 50,000 MW) of Peat Fulvic Acid.

6.3.3 Alum Coagulation Followed by Adsorption

Rate data for peat fulvic acid adsorption after coagulation with alum are presented in Figure 30. The continuous curves are the best fit of the batch reactor model. Comparison of the data in Figures 26 and 30 shows that coagulation with alum enhances the uptake rate of peat fulvic acid. Peat fulvic acid remaining after coagulation with alum was adsorbed at a faster rate and in greater amounts. For a fixed dose of carbon, the percentages of TOC remaining in solution were much lower than for peat fulvic acid remaining after coagulation with alum. For this type of fulvic acid the rate of uptake by the F-400 carbon was the best, followed by HD-3000 and WV-G, which had almost identical uptake rates. The WV-W carbon had the slowest adsorption kinetics and the lowest capacity. By comparing the rates of uptake of peat fulvic acid before and after alum coagulation, one can see that the rate of uptake by these carbons is greater than for peat fulvic acid without coagulation. The F-400 carbon provides the highest adsorption capacity for peat fulvic acid without coagulation (as shown in Figure 26) and also has the best uptake of this fulvic acid remaining after coagulation.

6.3.4 The Relationship between Surface Diffusion Coefficient and Adsorption Capacity

The film transfer and surface diffusion coefficients can be determined from the best fit of the mathematical model to the experimental data for uptake rate. The data for commercial humic acid, peat fulvic acid, higher and lower molecular fractions ($> 50,000$ and $< 1,000$ MW) of peat fulvic acids, and peat fulvic acid remaining after coagulation with alum were evaluated for the relationship between the surface diffusion coefficient and the Freundlich adsorption constant K .

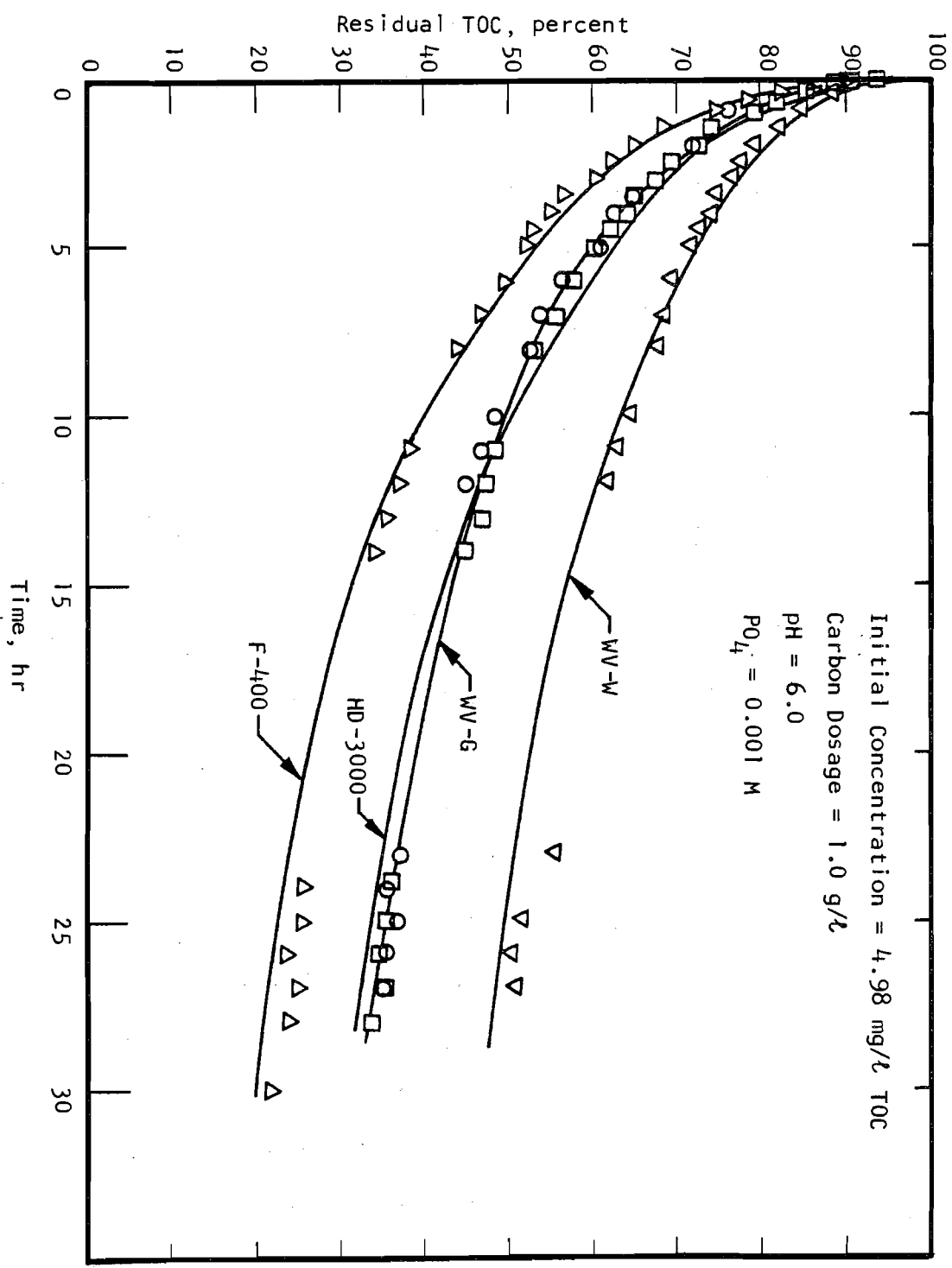


Figure 30. Rate of Adsorption of Peat Fulvic Acid after Coagulation with Alum.

Table 11 presents the adsorption constant K and the surface diffusion coefficient of different humic substances adsorbed by various activated carbons. The surface diffusion coefficient decreased as the adsorption constant K increased for the cases of peat fulvic acid and peat fulvic acid (< 1,000 MW). A similar decrease in surface diffusion coefficient with an increase in surface coverage of benzaldehyde on Amberlite particles was found by Komiyama and Smith (1974). This inverse correlation of humic substances may be related to the tendency of the humic materials to form aggregates on the carbon surface. The extent of aggregation would increase as surface coverage increased, and the rate of passage of molecules over the surface would be slowed by incorporation of molecules into and release from these aggregates. However, the surface diffusion coefficient only varied from 1.3 to 6.0×10^{-11} cm²/sec, and a wider range of diffusion coefficients corresponding to a wider range of surface coverages is needed to confirm this result.

6.4 Adsorption Column Studies

Column studies were essential to evaluate whether the adsorption effectiveness of the carbons could be observed in the columns as well as determined from the isotherm studies. Experimental column runs and mathematical model predictions are presented in the section that follows. The mathematical model predictions are also verified with the actual experimental runs.

6.4.1 Type of Humic Substances and Type of Carbon

The breakthrough curves for different humic substances adsorbed by the WV-G carbon are shown in Figure 31. Both column runs were kept at the same empty bed contact time of 7.50 minutes with a flow rate of 0.78 gpm/ft². The diameter and length of the column were 3.0 cm and 24 cm, respectively.

Table 11. Freundlich Constants and Surface Diffusion Coefficient of Different Humic Substances Adsorbed by Carbons

Humic substance	Carbon	Surface diffusion coefficient, 10^{-11} cm ² /sec	Freundlich constants	
			K	1/n
Commercial humic acid	HD-3000	5.8	6.617	1.022
	F-400	1.7	1.905	1.818
	WV-G	2.1	1.982	1.374
Peat fulvic acid	WV-W	3.8	1.098	1.524
	HD-3000	1.3	7.365	0.516
	F-400	2.7	5.282	0.519
Peat fulvic acid (< 1,000 MW)	WV-G	3.5	3.726	0.565
	WV-W	5.4	1.913	0.532
	HD-3000	3.2	18.535	0.553
Peat fulvic acid (> 50,000 MW)	F-400	2.3	31.146	0.610
	WV-G	2.7	21.184	0.621
	WV-W	4.0	11.018	0.733
Peat fulvic acid (Coagulated)	HD-3000	1.9	6.546	0.545
	F-400	6.0	4.163	0.555
	WV-G	3.3	1.493	1.285
Peat fulvic acid (Coagulated)	WV-W	3.1	0.725	1.465
	HD-3000	1.6	20.007	0.451
	F-400	3.0	20.224	0.592
Peat fulvic acid (Coagulated)	WV-G	2.0	15.123	0.624
	WV-W	2.4	5.913	1.006

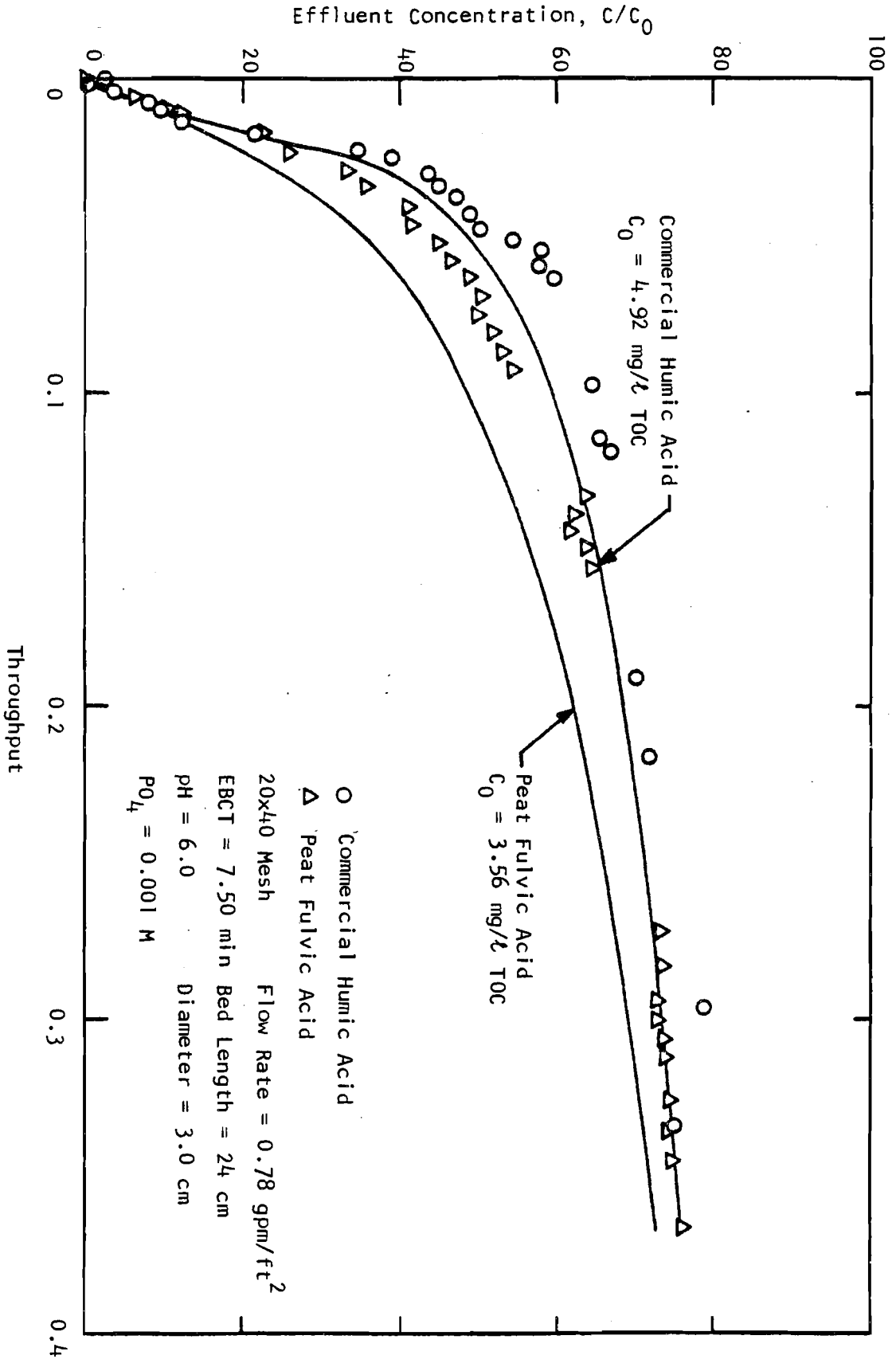


Figure 31. Breakthrough Curves for Different Humic Substances Adsorbed by WV-G Carbon.

The influent concentration for humic acid was 4.92 mg/l TOC which was higher than the concentration of 3.56 mg/l TOC for peat fulvic acid. Different amounts of carbon were used for these two different humic substances, namely, 45.26 grams carbon for commercial humic acid and 61.55 grams carbon for fulvic acid. Because different influent concentrations and amounts of carbon were used, the performance of the WV-G carbon on the adsorption of both commercial humic and peat fulvic acids was only slightly different. However, the major purpose of the test was to verify the model predictions, not to evaluate carbon performance.

The solid lines in Figure 31 are breakthrough curves predicted from the model. A slight deviation of the predicted data from the experimental data was observed. In Figure 31 the effluent concentration is expressed by the ratio of effluent concentration C to influent concentration C_0 . The time is expressed as mass throughput, which is defined as the mass of the solute fed to the column divided by the equilibrium capacity of the adsorbent in the column. When the quantity of solute fed to the adsorber is equal to the equilibrium capacity of the adsorber, the throughput equals 1.0. As shown in Figure 31, the value of throughput is only 0.4, while the effluent from the column reaches approximately 80% of the influent concentration. This suggests that slow rates of uptake of both humic and fulvic acids by WV-G carbon.

Column runs for peat fulvic acid adsorbed by different activated carbons were conducted under the same conditions with an empty bed contact time of 7.50 minutes and a flow rate of 0.78 gpm/ft²; the results are presented in Figure 32. Since the bed volume for these different carbons was fixed at the same empty bed contact time of 7.50 min, the amount of carbon packed into a fixed-volume bed varied with the type of carbon. Only 44.97 grams of HD-3000 were used, whereas 61.55 and 65.74 grams of WV-G and WV-W were used.

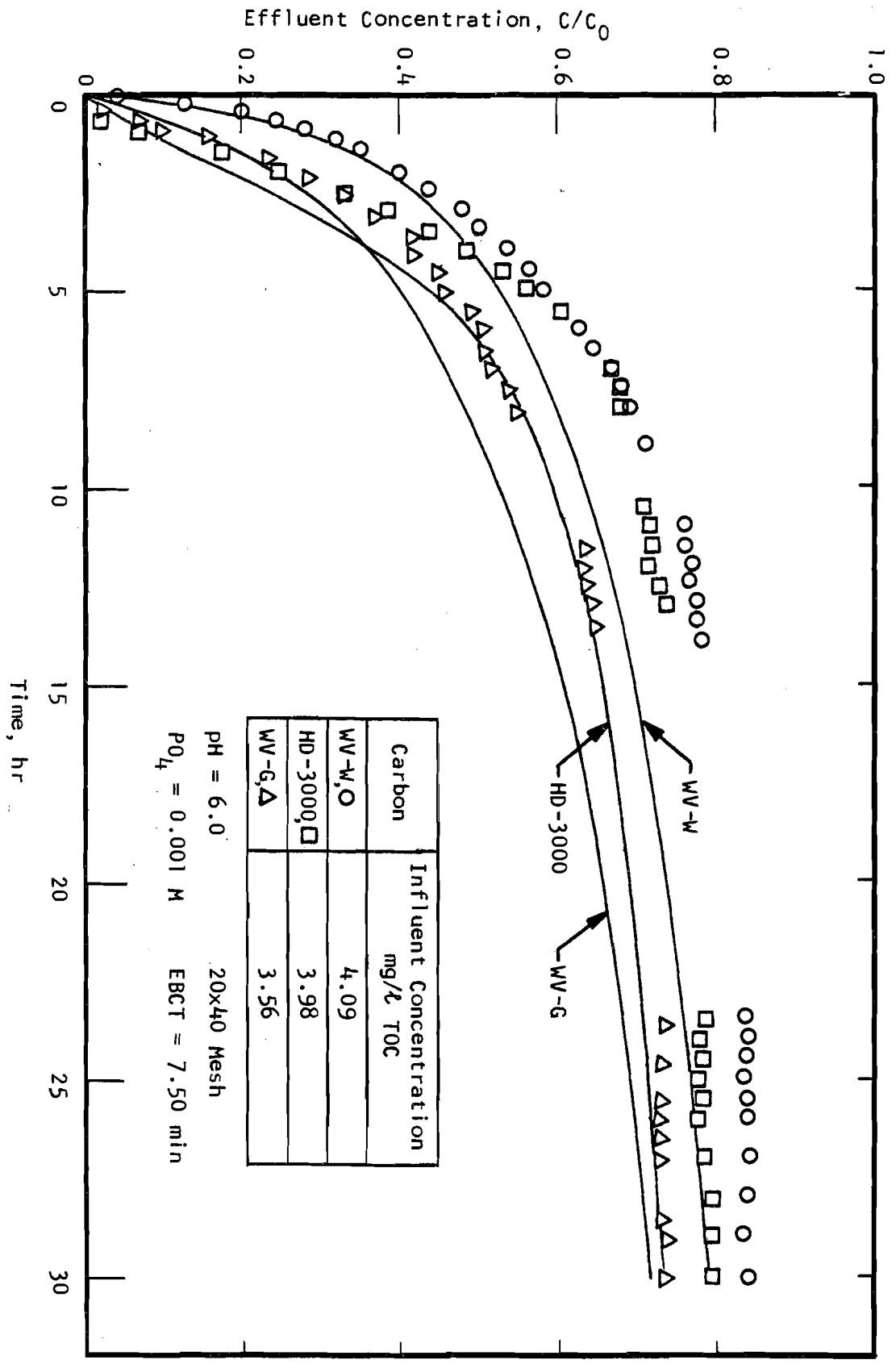


Figure 32. Breakthrough Curves for Peat Fulvic Acid Adsorbed by Different Activated Carbons.

The predicted breakthrough curves are presented in Figure 32. Although some deviations between the predicted data and the experimental data existed, the model predictions were able to describe the relative adsorption efficiency of each carbon. A possible explanation for the difference between actual and predicted effluent concentrations is the existence of a higher surface diffusion coefficient in the batch reactor as compared to the column reactor. As discussed above, the surface diffusion coefficient of humic substances was inversely related to the surface coverage of the carbon. A lower surface coverage is expected in the batch experiment because the initial concentration (equal to the column influent concentration) decreased with time; thus the column tended to equilibrate at a higher solution concentration than the batch reactor. As shown in Section 6.4.3b, a change in surface diffusion coefficient of 25 to 50 percent will make a significant difference in the predicted curve - enough to give good correspondence between actual and predicted column data. Further research in this area should be directed toward determining the surface diffusion coefficient as a function of surface coverage.

6.4.2 Alum Coagulation Followed by Adsorption

Breakthrough curves for peat fulvic acid before and after alum coagulation and adsorbed by WV-W carbon are shown in Figure 33. These two column runs were conducted using the same amount of carbon and the same operating conditions. The influent concentration was 4.52 mg/l TOC for fulvic acid remaining after coagulation and 3.56 mg/l TOC for fulvic acid without coagulation. Despite the slightly different influent concentrations, a significant difference in the adsorption of these two fulvic acids was observed. This finding is in agreement with the results of adsorption isotherm studies. Based on the isotherm tests, the adsorption capacity for peat fulvic acid remaining after alum

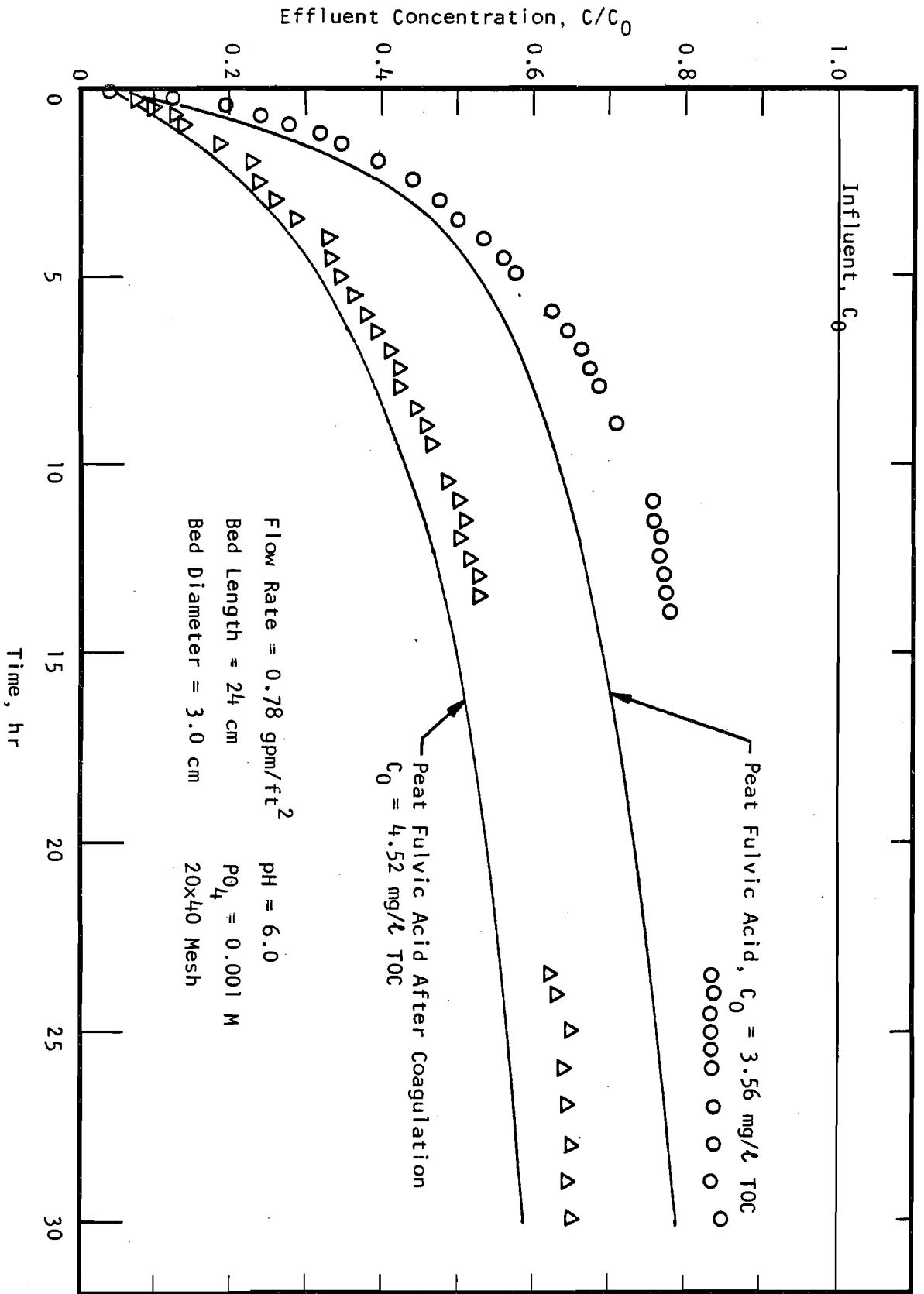


Figure 33. Breakthrough Curves for Peat Fulvic Acid Adsorbed by MW-M Carbon before and after Coagulation with Alum.

coagulation was three times the capacity of peat fulvic acid without coagulation. Similarly, the adsorption capacity of the carbon bed for the former solute was 2.16 times the capacity of the latter solute for 30 hours operation. The total adsorption capacity was evaluated by integrating the area occupied between the influent line and the breakthrough curve. Thus the findings of the isotherm studies matched the results of the column studies.

To test the model's ability to accurately predict effluent concentration of peat fulvic acid remaining after alum coagulation, the predicted curve was generated. The agreement between the experimental data and the predicted curve indicates that the model is able to describe the adsorption of peat fulvic acid remaining after coagulation in the column experiment.

6.4.3 The Application of the Mathematical Model

The mathematical model was verified in the previous section by comparing the column model predictions with experimental data. The model was able to describe the performance of carbon columns but some deviation between the experimental data and the predicted curve was found. Therefore, surface diffusion coefficients determined from batch reactor experiments were compared to those determined from the column data. The variation in hydraulic loading and bed length was also taken into consideration. Finally, the sensitivity of the model to adsorption isotherm constants and mass transfer coefficients is discussed in the section that follows.

a. Model Verification

Table 12 lists the respective values of surface diffusion coefficients determined from batch and column models for two different humic substances adsorbed by various activated carbons. Commercial humic and peat fulvic

Table 12. Comparison of Surface Diffusion Coefficients for Different Humic Substances and Various Activated Carbons Obtained from Batch and Column Models

Solute	Adsorbent	Model	Surface diffusion coefficient, cm^2/sec		
			A	B	C
Commercial humic acid	F-400 (60 x 80)	Batch	5.0×10^{-12}	6.0×10^{-12}	7.2×10^{-12}
		Column ^a	5.2×10^{-12}	7.0×10^{-12}	9.5×10^{-12}
		Column ^b	8.0×10^{-12}	10.0×10^{-12}	12.5×10^{-12}
Commercial humic acid	WV-G (20 x 40)	Batch	1.8×10^{-11}	2.1×10^{-11}	2.4×10^{-11}
		Column	1.4×10^{-11}	1.7×10^{-11}	2.0×10^{-11}
Peat fulvic acid	WV-G (20 x 40)	Batch	2.0×10^{-11}	3.5×10^{-11}	4.2×10^{-11}
		Column	2.25×10^{-11}	2.5×10^{-11}	2.8×10^{-11}
Peat fulvic acid	WV-W (20 x 40)	Batch	4.2×10^{-11}	5.4×10^{-11}	6.5×10^{-11}
		Column	3.5×10^{-11}	4.0×10^{-11}	4.7×10^{-11}

A, B, and C express the lower region of 95% confidence, best fit, and higher region of 95% confidence, respectively.

a Column runs with empty bed contact time of 6.93 min.

b Column runs with empty bed contact time of 2.21 min.

acids were used for this comparison. The surface diffusion coefficients were determined independently using data from the batch rate and column studies. As presented in Table 12, the surface diffusion coefficients obtained by the best fits with both batch and column models are fairly close. These coefficients obtained from the batch and column models had an overlapping 95% confidence region (except for column data designated by footnote b). Consequently, the surface diffusion coefficient determined from batch rate studies can be used in the model predictions.

In contrast, Weber et al. (1978) studied the modeling of the humic acid adsorption by activated carbon and found values of surface diffusion coefficients with a difference of one order of magnitude were between batch and column models. They suggested that the biological effect may explain this difference. It is possible that biological effects were significant in the 10-day column runs which they conducted because a different type of humic substance was used.

The length of the adsorber and flow rates are other important factors that must be verified for this column model. Two sets of experimental column data were collected from a 1.0 cm diameter column under different conditions. Run A was operated with a bed length of 18 cm and a flow rate of 10.83 mL/min (2.35 gpm/ft^2); run B was conducted with a longer bed length of 24 cm and a slower flow rate of 4.60 mL/min (1.44 gpm/ft^2). The corresponding empty bed contact time for runs A and B was 2.21 and 6.83 min, respectively. Figure 34 compares experimental column data with model predictions for commercial humic acid solution and F-400 (60 x 80) activated carbon. The dotted lines represent the best fit of the column model; the solid lines were obtained from the predictions of the column model. Few differences

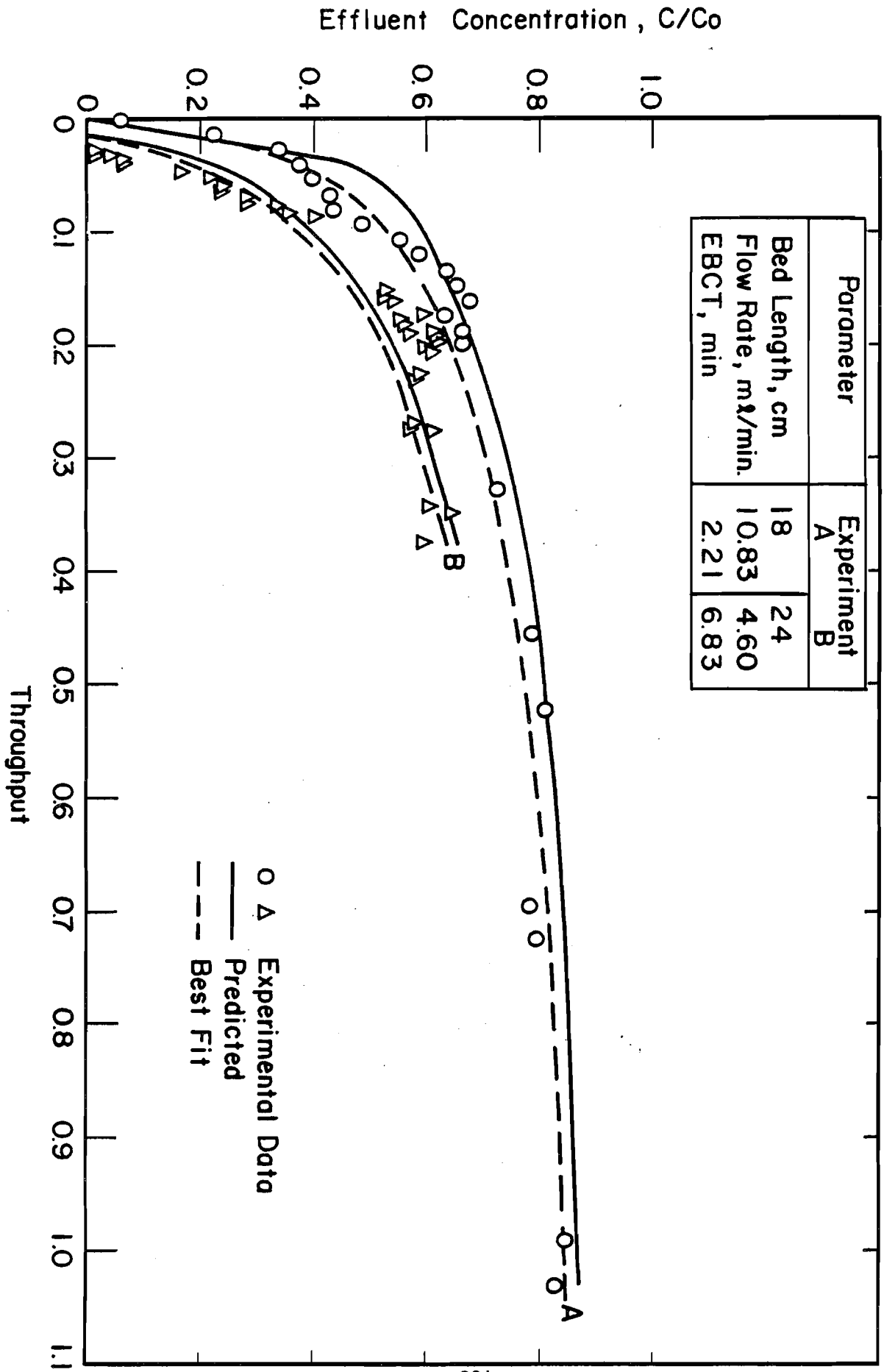


Figure 34. Breakthrough Curves for Commercial Humic Acid Adsorbed by F-400 (60x80) Carbon.

were observed between the model predictions and the experimental data.

b. Sensitivity Analyses

Model sensitivity to the Freundlich adsorption constant K is shown for peat fulvic acid in Figure 35. The center line represents the breakthrough curve using a K value of 3.29 mg/g and a Freundlich adsorption constant $1/n$ of 0.5653 determined from the isotherm data. The lines above and below the center line represent the predicted breakthrough curves with $\pm 25\%$ variation of K . The sensitivity of the model to the constant $1/n$ for peat fulvic acid is presented in Figure 36. The predicted curves are not as sensitive to $1/n$ as to K .

The effect of variation in the film transfer coefficient on the breakthrough curves is shown in Figure 37 for peat fulvic acid. Again, the film transfer coefficient is not very sensitive because the Sherwood number is high. The higher the Sherwood number, the less important the film transfer coefficient. Initially the model is more sensitive because the film transfer resistance is controlling the mass transfer. The effect of the surface diffusion coefficient is shown in Figure 38. The initial column run is not affected significantly by the variation in the surface diffusion coefficient. Substantially different predicted curves could result from a longer run. Similar results from the model's sensitivity to peat fulvic acid remaining after coagulation with alum were also observed.

c. Model Predictions

The breakthrough curves for peat fulvic acid adsorbed on different activated carbons are shown in Figure 39. These predicted curves were

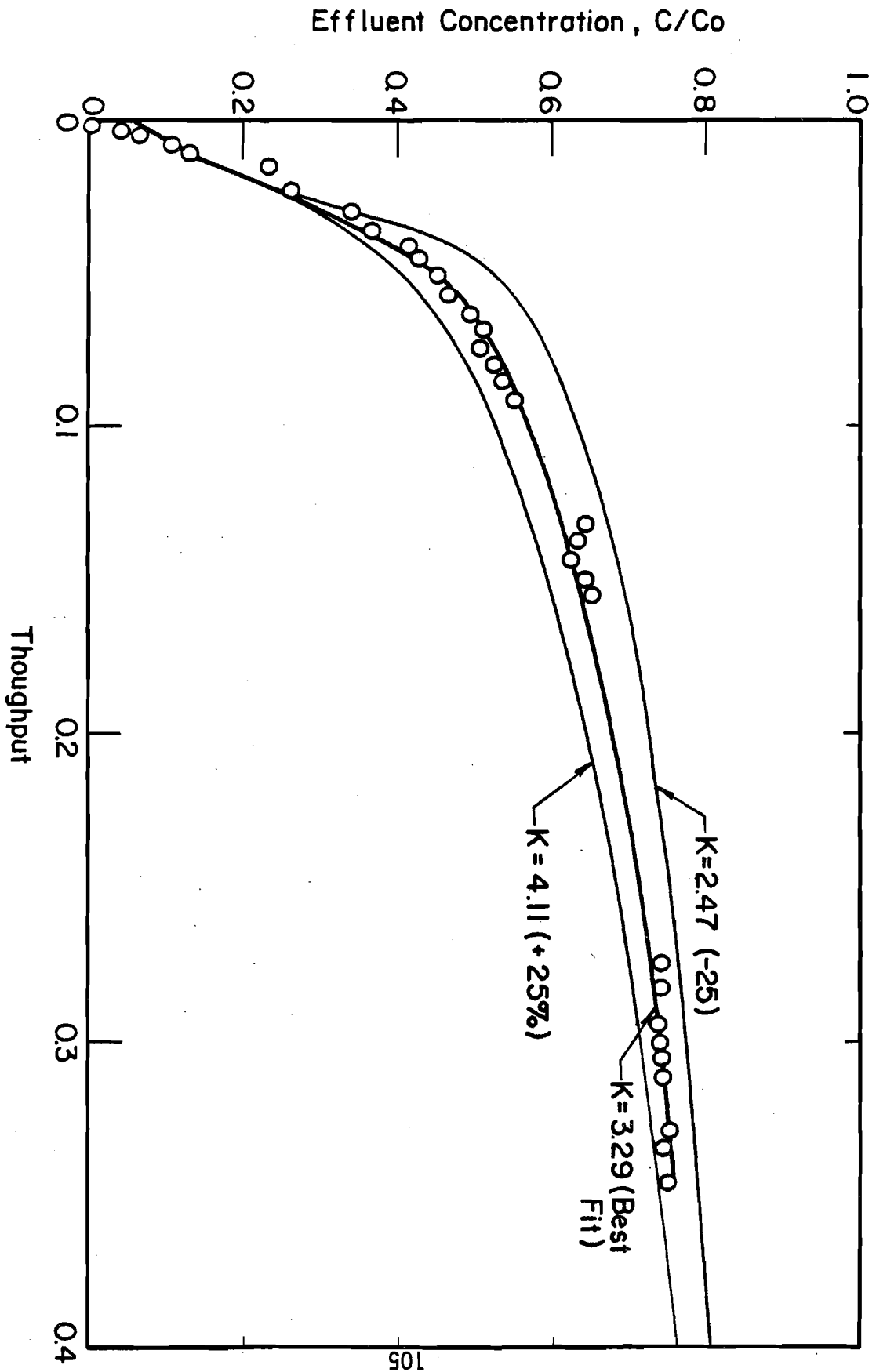


Figure 35. Sensitivity Analysis of the Adsorption Constant K , mg/g.

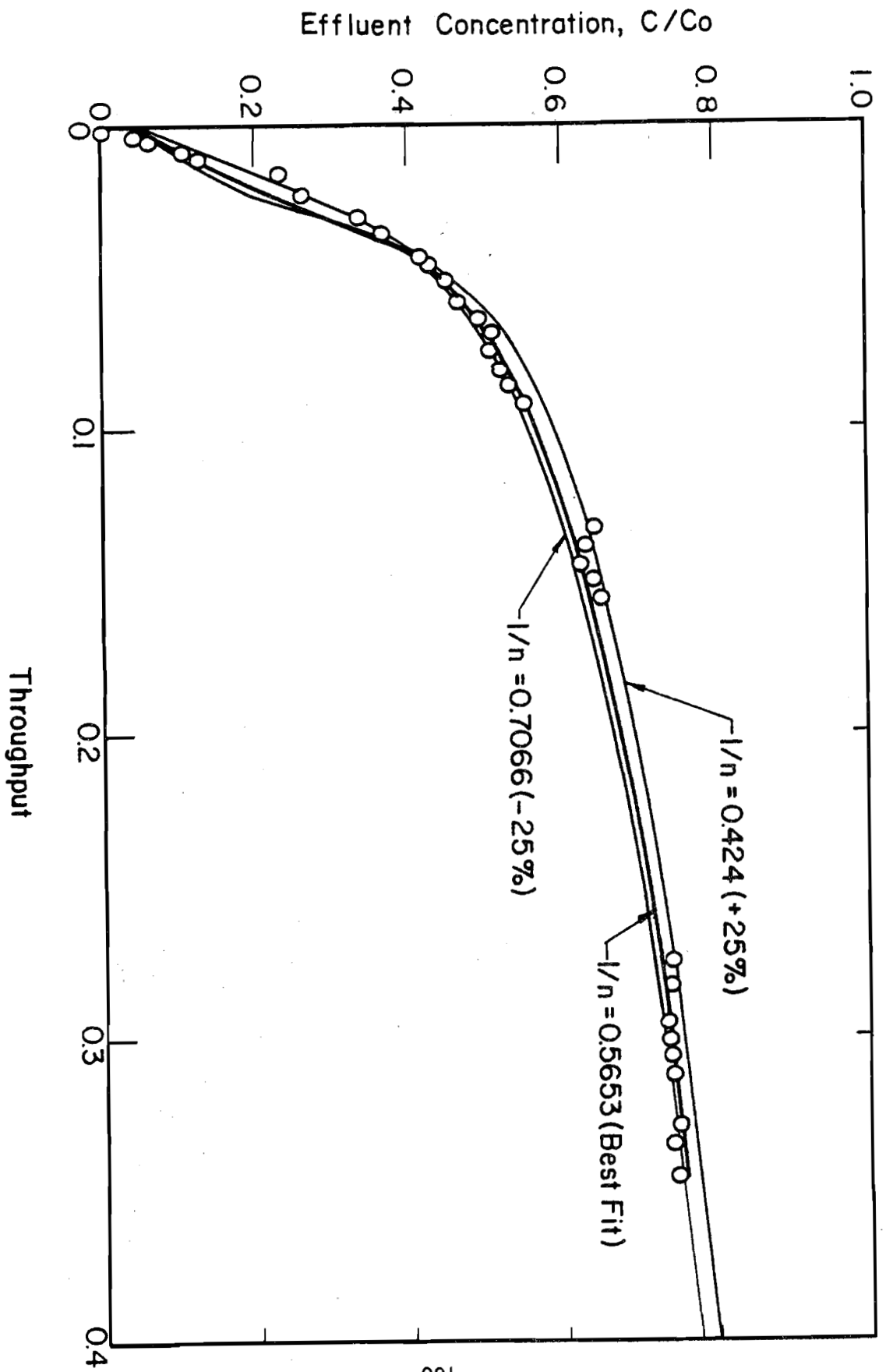


Figure 36. Sensitivity Analysis of the Adsorption Constant $1/n$.

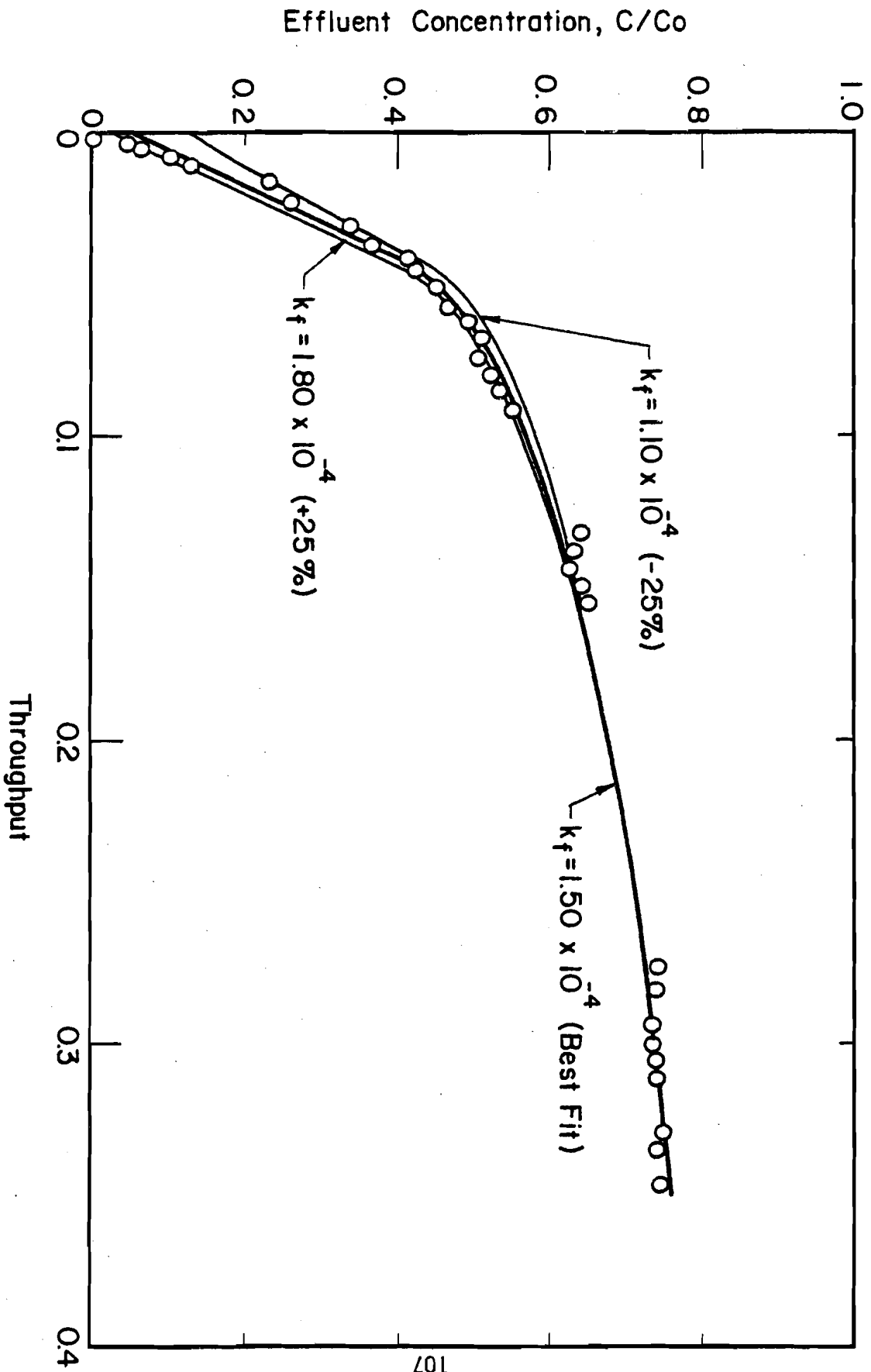


Figure 37. Sensitivity Analysis of the Film Transfer Coefficient k_f , cm/sec.

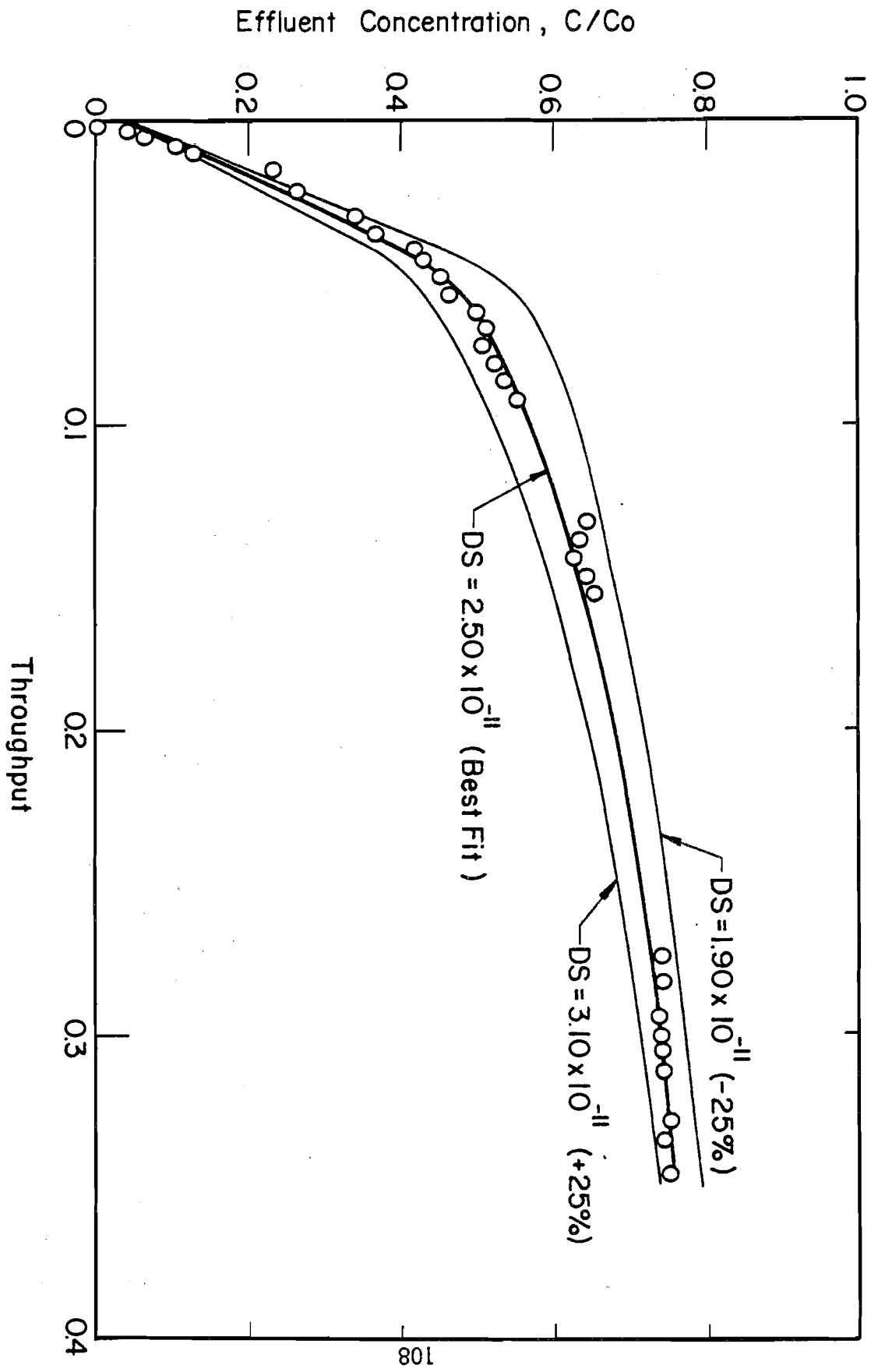


Figure 38. Sensitivity Analysis of the Surface Diffusion Coefficient D_s , cm^2/sec .

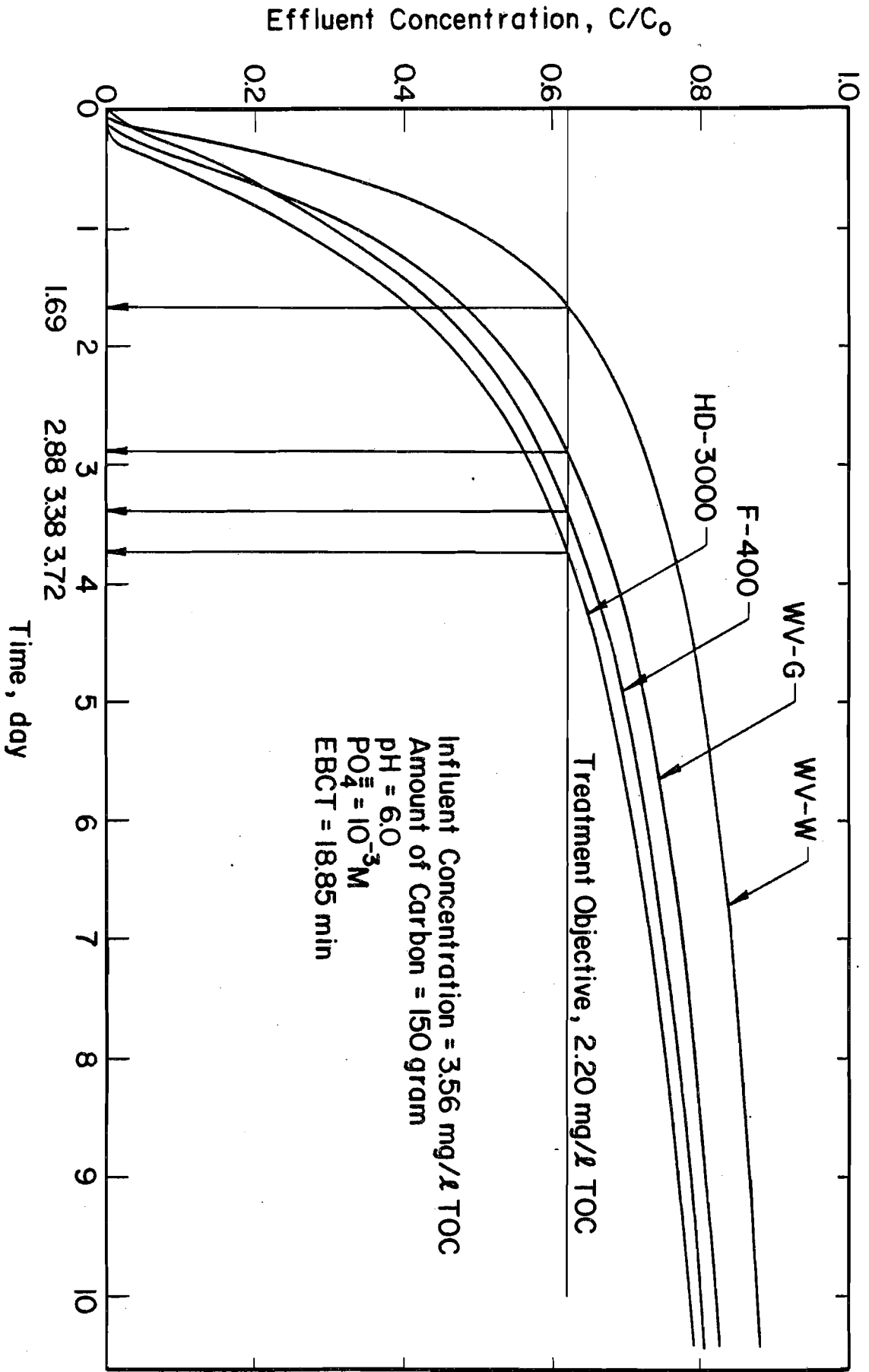


Figure 39. Predicted Breakthrough Curves for Peat Fulvic Acid.

generated using an initial concentration of 3.56 mg/l TOC and 150 grams of carbon. The flow rate and column length were varied to maintain the same empty bed contact time (EBCT) of 18.85 min. The surface diffusion coefficient of each carbon was obtained from the batch reactor study, and the column film transfer coefficient was determined from the equation proposed by Williamson et al. (1963). HD-3000, F-400, and WV-G performed better than the WV-W carbon, which has a faster breakthrough curve than the other carbons. For a particular treatment objective with 100 µg/l chloroform formation potential (CFP), the effluents of these carbon beds should not exceed 2.20 mg/l TOC, according to correlation of TOC and CFP shown in Figure 9. Using the line drawn for effluent concentration at 0.62 (corresponding to a TOC of 2.20 mg/l) in Figure 39, one can see that the service times for WV-W, WV-G, F-400, and HD-3000 carbon beds are 1.69, 2.88, 3.38, and 3.72 days. The total amount of water treated per gram of carbon corresponding to the above service times is 0.33, 0.61, 0.91, and 1.07 liters. When only the capacity is considered, HD-3000 is the best carbon for treating peat fulvic acid.

Since alum coagulation of peat fulvic acid prior to carbon adsorption was found to enhance the adsorption capacity of carbon almost threefold, it is of interest to predict column performance under this condition. Figure 40 gives the predicted breakthrough curves for peat fulvic acid remaining after coagulation with alum. These predicted curves are generated using an influent concentration of 3.56 mg/l as TOC of peat fulvic acid remaining after alum coagulation and 18.85 min EBCT with the same operating conditions described above. A notable difference in the predicted break-

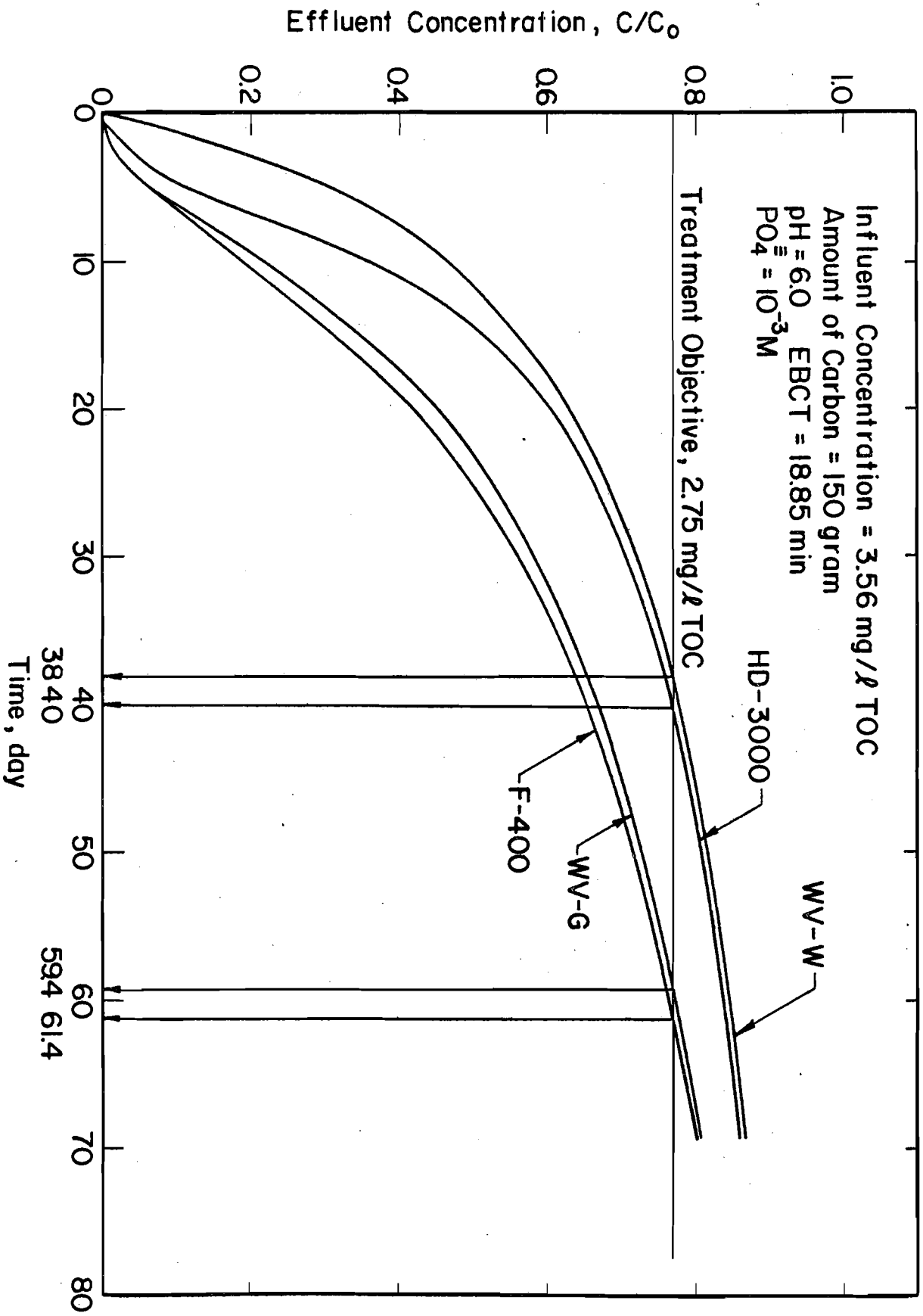


Figure 40. Predicted Breakthrough Curves for Peat Fulvic Acid Remaining after Coagulation with Alum.

through curves presented in Figure 40 is the service time for all four carbons. For the same treatment objective of 100 $\mu\text{g}/\ell$ CFP, the carbon bed effluents should not exceed 2.75 mg/ℓ TOC because peat fulvic acid remaining after coagulation with alum has a lower CFP. With this limit, the service times for WV-W, HD-3000, WV-G, and F-400 were 38, 40, 59.4, and 61.4 days, respectively. Of these four carbons, F-400 and WV-G perform the best. HD-3000 has a sharper breakthrough curve than the other carbons. The performance of this peat fulvic acid remaining after coagulation with alum on the carbon beds also corresponds somewhat with results from the adsorption isotherms. In the isotherm study, the surface concentrations of carbon at an equilibrium concentration of 3.56 mg/ℓ TOC for F-400, HD-3000, WV-G, and WV-W are 42.5, 35.0, 33.0, and 20.15 mg/g , respectively. Although the surface concentrations for HD-3000 and WV-G are similar, the predicted breakthrough curves for these two carbons are different because WV-G carbon has a larger surface diffusion coefficient than HD-3000 carbon. The surface diffusion coefficient was 2.0 and 1.6×10^{-11} cm^2/sec for WV-G and HD-3000, respectively.

It is of interest to compare the predicted breakthrough curves for peat fulvic acid before and after coagulation. As shown in Figures 39 and 40, the major difference between peat fulvic acid before and after coagulation is the service time of the carbon bed. For the same influent concentration and treatment objective, the service time before the regeneration of carbon bed for fulvic acid without coagulation pretreatment varies from 1.69 to 3.72 days, whereas for fulvic acid remaining after coagulation the time varies from 38 to 61.4 days. A significant increase in the service time of

the carbon bed resulted from the conjunctive use of carbon adsorption and coagulation.

To evaluate the effect of empty bed contact time (EBCT) on humic substance removal by the activated carbon bed, several model predictions were made using a fixed flow rate of 0.78 gpm/ft^2 and various bed lengths from 12 to 240 cm. Thus the contact times were between 3.77 and 75.4 min. The predicted breakthrough curves for peat fulvic acid adsorbed by WV-G carbon with various EBCTs are presented in Figure 41. The longer EBCT of the column, the better the performance. Diffusion of such large molecules inside the carbon particle takes a long time. The surface diffusion coefficient of humic substances within the carbon particle is of the order of $10^{-11} \text{ cm}^2/\text{sec}$, which is an extremely small number compared with the other organics reported by Crittenden and Weber (1978a,b). For a treatment objective of $100 \text{ }\mu\text{g}/\ell$ CFP of effluent, the service times for EBCTs of 3.77, 7.54, 11.3, 15.1, 18.9, 37.7 and 75.4 min are 2.4, 14, 33, 58, 82, 255, and 720 hours, respectively. Therefore, each doubling of EBCT resulted in a greater increase than doubling the operating times of the carbon beds.

The effect of EBCT on the removal of humic substances remaining after coagulation is more pronounced. Under the same conditions as for peat fulvic acid without coagulation, the predicted breakthrough curves for peat fulvic acid remaining after alum coagulation were determined and were plotted in Figure 42. For a treatment objective of $100 \text{ }\mu\text{g}/\ell$ CFP of effluent, the service times for EBCTs of 3.77 and 7.54 min are 169 and 465 hours. A great difference in the ability to treat more peat fulvic acid remaining after coagulation was noticed for the first doubling of EBCT.

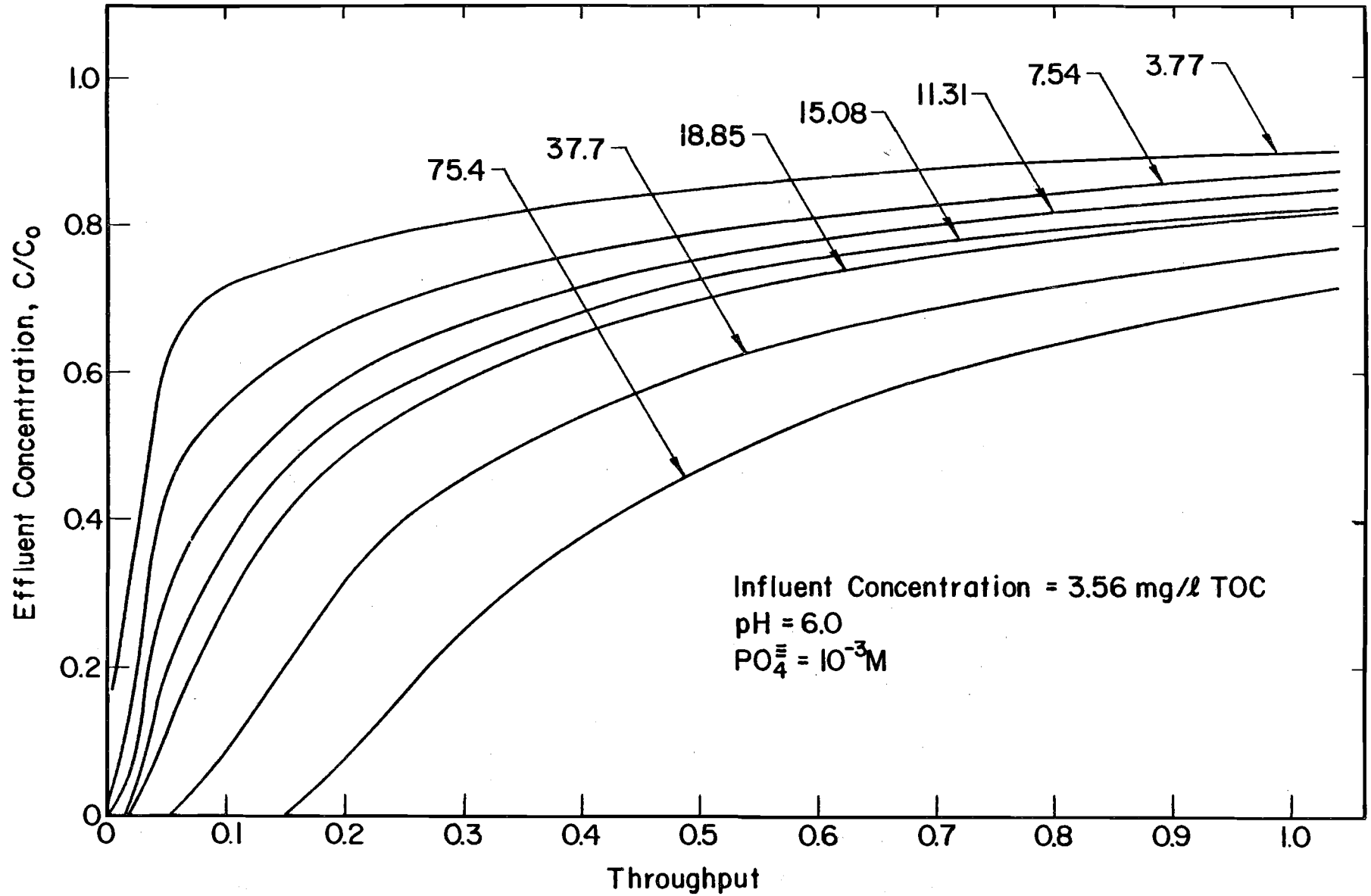


Figure 41. Predicted Breakthrough Curves of Peat Fulvic Acid Adsorbed by WV-G Carbon with Various Empty Bed Contact Times (min).

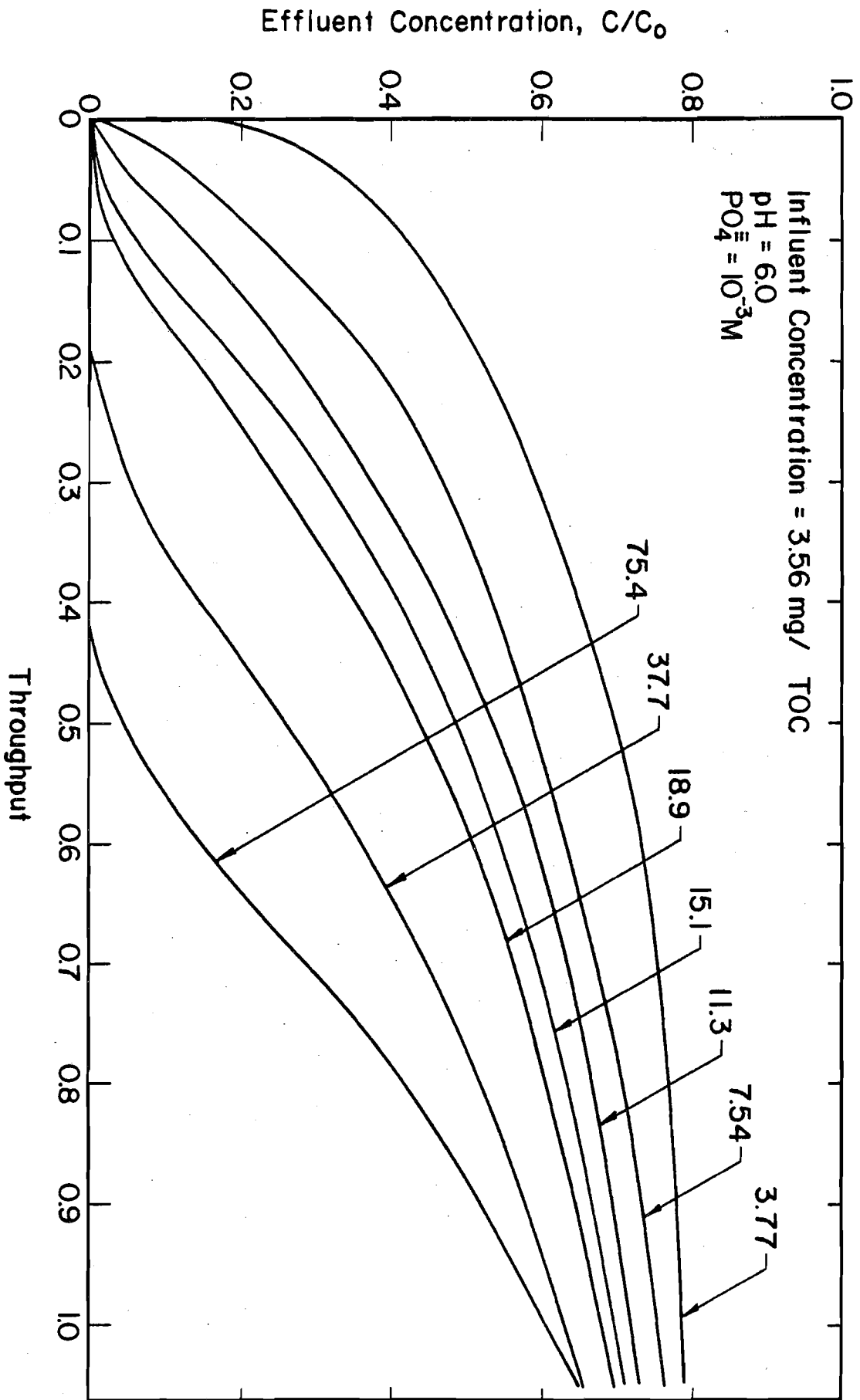


Figure 42. Predicted Breakthrough Curves of Peat Fulvic Acid Remaining after Alum Coagulation Adsorbed by W-6 Carbon with Various Empty Bed Contact Times (min).

For different influent concentrations, predicted breakthrough curves were generated using a 3 cm diameter (ID) and 60 cm long WV-G carbon bed with a 0.78 gpm/ft^2 flow rate and an EBCT of 18.85 min. The influent concentration was varied from 1.0 to 20 mg/l TOC. Both the column film transfer and surface diffusion coefficients were assumed to be $2 \times 10^{-4} \text{ cm/sec}$ and $2.5 \times 10^{-11} \text{ cm}^2/\text{sec}$, respectively. Figure 43 gives these breakthrough curves, the shape of which changes with the influent concentration. The higher the influent concentration, the sharper the breakthrough curve. For a 50% breakthrough of influent TOC, the service times for a carbon bed containing WV-G are 26, 58, and 109 hours for influent TOC values of 8.0, 4.0, and 2.0 mg/l. Thus the service time of the carbon bed was doubled for each 50% reduction of influent concentration. However, this prediction is only valid for constant column film transfer and surface diffusion coefficients of all different initial concentrations. As discussed in the adsorption kinetic section, the surface diffusion coefficient of humic substances may depend on the surface concentration on the carbon. With an increased initial concentration, the surface loading on the carbon is expected to be higher, thus leading to a decrease of the surface diffusion coefficient. A higher effluent concentration will be observed consequently, because of the decrease in the surface diffusion coefficient at higher influent concentrations.

The service time of a carbon bed can be extended significantly when humic substances are partially removed by alum coagulations before carbon adsorption. For an influent concentration of 3.56 mg/l TOC peat fulvic acid, a 3 x 60 cm carbon column containing 150 grams of F-400 carbon operated at

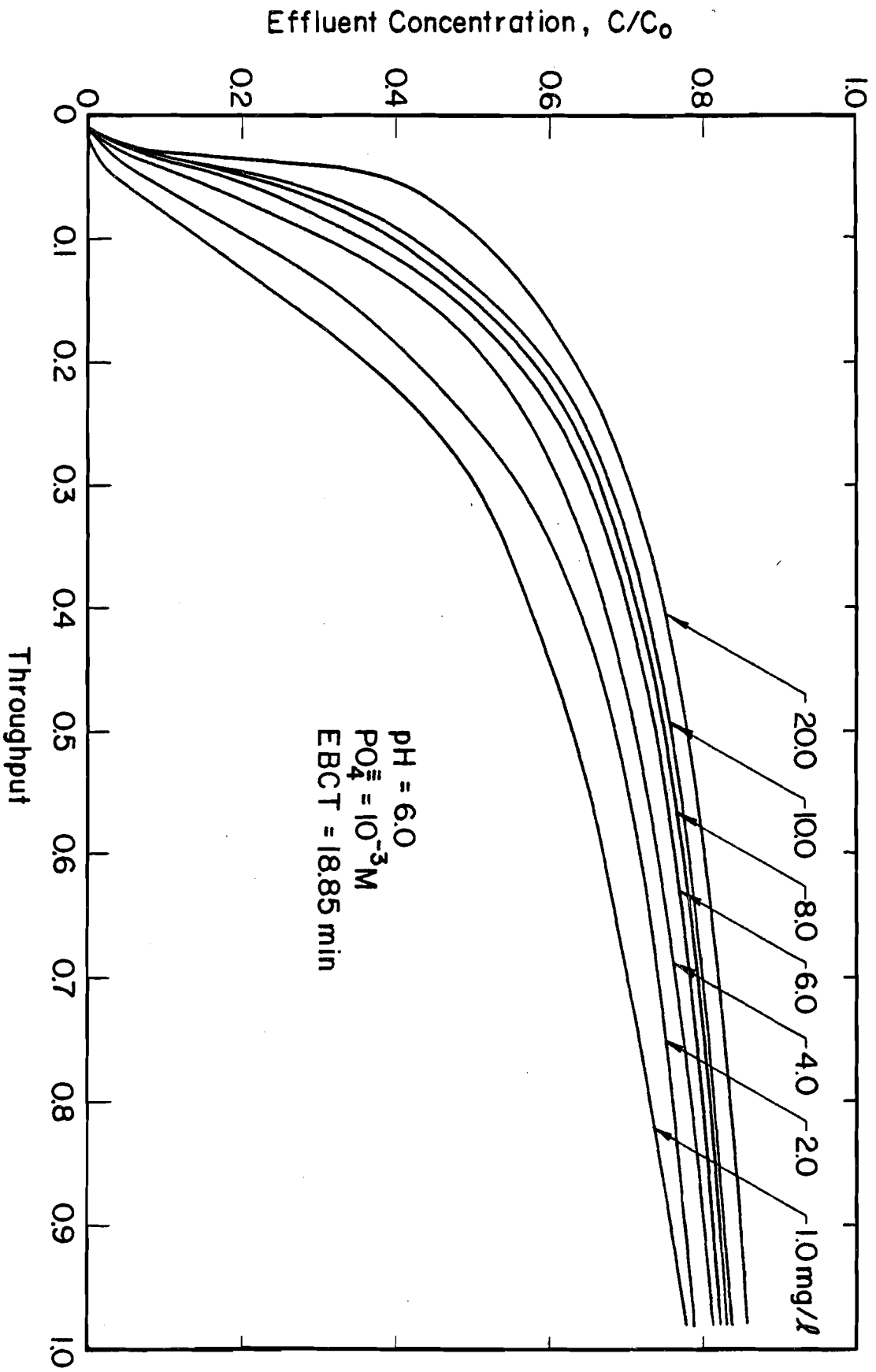


Figure 43. Predicted Breakthrough Curves for Peat Fulvic Acid Adsorbed by MW-G Carbon with Different Influent Concentrations (mg/l, TOC).

a flow rate of 0.78 gpm/ft^2 (EBCT = 18.85 min) was used for model predictions. Predicted service times for 0%, 10%, and 20% removal by alum coagulation are 0.1, 3.2, and 6.0 months. Therefore, a significant improvement in the carbon bed adsorption can result from a partial removal of humic substances by alum coagulation.

7. ENGINEERING SIGNIFICANCE

This study has demonstrated a simple procedure for evaluating the removal of humic substances by the process of carbon adsorption. The procedure includes bench-scale adsorption isotherm and rate studies and the application of a mathematical model to predict the performance of a pilot-scale carbon bed. Data obtained from the model predictions can be useful in designing a pilot-scale carbon bed. Since the behavior of each different humic substance varies with the source, a pilot-scale carbon bed is needed for each different water treatment plant location. On the basis of results obtained from pilot-scale studies, full-scale carbon beds for individual water treatment plants can be effectively designed and economically operated.

The conjunctive use of coagulation and carbon adsorption is also a very important process in considering the removal of humic substances from water. This study found a significant increase in isotherm capacity and rate of adsorption of peat fulvic acid remaining after alum coagulation. Based on the results of model prediction, a longer time between regeneration of a carbon bed could be achieved for a given treatment objective. By a similar approach, a pilot-scale plant can be set up for each individual water treatment plant to evaluate the suitability of the conjunction of these two processes. The coagulation and carbon adsorption processes of a full-scale water treatment plant can be optimized for humic substance, using findings from a pilot-scale study. In this way, the overall cost of water treatment may be reduced.

8. CONCLUSIONS

Based on the results of this study, the following conclusions may be drawn:

- (1) Both ultraviolet/visible adsorption and total organic carbon measurement can be used to indicate the chloroform formation potential of humic substances in the processes of chemical coagulation and activated carbon adsorption.
- (2) Different adsorption isotherms were found for commercial humic and peat fulvic acids. An unfavorable adsorption isotherm was found for commercial humic acid. A favorable adsorption isotherm was observed for peat fulvic acid.
- (3) A decrease of solution pH, particle size of carbon, molecular weight of the humic substance, and an increase of soluble alum were all found to increase the adsorption capacity.
- (4) Pore volumes of 100 to 500 Å radius correlated well with the adsorption capacity of activated carbon for humic substances.
- (5) Based on the same amount of carbon, the lignite base activated carbon, which has a large volume of macropores in a column, adsorbed humic substances before coagulation better than the other activated carbons.
- (6) The conjunctive use of alum coagulation and carbon adsorption improved the adsorption efficiency of carbon with respect to adsorption isotherm and column performance.
- (7) Based on the same amount of carbon in a column, the bituminous base activated carbons with a wide spectrum of pore sizes adsorbed humic substances remaining after coagulation better than the other carbons.

- (8) The application of a mathematical model described by Crittenden and Weber (1978a,b) was successful. The model parameter estimation technique gave satisfactory results and the model was satisfactorily verified. It was then possible to predict the performance of carbon adsorbers for humic substance adsorption.
- (9) This mathematical model was found to be sensitive to values of adsorption capacity of activated carbon and the surface diffusion coefficient of humic substance inside the adsorbent particle.
- (10) The empty bed contact time of the carbon column was one of the major factors that influenced the time to saturation by humic substances. The longer the empty bed contact time, the better the performance of the column.
- (11) The influent concentration of humic substances was another important factor. The lower the influent concentration, the longer the carbon bed can serve for a given TOC effluent. However, the breakthrough curves for lower influent concentrations were flatter than the higher influent concentrations. Consequently, the utilization of the carbon bed appeared less efficient when lower influent concentrations were introduced.

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