THE REMOVAL OF LOW LEVELS OF PHENOL BY ACTIVATED CARBON IN THE PRESENCE OF BIOLOGICAL ACTIVITY

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ABSTRACT

Bioregeneration of activated carbon was shown to occur in bench-scale carbon columns through use of parallel bacterially seeded and non-seeded, non-bioactive columns. Phenol degrading organisms were taken from an enrichment using phenol as sole carbon source. Mass balance calculations on phenol and dissolved oxygen were used to estimate amounts of pre-adsorbed phenol being biodegraded under different conditions, with a check made on this amount through the use of adsorption isotherm analysis. The amount of bioregeneration was found to be related to the influent dissolved oxygen concentration. Transient organic load experiments showed that the presence of a bacterial population could affect the effluent concentrations resulting from such transient loadings primarily through two mechanisms: increased carbon capacity due to bioregeneration, and reduction of solution concentration due to biodegradation of phenol in the bulk solution. End product analysis was performed via carbon extraction, gas chromatography, and mass spectroscopy. Total organic carbon analysis of column effluents was also performed.

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1. INTRODUCTION

The presence of trace amounts of organic compounds in drinking water and drinking water sources has been well documented (EPA, 1975; Symons et al., 1975). The health implications of the presence of trace organics in water has given rise to regulations limiting their presence (EPA, 1979). Granular activated carbon (GAC) adsorption is regarded as a promising method for removal of trace organic compounds from water (EPA, 1978; Symons, 1978). Fundamental questions remain, however, concerning the performance of GAC under the conditions of low organic load typical of water treatment plant operation.

The fact that microorganisms are ubiquitous in carbon beds used in water treatment processes has been recognized (Love and Symons, 1978; Hansen, 1975). A basic question remains to be answered: are bacteria harmful or beneficial to the operation of a carbon bed used in water treatment? Ozone pretreatment of carbon bed influent has been shown to increase organics removal, presumably via increased biodegradation of the organics present, but possibly by other means (Schulhof, 1979). The lack of understanding of the processes involved in the operation of carbon beds containing bacteria has made extensive pilot plant testing necessary for application of this process.

In order to lessen the need for pilot scale testing and to increase our understanding of the processes occurring when bacteria are active in carbon columns, carefully controlled experiments could be used to measure the removal of specific compounds by actived carbon

in the presence of bacteria. Such bench-scale experiments could then be used to answer basic questions about the removal process as it is occurring, with mass balances possible to quantify removal rates.

The objective of this study was to evaluate the process of carbon adsorption in the presence of biological activity. A bench-scale system was designed and applied using phenol as a model compound since it is both adsorbable and biodegradable. The importance of influent dissolved oxygen concentration as it affects bioregeneration of the carbon was investigated. The effects of the bacterial population on the resultant effluent profile from a transient influent organic load were also investigated, since in a real treatment plant the influent organic load is rarely constant. An attempt was also made to characterize the degradation products formed in this process to assess their potential health or treatment problems.

2. LITERATURE SURVEY

2.1 Organic Compounds in Drinking Water

Several recent surveys such as the National Organics Monitoring Survey (Symons et al., 1975) have shown that many different types of organic compounds are present in water supplies. A variety of these and other compounds are also present in finished drinking water (Arguello et al., 1978). The types of compounds present in water supplies and drinking water cover a wide range of size and properties, from humic acids to haloforms, and their concentrations range from below the limits of detection to several milligrams per liter, depending on the water and the compound (Smith et al., 1980; Arguello et al., 1979; Oliver and Lawrence, 1979; Rook, 1976).

Organics in water arise from many different sources. Many may be of autochthonous or other natural origin (Suida, 1980), but the majority of compounds identified in drinking water to date are of human origin. These compounds attributable to man's activity can be divided into two major groups: those which are in the raw water supply and those which are added during the water treatment process. Increasing reuse, both direct and indirect, of treated wastewater for human consumption increases the numbers of possibly hazardous organic chemicals present in a given water supply or finished water (State of California, 1976). The original sources of these compounds may be industrial discharge or municipal waste, and both surface waters and groundwaters may

carbon particles in typical water treatment applications is low, on the order of 1% surface coverage (Weber et al., 1978; Klotz et al., 1976; Kooij, 1976). The manipulations used to arrive at this number for percentage surface coverage are inherently flawed, however, so that the surface coverage may in fact be higher. Calculations based on enumeration of bacteria in carbon bed effluents should take into account the observation that techniques such as the Standard Plate Count Test may be only measuring part of the total bacterial population present (Cairo et al., 1970). Use of scanning electron micrographs to determine population densities on activated carbon particles may be misleading due to the extreme conditions used in sample preparation (Weber et al., 1977). These harsh conditions could remove bacteria or otherwise change the distribution of microorganisms on the carbon particles. The value of 1% surface coverage should therefore be treated as a minimum number, since both methods used to arrive at this number contain assumptions which may lead to artificially low results. The important point remains, however, that bacterial populations exist in activated carbon beds in numbers which indicate that the bacteria should have some modifying effect on the performance of carbon in adsorption.

Deliberate increasing of the influent dissolved oxygen (DO) levels for a GAC column results in the process called "Biological Activated Carbon (BAC)" (Symons, 1978). Since bacteria are ubiquitous in carbon beds, BAC is probably a misnomer. Aerobic bacteria will thrive in a GAC column as long as the influent stream contains enough DO and enough biodegradable organic matter. Since ozone in water decays to oxygen, and since ozonation breaks up large organic molecules, ozon-

ation has been used to treat carbon column influents. There has not been evidence which separates the effects of ozone into its two possible modes of action (increasing DO and decreasing size of organic molecules); nonetheless ozone is a popular treatment chemical. European workers have further developed the use of BAC via pretreatment of source water with ozone and manipulation of ozone contact time to increase the biodegradability of organics in water sources (Schulhof, 1979; Miller and Rice, 1978; Rice et al., 1978; Eberhardt, 1976; Kooij, 1976; Sontheimer, 1976). The advantages in using ozonation followed by granular activated carbon containing established microorganisms, as opposed to using GAC alone, are the following (Symons, 1978):

1) There is more effective removal of dissolved organics;
2) If the GAC can be kept free of halogenated organics, the operation life of the carbon, before regeneration is necessary, is increased;
3) Biological conversion of ammonia occurs in the columns;
4) Less ozone is required for removal of a given amount of organics than if ozone itself is used for organics removal.

It is not clear whether some of these benefits could also result merely from increasing the influent DO to a carbon column in use.

Recent work with bacteria in carbon beds following ozonation has concentrated on the gross parameters of bed operation, such as Standard Plate Counts (American Public Health Association, 1975) of the effluent and measurements of changes in dissolved oxygen, total organic carbon, ammonia concentration, and total inorganic carbon across pilot

plant columns operated with typical pretreated raw water input (Sontheimer et al., 1978). Attempts to define the chemical makeup of the influent and effluent to more closely determine the exact biodegradation processes which are occurring have not been made, and attempts to determine the role of bioregeneration in such systems have also not been made (see section 2.2.3).

Non-specific general enumeration techniques such as the Standard Plate Count Test (American Public Health Association, 1975), or modifications thereof, have been the most widely used means of monitoring bacterial numbers in a carbon bed (Rice et al., 1978; Sontheimer et al., 1978; Symons, 1978; Hutchinson and Ridgway, 1977; Klotz et al., 1976; Kooij, 1976). These methods do not recover the majority of bacteria in a carbon bed or its effluents (Cairo et al., 1979b; Benedek, 1978; Blanken, 1978), but their results are useful in comparing results from different studies if identical testing procedures are used. Numbers for a typical plant finished water range from zero to 100 bacteria/mℓ, with a mean value of 116 bacteria/mℓ over a period of four and one-half months (Rice et al., 1978). Standard Plate Count Test results from carbon bed effluents are usually much higher than this, from 10^2 to 10^5/mℓ of water, while in the bed itself the density of bacteria has been estimated to be 10^5 to 10^6/g of wet activated carbon. Plate counts have been found to be dependent on the empty bed contact time (EBCT) of a carbon bed; even after effects of volumetric flow rate were taken into account, it was found that the greater the EBCT, the greater the bacterial numbers in the effluents. In the same study, chlorination of the influent was found to decrease the numbers of bacteria in the bed

effluent (Cairo et al., 1979b).

Little work has been performed on identification of the organisms present in activated carbon beds or in their effluents. Clostridia perfringens was found in a single sample of effluent from a French plant (Rice et al., 1978), while Coliforms, Pseudomonas, and Actinomycetes varieties were isolated from activated carbon in the Netherlands (Kooij, 1976). In addition to these three groups, members of the groups Bacillus, Flavobacterium and Alcaligenes have been found in carbon beds or their effluents in the U.S. (Brewer and Carmichael, 1979; Cairo et al., 1979b; Love and Symons, 1978). These types of bacteria are predominantly saprophytic chemo-organotrophs common to soil or natural waters and have no pathogenic significance. Some species of Pseudomonas, Flavobacterium, and Alcaligenes are opportunistic pathogens, chlorine resistant, or suppressors of total coliform measurements, such that the significance of the presence of these bacteria as regards health effects or distribution system problems remains to be determined (Cairo et al., 1979b). Since some Pseudomonas have been shown to degrade a variety of organic compounds under laboratory conditions (Chapman, 1972; Tabak et al., 1964; Gray and Thornton, 1928), biodegradation of organic compounds could be expected to occur in a carbon bed under the appropriate conditions.

Detailed information about the performance of bacteria in activated carbon beds is lacking, but there are some data in the literature which reflect changes in gross parameters during the normal operation of the bed. In a pilot plant operation treating Ruhr River water with a variety of commercial activated carbons, the following

parameter changes were observed through the beds over a six-month period: dissolved organic carbon decreased an average 1.22 mg/ℓ, with values ranging from 0.92 to 1.26 mg/ℓ; dissolved inorganic carbon increased an average 1.04 mg/ℓ, with values ranging from 0.83 to 1.36 mg/ℓ; dissolved ammonia decreased an average 1.31 mg/ℓ, with values ranging from 1.31 to 1.34 mg/ℓ, and dissolved oxygen decreased an average 6.45 mg/ℓ, with values ranging from 5.99 to 6.95 mg/ℓ (Sontheimer et al., 1978). The oxygen demand seen was attributed to stoichiometric demands for the oxidation of NH_4^+ to nitrate and the dissolved organic carbon to carbon dioxide.

The lack of understanding involved in the operation of carbon beds containing bacteria has made pilot plant testing necessary for almost every application of this process. In the case of ozonation followed by activated carbon, performance is believed to be affected by the nature of the organics present, the influent biochemical oxygen demand (BOD) load, the influent dissolved oxygen levels, the amount and type of biological growth in the carbon bed, and the effects of pretreatment of the influent (Culp and Hansen, 1980). In the case of use of GAC beds without prior influent ozonation, performance is probably affected by the same parameters.

2.2.4 Bioregeneration of Activated Carbon

In this discussion, bioregeneration of activated carbon is defined as an increase in adsorption capacity of activated carbon due to biological degradation of organic molecules which were adsorbed on the carbon. Such removal of material from the carbon surface by the

action of microorganisms will reopen adsorption sites to occupation by other organic molecules in the bulk solution passing through the carbon column. The amount of bioregeneration which occurs on a given carbon can be measured by determining the adsorption isotherms for the same carbon before and after bioregeneration has taken place. It should be noted that biodegradation processes will have two sources from which degraded molecules will come: adsorbed molecules can be removed from the carbon surface, in which case bioregeneration occurs; or molecules can be removed from the bulk solution passing through the column. Both types of biodegradation will have the same effect on a breakthrough curve; if only breakthrough data are considered, it may be observed for each case that apparent carbon capacity is increased. Further analysis, such as adsorption isotherm tests, are necessary to determine if true bioregeneration has taken place. Since biodegradation of organics from the bulk influent often takes place at the same time that bioregeneration takes place, careful mass balance measurements are necessary to determine amounts of bioregeneration.

Many operators and experimenters have observed that breakthrough of organics in activated carbon beds or columns is delayed when biological activity is present (Schulhof, 1979; Eberhardt, 1976; Parkhurst et al., 1967). This phenomenon has been attributed to the activity of bacteria in the carbon beds. Much speculation has led to the assumption that bacteria can bioregenerate carbon during use, but there are no data in the literature to support this assumption. Observed breakthrough curves could be explained by the biodegradation of organics from the bulk influent, in which case carbon acts only as a support

et al., 1964; Gray and Thornton, 1928). The biodegradation of phenol by the bacterial population of a sand filter has been previously studied (Pipes, 1976). The types of bacteria found to degrade phenol include Pseudomonas and Bacillus, both which are genera which have been identified in carbon beds or carbon bed effluents (Love and Symons, 1978). Phenol degradation by bacteria has been studied via the activated sludge process, and the applications of the kinetics of such biodegradation have been used in wastewater treatment (Beltrame et al., 1980; Holladay et al., 1978).

The pathways by which phenol is degraded by Pseudomonas are well documented (Feist and Hegeman, 1969). A summary of the major intermediates produced via these pathways is shown in Figure 1. The use of such pathways cannot be assumed a priori, since divergent catabolic routes have often been observed in Pseudomonas, with some individual strains possessing two independent biochemical mechanisms for the dissimilation of a single compound. Convincing proof that a given metabolic pathway is indeed being used by a given organism requires considerable documentation (Ornston, 1971).

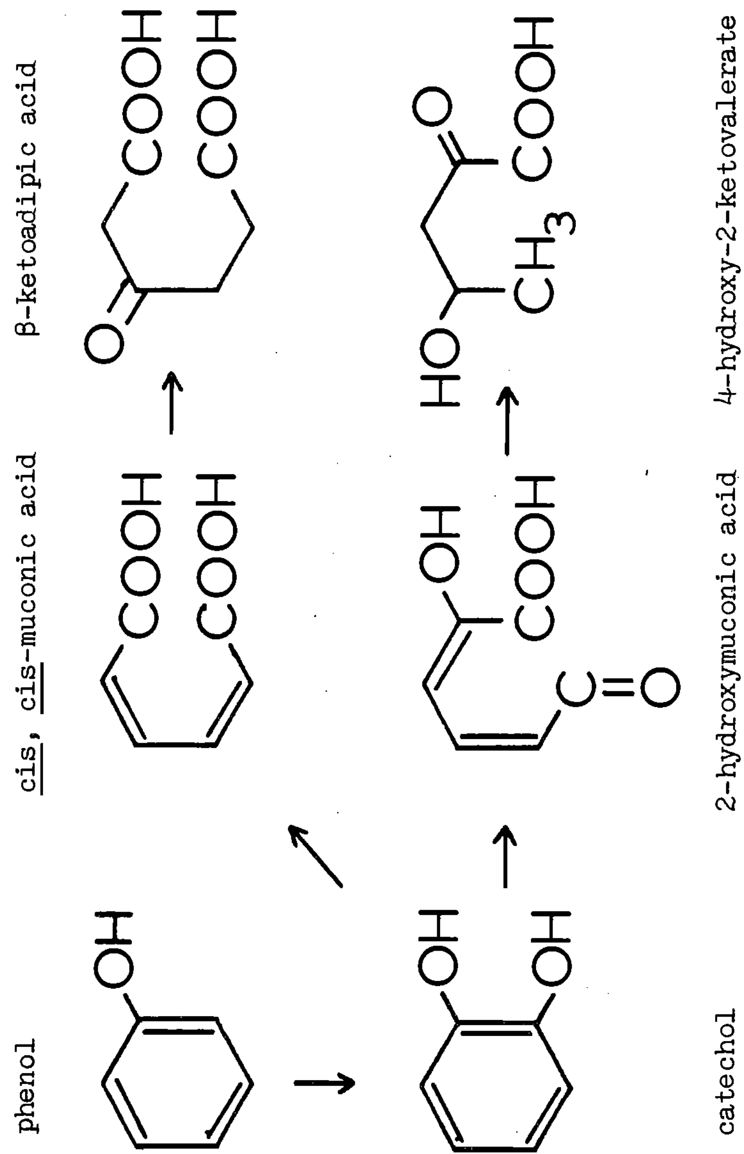


Figure 1. Degradation Products of Phenol

3. SCOPE OF THE INVESTIGATION

The main objective of this study was to determine the contribution of bacteria to the removal of phenol by granular activated carbon under conditions of low influent organic load. Once it was determined that a bacterial population could be established on a carbon column in a reproducible manner, aspects of bacterial performance under various influent conditions could be investigated. Therefore, the first objective of this work was to develop an experimental system which could be carefully controlled so as to be able to generate meaningful data concerning phenol removal and dissolved oxygen removal through a seeded column and a non-seeded, non-bioactive (preferably sterile) column for comparative purposes.

Once the experimental system was found to be adequate, the investigation into bacterial performance was initiated. This investigation was divided into three areas: first, the effects of varying influent dissolved oxygen levels; second, the effects of transient influent organic load; and third, an attempt to characterize end products of phenol degradation in the column.

The objective of the varied dissolved oxygen influent experiments was to determine if biological degradation of phenol adsorbed on activated carbon was oxygen limited. Mass balance calculations on phenol and dissolved oxygen could be used to measure amounts of pre-adsorbed phenol being biodegraded under different conditions, with a possible check through the use of adsorption isotherm analysis.

The objective of the transient organic load experiments was to determine if the presence of bacteria in an activated carbon column had an effect on such transient loads. Through the use of mass balances, quantitative assessment of the effects should be possible.

The final objectives to be considered were those associated with end product analysis. These were to determine the mass of end products formed and to chemically characterize the end products produced by bacterial degradation of phenol in activated carbon columns.

There are several questions to be answered by this study which should have immediate impact on the water treatment and advanced wastewater treatment industry. The major areas of concern are the following: are the bacteria which are known to exist in water treatment carbon beds performing any beneficial role in trace organics removal; what is the effect of influent dissolved oxygen levels on this role; and, how are bacteria affecting transient influent organic loads.

4. MATERIALS AND METHODS

4.1 Materials

4.1.1 Phenol

The reasons for using phenol in this study were listed in section 2.3.1, as was the commercial source of this compound.

4.1.2 Media Specifications

The Standard Plate Count medium and dilution buffer were prepared according to published means (American Public Health Association, 1975).

The solutions used for the enrichments and the influent for the column experiments were prepared using a mineral medium (adapted from Gray and Thornton, 1928) supplemented with phenol, e.g., 2 mg/ℓ, in a concentration noted in the data corresponding to each experiment. The composition of this medium is listed in Table 1. The pH of this medium was 7.5.

4.1.3 Source of Microorganisms

In the studies using seeded activated carbon, the organisms used to seed the columns were originally taken from an enrichment. The enrichment procedure involved inoculation of an aliquot of the mineral medium listed in Table 1, which was supplemented with 2 mg/ℓ phenol, with 1.0 mℓ water taken from the Saline Ditch at the Perkins Road bridge, which is approximately one kilometer downstream of the Urbana-

Table 1

Composition of Mineral Medium

g/ℓ	Component	Source
.5	K_2HPO_4	Mallinckrodt
.005	$(NH_4)_2SO_4$	Baker & Adamsen
.007	$CaCl_2 \cdot 2H_2O$	Mallinckrodt
.02	$MgCl_2 \cdot 6H_2O$	Mallinckrodt
.005	NaCl	J. T. Baker
.001	$FeCl_3$	Matheson

otherwise identical column was used in experiments of 3.1 g carbon mass (5 cm carbon bed length).

A continuous flow cell was designed and built to measure dissolved oxygen with a Yellow Springs Instrument Company Model 54 dissolved oxygen and temperature probe. Continuous pumping was supplied by a Buchler Polystaltic multichannel peristaltic pump.

Reservoirs were 12 ℓ Pyrex carboys modified by addition of a 3 mm teflon stopcock fitted with 6.4 mm OD glass tubing which could accommodate a Swagelok reducing connector in the same manner as the columns. By use of such a setup the solution flowing through the carbon column was in contact only with glass, teflon, or stainless steel, except for a 30 cm length of one-eighth inch Tygon tubing through the peristaltic pump. This setup reduced the introduction of unwanted organic compounds which may leach from plastic tubing and/or hardware (see Figure 2).

The amount of dissolved oxygen in the influent was determined by controlling the atmosphere over the reservoirs. For the 9 mg/ℓ influent, cotton plugs were used to allow free exchange of atmospheric oxygen into solution without allowing bacterial contamination of the sterile reservoirs. For the 4 mg/ℓ influent, a mixture of high purity nitrogen and oxygen was kept at positive pressure over the reservoir through use of teflon and glass lines through rubber stoppers connected to a mineral oil bubbler. For the 16 mg/ℓ influent, a custom blend of ultrahigh purity 30% oxygen and 70% nitrogen was used (Linde). It should be noted that Henry's Law predicts a DO of 13.4 mg/ℓ using this mixture; tests on this mixture and an unacceptable companion tank

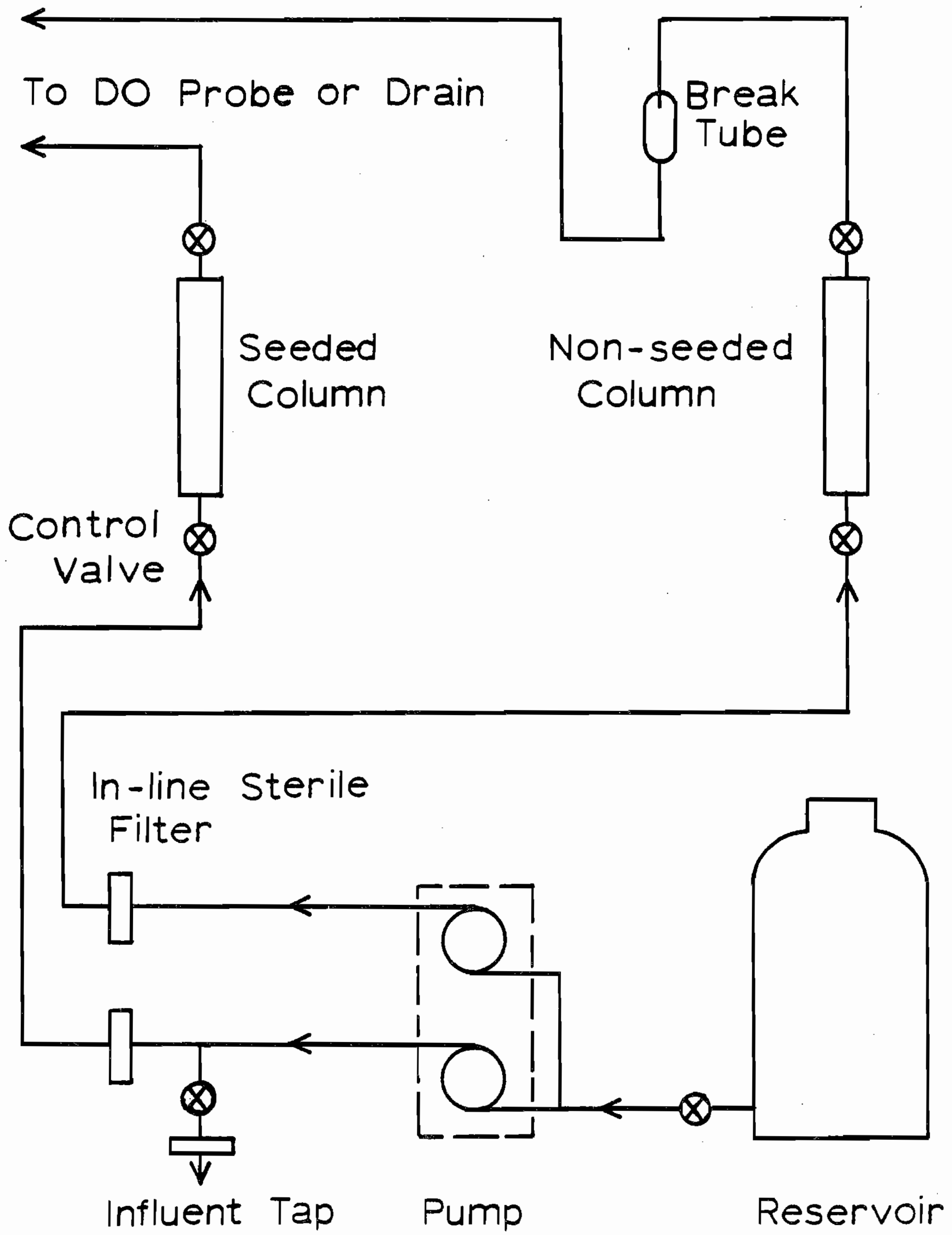


Figure 2. Column Setup

showed gas concentrations other than those on the label.

4.2 Methods

4.2.1 Phenol Measurements

Phenol measurements were performed by the 4-aminoantipyrine direct photometric method (American Public Health Association, 1975). Comparison testing of results obtained with standard solutions and samples led to omission of the distillation step generally included in this method. No differences in accuracy were detectable in samples analyzed without steam distillation when compared to the results obtained for the samples when the distillation step was used.

4.2.2 Total Organic Carbon Analysis

Samples to be analyzed for total organic carbon were stored at 1°C until analysis. Analysis was performed using a Dohrman DC-54 ultralow total organic carbon analyzer system (Dohrman Division of Envirotech Corporation, Santa Clara, California). Multiple measurements were made of each sample such that the standard deviation of the average obtained for a given sample was within 5% of the mean value of the measurement.

4.2.3 Dissolved Oxygen Measurements

Dissolved oxygen levels of the influent and effluent of the column experiments were measured using a continuous flow cell built to hold a Yellow Springs Instrument Company No. 5418 oxygen and temperature probe connected to a Model 54 oxygen meter. The meter was calibrated regularly (every other day) with air-saturated water and zero

oxygen water (American Public Health Association, 1975) and was found to regularly need little or no adjustment. Comparison of probe performance with the Winkler titrimetric procedure showed excellent agreement.

4.2.4 Standard Plate Counts

Bacteria were enumerated using the Standard Plate Count procedure (American Public Health Association, 1975). For column effluent samples from columns operated under ultraviolet (UV) lamps, the UV lamps were turned off 5 min prior to sampling to eliminate any effects of the UV on bacteria in the effluent lines of the column setup.

4.2.5 Column Operation

The carbon was pre-equilibrated with 2 mg/ℓ phenol (unless otherwise noted) under sterile conditions, while all glassware and fittings were autoclaved before use. Using sterile technique, the columns were packed with carbon in slurry form, using glass wool plugs at each end of the carbon mass for support. One column was then biologically seeded by addition of 0.2 g activated carbon which contained biological growth (see section 4.1.3). The other column was shielded from contamination via use of an effluent line break tube and an influent line Millipore No. XX4404700 in-line filter unit using Nuclepore No. 121106 4.7 cm 0.2 micron nitrocellulose filters and type P40 prefilters, in a manner similar to that used by previous investigators (Klotz _et al_., 1975).

All columns were operated in an upflow mode, and shielded

from light with aluminum foil to prevent algal growth. The varied influent oxygen experiments were operated at a flow rate of 2 mℓ/min through each column. This is equal to a flow of 0.19 mm/sec (0.28 gal/min·ft^2) and gives an empty bed contact time (EBCT) of over 14 min. This is significantly slower than the standard activated carbon bed flow rate of about 1.4 to 2.0 mm/sec (2 to 3 gal/min·ft^2) and EBCT under 7 min, although European experience has indicated that EBCT of 15 to 30 min is necessary for optimal growth of microorganisms in the use of biological activated carbon (Symons, 1978).

The varied influent phenol experiments were operated at a flow rate of 10 mℓ/min, while the carbon for these experiments was pre-equilibrated with 0.8 mg/ℓ phenol.

A tee and sample port were located in the influent line of the seeded column to allow influent sampling. Contamination through this line was blocked by a Nuclepore No. 420200 25 mm Swin-Lok Holder containing a 25 mm Nuclepore 0.2 micron nitrocellulose filter.

4.2.6 Batch Tests

Batch tests were performed on the carbon used in the variable influent oxygen column experiments. To eliminate the effects of biological growth, the carbon used in these tests was washed with sequential aliquots of 0.2 M HCl until the supernatant was at pH 3. The isotherm test solution was also adjusted to pH 3 with 0.2 M HCl after phenol had been added to the solution.

Individual isotherm samples were prepared by adding a measured amount of carbon to each of a series of eight 120 mℓ bottles.

The wet carbon (resulting from pre-equilibration with phenol and pH adjustment) was dewatered by following the procedure developed in this laboratory for repetitive wet weighing of synthetic resins (Chudyk et al., 1979). The carbon was not dried for batch tests so as to avoid losses of phenol due to vaporization. Sample bottles were filled, capped, and shaken as described above (see section 4.1.4).

4.2.7 Computer Evaluation of Column Experiment Data

A computer program developed and used to predict the performance of activated carbon columns in the removal of various compounds from solution (Thacker, 1980) was used to account for changes in capacity on the carbon produced by biodegradation of adsorbed phenol. This information was used in the transient loading experiments in order to be able to observe whether or not the effects of an established bacterial population on a transient load were restricted to capacity effects.

This computer model assumes: 1) that there is plug flow in the carbon column; and 2) that the rate of adsorption is controlled by film transfer and surface diffusion, i.e., that the solute molecule moves through a solvent film to the surface of the carbon particle where it attaches to the carbon surface according to the conditions of the known equilibrium isotherm, and then moves into the carbon particle via surface diffusion along the carbon pores. The simultaneous equations resulting from the mathematical expression of these assumptions were solved by orthogonal collocation and a numerical integration routine computer package known as GEAR.

This computer model predicts the effluent concentrations resulting from an established set of initial column conditions. The model does not take into account any of the effects expected to occur from the actions of a bacterial population present in the carbon column. The possible effects during a transient load experiment include bioregeneration of the carbon, which would increase the apparent capacity of the carbon, and biodegradation of phenol in the bulk influent, which would decrease the amount of mass in the phenol pulse which was introduced as part of the transient load experiment. If bioregeneration of the carbon takes place during a transient loading experiment, the resulting effluent phenol pulse shape would be lower and broader, with a later occurring concentration maximum, than would be predicted by the computer model. If biodegradation of phenol in the bulk influent occurs as the phenol pulse is passing through the column, the resulting effluent phenol pulse shape would also be lower than that predicted by the computer model.

If the presence of a biofilm on the surface of the carbon acts in any way to block or hinder adsorption of phenol, such action would be reflected in a higher and sharper effluent phenol pulse shape than that predicted by the computer model. If phenol adsorbs to an inert bacterial cell or to extracellular products which may act to modify the surface characteristics of the carbon, such additional adsorption would be difficult to distinguish from bioregeneration of the carbon surface or biodegradation of the bulk influent phenol during a transient loading experiment. To distinguish between the active adsorption and passive adsorption characteristics of a bacterial population

during a transient loading experiment, the bacterial population was rendered inactive by lowering the pH of the column and influent to pH 3. The isotherm parameters describing phenol adsorption at lower pH are also necessary for the model. The action of any passive bio-adsorption process would be reflected in a lower and broader effluent phenol pulse shape than that predicted by the computer, while a match between the predicted and experimental data would reinforce the idea that bioactive processes are the important factors acting to lower the effluent phenol concentration during a transient loading experiment.

In order to use this model, several variables describing the operating conditions were needed. The length and width of the column, flow rate, carbon particle radius (mean radius of 30 by 40 U.S. Standard Sieve Series after Fair et al., 1968), mass of carbon in the column, and apparent density of the carbon were all physical parameters associated with the column and carbon specifications. The film transfer coefficient was calculated using literature correlations to the flow conditions used in these experiments (Reid and Sherwood, 1966; Williamson et al., 1963). The value of surface diffusivity was determined by a best-fit analysis of two sets of adsorption kinetics data recorded at 150 and 10 mg/ℓ, respectively, using a method established in this laboratory (Thacker, 1980). The Freundlich isotherm constants from the appropriate isotherm (depending on pH; see Figure 3 and Figure 11) were also required. The condition of the carbon at the beginning of each experiment, as expressed as the equilibrium concentration of phenol which corresponds to the surface concentration present from pre-equilibration of the carbon with phenol, was calculated using mass

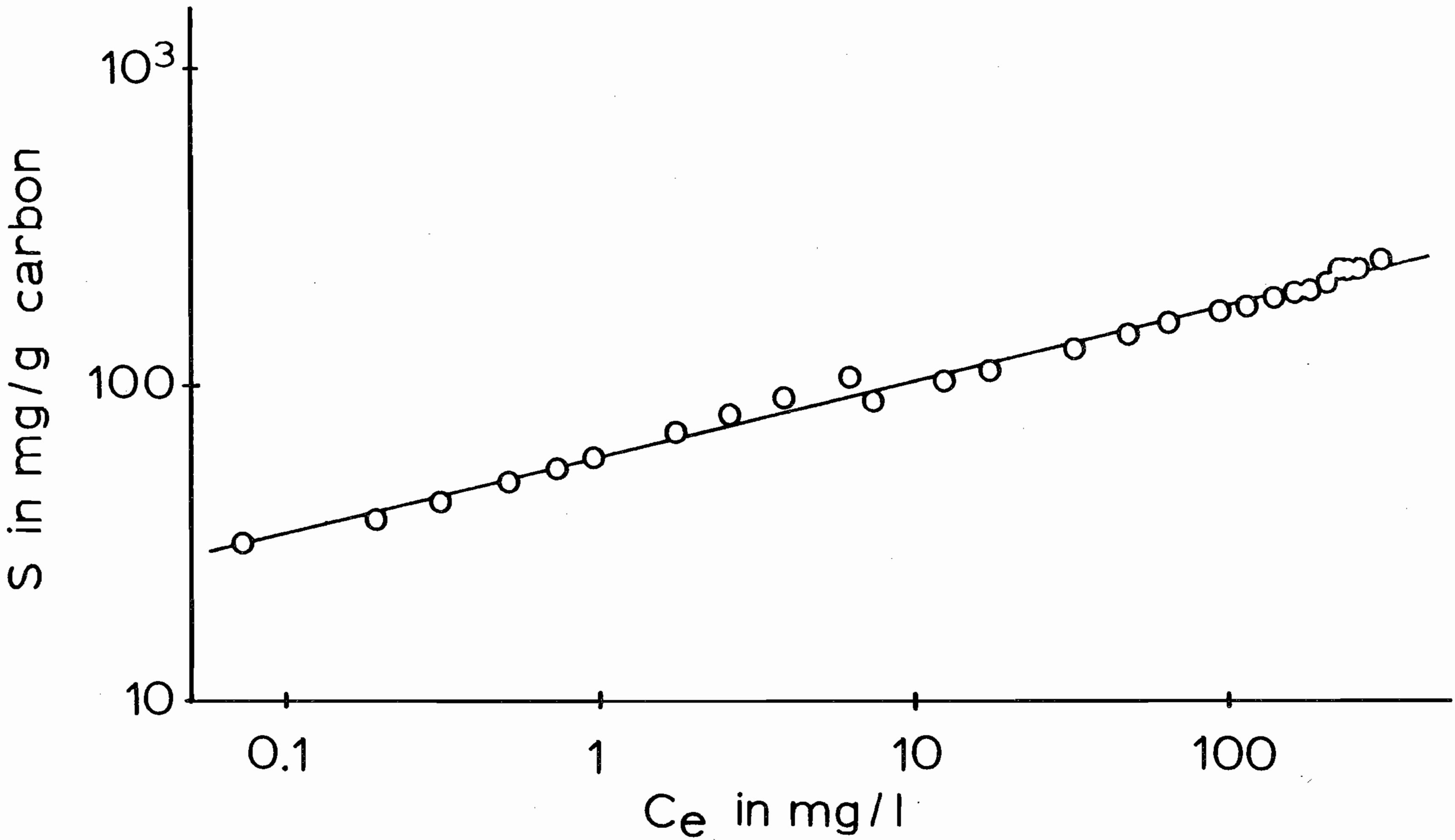


Figure 3. Freundlich Isotherm of Phenol on Filtrasorb 400 30 by 40, pH 7.5

balance considerations. The time and concentration profiles of the influent pulses were taken from laboratory data, since the influent pulses were similar but not identical in all cases.

Using the Freundlich isotherm obtained for phenol on the Filtrasorb 400 used in this study (see Figure 3), along with data collected during the transient loading experiments, the status of the carbon column at various times throughout the transient loading experiments was compared with the computer prediction. The results of these experiments are presented in section 5.

4.2.8 Carbon Extraction and Analysis

The carbon used in each column experiment was stored at 1°C after removal from the column. One gram aliquots of each batch of carbon were Soxhlet extracted for 48 hr with methylene chloride after wetting the carbon with methanol (where noted, an azeotrope of methylene chloride/methanol was used for extraction). Each extract was then concentrated to a volume of 2 mℓ in a Kuderna-Danish evaporator. The concentrate was methylated using diazomethane (Diazald, Aldrich) and further concentrated to 0.5 mℓ. The methylated concentrate was analyzed via gas chromatography (GC) and mass spectroscopy (MS) on an HP 5985 GC/MS system. The GC column was a 30 m WCOT SP2100 capillary column with a He gas flow rate of 1.5 mℓ/min. The column was temperature programmed as follows: initial temperature was 40°C and was held there for 5 min; the temperature was then increased at 4°/min up to 240°C (Supina, 1974; McNair and Bonelli, 1969). Splitless injection was used. Mass spectra were scanned starting 4 min after injection

in the range 35-500 amu.

Results were analyzed via use of the instrument's library search computer, by comparison with samples of known compounds (_trans_-muconic acid methyl ester was provided by Dr. R. Larson), comparison with known spectra, and by standard interpretation procedure (McLafferty, 1973).

5. RESULTS AND DISCUSSION

5.1 Design of Experimental System

There were three requirements of a system which would meet the objectives of this study. First, two columns in parallel, seeded and non-seeded, were needed to measure the effects of the presence of a bacterial population on a carbon column. In order to correctly perform such measurements, the non-seeded column must have remained sterile, or, alternatively, a small number of bacteria could be tolerated on the non-seeded column as long as it could be shown that this small population was not contributing to either phenol removal or dissolved oxygen use. This condition in the non-seeded column was required to remain in effect for periods of several weeks for each column experiment. Second, a flow rate and carbon mass were required which would allow changes in influent phenol levels to be observed in the effluent within a reasonable time. Third, the flow rate could also not be allowed to exceed the daily capacity for preparation of sterile influent. The details of this design were provided in an earlier section (see section 4.1.5).

5.2 Column Experiments

5.2.1 Variable Influent Dissolved Oxygen Experiments

Three levels of influent dissolved oxygen (DO) were chosen for this study: 4 mg/ℓ, 9 mg/ℓ, and 16 mg/ℓ. These three levels represent extremes typical of water treatment practice. In advanced

wastewater treatment, DO levels may often be below air saturation after biological treatment, so that a level of 4 mg/ℓ DO is not unusual. Air saturated water, typical of drinking water surface sources, would have a DO level of about 9 mg/ℓ. Increased oxygen concentrations are often used to enhance biological activity (as described in section 2.2.3), such that a 16 mg/ℓ DO could be the result in some cases of oxygenation or ozonation of the influent of an activated carbon column.

The results shown in the following figures are those typically obtained for two or more experiments performed under the same conditions. The influent and effluent DO and phenol levels were monitored for both the biologically seeded and the non-seeded columns in all three cases. Since oxygen is chemisorbed onto activated carbon (Prober et al., 1975), a breakthrough curve of DO on each column was to be expected.

The influent and effluent DO measurements for the 9 mg/ℓ influent DO experiment are presented in Figure 4. In the non-seeded column DO broke through after approximately 100 hr of operation. In the seeded column, the effluent DO originally was parallel to that of the non-seeded column. As the numbers of bacteria in the column increased, the effluent DO dropped below one mg/ℓ. The seeded column influent and effluent phenol measurements for the 9 mg/ℓ influent DO experiment are shown in Figure 5. The effluent phenol concentration dropped to zero mg/ℓ at approximately the same time that the effluent DO dropped below one mg/ℓ. This indicates that bacterial oxidation is removing the phenol which is entering the column, as well as any phenol which may have desorbed from the column due to equilibrium effects.

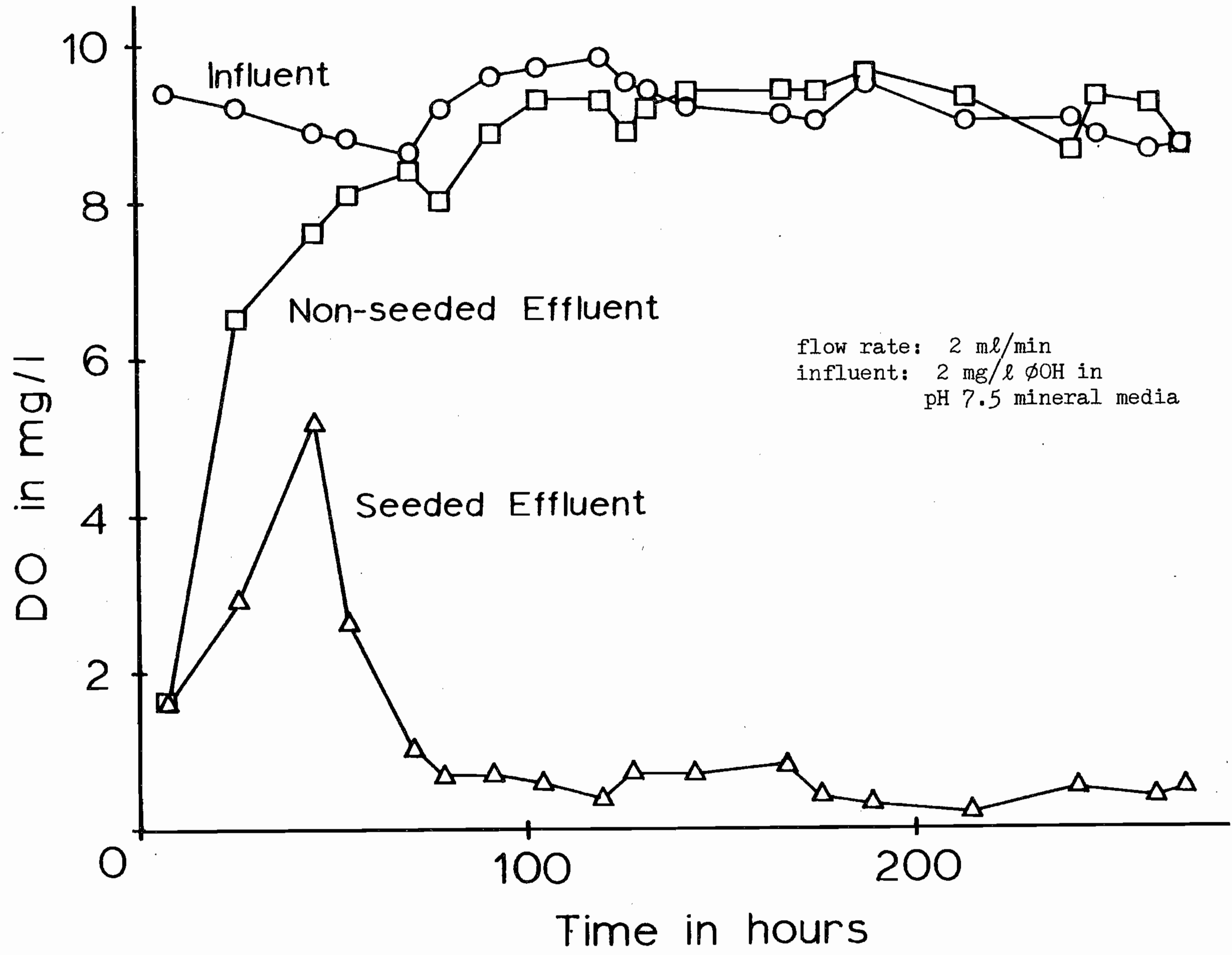


Figure 4. Dissolved Oxygen Data for the 9 mg/ℓ Experiment

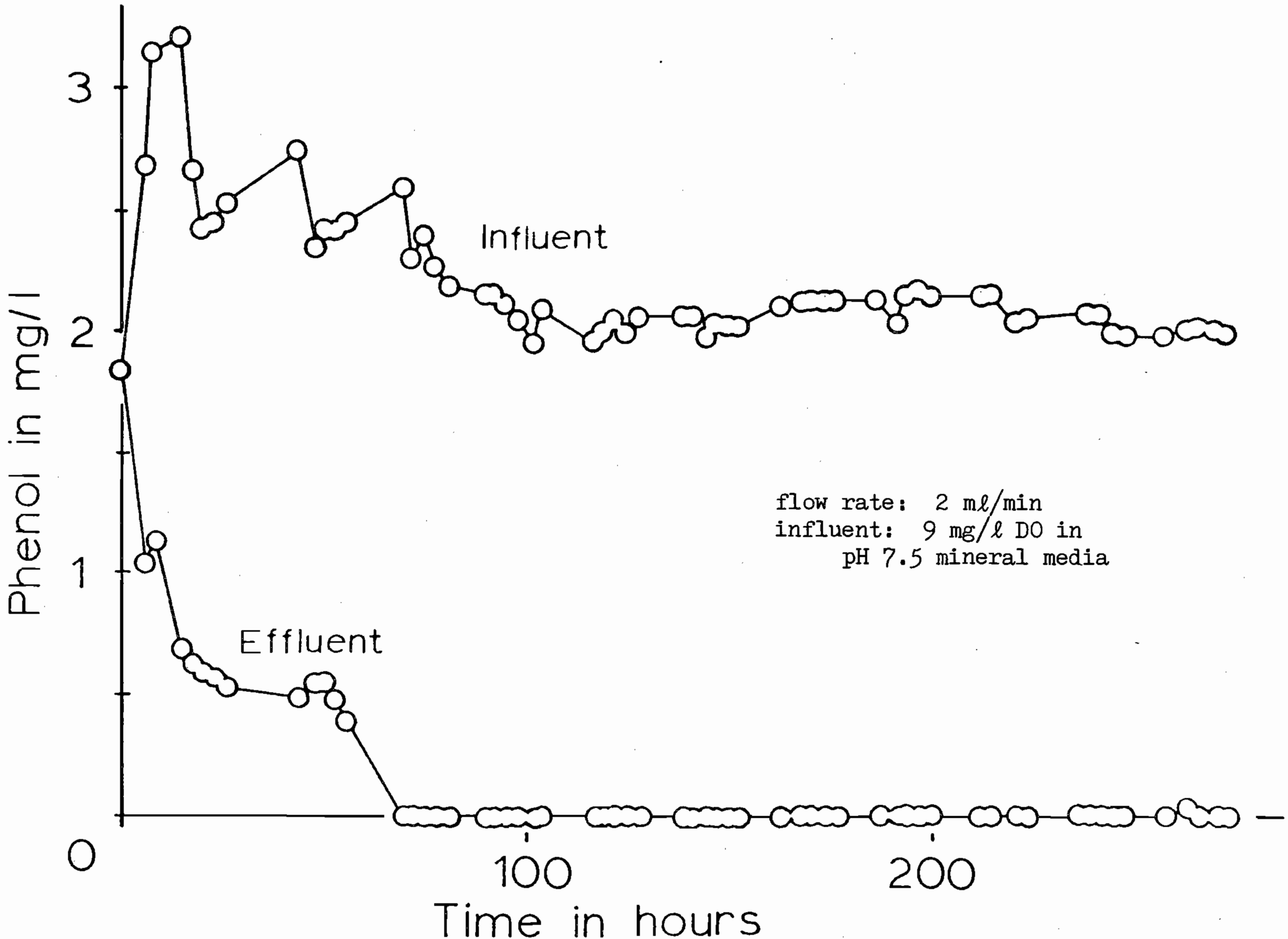
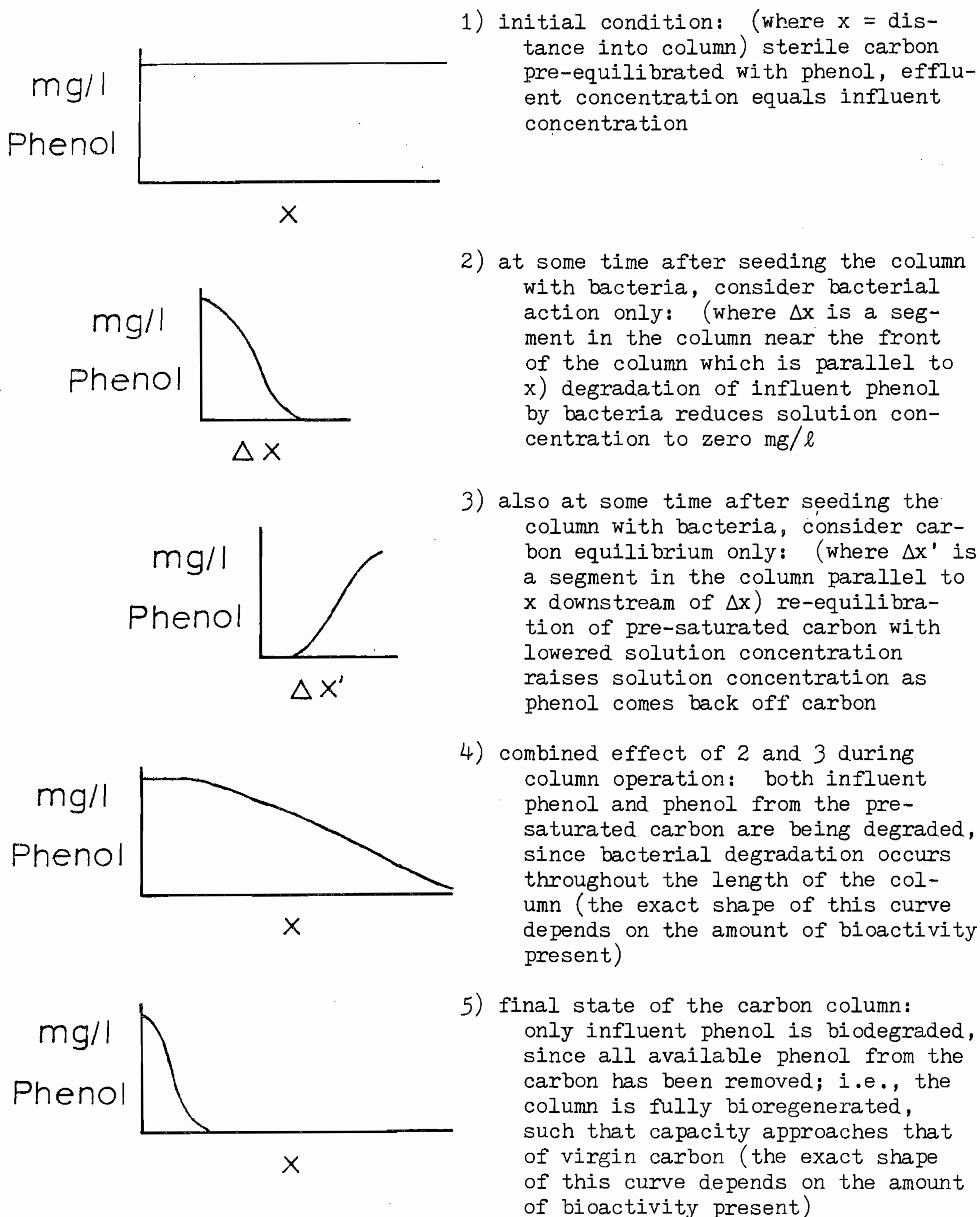


Figure 5. Phenol Data for the 9 mg/ℓ Experiment

The sequence of events in a typical column experiment is outlined in Figure 6. The observation that effluent phenol drops to and remains at zero mg/ℓ implies that microbial degradation of phenol is occurring throughout the entire length of the carbon column, until such time as the carbon is bioregenerated at the effluent end of the column. Bacterial activity is expected to remain constantly high at the influent end of the column where influent phenol and DO are available. As the bioregeneration of the column progresses from the effluent end to the influent end, the zone of bacterial activity in the column could also be expected to shrink towards the influent end of the column. This would continue until a final state is reached in which the column is fully bioregenerated and bacterial activity is confined to the influent section of the column. The effects of such shifts in zones of bacterial activity may have an effect on the number of bacteria in the effluent, but such an effect was not noted in the Standard Plate Count Test results as shown in Figure 7.

The influent and effleunt DO levels of the 4 mg/ℓ influent DO experiment are shown in Figure 8, while the influent and seeded column effluent phenol measurements are shown in Figure 9. The expected breakthrough curve of oxygen on carbon for the unseeded column is evident in Figure 8. From the pattern of the seeded 9 mg/ℓ influent DO column as shown in Figure 4, as well as the lower levels of bacterial numbers seen in the 4 mg/ℓ influent DO experiment compared to the 9 mg/ℓ influent DO experiment (see Figure 7), one might expect a higher curve for the seeded column effluent in Figure 8 than the observed pattern of rapid drop to near-zero effluent DO levels. However, the oxygen



1) initial condition: (where x = distance into column) sterile carbon pre-equilibrated with phenol, effluent concentration equals influent concentration

2) at some time after seeding the column with bacteria, consider bacterial action only: (where Δx is a segment in the column near the front of the column which is parallel to x) degradation of influent phenol by bacteria reduces solution concentration to zero mg/ℓ

3) also at some time after seeding the column with bacteria, consider carbon equilibrium only: (where Δx' is a segment in the column parallel to x downstream of Δx) re-equilibration of pre-saturated carbon with lowered solution concentration raises solution concentration as phenol comes back off carbon

4) combined effect of 2 and 3 during column operation: both influent phenol and phenol from the pre-saturated carbon are being degraded, since bacterial degradation occurs throughout the length of the column (the exact shape of this curve depends on the amount of bioactivity present)

5) final state of the carbon column: only influent phenol is biodegraded, since all available phenol from the carbon has been removed; i.e., the column is fully bioregenerated, such that capacity approaches that of virgin carbon (the exact shape of this curve depends on the amount of bioactivity present)

Figure 6. Sequence of Events in a Typical Column Experiment

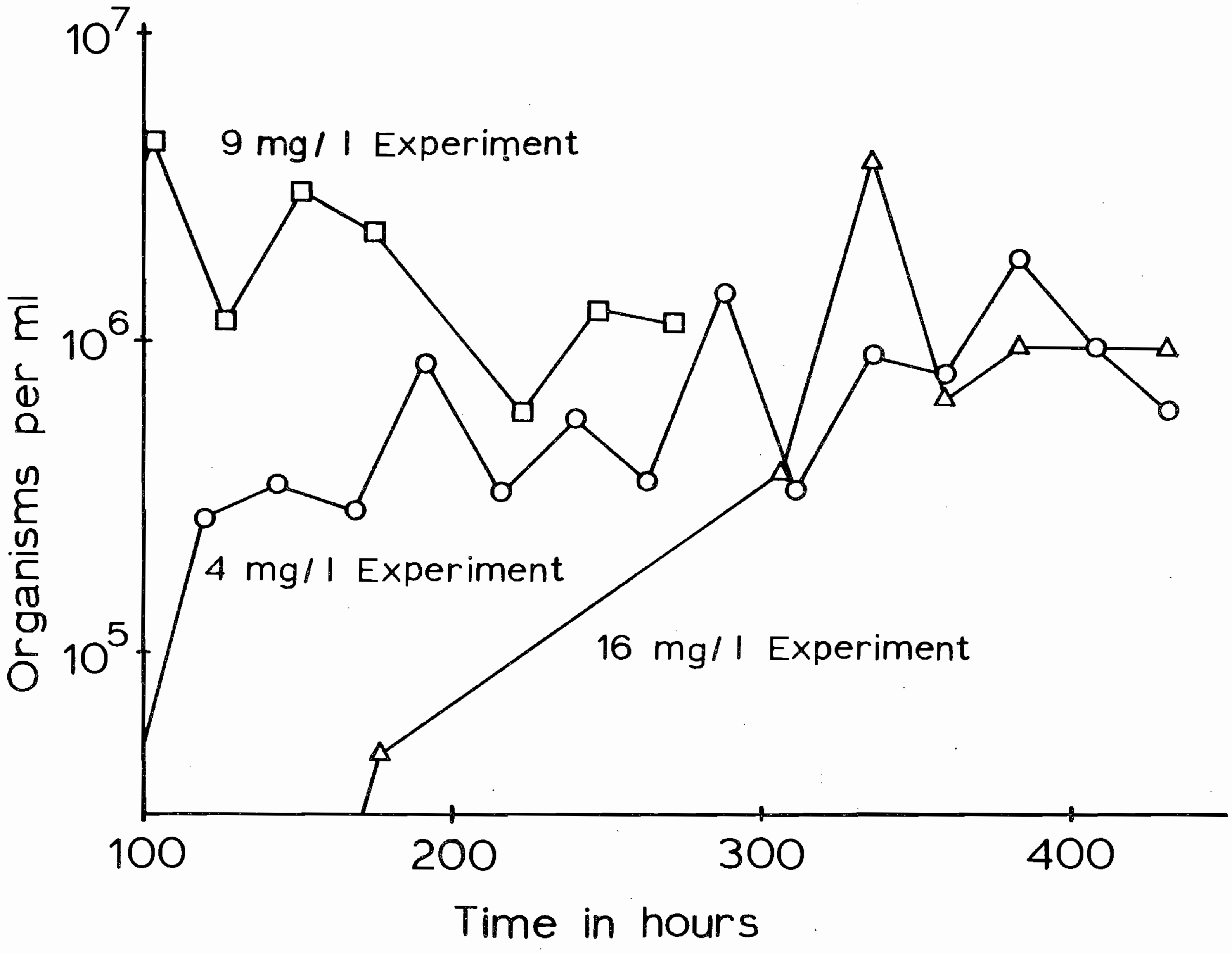


Figure 7. Effluent Standard Plate Counts

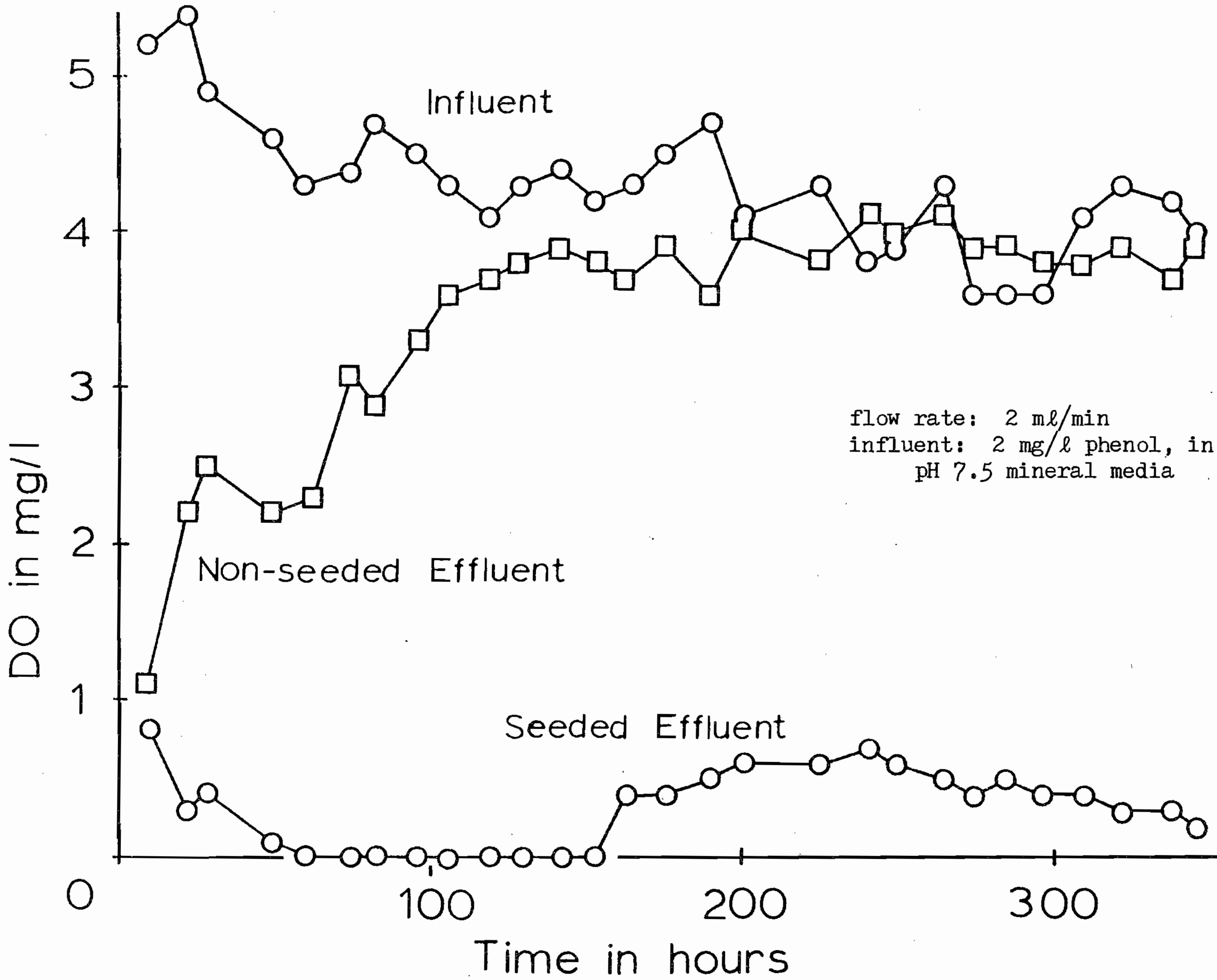


Figure 8. Dissolved Oxygen Data for the 4 mg/ℓ Experiment

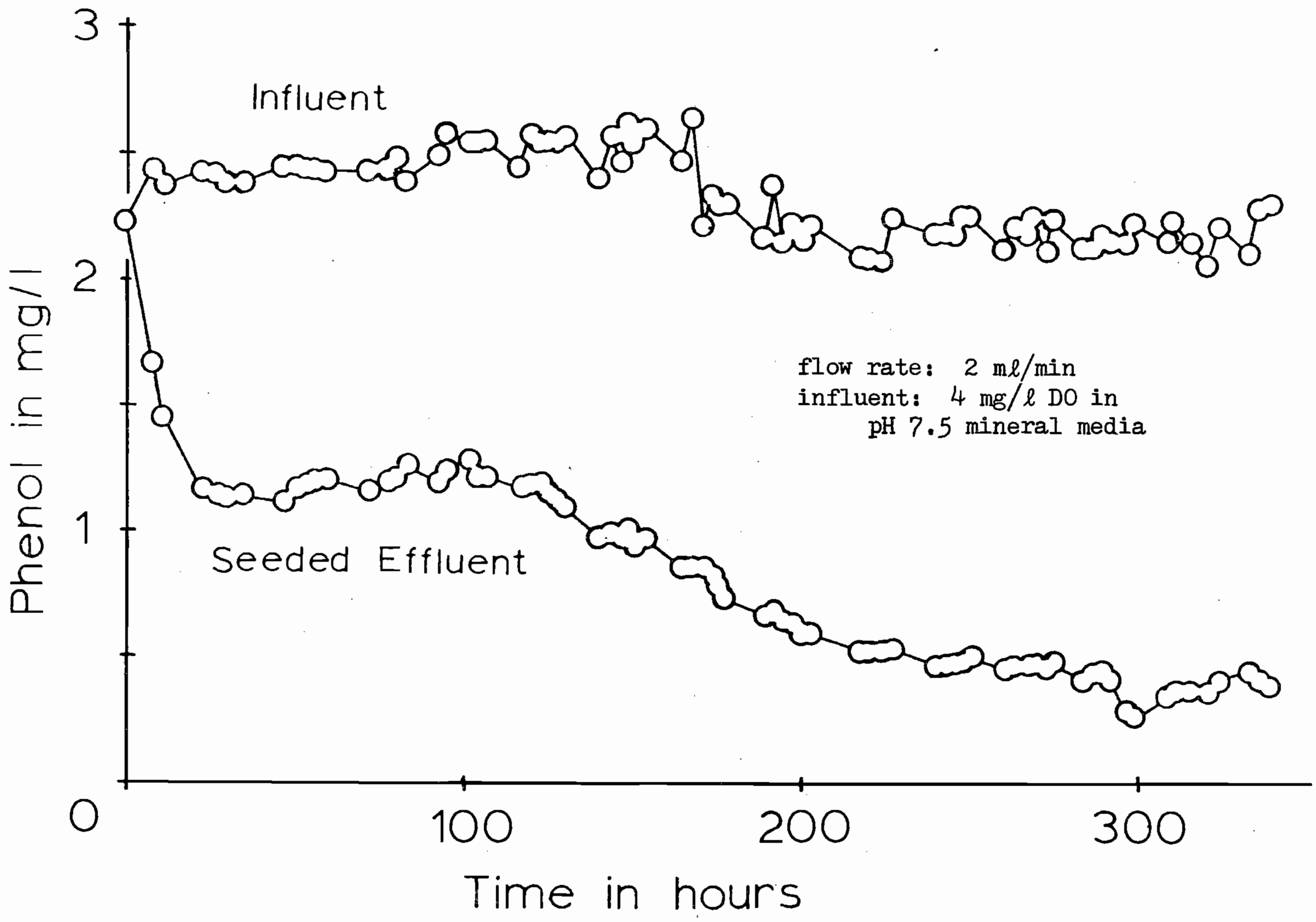


Figure 9. Phenol Data for the 4 mg/ℓ Experiment

available in the 4 mg/ℓ influent DO experiment is much lower than that available in the 9 mg/ℓ influent DO experiment. As shown in Figure 4, the amount of available DO in the period before about 50 hr is the difference between the Seeded Effluent and Non-seeded Effluent curves, i.e., between 2 and 3 mg/ℓ. The same amount of available DO use in the case of the 4 mg/ℓ influent DO experiment accounts for the rapid decrease in seeded effluent DO seen in Figure 8. There also may be effects due to differences in bacterial types on numbers during the early portions of these two experiments, but without further evidence, they are assumed to be minimal.

Figure 10 shows the influent and seeded effluent DO levels of the 16 mg/ℓ influent DO column. Since more influent DO was available the seeded effluent DO almost broke through by 100 hr. The non-seeded effluent DO, omitted from Figure 10 for purposes of clarity, reached breakthrough at about 100 hr in a manner similar to the patterns seen in Figures 4 and 8. As shown in Figure 7, the Standard Plate Count of the seeded effluent of the 16 mg/ℓ influent DO column, a first approximation of the population on the column, increased to levels approaching those levels seen in the other column experiments only after 100 hr. At the same time, as seen in Figure 10, the DO levels in the seeded effluent dropped to low levels after 150 hr, while Figure 11 shows that the seeded column effluent phenol levels dropped to between 0.25 and 0.10 mg/ℓ on their way to zero mg/ℓ at about 250 hr. Such performance indicates a much longer lag time for the 16 mg/ℓ influent DO experiment than was seen in the 4 mg/ℓ or 9 mg/ℓ influent DO experiments. There are two possible reasons for this, and both

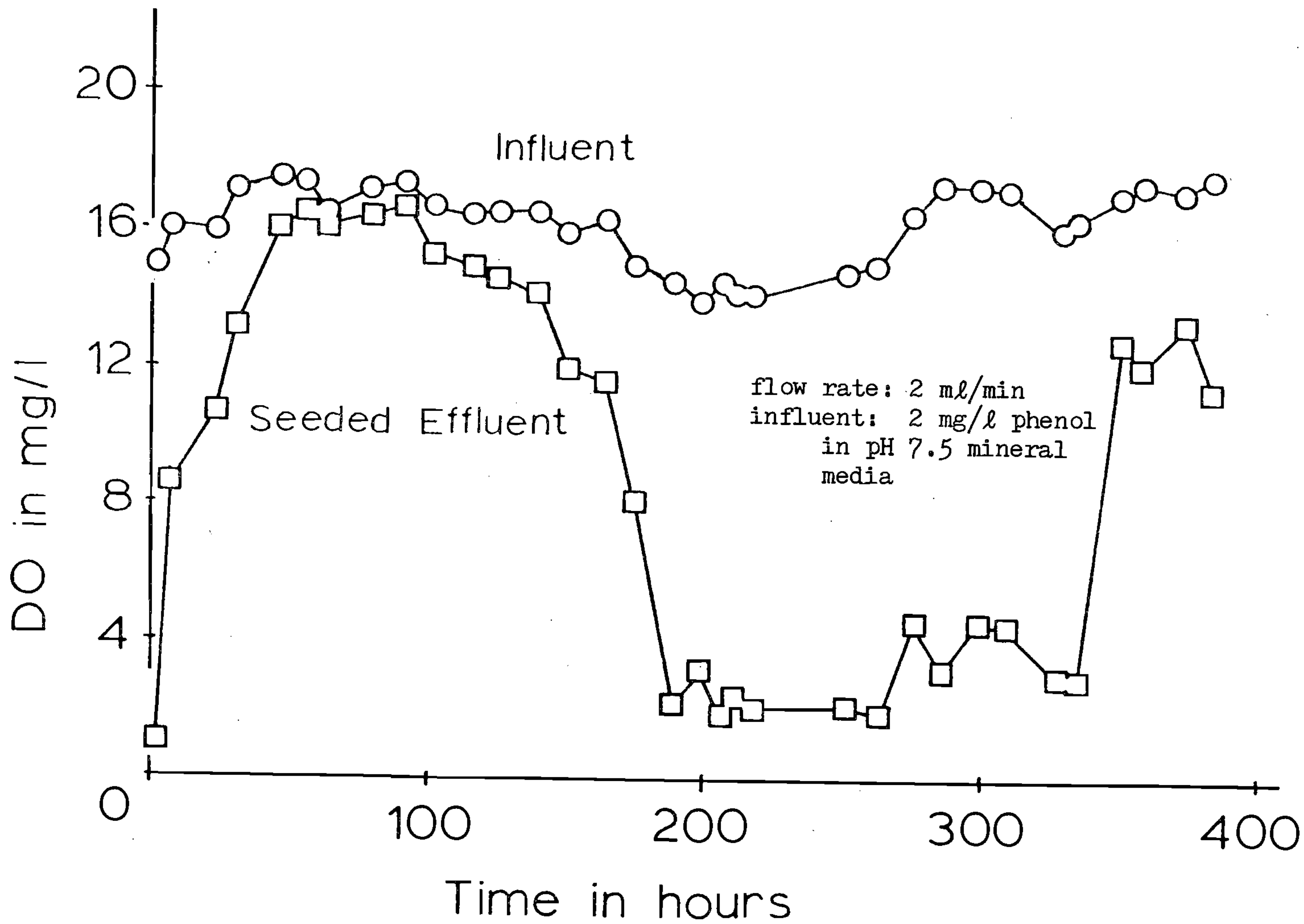


Figure 10. Dissolved Oxygen Data for the 16 mg/ℓ Experiment

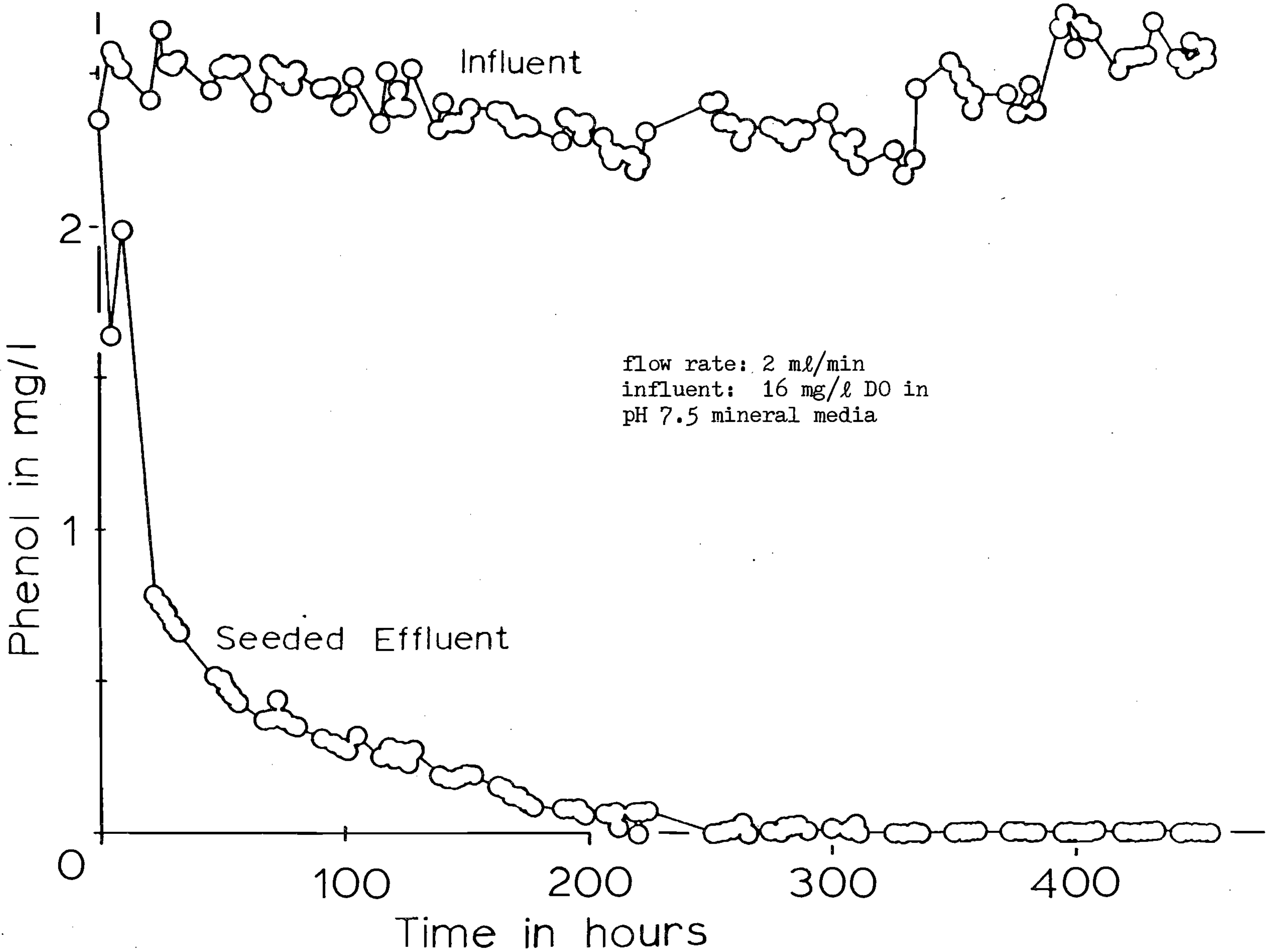


Figure 11. Phenol Data from the 16 mg/ℓ Experiment

mechanisms may be working at the same time. The first relevant difference between the 16 mg/ℓ influent DO experiment and the other two influent DO experiments was the time scale involved in the execution of each experiment. The same biological seed was used for each experiment, but the age of the seed at the time of use for the specific experiments depicted here as examples of typical results was as follows: for the 9 mg/ℓ influent DO experiment, 15 days; for the 4 mg/ℓ influent DO experiment, 70 days; and for the 16 mg/ℓ influent DO experiment, 99 days. If the viability of the bacterial seed diminished with time, so that there were actually fewer bacteria or bacteria of a different species distribution placed on the last carbon column than on earlier carbon columns, then an increase in the amount of time necessary for the bacteria to acclimate to the column would be expected.

Another factor which would delay acclimation of bacteria to growth in the 16 mg/ℓ influent DO experiment is that of oxygen toxicity. The enrichment from which the seed material was developed was performed at about 9 mg/ℓ DO. It is known that sudden increases in local oxygen tension can be toxic to certain types of bacteria (Kuenen et al., 1979), such that an increase from 9 to 16 mg/ℓ influent DO may have killed a significant proportion of the bacterial seed used in the 16 mg/ℓ influent DO experiment, resulting in an increased lag time as the remaining bacterial population adjusted to the new growth condition.

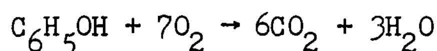
Once the population was established, as indicated by the combined evidence from the Standard Plate Counts, DO removals, and phenol removals, a period of high oxygen use was indicated by the pattern of DO removals seen in Figure 10. After a 150 hr period during which most

available influent DO was being used in the column, it can be seen that an effluent DO level about 4 mg/ℓ below that of the influent was then established. This pattern of DO removal suggests that both phenol from the influent and phenol which had been pre-adsorbed on the carbon were being biodegraded until such time as all available pre-adsorbed phenol was removed from the column. After this time only influent phenol was oxidized, reducing the amount of DO removal by the bacteria to that DO needed only to oxidize influent phenol. If after 340 hr most of the phenol available to bacteria in the column had been degraded, the amount of oxygen consumption would be expected to drop to a level which would be adequate for oxidation of the 2 mg/ℓ phenol influent.

The Standard Plate Count (SPC) results on the effluents of each column reflected the trends seen in DO measurements. The SPC results for the seeded column effluents can be seen in Figure 7 for the different influent DO experiments. Non-seeded column effluent SPCs were never above a few hundred organisms/mℓ, and were usually less than 100 organisms/mℓ. These numbers, along with the observation that no dissolved oxygen was being used in the non-seeded columns (e.g., see Figure 4, Non-seeded Effluent), led to the conclusion that there was no significant biodegradation occurring in the non-seeded columns. An adjustment period, during which time bacterial numbers were seen to increase to their steady-state values, was observed for all seeded columns. As could also be inferred form the DO data, this initial period took about 100 hr for the lower influent DO experiments, while it took about 200 hr for the 16 mg/ℓ influent DO experiment. In all three

cases a steady-state level between 10^5 and 10^6 SPC/mℓ was reached; these numbers are close to those seen in carbon bed effluents in water treatment (Cairo et al., 1979b).

The theoretical amount of biodegradation which occurred in each column can be calculated using a mass balance approach. Complete oxidation of phenol would follow the equation:



$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O$$

This equation can be used to calculate the amount of phenol being degraded at a given time. Bacterial oxidation may well stop short of the products CO_2 and H_2O (Ornston, 1971). Such oxidation would use less than seven molecules of oxygen per molecule of phenol, so that the amount of degradation calculated using the above relation must be stated as a minimum boundary value. This minimum boundary value can be used to get a number for the minimum amount of phenol degraded per mg/ℓ oxygen used. It is likely that more phenol was degraded than was calculated using the minimum value, but without more information, a more accurate value for amount of phenol biodegraded cannot be determined with confidence.

Using the molecular weight of phenol of 94.11 and that of oxygen of 31.9988, and using the oxidation equation above which assumes complete oxidation to CO_2 and H_2O, it can be seen that for each milligram per liter of oxygen which is used up, at least 94.11/(7[31.9988]) = 0.420 mg/ℓ phenol will be oxidized. In order to calculate the amount of pre-adsorbed phenol which is being removed from the carbon by the action of the bacteria, oxygen used to oxidize influent phenol must also be accounted for. Therefore, the equation expressing the minimum

amount of bioregeneration (M) which is occurring at a given instant is as follows:

$$M = 0.420(DO_{in} - DO_{out}) - (\phi OH_{in} - \phi OH_{out})$$

where all units are in milligrams per liter. This gives a number indicating the mg phenol being biodegraded per liter of throughput solution at a given time during a column experiment. Values of M were calculated for the three column experiments using different oxygen influents; these values are shown in Figure 12. Figure 12 indicates that for the 4 mg/ℓ oxygen influent experiment there was essentially no bioregeneration of the carbon, since virtually all available oxygen would be used up in oxidation of the 2 mg/ℓ phenol influent. The higher influent O_2 experiments showed bioregeneration amounts roughly proportional to the influent DO: for the 9 mg/ℓ influent DO, average M = 1.6 mg/ℓ phenol, while for the 16 mg/ℓ influent, average M = 3.0 mg/ℓ phenol.

In the 16 mg/ℓ influent DO experiment, Figure 12 shows that bioregeneration occurred for only a relatively short time, from 170 hr to about 340 hr, indicating that the period of low O_2 uptake after 340 hr seen in Figure 10 was due to the bacterial population's adjustment to a state in which they were only oxidizing the influent phenol. This would suggest that virtually all pre-adsorbed phenol which was available to the bacteria on the carbon had been oxidized. The amount of phenol which was pre-adsorbed on the carbon can be calculated using the isotherm determined for phenol on this activated carbon as presented in Figure 3. Using this isotherm, a surface concentration of 72.3 mg/g carbon corresponds to the initial equilibrium concentration of

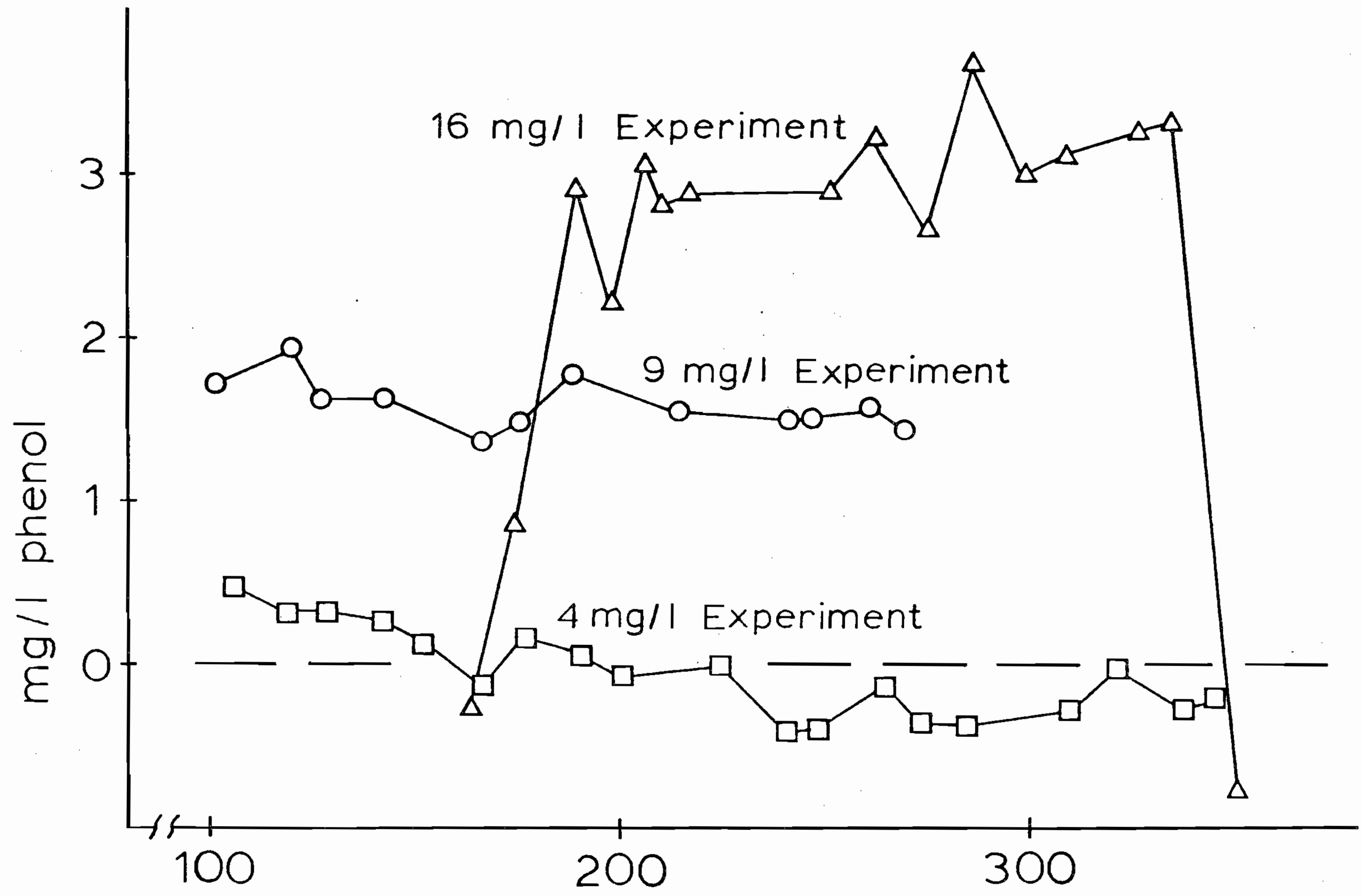


Figure 12. Minimum Milligrams per Liter Phenol Bioregenerated versus Time

2.35 mg/ℓ recorded at the start of the 16 mg/ℓ influent DO experiment. Since 10 g carbon were used in each of these experiments, 723 mg phenol was adsorbed on the carbon in this column. Summation of the area under the curve in Figure 12 corresponding to the 16 mg/ℓ influent DO experiment yields a minimum amount of phenol bioregenerated as 58.6 mg phenol. There are several possible reasons for this discrepancy between the calculated surface concentration of phenol and the calculated amount of phenol able to be removed by biodegradation. First, the amount of phenol removed by degradation was calculated as a minimum amount based on complete oxidation of phenol to CO_2 and H_2O. Since this is a minimum boundary value, the actual amount of phenol removed could have been higher if incomplete oxidation of phenol occurred. If only one molecule of oxygen was used per molecule of phenol oxidized, for example, then the amount of phenol bioregenerated could be calculated to be 807 mg phenol. This is done by using the same data as the previous calculation of M value for the 16 mg/ℓ influent DO experiment, after revising the equation used to calculate the value of M to account for using only one molecule of O_2 instead of seven per molecule of phenol biodegraded, and summing the area under the new "M" versus time curve generated.

If indeed only one molecule of oxygen were used per molecule of phenol biodegraded, a mixture of the products catechol, cis,cis-muconic acid, and/or 2-hydroxymuconic acid would be expected to be found in the column effluent or on the carbon itself. The low levels of TOC found in the column effluent (see section 5.3.1) compared to the amount of TOC entering the column as phenol (2 mg/ℓ phenol equals

1.6 mg/ℓ as TOC) suggest that if all of the phenol is being oxidized by an average of one molecule oxygen per molecule phenol, then the resulting oxidation products are not in the column effluent in the quantities expected from such oxidation. If such oxidation products were adsorbed onto the carbon, it was expected that analysis of the carbon extracts via gas chromatography/mass spectroscopy (GC/MS) would show the presence of such compounds. As discussed in section 5.3.2, GC/MS did not reveal the presence of any known biodegradation products of phenol. Similar reasoning applies to the other possible levels of oxidation of phenol, and the evidence from effluent and carbon extract analysis suggests that few if any oxidation intermediate products were made.

Phenol used by the microorganisms for cell synthesis would not be oxidized completely to CO_2 and H_2O, so it would not require much oxygen for removal. The products formed would be other than those expected from phenol degradation since the bacteria would be converting the phenol into cell mass. This would make tracing of the fate of this phenol difficult using the methods outlined in this study. Since the amount of cell mass produced was very small (see section 5.3.1), phenol lost to cell mass is considered to be negligible.

Another important consideration in evaluation of these data is that the carbon used in the column experiments may not have reached equilibrium during the pre-loading of phenol sequence before each of these experiments. The pitfalls associated with non-attainment of equilibrium in studies using phenol and activated carbon have recently been discussed (Peel and Benedek, 1980). If equilibrium was not

reached during pre-equilibration of the carbon with phenol, the remaining available capacity of the carbon for phenol would be reflected in an artificially higher apparent amount of biodegradation of the phenol as measured by mass balances on the carbon column.

The sequence of events during typical column operation, as outlined in Figure 6, indicated that if a biologically active column is operated long enough, a state will be reached in which activity is limited to the influent end of the column, with the rest of the column fully bioregenerated. The progression from step 4 to step 5 in Figure 6 may be a gradual one, with the zone of biological activity slowly being moved up the column from the effluent end to the influent end; the exact rate of the process, the distribution of phenol concentrations in the column, and the distribution of the bacterial numbers in the column may depend on column conditions. Regardless of the rate of such a process, one factor is common to all such processes: the observation that effluent phenol is zero indicates that the column is in transition between steps 4 and 5 and may be approaching the status of step 5. In such a state, bioactivity is not distributed uniformly along the column length, since the effluent end must be fully bioregenerated, or a non-zero phenol effluent would be observed. This would mean that at the end of these experiments, when isotherm analysis was performed, some of the carbon in the column was bioregenerated more than the rest. Since the carbon from each column was uniformly mixed during the process of unpacking each column, results of analysis both by the isotherms in this section and the extracts in section 5.3.2 are the average of characteristics over the entire length of the column. The

final consideration affecting bioregeneration amounts is the phenomenon of hysteresis. If phenol is not reversibly adsorbed to carbon, or in some manner becomes unavailable to microorganisms once it is adsorbed, a certain amount of the phenol will remain on the carbon even though bioregeneration is complete. Further investigation is required to determine if any or all of these considerations are important in affecting observed amounts of bioregeneration versus known carbon capacity.

If the oxygen uptake seen in these column experiments was due to bioregeneration of the carbon via oxidation of pre-adsorbed phenol, the capacity of the carbon for more phenol would have been changed by such bioregeneration. A check for biodegradation therefore requires a means of measuring changes in the capacity of the carbon which may have occurred during a given column experiment, such as Freundlich isotherms on the carbon used both before and after each experiment. The batches of carbon which had been pre-equilibrated with phenol (as described in section 4.1.4) were stored at 1°C until use. The carbon in each batch in excess of that required for column use was returned to storage until needed for further tests. Since slightly different values of equilibrium concentration were obtained for each batch, the excess carbon from batches corresponding to each column run were stored in their original equilibrium bottles in order to preserve the integrity of each batch used for each different column experiment. Once a column experiment was ended, there were then two subcategories of carbon resulting from the original batch of carbon used to pack the column: one was the original carbon which had been stored, and the other was the carbon which had been used in the column. Freundlich

isotherms were determined on each of these two subcategories of carbon for each of the three varied influent DO experiments. These isotherms should be described as apparent Freundlich isotherms for two reasons. First, this determination did not account for phenol which had been pre-adsorbed on the carbon. Second, no checks were made on whether or not equilibrium had been attained during the two weeks allowed for this isotherm determination. Without such checks, assumption of equilibrium of phenol adsorption in 30 by 40 mesh size carbon during such a short time period is questionable (Peel and Benedek, 1980). In addition, the presence of substances on carbon, such as end products, which result from column use may be inhibiting adsorption of phenol in each of the "After" cases. This would indicate a capacity for phenol which would be lower than that expected in the absence of such interference and would therefore lower the values calculated from these isotherms for amounts of bioregeneration. Since the carbon used in each column was compared only with carbon from the same original pre-equilibrium batch, only effects on the carbon capacity due to carbon column operation would be able to be observed. In this manner the presence or absence of any biodegradation which occurred during a column experiment could be demonstrated. If the pre-equilibrium step had not been complete (i.e., true equilibrium had not been reached), additional available capacity would affect the isotherm results in the same manner for both the "Before" and "After" subcategories of carbon tested from each experiment. Therefore, comparison of these apparent isotherms was a means of determining whether or not biodegradation took place during a given column experiment.

Figure 13 shows the isotherm results for the 4 mg/ℓ influent DO experiment. There was little or no change in the carbon's capacity for phenol. This reinforces the estimate of zero biodegradation seen for this experiment in Figure 12. Figure 14 shows the isotherm results for the 9 mg/ℓ influent DO experiment. The phenol capacity increased after the column experiment, a result reinforcing the fact that bioregeneration was calculated from mass balances as occurring in this column experiment. Figure 15 shows the isotherm results for the 16 mg/ℓ influent DO experiment along with the isotherm curve for virgin carbon (no phenol pre-adsorbed). The capacity of the carbon used in this column experiment was increased to an amount where the isotherm appears to be closer to the isotherm for virgin carbon than to the isotherm for the same carbon used in the column in its initial condition. The trend established by these sets of isotherms is that of increasing amounts of biodegradation resulting from increased influent DO levels. Since the isotherms presented in Figures 13, 14, and 15 were not necessarily at equilibrium, use of these curves for calculations of amounts of regeneration versus different influent DO conditions must be treated with caution. It would not be proper to use these curves in calculating absolute amounts of regeneration; rather, comparative amounts of regeneration seen as a result of determining this series of isotherms in parallel can be used to demonstrate the trends established in these experiments.

It should be pointed out that the isotherms labeled as "Before" lines in Figures 13, 14, and 15 may be misleading due to the manner in which they are presented. As is typical of Freundlich isotherm

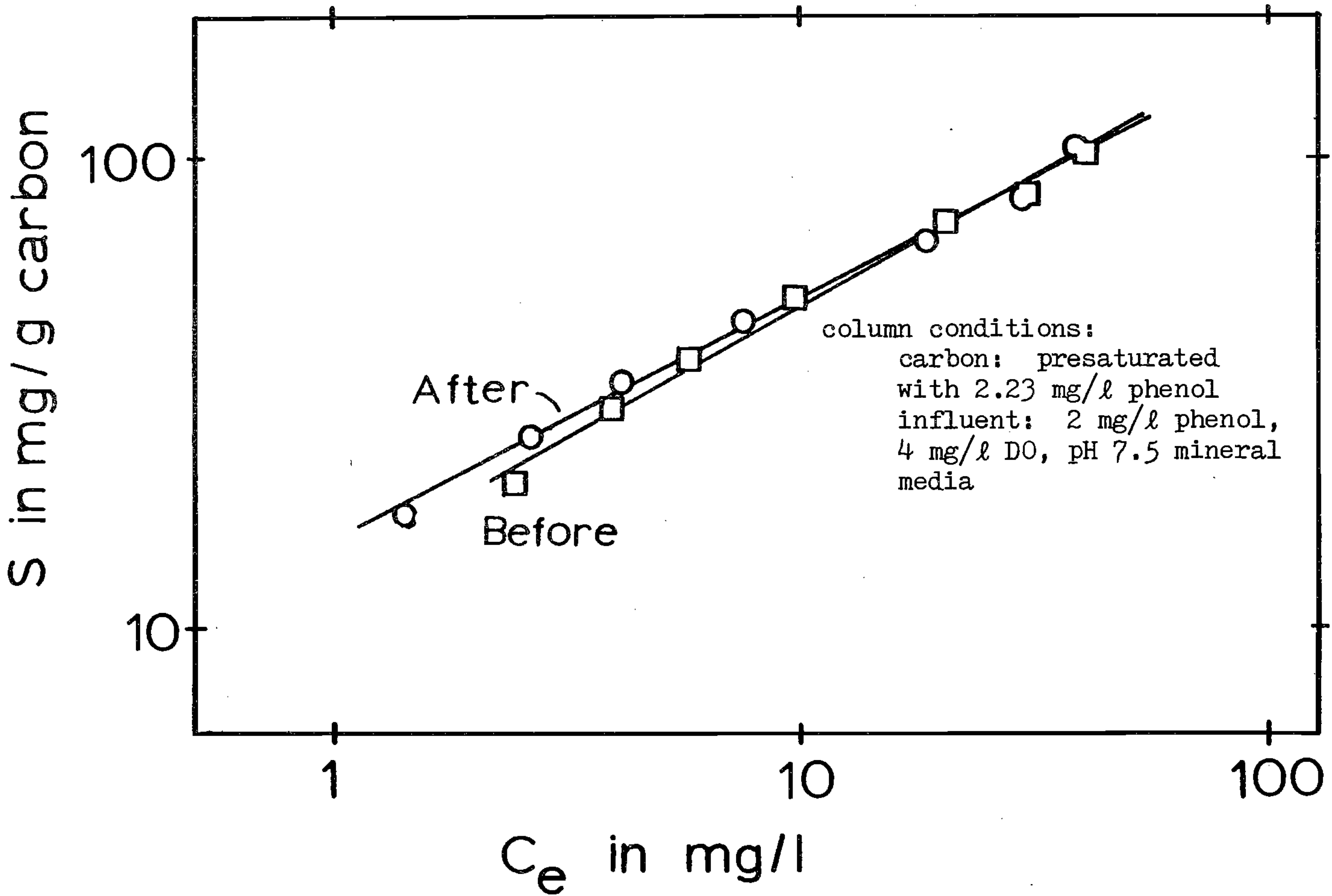


Figure 13. Freundlich Isotherm for the Carbon Batch Used in the 4 mg/ℓ Influent DO Experiment

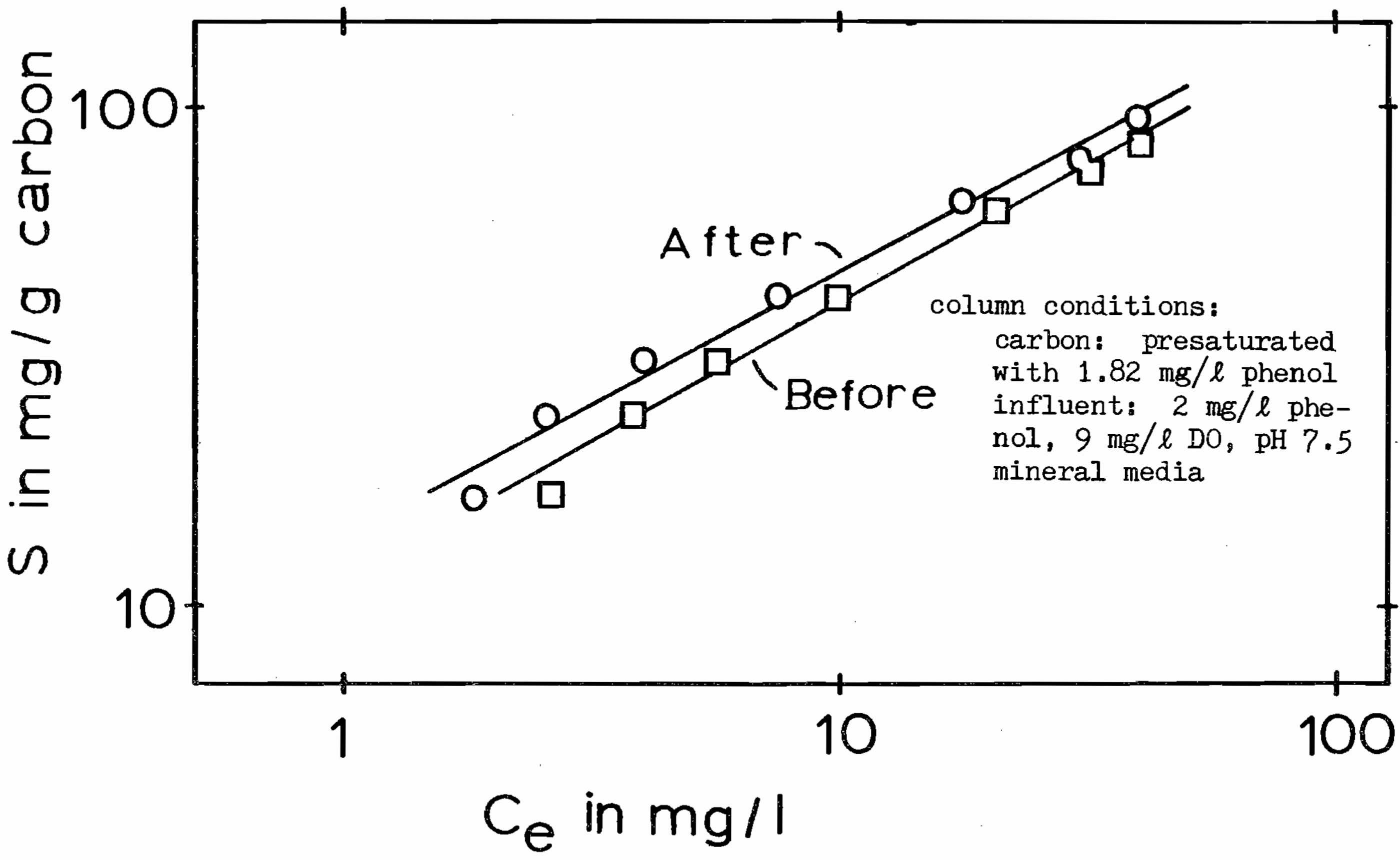


Figure 14. Freundlich Isotherm for the Carbon Batch Used in the 9 mg/ℓ Influent DO Experiment

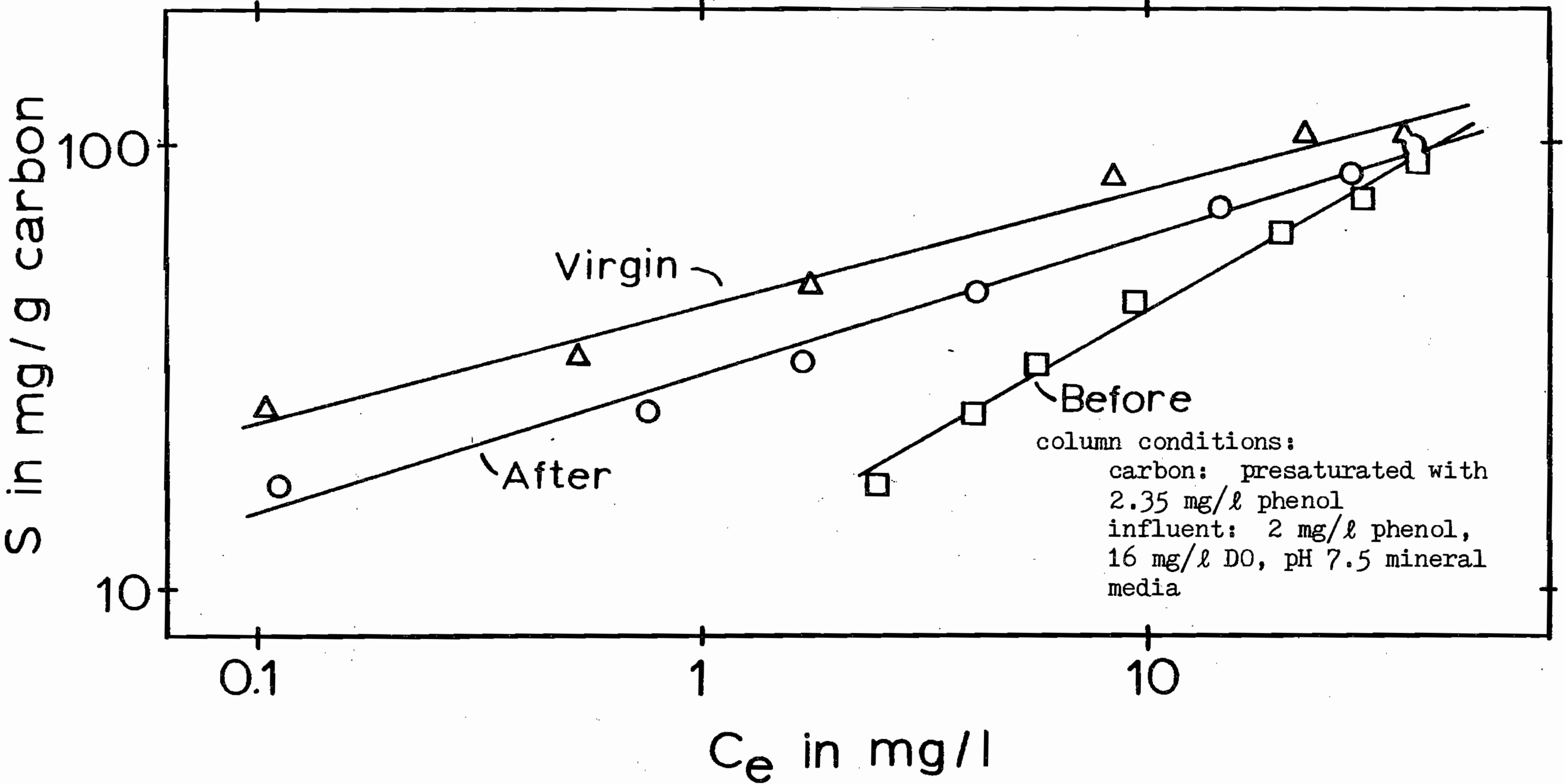


Figure 15. Freundlich Isotherm for the Carbon Batch Used in the 16 mg/ℓ Influent DO Experiment

depictions (Chudyk et al., 1979; Herzing et al., 1977), the data points obtained were overlaid by a linear least squares line generated by equal weighting of each appropriate data point. Since the carbon was pre-saturated with about 2 mg/ℓ phenol in these experiments, there should not be any capacity for phenol at or below a C_e value equal to the pre-saturation concentration. In each of the three cases there are no data points at or below the corresponding pre-saturation concentration. Extrapolation of the "Before" lines beyond the lowest data point measured would indicate capacity existing where there should be none, i.e., at or below C_e values equal to the pre-saturation condition; therefore, such extrapolation should not be performed.

A typical isotherm data point calculation is performed as follows. Known quantities are the amount of carbon in a given sample bottle, the final phenol concentration in that bottle, and an initial phenol concentration as determined by measuring the phenol concentration in a sample bottle, subjected to the same treatment as all other sample bottles, which contained no carbon (blank). All of the data points are then the result of a C_e value which is the concentration in solution as measured for each bottle, and an S value which is calculated from the difference between the C_e value for a particular bottle and the blank C_e value, divided by the amount of carbon in the bottle. At high values of C_e, the determination of S values is subject to error from two sources: the amount of phenol present is found as the small difference between the relatively large numbers corresponding to the C_e values of the sample and the blank, while the amount of carbon present is determined by weighing an amount of carbon which is small enough to be near

the limits of accuracy of a laboratory balance. These two sources of error tend to increase the uncertainty of the data points corresponding to higher C_e values, with greatest error associated with the highest C_e value on each graph. Consideration of this observation with the isotherms shown in Figures 13, 14, and 15 leaves open to question whether the data points shown for the "Before" lines actually would be better depicted as following a curve which asymptotically approaches the carbon presaturation C_e value.

The amount of regeneration of the carbon which occurred during each experiment was calculated from the isotherms shown in Figures 13, 14, and 15. After an equilibrium concentration (C_e) was selected, the difference between the "Before" and "After" values of surface concentration (S) was compared with the difference between the "Before" values and the "Virgin" value from Figure 15. The difference in S values between the "Before" values and that for virgin carbon is due to capacity occupied by the phenol which was pre-adsorbed on the carbon. If all of the pre-adsorbed phenol were removed, then this capacity would become available. This S value is then the maximum amount of bioregeneration possible. The difference in S values between the "Before" values and the "After" values is due to increased capacity as a result of bioregeneration of the carbon during each corresponding experiment. A value for "per cent bioregeneration" was calculated for C_e values of 5 and 10 mg/ℓ for each column experiment by dividing this second S value by the S value calculated using the virgin carbon isotherm and multiplying by 100% (see Table 2). The relative values of "per cent bioregeneration" calculated can be compared with the relative

Table 2

Increase in Capacity of Carbons Used in Column Experiments*

at C_e mg/ℓ	Influent O_2 mg/ℓ	ΔS mg/g C	ΔS' mg/g C	% Bioregenerated
5	4	2.7	33.1	8
	9	4.6	38.3	12
	16	22.1	37.7	59
10	4	1.8	30.8	6
	9	5.9	38.2	15
	16	20.3	37.1	55

*Calculated using the isotherms shown in Figures 13, 14, and 15; after selecting a C_e value, the difference between S values on the "After" and "Before" curves was measured on the appropriate isotherm (ΔS sbove). The difference between the S values on the "Before" curve and the S value on the "Virgin" curve for the same C_e was then measured (ΔS' above); ΔS was then divided by ΔS' to obtain % Bioregenerated.

amounts of bioregeneration found in each experiment illustrated in Figure 12. The trend established by this calculation parallels the trend shown in Figure 12, i.e., increasing amounts of bioregeneration result from increasing levels of influent DO. Drawbacks in using the actual amounts calculated can be illustrated by considering the 4 mg/ℓ influent DO experiment results: analysis of the M values calculated for this experiment presented in Figure 12 indicate that the amount of bioregeneration was negative or at best zero, while calculations using the corresponding isotherms, results of which are presented in Table 2, indicate that the column was 5-8% bioregenerated. If the carbon was not at equilibrium during pre-saturation, additional adsorption could have taken place; this may be the cause of this apparent bioregeneration.

Although some uncertainties exist in the amounts of bioregeneration which occurred under the various influent DO conditions, the trend established in each set of calculations is clear: higher influent DO levels resulted in higher amounts of bioregeneration. The implications of this observation are the following: bioregeneration can occur during the operation of a carbon column containing bacterial growth; the amount of bioregeneration depends on the influent DO, all other factors being equal; and, further work is necessary to determine the influence of these other factors as well as more precise determination of DO effects on bioregeneration amounts in order to apply these results to actual treatment.

A rate of biodegradation can be calculated for the varied influent DO experiments and compared to the literature. Degradation rates achieved in pilot studies have been reported to be in the range of

1-4 g TOC per m^3 carbon per hr (Eberhardt, 1976). Using mass balance, a rate in units of g ϕOH/$m^3 \cdot$hr can be found for the varied influent DO experiments:

$$\text{biodegradation rate} = \frac{\text{g } \phi\text{OH}}{\text{m}^3 \text{ carbon} \cdot \text{hr}} = \frac{\text{g } \phi\text{OH}}{\text{m}^3 \text{ solution}} \times \frac{\text{flow rate m}^3/\text{hr}}{\text{bed volume m}^3}$$

$$= \frac{\text{g } \phi\text{OH}}{\text{m}^3 \text{ solution}} \times \frac{\text{approach velocity m/hr}}{\text{bed depth m}}$$

The amount of phenol removed in mg/ℓ throughput solution is the same as g/m^3 throughput solution. The approach velocity in the carbon was calculated in section 4.2.5 to be 0.19 mm/sec which equals 0.68 m/hr. The length of the column used was 1.61×10^{-1} m. These terms can be combined to give:

$$\text{biodegradation rate} = 2 \text{ g/m}^3 \times \frac{0.68 \text{ m/hr}}{1.61 \times 10^{-1} \text{ m}}$$

$$= 8.45 \text{ g } \phi\text{OH/m}^3 \text{ carbon} \cdot \text{hr} \times \frac{1.6 \text{ g TOC}}{2 \text{ g } \phi\text{OH}}$$

$$= 6.7 \text{ g TOC/m}^3 \text{ carbon} \cdot \text{hr}$$

Since this rate measures only removal of influent phenol, but not bioregeneration, all three varied influent DO columns reached approximately the same rate described by this equation, since in all three cases a situation was reached in which most or all of the influent phenol was being removed, as shown in Figures 5, 9, and 11. Specifically, the 9 and 16 mg/ℓ influent DO experiments reached the same state in which all influent phenol was being removed, while the 4 mg/ℓ influent DO experiment reached a state in which all but 0.4 mg/ℓ of the influent phenol was being removed, which would give a biodegradation rate of

6.76 g $\phi OH/m^3$ carbon·hr. It is clear that this equation shows a difference in performance between the 4 mg/ℓ influent DO column and the other two different influent DO column experiments, but since bioregeneration is not included, this equation is not adequate to describe the differences in performance between the 9 mg/ℓ and 16 mg/ℓ influent DO experiments. In order to more closely describe the actual biodegradation rates which are applicable to these column experiments, a means to account for biodegradation of the phenol which had been pre-adsorbed on the column must be included in any rate determination. For the varied oxygen influent DO experiments, the values of M calculated in section 5.2.1 were good first approximations to use in estimating the amounts of phenol removed from the carbon by bioregeneration. In order to calculate total biodegradation rates, however, the influent phenol removed must also be accounted for since that is also apparently being degraded. The exact nature of the oxidation products of phenol in this system is not known, so that calculations using a given number of oxygen molecules per molecule of phenol degraded must be considered as approximations. Calculations which would yield results reflecting the contributions of both influent phenol and pre-adsorbed phenol biodegradation must be based directly on the amount of oxygen consumed in the column by the bacterial population. Once the oxygen breakthrough curve was complete, the main use of oxygen in the carbon column was for phenol oxidation. Therefore, a biodegradation rate based on oxygen consumption is most applicable in comparing performances of carbon columns under the conditions used in this study. Some caution is advised, however, in using such a rate determination for other data, since this method assumes

that oxygen use due to oxidation of ammonia and endogenous respiration is negligible. In the column experiments described here, ammonia oxidation was measured by testing ammonia concentrations of the columns' influent and effluent via the Phenate Method (American Public Health Association, 1975). There was always less than 1% difference between the values for the influent and effluent, which could account for a maximum of 0.1 mg/ℓ dissolved oxygen used in a given column. Because of the small amount of microbial mass in the column effluent (see section 5.3.1), endogenous respiration was also considered to be negligible.

The biodegradation rate based on oxygen consumption was calculated in a manner similar to the method used to calculate biodegradation rates based on phenol consumption, with the assumption used earlier in section 5.2.1 to calculate bioregeneration amounts, i.e.,

$$\frac{\text{bioregeneration rate in g } \phi\text{OH}}{\text{m}^3 \text{ carbon}\cdot\text{hr}} = \frac{\Delta \text{ g } O_2}{\text{m}^3 \text{ solution}} \times \frac{\text{approach velocity m/hr}}{\text{bed length m}} \times \frac{0.42 \text{ mg}/\ell\ \phi\text{OH}}{\text{mg}/\ell\ O_2}$$

where Δ g O_2/m^3 solution was the influent minus effluent DO levels. In the case of the varied influent DO experiments, these values were calculated at different times during each experiment. These rates are listed in Table 3. These rates follow the same trend established by the calculation of M in section 5.2.1 and presented in Figure 12. As in the case of Figure 12, the rate calculations in Table 3 indicate that the lowest rate of biodegradation occurred in the 4 mg/ℓ influent DO experiment, with increasing rates seen in the 9 mg/ℓ and 16 mg/ℓ influent DO experiments. In the 16 mg/ℓ influent DO experiment, the

Table 3

Biodegradation Rates in the Varied Oxygen Influent Experiments

Oxygen Influent mg/ℓ	Time hr	Rate* g ØOH/m^3 carbon·hr
4	100	6.12
	300	6.03
9	100	16.1
	200	16.3
16	100	2.48
	200	18.9
	350	7.45

*based on the equation:

$$\text{rate} = \frac{\Delta \text{ g } O_2}{m^3 \text{ solution}} \times \frac{\text{approach velocity m/hr}}{\text{bed length m}} \times \frac{\text{g/}\ell\ \text{ØOH degraded}}{\text{g/}\ell\ O_2 \text{ used}}$$

$$\text{rate} = \frac{\Delta \text{ g } O_2}{m^3 \text{ solution}} \times \frac{0.68 \text{ m/hr}}{0.161 \text{ m}} \times 0.42$$

rate of biodegradation was initially very low, then passed through a period of high biodegradation rate, and then dropped to a low rate again. Since this method of calculating rates takes into account flow rates, it was useful in calculation the rates of biodegradation involved in the transient loading experiments (see section 5.2.2).

5.2.2 Transient Loading Experiments

In order to allow effects of changes in influent phenol levels to be observed in the effluent within a reasonable time, 3.1 g carbon pre-equilibrated with 0.8 mg/ℓ phenol was used for all transient loading experiments, while the flow rate used was 10 mℓ/min (EBCT of 1.4 min, flow rate of 0.95 mm/sec or 1.4 gal/min·ft^2). Other aspects of the transient loading experiments, such as bacterial seed origin, were the same as in the 9 mg/ℓ influent DO experiment. The transient load selected for study was a pulse of phenol of 150 mg/ℓ for 1 hr, after which the influent concentration of 0.8 mg/ℓ was restored for the remainder of the experiment. Using the Freundlich isotherm of Figure 3 and the other characteristics known about the Filtrasorb 400 used in this study as imput, the computer model generated effluent concentrations for transient loads. Figure 16 shows the effluent phenol measurement for a sterile column and the computer generated effluent concentration curve for the same conditions. The column was pulsed at zero bed volumes. Since one bed volume was 14 mℓ and the flow rate was 10 mℓ/min, 3000 bed volumes required approximately 100 hr. The sterile column effluent phenol concentration peaked near 1000 bed volumes and then tailed off gradually. The influent concentration was reached after

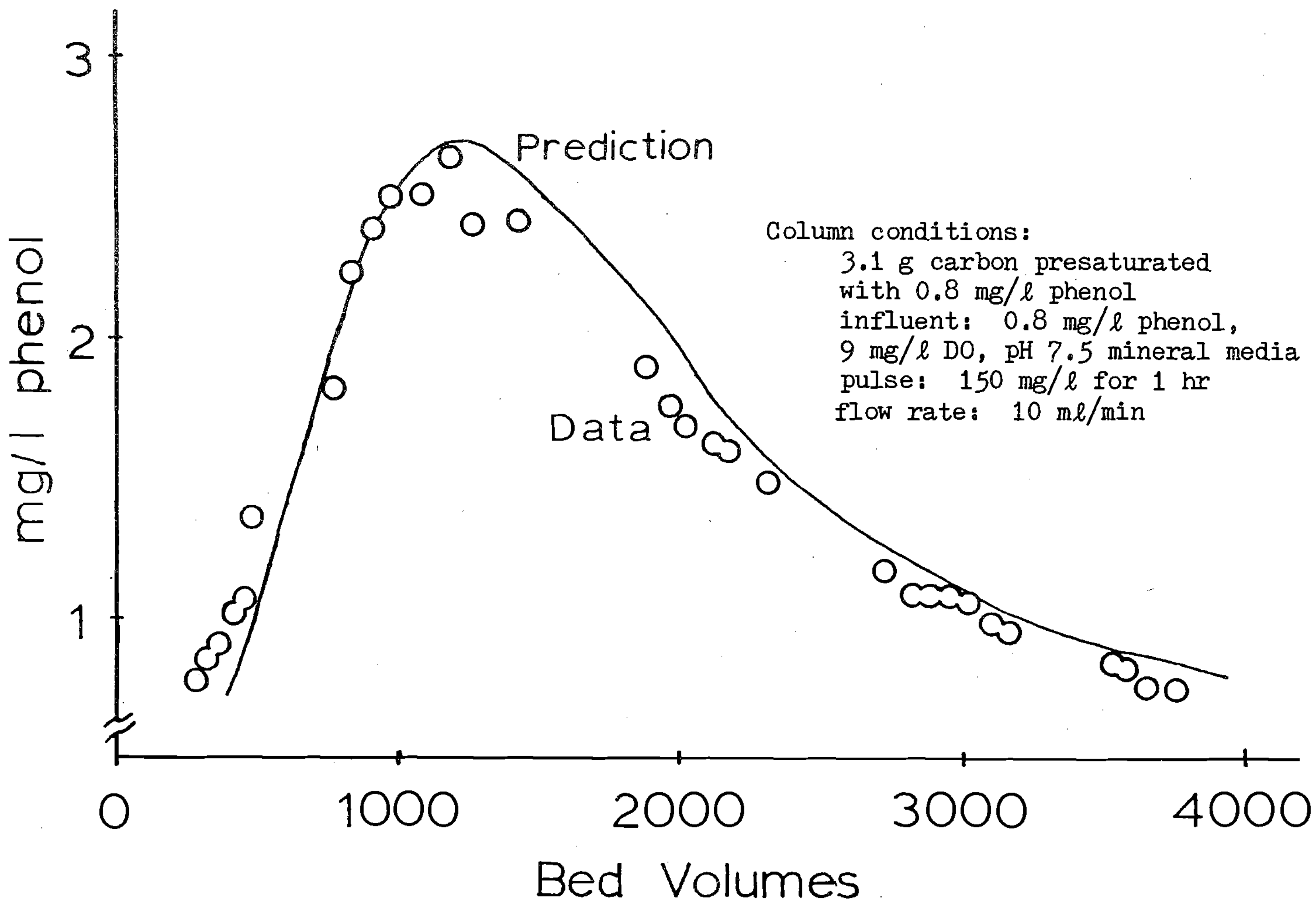


Figure 16. Effluent Phenol Data and Computer Generated Curve for the First Sterile Pulsed Column Experiment

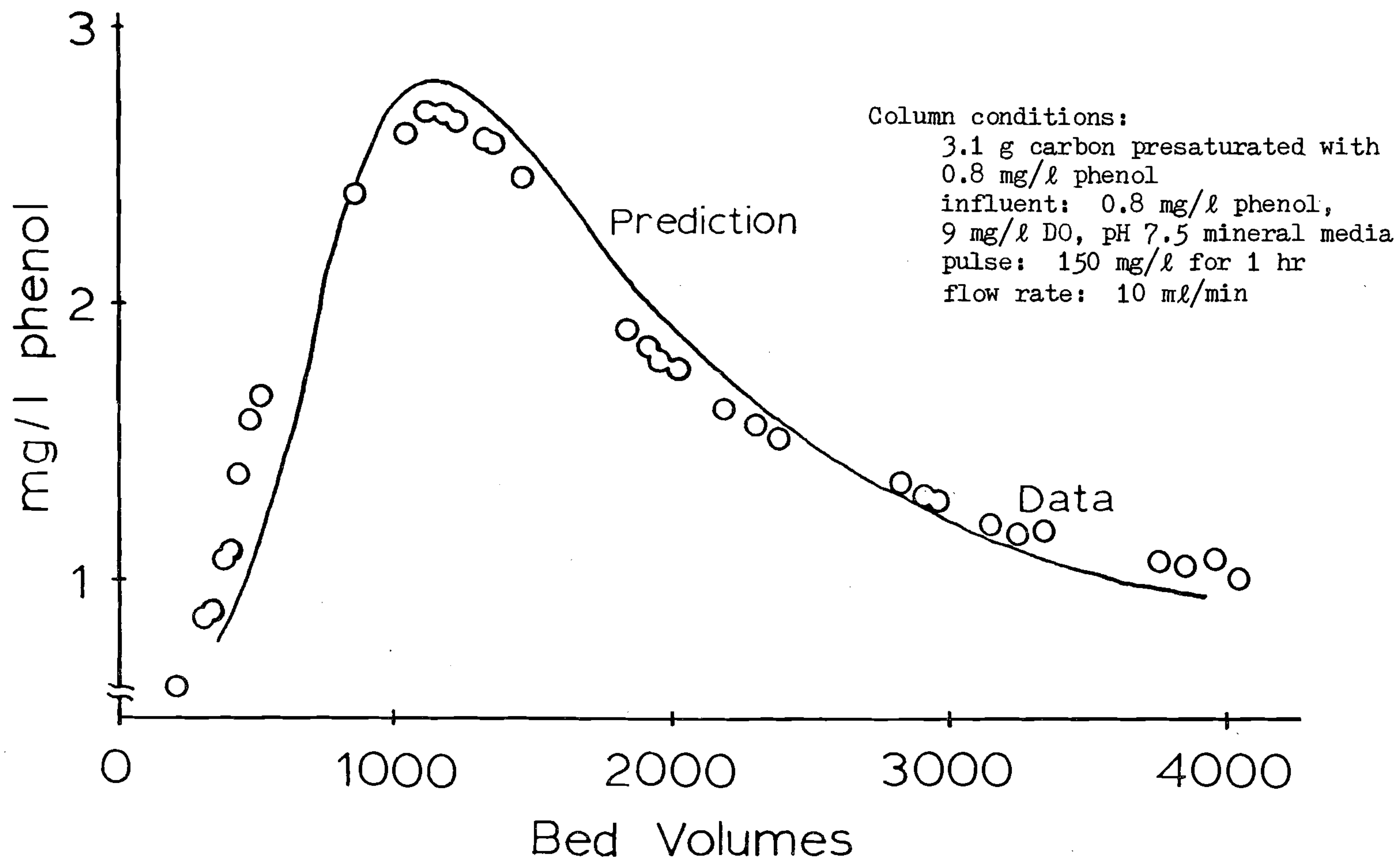


Figure 17. Effluent Phenol Data and Computer Generated Curve for the Second Sterile Pulsed Column Experiment

8000 bed volumes. Of the 85 mg phenol introduced into the column in the pulse, only 50 mg phenol came out, indicating that the column was not really saturated at a C_e of 0.8 mg/ℓ (i.e., pre-equilibrium of the carbon had not been completed). A second smaller transient load was then introduced into the same column. A similar pulse shape was seen for this second sterile pulse as for the first sterile pulse (see Figure 17). Of the 45 mg phenol introduced into the column in this second pulse, a total of 39 mg phenol had been eluted by 3000 bed volumes. This indicated that by the end of the end of the first sterile pulse, the column had been saturated with phenol at a surface concentration corresponding to a C_e of 0.8 mg/ℓ. The same sterile column was then seeded (as in section 4.1.3). The flow rate was reduced to 2 mℓ/min in order to reduce washout of bacteria and thus enhance the establishment of a stable bacterial population on the column. The column was operated for 18 days under these conditions, at which time the Standard Plate Count Test results showed a population of 6.6×10^5 bacteria/mℓ in the column effluent. The effluent phenol concentration was zero at this time. The DO drop across the column reached a maximum of 5.5 mg/ℓ oxygen, and then declined to 2.5 mg/ℓ oxygen, indicating that most of the available pre-adsorbed phenol had been oxidized and that the bacteria were using oxygen mainly to oxidize influent phenol. At this point the flow rate was increased again to 10 mℓ/min, and a third pulse of 150 mg/ℓ phenol was sent into the column for 1 hr. Figure 18 shows the entire history of this column. The effluent phenol concentration after this first seeded pulse was no longer zero, but no distinct pulse shape was seen either. This dramatic reduction of the effluent concentration,

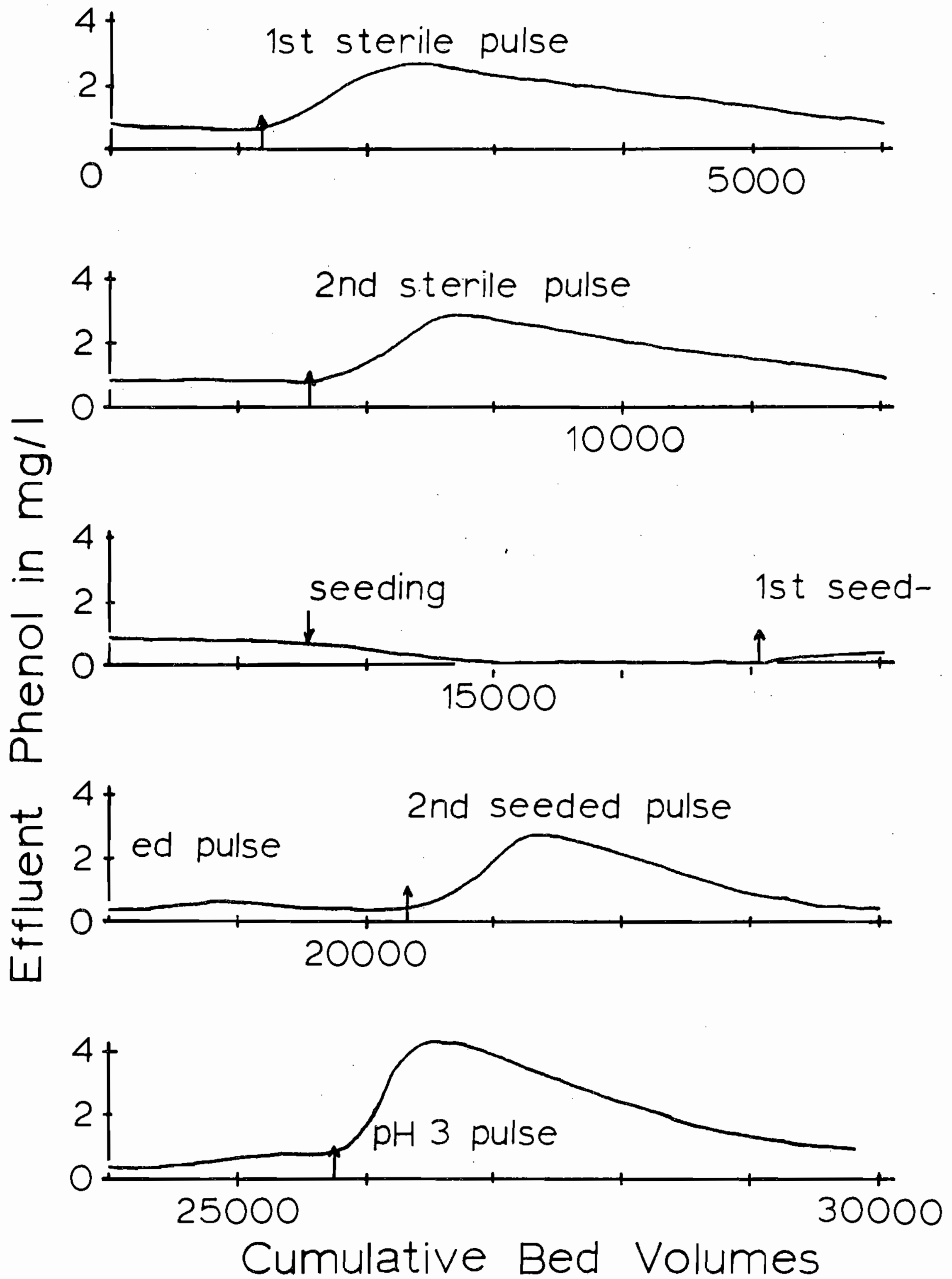


Figure 18. Entire History of the Column Used in the Transient Loading Experiments (for detail see Figures 16, 17, 19, and 21)

when compared to the effluent pattern of the sterile column, could only be attributed to the presence of the bacteria in the carbon column. The bacteria could have caused this phenomenon by one or both of two major mechanisms. The first possibility is that due to the bioregeneration of the carbon by the bacteria, the increase in capacity of the carbon was enough to adsorb the entire amount of phenol which was introduced during the pulse. The second possible mechanism is that of increased direct oxidation of the influent phenol by the bacteria as the increased phenol concentration passed into the column. Increased degradation rates should be reflected in increased removal of dissolved oxygen while the phenol peak was in the column. The number of bacteria in the column effluent remained fairly constant, as seen in Table 4. The measured degradation rates for the transient loading experiments are presented later in this section.

If the phenol in this first seeded column pulse was adsorbed on the column, a second immediately following pulse should not show any effects from bioregeneration, since the bacteria would not have had enough time to bioregenerate the carbon. The effluent phenol concentration data from two consecutive seeded column pulses is shown in Figure 19, along with the computer generated effluent concentration curves for the same conditions. Pulses were introduced at zero bed volumes and at 3270 bed volumes, respectively. At the end of the second sterile pulse, influent and effluent phenol concentrations were measured to be 0.8 mg/ℓ, so the surface concentration was calculated to be that which was in equilibrium with a solution concentration of 0.8 mg/ℓ or 55.8 mg/g C for a total of 173 mg on the carbon column.

Table 4

Standard Plate Counts During the Seeded Column Pulse Experiment

Bed Volumes	Count/mℓ
first pulse at zero	
442	4.9×10^5
1217	7.8×10^5
1878	2.09×10^6
2673	3.2×10^5
second pulse at 3270	
3589	3.32×10^5
4420	1.2×10^4
5363	3.59×10^5
6177	3.37×10^5
7011	4.7×10^5

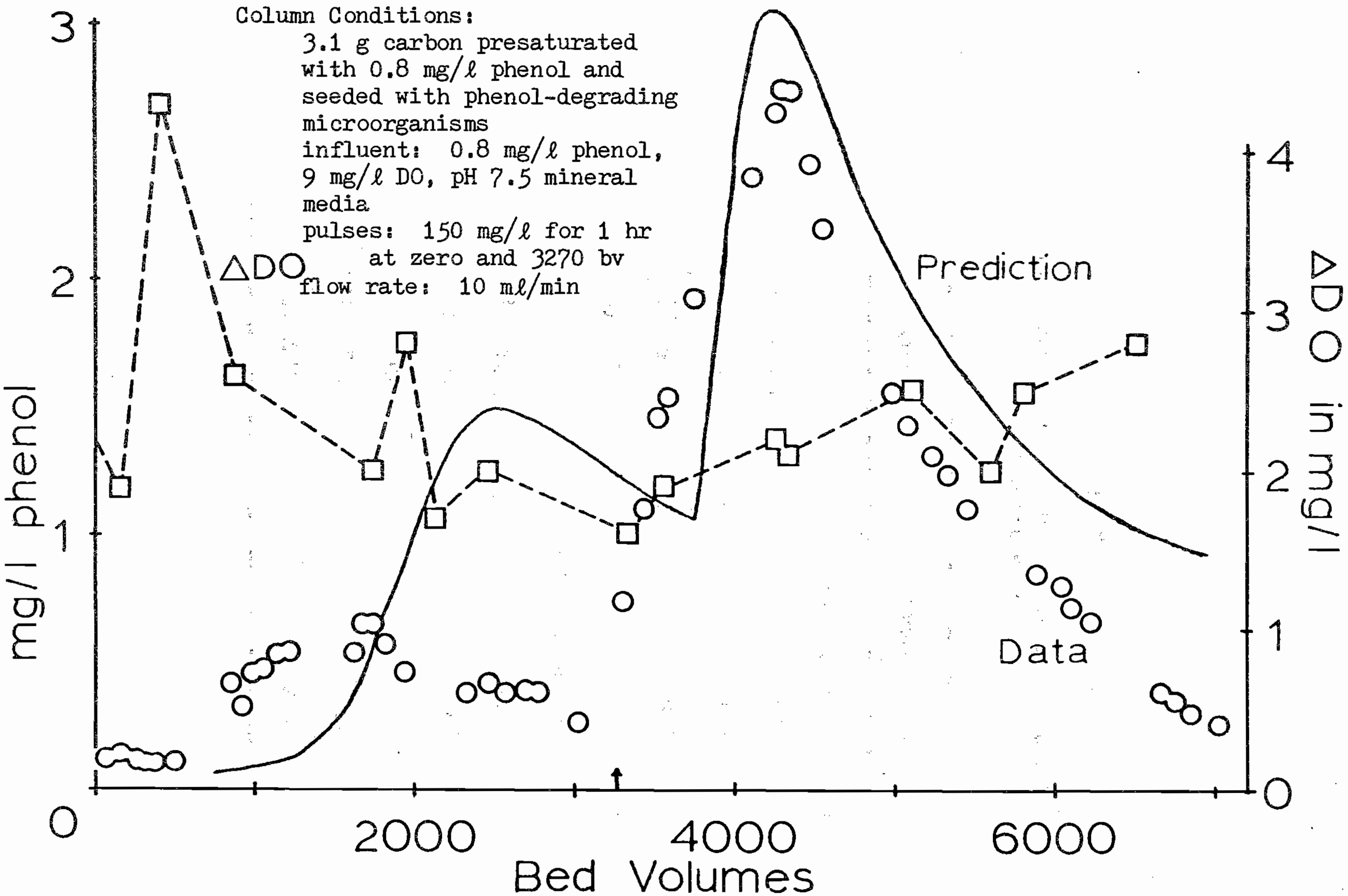


Figure 19. Effluent Phenol Data, Computer Generated Curve, and Dissolved Oxygen Uptake Data for the Seeded Pulsed Column Experiment

The calculations used to determine values of C_e used for the computer prediction of the seeded pulses and the pH 3 pulse were based on this calculation and the mass balances presented in Table 5.

The rate of biodegradation based on amount of oxygen used in this column was calculated during that part of the transient loading experiment in which bacterial activity was present, i.e., after seeding and until the end of the second seeded pulse. Figure 20 shows the biodegradation rate of phenol based on oxygen use versus time for this column during the period of column operation in which bacteria were present. Once the column was seeded, the biodegradation rate slowly increased until it reached a maximum of 9.8 g $\phi OH/m^3 \cdot hr$ at about 1800 bed volumes. The rate then decreased until the time of the first seeded pulse. It must be noted that the jump in flow rate from 2 $m\ell/min$ to 10 $m\ell/min$ greatly increased the amounts of both oxygen and phenol being introduced into the column per unit time, even when the concentration was not increased. This allowed higher biodegradation rates to occur at times of higher flow rates. After introduction of the first seeded pulse, the biodegradation rate jumped to a high point of 123 g $\phi OH/m^3$ carbon·hr. This value was over ten times the magnitude of the highest rate reached during seeding. This high rate was reached for only one point during the time of the transient loading experiments. It may be an artifact due to scatter in DO measurements. There were, however, five other measurements during this phase which reflected rates over 70 g $\phi OH/m^3$ carbon·hr, reinforcing the concept that biodegradation rates were greatly accelerated after introduction of the transient loads. There was no corresponding peak in activity after the second seeded

Table 5

Mass Balances on Phenol and Oxygen during the Bioactive Portion of the Transient Loading Experiment

Event	Total mg ØOH applied[1]	mg O_2 used[2]	mg ØOH equivalent of O_2 used[3]	mg ØOH left on column total[4]	mg ØOH left on column mg/g C[5]	mg/ℓ Corresponding[6]
Seeding	75.6	321.4	135	114	36.6	0.14
First Seeded Pulse	124.8	138.9	58.3	180	58.2	0.95
Second Seeded Pulse	61.1	140.1	58.8	182	58.8	0.95

[1]The difference between the summations of the total influent phenol and total effluent phenol measurements

[2]The difference between the summations of the total influent DO and total effluent DO measurements

[3]Assumes 0.42 mg/ℓ ØOH per mg/ℓ O_2 used

[4]Number resulting from the mg left on the column before the event minus the ØOH equivalent of O_2 used plus the total ØOH applied; before seeding, the surface concentration was 55.5 mg/g C for a total of 173 mg ØOH

[5]Total mg divided by 3.1 g GAC in the column

[6]Calculated using the isotherm shown in Figure 3, then used for the computer prediction of the immediately following pulse

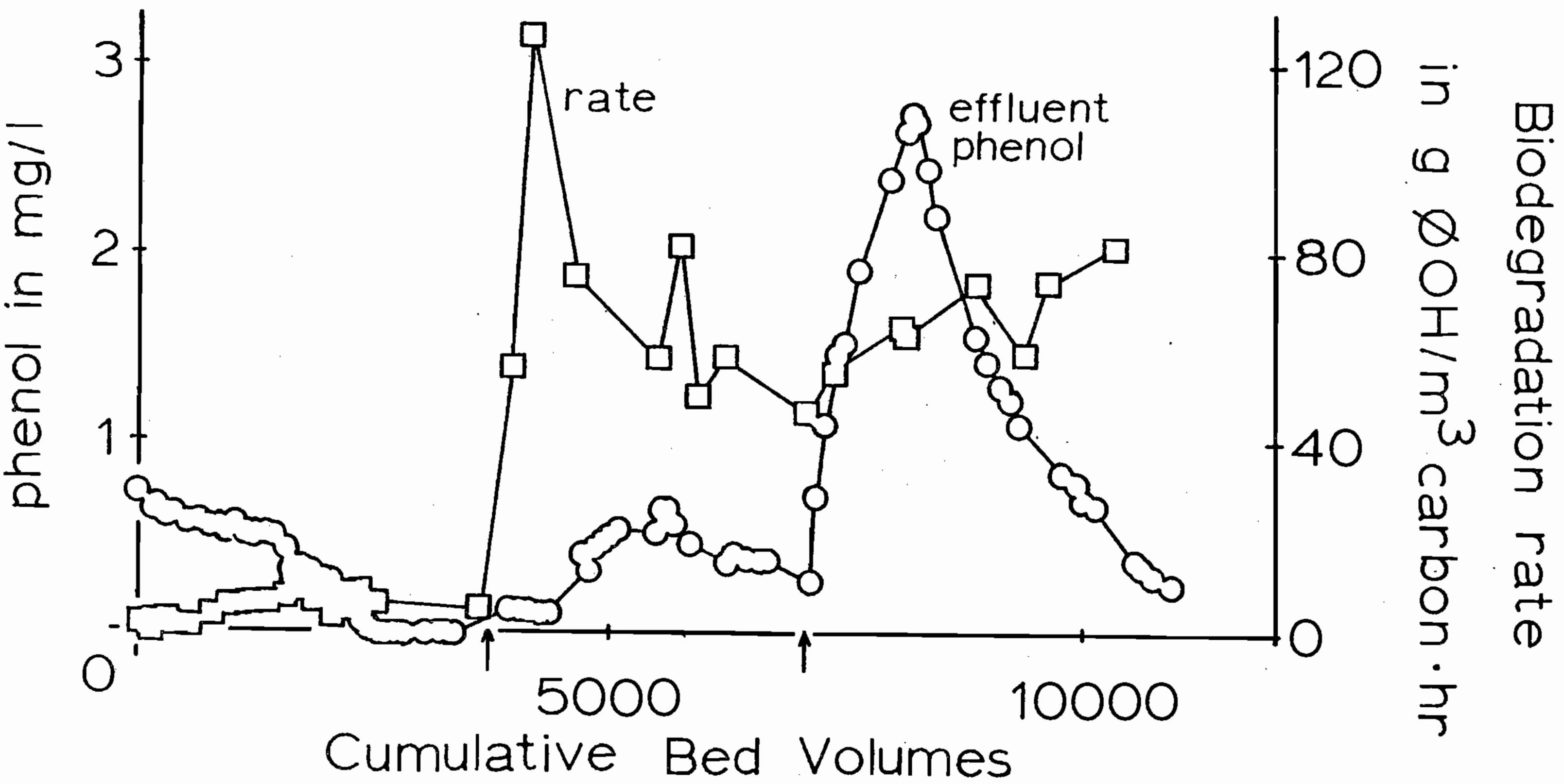


Figure 20. Biodegradation Rates Measured During the Bioactive Portion of the Transient Loading Experiments

pulse. Had a narrow peak in activity been present, it may have been missed by the normal span of time between DO measurements (an average of 460 bed volumes between samples during the second seeded pulse).

The great attenuation of the first seeded pulse was a result of two mechanisms: the capacity increase of the carbon from bioregeneration, and bacterial oxidation of phenol as it passed through the carbon. The computer model accounted for changes in capacity, but not for biodegradation of bulk influent phenol as it passed through the column. Therefore, it predicted that the effluent concentration would start low but later would show an attenuated pulse shape. Bioregeneration of the carbon during seeding did in fact increase the capacity of the carbon and therefore kept the effluent concentration low during the first 2000 bed volumes after the first seeded pulse. The computer model predicted that the effluent concentration of phenol would rise after 2000 bed volumes had passed, but this was not observed. The removal of phenol in the column after this point could not be accounted for by any increased capacity of the carbon, but must have been due to biodegradation of the phenol in solution as it passed through the carbon column.

After the first seeded pulse it was assumed that some phenol had been re-adsorbed onto the carbon, as was described above. Since the second seeded pulse immediately followed the first seeded pulse, it was expected that there would not be any effects due to bioregeneration possible on the effluent phenol curve. As is seen in Figure 19, the observed effluent profile follows the predicted curve closely between the time of pulsing at 3270 bed volumes and about 4500 bed volumes. The effluent data in Figure 19 after 4500 bed volumes show a rapid

decrease in phenol concentration such that the effluent concentration dropped below the influent concentration at about 6000 bed volumes. The computer prediction indicated that the effluent would match the influent only after about 8000 bed volumes. The observed rapid drop in concentration must have been a result of biological oxidation of phenol. Therefore biodegradation of the phenol in solution contributed to phenol removal during the second seeded pulse, as well as during the first seeded pulse.

In order to evaluate the effects of the biological population on the carbon, the influent to the same column was changed to pH 3 with HCl, and the column was allowed to reach pH 3 in the effluent. This operation took less than 100 bed volumes and effectively stopped bacterial activity in the column, as reflected by zero DO demand across the column and effluent Plate Counts of less than 50 bacteria/mℓ. Another 150 mg/ℓ 1 hr pulse was introduced into the column at this time. Figure 21 shows the effluent phenol measurements of this column experiment and the computer generated effluent concentration curve for the same conditions. The carbon's capacity for phenol is decreased with decreasing pH. This can be seen by comparing the Freundlich isotherms at pH 7.5 presented in Figure 3 and pH 3 presented in Figure 15 (isotherm labeled "Virgin"). For example, at an equilibrium concentration (C_e) of 0.10 mg/ℓ, at pH 7.5 the surface concentration (S) is 33.9 mg/g C, while at pH 3, the corresponding S value is only 23.8 mg/g C. This reduced capacity at lower pH should cause the effluent pulse height to increase compared to the effluent pulse height seen for a sterile pulse at pH 7.5 (see Figures 16 and 17). The effluent phenol data and

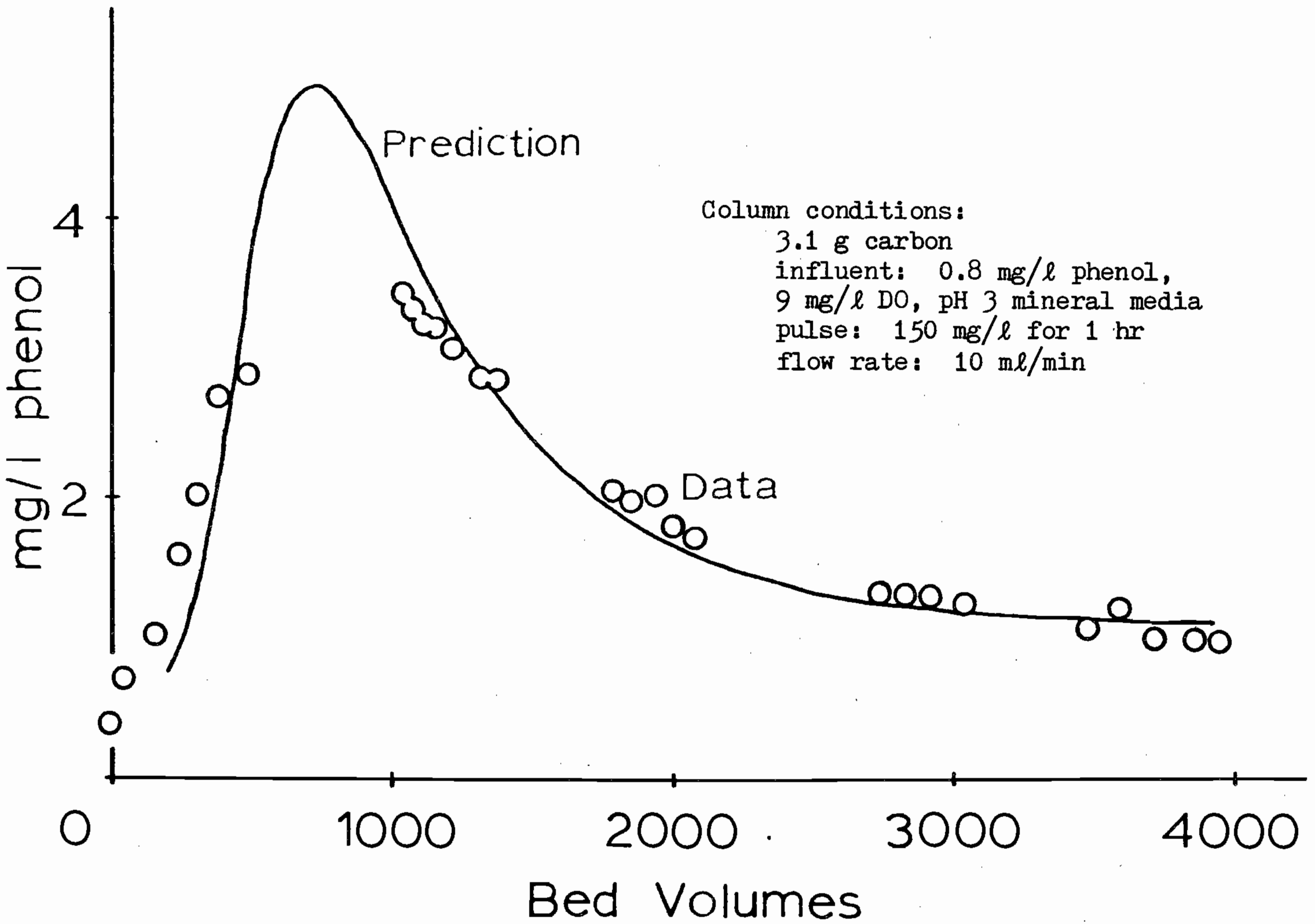


Figure 21. Effluent Phenol Data and Computer Generated Curve for the Pulsed pH 3 Column Experiment

computer predicted curve for the pH 3 pulse are shown in Figure 21. Since the pattern of the effluent phenol data matches that of the computer generated pulse, even after 1500 bed volumes, the rapid drop in phenol concentration which was seen in Figure 19 could only have been due to the microbial population, and not, for example, due to some change in the character of the carbon surface. This result indicates that the bacterial population plays an active role in removal of phenol from the bulk solution as it passes through the column. Since the bacteria need to be alive in order to affect the apparent capacity of the carbon due to bioregeneration, biodegradation, or both, the carbon may be acting as a concentration buffer in protecting the bacterial population from the high influent phenol levels of the pulse. Such phenol concentrations could kill many types of bacteria (Nester et al., 1973), so that the bacterial population could be gaining a benefit from using carbon as an attachment surface rather than using a non-adsorbing support medium.

The transient loading experiments have answered some important questions. They have also indicated a need for further investigation. It has been shown that a bacterial population will contribute to the reduction in effluent phenol concentrations of a pulsed carbon column in two ways. Increased capacity due to bioregeneration of the carbon is important especially if there is enough time for such bioregeneration to occur between transient loads. Biodegradation of phenol in solution as it passes through the column is also important in reduction of effluent concentration, and can occur independently of bioregeneration. Such biodegradation requires a viable population of bacteria

on the column, which requires the tailoring of treatment system conditions to permit enhanced biological activity. Hence, there is a need to more closely investigate biodegradation rates as they relate to influent DO, type of substrate, and type of bacterial population.

5.3 End Product Analysis

5.3.1 Total Organic Carbon Analysis

Effluent samples from each of the varied oxygen influent experiments were collected and stored at 1°C until Total Organic Carbon (TOC) analysis was performed. Since phenol was in most samples, the amount of TOC which is actually phenol can be accounted for using the TOC response of phenol as shown in Figure 22. Using the straight line generated by the linear least squares analysis of the points in Figure 22, the TOC response for a given phenol concentration can be calculated. For example, the 196 hr sample taken during the 4 mg/ℓ DO influent experiment contained 0.504 mg/ℓ phenol, which corresponds to a TOC response of 0.387 mg/ℓ. Therefore, the non-phenol portion of organic carbon measured by TOC analysis must be the TOC measurement minus the phenol present (expressed as TOC), or 0.527 mg/ℓ - 0.386 mg/ℓ or 0.141 mg/ℓ. This result can also be expressed as a percentage of the total TOC present. Continuing with the same example,

$$\text{non-phenol TOC} = \frac{0.141 \text{ mg}/\ell}{0.527 \text{ mg}/\ell} \times 100\% = 27\%$$

Calculations were made in a similar manner for the other data points, with all results presented in Table 6.

The apparent trend in these data is that for the two higher influent DO experiments, once the bacterial population was established,

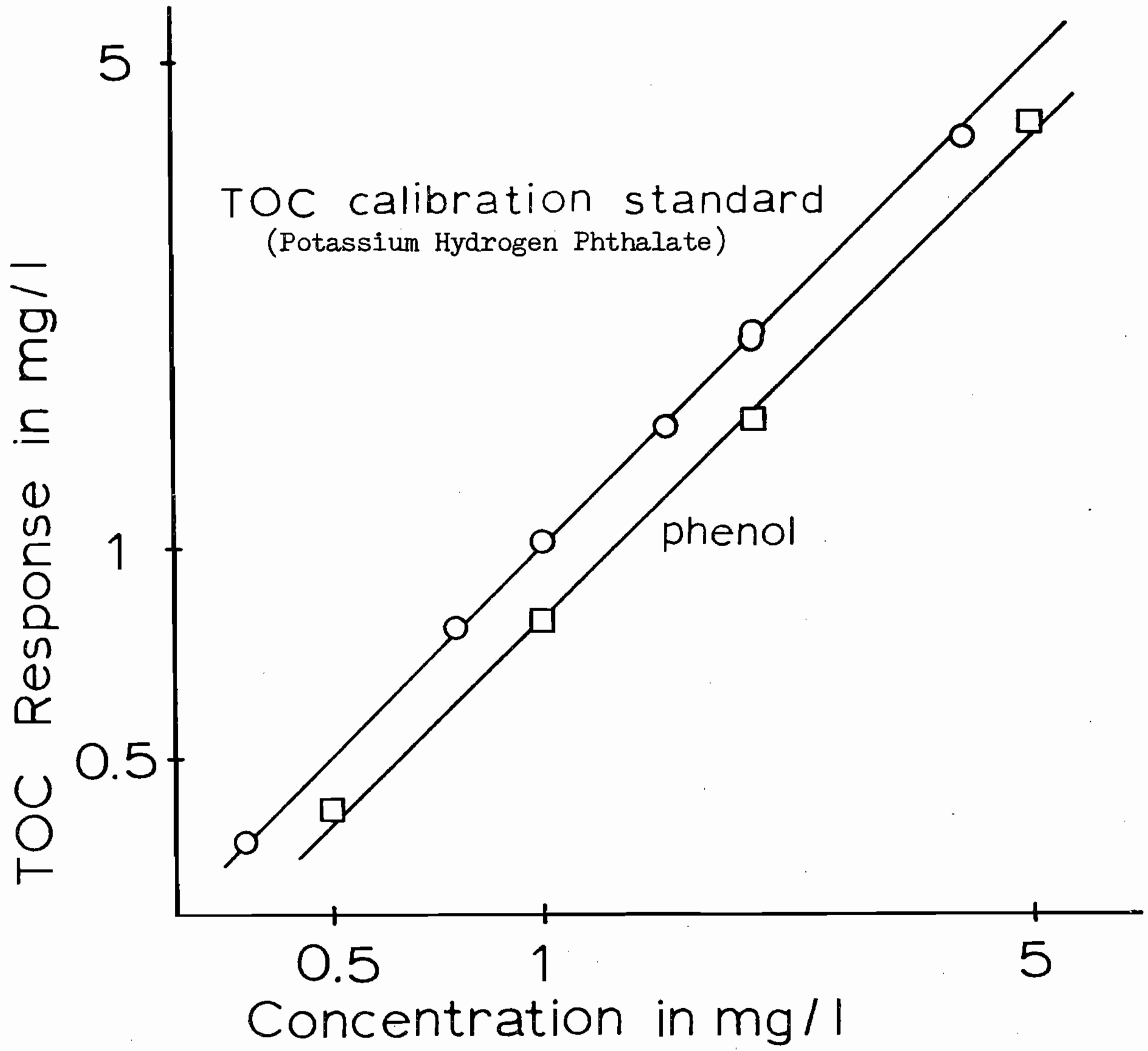


Figure 22. TOC Response versus Concentration

Table 6

Total Organic Carbon (TOC) Analysis of Effluent from the Varied Oxygen Influent Experiments

Time	Phenol		TOC	Non-Phenol TOC	
hr	mg/ℓ as Phenol	mg/ℓ as TOC	mg/ℓ	mg/ℓ	% of total
4 mg/ℓ DO Influent					
196	.504	.386	.527	.141	27
239	.362	.271	.490	.219	45
260	.352	.263	.384	.121	32
284	.321	.238	.368	.130	35
313	.280	.205	.296	.091	31
332	.347	.259	.381	.122	32
9 mg/ℓ DO Influent					
243	.03	.003	.201	.198	99
265	.04	.011	.214	.203	95
290	.017	<.001	.100	.100	100
313	.017	<.001	.165	.165	100
336	.031	.004	.090	.086	96
358	0	0	.107	.107	100
16 mg/ℓ DO Influent					
100	.211	.149	.305	.156	51
150	.147	.098	.202	.104	51
174	.075	.039	.148	.109	74
217	.050	.019	.214	.195	91
279	.015	<.001	.123	.123	100

there was an increased proportion of the effluent TOC which cannot be accounted for by the measured phenol concentrations of the same samples. This excess effluent TOC is a very small amount, however, on the average about 0.14 mg/ℓ for all cases.

Approximations can also be made in order to estimate the contribution of biomass to the TOC found in the effluents from the columns used in the varied oxygen influent experiments. The assumptions necessary for such calculations are that a typical cell's volume is 1 μm^3, or 10^{-12} cm^3, and that the specific gravity of a cell is near that of water, or 1 g/cm^3 (Nester et al., 1973). With a specific gravity of 1.0, the mass of one cell is 1×10^{-12} g/cell, or 1×10^{-9} mg/cell. The amount of organic carbon in a bacterial cell is about 9% (Metcalf & Eddy, Inc., 1972), so that the contribution of bacteria to TOC would be 9×10^{-11} mg/cell. For example, the 196 hr sample taken during the 4 mg/ℓ influent DO experiment was seen to contain 8.5×10^5 bacteria/mℓ (see Figure 9). This number of bacteria would have a biomass of 8.5×10^8 cell/ℓ x 9×10^{-11} mg/cell = 0.077 mg/ℓ. This was subtracted from the non-phenol TOC value calculated and shown in Table 6, leaving a non-phenol, non-biomass TOC equivalent to 0.064 mg/ℓ which is 12% of the total TOC measured. Calculations were made in a similar manner for the other data points, with the results listed in Table 7. Trends in these data are similar to the trends observed for the data presented in Table 6. Since there were many assumptions involved in determining the numbers shown in Table 7, use of these numbers for purposes other than observing general trends would not be appropriate. The remainder of the non-phenol TOC may be

Table 7

Contributions of Biomass to Effluent TOC Values from the Varied Oxygen Influent Experiments

Time	Biomass (est.)	Non-Phenol, Non-Biomass TOC	
hr	mg/ℓ	mg/ℓ	% of total
4 mg/ℓ DO Influent			
196	.077	.064	12
239	.051	.168	34
260	.031	.090	23
284	.126	.004	1
313	.020	.061	21
332	.082	.040	10
9 mg/ℓ DO Influent			
243	.118	.080	40
265	.100	.103	48
290	.100	0	0
313	.100	.065	39
336	.100	0	0
358	.100	.007	7
16 mg/ℓ DO Influent			
100	<.001	.156	51
150	<.001	.104	51
174	.004	.105	71
217	.004	.191	89
279	.034	.089	72

due to the presence of microorganisms in the effluent which are not measured by the Standard Plate Count Test. Without additional investigation, the actual amount of biomass in the effluent can only be approximated as above.

Because of the small amount of material measured in the effluent during these column experiments, efforts to identify specific end products were concentrated on analysis of materials which could be extracted from the carbon, the results of which are presented in the next section.

5.3.2 Carbon Extract Analysis

The carbons used in a seeded 9 mg/ℓ DO influent column experiment, a seeded pulsed pH 7.5 column experiment, and a non-seeded 9 mg/ℓ DO influent column experiment were extracted with organic solvent. After methylation, and optionally after reaction with aminoantipyrine (aap) to sequester phenol, the concentrated extract was analyzed via GC/MS. The results of this analysis are shown in Table 8. A sample of trans-muconic acid methyl ester in methylene chloride gave clearly identifiable results using the same GC/MS analysis conditions. It should be noted that this method will detect less than 5% of the organics in a given water sample; thus it is by no means an exhaustive investigation into all possible organic compounds present (Giger *et al.*, 1976).

None of the compounds known to be biodegradation products of phenol (see section 2.3.2) were found in the carbon extracts. Compounds found in the non-seeded column extract can be assumed to be con-

Table 8

Compounds Tentatively Identified via GC/MS

Identity	Column s = seeded ns = non-seeded p = pulsed	Solvent used for Extraction mc = methylene chloride m/m = methylene chloride/ methanol azeotrope	aap Reaction yes = used no = not used
anisole	s, ns, p	mc, m/m	yes, no
phenol	s, ns, p	mc, m/m	yes, no
acetophenone	s	mc, m/m	yes
methyl salicylate	s, p	mc	no
methyl-p-methoxybenzoate	s, p	mc, m/m	yes, no
4-methoxy diphenyl ether	s, p	mc	no
2,2'-dimethoxybiphenyl	s, p	mc	yes, no
m-cresol	p	mc	no
2,4,5-trichloroanisole	p	mc	yes
benzyl alcohol	p	mc	no
C_{17} fatty acid methyl ester (FAME)	s	mc	no
C_{11} FAME	p	mc	no
C_{13} FAME	p	mc	no
C_{16} FAME	p	mc	no
2-hexyne	ns	mc	no
diethyl phthalate	ns, s	mc	no
di-n-butyl phthalate	ns, s	mc	no
methyl butyl phthalate	ns	mc	no

taminants of the system. A list of compounds found in methylated distilled water is shown in Table 9 (A. Chen, personal communication) and can be compared with the compounds found in the non-seeded column extract. Contaminant compounds could have come from the distilled water or from leaching from the small amount of plastic tubing and hardware used in the column setup. The compounds found in the seeded column and the seeded pulsed column could be attributed to some effect of the microbial population, but without more definitive results, such assignment can only be speculation at this point. Failure to find any of the known biodegradation products of phenol could be due to one reason or to a combination of reasons. 1) Biodegradation of phenol to carbon dioxide and water may have been complete. 2) The biodegradation pathways used by the bacteria in the column could be other than those established to be used by some Pseudomonas species. 3) If the known pathways were used, the intermediate products may not have adsorbed well on the carbon, such that there was little there to extract. 4) Conversely, strong adsorption of the intermediates may have led to failure of the methylene chloride or azeotropic mixture to extract the compounds from the carbon. It is clear that perusal of this line of investigation will require much perseverance to answer merely some of the questions which have been encountered here.

Table 9

Compounds Found in Distilled Water after Methylation

Acetophenone
Methylbenzoate
Dimethoxybenzene
o-Methoxyphenol
1,4-Dimethoxy-2-chlorobenzene
Dimethyl phthalate
Diethyl phthalate
Dibutyl phthalate
C_8 through C_{11} FAME

6. ENGINEERING SIGNIFICANCE

The results of this study have shown that biological activity can be beneficial to the operation of an activated carbon column under bench-scale conditions. If the influent dissolved oxygen is kept at air saturation levels or above and the concentration of biodegradable organics in the influent is kept below an average of about 3 mg/ℓ TOC, biological activity in a carbon bed will be enhanced without causing anaerobic conditions. During normal water or advanced wastewater treatment operations, the influent TOC can fluctuate widely (Culp and Hansen, 1980; Trussell and Umphres, 1978). During periods of low concentration, the biological activity may bioregenerate the carbon in place, depending on the type of organics present, thus increasing the apparent capacity of the carbon for adsorption. Apparent capacity will also be increased at all times due to ongoing biodegradation of organics in the bulk influent as it passes through the column. If it can be shown that the lifetime of an activated carbon bed can be extended by enhancement of the biological activity present in the carbon bed, such activity will be of economic importance.

7. CONCLUSIONS

The results of this study lead to the following conclusions:

1) Bioregeneration of activated carbon occurs in bench-scale carbon columns when carbon pre-saturated with phenol is fed an influent composed of a pH 7.5 mineral medium and 2 mg/ℓ phenol and the influent DO is at air saturation or higher (9 mg/ℓ). The amount of bioregeneration is related to the influent DO when all other conditions are equal. Amounts of bioregeneration can be calculated using mass balances on phenol and oxygen or measured from changes in adsorption capacity of the carbon before and after use.

2) During transient influent phenol loading, the bacterial activity in a bench-scale column affects the effluent phenol profile by two mechanisms. These are biodegradation of phenol in the bulk influent solution as it passes through the column and bioregeneration of the carbon by removal of adsorbed phenol. When an influent pulse is preceded by a period of low influent load, bioregeneration will be important in reducing effluent concentrations from the subsequent pulse load. If there has not been enough time between influent pulses, bioregeneration will not be effective in reducing effluent pulse amplitude as would be biodegradation alone.

3) An adsorbing support medium, such as activated carbon, is superior to a relatively non-adsorbing support medium, such as sand, for growth of bacteria under transient loading conditions, The carbon will buffer concentrations in the column, even to the point of reducing

potentially lethal concentrations of biocides down to levels tolerable to bacteria. This was demonstrated for phenol: an influent pulse concentration of 150 mg/ℓ was reduced to less than 3 mg/ℓ in the effluent by the action of the carbon alone. Such concentration buffering should also allow more biodegradation to occur in a carbon column than in a sand column since the adsorption equilibrium characteristics of carbon would lengthen the amount of time an influent pulse of adsorbable organic material would remain in the column compared to the residence time of an equivalent pulse in a non-adsorbing (e.g., sand) column.

4) Further research is needed in order to fully understand the processes involved in biologically active carbon columns. The nature of the relation between biodegradation rate and DO concentration needs to be explored in order to efficiently apply the results of this study to actual practice. Other aspects left unclear at this point are the effects of changing bacterial varieties on biodegradation rates, the exact nature of degradation products under different column conditions, and the effects of a mixture of organic compounds in the influent on effluent profiles. Ideally, sophistication of computer modeling to account for biodegradation and bioregeneration may allow rapid visualization of the results of the influent variations possibly encountered in practice.

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