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Effect of dissolved oxygen on activated carbon uptake

Abuzaid, Nabil Said Fuad, Ph.D.

King Fahd University of Petroleum and Minerals (Saudi Arabia), 1993

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EFFECT OF DISSOLVED OXYGEN ON ACTIVATED CARBON UPTAKE

BY

NABIL SAID FUAD ABUZAID

A Dissertation Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

IN

CIVIL ENGINEERING

July 1993

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

This Dissertation, written by **Nabil Said Fuad Abuzaid** *under the direction of his Dissertation Advisor and approved by his Dissertation committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of* **DOCTOR OF PHILOSOPHY IN CIVIL ENGINEERING**

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كلية الدراسات العليا
COLLEGE OF GRADUATE STUDIES

This dissertation is dedicated

to

my parents and my wife

ACKNOWLEDGEMENTS

Praise and gratitude be to **ALLAH**, Almighty, without whose gracious help it would have been impossible to accomplish this work. Acknowledgement is due to King Fahd University of Petroleum & Minerals for extending the facilities to carry out this research.

I would like to express my gratitude and appreciation to my advisor Dr. Girgis F. Nakhla for his guidance and helpful suggestions throughout this study. Thanks are due to my co-advisor Dr. Shaukat Farooq , and the committee members, Dr. Rasheed I. Allayla, Dr. Kevin F. Loughlin, and Dr. Emmanuel Osei-Twum for their invaluable suggestions and significant contributions. Special thanks are due to Dr. Kevin F. Loughlin for his invaluable contribution to the theoretical aspects of the work, and Dr. Emmanuel Osei-Twum who provided assistance in the chemical analysis and helped lay the chemical framework for the interpretation of the findings.

Acknowledgement is also due to Mr. Essam Al-Deeb and Mr. M.K. Abdulappa of Environmental Engineering Laboratory for their assistance during the experimentation.

I owe my family an expression of gratitude for their patience and understanding during my studies in KFUPM.

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خلاصة الرسالة

اسم الطالب : نبيل سعيد فؤاد أبوزيد
عنوان الدراسة : تأثير الاكسجين المذاب على قدرة الكربون المنشط .
التخصص : هندسة مدنية (مصادر المياه والبيئة) .
تاريخ الشهادة : يوليو ١٩٩٣م .

بينت دراسات الحرارة المتساوية على الفينول والاكريسول والنيتروفينول نسبة ٢٠ - ١١٥٪ زيادة في قدرة الكربون نتيجة لوجود الاكسجين المذاب . وقد تم التوصل إلى نفس هذه الظاهرة عندما استعملت عوامل الاكسدة مثل بوركسيد الهيدروجين وبيرمنجنات البوتاسيوم بدلاً من الاكسجين الجزيئي .

بينما دلت الدراسة على عدم وجود تاثير يذكر للاكسجين المذاب على قدرة الكربون على امتصاص المواد الأليفية .

وقد افترضت التلمرة على سطح الكربون كسبب مقترح لهذه الظاهرة بعد الكشف عن ثنائيات وثلاثيات الفينول بعد استخلاصها من الكربون في تجربة الاكسجين ، وبناء على ذلك تم إقتراح وسيلتين للتفاعل لتمثيل التفاعل بين الاكسجين وعامل الأكسدة مع الفينول .

ولقد أشارت التجارب إلى أن الإمتزاز الفيزيائي يزيد عند درجة حموضة منخفضة في حين أن تفاعلات التلمرة زادت عند الحموضة العالية ولكن الحموضة المتعادلة أعطت أعلى زيادة في قدرة الكربون . أما بالنسبة لتجارب تأثير الحرارة فقد أشارت إلى تحسن الامتزاز الفيزيائي مع إنخفاض الحرارة وتزايد التلمرة مع إزدياد الحرارة . ولقد وجد أن الزيادة في القدرة على الامتزاز لمركبات الفينول تتناسب مع زيادة الاكسجين المذاب كما تزداد كذلك مركبات الفينول الثنائية . وقد وجد أن كفاءة استرجاع الفينول من الكربون انخفضت في حالة وجود الاكسجين من ٧٠٪ إلى ٢٥٪ . وأن القدرة الاضافية قد اعتمدت على كمية الاكسجين المذاب وكتلة الكربون .

هذا وقد تم التوصل إلى نموذجين رياضيين للربط بين القدرة تحت جو الاكسجين وكلاً من كمية الاكسجين المذاب والقدرة بدون الأكسجين المذاب .

وقد بينت التجارب الزمنية أن عامل الانتشار الظاهري قد قُل مع زيادة كمية الاكسجين المذاب وإزدادت مدة التوازن الفيزيائي مع زيادة الحموضة وانخفاض الحرارة وإزدادت قيمة معامل الإنتشار تحت جو الأكسجين طردياً مع درجة الحرارة وعكسياً مع الحموضة ، في حين أن أعلى فرق في الإنتشار في حالتي وجود الاكسجين وعدمه كانت عند الحموضة المتعادلة ودرجة حرارة ٣٥ درجة مئوية .

وقد تم عمل نموذج رياضي يحتوي على التفاعلات الناتجة عن الاكسجين المذاب مع الامتزاز حيث أفترض أن التفاعل من الدرجة الأولى لا يعتمد على كمية الأكسجين . وقد أثبتت تجارب أعمدة الكربون أن الأكسجين المذاب يؤخر منحنى الظهور مؤدياً إلى منحنى مختلف كلياً .

أن موضوع الاختلاف بين قدرة الكربون في حالة تجارب المزجاجات والأعمدة قد حلّ نهائياً ، وقد وجد أن النموذج المعروف بـ هـ . س . د . م قدرة جيدة على التنبؤ بالنتائج المخبرية .

درجة الدكتوراة في الفلسفة

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكة العربية السعودية

يوليو ١٩٩٣م

DISSERTATION ABSTRACT

Name: Nabil Said Fuad Abuzaid

Title of Study: Effect of Dissolved Oxygen on Activated Carbon Uptake
Major Field: Civil Engineering (Water Resources & Environmental)
Date of Degree: July 1993

Isotherm studies on phenolics show a 20-115% increase in uptake due to the presence of oxygen in the test environment, with the additional uptake increasing with decreasing equilibrium concentrations. The same phenomenon is found when oxidizing agents such as hydrogen peroxide and potassium permanganate are used. Equilibrium data show no such effect on aliphatics. Uptake of domestic and industrial wastewater improve similarly.

Telomerization of adsorbates on the carbon surface is suggested as a potential reason for this phenomenon. Two reaction mechanisms are proposed to present the reaction between oxygen and oxidizing agents with phenol on the carbon surface.

Experimental data indicate that low pH favors physical adsorption, while high pH promotes telomerization. The optimum pH for adsorption of phenolics under oxic conditions is pH 7. Lower temperatures favored physical adsorption and higher temperature results in significant enhancement in the uptake under oxic conditions.

Uptakes of phenol and o-cresol increase with the increase in the DO concentration. The quantities of dimers and trimers formed on the carbon surface are a function of the DO level. Phenol yield efficiencies around 70% and 25% are observed for anoxic and oxic loadings, respectively. The additional uptake attained under oxic conditions is limited by the mass of DO as well as the mass of GAC in the test environment. Two models relating the oxic uptake to the ratio of DO to GAC mass and the anoxic capacities are developed.

The apparent surface diffusivity coefficient for phenol and o-cresol in GAC decreases with increasing DO levels in the sorbate solution. Equilibration time for physical adsorption increases proportionally with pH and inversely with temperature, while, for the oxic case, the equilibration time occurs in the time range of (7.5-11) days from the beginning of the experiment. D_s values for the oxic cases increase proportionally with temperature and inversely with pH, with the highest difference between oxic and anoxic diffusivities at pH 7 and 35°C.

A mathematical model which incorporates the observed reactions with adsorption is formulated. In that model the reaction is assumed to be first order with respect to the capacity and not limited by dissolved oxygen existence.

The column experiments have shown that DO causes a delay in the breakthrough curve (BTC), resulting in a completely different BTC. The issue of discrepancies between isotherm capacities and column capacities is resolved. The HSDM is found to have good prediction capability (before tailing).

DOCTOR OF PHILOSOPHY DEGREE
KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
Dhahran, Saudi Arabia
July 1993

CHAPTER 1

INTRODUCTION

1.1 Introduction

Adsorption on activated carbon (AC) is a useful and effective process for the purification of industrial and hazardous wastewaters, for advanced treatment of secondary effluents, as well as for the removal of organic pollutants from drinking water. Activated carbon is the most commonly used adsorbent in the area of environmental engineering due to its excellent adsorption characteristics, and is also frequently employed in biological reactors because of its superior microbial attachment properties.

Activated carbon is used in aerobic fixed film reactors, activated sludge systems, and fluidized-bed anaerobic reactors for toxic wastewater treatment. The relatively high cost of AC has motivated researchers to investigate and attempt to maximize the adsorptive capacity of AC for hazardous organic compounds. Factors affecting the adsorptive capacity of such compounds were also investigated in order to fully utilize activated carbon under operational conditions.

The design of contact systems and the prediction of their performance have been largely dependent on laboratory data for the equilibrium capacity of the activated carbon for the pollutant. Both the concentrations of dissolved oxygen and the composition of the wastewater amenable to treatment vary appreciably from one process to

another.

Discrepancies between equilibrium data obtained using the commonly employed bottle-point and column techniques have long baffled researchers although several explanations, such as irreversible adsorption, existence of easily accessible macropores and unaccessible micropores, and surface diffusion limitation have been postulated. Our limited understanding of the impact of dissolved oxygen (DO) on the adsorptive capacity of activated carbon may have contributed to this dependence of equilibrium data on the procedure of attaining equilibrium because DO in a continuous flow AC column is likely to differ from that prevalent in a closed bottle. In the literature review, it will be shown that the role of DO on the adsorption process has long been considered negative, but recently, work done in this university and elsewhere, has proven that the existence of DO has a positive effect on the adsorption of phenolics on activated carbon.

The broad objectives of this research are to ascertain the role of DO in the adsorption of organic pollutants by Granular Activated Carbon (GAC) and provide more insight into the nature of the oxygen induced-adsorption phenomenon. The specific objectives of this study are to:

1. Establish the dependance of the adsorption enhancement phenomenon due to dissolved oxygen on several chemical parameters such as group type, substitutes type, number of substitutions, and functional groups type.

2. Investigate the effect of oxidizing agents and their concentrations on adsorption.
3. Ascertain the effect of environmental and operational variables such as pH, temperature, and DO on adsorption equilibrium and kinetics.

4. Model the relation between the additional capacity and the dissolved oxygen content.

5. Test the predictability of breakthrough curves using the equilibrium and kinetic data obtained in batch experiments.

This is a fundamental research which will furnish invaluable insight into the oxygen-induced enhancement of the adsorption phenomenon. The outcome of this study will elucidate the role of molecular oxygen in the adsorption of pollutants on granular activated carbon as well as providing a comprehensive understanding of the effect of several water quality parameters and process design variables on the enhancement phenomenon. The findings of this study will not only be important from a theoretical viewpoint, but also from a practical standpoint. The concept of oxygen-induced improvement in adsorptive capacity may have tremendous economic implications. For example, increasing the dissolved oxygen in the influent wastewater to a GAC filter may furnish additional adsorptive capacity and significantly prolong filter runs. Increasing the dissolved oxygen in a powdered activated carbon treatment may increase the capacity by as much as 50-60% at very low concentrations.

1.2 Literature Review

Oxygen is known to react to a significant extent with activated carbon (1,2,3,4). It has been shown that carbons activated in an atmosphere of pure CO_2, or in a vacuum, react with molecular oxygen at and below room temperature, causing formation of organic oxygen functional groups on the carbon surface (1,2). Mattson et al. (5) detected the presence of significant amounts of carbonyl and carboxyl groups on acti-

vated carbon surfaces. The behavior of activated carbon as an adsorbent has to be related to surface functionality; the evidence for chemical interaction at the surface between carbonyl and carboxyl groups and organic adsorbates is convincing (6). Enhancement of the adsorptive capacity of activated carbon may well be accomplished by increasing the concentration of the appropriate surface functional groups.

While the issue of wastewater complexity and multi-solute adsorption has been addressed by numerous studies aimed at improving the understanding of the phenomenon of competitive adsorption, work towards elucidating the role of oxygen in the process of adsorption of organics has been limited. Prober et al. (7) found that molecular oxygen increases base sorption capacity due to the formation of acidic surface oxides. The same phenomenon was confirmed by Coughlin and Ezra (8) who observed reduction in adsorption capacity for phenol and nitrobenzene and Snoeyink et al. (9) who reported a 50% reduction in adsorptive capacity of phenol and nitrophenol due to the formation of acidic surface oxides.

Recently, Vidic et al. (10), and Nakhla et al. (11) have studied the effect of DO on the adsorption of phenolics by GAC. The standard static-bottle procedure was modified to include initial purging of the activated carbon and the adsorbate solution to obtain equilibrium data in the absence of oxygen. From both of the studies, it was reported that DO increased the capacity of activated carbon for phenolics by as much as 100%. In a study on phenol and o-cresol, Abuzaid and Harazin (12) concluded that when the sparger gases were carbon dioxide, the adsorbate solution which contained DO had about 40% increase in the retention capacity compared to the solution with zero DO concentration (CO_2 purged). The causes of this enhancement were investigated by Grant and King (13) and Vidic and Suidan (14). Both studies showed that dis-

solved oxygen promotes telomer formation of phenolics on the carbon surface.

Literature on the oxygen induced enhancement phenomenon of the adsorptive capacity are very recent as well as limited. For the purpose of good establishment of the phenomenon and the substantiation of previous work, several compounds should be studied. These compounds which should belong to different chemical groups are thus chosen according to their pollution potential, availability, and ease of analysis. Weber and Pirbazari (15) studied the adsorption characteristics of benzene, p-dichlorobenzene, carbon tetrachloride, dieldrin and two PCBs in water. The Freundlich model was found to fit the equilibrium data accurately, and the constants were calculated and used as inputs in the Michigan Adsorption Design and Application Model (MADAM) for the kinetic determination. Eldib and Badawi (16) found that the adsorption of benzene, toluene, o-xylene, and ethylbenzene on activated carbon proceeded in accordance with the Freundlich model. Model constants as well as the coefficients of determinations were calculated and listed.

Moreover, there are several variables which greatly affect the performance of GAC and are usually studied; most important are the pH of the solution, temperature, initial concentration of the adsorbates, flow rate of adsorbate solution, and competition of solutes on the surface of GAC. In general, adsorption of typical organic pollutants from water is increased with decreasing pH. Garten and coworkers (17,18,19) have shown that acid and alkali sorption is related to surface functional groups which form during the preparation of the carbon. Alkali-sorption occurs principally on carbons activated at temperatures near 400°C while, acid sorption occurs on these activated at 1000°C. Weber (20) studied the effect of pH on adsorption in an activated carbon column. A solution of sulfonated alkyl-benzene with an unadjusted pH slightly below neu-

tral was passed through the column until the ratio of effluent concentration to influent concentration (C/C_0) reached 0.55. At this point the pH was decreased to 2.5. The effect of the reduced pH was to considerably increase adsorption and sharply decrease the concentration of the solute escaping in the effluent. The removal of fluoride from water by activated carbon was investigated by Wu (21), who reported that the highest capacity simulated by the Langmuir isotherm was at pH 5.0.

Alhert and Gorgol (22) investigated the adsorption of the supernatant of two landfill leachates on GAC. The supernatant exhibited a weak pH effect on the adsorptive capacity of GAC for TOC with the adsorptive capacity at pH 7 greater than at pH 12. A differential bed reactor was used to determine the kinetic of the removal of orthophosphates from wastewater by activated carbon by Koh and Chung (23). The kinetic reaction at a pH of 4 was faster than at pH 8 and 12. Unlike the findings of most researchers, Herzing et al. (24) reported no major effect of pH on the adsorption of 2-methylisoborneol and geosmin (Q) on activated carbon.

Physical adsorption is an exothermic process, thus the extent of adsorption generally increases with decreasing temperature. By comparing viable cell counts in activated carbon columns operated at 5° and 25°C, Maqsood and Benedek (25) showed that the greater total organic carbon removals occurring at higher temperatures was partially due to a larger preponderance of microbes. Alben et al. (26) observed decreases in the adsorption capacity of trihalomethanes on granular activated carbon with increasing temperature in the range of 4 to 45°C.

Recent literature on the effect of temperature on the enhancement is conflicting. While Vidic et al. (14) found that temperature variations had no effect on the enhancement, Grant and King (13) found that higher temperature enhances the telomerization

reaction and hence increases the adsorption capacity. In the same study, it was found that these reactions are favored by higher pH conditions. However, in their experimental scheme, effect of pH and temperature was not separated from the effect of dissolved oxygen. Very extreme values, such as pH values of 1.8 and 12, and temperatures as high as 80°C were studied. Furthermore, the effect of pH was studied at a temperature of 80°C. These pH and temperature ranges pertain more to chemical engineering applications and are unrealistic in waste treatment systems.

Another important variable is the presence of a number of compounds that are simultaneously adsorbable on GAC in the solution. These compounds may mutually enhance adsorption, may act relatively independently, or may interfere with one another. The effect of having a mixture of solutes compared to a single solute depends on the nature and characteristics of the competing solutes. In this regard, Weber (20) concluded from a column study that the presence of other solutes in the mixture adversely affects the adsorption of the first, leading to a much more rapid breakthrough of this material. Martin and Al-Bahrani (27) showed from batch experiment that the overall carbon capacity for adsorption was barely affected by an increase in the number of solutes in solution, whereas in column experiments the overall carbon capacity for adsorption was considerably enhanced by an increase in the number of solutes in solution.

The dependance of adsorption on flow rate was studied by several researchers. Bhargava et al. (28) investigated the adsorption kinetics of phenol in a countercurrent carbon system which maximized the adsorptive capacity of activated carbon. The system achieved 40-70% removal with % removal decreasing with increasing flow rates. McKay (29) found that the capacity of a fluidized bed of activated carbon for acidic

and alkaline dyes increased with a decrease in the flow rate of the dye solution.

McKay developed a model to determine the external mass transfer coefficient of pollutants from water onto activated carbon (30). Agitation, initial pollutant concentration, carbon mass, carbon particle size, and solution temperature were variables used to evaluate the two constants in the dimensionless equation developed. The surface mass transfer coefficients for the adsorption of acidic and basic high tinctorial dyes varied linearly with agitation, initial dye concentration and contact time; reciprocally with absolute temperature; and independently with dye solution pH between 5.2 and 8.5 (31,32).

The HSDM model derived by Rosen (33) has been successfully used to model the dynamics of adsorption for various compounds on GAC (34,35,36). In contrast to the pore diffusion model (PDM) (37), where the adsorbate is assumed to diffuse into a liquid phase within the carbon particle and equilibrate locally along the pore wall, the HSDM assumes that molecules creep along the inner surface and migrate into the particle in the adsorbed state. Equilibrium between liquid phase and solid phase adsorbate concentration is assumed to exist only at the outer surface of the adsorbent particle. The mathematical formulation of the HSDM is readily available in the literature (33,34,35) and will be presented later in this chapter.

Besides equilibrium data that are normally fitted to Freundlich or Langmuir isotherms, knowledge of the values of kinetic parameters is necessary in order to accurately describe the performance of adsorbers. Closed batch tests are often performed for this task. The liquid-film mass transfer coefficient, k_f , and the surface diffusion coefficient, D_s are then found by minimizing the differences between data and model output. This minimization procedure is usually done by intuitively varying the kinetic coefficient in

the mathematical model until the experimental data and model results agree satisfactorily (34,35). This method works well if only one unknown parameter has to be determined (k_f or D_s alone), but becomes more troublesome if several parameters have to be found simultaneously.

When surface diffusion is the limiting transport mechanism, Hand et al. (38) have developed a procedure for determining surface diffusion coefficients by experimentally eliminating the liquid film resistance and comparing empirical solutions of the HSDM model and batch adsorption data. The procedure developed is as follows:

1. conduct isotherm tests and determine Freundlich isotherm parameters,
2. calculate dosage of adsorbent required to achieve a C_e/C_o equal to 0.5 ,
3. conduct rate tests at several mixing intensities and demonstrate experimentally that liquid-phase mass transfer resistance has been eliminated.
4. after that, calculate model predicted dimensionless times using developed empirical equations.
5. calculate the Biot number based on determination of local diffusivity.
6. check if the Biot number is greater than a table value. If it is not, then the rate test should be repeated at a higher mixing intensity.
7. calculate the residual sum of squares (S^2) for several values of D_s and plot (S^2) versus D_s. Estimate D_s where S^2 is the lowest (S^2_{min}) which is the best estimate for D_s, and calculate the 95 % confidence interval for the D_s estimate. Check and ensure that S_{min} is less than 0.1, if it is not, then causes of errors, such as excessive scatter in the rate test data, should be evaluated. If necessary, rerun isotherm and rate studies, or both.
8. plot the best fit D_s model simulation versus the data.

9. the D_s values required for model simulations are D_s for the best fit and the D_s values which bracket the 95% confidence interval.

In instances where surface diffusion is the rate limiting transport mechanism, liquid film mass transfer coefficient can be estimated from generalized correlations (39). The shortcoming of both methods, however, is that it is not always possible to establish conditions during an experiment that permit the separate determination of kinetic parameters. This is specially true when kinetic parameters are to be evaluated for new conditions like in the case of the proposed study where several variables such as pH, temperature, and DO concentration interact and influence the adsorption process. In this study, the procedure developed by Traegner and Suidan (40) will be used for the determination of the diffusivity coefficients for the cases under study. Their procedure uses the Levenberg-Marquardt numerical algorithm to accomplish this task. Unlike standard procedures where only one of the kinetic parameters, either k_f or D_s, is determined, the proposed method allows for simultaneous estimation of batch kinetic constants. Such a computerized procedure is useful since the results of batch kinetic tests usually fall in the range of 1 to 100 (40), where mass transport is influenced by both liquid mass transfer and intraparticle mass transfer resistance. With the help of the residual surface plots it was shown that the solution optimum to the HSDM is unique, i.e there exists one unique set of parameter values where the model solution best fits the experimental data. However, care must be exercised in accepting iterated parameters. Numerical values obtained for k_f if the Biot number $>>$ 100, should be rejected as inaccurate since at this Biot number only intraparticle mass transport is the dominant factor.

Continuous-flow operations have advantages over batch-type operations because

rates of adsorption in batches depend upon the concentration of adsorbate in solution, and because they are capable of treating large volumes of wastewaters (41). Most continuous-flow systems are operated as fixed-bed adsorption columns. Fixed-bed adsorbers may be operated in either the upflow or downflow mode. In downflow systems the carbon can serve for adsorption and for filtration of suspended solids, and hence, is used when the wastewater contains suspended solids (42).

A substantial fraction of the time and expense associated with planning and designing adsorption facilities is involved in predicting or forecasting the operational dynamics of the process (38). Extensive experimental studies to examine the effect of each system variable on the adsorption process is needed. Inspite of the long duration and high costs for such pilot studies, they fail some times to predict adsorbers behavior (34). The need for pilot scale column studies arises from the fact that no rational design basis utilizing the fundamental adsorptive properties of GAC (i.e equilibrium and kinetics) exists. Scale-up from laboratory to pilot scale is likely to be erroneous given the discrepancies between isotherms and column capacities (43,44,45,46). This discrepancy was attributed to the irreversibility of the adsorption process (43), to a decline in the intraparticle diffusivity during the later part of a breakthrough experiment (44), and to the continuously decreasing adsorbate concentration in the liquid phase during an isotherm experiment (45).

To reduce the time and expense associated with the pilot-plant studies, several mathematical models have been developed to forecast the impact of process variables on adsorber performance. These fixed-bed adsorber models differ in the way they describe possible combinations of external and internal mass transfer resistances, nonlinearity of adsorption isotherms, and axial dispersion. Weber and Chakrovorti (37) and Fritz and Schluender (47) proposed a combination of surface diffusion and pore

diffusion transport, which they assume take place simultaneously. This model is known as the heterogenous diffusion mode or pore and surface diffusion model. The shortcoming of the latter model is that surface and pore diffusion parameters cannot be determined uniquely.

Fixed-bed adsorber dynamics have been predicted successfully using the HSDM model for over 100 adsorbate-adsorbent systems which included a number of organics found in drinking water and wastewater treatment (38). Concentration history profiles for complex mixtures such as humic substances, expressed in terms of surrogate parameters such as Total Organic Carbon (TOC), single components with or without background organics, and multicomponent systems have been predicted using the HSDM model (38). Accordingly, the HSDM model can be used as an effective engineering tool for preliminary design purposes and if available to design engineer, it may be used for: 1) to plan the scope of pilot-scale studies, 2) interpret pilot-scale test results, 3) investigate multistage adsorber configuration, and 4) estimate preliminary costs of fixed bed adsorbers (38). Many researchers reported the disagreement between the GAC adsorptive capacities determined from isotherm runs and from column and batch experiments (43,44,45,46). As a result, serious problems were experienced in attempting to use the single-rate HSDM model to predict GAC adsorber breakthrough curves (BTC's) for some adsorbate adsorbent systems. Crittenden and Weber (34) had to adjust the adsorptive capacity of activated carbon as given by the adsorption isotherm in order to fit column breakthrough data. Furthermore, they assumed the ratio of the capacities given by that new pseudo isotherm and the isotherm obtained using the standard bottle-point technique to be constant. Later, Liu and Weber (43) concluded that only column studies can be used to determine single-solute adsorption isotherms that would permit accurate prediction of BTC's. Seidel and Gelbin (48) and Liu and

Weber (43) noted that during BTC experiments the effluent adsorbate concentration approaches some asymptotic value that is below the influent concentration.

Peel and Benedek (49) proposed a dual-rate kinetic model that assumes the existence of two types of pores within the carbon particle: macropores, where fast adsorption occurs, and micropores which contribute to the removal of adsorbate in the latter part of a column ru The shortcoming of this model was that the distribution of pore volume between macropores and micropores was found to depend on the liquid-phase adsorbate concentration.

1.3 Theoretical Background

1.3.1 Adsorption Isotherms

An adsorption isotherm specifies the equilibrium surface concentration of adsorbate on adsorbent as a function of bulk concentration of adsorbate in solution. It is called an isotherm because it describes the equilibrium state of adsorbate, adsorbent, and solute at a given temperature as implied by the name. The Langmuir adsorption isotherm describes reversible equilibrium between a surface and solution. The adsorbent surface is considered to be made up of identical individual sites where molecules of the adsorbate are physically bound. The Langmiur equation is:

$$q = \frac{Q_1 bC}{1 + bC} \qquad (1.1)$$

where;

q = adsorbed solute, mg/g

C = final liquid phase concentrations of adsorbate in solution, mg/l

Q_1 = maximum number of mg adsorbed per gms adsorbent when the surface sites are saturated with adsorbate (i.e., a full monolayer) Langmuir isotherm constants, and

b = empirical equilibrium constant related to the energy or net enthalpy of adsorption with units of inverse concentration.

The Langmuir model can be transformed to the following linear forms in order to determine model parameters :

$$\frac{1}{q} = \frac{1}{Q_1 * b}\frac{1}{C} + \frac{1}{Q_1} \qquad (1.2)$$

or

$$\frac{C}{q} = \frac{1}{Q_1 * b} + \frac{C}{Q_1} \qquad (1.3)$$

The Langmuir adsorption isotherm has found wide applicability to adsorption of compounds in water treatment. Its advantages include simplicity, physical basis, and ability to fit a broad range of experimental data. Its limitations include (1) the assumption that the energy of adsorption is independent of degree of coverage, and (2) allowance for at most only one monolayer. The mass adsorbed, q, is assumed to approach a saturation value, Q', when C becomes very large

The Langmuir model incorporates an assumption that the energy of adsorption is the same for all surface sites and not dependent on degree of coverage. In reality, energy of adsorption may vary because real surfaces are heterogeneous. The Freundlich adsorption isotherm attempts to account for this. Assuming that the frequency of sites associated with a free energy of adsorption decreases exponentially with increasing free

energy, one can demonstrate that the isotherm will have the form:

$$q = kC^{1/n} \tag{1.4}$$

where; k and n are constants. The log-log plot of q against C for this equation is linear. The intercept, k, is roughly an indicator of sorption capacity and the slope, n, of adsorption intensity. The Fruendlich equation generally, agrees quite well with the Langmuir equation and experimental data over moderate ranges of concentrations. Unlike the Langmuir equation, however, it does not reduce to a linear adsorption expression at very low concentrations and is thus not thermodynamically sound. Nor does it agree well with the Langmuir equation at very high concentrations, since n must reach some limit when the surface is fully covered. Here, the surface concentration of adsorbate does not approach a saturating value as C increases, since there are always surface sites with higher free energies of adsorption to fill. The Freundlich isotherm is very widely used to fit observed data empirically even when there is no basis for its underlying assumptions.

In water treatment the ideal case of one adsorbate being removed onto an adsorbent is seldom encountered; the objective of adsorption in most real systems is to remove several adsorbates. This complicates both, the theoretical picture of equilibrium among adsorbates and adsorbent and the ability of the engineer to apply the theory in practice. The Langmuir model may be generalized from single- to multi-component adsorption. The assumptions for specific sites, reversible adsorption, and homogeneous free energies of adsorption remain the same as for the case of a single component but are now applied to several adsorbates so that the mass of adsorbate i is given by:

$$q_i = \frac{Q_1 b_i C_i}{1 + \sum_{i=0}^{n} b_i C_i} \qquad (1.5)$$

Using this equation, one can in theory estimate the equilibrium capacity of an adsorbent for a complex mixture of compounds from the constants determined for a single solute.

1.3.2 Kinetics of Adsorption.

One of the main requirements for the design of a GAC adsorption system is a knowledge of the kinetics of the adsorption process. Many mathematical models have been developed to describe adsorption on activated carbon. The most widely used are the Homogenous Surface Diffusion Model (HSDM) and the Pore Diffusion Model (PDM). The following are general simplifying assumptions that apply to both models:

1. The adsorption process is isothermal and reversible.
2. Transport inside the particle is only due to diffusion of the adsorbate.
3. Instantaneous equilibrium occurs at active adsorption sites.
4. Particles are assumed to be spherical and isotropic.

Both models assume the presence of a stagnant liquid film layer surrounding the carbon particle, through which the adsorbate diffuses before reaching the outer carbon surface.

1.3.2.1 Pore Diffusion Model (PDM)

A schematic representation of the adsorption process on a carbon particle using the mechanism assumed by the PDM is shown in Figure 1.1.

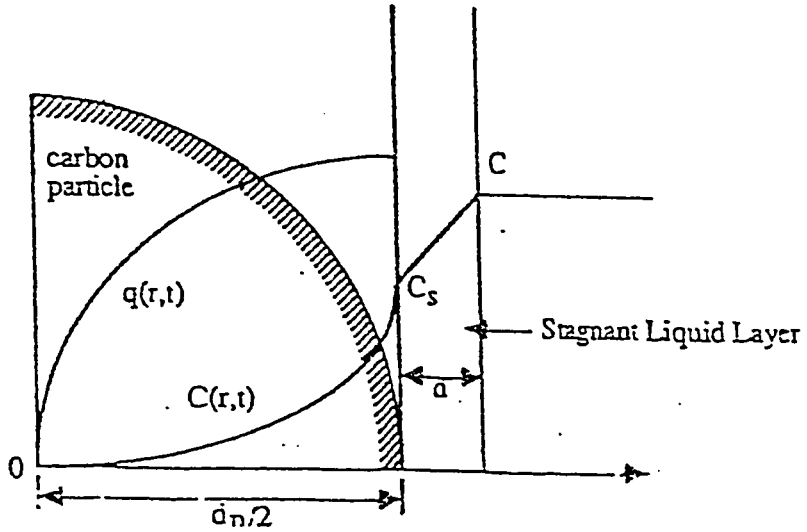


Figure 1.1: Schematic Representation of the PDM Model

The main assumption of the Pore Diffusion Model is that, after diffusing through the stagnant liquid film layer, the adsorbate diffuses through the aqueous phase inside the pore of the carbon particle and reaches instantaneous equilibrium with the solid concentration of the adsorbate on the inner surface of the pore. Therefore, the two possible rate limiting steps in the adsorption process are the diffusion of the adsorbate through the stagnant liquid layer surrounding the carbon particle, characterized by the external mass transfer coefficient, k_f, and the diffusion of the adsorbate through the liquid phase inside the pores, characterized by the pore diffusion coefficient, D_p.

The equation describing the pore diffusion of adsorbate into a spherical granule is given by:

$$\rho_p \frac{\partial q}{\partial t} + \varepsilon_p \frac{\partial C_p}{\partial t} = D_p \left(\frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right) \tag{1.6}$$

where;

ρ_p = density of the carbon particle, M/L^3,

q = carbon loading, M adsorbate/M adsorbent,

ε_p = particle porosity,

D_p = pore diffusion coefficient, L^2/T,

C_p = pore liquid-phase concentration, M/L^3,

r = distance from the center of the spherical particle, L.

The two boundary conditions for the above equation are:

$$@\ r = 0, t: \quad \frac{\partial C_p}{\partial r} = 0 \tag{1.7}$$

and,

$$@\ r = r_0: \quad D_p \frac{\partial C_p}{\partial r} = k_f (C - C_s) \tag{1.8}$$

where;

d_p = diameter of the spherical GAC particle, L,

C = bulk liquid concentration, M/L^3,

C_s = adsorbate in the liquid film at the solid-liquid interface, M/L^3,

k_f = external mass transfer coefficient, L/T.

The initial condition for Equation 1.7 is

$$@\ t = 0, 0 \le r \le r_0: \quad C_p = 0 \tag{1.9}$$

The first term of the right hand side of Equation 1.6, describing the solid phase storage capacity, is much larger than the second term describing the liquid phase storage capacity. Therefore, one way of simplifying Equation 1.6 is by approximating the two terms by the first term only. Another simplifying procedure is to substitute C_p by q using an isotherm relationship.

1.3.2.2 Homogeneous Surface Diffusion Model (HSDM)

A schematic diagram describing the adsorption profile of an adsorbate on a carbon particle using the mechanisms assumed by the HSDM is shown in Figure 1.2 The HSDM is based on the assumption that equilibrium between the carbon and the adsorbate occurs only at the outer surface of the carbon particle, and that the adsorbate then migrates along the inner carbon surface to available active sites.

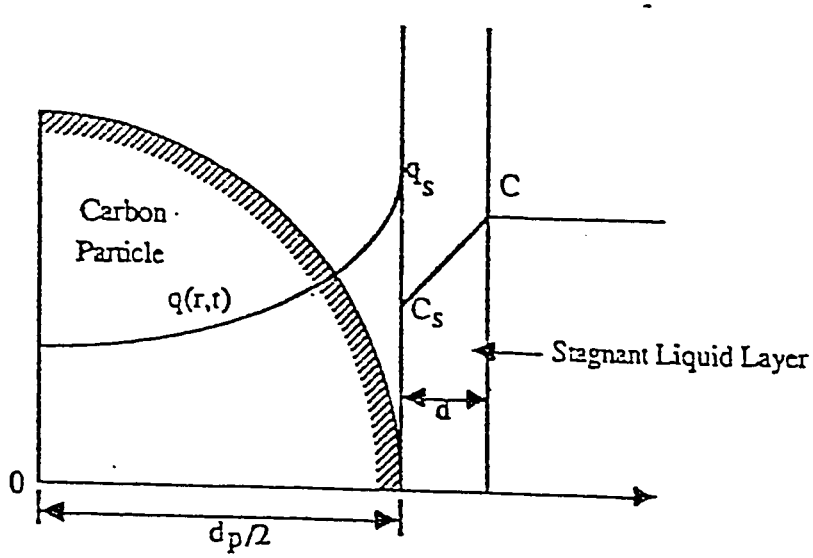


Figure 1.2: Schematic Representation of the HSDM Model

The kinetic parameters incorporated in this model are the stagnant liquid film mass transfer coefficient, k_f, which describes the rate of diffusion of the adsorbate through the stagnant liquid film layer around the carbon particle, and the surface diffusion coefficient, D_s, which describes the rate of diffusion of the adsorbate on the carbon surface.

The equation describing the surface diffusion of adsorbate into a spherical granule is given by:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) \tag{1.10}$$

where;

q = carbon loading, M adsorbate/M adsorbent,

D_s = surface diffusion coefficient assumed independent of concentration, L^2/T,

r = distance from the center of the spherical particle, L.

The initial condition (Equation 1.11) assumes the presence of no adsorbate in the particle, while the boundary conditions (Equations 1.12 and 1.13) state that the flux at the center of the particle is always equal to zero because of symmetry, and that the rate of adsorption into the particle is equal to the flux of adsorbate from the stagnant liquid.

$$@\ t = 0,\ 0 \le r \le r_0 :\ q = 0 \tag{1.11}$$

$$@\ t \ge 0,\ r = 0:\ \frac{\partial q}{\partial r} = 0 \tag{1.12}$$

$$@\ t \ge 0,\ r = \frac{r_0}{2} :\ 4\pi r_0^2 \int_0^t \left(-D_s \frac{\partial q}{\partial r}\right) dt = V_l (C_0 - C) \tag{1.13}$$

The HSDM assumes that an equilibrium relationship is only satisfied at the outer surface of the particle. Therefore the boundary condition for Equation 1.13 is the isotherm

equation at the outer surface:

$$@\ r = \frac{r_0}{2}:\ C_s = f(q_s) \tag{1.14}$$

1.3.2.3 Packed Bed Kinetics

Crittenden and co-workers (34) have developed the homogeneous surface diffusion model (HSDM). The following assumptions are made in the fixed bed model:

1. There is no radial dispersion or channeling
2. Surface diffusion flux is much bigger than pore diffusion flux. Therefore, pore diffusion flux is neglected. In addition, the adsorbent is assumed to be homogeneous and the surface diffusion flux can be described by Fick's law: Flux = $-D_s(\frac{\partial C}{\partial x})$
3. The liquid phase diffusion flux can be described by the linear driving force approximation, using estimates for the film transfer coefficient k_f
4. The adsorbent is fixed in the adsorber (back-washing is not considered).
5. Adsorption equilibria can be described by the Freundlich isotherm.
6. Plug flow exists within the bed.

Dimensionless groups are defined to simplify solution of the differential equations and reduce the number of independent variables. Mass throughput or dimensionless time is defined as:

$$T = \frac{\text{rate of mass of adsorbate fed}}{\text{total mass of adsorbate at equilibrium}}$$

$$= \frac{QC_0t}{Mq_e + \varepsilon VC_0}$$

where;

Q = influent flowrate, L^3/T

C_0 = fluid phase concentration of adsorbate in influent, M/L^3

t = elapsed time, T

M = total mass of adsorbent in the bed, M

q_e = adsorbent phase concentration at equilibrium with C_0, in the fluid phase, M adsorbate/ M adsorbent

ε = ratio of void volume to total bed volume

V = total bed volume, L^3

The dimensionless solute distribution parameter D_g is defined as

$$D_g = \frac{\text{mass of adsorbate in solid phase at equilibrium}}{\text{mass of adsorbate in liquid phase at equilibrium}} = \frac{\rho_a q_e (1 - \varepsilon)}{\varepsilon C_0}$$

where, ρ_p = pellet density (includes pore volume)

The dimensionless Biot number, B_i, is defined as:

$$B_i = \frac{\text{rate of liquid phase mass transfer}}{\text{rate of surface diffusion within the particle}}$$

$$= \frac{(1 - \varepsilon) k_f r_0}{\varepsilon D_s D_g \theta_1}$$

where;

k_f = film transfer coefficient, L/T

D_s = surface diffusion coefficient, L^2/T

θ_1 = sphericity (dimensionless ratio of the surface area of the equivalent volume sphere to the actual surface area of the particle).

r_0 = particle radius, L.

The modified Stanton number, St, is a dimensionless measure of the bed length as compared to the length of the mass transfer zone in the case where liquid phase mass transfer resistance controls the adsorption rate:

$$St = \frac{k_f \tau (1 - \varepsilon)}{r_0 \varepsilon \theta_i}$$

where, τ = hydraulic residence time in the bed.

The surface diffusion modulus B_d is a dimensionless measure of bed length compared to the length of the mass transfer zone in the case where intraparticle diffusion controls adsorption rate:

$$B_d = \frac{D_s D_g \tau}{r_0^2} = \frac{St}{B_i}$$

Assuming the adsorbent phase, including the pore volume is homogeneous solid, the surface diffusion flux J_s is

$$J_s = -D_s \rho_p \frac{\partial q}{\partial r}$$

A mass balance for the adsorbate in the solid phase system is

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r}\right) \qquad (1.10)$$

where;

r = distance from the center of the spherical particle, L.

t = time.

The initial condition (Equation 1.12) assumes the presence of no adsorbate in the particle, while the boundary conditions (Equations 1.13 and 1.19) state that the flux at the

center of the particle is always equal to zero, and that the rate of adsorption into the particle is equal to the flux of adsorbate across the stagnant liquid layer.

$$@\ t = 0, 0 \le r \le \frac{r_0}{2} :\ q = 0 \tag{1.11}$$

$$@\ t \ge 0, r = 0: \frac{\partial q}{\partial r} = 0 \tag{1.12}$$

$$@\ t \ge 0, (r = r_0, t): \frac{\partial q}{\partial r} = \frac{k_f}{\rho_p D_s \theta}(C - C_s) \tag{1.15}$$

Assuming the linear driving force approximation. The liquid phase mass flux J_1 can be written as $J_1 = k_f(C_b - C_s)$, where, C_b = bulk fluid phase concentration of adsorbate.

The mass balance equation for a packed bed exhibiting plug flow is

$$\frac{\partial C}{\partial t} = - V\frac{\partial c}{\partial Z} - \frac{3(1 - \varepsilon_B)}{r\ R} k_f (C - C_s) \tag{1.16}$$

where,

V = interstitial velocity

Z = longitudinal dimension

The initial condition of Equation 1.16 is

$$@\ t < \tau, L_0 \le Z \le L_B :\ C = 0$$

and the boundary condition is

$$@\ t \ge 0, Z = 0 :\ C = C_0$$

To couple the solid and liquid phase mass balance equations, the surface concentration of adsorbate in the liquid phase $C_s(t)$ must be expressed in terms of the surface concentration of adsorbate in the solid phase $q(r = R, t)$. This equation is developed from the assumption of local adsorption equilibria adjacent to the exterior adsorbent surface, as described by the nonlinear Freundlich isotherm

$$q = KC_s^{1/n}$$

The three main equations contain three independent variables, mass throughput T, radial position r, and axial position Z. Dependent variables are liquid phase concentration C(Z, T), liquid phase concentration at the exterior surface of the adsorbent C_s (Z, T), and solid phase concentration q(r,Z,T). Simultaneous solution of the system of equations results in a predictive model of fixed bed concentration history profiles for a given set of physical and chemical properties. Those equations cannot be solved analytically. Solutions may be obtained using orthogonal collocation techniques (35). This numerical method reduces the system of partial differential equations to a set of ordinary differential equations which may be integrated.

1.4 Research Outline

Stage I

Enhancement of the adsorptive capacity of activated carbon caused by the presence of oxygen is barely established, mainly, because very few compounds were studied. Hence, in the first stage of the research, it is proposed to conduct isotherm studies for several compounds. Alkylphenolics, alkylaliphatics, and wastewater from a petrochemical industry and domestic sources will be investigated. The selected compounds are

listed in Table 1.1. These synthetic organic compounds are selected for the purpose of this study because they are common constituents of industrial wastewater effluents, particularly, in oil and petrochemicals related industries (50), as well as being potentially hazardous to human beings and hence, appear on the priority pollutants list (50). Concentrations as low as 1 mg/l are considered hazardous (51, 52) and have even been detected in drinking water (53, 54). Since some of those compounds are known by some common names. Table 1.2 lists their common names and structural formulas, and facilitates a comparison between the compounds.

The choice was also designed to investigate the dependance of the adsorption enhancement phenomenon on the following chemical parameters:

1. types of compounds (aromatics versus aliphatics).
2. functional groups (phenolics versus alkanes).
3. number of identical alkyl derivatives (tri. versus tetra.).
4. type of substitution (methyl versus nitro, chloro versus bromo).

For each of the above compounds, two isotherms (zero and saturation level of dissolved oxygen) were conducted under room temperature, neutral pH. Comparative analysis of the data is used to assess the impact of the aforementioned parameters on the adsorption enhancement.

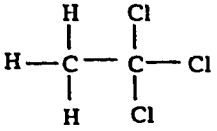
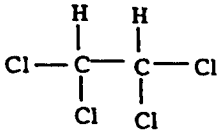
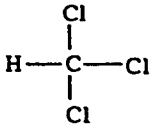
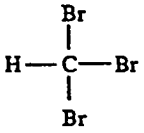
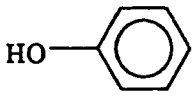
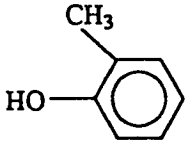
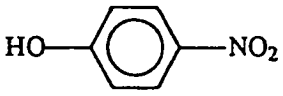
Stage II

This stage will address the role of oxidizing agents such as hydrogen peroxide and potassium permanganate on the adsorption process. For each of the oxidizing agents two isotherms (zero and concentration equivalent to saturation level of pure dissolved oxygen) are conducted under room temperature at neutral pH.

Table 1.1 Chemical Compounds Involved in Stage 1.

Aliphatics	Alkylphenols	Wastewater
1,1,1-Trichloroethane	Phenol	domestic
1,1,2,2-Tetrachloroethane	1-Methylphenol	petrochemicals
Trichloromethane	2-Nitrophenol	
Tribromomethane		

Table 1.2: Compounds Common Names and Structural Formulae

Compound	Common Name	Structural Formula
1,1,1-Trichloroethane	Methylchloroform	
1,1,2,2-Tetrachloroethane		
Trichloromethane	Chloroform	
Tribromomethane	Bromoform	
Phenol		
2-Methylphenol	o-Cresol	
4-Nitrophenol		
Domestic Wastewater		
Petrochemical Wastewater		

Stage III

On the basis of the isotherms study, two compounds namely phenol and o-cresol are chosen for further testing. The choice is on the basis of highest attainable percentage improvement in adsorptive capacity. In this stage, research is focussed on investigating the effect of different operational variables on the enhancement phenomenon. Isotherm as well as batch kinetic studies are conducted for two levels of dissolved oxygen (zero and saturation). Those levels are chosen because they are expected to amplify the difference in the adsorption capacity. After investigating the enhancement phenomenon under different levels of each variable, one level will be chosen and denoted as optimum. The choice of the optimum value for each variable will be based on two criteria; first, maximum enhancement in the adsorption capacity; and second, relative to prevalent conditions of industrial effluents. From the equilibrium data, an attempt is made to relate the additional capacity to the dissolved oxygen level. Following are the variables studied ;

1. pH

The effect of pH is assessed by running adsorption experiments under room temperature at pH levels of 3, 7, and 11. Deionized water is buffered at the required pH using a suitable buffer. After the addition of the buffer, the specific pH is reached by careful addition of a strong acid or base.

2. Temperature

Temperature dependance of the adsorption enhancement phenomenon is investigated by running adsorption experiments for temperatures of 8°C, room temperature

(about 21°C), and 35°C under the optimum pH found earlier. Temperature controlled water baths are used in order to maintain the required temperature.

3. Effect of Different Levels of Dissolved Oxygen

Four levels of dissolved oxygen are chosen, the effect of those levels on the adsorption capacity is investigated under neutral pH and room temperature. DO levels of zero, moderate, saturation with air, and saturation with pure oxygen were chosen.

Stage IV

In this stage, column studies are performed under oxic and anoxic conditions at room temperature and neutral pH. The experimental results are compared with those predicted using the equilibrium, and kinetic data obtained from stage III.

The thesis will be divided to eight chapters. Chapter 1 is the introduction, chapter 2 is the experimental procedure, while, the isotherm studies are presented in chapters 3, 4, and 5. Chapter 3 is about the relation of the phenomenon (enhancement in the uptake) with the types of chemical compounds, chapter 4 is about the effect of pH and temperature on the phenomenon, and chapter 5 is related to the response of different DO levels to the enhancement in uptake. Chapter 6 deals with the kinetics related to the effect of DO, while, chapter 7 is about the effect of DO on adsorption columns. Finally, Chapter 8 will include conclusions and recomendations for further research.

Chapter 2

APPARATAS AND EXPERIMENTAL PROCEDURE

2.1 General

2.1.1 Chemicals and Materials

The adsorbate chemicals (phenol, o-cresol, 4-nitrophenol 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloromethane, and tribromomethane) of Analytical Grade (ANALAR) quality were obtained from Fisher Scientific, USA. Methylene chloride and ethanol were used in the extraction experiments as received from Fisher Scientific.

Activated carbon was purchased from Fisher Scientific, USA. Table 2.1 gives the physical properties of the carbon used.

2.1.2 Apparatus

2.1.2.1 Shakers

Karl Kolb shakers, purchased from Scientific Technical Supplies, West Germany, were used in the loading experiment. The shakers were equipped with temperature control from zero to 100°C and a variable shaking frequency.

Table. 2.1 Physical Properties of Filtrasorb-400 Activated Carbon

Total Surface Area (N_2 BET Method), m^2/g	824
Bulk Density, g/cm^3	0.74
Particle Density Wetted in Water, gm/ cm^3	1.3-1.4
Pore Volume, cm^2/gm	0.94
Effective Size (d_{10}), cm	0.055-0.065
Uniformity Coefficient (d_{60}/d_{10})	1.6-2.1
Particle Size Used in Experiments (d_o), cm	0.156

2.1.2.2 Mixers

Six closed mixers were manufactured in the KFUPM workshop. They were made from plexy glass with a volume of 5 liters. The GAC particles were trapped in a basket around the wall of the mixer, and the liquid was agitated by mixers at 200 rev/min. The system was sealed with facilities to measure temperature and withdraw samples for measurements. The mixer temperature was controlled by water circulating from temperature controlled water baths in surrounding water jackets. Figure 2.1 shows a schematic diagram of the kinetics experimental setup.

2.1.2.3 Columns

Four plexy glass columns (60 cm long and 2.54 cm I.D.) were manufactured and placed on a wooden frame. One variable speed pump with four heads was used to transfer the adsorbate to the columns. The feed solution was placed in barrels with about 200 L capacity. The barrels were sealed from the atmosphere and connected to plastic bags containing oxygen or nitrogen in order to keep the proper head space. Figure 2.2 shows a schematic diagram of the column setup.

2.1.2.4 GC-MS

The samples were analysed using the HX100 (JEOL, Japan) mass spectrometer equipped with a Carlo Erba (Italy) gas chromatograph. The gas chromatograph was equipped with a split/spiltless injector at 250°C. The column was DB-1, 25 m x 0.25 mm i.d., with a 0.3 μm film thickness. The carrier gas was Helium at a flow rate of 6 mL/min. The oven temperature was programmed from 50°C to 300°C at 10°C /min with a zero initial time and 5 min. final time. The ion source temperature was 250°C, the emission was 100 μA, and the acceleration voltage was 5 KV.

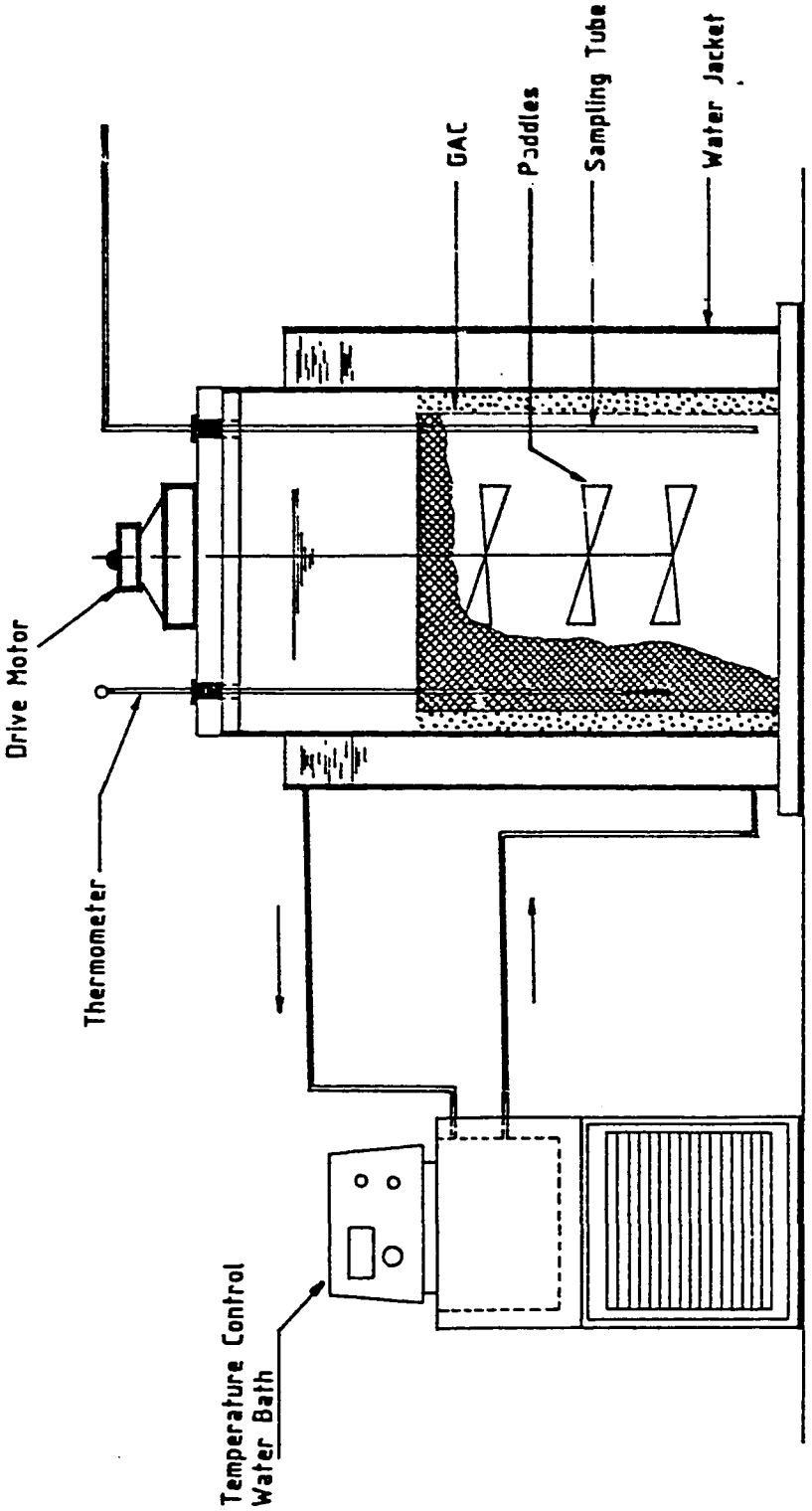


Figure 2.1: Schematic Diagram of the Kinetics Experimental setup

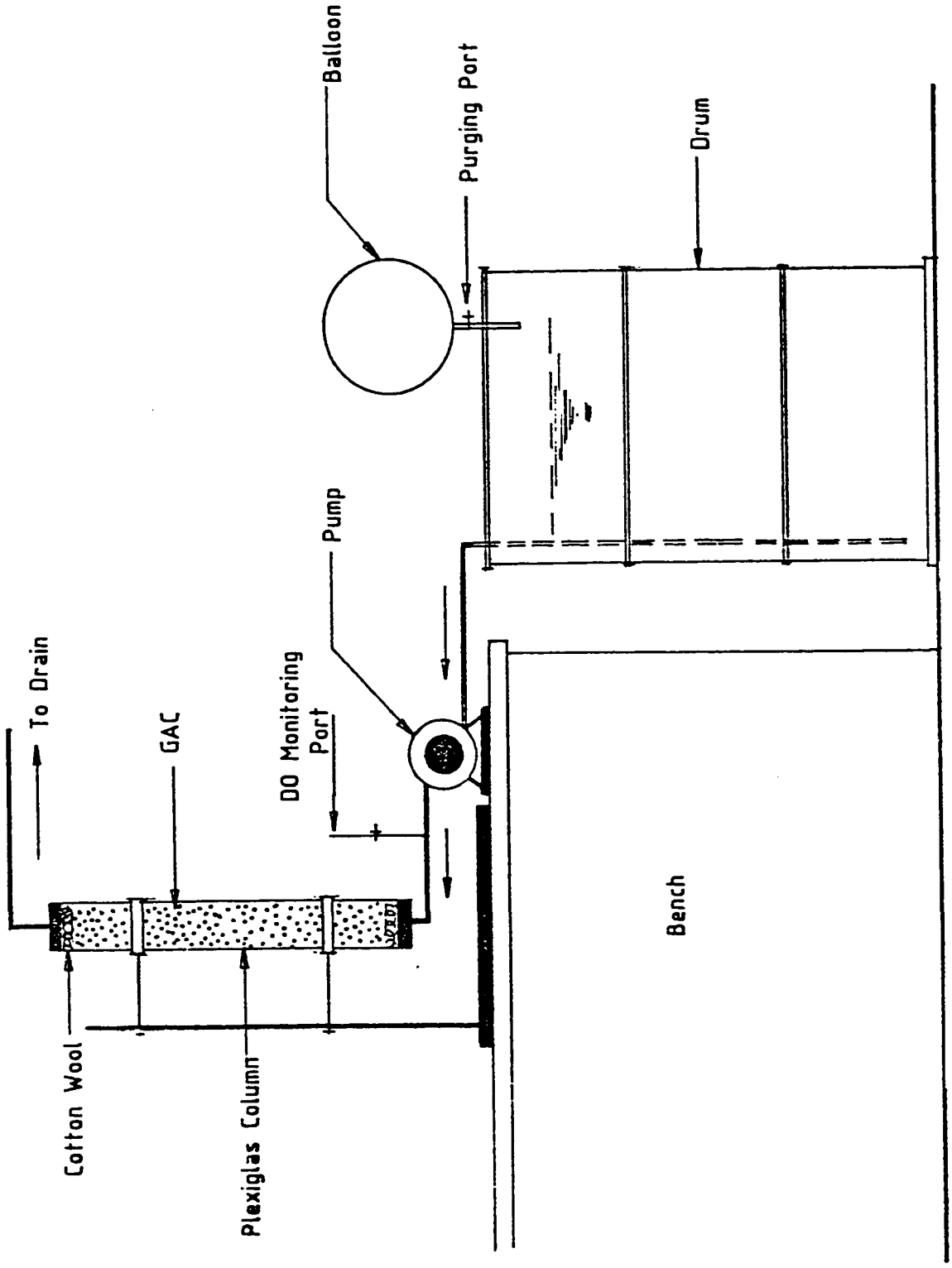


Figure 2.2: Schematic Diagram of the Columns setup

Data acquisition was carried out with a DS5000 data system. For qualitative analysis of the sample, data were acquired for 30 min. For quantitative analysis of phenol yield, data acquisition was carried out for only 10 min.

2.1.2.5 UV Spectrophotometry

Spectronic 21 spectrophotometer (Bausch and Lomb Model UV-D) was used at a wavelength of 270 nm for phenol and o-cresol under all temperature and pH conditions with the exception of the pH 11 phenol solution which was measured at a wavelength of 288 nm. 4-nitrophenol was measured at 318 nm. Blanks of distilled water were measured before any analysis to check for zero readings. Standards were prepared in order to draw calibration curves so as to to convert absorbances in to concentration readings

2.1.2.6 Total Organic Carbon Analyzer

Beckmen Model 915 Total Carbon Analyzer was used for the analysis of total organic carbon (TOC) content and total inorganic carbon (TIC) content. Calibration curves were to be prepared before direct measurements.

2.2 Loading Experiments

2.2.1 Screening stage

The Carbon was washed several times with deionized water to remove all fines. It was then dried in an oven at 110°C for 24 hours and allowed to cool at room temperature for about 10 minutes. Finally, it was stored in a dessicator prior to use.

2.2.1.1 Aromatics

Single-solute stock solutions (1000 mg/l each) of phenol, o-cresol, and 4-nitrophenol were prepared. 1.3 g/l of KH_2PO_4 was added to each solution and the pH was raised to 7 with NaOH 1 N. per liter For each compound, two sets of 160-ml bottles containing identical amounts of 10 x 16 U.S. mesh size activated carbon were prepared and subsequently filled with 100 ml of adsorbate solution. One set was purged with nitrogen until a zero level of DO was attained, and the bottles were quickly closed with a rubber stopper. This procedure will be denoted henceforth as anoxic. Oxygen was purged in the other set until saturation was achieved as evidenced by a DO concentration around 30 mg/l. This procedure will be denoted henceforth as oxic. For phenol, four other sets were prepared by separately adding two levels of hydrogen peroxide and potassium permanganate to each set. The two levels of hydrogen peroxide were 31.88 mg/l and 63.75 mg/l, while for potassium permanganate they were 6.0 mg/l and 12 mg/l. Each set of bottles included two bottles without activated carbon to serve as blanks to check for sorbate volatilization, and adsorption of sorbate onto walls of the container. All bottles were placed in a shaker for a period of 14 days. At the end of the equilibration period, samples were withdrawn from each bottle, filtered through 0.45 μm Millipore filter paper, and analyzed for sorbate residual concentrations. Spectronic 21 spectrophotometer (Bausch and Lomb) was used at a wavelength of 270 nm for phenol and o-cresol, and 318 nm for 4-nitrophenol.

2.2.1.2 Aliphatics

The same procedure mentioned for aromatics was repeated for each of 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloromethane, and and tribromomethane,

with the following modifications; the purging process was applied to the buffer solution before the addition of the chemicals and the 160-ml bottles were filled completely with the adsorbates to avoid evaporation. Direct measurement of total carbon was done by quickly injecting the sample into a Beckmen Model 915 Total Carbon Analyzer. For each sample, inorganic carbon was measured twice, at the beginning and the end of the equilibration period, to check for the possibility of biological activity. The organic carbon was calculated by subtracting inorganic carbon (if any) from the total carbon. Total Organic Carbon (TOC) measurements of known concentrations of target compounds indicated that the ratio of measured to theoretical TOC was in the range of 0.9-0.97, while the conversion factors between measured TOC and concentrations in mg/l were, 5.92, 7.25, 11.36, and 19.23 for 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloromethane, and tribromomethane, respectively.

2.2.1.3 Wastewater

The procedure applied to aliphatics was followed here with the following modifications; since the industrial wastes contained volatile chemicals, purging with gases was not a suitable way for introducing or excluding dissolved oxygen. Alternatively, the oxygen free sets were prepared by adding sodium thiosulphate in a quantity sufficient to totally consume the DO. The other sets were operated at the normal level of DO (about 6 mg/l). This alternative was applied to phenol solution as a check for its effectiveness and validity, and to insure no interaction between sodium thiosulphate and the sorbate solution. The filtered domestic wastewater was sterilized prior to use, to preclude biological activity.

2.2.2 Effect of pH and Temperature

In the case of various pH loadings, the procedure of section 2.2.1.1 for phenol and o-cresol was repeated at pH 3, 7, and 11. pH values of 3, and 11 were obtained by KCl/HCl and NaHCO3/NaOH mixtures, respectively. The KCl/HCl mixture was prepared by mixing 25 ml 0.2 M KCl with 6.5 ml 0.2 M HCl and dilute to 100 ml, while the NaHCO3/NaOH mixture was prepared by mixing 50 ml 0.05 M NaHCO3 with 22.7 ml 0.1 M NaOH and diluting to 100 ml. The pH effect was studied at room temperature.

The loading procedure of section 2.2.1.1 was repeated twice for phenol and o-cresol with the exception that after purging with gases, the bottles were put in temperature controlled shakers, one at 8°C and the other at 35°C.

At the end of the equilibration period, samples were withdrawn from each bottle, filtered through 0.45 μm Millipore filter paper, and analyzed for sorbate residual concentrations. Spectronic 21 spectrophotometer (Bausch and Lomb Model UV-D) was used at a wavelength of 270 nm for phenol and o-cresol under all temperature and pH conditions with the exception of the pH 11 phenol solution which was measured at a wavelength of 288 nm.

2.2.3 Effect of Different Levels of Dissolved Oxygen

In addition to the oxic and anoxic conditions, two other DO levels were introduced for phenol and o-cresol. Nitrogen was slightly purged until a moderate amount of DO (3-4 mg/l) was achieved. Air was purged so that saturation with air (9.0 mg/l) can be achieved. By this, four levels of DO were achieved and denoted as DO 1

(anoxic), DO 2 (moderate), DO 3 (purged with air), and DO 4 (purged with pure oxygen (oxic)). Each set of bottles included two bottles without activated carbon to serve as blanks to check for sorbate volatilization, and adsorption of sorbate onto walls of the container. All bottles were placed on a shaker at room temperature of about 21°C for a period of 14 days. At the end of the equilibration period, samples were withdrawn from each bottle, treated and analyzed similar to the procedure mentioned above.

2.3 Extraction Experiments

GAC samples used in the anoxic (DO 1) and "pure oxygen purged" (DO 4) phenol solutions and those used in the anoxic, "air purged" (DO 3), and "pure oxygen purged" o-cresol solutions were extracted in a Soxhlet extractor. GAC samples were first extracted for 24 hours with methanol and then with methylene chloride for 3 days following the procedure of Vidic et. al. (14). The extracts were dried with anhydrous Na_2SO_4, filtered and concentrated for GC-MS analysis.

Virgin GAC samples and the pure chemicals used in the preparation of the sorbate solutions were also treated and analyzed similarly.

While the above work was for samples of pH 7, sample from "oxic, pH 3" phenol experiment was extracted and analyzed following the procedure mentioned above.

2.4 Kinetic experiments

The rate experiments were conducted for phenol and o-cresol in completely mixed tanks in which the GAC particles were trapped in a basket. Freely mixing with the solution would have resulted in very low (if not zero) relative velocity between the adsorbents and the adsorbate solutions. The objective here was to increase external mass transfer by maximizing the fluid relative velocity.

In the study of the effect of different DO levels, four closed mixers with the same mixing conditions, same initial sorbate concentration and volume, and identical GAC masses, but different DO concentrations were run simultaneously at neutral pH and a temperature of 21°C. The four different DO levels were achieved by a purging procedure similar to that used in the loading experiments.

In the case of experiments which studied the effects of pH on kinetics, the kinetics experiment procedure was followed with the exception that there were two mixing tanks for each pH condition, one mixer with anoxic condition (zero level of DO in the adsorbate solution) and the other with oxic condition (DO around 30 mg/l). pH values of 3, 7, and 11 were maintained following the procedure performed in the loading tests.

For the case of batch kinetic experiments under varied temperature, temperatures of 8°C and 35°C were controlled with water circulating from temperature controlled water baths surrounding water jackets. The mixing tanks were connected to the water baths after finishing the purging process and maintaining the the required DO concentration. Samples were taken at predetermined time intervals for concentration measurements until equilibrium, indicated by constant concentration for three consecutive samples, was attained. The cumulative volume of these samples constituted less than 5

percent of the total initial volume in the mixer.

2.5 Column Experiments

Phenol and o-cresol breakthrough curves (BTCs) were obtained under oxic and anoxic conditions using (60 cm long and 2.54 cm I.D.) glass columns charged with 130 g of activated carbon. The influent adsorbate concentrations were maintained at 70 mg/l for all column experiments. The feed solution to the columns was prepared using deionized water buffered similar to the loading experiments in order to keep neutral pH. The activated carbon columns were operated in an upflow mode at a flow rate of 100 ml/min resulting in 0.197 m/min (superficial velocity) at room temperature. The anoxic experiments were performed by purging the feed solution with nitrogen and keeping the solution under a head space of nitrogen. Due to the fact that 144 L of feed solution was pumped through the column per day it was not possible to completely remove DO from the adsorbate solution and have zero DO content; and hence, DO concentration was in the range of (0.1-0.4) mg/l. The oxic column experiments were performed by purging the adsorbate solution with pure oxygen until saturation was reached and a DO concentration of 30 mg/l was measured. Samples were taken from the effluents for concentration measurements.

Chapter 3

EFFECT OF DISSOLVED OXYGEN ON ACTIVATED CARBON ADSORPTION OF DIFFERENT CHEMICALS

3.1 Introduction

Adsorption on granular activated carbon (GAC) is one of the most commonly used methods for water and wastewater treatment, especially, those containing refractory organic compounds that persist in the environment and resist biodegradation. The equilibrium uptake by GAC of target compounds is the major factor influencing the design of full scale adsorption columns, and the decision regarding its economic feasibility. This fact has motivated researchers to investigate the uptake by GAC of a large number of compounds as well as factors affecting it. Among those are: carbon particle size, initial concentration, pH, and temperature.

While the aforementioned variables have been thoroughly researched, a major parameter namely dissolved oxygen (DO) has not received due attention. A few studies have shown that the existence of DO in the adsorbate solution enhances the uptake of phenolics by GAC (10,11,13).

From the previous work, it was felt that this phenomenon needed more investigation, particularly, because the number of compounds studied was not deemed sufficient to arrive at solid conclusions. Accordingly, in this study, another aromatic compound,

4-nitrophenol, is investigated in addition to phenol and o-cresol. In order to increase understanding of the enhancement nature, oxidizing agents were applied to the phenol solution to investigate their effect on the uptake. Hydrogen peroxide and potassium permanganate were used for this purpose. The adsorption of four aliphatic compounds is also studied, namely, trichloromethane (chloroform), tribromomethane (bromoform), 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane. The aforementioned organic compounds were selected for the purpose of this study because they are common constituents of industrial wastewater effluents, particularly, oil and petrochemicals related industries. The selection was also designed to investigate the dependence of the adsorption enhancement phenomenon, if existent, on the following chemical parameters:

1. types of compounds (aromatics versus aliphatics)
2. groups (methanes versus ethanes)
3. number of halogen identical alkyl derivatives (tri. versus tetra.)
4. type of substitution (methyl,nitro, chloro, and bromo).

The practical importance of the oxygen-induced enhancement in uptake was tested on four different wastewater samples, namely; domestic wastewater (DWW), and three different streams from a petrochemical industry located in the eastern province of Saudi Arabia. Figure 3.1 shows a layout of the styrene unit plant along with the locations of two of the streams under study. Location 1 is a stream highly polluted with benzene and related compounds, location 2 is after stripping the stream of location 1 for benzene yield, and, finally, location 3 which is not shown on the figure is the last stream or effluent from the whole plant.

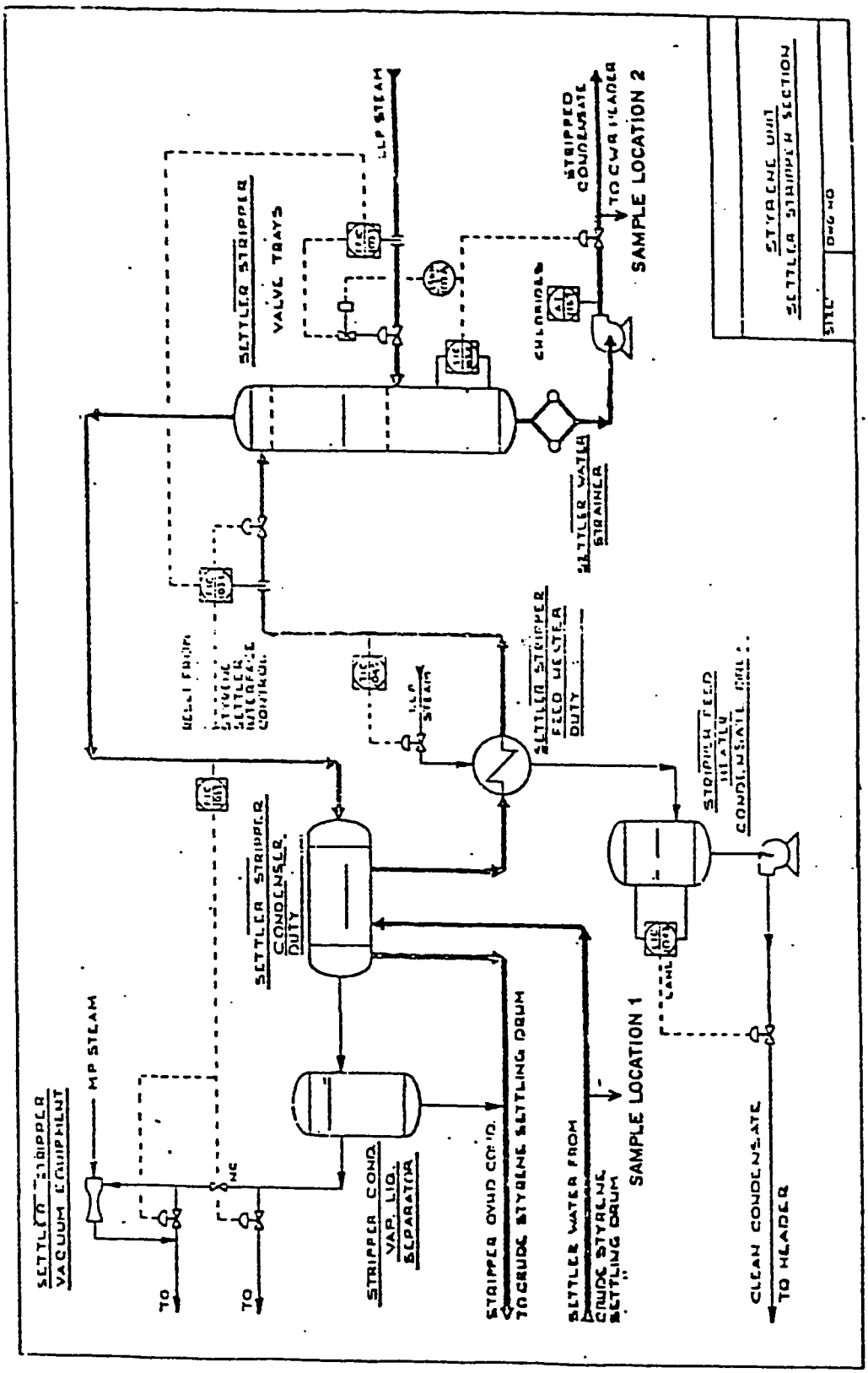


Figure 3.1: Layout of the Styrene Plant With Sample Locations.

3.2 Results and Discussion

3.2.1 Adsorption of Aromatics

After the determination of residual concentration of adsorbates, the single-solute isotherms for each of the compounds under study obtained at 21°C were modelled by the Freundlich equation; $q = kc^{1/n}$. The close agreement between the concentration of adsorbates in the blank bottles and the stock solutions indicated the lack of volatility and biodegradation of the adsorbates under the conditions of the experiment. The possibility of biological activity was also tested by monitoring the increase in the inorganic carbon content during the equilibration period.

The data of the Freundlich curves for phenol, o-cresol, and 4-nitrophenol are presented in figures 3.2, 3.3, and 3.4 for the cases of zero, and saturation levels of oxygen (30 mg/l). The figures clearly depict that the existence of dissolved oxygen in the environment tremendously enhances the uptake of the three phenolics by GAC. This statistically-significant oxygen-induced uptake is not attributable to biological degradation since no increase in the inorganic carbon content was observed during equilibration. Generally, the percentage enhancement increases with decreasing equilibrium concentration. For example, the oxic equilibrium uptake for phenol at a concentration of 1000 mg/l is 74% more than the anoxic uptake, while at 1 mg/l it is 263 % more than the anoxic uptake. The corresponding figures for o-cresol are 42% and 215%, respectively. On the other hand, nitrophenol exhibited a modest 11% increase in uptake under oxic conditions at 1000 mg/l and 18% at 1 mg/l. The explanation for that will be discussed latter in this chapter. While the general trend of increasing enhancement of the adsorptive uptake of GAC with lower equilibrium liquid phase concentration agrees with the observations of Vidic and Suidan (14), the order of enhancement for the three

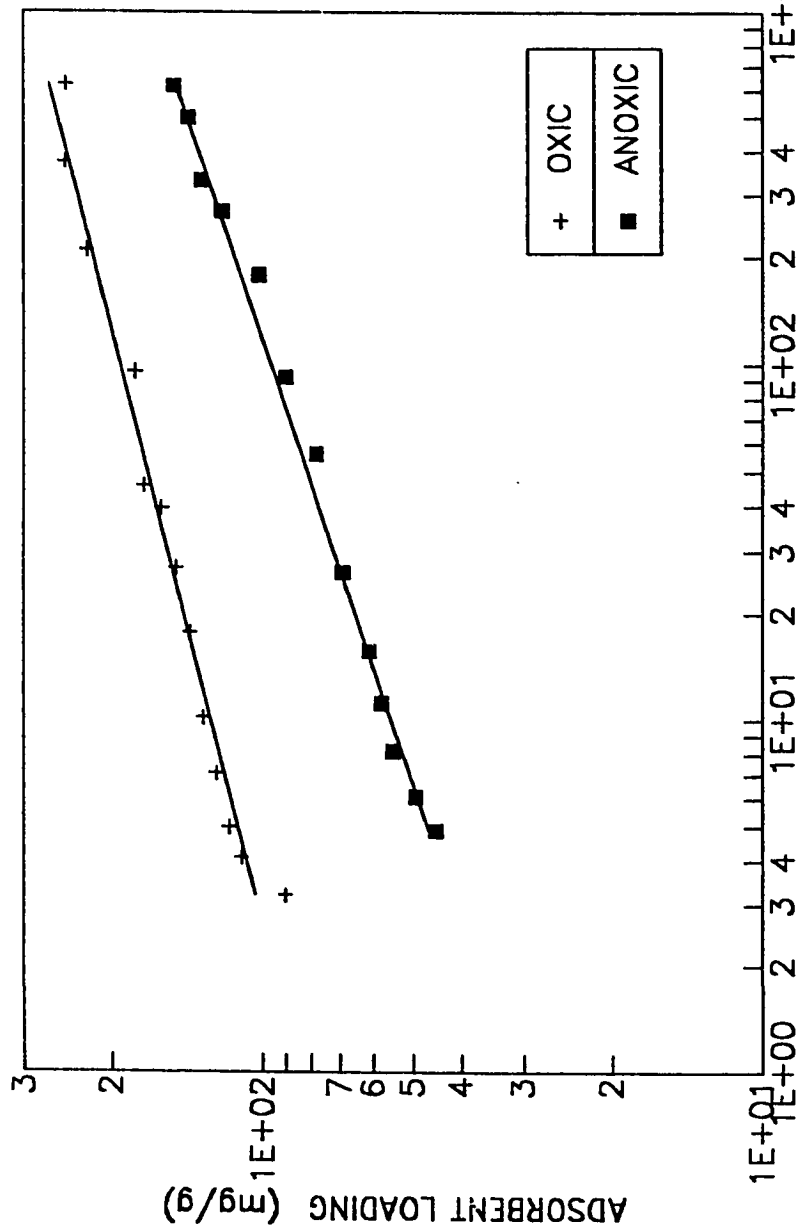


Figure 3.2: Uptakes of Phenol at T = 21°C and pH of 7 Along with Best Fit Freundlich Curves Using constants Given in Table 3.1.

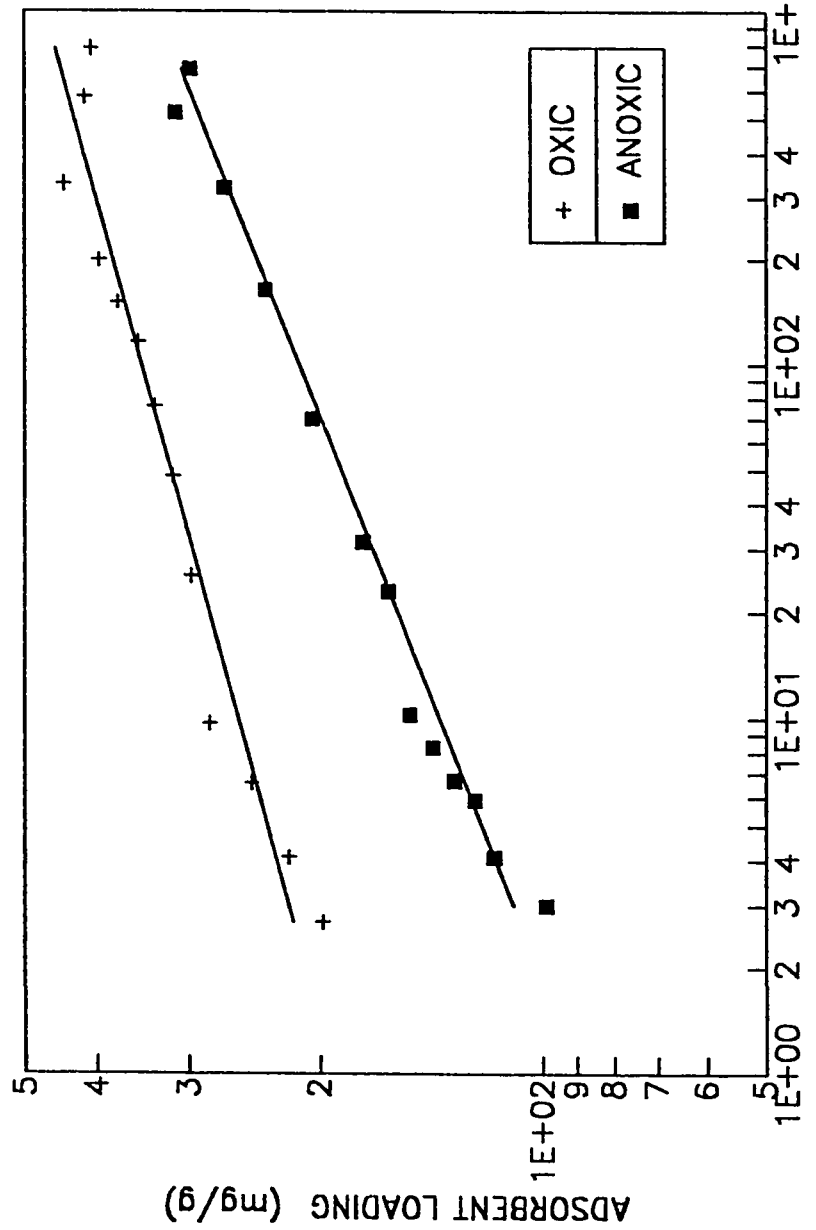


Figure 3.3: Uptakes of o-Cresol at T = 21°C and pH of 7, Along with Best Fit Freundlich Curves Using Constants Given in Table 3.1.

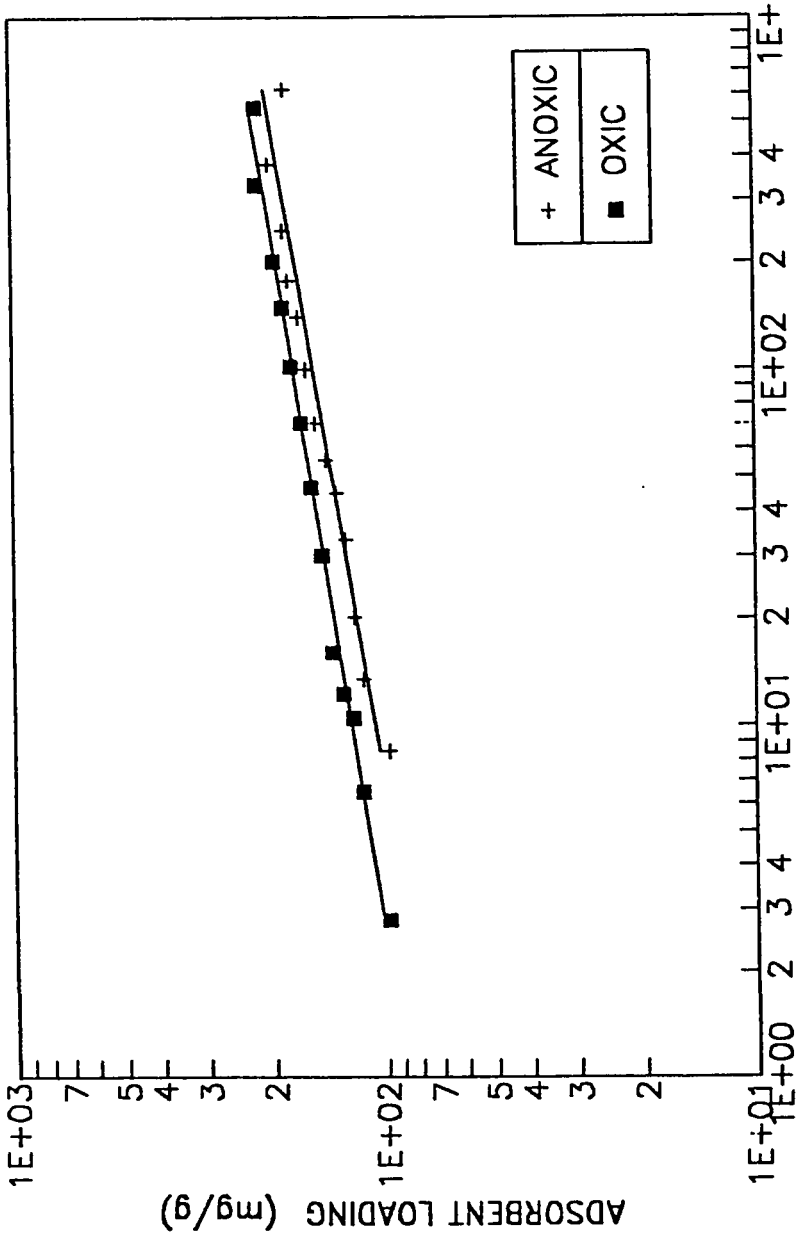


Figure 3.4: Uptakes of 4-Nitrophenol at 21° C and pH of 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 3.1.

phenolics does not. In their work on Filtrasob 400 GAC (Calgon Corp., PA, USA) Vidic and Suidan (14) have reported increased percentage enhancement for substituted phenols such as o-cresol, chlorophenol, and ethylphenol. The discrepancies between the results of this work and those reported by Vidic et al. (14) in terms of enhancement for phenol and substituted phenols may be attributable to the differences in GAC characteristics as well as the purity of the chemicals since GC-MS analysis of the nitrophenol indicated the presence of impurities.

3.2.2 Extraction Studies

Phenol yield efficiencies of around 70% were attained for the anoxic isotherm while only 23% of the phenol previously adsorbed on the GAC used in the oxic procedure was extracted suggesting the formation of more strongly adsorbable compounds on the activated carbon surface. Figures 3.5 and 3.6 show the chromatograms for the GC-MS analysis of the extracts of the GAC samples used in the oxic and anoxic phenol experiments which revealed the presence of significant quantities of two dimers, identified as 2,2-dihydroxy-1,1-biphenyl and 4-phenoxyphenol and a trimer on the GAC used in the oxic experiments while only traces of dimers were detected in the anoxic extracts. For o-cresol, dimers and trimers were detected in the case of oxygen purged samples while only traces of dimers were found on the GAC used in the oxygen free experiment. It must be emphasized that no such compounds were found either in the extracts of virgin carbon or in the original stock solutions which suggests that telomerization reaction took place on the activated carbon surface in the presence of molecular oxygen which may explain the higher oxic uptakes.

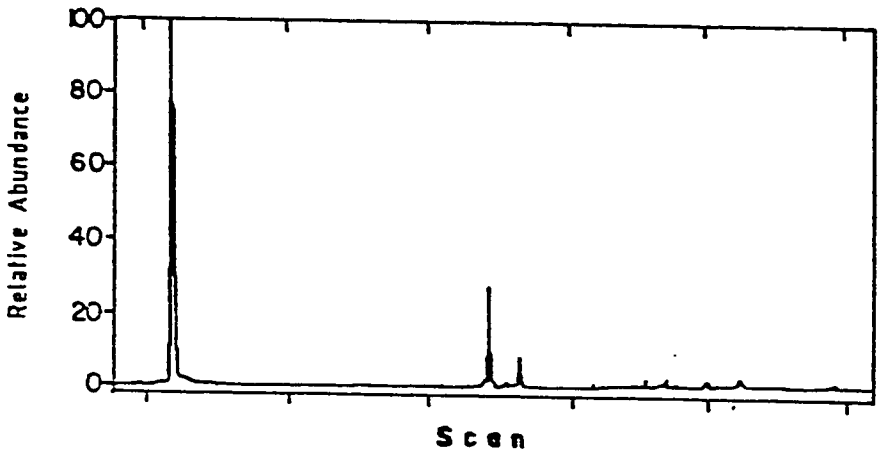


Figure 3.5: GC–MS Total Ion Chromatogram for the Anoxic GAC Sample of Phenol

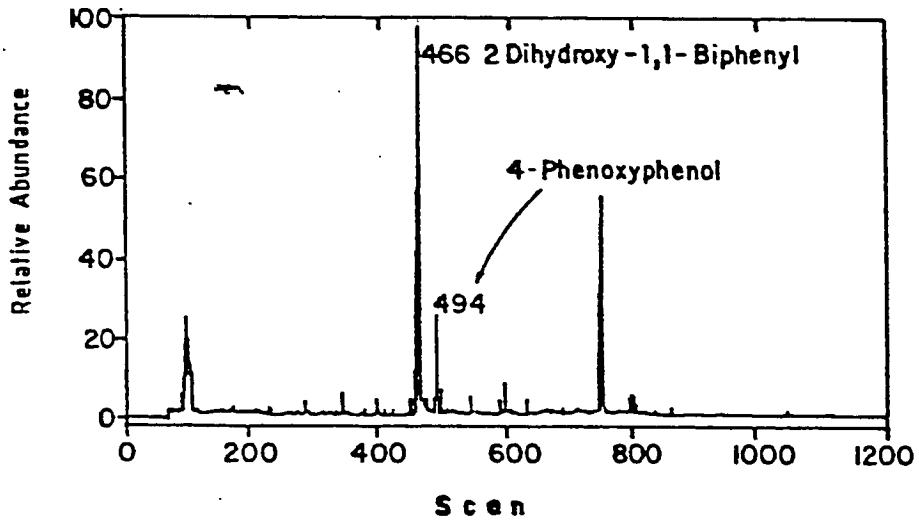


Figure 3.6: GC–MS Total Ion Chromatogram for the Oxic GAC Sample of Phenol

3.2.3 Oxidizing Agents

The oxygen-induced enhancement in the uptake of GAC for the phenolics has stimulated work on use of other oxidizing agents. Figure 3.7 and 3.8 depicts the anoxic phenol isotherms and those conducted with hydrogen peroxide and potassium permanganate, respectively. Both oxidizing agents have appreciably increased the uptake of phenol by GAC without marked difference between their two levels, thus precluding the limitation of their amounts in the test bottles.

Recovery analysis performed on GAC extracts from both isotherms, indicated that only 26% of the adsorbed phenol in the case of hydrogen peroxide and a meager 2.1% in the case of potassium permanganate was extractable. Furthermore, GC-MS analysis of such extracts confirmed the presence of significant quantities of the same dimers and trimers observed in the oxic isotherms, on the carbon surface.

The results of this study appears contradictory to the findings of Coughlin (67) who used potassium permanganate to increase the acidic oxides on a commercial activated carbon from 0.38 to 4.15 meq/g which lowered the adsorptive uptake of GAC for phenol, and Snoeyink et al. (9) who reported that oxidation with aqueous chlorine lowered the sorption uptake for phenol. However, The reason for this difference may be due to the fact that those researchers treated the activated carbon with oxidizing agents prior to mixing with the adsorbate solution, which may have resulted in changes of the functional groups present in the activated carbon lattice. In the work published by Coughlin and Ezra (8), the surface of the carbons were modified by wet oxidation and reduction. Oxidation was carried out by stirring the carbon samples in $(NH_4)_2S_2O_8$ 0.1 N solution for two weeks. The amounts of acidic and basic functional groups were then determined by specific titration techniques.

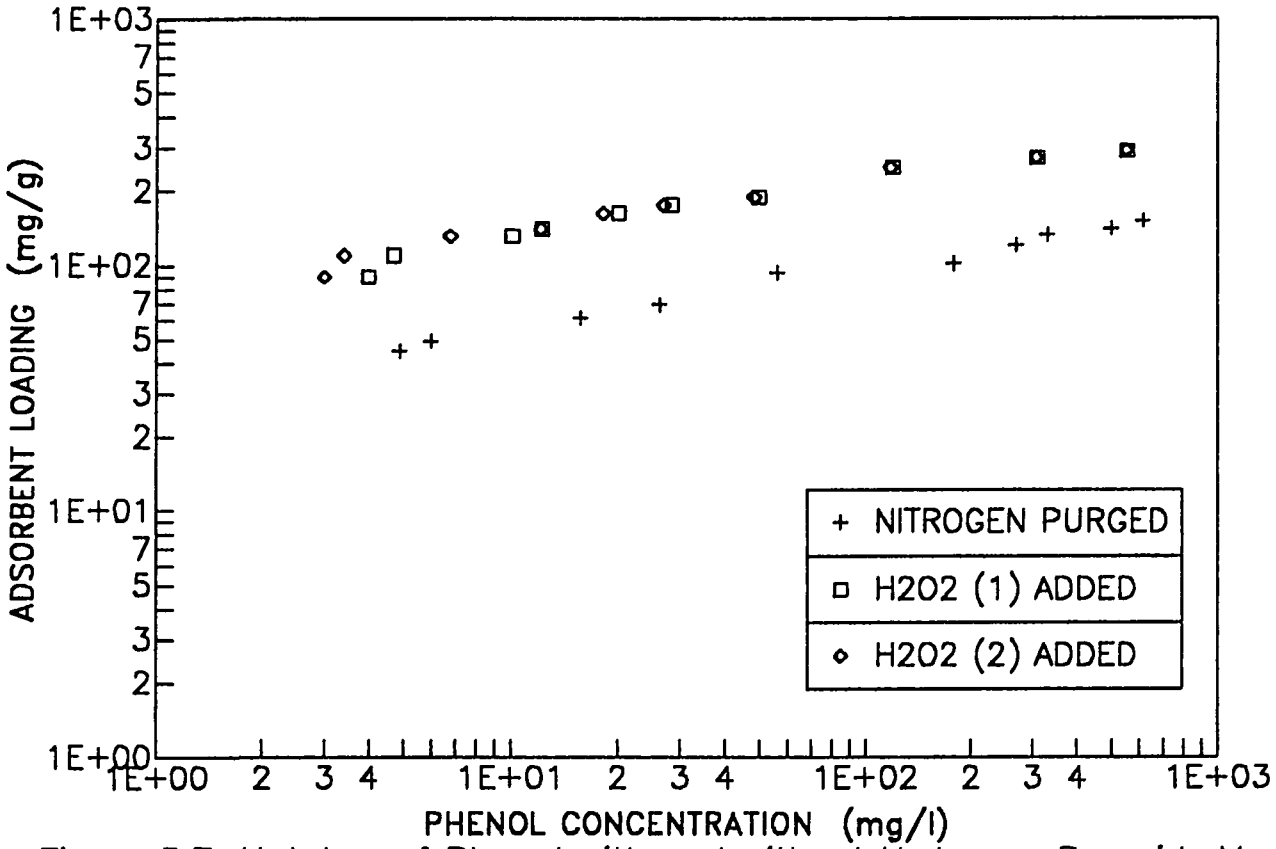


Figure 3.7: Uptakes of Phenol with and without Hydrogen Peroxide Versus Residual Concentration at T = 21°C and pH of 7.

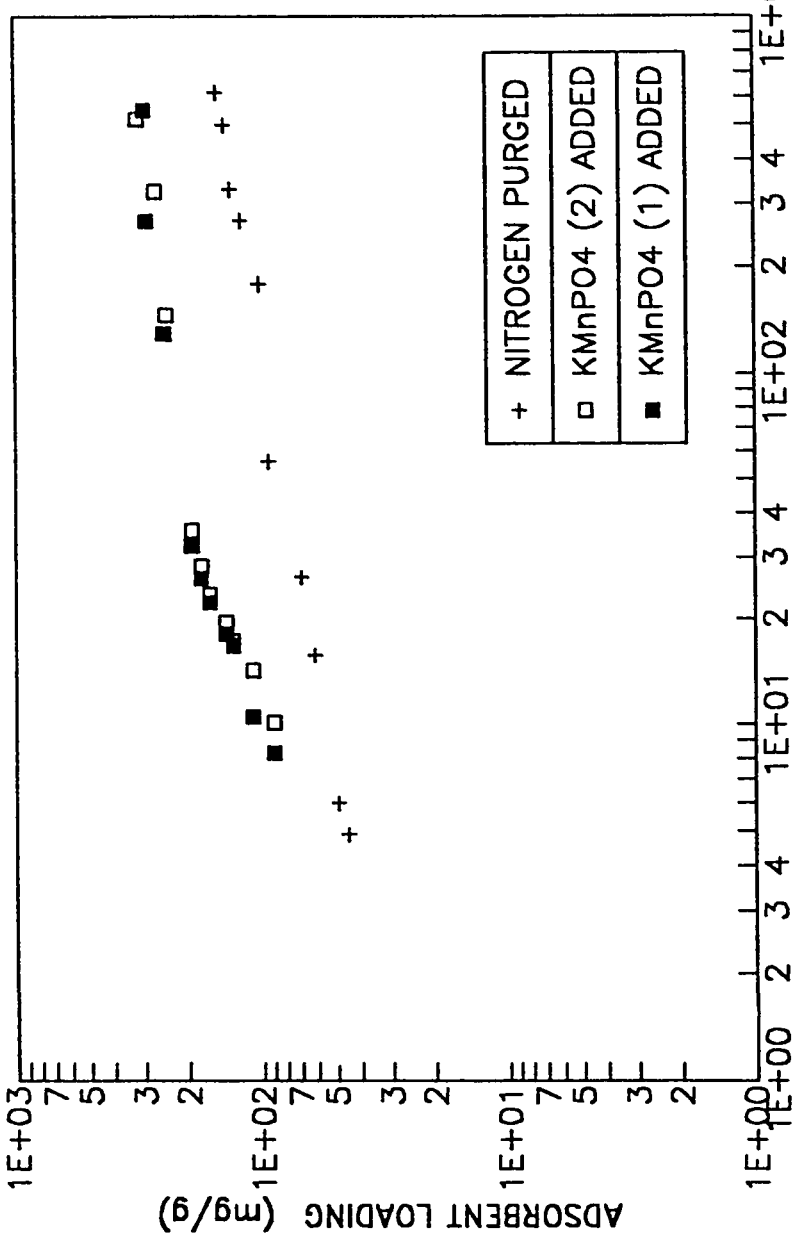


Figure 3.8: Uptakes of Phenol with and without Potasium Permanganate Versus Residual Concentration at T = 21°C and pH of 7.

After that, adsorption isotherms experiments were carried out for phenol and nitrobenzene. The results of such experiments showed that the increase of acidic functional groups caused by oxidation decreased the adsorption capacities for the above compounds by about 50 %. This was attributed to their acidic properties which do not undergo chemi-sorption on an acidic surface. However, the increase of basic functional groups on the carbon surface by the addition of a reduction treatment step showed an inverse effect (i.e. increased the adsorption capacity of GAC for phenol and nitrobenzene).

Evangelos et al. (68) reported that batch reaction products of the free chlorine-phenolic compounds reaction are mono-, di-, and trichloro derivatives, while when chlorine reacts with phenolic compounds adsorbed on GAC, many additional products are formed. It was concluded that GAC exposed to chlorine becomes capable of promoting reactions such as hydroxylation of the aromatic ring, oxidation to quinones, chlorine substitution, carboxylation, and oxidative coupling (dimer formation).

The above discussion clearly show that the researchers who had contradictory results to this study were dealing with another phenomenon which is the formation of acidic or basic functional groups on the GAC surface which had an effect on the chemi-sorption of acidic and basic compounds.

3.2.4 Reaction Mechanisms

The formation of the dimers found in the GC-MS analysis can arise as a result o a free radical reaction in the case of oxygen and as a result of ionic reaction in the case of hydrogen peroxide and potassium permanganate.

Two free radical mechanisms for the reaction of phenol with oxygen and potassium permanganate are proposed and presented in Schemes 1 and 2, respectively. The two reaction mechanisms produces a final product of the dimer 4-phenoxyphenol which was detected on the carbon surface.

The over all reaction presented in scheme 1 can be shown as

$$2\,C_6H_5OH + \frac{1}{2}\,O_2 \longrightarrow C_{12}O_2H_{10} + H_2O$$

From the previous chemical equation, 1 mg/l of DO consumes 11.75 of phenol, while from the isotherm experiments, the real ratio of oxygen to phenol consumed (difference in uptake) is 1:3.1 and 1:7.8 for Carbon masses of 1000, 500 mg, respectively. This clearly shows that DO is not limiting the telomerization reactions.

Since telomerization was observed to occur on the activated carbon surface, the essential elements for the initiation and progression of such reactions are oxygen, adsorbate, and reaction sites. For a given adsorbate-adsorbent system at known conditions of pH and temperature, the extent of telomerization is most strongly influenced by two parameters namely the mass of oxygen needed for the reaction and the availability of adsorption sites i.e. mass of GAC. This dual-limitation of the adsorptive uptake enhancement, attributed to telomerization is best illustrated by Figure 3.9 which shows the additional sorptive uptake attained under oxic conditions versus the initial DO to GAC mass. The data show that for all the three compounds, the additional uptake initially increased with increasing DO to GAC mass ratio to a point beyond which the DO to GAC ratio did not exert any appreciable influence on the additional uptake.

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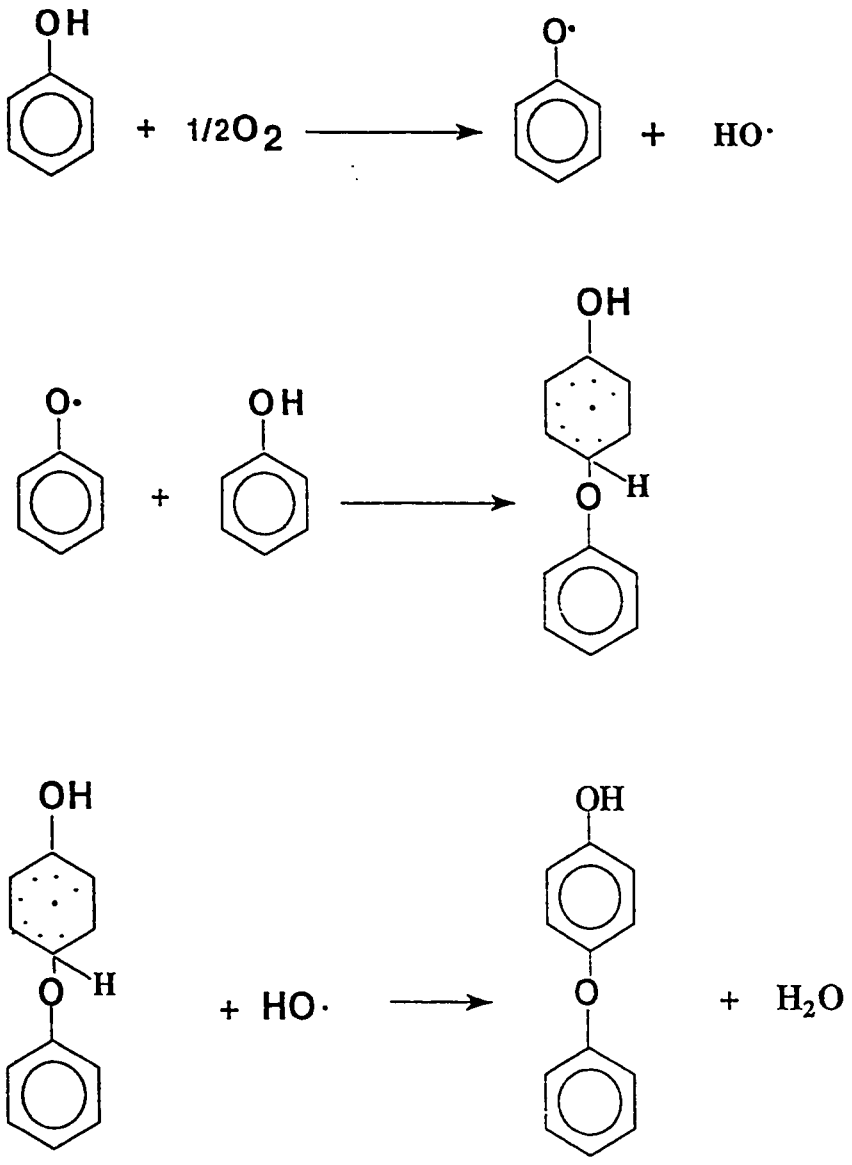
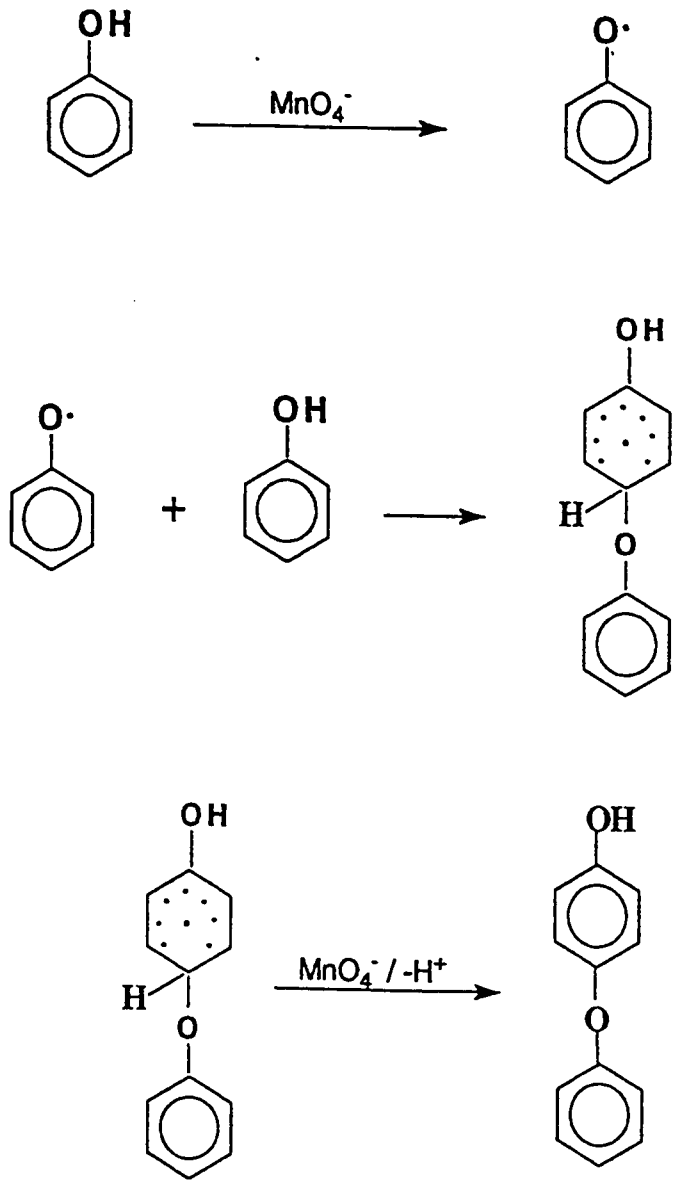


Scheme 1. Free Radical Mechanismfor the reaction of oxygen with phenol



Scheme 2. Free Radical Mechanism for the Reaction of Potassium Permanganate with Phenol

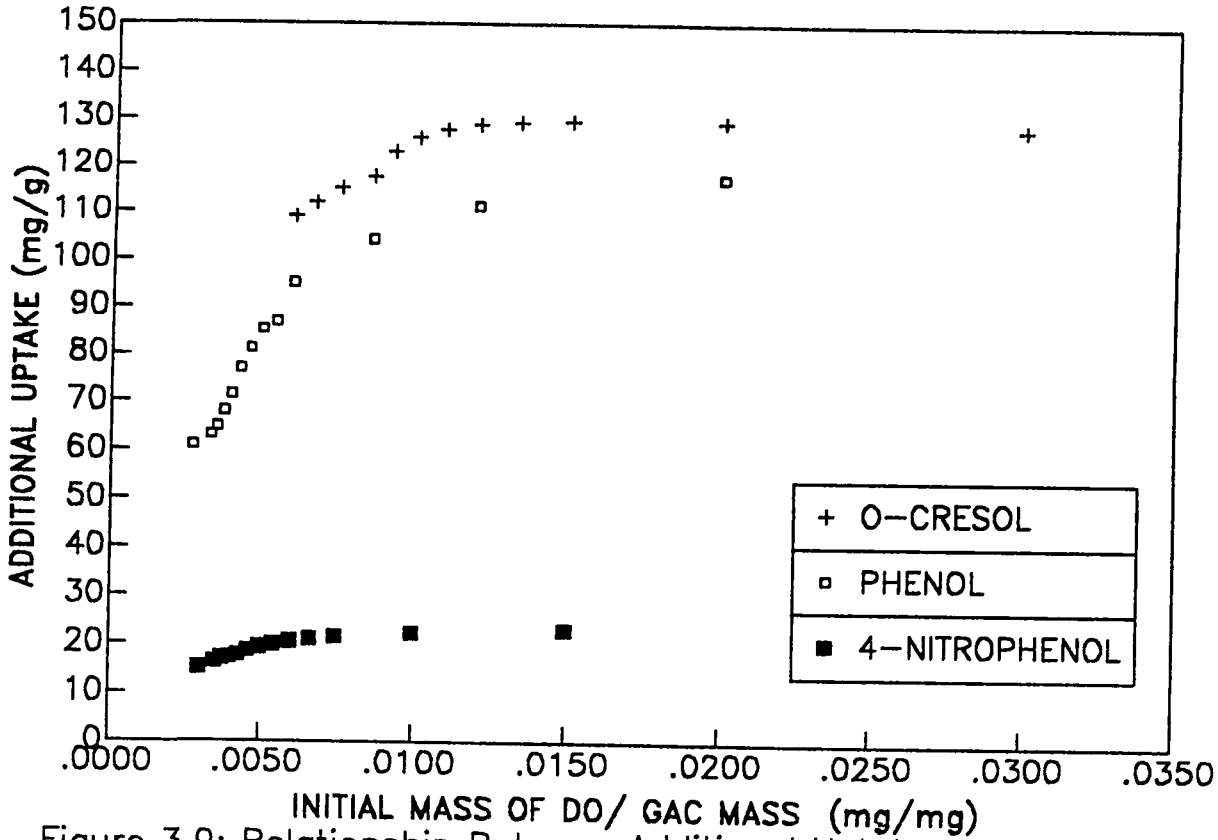


Figure 3.9: Relationship Between Additional Uptake and the Ratio of Initial DO to GAC Mass at T = 21°C and pH of 7.

Evidently then, at low DO to GAC mass ratio, the enhancement in uptake is limited by the mass of oxygen present in the test environment while at high DO to GAC mass ratio, corresponding to low GAC mass the additional uptake is limited by the mass of GAC or availability of adsorption sites for the telomerization reactions to take place.

Another important parameter that appears to influence this enhancement in uptake under oxic conditions is the adsorbability of the compound as reflected by its retention capacity. The additional uptake attained in the presence of oxygen expressed as a percentage of the anoxic uptake is a decreasing nonlinear function of the anoxic uptake (Figure 3.10). However, such representation of the oxygen-induced enhancement in the uptake of the GAC although readily interpretable in terms of the percentage increase in the extended service life of an adsorber, is misleading since the low anoxic capacities corresponding to high GAC masses and relatively low DO to GAC mass ratio exhibit the highest incremental capacities. To provide more insight into this phenomenon and its dependence on the adsorbability of the pollutant, the actual additional uptake is plotted as a function of the anoxic isotherm uptake in Figure 3.11, since it is directly related to the stoichiometry of the telomerization reactions responsible for this enhancement in view of the limited amount of molecular oxygen and adsorption sites available in the test environment. Figure 3.11 indicates that the additional uptake attained by the presence of oxygen in the test environment is initially an increasing function of the anoxic adsorptive uptake of GAC. Such relationship suggests that the extent of the telomerization taking place on the activated carbon surface is strongly influenced by the retained adsorbate. The data for o-cresol and nitrophenol clearly show that at high oxic capacities the aforementioned additional uptake becomes independent of the amount of adsorbate retained under anoxic conditions.

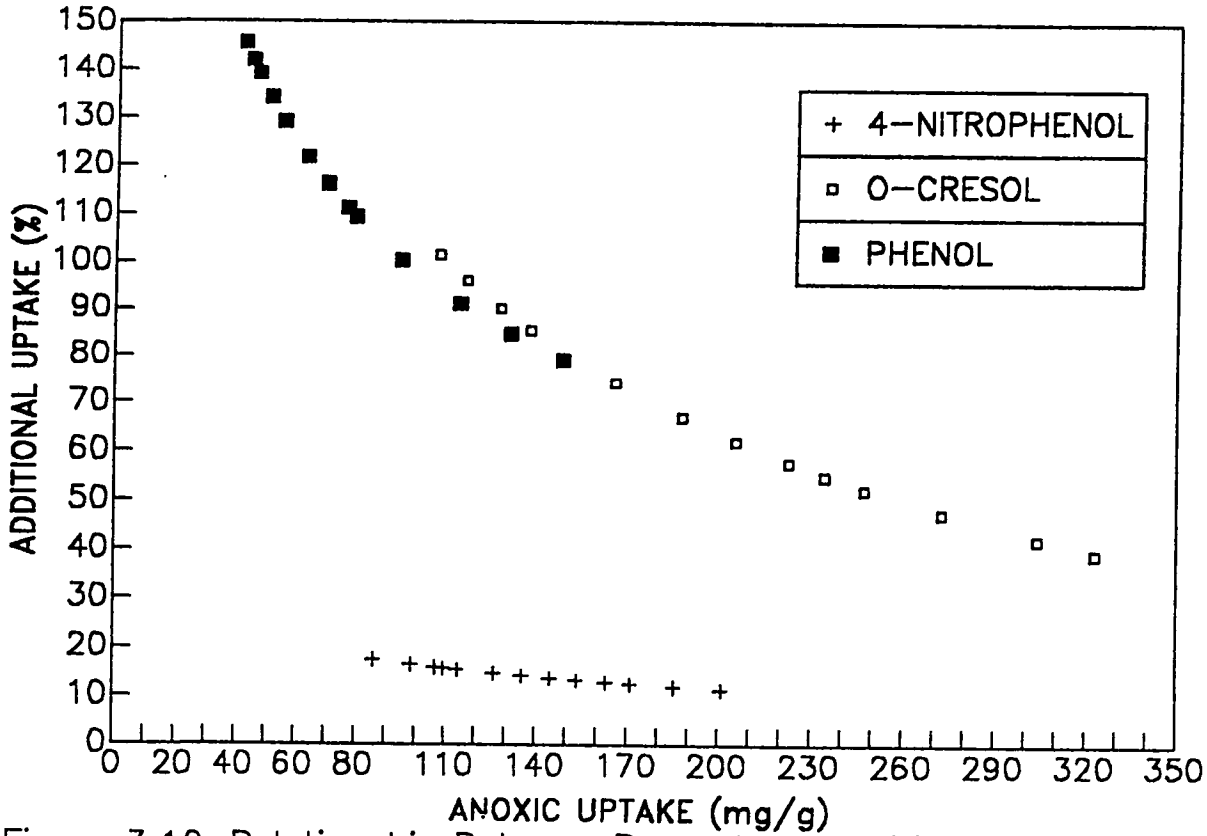


Figure 3.10: Relationship Between Percentage Additional Uptake and the Anoxic Uptake at T = 21 °C and pH of 7.

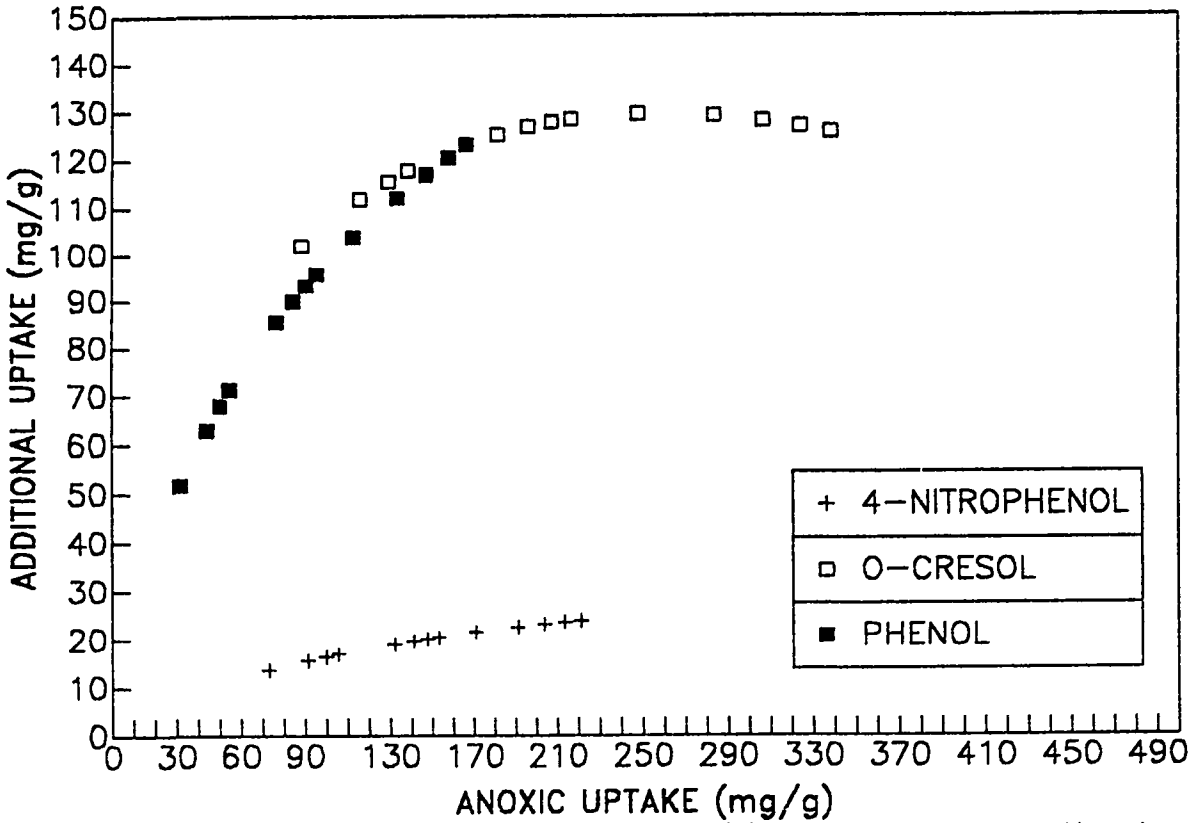


Figure 3.11: Relationship Between Additional Uptake and the Anoxic Uptake at T = 21° C and pH of 7.

from mod21

The high anoxic capacities corresponds to high DO to GAC mass ratio and therefore this "hindrance" of extended uptake is not attributable to oxygen limitation. It is thus hypothesized that only a limited number of adsorption sites where conditions favor telomerization exist and therefore percentage additional uptake is likely to decrease with increasing adsorbate retention uptake which is consistent with the observations of Figure 3.10. In fact, based on the isotherm equation (1.5) for competitive adsorption, and the low phenol yield in the oxic isotherm, it can be concluded that while DO enhances the overall uptake by the formation of telomers, it reduces the physical adsorption of the phenolic compound.

3.2.5 Aliphatics

The isotherms for the aliphatic compounds presented in figures 3.12-3.15 show the isotherms for the aliphatic compounds. The data agree with those found by Urano et al. (55) and Suffet (56). It is apparent that no enhancement of the adsorptive uptake of GAC for the aliphatic compounds was observed regardless of the type of functional group, type of substitution, and number of substitutions.

3.2.6 Wastewater

To corroborate the findings of this study and its practical applications, isotherms studies were performed on three industrial wastewater streams and a domestic wastewater sample. The equilibrium adsorption isotherms for the wastewater samples are presented in Figures 3.16-3.19. The data point to a significant enhancement in the uptake of GAC for organics compounds when oxygen is available in the test environment.

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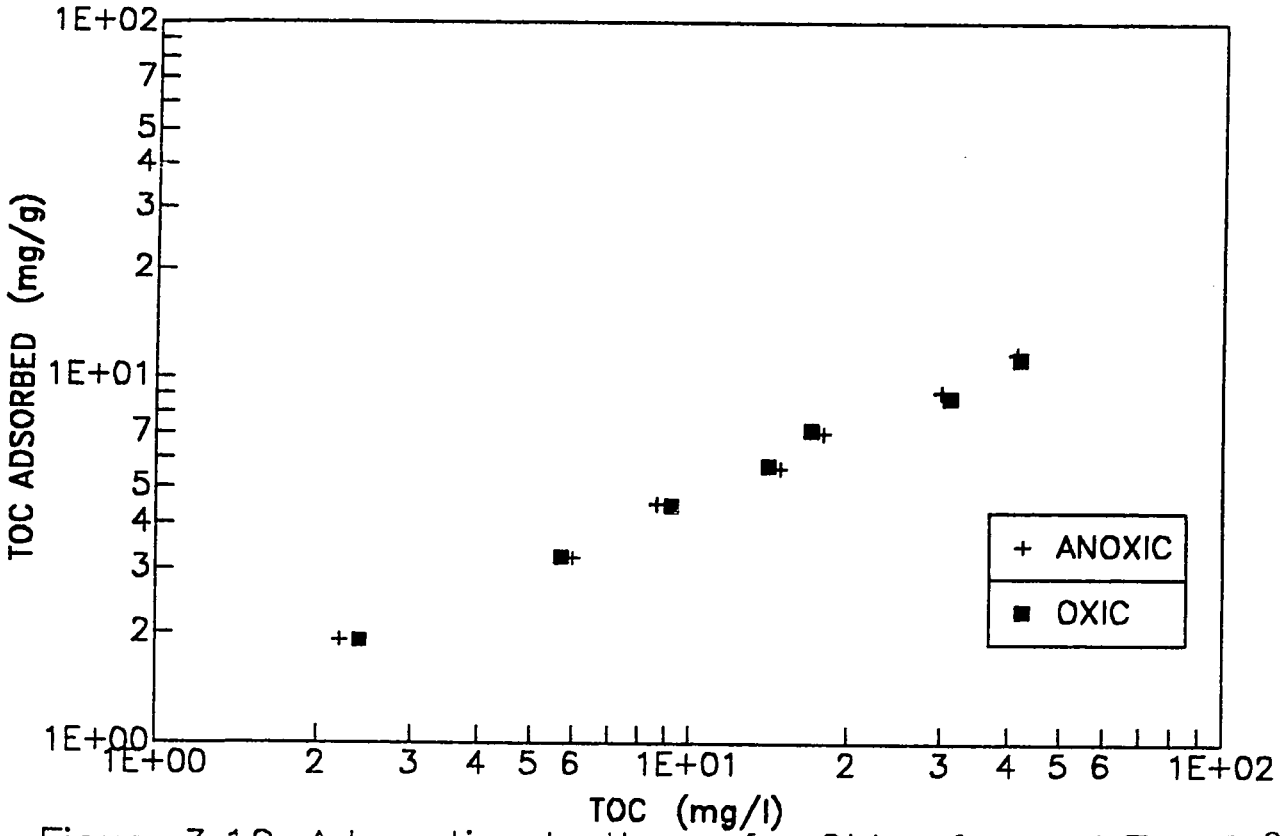

Figure 3.12: Adsorption Isotherm for Chloroform at T = 21° C and pH of 7.

from fob11

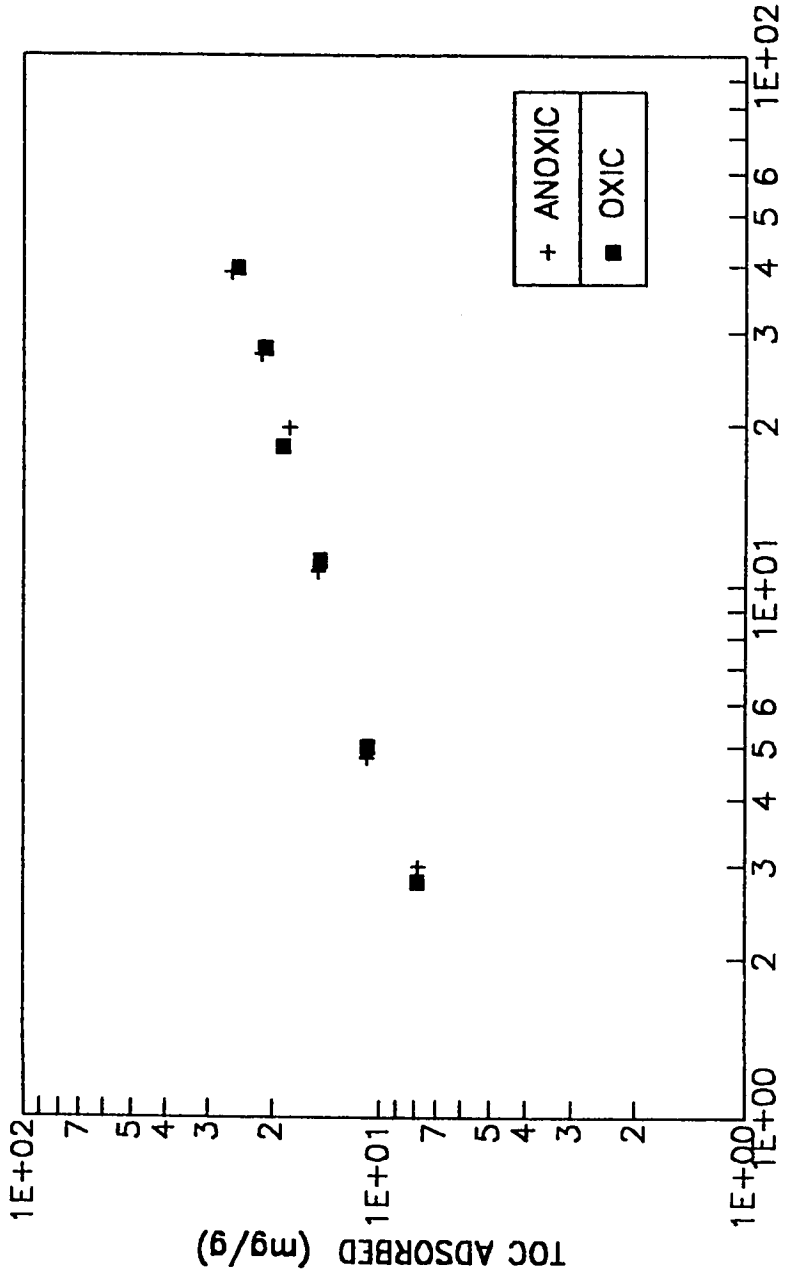

Figure 3.13: Adsorption Isotherm for Bromoform at T = 21° C and pH of 7.

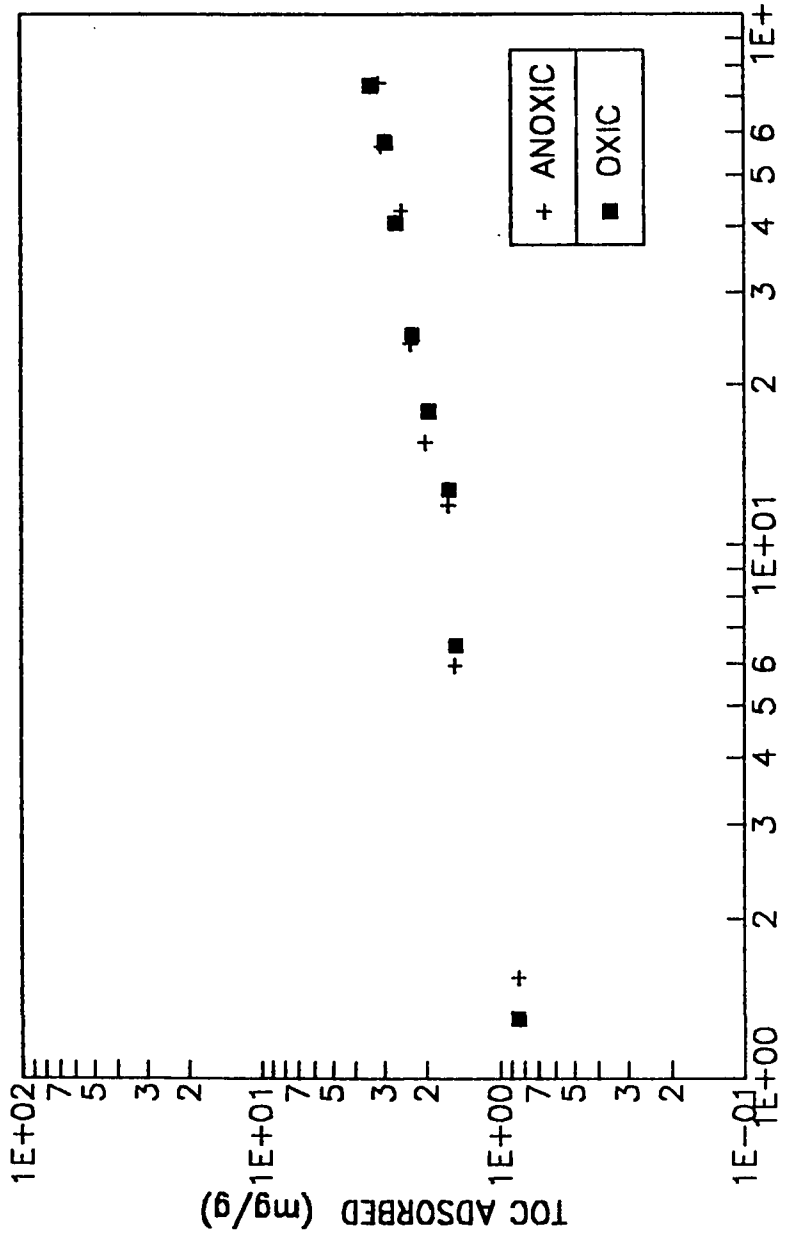

Figure 3.14: Adsorption Isotherm for 1,1,1-Trichloroethane at T = 21° C and pH of 7.

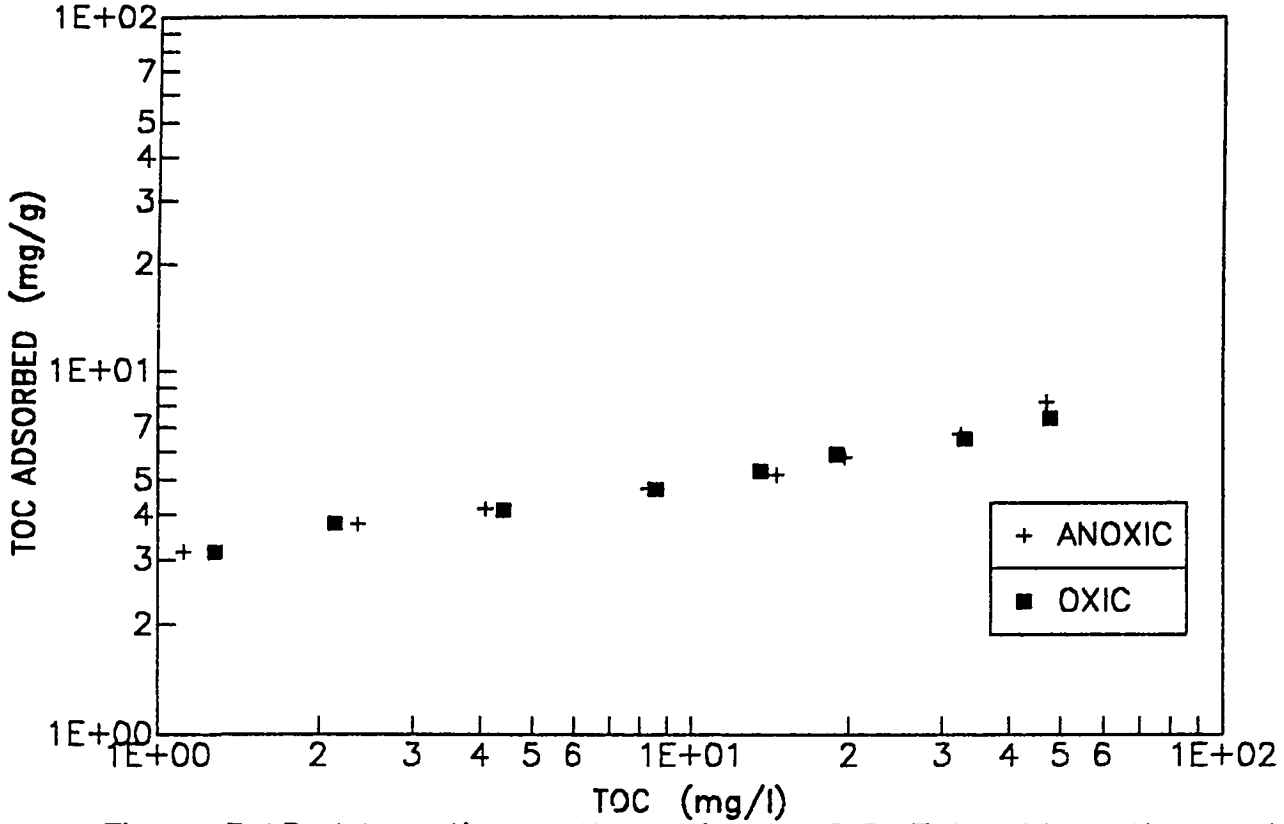

Figure 3.15: Adsorption Isotherm for 1,1,2,2—Tetrachloroethane at T = 21° C and pH of 7.

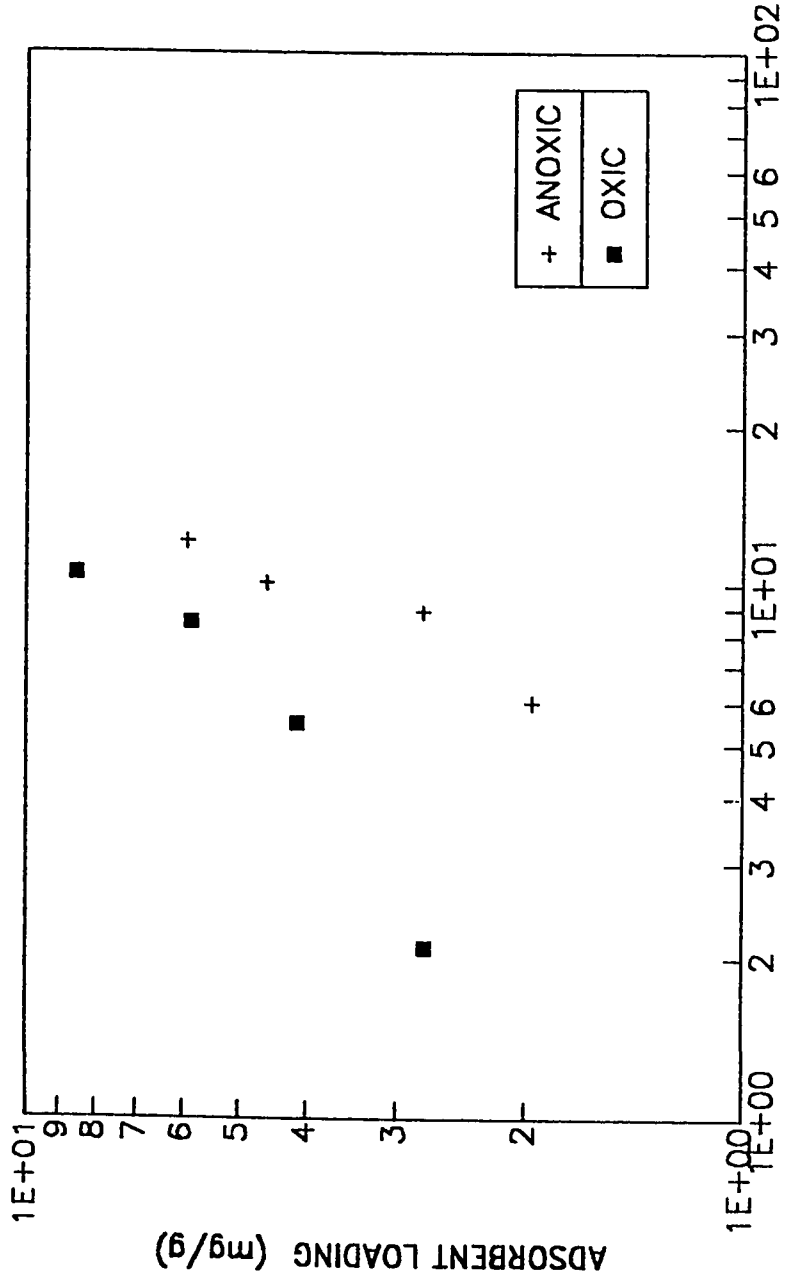

Figure 3.16: Uptakes of TOC for I.W.W, Sample Location 1, at T = 21° C and pH of 7.

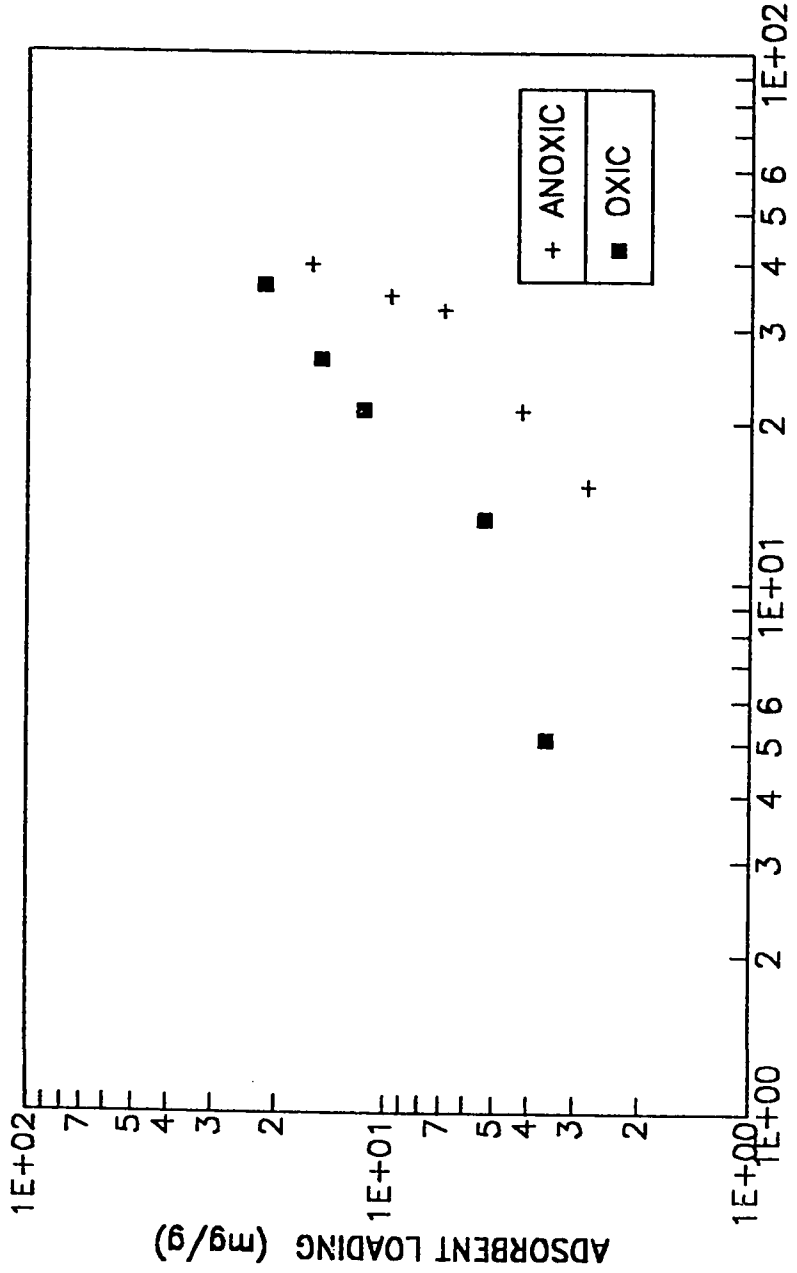

Figure 3.17: Uptakes of TOC for I.W.W, Sample Location 2, at T = 21 °C and pH of 7.

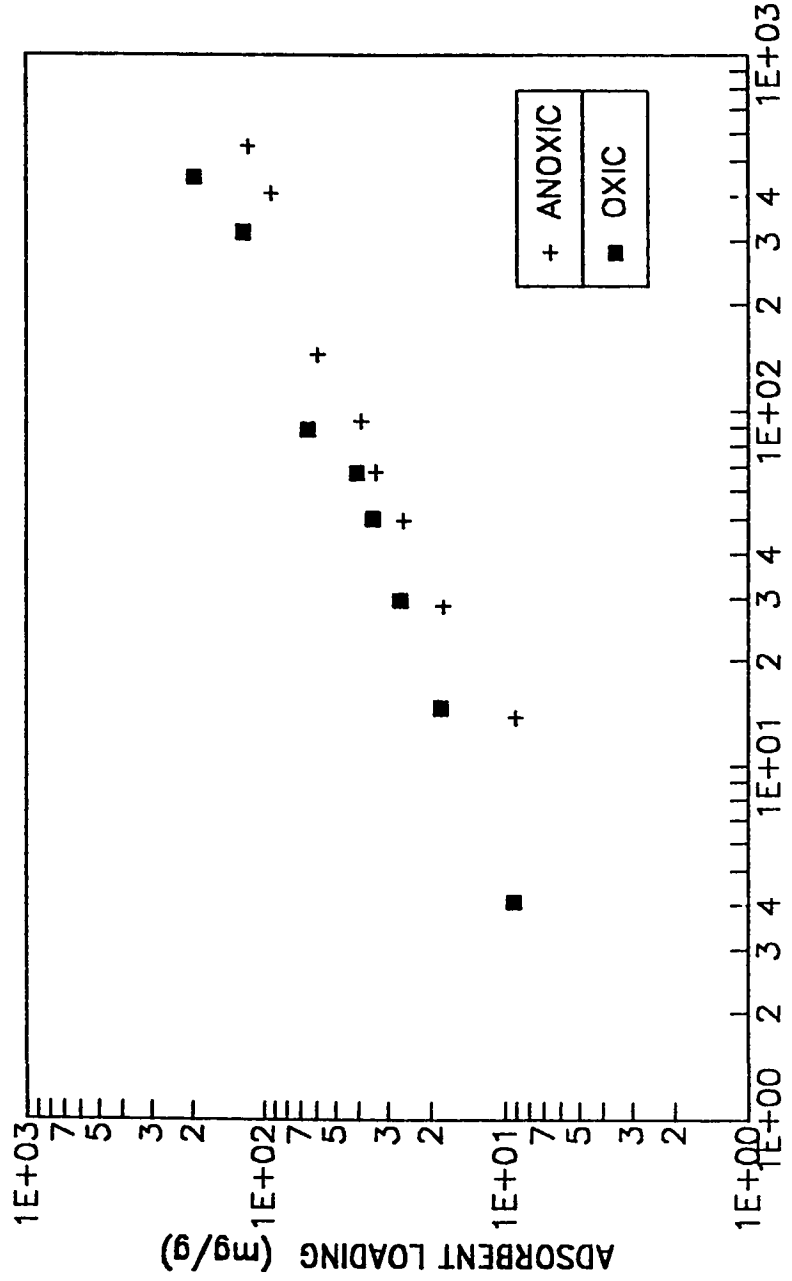

Figure 3.18: Uptakes of TOC for I.W.W, Sample locationon 3, at T = 21° C and pH of 7.

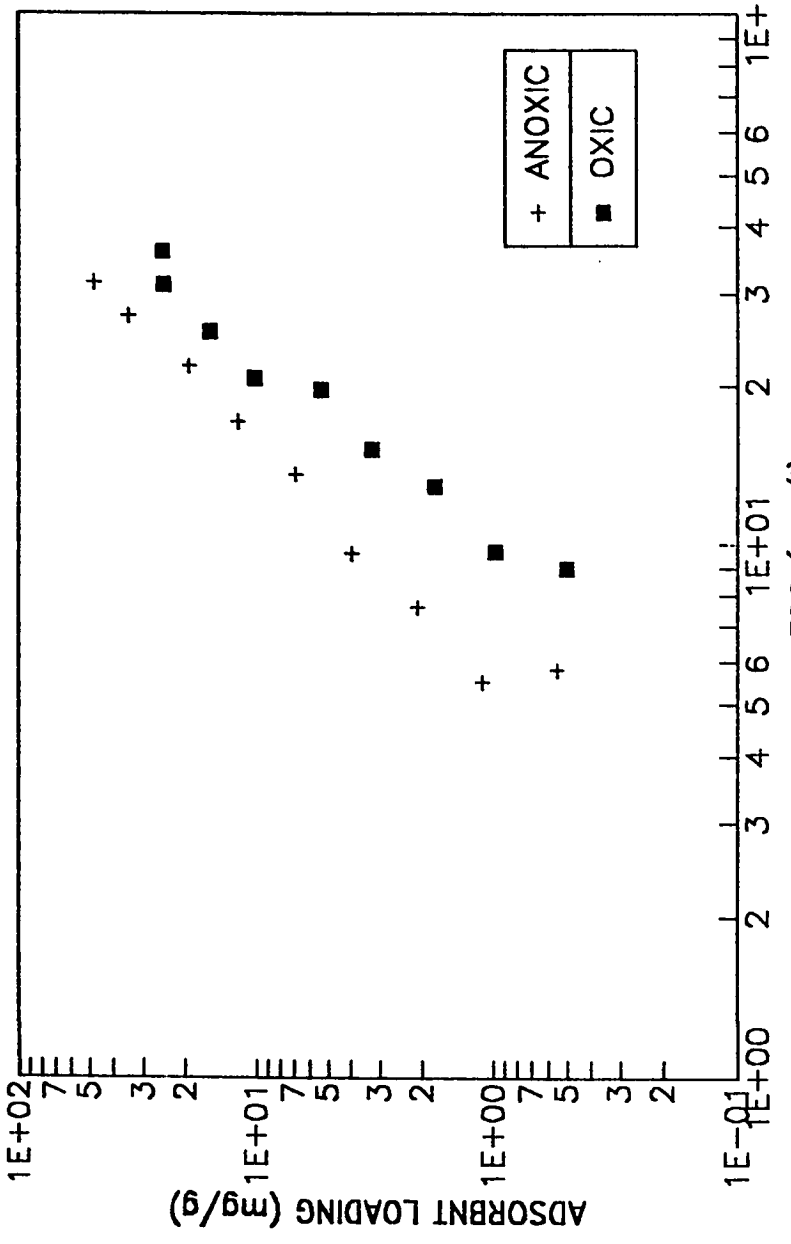

Figure 3.19: Uptakes of TOC for D.W.W at T = 21 °C and pH of 7.

Biodegradation was discounted as a possible cause for this increase in uptake through monitoring of inorganic carbon. Once again the impact of oxygen on the retention uptake of GAC was more pronounced at low concentrations. Thus in a practical operation of GAC adsorbers which are usually designed to meet stringent effluent criteria, the addition of oxygen to the feed water results in a significant extension of their service life. The reason for the I.W.W response is that the samples contained aromatics which have similar characteristics to the phenolics, while, for the D.W.W, the reason might be the existence of chemicals in the influent stream coming from ARAMCO facilities. Table 3.1 presents the Freundlich model constants for the compounds and waste water samples studied.

To corroborate the findings of this study and to make sure that these differences are not due to experimental errors, statistical analysis was carried out, and the null hypothesis that attributes the differences in uptakes of activated carbon due to the presence of DO to random error was tested. The Analysis of Variance was constructed following the methodology of Montgomery (57), whereby the ratio of the mean squares of the variable of interest (residual concentration) to that of the error is calculated. The F-value is then compared with a corresponding value from a table under the same degrees of freedom as the data and a specified probability of error. The result of the analysis showed that the null hypothesis was strictly rejected.

Table 3.1. Freundlich Model Constants for the Compounds Studied at pH = 7 and a temperature of 21°C.

Compound	Isotherm Type	k (mg/g)(L/mg)$^{1/n}$	n	R^2
chloroform	oxic	1.09	0.63	0.99
	anoxic	1.14	0.61	0.99
bromoform	oxic	5.19	0.43	0.98
	anoxic	5.33	0.42	0.99
1,1,1trichloroethane	oxic	0.76	0.34	0.99
	anoxic	0.77	0.33	0.98
1,1,2,2tetrachloroethane	oxic	3.01	0.22	0.98
	anoxic	2.99	0.23	0.97
D.W.W	oxic	0.016	2.3	0.94
	anoxic	0.0013	2.9	0.95
I.W.W loc. 1	oxic	0.26	0.64	0.93
	anoxic	1.84	0.67	0.94
I.W.W loc. 2	oxic	0.66	0.94	0.96
	anoxic	0.03	1.65	0.94
I.W.W loc. 3	oxic	1.58	0.65	0.97
	anoxic	0.1	1.59	0.95
o-cresol	oxic	190.4	0.13	0.94
	anoxic	88.6	0.19	0.98
phenol	oxic	83.5	0.18	0.97
	anoxic	31.7	0.24	0.99
4-nitrophenol	oxic	87.0	0.15	0.99
	anoxic	73.3	0.16	0.94

* R^2 is the coefficient of determination

Chapter 4

ACTIVATED CARBON ADSORPTION OF PHENOLICS IN OXIC SYSTEMS: EFFECT OF PH AND TEMPERATURE VARIATIONS ON EQUILIBRIUM

4.1 Introduction

In the previous chapter, the enhancement of uptake of phenolics by AC in the presence of DO was established. This enhancement influences the prediction of the breakthrough curves leading to a fallible design of adsorption columns, i.e. taking into account the additional uptake gained by the presence of DO yields a shorter column for a given throughput waste volume or a longer run time which means less consumption of GAC. This enhancement in retention capacities was primarily attributed to oxidative coupling reactions taking place on the carbon surface. The production of irreversibly adsorbed telomeric products, while prolonging adsorber runs gives rise to a major drawback of this enhancement phenomenon, namely low or negligible regeneration efficiencies.

In view of the scarcity of information in the literature, the objective in this chapter is to delineate the impact of the solution pH and temperature on the enhancement in sorption uptake attributed to adsorbate telomerization. Isotherm studies are conducted for phenol and o-cresol at room temperature and pH values of 3, 7, and 11 in oxic and anoxic conditions. Isotherm studies are also conducted for the same sorbates at

neutral pH and temperatures of 8°C, 21°C, and 35°C in both oxic and anoxic conditions. GC-MS analysis was performed on the GAC extracts for phenol and o-cresol to characterize the adsorbate phase and study the extent of telomerization.

4.2 Results and Discussion

After the determination of residual concentration of adsorbates, the single-solute isotherms for each of the cases under study are well represented by the Freundlich equation: $q = kc^{1/n}$.

4.2.1 pH Variation

The phenol adsorption data and Freundlich phenol curves at pH values of 3, 7, and 11, are shown in figures 4.1, 4.2, and 4.3 respectively, while the o-cresol data and freundlich curves at pH values of 3, 7, and 11, are shown in Figures 4.4, 4.5, and 4.6, respectively. The previous figures show higher retention capacities under oxic conditions compared to the anoxic one for the three pH values. However, the increase in uptake differed in magnitude depending on the pH value. For o-cresol, the percentage enhancement at 1 mg/l residual concentration was 22.5%, 115%, and 122% at pH values of 3, 7, and 11, respectively. While for phenol, the percentage enhancement at 1 mg/l residual concentration was 70%, 163%, and 162.4% at pH values of 3, 7, and 11, respectively. Table 4.1 lists the Freundlich model constants for these cases. The values of k and 1/n for phenol and o-cresol, and the fact that 1/n was higher in the case of oxygen-free isotherm agrees well with the findings of Vidic et al. (10, 14, 58) and Nakhla et al. (11, 59).

Table 4.1. Freundlich Constants for Phenol and o-Cresol at Various pHs and temperature of 21°C.

Compound	Isotherm Type	k $(mg/g)(L/mg)^{1/n}$	1/n	R^2
o-cresol	oxic, pH 3	134.3	0.14	0.94
	anoxic, pH 3	109.6	0.17	0.97
o-cresol	oxic, pH 7	190.4	0.13	0.99
	anoxic, pH 7	88.6	0.19	0.96
o-cresol	oxic, pH 11	65.4	0.20	0.97
	anoxic, pH 11	29.4	0.19	0.96
phenol	oxic, pH 3	61.4	0.19	0.95
	anoxic, pH 3	36.1	0.24	0.96
phenol	oxic, pH 7	83.5	0.18	0.97
	anoxic, pH 7	31.7	0.24	0.99
phenol	oxic, pH 11	32.8	0.31	0.96
	anoxic, pH 11	12.5	0.37	0.95

* R^2 is the coefficient of determination

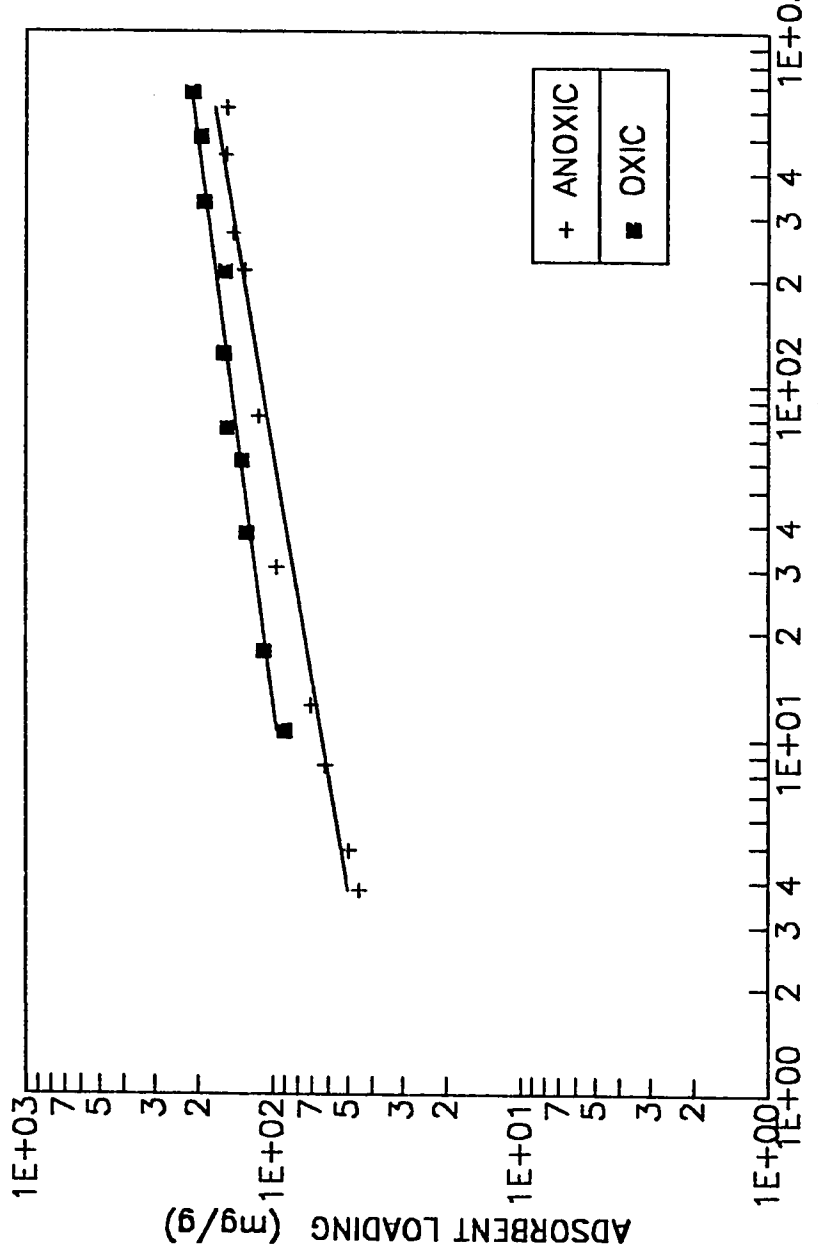

Figure 4.1: Phenol Uptakes at pH 3 and T = 21° C. Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.

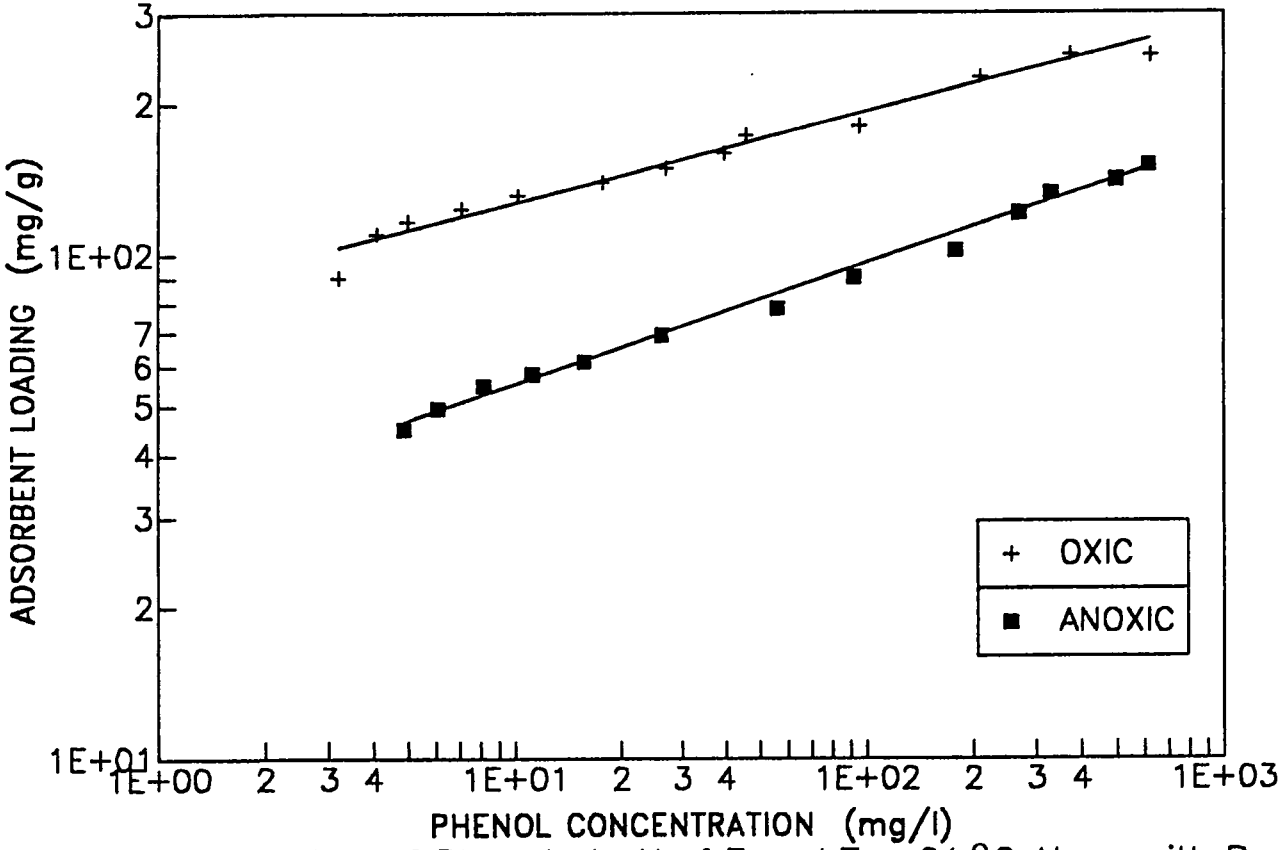

Figure 4.2: Uptakes of Phenol at pH of 7 and T = 21 °C Along with Best Fit Freundlich Curves Using constants Given in Table 4.1.

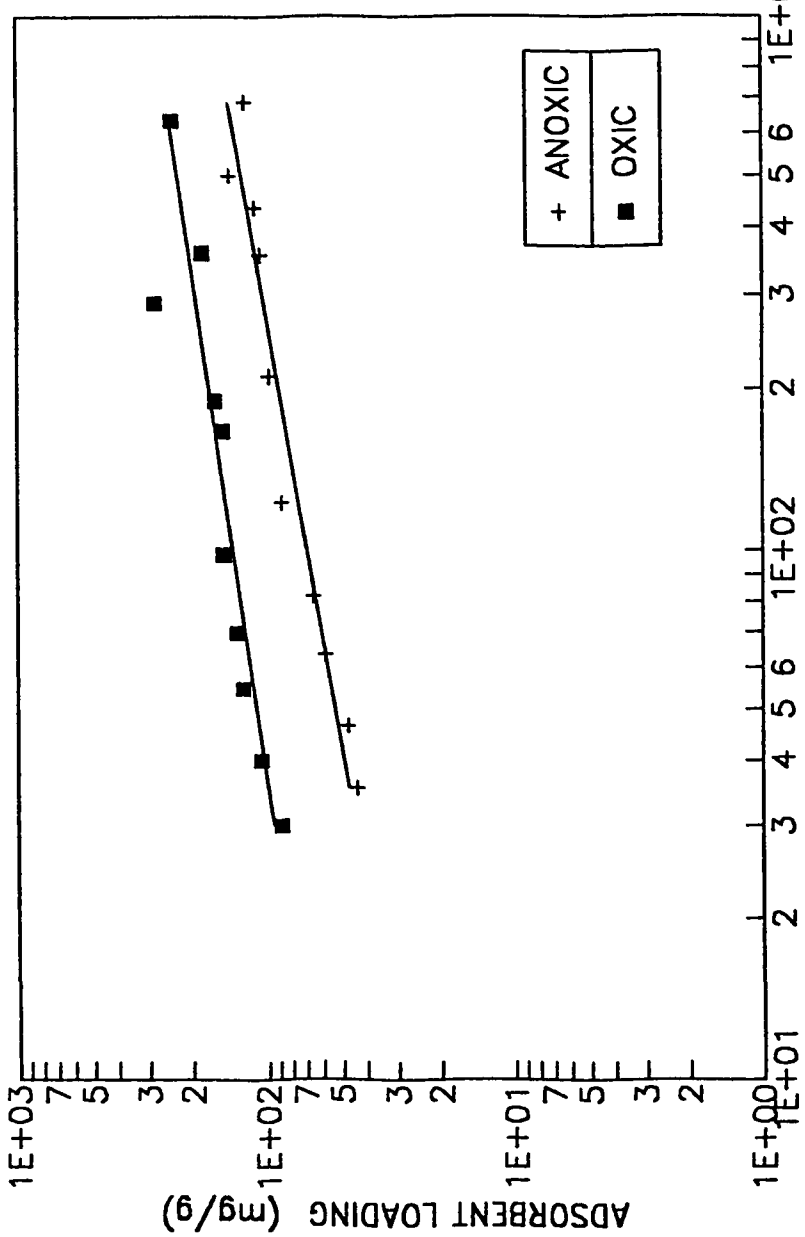

Figure 4.3: Phenol Uptakes at pH 11 and T = 21 °C. Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.

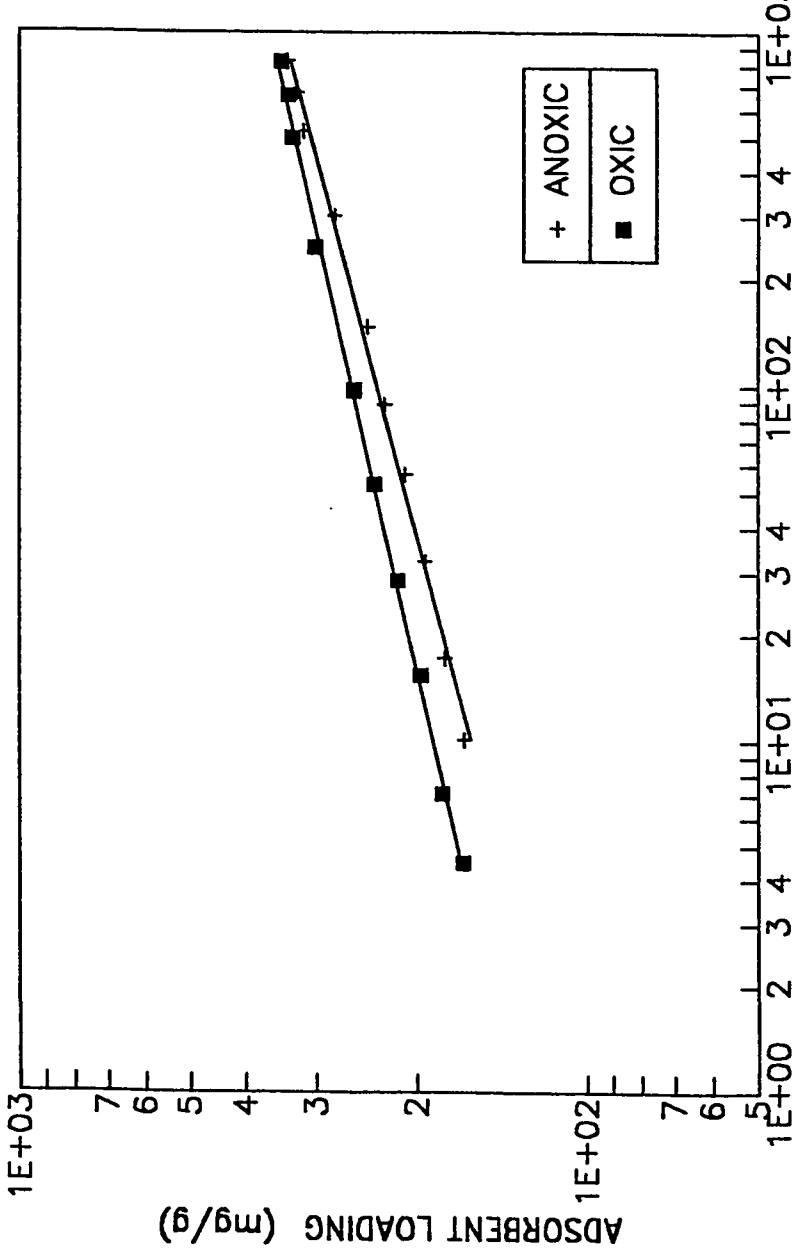

Figure 4.4: o-Cresol Uptakes at pH 3 and T = 21 °C Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.

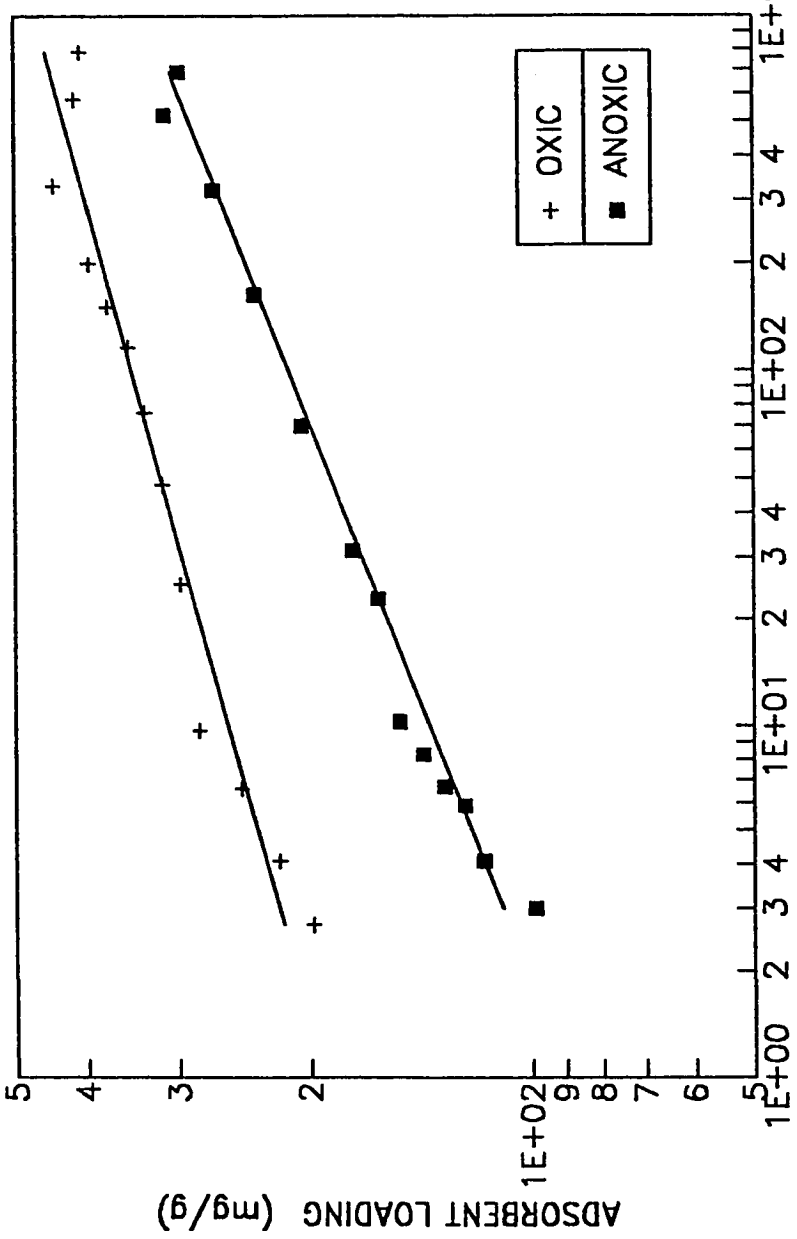

Figure 4.5: Uptakes of o-Cresol at pH of 7 and T = 21 °C. Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.

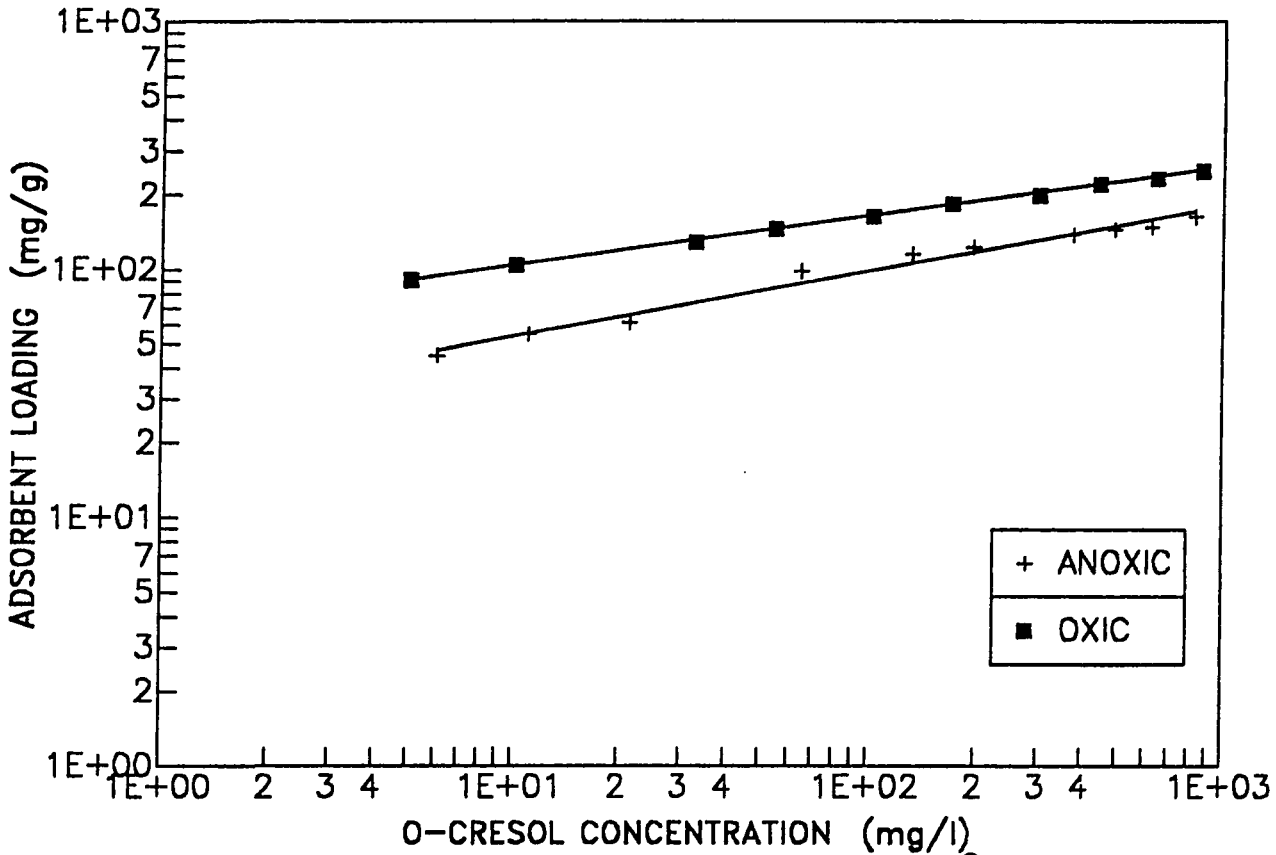

Figure 4.6: Uptakes of o-Cresol at pH 11 and T = 21° C. Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.

The extraction efficiency of the adsorbates from the GAC was generally lower in the oxic case compared to the anoxic one, thus confirming the findings of Grant and King (13) and Vidic and Suidan (14).

Results of the GC-MS analyses performed on the extracts from the carbon used in oxic and anoxic phenol and o-cresol isotherms suggested that a telomerization reaction promoted by the presence of dissolved oxygen in the test environment is a possible explanation for the observed low phenol recovery (adsorption irreversibility) and the subsequent enhancement in uptake. Significant amounts of dimers and trimers of phenol and o-cresol not originating from the stock solutions or the carbon surface were detected in the oxic samples while only traces of dimers were formed in the anoxic samples.

Figures 4.7 and 4.8 present the additional uptake as a percentage of the anoxic uptake versus the anoxic uptake for the various pH phenol and o-cresol cases, respectively. From the figures, it is seen that all the curves decrease nonlinearly with increase in the anoxic uptake. The data strongly suggests that at high sorbate concentrations most of the adsorption sites are occupied by the parent compound and thus relatively fewer sites are available for the oxygen-induced telomerization products. It can also be noted that the order of enhancement is pH 7 > pH 11 > pH 3 for both phenol and o-cresol. Figures 4.9 and 4.10 present the theoretical pC-pH diagrams calculated by the following relation; pH = pKa + Log {salt/acid}. The salt and acid in the aforementioned equation are the conjugate base and acid. To be able to understand and rationalize the observed trends in Figures 4.7 and 4.8, it is essential to know the consequences of pH variations on adsorption and reaction of the selected phenols. Low pH means abundance of protons in the sorbate solution and completely acid forms of phenol or o-cresol.

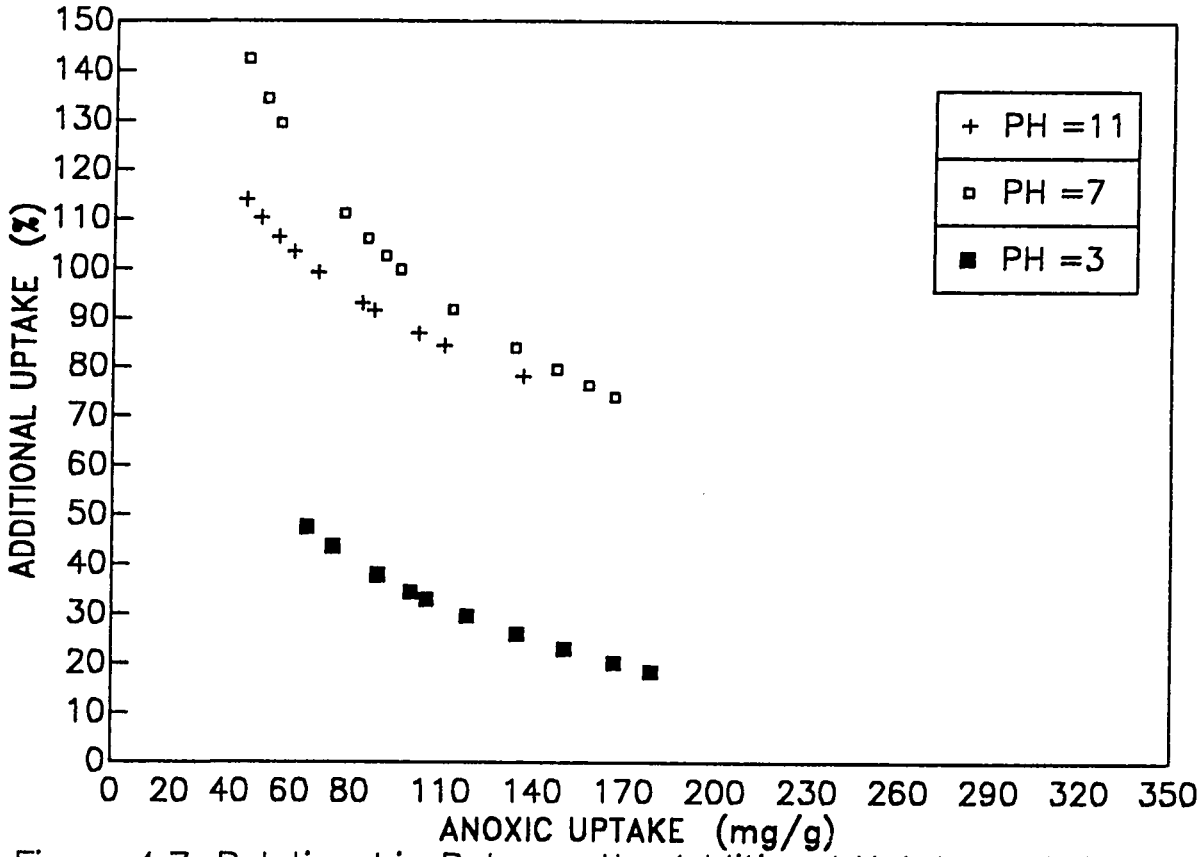

Figure 4.7: Relationship Between the Additional Uptake and the Anoxic Uptake for Phenol at Different pHs and T = 21° C.

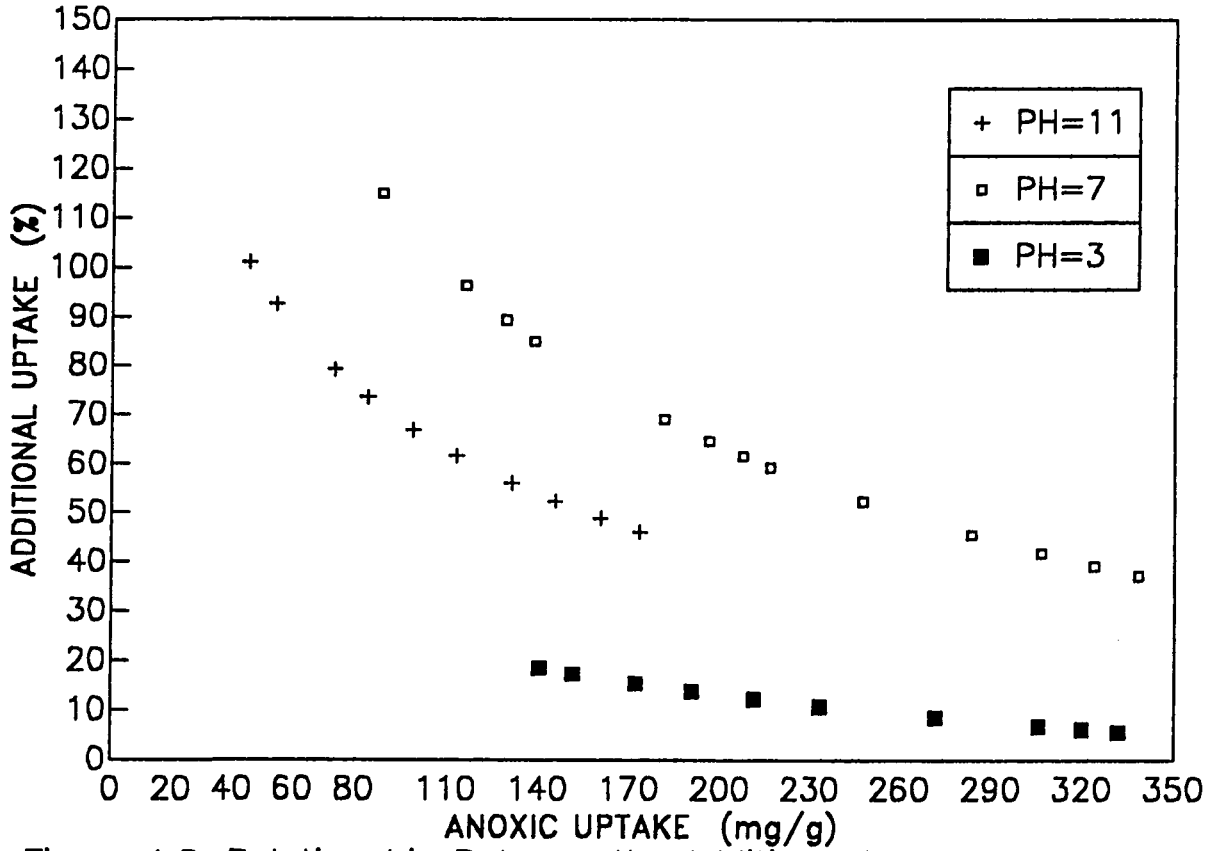

Figure 4.8: Relationship Between the Additional Uptake and the Anoxic Uptake for o-Cresol at Different pHs and T = 21 °C.

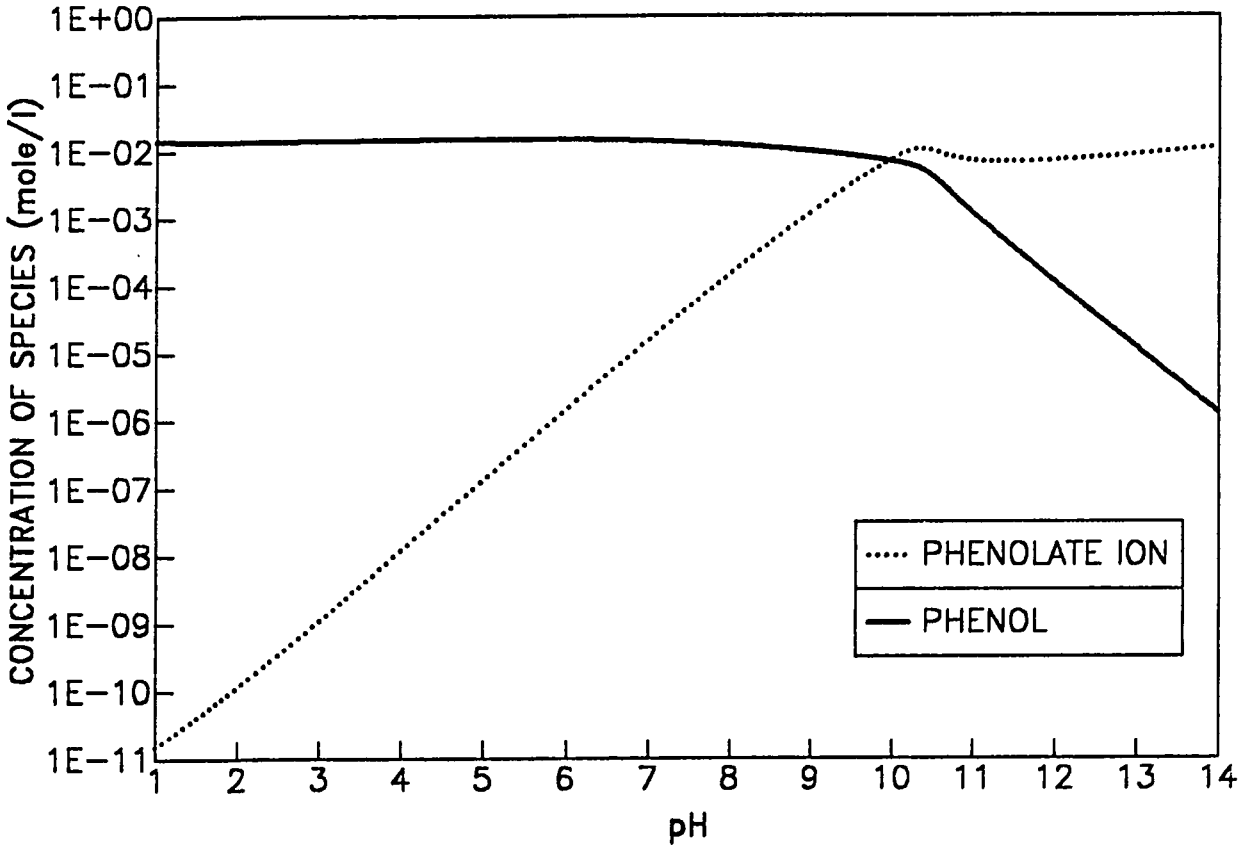

Figure 4.9: pC−pH Diagram for Phenol

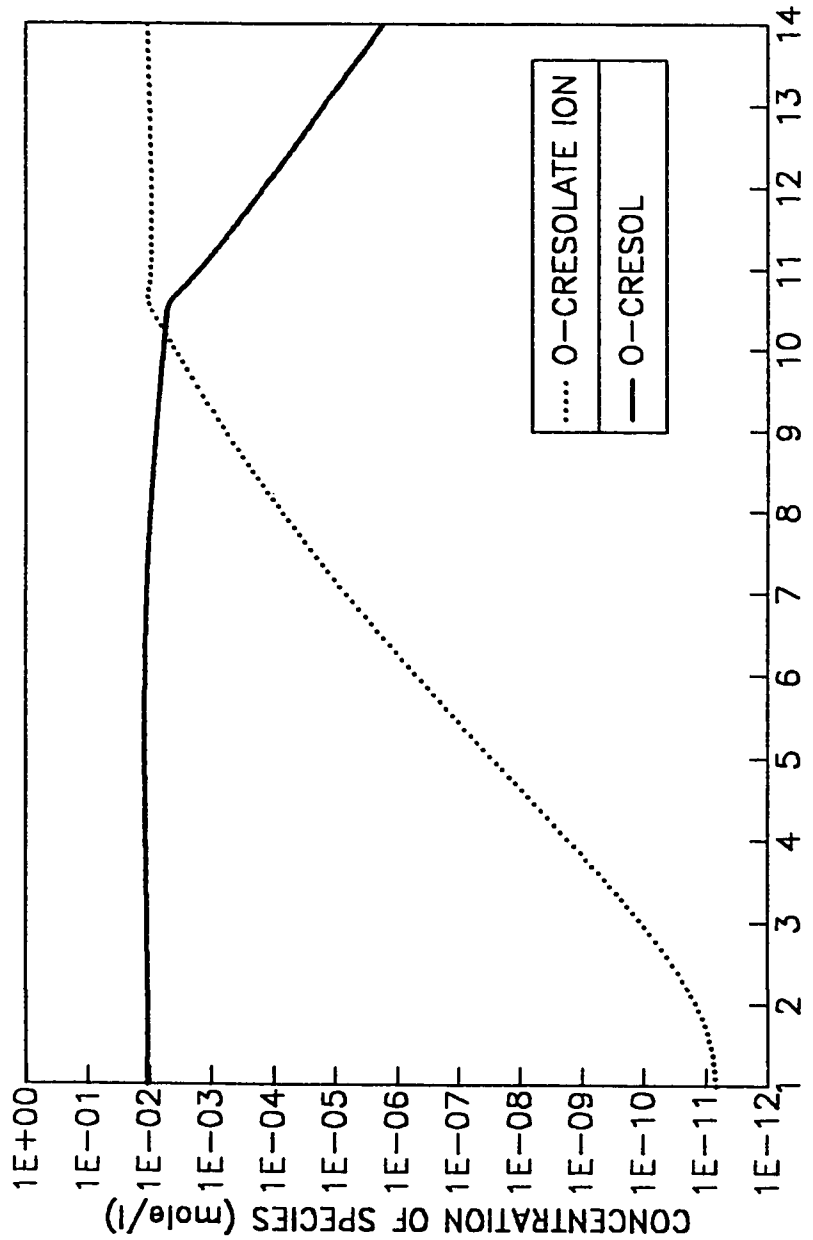

Figure 4.10: pC–pH Diagram for o–Cresol

pH 7 means neutral solution and mostly acid forms of the compounds, while at pH 11 there are very few protons and the compounds are expected to be in the salt forms. Phenol is expected to ionize more than o-cresol because phenol has a lower pKa (9.96) compared to o-cresol (10.2) (60). Actually, the scanning performed in order to find the optimum wavelength for the spectrophotometric determination of phenol and o-cresol at pH 11 showed that for phenol the wavelength corresponding to maximum absorbance shifted from 270 nm to 288 nm, which is an indication of significant ionization, and hence, formation of phenolate ions, while no change was observed for o-cresol. It can be stated that phenol ionizes more easily than o-cresol which can also be explained by the electron donation property of the methyl group in the case of o-cresol (60). The response of adsorption and chemical reactions to the above solute conditions is as follows: adsorption increases when the number of protons increase (low pH) and vice versa which agrees with the findings of many researchers (17, 18, 19, 22). While, the adsorption of unionized compounds is more than the ionized forms, ions have higher affinity for reaction than unionized compounds (13). Extracts of the carbon used in the oxic pH 3 isotherm were analyzed via GC-MS and found to contain only traces of the dimers and trimers observed in the isotherm extracts at pH 7. The explanation for this finding can best be illustrated graphically. Figure 4.11 illustrates the response of adsorption, reaction, and adsorption-reaction combination to pH variation. In fact, the curve of adsorption-reaction shows that increasing pH has two opposing effects on the phenomenon (i.e increasing reaction and decreasing adsorption), which yields the trend found in Figures 4.7 and 4.8 for the oxic cases.

The ratio of sorptive uptake at different pH and DO levels to the uptake of the anoxic isotherm at pH 7 versus the residual sorbate concentration is depicted in Figures 4.12 and 4.13.

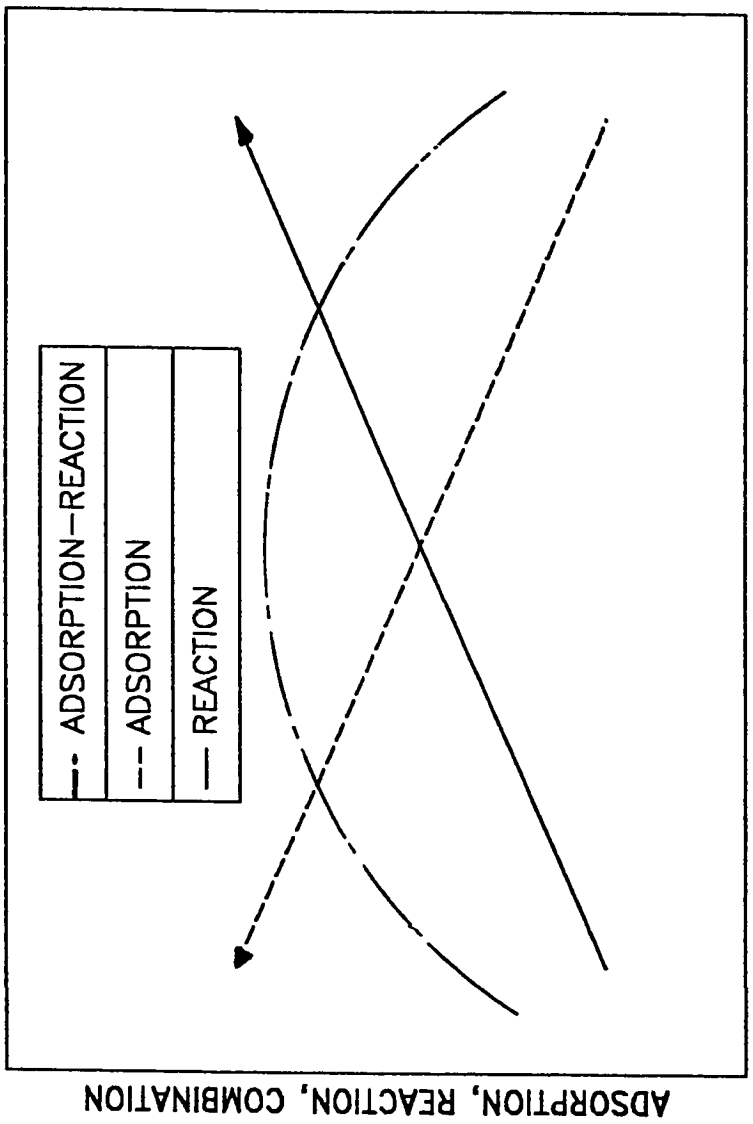

Figure 4.11: Hypothetized Effect of pH on Adsorption–Reaction Combination.

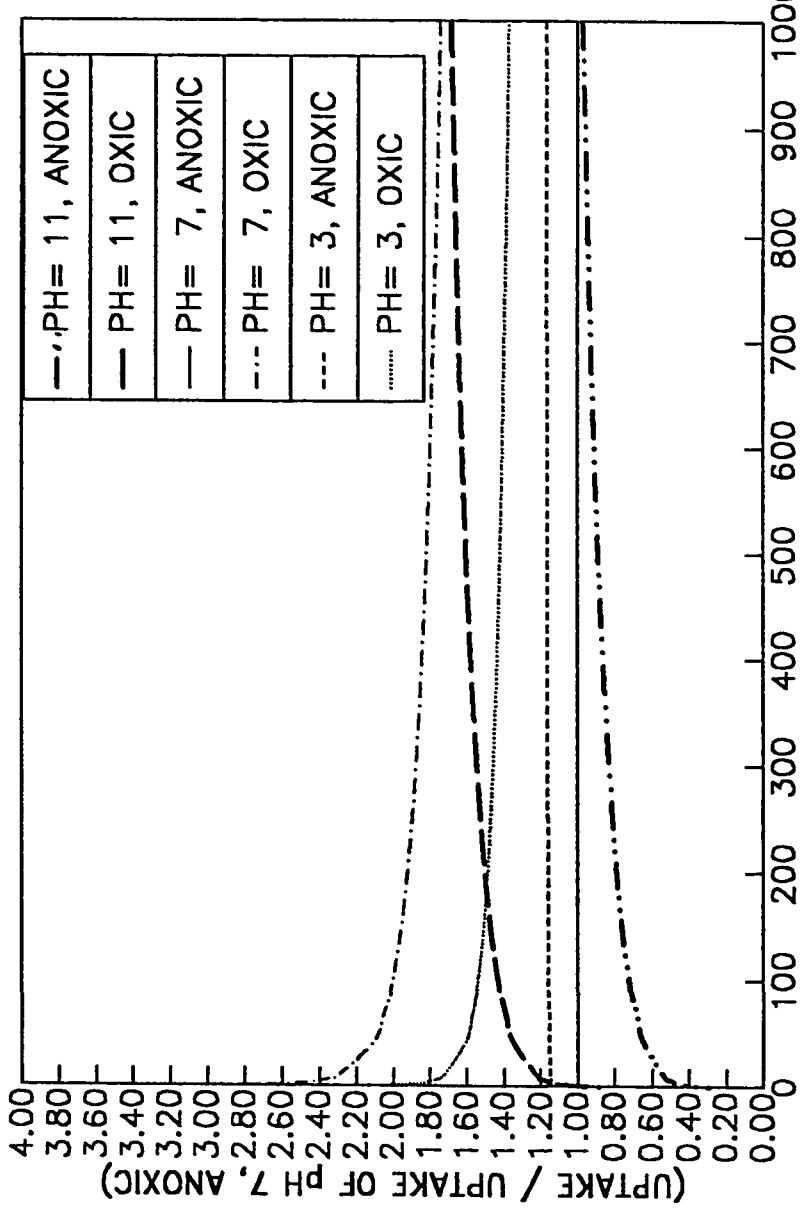

Figure 4.12: Phenol Uptakes at Different pHs Rlative to the Uptake at Neutral pH Versus Residual Concentration, at T = 21 ^{o}C.

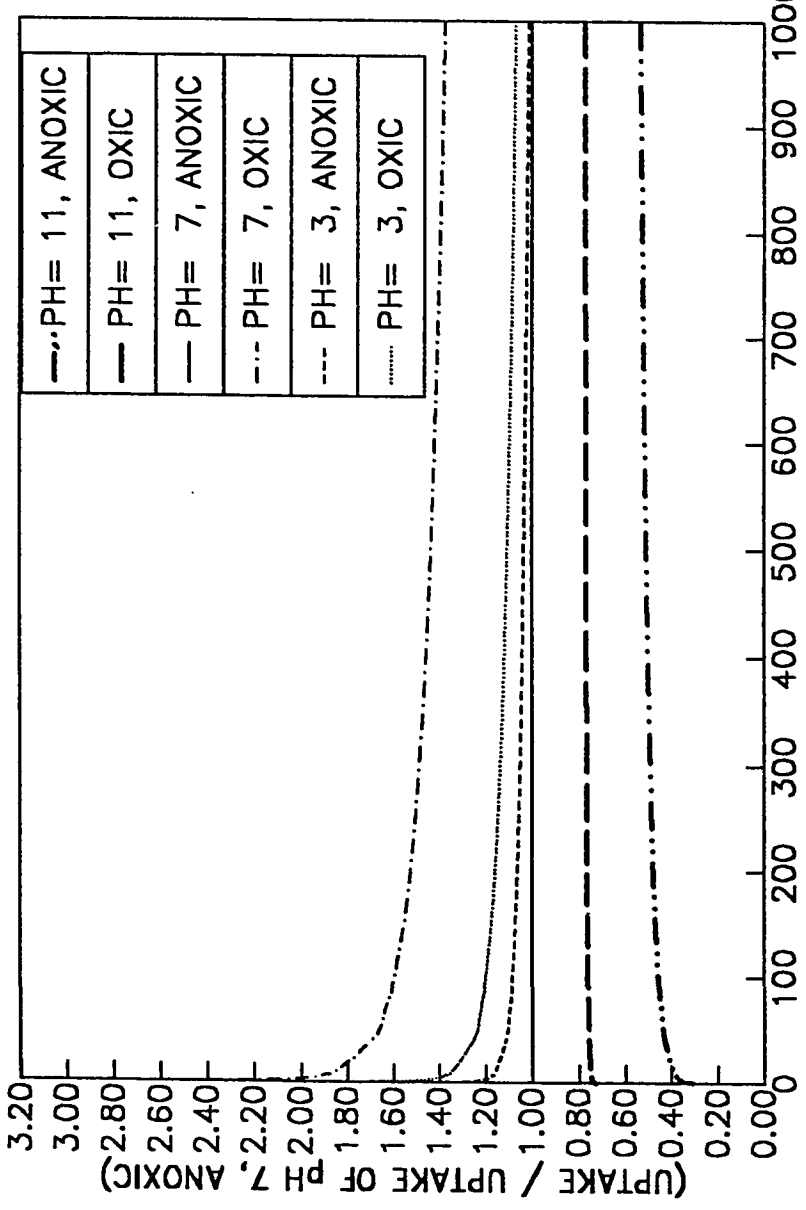

Figure 4.13: o-Cresol Uptakes at different pHs Relative to the Upatke at Neutral pH Versus Residual Concentration, at T = 21° C.

The utility of plotting the data in the manner shown is quite conspicuous as it enables one to determine the uptake at any concentration at various test conditions given only the sorptive uptake at neutral pH. The aforementioned discussion will be used as a basis for the explanation of the results shown in Figure 4.12. The fact that the uptake of phenol and o-cresol can be increased by about two to three folds simply through modifying the solution pH and its dissolved oxygen content is noteworthy. It can be seen that generally the two sorbates exhibited similar trends. The ratio of the respective capacities to the anoxic uptake at pH 7 decreased rapidly at low concentrations and remained relatively constant thereafter. The capacities at pH 11 exhibited a slightly different trend in the sense that their ratios to the anoxic isotherm at pH 7 increased sharply at low concentrations and subsequently stabilized. At low residual concentrations corresponding to relatively low initial DO to GAC mass ratio, although the extent of the telomerization is enhanced at pH 11, this reaction is limited by the availability of oxygen for its progression.

The relative independence of this uptake ratio at high concentrations suggests that the pH effect on adsorption may be hypothetically modelled as;

$$\Delta q = K_1 [\{H^+ - 10^{-7}\}^m C_e^{\frac{1}{n_1}} \quad (4.1)$$

where, Δq is the change in uptake relative to anoxic uptake at pH 7, mg/g, K_1, m, and $\frac{1}{n_1}$ are constants, $\{H^+\}$ is the hydrogen ion concentration, mole/l, and C_e is the sorbate equilibrium concentration, mg/l.

Thus, the ratio plotted as the ordinate of Figure 4.12 is given by

$$1 + \frac{K_1 [H^+ - 10^{-7}]^m C_e^{(\frac{1}{n_1} - \frac{1}{n_2})}}{K_2} \quad (4.2)$$

where, K_2 and $\frac{1}{n_2}$ are the Freundlich isotherm constants at neutral pH. For a given pH, all the terms in Equation (4.2) are constant except the C_e term. Given the low values of $\frac{1}{n_2}$ for the two adsorbates listed in Table 4.1, this ratio in uptake becomes relatively insensitive to the changes in residual concentrations. The value of the ratio given by Equation 4.2 can be greater or less than 1 depending on the value of the pH term between parenthesis. The validity of this representation is emphasized by the data shown depicting the anoxic isotherm at pH 3 and pH 11, respectively, above and below 1. However, in the presence of oxygen, Equation 4.1 must be modified to include a term that accounts for the incremental uptake due to telomerization reactions. This reaction term strongly influences the aforementioned ratio and in extreme cases as for phenol it could counterbalance the negative pH effect at high pH values and result in ratios exceeding 1. While o-cresol acted similarly, the reaction term at pH 11 was not very high due to a lower degree of ionization of o-cresol relative to phenol.

4.2.2 Temperature Variation

The Freundlich phenol curves and data at pH of 7 and temperatures of 8°C, 21°C, and 35°C are shown in figures 4.14, 4.15, and 4.16 respectively, while the the Freundlich o-cresol curves at pH 7 and temperatures of 8°C, 21°C, and 35°C are shown in figures 4.17, 4.18, and 4.19, respectively. It was found experimentally that the increase in temperature from 21°C to 35°C reduces the saturation concentration of DO from 32 mg/l to about 28 mg/l so, here, the term oxic presents DO concentration of 28 mg/l. As in the case of pH variations, the aforementioned figures show higher capacities for oxic conditions compared to the anoxic ones for the three temperature values.

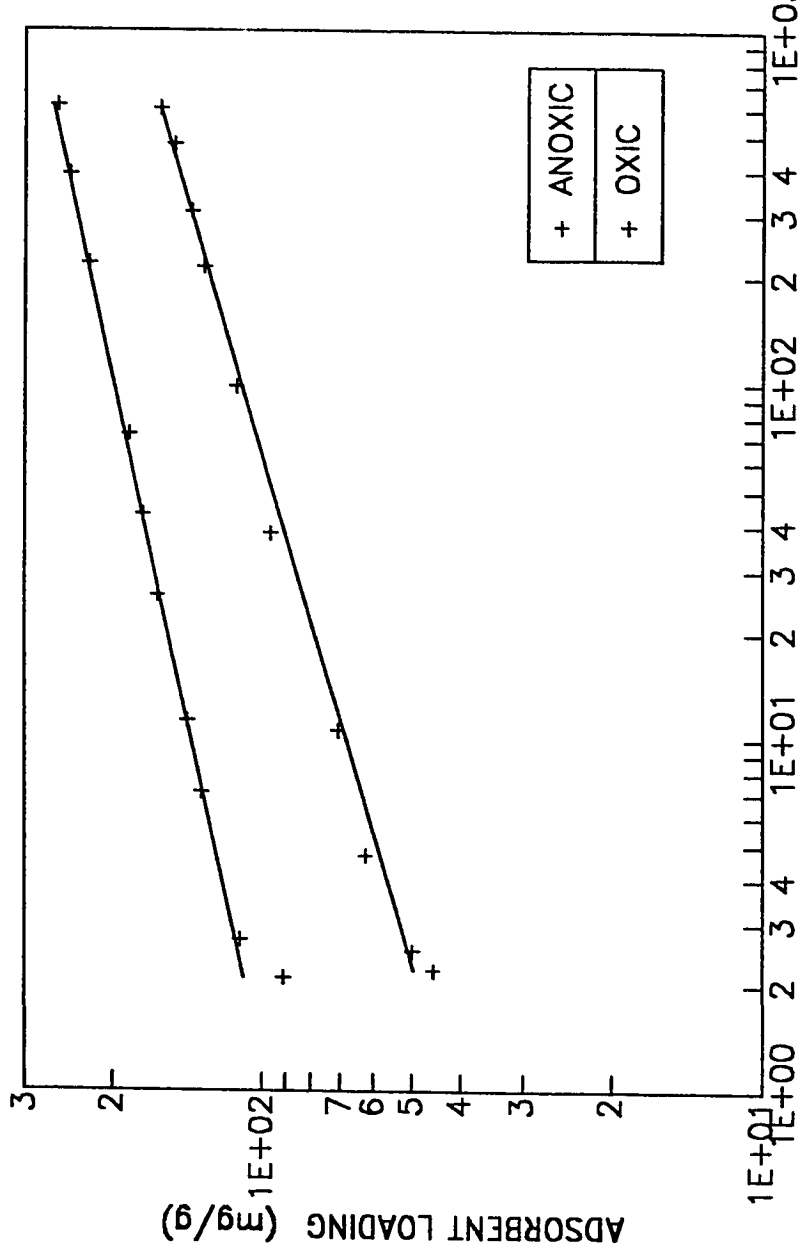

Figure 4.14: Phenol Uptakes at T = 8 °C. and pH of 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.

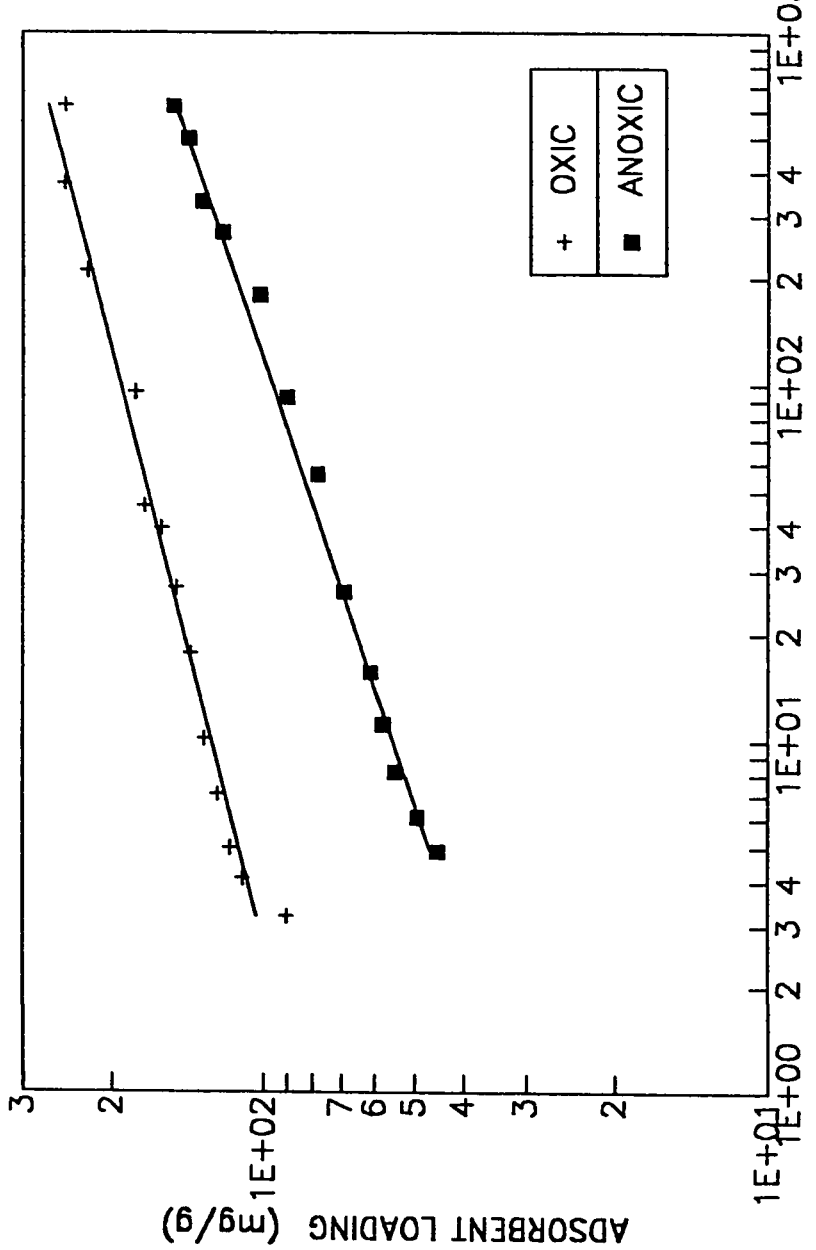

Figure 4.15: Uptakes of Phenol at T = 21° C and pH of 7 Along with Best Fit Freundlich Curves Using constants Given in Table 4.2.

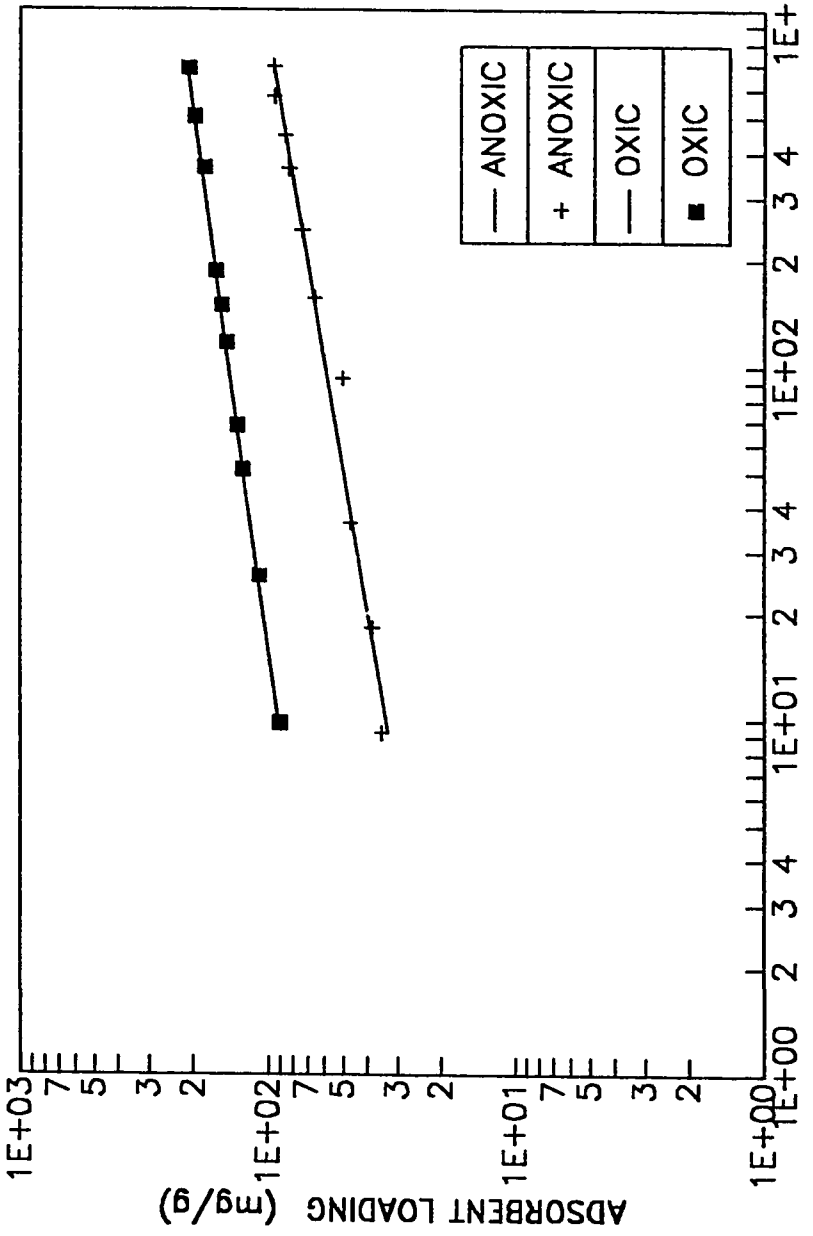

Figure 4.16: Phenol Uptakes at T 35°C. and pH 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.

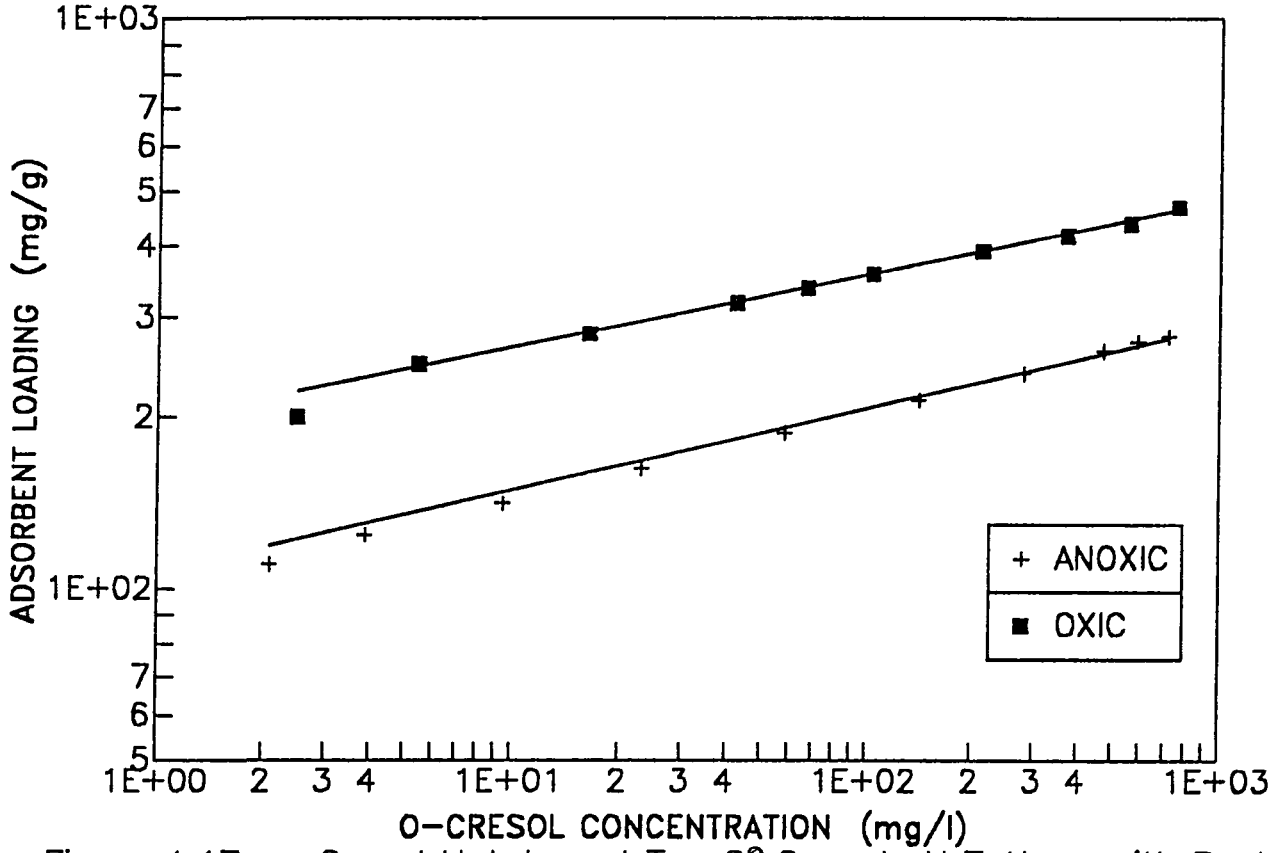

Figure 4.17: o-Cresol Uptakes at T = 8° C. and pH 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.

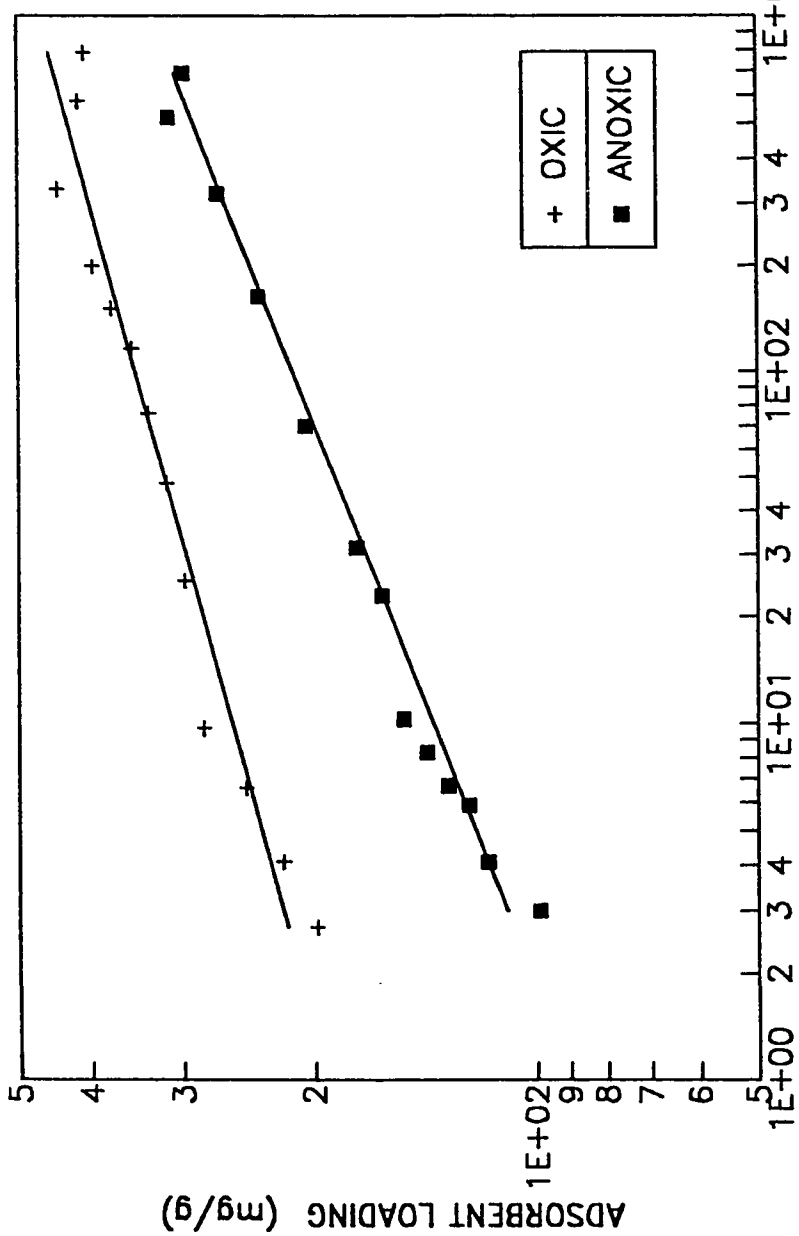

Figure 4.18: o-Cresol Uptakes at T = 21 °C. and pH 7, Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.

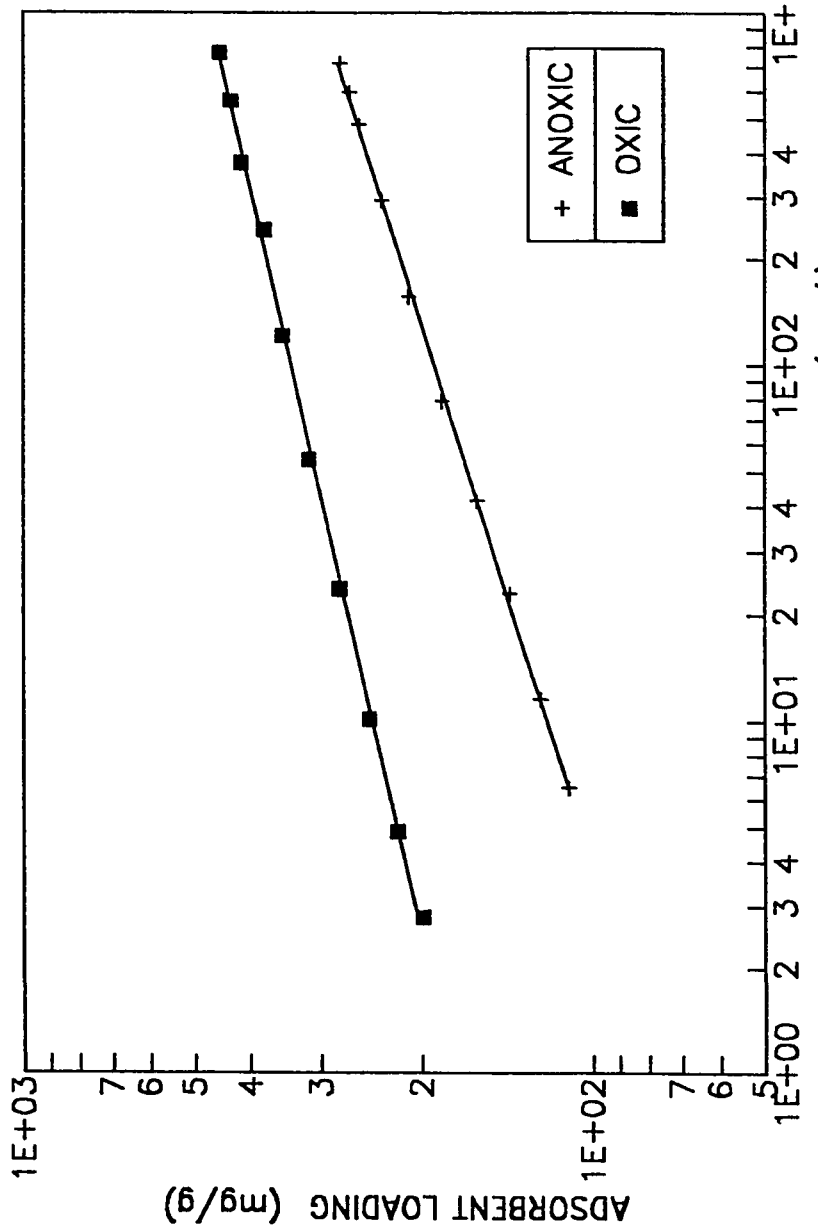

Figure 4.19: o-Cresol Uptakes at T = 35° C. and pH 7 Along with Best Fit Freundlich Curves Using Constants given in Table 4.2.

However, the increase in sorptive uptake was strongly dependent upon temperature. For phenol, the percentage enhancement in sorptive uptake at 1 mg/l residual concentration was 134%, 163%, and 200% at temperatures of 8°C, 21°C, and 35°C, respectively, while for o-cresol, the percentage enhancement in uptake at 1 mg/l residual concentration was 90%, 115%, and 130% at temperatures of 8°C, 21°C, and 35°C, respectively. Table 4.2 lists the Freundlich model constants for the data already shown in the aforementioned Figures. It is noted from the table that the value of 1/n was higher in the case of anoxic compared to oxic isotherms. It is also seen that the value of 1/n reflecting the dependence of the sorptive uptake on the liquid phase concentration increased with temperature. The percentage additional uptake caused by the presence of DO is shown as a function of the anoxic uptake in Figure 4.20 and 4.21 for phenol and o-cresol, respectively. It is apparent that the relative enhancement in uptake is a nonlinearly decreasing function of the anoxic uptake, which can be attributed to sites limitation at high anoxic capacities. It is also noted from Figures 4.20 and 4.21 that the order of percentage enhancement was at T = 8°C < T = 21°C < T = 35°C. Not only do the relative increases depicted in Figures 4.22 and 4.23 suggest that increasing temperatures favor the telomerization reaction but also the actual magnitudes of these incremental capacities point to the same finding which is consistent with the observation of Grant and King (13). An endothermic telomerization reaction would rationalize the observed effects of temperature on adsorption under oxic conditions. However, the differences between the additional capacities at 21° and 35°C are much more pronounced at high anoxic capacities than at low ones, and this is also true between 21° and 8°C. At low anoxic capacities corresponding to low DO to GAC mass ratios, oxygen limitation effects on telomerization become significant, and thus reduction in solubility of oxygen at high temperatures tend to accent such limitation.

Table 4.2. Freundlich Constants for Phenol and o-Cresol at Various Temperatures and pH 7.

Compound	Isotherm Type	k (mg/g)(L/mg)$^{1/n}$	1/n	R^2
o-cresol	oxic, T= 8°C	197.5	0.13	0.95
	anoxic, T= 8°C	104.0	0.18	0.96
o-cresol	oxic, T= 21°C	190.4	0.13	0.99
	anoxic, T= 21°C	88.6	0.19	0.96
o-cresol	oxic, T= 35°C	175.0	0.14	0.94
	anoxic, T= 35°C	76.1	0.20	0.97
phenol	oxic, T= 8°C	96.7	0.16	0.95
	anoxic, T= 8°C	41.8	0.21	0.96
phenol	oxic, T= 21°C	83.5	0.18	0.97
	anoxic, T= 21°C	31.7	0.24	0.99
phenol	oxic, T= 35°C	57.3	0.20	0.96
	anoxic, T= 35°C	19.0	0.25	0.94

* R^2 is the coefficient of determination

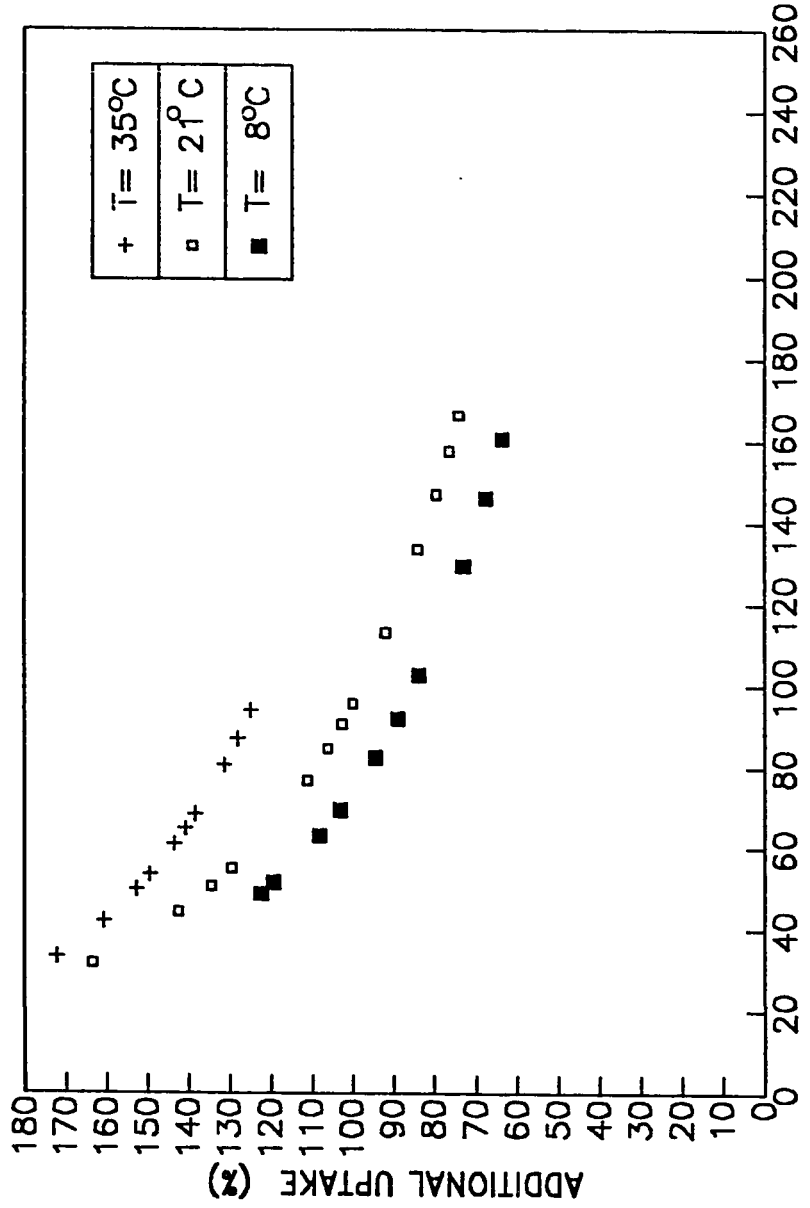

Figure 4.20: Relationship Between the Additional Uptake and the Anoxic Uptake for Phenol at Different Temperatures and pH 7.

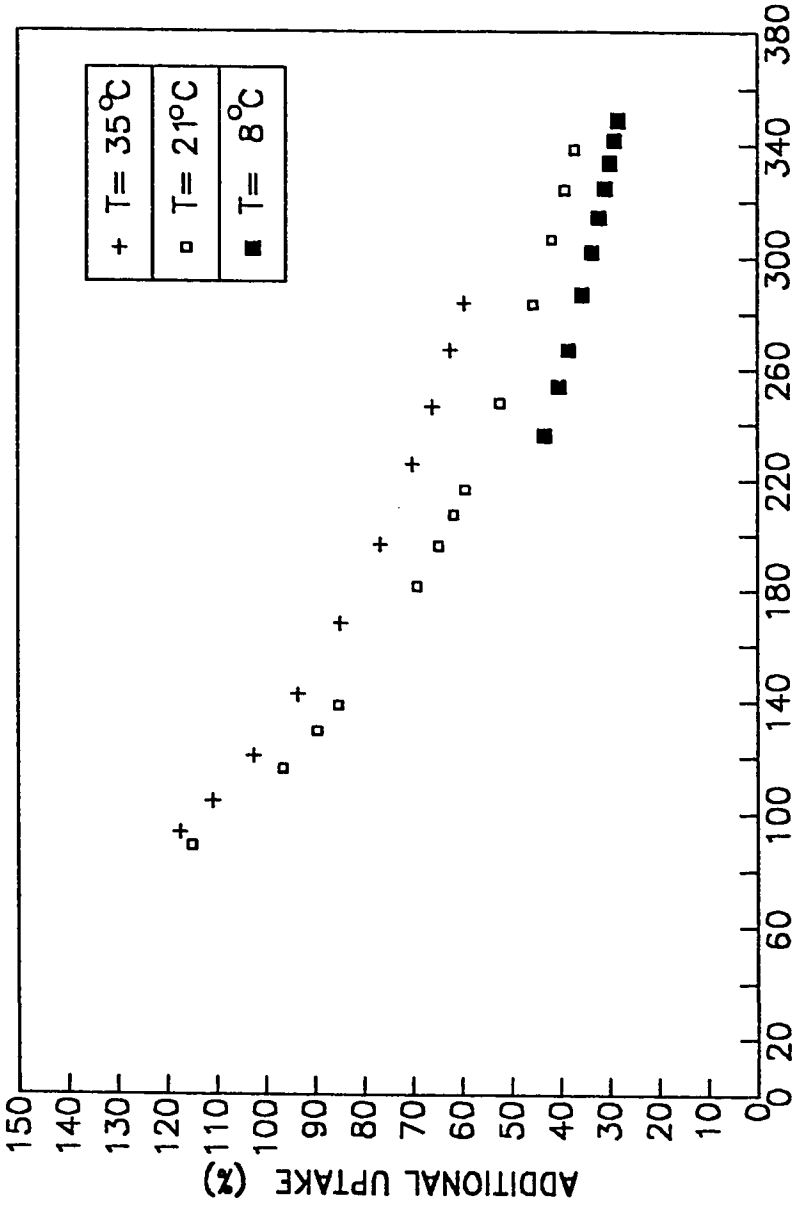

Figure 4.21: Relationship Between the Additional Uptake and the Anoxic Uptake for o-Cresol at Different Temperatures and pH 7.

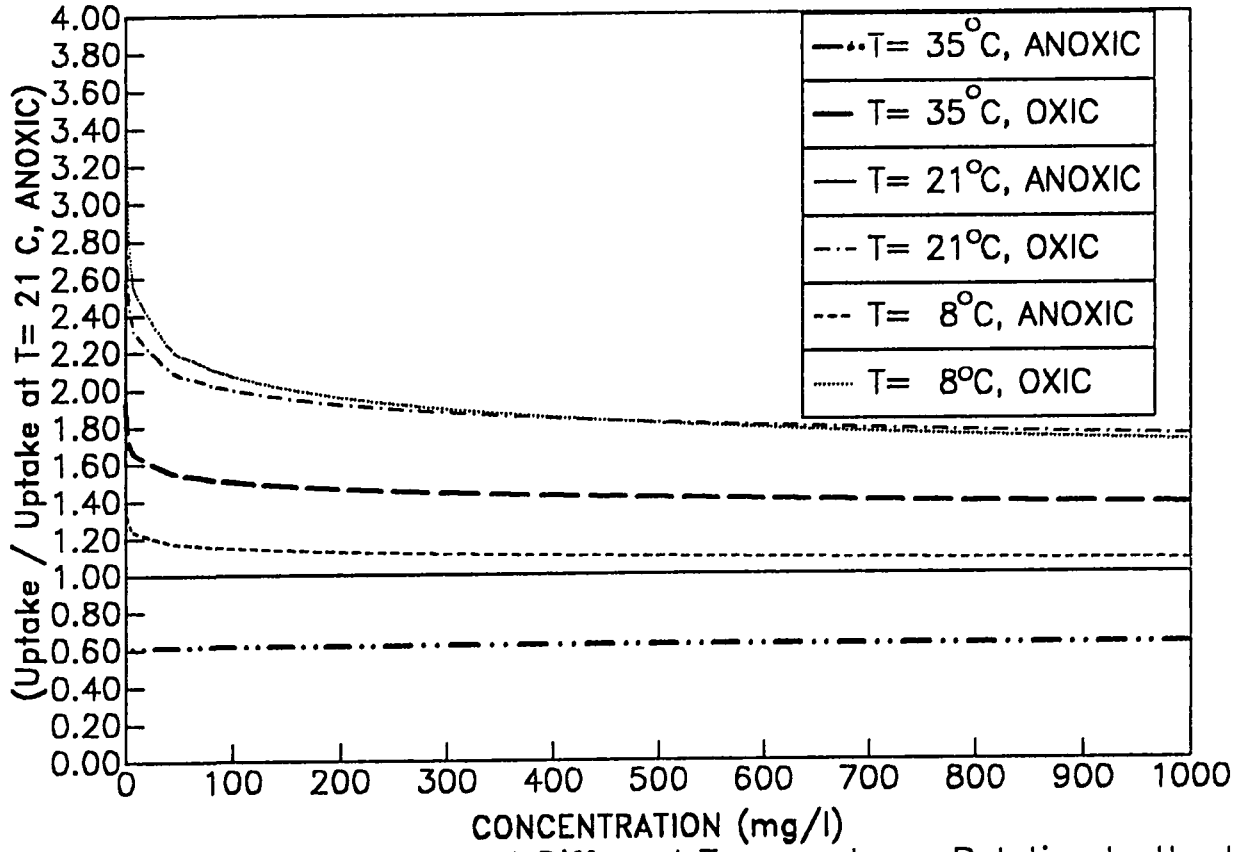

Figure 4.22: Phenol Uptakes at Different Temperatures Relative to the Uptake at Room Temperature Versus Residual Concentration.

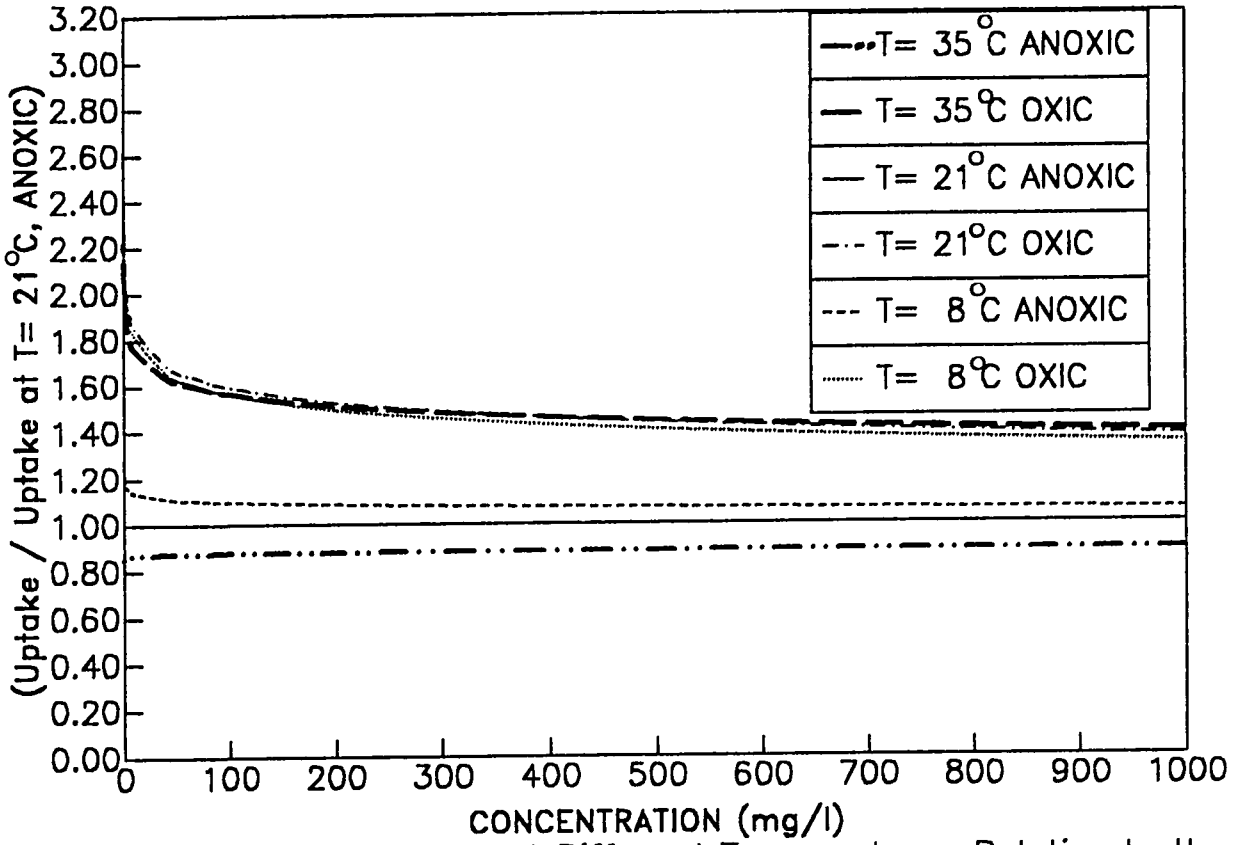

Figure 4.23: o-Cresol Uptakes at Different Temperatures Relative to the Uptake at Room Temperature Versus Residual Concentration.

These results are contradictory to those of Vidic and Suidan (14) who noted that increasing the temperature from 21°C to 35°C did not have significant effects on the adsorption-enhancement phenomenon attributed to sorbate telomerization.

The net effect of temperature on adsorption of phenolics may be evidenced as a combination of physical adsorption and oxygen-induced telomerization. Figures 4.22 and 4.23 represent the ratio of oxic and anoxic capacities at different temperatures versus the residual adsorbate concentration for phenol and o-cresol. The additional retention uptake due to sorbate telomerization can be readily deduced from Figures 4.22 and 4.23. For the anoxic systems, the uptake increased with the decrease in temperature, thus agreeing with the commonly known fact that adsorption is an exothermic process (61). For the oxic cases, phenol and o-cresol behaved differently, while the net effect of temperature on the oxic sorbate uptake of o-cresol was the same for the three temperatures studied, i.e. 8°C, 21°C, and 35°C, the oxic capacities for phenol were lower at 35°C than at 8°C and 21°C. The loading data for o-cresol suggests that the positive effect of temperature on telomerization is counterbalanced by the reduction in physical adsorption at 35°C, and vice-versa at 8°C. The slight difference in behavior between phenol and o-cresol can be explained by considering the relative ratios of the anoxic loading at 35°C to the reference uptake at 21°C. For o-cresol, the anoxic uptake at 35°C was 85% while for phenol, it was about 60% of the reference uptake. Thus despite the significant enhancement attained by the presence of DO, the oxic uptake at 35°C fails to approach that at 21°C.

In an attempt to determine the heat of adsorption for phenol and o-cresol, the Arrhenious equation was used. The equation is:

$$k = k_0 \exp\left(\frac{-\Delta H}{R_g T}\right) \tag{4.3}$$

which can linearized as;

$$\log k = k_0 - \frac{\Delta H}{2.3\, R_g T} \tag{4.4}$$

where, k is the Freundlich constant, k_0 is the intercept, R_g is the universal gas constant = 8.31 J/(mol.K), $-\Delta H$ is the heat of adsorption, and T is temperature in kelvin. Figure 4.24 presents the relation in Equation 4.4 for phenol and o-cresol, from which the intercept k_0 was = -2.3 and 0.5 for phenol and o-cresol, respectively, while, the heat of adsorption $-\Delta H$ was calculated from the slope and found to be -8124 J/mole and -21170 J/mole for phenol and o-cresol, respectively. The use of the aforementioned relation enables one to predict the capacities at different temperatures using the following equation:

$$q = k_0 \exp\left(-\frac{\Delta H}{R_g T}\right) C^{\frac{1}{n}} \tag{4.5}$$

providing the appropriate constants are used.

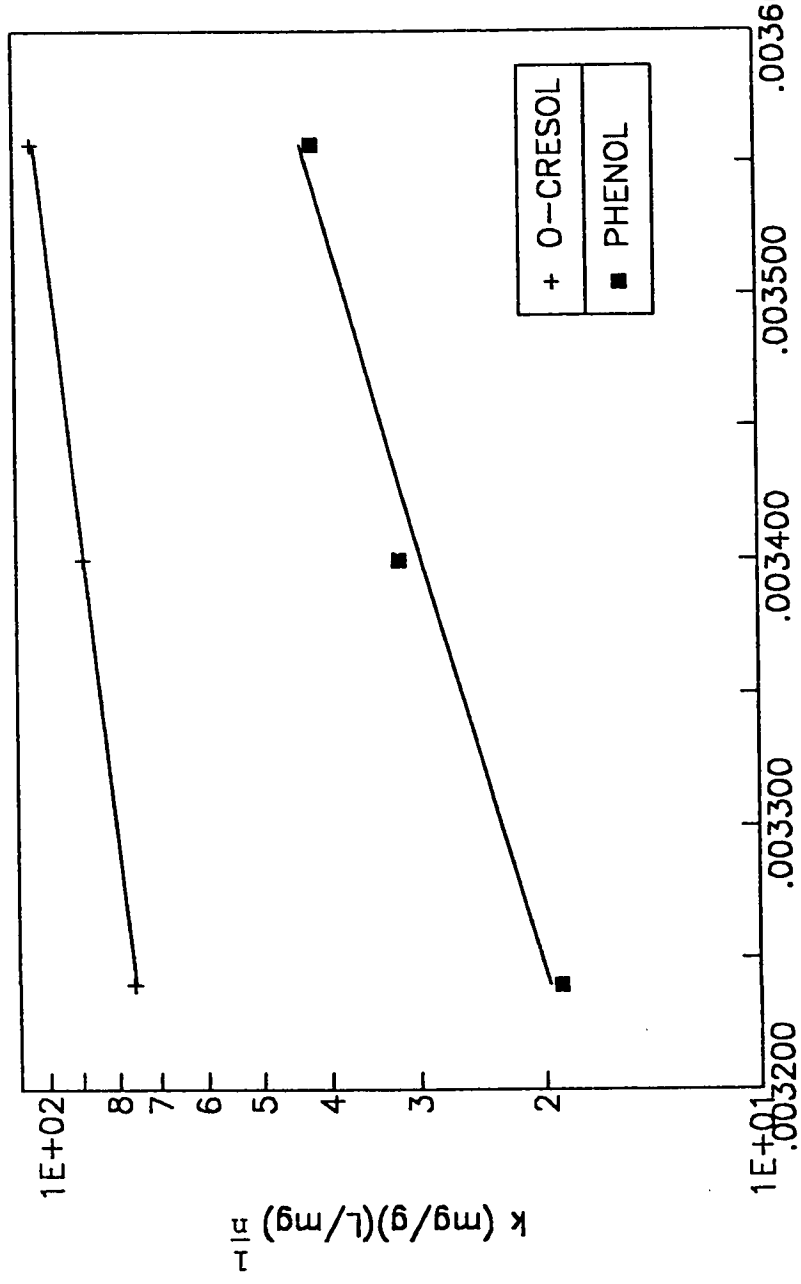

Figure 4.24: Relationship Between Freundlich Constants and Temperature for Phenol and o-Cresol Along with Lines of Best Fit.

Chapter 5

EFFECTS OF DISSOLVED OXYGEN LEVELS ON EQUILIBRIUM OF PHENOLICS ADSORPTION BY ACTIVATED CARBON

5.1 Introduction

The recent work addressing the role of oxygen in the adsorption of phenolics on AC has been conducted at two levels of DO; zero and saturation with oxygen (DO concentration around 30 mg/l), and thus does not permit precise modelling of DO effects on adsorption equilibrium. The objective of this study is to provide further insight into the effect of DO on the kinetics and adsorption equilibrium of phenol and o-cresol by AC. A secondary objective of this study is to present a mathematical model of such effects that could be used to describe adsorption uptakes at various DO concentrations. Four levels of dissolved oxygen were selected namely; zero, 4 mg/l, saturation with air corresponding to DO about 9 mg/l, and saturation with pure oxygen (DO concentration around 30 mg/l). Those DO levels will be denoted hereafter as DO levels 1, 2, 3, and 4, respectively.

In order to study the effect of the different oxygen levels on kinetics of adsorption, closed batch studies were performed on the adsorption of phenol on GAC under the aforementioned four levels of dissolved oxygen.

5.2 Results and Discussion

5.2.1 Equilibrium Studies

After the determination of residual concentration of adsorbates, the single-solute loadings for each of the cases under study were described by the Freundlich equation; $q = kc^{1/n}$.

The phenol uptakes are plotted against the residual concentration in Figures 5.1 and 5.2 on logarithmic scale (Freundlich loading) and linear scale (to accent the differences) at the four levels of DO, while Figures 5.3 and 5.4 represents the o-cresol case. In the following discussion, the term "anoxic" and "oxic" refer to DO levels 1 and 4 corresponding to concentrations of 0, around 30 mg/l, respectively. The two figures clearly show that the uptake increases with the increase in the DO level. For o-cresol, the percentage enhancement at 1 mg/l residual concentration was 43%, 71%, and 115% of the base anoxic uptake at DO levels 2, 3, and 4, respectively,. while for phenol, the percentage enhancement at 1 mg/l residual concentration was 52%, 93%, and 163% of the anoxic uptake at DO levels 2, 3, and 4, respectively. Table 5.1 lists the Freundlich model constants for the cases already shown in Figures 5.1 and 5.3. From Table 5.1 it is apparent that while the values of k are increasing with the increase in DO content 1/n values are decreasing for phenol and o-cresol. This agrees with the findings of Vidic and Suidan (14) who observed in two DO levels experiment (oxic and anoxic) that 1/n was higher in the case of oxygen-free loading.

Table 5.1. Freundlich Constants at Different DO Levels for Phenol and o-Cresol, at temperature of 21°C, and pH 7.

Compound	Isotherm Type	k (mg/g)(L./mg)	1/n	R^2
o-cresol	anoxic, DO 1	88.6	0.190	0.96
	oxic, DO 2	126.8	0.173	0.95
	oxic, DO 3	151.7	0.154	0.96
	oxic, DO 4	190.4	0.130	0.99
phenol	anoxic, DO 1	31.7	0.240	0.99
	oxic, DO 2	48.3	0.223	0.95
	oxic, DO 3	61.1	0.203	0.96
	oxic, DO 4	83.5	0.180	0.97

* R^2 is the coefficient of determination

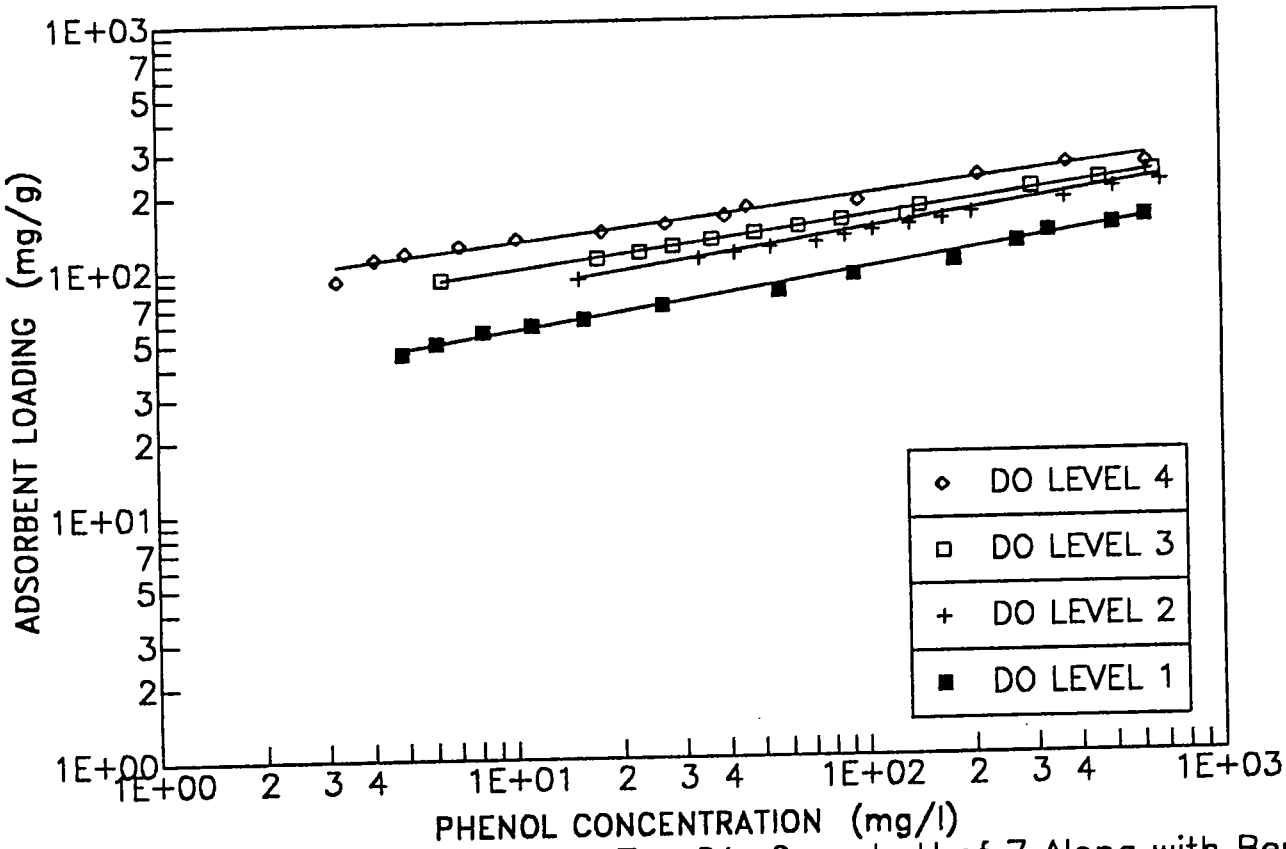

Figure 5.1: Uptakes of Phenol at T = 21 C. and pH of 7 Along with Best Fit Freundlich Curves Using constants Given in Table 5.1.

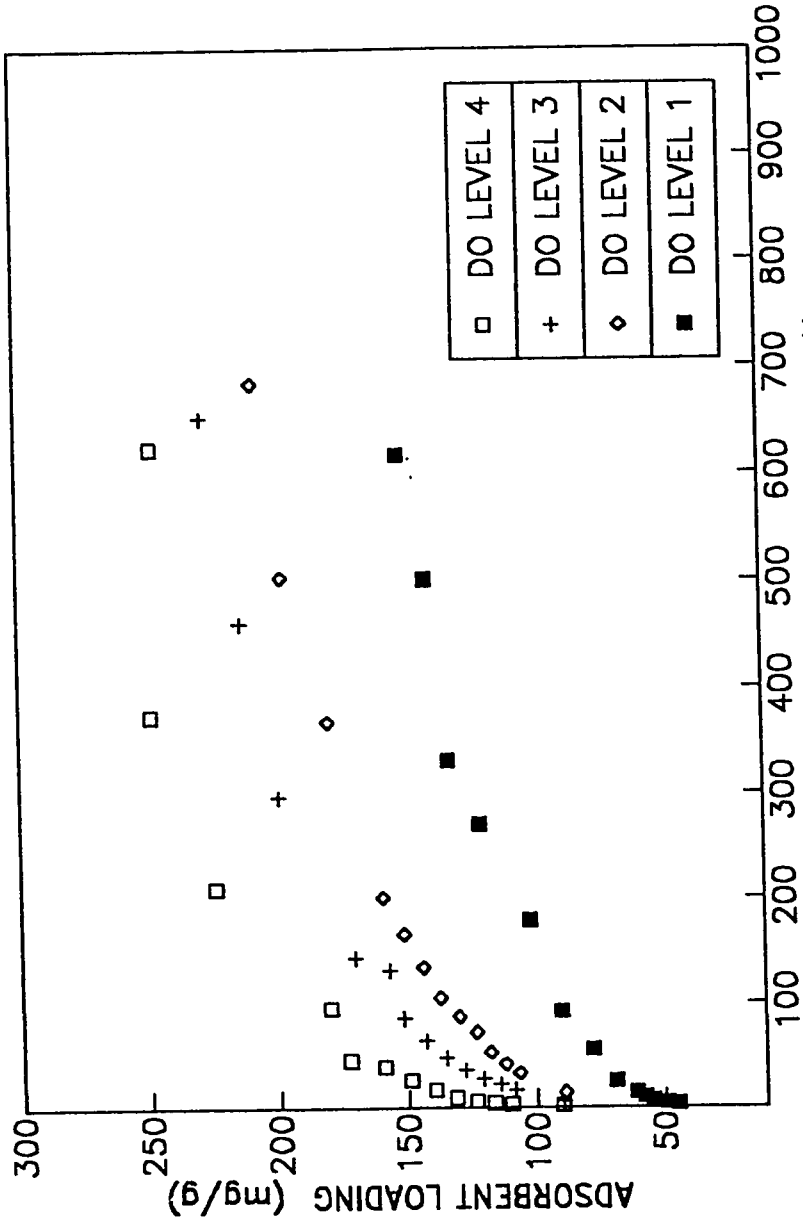

Figure 5.2: Uptakes of Phenol Under Different Oxygen Levels at T = 21° C. and pH of 7.

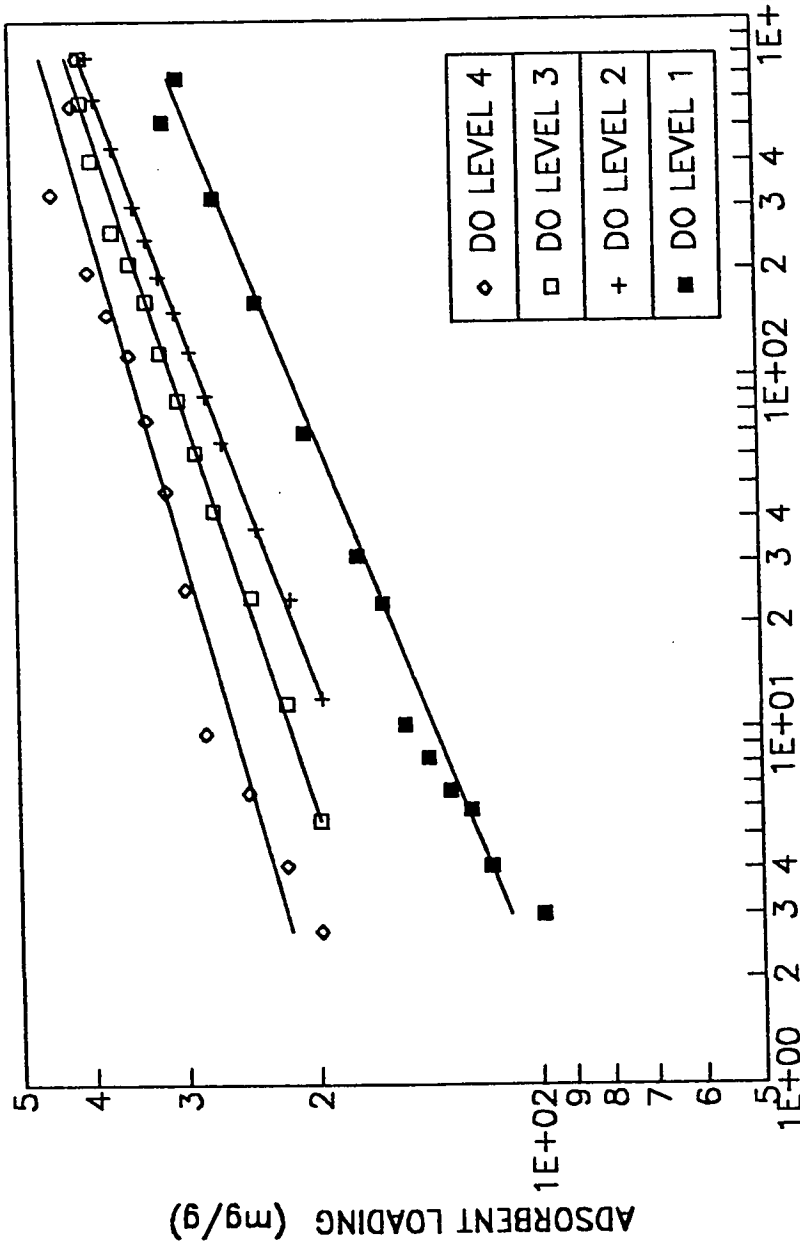

Figure 5.3: Uptakes of o-Cresol at T = 21°C. and pH of 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 5.1.

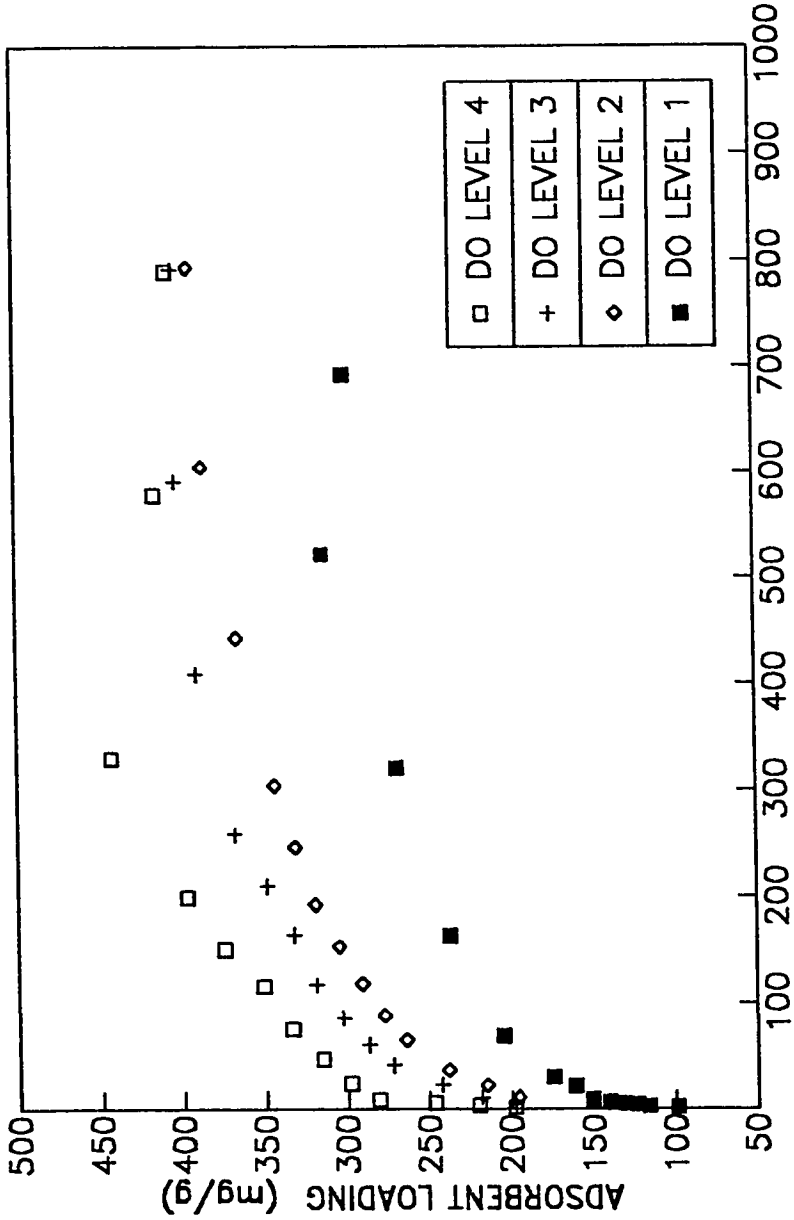

Figure 5.4: Uptakes of o-Cresol Under Different Oxygen Levels at T = 21° C. and pH of 7.

5.2.2 Extraction Studies

As mentioned in chapter 3, GC-MS analysis of the extracts of the GAC samples used in the oxic and anoxic phenol experiments resulted in dimers which could be identified as; 2,2-dihydroxy-1,1-biphenyl and 4-phenoxyphenol and a trimer on the GAC used in the oxic loading while only traces of the dimers were detected in the anoxic extracts. However, more work was done in this stage. For o-cresol, the above analysis was performed on the cases of DO levels 1, 3, and 4 (i.e anoxic, "purged with air", and "purged with pure oxygen". Results of the GC-MS scans are presented for the anoxic, "purged with air", and oxic cases in Figures 5.5, 5.6, and 5.7 ,respectively. It is apparent that the anoxic extracts contained much higher concentration of o-cresol (peak at 120 nm) and trace amounts of the dimers represented by the peaks at scan numbers 342 and 364 relative to the oxygenated samples. Significant amounts of the above two dimers, trimers represented by the peaks at scan numbers 462 and 475, and higher telomers were detected in the two extracts from the partially and fully oxygenated samples. Interestingly, the intensity of the peaks showing such dimers and trimer was higher in DO level 4 sample (DO around 30 mg/l) compared to DO level 3 (DO around 9 mg/l) as shown in Figures 5.6 and 5.7. This telomerization coupled with lower recovery of the original adsorbate explains the results of the loadings presented in Figures 5.1 and 5.3 and Table 5.1. It must be emphasized that no such telomers were found either in the extracts of virgin carbon or in the original stock solutions which suggests that occurrence of telomerization reaction on the activated carbon surface in the presence of molecular oxygen is the reason for the higher oxic uptakes.

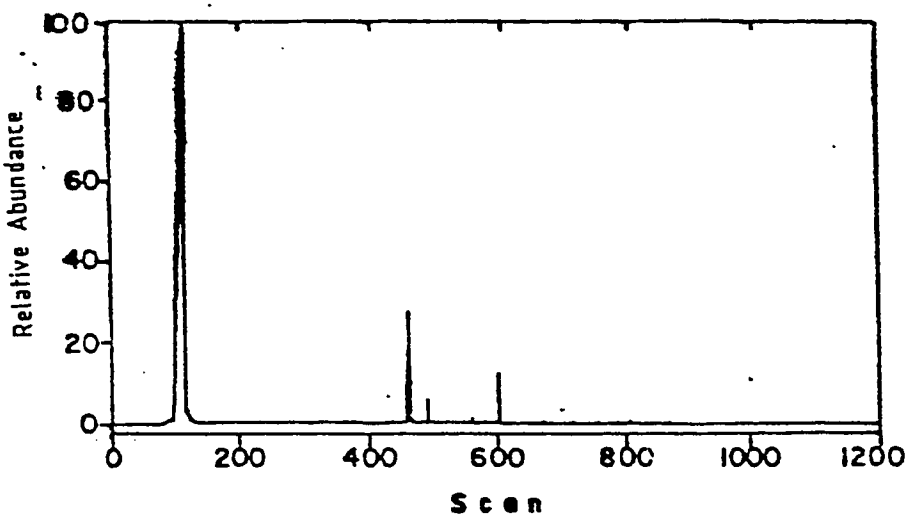

Figure 5.5: GC–MS Total Ion Chromatogram for the Anoxic GAC Sample of o–Cresol

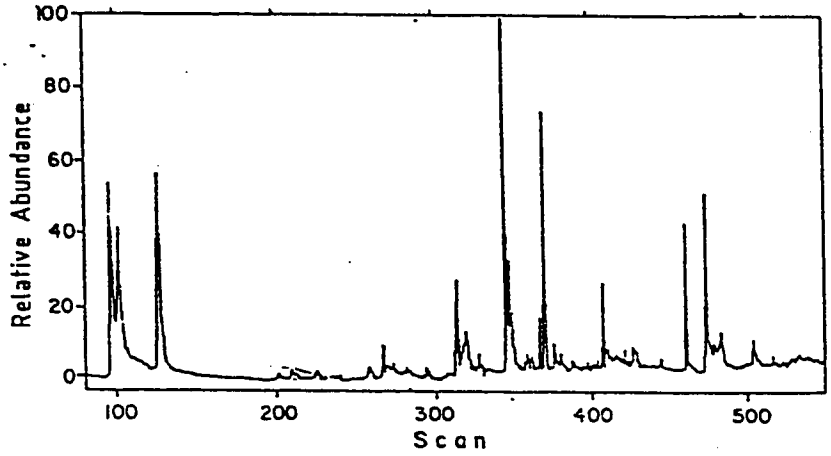

Figure 5.6: GC–MS Total Ion Chromatogram for the "Air Purged" GAC Sample of o–Cresol

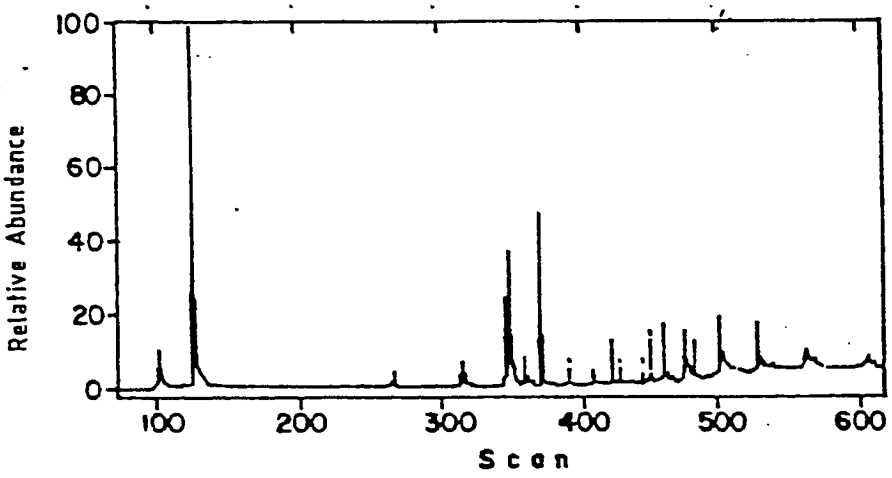

Figure 5.7: GC–MS Total Ion Chromatogram for the Oxic GAC Sample of o–Cresol

Since the telomerization was observed to occur on the activated carbon surface, the essential elements for the initiation and progression of such reactions are oxygen, the adsorbate, and reaction sites. For a given adsorbate-adsorbent system at known conditions of pH and temperature, the extent of telomerization is most strongly influenced by two parameters namely the mass of oxygen needed for the reaction and the availability of adsorption sites i.e. mass of GAC. This dual-limitation of the uptake enhancement, attributed to telomerization is best illustrated by Figures 5.8 and 5.9 which shows the additional sorptive uptake attained under oxic conditions versus the DO to GAC mass ratio at the three oxic conditions (DO levels; 2,3, and 4) for phenol and o-cresol. The data shows that for DO level 2 (lowest amount of oxygen), the increase in the additional uptake relative to the increase in DO to GAC mass was the highest; since the amount of DO was low and thus the ratio of DO to GAC mass was low, the enhancement in uptake is limited by the mass of oxygen present in the test environment. On the other hand, in the case of DO level 4 (highest amount of oxygen), there is almost no effect of DO to GAC mass ratio on the additional uptake after a DO/GAC mass ratio of 0.007 and 0.0117 for phenol and o-cresol, respectively. This can be explained by the sites limitation at this high ratio of DO to GAC mass and hence the additional uptake is limited by the mass of GAC or availability of adsorption sites for the telomerization reaction to take place. Interestingly, and inspite of some scatter, the data of DO level 3 is in between the two trends, in agreement with the plausible explanation given. In fact, the three curves can be taken as one continuous curve reflecting the relation between the additional uptake and the normalized DO contents.

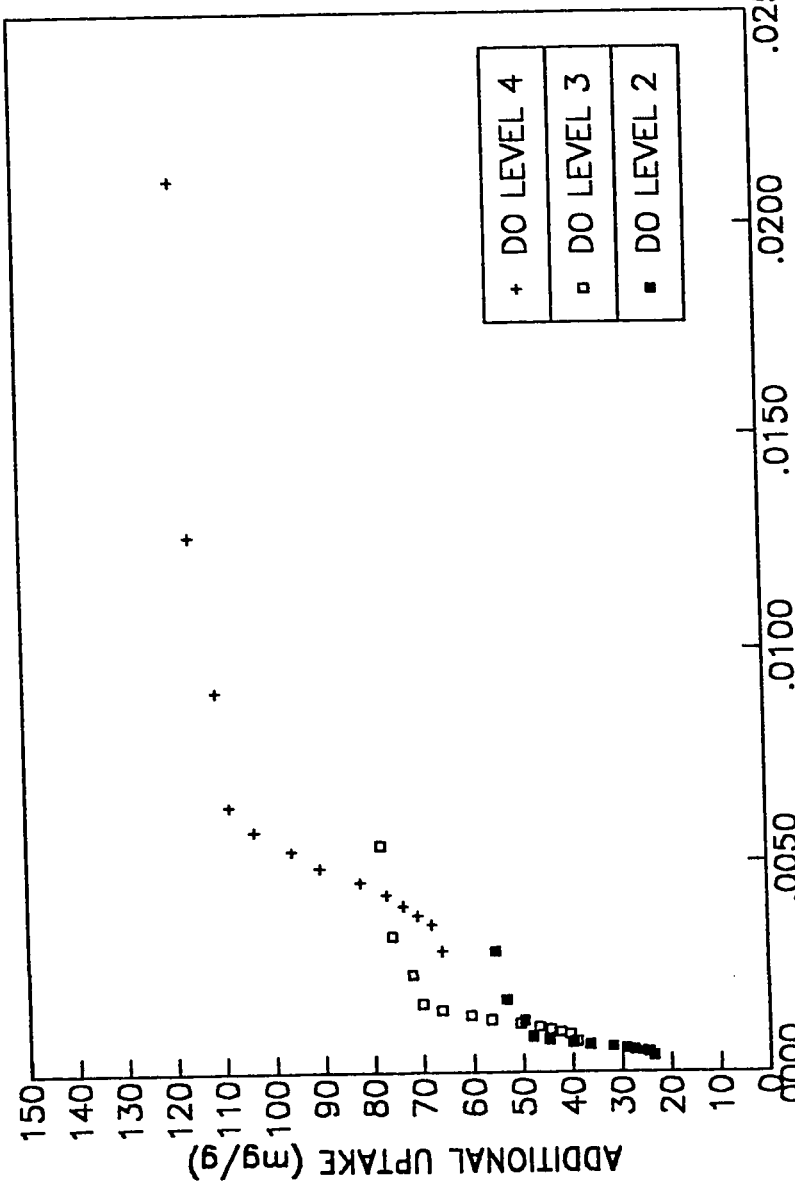

Figure 5.8: Relationship Between Additional Uptake and the Ratio of DO to the GAC Mass for Phenol at T = 21 °C. and pH of 7.

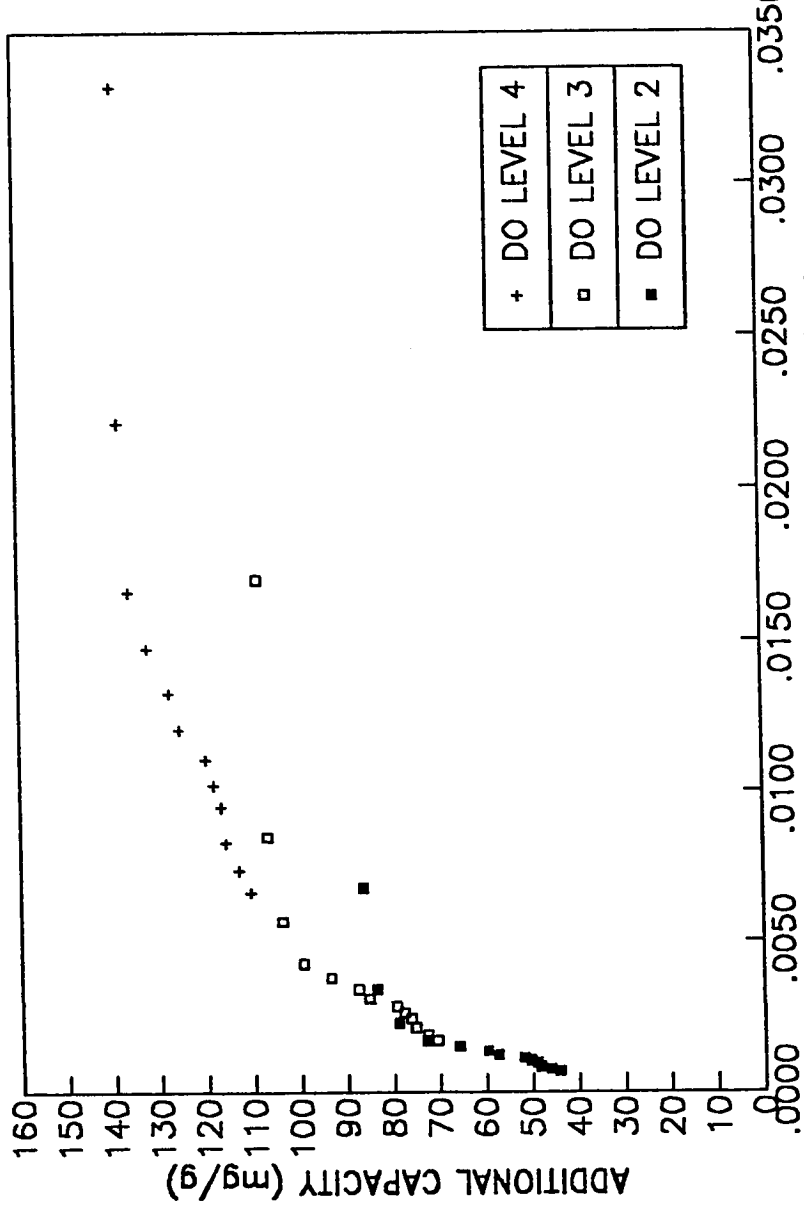

Figure 5.9: Relationship Between Additional Uptake and the Ratio of DO to the GAC Mass for o-Cresol at T = 21° C. and pH of 7.

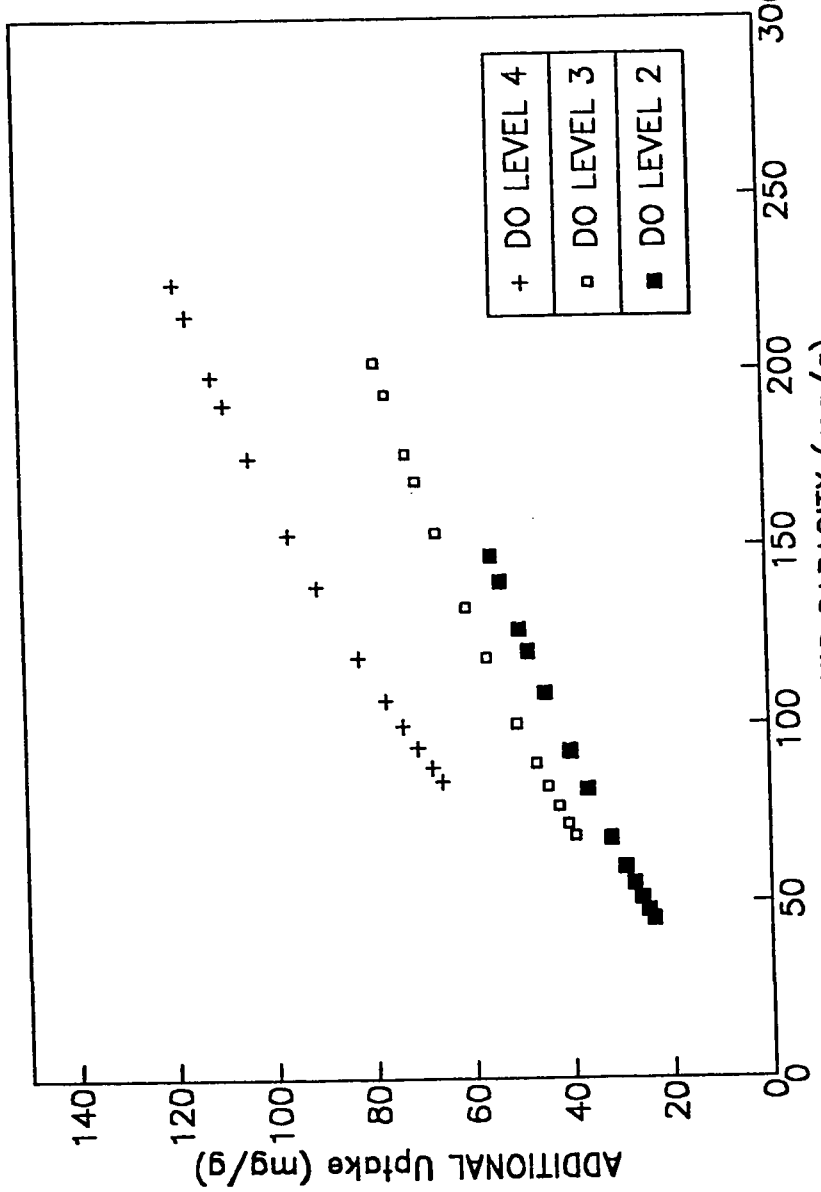

Figure 5.10: Relationship Between the Additional Uptake and the Anoxic Capacity for Phenol at T = 21° C. and pH 7.

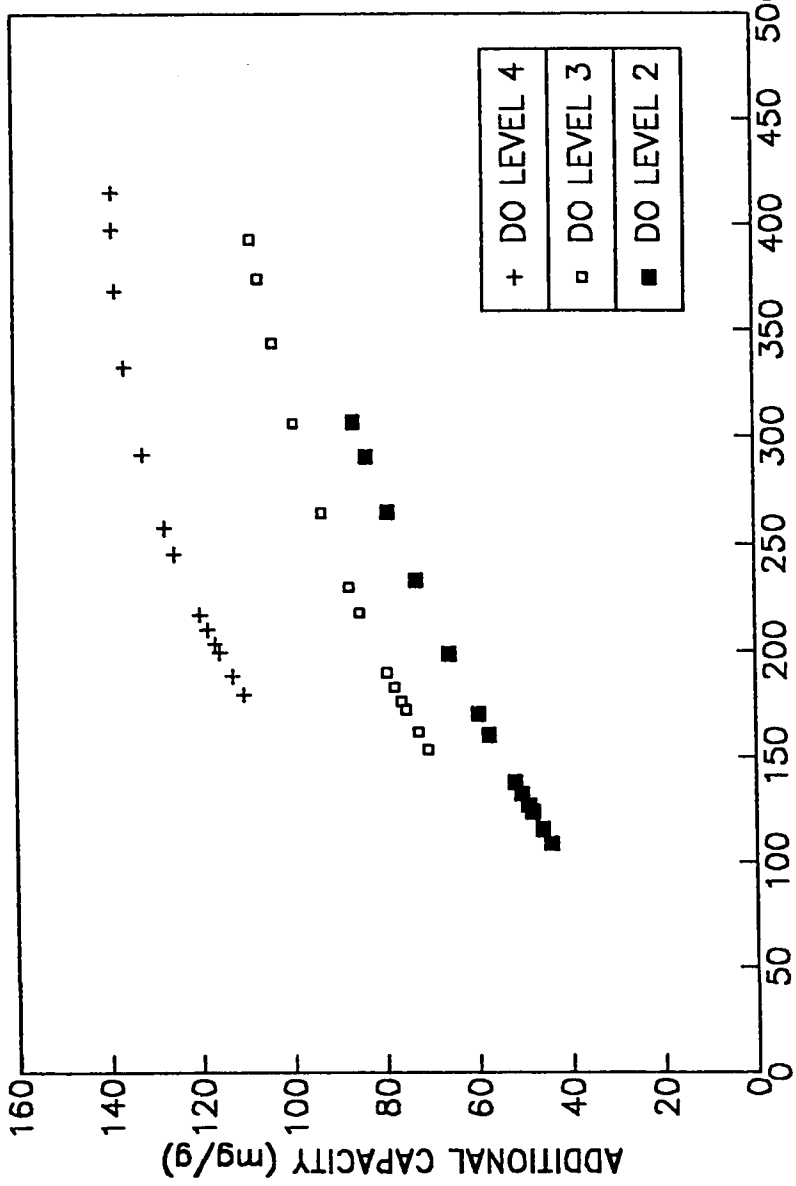

Figure 5.11: Relationship Between the Additional Uptake and the Anoxic Capacity for o-Cresol at T = 21° C. and pH 7.

from difmo4

Another important parameter that appears to influence this enhancement in uptake under oxic conditions is the adsorbability of the compound as reflected by its retention uptake. The additional uptake attained in the presence of the three oxygen levels is plotted as a function of the anoxic loading uptake for phenol and o-cresol in Figures 5.10 and 5.11. The two figures clearly depict that at low uptakes, the additional uptake attained by the presence of oxygen in the test environment is an increasing function of the anoxic adsorption uptake, while at high anoxic uptakes the additional uptake becomes independent of the amount of adsorbate retained under anoxic conditions. At this high level of oxygen content, the hindrance of extended adsorption uptake is not attributable to oxygen limitation, and therefore, the other limitation (i.e surface sites) is controlling. The above findings are supported by an experiment performed by Vidic and Suidan (14). In that experiment, bottles were filled with adsorbate solution containing 1000 mg/l o-cresol and 9 mg/l DO. GAC masses were chosen 150, 380, and 500 mg. DO level in each set of bottles were monitored with time (Figure 5.12). From the figure, it is clear that DO consumption is a function of GAC masses (i.e. adsorption sites).

5.2.3 Modeling

Based on the trends depicted in Figures 5.8 and 5.9 a mathematical relationship between the additional uptake gained by the presence of DO and the ratio of DO to GAC mass for phenol and o-cresol can be determined. The SAS package (62) was used to perform the nonlinear regression analysis, and the following general relationship was found

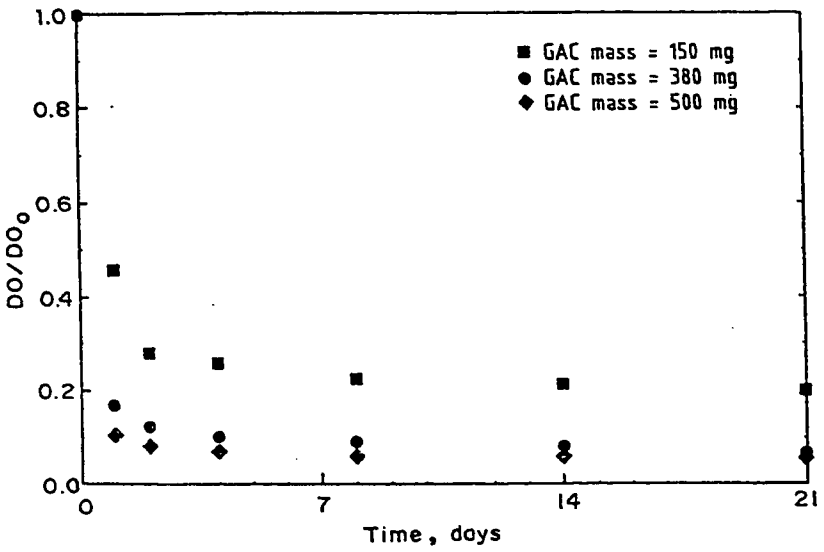

Figure 5.12: Oxygen Uptake with Time (Ref. 14)

$$\Delta q = M_1 | R_o |^{b}_{1} \tag{5.1}$$

where, Δq is the change in uptake relative to the anoxic uptake, mg/g. R sub o is the ratio of DO to GAC mass, M_1 is the model constant (= 827 and 426 for phenol and o-cresol, respectively), while b_1 is the model exponent (= 0.427 and 0.23 for phenol and o-cresol), respectively. Another nonlinear relationship was tested in which the oxic uptake was the dependent variable while the anoxic uptake and the GAC mass ratio were the independent variables. The equation took the form:

$$q = q_0 + L\,|q_0|^{h}\,|R_o|^{d} \tag{5.2}$$

where, q and q_0 are the oxic and anoxic uptakes, respectively, L is the model coefficient (= 378 and 442 for phenol and o-cresol, respectively) while h and d are model exponents. (h = 0.345 and 0.329 for phenol and o-cresol, respectively, and d = 0.069 and 0.042 for phenol and o-cresol, respectively). Equation 5.1 and 5.2 will be denoted henceforth as model 1 and model 2, respectively. It should be noted that Equation 5.1 can be expressed as;

$$q = q_0 + \{M\,|\,R\,|^{b}\} \tag{5.3}$$

while Equation 5.2 can be expressed as;

$$\Delta q = L\,|q_0|^{h}\,|R|^{d} \tag{5.4}$$

Figures 5.13 and 5.14 depict the theoretical models predictions along with the experimental data of phenol on logarithmic and normal scales, respectively, while Figures 5.15 and 5.16 represent the case of o-cresol. These data were reported by Vidic and Suidan (14). The anoxic loading given in that study was used to calculate the GAC masses given the sorbate volume and initial concentration. The DO content provided in the study was divided by the GAC masses in order to calculate the ratio of DO to GAC mass ratio which is denoted by the independent variable R in the two models.

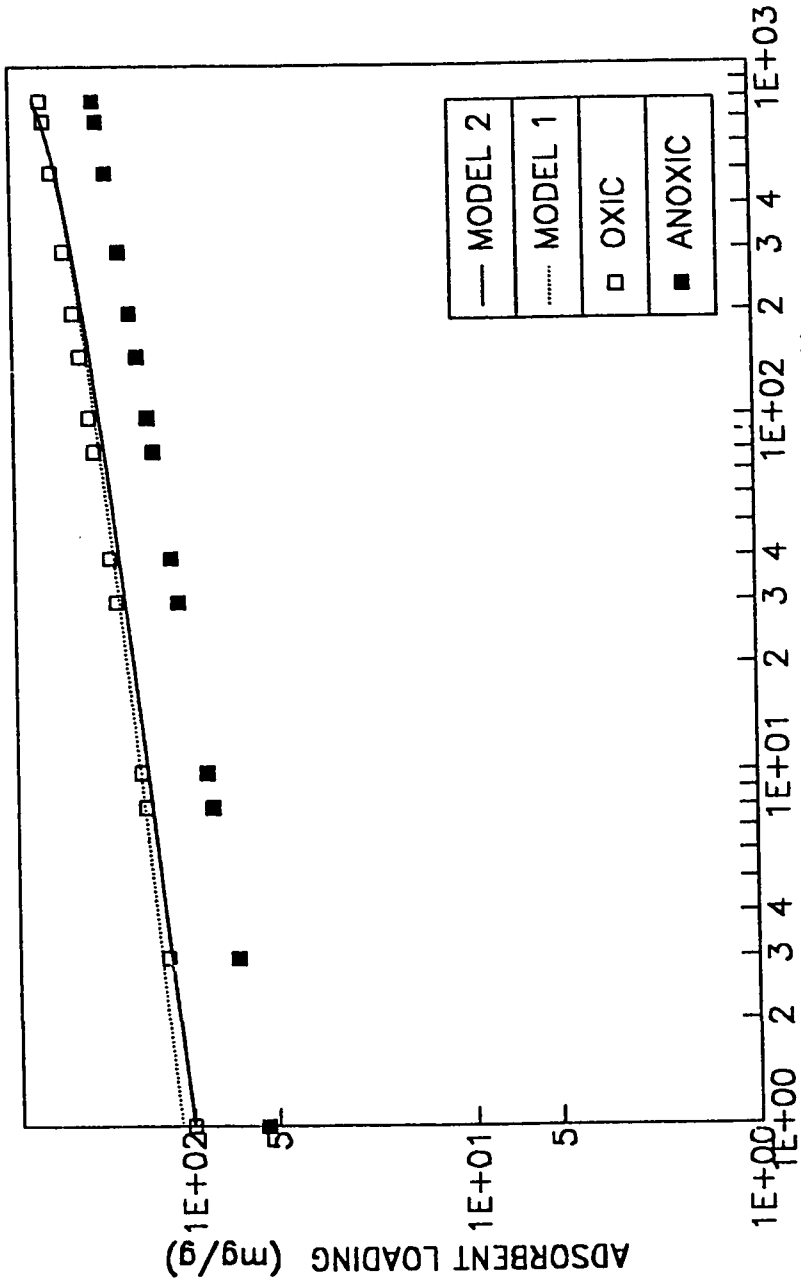

Figure 5.13: Observed and Predicted Phenol Uptakes, Data from Ref. 14.

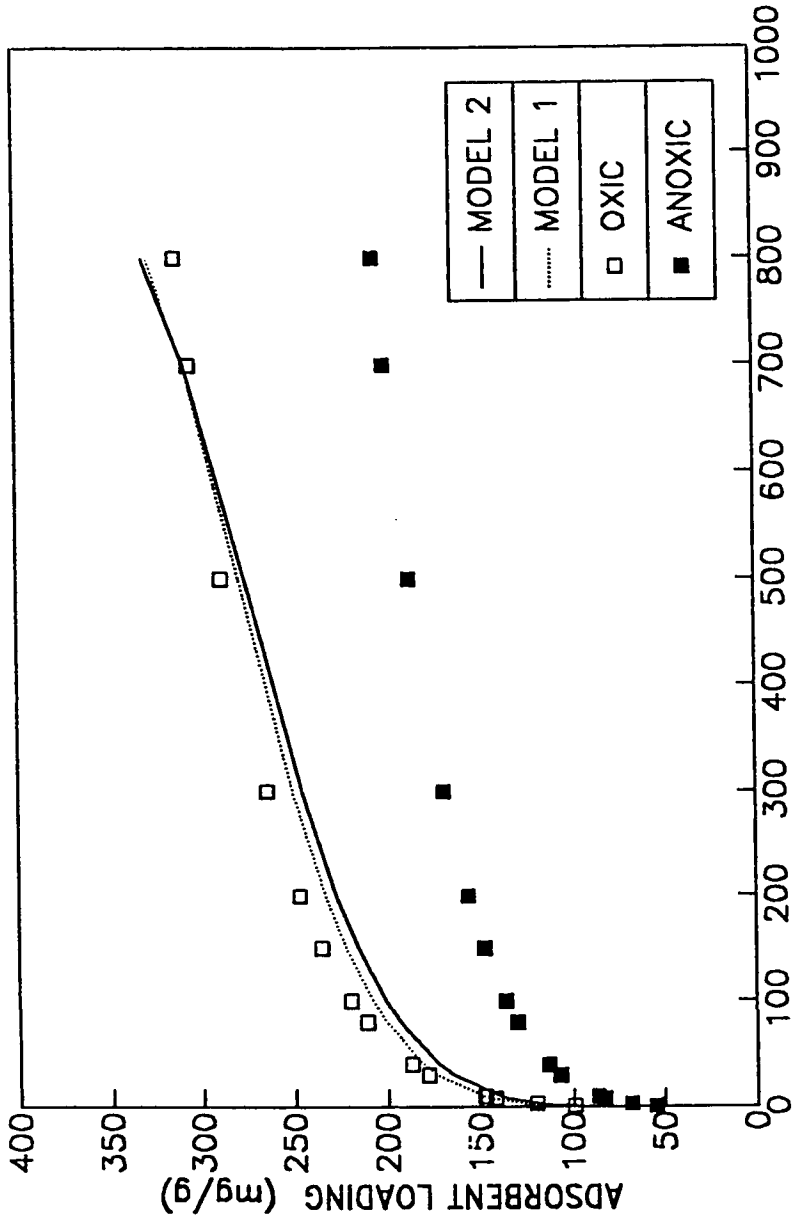

Figure 5.14: Observed and Predicted Phenol Uptakes, Data from Ref. 14.

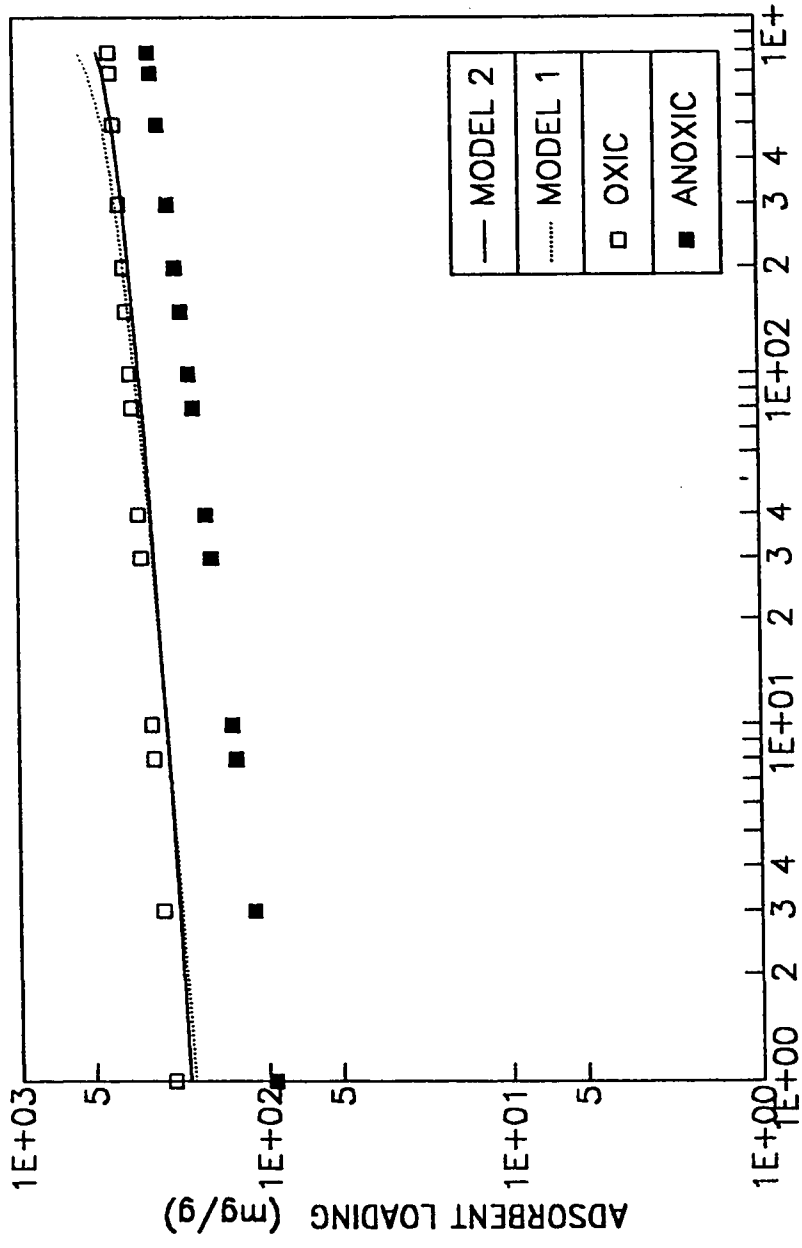

Figure 5.15: Observed and Predicted Uptakes for o-Cresol, Data from Ref. 14.

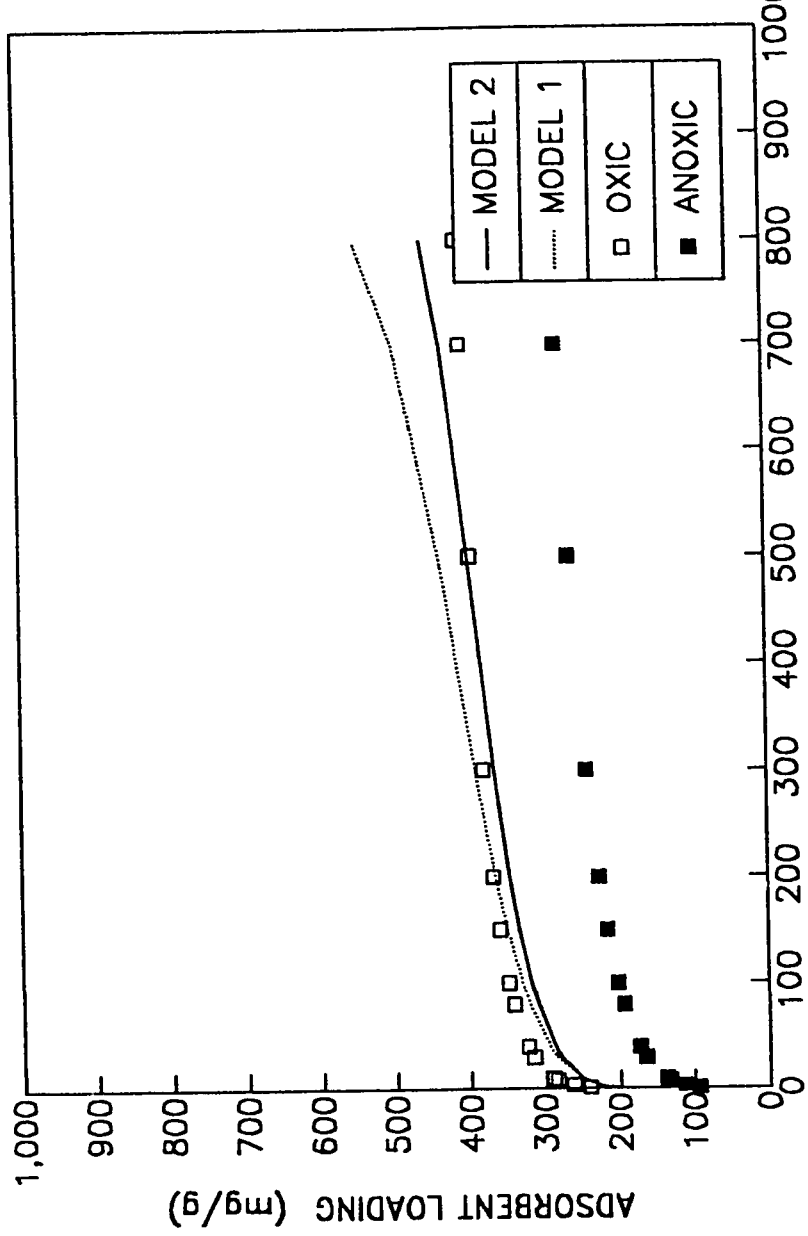

Figure 5.16: Observed and Predicted Uptakes for o-Cresol, Data from Ref. 14.

Using the aforementioned values of R and the anoxic uptakes given by the anoxic loading the oxic loading was predicted by the use of Models 1 and 2. The objective of presenting the data on both logarithmic and linear scales is to clarify the whole range of data, since the logarithmic scale will take care of the low values while the high values will be better illustrated by the linear scale. Figure, 5.13 and 4.14 show that the two models predicted the phenol oxic loading very well while the prediction capability was somewhat weaker in the case of o-cresol as shown in Figures 5.15 and 5.16. This is supported by higher chi-square values in the case of o-cresol prediction compared to that of phenol. The utility of the above models is quite conspicuous, since the oxic loading can be calculated knowing the anoxic loading and the initial DO content.

Chapter 6

KINETICS OF PHENOLICS UPTAKE BY ACTIVATED CARBON

6.1 Introduction

Knowledge of adsorption kinetics for adsorption systems is essential for the design and operation of adsorbers. Furthermore, like in the case of equilibrium uptake, it is also important to study factors affecting the kinetics such as temperature, pH, and more recently dissolved oxygen content which has been demonstrated to strongly influence the adsorption process.

In the previous chapters, dissolved oxygen (DO) was shown to induce telomerization reactions for phenolics on the activated carbon surface, improving their uptake. The effect of pH and temperature and different levels of DO on the enhancement in the uptake was also investigated in the previous chapters. The objective of this chapter is to investigate the effect of the aforementioned variables (e.g. pH, temperature, and different DO levels) on the kinetics of physical adsorption and the kinetics of adsorption-reaction combination. The homogeneous surface diffusion model (HSDM) will be used in order to calculate the diffusivity coefficients related to the batch experiments.

6.2 Results and Discussion

6.2.1 Effect of DO Levels

The apparent surface diffusivities for phenol and o-cresol were determined from the batch test data presented in Figures 6.1 and 6.2. It is apparent that rapid uptake of adsorbate, that was independent of the presence of DO in the test environment, occurred during the first 12 hours, followed by a much slower uptake until equilibrium was attained. It is worth noting that equilibrium was attained after only 48 hours in the anoxic batch while taking about 14 days in the oxic batch. Furthermore, the strong dependence of the equilibrium uptake on the DO concentration corroborates the findings of the isotherms discussed earlier. Similar results were observed for phenol at pH 12 by Cooney and Xi (63). The rapid initial uptake is primarily due to physical adsorption of phenol onto activated carbon and the subsequent prolonged uptake is explained by the telomerization reactions which have been reported by Grant and King (13) to be promoted by longer contact times. It is therefore, apparent that telomerization is the rate limiting step in the overall uptake of phenol and o-cresol. The phenol and o-cresol uptake rates in all three batches containing dissolved oxygen were identical for the first two days and remained similar for another day in the two batches containing DO concentrations of 9 and 30 mg/l (DO levels of 3 and 4, respectively) after which time marked differences in uptake were observed. It is conceivable that the rate of diffusion of oxygen, necessary to promote telomerization increases with increasing DO concentrations but it appears that the extent of of telomerization governs the equilibration time i.e. longer times are needed for higher concentrations of DO as evident by the data in Figures 6.1 and 6.2. In the first two days when the additional uptake due to reaction is low, differences in residual concentrations between the three DO levels

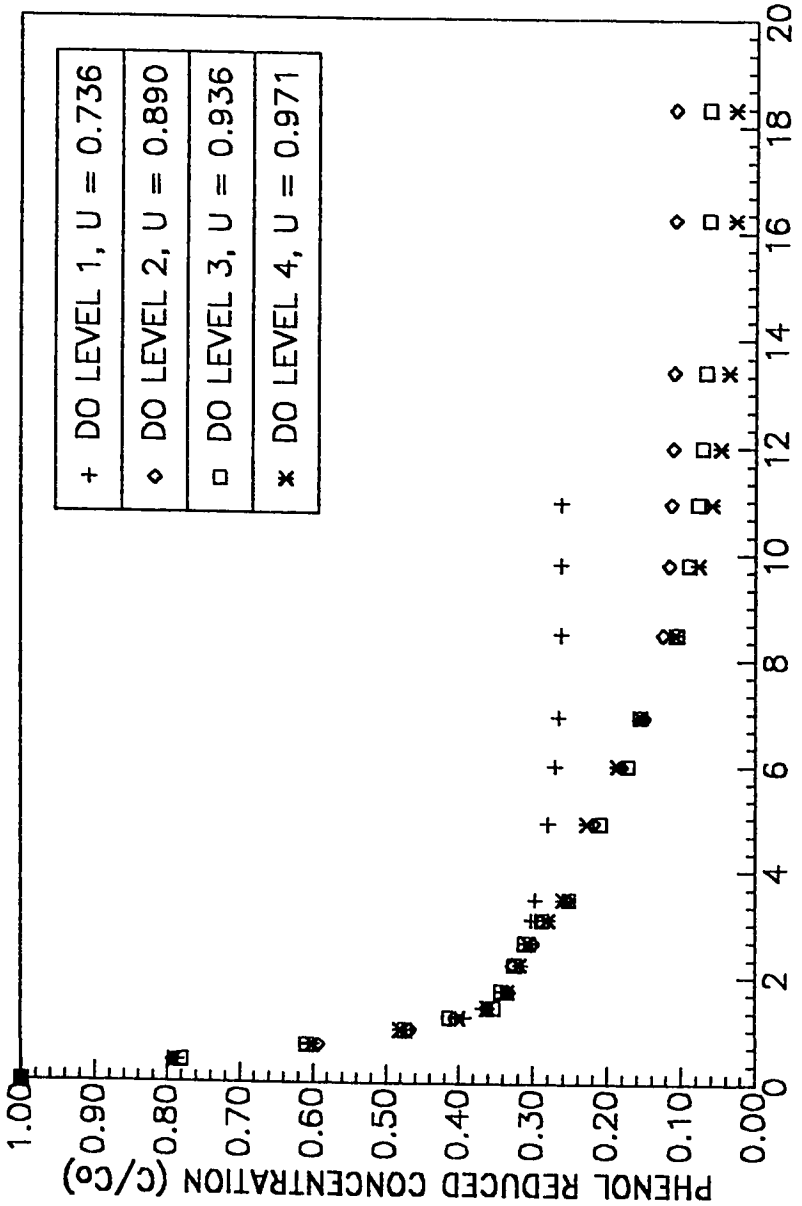

Figure 6.1: Closed Batch Kinetic Experiment for Phenol at T = 21°C. and pH of 7.

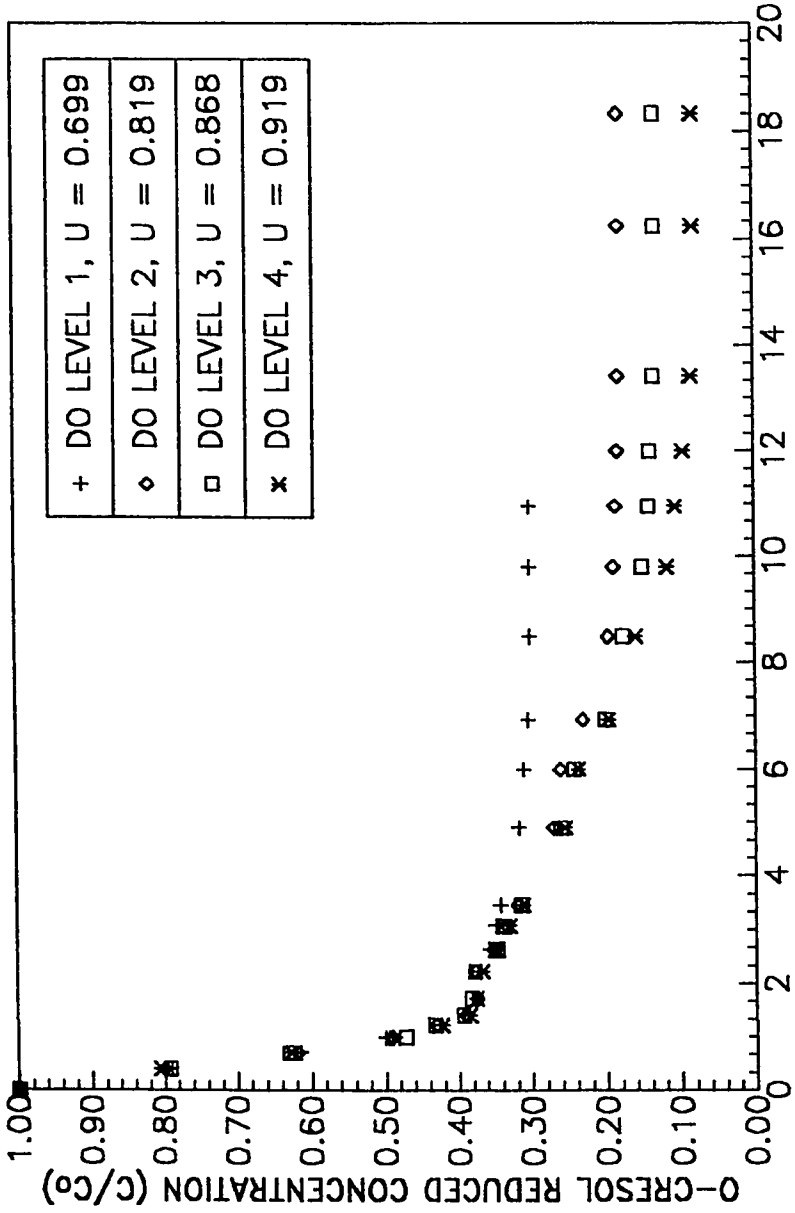

Figure 6.2: Closed Batch Kinetics Experiment for o-Cresol at T = 21° C. and pH 7.

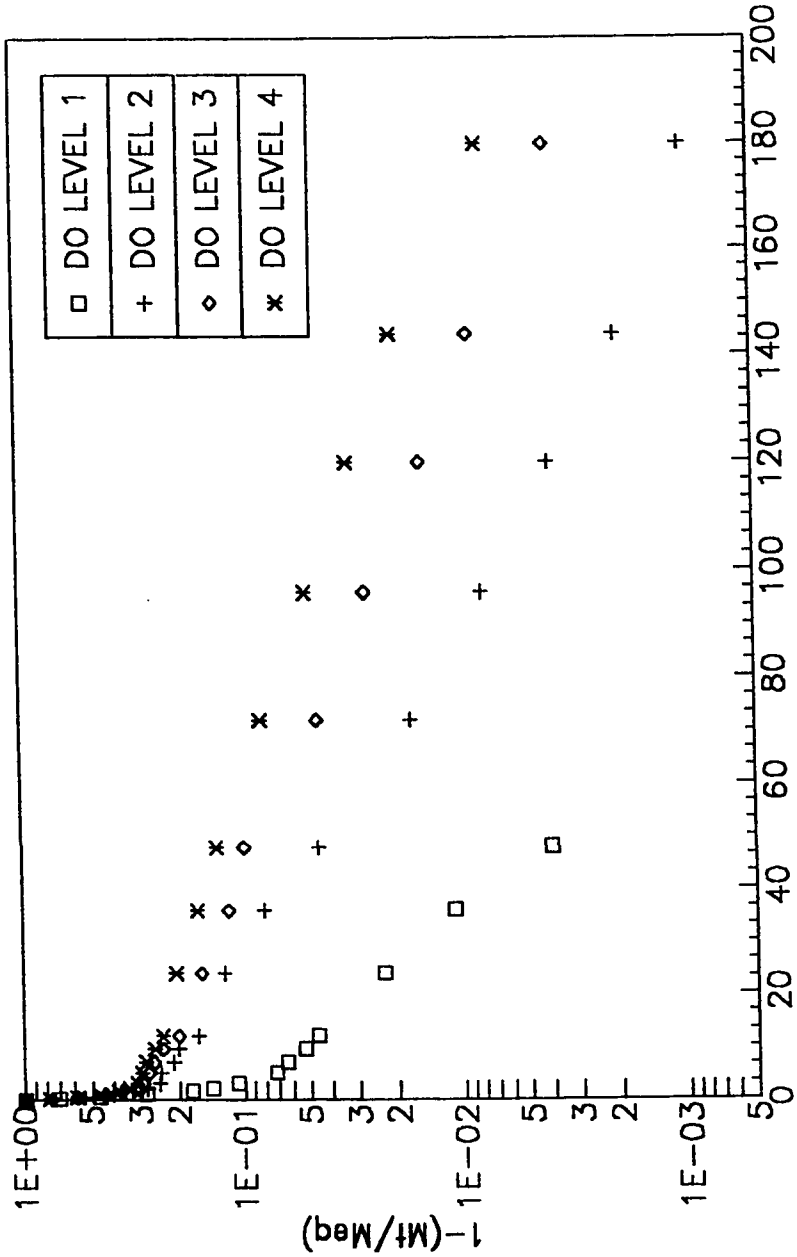

Figure 6.3: Linearized Rate of Phenol Uptake at T = 21°C. and pH of 7 from CRANKP

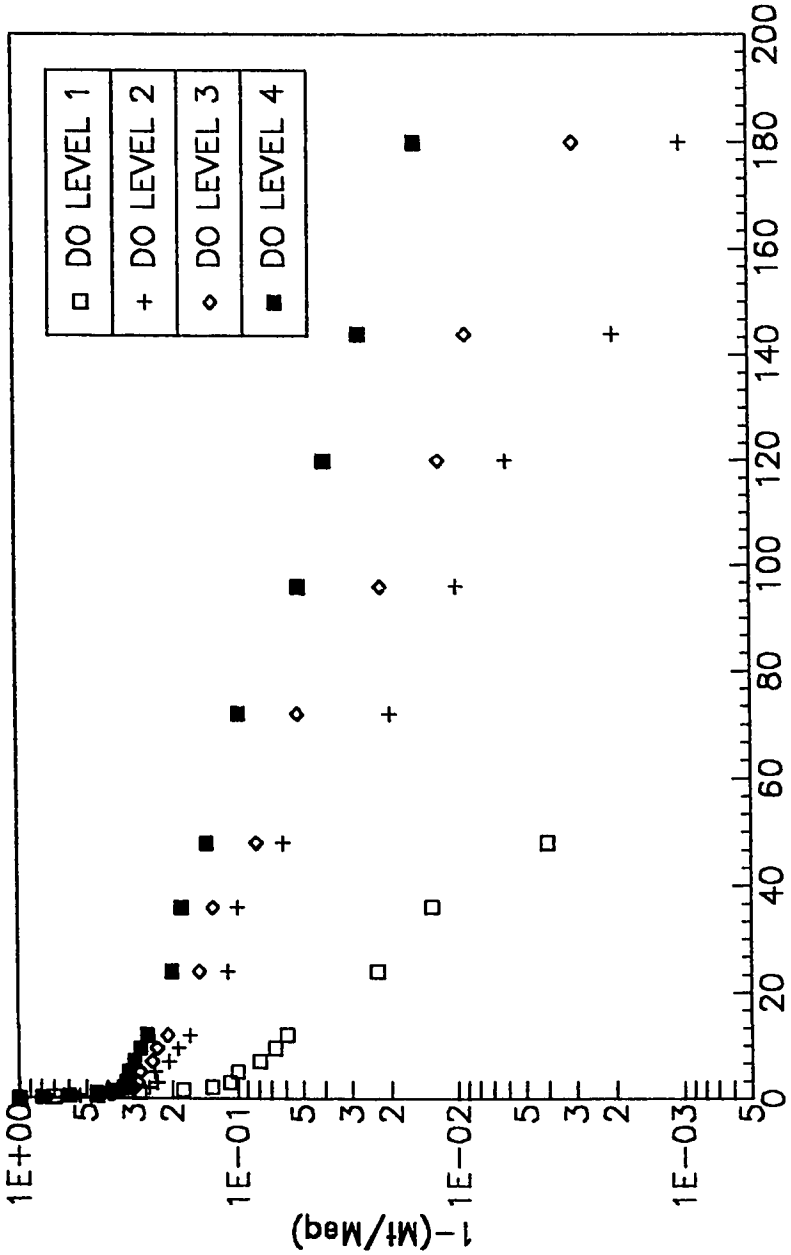

Figure 6.4: Linearized Rate of o-Cresol Uptake at T = 21 °C. and $pH_{from\ lac1}$ of 7

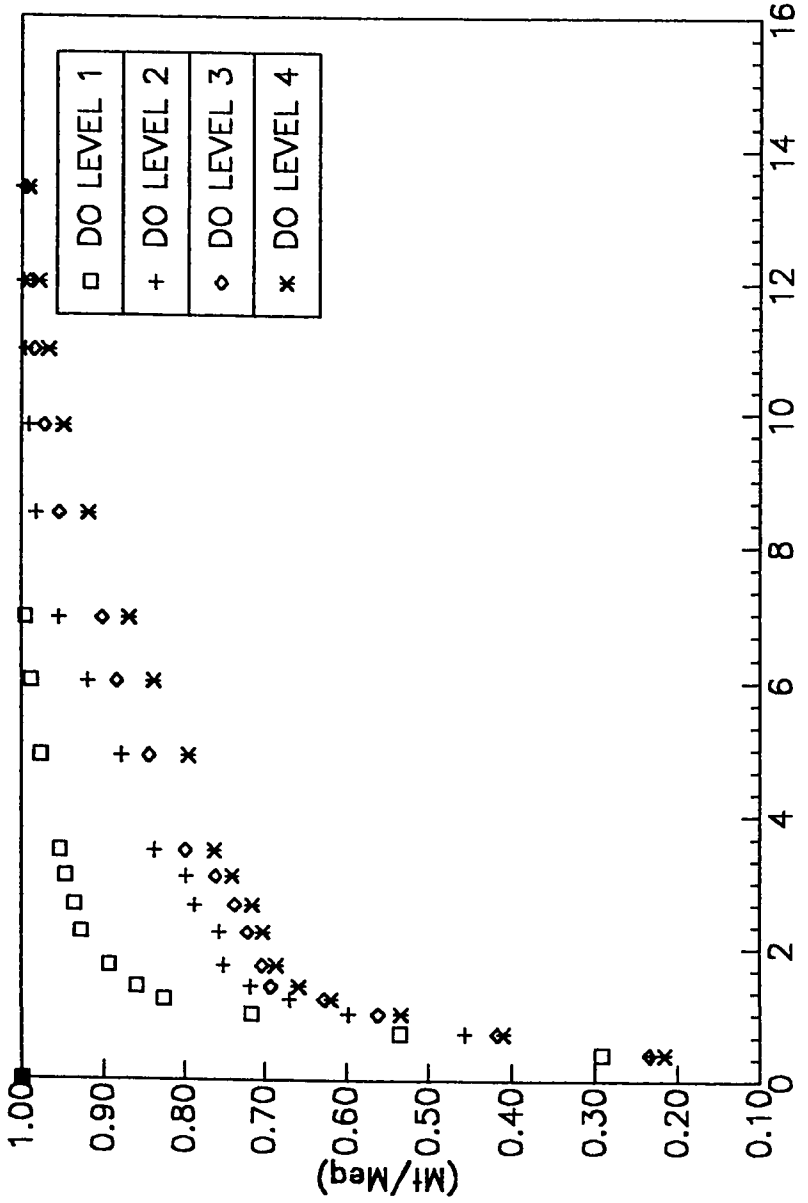

Figure 6.5: Linearized Uptake Rate of Phenol at T = 21° C. and pH of 7 from CRANLPL

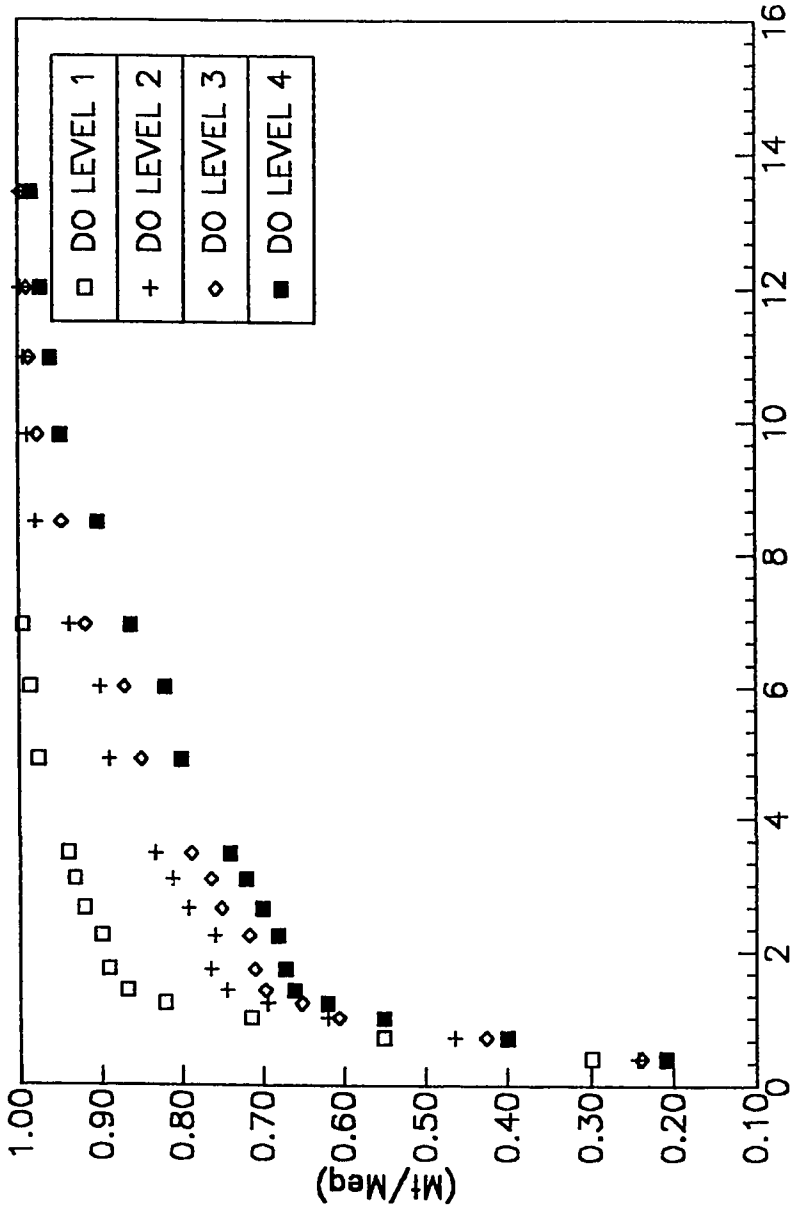

Figure 6.6: Linearized Uptake Rate of o-Cresol at T = 21° C. and pH of Z from Lake

are masked. As time increase, such differences become more pronounced as a result of of progression of the telomerization process at widely varying rates. The kinetic data were analyzed using the procedure described by Traegner and Suidan (40). A two parameter search-approach was used to accomplish the best fit of the HSDM to the experimental data (Figures 6.1 and 6.2). The aforementioned procedure had the following statistical criteria

$$r_i = y_i - v(x,t_i) \tag{6.1}$$

where, y_i are the experimental data at certain selected times t_i and $v(x,t_i)$ the corresponding output of the HSDM. The residual r_i is a measure for the standard deviation at times t_i and is only due to noise in the data and should exhibit random character. The nonlinear least square problem consists now of choosing x, the parameter vector so that the fit is as close as possible to the y_i values in the sense that the sum of squares of the residuals r_i (x)'s is minimized:

$$\text{minimize} = \frac{1}{2} R(x)^T R(x) = \frac{1}{2} \sum_{i=1}^{m_i} r_i(x)^2 = f(x) \tag{6.2}$$

where, $m_i < n$ and m_i is the number observations, n the number of parameters to be determined, and R(x) is the residual vector.

In the long time region a plot of $\log(1 - \frac{m_t}{m_\infty})$ versus t should be linear with a slope related to the inverse time constants of the combined diffusion-reaction phenomenon and to the uptake, here,

$$1 - \frac{m_t}{m_\infty} = 1 - \left|\frac{c_t - c_\infty}{c_0 - c_\infty}\right|,$$

where, c_0, and c_∞ are the initial and equilibrium concentrations, respectively, while c_t is the concentration measured at any time as shown in Figures 6.3 and 6.4 for the data previously presented in Figures 6.1 and 6.2. In another presentation, $\frac{m_t}{m_\infty}$ was plotted against square root of time in Figures 6.5 and 6.6 for phenol and o-cresol, respectively. The two presentations shown in Figures 6.3-6.6 illustrate very clearly the nature of the phenomena, Figures 6.3 and 6.4 have shown different apparent diffusivity with different DO levels in the long time range which is attributed to the reactions and uptake, Figures 6.5 and 6.6 demonstrated that in the short time region, the four curves related to different DO levels had the same slope which means that the diffusivity was constant and not a function of DO level. As a result, it is postulated that in the beginning, physical adsorption controls. Surface diffusivities (D_s) were found by the HSDM model for the four DO levels and presented in Table 6.1 along with χ^2 values calculated for the data and from the tables for both phenol and o-cresol. The χ^2 values were lower than the table values for both the oxic and anoxic experiment which means that data is fairly predicted by the HSDM model. However, the χ^2 values for the anoxic cases were much lower than the oxic ones and the χ^2 values increase with the increase in the DO level. This shows that the HSDM prediction capability is excellent for the anoxic experiments (physical adsorption) and this capability decreases with more interference from telomerization reactions. The resulting diffusivities for phenol and o-cresol are in agreement with the literature values (35,40) found at neutral pH and room temperature as 3.53×10^{-8} and 2.41×10^{-8} for phenol and o-cresol, respectively. Figures 6.7 and 6.8 show the closed batch kinetics under different DO levels along with HSDM predictions for phenol and o-cresol, respectively, Figures 6.7 and 6.8 depict the good prediction capability HSDM model has for physical adsorption (anoxic curves), while this

Table 6.1. Apparent Diffusivities of Phenol and o-Cresol Evaluated by the HSDM Model Under Different DO Levels at temperature of 21°C and pH 7.

Compound	Operational Conditions	HSDM (Ds) cm^2/sec	χ^2	$\chi^2_{n,\alpha\ 0.95}$
o-cresol	oxic (DO 4)	1.4E-08	0.89	8.05
	oxic (DO 3)	2.0E-08	0.48	8.05
	oxic (DO 2)	2.5E-08	0.36	8.05
	anoxic (DO 1)	8.3E-08	0.036	5.7
phenol	oxic (DO 4)	7.6E-09	2.1	8.05
	oxic (DO 3)	1.4E-08	0.67	8.05
	oxic (DO 2)	1.6E-08	0.36	8.05
	anoxic (DO 1)	6.3E-08	0.054	5.7

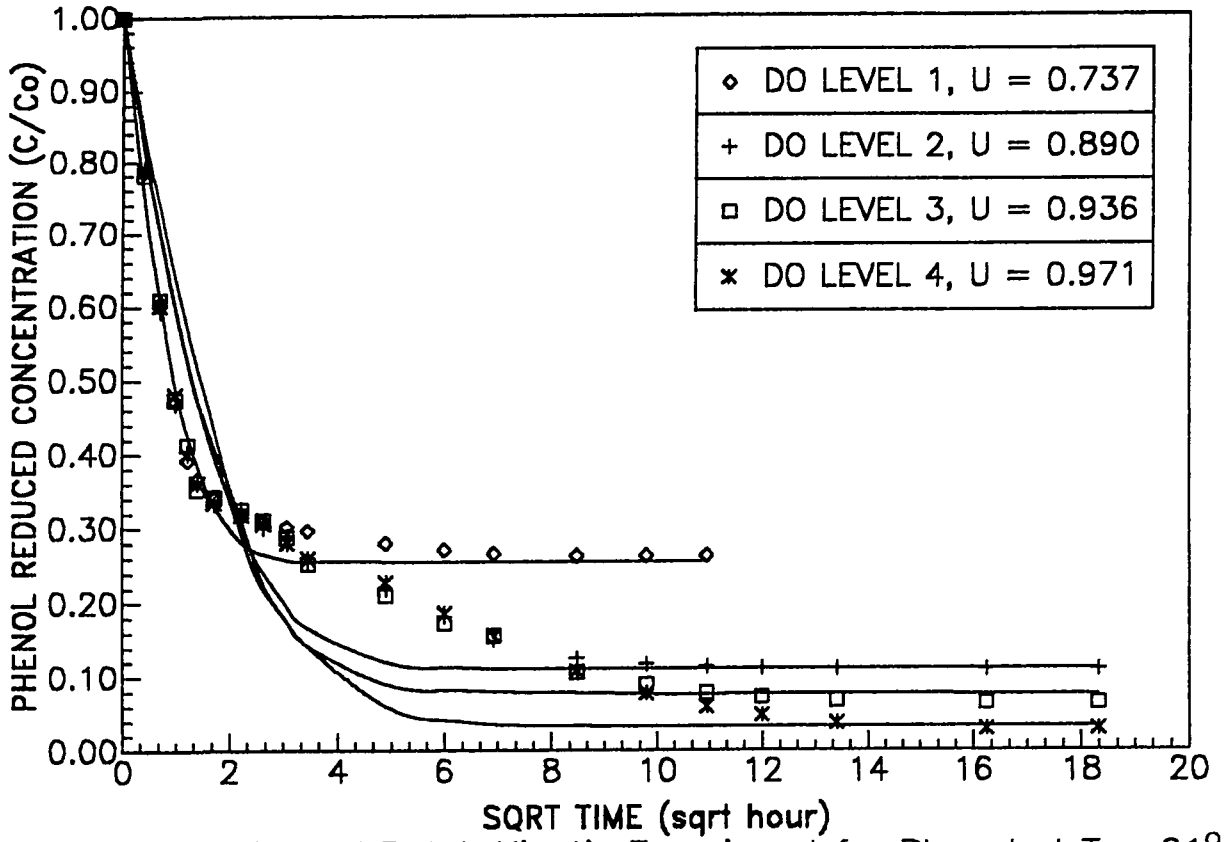

Figure 6.7: Closed Batch Kinetic Experiment for Phenol at T = 21° C. and pH 7 Along with HSDM Predictions.

HSDM1S

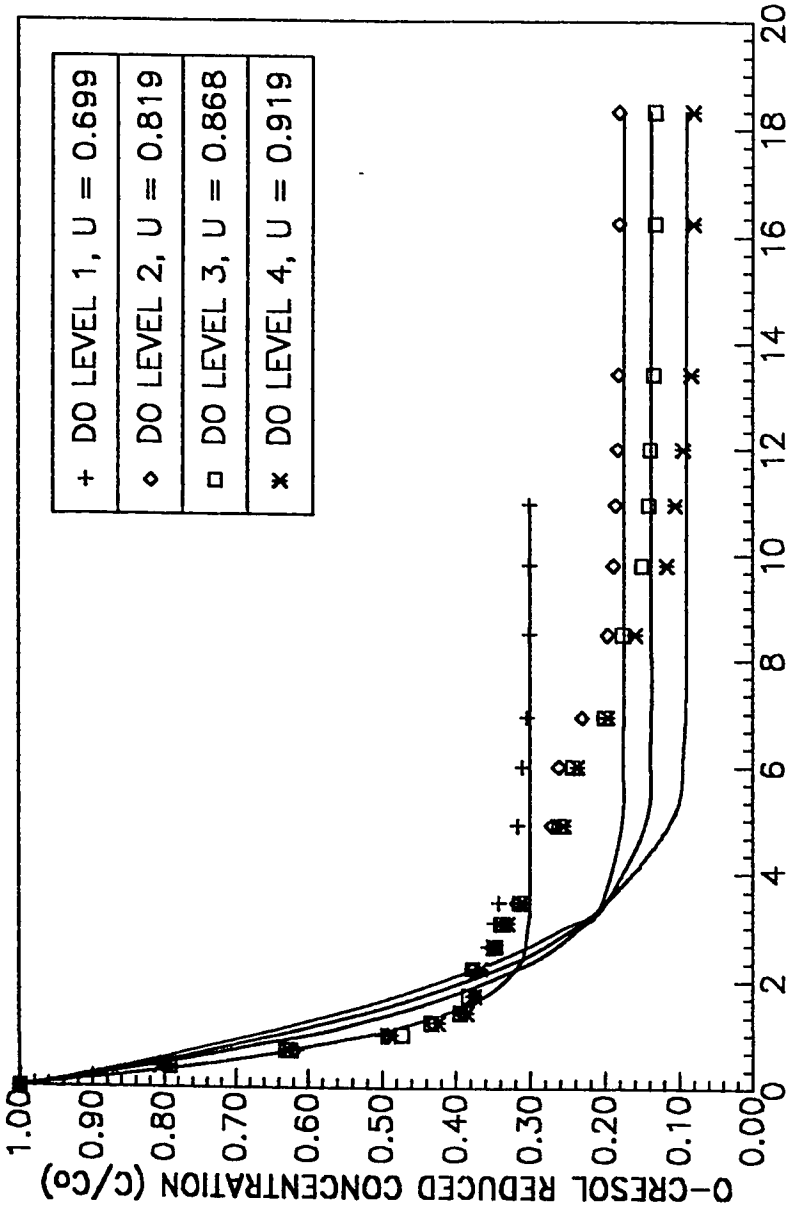

Figure 6.8: Closed Batch Kinetics Experiment for o-Cresol at T = 21° C. and pH 7 Along with HSDM Predictions.

was not always the case for the oxic curves. The reason is that the HSDM model is based on physical adsorption assumptions only, and, therefore, does not include any reaction term in the mathematical formulation, however; the diffusivity coefficients calculated for the oxic case, although they do not reflect the nature of the process very well give a way of comparison for the effects of environmental conditions on the telomerization reactions. The diffusivity coefficients found by the HSDM model were plotted against DO to GAC mass ratios in Figures 6.9 and 6.10 for phenol and o-cresol, respectively. The previous Figures clearly indicate that the apparent diffusivity coefficient decreases with increasing DO concentrations. It is also noted that the largest drop in the diffusivity was between the DO level 1 (anoxic) and the other levels, while the difference between the diffusivity values in the oxic levels were not as high. Such decrease in diffusivity, a measure of how fast equilibrium is attained, with increasing DO concentrations, is obviated by the slow telomerization rate controlling the uptake process and resulting in relatively long equilibration time.

6.2.2 Effect of pH Variation

The anoxic and oxic closed batch kinetic experiments for phenol at pH values of 3, 7, and 11 are shown in Figures 6.11, 6.12, and 6.13, respectively, while Figures 6.14, 6.15, and 6.16 represent the o-cresol case. From the aforementioned Figures, it is clear that pH variations affect the kinetics of adsorption presented by the anoxic case as well as the kinetics of adsorption-reaction combination presented by the oxic one. The data in Figures 6.17-6.22 show that the equilibration time for physical adsorption increases with the increase in pH, while, on the other hand, for the oxic case in which telomerization reaction is taking place, the equilibration time is unaffected by the pH variations. However, while at all the pHs equilibrium was attained on the eleventh day of

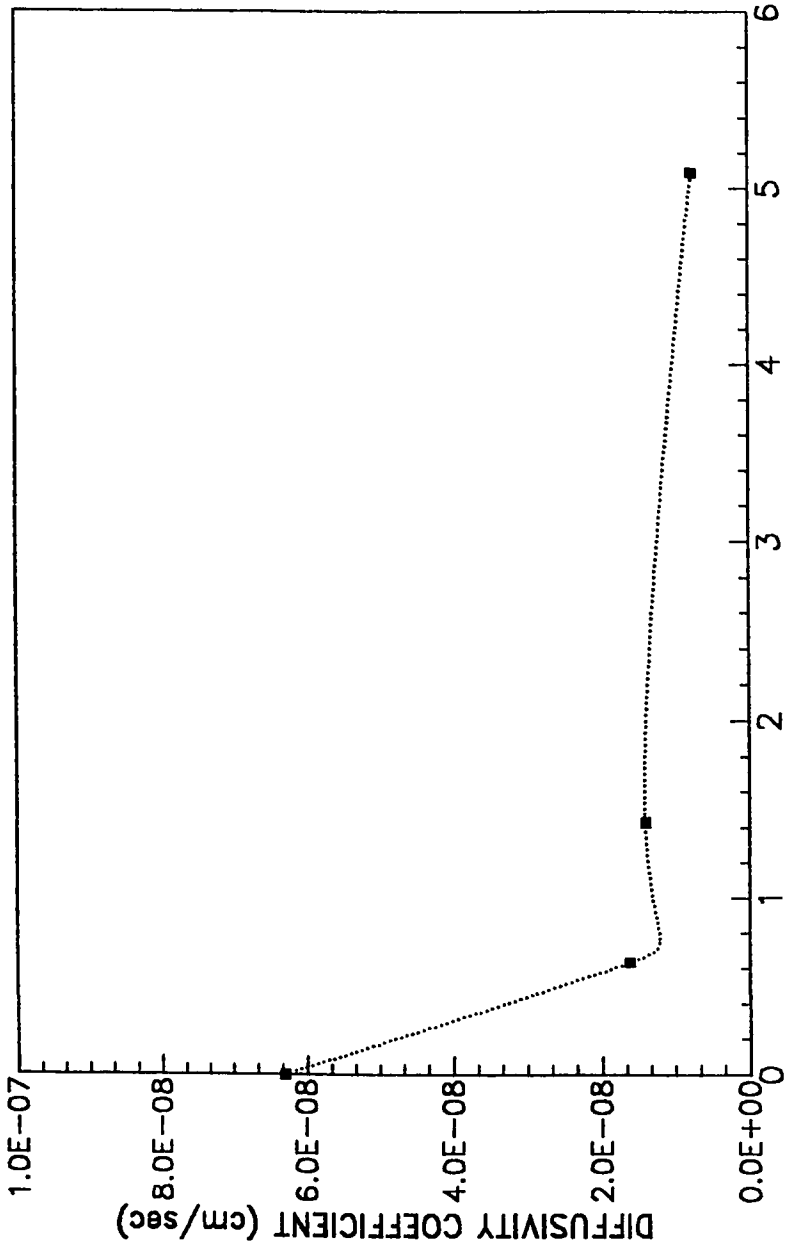

Figure 6.9: Relationship Between the Phenol Apparent Diffusivity (HSDM) and the Ratio of DO to GAC Mass at T = 21° C. and pH 7.

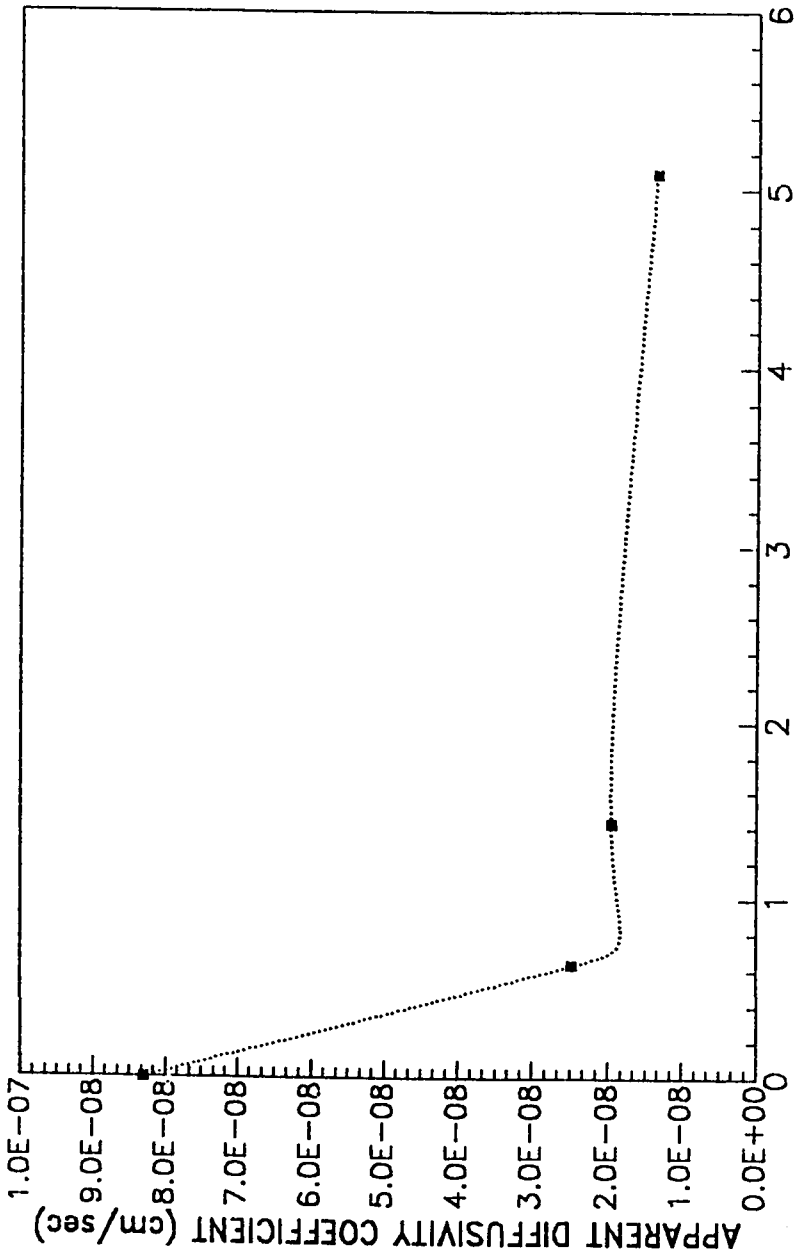

Figure 6.10: Relationship Between the o-Cresol Apparent Diffusivity (HSDM) and the Ratio of DO to GAC Mass at T = 21° C. and pH 7.

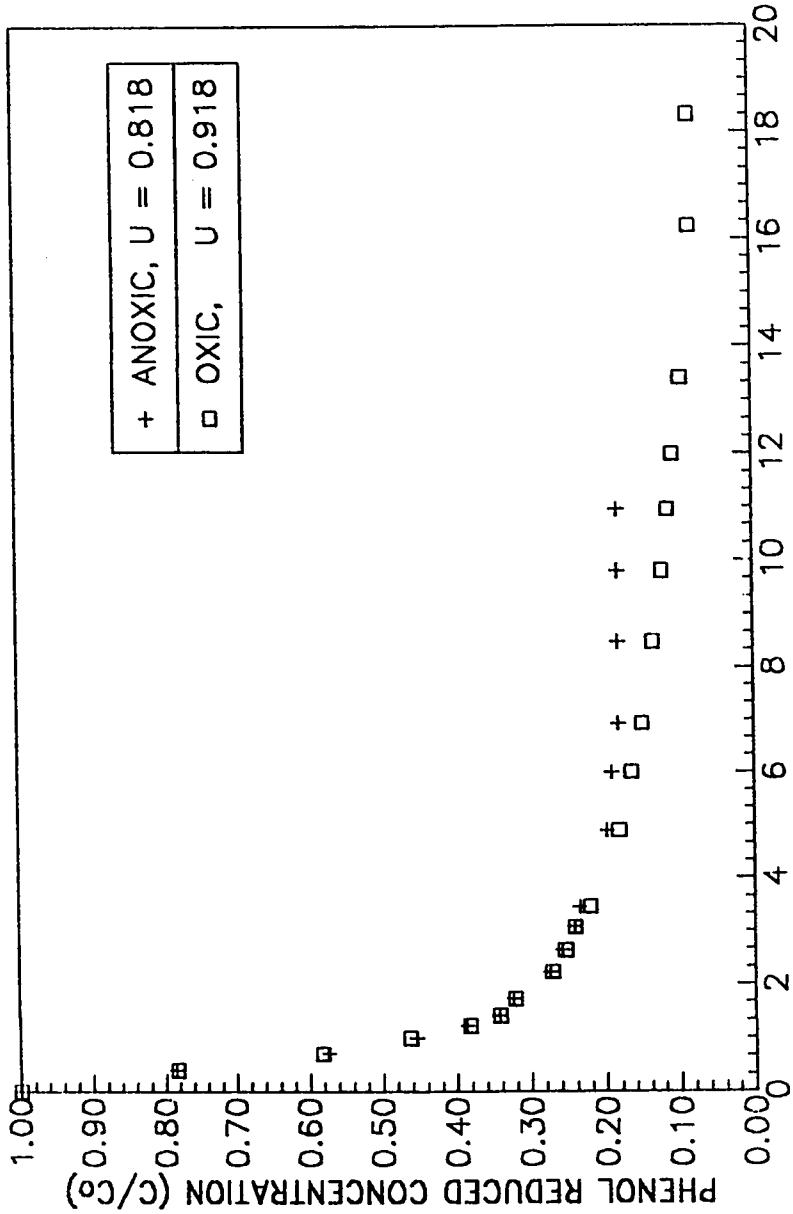

Figure 6.11: Closed Batch Kinetics Experiment for Phenol at pH 3 and T = 21° C.

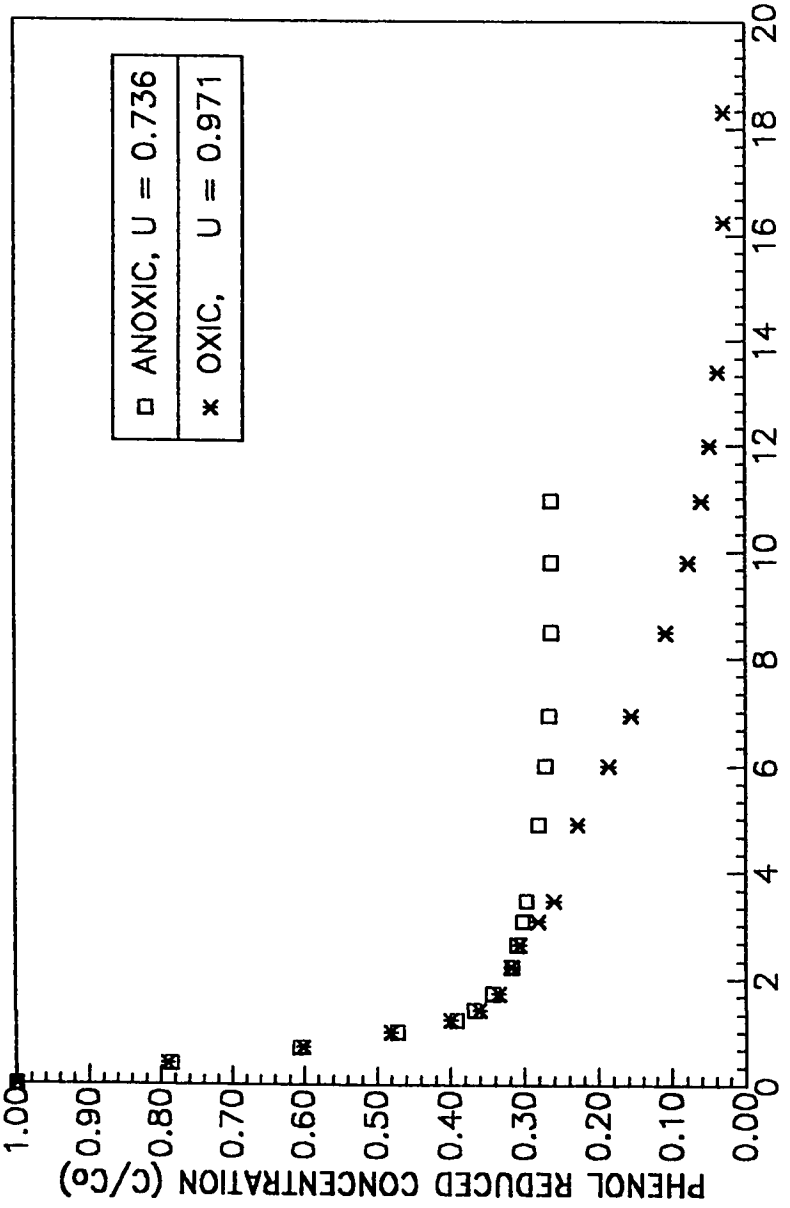

Figure 6.12: Closed Batch Kinetic Experiment for Phenol at pH 7 and T = 21° C.

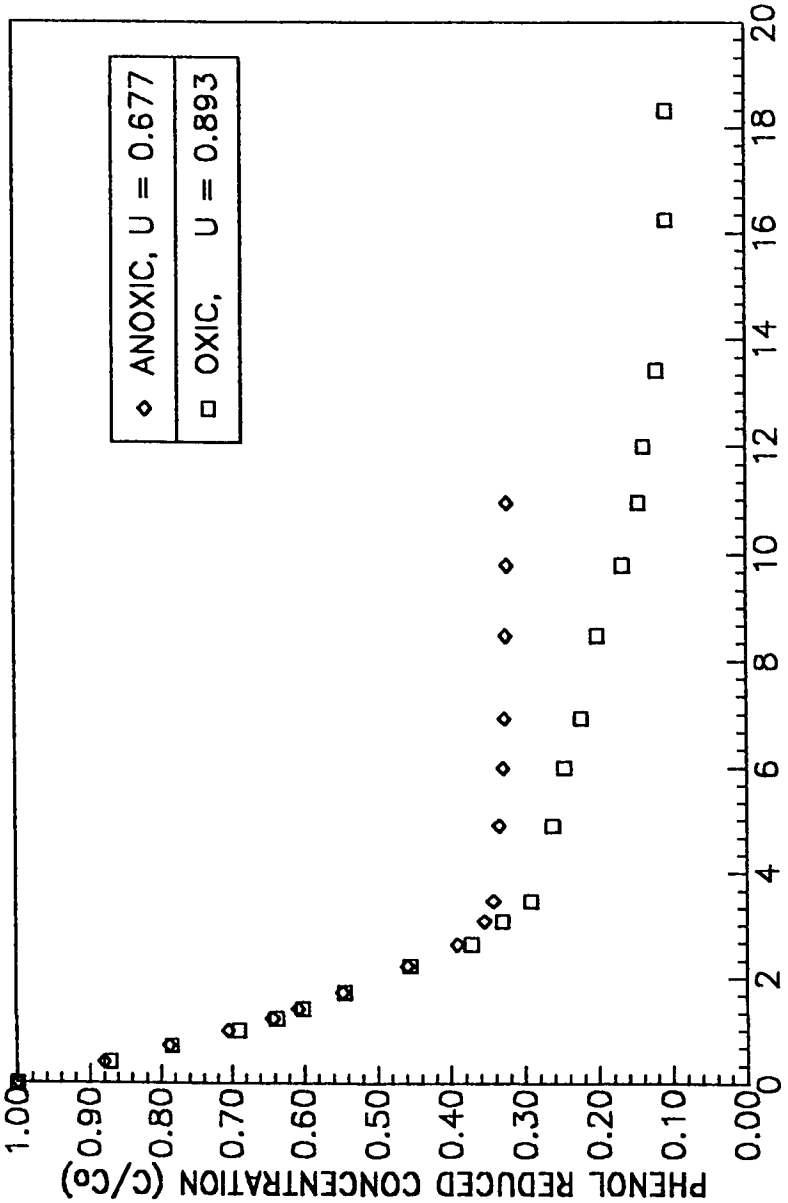

Figure 6.13: Closed Batch Kinetics Experiment for Phenol at pH 11 and T = 21 °C.

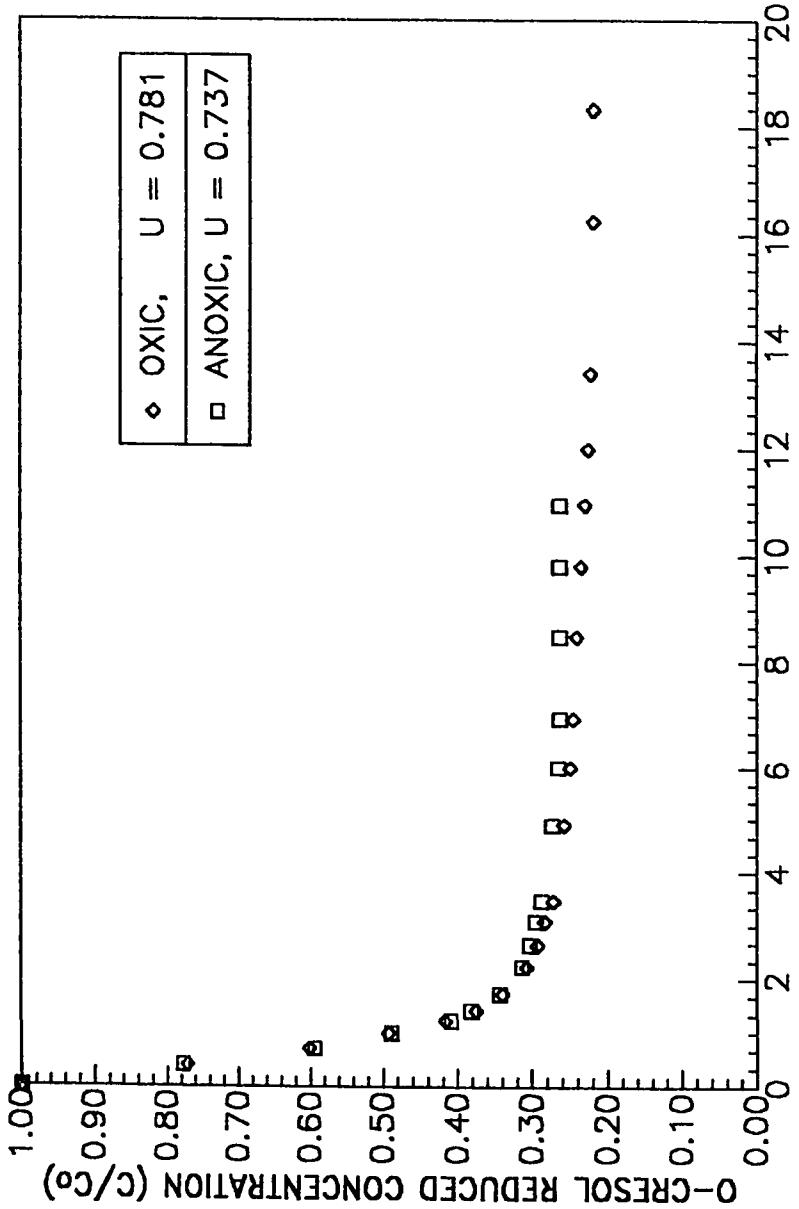

Figure 6.14: Closed Batch Kinetics Experiment for o-Cresol at pH 3 and T = 21° C.

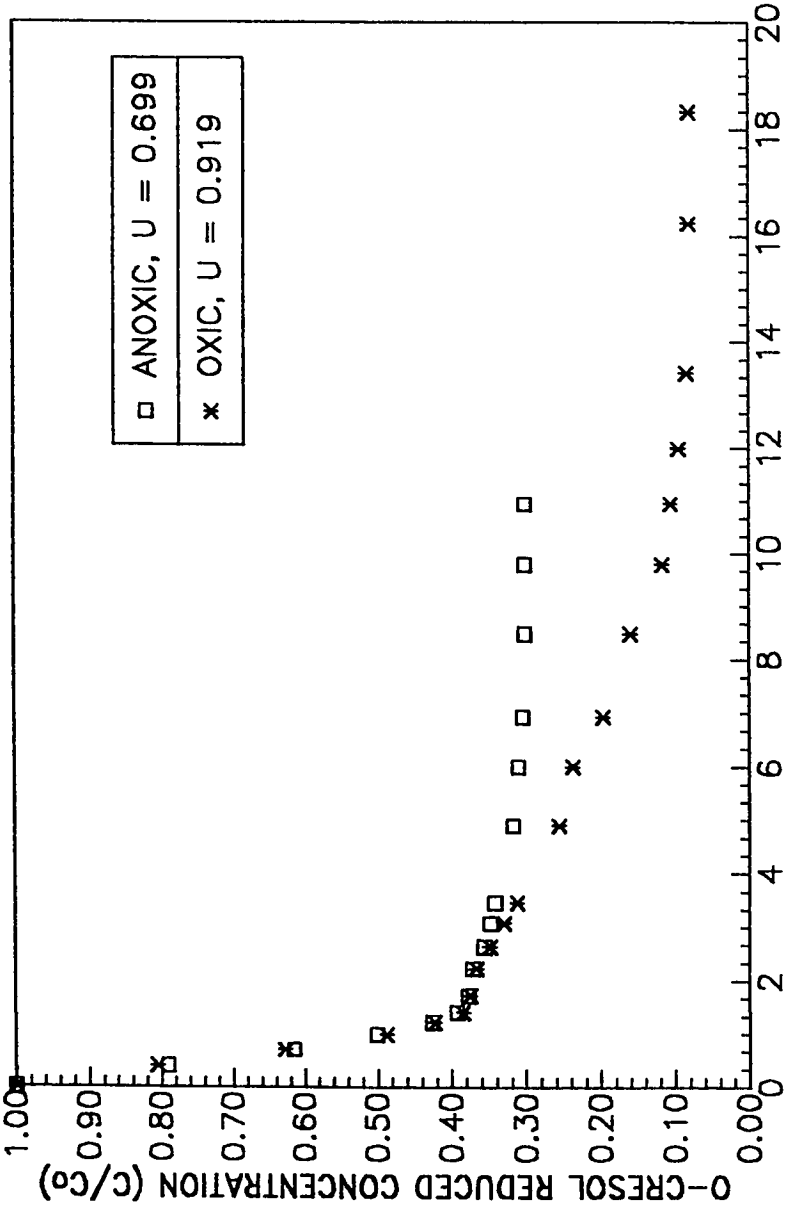

Figure 6.15: Closed Batch Kinetics Experiment for o-Cresol at pH 7 and T = 21° C.

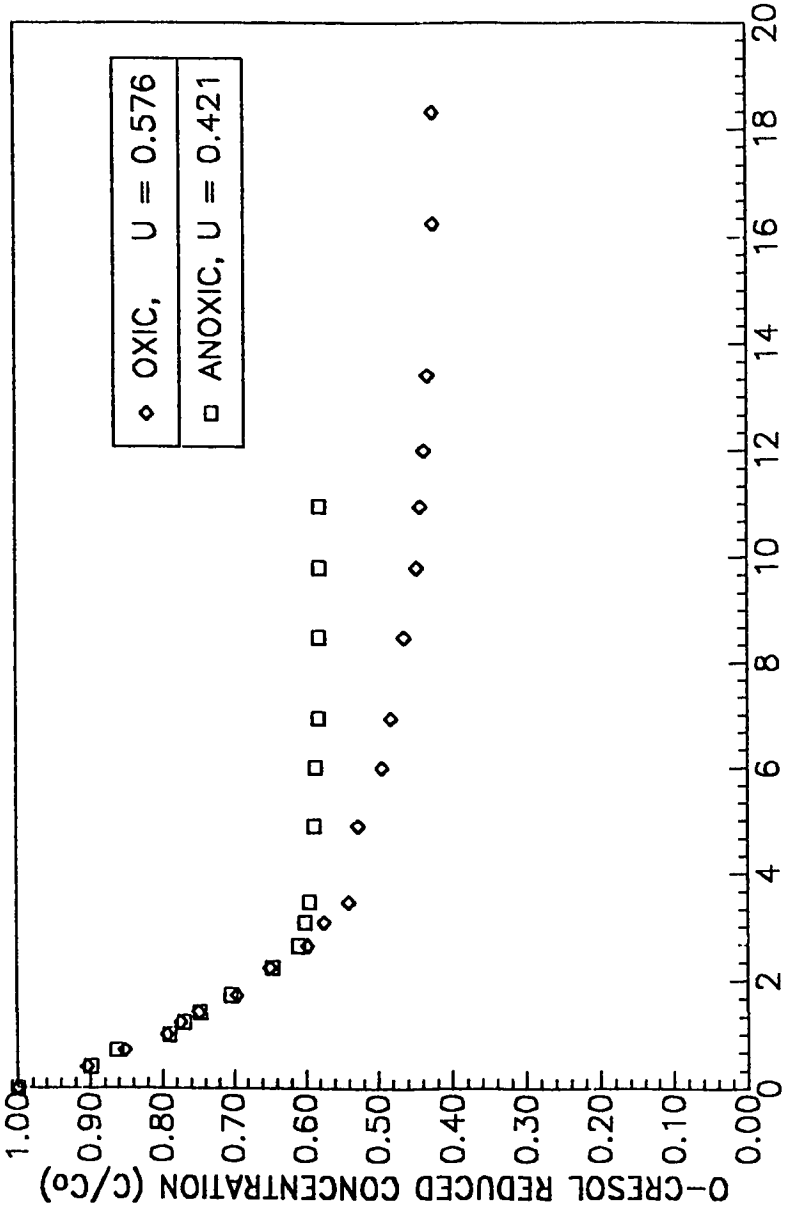

Figure 6.16: Closed Batch Kinetics Experiment for o-Cresol at pH 11 and T = 21 °C.

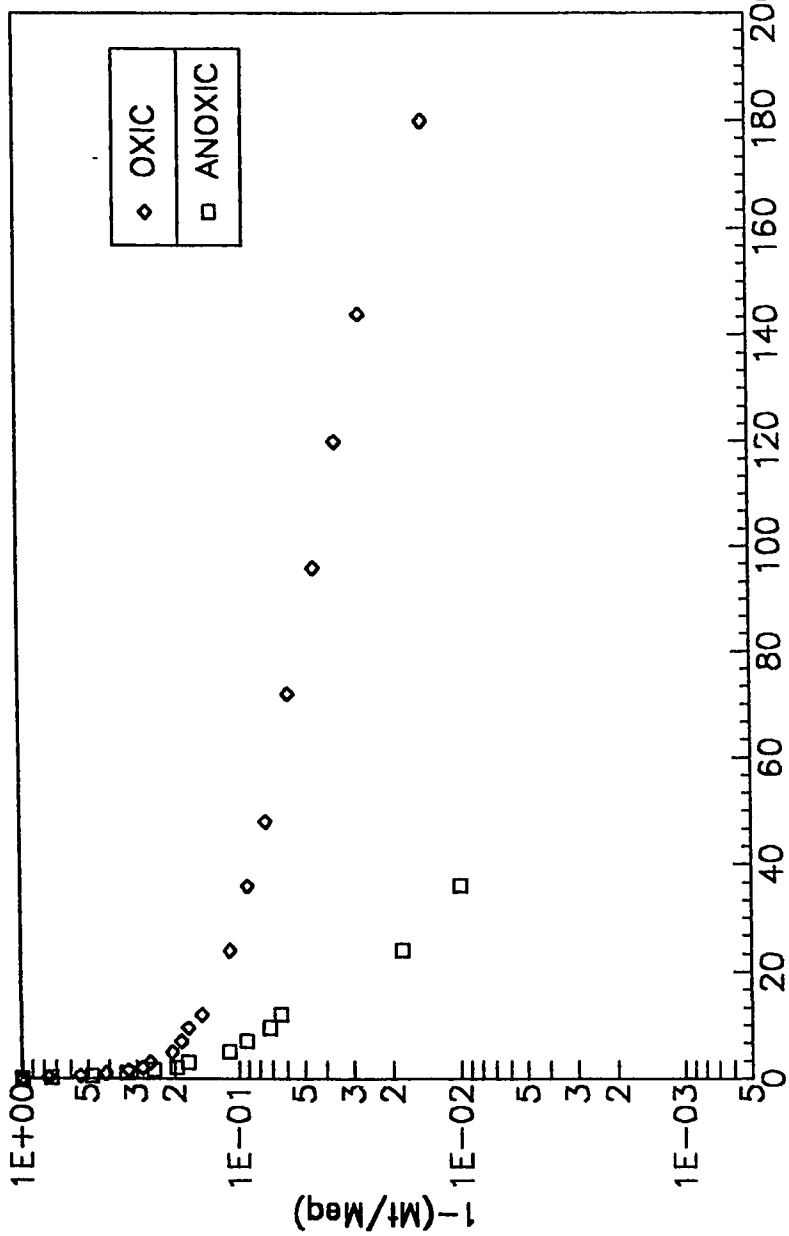

Figure 6.17: Linearized Rate of Phenol Uptake at pH 3and T = $21^{\circ}C_{\text{from oah13}}$

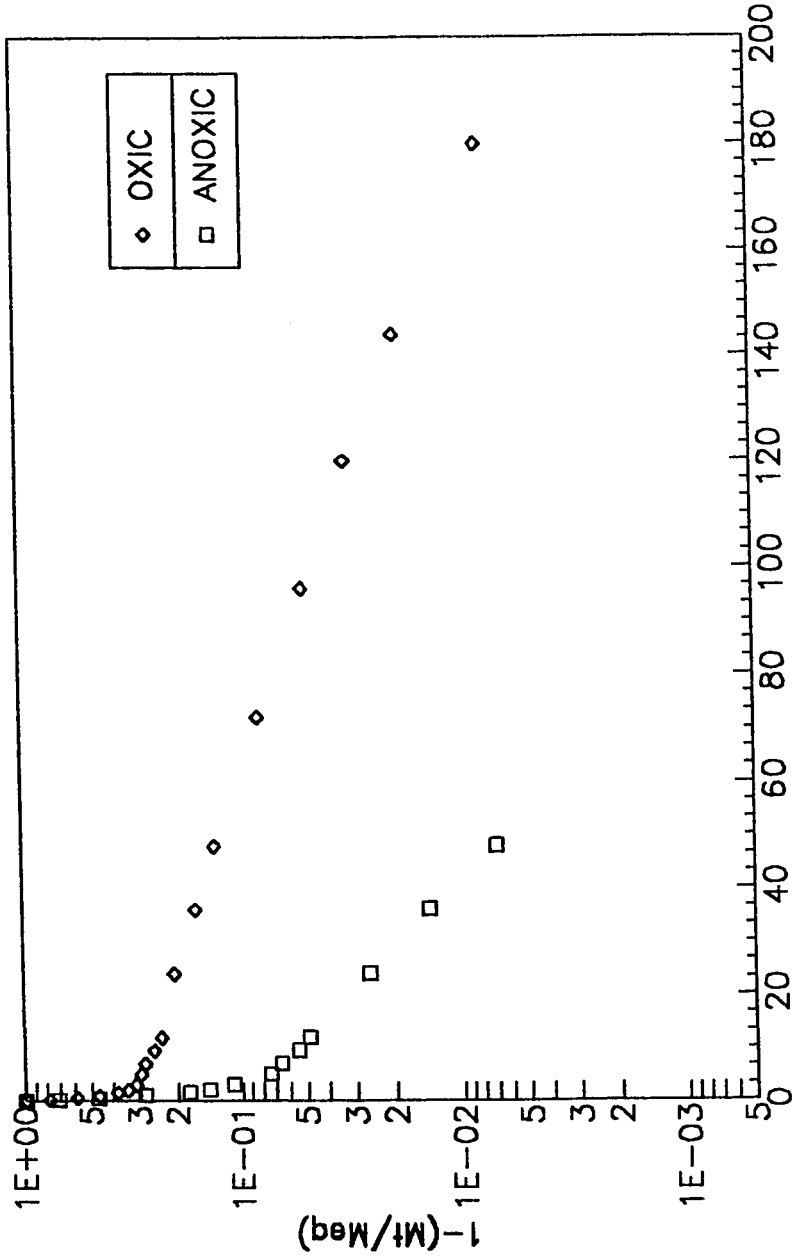

Figure 6.18: Linearized Rate of Phenol Uptake at pH 7and T = 21°C from ash17

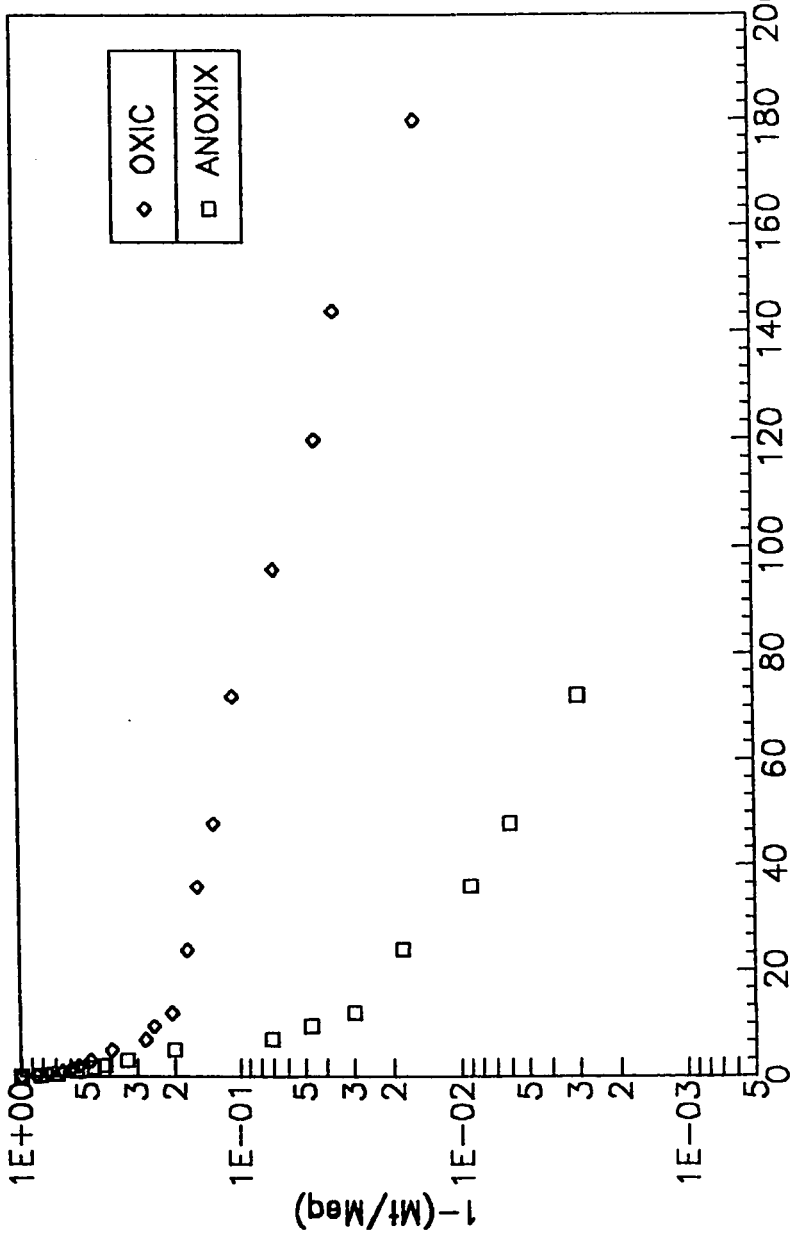

Figure 6.19: Linearized Rate of Phenol Uptake at pH 11 and T = 21°C from 66h111

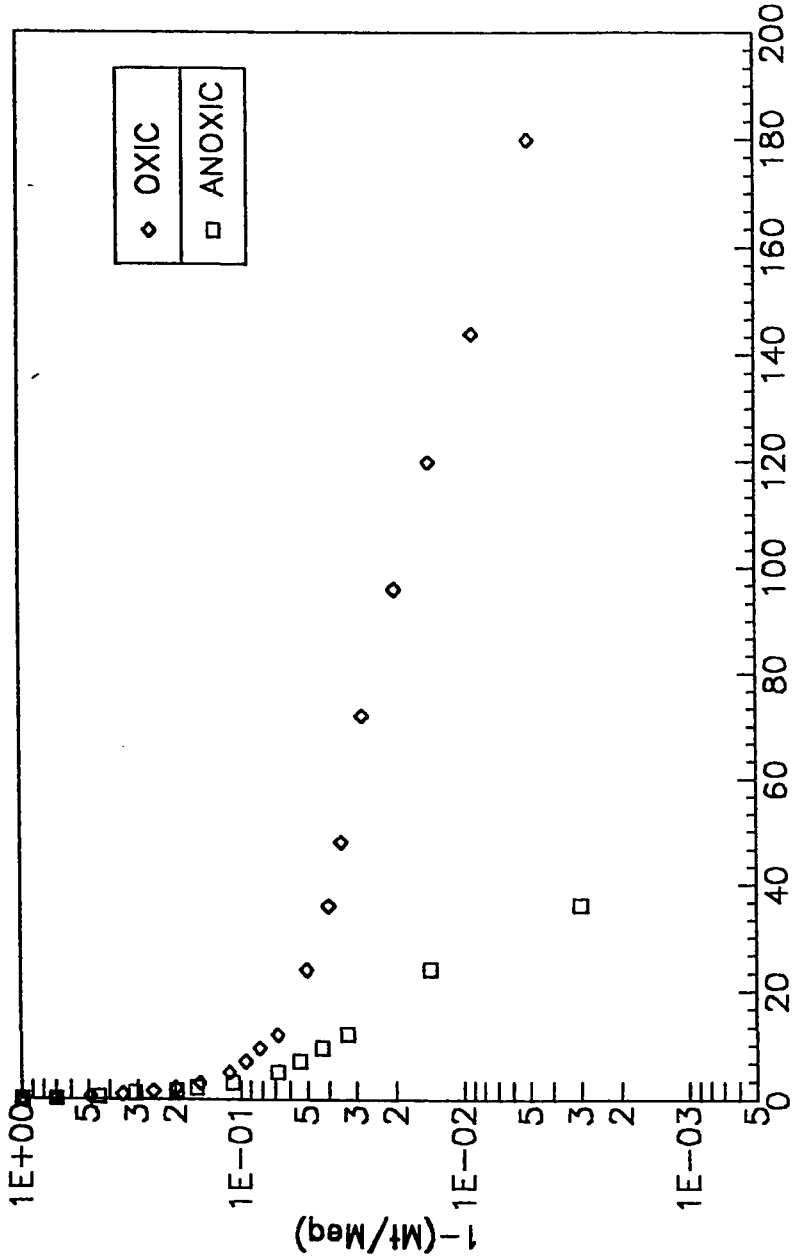

Figure 6.20: Linearized Rate of o-Cresol Uptake at pH 3 and T = $21^{\circ}C_{\text{from data13}}$

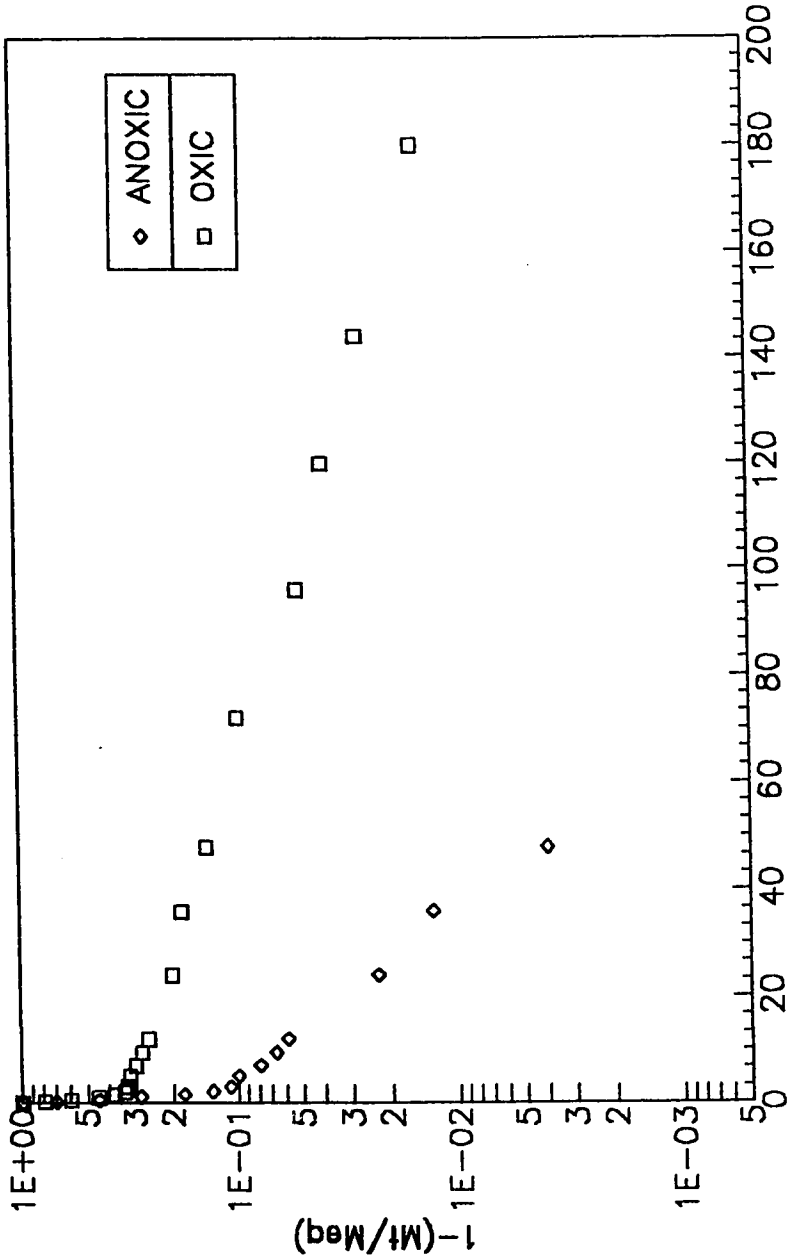

Figure 6.21: Linearized Rate of o-Cresol Uptake at pH 7 and T = $21^{\circ}C_{from\ Gbh17}$

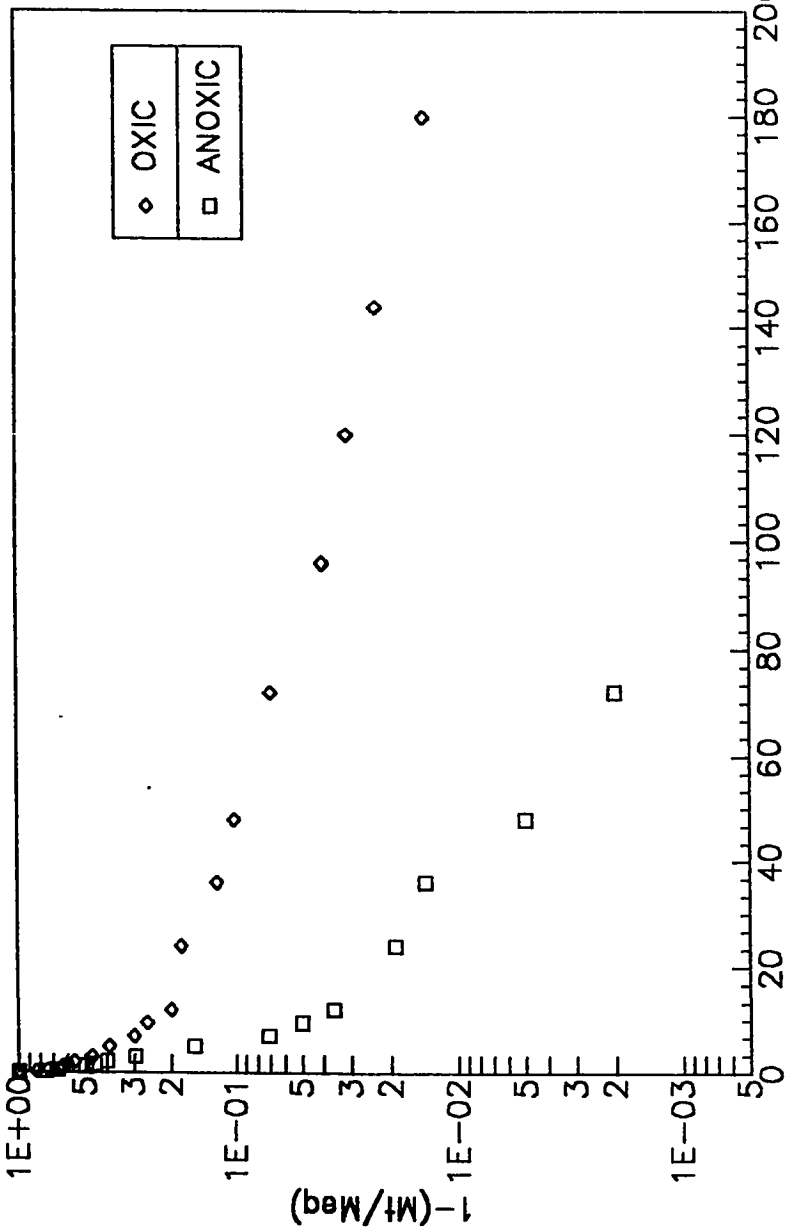

Figure 6.22: Linearized Rate of o-Cresol Uptake at pH 11 and T = 21 °C from ash111

the experiment, the last measurement before this time was after 7.5 days from the start of the experiment. So, one can only conclude that equilibrium was maintained in the four cases in the period of (7.5-11) days from the start of the experiment.

The data presented in Figures 6.11-6.16 will be shown in terms of linearized uptakes. Phenol linearized uptakes at pH values of 3, 7, and 11 are plotted and shown in Figures 6.17, 6.18, and 6.19, respectively, while Figures 6.20, 6.21, and 6.22 present the case of o-cresol. The different long time slopes in the figures suggests the effect of pH variation on both physical adsorption and reactions. Surface diffusivities (D_s) were found by the HSDM model for the three pH values under the oxic and anoxic conditions and are presented in Table 6.2 for both phenol and o-cresol. The HSDM model was used to predict the data presented in the figures of this section; so, the experimental data for phenol and o-cresol under oxic and anoxic conditions at the different pH values are presented again along with the HSDM predictions in Figures 6.23-6.28. Those figures depict the good prediction capability HSDM model has for physical adsorption (anoxic curves), while this was not always the case for the oxic curves. The reason for that was discussed in the previous section. However, the χ^2 values were lower than the table values for both the oxic and anoxic experiment which statistically means that data is fairly predicted by the HSDM model.

To be able to analyze the effect of pH on the oxic and anoxic adsorption, D_s values are plotted versus pH for phenol and o-cresol in Figures 6.29 and 6.30, respectively. From the figures it is clear that for the anoxic case (physical adsorption) the highest surface diffusivities were attained at pH 7 and the order of D_s values was at pH 7 > pH 3 > pH 11 which conflicts with the findings of Koh and Chung (23) who observed that the kinetics were increasing with the decrease in pH. For the oxic condition, D_s

Table 6.2. Apparent Diffusivities of Phenol and o-Cresol Evaluated by the HSDM Model at Various pHs and temperature of 21°C.

Compound	Operational Conditions	HSDM (Ds) cm^2/sec	χ^2	$\chi^2_{n,\alpha\ 0.05}$
o-cresol	oxic, pH 3	5.9E-08	0.31	8.05
	anoxic, pH 3	7.8E-08	0.025	5.7
o-cresol	oxic, pH 7	1.4E-08	0.89	8.05
	anoxic, pH 7	8.3E-08	0.036	5.7
o-cresol	oxic, pH 11	1.1E-08	0.38	8.05
	anoxic, pH 11	3.3E-08	0.0045	5.7
phenol	oxic, pH 3	1.8E-08	0.4	8.05
	anoxic, pH 3	4.2E-08	0.055	5.7
phenol	oxic, pH 7	7.6E-09	2.07	8.05
	anoxic, pH 7	6.3E-08	0.054	5.7
phenol	oxic, pH 11	3.5E-09	0.21	8.05
	anoxic, pH 11	2.4E-08	0.014	5.7

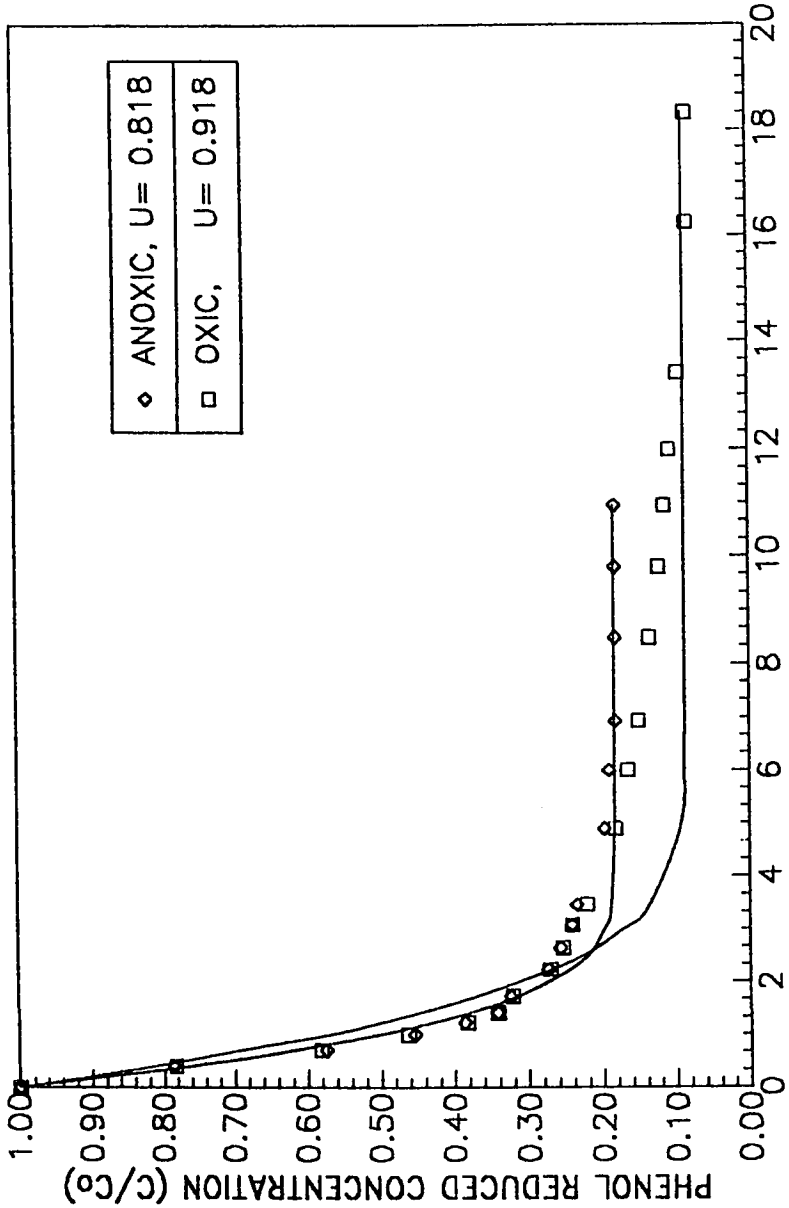

Figure 6.23: Closed Batch Kinetics Experiment for Phenol at pH 3 and T = 21°C. Along with HSDM Predictions.

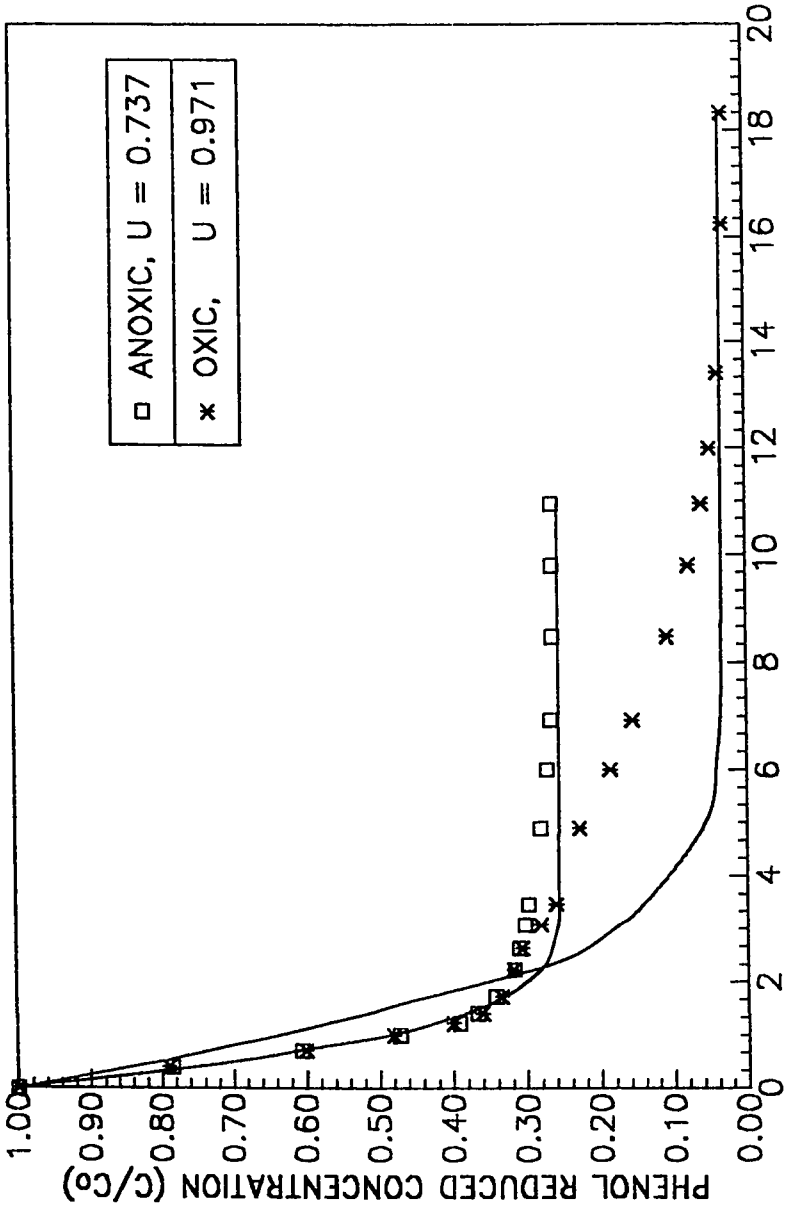

Figure 6.24: Closed Batch Kinetic Experiment for Phenol at pH 7 and T = 21 °C. Along with HSDM Predictions.

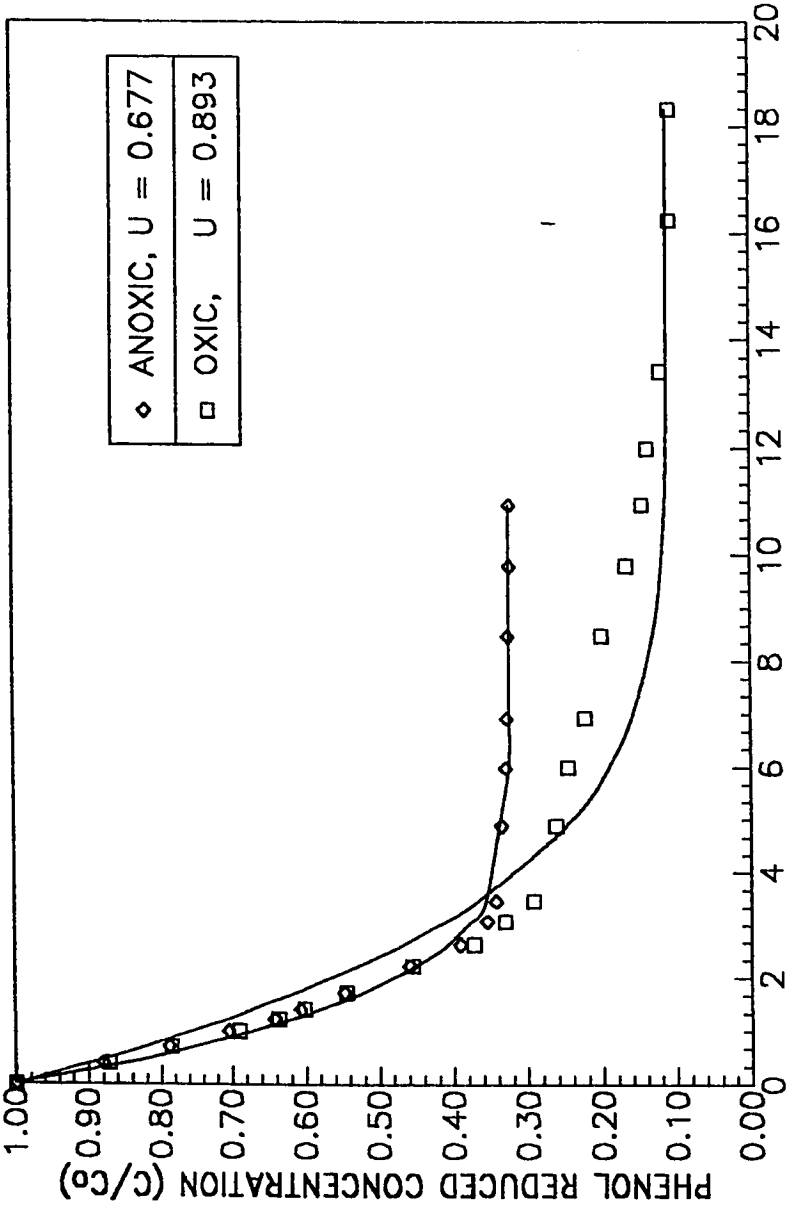

Figure 6.25: Closed Batch Kinetics Experiment for Phenol at pH 11 and T = 21° C. Along with HSDM Predictions.

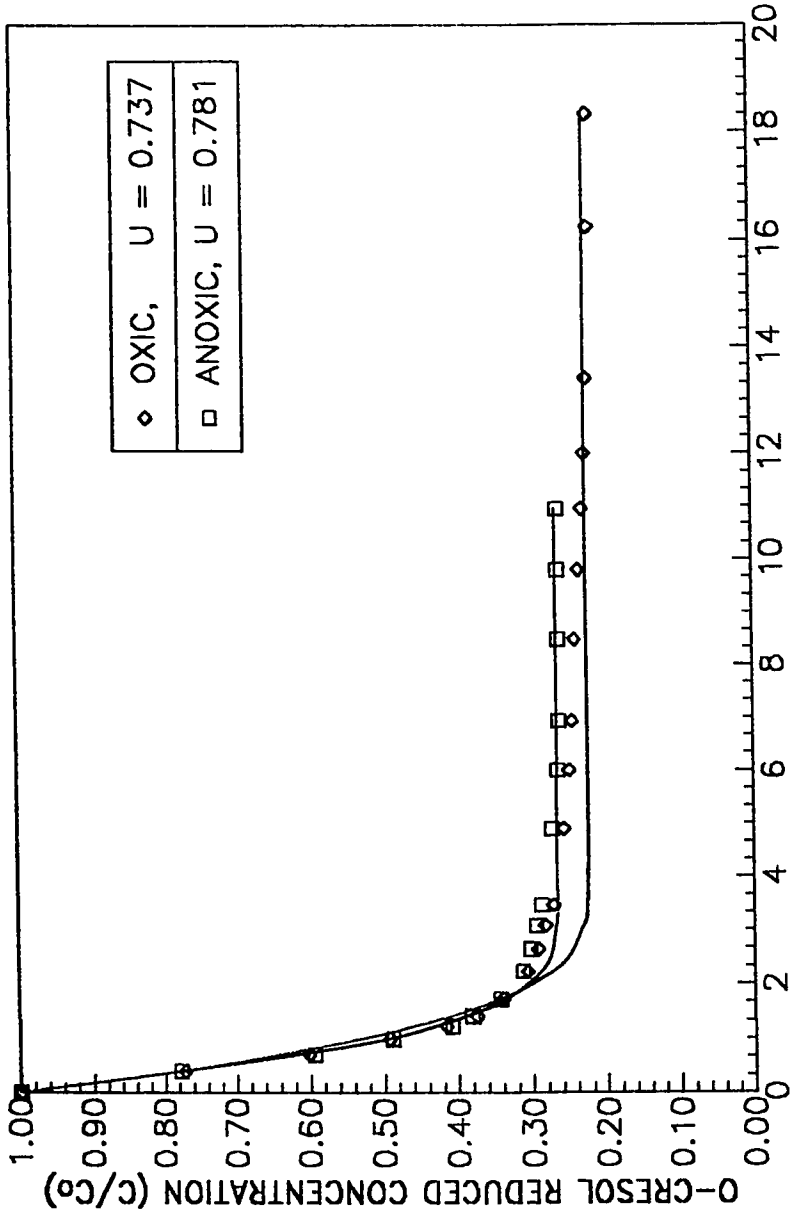

Figure 6.26: Closed Batch Kinetics Experiment for o-Cresol at pH 3 and T = 21 °C. Along with HSDM Predictions.

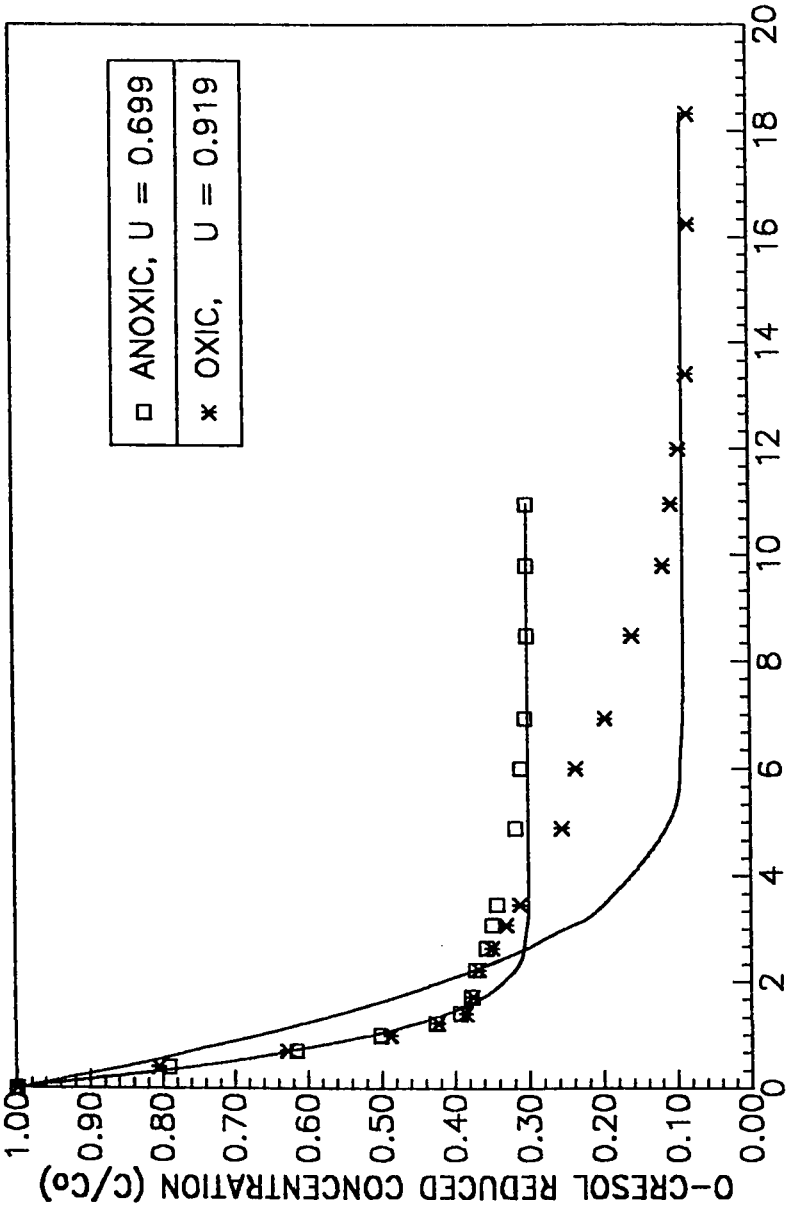

Figure 6.27: Closed Batch Kinetics Experiment for o-Cresol at pH 7 and T = 21°C. Along with HSDM Predictions.

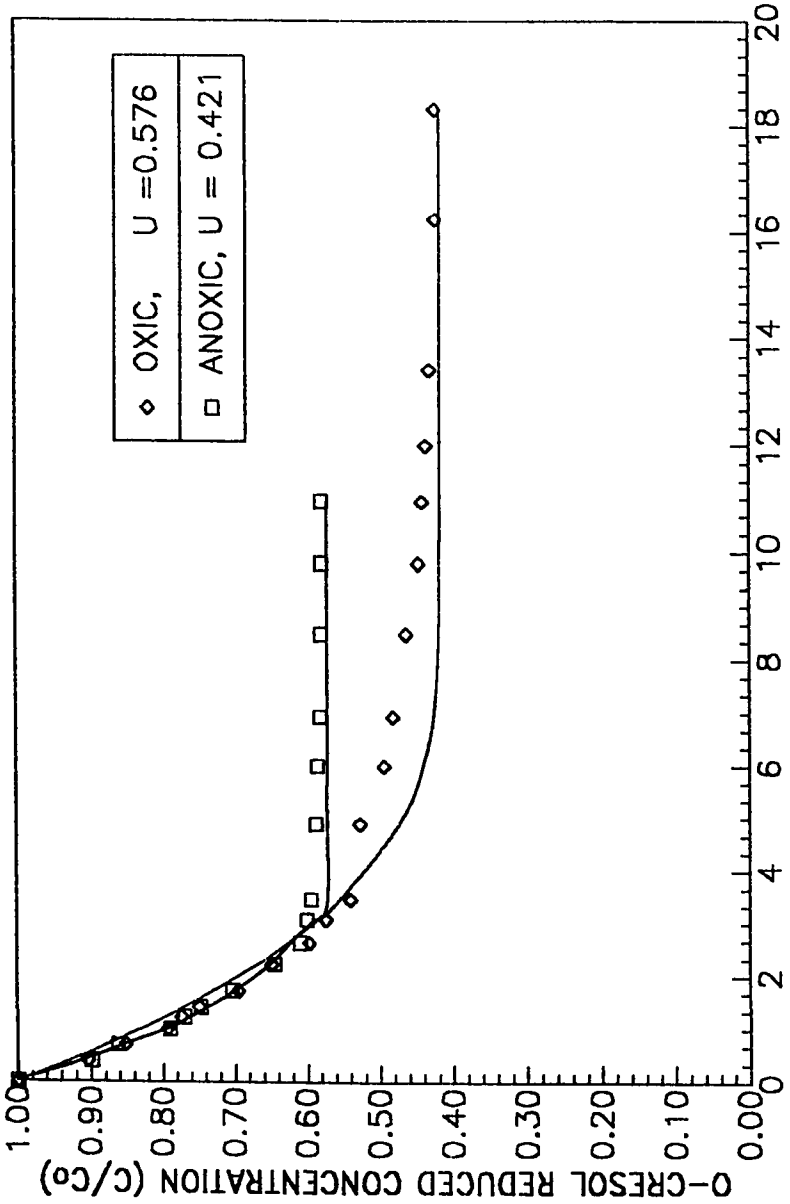

Figure 6.28: Closed Batch Kinetics Experiment for o-Cresol at pH 11 and T = 21° C. Along with HSDM Predictions.

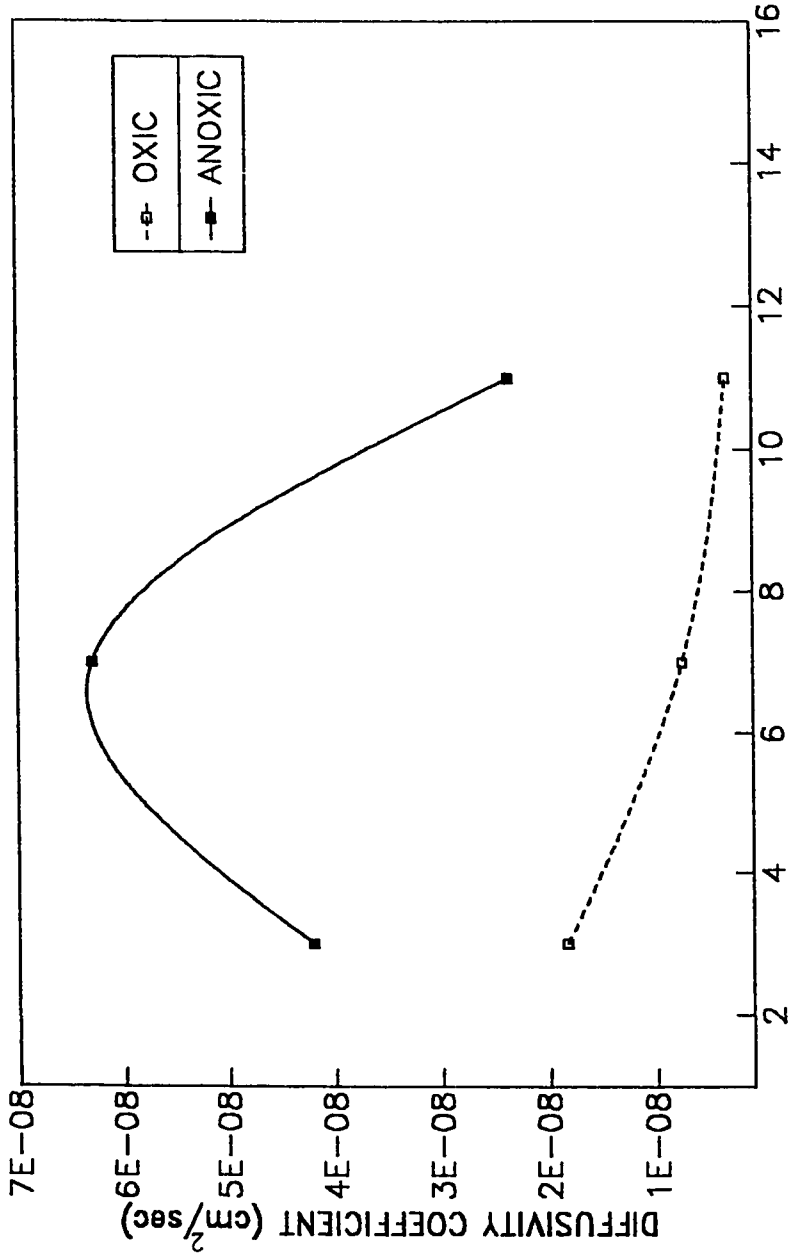

Figure 6.29: Relationship Between Phenol Apparent Diffusivities (HSDM) and pH at $\bar{T} = 21^{\circ}$ C.

from PPHS

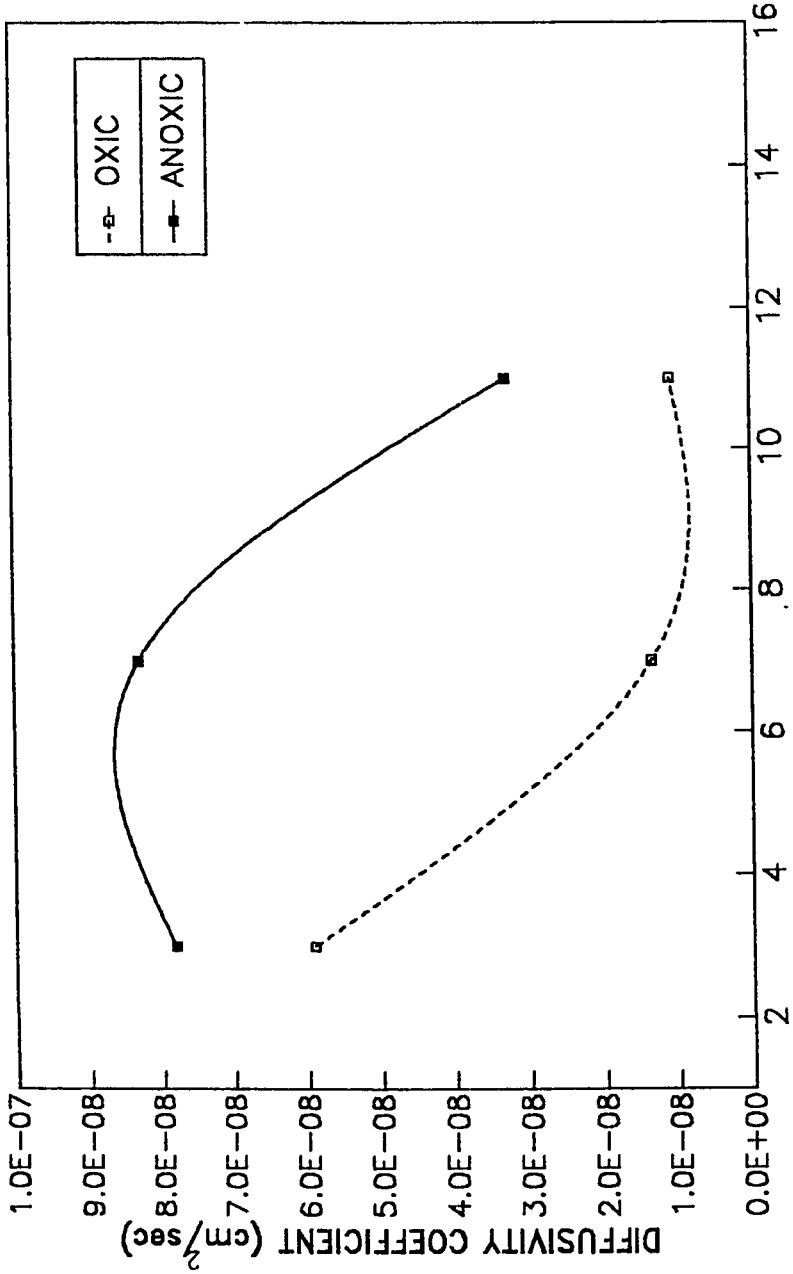

Figure 6.30: Relationship Between o-Cresol Apparent Diffusivities (HSDM) and pH at T = 21° C.

from OPHS

values were decreasing with the increase in pH which agrees with the findings in the literature (23,61). The reason is due to the fact that in the standard experiments oxic conditions are maintained, since, there is no DO removal step. D_s values in the oxic conditions were always lower than the anoxic case which is attributed to the delay in the equilibration time resulting from the telomerization reaction on the carbon surface. However, the difference between D_s values in the oxic and anoxic uptakes was highest at pH 7 which means that the rate of the reaction is highest at pH 7 compared to pH 3 and pH 11.

6.2.3 Effect of Temperature Variation

The anoxic and oxic closed batch kinetic experiments for phenol at temperature values of 8°C, 21°C, and 35°C are shown in Figures 6.31, 6.32, and 6.33, respectively, while Figures 6.34, 6.35, and 6.36 represent the o-cresol data. From these figures, it is clear that temperature variations affect the kinetics of adsorption presented by the anoxic case as well as the kinetics of adsorption-reaction combination presented by the oxic case. The data show that the equilibration time for physical adsorption increases with the decrease in temperature. Consistent with the lower values of d_s expected. On the other hand, for the oxic case, equilibrium was maintained for the three different temperatures for both phenol or o-cresol in the time period of (7.5-11) days from the beginning of the kinetic experiments.

The data presented in Figures 6.37-6.42 are shown in terms of linearized uptakes. Linearized phenol uptake curves at temperature values of 8°C, 21°C, and 35°C are plotted in Figures 6.37, 6.38, and 6.39, respectively, while Figures 6.40, 6.41, and 6.42 present the data for o-cresol. The different long time slopes in the figures suggests the

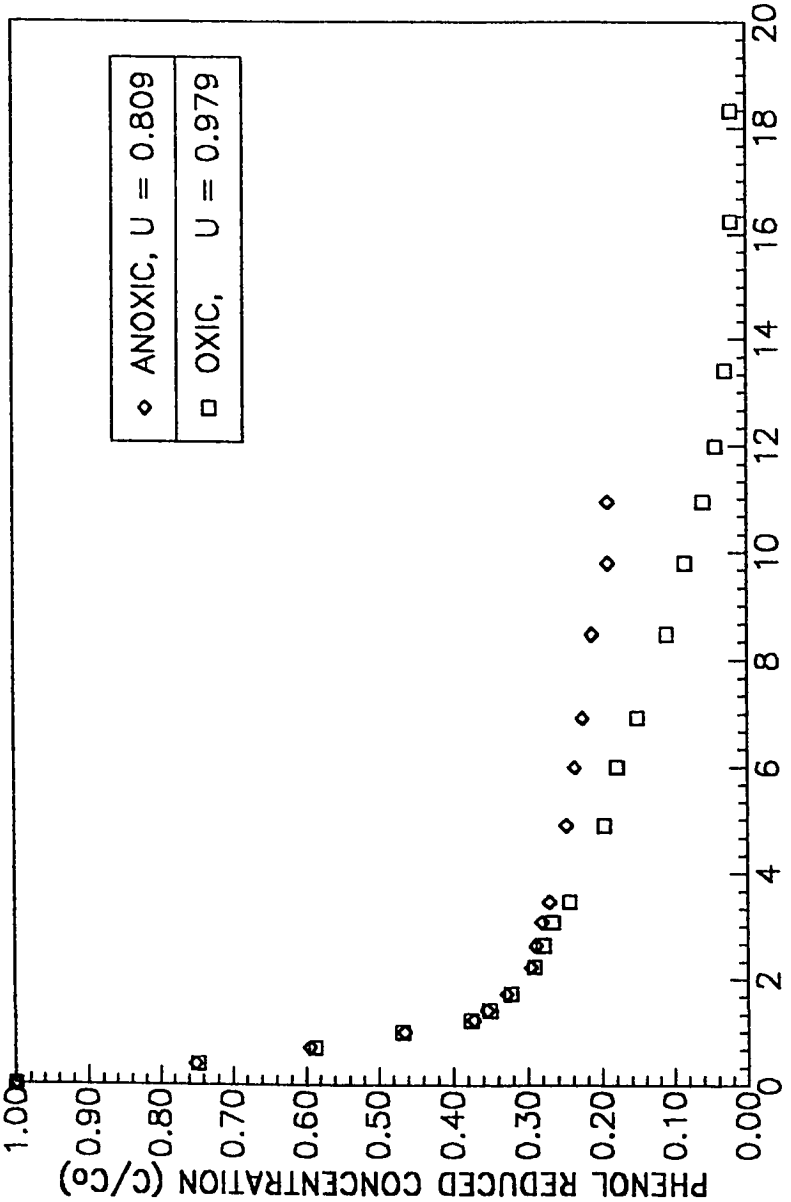

Figure 6.31: Closed Batch Kinetics Experiment for Phenol at T = 8 °C. and pH 7.

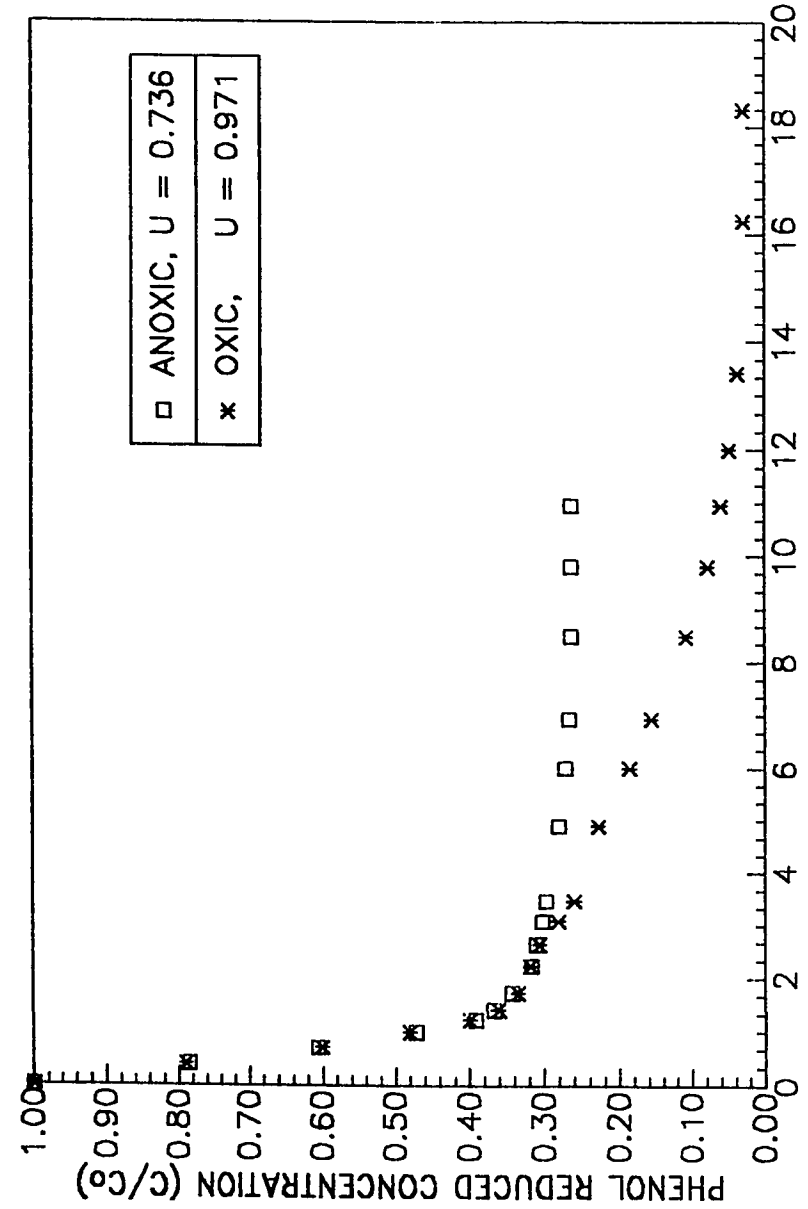

Figure 6.32: Closed Batch Kinetic Experiment for Phenol at T = 21° C. and pH 7.

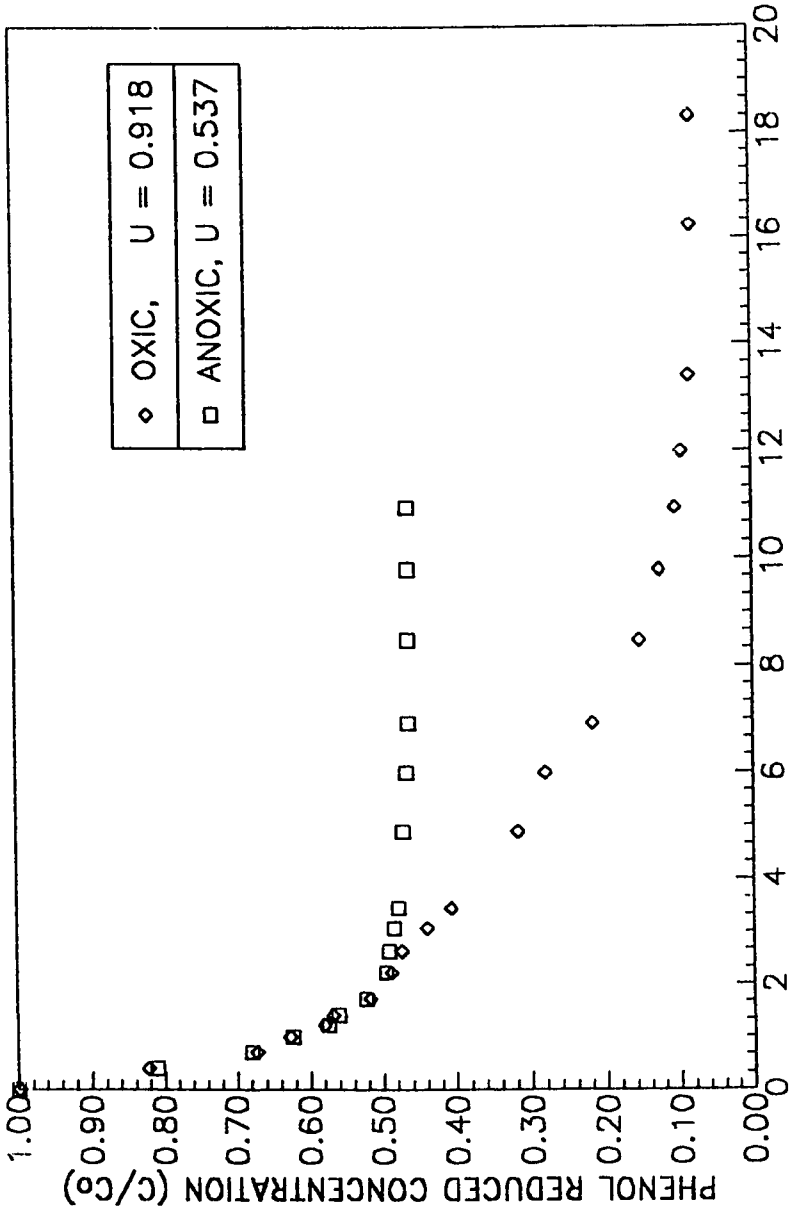

Figure 6.33: Closed Batch Kinetics Experiment for Phenol at T = 35° C. and pH 7.

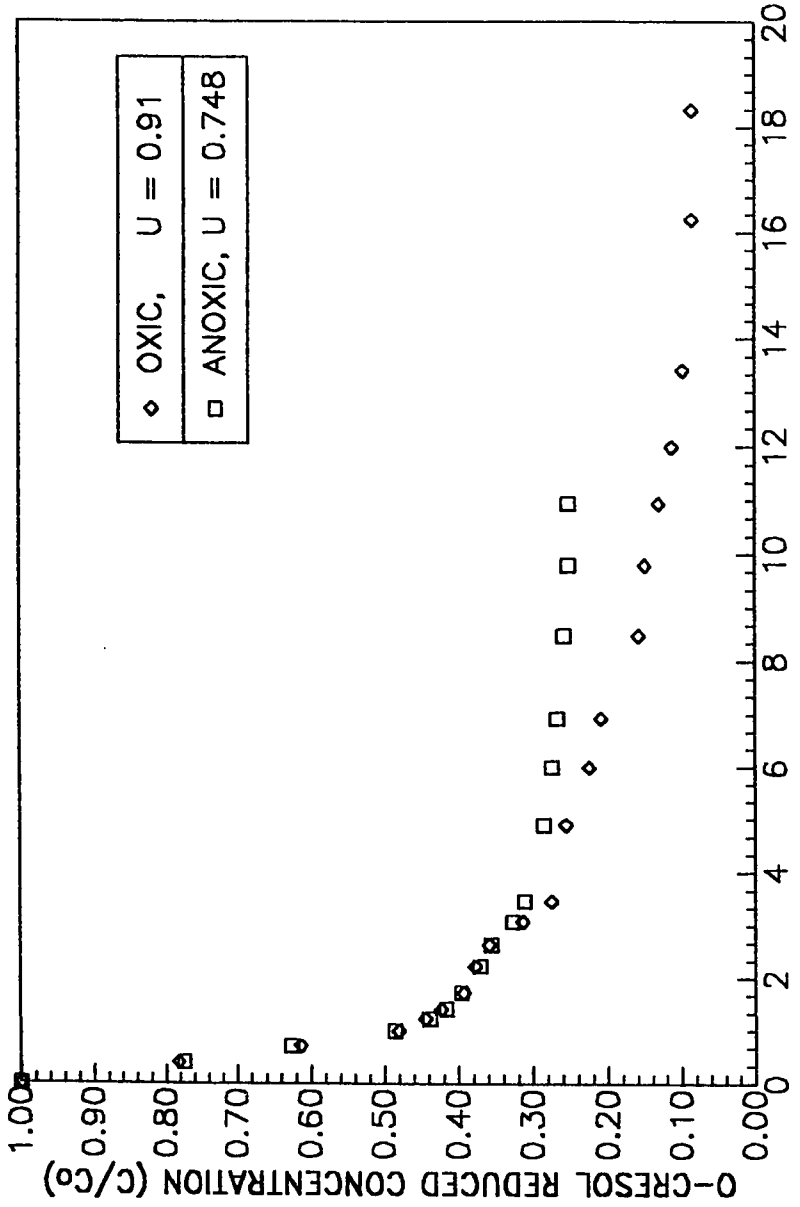

Figure 6.34: Closed Batch Kinetics Experiment for o-Cresol at T= 8° C. and pH 7.

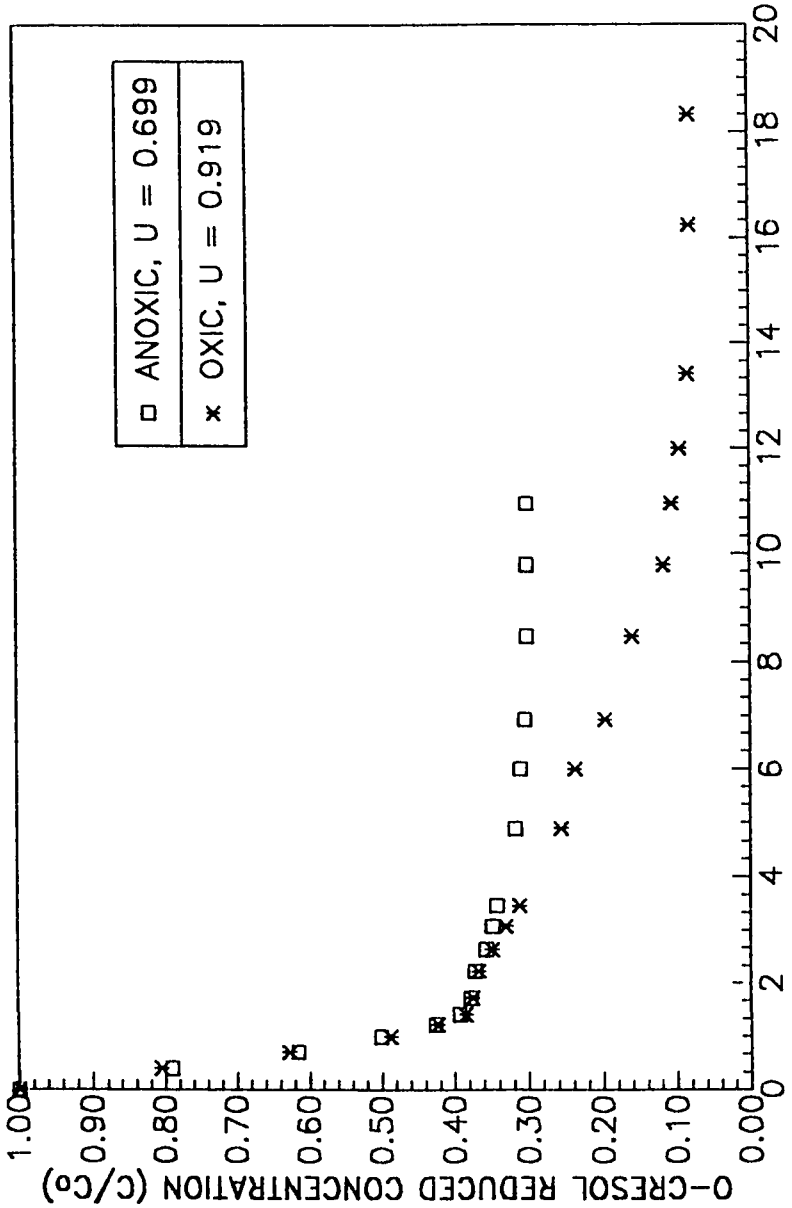

Figure 6.35: Closed Batch Kinetics Experiment for o-Cresol at T = 21° C. and pH 7.

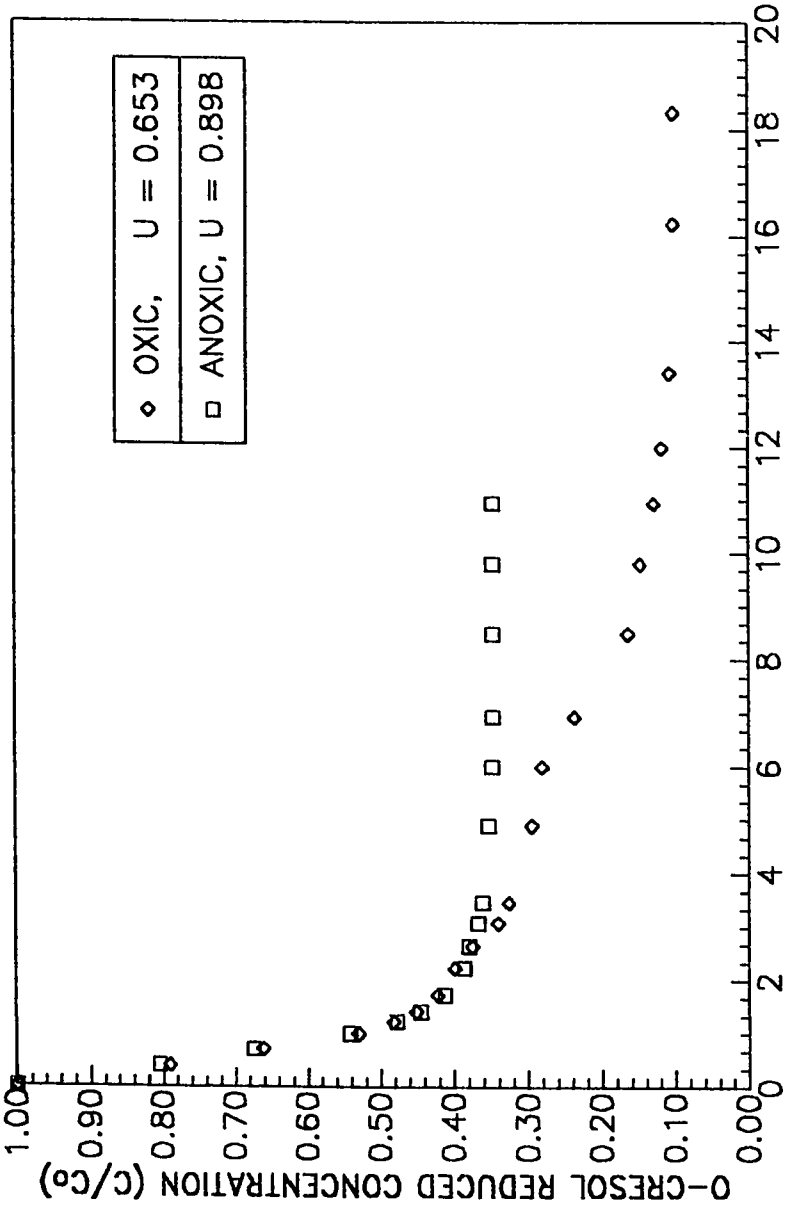

Figure 6.36: Closed Batch Kinetics Experiment for o-Cresol at T = 35 °C. and PH 7.

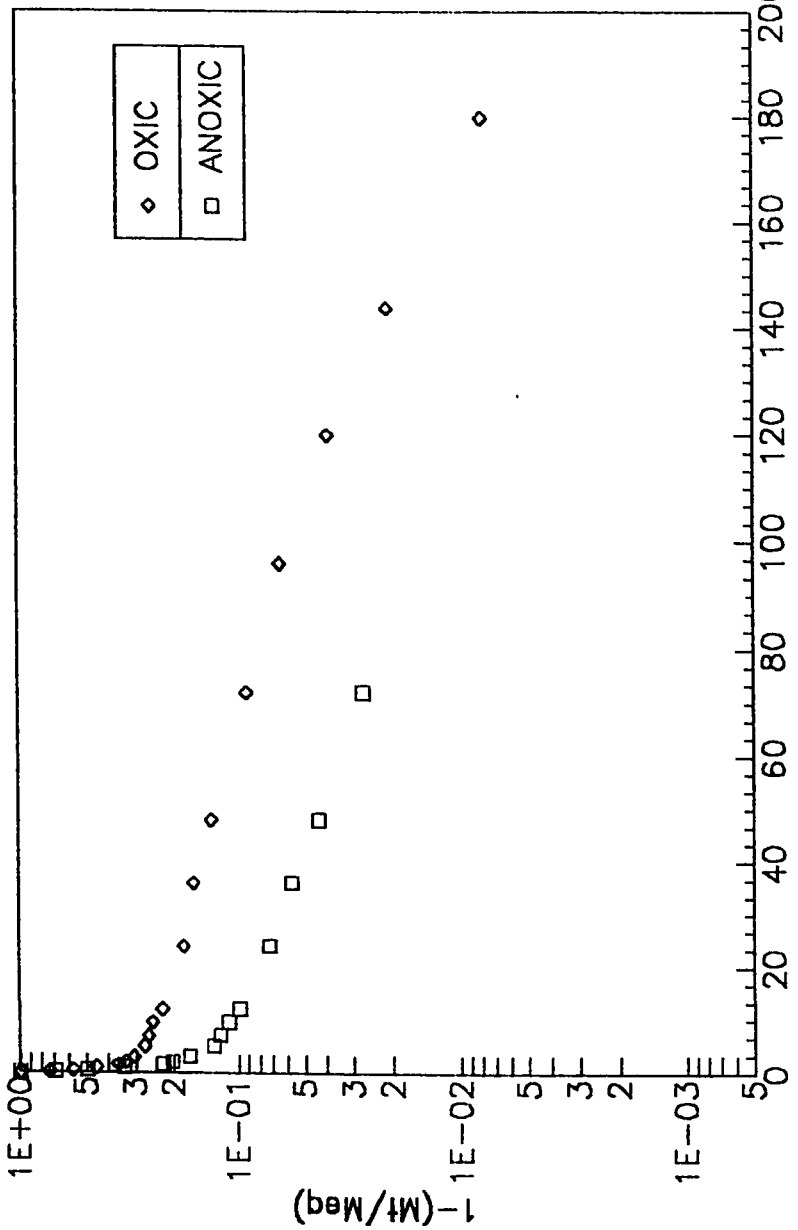

Figure 6.37: Linearized Rate of Phenol Uptake at T = 8°C. and pH 7 from bbh18

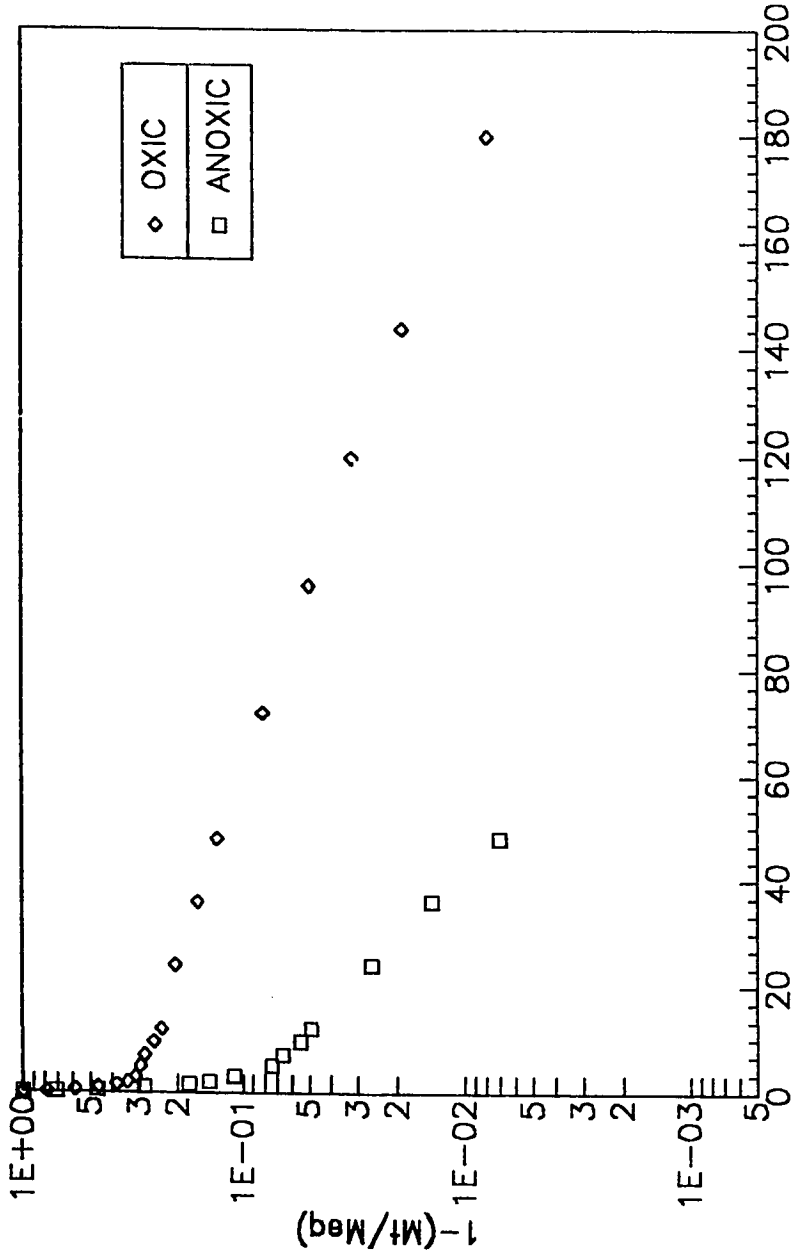

Figure 6.38: Linearized Rate of Phenol Uptake at T = 21°C.and pH 7 from oah121

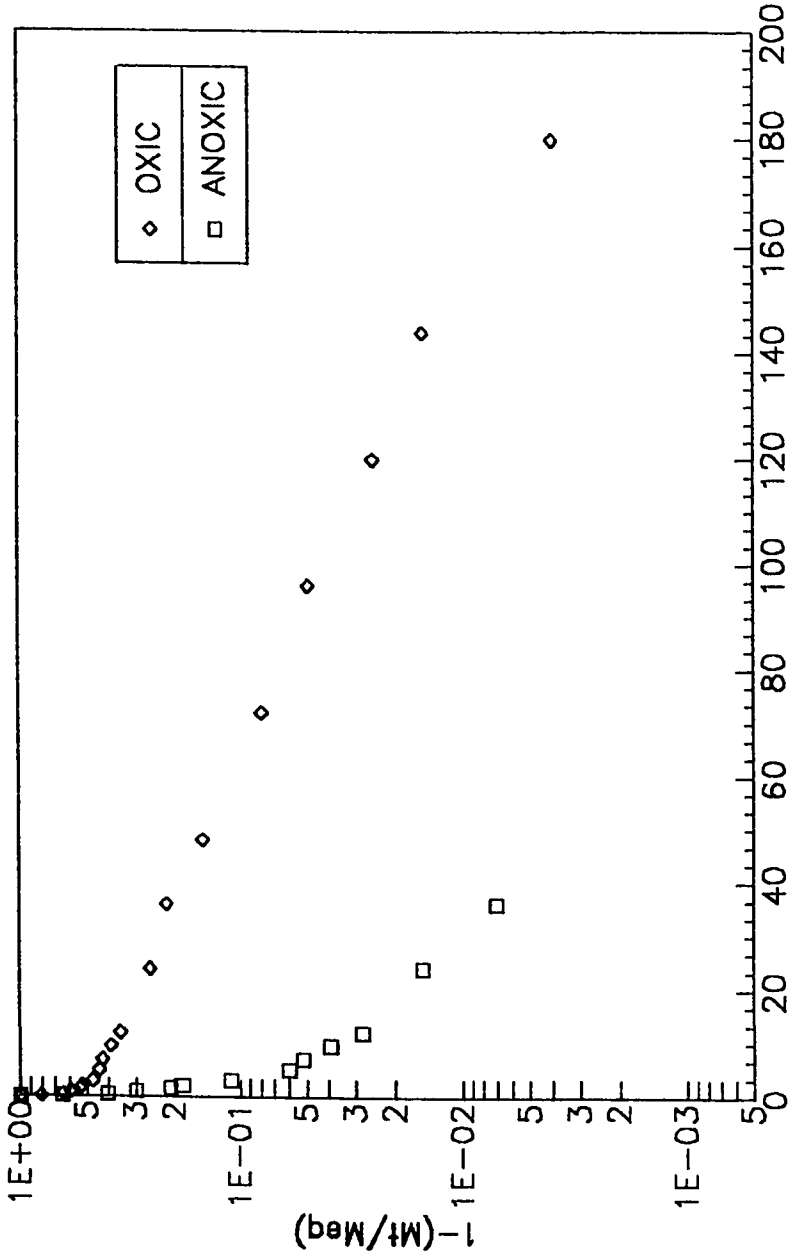

Figure 6.39: Linearized Rate of Phenol Uptake at T = 35° C. and pH 7 from ppb35

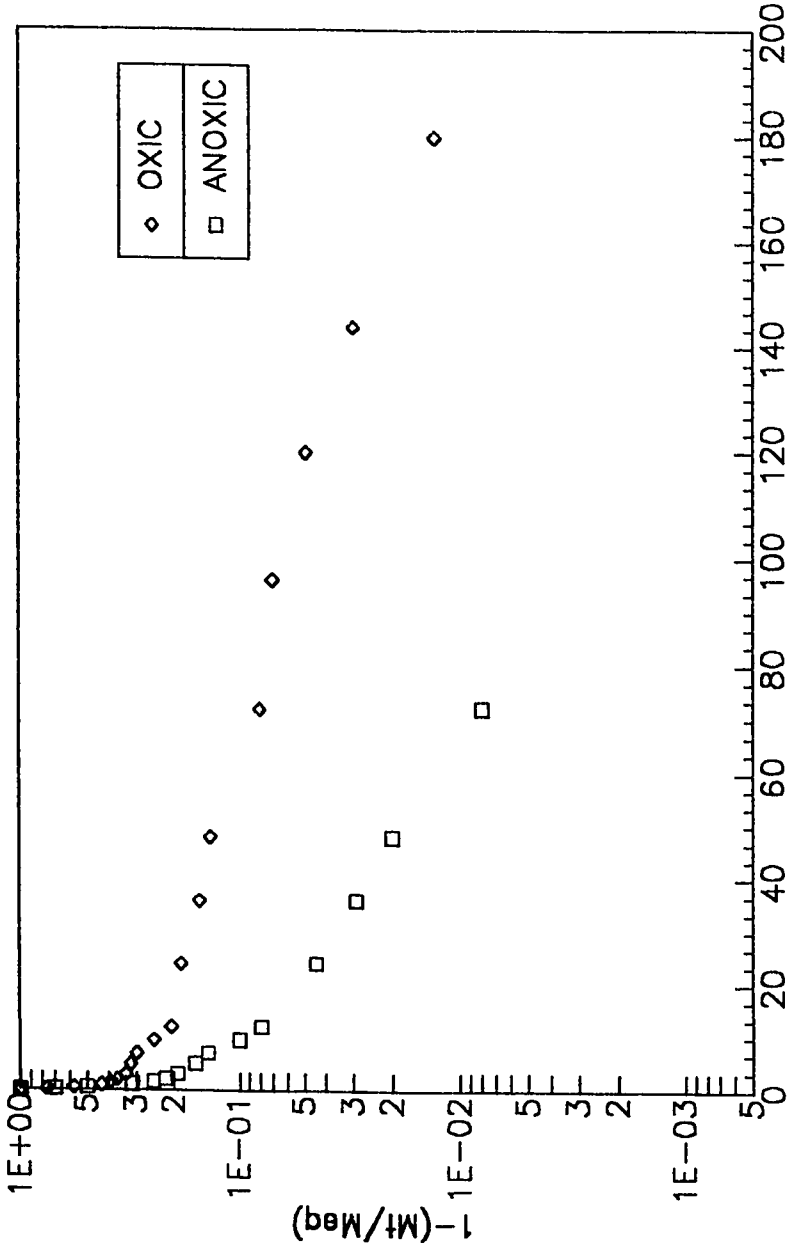

Figure 6.40: Linearized Rate of o-Cresol Uptake at T= 8° C. and pH 7 $_{\text{from OT18}}$

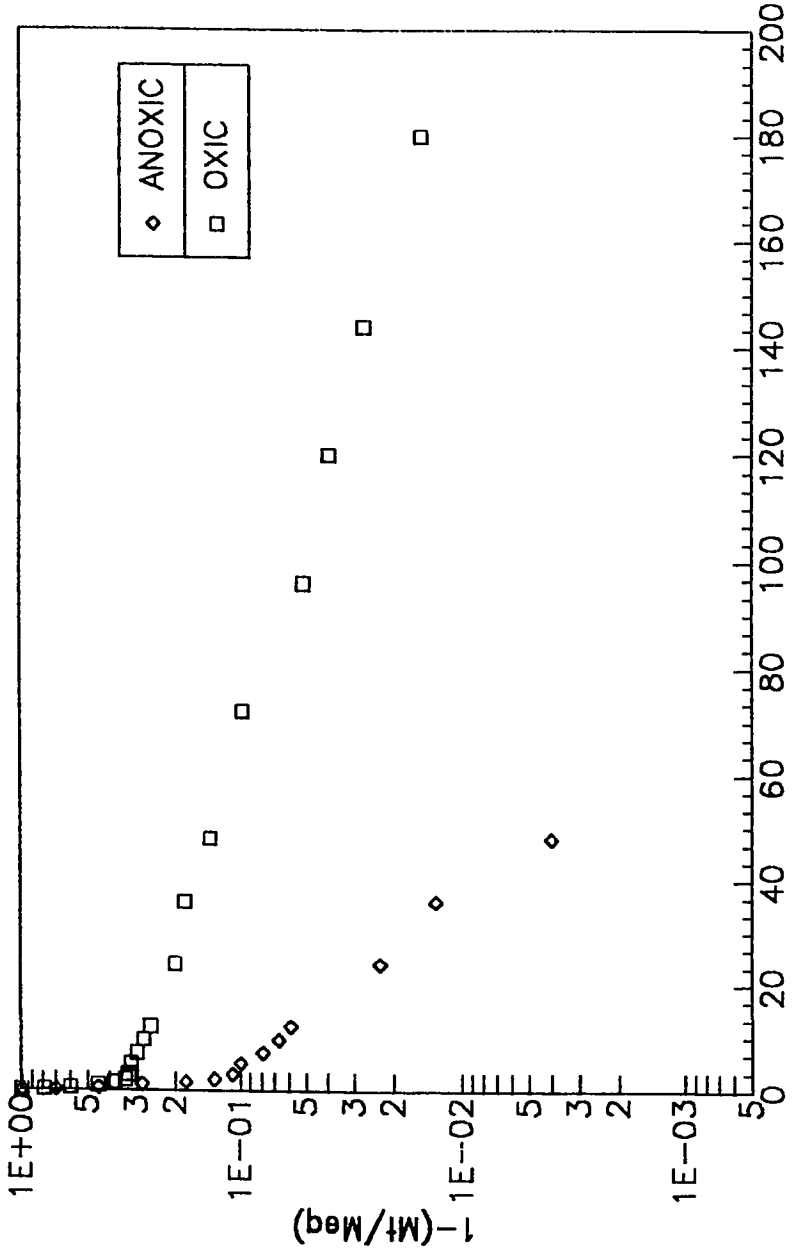

Figure 6.41: Linearized Rate of o-Cresol Uptake T = 21 °C. and pH 7. from OT121

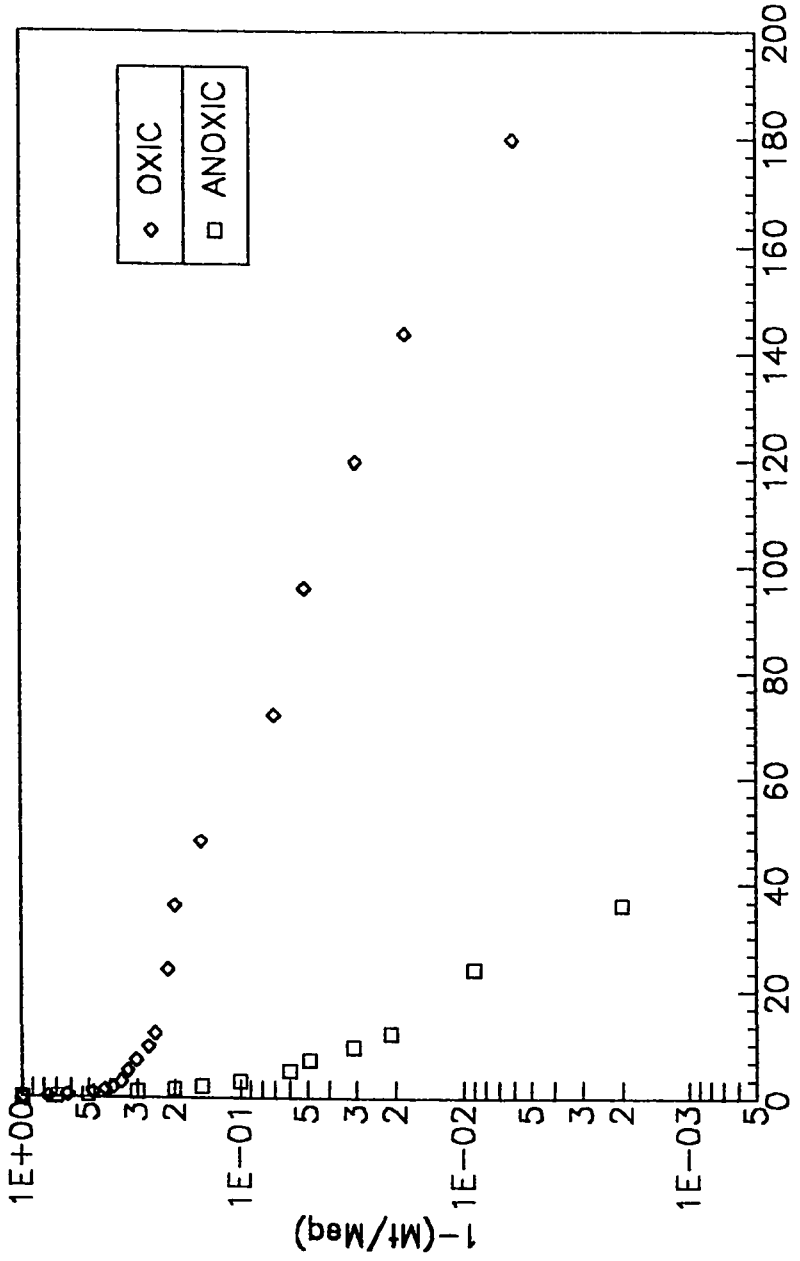

Figure 6.42: Linearized Rate of o-Cresol Uptake at T = 35° C. and $pH_{Z_{from\ OT135}}$

effect of temperature variation on both physical adsorption and reactions. Surface diffusivities (D_s) were found by the HSDM model for the three temperature values under the oxic and anoxic conditions and are presented in Table 6.3 for both phenol and o-cresol. The χ^2 values were higher than the table values for both the oxic and anoxic experiment which again statistically means that data is fairly predicted by the HSDM model. The HSDM model was used to predict the data presented in the figures of this section, so; the experimental data for phenol and o-cresol under oxic and anoxic conditions at the different temperature values were presented again along with the HSDM predictions in Figures 6.43-6.48. Like the case in the previous section, the HSDM model predicted the data for physical adsorption (anoxic curves) satisfactorily for most of the cases, while this was not always the case for the oxic curves. The reason was explained in the previous sections. However, it can be added here that while the experimental and theoretical equilibrium concentrations were similar which is due to the isotherm data provided in the model, the HSDM has to give lower theoretical concentration compared to the experimental ones before equilibrium is reached. This happens because the HSDM model deals with it as a pure adsorption process in which the rate of uptake is lower than that in the adsorption-reaction combination case (oxic experimental data).

To be able to analyze the effect of temperature on the oxic and anoxic adsorption, D_s values were plotted versus temperature for phenol and o-cresol in Figures 6.49 and 6.50, respectively. From the figures it is clear that for the anoxic case (physical adsorption), D_s for phenol and o-cresol increasing with temperature. For the oxic condition, D_s was highest at 21°C. This might be due to the fact that temperature had two opposite effects on DO. While the increase in temperature reduces oxygen solubility, it

Table 6.3. Apparent Diffusivities of Phenol and o-Cresol Evaluated by the HSDM Model at Various Temperatures and pH of 7.

Compound	Operational Conditions	HSDM (Ds) cm^2/sec	χ^2	$\chi^2_{n,\alpha=0.05}$
o-cresol	oxic, T= 8°C	1.1E-08	0.97	8.05
	anoxic, T= 8°C	4.8E-08	0.247	5.7
o-cresol	oxic, T= 21°C	1.4E-08	0.89	8.05
	anoxic, T= 21°C	8.3E-08	0.036	5.7
o-cresol	oxic, T= 35°C	9.9E-09	0.82	8.05
	anoxic, T= 35°C	8.7E-08	0.0058	5.7
phenol	oxic, T= 8°C	6.7E-09	2.7	8.05
	anoxic, T= 8°C	4.9E-08	0.18	5.7
phenol	oxic, T= 21°C	7.6E-09	2.1	8.05
	anoxic, T= 21°C	6.3E-08	0.054	5.7
phenol	oxic, T= 35°C	2.9E-09	0.28	8.05
	anoxic, T= 35°C	8.8E-08	0.009	5.7

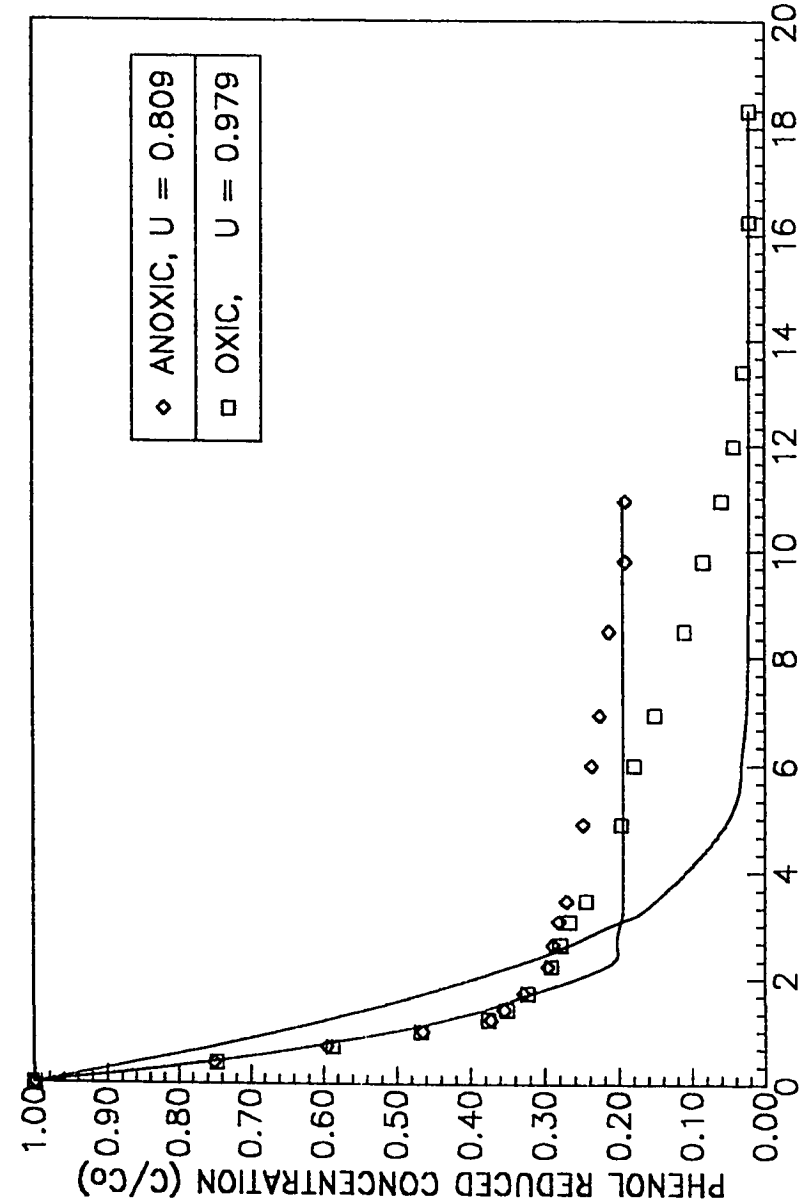

Figure 6.43: Closed Batch Kinetics Experiment for Phenol at T = 8 °C. and pH 7 Along with HSDM Predictions.

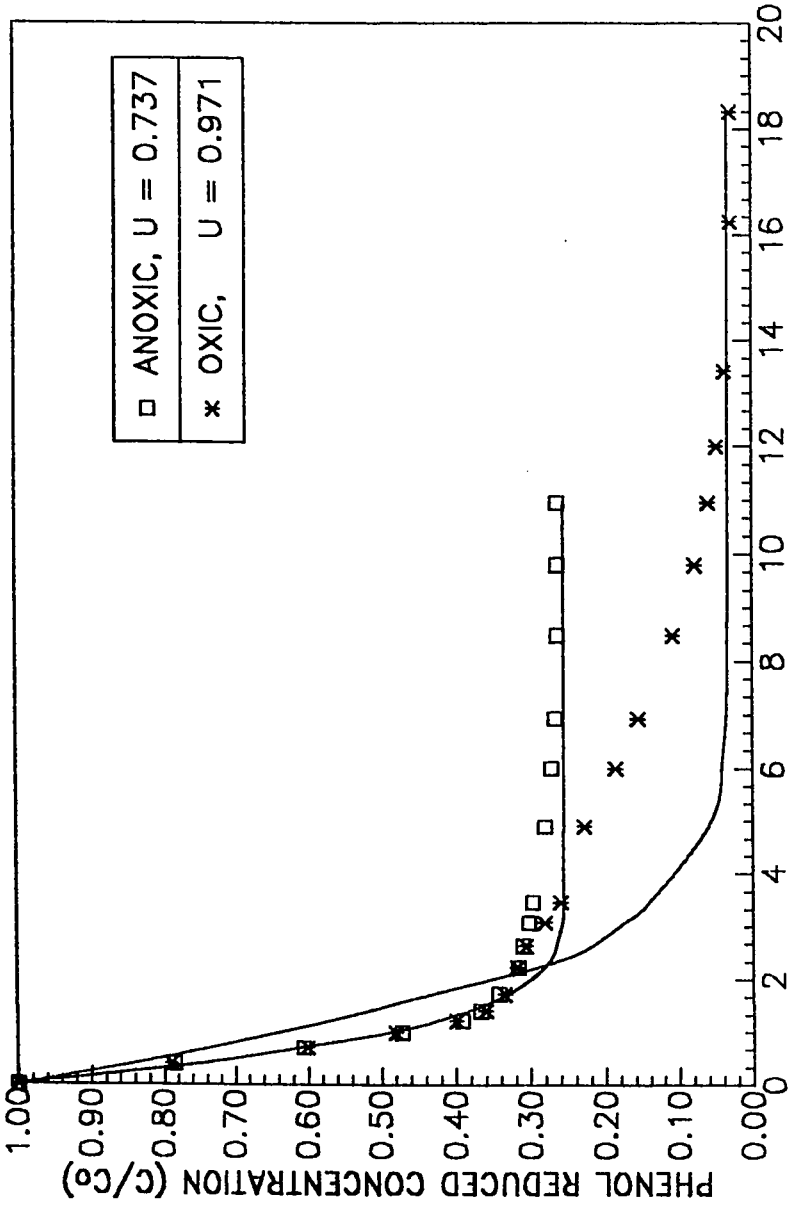

Figure 6.44: Closed Batch Kinetic Experiment for Phenol at at T = 21° C. and pH 7 Along with HSDM Predictions.

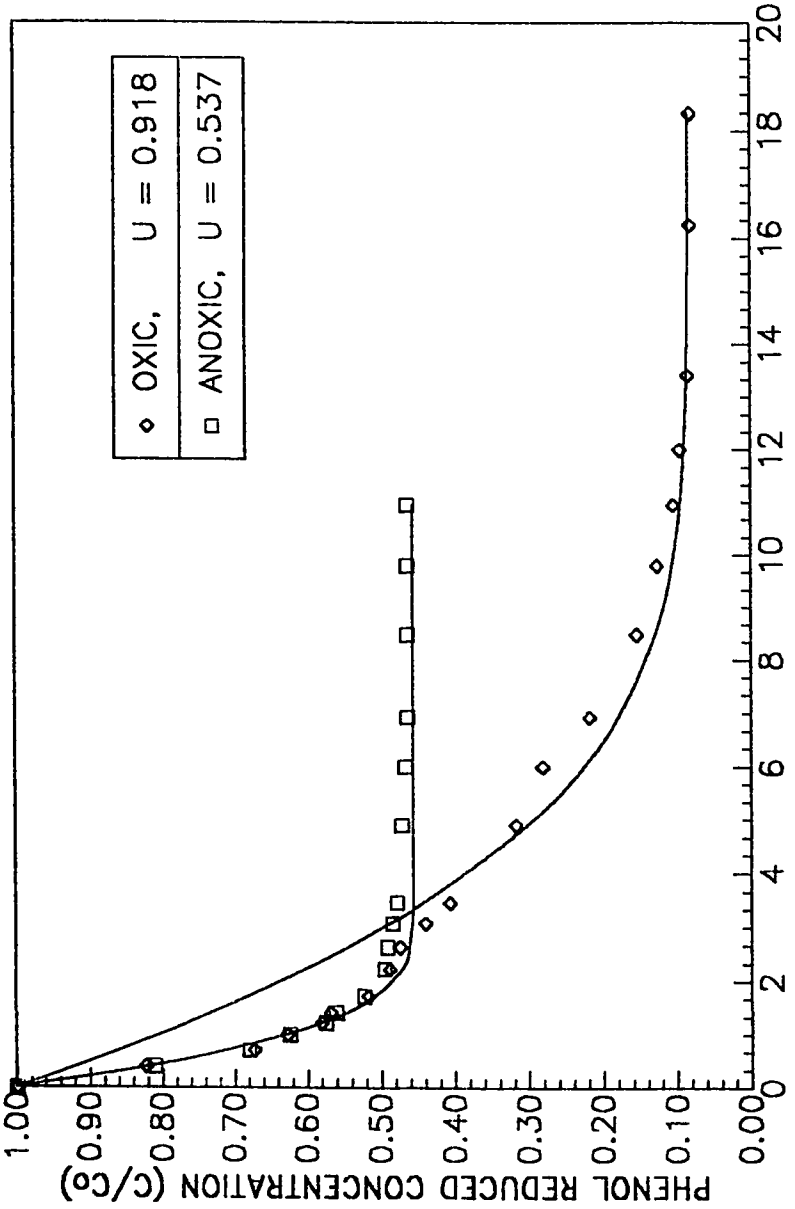

Figure 6.45: Closed Batch Kinetics Experiment for Phenol at T = 35° C. and pH 7 Along with HSDM Prediction.

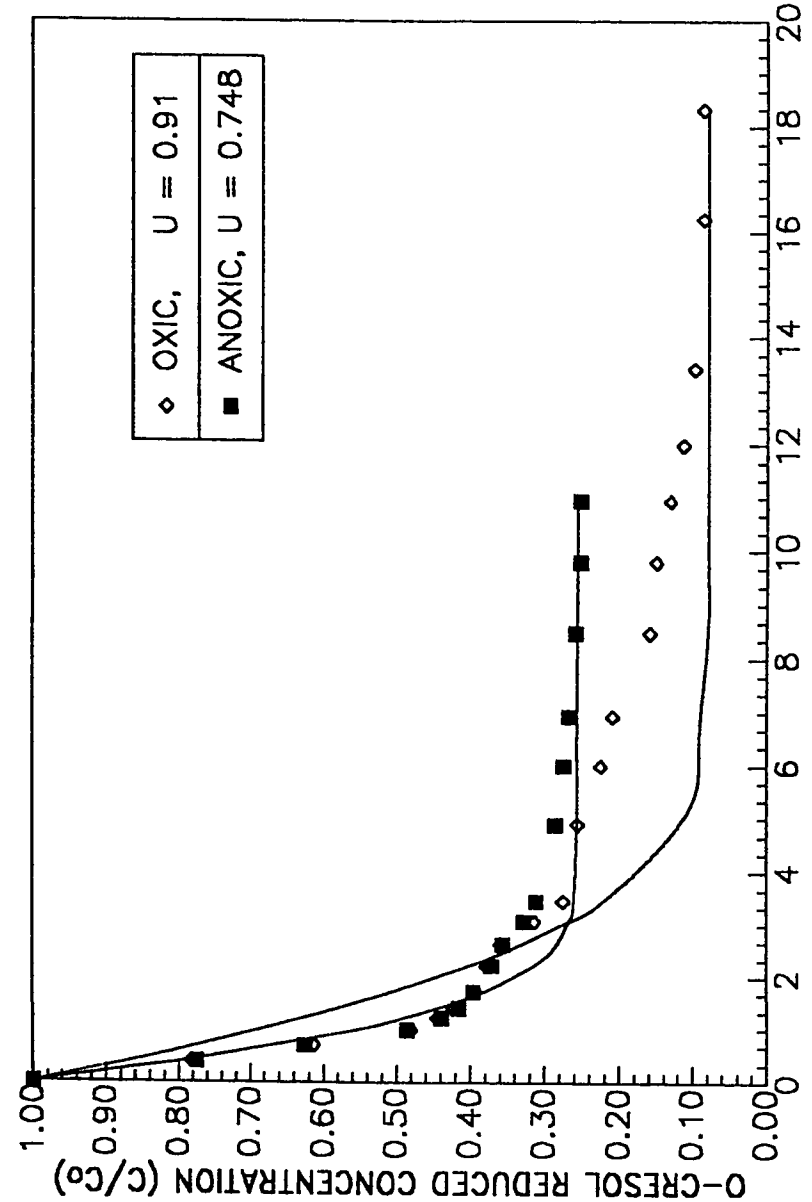

Figure 6.46: Closed Batch Kinetics Experiment for o-Cresol at T= 8° C. and pH 7 Along with HSDM Predictions.

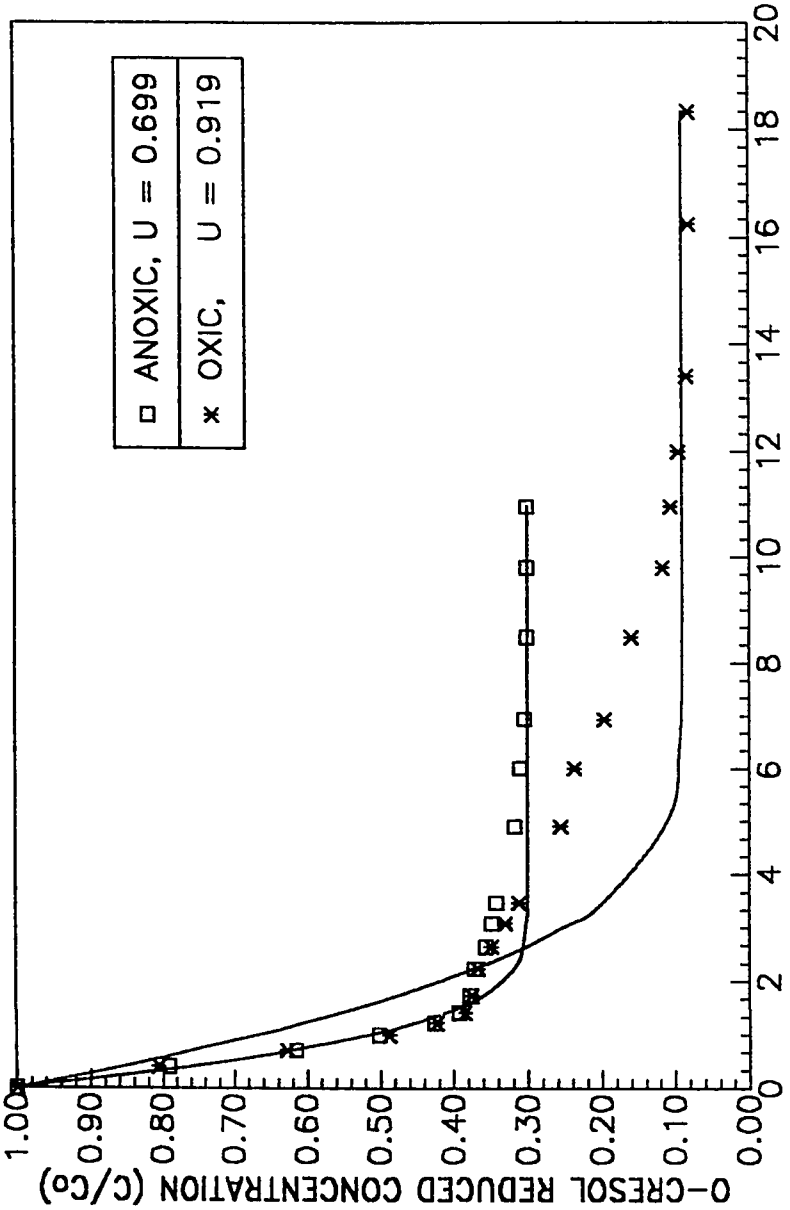

Figure 6.47: Closed Batch Kinetics Experiment for o-Cresol at T = 21° C. and pH 7 Along with HSDM Predictions.

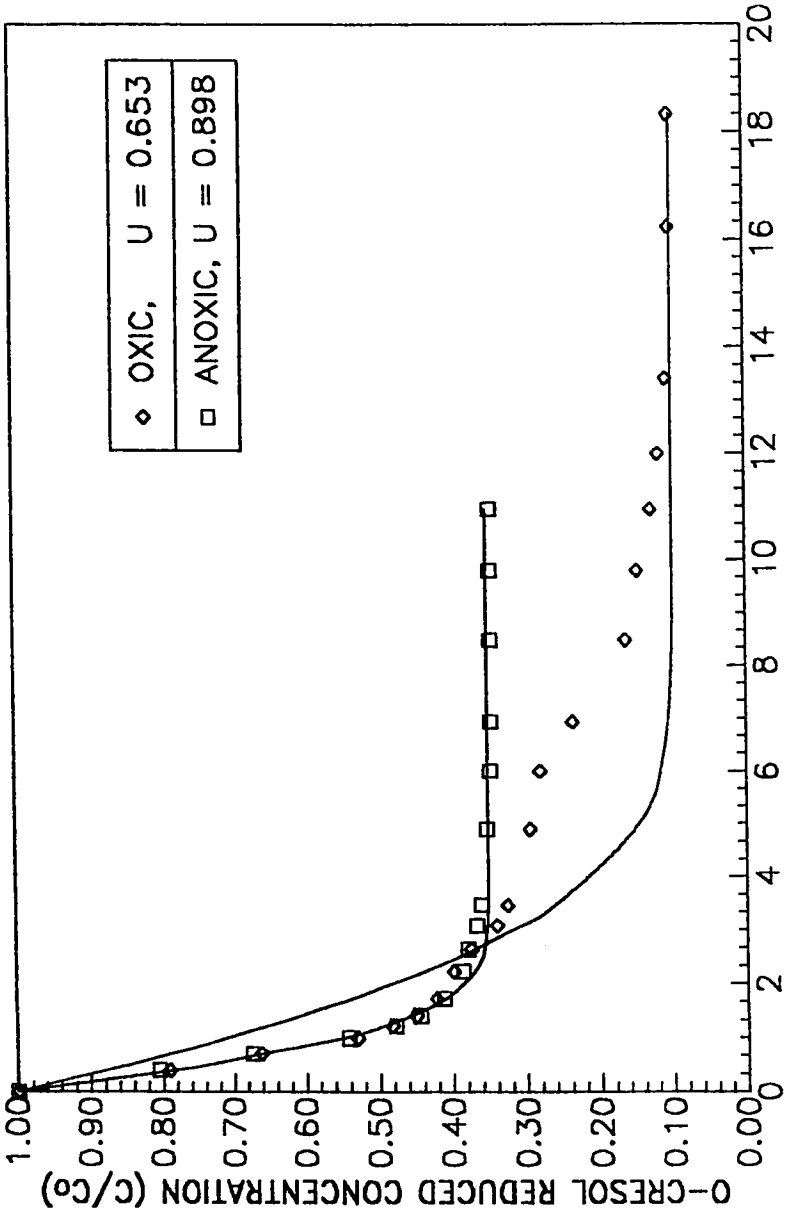

Figure 6.48: Closed Batch Kinetics Experiment for o-Cresol at T = 35° C. and pH 7 Along with HSDM Predictions.

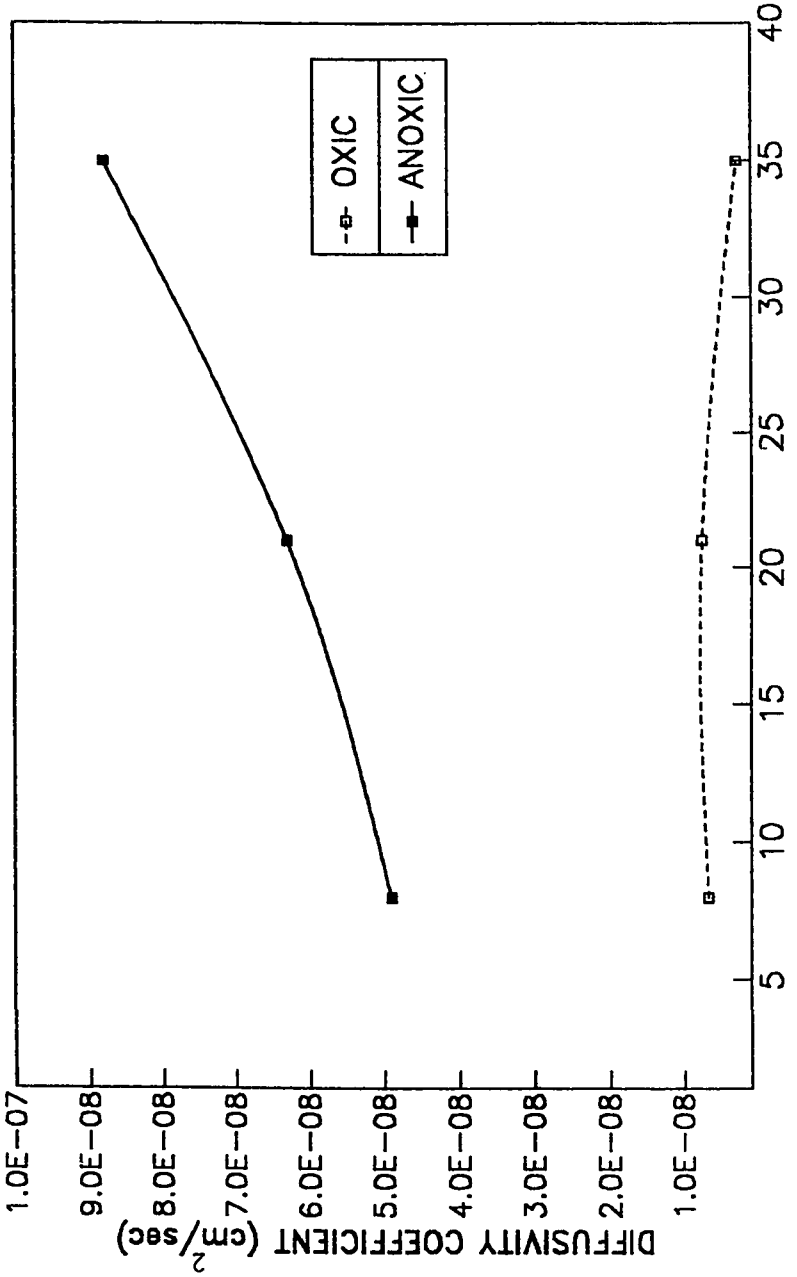

Figure 6.49: Relationship Between Phenol Apparent Diffusivities (HSDM) and Temperature at pH 7.

from PTHS

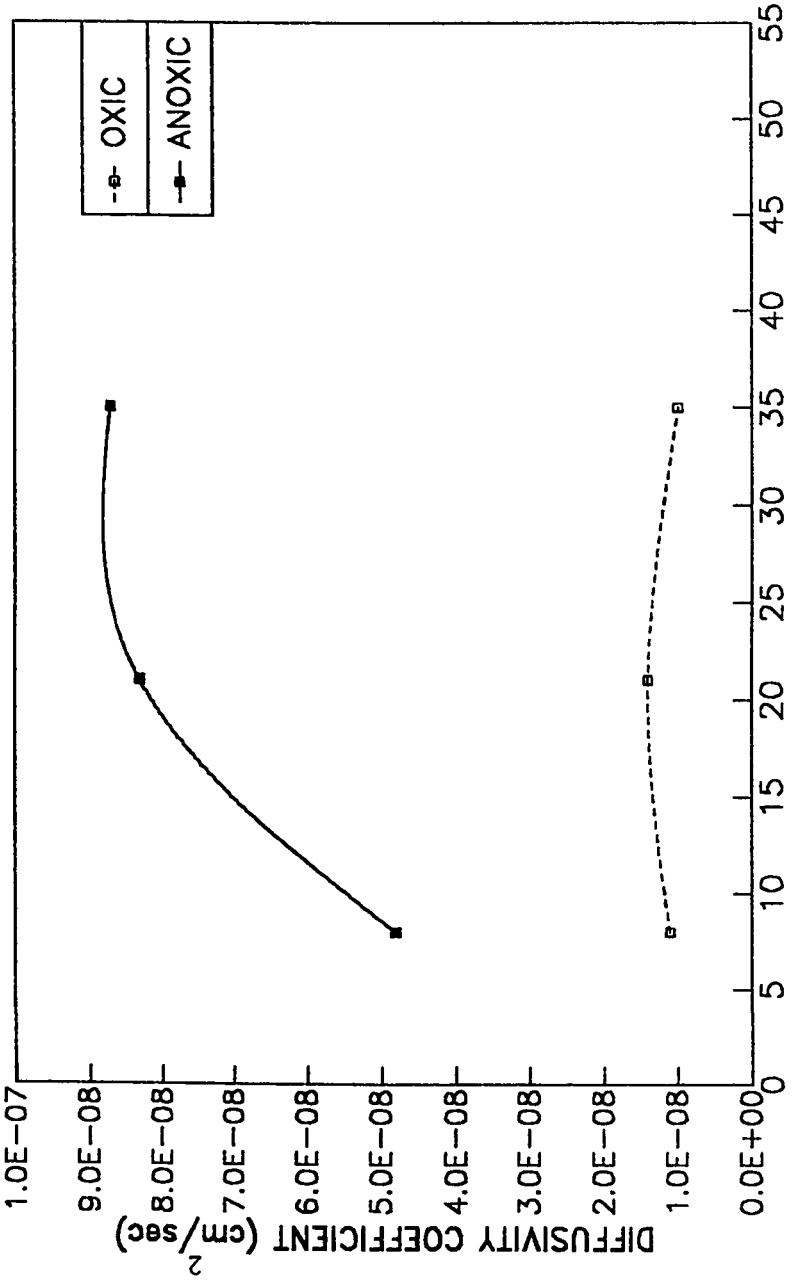

Figure 6.50: Relationship Between o-Cresol Apparent Diffusivities (HSDM) and Temperature at pH 7.

from OTHS

increases its diffusivity. Furthermore, under the oxic condition D_s values were always lower than the anoxic case which is attributed to the delay in the equilibration time resulting from the telomerization reaction on the carbon surface. However, the differences between D_s values in the oxic and anoxic conditions were increase with he temperature implying that the rate of the reaction is increasing with temperature.

In order to determine the activation energy for phenol and o-cresol, the rate equation was used. The equation is:

$$D_s = D_{s0} \exp\frac{-E_a}{R_g T} \tag{6.3}$$

which can linearized as;

$$\text{Log}(D_s) = \text{Log}D_{s0} - \frac{E_a}{2.3\, R_g T} \tag{6.4}$$

where, D_s is the diffusivity coefficient, D_{s0} is the intercept, R_g is the universal gas constant = 8.31 Jol/(mole.k), E_a is the activation energy, and T is temperature in kelvin. Figure 6.51 presents the relation in Equation 6.4 for phenol and o-cresol, from which the intercept k_0 was = -4.48 and -4.05 for phenol and o-cresol, respectively, while, the activation energies were calculated from the slopes and found 15238.7 J/mole and 15355.4 J/ mole for phenol and o-cresol, respectively The close values for E_a in the case of phenol and o-cresol reflects similar responses for the kinetics to temperature variation.

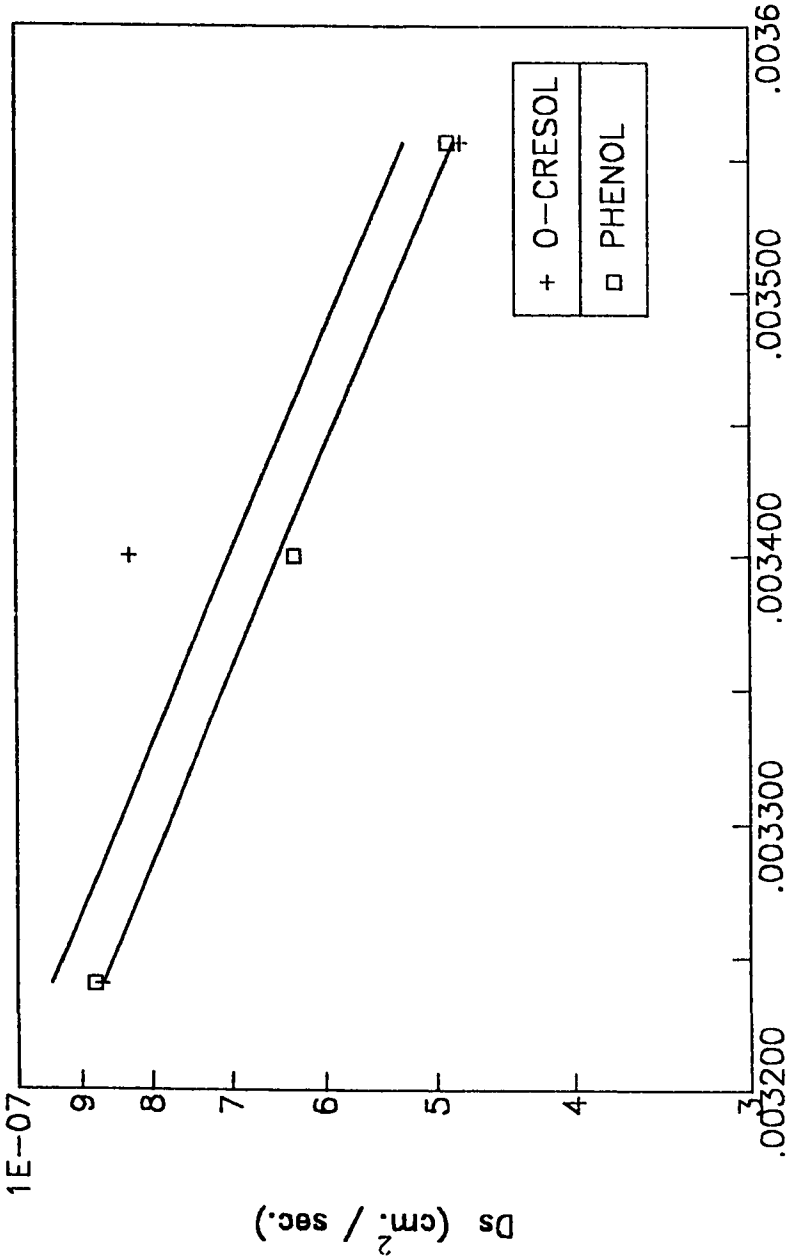

Figure 6.51: Relationship Between Diffusivities and Temperature for Phenol and o-Cresol Along with Lines of Best Fit.

6.3 Model Formulation

The diffusion model considering adsorption only was discussed in section 1.3.2.2 and took the form:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) \qquad (6.5)$$

where;

q = carbon loading, M adsorbate/M adsorbent,

D_s = surface diffusion coefficient, L^2/T,

r = distance from the center of the spherical particle, L, and

t = time, T.

The initial condition (Equation 6.6) assumes the presence of no adsorbate in the particle, while the boundary conditions (Equations 6.7 and 6.8) state that the flux at the center of the particle is always equal to zero because of symmetry, and that the rate of adsorption into the particle is equal to the uptake from the bulk fluid.

$$@\ t = 0, 0 \le r \le r_0: \quad q = 0 \qquad (6.6)$$

$$@\ t \ge 0, r = 0: \quad \frac{\partial q}{\partial r} = 0 \qquad (6.7)$$

$$@\ t \ge 0, r = r_0: \quad 4\pi r_0^2 \int_0^t \left(-D_s \frac{\partial q}{\partial r}\, dt\right) = V_l (C_0 - C) \qquad (6.8)$$

where; V_l is the volume of liquid, r_0 is the radius of the carbon particle, and C_0 and C are the concentrations initially and at any time, respectively.

In order to model the oxygen induced increase in the uptake, which was found to be caused by telomerization reactions on the carbon surface, a reaction term must be added to Equation (6.5). The equation governing the adsorption-reaction combination is:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) - k_r(q - q_\infty) \qquad (6.9)$$

with the same initial and boundary conditions of Equation 6.5

where;

k_r = reaction constant, 1/T, and,

q_∞ = carbon loading at equilibrium, M adsorbate/M adsorbent.

The reaction in the aforementioned equation was assumed to be first order and not limited by oxygen concentration or diffusion.

Defining the dimensionless variables:

$$Q = \frac{q - q_\infty}{q_0 - q_\infty}$$

$$R = \frac{r}{r_0}$$

$$\tau = \frac{D_s t}{r_0^2}$$

$$\frac{\partial Q}{\partial \tau} = \frac{\partial Q}{\partial t}\cdot\frac{\partial t}{\partial \tau} = \frac{\partial Q}{\partial t}\cdot\frac{r_0^2}{D_s}$$

$$\frac{\partial Q}{\partial t} = \frac{\partial Q}{\partial \tau} \cdot \frac{\partial \tau}{\partial t} = \frac{\partial Q}{\partial \tau} \cdot \frac{D_s}{r_0^2}$$

$$\frac{\partial Q}{\partial \tau} \cdot \frac{D_s}{r_0^2} = \frac{D_s}{r_0^2 R^2} \frac{\partial}{\partial R}\left(R^2 \frac{\partial Q}{\partial R}\right) - k_r Q$$

$$\frac{\partial Q}{\partial \tau} = \frac{1}{R^2} \frac{\partial}{\partial R}\left(R^2 \frac{\partial Q}{\partial R}\right) - k_r \left(\frac{r_0^2}{D_s}\right) Q$$

$$\frac{\partial Q}{\partial \tau} = \frac{1}{R^2} \frac{\partial}{\partial R}\left(R^2 \frac{\partial Q}{\partial R}\right) - \varphi^2 Q \qquad (6.10)$$

where, φ^2 is the Thiele modulus. Equation (6.10) is the dimensionless form of Equation (6.9).

where, $\varphi = \sqrt{k_r r_0^2 / D_s}$

$$\varphi^2 = \frac{\text{diffusion time constant}}{\text{reaction time constant}}$$

at $\varphi = 1$, both diffusion and reaction have equal importance,

at $\varphi < 0.1$, reaction mechanism dominates, and

at $\varphi > 10$, diffusion mechanism dominates

The initial condition becomes:

$$@\ \tau = 0, 0 \le R \le 1:\ Q = 0 \qquad (6.11)$$

and the boundary conditions are:

$$@\ \tau \geq 0,\ R = 0 : \frac{\partial Q}{\partial R} = 0 \tag{6.12}$$

$$@\ \tau \geq 0,\ R = 1 : \frac{\partial \overline{Q}}{\partial \tau} = -3\frac{\partial Q}{\partial R} \tag{6.13}$$

where, $\overline{Q} = 3\int_0^1 Q\, R^2\, dR$

The aforementioned boundary condition can be linked to the Freundlich isotherm relation and the batch system by:

$$\int_0^\tau \frac{\partial Q}{\partial R}\, d\tau = -\frac{1}{3}\left(\frac{U}{\alpha - U} + \overline{Q}\right) \tag{6.14}$$

where the total fractional uptake is

$$U = \frac{C_0 - C_\infty}{C_0}$$

and,

$$\alpha = \frac{V_s\, k\, c_0^{n-1}}{V_l}$$

where, V_s and V_l are volume of sorbent and liquid, respectively, and k and n are the Freundlich model constants.

The above differential equations cannot be solved analytically, and a numerical procedure e. g. finite difference or finite element should be used. This is outside the scope of the dissertation, and hence, this effort is recommended for future research.

Chapter 7

EFFECT OF DISSOLVED OXYGEN ON THE BREAKTHROUGH OF PHENOLICS FROM ACTIVATED CARBON

7.1 Introduction

Granular activated carbon (GAC) is an excellent adsorbent for many of the organic contaminants present in water supplies and wastewater discharges. GAC use is frequently considered when concentrations of organic pollutants, particularly, those of the relatively nonbiodegradable type, must be reduced to low levels as a result of the increasingly stringent effluent standards.

Carbon adsorption can be operated on either a batch or continuous-flow basis. In batch processes the carbon and wastewater are mixed together in a suitable reaction vessel until the concentration of the solute has been reduced to the desired level. Most continuous-flow systems are operated as fixed-bed adsorption columns. Continuous-flow operations have advantages over batch-type operations because rates of adsorption in batches depend upon the concentration of adsorbate in solution, and because they are capable of treating large volumes of wastewaters. Fixed-bed adsorbers may be operated in either the upflow or downflow mode. In downflow systems the carbon can serve for adsorption and for filtration of suspended solids; hence, it is used when the

wastewater contains suspended solids. Upflow columns may be operated either as packed or expanded beds. Packed-beds require a high-quality influent to prevent clogging, whereas expanded beds are capable of handling wastewater high in suspended solids. For the purpose of this study the upflow packed bed system was chosen because the adsorbate solutions did not contain any suspended solids.

The design of fixed bed adsorbers involves estimation of the shape of the breakthrough curve (BTC) and the appearance of the breakpoint. A substantial fraction of the time and expense associated with planning and designing adsorption facilities is involved in predicting or forecasting the operational dynamics of the process. The approach involves the conduction of extensive experimental pilot studies to examine the effect of each system variable. Inspite of the long duration and high costs for such pilot studies, sometimes they fail to predict adsorber behavior. This failure is attributable to difference in the operational characteristics between the experimental and full scale adsorbers. The need for pilot scale column studies stemmed from the lack of a rational design basis utilizing the fundamental adsorptive parameters of GAC (i.e equilibrium and kinetics). Discrepancies between the isotherm capacities involved in the design and the actual column capacity were always noticed and attributed to irreversibility of the adsorption process, to a decline in the intraparticle diffusivity during the latter part of the breakthrough curve and to the continuously decreasing adsorbate concentration in the liquid phase during an isotherm experiment. Currently, several mathematical models that utilize relatively inexpensive and much less laborious experimentation have been postulated to facilitate scale-up and reduce the cost of adsorber design. Some of these models that have been widely successful in breakthrough prediction of adsorber columns include the pore diffusion model (PDM) and the homogeneous surface diffusion model (HSDM).

It was shown in the previous chapters that dissolved oxygen DO affects equilibrium and kinetics of phenolics adsorption on GAC. In real application, the system condition with regard to DO content can vary appreciably. While, the application of powdered activated carbon in activated sludge processes can provide oxic conditions, anaerobic GAC contactors will result in complete anoxic conditions. In addition, biological activity in fixed bed adsorbers can lead to exhaustion of some of the DO content resulting in different amounts of DO in the adsorber environment. In this chapter, the effect of DO on the BTC's of phenol and o-cresol from GAC will be investigated, and the validity the homogeneous surface diffusion model (HSDM) will be tested.

7.2 Results and Discussion

7.2.1 Determination of External Mass Transfer Coefficients

For phenol and o-cresol, the surface diffusion coefficients have been determined experimentally using closed batch kinetics. The external mass transfer coefficients k_f must be evaluated using correlations. The following equation (64) was developed for Reynolds numbers between 3 and 1000 ;

$$\frac{2\,k_f\,r}{D_l} = 2 + 1.1\,R^{0.6}\,S^{0.333} \qquad (7.1)$$

where,ch k_f is the liquid-phase mass transfer coefficient, R is Reynolds number, and S is Schmidt number. These dimensionless groups are defined in the following equations:

$$S = \frac{\mu}{\rho_l\,D_l} \qquad (7.2)$$

$$R = \frac{2\,\rho_l\,r\,v}{\mu} \qquad (7.3)$$

where, μ is viscosity of water = 0.00098 kg.s/m, ρ_l is density of water = 997.8 kg/m^3 , r

is mean radius of adsorbent particle = 0.00078 m, v is the superficial velocity = 3.285E-3 m/sec, and D_l is the diffusivity of the adsorbate in water calculated using the Wilke-Chang equation (65) to be 8.792E-10 m^2/sec and 7.808E-10 m^2/sec , for phenol and o-cresol, respectively. The correlation that best matched the experimental column data in a study performed by Crittenden and Weber (34) on phenol was that proposed by Williamson et al. (66) given in

$$\frac{k_f S^{0.58}}{v} = 2.40\ R^{-0.66} \tag{7.4}$$

(Reynolds number range of applicability, 0.08-125)

Here,

$$R = \frac{\rho_l r v}{\varepsilon \mu} \tag{7.5}$$

where, ε is the void ratio =0.39. The correlation presented in Equations 7.1 and 7.4 are denoted henceforth, correlation 1 and correlation 2, respectively. The external mass transfer coefficients for phenol and o-cresol calculated using these correlations are presented in Table 7.1.

7.2.2 Column Studies

Column experiments show that in addition to the effect on the capacity and kinetics of GAC adsorbers, dissolved oxygen tremendously affects column performance. It does not only affect the shape of the BTC but also causes a delay in it, resulting in a completely different BTC. This finding is depicted in Figures 7.1-7.4 for phenol and o-cresol under oxic and anoxic conditions. The anoxic conditions are related to about 0 and 30 mg/l DO, respectively. For mor clarity, the oxic and anoxic behavior are combined together in Figures 7.5 and 7.6, respectively. As shown in the figures, in the

Table 7.1. External Mass Transfer Coefficients for Phenol and o-Cresol for Conditions Used in this Work

Compound	k (Corr. 1) cm^2/sec	k (Corr. 2) cm^2/sec
o-cresol	1.72E-03	3.60E-3
phenol	1.86E-03	3.88E-3

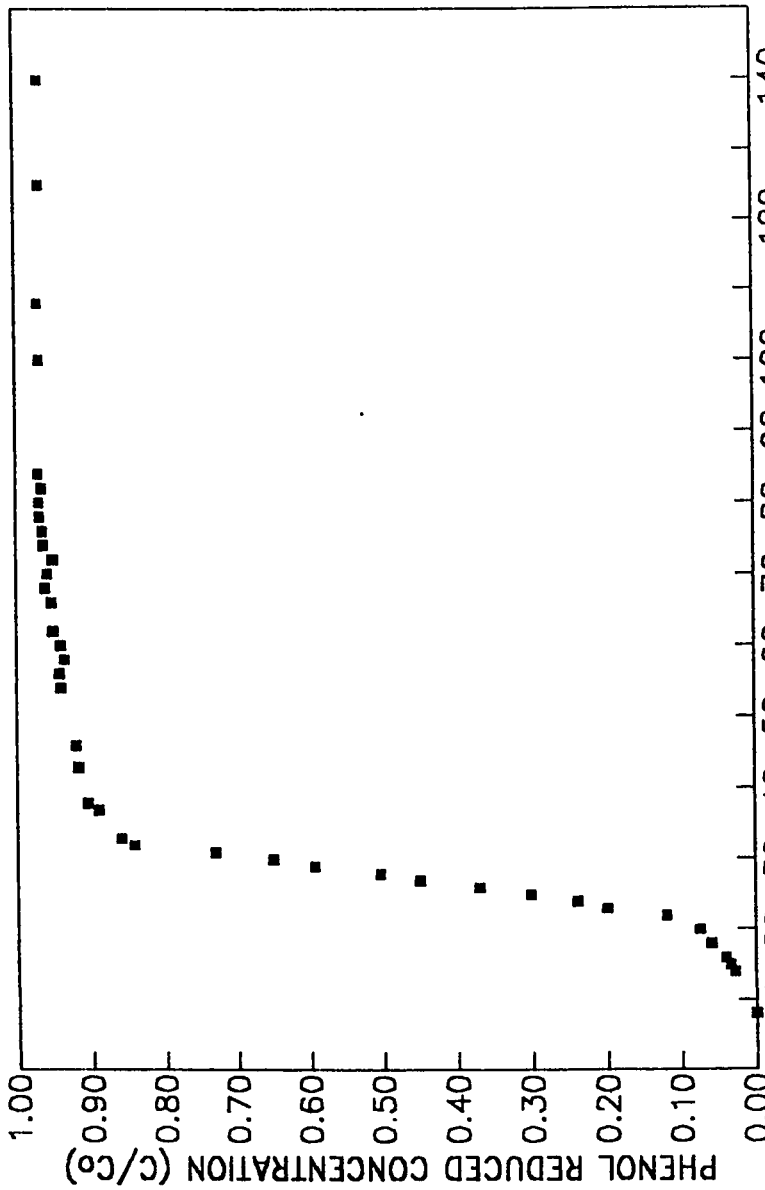

Figure 7.1: Breakthrough of Phenol Under Anoxic Condition at T = 21° C. and pH 7.

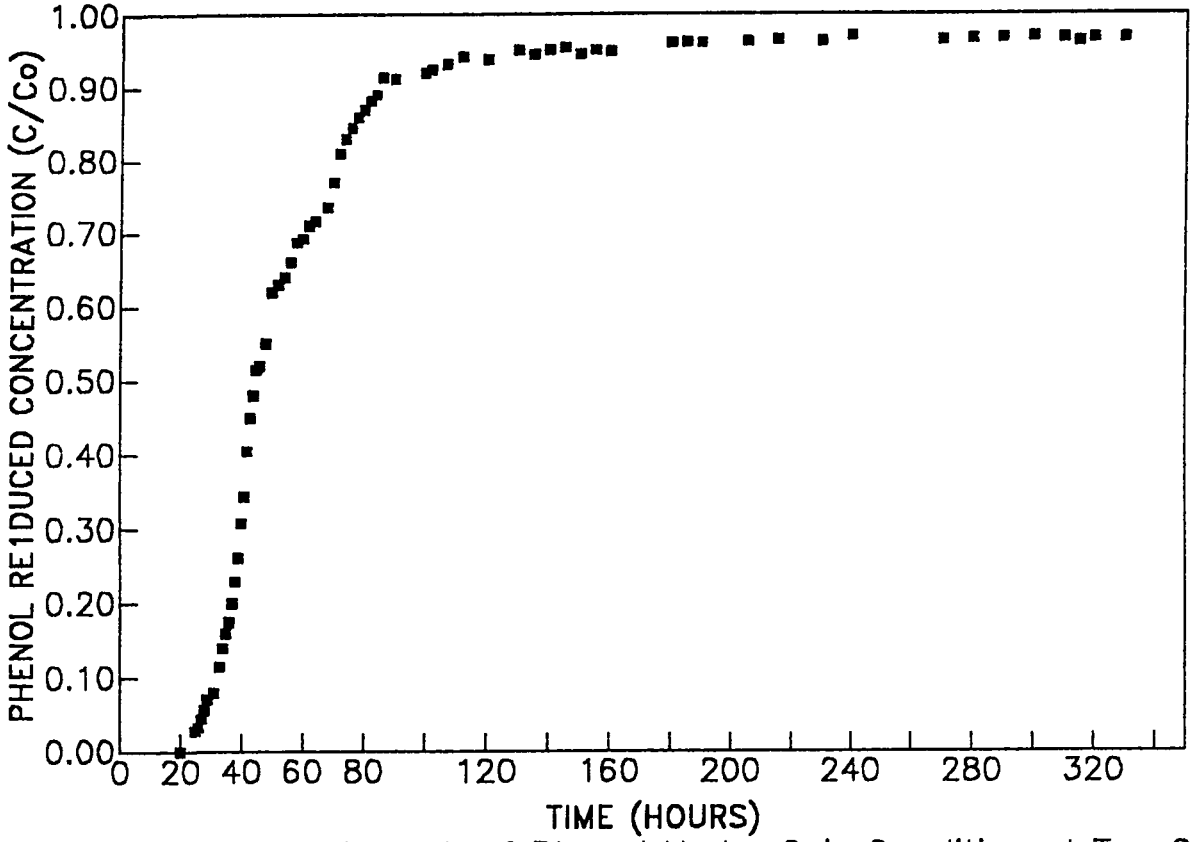

Figure 7.2: Breakthrough of Phenol Under Oxic Condition at T = 21° C. and pH 7.

PCOLO6

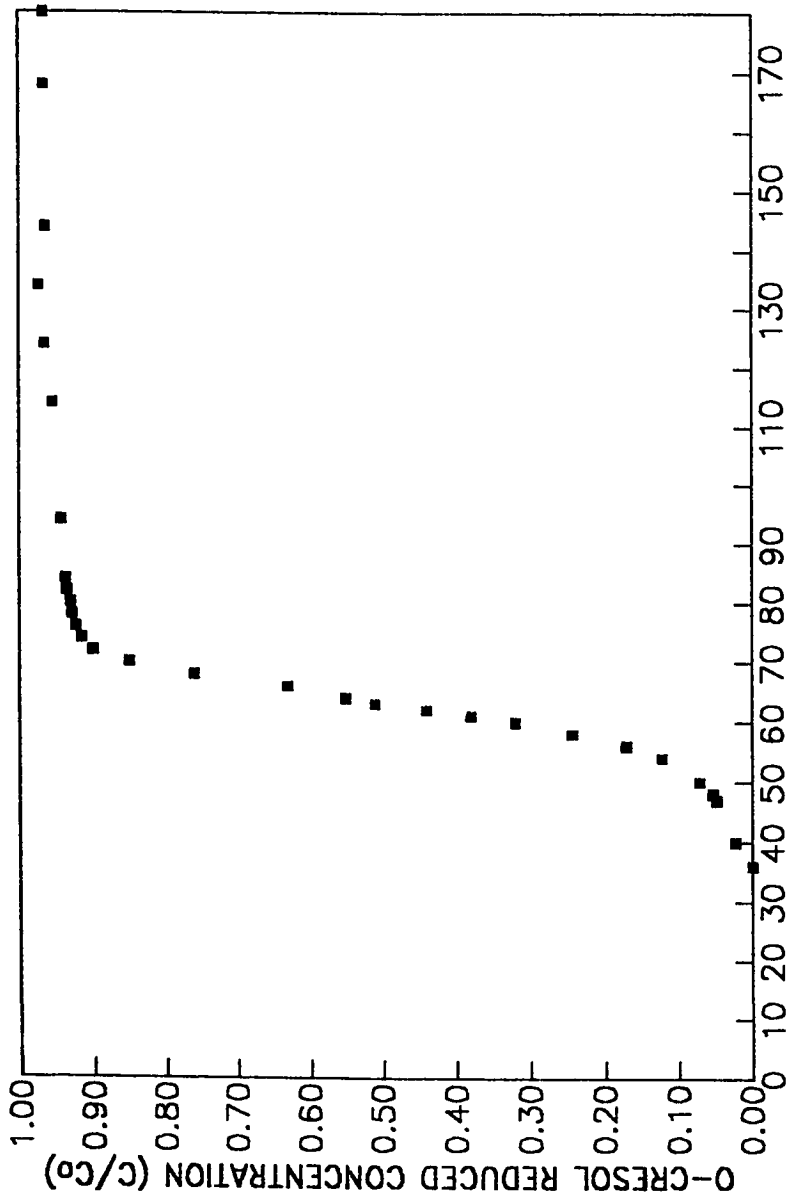

Figure 7.3: Breakthrough of o-Cresol Under Anoxic Condition at T = 21° C. and pH 7.

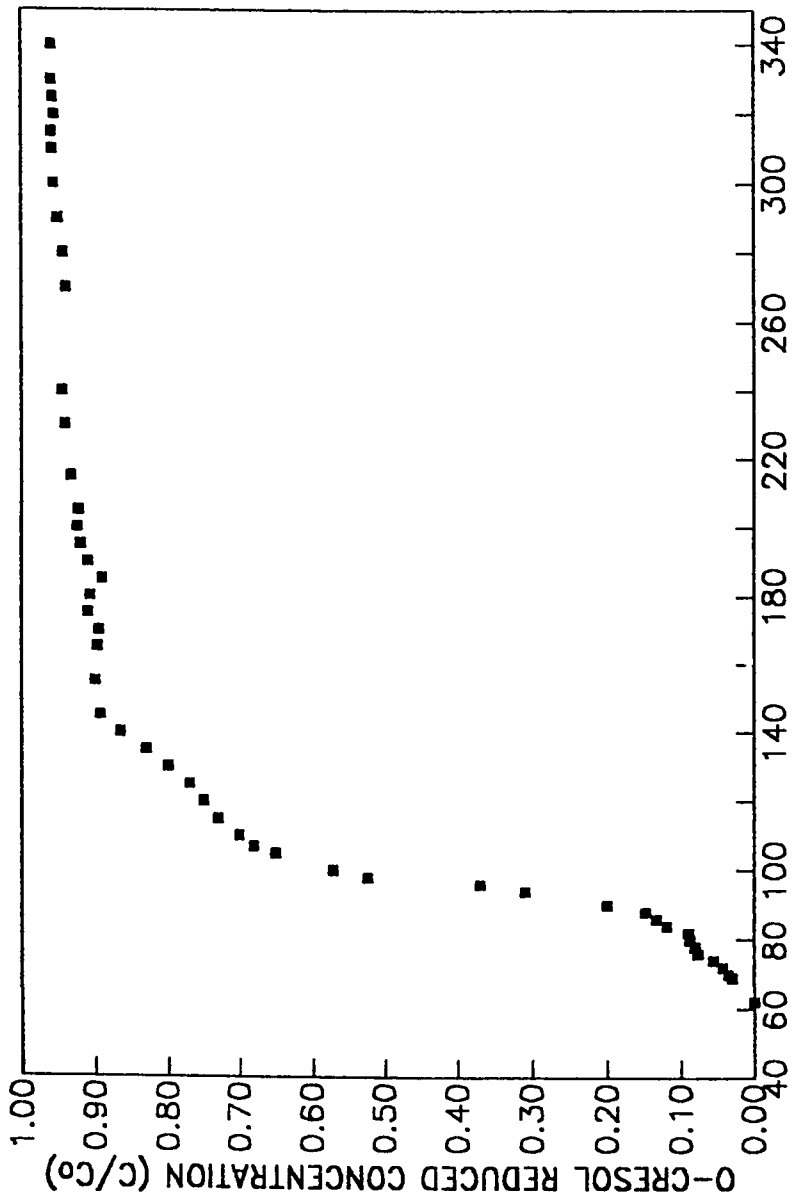

Figure 7.4: Breakthrough of o-Cresol Under Oxic Condition at T = 21° C. and pH 7.

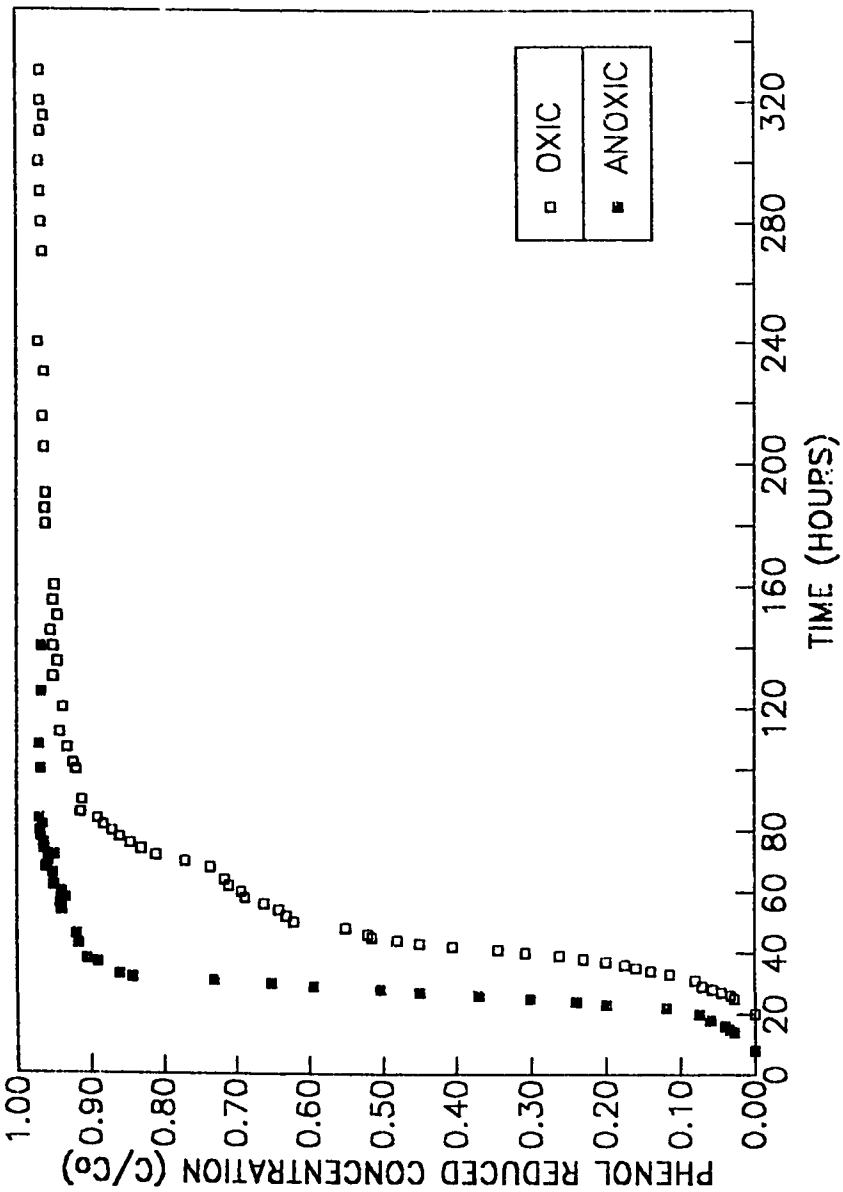

Figure 7.5: Breakthrough Curves for Phenol at T = 21 °C. and pH γ_{COL}

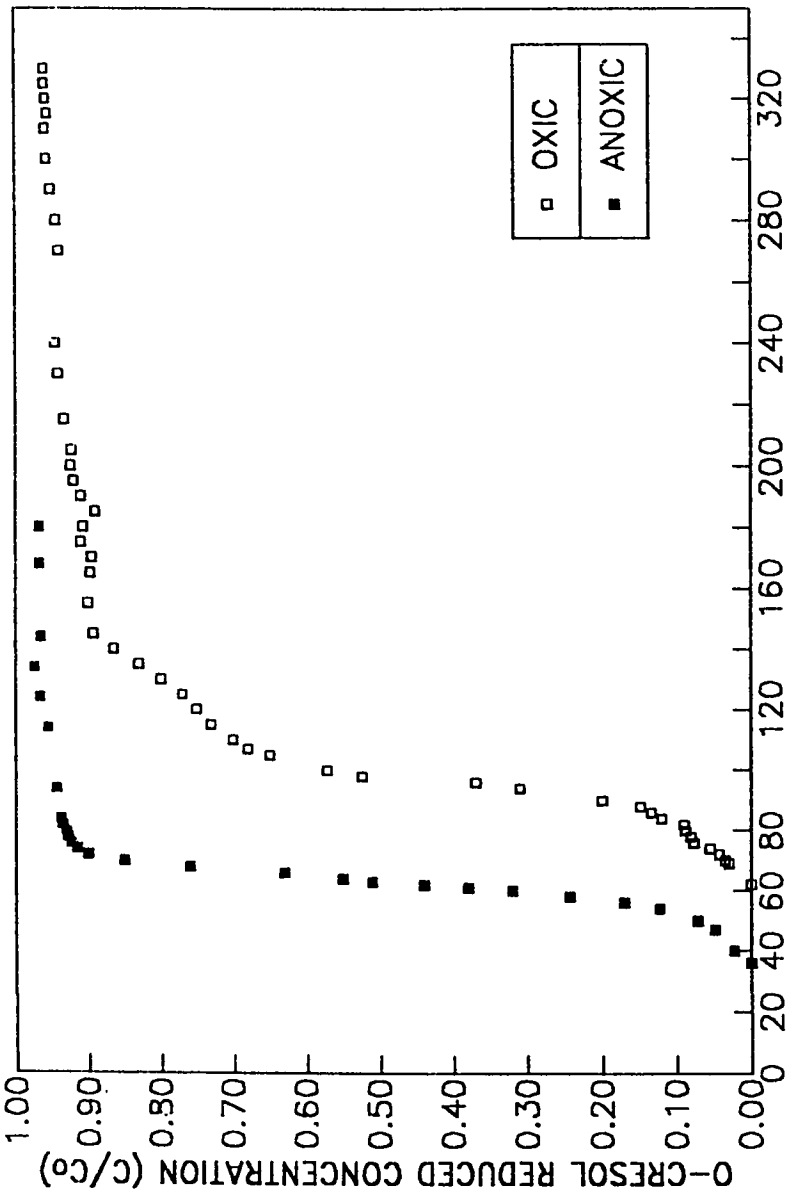

Figure 7.6: Breakthrough Curves for o-Cresol at T = 21° C. and pH_{ZOCOL}

anoxic experiments, the initial breakthrough started after 8 hours and 36 hours for phenol and o-cresol, respectively while for the oxic experiments, the corresponding figures were 20 hours and 62 hours. The 50% breakthrough in the anoxic columns occurred after 28 hours and 65 hours for phenol and o-cresol, respectively while for the oxic experiments, the corresponding figures were 50 hours and 100 hours. Finally, column exhaustion characterized by 95 % breakthrough capacities occurred in the anoxic column experiments after 50 hours and 93 hours for phenol and o-cresol, respectively while for the oxic experiments, the corresponding figures were 130 hours and 215 hours for phenol and o-cresol respectively. These times were measured from the beginning of the experiment and give a very good indication about the tremendous additional capacity available in the column in the case of oxic conditions compared to the anoxic conditions if any particular effluent (phenolic type) standard is to be achieved. The ratio for those times (oxic/anoxic) for phenol and o-cresol were 2.6 and 2.31 for phenol and o-cresol, respectively. The above figures show that the existence of DO in the adsorbate solution not only prolongs the time needed to reach certain breakthrough point or increase the capacity of the adsorber column but also affect the shape of the BTC resulting in a flatter BTC, which again can be attributed to telomerization reactions rather than pure adsorption in which the BTC is usually sharp and little flattening is expected. Flat BTCs of phenolics from GAC column have also been found by other researches (34,58). The above discussion is applicable to serial column operation in which exhaustion is the criteria for their design. However, in order to investigate the effect of DO on the shape of the early part of the BTC's interest should be focused on the time between the start of the BTC to the time needed to reach 50 % breakthrough capacity. For the anoxic conditions this time was 20 hours and 29 hours for phenol and o-cresol, respectively while for the oxic condition the corresponding figures were 30 hours and 38 hours, hence, the ratio for those times (oxic/anoxic) for phenol and

o-cresol were 1.5 and 1.31 for phenol and o-cresol, respectively. The above figures show that the existence of DO in the adsorbate solution affects the shape of the early BTC resulting in a flatter BTC, and delays the initial breakthrough point which is very important in single column operation in which the adsorber column has to meet an effluent criteria which is usually low; accordingly time to reach the initial breakthrough is the design criteria.

In order to compare between the capacities obtained from BTC's and isotherm capacities, the areas above each BTC were calculated and are presented along with the isotherm capacities in Table 7.2. From Table 7.2, and by calculating the ratios of oxic to anoxic capacities at exhaustion and comparing them to the oxic to anoxic exhaustion time ratios for phenol and o-cresol (Figures 7.1 and 7.2) it was found that the ratios of capacities and the those of exhaustion times are not identical as higher time ratios are found. This is an indirect proof that the aforementioned time differences are not merely due to the difference in adsorptive capacities but also to the differences in the adsorption rates as well. This is consistent with the findings of batch kinetic experiments reported in chapter 6 which emphasized that the "apparent" or observed rate of adsorption decreases as a result of telomerization in the presence of DO. It is also depicted from the aforementioned table that the anoxic column capacities were higher than the anoxic isotherm capacities by 7.5 % and 4 % for phenol and o-cresol, respectively. The reason is thought to be due to the DO residual in the anoxic experiments (0.1-0.4) which might have resulted in some telomerization of the phenolics on the GAC surface in the adsorption column. Oxic column capacities for phenol were 4 % lower than that of the isotherm while for o-cresol, they were 7 % higher. In fact, no valid explanation for this is available, but since those differences are very low, they could be due to human errors and material inconsistency. Table 7.3 is similar to the

Table 7.2. Isotherm and Column Capacities at Exhaustion for Phenol and o-Cresol Under Oxic and Anoxic Conditions.

Compound	Operational Conditions	Iso. Cap. mg/g	Col. Cap. mg/g
o-cresol	oxic	330.77	356.67
	anoxic	198.6	207.3
phenol	oxic	179.39	171.90
	anoxic	87.88	94.380

Table 7.3. Isotherm and Column Capacities at 50 % BTC for Phenol and o-Cresol Under Oxic and Anoxic Conditions.

Compound	Operational Conditions	Iso. Cap. mg/g	Col. Cap. mg/g
o-cresol	oxic	330.77	295.5
	anoxic	196.60	193.70
phenol	oxic	179.39	148.8
	anoxic	87.88	84.6

previous table with the exception that the listed capacities are those obtained using a square wave passing through the 50 % breakthrough point. From Table 7.3 it is noted that the for the 50 % capacity the isotherm and column capacities were very close in the anoxic case and the ratios of column capacities to isotherm capacities were 0.963 and 0.975 for phenol and o-cresol, respectively, while for the oxic condition the corresponding figures were 0.89 and 0.83. This shows some deviation from the square wave in the case of oxic conditions compared to the anoxic conditions. This is expected since under oxic conditions, the column behavior is not only affected by physical adsorption but also by the telomerization reactions.

Another characteristic which has been long related to the adsorption of phenolic compounds on activated carbon is the tailing in the BTC (58). The capacity above the tails of phenol oxic and anoxic BTC's were 24.23 mg/g and 7.5 mg/g, respectively while the corresponding figures for o-cresol were 38.84 mg/g and 8.07 mg/g. The start of the tail was characterized by the initial flattening in the BTC generally occurring after 90-94 % breakthrough capacity. This shows that although tailing was found in both oxic and anoxic conditions, the capacities involved are much higher in the oxic experiments compared to the anoxic experiments.

Modeling the BTC's was performed using the plug-flow homogenous surface diffusion model (PFHSDM). Model predictions for the BTCs were obtained using two sets of independently determined adsorption parameters. The input to the model included adsorption equilibria data described by the Freundlich adsorption isotherm equation for both oxic and anoxic conditions, adsorption kinetic parameters such as surface diffusion coefficients determined from the oxic and anoxic batch experiments, and the external mass transfer coefficient determined from correlations, and physical parameters such as the mass of carbon, length of the column, internal diameter of the column,

molecular weight of the solute, no of compounds in solution, density of carbon, flow-rate of feed solution, initial concentration of sorbate solution, and density of solution, as well as some model related variables such as time for calculation of BTC, accuracy needed, and number of collocation points. The output of the model is the prediction of the BTC with time. It is worth mentioning that while the case under study consisted of single solute and constant influent concentration, the available model is capable of predicting multi-solute adsorption with various influent concentrations. Model predictions, using these two sets of parameters (oxic and anoxic), are shown together with the corresponding experimental BTC's in Figures 7.7-7.10 for phenol and o-cresol, respectively. From these figures it is clear that the PFHSDM model gives very good prediction for the oxic and anoxic conditions especially before tailing, provided that the appropriate parameters, especially, apparent diffusivity are used. This good prediction capability was valid for the cases of film transfer coefficients calculated from both correlations with correlation 2 giving better prediction of the initial BTC's in the all of the cases. As a result, it can be concluded that the use of correlation 2 yields film transfer coefficients that predicts the BTC very well, especially the earlier stage. This supports the finding of Crittenden and Weber (34) who found that correlation 2 best matched their experimental data on adsorption of phenolics. The good predictability the PFHSDM model has for oxic and anoxic conditions conflicts with the findings of Vidic and Suidan (58) who found that only the anoxic parameters would predict the early portion of BTC of the adsorption column operating under oxic conditions. The reason for their findings and hence for this conflict is very obvious, since in their work, they used low mass of carbon (50 g) and relatively high initial o-cresol concentration (200 mg/l) resulting in a rapid BTC which started and finished within 12 hours. This where the intrinsic diffusion controls even with telomerization reactions present, hence, the actual BTC was mostly under anoxic conditions, which was best predicted by the

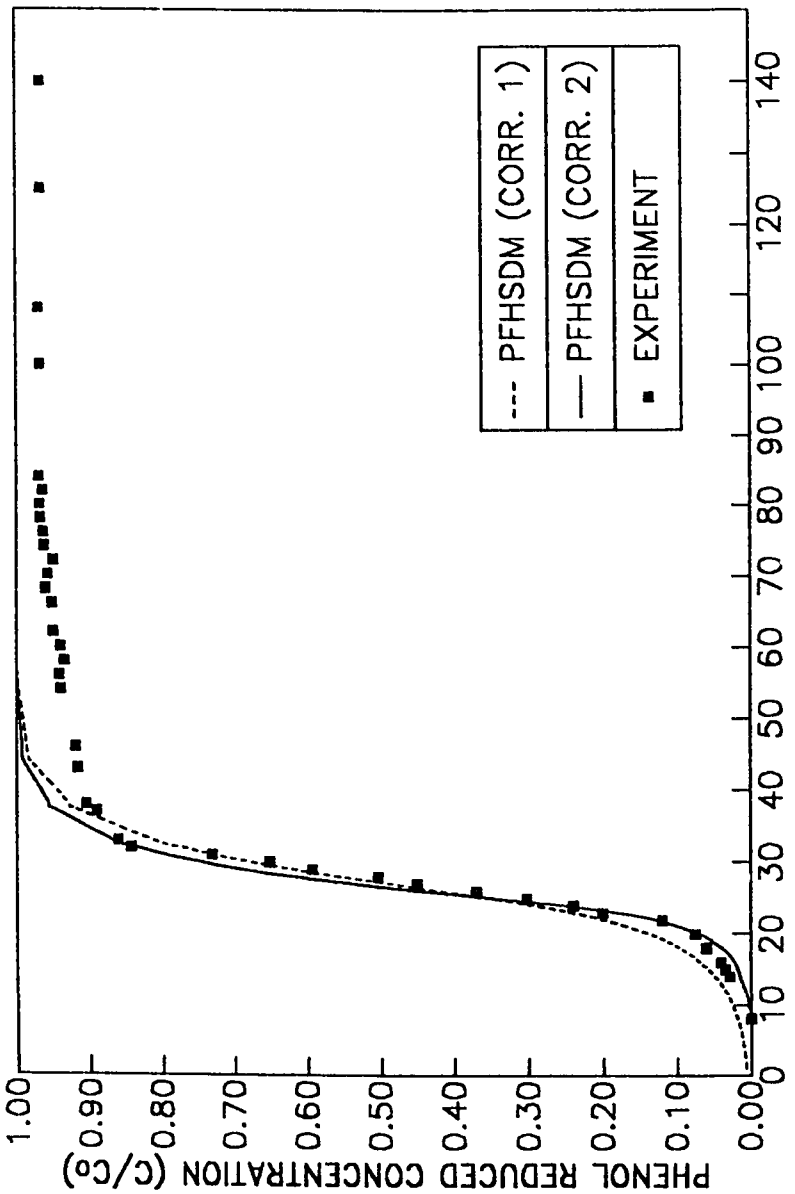

Figure 7.7: Breakthrough of Phenol Under Anoxic Condition at T = 21 °C and pH 7 Along with PFHSDM Predictions.

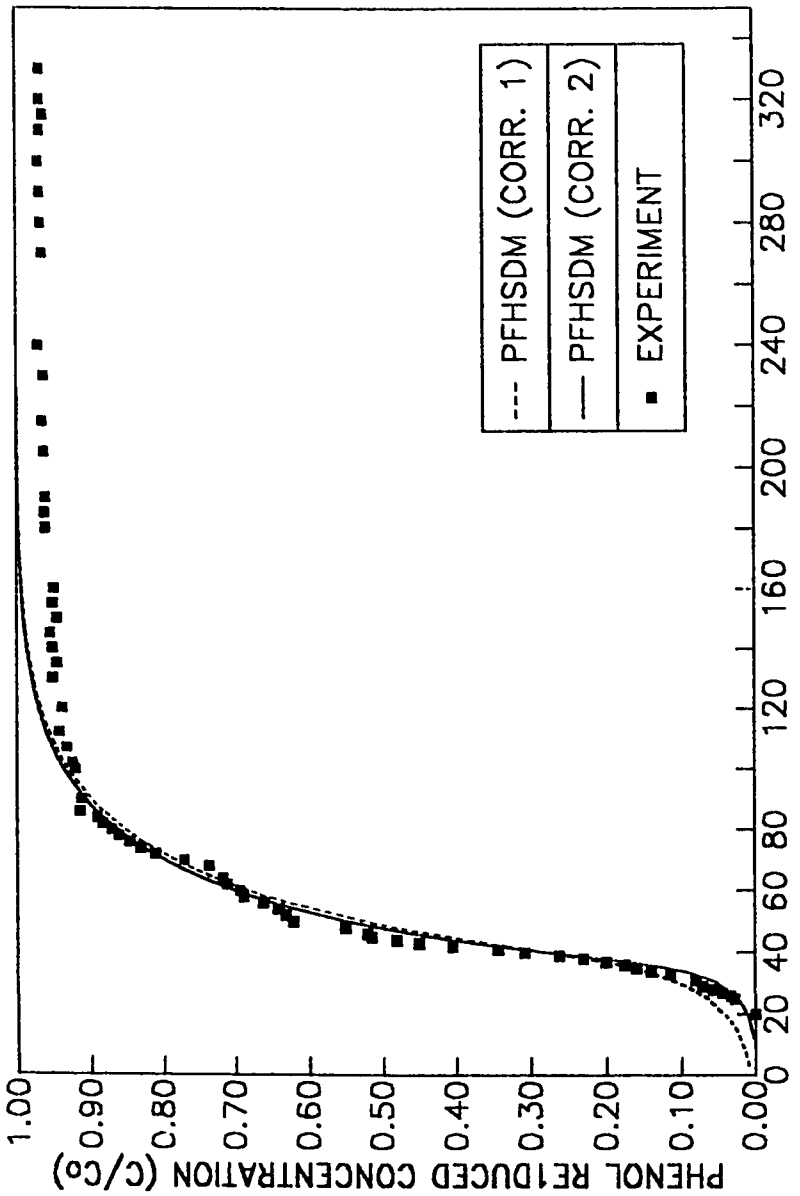

Figure 7.8: Breakthrough of Phenol Under Oxic Condition at T = 21 °C. and pH 7 Along with PFHSDM Predictions.

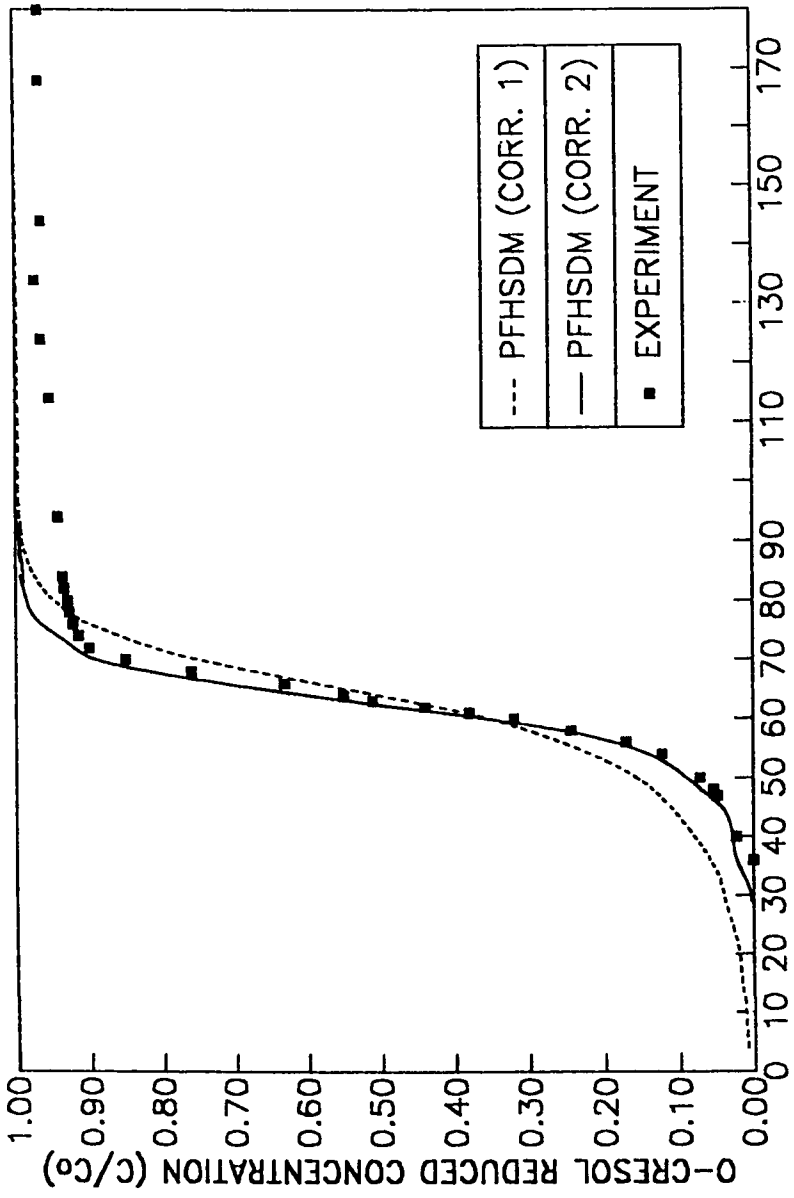

Figure 7.9: Breakthrough of o-Cresol Under Anoxic Condition at T = 21 ^{o} C. and pH 7 Along with PFHSDM Predictions.

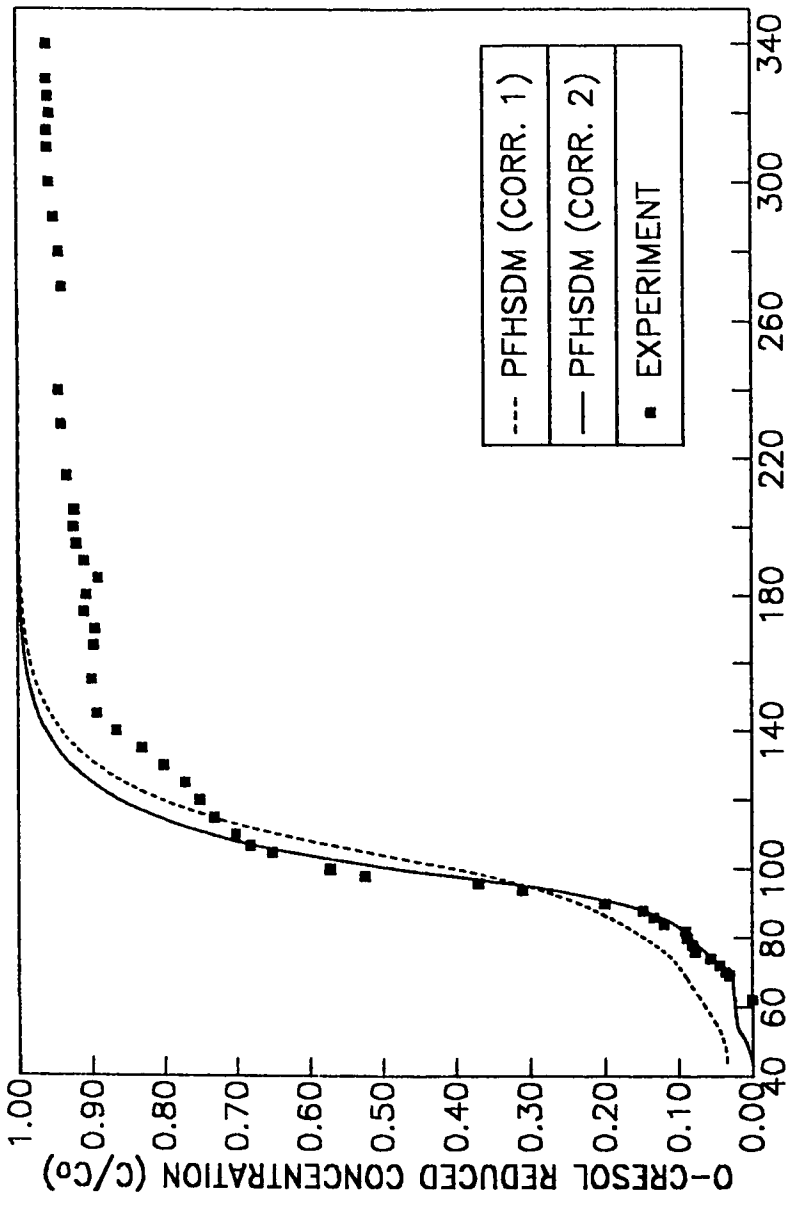

Figure 7.10: Breakthrough of o-Cresol Under Oxic Conditions at T = 21° C. and pH 7 Along with PFHSDM Predictions.

anoxic parameters. However, the oxic condition effects started in the tailing stage resulting in a high portion of the column capacity in the tailing stage. In the case of this study, columns were so designed as to delay BTC's, allowing telomerization reactions to proceed along with physical adsorption right from the beginning of the BTC.

The finding that totally different BTCs as well as different time characteristics are observed under varying levels of DO is extremely important from a practical standpoint. If parallel or short column operation is proposed for design, then the early portion of BTC governs design, while, for series operation or long columns the entire BTC controls the design and number of columns. As has been demonstrated above, the level of DO in the feed wastewater strongly influences both the earlier and later portions of the BTC. Thus, utilizing knowledge of adsorption equilibria and kinetics of diffusion and reaction under ambient DO conditions to design adsorbers so as to prolong adsorber runs sufficiently to permit telomerization, substantially delays times to breakthrough and exhaustion.

Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

1. This study demonstrates that the uptake of GAC for phenolic compounds is strongly influenced by the presence of oxidizing agents in the test environment. The uptakes of GAC for phenol, o-cresol, and nitrophenol at 1 mg/l under oxic conditions were 163%, 114%, and 18% higher than the anoxic oxygen uptake. This oxygen-induced enhancement in the uptake of GAC for phenolics were more pronounced low equilibrium concentrations. At higher loading the GAC retention capacities for phenol, o-cresol, and nitrophenol exhibited 74%, 42%, and a modest of 11% increase over the respective anoxic capacities at 1000 mg/l. The additional uptake attained under oxic conditions was strongly dependent on the anoxic sorption uptake and was limited by the mass of oxygen as well the mass of activated carbon in the test environment. Oxidizing agents such as hydrogen peroxide and potassium permanganate behaved similar to oxygen with respect to enhancing the phenol uptake. On the other hand, this phenomena of increased retention uptake due to the presence of dissolved oxygen in the test environment was not applicable in the case of alphatics. regardless of their chemical and substitutional properties. Testing of actual industrial and domestic wastewater cor-

roborated the influence of dissolved oxygen on the retention uptake of GAC for organics, which was accentuated at low concentrations.

2. Phenol yield efficiencies around 70% were observed for the anoxic isotherm and 23% for the oxic isotherm. Extraction suggest the formation of more strongly adsorbable compounds on the activated carbon surface in the oxic case. Results of the GC-MS analysis of the extracts of the GAC samples used in the oxic and anoxic phenol experiments revealed the presence of significant quantities of two dimers, identified as 2,2-dihydroxy-1,1-biphenyl and 4-phenoxyphenol and a trimer on the GAC used in the oxic isotherm while only traces of the dimer were detected in the anoxic extracts. For o-cresol, the above analysis was performed on the cases of DO levels 1, 3, and 4 (i.e anoxic, "purged with air", and "purged with pure oxygen". It was found that the anoxic extracts contained much higher concentration of o-cresol and trace amounts of the dimers Interestingly, the intensity of the peaks showing dimers and trimer was higher in DO level 4 sample (DO around 30 mg/l) compared to DO level 3 (DO around 9 mg/l). Two reaction mechanisms were proposed for the reaction between oxygen or oxidizing agents with phenol on the carbon surface.

3. The solution pH and temperature appear to strongly influence such chemical reactions. The net effect of pH and temperature on activated carbon adsorption is a combination of their influence on both physical adsorption and chemical reactions. While a pH of 3 was observed to favor physical adsorption, pH of 11 favored oxidation reactions, and the optimal pH for adsorption of phenolics by activated carbon under oxic conditions was pH 7. The anoxic uptake of phenol and o-cresol increased with decreasing temperatures and was highest at the low-

est temperature studied of 8°C. Adsorption enhancement due to telomerization was highest at a temperature of 35°C. Oxic isotherms capacities were found to be relatively independent of temperature thus suggesting that the positive and adverse impact of temperature on chemical reactions and physical adsorption, respectively, tend to balance.

4. The tests performed at different levels of dissolved oxygen have shown uptakes to be a direct function of the DO level. For o-cresol, the percentage enhancement at 1 mg/l residual concentration was 43%, 71%, and 115% of the base anoxic uptake at initial DO concentrations of 4, 9, and 32 mg/l, respectively. The corresponding figures for phenol were 52%, 93%, and 163% of the anoxic uptake at initial DO concentrations of 4, 9, and 32 mg/l, respectively. This enhancement in the sorption uptake of the GAC was attributed to the formation of dimers and trimers, (the magnitude of which increased with the increase in DO), on the carbon surface in the presence of oxygen. Two models were developed relating the oxic uptake with the ratio of initial DO to GAC mass and the anoxic uptakes. The prediction capability of those models for the literature data was high.

5. The batch kinetics studies have shown that the apparent diffusivity coefficient for phenol on GAC is highly influenced by the initial DO concentration. The higher the initial DO content in the sorbate solution the lower the apparent diffusivity coefficient, which was explained in terms of the delay in equilibration time with the increase in the DO content due to telomerization.

6. Equilibration time for physical adsorption increased proportionally with pH and inversely with temperature. For the adsorption-reaction combination the equilibration time occurred in the time range of (7.5-11) days from the beginning of

the experiment, for all pH and temperature variations. D_s values for the oxic cases increased proportionally with temperature and inversely with pH, while the highest difference between oxic and anoxic diffusivities were at pH 7 and temperature 35°C.

A mathematical model which incorporate the reactions due to dissolved oxygen with adsorption was formulated. In that model which is basically a surface diffusion model, the reaction was assumed to be first order and not limited by dissolved oxygen existence.

7. The column experiments have shown that in addition to the effect on the capacity and kinetics of GAC adsorbers, dissolved oxygen tremendously affect column performance. It does not only affect the shape of the breakthrough curve but also causes a delay in the breakthrough curve, resulting in a completely different BTC. The issue of discrepancies between isotherm capacities and column capacities which have long baffled researchers was resolved. Column capacities agree well with the isotherm capacities run at identical environmental conditions.

8. The finding that totally different BTCs as well as different time characteristics are observed under varying levels of DO is extremely important from a practical standpoint. If parallel column operation is proposed for design, then the early portion of BTC governs design, while, for series operation the entire BTC controls the design and number of columns. As has been demonstrated above, the level of DO in the feed wastewater strongly influences both the earlier and later portions of the BTC. Thus, adsorbers can be designed to take advantage of the simultaneous adsorption-reaction phenomenon to substantially delay times to breakthrough and exhaustion.

9. The HSDM was found to have good prediction capability (before tailing) when the appropriate equilibrium and rate parameters are used and when the telomerization reaction starts with adsorption from the start of the BTC.

8.2 Recommendations for Further Research

1. In this study, effects of different DO levels were studied at neutral pH and room temperature while the effect of pH variations was investigated at room temperature and those of temperature was studies at neutral pH. It might be worthy to study the interactions between DO, pH, and temperature under different levels of the three variables.

2. Although, it was concluded from the study that DO existence affects the regeneration efficiency of the carbon, much more work can be done to explore this area.

3. The leachability and toxicity of the polymers formed on the carbon surface can be another point of research

4. The effect of DO existence on other adsorbate-adsorbent system e.g. activated alumina systems

5. Study of other aromatics, especially, large compounds.

APPENDIX A.1

RAW DATA

APPENDIX A.1.1

RAW DATA FOR THE SCREENING STAGE (isotherms)

Type of experiment: isotherm

Name of solute: 4-nitrophenol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 21°C.

Date started: 4/1/1992

Date ended: 18/1/1992

Method of analysis: uv spectrophotometer (318 wavelength)

	initial DO = 31.1 mg/l		initial DO = 0.0 mg/l		
Carbon Mass mg	Abs.	Conc. mg/l	Abs.	Conc. mg/l	
0.0	1.105	984.5 a	1.104	983.0 a	
0.0	1.107	985.0 a	1.108	985.9 a	
200.0	0.618	550.2 a	6.978	621.0 a	
300.0	0.374	332.4 a	4.278	380.7 a	c
400.0	0.227	201.6 b	2.776	247.1 b	
450.0	0.168	149.2 b	1.997	177.7 b	
500.0	1.146	102.0 b	1.573	140.0 b	c
550.0	0.798	71.0 b	1.125	100.1 b	
600.0	0.527	46.9 b	0.794	70.7 b	
650.0	0.339	30.2 b	0.628	55.9 b	c
700.0	0.181	16.1	0.507	45.1 b	
750.0	0.138	12.3	0.375	33.4 b	
800.0	0.118	10.5	0.227	20.2	
850.0	0.073	6.5	0.152	13.5	
1000.0	0.031	2.8	0.096	8.5	

Remarks:

a: 100 dilutions

b: 10 dilutions

c: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: phenol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 21°C.

Date started: 21/1/1992

Date ended: 5/2/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 33.2 mg/l				initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l		Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.159	996.7	a	0.0	1.157	995.5	a
0.0	1.152	990.1	a	0.0	1.153	991.7	a
150.0	7.250	623.5	a	250.0	7.179	617.4	a b
250.0	4.341	373.3	a	350.0	5.829	501.3	a
350.0	2.443	210.1	a	500.0	3.849	331.0	a
500.0	1.113	95.7		600.0	3.143	270.3	a
550.0	0.534	45.9		800.0	2.086	179.4	a
600.0	0.462	39.7		1000.0	1.078	92.7	
650.0	0.314	27.0		1200.0	0.656	56.4	
700.0	0.206	17.7		1400.0	0.306	26.3	b
750.0	0.119	10.2		1600.0	0.183	15.7	
800.0	0.083	7.1		1700.0	0.130	11.2	
850.0	0.058	5.0		1800.0	0.095	8.2	b
900.0	0.048	4.1		2000.0	0.071	6.1	
1100.0	0.037	3.2		2200.0	0.057	4.9	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

- Extraction was performed for two points from each isotherm.

Type of experiment: isotherm

Name of solute: o-cresol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 21°C.

Date started:21/1/1992

Date ended: 5/2/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 31.2 mg/l			initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l	Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.068 a	987.3	0.0	1.073	992.5 a	
0.0	1.075 a	994.5	0.0	1.072	991.6 a	
50.0	0.854 a	789.900	100.0	0.749	692.9 a	
100.0	0.625 a	578.300	150.0	0.565	522.4 a	b
150.0	0.356 a	329.200	250.0	0.347	320.6 a	
200.0	0.216 a	199.500	350.0	0.177	163.7 a	
225.0	0.163 a	151.100	450.0	0.760	70.3 a	
250.0	0.126 a	116.300	550.0	0.339	31.4	b
275.0	0.826	76.400	600.0	0.248	22.9	
300.0	0.520	48.100	650.0	0.111	10.3	
325.0	0.272	25.200	700.0	0.090	8.3	
350.0	0.105	9.700	750.0	0.072	6.7	
400.0	0.071	6.600	800.0	0.064	5.9	b
450.0	0.044	4.100	850.0	0.044	4.1	
500.0	0.029	2.700	1000.0	0.032	3.0	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: chloroform

Initial concentration: 700 mg/l

Volume of solution: 160 ml

pH: 7

Temperature: 21°C.

Date started: 24/1/1992

Date ended: 8/2/1992

Method of analysis: TOC analyzer

	initial DO = 30.1 mg/l		initial DO = 0.0 mg/l		
Carbon Mass mg	TOC mg/l	Conc. mg/l	TOC mg/l	Conc. mg/l	
0.0	61.2	695.2	61.9	703.2	
0.0	61.7	700.9	61.5	698.6	
250.0	42.2	479.0	41.5	471.7	
500.0	31.3	355.4	30.1	341.7	a
900.0	17.1	193.8	18.0	204.5	
1200.0	14.1	160.7	14.9	169.0	a
1700.0	9.3	105.2	8.7	98.6	
2500.0	5.7	65.0	6.0	68.2	
4500.0	2.4	27.4	2.2	25.1	a
10000.0	0.7	7.4	0.8	8.6	

Remarks:

a: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: bromoform

Initial concentration: 1100 mg/l

Volume of solution: 160 ml.

pH: 7

Temperature: 21°C.

Date started: 24/1/1992

Date ended: 8/2/1992

Method of analysis: TOC analyzer

Carbon Mass mg	initial TOC mg/l	initial Conc. mg/l	TOC mg/l	Conc. mg/l	
0.0	56.3	1082.7	57.1	1098.0	
0.0	57.4	1103.8	55.8	1073.6	
100.0	39.8	765.1	39.0	750.3	a
200.0	28.1	539.7	27.3	525.5	
300.0	18.2	350.6	19.8	380.1	a
450.0	11.2	215.0	10.7	205.3	
700.0	5.0	96.2	4.8	92.0	
1000.0	2.8	53.9	3.0	57.5	a
1500.0	0.8	15.5	0.7	13.3	
2500.0	0.5	8.7	0.4	8.2	

Remarks:

a: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: 1,1,1 trichloroethane

Initial concentration: 500 mg/l

Volume of sample: 160 ml.

pH: 7

Temperature: 21°C.

Date started: 9/2/1992

Date ended: 23/2/1992

Method of analysis: TOC analyzer

	initial DO = 29.1 mg/l		initial DO = 0.0 mg/l		
Carbon Mass mg	TOC mg/l	Conc. mg/l	TOC mg/l	Conc. mg/l	
0.0	82.7	489.5	83.4	493.7	
0.0	83.1	491.2	82.3	487.2	
400.0	73.7	436.1	74.4	440.3	a
1250.0	57.7	341.6	56.7	335.5	
2300.0	40.8	241.3	42.9	253.9	
3700.0	24.9	147.6	23.9	141.6	a
4850.0	17.9	105.8	15.6	92.3	
6350.0	12.7	75.4	11.9	70.5	
7350.0	6.5	38.5	6.0	35.3	
14000.0	1.3	7.7	1.6	9.2	a

Remarks:

a: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: 1,1,2,2 tetrachloroethane

Initial concentration: 400 mg/l

Volume of solution: 160 ml.

pH: 7

Temperature: 21°C.

Date started: 9/2/1992

Date ended: 23/2/1992

Method of analysis: TOC analyzer

	initial DO = 33.6 mg/l		initial DO = 0.0 mg/l		
Carbon Mass mg	TOC mg/l	Conc. mg/l	TOC mg/l	Conc. mg/l	
0.0	55.3	400.9	55.5	402.4	
0.0	55.7	403.8	55.9	405.3	
150.0	47.9	347.4	47.1	341.5	a
500.0	33.1	240.3	32.5	235.5	
900.0	19.0	137.8	19.7	142.5	
1150.0	13.6	98.5	14.6	105.7	
1450.0	8.6	62.4	8.3	60.3	a
1800.0	4.4	32.1	4.1	29.7	
2050.0	2.2	15.6	2.4	17.2	a
2500.0	1.3	9.3	1.1	8.1	

Remarks:

a: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: Domestic wastewater

Initial concentration: 41.5 mg/l as TOC

Quantity of sodium thiosulphate (0.025 N) added: 15 mg/l

pH: 7

Temperature: 21°C.

Date started: 15/4/1992

Date ended: 29/4/1992

Method of analysis: TOC analyzer

	initial DO = 6.2 mg/l (normal DO level)		initial DO = 0.0 mg/l		
Carbon Mass mg	TOC reading	TOC mg/l	TOC reading	Conc. mg/l	
0.0	37.5	41.7	37.1	41.2	
0.0	37.0	41.1	36.5	40.5	
20.0	32.5	36.1	28.3	31.5	
40.0	28.1	31.2	24.5	27.2	a
100.0	22.9	25.4	19.6	21.8	
200.0	18.6	20.7	15.4	17.1	
400.0	17.7	19.7	12.2	13.6	a
800.0	13.7	15.2	8.6	9.6	
1600.0	11.6	12.9	6.8	7.6	
3200.0	8.7	9.7	4.9	5.5	a
6400.0	8.1	9.0	5.2	5.8	

Remarks:

a: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: Industrial wastewater (loc. 1)

Initial concentration: 41.5 mg/l as TOC

Quantity of sodium thiosulphate (0.025 N) added: 15 mg/l

Volume of solution: 160 ml

pH: 7

Temperature: 21°C.

Date started: 1/5/1992

Date ended: 15/5/1992

Method of analysis: TOC analyzer

	initial DO = 5.1 mg/l (normal DO level)		initial DO = 0.0 mg/l		
Carbon Mass mg	TOC reading	TOC mg/l	TOC reading	Conc. mg/l	
0.0	647.1	695.8	649.2	698.1	
0.0	648.7	697.5	645.3	693.9	a
200.0	421.3	453.0	513.2	551.8	
500.0	295.8	318.1	379.4	408.0	
1500.0	83.3	89.6	134.5	144.6	a
2500.0	63.1	67.8	87.9	94.5	
3000.0	47.1	50.6	63.2	68.0	
4000.0	27.6	29.7	46.4	49.9	a
6000.0	13.7	14.7	26.6	28.6	
12000.0	3.8	4.1	12.8	13.8	

Remarks:

a: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: Industrial wastewater (loc. 2)

Initial concentration: 41.5 mg/l as TOC

Quantity of sodium thiosulphate (0.025 N) added: 15 mg/l

Volume of solution: 160 ml

pH: 7

Temperature: 21°C.

Date started: 1/5/1992

Date ended: 15/5/1992

Method of analysis: TOC analyzer

	initial DO = 4.9 mg/l (normal DO level)		initial DO = 0.0 mg/l		
Carbon Mass mg	TOC reading	TOC mg/l	TOC reading	Conc. mg/l	
0.0	46.1	49.6	46.4	49.9	
0.0	46.7	50.2	46.0	49.5	a
100.0	33.8	36.3	37.0	39.8	
250.0	24.5	26.3	32.3	34.7	a
400.0	19.6	21.1	30.3	32.6	
1100.0	12.3	13.2	19.5	21.0	
2000.0	4.7	5.1	14.1	15.2	a

Remarks:

a: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: Industrial wastewater (loc. 3)

Initial concentration: 15.75 mg/l as TOC

Quantity of sodium thiosulphate (0.025 N) added: 15 mg/l

Volume of solution: 160 ml

pH: 7

Temperature: 21°C.

Date started: 1/5/1992

Date ended: 15/5/1992

Method of analysis: TOC analyzer

	initial DO = 5.7 mg/l (normal DO level)		initial DO = 0.0 mg/l		
Carbon Mass mg	TOC reading	TOC mg/l	TOC reading	Conc. mg/l	
0.0	14.6	15.7	14.5	15.6	
0.0	14.7	15.8	15.0	16.1	a
100.0	9.8	10.5	11.3	12.1	
200.0	7.9	8.5	9.4	10.1	a
400.0	5.1	5.5	8.3	8.9	
800.0	2.0	2.1	5.6	6.0	a

Remarks:

a: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

APPENDIX A.1.2

RAW DATA FOR THE EFFECT OF VARIABLES (isotherms)

APPENDIX A.1.2.1

RAW DATA FOR THE EFFECT OF PH

Type of experiment: isotherm

Name of solute: phenol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 3

Temperature: 21°C.

Date started: 18/5/1992

Date ended: 2/6/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 30.7 mg/l				initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l		Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.128	996.3	a	0.0	1.125	993.1	a
0.0	1.112	991.1	a	0.0	1.127	995.5	a
150.0	0.763	675.6	a	250.0	0.690	610.4	a b
250.0	0.574	505.7	a	350.0	0.509	450.3	a
350.0	0.373	330.1	a	500.0	0.305	270.0	a
500.0	0.238	210.4	a	600.0	0.240	212.3	a
550.0	0.139	123.2	a	800.0	0.921	81.5	b
600.0	0.855	75.7		1000.0	0.344	30.4	
700.0	0.692	61.2		1400.0	0.141	12.5	
750.0	0.431	38.1		1600.0	0.096	8.5	
900.0	0.200	17.7		2000.0	0.055	4.9	
1100.0	0.120	10.6		2200.0	0.043	3.8	b

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: phenol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 21°C.

Date started: 21/1/1992

Date ended: 5/2/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 33.2 mg/l				initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l		Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.159	996.7	a	0.0	1.157	995.5	a
0.0	1.152	990.1	a	0.0	1.153	991.7	a
150.0	7.250	623.5	a	250.0	7.179	617.4	a b
250.0	4.341	373.3	a	350.0	5.829	501.3	a
350.0	2.443	210.1	a	500.0	3.849	331.0	a
500.0	1.113	95.7		600.0	3.143	270.3	a
550.0	0.534	45.9		800.0	2.086	179.4	a
600.0	0.462	39.7		1000.0	1.078	92.7	
650.0	0.314	27.0		1200.0	0.656	56.4	
700.0	0.206	17.7		1400.0	0.306	26.3	b
750.0	0.119	10.2		1600.0	0.183	15.7	
800.0	0.083	7.1		1700.0	0.130	11.2	
850.0	0.058	5.0		1800.0	0.095	8.2	b
900.0	0.048	4.1		2000.0	0.071	6.1	
1100.0	0.037	3.2		2200.0	0.057	4.9	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

- Extraction was performed for two points from each isotherm.

Type of experiment: isotherm

Name of solute: phenol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 11

Temperature: 21°C.

Date started: 12/5/1992

Date ended: 2/6/1992

Method of analysis: uv spectrophotometer (288 wavelength)

initial DO = 33.2 mg/l				initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l		Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.109	990.5	a	0.0	1.112	993.3	a
0.0	1.115	995.7	a	0.0	1.116	996.5	a
150.0	0.711	635.6	a	250.0	0.772	689.4	a b
250.0	0.325	290.5	a	350.0	0.561	501.3	a
350.0	0.403	360.1	a	500.0	0.489	436.7	a
500.0	0.213	190.2	a	600.0	0.399	356.6	a b
550.0	0.187	167.1	a	800.0	0.237	211.3	a
600.0	1.102	98.4		1000.0	0.138	123.1	a
700.0	0.782	69.8		1400.0	0.916	81.8	
750.0	0.614	54.8		1600.0	0.710	63.4	
900.0	0.449	40.1		2000.0	0.522	46.6	
1100.0	0.337	30.1		2200.0	0.398	35.5	b

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment

Type of experiment: isotherm

Name of solute: o-cresol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 3

Temperature: 21°C.

Date started: 18/5/1992

Date ended: 2/6/1992

Method of analysis: uv spectrophotometer (270 wavelength)

	initial DO = 30.9 mg/l		initial DO = 0.0 mg/l		
Carbon Mass mg	Abs.	Conc. mg/l	Abs.	Conc. mg/l	
0.0	1.058	998.1 a	1.055	994.7 a	
0.0	1.053	992.6 a	1.057	996.6 a	
50.0	0.876	825.8 a	0.808	830.1 a	b
100.0	0.702	662.4 a	0.715	673.9 a	
150.0	0.533	502.4 a	0.555	523.6 a	
250.0	0.260	245.6 a	0.330	311.5 a	
350.0	1.034	97.5	0.166	156.7 a	b
400.0	0.564	53.2	1.050	99.0	
450.0	0.303	28.6	0.707	66.7	
500.0	0.163	15.4	0.343	32.3	
550.0	0.075	7.1	0.182	17.2	b
600.0	0.048	4.5	0.107	10.1	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: o-cresol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 21°C.

Date started:21/1/1992

Date ended: 5/2/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 31.2 mg/l				initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l		Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.068 a	987.3		0.0	1.073	992.5 a	
0.0	1.075 a	994.5		0.0	1.072	991.6 a	
50.0	0.854 a	789.900		100.0	0.749	692.9 a	
100.0	0.625 a	578.300		150.0	0.565	522.4 a	b
150.0	0.356 a	329.200		250.0	0.347	320.6 a	
200.0	0.216 a	199.500		350.0	0.177	163.7 a	
225.0	0.163 a	151.100		450.0	0.760	70.3 a	
250.0	0.126 a	116.300		550.0	0.339	31.4	b
275.0	0.826	76.400		600.0	0.248	22.9	
300.0	0.520	48.100		650.0	0.111	10.3	
325.0	0.272	25.200		700.0	0.090	8.3	
350.0	0.105	9.700		750.0	0.072	6.7	
400.0	0.071	6.600		800.0	0.064	5.9	b
450.0	0.044	4.100		850.0	0.044	4.1	
500.0	0.029	2.700		1000.0	0.032	3.0	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: o-cresol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 11

Temperature: 21°C.

Date started: 18/5/1992

Date ended: 2/6/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 33.2 mg/l				initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l		Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.076	996.8	a	0.0	1.079	999.5	a
0.0	1.083	1002.6	a	0.0	1.075	995.9	a
50.0	0.943	873.4	a	100.0	0.902	835.2	a
150.0	0.700	648.7	a	250.0	0.677	626.7	a b
250.0	0.481	445.6	a	350.0	0.531	491.3	a
350.0	0.326	301.5	a	450.0	0.406	375.7	a
450.0	0.185	171.6	a	650.0	0.213	196.9	a b
550.0	1.111	102.9		750.0	0.143	132.6	a
650.0	0.595	55.1		950.0	0.702	65.0	
750.0	0.355	32.9		1600.0	0.231	21.4	
950.0	0.110	10.2		1800.0	0.120	11.1	
1100.0	0.055	5.100		2200.0	0.066	6.1	b

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

APPENDIX A.1.2.2

RAW DATA FOR THE EFFECT OF TEMPERATURE

Type of experiment: isotherm .

Name of solute: phenol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 8°C.

Date started: 1/9/1992

Date ended: 15/9/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 29.7 mg/l				initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l		Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.097	1004.2	a	0.0	1.094	1001.4	a
0.0	1.090	997.1	a	0.0	1.085	993.7	a
150.0	0.668	611.3	a	250.0	0.654	598.3	a b
250.0	0.427	389.4	a	350.0	0.517	473.4	a
350.0	0.239	218.5	a	500.0	0.335	306.1	a
500.0	0.790	72.3		600.0	0.233	213.4	a
550.0	0.472	43.2		800.0	1.075	98.4	
600.0	0.280	25.6		1000.0	0.419	38.3	b
700.0	0.123	11.3		1400.0	0.116	10.6	
750.0	0.078	7.1		1600.0	0.051	4.7	
900.0	0.030	2.7		2000.0	0.027	2.5	b
1100.0	0.023	2.1		2200.0	0.024	2.2	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: phenol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 21°C.

Date started: 21/1/1992

Date ended: 5/2/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 33.2 mg/l				initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l		Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.159	996.7	a	0.0	1.157	995.5	a
0.0	1.152	990.1	a	0.0	1.153	991.7	a
150.0	7.250	623.5	a	250.0	7.179	617.4	a b
250.0	4.341	373.3	a	350.0	5.829	501.3	a
350.0	2.443	210.1	a	500.0	3.849	331.0	a
500.0	1.113	95.7		600.0	3.143	270.3	a
550.0	0.534	45.9		800.0	2.086	179.4	a
600.0	0.462	39.7		1000.0	1.078	92.7	
650.0	0.314	27.0		1200.0	0.656	56.4	
700.0	0.206	17.7		1400.0	0.306	26.3	b
750.0	0.119	10.2		1600.0	0.183	15.7	
800.0	0.083	7.1		1700.0	0.130	11.2	
850.0	0.058	5.0		1800.0	0.095	8.2	b
900.0	0.048	4.1		2000.0	0.071	6.1	
1100.0	0.037	3.2		2200.0	0.057	4.9	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: phenol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 35°C.

Date started:15/6/1992

Date ended: 29/6/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 30.7 mg/l				initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l		Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.106	996.9	a	0.0	1.105	995.7	a
0.0	1.112	1002.5	a	0.0	1.127	1000.5	a
150.0	0.761	685.3	a	250.0	0.770	693.5	a b
250.0	0.559	503.7	a	350.0	0.636	572.6	a
350.0	0.405	364.7	a	500.0	0.495	446.3	a
500.0	0.208	187.1	a	600.0	0.401	361.3	a
550.0	0.166	149.6	a	800.0	0.270	243.1	a b
600.0	1.303	117.4		1000.0	0.175	157.2	a
700.0	0.759	68.4		1400.0	1.032	93.0	
750.0	0.569	51.3		1600.0	0.402	36.2	
900.0	0.284	25.6		2000.0	0.202	18.2	b
1100.0	0.109	9.8		2200.0	0.102	9.2	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: o-cresol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 8°C.

Date started: 1/9/1992

Date ended: 15/9/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 30.7 mg/l				initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l		Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.029	998.3	a	0.0	1.032	1002.2	a
0.0	1.026	995.2	a	0.0	1.027	996.5	a
50.0	7.872	763.6	a	100.0	0.706	685.3	a b
100.0	5.774	560.1	a	150.0	0.553	536.3	a
150.0	3.829	371.4	a	200.0	0.424	411.2	a
200.0	2.195	212.9	a	300.0	1.231	119.4	a
250.0	1.070	103.4		400.0	0.877	85.1	b
275.0	0.696	67.5		500.0	0.375	36.4	
300.0	0.440	42.7		600.0	0.126	12.2	
350.0	0.169	16.4		700.0	0.057	5.5	
400.0	0.057	5.5		800.0	0.027	2.6	
450.0	0.026	2.5		900.0	0.021	2.0	b

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: o-cresol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 21°C.

Date started:21/1/1992

Date ended: 5/2/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 31.2 mg/l			initial DO = 0.0 mg/l			
Carbon Mass mg	Abs.	Conc. mg/l	Carbon Mass mg	Abs.	Conc. mg/l	
0.0	1.068 a	987.3	0.0	1.073	992.5 a	
0.0	1.075 a	994.5	0.0	1.072	991.6 a	
50.0	0.854 a	789.9	100.0	0.749	692.9 a	
100.0	0.625 a	578.3	150.0	0.565	522.4 a	b
150.0	0.356 a	329.2	250.0	0.347	320.6 a	
200.0	0.216 a	199.5	350.0	0.177	163.7 a	
225.0	0.163 a	151.1	450.0	0.760	70.3 a	
250.0	0.126 a	116.3	550.0	0.339	31.4	b
275.0	0.826	76.4	600.0	0.248	22.9	
300.0	0.520	48.1	650.0	0.111	10.3	
325.0	0.272	25.2	700.0	0.090	8.3	
350.0	0.105	9.7	750.0	0.072	6.7	
400.0	0.071	6.6	800.0	0.064	5.9	b
450.0	0.044	4.1	850.0	0.044	4.1	
500.0	0.029	2.7	1000.0	0.032	3.0	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: o-cresol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 35°C.

Date started:17/5/1992

Date ended: 1/6/1992

Method of analysis: uv spectrophotometer (270 wavelength)

initial DO = 30.2 mg/l			initial DO = 0.0 mg/l		
Carbon Mass mg	Abs.	Conc. mg/l	Carbon Mass mg	Abs.	Conc. mg/l
0.0	1.032	995.7 a	0.0	1.033	995.9 a
0.0	1.036	999.1 a	0.0	1.040	1002.1 a b
50.0	8.015	772.6 a	100.0	7.472	720.3 a
100.0	5.872	566.1 a	150.0	6.194	597.1 a
150.0	3.905	376.4 a	200.0	5.013	483.3 a
200.0	2.511	242.1 a	300.0	3.047	293.7 a b
250.0	1.254	120.9 a	400.0	1.616	155.8 a
300.0	0.564	54.4	500.0	0.822	79.2
350.0	0.245	23.6	600.0	0.433	41.7
400.0	0.106	10.2	700.0	0.238	22.9 b
450.0	0.051	4.9	800.0	0.120	11.6

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

APPENDIX A.1.2.3

RAW DATA FOR THE DIFFERENT LEVELS OF OXYGEN

Type of experiment: isotherm

Name of solute: phenol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 21°C.

Date started:15/8/1992

Date ended: 29/9/1992

Method of analysis: uv spectrophotometer (270 wavelength)

no initial oxygen			initial oxygen exists							
	0.0 mg/l			3.8 mg/l		8.9 mg/l		31.4 mg/l		
carbon mg.	Abs.	Conc. mg/l	Carbon mg.	Abs.	Conc. mg/l	Abs.	Conc.	Abs	Conc. mg/l	
0	1.116	997.4a	0	1.137	994.4a	1.138	995.7a	1.154	992.3	a
0	1.115	991.2a	0	1.135	992.8a	1.137	995.1a	1.157	994.7	a
250	.718	617.7a	150	.683	597.1a	.740	647.2a	.725	623.5	a
350	.683	501.3a	250	.455	398.5a	.379	331.5a	.434	373.3	a
500	.385	331.0a	350	.256	224.3a	.271	237.5a	.244	210.1	a
600	.314	270.3a	500	.928	81.2	1.001	87.6	1.113	95.7	
800	.209	179.4a	550	.682	59.7	.783	68.5	.534	45.9	
1000	1.07	92.7	600	.350	30.6	.519	45.4	.462	39.7	
1200	0.65	56.4	650	.393	34.4	.270	23.6	.314	27.0	
1400	0.30	26.3	700	.174	15.2	.248	21.7	.206	17.7	
1600	0.18	15.7 b	750	.141	12.3 b	.093	8.1 b	.119	10.3	b
1700	0.13	11.2	800	.078	6.8	.069	6.0	.083	7.1	
1800	0.09	8.2	850	.059	5.2	.067	5.9	.058	5.0	
2000	0.07	6.1 b	900	.056	4.9 b	.050	4.4 b	.048	4.1	b
2200	0.05	4.9	1100	.046	4.0	.045	3.9	.037	3.2	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

Type of experiment: isotherm

Name of solute: o-cresol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 21°C.

Date started 30/9/1992

Date ended: 13/9/1992

Method of analysis: uv spectrophotometer (270 wavelength)

no initial oxygen			initial oxygen exists							
	0.0 mg/l			3.8 mg/l		8.9 mg/l		31.4 mg/l		
carbon mg.	Abs.	Conc. mg/l	Carbon mg.	Abs.	Conc. mg/l	Abs.	Conc.	Abs.	Conc. mg/l	
0	1.157	994.6a	0	1.133	991.6a	1.133a	991.6	1.155	993.4a	
0	1.155	993.4a	0	1.134	992.7a	1.135a	992.8	1.152	990.0a	
100	.806	692.9a	50	.871	762.5a	.913a	799.3	.919	789.9a	
150	.607	522.4a	100	.678	593.1a	.634a	554.6	.674	578.3a	
250	.373	320.6a	150	.405	354.5a	.356a	311.2	.383	329.2a	
350	.190	163.7a	200	.200	174.9a	.249a	217.6	.232	199.5a	
450	.817	70.3	225	.186	162.4a	.152a	133.4	.176	151.1a	
550	.365	31.4	250	1.158	101.3	.148a	129.6	.135	116.3a	
600	.266	22.9	275	.921	80.6	.751	65.9	.88	76.4	
650	.120	10.3 b	300	.511	44.7 b	.606	53.0 b	.55	48.1 b	
700	.097	8.3	325	.195	17.1	.317	27.7	.29	25.2	
750	.078	6.7	350	.125	10.9	.094	8.2	.11	9.7	
800	.069	5.9 b	400	.087	7.6 b	.066	5.8 b	.07	6.6 b	
850	.048	4.1	450	.051	4.5	.055	4.8	.04	4.1	
1000	.035	3.0	500	.035	3.1	.034	3.0	.03	2.7	

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment showed zero difference for biological activity.

APPENDIX A.1.3

RAW DATA FOR THE EFFECT OF VARIABLES (Batch Kinetics)

APPENDIX A.1.3.1

RAW DATA FOR THE EFFECT OF PH

Reactor no. 1

Date started: 15/8/1992

Phenol at pH 3

Initial concentration : 1000 mg/l

Mass of carbon: 28.6 gm

Initial oxygen purged (32.7 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0		
0.000	1.143	996.400	1.000	a	b
0.160	0.895	780.181	0.783	a	
0.500	0.665	579.905	0.582	a	
1.000	0.529	461.333	0.463	a	
1.500	0.438	381.621	0.383	a	
2.000	0.391	340.769	0.342	a	
3.000	0.367	319.844	0.321	a	
5.000	0.310	270.024	0.271	a	
7.000	0.290	253.086	0.254	a	
9.500	0.275	240.132	0.241	a	
12.000	0.251	219.208	0.220	a	
24.000	0.208	181.345	0.182	a	b
36.000	0.189	164.406	0.165	a	
48.000	0.171	149.460	0.150	a	
72.000	0.154	134.514	0.135	a	
96.000	0.139	121.561	0.122	a	
120.000	0.130	113.590	0.114	a	
144.000	0.122	106.615	0.107		
180.000	0.109	94.658	0.095		
264.000	0.940	81.705	0.082		
336.000	0.940	81.705	0.082		b

Date ended: 29/8/1992

Remarks:

a: Ten times dilution was made

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 4

Date started: 15/8/1992

Phenol at pH 3

Initial concentration : 1000 mg/l

Mass of carbon: 28.6 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0		
0.000	1.140	994.000	1.000	a	b
0.160	0.896	781.284	0.786	a	
0.500	0.655	571.550	0.575	a	
1.083	0.519	452.270	0.455	a	
1.583	0.441	384.678	0.387	a	
2.083	0.391	340.942	0.343	a	
3.083	0.369	322.056	0.324	a	
5.083	0.312	272.356	0.274	a	
7.083	0.294	256.452	0.258	a	
9.583	0.276	240.548	0.242	a	
12.083	0.268	233.590	0.235	a	
24.083	0.226	196.812	0.198	a	
36.083	0.218	189.854	0.191	a	
48.083	0.207	180.908	0.182	a	b
72.083	0.207	180.908	0.182	a	
96.083	0.207	180.908	0.182	a	
120.083	0.207	180.908	0.182	a	b

Date ended: 19/8/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 2

Date started: 15/8/1992

phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6gm

Initial oxygen purged (32.3 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0		
0.000	1.120	1001.000	1.000	a	b
0.160	0.885	790.790	0.790	a	
0.500	0.673	601.601	0.601	a	
1.000	0.539	481.481	0.481	a	
1.500	0.448	400.400	0.400	a	
2.000	0.404	361.361	0.361	a	
3.000	0.374	334.334	0.334	a	
5.000	0.356	318.318	0.318	a	
7.000	0.343	306.306	0.306	a	
9.500	0.315	281.281	0.281	a	
12.000	0.291	260.260	0.260	a	
24.000	0.255	228.228	0.228	a	b
36.000	0.208	186.186	0.186	a	
48.000	0.175	156.156	0.156	a	
72.000	0.121	108.108	0.108	a	
96.000	0.871	78.078	0.078		
120.000	0.670	60.060	0.060		
144.000	0.542	48.048	0.048		
180.000	0.411	37.037	0.037		b
264.000	0.330	29.129	0.029		
336.000	0.330	29.129	0.029		b

Date ended: 29/8/1992

Remarks:

a: Ten times dilution was made

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 4

Date started: 20/8/1992

Phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0		
0.000	1.122	1002.700	1.000	a	b
0.160	0.880	787.119	0.785	a	
0.500	0.679	606.633	0.605	a	
1.083	0.528	472.271	0.471	a	
1.583	0.437	391.053	0.390	a	
2.083	0.409	365.985	0.365	a	
3.083	0.381	340.918	0.340	a	
5.083	0.352	314.848	0.314	a	
7.083	0.341	304.821	0.304	a	
9.583	0.336	300.810	0.300	a	
12.083	0.331	295.796	0.295	a	
24.083	0.316	282.761	0.282	a	b
36.083	0.312	278.750	0.278	a	
48.083	0.297	265.715	0.265	a	
72.083	0.293	261.705	0.261	a	
96.083	0.293	261.705	0.261	a	
120.083	0.293	261.705	0.261	a	b

Date ended: 24/8/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 3

Date started: 15/8/1992

phenol at pH 11

Initial concentration : 1000 mg/l

Mass of carbon: 28.6gm

Initial oxygen purged (30.8 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0		
0.000	1.099	995.000	1.000	a	b
0.160	0.958	866.645	0.871	a	
0.500	0.863	781.075	0.785	a	
1.000	0.759	686.550	0.690	a	
1.500	0.700	633.815	0.637	a	
2.000	0.661	597.995	0.601	a	
3.000	0.598	541.280	0.544	a	
5.000	0.500	452.725	0.455	a	
7.000	0.387	350.240	0.352	a	
9.500	0.363	328.350	0.330	a	
12.000	0.321	290.540	0.292	a	
24.000	0.288	260.690	0.262	a	b
36.000	0.270	244.770	0.246	a	
48.000	0.245	221.885	0.223	a	
72.000	0.221	199.995	0.201	a	
96.000	0.184	166.165	0.167	a	
120.000	0.159	144.275	0.145	a	
144.000	0.152	137.310	0.138	a	
180.000	0.132	119.400	0.120	a	b
264.000	0.118	106.465	0.107	a	
336.000	0.118	106.465	0.107	a	b

Date ended: 29/8/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 4

Date started: 25/8/1992

Phenol at pH 11

Initial concentration : 1000 mg/l

Mass of carbon: 28.6 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0		
0.000	1.097	992.700	1.000	a	b
0.160	0.965	873.576	0.880	a	
0.500	0.865	783.240	0.789	a	
1.083	0.773	699.853	0.705	a	
1.583	0.705	638.306	0.643	a	
2.083	0.666	602.569	0.607	a	
3.083	0.600	543.007	0.547	a	
5.083	0.503	455.649	0.459	a	
7.083	0.407	368.292	0.371	a	
9.583	0.389	352.408	0.355	a	
12.083	0.376	340.496	0.343	a	
24.083	0.367	332.554	0.335	a	b
36.083	0.361	326.598	0.329	a	
48.083	0.359	324.613	0.327	a	
72.083	0.356	322.627	0.325	a	
96.083	0.354	320.642	0.323	a	
120.083	0.354	320.642	0.323	a	b

Date ended: 29/8/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 5

Date started: 15/8/1992

o-cresol at pH 3

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial oxygen purged (30.7 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.802	772.000	0.772
0.500	0.625	602.000	0.602
1.000	0.512	493.000	0.493
1.500	0.433	417.000	0.417
2.000	0.389	375.000	0.375
3.000	0.353	340.000	0.340
5.000	0.319	307.000	0.307
7.000	0.408	393.000	0.393
9.500	0.398	383.000	0.383
12.000	0.386	372.000	0.372
24.000	0.268	258.000	0.258
36.000	0.260	250.000	0.250
48.000	0.255	246.000	0.246
72.000	0.250	241.000	0.241
96.000	0.244	235.000	0.235
120.000	0.239	230.000	0.230
144.000	0.235	226.000	0.226
180.000	0.232	223.000	0.223
264.000	0.227	219.000	0.219
336.000	0.227	219.000	0.219

Date ended: 29/8/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 3

Date started: 30/8/1992

o-cresol at pH 3

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.808	778.000	0.778
0.500	0.617	594.000	0.594
1.089	0.508	489.000	0.489
1.589	0.425	409.000	0.409
2.089	0.396	381.000	0.381
3.089	0.356	343.000	0.343
5.089	0.325	313.000	0.313
7.089	0.315	303.000	0.303
9.589	0.306	295.000	0.295
12.089	0.298	287.000	0.287
24.089	0.283	273.000	0.273
36.089	0.322	310.000	0.310
48.089	0.275	265.000	0.265
72.089	0.273	263.000	0.263
96.089	0.273	263.000	0.263
120.089	0.273	263.000	0.263

Date ended: 3/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 1

Date started: 30/8/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial oxygen purged: (31.5 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.837	806.000	0.806
0.500	0.652	628.000	0.628
1.000	0.507	488.000	0.488
1.500	0.439	423.000	0.423
2.000	0.400	385.000	0.385
3.000	0.389	375.000	0.375
5.000	0.381	367.000	0.367
7.000	0.362	349.000	0.349
9.500	0.343	330.000	0.330
12.000	0.324	312.000	0.312
24.000	0.266	256.000	0.256
36.000	0.246	237.000	0.237
48.000	0.205	197.000	0.197
72.000	0.166	160.000	0.160
96.000	0.121	117.000	0.117
120.000	0.110	106.000	0.106
144.000	0.099	95.000	0.095
180.000	0.087	84.000	0.084
264.000	0.084	81.000	0.070
336.000	0.084	81.000	0.070

Date ended: 13/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 3

Date started: 14/9/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.042	1000.000	1.000
0.160	0.824	791.000	0.791
0.500	0.641	615.000	0.615
1.089	0.522	501.000	0.501
1.589	0.444	426.000	0.426
2.089	0.409	393.000	0.393
3.089	0.393	377.000	0.377
5.089	0.386	371.000	0.371
7.089	0.371	356.000	0.356
9.589	0.362	348.000	0.348
12.089	0.356	342.000	0.342
24.089	0.330	317.000	0.317
36.089	0.323	310.000	0.310
48.089	0.317	304.000	0.304
72.089	0.314	301.000	0.301
96.089	0.314	301.000	0.301
120.089	0.314	301.000	0.301

Date ended: 18/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 2

Date started: 30/8/1992

o-cresol at pH 11

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial oxygen purged : (DO = 31.1 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.940	905.000	0.905
0.500	0.885	852.000	0.852
1.000	0.825	794.000	0.794
1.500	0.805	775.000	0.775
2.000	0.778	749.000	0.749
3.000	0.722	695.000	0.695
5.000	0.674	649.000	0.649
7.000	0.620	597.000	0.597
9.500	0.596	574.000	0.574
12.000	0.561	540.000	0.540
24.000	0.547	527.000	0.527
36.000	0.513	494.000	0.494
48.000	0.501	482.000	0.482
72.000	0.482	464.000	0.464
96.000	0.464	447.000	0.447
120.000	0.459	442.000	0.442
144.000	0.454	437.000	0.437
180.000	0.449	432.000	0.432
264.000	0.440	424.000	0.424
336.000	0.440	424.000	0.424

Date ended: 13/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 3

Date started: 19/9/1992

o-cresol at pH 11

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial nitrogen purged (0.0 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.934	899.000	0.899
0.500	0.896	863.000	0.863
1.089	0.820	790.000	0.790
1.589	0.800	770.000	0.770
2.089	0.776	747.000	0.747
3.089	0.730	703.000	0.703
5.089	0.670	645.000	0.645
7.089	0.632	609.000	0.609
9.589	0.623	600.000	0.600
12.089	0.617	594.000	0.594
24.089	0.610	587.000	0.587
36.089	0.607	585.000	0.585
48.089	0.292	281.000	0.281
72.089	0.602	580.000	0.580
96.089	0.601	579.000	0.579
120.089	0.601	579.000	0.579

Date ended: 23/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

APPENDIX A.1.3.2

RAW DATA FOR THE EFFECT OF TEMPERATURE

Reactor no. 4

Date started: 30/8/1992

phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6 gm

Initial oxygen purged (31.4 mg/l)

Temperature: 8°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.084	994.000	1.000
0.160	0.810	742.518	0.747
0.500	0.636	583.478	0.587
1.000	0.506	464.198	0.467
1.500	0.408	373.744	0.376
2.000	0.380	348.894	0.351
3.000	0.349	320.068	0.322
5.000	0.315	289.254	0.291
7.000	0.302	277.326	0.279
9.500	0.289	265.398	0.267
12.000	0.264	242.536	0.244
24.000	0.214	195.818	0.197
36.000	0.194	177.926	0.179
48.000	0.164	150.094	0.151
72.000	0.119	109.340	0.110
96.000	0.091	83.496	0.084
120.000	0.064	58.646	0.059
144.000	0.046	41.748	0.042
180.000	0.031	28.826	0.029
264.000	0.023	20.874	0.021
336.000	0.023	20.874	0.021

Date ended: 15/9/1992

Remarks:

a: Ten times dilution was made

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 3

Date started: 4/9/1992

Phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 8°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0		
0.000	1.122	1002.700	1.000	a	b
0.160	0.817	748.747	0.751		
0.500	0.647	593.215	0.595		
1.083	0.506	463.605	0.465		
1.583	0.406	371.881	0.373		
2.083	0.386	353.935	0.355		
3.083	0.357	327.016	0.328		
5.083	0.322	295.112	0.296		
7.083	0.314	288.133	0.289		
9.583	0.306	280.157	0.281		
12.083	0.295	270.187	0.271		
24.083	0.271	248.253	0.249		
36.083	0.258	236.289	0.237		
48.083	0.246	225.322	0.226		
72.083	0.232	212.361	0.213		
96.083	0.208	190.427	0.191		
120.083	0.208	190.427	0.191		

Date ended: 8/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 2

Date started: 15/8/1992

phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6gm

Initial oxygen purged (32.3 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0		
0.000	1.120	1001.000	1.000	a	b
0.160	0.885	790.790	0.790	a	
0.500	0.673	601.601	0.601	a	
1.000	0.539	481.481	0.481	a	
1.500	0.448	400.400	0.400	a	
2.000	0.404	361.361	0.361	a	
3.000	0.374	334.334	0.334	a	
5.000	0.356	318.318	0.318	a	
7.000	0.343	306.306	0.306	a	
9.500	0.315	281.281	0.281	a	
12.000	0.291	260.260	0.260	a	
24.000	0.255	228.228	0.228	a	b
36.000	0.208	186.186	0.186	a	
48.000	0.175	156.156	0.156	a	
72.000	0.121	108.108	0.108	a	
96.000	0.871	78.078	0.078		
120.000	0.670	60.060	0.060		
144.000	0.542	48.048	0.048		
180.000	0.411	37.037	0.037		b
264.000	0.330	29.129	0.029		
336.000	0.330	29.129	0.029		b

Date ended: 29/8/1992

Remarks:

a: Ten times dilution was made

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 4

Date started: 20/8/1992

Phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0		
0.000	1.122	1002.700	1.000	a	b
0.160	0.880	787.119	0.785	a	
0.500	0.679	606.633	0.605	a	
1.083	0.528	472.271	0.471	a	
1.583	0.437	391.053	0.390	a	
2.083	0.409	365.985	0.365	a	
3.083	0.381	340.918	0.340	a	
5.083	0.352	314.848	0.314	a	
7.083	0.341	304.821	0.304	a	
9.583	0.336	300.810	0.300	a	
12.083	0.331	295.796	0.295	a	
24.083	0.316	282.761	0.282	a	b
36.083	0.312	278.750	0.278	a	
48.083	0.297	265.715	0.265	a	
72.083	0.293	261.705	0.261	a	
96.083	0.293	261.705	0.261	a	
120.083	0.293	261.705	0.261	a	b

Date ended: 14/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 1

Date started: 14/9/1992

phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6gm

Initial oxygen purged (32.3 mg/l)

Temperature: 35°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.080	997.000	1.000
0.160	0.889	820.531	0.823
0.500	0.727	670.981	0.673
1.000	0.678	626.116	0.628
1.500	0.628	579.257	0.581
2.000	0.615	567.293	0.569
3.000	0.558	515.449	0.517
5.000	0.527	486.536	0.488
7.000	0.512	472.578	0.474
9.500	0.475	438.680	0.440
12.000	0.440	405.779	0.407
24.000	0.343	317.046	0.318
36.000	0.304	280.157	0.281
48.000	0.235	217.346	0.218
72.000	0.167	154.535	0.155
96.000	0.137	126.619	0.127
120.000	0.113	104.685	0.105
144.000	0.104	95.712	0.096
180.000	0.094	86.739	0.087
264.000	0.089	81.754	0.082
336.000	0.089	81.754	0.082

Date ended: 28/9/1992

Remarks:

a: Ten times dilution was made

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 3

Date started: 14/9/1992

Phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 35°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.081	998.000	1.000
0.160	0.877	809.378	0.811
0.500	0.735	678.640	0.680
1.083	0.675	622.752	0.624
1.583	0.622	573.850	0.575
2.083	0.607	559.878	0.561
3.083	0.564	520.956	0.522
5.083	0.535	494.010	0.495
7.083	0.531	490.018	0.491
9.583	0.523	483.032	0.484
12.083	0.517	477.044	0.478
24.083	0.509	470.058	0.471
36.083	0.501	462.074	0.463
48.083	0.501	462.074	0.463
72.083	0.501	462.074	0.463
96.083	0.501	462.074	0.463
120.083	0.501	462.074	0.463

Date ended: 18/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 2

Date started: 30/8/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial oxygen purged : (DO = 31.1 mg/l)

Temperature: $8^{o}C$.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.813	783.000	0.783
0.500	0.638	614.000	0.614
1.000	0.499	481.000	0.481
1.500	0.462	445.000	0.445
2.000	0.439	423.000	0.423
3.000	0.408	393.000	0.393
5.000	0.393	378.000	0.378
7.000	0.373	359.000	0.359
9.500	0.326	314.000	0.314
12.000	0.286	275.000	0.275
24.000	0.266	256.000	0.256
36.000	0.234	225.000	0.225
48.000	0.217	209.000	0.209
72.000	0.165	159.000	0.159
96.000	0.156	150.000	0.150
120.000	0.136	131.000	0.131
144.000	0.117	113.000	0.113
180.000	0.102	98.000	0.098
264.000	0.089	86.000	0.086
336.000	0.089	86.000	0.086

Date ended: 13/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 3

Date started: 19/9/1992

o-Cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial nitrogen purged (0.0 mg/l)

Temperature: 8°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.805	775.000	0.775
0.500	0.650	626.000	0.626
1.089	0.505	486.000	0.486
1.589	0.456	439.000	0.439
2.089	0.432	416.000	0.416
3.089	0.411	396.000	0.396
5.089	0.385	371.000	0.371
7.089	0.370	356.000	0.356
9.589	0.340	327.000	0.327
12.089	0.323	311.000	0.311
24.089	0.296	285.000	0.285
36.089	0.285	274.000	0.274
48.089	0.277	267.000	0.267
72.089	0.268	258.000	0.258
96.089	0.262	252.000	0.252
120.089	0.272	262.000	0.262

Date ended: 23/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 1

Date started: 30/8/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial oxygen purged: (31.5 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.837	806.000	0.806
0.500	0.652	628.000	0.628
1.000	0.507	488.000	0.488
1.500	0.439	423.000	0.423
2.000	0.400	385.000	0.385
3.000	0.389	375.000	0.375
5.000	0.381	367.000	0.367
7.000	0.362	349.000	0.349
9.500	0.343	330.000	0.330
12.000	0.324	312.000	0.312
24.000	0.266	256.000	0.256
36.000	0.246	237.000	0.237
48.000	0.205	197.000	0.197
72.000	0.166	160.000	0.160
96.000	0.121	117.000	0.117
120.000	0.110	106.000	0.106
144.000	0.099	95.000	0.095
180.000	0.087	84.000	0.084
264.000	0.084	81.000	0.070
336.000	0.084	81.000	0.070

Date ended: 13/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 3

Date started: 14/9/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.042	1000.000	1.000
0.160	0.824	791.000	0.791
0.500	0.641	615.000	0.615
1.089	0.522	501.000	0.501
1.589	0.444	426.000	0.426
2.089	0.409	393.000	0.393
3.089	0.393	377.000	0.377
5.089	0.386	371.000	0.371
7.089	0.371	356.000	0.356
9.589	0.362	348.000	0.348
12.089	0.356	342.000	0.342
24.089	0.330	317.000	0.317
36.089	0.323	310.000	0.310
48.089	0.317	304.000	0.304
72.089	0.314	301.000	0.301
96.089	0.314	301.000	0.301
120.089	0.314	301.000	0.301

Date ended: 18/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 1

Date started: 30/8/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial oxygen purged: (31.5 mg/l)

Temperature: 35°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.821	791.000	0.791
0.500	0.687	662.000	0.662
1.000	0.551	531.000	0.531
1.500	0.502	483.000	0.483
2.000	0.468	451.000	0.451
3.000	0.438	422.000	0.422
5.000	0.414	399.000	0.399
7.000	0.389	375.000	0.375
9.500	0.354	341.000	0.341
12.000	0.339	326.000	0.326
24.000	0.306	295.000	0.295
36.000	0.292	281.000	0.281
48.000	0.246	237.000	0.237
72.000	0.171	165.000	0.165
96.000	0.154	148.000	0.148
120.000	0.134	129.000	0.129
144.000	0.123	118.000	0.118
180.000	0.111	107.000	0.107
264.000	0.106	102.000	0.102
336.000	0.106	102.000	0.102

Date ended: 13/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 3

Date started: 14/9/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 35^{o}C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.836	805.000	0.805
0.500	0.701	675.000	0.675
1.089	0.563	542.000	0.542
1.589	0.496	478.000	0.478
2.089	0.462	445.000	0.445
3.089	0.428	412.000	0.412
5.089	0.401	386.000	0.386
7.089	0.394	379.000	0.379
9.589	0.381	367.000	0.367
12.089	0.375	361.000	0.361
24.089	0.367	353.000	0.353
36.089	0.361	348.000	0.348
48.089	0.360	347.000	0.347
72.089	0.360	347.000	0.347
96.089	0.360	347.000	0.347
120.089	0.360	347.000	0.347

Date ended: 18/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

APPENDIX A.1.3.3

RAW DATA FOR THE EFFECT OF DO LEVELS

Reactor no. 2

Date started: 15/8/1992

phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6gm

Initial oxygen purged (32.3 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0		
0.000	1.120	1001.000	1.000	a	b
0.160	0.885	790.790	0.790	a	
0.500	0.673	601.601	0.601	a	
1.000	0.539	481.481	0.481	a	
1.500	0.448	400.400	0.400	a	
2.000	0.404	361.361	0.361	a	
3.000	0.374	334.334	0.334	a	
5.000	0.356	318.318	0.318	a	
7.000	0.343	306.306	0.306	a	
9.500	0.315	281.281	0.281	a	
12.000	0.291	260.260	0.260	a	
24.000	0.255	228.228	0.228	a	b
36.000	0.208	186.186	0.186	a	
48.000	0.175	156.156	0.156	a	
72.000	0.121	108.108	0.108	a	
96.000	0.871	78.078	0.078		
120.000	0.670	60.060	0.060		
144.000	0.542	48.048	0.048		
180.000	0.411	37.037	0.037		b
264.000	0.330	29.129	0.029		
336.000	0.330	29.129	0.029		b

Date ended: 29/8/1992

Remarks:

a: Ten times dilution was made

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 2

Date started: 15/8/1992

phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6gm

Initial oxygen purged (8.5 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.120	998.100	1.000
0.160	0.874	778.586	0.780
0.500	0.682	607.646	0.609
1.000	0.531	473.136	0.474
1.500	0.463	412.419	0.413
2.000	0.395	351.703	0.352
3.000	0.383	341.427	0.342
5.000	0.364	324.614	0.325
7.000	0.348	309.668	0.310
9.500	0.322	287.250	0.288
12.000	0.283	251.754	0.252
24.000	0.235	209.720	0.210
36.000	0.193	172.356	0.173
48.000	0.175	155.542	0.156
72.000	0.119	106.035	0.106
96.000	0.100	89.221	0.089
120.000	0.088	78.012	0.078
144.000	0.081	72.407	0.073
180.000	0.076	67.737	0.068
264.000	0.071	62.880	0.063
336.000	0.071	62.880	0.063

Date ended: 29/8/1992

Remarks:

a: Ten times dilution was made

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 2

Date started: 15/8/1992

phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6gm

Initial oxygen purged (4 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.113	997.000	1.000
0.160	0.882	790.621	0.793
0.500	0.660	591.221	0.593
1.000	0.521	466.596	0.468
1.500	0.451	403.785	0.405
2.000	0.403	360.914	0.362
3.000	0.369	331.004	0.332
5.000	0.364	326.019	0.327
7.000	0.334	299.100	0.300
9.500	0.323	289.130	0.290
12.000	0.284	254.235	0.255
24.000	0.244	218.343	0.219
36.000	0.203	181.454	0.182
48.000	0.167	149.550	0.150
72.000	0.139	124.625	0.125
96.000	0.130	116.649	0.117
120.000	0.127	113.658	0.114
144.000	0.125	111.664	0.112
180.000	0.124	110.667	0.111
264.000	0.122	109.670	0.110
335.000	0.122	109.670	0.110

Date ended: 29/8/1992

Remarks:

a: Ten times dilution was made

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 4

Date started: 20/8/1992

Phenol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 28.6 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.122	1002.700	1.000
0.160	0.880	787.119	0.785
0.500	0.680	607.636	0.606
1.083	0.529	473.274	0.472
1.583	0.440	393.058	0.392
2.083	0.412	367.991	0.367
3.083	0.384	342.923	0.342
5.083	0.354	316.853	0.316
7.083	0.348	310.837	0.310
9.583	0.339	302.815	0.302
12.083	0.333	297.802	0.297
24.083	0.314	280.756	0.280
36.083	0.304	271.732	0.271
48.083	0.298	266.718	0.266
72.000	0.295	263.710	0.263
96.083	0.295	263.710	0.263
120.083	0.295	263.710	0.263

Date ended: 24/8/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 1

Date started: 30/8/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial oxygen purged: (31.5 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.038	1000.000	1.000
0.160	0.837	806.000	0.806
0.500	0.652	628.000	0.628
1.000	0.507	488.000	0.488
1.500	0.439	423.000	0.423
2.000	0.400	385.000	0.385
3.000	0.389	375.000	0.375
5.000	0.381	367.000	0.367
7.000	0.362	349.000	0.349
9.500	0.343	330.000	0.330
12.000	0.324	312.000	0.312
24.000	0.266	256.000	0.256
36.000	0.246	237.000	0.237
48.000	0.205	197.000	0.197
72.000	0.166	160.000	0.160
96.000	0.121	117.000	0.117
120.000	0.110	106.000	0.106
144.000	0.099	95.000	0.095
180.000	0.087	84.000	0.084
264.000	0.084	81.000	0.070
336.000	0.084	81.000	0.070

Date ended: 13/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 1

Date started: 30/8/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial oxygen purged: (8.5 mg/l)

Temperature: 21^{o}C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.030	1000.000	1.000
0.160	0.816	792.000	0.792
0.500	0.649	630.000	0.630
1.000	0.487	473.000	0.473
1.500	0.446	433.000	0.433
2.000	0.406	394.000	0.394
3.000	0.394	383.000	0.383
5.000	0.388	377.000	0.377
7.000	0.357	347.000	0.347
9.500	0.346	336.000	0.336
12.000	0.323	314.000	0.314
24.000	0.269	261.000	0.261
36.000	0.250	243.000	0.243
48.000	0.207	201.000	0.201
72.000	0.181	176.000	0.176
96.000	0.154	150.000	0.150
120.000	0.145	141.000	0.141
144.000	0.143	139.000	0.139
180.000	0.138	134.000	0.134
264.000	0.135	131.000	0.131
336.000	0.135	131.000	0.131

Date ended: 13/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 1

Date started: 30/8/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 12 gm

Initial oxygen purged: (4.0 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.116	1000.000	1.000
0.160	0.894	801.000	0.801
0.500	0.692	620.000	0.620
1.000	0.549	492.000	0.492
1.500	0.482	432.000	0.432
2.000	0.436	391.000	0.391
3.000	0.417	374.000	0.374
5.000	0.422	378.000	0.378
7.000	0.392	351.000	0.351
9.500	0.374	335.000	0.335
12.000	0.355	318.000	0.318
24.000	0.302	271.000	0.271
36.000	0.292	262.000	0.262
48.000	0.258	231.000	0.231
72.000	0.220	197.000	0.197
96.000	0.211	189.000	0.189
120.000	0.208	186.000	0.186
144.000	0.204	183.000	0.183
180.000	0.203	182.000	0.182
264.000	0.202	181.000	0.181
336.000	0.202	181.000	0.181

Date ended: 13/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

Reactor no. 3

Date started: 14/9/1992

o-cresol at pH 7

Initial concentration : 1000 mg/l

Mass of carbon: 15 gm

Initial nitrogen purged (DO = 0.0)

Temperature: 21°C.

Time (Hour)	Abs.	conc. (c) (mg/l)	c/c0
0.000	1.042	1000.000	1.000
0.160	0.824	791.000	0.791
0.500	0.641	615.000	0.615
1.089	0.522	501.000	0.501
1.589	0.444	426.000	0.426
2.089	0.409	393.000	0.393
3.089	0.393	377.000	0.377
5.089	0.386	371.000	0.371
7.089	0.371	356.000	0.356
9.589	0.362	348.000	0.348
12.089	0.356	342.000	0.342
24.089	0.330	317.000	0.317
36.089	0.323	310.000	0.310
48.089	0.317	304.000	0.304
72.089	0.314	301.000	0.301
96.089	0.314	301.000	0.301
120.089	0.314	301.000	0.301

Date ended: 18/9/1992

Remarks:

a: Ten times dilution was made for all the samples

b: Inorganic carbon measurements were performed and no increase was noticed (no biological activity)

APPENDIX A.1.4

RAW DATA FOR THE COLUMN EXPERIMENTS

Column no. 1

Date started: 12/3/1993

o-Cresol at pH 7

Initial concentration : 70 mg/l

Mass of carbon: 130 gm

Nitrogen purged (DO = 0.04 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	Conc. (C) (mg/l)	C/C0
36.000	0.000	0.000	0.000
40.000	0.025	1.610	0.023
47.000	0.054	3.430	0.049
50.000	0.080	5.040	0.072
54.000	0.136	8.610	0.123
56.000	0.189	11.970	0.171
58.000	0.270	17.080	0.244
60.000	0.354	22.400	0.320
61.000	0.420	26.600	0.380
62.000	0.486	30.800	0.440
63.000	0.564	35.700	0.510
64.000	0.608	38.500	0.550
66.000	0.696	44.100	0.630
68.000	0.839	53.130	0.759
70.000	0.939	59.500	0.850
72.000	0.994	63.000	0.900
74.000	1.011	64.050	0.915
76.000	1.020	64.610	0.923
78.000	1.025	64.960	0.928
80.000	1.028	65.100	0.930
82.000	1.033	65.450	0.935
84.000	1.035	65.590	0.937
94.000	1.042	66.010	0.943
114.000	1.055	66.850	0.955
124.000	1.067	67.620	0.966
134.000	1.076	68.180	0.974
144.000	1.066	67.550	0.965
168.000	1.069	67.690	0.967
180.000	1.069	67.690	0.967

Date ended: 25/3/1993

Column no. 2

Date started: 12/3/1993

o-Cresol at pH 7

Initial concentration : 70 mg/l

Mass of carbon: 130 gm

Oxygen purged (DO = 31.4 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	Conc. (C) (mg/l)	C/C0
62.000	0.000	0.000	0.000
69.000	0.033	2.100	0.030
70.000	0.038	2.450	0.035
72.000	0.047	3.010	0.043
74.000	0.061	3.920	0.056
76.000	0.083	5.390	0.077
78.000	0.088	5.670	0.081
80.000	0.095	6.160	0.088
82.000	0.098	6.300	0.090
84.000	0.130	8.400	0.120
86.000	0.145	9.380	0.134
88.000	0.161	10.430	0.149
90.000	0.217	14.000	0.200
94.000	0.336	21.700	0.310
96.000	0.401	25.900	0.370
98.000	0.568	36.680	0.524
100.000	0.619	39.970	0.571
105.000	0.704	45.500	0.650
107.000	0.737	47.600	0.680
110.000	0.758	49.000	0.700
115.000	0.791	51.100	0.730
120.000	0.813	52.500	0.750
125.000	0.834	53.900	0.770
130.000	0.867	56.000	0.800
135.000	0.899	58.100	0.830
140.000	0.937	60.550	0.865
145.000	0.967	62.510	0.893
155.000	0.975	63.000	0.900
165.000	0.972	62.790	0.897
170.000	0.970	62.650	0.895
175.000	0.986	63.700	0.910
180.000	0.983	63.490	0.907
185.000	0.964	62.300	0.890
190.000	0.986	63.700	0.910
195.000	0.997	64.400	0.920

200.000	1.001	64.680	0.924
205.000	1.000	64.610	0.923
215.000	1.011	65.310	0.933
230.000	1.020	65.870	0.941
240.000	1.024	66.150	0.945
270.000	1.018	65.800	0.940
280.000	1.023	66.080	0.944
290.000	1.030	66.570	0.951
300.000	1.037	66.990	0.957
310.000	1.039	67.130	0.959
315.000	1.036	66.920	0.956
320.000	1.038	67.060	0.958
325.000	1.040	67.200	0.960
330.000	1.040	67.200	0.960

Date ended: 25/3/1993

Column no. 3

Date started: 12/3/1993

Phenol at pH 7

Initial concentration : 70 mg/l

Mass of carbon: 130 gm

Nitrogen purged (DO = 0.04 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	Conc. (C) (mg/l)	C/C0
8.000	0.000	0.000	0.000
14.000	0.031	1.960	0.028
15.000	0.037	2.380	0.034
16.000	0.044	2.800	0.040
18.000	0.066	4.200	0.060
20.000	0.082	5.250	0.075
22.000	0.132	8.400	0.120
23.000	0.219	14.000	0.200
24.000	0.263	16.800	0.240
25.000	0.331	21.140	0.302
26.000	0.406	25.900	0.370
27.000	0.493	31.500	0.450
28.000	0.552	35.210	0.503
29.000	0.650	41.510	0.593
30.000	0.713	45.500	0.650
31.000	0.800	51.100	0.730
32.000	0.923	58.940	0.842
33.000	0.943	60.200	0.860
37.000	0.976	62.300	0.890
38.000	0.992	63.350	0.905
43.000	1.005	64.190	0.917
46.000	1.009	64.400	0.920
54.000	1.031	65.800	0.940
56.000	1.033	65.940	0.942
58.000	1.025	65.450	0.935
60.000	1.031	65.800	0.940
62.000	1.042	66.500	0.950
66.000	1.044	66.640	0.952
68.000	1.054	67.270	0.961
70.000	1.050	67.060	0.958
72.000	1.042	66.500	0.950
74.000	1.056	67.410	0.963
76.000	1.057	67.480	0.964
78.000	1.061	67.760	0.968
80.000	1.062	67.830	0.969

82.000	1.058	67.550	0.965
84.000	1.064	67.900	0.970
100.000	1.061	67.760	0.968
108.000	1.064	67.900	0.970
125.000	1.060	67.690	0.967
140.000	1.060	67.690	0.967

Date ended: 25/3/1993

Column no. 4

Date started: 12/3/1993

Phenol at pH 7

Initial concentration : 70 mg/l

Mass of carbon: 130 gm

Oxygen purged (DO = 31.1 mg/l)

Temperature: 21°C.

Time (Hour)	Abs.	Conc. (C) (mg/l)	C/C0
20.000	0.000	0.000	0.000
25.000	0.031	1.960	0.028
26.000	0.036	2.310	0.033
27.000	0.050	3.150	0.045
28.000	0.063	3.990	0.057
29.000	0.078	4.970	0.071
31.000	0.088	5.600	0.080
33.000	0.127	8.050	0.115
34.000	0.155	9.800	0.140
35.000	0.177	11.200	0.160
36.000	0.193	12.250	0.175
37.000	0.221	14.000	0.200
38.000	0.254	16.100	0.230
39.000	0.290	18.340	0.262
40.000	0.340	21.560	0.308
41.000	0.380	24.080	0.344
42.000	0.448	28.350	0.405
43.000	0.497	31.500	0.450
44.000	0.530	33.600	0.480
45.000	0.568	35.980	0.514
46.000	0.575	36.400	0.520
48.000	0.608	38.500	0.550
50.000	0.685	43.400	0.620
52.000	0.696	44.100	0.630
54.000	0.707	44.800	0.640
56.000	0.729	46.200	0.660
58.000	0.759	48.090	0.687
60.000	0.765	48.440	0.692
62.000	0.785	49.700	0.710
64.000	0.791	50.120	0.716
68.000	0.812	51.450	0.735
70.000	0.851	53.900	0.770
72.000	0.895	56.700	0.810
74.000	0.917	58.100	0.830
76.000	0.934	59.150	0.845

78.000	0.950	60.200	0.860
80.000	0.961	60.900	0.870
82.000	0.975	61.740	0.882
84.000	0.983	62.300	0.890
86.000	1.010	63.980	0.914
90.000	1.008	63.840	0.912
100.000	1.017	64.400	0.920
102.000	1.021	64.680	0.924
107.000	1.030	65.240	0.932
112.000	1.041	65.940	0.942
120.000	1.036	65.660	0.938
130.000	1.051	66.570	0.951
135.000	1.044	66.150	0.945
140.000	1.051	66.570	0.951
145.000	1.055	66.850	0.955
150.000	1.044	66.150	0.945
155.000	1.051	66.570	0.951
160.000	1.049	66.430	0.949
180.000	1.062	67.270	0.961
185.000	1.063	67.340	0.962
190.000	1.062	67.270	0.961
205.000	1.064	67.410	0.963
215.000	1.066	67.550	0.965
230.000	1.064	67.410	0.963
240.000	1.073	67.970	0.971
270.000	1.066	67.550	0.965
280.000	1.069	67.690	0.967
290.000	1.070	67.760	0.968
300.000	1.072	67.900	0.970
310.000	1.070	67.760	0.968
315.000	1.064	67.410	0.963
320.000	1.070	67.760	0.968
330.000	1.070	67.760	0.968

Date ended: 25/3/1993

APPENDIX A.2

COMPUTER PROGRAMS FOR THE PREDICTION OF THE BATCH EXPERIMENTS

```
**************************************************************************
*  In order to determine the surface diffusion coefficient two programs
*  are required to be run.
*  The two programs are:
*  HSDM.EXE and SHSDM.EXE
**************************************************************************
The first step:
Run HSDM.EXE
This program uses the following input files
   -HSDM.IN
   -PART.COL
HSDM.IN IS YOUR INPUT FILE. DETAILS ARE SHOWN IN THE FILE ITSELF. USUALLY
USE FOR THE RUN TIME A LARGE LENGTH OF TIME TO OBTAIN THE BEST ESTIMATE
the surface diffusiuon coefficient Ds.
PART.COL is the collocation matrices file
YOUR OUTPUT FILE IS HSDM.OUT.  FROM THIS FILE GET THE
FINAL ESTIMATE OF DS
**************************************************************************
The second step :
Run SHSDM.EXE
This program uses the following input files
SHSDM.CTR
SHSDM.IN
INPUT.DAT
PART.COL
THE ONLY INPUT FILE YOU NEED TO ADJUST IS INPUT.DAT.
AGAIN THE DETAILS ARE
SHOWN IN THE FILE ITSELF. HERE PUT THE DS ESTIMATE OBTAINED FROM  THE
PROGRAM.
THE OUTPUT FILES ARE TWO: SHSDM.OUT AND OUTPUT.DAT
SHSDM.OUT will give you the final Ds value.
OUTPUT.DAT will give you a table (found at the end of the file) showing
THE TIME, EXP C/CO, AND PREDICTED C/CO
**************************************************************************
```

```
 0  1   1       /IPRC,IPRI,IPRO  DON'T CHANGE
200.98D0     /C0 ,INITIAL CONC       (mg/L)
1.224   /CARBON CONC  (g/L)
0.517756d-05    /DS, SURFACE DIFFUSION ESTIMATE    (cm2/min)
0.207473D0  /XKF, FILM TRANSFER ESTIMATE    (cm/min)
50.25    /XK , FREUNDLICK K PARAMETER   (mg/g - mg/l)
0.214       /XN, FREUNDLICH EXPONENT PARAMETER  (mg/g - mg/l)
0.050019D0     /RADP, RADIUS OF GAC PARTICLE  (cm)
0.74D0     /RHOP, DENSITY OF GAC PARTICLE      (g/cm3)
 10         /NCP, NUMBER OF COLLOCATION POINTS-  DON'T CHANGE
  0.1D-04  2  2           /TOL,METH,MITER  DON'T CHANGE
 1.0D-10    /DTINIT     (min)     DON'T CHANGE
 2.50D0         /DTOUT   (min)     DELTA TIME OUT
 9000.0D0    /TFINAL    (min)      TOTAL RUN TIME
 10000       /ITMAX                MAX NUMBER OF ITERATIONS
```

```
12 200.98 1   / NUMBER OF DATA POINTS,  INITIAL CONCENTRATION. ALWAYS USE
THE THIRD PARAMETER
0.0 1.0       / TIME, MIN     C/Co
30.0 0.597
60.0 0.438
90.0 0.356
120.0 0.328
150.0 0.305
180.0 0.293
210.0 0.281
270.0 0.275
390.0 0.262
630.0 0.258
1133.0 0.244
1.2240      /carbon conc ,g/L
0.050019    /particle radius, cm
0.74        /GAC particle density,  g/cm3
50.25      /Freundlich K parameter ((q in mg/g) - (C in mg/L))
0.214      /Freundlich n parameter
0.22       /film transfer coefficient cm/min
5.2d-06    /surface diffusion coefficient, cm2/min
```

```
      PROGRAM HSDM                                                      HSD00010
C                                                                       HSD00020
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               HSD00030
C                                                                       HSD00040
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                       HSD00050
      COMMON /COL/ NCP,WP(14),BP(14,14)                                 HSD00060
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,                                 HSD00070
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                      HSD00080
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                      HSD00090
      COMMON /VAR/ Y(15),NTOT                                           HSD00100
C                                                                       HSD00110
C                                                                       HSD00120
      OPEN(30,FILE='HSDM.IN',STATUS='OLD')                              HSD00130
      OPEN(31,FILE='PART.COL',STATUS='OLD')                             HSD00140
      OPEN(32,FILE='HSDM.OUT',STATUS='NEW')                             HSD00150
C                                                                       HSD00160
      CALL INPUT                                                        HSD00170
C                                                                       HSD00180
      CALL INCOL                                                        HSD00190
C                                                                       HSD00200
      CALL INIT                                                         HSD00210
C                                                                       HSD00220
      CALL CALCC                                                        HSD00230
C                                                                       HSD00240
      STOP '           ALL DONE'                                        HSD00250
C                                                                       HSD00260
      END                                                               HSD00270
C-------------------------------------------------------------          HSD00280
      SUBROUTINE INPUT                                                  HSD00290
C                                                                       HSD00300
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               HSD00310
C                                                                       HSD00320
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                       HSD00330
      COMMON /COL/ NCP,WP(14),BP(14,14)                                 HSD00340
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,                                 HSD00350
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                      HSD00360
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                      HSD00370
      COMMON /VAR/ Y(15),NTOT                                           HSD00380
C                                                                       HSD00390
      READ(30,*) IPRC,IPRI,IPRO                                         HSD00400
C                                                                       HSD00410
C     PHYSICAL PARAMETER                                                HSD00420
C                                                                       HSD00430
      READ(30,*) CO                                                     HSD00440
      READ(30,*) CCONC                                                  HSD00450
      READ(30,*) DS                                                     HSD00460
      READ(30,*) XKF                                                    HSD00470
      READ(30,*) XK                                                     HSD00480
      READ(30,*) XN                                                     HSD00490
      READ(30,*) RADP                                                   HSD00500
      READ(30,*) RHOP                                                   HSD00510
C                                                                       HSD00520
C     CONTROL PARAMETER                                                 HSD00530
C                                                                       HSD00540
      READ(30,*) NCP                                                    HSD00550
```

```
      READ(30,*) TOL,METH,MITER                                          HSD00560
      READ(30,*) DTINIT                                                  HSD00570
      READ(30,*) DTOUT                                                   HSD00580
      READ(30,*) TFINAL                                                  HSD00590
      READ(30,*) ITMAX                                                   HSD00600
C                                                                        HSD00610
      RETURN                                                             HSD00620
      END                                                                HSD00630
C-------------------------------------------------------------           HSD00640
      SUBROUTINE INCOL                                                   HSD00650
C                                                                        HSD00660
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                                HSD00670
C                                                                        HSD00680
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                        HSD00690
      COMMON /COL/ NCP,WP(14),BP(14,14)                                  HSD00700
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,                                  HSD00710
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                       HSD00720
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                       HSD00730
      COMMON /VAR/ Y(15),NTOT                                            HSD00740
C                                                                        HSD00750
      DIMENSION IDL(2)                                                   HSD00760
      DIMENSION DUMMY(14)                                                HSD00770
C                                                                        HSD00780
      IFL1=0                                                             HSD00790
      IFL2=0                                                             HSD00800
   10 CONTINUE                                                           HSD00810
C                                                                        HSD00820
      READ(31,*) ID                                                      HSD00830
      IF(ID .EQ. 999) THEN                                               HSD00840
C     SOMETHING IS WRONG                                                 HSD00850
      WRITE(*,*) ' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'        HSD00860
      STOP ' ERROR - ALL DONE '                                          HSD00870
      END IF                                                             HSD00880
      IF(ID .EQ. NCP) THEN                                               HSD00890
      IFL1=1                                                             HSD00900
      END IF                                                             HSD00910
C                                                                        HSD00920
C     READ IN AND DISTRIBUTE                                             HSD00930
C                                                                        HSD00940
      IF(IFL1 .NE. 0) THEN                                               HSD00950
C                                                                        HSD00960
      READ(31,1001) (WP(I),I=1,ID)                                       HSD00970
      DO 2 I=1,ID                                                        HSD00980
      READ(31,1001) (BP(I,J),J=1,ID)                                     HSD00990
    2 CONTINUE                                                           HSD01000
C                                                                        HSD01010
      IF(IFL1 .EQ. 0) GO TO 10                                           HSD01020
      IF(IFL1 .EQ. 1) GO TO 11                                           HSD01030
C                                                                        HSD01040
      END IF                                                             HSD01050
C                                                                        HSD01060
      IF(IFL1 .EQ. 0) THEN                                               HSD01070
      READ(31,1001) (DUMMY(I),I=1,ID)                                    HSD01080
      DO 6 I=1,ID                                                        HSD01090
      READ(31,1001) (DUMMY(J),J=1,ID)                                    HSD01100
```

```
    6 CONTINUE                                                        HSD01110
      GO TO 10                                                        HSD01120
      END IF                                                          HSD01130
C                                                                     HSD01140
   11 CONTINUE                                                        HSD01150
C     WRITE THE MATRIXES                                              HSD01160
      IF(IPRC .EQ. 1) THEN                                            HSD01170
      WRITE(*,*) ' WEIGHTS  '                                         HSD01180
      WRITE(*,1001) (WP(I),I=1,NCP)                                   HSD01190
      WRITE(*,*) ' COLLOCATION MATRIX (B)'                            HSD01200
      DO 13 I=1,NCP                                                   HSD01210
      WRITE(*,1001) (BP(I,J),J=1,NCP)                                 HSD01220
   13 CONTINUE                                                        HSD01230
      END IF                                                          HSD01240
C                                                                     HSD01250
 1001 FORMAT(4D20.12)                                                 HSD01260
C                                                                     HSD01270
      RETURN                                                          HSD01280
      END                                                             HSD01290
C-----------------------------------------                            HSD01300
      SUBROUTINE INIT                                                 HSD01310
C                                                                     HSD01320
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                             HSD01330
C                                                                     HSD01340
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                     HSD01350
      COMMON /COL/ NCP,WP(14),BP(14,14)                               HSD01360
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,                               HSD01370
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                    HSD01380
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                    HSD01390
      COMMON /VAR/ Y(15),NTOT                                         HSD01400
C                                                                     HSD01410
      NTOT=NCP+1                                                      HSD01420
C                                                                     HSD01430
C     INITIAL CONDITION FOR SOLID PHASE                               HSD01440
C                                                                     HSD01450
      DO 11 I=1,NTOT-1                                                HSD01460
      Y(I)=0.0D0                                                      HSD01470
   11 CONTINUE                                                        HSD01480
C                                                                     HSD01490
C     LIQUID PHASE                                                    HSD01500
C                                                                     HSD01510
      Y(NTOT)=1.0D0                                                   HSD01520
C                                                                     HSD01530
C     COMPUTE DEPENDENT PARAMETERS                                    HSD01540
C                                                                     HSD01550
      Q0=XK*C0**XN                                                    HSD01560
C                                                                     HSD01570
      CD=CCONC*Q0/C0                                                  HSD01580
C                                                                     HSD01590
      B1=XKF*RADP*C0                                                  HSD01600
      B2=DS*RHOP*Q0*1000.0D0                                          HSD01610
      BIOT=B1/B2                                                      HSD01620
C                                                                     HSD01630
      TFAC=DS/(RADP*RADP)                                             HSD01640
C                                                                     HSD01650
```

```
      IF(IPRI .EQ. 1) THEN                                              HSD01660
      WRITE(32,1001) CO,CCONC,CD                                        HSD01670
      WRITE(32,1004) DS                                                 HSD01680
      WRITE(32,1005) XKF                                                HSD01690
      WRITE(32,1006) BIOT                                               HSD01700
      WRITE(32,1007) RADP                                               HSD01710
      WRITE(32,1008) RHOP                                               HSD01720
      WRITE(32,1009) XK                                                 HSD01730
      WRITE(32,1010) XN                                                 HSD01740
      WRITE(32,1011) TFAC                                               HSD01750
C                                                                       HSD01760
C     CONTROL PARAMETER                                                 HSD01770
      WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL            HSD01780
       END IF                                                           HSD01790
C                                                                       HSD01800
C    FORMAT STATEMENTS                                                  HSD01810
C                                                                       HSD01820
 1001 FORMAT(2X,'CO    = ',E12.6,/,                                     HSD01830
     &2X,'CCONC = ',E12.6,/,                                            HSD01840
     &2X,'CD    = ',E12.6,/)                                            HSD01850
C                                                                       HSD01860
 1004 FORMAT(1X,'DS    = ',E12.5)                                       HSD01870
 1005 FORMAT(1X,'XKF   = ',E12.5)                                       HSD01880
 1006 FORMAT(1X,'BIOT  = ',E12.5)                                       HSD01890
 1007 FORMAT(1X,'RADP  = ',E12.5)                                       HSD01900
 1008 FORMAT(1X,'RHOP  = ',E12.5)                                       HSD01910
 1009 FORMAT(1X,'XK    = ',E12.5)                                       HSD01920
 1010 FORMAT(1X,'XN    = ',E12.5)                                       HSD01930
 1011 FORMAT(1X,'TFAC  = ',E12.5)                                       HSD01940
C                                                                       HSD01950
 1013 FORMAT(1X,'NTOT =',I4,/,                                          HSD01960
     & 1X,'TOL   =',E16.6,/,                                            HSD01970
     & 1X,'METH  =',I4,/,                                               HSD01980
     & 1X,'MITER =',I4,/,                                               HSD01990
     & 1X,'DTINIT =',E16.6,/,                                           HSD02000
     & 1X,'DTOUT =',E16.6,/,                                            HSD02010
     & 1X,'TFINAL =',E16.6,/,                                           HSD02020
     & 1X,'NULL')                                                       HSD02030
C                                                                       HSD02040
      RETURN                                                            HSD02050
      END                                                               HSD02060
C-----------------------------------------                              HSD02070
      SUBROUTINE CALCC                                                  HSD02080
C                                                                       HSD02090
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               HSD02100
C                                                                       HSD02110
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                       HSD02120
      COMMON /COL/ NCP,WP(14),BP(14,14)                                 HSD02130
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,                                 HSD02140
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                      HSD02150
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                      HSD02160
      COMMON /VAR/ Y(15),NTOT                                           HSD02170
C                                                                       HSD02180
      DIMENSION WK(390),IWK(29)                                         HSD02190
C                                                                       HSD02200
```

```
      EXTERNAL FCN,FCNJ                                                 HSD02210
C                                                                       HSD02220
      N=NTOT                                                            HSD02230
      HH=DTINIT                                                         HSD02240
      INDEX=1                                                           HSD02250
C                                                                       HSD02260
      T=0.0D0                                                           HSD02270
C                                                                       HSD02280
      ITRY=0                                                            HSD02290
      ITRYT=0                                                           HSD02300
      TPHYS=0.0D0                                                       HSD02310
      ITER=0                                                            HSD02320
C                                                                       HSD02330
      WRITE(*,2001) ITER,ITRY,T,TPHYS,Y(NTOT)                           HSD02340
      WRITE(32,*) ITER,ITRY,T,TPHYS,Y(NTOT)                             HSD02350
C                                                                       HSD02360
  100 CONTINUE                                                          HSD02370
C                                                                       HSD02380
      ITER=ITER+1                                                       HSD02390
      TEND=T+DTOUT*TFAC                                                 HSD02400
C                                                                       HSD02410
      ITRY=0                                                            HSD02420
      CALL DGEAR(N,FCN,FCNJ,T,HH,Y,TEND,                                HSD02430
     &TOL,METH,MITER,INDEX,IWK,WK,IER)                                  HSD02440
C                                                                       HSD02450
      ITRYT=ITRYT+ITRY                                                  HSD02460
      T=TEND                                                            HSD02470
      TPHYS=T/TFAC                                                      HSD02480
CC      WRITE(*,*) (Y(LL),LL=1,NCP)                                     HSD02490
      WRITE(*,2001) ITER,ITRY,T,TPHYS,Y(NTOT)                           HSD02500
C                                                                       HSD02510
CC      WRITE(32,*) (Y(LL),LL=1,NCP)                                    HSD02520
      WRITE(32,*) ITER,ITRY,T,TPHYS,Y(NTOT)                             HSD02530
      IF (T/TFAC .LT. TFINAL)  GO TO 100                                HSD02540
C                                                                       HSD02550
      WRITE(*,*) 'ITRYT = ',ITRYT                                       HSD02560
      WRITE(32,*) ' 999  999  999  999  999  999  999'                  HSD02570
 2001 FORMAT(1X,I4,I5,3E12.4)                                           HSD02580
      RETURN                                                            HSD02590
      END                                                               HSD02600
C-----------------------------------------------                        HSD02610
      SUBROUTINE FCNJ(N,T,Y,PD)                                         HSD02620
C                                                                       HSD02630
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               HSD02640
C                                                                       HSD02650
      DIMENSION Y(N),PD(N,N)                                            HSD02660
C                                                                       HSD02670
      RETURN                                                            HSD02680
      END                                                               HSD02690
C-----------------------------------------                              HSD02700
      SUBROUTINE FCN(N,T,Y,YPRIME)                                      HSD02710
C                                                                       HSD02720
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               HSD02730
C                                                                       HSD02740
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                       HSD02750
```

```
      COMMON /COL/ NCP,WP(14),BP(14,14)                                 HSD02760
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,                                 HSD02770
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                      HSD02780
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                      HSD02790
C                                                                       HSD02800
      DIMENSION Y(N),YPRIME(N)                                          HSD02810
      DIMENSION BB(14)                                                  HSD02820
C                                                                       HSD02830
      ITRY=ITRY+1                                                       HSD02840
C                                                                       HSD02850
      NTOT=N                                                            HSD02860
      KK=0                                                              HSD02870
      II=0                                                              HSD02880
C                                                                       HSD02890
      NICP=NCP-1                                                        HSD02900
C                                                                       HSD02910
      DO 30 J=1,NICP                                                    HSD02920
      BB(J)=0.0D0                                                       HSD02930
   30 CONTINUE                                                          HSD02940
      WW=0.0D0                                                          HSD02950
C                                                                       HSD02960
      DO 50 I=1,NICP                                                    HSD02970
      II=II+1                                                           HSD02980
      LL=0                                                              HSD02990
C                                                                       HSD03000
      DO 40 J=1,NCP                                                     HSD03010
      LL=LL+1                                                           HSD03020
      BB(I)=BB(I)+BP(I,J)*Y(LL)                                         HSD03030
   40 CONTINUE                                                          HSD03040
C                                                                       HSD03050
C    MASS BALANCE INSIDE PARTICLE (EXCEPT BOUNDARY)                     HSD03060
C                                                                       HSD03070
      YPRIME(II)=BB(I)                                                  HSD03080
C                                                                       HSD03090
      WW=WW+WP(I)*YPRIME(II)                                            HSD03100
   50 CONTINUE                                                          HSD03110
C                                                                       HSD03120
C     SOLID-LIQUID INTERFACE                                            HSD03130
C                                                                       HSD03140
      II=II+1                                                           HSD03150
CC      YPRIME(II) = ((BIOT*(Y(NTOT)-(Y(II)**(1.0D0/XN)))-WW)/          HSD03160
CC     &WP(NCP))                                                        HSD03170
C                                                                       HSD03180
      IGO=0                                                             HSD03190
C    HEAT EQ AT INTERFACE                                               HSD03200
      BSUM=0.0D0                                                        HSD03210
      DO 11 KKK=1,NCP                                                   HSD03220
      BSUM=BSUM+BP(NCP,KKK)*Y(KKK)                                      HSD03230
   11 CONTINUE                                                          HSD03240
C                                                                       HSD03250
      IF (IGO .EQ. 0) THEN                                              HSD03260
      IF(Y(II) .LT. 1.0D-15) THEN                                       HSD03270
CC      YPRIME(II) = ((BIOT*(Y(NTOT)-Y(II))-WW)/WP(NCP))                HSD03280
CC      YPRIME(II) = ((BIOT*(Y(NTOT)-0.0D0)-WW)/WP(NCP))                HSD03290
      YPRIME(II) = (((BIOT*(Y(NTOT)-0.0D0)-WW)/WP(NCP))+BSUM)*0.5HSD03300
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```
C                                                                       HSD03310
      ELSE                                                              HSD03320
      YPRIME(II) = (((BIOT*(Y(NTOT)-(Y(II)**(1.0D0/XN)))-WW)/           HSD03330
     &WP(NCP))+BSUM)*0.5D0                                              HSD03340
      END IF                                                            HSD03350
      END IF                                                            HSD03360
C                                                                       HSD03370
C     LIQUID PHASE MASS BALANCE                                         HSD03380
C                                                                       HSD03390
      YPRIME(NTOT)=-3.0D0*CD*(WW+                                       HSD03400
     &(YPRIME(II)*WP(NCP)))                                             HSD03410
C                                                                       HSD03420
      RETURN                                                            HSD03430
      END                                                               HSD03440
                                                                        HSD03450
                                                                        HSD03460
                                                                        HSD03470
                                                                        HSD03480
```

```
      PROGRAM SEARCH                                                    SHS00010
C                                                                       SHS00020
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               SHS00030
C                                                                       SHS00040
      COMMON /PAR1/ COV(10),CCONCV(10),RADPV(10),RHOPV(10),             SHS00050
     &PARV(4,10),NDPV(10),NDSET,IPS(4),ISCALE(4),TM(50,10),             SHS00060
     &YM(50,5,10),IDREP(10),NDPSV(10),YF(50,10)                         SHS00070
C                                                                       SHS00080
      CHARACTER*80 IFNAME(10)                                           SHS00090
C                                                                       SHS00100
      DIMENSION X(4),PARM(4),F(500),XJAC(500,4),XJTJ(10),WORK(103       SHS00110
C                                                                       SHS00120
      EXTERNAL FIND                                                     SHS00130
C                                                                       SHS00140
      IXJAC=500                                                         SHS00150
C                                                                       SHS00160
      OPEN(1,FILE='SHSDM.IN',STATUS='OLD')                              SHS00170
      OPEN(97,FILE='SHSDM.CTR',STATUS='OLD')                            SHS00180
C                                                                       SHS00190
C     INPUT SEARCH ROUTINE CONTROL PARAMETER                            SHS00200
      READ(97,*) NSIG                                                   SHS00210
      READ(97,*) EPS                                                    SHS00220
      READ(97,*) DELTA                                                  SHS00230
      READ(97,*) MAXFN                                                  SHS00240
      READ(97,*) IOPT                                                   SHS00250
      READ(97,*) PARM(1)                                                SHS00260
      READ(97,*) PARM(2)                                                SHS00270
      READ(97,*) PARM(3)                                                SHS00280
      READ(97,*) PARM(4)                                                SHS00290
C                                                                       SHS00300
      K=1                                                               SHS00310
  123 CONTINUE                                                          SHS00320
      READ(1,1000) IFNAME(K)                                            SHS00330
      IF(IFNAME(K) .NE. 'NULL') THEN                                    SHS00340
C     READ IN THE NAME OF THE DATA FILES                                SHS00350
      NDSET=K                                                           SHS00360
      K=K+1                                                             SHS00370
      GO TO 123                                                         SHS00380
      ELSE                                                              SHS00390
C     NAME OF OUTPUT FILE                                               SHS00400
      READ(1,1000) IFNAME(K)                                            SHS00410
      END IF                                                            SHS00420
C                                                                       SHS00430
      READ(1,*) (IPS(I),I=1,4)                                          SHS00440
C                                                                       SHS00450
      WRITE(*,*) ' YOUR INPUT ',NDSET, ' DATA FILE(S):'                 SHS00460
      DO 1 K=1,NDSET                                                    SHS00470
      WRITE(*,*) IFNAME(K)                                              SHS00480
    1 CONTINUE                                                          SHS00490
C                                                                       SHS00500
      WRITE(*,*) ' YOUR OUTPUT DATA FILE IS:'                           SHS00510
      WRITE(*,*) IFNAME(NDSET+1)                                        SHS00520
C                                                                       SHS00530
      IPSSUM=0                                                          SHS00540
      DO 2 K=1,4                                                        SHS00550
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```
      IF(IPS(K) .EQ. 1) THEN                                          SHS00560
      IPSSUM=IPSSUM+1                                                 SHS00570
      END IF                                                          SHS00580
    2 CONTINUE                                                        SHS00590
C                                                                     SHS00600
      DO 11 K=1,NDSET                                                 SHS00610
      OPEN(K,FILE=IFNAME(K),STATUS='OLD')                             SHS00620
      REWIND(K)                                                       SHS00630
      READ(K,*) NDPV(K),COV(K),IDREP(K)                               SHS00640
      DO 22 IP=1,NDPV(K)                                              SHS00650
      READ(K,*) TM(IP,K),(YM(IP,I,K),I=1,IDREP(K))                    SHS00660
   22 CONTINUE                                                        SHS00670
      READ(K,*) CCONCV(K)                                             SHS00680
      READ(K,*) RADPV(K)                                              SHS00690
      READ(K,*) RHOPV(K)                                              SHS00700
      READ(K,*) PARV(3,K)                                             SHS00710
      READ(K,*) PARV(4,K)                                             SHS00720
      READ(K,*) PARV(1,K)                                             SHS00730
      READ(K,*) PARV(2,K)                                             SHS00740
   11 CONTINUE                                                        SHS00750
C                                                                     SHS00760
C    COUNT TOTAL NUMBER OF DATA POINTS                                SHS00770
                                                                      SHS00780
      DO 94 II=1,NDSET                                                SHS00790
      NDPSV(II)=0                                                     SHS00800
      DO 95 IJ=1,NDPV(II)                                             SHS00810
      DO 95 JJ=1,IDREP(II)                                            SHS00820
      IF(YM(IJ,JJ,II) .LE. 1.1D0) THEN                                SHS00830
      NDPSV(II)=NDPSV(II)+1                                           SHS00840
      END IF                                                          SHS00850
   95 CONTINUE                                                        SHS00860
   94 CONTINUE                                                        SHS00870
C                                                                     SHS00880
      M1=0                                                            SHS00890
      DO 211 KK=1,NDSET                                               SHS00900
      M1=M1+NDPV(KK)                                                  SHS00910
  211 CONTINUE                                                        SHS00920
C                                                                     SHS00930
      M=0                                                             SHS00940
      DO 21 KK=1,NDSET                                                SHS00950
      M=M+NDPSV(KK)                                                   SHS00960
   21 CONTINUE                                                        SHS00970
C                                                                     SHS00980
      WRITE(*,*) ' TOTAL OBSERVATION TIMES :',M1                      SHS00990
      WRITE(*,*) ' TOTAL DATA POINTS :',M                             SHS01000
      WRITE(*,*) ' YOU ARE SEARCHING FOR ',IPSSUM ,' PARAMETERS'      SHS01010
C                                                                     SHS01020
      K=1                                                             SHS01030
      IF(IPS(1) .EQ. 1) THEN                                          SHS01040
      SCALE=DLOG10(PARV(1,1))                                         SHS01050
      IF(SCALE .GT. 0.0D0) THEN                                       SHS01060
      ISCALE(K)=DINT(SCALE)+1                                         SHS01070
      ELSE                                                            SHS01080
      ISCALE(K)=DINT(SCALE)                                           SHS01090
      END IF                                                          SHS01100
```

```
      X(K)=PARV(1,1)/(10.0D0**ISCALE(K))                                SHS01110
      XXX=X(K)*10.0D0**ISCALE(K)                                        SHS01120
      WRITE(*,*) ' PARAMETER # ',K,' == KF',' ;  IG: ',XXX              SHS01130
      K=K+1                                                             SHS01140
      END IF                                                            SHS01150
C                                                                       SHS01160
      IF(IPS(2) .EQ. 1) THEN                                            SHS01170
      SCALE=DLOG10(PARV(2,1))                                           SHS01180
      IF(SCALE .GT. 0.0D0) THEN                                         SHS01190
      ISCALE(K)=DINT(SCALE)+1                                           SHS01200
      ELSE                                                              SHS01210
      ISCALE(K)=DINT(SCALE)                                             SHS01220
      END IF                                                            SHS01230
      X(K)=PARV(2,1)/(10.0D0**ISCALE(K))                                SHS01240
      XXX=X(K)*10.0D0**ISCALE(K)                                        SHS01250
      WRITE(*,*) ' PARAMETER # ',K,' == DS',' ;  IG: ',XXX              SHS01260
      K=K+1                                                             SHS01270
      END IF                                                            SHS01280
C                                                                       SHS01290
      IF(IPS(3) .EQ. 1) THEN                                            SHS01300
      SCALE=DLOG10(PARV(3,1))                                           SHS01310
      IF(SCALE .GT. 0) THEN                                             SHS01320
      ISCALE(K)=DINT(SCALE)+1                                           SHS01330
      ELSE                                                              SHS01340
      ISCALE(K)=DINT(SCALE)                                             SHS01350
      END IF                                                            SHS01360
      X(K)=PARV(3,1)/(10.0D0**ISCALE(K))                                SHS01370
      XXX=X(K)*10.0D0**ISCALE(K)                                        SHS01380
      WRITE(*,*) ' PARAMETER # ',K,' == K',' ;  IG: ',XXX               SHS01390
      K=K+1                                                             SHS01400
      END IF                                                            SHS01410
C                                                                       SHS01420
      IF(IPS(4) .EQ. 1) THEN                                            SHS01430
      SCALE=DLOG10(PARV(4,1))                                           SHS01440
      IF(SCALE .GT. 0) THEN                                             SHS01450
      ISCALE(K)=DINT(SCALE)+1                                           SHS01460
      ELSE                                                              SHS01470
      ISCALE(K)=DINT(SCALE)                                             SHS01480
      END IF                                                            SHS01490
      X(K)=PARV(4,1)/(10.0D0**ISCALE(K))                                SHS01500
      XXX=X(K)*10.0D0**ISCALE(K)                                        SHS01510
      WRITE(*,*) ' PARAMETER # ',K,' == N',' ;  IG: ',XXX               SHS01520
      END IF                                                            SHS01530
C                                                                       SHS01540
C     CALL TO THE SEARCH ROUTINE                                        SHS01550
C                                                                       SHS01560
      OPEN(NDSET+1,FILE=IFNAME(NDSET+1),STATUS='NEW')                   SHS01570
C                                                                       SHS01580
      N=IPSSUM                                                          SHS01590
C                                                                       SHS01600
      CALL ZXSSQ(FIND,M,N,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,X,             SHS01610
     &SSQ,F,XJAC,IXJAC,XJTJ,WORK,INFER,IER)                             SHS01620
C                                                                       SHS01630
C     OUTPUT TO DATA FILE                                               SHS01640
      DO 111 K=1,NDSET                                                  SHS01650
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      DO 222 IP=1,NDPV(K)                                              SHS01660
      WRITE(NDSET+1,1001) TM(IP,K),(YM(IP,II,K),II=1,IDREP(K)),        SHS01670
     &YF(IP,K)                                                         SHS01680
  222 CONTINUE                                                         SHS01690
  111 CONTINUE                                                         SHS01700
C                                                                      SHS01710
 1000 FORMAT(A)                                                        SHS01720
 1001 FORMAT(2X,6E16.6)                                                SHS01730
C                                                                      SHS01740
      STOP '  ALL DONE'                                               SHS01750
      END                                                              SHS01760
C-------------------------------------------------------              SHS01770
      SUBROUTINE FIND(X,M,N,F)                                         SHS01780
C                                                                      SHS01790
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                              SHS01800
C                                                                      SHS01810
      COMMON /PAR1/ COV(10),CCONCV(10),RADPV(10),RHOPV(10),            SHS01820
     &PARV(4,10),NDPV(10),NDSET,IPS(4),ISCALE(4),TM(50,10),            SHS01830
     &YM(50,5,10),IDREP(10),NDPSV(10),YF(50,10)                        SHS01840
C                                                                      SHS01850
      DIMENSION X(4),F(500)                                            SHS01860
      DIMENSION TT(50),YY(50)                                          SHS01870
      DIMENSION SSQV(10),XXV(4)                                        SHS01880
C                                                                      SHS01890
      DATA ICALL /0/                                                   SHS01900
C                                                                      SHS01910
      ICALL=ICALL+1                                                    SHS01920
C                                                                      SHS01930
C     IF TROBLE LIMIT THE PARAMETERS TO                                SHS01940
C     THE SMALLEST VALUE OF 10D-30                                     SHS01950
      DO 1 KK=1,N                                                      SHS01960
      X(KK)=DMAX1(X(KK),1.0D-30)                                       SHS01970
    1 CONTINUE                                                         SHS01980
C                                                                      SHS01990
      WRITE(*,1000) ICALL,(X(KK)*10.0D0**ISCALE(KK),KK=1,N)            SHS02000
      WRITE(NDSET+1,1000) ICALL,(X(KK)*10.0D0**ISCALE(KK),KK=1,N)      SHS02010
C                                                                      SHS02020
      LL=1                                                             SHS02030
      DO 111 K=1,NDSET                                                 SHS02040
C     LOAD TIME VECTOR FOR THE K'S DATA SET                            SHS02050
      DO 2 L=1,NDPV(K)                                                 SHS02060
      TT(L)=TM(L,K)                                                    SHS02070
    2 CONTINUE                                                         SHS02080
C                                                                      SHS02090
      DO 9 II=1,4                                                      SHS02100
      IF(IPS(II) .EQ. 1) THEN                                          SHS02110
      XXV(II)=X(II)*10.0D0**ISCALE(II)                                 SHS02120
      ELSE                                                             SHS02130
      XXV(II)=PARV(II,K)                                               SHS02140
      END IF                                                           SHS02150
    9 CONTINUE                                                         SHS02160
C                                                                      SHS02170
      CALL HSDM(COV(K),CCONCV(K),RADPV(K),RHOPV(K),XXV(1),XXV(2)       SHS02180
     &,XXV(3),XXV(4),TT,YY,NDPV(K))                                    SHS02190
C                                                                      SHS02200
```

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C    SET UP THE RESIDUAL VECTOR F                                    SHS02210
C                                                                    SHS02220
      SSQV(K)=0.0D0                                                  SHS02230
      DO 3 L=1,NDPV(K)                                               SHS02240
      YF(L,K)=YY(L)                                                  SHS02250
      DO 4 ID=1,IDREP(K)                                             SHS02260
      IF(YM(L,ID,K) .LE. 1.1D0) THEN                                 SHS02270
      F(LL)=(YM(L,ID,K)-YY(L))/YM(L,ID,K)                            SHS02280
CC      WRITE(*,*) LL,F(LL)                                          SHS02290
      SSQV(K)=SSQV(K)+F(LL)*F(LL)                                    SHS02300
      LL=LL+1                                                        SHS02310
      END IF                                                         SHS02320
    4 CONTINUE                                                       SHS02330
    3 CONTINUE                                                       SHS02340
  111 CONTINUE                                                       SHS02350
C                                                                    SHS02360
      WRITE(*,1000) ICALL,(SSQV(I),I=1,NDSET)                        SHS02370
      WRITE(NDSET+1,1000) ICALL,(SSQV(I),I=1,NDSET)                  SHS02380
 1000 FORMAT(1X,I5,6E16.6)                                           SHS02390
C                                                                    SHS02400
      RETURN                                                         SHS02410
      END                                                            SHS02420
C-------------------------------------------------------------       SHS02430
      SUBROUTINE HSDM(CO1,CCONC1,RADP1,RHOP1,XKF1,DS1,XK1,XN1,       SHS02440
     &TT,YY,NDP)                                                     SHS02450
C                                                                    SHS02460
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                            SHS02470
C                                                                    SHS02480
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                    SHS02490
      COMMON /COL/ NCP,WP(14),BP(14,14)                              SHS02500
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,                              SHS02510
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                   SHS02520
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                   SHS02530
      COMMON /VAR/ Y(15),NTOT                                        SHS02540
C                                                                    SHS02550
      DIMENSION TT(1),YY(1)                                          SHS02560
C                                                                    SHS02570
      DATA ICALL /0/                                                 SHS02580
C                                                                    SHS02590
      OPEN(31,FILE='PART.COL',STATUS='OLD')                          SHS02600
      OPEN(32,FILE='SHSDM.OUT',STATUS='NEW')                         SHS02610
C                                                                    SHS02620
      IF(ICALL .EQ. 0) THEN                                          SHS02630
C                                                                    SHS02640
      CALL INPUT                                                     SHS02650
C                                                                    SHS02660
      CALL INCOL                                                     SHS02670
C                                                                    SHS02680
      ICALL=1                                                        SHS02690
      END IF                                                         SHS02700
C                                                                    SHS02710
      CO=CO1                                                         SHS02720
      CCONC=CCONC1                                                   SHS02730
      RADP=RADP1                                                     SHS02740
      RHOP=RHOP1                                                     SHS02750
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      XK=XK1                                                          SHS02760
      XN=XN1                                                          SHS02770
      XKF=XKF1                                                        SHS02780
      DS=DS1                                                          SHS02790
C                                                                     SHS02800
      CALL INIT                                                       SHS02810
C                                                                     SHS02820
      CALL CALCC(TT,YY,NDP)                                           SHS02830
C                                                                     SHS02840
      RETURN                                                          SHS02850
C                                                                     SHS02860
      END                                                             SHS02870
C-------------------------------------------------------------        SHS02880
      SUBROUTINE INPUT                                                SHS02890
C                                                                     SHS02900
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                             SHS02910
C                                                                     SHS02920
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                     SHS02930
      COMMON /COL/ NCP,WP(14),BP(14,14)                               SHS02940
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,                               SHS02950
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                    SHS02960
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                    SHS02970
      COMMON /VAR/ Y(15),NTOT                                         SHS02980
C                                                                     SHS02990
CC      OPEN(30,FILE='SHSDM.CTR',STATUS='OLD')                        SHS03000
CC      REWIND (30)                                                   SHS03010
      READ(97,*) IPRC,IPRI,IPRO                                       SHS03020
C                                                                     SHS03030
C    PHYSICAL PARAMETER                                               SHS03040
C                                                                     SHS03050
CC      READ(30,*) CO                                                 SHS03060
CC      READ(30,*) CCONC                                              SHS03070
CC      READ(30,*) DS                                                 SHS03080
CC      READ(30,*) XKF                                                SHS03090
CC      READ(30,*) XK                                                 SHS03100
CC      READ(30,*) XN                                                 SHS03110
CC      READ(30,*) RADP                                               SHS03120
CC      READ(30,*) RHOP                                               SHS03130
C                                                                     SHS03140
C     CONTROL PARAMETER                                               SHS03150
C                                                                     SHS03160
      READ(97,*) NCP                                                  SHS03170
      READ(97,*) TOL,METH,MITER                                       SHS03180
      READ(97,*) DTINIT                                               SHS03190
CC      READ(30,*) DTOUT                                              SHS03200
CC      READ(30,*) TFINAL                                             SHS03210
CC      READ(30,*) ITMAX                                              SHS03220
C                                                                     SHS03230
      CLOSE (30)                                                      SHS03240
C                                                                     SHS03250
      RETURN                                                          SHS03260
      END                                                             SHS03270
C-------------------------------------------------------------        SHS03280
      SUBROUTINE INCOL                                                SHS03290
C                                                                     SHS03300
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      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                                SHS03310
C                                                                        SHS03320
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                        SHS03330
      COMMON /COL/ NCP,WP(14),BP(14,14)                                  SHS03340
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,                                  SHS03350
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                       SHS03360
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                       SHS03370
      COMMON /VAR/ Y(15),NTOT                                            SHS03380
C                                                                        SHS03390
      DIMENSION IDL(2)                                                   SHS03400
      DIMENSION DUMMY(14)                                                SHS03410
C                                                                        SHS03420
      IFL1=0                                                             SHS03430
      IFL2=0                                                             SHS03440
   10 CONTINUE                                                           SHS03450
C                                                                        SHS03460
      READ(31,*) ID                                                      SHS03470
      IF(ID .EQ. 999) THEN                                               SHS03480
C     SOMETHING IS WRONG                                                 SHS03490
      WRITE(*,*) ' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'        SHS03500
      STOP ' ERROR - ALL DONE '                                          SHS03510
      END IF                                                             SHS03520
      IF(ID .EQ. NCP) THEN                                               SHS03530
      IFL1=1                                                             SHS03540
      END IF                                                             SHS03550
C                                                                        SHS03560
C     READ IN AND DISTRIBUTE                                             SHS03570
C                                                                        SHS03580
      IF(IFL1 .NE. 0) THEN                                               SHS03590
C                                                                        SHS03600
      READ(31,1001) (WP(I),I=1,ID)                                       SHS03610
      DO 2 I=1,ID                                                        SHS03620
      READ(31,1001) (BP(I,J),J=1,ID)                                     SHS03630
    2 CONTINUE                                                           SHS03640
C                                                                        SHS03650
      IF(IFL1 .EQ. 0) GO TO 10                                           SHS03660
      IF(IFL1 .EQ. 1) GO TO 11                                           SHS03670
C                                                                        SHS03680
      END IF                                                             SHS03690
C                                                                        SHS03700
      IF(IFL1 .EQ. 0) THEN                                               SHS03710
      READ(31,1001) (DUMMY(I),I=1,ID)                                    SHS03720
      DO 6 I=1,ID                                                        SHS03730
      READ(31,1001) (DUMMY(J),J=1,ID)                                    SHS03740
    6 CONTINUE                                                           SHS03750
      GO TO 10                                                           SHS03760
      END IF                                                             SHS03770
C                                                                        SHS03780
   11 CONTINUE                                                           SHS03790
C     WRITE THE MATRIXES                                                 SHS03800
      IF(IPRC .EQ. 1) THEN                                               SHS03810
      WRITE(*,*) ' WEIGHTS  '                                            SHS03820
      WRITE(*,1001) (WP(I),I=1,NCP)                                      SHS03830
      WRITE(*,*) ' COLLOCATION MATRIX (B)'                               SHS03840
      DO 13 I=1,NCP                                                      SHS03850
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      WRITE(*,1001) (BP(I,J),J=1,NCP)                                   SHS03860
   13 CONTINUE                                                          SHS03870
      END IF                                                            SHS03880
C                                                                       SHS03890
 1001 FORMAT(4D20.12)                                                   SHS03900
C                                                                       SHS03910
      RETURN                                                            SHS03920
      END                                                               SHS03930
C-----------------------------------------                              SHS03940
      SUBROUTINE INIT                                                   SHS03950
C                                                                       SHS03960
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               SHS03970
C                                                                       SHS03980
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                       SHS03990
      COMMON /COL/ NCP,WP(14),BP(14,14)                                 SHS04000
      COMMON /PARM/ C0,Q0,CCONC,DS,XKF,                                 SHS04010
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                      SHS04020
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                      SHS04030
      COMMON /VAR/ Y(15),NTOT                                           SHS04040
C                                                                       SHS04050
      NTOT=NCP+1                                                        SHS04060
C                                                                       SHS04070
C     INITIAL CONDITION FOR SOLID PHASE                                 SHS04080
C                                                                       SHS04090
      DO 11 I=1,NTOT-1                                                  SHS04100
      Y(I)=0.0D0                                                        SHS04110
   11 CONTINUE                                                          SHS04120
C                                                                       SHS04130
C     LIQUID PHASE                                                      SHS04140
C                                                                       SHS04150
      Y(NTOT)=1.0D0                                                     SHS04160
C                                                                       SHS04170
C     COMPUTE DEPENDENT PARAMETERS                                      SHS04180
C                                                                       SHS04190
      Q0=XK*C0**XN                                                      SHS04200
C                                                                       SHS04210
      CD=CCONC*Q0/C0                                                    SHS04220
C                                                                       SHS04230
      B1=XKF*RADP*C0                                                    SHS04240
      B2=DS*RHOP*Q0*1000.0D0                                            SHS04250
      BIOT=B1/B2                                                        SHS04260
C                                                                       SHS04270
      TFAC=DS/(RADP*RADP)                                               SHS04280
C                                                                       SHS04290
      IF(IPRI .EQ. 1) THEN                                              SHS04300
      WRITE(32,1001) C0,CCONC,CD                                        SHS04310
      WRITE(32,1004) DS                                                 SHS04320
      WRITE(32,1005) XKF                                                SHS04330
      WRITE(32,1006) BIOT                                               SHS04340
      WRITE(32,1007) RADP                                               SHS04350
      WRITE(32,1008) RHOP                                               SHS04360
      WRITE(32,1009) XK                                                 SHS04370
      WRITE(32,1010) XN                                                 SHS04380
      WRITE(32,1011) TFAC                                               SHS04390
C                                                                       SHS04400
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C     CONTROL PARAMETER                                                 SHS04410
      WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL            SHS04420
       END IF                                                           SHS04430
C                                                                       SHS04440
C    FORMAT STATEMENTS                                                  SHS04450
C                                                                       SHS04460
 1001 FORMAT(2X,'CO    = ',E12.6,/,                                     SHS04470
     &2X,'CCONC = ',E12.6,/,                                            SHS04480
     &2X,'CD    = ',E12.6,/)                                            SHS04490
C                                                                       SHS04500
 1004 FORMAT(1X,'DS    = ',E12.5)                                       SHS04510
 1005 FORMAT(1X,'XKF   = ',E12.5)                                       SHS04520
 1006 FORMAT(1X,'BIOT  = ',E12.5)                                       SHS04530
 1007 FORMAT(1X,'RADP  = ',E12.5)                                       SHS04540
 1008 FORMAT(1X,'RHOP  = ',E12.5)                                       SHS04550
 1009 FORMAT(1X,'XK    = ',E12.5)                                       SHS04560
 1010 FORMAT(1X,'XN    = ',E12.5)                                       SHS04570
 1011 FORMAT(1X,'TFAC  = ',E12.5)                                       SHS04580
C                                                                       SHS04590
 1013 FORMAT(1X,'NTOT =',I4,/,                                          SHS04600
     & 1X,'TOL   =',E16.6,/,                                            SHS04610
     & 1X,'METH  =',I4,/,                                               SHS04620
     & 1X,'MITER =',I4,/,                                               SHS04630
     & 1X,'DTINIT =',E16.6,/,                                           SHS04640
     & 1X,'DTOUT =',E16.6,/,                                            SHS04650
     & 1X,'TFINAL =',E16.6,/,                                           SHS04660
     & 1X,'NULL')                                                       SHS04670
C                                                                       SHS04680
      RETURN                                                            SHS04690
      END                                                               SHS04700
C-----------------------------------------                              SHS04710
      SUBROUTINE CALCC(TT,YY,NDP)                                       SHS04720
C                                                                       SHS04730
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               SHS04740
C                                                                       SHS04750
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                       SHS04760
      COMMON /COL/ NCP,WP(14),BP(14,14)                                 SHS04770
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,                                 SHS04780
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                      SHS04790
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                      SHS04800
      COMMON /VAR/ Y(15),NTOT                                           SHS04810
C                                                                       SHS04820
      DIMENSION TT(1),YY(1)                                             SHS04830
C                                                                       SHS04840
      DIMENSION WK(390),IWK(29)                                         SHS04850
C                                                                       SHS04860
      EXTERNAL FCN,FCNJ                                                 SHS04870
C                                                                       SHS04880
CC      DO 98 KK=1,NDP                                                  SHS04890
CC      WRITE(*,*) KK,TT(KK)                                            SHS04900
CC   98 CONTINUE                                                        SHS04910
C                                                                       SHS04920
      N=NTOT                                                            SHS04930
      HH=DTINIT                                                         SHS04940
      INDEX=1                                                           SHS04950
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C                                                                       SHS04960
      T=0.0D0                                                           SHS04970
C                                                                       SHS04980
      ITRY=0                                                            SHS04990
      ITRYT=0                                                           SHS05000
      TPHYS=0.0D0                                                       SHS05010
      ITER=0                                                            SHS05020
C                                                                       SHS05030
CC      WRITE(*,*) ITER,ITRY,T,TPHYS,Y(NTOT)                            SHS05040
CC      WRITE(32,*) ITER,ITRY,T,TPHYS,Y(NTOT)                           SHS05050
C                                                                       SHS05060
      DO 100 IP=1,NDP                                                   SHS05070
C                                                                       SHS05080
      ITER=ITER+1                                                       SHS05090
      TEND=TT(IP)*TFAC                                                  SHS05100
C                                                                       SHS05110
      IF(TT(IP) .LE. 0.01) THEN                                         SHS05120
      YY(IP)=1.0D0                                                      SHS05130
      GO TO 100                                                         SHS05140
      END IF                                                            SHS05150
C                                                                       SHS05160
      ITRY=0                                                            SHS05170
      CALL DGEAR(N,FCN,FCNJ,T,HH,Y,TEND,                                SHS05180
     &TOL,METH,MITER,INDEX,IWK,WK,IER)                                  SHS05190
C                                                                       SHS05200
      ITRYT=ITRYT+ITRY                                                  SHS05210
      T=TEND                                                            SHS05220
      TPHYS=T/TFAC                                                      SHS05230
CC      WRITE(*,*) (Y(LL),LL=1,NCP)                                     SHS05240
      WRITE(*,1000) ITER,ITRY,T,TPHYS,Y(NTOT)                           SHS05250
 1000 FORMAT(1X,I5,I5,3E16.6)                                           SHS05260
C                                                                       SHS05270
CC      WRITE(32,*) (Y(LL),LL=1,NCP)                                    SHS05280
CC      WRITE(32,*) ITER,ITRY,T,TPHYS,Y(NTOT)                           SHS05290
CC      IF (T/TFAC .LT. TFINAL)  GO TO 100                              SHS05300
C                                                                       SHS05310
      YY(IP)=Y(NTOT)                                                    SHS05320
C                                                                       SHS05330
  100 CONTINUE                                                          SHS05340
C                                                                       SHS05350
CC      WRITE(*,*) 'ITRYT = ',ITRYT                                     SHS05360
CC      WRITE(32,*) ' 999  999  999  999  999  999  999'                SHS05370
      RETURN                                                            SHS05380
      END                                                               SHS05390
C-----------------------------------------------                        SHS05400
      SUBROUTINE FCNJ(N,T,Y,PD)                                         SHS05410
C                                                                       SHS05420
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               SHS05430
C                                                                       SHS05440
      DIMENSION Y(N),PD(N,N)                                            SHS05450
C                                                                       SHS05460
      RETURN                                                            SHS05470
      END                                                               SHS05480
C---------------------------------------                                SHS05490
      SUBROUTINE FCN(N,T,Y,YPRIME)                                      SHS05500
```

```
C                                                                       SHS05510
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               SHS05520
C                                                                       SHS05530
      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER                       SHS05540
      COMMON /COL/ NCP,WP(14),BP(14,14)                                 SHS05550
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,                                 SHS05560
     &XK,XN,RADP,RHOP,BIOT,CD,TFAC                                      SHS05570
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY                      SHS05580
C                                                                       SHS05590
      DIMENSION Y(N),YPRIME(N)                                          SHS05600
      DIMENSION BB(14)                                                  SHS05610
C                                                                       SHS05620
      ITRY=ITRY+1                                                       SHS05630
C                                                                       SHS05640
      NTOT=N                                                            SHS05650
      KK=0                                                              SHS05660
      II=0                                                              SHS05670
C                                                                       SHS05680
      NICP=NCP-1                                                        SHS05690
C                                                                       SHS05700
      DO 30 J=1,NICP                                                    SHS05710
      BB(J)=0.0D0                                                       SHS05720
   30 CONTINUE                                                          SHS05730
      WW=0.0D0                                                          SHS05740
C                                                                       SHS05750
      DO 50 I=1,NICP                                                    SHS05760
      II=II+1                                                           SHS05770
      LL=0                                                              SHS05780
C                                                                       SHS05790
      DO 40 J=1,NCP                                                     SHS05800
      LL=LL+1                                                           SHS05810
      BB(I)=BB(I)+BP(I,J)*Y(LL)                                         SHS05820
   40 CONTINUE                                                          SHS05830
C                                                                       SHS05840
C    MASS BALANCE INSIDE PARTICLE (EXCEPT BOUNDARY)                     SHS05850
C                                                                       SHS05860
      YPRIME(II)=BB(I)                                                  SHS05870
C                                                                       SHS05880
      WW=WW+WP(I)*YPRIME(II)                                            SHS05890
   50 CONTINUE                                                          SHS05900
C                                                                       SHS05910
C     SOLID-LIQUID INTERFACE                                            SHS05920
C                                                                       SHS05930
      II=II+1                                                           SHS05940
CC      YPRIME(II) = ((BIOT*(Y(NTOT)-(Y(II)**(1.0D0/XN)))-WW)/          SHS05950
CC     &WP(NCP))                                                        SHS05960
C                                                                       SHS05970
      IGO=0                                                             SHS05980
C    HEAT EQ AT INTERFACE                                               SHS05990
      BSUM=0.0D0                                                        SHS06000
      DO 11 KKK=1,NCP                                                   SHS06010
      BSUM=BSUM+BP(NCP,KKK)*Y(KKK)                                      SHS06020
   11 CONTINUE                                                          SHS06030
C                                                                       SHS06040
      IF (IGO .EQ. 0) THEN                                              SHS06050
```

```
      IF(Y(II) .LT. 1.0D-10) THEN                                       SHS06060
CC      YPRIME(II) = ((BIOT*(Y(NTOT)-Y(II))-WW)/WP(NCP))                SHS06070
CC      YPRIME(II) = ((BIOT*(Y(NTOT)-0.0D0)-WW)/WP(NCP))                SHS06080
      YPRIME(II) = (((BIOT*(Y(NTOT)-0.0D0)-WW)/WP(NCP))+BSUM)*0.5SHS06090
C                                                                       SHS06100
      ELSE                                                              SHS06110
CC      YPRIME(II) = (((BIOT*(Y(NTOT)-(Y(II)**(1.0D0/XN)))-WW)/         SHS06120
      XS=DEXP((1.0D0/XN)*DLOG(Y(II)))                                   SHS06130
CC      WRITE(*,*) ' XS ,Y(II)',XS,Y(II)                                SHS06140
      YPRIME(II) = (((BIOT*(Y(NTOT)-XS)-WW)/                            SHS06150
     &WP(NCP))+BSUM)*0.5D0                                              SHS06160
      END IF                                                            SHS06170
      END IF                                                            SHS06180
C                                                                       SHS06190
C     LIQUID PHASE MASS BALANCE                                         SHS06200
C                                                                       SHS06210
      YPRIME(NTOT)=-3.0D0*CD*(WW+                                       SHS06220
     &(YPRIME(II)*WP(NCP)))                                             SHS06230
C                                                                       SHS06240
      RETURN                                                            SHS06250
      END                                                               SHS06260
                                                                        SHS06270
                                                                        SHS06280
                                                                        SHS06290
                                                                        SHS06300
```

APPENDIX A.3

COMPUTER PROGRAMS FOR THE PREDICTION OF THE BREAKTHROUGH CURVES IN COLUMNS

```
Subject: Program - Info

Program Plug

-Description-

 This program predicts the effluent concentration profile for
a single or multicomponent fixed bed adsorber. The mechanism incorporated
in the mathematical model include:
 1-Plug Fow Homogeneous Surface Diffusion Model - Intraparticle
   transport described by Surface Diffusion only.
 2- Film transfer resistance at adsorbent surface.
       3- Local equilibrium exists at adsorbent surface.
 4- Multicomponent equilibrium described by the ideal adsorbed
    solution theory (IAST).
 5- The single solute isotherms are represented by the Freundlich
    equation or the Myers equation.
The system of the partial differential equations are solved in the progra
by converting them to a system of ordinary differential equations using
the orthogonal collocation then integrated by the GEAR method using the
subroutine 'DGEAR'.
**************************************************************************
* The program is supplied in two files. One is called Plug.for    *
* and the other is Dgearb.for.                                           *
*########################################################################*
* The file PLUG.FOR contains the following subroutines:                  *
*                                                                        *
* 1- Subroutine ORTHOG (N): This subroutine combines the collocation     *
*    constants and the dimensionless groups calculated in the main       *
*    program to save computation time.                                   *
* 2- Subroutine DIFFUN (N,T,YO,YDOT): This subroutine is called by       *
*    Dgear in the integration process. It receives the values of the     *
*    dependent variables from Dgear and returns the values of the        *
*    derivatives of the dependent variables. This continues until the    *
*    total run time is met.                                              *
* 3- Subroutine OBJFUN(TD,NDATA,NP): This subroutine calculates the      *
*    standard deviation between the predicted and experimental data,     *
*    if any is given. If no data is given this subroutine is ignored.    *
* 4- Function CINF (I,T): This function calculates the influent conc.    *
*    to the column for each component at each time interval T. If no     *
*    varying influent data is given this subroutine is ignored.          *
* 5- Subroutine PEDERV (N,T,Y,PD,NO): This subroutine is a dummy         *
*    subprogram used by GEAR.                                            *
* 6- Subroutine MYERS(CO,QO,J): This subroutine is a search routine      *
*    for calculating the equilibrium solid phase concentration using     *
*    the Myers isotherm equation for the single solute system.           *
*########################################################################*
*The file DGEARB.FOR contains the subroutines utilizing the Gear method *
*for solving a system of first order ordinary differential equations. It*
*also contains the subroutines for IAST calculations using the Myers    *
*isotherm equation up to THREE COMPONENT MIXTURE.  The main subroutines *
*for the IAST calculations are:                                         *
*$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$*
*IASTMC : IAST calculation if the liquid phase concentrations are known.*
*Here initial guesses for the adsorbed phase are made.                  *
```

```
*          If program stalls change these initial guesses.              *
*IASTMQ: IAST calculation if the solid phase concentrations are known.  *
*Here initial guesses for the liquid phase concentrations are made.     *
*                         If program stalls change these initial        *
*guesses.                                                               *
*$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$*
**************************************************************************
*-COMPILING THE PROGRAM-                                                 *
*First compile the file GEARB.FOR without linking to the fortran        *
*library, then compile the file PLUG.FOR with linking to the fortran    *
*library + DGEARB.OBJ                                                   *
**************************************************************************
*-EXECUTION-                                                             *
*To execute the program three sets of data must be supplied:            *
*A- The data file PLUG.DAT. This file can have any other name but the   *
*   format must be according to the PLUG.DAT. Some notes are written at *
*   the top of the file and must be followed.  Hereunder please find    *
*   some additional notes:                                              *
*   1- If experimental Ds and Kf values are supplied put under PSDFR 0.0*
*      otherwise PSDFR has to be specified  in order to use emperical   *
*      correlations for Ds and Kf. In that case any values given for Ds *
*      and Kf won't be used for model calculations.                     *
*   2- The following constants are not used if experimental Kf and Ds   *
*      are given and PSDFR set to 0.0 :                                 *
*      a- temperature                                                   *
*      b- water density                                                 *
*      c- water viscosity                                               *
*      d- particle porosity                                             *
*      however the above constants are important if emperical correla-  *
*      tions for Ds and Kf are to be used.                              *
*   3- If NCOL = 1 print out of collocation constants are given under   *
*      unit 6, for any other value of NCOL no print out constants are   *
*      given.                                                           *
*   4- If the number of varying influent concentration is assigned a    *
*      zero no read out will be taken from the varying influent conc.   *
*      values table.                                                    *
*B- The collocation constants. These are read from two files. The files *
*   under the name of AUCOL are the axial matrices and the files under  *
*   the name COL are the radial matrices. The number given after AUCOL  *
*   or COL is the number of axial or radial collocation points. The     *
*   following files are supplied for the axial matrices:
*   AUCOL6.TXT, AUCOL7.TXT, AUCOL8.TXT, AUCOL10.TXT, AUCOL12.TXT,       *
*   AUCOL14.TXT AND AUCOL18.TXT                                         *
*   The following files are supplied for the radial matrices :          *
*   COL2.TXT, COL3.TXT, COL4.TXT, COL5.TXT, COL7.TXT                    *
* The program also writes to two output files:                          *
* UNIT 6 - used if NCOL is set to 01 for printing out collocation       *
* constants and any messages given by the program to the user.          *
* UNIT 7 - used for the output produced by the program.                 *
**************************************************************************
* - PROGRAM DIMENSIONS -                                                *
*The program has been dimensioned for 3 components. Any number of      *
*components up to 3 may be used. The program is also dimensioned for   *
*using up to 7 RADIAL collocation points and up to 18 AXIAL collocation *
*points. It is also dimensioned to solve up to 147 equations where the  *
```

```
* number of equations is given by:                                    *
*    NEQ = ((NC+1)*MC)-1)*NCOMP                                       *
* where:                                                              *
*    NEQ =number of equations                                         *
*     NC = number of radial collocation points                        *
*     MC = number of axial collocation points                         *
*  NCOMP = number of components                                       *
* If more than 147 equations are to be solved the following arrays    *
* in the file DGEARB.FOR must be redimensioned according to the value of*
* NEQ:                                                                *
* YMAX, ERROR, SAVE1, SAVE2 AND IPIV                                  *
* Also the following array must be dimensioned according to NEQ squared:*
* PW.                                                                 *
* Hence when choosing the number of radial and axial points make sure *
* that NEQ does not exceed 147 otherwise redimensiong of DGEARB.for has *
* to be made.                                                         *
* The program is also dimensioned to read up to 75 points of varying  *
* influent concentrations and 900 TIME STEPS.                         *
***********************************************************************
```

```
*******PLUG FLOW HOMOGENEOUS SURFACE DIFFUSION Model DATA FILE**********
N.B.:1-FOR INTEGER NUMBERS USE TWO FIGURES i.e. IF THE NUMBER IS 0 PUT 0
     2-FOR THE E-SPECIFICATION FORMAT USE FIVE DECIMAL PLACES
     3-IF THE FREUNDLICH ISOTHERM IS TO BE USED FOR MODEL CAL. PUT UNDER
     4-IF THE MYERS ISOTHERM IS TO BE USED FOR MODEL CAL. PUT UNDER ISO
     5-WHEN REPLACING A NUMBER IN THE FILE MAKE SURE THE ASTERISKS ARE B
       IN THEIR PLACE.
*************BREAKTHROUGH CURVE FOR THE BINARY MIXTURE*****************
------------------------------------------------------------------------
****COLLOCATION MATRICES FILES AUCOL=AXIAL, COL=RADIAL
AUCOL10 TXT*COL2 TXT   ***
------------------------------------------------------------------------
  Iso      *   Ncomp   *part.radius* particle  *   PSDFR    ***
-----------*-----------*cm          * porosity  *-----------***
00         *03         *0.154      *0.641      *0.0         ***
------------------------------------------------------------------------
  TEMP     *W.DENSITY  *VICOSITY   *APP.DENSITY*LENGTH     *FLOW RATE  *
   C       * g/cu cm   *g/cm.sec   *g/cu cm    *cm         *ml/min     *
 23.01     *0.9994     *0.01206    *0.74       * 20.54     *104.7198   *
------------------------------------------------------------------------
  DIA.     * MASS OF C.*ERROR CRIT.*TIME STEP  *   NCOL    *T.STEP AD. *
  cm       * grams     *-----------* min       * ----------*-----------*
4.0        *120.0      *0.00001    *0.10000E-05*02         *60.0       *
------------------------------------------------------------------------
TOTAL TIME *START.TIME *1STOUT.TIME*NO.TIME CHANGED*
min        * min       * min       *-----------*
2.88000E+04*0.0        *0.1        *02         *
------------------------------------------------------------------------
NO. VARYING INF. CONC. *  NO. OF COLUMN DATA   *
19                     *00                     *
------------------------------------------------------------------------
COMPONENT1 *COMPONENT2 *COMPONENT3    ***
   DCE     * TCE       *PCE           ***
------------------------------------------------------------------------
Adsorbates molecular weights
   XWT(I)  *---------- * --------- ***
96.94      *131.39     *165.83     ***
------------------------------------------------------------------------
   DS(I)   * sq cm/sec *  -------- ***
8.62920E-08*5.27500E-08*3.34970E-08***
------------------------------------------------------------------------
   KF(I)   * cm/sec    *  ------- ***
0.36667E-02*0.43383E-02*0.35667E-02***
------------------------------------------------------------------------
MOLAL VOL  *gmol/cu cm * -------   ***
118.4      *140.6      *166.5      ***
------------------------------------------------------------------------
   CBO(I)  *mg/L       * -------   ***
1000.0     *1000.0     *1000.0     ***
------------------------------------------------------------------------
                                  n
Freundlich K, (mmol/g)/(mmol/L)
Fr.(K(I))  *--------   *--------   ***
30.544     *159.81     * 341.3014  ***
------------------------------------------------------------------------
```

```
   n(I)     *--------   *---------  ***
0.587       *0.482      *0.516     ***
-------------------------------------------------------------------------
MY. H(L/g) *------     * -------   ***
1.81809E+02*2.42612E+02*1.58575E+03***
-------------------------------------------------------------------------
                    -p
MY. K       *(mmol/g)  * -------   ***
3.553       *2.1016     *3.6443    ***
-------------------------------------------------------------------------
MY. P       * --------  *-------    ***
0.808       *1.2496     *0.7476    ***
-------------------------------------------------------------------------
vector of output time values at which a new time step will be used, min.
   TIE(I)  * ------    *--------  *---------  *-------   *------     *
0.0         *6.00000E+03*          *          *          *           *
-------------------------------------------------------------------------
vector of new time steps for integration, min.
   TINC(I) * ------    *-------   * -----     * ------   *------     *
 60.0       *300.0     *          *           *          *           *
-------------------------------------------------------------------------
-------------------------------------------------------------------------
VARYING INFLUENT CONC. VALUES
TIME        *COMPONENT1 *COMPONENT2 * COMPONENT3*
min         * mg/L      * mg/L      * mg/L      *
-----------*-----------*-----------*-----------*-------------------------
-----------*-----------*-----------*-----------*-------------------------
0.0         *97.759     *100.475    *0.0        *
780.0       *97.04      *100.575    *0.0        *
1320.0      *96.567     *99.841     *0.0        *
2170.0      *95.482     *99.187     *0.0        *
2770.2      *95.47      *98.184     *0.0        *
3640.2      *96.849     *98.474     *0.0        *
4180.2      *96.961     *100.836    *0.0        *
5080.2      *94.69      *99.104     *0.0        *
6460.2      *96.15      *99.5       *0.0        *
7669.1      *96.139     *97.243     *0.0        *
7669.2      *96.139     *97.243     *86.363     *
8628.0      *95.769     *96.656     *86.304     *
9108.0      *97.084     *99.006     *88.06      *
9888.0      *95.941     *96.764     *88.323     *
10728.0     *96.293     *98.701     *88.389     *
11328.0     *95.135     *97.515     *86.342     *
11928.0     *95.598     *104.44     *95.011     *
12948.0     *97.786     *102.606    *90.963     *
14388.0     *96.453     *105.116    *94.453     *
-------------------------------------------------------------------------
*************************************************************************
```

```
CC   SUBJECT: PROGRAM - PLUG.FOR                                          PLU00010
      CC                                                                  PLU00020
      CC       PROGRAM PLUG                                               PLU00030
      C          PLUG FLOW HOMOGENEOUS SURFACE DIFFUSION MODEL            PLU00040
      C                                                                   PLU00050
      C....declaration block                                              PLU00060
      C                                                                   PLU00070
            IMPLICIT DOUBLE PRECISION (A-H,O-Z)                           PLU00080
            DOUBLE PRECISION KF(3),L                                      PLU00090
            CHARACTER*25 CHAR(3),FILEIN,FILEOUT,AUCOL,COL                 PLU00100
            CHARACTER*80 TITLE                                            PLU00110
            DIMENSION YO(400),TDATA(75),VB(3),DS(3),                      PLU00120
           +          BIS(3),TIE(3),TINC(3),XWT(3),DIFL(3),SC(3)          PLU00130
            COMMON/BLOCKA/DGS(3),ST(3),EDS(3),BR(7,7)                     PLU00140
            COMMON/BLOCKB/YM(3),XNI(3),XN(3),WR(7),AZ(18,18),A1(3),A2(3)PLU00150
           +QE(3),XK(3),A3(3)                                             PLU00160
            COMMON/BLOCKC/FMIN(3),TP(900),CP(3,900),CD(3,75),CINT(3,75) PLU00170
            COMMON/BLOCKD/CIN(3,75),TIN(75)                               PLU00180
            COMMON MC,NC,NCOMP,N1,DGT,NIN,ISO,CBO(3)                      PLU00190
            DATA INDEX/1/, MF/22/, NSTEPS/900/                            PLU00200
            WRITE(*,*) 'PLUG DATA'                                        PLU00210
            READ(*,2) FILEIN                                              PLU00220
            OPEN(4,FILE=FILEIN,STATUS='OLD')                              PLU00230
            WRITE(*,*) ' OUT DATA'                                        PLU00240
            READ(*,2) FILEOUT                                             PLU00250
            OPEN(7,FILE=FILEOUT,STATUS='NEW')                             PLU00260
      C                                                                   PLU00270
      C.....read in data from DATA FILE                                   PLU00280
      C                                                                   PLU00290
            READ(4,173) TITLE                                             PLU00300
            READ(4,174) AUCOL,COL                                         PLU00310
            READ(4,175) ISO,NCOMP,RAD,EPOR,PSDFR                         PLU00320
            READ(4,176) TEMP,DW,VW,RHOP,L,FLRT                            PLU00330
            READ(4,177) DIA,WT,EPS,DHO,NCOL,DSTEP                         PLU00340
            READ(4,178) DTOL,DTO,DOUT,NM                                  PLU00350
            READ(4,179) NIN,NDATA                                         PLU00360
            READ(4,180) (CHAR(I), I = 1,NCOMP)                            PLU00370
            READ(4,181) (XWT(I), I = 1,NCOMP)                             PLU00380
            READ(4,182) (DS(I), I = 1,NCOMP)                              PLU00390
            READ(4,182) (KF(I),I=1,NCOMP)                                 PLU00400
            READ(4,182) (VB(I), I = 1,NCOMP)                              PLU00410
            READ(4,182) (CBO(I), I = 1,NCOMP)                             PLU00420
            READ(4,183) (XK(I), I = 1,NCOMP)                              PLU00430
            READ(4,182) (XN(I), I = 1,NCOMP)                              PLU00440
            READ(4,182) (A1(I), I=1,NCOMP)                                PLU00450
            READ(4,181) (A2(I),I=1,NCOMP)                                 PLU00460
            READ(4,182) (A3(I),I=1,NCOMP)                                 PLU00470
            READ(4,187) (TIE(I), I = 1 , NM)                              PLU00480
            READ(4,176) (TINC(I), I = 1 , NM)                             PLU00490
            READ(4,184)                                                   PLU00500
            IF (NIN .EQ. 0) GO TO 812                                     PLU00510
            DO 1 J = 1,NIN                                                PLU00520
               READ(4,185) TIN(J), (CIN(I,J), I = 1,NCOMP)                PLU00530
          1 CONTINUE                                                      PLU00540
        812   IF (NDATA .EQ. 0) GO TO 813                                 PLU00550
```

```
      DO 3 J = 1,NDATA                                                  PLU00560
         READ(4,185) TDATA(J), (CD(I,J), I = 1,NCOMP)                   PLU00570
    3 CONTINUE                                                          PLU00580
C                                                                       PLU00590
C.....read in collocation constants                                     PLU00600
C                                                                       PLU00610
813   OPEN(2,FILE=AUCOL,STATUS='OLD')                                   PLU00620
      OPEN(3,FILE=COL,STATUS='OLD')                                     PLU00630
      READ(3,*) NC                                                      PLU00640
      READ(3,101) (WR(J),J = 1,NC)                                      PLU00650
      DO 5 I = 1, NC                                                    PLU00660
         READ(3,101) (BR(I,J),J = 1,NC)                                 PLU00670
    5 CONTINUE                                                          PLU00680
      READ(2,*) MC                                                      PLU00690
      DO 10 I = 1,MC                                                    PLU00700
         READ(2,101) (AZ(I,J),J = 1,MC)                                 PLU00710
   10 CONTINUE                                                          PLU00720
      NEQ = (((NC + 1)*MC) - 1)*NCOMP                                   PLU00730
C                                                                       PLU00740
C.....print out collocation constants if NCOL = 1                       PLU00750
C.....otherwise skip to statement number 25                             PLU00760
C                                                                       PLU00770
      IF ( NCOL .NE. 1) GO TO 25                                        PLU00780
      WRITE(*,*) ' '                                                    PLU00790
      WRITE(*,*) 'RADIAL W VECTOR'                                      PLU00800
      WRITE(*,102) (WR(J),J=1,NC)                                       PLU00810
      WRITE(*,*) ' '                                                    PLU00820
      WRITE(*,*) 'RADIAL B MATRIX'                                      PLU00830
      DO 15 I = 1,NC                                                    PLU00840
         WRITE(*,102) (BR(I,J),J = 1,NC)                                PLU00850
   15 CONTINUE                                                          PLU00860
      WRITE(*,*) ' '                                                    PLU00870
      WRITE(*,*) 'AXIAL A MATRIX'                                       PLU00880
      DO 20 I = 1,MC                                                    PLU00890
         WRITE(*,102) (AZ(I,J),J = 1,MC)                                PLU00900
   20 CONTINUE                                                          PLU00910
C                                                                       PLU00920
C                                                                       PLU00930
C.....calculate the fixed-bed parameters                                PLU00940
C                                                                       PLU00950
25    DO 212, I = 1, NCOMP                                              PLU00960
         CBO(I) = CBO(I)/XWT(I)                                         PLU00970
212   CONTINUE                                                          PLU00980
      AREA = 3.141592654D0*DIA*DIA/4.0D0                                PLU00990
      BEDVOL = L*AREA                                                   PLU01000
      EBED = 1.0D0 - WT/(BEDVOL*RHOP)                                   PLU01010
      EBCT = BEDVOL/FLRT                                                PLU01020
      TAU = BEDVOL*EBED*60.0D0/FLRT                                     PLU01030
      SF = .24542387D0*FLRT/AREA                                        PLU01040
      VS = FLRT/(60.0D0*AREA)                                           PLU01050
      IF(PSDFR.EQ.0.0D0) GOTO 69                                        PLU01060
      RE = (2.0D0*RAD*VS*DW)/(EBED*VW)                                  PLU01070
69    DO 68, I = 1 , NCOMP                                              PLU01080
      IF(PSDFR.LE.0.0D0) THEN                                           PLU01090
      PSDFR=0.0D0                                                       PLU01100
```

```
      GOTO 68                                                          PLU01110
      ELSE                                                             PLU01120
      DIFL(I) = 13.26D-05/(((VW*100.0D0)**1.14D0)*(VB(I)**5.89D-01)PLU01130
      SC(I) = VW/(DW*DIFL(I))                                          PLU01140
      END IF                                                           PLU01150
      IF (KF(I).LE.0.0D0) THEN                                         PLU01160
      KF(I) = (2.4D0*VS)/((RE**.66D0)*(SC(I)**.58D0))                  PLU01170
      ENDIF                                                            PLU01180
      IF (PSDFR.LE.0.0D0) THEN                                         PLU01190
      PSDFR = 0.0D0                                                    PLU01200
      GO TO 68                                                         PLU01210
      ELSE                                                             PLU01220
      DS(I) = (EPOR*DIFL(I)*CBO(I)*PSDFR)/(1.0D+03*RHOP*XK(I)*CBO(PLU01230
     +(I))                                                             PLU01240
      ENDIF                                                            PLU01250
68    CONTINUE                                                         PLU01260
C                                                                      PLU01270
C.....print out fixed bed parameters                                   PLU01280
C                                                                      PLU01290
      WRITE(7,143)                                                     PLU01300
      WRITE(*,143)                                                     PLU01310
      IF(ISO.EQ.0) THEN                                                PLU01320
      WRITE(7,188)                                                     PLU01330
      WRITE(*,188)                                                     PLU01340
      ELSE                                                             PLU01350
      WRITE(7,189)                                                     PLU01360
      WRITE(*,189)                                                     PLU01370
      END IF                                                           PLU01380
      WRITE(7,103) NC,MC,NEQ,RAD,WT,RHOP,EPOR,L,EBED,DIA,SF,TAU.EBPLU01390
      WRITE(7,1003)DHO,DOUT,RE,TEMP,DW,VW,PSDFR                        PLU01400
      WRITE(*,103) NC,MC,NEQ,RAD,WT,RHOP,EPOR,L,EBED,DIA,SF,TAU,EBPLU01410
      WRITE(*,1003)DHO,DOUT,RE,TEMP,DW,VW,PSDFR                        PLU01420
C                                                                      PLU01430
C.....calculate and print out dimensionless groups                     PLU01440
C                                                                      PLU01450
      QTE=0.0D0                                                        PLU01460
      IF(ISO.EQ.0) THEN                                                PLU01470
      DO 30 I = 1,NCOMP                                                PLU01480
         QE(I) = XK(I)*CBO(I)**XN(I)                                   PLU01490
         QTE   = QTE + QE(I)                                           PLU01500
30    CONTINUE                                                         PLU01510
       ELSE                                                            PLU01520
       IF(NCOMP.EQ.1) THEN                                             PLU01530
       CALL MYERS(CBO(1),QE(1),1)                                      PLU01540
       QTE=QE(1)                                                       PLU01550
       ELSE                                                            PLU01560
       IF (NCOMP.EQ.2) THEN                                            PLU01570
      CALL IASTMC(CBO,QE,A1,A2,A3,2)                                   PLU01580
      QTE=QE(1)+QE(2)                                                  PLU01590
      ELSE                                                             PLU01600
      CALL IASTMC(CBO,QE,A1,A2,A3,3)                                   PLU01610
      QTE=QE(1)+QE(2)+QE(3)                                            PLU01620
      END IF                                                           PLU01630
      END IF                                                           PLU01640
      END IF                                                           PLU01650
```

```
      DO 31 I=1,NCOMP                                                   PLU01660
         DGS(I) = (RHOP*QE(I)*(1.0D0 - EBED)*1000.0D0)/(EBED*CBO(I      PLU01670
         EDS(I) = DS(I)*DGS(I)*TAU/(RAD**2.0D0)                         PLU01680
         ST(I)  = KF(I)*(1.0D0 - EBED)*TAU/(EBED*RAD)                   PLU01690
         BIS(I) = ST(I)/EDS(I)                                          PLU01700
         XNI(I) = 1.0D0/XN(I)                                           PLU01710
         WRITE(7,104) CHAR(I),VB(I),XWT(I),CBO(I),XK(I),XN(I),DIFL      PLU01720
     +               KF(I),DS(I),ST(I),DGS(I),BIS(I),EDS(I),SC(I)       PLU01730
         WRITE(*,104) CHAR(I),VB(I),XWT(I),CBO(I),XK(I),XN(I),DIFL      PLU01740
     +               KF(I),DS(I),ST(I),DGS(I),BIS(I),EDS(I),SC(I)       PLU01750
         WRITE(7,190) A1(I),A2(I),A3(I)                                 PLU01760
         WRITE(*,190) A1(I),A2(I),A3(I)                                 PLU01770
   31 CONTINUE                                                          PLU01780
      WRITE(7,141)                                                      PLU01790
      WRITE(*,141)                                                      PLU01800
      WRITE(7,142) (I,CHAR(I), I = 1, NCOMP)                            PLU01810
      WRITE(*,142) (I,CHAR(I), I = 1, NCOMP)                            PLU01820
      WRITE(7,106) (I,I, I = 1 , NCOMP)                                 PLU01830
      WRITE(*,106) (I,I, I = 1 , NCOMP)                                 PLU01840
C                                                                       PLU01850
C.....total solute dist. parameter and bed volumes fed to column        PLU01860
C                                                                       PLU01870
      DGT = 0.0D0                                                       PLU01880
      DO 33 I = 1,NCOMP                                                 PLU01890
      DGT = DGT + DGS(I)                                                PLU01900
   33 CONTINUE                                                          PLU01910
      BVF = EBED*DGT                                                    PLU01920
C                                                                       PLU01930
C.....calculate equilibrium adsorbent phase concentration fraction      PLU01940
C                                                                       PLU01950
      DO 35 I = 1,NCOMP                                                 PLU01960
         YM(I) = QE(I)/QTE                                              PLU01970
   35 CONTINUE                                                          PLU01980
C                                                                       PLU01990
C.....call subroutine ORTHOG to combine collocation constants           PLU02000
C.....and dimensionless groups and to determine total number            PLU02010
C.....of differential equations being solved for by GEAR                PLU02020
C                                                                       PLU02030
      CALL ORTHOG ( N )                                                 PLU02040
C                                                                       PLU02050
C.....convert independent variables to dimensionless form               PLU02060
C                                                                       PLU02070
      TCONV = 60.0D0/(TAU*(DGT + 1.0D0))                                PLU02080
      TSTEP = DSTEP*TCONV                                               PLU02090
      TTOL  = DTOL*TCONV                                                PLU02100
      TOUT  = DOUT*TCONV                                                PLU02110
      HO    = DHO*TCONV                                                 PLU02120
      TO    = DTO*TCONV                                                 PLU02130
      DO 40 I = 1,NM                                                    PLU02140
         TIE(I)  = TIE(I)*TCONV                                         PLU02150
         TINC(I) = TINC(I)*TCONV                                        PLU02160
   40 CONTINUE                                                          PLU02170
C                                                                       PLU02180
C.....convert influent and experimental data to dimensionless form      PLU02190
C                                                                       PLU02200
```

```
      DO 50 J = 1,NDATA                                                 PLU02210
         TDATA(J) = TDATA(J)*TCONV                                      PLU02220
         DO 45 I = 1,NCOMP                                              PLU02230
            CD(I,J) = CD(I,J)/(CBO(I)*XWT(I))                           PLU02240
   45    CONTINUE                                                       PLU02250
   50 CONTINUE                                                          PLU02260
      DO 60 J = 1,NIN                                                   PLU02270
         TIN(J) = TIN(J)*TCONV                                          PLU02280
         DO 55 I = 1,NCOMP                                              PLU02290
            CIN(I,J) = CIN(I,J)/(CBO(I)*XWT(I))                         PLU02300
   55    CONTINUE                                                       PLU02310
   60 CONTINUE                                                          PLU02320
C                                                                       PLU02330
C.....Initialize dependent variables                                   PLU02340
C                                                                       PLU02350
      DO 65  I = 1, N                                                   PLU02360
         YO(I) = 0.0D0                                                  PLU02370
   65 CONTINUE                                                          PLU02380
C                                                                       PLU02390
C.....loop for calling GEAR to integrate differential equations        PLU02400
C                                                                       PLU02410
      ITP = 0                                                           PLU02420
      MA  = 1                                                           PLU02430
   70 ITP = ITP + 1                                                     PLU02440
      CALL DGEAR (N,TO,HO,YO,TOUT,EPS,MF,INDEX)                         PLU02450
      DO 75 I = 1,NCOMP                                                 PLU02460
         CP(I,ITP) = YO(N1*I)                                           PLU02470
   75 CONTINUE                                                          PLU02480
      TP(ITP) = TOUT                                                    PLU02490
      DOUT = TOUT/TCONV                                                 PLU02500
      WRITE(7,150) DOUT,TOUT*BVF,(YO(N1*I),I=1,NCOMP)                   PLU02510
      WRITE(*,150) DOUT,TOUT*BVF,(YO(N1*I),I=1,NCOMP)                   PLU02520
      IF ( ITP .LT. NSTEPS ) THEN                                       PLU02530
         IF ( TOUT .LT. TTOL ) THEN                                     PLU02540
            IF ( NM .NE. 0 .AND. TOUT .GE. TIE(MA) ) THEN               PLU02550
               TSTEP = TINC(MA)                                         PLU02560
               IF ( MA .EQ. NM ) THEN                                   PLU02570
                  NM = 0                                                PLU02580
               ELSE                                                     PLU02590
                  MA = MA + 1                                           PLU02600
               ENDIF                                                    PLU02610
            ENDIF                                                       PLU02620
            TOUT = TOUT + TSTEP                                         PLU02630
            IF ( TOUT .GT. TTOL ) TOUT = TTOL                           PLU02640
            GO TO 70                                                    PLU02650
         ENDIF                                                          PLU02660
      ELSE                                                              PLU02670
         IF ( TOUT .NE. TTOL ) THEN                                     PLU02680
            WRITE(6,108) NSTEPS, DOUT                                   PLU02690
            GO TO 90                                                    PLU02700
         ENDIF                                                          PLU02710
      ENDIF                                                             PLU02720
C                                                                       PLU02730
C.....if experimental data is given call OBJFUN to determine FMIN      PLU02740
C.....for each component and print out results                          PLU02750
```

```
C                                                                       PLU02760
      IF ( NDATA .EQ. 0 ) GO TO 90                                      PLU02770
      WRITE(7,109)                                                      PLU02780
      CALL OBJFUN ( TDATA,NDATA,ITP )                                   PLU02790
      DO 85 I = 1,NCOMP                                                 PLU02800
         WRITE(7,110) I                                                 PLU02810
         DO 80 J = 1,NDATA                                              PLU02820
            RES = ((CINT(I,J) - CD(I,J))/CD(I,J))*100.0D0               PLU02830
            WRITE(7,111) TDATA(J)/TCONV,CD(I,J),CINT(I,J),RES           PLU02840
   80    CONTINUE                                                       PLU02850
         WRITE(7,112) NDATA,FMIN(I)                                     PLU02860
   85 CONTINUE                                                          PLU02870
   90 STOP                                                              PLU02880
C                                                                       PLU02890
C                                                                       PLU02900
C                      ---- FORMAT BLOCK ----                          PLU02910
C                                                                       PLU02920
C                                                                       PLU02930
  2   FORMAT (A)                                                        PLU02940
  101 FORMAT(4F20.12)                                                   PLU02950
  102 FORMAT(1X,4F20.12)                                                PLU02960
  103 FORMAT(////                                                       PLU02970
     +' NUMBER OF RADIAL COLLOCATION POINTS, NC... = ',I15/             PLU02980
     +' NUMBER OF AXIAL COLLOCATION POINTS, MC.... = ',I15/             PLU02990
     +' TOTAL NO. OF DIFFERENTIAL EQUATIONS, NEQ.. = ',I15/             PLU03000
     +' RADIUS OF ADSORBENT PARTICLE, RAD (CM.)... = ',E15.5/           PLU03010
     +' MASS OF ADSORBENT, WT (GRAMS)............. = ',E15.5/           PLU03020
     +' APPARENT PARTICLE DENSITY, RHOP (GM/CM**3) = ',E15.5/           PLU03030
     +' VOID FRACTION OF THE CARBON. EPOR (DIM.) . = ',E15.5/           PLU03040
     +' LENGTH OF BED, L (CM.).................... = ',E15.5/           PLU03050
     +' VOID FRACTION OF BED, EBED (DIM.)......... = ',E15.5/           PLU03060
     +' DIAMETER OF FIXED-BED, DIA, (CM.) ........ = ',E15.5/           PLU03070
     +' SURFACE LOADING, SF (GPM/FT**2)........... = ',E15.5/           PLU03080
     +' PACKED BED CONTACT TIME. TAU (SEC.)....... = ',E15.5/           PLU03090
     +' EMPTY BED CONTACT TIME, EBCT (MIN.)....... = ',E15.5)           PLU03100
 1003  FORMAT(/                                                         PLU03110
     +' INITIAL INTEGRATION STEP, DHO (MIN.)...... = ',E15.5/           PLU03120
     +' INITIAL OUTPUT TIME, DOUT (MIN.).......... = ',E15.5/           PLU03130
     +' REYNOLDS NUMBER, RE, (DIM.) .............. = ',E15.5/           PLU03140
     +' TEMPERATURE OF WATER, TEMP, (DEG C.) ..... = ',E15.5/           PLU03150
     +' DENSITY OF WATER, DW, (GM/CU.CM) ......... = ',E15.5/           PLU03160
     +' VISCOSITY OF WATER, VW, (GM/CM-SEC) ...... = ',E15.5/           PLU03170
     +' PORE SURFACE DIFFUSION FLUX RATIO, PSDFR . = ',E15.5/)          PLU03180
  104 FORMAT(/' PARAMETERS FOR  ',A20/                                  PLU03190
     +  4X,'MOLAL VOLUME AT THE BOILING PT. (CU. CM./GMOL). = ',E1PLU03200
     +  4X,'MOLECULAR WEIGHT OF COMPOUND, XWT ............. = ',E1PLU03210
     +  4X,'INITIAL BULK LIQUID-PHASE CONC., (MMOL/L) ..... = ',E1PLU03220
     +  4X,'FREUNDLICH ISO. CAP., XK (MMOL/GM)/(L/MMOL)**XN = ',E1PLU03230
     +  4X,'FREUNDLICH ISOTHERM CONSTANT, XN, (DIM.) ...... = ',E1PLU03240
     +  4X,'LIQUID DIFFUSIVITY, DIFL, (SQ.CM./SEC)......... = ',E1PLU03250
     +  4X,'FILM TRANSFER COEFFICIENT, KF, (CM./SEC) ...... = ',E1PLU03260
     +  4X,'SURFACE DIFFUSION COEFFICIENT, DS, (SQ.CM./SEC) = ',E1PLU03270
     +  4X,'STANTON NUMBER, ST, (DIM.) ..................... = ',E1PLU03280
     +  4X,'SOLUTE DISTRIBUTION PARAMETER, DGS, (DIM.) .... = ',E1PLU03290
     +  4X,'BIOT NUMBER, BIS, (DIM.) ....................... = ',E1PLU03300
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     +  4X,'DIFFUSIVITY MODULUS, EDS, (DIM.) ..... = ',E1PLU03310
     +  4X,'SCHMIDT NUMBER, SC, (DIM.) ..... = ',E1PLU03320
   190 FORMAT(                                                    PLU03330
     +  4X,'MYERS ISOTHERM CONSTANT, H, (L/g)..... = ',E1PLU03340
     +  4X,'MYERS ISOTHERM CONSTANT, K, (MMOL/G)**-P.....= ',E1PLU03350
     +  4X,'MYERS ISOTHERM CONSTANT, P, (DIM.) .....= ',E1PLU03360
   141 FORMAT(///20X,'MODEL PREDICTION:',//,5X,'COMPONENT NUMBER ',PLU03370
     +'COMPOUND NAME'/)                                           PLU03380
   142 FORMAT(3(13X,I1,13X,A20,//))                               PLU03390
   106 FORMAT(1X,'TIME(min.)',3X,'BED VOLUMES',2X,3(2X,'C(',I1,')/CPLU03400
     +,')'))                                                      PLU03410
   150 FORMAT(1X,G12.5,2X,F10.1,4X,3(1X,F7.4))                    PLU03420
   108 FORMAT(' WARNING MORE STEPS ATTEMPTED THAN NSTEPS; TTOL NOT PLU03430
     +   'REACHED:'/6X,'NSTEPS = ',I3,', AND TOUT(min) = ',F10.6) PLU03440
   109 FORMAT(///15X,'MODEL PREDICTION vs DATA'//)                PLU03450
   110 FORMAT(/5X,'RESULTS FOR COMPONENT  :',A20///               PLU03460
     +       5X,'TIME(min.)',9X,'CONC(data)',5X,'CONC(pred)',    PLU03470
     +       4X,'RESIDUAL'/)                                     PLU03480
   111 FORMAT(5X,G12.3,5X,F9.4,5X,F9.4,6X,F10.5)                  PLU03490
   112 FORMAT(//5X,'FMIN BASED ON',I4,2X,'DATA POINTS:',          PLU03500
     +       3X,'FMIN = ',F10.6)                                 PLU03510
   143 FORMAT(/2X,'PLUG FLOW HOMOGENEOUS SURFACE DIFFUSION MODEL CAPLU03520
     +IONS')                                                      PLU03530
   173 FORMAT(///////,A80)                                        PLU03540
   174 FORMAT(//,2(A11,1X))                                       PLU03550
   175 FORMAT(///,2(I2,10X),3(G11.5,1X))                          PLU03560
   176 FORMAT(///,6(G11.5,1X))                                    PLU03570
   177 FORMAT(///,4(G11.5,1X),I2,10X,G11.5,1X)                    PLU03580
   178 FORMAT(///,3(G11.5,1X),I2,10X)                             PLU03590
   179 FORMAT(//,2(I2,22X))                                       PLU03600
   180 FORMAT(//,2(A11,1X),A14,1X)                                PLU03610
   181 FORMAT(///,3(G11.5,1X))                                    PLU03620
   182 FORMAT(//,3(G11.5,1X))                                     PLU03630
   183 FORMAT(////,3(G11.5,1X))                                   PLU03640
   184 FORMAT(//////)                                             PLU03650
   185 FORMAT(4(G11.5,1X))                                        PLU03660
   187 FORMAT(///,6(G11.5,1X))                                    PLU03670
   188 FORMAT(/'  MODEL CALCULATION USING THE FREUNDLICH EQUATION')PLU03680
   189 FORMAT(/'  MODEL CALCULATION USING THE MYERS EQUATION')    PLU03690
       END                                                        PLU03700
C                                                                 PLU03710
C                                                                 PLU03720
C                     ----------------------                      PLU03730
C                     | END OF MAIN PROGRAM |                     PLU03740
C                     ----------------------                      PLU03750
C                                                                 PLU03760
C                                                                 PLU03770
C                                                                 PLU03780
                      SUBROUTINE ORTHOG ( N )                     PLU03790
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                         PLU03800
      COMMON/BLOCKA/DGS(3),ST(3),EDS(3),BR(7,7)                   PLU03810
      COMMON/BLOCKE/STD(3),BEDS(3,7,7),DGI(3),MND,ND,MD,DG1       PLU03820
      COMMON MC,NC,NCOMP,N1,DGT,NIN,ISO,CBO(3)                    PLU03830
      DIMENSION EDD(3)                                            PLU03840
      ND  = NC - 1                                                PLU03850
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      MD  = MC - 1                                                      PLU03860
      MND = MC*ND                                                       PLU03870
      N1  = MND + MC + MD                                               PLU03880
      N   = N1*NCOMP                                                    PLU03890
      DO 30 I = 1,NCOMP                                                 PLU03900
         DG1    = 1.0D0 + DGT                                           PLU03910
         DGI(I) = 1.0D0/DGS(I)                                          PLU03920
         STD(I) = ST(I)*DG1                                             PLU03930
         EDD(I) = DG1*DGI(I)*EDS(I)                                     PLU03940
         DO 20 J = 1,ND                                                 PLU03950
            DO 10 K = 1,NC                                              PLU03960
               BEDS(I,J,K) = EDD(I)*BR(J,K)                             PLU03970
   10       CONTINUE                                                    PLU03980
   20    CONTINUE                                                       PLU03990
   30 CONTINUE                                                          PLU04000
      RETURN                                                            PLU04010
      END                                                               PLU04020
C                                                                       PLU04030
C                                                                       PLU04040
C                  ----------------------------                         PLU04050
C                  | END OF SUBROUTINE ORTHOG |                         PLU04060
C                  ----------------------------                         PLU04070
C                                                                       PLU04080
C                                                                       PLU04090
C                                                                       PLU04100
                SUBROUTINE DIFFUN ( N,T,YO,YDOT )                       PLU04110
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               PLU04120
      DIMENSION YO(1),YDOT(1),WW(18),AAU(18),BB(7,18),CS(3,18),         PLU04130
     +          Z1(3),ZZ(3),CSS(3),QO(3),CBS(3,18),Z(3,18)              PLU04140
      COMMON/BLOCKA/DGS(3),ST(3),EDS(3),BR(7,7)                         PLU04150
      COMMON/BLOCKB/YM(3),XNI(3),XN(3),WR(7),AZ(18,18),A1(3),A2(3)PLU04160
     +QE(3),XK(3),A3(3)                                                 PLU04170
      COMMON/BLOCKE/STD(3),BEDS(3,7,7),DGI(3),MND,ND,MD,DG1             PLU04180
      COMMON MC,NC,NCOMP,N1,DGT,NIN,ISO,CBO(3)                          PLU04190
      DO 15 K = 1,MC                                                    PLU04200
         QTE = 0.0D0                                                    PLU04210
         QTO = 0.0D0                                                    PLU04220
         KK = MND + K                                                   PLU04230
         IF(ISO.EQ.1) GOTO 12                                           PLU04240
         DO 5 I = 1,NCOMP                                               PLU04250
            II = KK + (I-1)*N1                                          PLU04260
            Z1(I) =YM(I)*YO(II)                                         PLU04270
            QTE = QTE + Z1(I)                                           PLU04280
            QTO = QTO + XNI(I)*Z1(I)                                    PLU04290
    5    CONTINUE                                                       PLU04300
         DO 10 I = 1,NCOMP                                              PLU04310
            IF ( QTE .LE. 0.0D0 .OR. QTO .LE. 0.0D0 ) THEN              PLU04320
               CS(I,K) = 0.0D0                                          PLU04330
            ELSE                                                        PLU04340
               Z1(I) = Z1(I)/QTE                                        PLU04350
               QO(I) = QTO*XN(I)/YM(I)                                  PLU04360
               IF ( XNI(I)*DLOG10(QO(I)) .LT. -20.0D0 ) THEN            PLU04370
                  CS(I,K) = 0.0D0                                       PLU04380
                  ELSE                                                  PLU04390
                  CS(I,K) = Z1(I) * QO(I)**XNI(I)                       PLU04400
```

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            ENDIF                                                          PLU04410
           ENDIF                                                           PLU04420
10          CONTINUE                                                       PLU04430
           GOTO 15                                                         PLU04440
12         DO 6 I=1,NCOMP                                                  PLU04450
           II=KK+(I-1)*N1                                                  PLU04460
           Z(I,K)=(QE(I))*YO(II)                                           PLU04470
6          CONTINUE                                                        PLU04480
           IF(Z(1,K).LE.0.0D0) THEN                                        PLU04490
           CS(1,K)=0.0D0                                                   PLU04500
           CS(2,K)=0.0D0                                                   PLU04510
           CS(3,K)=0.0D0                                                   PLU04520
           ELSE                                                            PLU04530
           IF(Z(2,K).LE.0.0D0.AND.Z(1,K).GT.0.0D0) THEN                    PLU04540
           CS(1,K)=((Z(1,K)/A1(1))*DEXP(A2(1)*Z(1,K)**A3(1)))/CBO(1)       PLU04550
           CS(2,K)=0.0D0                                                   PLU04560
           CS(3,K)=0.0D0                                                   PLU04570
           ELSE                                                            PLU04580
          IF(Z(1,K).GT.0.0D0.AND.Z(2,K).GT.0.0D0.AND.                      PLU04590
     +      Z(3,K).LE.0.0D0) THEN                                          PLU04600
          ZZ(1)=Z(1,K)                                                     PLU04610
          ZZ(2)=Z(2,K)                                                     PLU04620
         CALL IASTMQ(CSS,ZZ,A1,A2,A3,2)                                    PLU04630
         CS(1,K)=CSS(1)/CBO(1)                                             PLU04640
         CS(2,K)=CSS(2)/CBO(2)                                             PLU04650
         CS(3,K)=0.0D0                                                     PLU04660
          ELSE                                                             PLU04670
          ZZ(1)=Z(1,K)                                                     PLU04680
          ZZ(2)=Z(2,K)                                                     PLU04690
          ZZ(3)=Z(3,K)                                                     PLU04700
         CALL IASTMQ(CSS,ZZ,A1,A2,A3,3)                                    PLU04710
        CS(1,K)=CSS(1)/CBO(1)                                              PLU04720
        CS(2,K)=CSS(2)/CBO(2)                                              PLU04730
        CS(3,K)=CSS(3)/CBO(3)                                              PLU04740
        ENDIF                                                              PLU04750
         ENDIF                                                             PLU04760
        ENDIF                                                              PLU04770
15     CONTINUE                                                            PLU04780
       DO 60 I = 1,NCOMP                                                   PLU04790
          II = (I-1)*N1                                                    PLU04800
          III = II + MND                                                   PLU04810
          IIII = III + MD                                                  PLU04820
          IF ( NIN .EQ. 0 ) THEN                                           PLU04830
             CINFL = 1.0D0                                                 PLU04840
          ELSE                                                             PLU04850
             CINFL = CINF(I,T)                                             PLU04860
          ENDIF                                                            PLU04870
          DO 20 K = 2,MC                                                   PLU04880
          IF ( CS(I,K) .LE. 0.0D0 ) THEN                                   PLU04890
             CBS(I,K) = STD(I)*YO(IIII + K)                                PLU04900
          ELSE                                                             PLU04910
             CBS(I,K) = STD(I)*(YO(IIII + K) - CS(I,K))                    PLU04920
          ENDIF                                                            PLU04930
    20    CONTINUE                                                         PLU04940
          DO 40 K = 1,MC                                                   PLU04950
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            WW(K) = 0.0D0                                                PLU04960
            AAU(K) = 0.0D0                                               PLU04970
            KK = II + (K-1)*ND                                           PLU04980
            DO 30 J = 1,ND                                               PLU04990
               BB(J,K) = 0.0D0                                           PLU05000
               DO 25 M = 1,ND                                            PLU05010
                  BB(J,K) = BB(J,K) +BEDS(I,J,M)*YO(KK + M)              PLU05020
   25          CONTINUE                                                  PLU05030
               BB(J,K) = BB(J,K) +BEDS(I,J,NC)*YO(III + K)               PLU05040
   30          CONTINUE                                                  PLU05050
            DO 35 J = 1,ND                                               PLU05060
               JJ = KK + J                                               PLU05070
C                                                                        PLU05080
C.....Intraparticle Phase Mass Balance(excluding boundary)               PLU05090
C                                                                        PLU05100
               YDOT(JJ) = BB(J,K)                                        PLU05110
C                                                                        PLU05120
               WW(K) = WW(K) + WR(J)*YDOT(JJ)                            PLU05130
   35       CONTINUE                                                     PLU05140
   40    CONTINUE                                                        PLU05150
C                                                                        PLU05160
C.....Liquid-Solid Boundary Layer Mass Balance at column entrance        PLU05170
C                                                                        PLU05180
         YDOT(III+1) = (STD(I)*DGI(I)*(CINFL - CS(I,1))                  PLU05190
     +                 - WW(1)) / WR(NC)                                 PLU05200
C                                                                        PLU05210
         DO 55 K = 2,MC                                                  PLU05220
C                                                                        PLU05230
C.....Liquid-Solid Boundary Layer Mass Balance within column             PLU05240
C                                                                        PLU05250
            YDOT(III+K) = (CBS(I,K)*DGI(I) - WW(K)) / WR(NC)             PLU05260
C                                                                        PLU05270
            DO 50 M = 2,MC                                               PLU05280
               AAU(K) = AAU(K) + AZ(K,M)*YO(IIII+M)                      PLU05290
   50       CONTINUE                                                     PLU05300
C                                                                        PLU05310
C.....Liquid Phase Mass Balance                                          PLU05320
C                                                                        PLU05330
            YDOT(IIII+K) = -DG1*(AZ(K,1)*CINFL + AAU(K))                 PLU05340
     +                     - 3.0D0*CBS(I,K)                              PLU05350
C                                                                        PLU05360
   55    CONTINUE                                                        PLU05370
   60 CONTINUE                                                           PLU05380
      RETURN                                                             PLU05390
      END                                                                PLU05400
C                                                                        PLU05410
C                  ----------------------------                          PLU05420
C                  | END OF SUBROUTINE DIFFUN |                          PLU05430
C                  ----------------------------                          PLU05440
C                                                                        PLU05450
C                                                                        PLU05460
C                                                                        PLU05470
                SUBROUTINE OBJFUN ( TD,NDATA,NP )                        PLU05480
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                                PLU05490
      DIMENSION TD(1)                                                    PLU05500
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```
      COMMON/BLOCKC/ FMIN(3),TP(900),CP(3,900),CD(3,75),CINT(3,75)PLU05510
      COMMON MC,NC,NCOMP,N1,DGT,NIN,ISO,CBO(3)                   PLU05520
      DO 15 K = 1,NCOMP                                          PLU05530
         FMIN(K) = 0.0D0                                         PLU05540
         NP1 = NP - 1                                            PLU05550
         DO 10 J = 1,NDATA                                       PLU05560
            DO 5 I = 1,NP1                                       PLU05570
               IF( TD(J) .LT. TP(I) .OR. TD(J) .GT. TP(I+1) ) GO TPLU05580
               CAP = CP(K,I) + ((TD(J)-TP(I))/(TP(I+1)-TP(I)))*  PLU05590
     +               (CP(K,I+1)-CP(K,I))                         PLU05600
               CINT(K,J) = CAP                                   PLU05610
               FMIN(K) = FMIN(K) + ((CAP-CD(K,J))/CD(K,J))**2.0D0 PLU05620
               GO TO 10                                          PLU05630
    5       CONTINUE                                             PLU05640
   10    CONTINUE                                                PLU05650
   15 CONTINUE                                                   PLU05660
      DO 20 K = 1,NCOMP                                          PLU05670
         FMIN(K) = SQRT(FMIN(K)/FLOAT(NDATA-1))*100.0D0          PLU05680
   20 CONTINUE                                                   PLU05690
      RETURN                                                     PLU05700
      END                                                        PLU05710
C                                                                PLU05720
C                  ----------------------------                  PLU05730
C                  | END OF SUBROUTINE OBJFUN |                  PLU05740
C                  ----------------------------                  PLU05750
C                                                                PLU05760
C                                                                PLU05770
C                                                                PLU05780
                        FUNCTION CINF(I,T)                       PLU05790
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                        PLU05800
      COMMON/BLOCKD/CIN(3,75),TIN(75)                            PLU05810
      COMMON MC,NC,NCOMP,N1,DGT,NIN,ISO,CBO(3)                   PLU05820
      IF (T .LE. TIN(1) ) THEN                                   PLU05830
         CINF = 1.0D0                                            PLU05840
      ELSE IF (T .GE. TIN(NIN) ) THEN                            PLU05850
         CINF = CIN(I,NIN)                                       PLU05860
      ELSE                                                       PLU05870
         J = 1                                                   PLU05880
   10    J = J + 1                                               PLU05890
            IF(T .GE. TIN(J-1) .AND. T .LE. TIN(J) ) THEN        PLU05900
               CINF = CIN(I,J-1) + (CIN(I,J)-CIN(I,J-1))*(T-TIN(J-PLU05910
     +            (TIN(J)-TIN(J-1))                             PLU05920
            ELSE IF (J .LT. NIN ) THEN                           PLU05930
               GO TO 10                                          PLU05940
            ENDIF                                                PLU05950
         ENDIF                                                   PLU05960
      RETURN                                                     PLU05970
      END                                                        PLU05980
               SUBROUTINE PEDERV ( N,T,Y,PD,NO )                 PLU05990
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                        PLU06000
      RETURN                                                     PLU06010
      END                                                        PLU06020
C                                                                PLU06030
C                  ----------------------------                  PLU06040
C                  | END OF SUBROUTINE PEDERV |                  PLU06050
```

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C                    ----------------------------                    PLU06060
C                                                                    PLU06070
      SUBROUTINE MYERS(CO,QO,J)                                      PLU06080
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                            PLU06090
      COMMON MC,NC,NCOMP,N1,DGT,NIN,ISO,CBO(3)                       PLU06100
      COMMON/BLOCKB/YM(3),XNI(3),XN(3),WR(7),AZ(18,18),A1(3),A2(3)PLU06110
     +QE(3),XK(3),A3(3)                                              PLU06120
      DIMENSION A(3)                                                 PLU06130
      GOTO(20,30) J                                                  PLU06140
20    A(1)=A1(1)                                                     PLU06150
      A(2)=A2(1)                                                     PLU06160
      A(3)=A3(1)                                                     PLU06170
      GOTO 40                                                        PLU06180
30    A(1)=A1(2)                                                     PLU06190
      A(2)=A2(2)                                                     PLU06200
      A(3)=A3(2)                                                     PLU06210
40    EPSMY=1D-10                                                    PLU06220
      QEO=0.1                                                        PLU06230
      ITRY=0                                                         PLU06240
100   CONTINUE                                                       PLU06250
      ARG=A(2)*QEO**A(3)                                             PLU06260
      F=CO-QEO/A(1)*DEXP(ARG)                                        PLU06270
      FP=-(2.0D0*DEXP(ARG)+QEO*A(2)*A(3)*QEO**(A(3)-1.0))            PLU06280
      FSTEP=F/FP                                                     PLU06290
      IF(DABS(F/QEO).GT.EPSMY) THEN                                  PLU06300
      QE1=QEO-FSTEP                                                  PLU06310
      IF(QE1.LT.0.0) THEN                                            PLU06320
      QEO=QEO*0.5D0                                                  PLU06330
      GOTO 100                                                       PLU06340
      ENDIF                                                          PLU06350
      QEO=QE1                                                        PLU06360
      GOTO 100                                                       PLU06370
      ENDIF                                                          PLU06380
      QO=QE1                                                         PLU06390
      CE=QE1/A(1)*DEXP(A(2)*QE1**A(3))                               PLU06400
      RETURN                                                         PLU06410
      END                                                            PLU06420
```

```
      SUBROUTINE DGEAR (N,TO,HO,YO,TOUT,EPS,MF,INDEX)                    DGE00010
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                                DGE00020
      INTEGER N,MF,INDEX                                                 DGE00030
      INTEGER NC,MFC,KFLAG,JSTART,IPIV,NSQ,NQUSED,NSTEP,NFE,NJE          DGE00040
      INTEGER LOUT,I,NO,NHCUT,KGO                                        DGE00050
      DOUBLE PRECISION TO,HO,YO,TOUT,EPS                                 DGE00060
      DOUBLE PRECISION T,H,HMIN,HMAX,EPSC,UROUND,YMAX,ERROR,SAVE1        DGE00070
      DOUBLE PRECISION SAVE2,PW,EPSJ,HUSED                               DGE00080
      DOUBLE PRECISION Y,TOUTP,AYI,D                                     DGE00090
      COMMON /GEAR1/ T,H,HMIN,HMAX,EPSC,UROUND,NC,MFC,KFLAG,JSTARTDGE00100
      COMMON /GEAR2/ YMAX(147)                                           DGE00110
      COMMON /GEAR3/ ERROR(147)                                          DGE00120
      COMMON /GEAR4/ SAVE1(147)                                          DGE00130
      COMMON /GEAR5/ SAVE2(147)                                          DGE00140
      COMMON /GEAR6/ PW(21609)                                           DGE00150
      COMMON /GEAR7/ IPIV(147)                                           DGE00160
      COMMON /GEAR8/ EPSJ,NSQ                                            DGE00170
      COMMON /GEAR9/ HUSED,NQUSED,NSTEP,NFE,NJE                          DGE00180
      DIMENSION YO(N)                                                    DGE00190
      DIMENSION Y(147,6)                                                 DGE00200
      DATA LOUT/6/                                                       DGE00210
      IF (INDEX.EQ.0) GO TO 20                                           DGE00220
      IF (INDEX.EQ.2) GO TO 25                                           DGE00230
      IF (INDEX.EQ.-1) GO TO 30                                          DGE00240
      IF (INDEX.EQ.3) GO TO 40                                           DGE00250
      IF (INDEX.NE.1) GO TO 430                                          DGE00260
      IF (EPS.LE.0.0D0) GO TO 400                                        DGE00270
      IF (N.LE.0) GO TO 410                                              DGE00280
      IF ((TO-TOUT)*HO.GE.0.0D0) GO TO 420                               DGE00290
      UROUND=.10842D-18                                                  DGE00300
      DO 10 I=1,N                                                        DGE00310
        YMAX(I)=ABS(YO(I))                                               DGE00320
        IF (YMAX(I).EQ.0.0D0) YMAX(I)=1.0D0                              DGE00330
   10   Y(I,1)=YO(I)                                                     DGE00340
      NC=N                                                               DGE00350
      T=TO                                                               DGE00360
      H=HO                                                               DGE00370
      IF ((T+H).EQ.T) WRITE (LOUT,15)                                    DGE00380
      HMIN=ABS(HO)                                                       DGE00390
      HMAX=ABS(TO-TOUT)*10.0D0                                           DGE00400
      EPSC=EPS                                                           DGE00410
      MFC=MF                                                             DGE00420
      JSTART=0                                                           DGE00430
      NO=N                                                               DGE00440
      NSQ=NO*NO                                                          DGE00450
      EPSJ=SQRT(UROUND)                                                  DGE00460
      NHCUT=0                                                            DGE00470
      GO TO 50                                                           DGE00480
   20 HMAX=ABS(TOUT-TOUTP)*10.0D0                                        DGE00490
      GO TO 80                                                           DGE00500
   25 HMAX=ABS(TOUT-TOUTP)*10.0D0                                        DGE00510
      IF ((T-TOUT)*H.GE.0.0D0) GO TO 500                                 DGE00520
      GO TO 85                                                           DGE00530
C                                                                        DGE00540
   30 IF ((T-TOUT)*H.GE.0.0D0) GO TO 440                                 DGE00550
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```
      JSTART=-1                                                        DGE00560
      NC=N                                                             DGE00570
      EPSC=EPS                                                         DGE00580
      MFC=MF                                                           DGE00590
C                                                                      DGE00600
   40 IF ((T+H).EQ.T) WRITE (LOUT,15)                                  DGE00610
C                                                                      DGE00620
   50 CALL NGE002 (Y,NO)                                               DGE00630
C                                                                      DGE00640
      KGO=1-KFLAG                                                      DGE00650
      GO TO (60,100,200,300), KGO                                      DGE00660
C  KFLAG =   0,  -1,  -2,  -3                                          DGE00670
C                                                                      DGE00680
   60 CONTINUE                                                         DGE00690
      D=0.0D0                                                          DGE00700
      DO 70 I=1,N                                                      DGE00710
        AYI=ABS(Y(I,1))                                                DGE00720
        YMAX(I)=DMAX1(YMAX(I),AYI)                                     DGE00730
   70   D=D+(AYI/YMAX(I))**2                                           DGE00740
      D=D*(UROUND/EPS)**2                                              DGE00750
      IF (D.GT.FLOAT(N)) GO TO 250                                     DGE00760
      IF (INDEX.EQ.3) GO TO 500                                        DGE00770
      IF (INDEX.EQ.2) GO TO 85                                         DGE00780
   80 IF ((T-TOUT)*H.LT.0.0D0) GO TO 40                                DGE00790
C                                  CALL INTERP                         DGE00800
      CALL NGE001 (TOUT,Y,NO,YO)                                       DGE00810
      GO TO 520                                                        DGE00820
   85 IF (((T+H)-TOUT)*H.LE.0.0D0) GO TO 40                            DGE00830
      IF (ABS(T-TOUT).LE.100.0D0*UROUND*HMAX) GO TO 500                DGE00840
      IF ((T-TOUT)*H.GE.0.0D0) GO TO 500                               DGE00850
      H=(TOUT-T)*(1.0D0-4.0D0*UROUND)                                  DGE00860
      JSTART=-1                                                        DGE00870
      GO TO 40                                                         DGE00880
  100 WRITE (LOUT,105) T                                               DGE00890
  110 IF (NHCUT.EQ.10) GO TO 150                                       DGE00900
      NHCUT=NHCUT+1                                                    DGE00910
      HMIN=HMIN*.10D0                                                  DGE00920
      H=H*.10D0                                                        DGE00930
      WRITE (LOUT,115) H                                               DGE00940
      JSTART=-1                                                        DGE00950
      GO TO 40                                                         DGE00960
C                                                                      DGE00970
  150 WRITE (LOUT,155)                                                 DGE00980
      GO TO 500                                                        DGE00990
C                                                                      DGE01000
  200 WRITE (LOUT,205) T,H                                             DGE01010
      GO TO 500                                                        DGE01020
C                                                                      DGE01030
  250 WRITE (LOUT,255) T                                               DGE01040
      KFLAG=-2                                                         DGE01050
      GO TO 500                                                        DGE01060
C                                                                      DGE01070
  300 WRITE (LOUT,305) T                                               DGE01080
      GO TO 110                                                        DGE01090
C                                                                      DGE01100
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  400 WRITE (LOUT,405)                                                  DGE01110
      INDEX=-4                                                          DGE01120
      RETURN                                                            DGE01130
C                                                                       DGE01140
  410 WRITE (LOUT,415)                                                  DGE01150
      INDEX=-4                                                          DGE01160
      RETURN                                                            DGE01170
C                                                                       DGE01180
  420 WRITE (LOUT,425)                                                  DGE01190
      INDEX=-4                                                          DGE01200
      RETURN                                                            DGE01210
C                                                                       DGE01220
  430 WRITE (LOUT,435) INDEX                                            DGE01230
      INDEX=-4                                                          DGE01240
      RETURN                                                            DGE01250
C                                                                       DGE01260
  440 WRITE (LOUT,445) T,TOUT,H                                         DGE01270
C                                 CALL INTERP                           DGE01280
      CALL NGE001 (TOUT,Y,NO,YO)                                        DGE01290
      INDEX=-5                                                          DGE01300
      RETURN                                                            DGE01310
C                                                                       DGE01320
  500 TOUT=T                                                            DGE01330
      DO 510 I=1,N                                                      DGE01340
  510   YO(I)=Y(I,1)                                                    DGE01350
  520 INDEX=KFLAG                                                       DGE01360
      TOUTP=TOUT                                                        DGE01370
      HO=HUSED                                                          DGE01380
      IF (KFLAG.NE.0) HO=H                                              DGE01390
      RETURN                                                            DGE01400
C                                                                       DGE01410
   15 FORMAT (35H WARNING..  T + H = T ON NEXT STEP.)                   DGE01420
  105 FORMAT (//35H KFLAG = -1 FROM INTEGRATOR AT T = ,E16.8/39H        DGE01430
     1TEST FAILED WITH DABS(H) = HMIN/)                                 DGE01440
  115 FORMAT (24H  H HAS BEEN REDUCED TO ,E16.8,26H  AND STEP WILLDGE01450
     1TRIED//)                                                          DGE01460
  155 FORMAT (//44H PROBLEM APPEARS UNSOLVABLE WITH GIVEN INPUT//)DGE01470
  205 FORMAT (//35H KFLAG = -2 FROM INTEGRATOR AT T = ,E16.8,5H  HDGE01480
     1.8/52H  THE REQUESTED ERROR IS SMALLER THAN CAN BE HANDLED//DGE01490
  255 FORMAT (//37H INTEGRATION HALTED BY DRIVER AT T = ,E16.8/56HDGE01500
     1TOO SMALL TO BE ATTAINED FOR THE MACHINE PRECISION/)          DGE01510
  305 FORMAT (//35H KFLAG = -3 FROM INTEGRATOR AT T = ,E16.8/45H  DGE01520
     1TOR CONVERGENCE COULD NOT BE ACHIEVED/)                           DGE01530
  405 FORMAT (//28H ILLEGAL INPUT.. EPS .LE. 0.//)                      DGE01540
  415 FORMAT (//25H ILLEGAL INPUT.. N .LE. 0//)                         DGE01550
  425 FORMAT (//36H ILLEGAL INPUT.. (TO-TOUT)*H .GE. 0.//)              DGE01560
  435 FORMAT (//24H ILLEGAL INPUT.. INDEX =,I5//)                       DGE01570
  445 FORMAT (//44H INDEX = -1 ON INPUT WITH (T-TOUT)*H .GE. 0./4HDGE01580
     116.8,9H   TOUT =,E16.8,6H   H =,E16.8/44H INTERPOLATION WAS DGE01590
     2S ON NORMAL RETURN./41H DESIRED PARAMETER CHANGES WERE NOT MDGE01600
      END                                                               DGE01610
      SUBROUTINE NGE001 (TOUT,Y,NO,YO)                                  DGE01620
C                                                                       DGE01630
C  THIS IS CALLED BY "GEAR". IT WAS "INTERP" IN THE DISTRIBUTED VEDGE01640
C                                                                       DGE01650
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      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                                DGE01660
      INTEGER NO,N,IDUMMY,JSTART,I,L,J                                   DGE01670
      DOUBLE PRECISION TOUT,Y,YO,T,H,DUMMY,S,S1                          DGE01680
      COMMON /GEAR1/ T,H,DUMMY(4),N,IDUMMY(2),JSTART                     DGE01690
      DIMENSION YO(NO), Y(NO,6)                                          DGE01700
      DO 10 I=1,N                                                        DGE01710
   10   YO(I)=Y(I,1)                                                     DGE01720
      L=JSTART+1                                                         DGE01730
      S=(TOUT-T)/H                                                       DGE01740
      S1=1.0D0                                                           DGE01750
      DO 30 J=2,L                                                        DGE01760
        S1=S1*S                                                          DGE01770
        DO 20 I=1,N                                                      DGE01780
   20     YO(I)=YO(I)+S1*Y(I,J)                                         DGE01790
   30   CONTINUE                                                        DGE01800
      RETURN                                                             DGE01810
      END                                                                DGE01820
      SUBROUTINE NGE002 (Y,NO)                                           DGE01830
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                                DGE01840
C                                                                        DGE01850
      INTEGER NO,N,MF,KFLAG,JSTART,IPIV,NQUSED,NSTEP,NFE,NJE             DGE01860
      INTEGER I,METH,MITER,NQ,L,IDOUB,MFOLD,NOLD,IRET,MEO,MIO,IWEVDGE01870
     1DER,LMAX,IREDO,J,NSTEPJ,J1,J2,M,IER,NEWQ                           DGE01880
      DOUBLE PRECISION Y,T,H,HMIN,HMAX,EPS,UROUND,YMAX,ERROR,SAVE1DGE01890
      DOUBLE PRECISION SAVE2,PW,HUSED                                    DGE01900
      DOUBLE PRECISION EL,OLDLO,TOLD,RMAX,RC,CRATE,EPSOLD,HOLD,FN,DGE01910
     1E,EUP,BND,RH,R1,CON,R,HLO,RO,D,PHLO,PR3,D1,ENQ3,ENQ2,PR2,PR1DGE01920
      DOUBLE PRECISION TQ                                                DGE01930
      COMMON /GEAR1/ T,H,HMIN,HMAX,EPS,UROUND,N,MF,KFLAG,JSTART          DGE01940
      COMMON /GEAR2/ YMAX(147)                                           DGE01950
      COMMON /GEAR3/ ERROR(147)                                          DGE01960
      COMMON /GEAR4/ SAVE1(147)                                          DGE01970
      COMMON /GEAR5/ SAVE2(147)                                          DGE01980
      COMMON /GEAR6/ PW(21609)                                           DGE01990
      COMMON /GEAR7/ IPIV(147)                                           DGE02000
      COMMON /GEAR9/ HUSED,NQUSED,NSTEP,NFE,NJE                          DGE02010
      DIMENSION Y(NO,6)                                                  DGE02020
      DIMENSION EL(13), TQ(4)                                            DGE02030
      DATA EL(2)/1.0D0/,OLDLO/1.0D0/                                     DGE02040
      KFLAG=0                                                            DGE02050
      TOLD=T                                                             DGE02060
      IF (JSTART.GT.0) GO TO 200                                         DGE02070
      IF (JSTART.NE.0) GO TO 120                                         DGE02080
      CALL DIFFUN (N,T,Y,SAVE1)                                          DGE02090
      DO 110 I=1,N                                                       DGE02100
  110   Y(I,2)=H*SAVE1(I)                                                DGE02110
      METH=MF/10                                                         DGE02120
      MITER=MF-10*METH                                                   DGE02130
      NQ=1                                                               DGE02140
      L=2                                                                DGE02150
      IDOUB=3                                                            DGE02160
      RMAX=1.D+04                                                        DGE02170
      RC=0.0D0                                                           DGE02180
      CRATE=1.0D0                                                        DGE02190
      EPSOLD=EPS                                                         DGE02200
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      HOLD=H                                                        DGE02210
      MFOLD=MF                                                      DGE02220
      NOLD=N                                                        DGE02230
      NSTEP=0                                                       DGE02240
      NSTEPJ=0                                                      DGE02250
      NFE=1                                                         DGE02260
      NJE=0                                                         DGE02270
      IRET=1                                                        DGE02280
      GO TO 130                                                     DGE02290
  120 IF (MF.EQ.MFOLD) GO TO 150                                    DGE02300
      MEO=METH                                                      DGE02310
      MIO=MITER                                                     DGE02320
      METH=MF/10                                                    DGE02330
      MITER=MF-10*METH                                              DGE02340
      MFOLD=MF                                                      DGE02350
      IF (MITER.NE.MIO) IWEVAL=MITER                                DGE02360
      IF (METH.EQ.MEO) GO TO 150                                    DGE02370
      IDOUB=L+1                                                     DGE02380
      IRET=1                                                        DGE02390
  130 CALL NGE003 (METH,NQ,EL,TQ,MAXDER)                            DGE02400
      LMAX=MAXDER+1                                                 DGE02410
      RC=RC*EL(1)/OLDL0                                             DGE02420
      OLDL0=EL(1)                                                   DGE02430
  140 FN=FLOAT(N)                                                   DGE02440
      EDN=FN*(DBLE(TQ(1))*EPS)**2                                   DGE02450
      E=FN*(DBLE(TQ(2))*EPS)**2                                     DGE02460
      EUP=FN*(DBLE(TQ(3))*EPS)**2                                   DGE02470
      BND=FN*(DBLE(TQ(4))*EPS)**2                                   DGE02480
      GO TO (160,170,200), IRET                                     DGE02490
  150 IF ((EPS.EQ.EPSOLD).AND.(N.EQ.NOLD)) GO TO 160                DGE02500
      EPSOLD=EPS                                                    DGE02510
      NOLD=N                                                        DGE02520
      IRET=1                                                        DGE02530
      GO TO 140                                                     DGE02540
  160 IF (H.EQ.HOLD) GO TO 200                                      DGE02550
      RH=H/HOLD                                                     DGE02560
      H=HOLD                                                        DGE02570
      IREDO=3                                                       DGE02580
      GO TO 175                                                     DGE02590
  170 RH=DMAX1(RH,HMIN/ABS(H))                                      DGE02600
  175 RH=DMIN1(RH,HMAX/ABS(H),RMAX)                                 DGE02610
      R1=1.0D0                                                      DGE02620
      DO 180 J=2,L                                                  DGE02630
        R1=R1*RH                                                    DGE02640
        DO 180 I=1,N                                                DGE02650
  180   Y(I,J)=Y(I,J)*R1                                            DGE02660
      H=H*RH                                                        DGE02670
      RC=RC*RH                                                      DGE02680
      IDOUB=L+1                                                     DGE02690
      IF (IREDO.EQ.0) GO TO 690                                     DGE02700
  200 IF (ABS(RC-1.0D0).GT.0.30D0) IWEVAL=MITER                     DGE02710
      IF (NSTEP.GE.NSTEPJ+20) IWEVAL=MITER                          DGE02720
      T=T+H                                                         DGE02730
      DO 210 J1=1,NQ                                                DGE02740
        DO 210 J2=J1,NQ                                             DGE02750
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      J=(NQ+J1)-J2                                                    DGE02760
      DO 210 I=1,N                                                    DGE02770
  210 Y(I,J)=Y(I,J)+Y(I,J+1)                                          DGE02780
  220 DO 230 I=1,N                                                    DGE02790
  230 ERROR(I)=0.0D0                                                  DGE02800
      M=0                                                             DGE02810
      CALL DIFFUN (N,T,Y,SAVE2)                                       DGE02820
      NFE=NFE+1                                                       DGE02830
      IF (IWEVAL.LE.0) GO TO 290                                      DGE02840
      IWEVAL=0                                                        DGE02850
      RC=1.                                                           DGE02860
      NJE=NJE+1                                                       DGE02870
      NSTEPJ=NSTEP                                                    DGE02880
      GO TO (250,240,260), MITER                                      DGE02890
  240 NFE=NFE+N                                                       DGE02900
  250 CON=-H*EL(1)                                                    DGE02910
C                                 CALL PSET                         DGE02920
      CALL NGE004 (Y,NO,CON,MITER,IER)                                DGE02930
      IF (IER.NE.0) GO TO 420                                         DGE02940
      GO TO 350                                                       DGE02950
  260 R=EL(1)*.10D0                                                   DGE02960
      DO 270 I=1,N                                                    DGE02970
  270 PW(I)=Y(I,1)+R*(H*SAVE2(I)-Y(I,2))                              DGE02980
      CALL DIFFUN (N,T,PW,SAVE1)                                      DGE02990
      NFE=NFE+1                                                       DGE03000
      HLO=H*EL(1)                                                     DGE03010
      DO 280 I=1,N                                                    DGE03020
        RO=H*SAVE2(I)-Y(I,2)                                          DGE03030
        PW(I)=1.0D0                                                   DGE03040
        D=.10D0*RO-H*(SAVE1(I)-SAVE2(I))                              DGE03050
        SAVE1(I)=0.0D0                                                DGE03060
        IF (ABS(RO).LT.UROUND*YMAX(I)) GO TO 280                      DGE03070
        IF (ABS(D).EQ.0.0D0) GO TO 420                                DGE03080
        PW(I)=.10D0*RO/D                                              DGE03090
        SAVE1(I)=PW(I)*RO                                             DGE03100
  280 CONTINUE                                                        DGE03110
      GO TO 370                                                       DGE03120
  290 IF (MITER.NE.0) GO TO (350,350,310), MITER                      DGE03130
      D=0.0D0                                                         DGE03140
      DO 300 I=1,N                                                    DGE03150
        R=H*SAVE2(I)-Y(I,2)                                           DGE03160
        D=D+((R-ERROR(I))/YMAX(I))**2                                 DGE03170
        SAVE1(I)=Y(I,1)+EL(1)*R                                       DGE03180
  300 ERROR(I)=R                                                      DGE03190
      GO TO 400                                                       DGE03200
C-----------------------------------------------------------------DGE03210
  310 PHLO=HLO                                                        DGE03220
      HLO=H*EL(1)                                                     DGE03230
      IF (HLO.EQ.PHLO) GO TO 330                                      DGE03240
      R=HLO/PHLO                                                      DGE03250
      DO 320 I=1,N                                                    DGE03260
        D=1.0D0-R*(1.0D0-1.0D0/PW(I))                                 DGE03270
        IF (ABS(D).EQ.0.0D0) GO TO 440                                DGE03280
  320 PW(I)=1.0D0/D                                                   DGE03290
  330 DO 340 I=1,N                                                    DGE03300
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  340   SAVE1(I)=PW(I)*(H*SAVE2(I)-(Y(I,2)+ERROR(I)))                DGE03310
      GO TO 370                                                      DGE03320
  350 DO 360 I=1,N                                                   DGE03330
  360   SAVE1(I)=H*SAVE2(I)-(Y(I,2)+ERROR(I))                        DGE03340
C                                 CALL SOL                         DGE03350
      CALL NGE006 (N,NO,PW,SAVE1,IPIV)                               DGE03360
  370 D=0.0D0                                                        DGE03370
      DO 380 I=1,N                                                   DGE03380
        ERROR(I)=ERROR(I)+SAVE1(I)                                   DGE03390
        D=D+(SAVE1(I)/YMAX(I))**2                                    DGE03400
  380   SAVE1(I)=Y(I,1)+EL(1)*ERROR(I)                               DGE03410
C-------------------------------------------------------------------DGE03420
  400 IF (M.NE.0) CRATE=DMAX1(.90D0*CRATE,D/D1)                      DGE03430
      IF ((D*DMIN1(1.0D0,2.0D0*CRATE)).LE.BND) GO TO 450             DGE03440
      D1=D                                                           DGE03450
      M=M+1                                                          DGE03460
      IF (M.EQ.3) GO TO 410                                          DGE03470
      CALL DIFFUN (N,T,SAVE1,SAVE2)                                  DGE03480
      GO TO 290                                                      DGE03490
C-------------------------------------------------------------------DGE03500
  410 NFE=NFE+2                                                      DGE03510
      IF (IWEVAL.EQ.-1) GO TO 440                                    DGE03520
  420 T=TOLD                                                         DGE03530
      RMAX=2.0D0                                                     DGE03540
      DO 430 J1=1,NQ                                                 DGE03550
        DO 430 J2=J1,NQ                                              DGE03560
        J=(NQ+J1)-J2                                                 DGE03570
        DO 430 I=1,N                                                 DGE03580
  430   Y(I,J)=Y(I,J)-Y(I,J+1)                                       DGE03590
      IF (ABS(H).LE.HMIN*1.000010D0) GO TO 680                       DGE03600
      RH=.250D0                                                      DGE03610
      IREDO=1                                                        DGE03620
      GO TO 170                                                      DGE03630
  440 IWEVAL=MITER                                                   DGE03640
      GO TO 220                                                      DGE03650
  450 IF (MITER.NE.0) IWEVAL=-1                                      DGE03660
      NFE=NFE+M                                                      DGE03670
      D=0.0D0                                                        DGE03680
      DO 460 I=1,N                                                   DGE03690
  460   D=D+(ERROR(I)/YMAX(I))**2                                    DGE03700
      IF (D.GT.E) GO TO 500                                          DGE03710
      KFLAG=0                                                        DGE03720
      IREDO=0                                                        DGE03730
      NSTEP=NSTEP+1                                                  DGE03740
      HUSED=H                                                        DGE03750
      NQUSED=NQ                                                      DGE03760
      DO 470 J=1,L                                                   DGE03770
        DO 470 I=1,N                                                 DGE03780
  470   Y(I,J)=Y(I,J)+EL(J)*ERROR(I)                                 DGE03790
      IF (IDOUB.EQ.1) GO TO 520                                      DGE03800
      IDOUB=IDOUB-1                                                  DGE03810
      IF (IDOUB.GT.1) GO TO 700                                      DGE03820
      IF (L.EQ.LMAX) GO TO 700                                       DGE03830
      DO 490 I=1,N                                                   DGE03840
  490   Y(I,LMAX)=ERROR(I)                                           DGE03850
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      GO TO 700                                                          DGE03860
  500 KFLAG=KFLAG-1                                                      DGE03870
      T=TOLD                                                             DGE03880
      DO 510 J1=1,NQ                                                     DGE03890
        DO 510 J2=J1,NQ                                                  DGE03900
        J=(NQ+J1)-J2                                                     DGE03910
        DO 510 I=1,N                                                     DGE03920
  510   Y(I,J)=Y(I,J)-Y(I,J+1)                                           DGE03930
      RMAX=2.0D0                                                         DGE03940
      IF (ABS(H).LE.HMIN*1.000010D0) GO TO 660                           DGE03950
      IF (KFLAG.LE.-3) GO TO 640                                         DGE03960
      IREDO=2                                                            DGE03970
      PR3=1.D20                                                          DGE03980
      GO TO 540                                                          DGE03990
  520 PR3=1.D20                                                          DGE04000
      IF (L.EQ.LMAX) GO TO 540                                           DGE04010
      D1=0.0D0                                                           DGE04020
      DO 530 I=1,N                                                       DGE04030
  530   D1=D1+((ERROR(I)-Y(I,LMAX))/YMAX(I))**2                          DGE04040
      ENQ3=.50D0/FLOAT(L+1)                                              DGE04050
      PR3=((D1/EUP)**ENQ3)*1.40D0+1.4D-06                                DGE04060
  540 ENQ2=.50D0/FLOAT(L)                                                DGE04070
      PR2=((D/E)**ENQ2)*1.20D0+1.2D-06                                   DGE04080
      PR1=1.D20                                                          DGE04090
      IF (NQ.EQ.1) GO TO 560                                             DGE04100
      D=0.0D0                                                            DGE04110
      DO 550 I=1,N                                                       DGE04120
  550   D=D+(Y(I,L)/YMAX(I))**2                                          DGE04130
      ENQ1=.50D0/FLOAT(NQ)                                               DGE04140
      PR1=((D/EDN)**ENQ1)*1.30D0+1.3D-06                                 DGE04150
  560 IF (PR2.LE.PR3) GO TO 570                                          DGE04160
      IF (PR3.LT.PR1) GO TO 590                                          DGE04170
      GO TO 580                                                          DGE04180
  570 IF (PR2.GT.PR1) GO TO 580                                          DGE04190
      NEWQ=NQ                                                            DGE04200
      RH=1.0D0/PR2                                                       DGE04210
      GO TO 620                                                          DGE04220
  580 NEWQ=NQ-1                                                          DGE04230
      RH=1.0D0/PR1                                                       DGE04240
      GO TO 620                                                          DGE04250
  590 NEWQ=L                                                             DGE04260
      RH=1.0D0/PR3                                                       DGE04270
      IF (RH.LT.1.10D0) GO TO 610                                        DGE04280
      DO 600 I=1,N                                                       DGE04290
  600   Y(I,NEWQ+1)=ERROR(I)*EL(L)/FLOAT(L)                              DGE04300
      GO TO 630                                                          DGE04310
  610 IDOUB=10                                                           DGE04320
      GO TO 700                                                          DGE04330
  620 IF ((KFLAG.EQ.0).AND.(RH.LT.1.10D0)) GO TO 610                     DGE04340
      IF (NEWQ.EQ.NQ) GO TO 170                                          DGE04350
  630 NQ=NEWQ                                                            DGE04360
      L=NQ+1                                                             DGE04370
      IRET=2                                                             DGE04380
      GO TO 130                                                          DGE04390
  640 IF (KFLAG.EQ.-7) GO TO 670                                         DGE04400
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      RH=.10D0                                                          DGE04410
      RH=DMAX1(HMIN/ABS(H),RH)                                          DGE04420
      H=H*RH                                                            DGE04430
      CALL DIFFUN (N,T,Y,SAVE1)                                         DGE04440
      NFE=NFE+1                                                         DGE04450
      DO 650 I=1,N                                                      DGE04460
  650   Y(I,2)=H*SAVE1(I)                                               DGE04470
      IWEVAL=MITER                                                      DGE04480
      IDOUB=10                                                          DGE04490
      IF (NQ.EQ.1) GO TO 200                                            DGE04500
      NQ=1                                                              DGE04510
      L=2                                                               DGE04520
      IRET=3                                                            DGE04530
      GO TO 130                                                         DGE04540
  660 KFLAG=-1                                                          DGE04550
      GO TO 700                                                         DGE04560
  670 KFLAG=-2                                                          DGE04570
      GO TO 700                                                         DGE04580
  680 KFLAG=-3                                                          DGE04590
      GO TO 700                                                         DGE04600
  690 RMAX=10.0D0                                                       DGE04610
  700 HOLD=H                                                            DGE04620
      JSTART=NQ                                                         DGE04630
      RETURN                                                            DGE04640
      END                                                               DGE04650
      SUBROUTINE NGE003 (METH,NQ,EL,TQ,MAXDER)                          DGE04660
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               DGE04670
      INTEGER METH,NQ,MAXDER,K                                          DGE04680
      DOUBLE PRECISION EL                                               DGE04690
      DOUBLE PRECISION TQ,PERTST                                        DGE04700
      DIMENSION PERTST(12,2,3), EL(13), TQ(4)                           DGE04710
      DATA PERTST/1.0D0,1.0D0,2.0D0,1.0D0,.31580D0,.07407D0,.0139DGE04720
     $.002182D0,.0002945D0,.00003492D0,.000003692D0,.000000352DGE04730
     $1.0D0,1.0D0,.50D0,.16670D0,.041670D0,1.0D0,1.0D0,1.0D0,1.0D0DGE04740
     $1.0D0,1.0D0,1.0D0,2.0D0,12.0D0,24.0D0,37.890D0,53.330D0,70.0DGE04750
     $87.970D0,106.90D0,126.70D0,147.40D0,168.80D0,191.0D0,2.0D0,4DGE04760
     $7.3330D0,10.420D0,13.70D0,1.0D0,1.0D0,1.0D0,1.0D0,1.0D0,1.0DDGE04770
     $1.0D0,12.0D0,24.0D0,37.890D0,53.330D0,70.080D0,87.970D0,106.DGE04780
     $126.70D0,147.40D0,168.80D0,191.0D0,1.0D0,3.0D0,6.0D0,9.1670DDGE04790
     $12.50D0,1.0D0,1.0D0,1.0D0,1.0D0,1.0D0,1.0D0,1.0D0,1.0D0/     DGE04800
       GO TO (1,2), METH                                                DGE04810
    1 MAXDER=12                                                         DGE04820
       GO TO (101,102,103,104,105,106,107,108,109,110,111,112), NQ      DGE04830
    2 MAXDER=5                                                          DGE04840
       GO TO (201,202,203,204,205), NQ                                  DGE04850
  101 EL(1)=1.0D0                                                       DGE04860
      GO TO 900                                                         DGE04870
  102 EL(1)=0.50D0                                                      DGE04880
      EL(3)=0.50D0                                                      DGE04890
      GO TO 900                                                         DGE04900
  103 EL(1)=4.1666666666666667D-01                                      DGE04910
      EL(3)=0.750D0                                                     DGE04920
      EL(4)=1.6666666666666667D-01                                      DGE04930
      GO TO 900                                                         DGE04940
  104 EL(1)=0.3750D0                                                    DGE04950
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      EL(3)=9.1666666666666667D-01                                      DGE04960
      EL(4)=3.3333333333333333D-01                                      DGE04970
      EL(5)=4.1666666666666667D-02                                      DGE04980
      GO TO 900                                                         DGE04990
  105 EL(1)=3.4861111111111111D-01                                      DGE05000
      EL(3)=1.0416666666666670D0                                        DGE05010
      EL(4)=4.8611111111111111D-01                                      DGE05020
      EL(5)=1.0416666666666667D-01                                      DGE05030
      EL(6)=8.3333333333333333D-03                                      DGE05040
      GO TO 900                                                         DGE05050
  106 EL(1)=3.2986111111111111D-01                                      DGE05060
      EL(3)=1.1416666666666670D0                                        DGE05070
      EL(4)=0.6250D0                                                    DGE05080
      EL(5)=1.7708333333333333D-01                                      DGE05090
      EL(6)=0.0250D0                                                    DGE05100
      EL(7)=1.3888888888888889D-03                                      DGE05110
      GO TO 900                                                         DGE05120
  107 EL(1)=3.1559193121693122D-01                                      DGE05130
      EL(3)=1.2250D0                                                    DGE05140
      EL(4)=7.5185185185185185D-01                                      DGE05150
      EL(5)=2.5520833333333333D-01                                      DGE05160
      EL(6)=4.8611111111111111D-02                                      DGE05170
      EL(7)=4.8611111111111111D-03                                      DGE05180
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  111 EL(1)=2.80189596443936720-01                                      DGE05510
      EL(3)=1.46448412698412700                                         DGE05520
      EL(4)=1.17151455026455030D0                                       DGE05530
      EL(5)=5.79358190035273370-01                                      DGE05540
      EL(6)=1.88322861552028220-01                                      DGE05550
      EL(7)=4.14303626543209880-02                                      DGE05560
      EL(8)=6.21114417989417990-03                                      DGE05570
      EL(9)=6.25206679894179890-04                                      DGE05580
      EL(10)=4.04174015285126400-05                                     DGE05590
      EL(11)=1.51565255731922400-06                                     DGE05600
      EL(12)=2.50521083854417190-08                                     DGE05610
      GO TO 900                                                         DGE05620
  112 EL(1)=2.74265540031599060-01                                      DGE05630
      EL(3)=1.50993867243867240D0                                       DGE05640
      EL(4)=1.26027116402116400D0                                       DGE05650
      EL(5)=6.59234182098765430-01                                      DGE05660
      EL(6)=2.30458002645502650-01                                      DGE05670
      EL(7)=5.56972461052322160-02                                      DGE05680
      EL(8)=9.43948412698412700-03                                      DGE05690
      EL(9)=1.11927496693121690-03                                      DGE05700
      EL(10)=9.09391534391534390-05                                     DGE05710
      EL(11)=4.82253086419753090-06                                     DGE05720
      EL(12)=1.50312650312650310-07                                     DGE05730
      EL(13)=2.08767569878680990-09                                     DGE05740
      GO TO 900                                                         DGE05750
C                                                                       DGE05760
  201 EL(1)=1.0D0                                                       DGE05770
      GO TO 900                                                         DGE05780
  202 EL(1)=6.66666666666666700-01                                      DGE05790
      EL(3)=3.33333333333333300-01                                      DGE05800
      GO TO 900                                                         DGE05810
  203 EL(1)=5.45454545454545450-01                                      DGE05820
      EL(3)=EL(1)                                                       DGE05830
      EL(4)=9.09090909090909090-02                                      DGE05840
      GO TO 900                                                         DGE05850
  204 EL(1)=0.480D0                                                     DGE05860
      EL(3)=0.70D0                                                      DGE05870
      EL(4)=0.20D0                                                      DGE05880
      EL(5)=0.020D0                                                     DGE05890
      GO TO 900                                                         DGE05900
  205 EL(1)=4.37956204379562040-01                                      DGE05910
      EL(3)=8.21167883211678830-01                                      DGE05920
      EL(4)=3.10218978102189780-01                                      DGE05930
      EL(5)=5.47445255474452550-02                                      DGE05940
      EL(6)=3.64963503649635040-03                                      DGE05950
C                                                                       DGE05960
  900 DO 910 K=1,3                                                      DGE05970
  910   TQ(K)=PERTST(NQ,METH,K)                                         DGE05980
      TQ(4)=.50D0*TQ(2)/FLOAT(NQ+2)                                     DGE05990
      RETURN                                                            DGE06000
      END                                                               DGE06010
      SUBROUTINE NGE004 (Y,NO,CON,MITER,IER)                            DGE06020
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                               DGE06030
      INTEGER NO,MITER,IER,N,IDUMMY,IPIV,NSQ,I,J1,J                     DGE06040
      DOUBLE PRECISION Y,CON,T,H,DUMMY,UROUND,YMAX,SAVE1,SAVE2,PW       DGE06050
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      DOUBLE PRECISION EPSJ,D,RO,YJ,R                                   DGE06060
      DIMENSION Y(NO,6)                                                 DGE06070
      COMMON /GEAR1/ T,H,DUMMY(3),UROUND,N,IDUMMY(3)                    DGE06080
      COMMON /GEAR2/ YMAX(147)                                          DGE06090
      COMMON /GEAR4/ SAVE1(147)                                         DGE06100
      COMMON /GEAR5/ SAVE2(147)                                         DGE06110
      COMMON /GEAR6/ PW(21609)                                          DGE06120
      COMMON /GEAR7/ IPIV(147)                                          DGE06130
      COMMON /GEAR8/ EPSJ,NSQ                                           DGE06140
      IF (MITER.EQ.2) GO TO 20                                          DGE06150
      CALL PEDERV (N,T,Y,PW,NO)                                         DGE06160
      DO 10 I=1,NSQ                                                     DGE06170
   10   PW(I)=PW(I)*CON                                                 DGE06180
      GO TO 60                                                          DGE06190
   20 D=0.0D0                                                           DGE06200
      DO 30 I=1,N                                                       DGE06210
   30   D=D+SAVE2(I)**2                                                 DGE06220
      RO=ABS(H)*SQRT(D)*1.D+03*UROUND                                   DGE06230
      J1=0                                                              DGE06240
      DO 50 J=1,N                                                       DGE06250
        YJ=Y(J,1)                                                       DGE06260
        R=EPSJ*YMAX(J)                                                  DGE06270
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      IP(N)=-IP(N)                                                    DGE06610
      A(M,K)=A(K,K)                                                   DGE06620
      A(K,K)=T                                                        DGE06630
   20 IF (T.EQ.0.0D0) GO TO 80                                        DGE06640
      T=1.0D0/T                                                       DGE06650
      DO 30 I=KP1,N                                                   DGE06660
   30   A(I,K)=-A(I,K)*T                                             DGE06670
      DO 50 J=KP1,N                                                   DGE06680
        T=A(M,J)                                                      DGE06690
        A(M,J)=A(K,J)                                                 DGE06700
        A(K,J)=T                                                      DGE06710
        IF (T.EQ.0.0D0) GO TO 50                                      DGE06720
        DO 40 I=KP1,N                                                 DGE06730
   40     A(I,J)=A(I,J)+A(I,K)*T                                     DGE06740
   50   CONTINUE                                                     DGE06750
   60 CONTINUE                                                       DGE06760
   70 K=N                                                            DGE06770
      IF (A(N,N).EQ.0.0D0) GO TO 80                                  DGE06780
      RETURN                                                         DGE06790
   80 IER=K                                                          DGE06800
      IP(N)=0                                                        DGE06810
      RETURN                                                         DGE06820
      END                                                            DGE06830
      SUBROUTINE NGE006 (N,NDIM,A,B,IP)                              DGE06840
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)                            DGE06850
      INTEGER N,NDIM,IP,NM1,K,KP1,M,I,KB,KM1                         DGE06860
      DOUBLE PRECISION A,B,T                                         DGE06870
      DIMENSION A(NDIM,N), B(N), IP(N)                               DGE06880
      IF (N.EQ.1) GO TO 50                                           DGE06890
      NM1=N-1                                                        DGE06900
      DO 20 K=1,NM1                                                  DGE06910
        KP1=K+1                                                      DGE06920
        M=IP(K)                                                      DGE06930
        T=B(M)                                                       DGE06940
        B(M)=B(K)                                                    DGE06950
        B(K)=T                                                       DGE06960
        DO 10 I=KP1,N                                                DGE06970
   10     B(I)=B(I)+A(I,K)*T                                         DGE06980
   20   CONTINUE                                                     DGE06990
      DO 40 KB=1,NM1                                                 DGE07000
        KM1=N-KB                                                     DGE07010
        K=KM1+1                                                      DGE07020
        B(K)=B(K)/A(K,K)                                             DGE07030
        T=-B(K)                                                      DGE07040
        DO 30 I=1,KM1                                                DGE07050
   30     B(I)=B(I)+A(I,K)*T                                         DGE07060
   40   CONTINUE                                                     DGE07070
   50 B(1)=B(1)/A(1,1)                                               DGE07080
      RETURN                                                         DGE07090
      END                                                            DGE07100
      SUBROUTINE IASTMC(CE,QE,XMI1,XMK1,XMP1,N)                      DGE07110
C                                                                    DGE07120
C     IAST CALCULATION FOR MYERS ISOTHERMS                           DGE07130
C     IF THE LIQUID PHASE ADSORBATE                                  DGE07140
C     CONCENTRATIONS ARE KNOWN                                       DGE07150
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      IMPLICIT DOUBLE PRECISION(A-H,O-Z)                                DGE07160
C                                                                       DGE07170
C                                                                       DGE07180
      DIMENSION WK(33),X(3),Y(3),CO(3),QE(N),CF(N),                     DGE07190
     +XMH1(N),XMK1(N),XMP1(N)                                           DGE07200
C                                                                       DGE07210
      EXTERNAL FCNM                                                     DGE07220
      EXTERNAL FCNJM                                                    DGE07230
C                                                                       DGE07240
C     READ INITIAL GUESSES FOR ADSORBED PHASE                           DGE07250
C     ADSORBATE CONCENTRATIONS                                          DGE07260
C                                                                       DGE07270
      DO 3 I=1,N                                                        DGE07280
      X(I)=0.5*CE(I)                                                    DGE07290
3     CONTINUE                                                          DGE07300
      NSIG=4                                                            DGE07310
      ITMAX=300                                                         DGE07320
C                                                                       DGE07330
      CALL NMAJLS(N,FCNM,FCNJM,NSIG,                                    DGE07340
     &X,FNORM,ITMAX,WK,IER,XMH1,XMK1,XMP1,CE)                           DGE07350
C                                                                       DGE07360
      IF(IER .NE. 0) THEN                                               DGE07370
      WRITE(*,*) ' IER = ',IER                                          DGE07380
      WRITE(*,*) ' X = ', (X(I),I=1,N)                                  DGE07390
      WRITE(*,*) ' FNORM = ',FNORM                                      DGE07400
      WRITE(*,*) ' SUBROUTINE IAST MYERS'                               DGE07410
      STOP ' something is wrong '                                       DGE07420
      END IF                                                            DGE07430
C                                                                       DGE07440
C     COMPUTE  HYPOTHETICAL LIQUID PHASE CONC'S                         DGE07450
C     AND THE LIQUID PHASE MOLE FRACTIONS                               DGE07460
C                                                                       DGE07470
      DO 4 I=1,N                                                        DGE07480
      ARG=XMK1(I)*X(I)**XMP1(I)                                         DGE07490
      CO(I)=(X(I)/XMH1(I))*DEXP(ARG)                                    DGE07500
      Y(I)=CE(I)/CO(I)                                                  DGE07510
    4 CONTINUE                                                          DGE07520
C                                                                       DGE07530
C     TOTAL CARBON COVERAGE                                             DGE07540
C                                                                       DGE07550
      SUM=0.0D0                                                         DGE07560
      DO 5 I=1,N                                                        DGE07570
      SUM=SUM+Y(I)/X(I)                                                 DGE07580
    5 CONTINUE                                                          DGE07590
      QT=1.0D0/SUM                                                      DGE07600
C                                                                       DGE07610
C     ADSORBED PHASE ADSORPTION CONCENTRATION                           DGE07620
      DO 6 I=1,N                                                        DGE07630
      QE(I)=Y(I)*QT                                                     DGE07640
    6 CONTINUE                                                          DGE07650
      RETURN                                                            DGE07660
      END                                                               DGE07670
C-----------------------------------------                              DGE07680
      SUBROUTINE FCNM(X,F,XMH1,XMK1,XMP1,CE,N)                          DGE07690
C                                                                       DGE07700
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      IMPLICIT DOUBLE PRECISION(A-H,O-Z)                                DGE07710
C                                                                       DGE07720
      DIMENSION XMH1(N),XMK1(N),XMP1(N),CE(N)                           DGE07730
C                                                                       DGE07740
      DIMENSION X(N),F(N),H(3),P(3),ARG(3),FR(3),P1(3)                  DGE07750
C                                                                       DGE07760
      DO 1 I=1,N                                                        DGE07770
      X(I)=DMAX1(X(I),1.0D-20)                                          DGE07780
    1 CONTINUE                                                          DGE07790
C                                                                       DGE07800
      DO 2 I=1,N                                                        DGE07810
      H(I)=XMK1(I)*XMP1(I)/(XMP1(I)+1.0D0)                              DGE07820
      P(I)=X(I)+H(I)*X(I)**(XMP1(I)+1.0D0)                              DGE07830
2     CONTINUE                                                          DGE07840
      DO 3 I=1,N-1                                                      DGE07850
      F(I)=P(I)-P(I+1)                                                  DGE07860
3     CONTINUE                                                          DGE07870
C                                                                       DGE07880
      SUM=0.0D0                                                         DGE07890
      DO 4 I=1,N                                                        DGE07900
      ARG(I)=XMK1(I)*X(I)**XMP1(I)                                      DGE07910
      FR(I)=X(I)/XMH1(I)                                                DGE07920
      P1(I)=CE(I)/(FR(I)*DEXP(ARG(I)))                                  DGE07930
      SUM=SUM+P1(I)                                                     DGE07940
4     CONTINUE                                                          DGE07950
      F(N)=SUM-1.0D0                                                    DGE07960
C                                                                       DGE07970
      RETURN                                                            DGE07980
      END                                                               DGE07990
C---------------------------------------                                DGE08000
      SUBROUTINE FCNJM(X,FJ,XMH1,XMK1,XMP1,CE,N)                        DGE08010
C                                                                       DGE08020
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)                                DGE08030
C                                                                       DGE08040
      DIMENSION XMH1(N),XMK1(N),XMP1(N),CE(N),F1(3),F2(3)               DGE08050
C                                                                       DGE08060
      DIMENSION X(N),FJ(N,N),PR(3),ARG(3),XNOM(3)                       DGE08070
C                                                                       DGE08080
      DO 1 I=1,N                                                        DGE08090
      X(I)=DMAX1(X(I),1.0D-20)                                          DGE08100
    1 CONTINUE                                                          DGE08110
C                                                                       DGE08120
      DO 2 I=1,N                                                        DGE08130
      PR(I)=XMK1(I)*XMP1(I)*X(I)**XMP1(I)                               DGE08140
      ARG(I)=XMK1(I)*X(I)**XMP1(I)                                      DGE08150
      XNOM(I)=-CE(I)*XMH1(I)*(1.0D0+PR(I))                              DGE08160
2     CONTINUE                                                          DGE08170
C                                                                       DGE08180
      IF (N.EQ.2) THEN                                                  DGE08190
      FJ(1,1)=1.0D0+PR(1)                                               DGE08200
      FJ(2,1)=XNOM(1)/(X(1)*X(1)*DEXP(ARG(1)))                          DGE08210
      FJ(1,2)=-1.0D0-PR(2)                                              DGE08220
      FJ(2,2)=XNOM(2)/(X(2)*X(2)*DEXP(ARG(2)))                          DGE08230
      END IF                                                            DGE08240
      IF (N.EQ.3) THEN                                                  DGE08250
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      FJ(1,1)=1.0D0+PR(1)                                              DGE08260
      FJ(2,1)=0.0D0                                                    DGE08270
      FJ(3,1)=XNOM(1)/(X(1)*DEXP(ARG(1)))                              DGE08280
      FJ(1,2)=-1.0D0-PR(2)                                             DGE08290
      FJ(2,2)=1.0D0+PR(2)                                              DGE08300
      FJ(3,2)=XNOM(2)/(X(2)*DEXP(ARG(2)))                              DGE08310
      FJ(1,3)=0.0D0                                                    DGE08320
      FJ(2,3)=-1.0D0-PR(3)                                             DGE08330
      FJ(3,3)=XNOM(3)/(X(3)*DEXP(ARG(3)))                              DGE08340
      END IF                                                           DGE08350
C                                                                      DGE08360
      RETURN                                                           DGE08370
      END                                                              DGE08380
C--------------------------------                                      DGE08390
      SUBROUTINE IASTMQ(CE,QE,XMH1,XMK1,XMP1,N)                        DGE08400
C                                                                      DGE08410
C     IAST CALCULATION FOR MYERS ISOTHERMS                             DGE08420
C     IF THE SOLID PHASE ADSORBATE                                     DGE08430
C     CONCENTRATIONS ARE KNOWN                                         DGE08440
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)                               DGE08450
C                                                                      DGE08460
      DIMENSION XMH1(N),XMK1(N),XMP1(N),QE(N)                          DGE08470
C                                                                      DGE08480
      DIMENSION WK(33),X(3)                                            DGE08490
C                                                                      DGE08500
      DIMENSION Y(3),CO(3),CE(N)                                       DGE08510
C                                                                      DGE08520
      EXTERNAL FQNM                                                    DGE08530
      EXTERNAL FQNJM                                                   DGE08540
C     READ INITIAL GUESSES FOR LIQUID PHASE                            DGE08550
C     ADSORBATE CONCENTRATIONS                                         DGE08560
C                                                                      DGE08570
      DO 2 I=1,N                                                       DGE08580
      X(I)=0.5*QE(I)                                                   DGE08590
2     CONTINUE                                                         DGE08600
C                                                                      DGE08610
      NSIG=4                                                           DGE08620
      ITMAX=1000                                                       DGE08630
C                                                                      DGE08640
      CALL NMAJLS(N,FQNM,FQNJM,NSIG,                                   DGE08650
     &X,FNORM,ITMAX,WK,IER,XMH1,XMK1,XMP1,QE)                          DGE08660
C                                                                      DGE08670
      IF(IER .NE. 0) THEN                                              DGE08680
      WRITE(*,*) ' IER = ',IER                                         DGE08690
      WRITE(*,*) ' X = ', (X(I),I=1,N)                                 DGE08700
      WRITE(*,*) ' FNORM = ',FNORM                                     DGE08710
      WRITE(*,*) ' SUBROUTINE IAST MYERS'                              DGE08720
      STOP ' something is wrong '                                      DGE08730
      END IF                                                           DGE08740
C                                                                      DGE08750
C     COMPUTE  HYPOTHETICAL LIQUID PHASE CONC'S                        DGE08760
C     AND THE LIQUID PHASE MOLE FRACTIONS                              DGE08770
C                                                                      DGE08780
      DO 4 I=1,N                                                       DGE08790
      ARG=XMK1(I)*X(I)**XMP1(I)                                        DGE08800
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      CO(I)=(X(I)/XMH1(I))*DEXP(ARG)                                    DGE08810
    4 CONTINUE                                                          DGE08820
C                                                                       DGE08830
C     TOTAL CARBON COVERAGE                                             DGE08840
C                                                                       DGE08850
      SUM=0.0D0                                                         DGE08860
      DO 5 I=1,N                                                        DGE08870
      SUM=SUM+QE(I)                                                     DGE08880
    5 CONTINUE                                                          DGE08890
      QT=1.0D0/SUM                                                      DGE08900
C                                                                       DGE08910
C     LIQUID PHASE CONCENTRATION                                        DGE08920
      DO 6 I=1,N                                                        DGE08930
      CE(I)=QE(I)*CO(I)*QT                                              DGE08940
    6 CONTINUE                                                          DGE08950
      RETURN                                                            DGE08960
      END                                                               DGE08970
C-----------------------------------------                              DGE08980
      SUBROUTINE FQNM(X,F,XMH1,XMK1,XMP1,QE,N)                          DGE08990
C                                                                       DGE09000
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)                                DGE09010
C                                                                       DGE09020
      DIMENSION XMH1(N),XMK1(N).XMP1(N),QE(N)                           DGE09030
C                                                                       DGE09040
      DIMENSION X(N),F(N),H(3),P(3),ARG(3),FR(3),P1(3)                  DGE09050
C                                                                       DGE09060
      DO 1 I=1,N                                                        DGE09070
      X(I)=DMAX1(X(I),1.0D-20)                                          DGE09080
    1 CONTINUE                                                          DGE09090
C                                                                       DGE09100
      DO 2 I=1,N                                                        DGE09110
      H(I)=XMK1(I)*XMP1(I)/(XMP1(I)+1.0D0)                              DGE09120
      P(I)=X(I)+H(I)*X(I)**(XMP1(I)+1.0D0)                              DGE09130
2     CONTINUE                                                          DGE09140
      DO 3 I=1,N-1                                                      DGE09150
      F(I)=P(I)-P(I+1)                                                  DGE09160
3     CONTINUE                                                          DGE09170
C                                                                       DGE09180
      SUM=0.0D0                                                         DGE09190
      DO 4 I=1,N                                                        DGE09200
      P1(I)=QE(I)/X(I)                                                  DGE09210
      SUM=SUM+P1(I)                                                     DGE09220
4     CONTINUE                                                          DGE09230
      F(N)=SUM-1.0D0                                                    DGE09240
C                                                                       DGE09250
      RETURN                                                            DGE09260
      END                                                               DGE09270
C-----------------------------------------                              DGE09280
      SUBROUTINE FQNJM(X,FJ,XMH1,XMK1,XMP1,QE,N)                        DGE09290
C                                                                       DGE09300
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)                                DGE09310
C                                                                       DGE09320
      DIMENSION XMH1(N),XMK1(N),XMP1(N),QE(N)                           DGE09330
C                                                                       DGE09340
      DIMENSION X(N),FJ(N,N),PR(3),F1(3),F2(3)                          DGE09350
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C                                                                       DGE09360
      DO 1 I=1,N                                                        DGE09370
      X(I)=DMAX1(X(I),1.0D-20)                                          DGE09380
    1 CONTINUE                                                          DGE09390
      DX=1.80D0*(1.0D-6)**(1.0D0/3.0D0)                                 DGE09400
C                                                                       DGE09410
      DO 2 I=1,N                                                        DGE09420
      PR(I)=XMK1(I)*XMP1(I)*X(I)**XMP1(I)                               DGE09430
2     CONTINUE                                                          DGE09440
C                                                                       DGE09450
      IF (N.EQ.2) THEN                                                  DGE09460
      FJ(1,1)=1.0D0+PR(1)                                               DGE09470
      FJ(2,1)=-QE(1)/X(1)**2.0D0                                        DGE09480
      FJ(1,2)=-1.0D0-PR(2)                                              DGE09490
      FJ(2,2)=-QE(2)/X(2)**2.0D0                                        DGE09500
      END IF                                                            DGE09510
      IF (N.EQ.3) THEN                                                  DGE09520
      FJ(1,1)=1.0D0+PR(1)                                               DGE09530
      FJ(2,1)=0.0D0                                                     DGE09540
      FJ(3,1)=-QE(1)/X(1)**2.0D0                                        DGE09550
      FJ(1,2)=-1.0D0-PR(2)                                              DGE09560
      FJ(2,2)=1.0D0+PR(2)                                               DGE09570
      FJ(3,2)=-QE(2)/X(2)**2.0D0                                        DGE09580
      FJ(1,3)=0.0D0                                                     DGE09590
      FJ(2,3)=-1.0D0-PR(3)                                              DGE09600
      FJ(3,3)=-QE(3)/X(3)**2.0D0                                        DGE09610
      END IF                                                            DGE09620
C                                                                       DGE09630
      RETURN                                                            DGE09640
      END                                                               DGE09650
      SUBROUTINE NMAJLS(N,FCN,FCNJ,NSIG,X,FNORM,ITMAX,WK,IER            DGE09660
     +,XMH1,XMK1,XMP1,CE)                                               DGE09670
C                                                                       DGE09680
C     NEWTONS METHOD WITH GLOBALLY CONVERGENCE                          DGE09690
C     STRATEGY FOR SYSTEM OF NONLINEAR EQUATIONS                        DGE09700
C                                                                       DGE09710
C     N - NUMBER OF NONLINEAR EQUATIONS                                 DGE09720
C     X - UNKNOWN VECTOR                                                DGE09730
C     WK - WORK VECTOR OF LENGTH OF N*(5+2*N)                           DGE09740
C     FCN - SUBROUTINE FOR FUNCTIONAL EVALUATION                        DGE09750
C     FCNJ - ANALYTICAL JACOBEAN                                        DGE09760
C     NSIG - SIGNIFICANT DIGITS OF UNKNOWNS                             DGE09770
C     FNORM - NORM OF FUNCTION VECTOR                                   DGE09780
C     ITMAX - MAXIMUM ALLOWABLE NUMBER OF ITERATIONS                    DGE09790
C     IER - 0 - SUCCESSFULL ITERATION                                   DGE09800
C             100 - NORM NOT SUFFICIENTLY SMALL (OPTIMUM)               DGE09810
C             110 - EXCEEDS MAXIMAL NUMBER OF ITERATIONS                DGE09820
C                                                                       DGE09830
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)                                DGE09840
C                                                                       DGE09850
      DIMENSION WK(1),X(N),XMH1(N),XMK1(N),XMP1(N),CE(N)                DGE09860
C                                                                       DGE09870
      IER=0                                                             DGE09880
      ITER=0                                                            DGE09890
C                                                                       DGE09900
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      IFOL=1                                                          DGE09910
      IFOU=N                                                          DGE09920
      IFJL=N+1                                                        DGE09930
      IFJU=N+N*N                                                      DGE09940
      ISL=N+N*N+1                                                     DGE09950
      ISU=N+N*N+N                                                     DGE09960
      IXNL=ISU+1                                                      DGE09970
      IXNU=ISU+N                                                      DGE09980
      IFNL=IXNU+1                                                     DGE09990
      IFNU=IXNU+N                                                     DGE10000
      IWKGL=IFNU+1                                                    DGE10010
C                                                                     DGE10020
C     I.) FUNCTIONAL EVALUATION AND RES. FUNCTION                     DGE10030
C                                                                     DGE10040
      CALL FCN(X,WK(IFOL),XMH1,XMK1,XMP1,CE,N)                        DGE10050
C                                                                     DGE10060
      GO=0.0D0                                                        DGE10070
      DO 1 I=IFOL,IFOU                                                DGE10080
      GO=GO+WK(I)*WK(I)                                               DGE10090
    1 CONTINUE                                                        DGE10100
      GO=GO*0.5                                                       DGE10110
C                                                                     DGE10120
  200 CONTINUE                                                        DGE10130
C                                                                     DGE10140
      ITER=ITER+1                                                     DGE10150
C                                                                     DGE10160
C                                                                     DGE10170
C     II.) CALCULATE JACOBEAN                                         DGE10180
C                                                                     DGE10190
      CALL FCNJ(X,WK(IFJL),XMH1,XMK1,XMP1,CE,N)                       DGE10200
C                                                                     DGE10210
C                                                                     DGE10220
C     III.) SOLVE FOR NEWTON STEP                                     DGE10230
C                                                                     DGE10240
      CALL GAUSPI(WK(IFJL),WK(ISL),WK(IFOL),N,WK(IWKGL))              DGE10250
C                                                                     DGE10260
C                                                                     DGE10270
C     IV.) CHECK FOR ACCEPTABILITY                                    DGE10280
C                                                                     DGE10290
      XL=1.0                                                          DGE10300
      ITERI=0                                                         DGE10310
C                                                                     DGE10320
  100 CONTINUE                                                        DGE10330
      ITERI=ITERI+1                                                   DGE10340
C                                                                     DGE10350
      DO 2 I=1,N                                                      DGE10360
      WK(IXNL+I-1)=X(I)-XL*WK(ISL+I-1)                                DGE10370
    2 CONTINUE                                                        DGE10380
C                                                                     DGE10390
      CALL FCN(WK(IXNL),WK(IFNL),XMH1,XMK1,XMP1,CE,N)                 DGE10400
C                                                                     DGE10410
      GN=0.0D0                                                        DGE10420
      DO 3 I=IFNL,IFNU                                                DGE10430
      GN=GN+WK(I)*WK(I)                                               DGE10440
    3 CONTINUE                                                        DGE10450
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      GN=GN*0.5D0                                                    DGE10460
C                                                                    DGE10470
      A=GN-GO-1.0D-04*XL*2.0D0*GO                                    DGE10480
C                                                                    DGE10490
C                                                                    DGE10500
      IF(A .GT. 0.0D0) THEN                                          DGE10510
      IF(ITERI .GT. 50) THEN                                         DGE10520
      WRITE(*,*) ' Program stalls '                                  DGE10530
      WRITE(*,*) ' try new initial guess '                           DGE10540
      STOP                                                           DGE10550
      END IF                                                         DGE10560
C     APPLY FORMULA                                                  DGE10570
      XLN=GO/(GN-GO+2.0*GO)                                          DGE10580
      IF(XLN .LT. 0.1D0*XL) XL=XL*0.1                                DGE10590
      IF(XLN .GT. 0.5D0*XL) XL=XL*0.5                                DGE10600
      IF(XLN .GE. 0.1*XL .AND. XLN .LE. 0.5*XL) THEN                 DGE10610
      XL=XLN                                                         DGE10620
      END IF                                                         DGE10630
      GO TO 100                                                      DGE10640
      END IF                                                         DGE10650
C                                                                    DGE10660
C     PREPARE TO RETURN TO STEP I.)                                  DGE10670
C                                                                    DGE10680
      DO 4 I=1,N                                                     DGE10690
      WK(I)=WK(IFNL+I-1)                                             DGE10700
      X(I)=WK(IXNL+I-1)                                              DGE10710
    4 CONTINUE                                                       DGE10720
      GO=GN                                                          DGE10730
C     V.) CONVERGENCE TEST                                           DGE10740
C                                                                    DGE10750
      IF(ITER .GT. ITMAX) THEN                                       DGE10760
      WRITE(*,*) ' Iteration stalled or ITMAX too small'             DGE10770
      FNORM=2.0D0*GN                                                 DGE10780
      IER=110                                                        DGE10790
      RETURN                                                         DGE10800
      END IF                                                         DGE10810
C                                                                    DGE10820
      DO 5 I=1,N                                                     DGE10830
      CRIT=DABS(10.0D0**(-NSIG)*X(I))                                DGE10840
      IF(DABS(WK(ISL+I-1)) .GT. CRIT) GO TO 200                      DGE10850
    5 CONTINUE                                                       DGE10860
C                                                                    DGE10870
      FNORM=2.0D0*GN                                                 DGE10880
C                                                                    DGE10890
      IF(FNORM .LT. 10.0D0**(-NSIG)) THEN                            DGE10900
      IER=0                                                          DGE10910
      ELSE                                                           DGE10920
      IER=100                                                        DGE10930
      END IF                                                         DGE10940
C                                                                    DGE10950
      RETURN                                                         DGE10960
      END                                                            DGE10970
C-------------------------------------------                         DGE10980
      SUBROUTINE GAUSPI(A,X,B,N,W)                                   DGE10990
C                                                                    DGE11000
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C     A - COEFFICIENT MATRIX (UNCHANGED ON RETURN)                    DGE11010
C     B - CONSTANT VECTOR                                             DGE11020
C     X - SOLUTION VECTOR                                             DGE11030
C     W - WORK VECTOR DIMENSIONED (N,N+1)                             DGE11040
C         - IN CALLING PROGRAM N*N+1                                  DGE11050
C     C - DIMENSION OF MATRIX                                         DGE11060
C                                                                     DGE11070
C     ALGORITHM USES PARTIAL PIVOTING                                 DGE11080
C     BUT DOES NOT CHECK FOR SINGULARITY                              DGE11090
C     NO ACCURACY CHECK OR ITERATIVE IMPROVEMENT                      DGE11100
C     OF SOLUTION IS PERFORMED                                        DGE11110
C                                                                     DGE11120
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)                              DGE11130
C                                                                     DGE11140
      DIMENSION A(N,N),X(N),B(N),W(N,*)                               DGE11150
C                                                                     DGE11160
      DO 1 I=1,N                                                      DGE11170
      DO 2 J=1,N                                                      DGE11180
      W(I,J)=A(I,J)                                                   DGE11190
    2 CONTINUE                                                        DGE11200
      W(I,N+1)=B(I)                                                   DGE11210
    1 CONTINUE                                                        DGE11220
C                                                                     DGE11230
      DO 15 KK=1,N-1                                                  DGE11240
C                                                                     DGE11250
      JP=KK                                                           DGE11260
      IP=KK                                                           DGE11270
      IIS=KK                                                          DGE11280
      JJS=KK                                                          DGE11290
C                                                                     DGE11300
C     PARTIAL PIVOTING                                                DGE11310
C                                                                     DGE11320
      PMAX=DABS(W(IIS,JP))                                            DGE11330
      DO 11 II=IIS+1,N                                                DGE11340
      PCOMP=DABS(W(II,JP))                                            DGE11350
      IF(PMAX .LT. PCOMP) THEN                                        DGE11360
      PMAX=PCOMP                                                      DGE11370
      IP=II                                                           DGE11380
      END IF                                                          DGE11390
   11 CONTINUE                                                        DGE11400
C                                                                     DGE11410
      IF(IP .NE. IIS) THEN                                            DGE11420
      DO 12 JJ=JP,N+1                                                 DGE11430
      H=W(IIS,JJ)                                                     DGE11440
      W(IIS,JJ)=W(IP,JJ)                                              DGE11450
      W(IP,JJ)=H                                                      DGE11460
   12 CONTINUE                                                        DGE11470
      END IF                                                          DGE11480
C                                                                     DGE11490
C     TRIANGULATION STEP                                              DGE11500
C                                                                     DGE11510
      DO 13 I=IIS+1,N                                                 DGE11520
      DO 14 J=JJS+1,N+1                                               DGE11530
      W(I,J)=W(I,J)-W(I,JJS)/W(IIS,JJS)*W(IIS,J)                      DGE11540
   14 CONTINUE                                                        DGE11550
```

```
   13 CONTINUE                                                    DGE11560
C                                                                 DGE11570
   15 CONTINUE                                                    DGE11580
C                                                                 DGE11590
C     GAUSSIAN ELIMINATION                                        DGE11600
C                                                                 DGE11610
      X(N)=W(N,N+1)/W(N,N)                                        DGE11620
C                                                                 DGE11630
      DO 16 K1=1,N-1                                              DGE11640
      K=N-K1                                                      DGE11650
      SUM=0.0D0                                                   DGE11660
      DO 17 J=K+1,N                                               DGE11670
      SUM=SUM+W(K,J)*X(J)                                         DGE11680
   17 CONTINUE                                                    DGE11690
      X(K)=(W(K,N+1)-SUM)/W(K,K)                                  DGE11700
   16 CONTINUE                                                    DGE11710
C                                                                 DGE11720
      RETURN                                                      DGE11730
      END                                                         DGE11740
C-----------------------------------------                        DGE11750
```

NOMENCLATURE

b	equilibrium constant
B_i	Biot number
BTC	breakthrough curve
C	bulk liquid concentration
C_b	bulk liquid concentration
C_0	initial bulk liquid concentration
C_e	residual concentration
C_p	pore liquid phase concentration
C_s	adsorbate in the liquid film at the solid-liquid interface
d	exponent in Equation 5.4
d_p	particle diameter
D_g	dimensionless distribution parameter
D_l	diffusivity of adsorbate in water
D_p	pore diffusivity
D_s	surface diffusivity
DO	dissolved oxygen
h	exponent in equation 5.4
{H'}	Hydrogen ion concentration
J_l	Liquid phase mass flux

J_s	surface diffusion flux
GAC	granular activated carbon
k_r	rate constant in Equation 6.5
$K_{1,2}$	constants in Equations 4.1 and 4.2
k_f	external mass transfer coefficient
K_o	constant in Equation 4.3
k	Freundlich constant
L	constant in Equations 5.4
m	exponent in Equations 4.1 and 4.2
m_t	mass adsorbed at time t
m_∞	mass adsorbed at equilibrium
n	Freundlich exponent
q	carbon loading
q_0	initial capacity
q_∞	capacity at equilibrium
Q	dimensionless solid phase concentration in particles.
$\overline{Q}$	average dimensionless solid phase concentration in particles.
Q_1	Langmuir Constant
q^*	equilibrium solid phase concentration
r_i	measure for the standard deviation in Equation in Equation 6.1
R	dimensionless distance from the center of carbon particle
R_G	universal gas constant
R_o	ratio of dissoved oxygen to GAC mass

S	Schmidt number
St	Stanton number
t	time
T	temperature
TOC	total organic carbon
U	uptake
v	superficial velocity
V	total bed volume
V_l	volume of liquid
V_s	volume of solids
x	parameter vector in Equation 6.1
y_i	Experimental reading in Equation 6.1
Z	Longitudinal dimension in the column

GREEK LETTERS

$-\Delta H$	heat of adsorption
Δq	increase in the carbon uptake
ε	bed voidage
ε_p	particle porosity
μ	viscosity of water
τ	dimensionless time
θ_1	sphericity
φ	Thiele modulus

ρ_l	density of water
ρ_p	density of the carbon particle
χ^2	chi square statistics

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