

# **Effect of dissolved oxygen on activated carbon uptake**

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Civil Engineering

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## **Abstract**

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.

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.

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**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  
DHAIRAN, SAUDI ARABIA**

**In Partial Fulfillment of the  
Requirements for the Degree of**

**DOCTOR OF PHILOSOPHY**

**IN**

**CIVIL ENGINEERING**

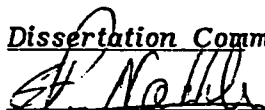
**July 1993**

**KING FAHD UNIVERSITY OF PETROLEUM & MINERALS**

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*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*

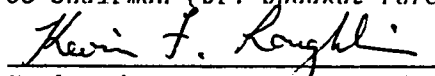
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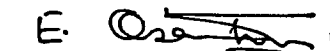
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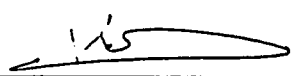
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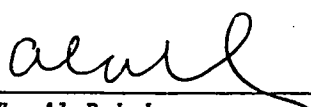


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Date : September, 1993



This dissertation is dedicated

to

*my parents and my wife*

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## ملخص الرسالة

اسم الطالب : نبيل سعيد فؤاد أبوزيد  
عنوان الدراسة : تأثير الأكسجين المذاب على قدرة الكربون المنشط .  
التخصص : هندسة مدنية ( مصادر المياه والبيئة ) .  
تاريخ الشهادة : يوليو ١٩٩٢ م .

بينت دراسات الحرارة المتساوية على الفينول والأكريستول والنيتروفينول نسبة ٢٠ - ١١٥٪ زيادة في قدرة الكربون نتيجة لوجود الأكسجين المذاب . وقد تم التوصل إلى نفس هذه الظاهرة عندما استعملت عوامل الأكسدة مثل بيوركسيد الهيدروجين وبيرومنجنات البوتاسيوم بدلاً من الأكسجين الجزيئي .  
بينما دلت الدراسة على عدم وجود تأثير يذكر للأكسجين 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 الأكسجين ، وبناء على ذلك تم اقتراح وسيلتين للتفاعل لتمثيل التفاعل بين الأكسجين 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 الإمتزاز الفيزيائي مع إنخفاض الحرارة وتزايد التلمرة مع إزدياد الحرارة . ولقد وجد أن الزيادة في القدرة على الإمتزاز لمركبات الفينول تتناسب مع زيادة الأكسجين المذاب كما تزداد كذلك مركبات الفينول الثنائية . وقد وجد أن كفاءة استرجاع الفينول من الكربون انخفضت في حالة وجود الأكسجين من ٧٠٪ إلى ٢٥٪ . وأن القدرة الإضافية قد اعتمدت على كمية الأكسجين المذاب وكتلة الكربون .  
هذا وقد تم التوصل إلى نموذجين رياضيين للربط بين القدرة تحت جو الأكسجين وكلاً من كمية الأكسجين المذاب والقدرة بدون الأكسجين المذاب .  
وقد بينت التجارب الزمنية أن عامل الانتشار الظاهري قد قل مع زيادة كمية الأكسجين 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 الأكسجين وعدمه كانت عند الحموضة المتعادلة ودرجة حرارة ٣٥ درجة مئوية .  
وقد تم عمل نموذج رياضي يحتوي على التفاعلات الناتجة عن الأكسجين المذاب مع الإمتزاز حيث افترض أن التفاعل من الدرجة الأولى لا يعتمد على كمية الأكسجين . وقد أثبتت تجارب أعمدة الكربون أن الأكسجين المذاب يؤخر منحني الظهور مؤدياً إلى منحني مختلف كلياً .  
أن موضوع الاختلاف بين قدرة الكربون في حالة تجارب المزججات 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 نهد للبتروك والمعادن

الطهران ، المملكة العربية السعودية

يولي ١٩٩٢ م

## 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  
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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 inaccessible 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  $\text{CO}_2$ , 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 ( $\text{CO}_2$  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  $C_e/C_0$  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 ( $S_{min}^2$ ) 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  $D_p$  values required for model simulations are  $D_p$  for the best fit and the  $D_p$  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  $D_p$ , 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  $\gg 100$ , 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. In spite 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, non-linearity of adsorption isotherms, and axial dispersion. Weber and Chakrovorti (37) and Fritz and Schlunder (47) proposed a combination of surface diffusion and pore

diffusion transport, which they assume take place simultaneously. This model is known as the heterogeneous 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 IISDM 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 IISDM model (38). Accordingly, the IISDM 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 IISDM 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 run. 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 Langmuir equation is:

$$q = \frac{Q_1 b C}{1 + b C} \quad (1.1)$$

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 :

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

or

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

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:

$$q = kC^{1/n} \quad (1.4)$$

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 Freundlich 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:

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

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.

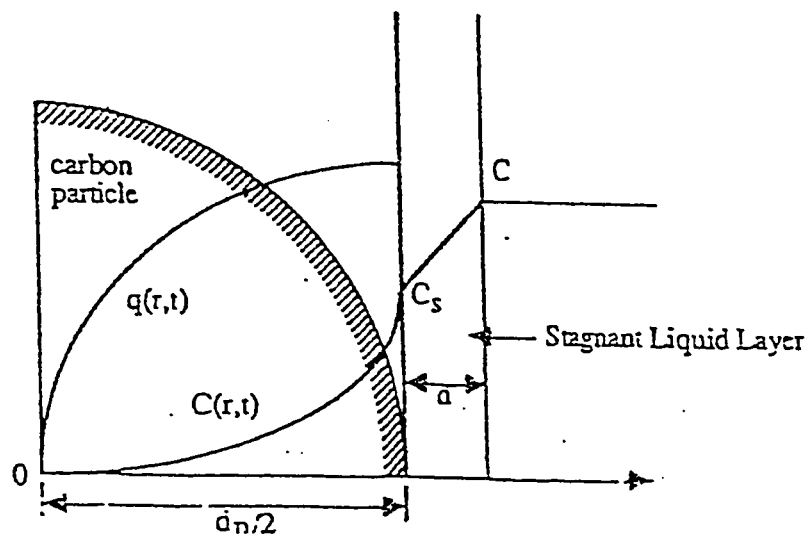


Figure 1.1: Schematic Representation of the PDM Model

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,  $k_p$ , 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:

$$\rho_p \frac{\partial q}{\partial t} + \epsilon_p \frac{\partial C_p}{\partial t} = D_p \left[ \frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right] \quad (1.6)$$

where;

$\rho_p$  = density of the carbon particle, M/L<sup>3</sup>,

$q$  = carbon loading, M adsorbate/M adsorbent,

$\epsilon_p$  = particle porosity,

$D_p$  = pore diffusion coefficient, L<sup>2</sup>/T,

$C_p$  = pore liquid-phase concentration, M/L<sup>3</sup>,

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

The two boundary conditions for the above equation are:

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

and,

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

where;

$d_p$  = diameter of the spherical GAC particle, L,

$C$  = bulk liquid concentration, M/L<sup>3</sup>,

$C_s$  = adsorbate in the liquid film at the solid-liquid interface, M/L<sup>3</sup>,

$k_f$  = external mass transfer coefficient, L/T.

The initial condition for Equation 1.7 is

$$@ t = 0, 0 \leq r \leq r_0: C_p = 0 \quad (1.9)$$

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.

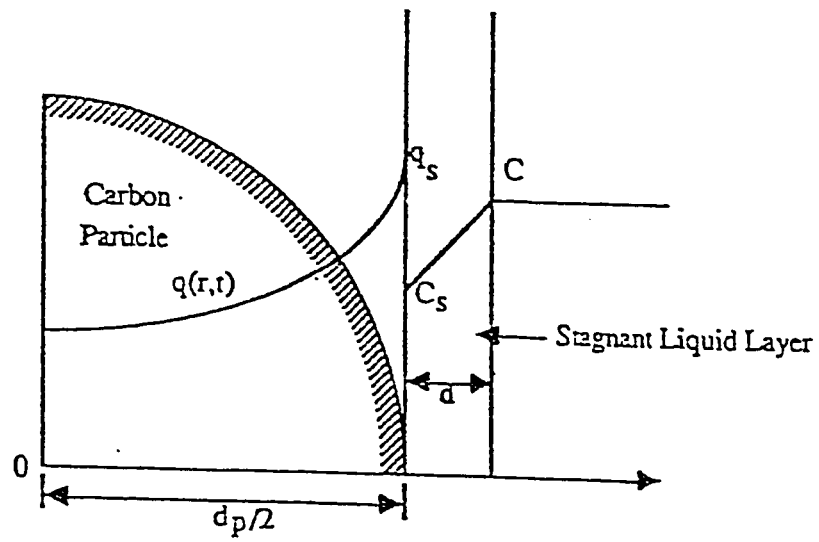


Figure 1.2: Schematic Representation of the HSDM Model

The kinetic parameters incorporated in this model are the stagnant liquid film mass transfer coefficient,  $k_p$ , 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:

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

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.

$$@ t = 0, 0 \leq r \leq r_0 : q = 0 \quad (1.11)$$

$$@ t \geq 0, r = 0: \frac{\partial q}{\partial r} = 0 \quad (1.12)$$

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

The IISDM 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:

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

### 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:  $\text{Flux} = -D_s \left( \frac{\partial C}{\partial x} \right)$
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:

$$\begin{aligned} T &= \frac{\text{rate of mass of adsorbate fed}}{\text{total mass of adsorbate at equilibrium}} \\ &= \frac{QC_0 t}{Mq_c + \epsilon VC_0} \end{aligned}$$

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

$\epsilon$  = ratio of void volume to total bed volume

$V$  = total bed volume,  $L^3$

The dimensionless solute distribution parameter  $D_g$  is defined as

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

where,  $\rho_p$  = pellet density (includes pore volume)

The dimensionless Biot number,  $B_i$ , is defined as:

$$B_i = \frac{\text{rate of liquid phase mass transfer}}{\text{rate of surface diffusion within the particle}} \\ = \frac{(1 - \epsilon)k_f r_0}{\epsilon D_s D_g \theta_1}$$

where;

$k_f$  = film transfer coefficient,  $L/T$

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

$\theta_1$  = 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:

$$St = \frac{k_f \tau (1 - \epsilon)}{r_0 \epsilon \theta_1}$$

where,  $\tau$  = hydraulic residence time in the bed.

The surface diffusion modulus  $E_d$  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:

$$E_d = \frac{D_s D_f \tau}{r_0^2} = \frac{St}{B_i}$$

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

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

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.

$$@ t = 0, 0 \leq r \leq \frac{r_0}{2} : q = 0 \quad (1.11)$$

$$@ t \geq 0, r = 0: \frac{\partial q}{\partial r} = 0 \quad (1.12)$$

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

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

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

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial Z} - \frac{3(1 - \epsilon_p)}{\epsilon_p R} k_f (C - C_s) \quad (1.16)$$

where,

$V$  = interstitial velocity

$Z$  = longitudinal dimension

The initial condition of Equation 1.16 is

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

and the boundary condition is

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

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.

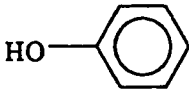
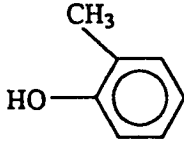
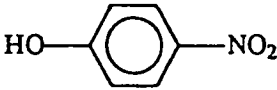
## Stage II

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	$  \begin{array}{c}  \text{H} \quad \text{Cl} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{H} \quad \text{Cl}  \end{array}  $
1,1,2,2-Tetrachloroethane		$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{Cl}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{Cl} \quad \text{Cl}  \end{array}  $
Trichloromethane	Chloroform	$  \begin{array}{c}  \text{Cl} \\    \\  \text{H}-\text{C}-\text{Cl} \\    \\  \text{Cl}  \end{array}  $
Tribromomethane	Bromoform	$  \begin{array}{c}  \text{Br} \\    \\  \text{H}-\text{C}-\text{Br} \\    \\  \text{Br}  \end{array}  $
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 recommendations for further research.

## **Chapter 2**

### **APPARATUS 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 <sub>2</sub> BET Method), m <sup>2</sup> /g	824
Bulk Density, g/cm <sup>3</sup>	0.74
Particle Density Wetted in Water, gm/ cm <sup>3</sup>	1.3-1.4
Pore Volume, cm <sup>3</sup> /gm	0.94
Effective Size (d <sub>10</sub> ), cm	0.055-0.065
Uniformity Coefficient (d <sub>90</sub> /d <sub>10</sub> )	1.6-2.1
Particle Size Used in Experiments (d <sub>0</sub> ), 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  $\mu$ m 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  $\mu$ A, and the acceleration voltage was 5 KV.

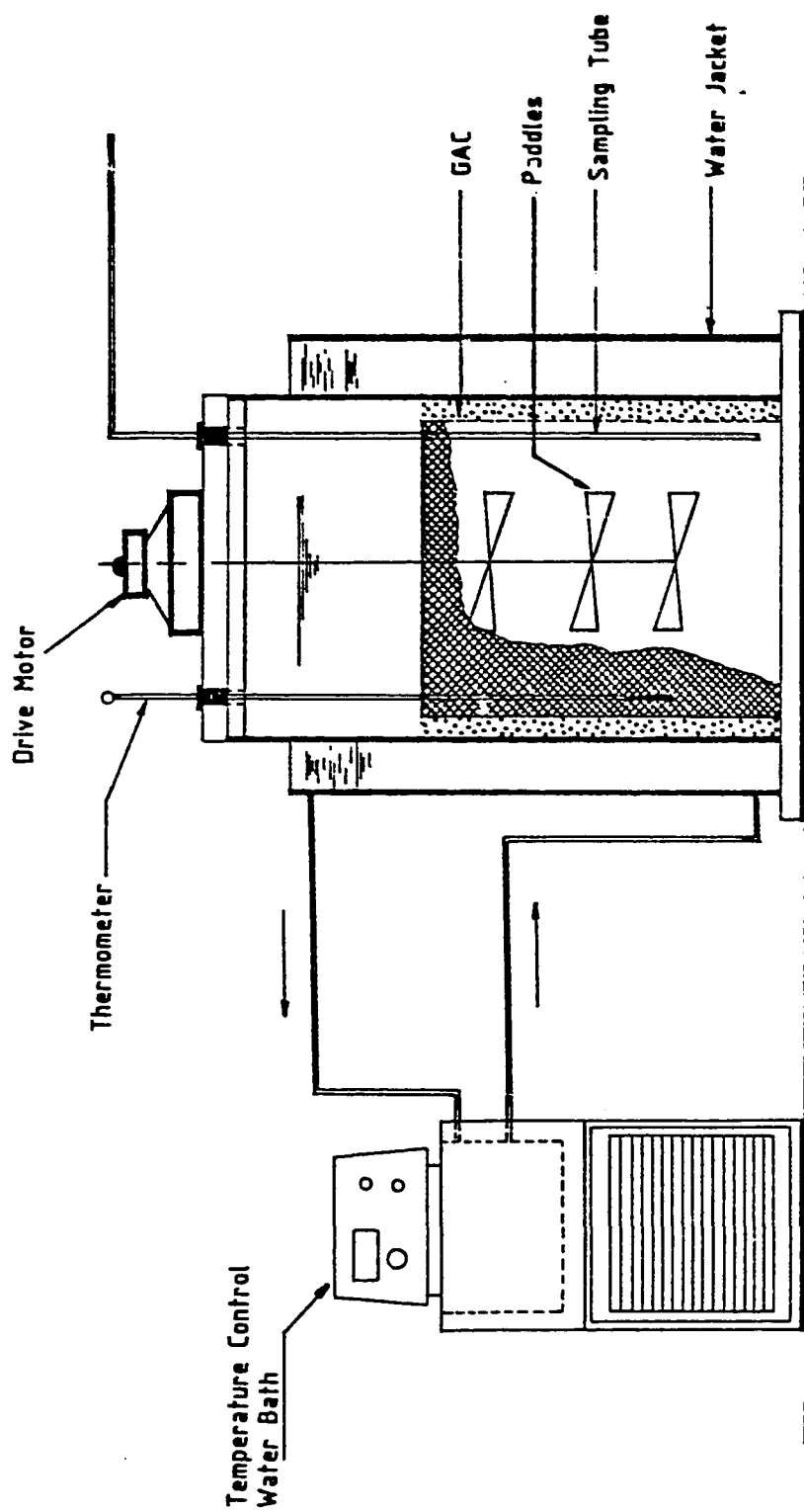


Figure 2.1: Schematic Diagram of the Kinetics Experimental setup

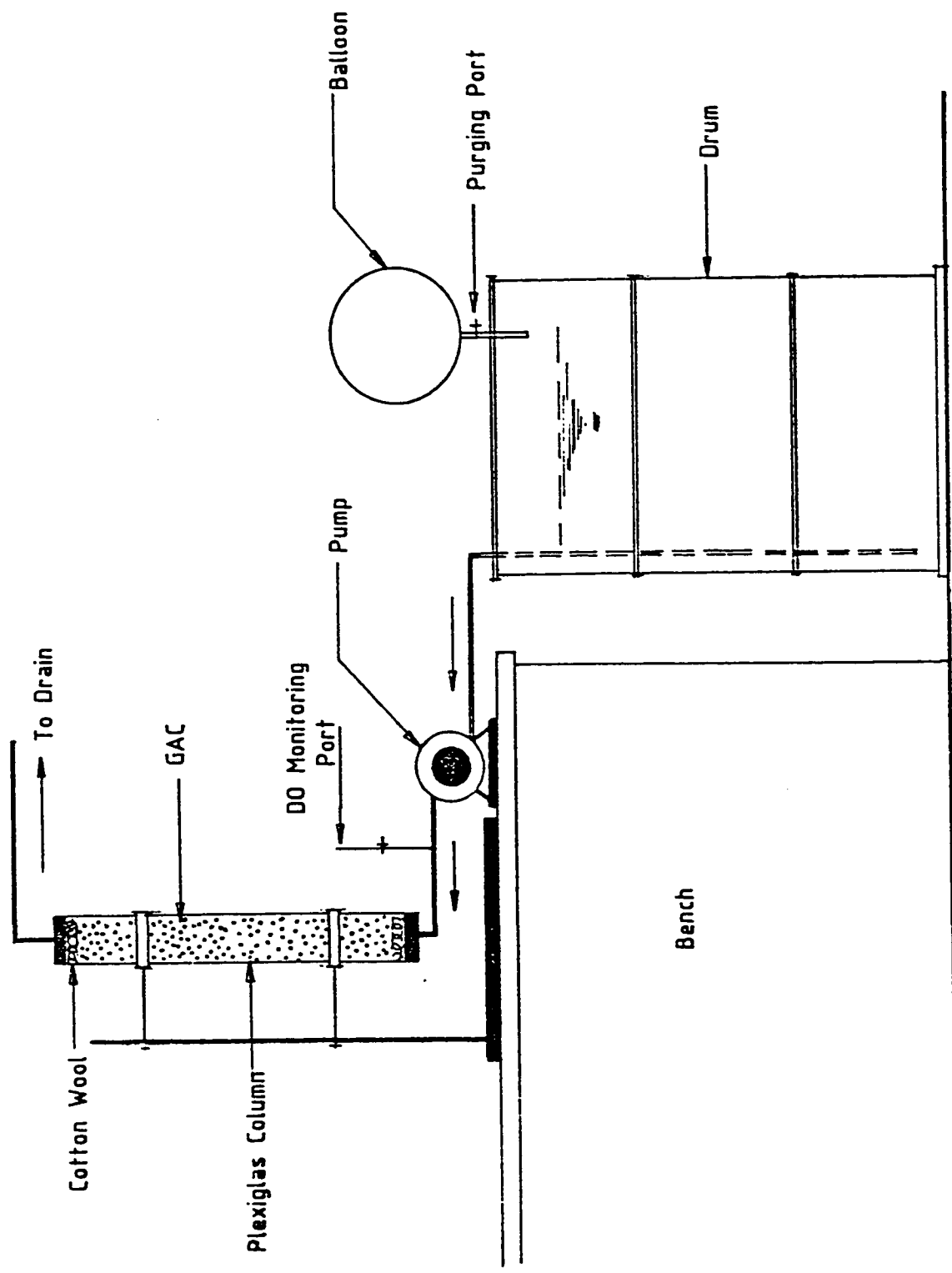


Figure 2.2: Schematic Diagram of the Columns setup

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 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  $\text{KH}_2\text{PO}_4$  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  $\mu\text{m}$  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 NaHCO<sub>3</sub>/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 NaHCO<sub>3</sub>/NaOH mixture was prepared by mixing 50 ml 0.05 M NaHCO<sub>3</sub> 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  $\text{Na}_2\text{SO}_4$ , 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 (IDWW), 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.

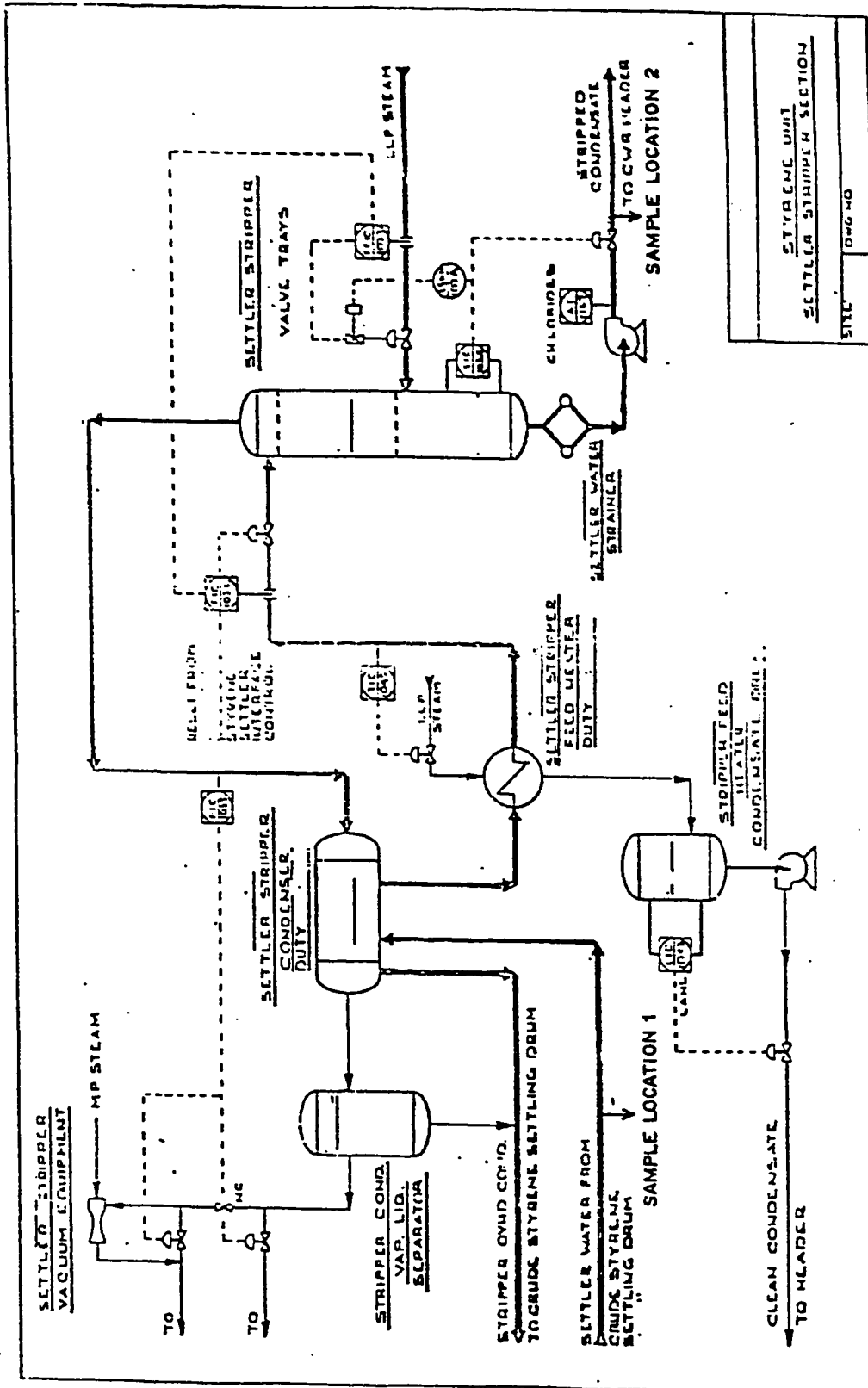


Figure 3.1: Layout of the Styrene Plant With Sample Locations.

## 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

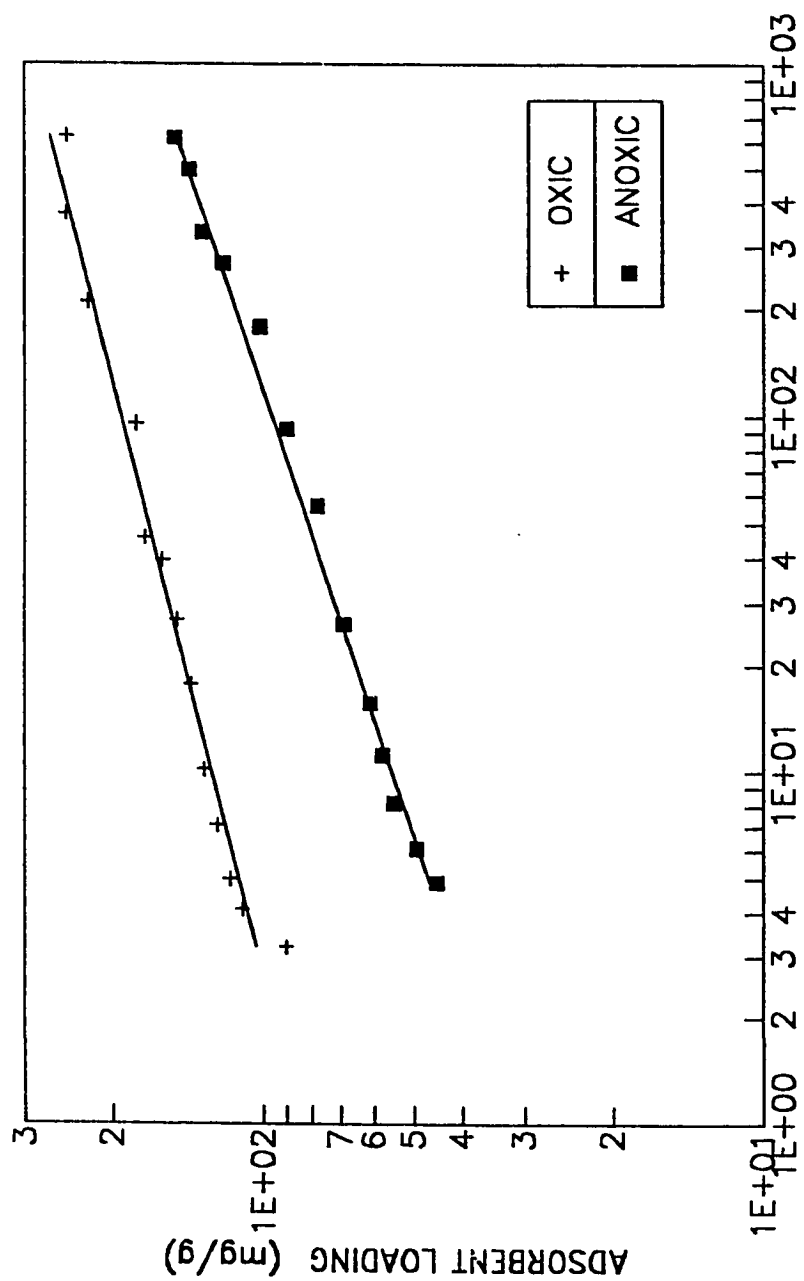


Figure 3.2: Uptakes of Phenol at  $T = 21^{\circ}\text{C}$  and pH of 7 Along with Best Fit Freundlich Curves Using constants Given in Table 3.1.

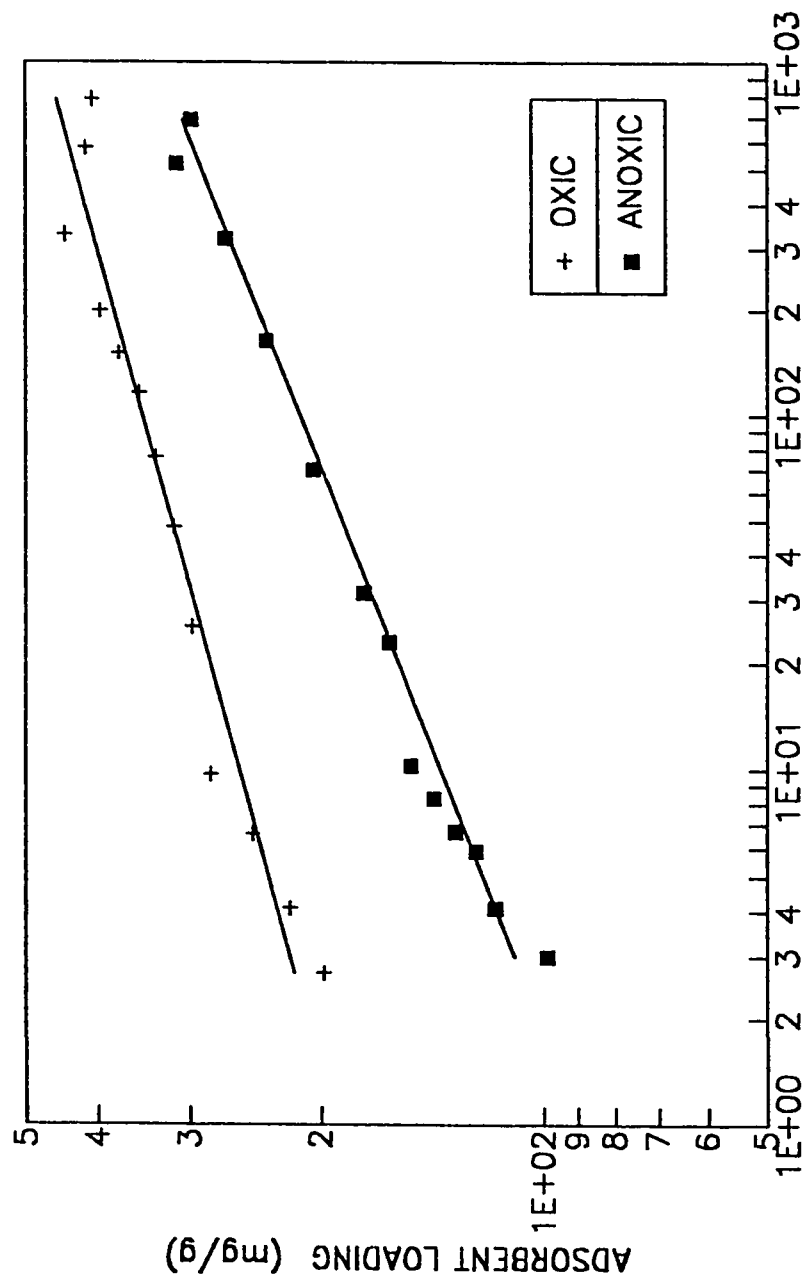
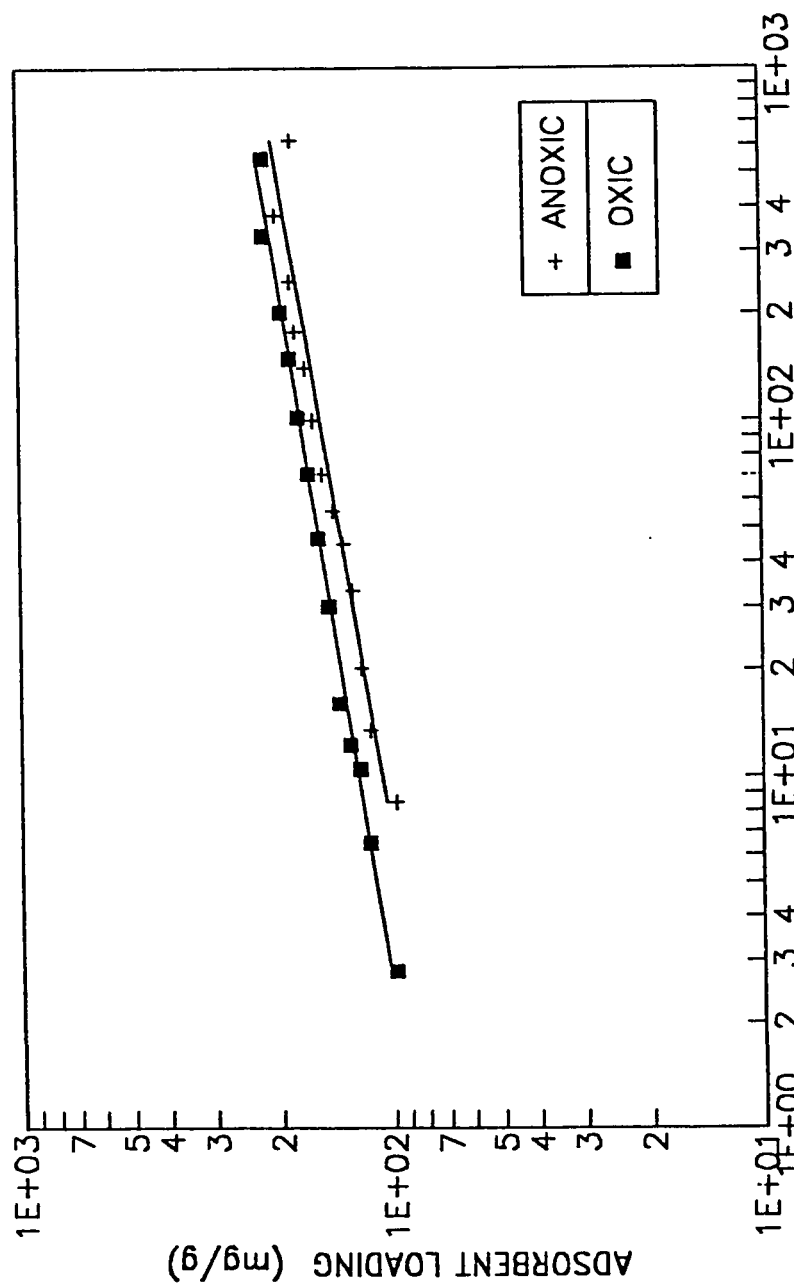


Figure 3.3: Uptakes of o-Cresol at T = 21°C and pH of 7, Along with Best Fit Freundlich Curves Using Constants Given in Table 3.1.

from ENR



2,4-NITROPHENOL CONCENTRATION (mg/l)

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 Filtrasorb 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.

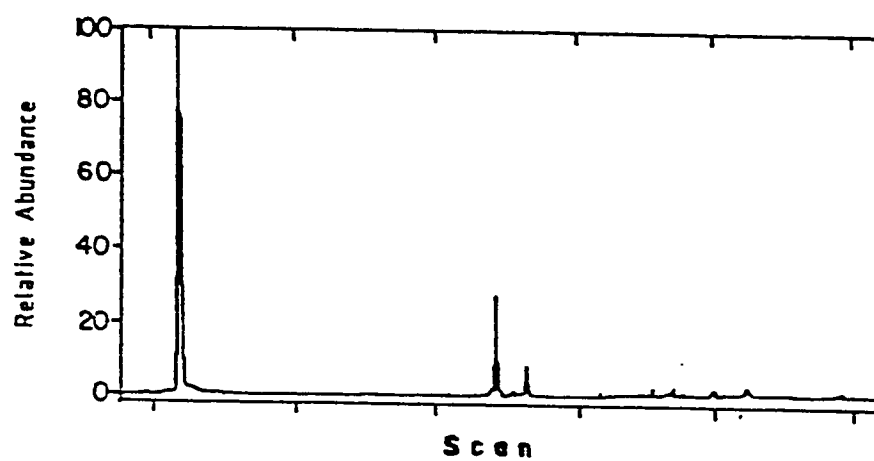


Figure 3.5: GC-MS Total Ion Chromatogram for the Anoxic GAC Sample of Phenol

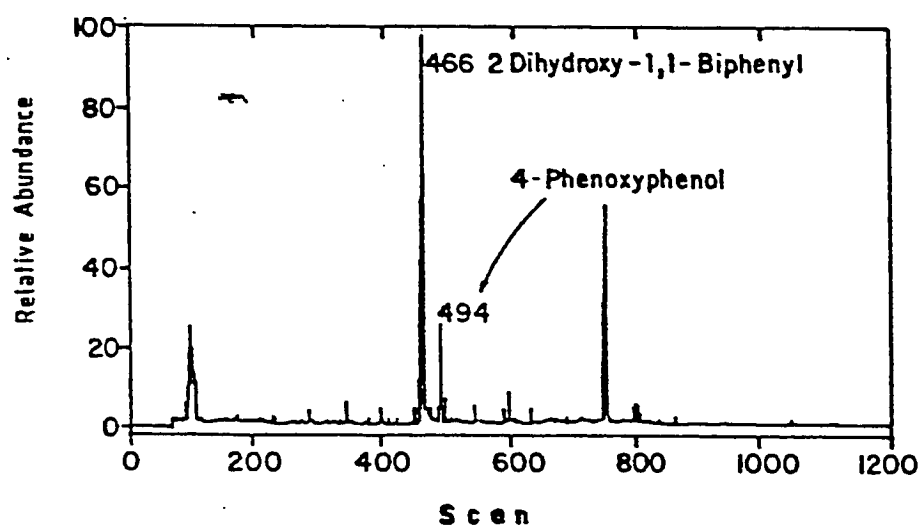


Figure 3.6: GC-MS Total Ion Chromatogram for the Oxidized GAC Sample of Phenol

### 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  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  0.1 N solution for two weeks. The amounts of acidic and basic functional groups were then determined by specific titration techniques.

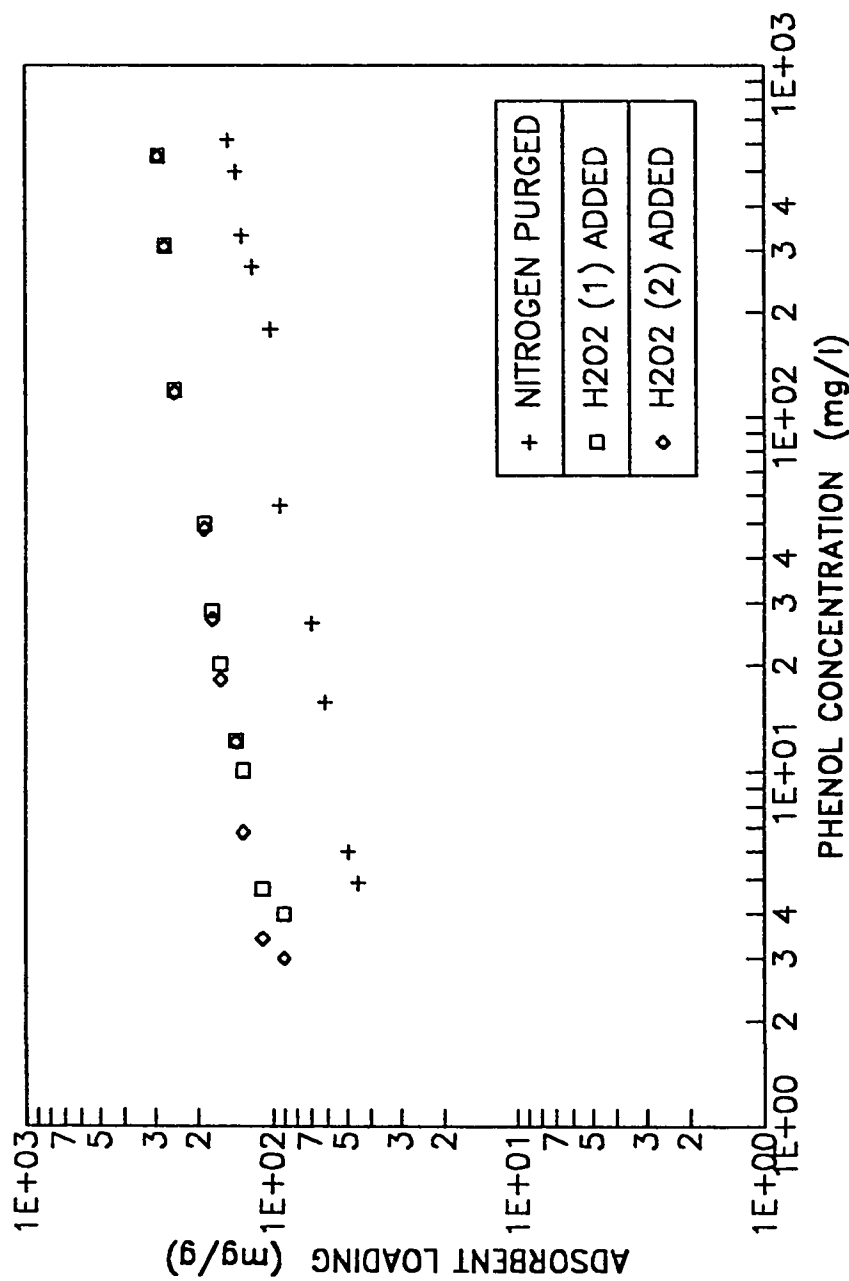


Figure 3.7: Uptakes of Phenol with and without Hydrogen Peroxide Versus Residual Concentration at  $T = 21^{\circ}\text{C}$  and pH of 7.

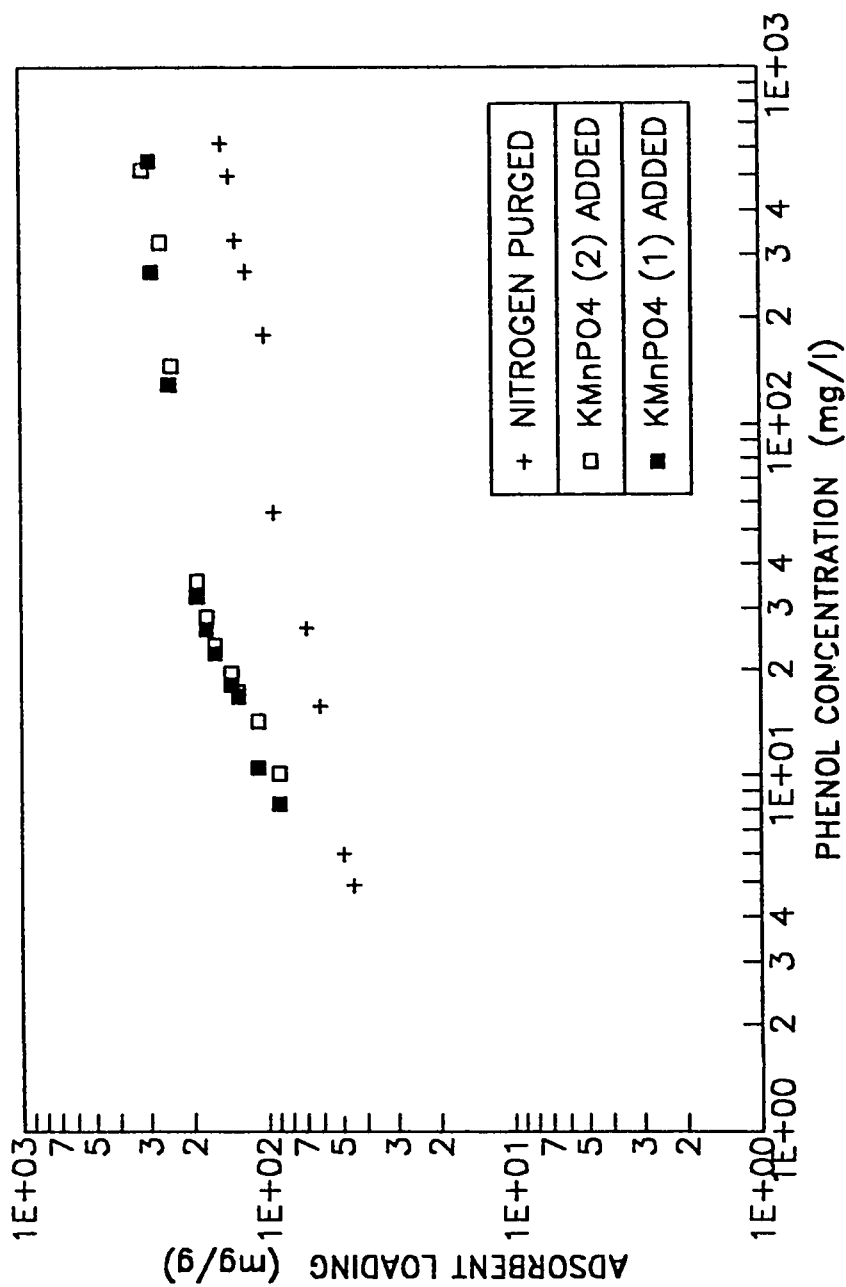


Figure 3.8: Uptakes of Phenol with and without Potassium Permanganate Versus Residual Concentration at  $T = 21^{\circ}\text{C}$  and pH of 7.

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 chemisorption 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 shows 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 chemisorption 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 of 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.

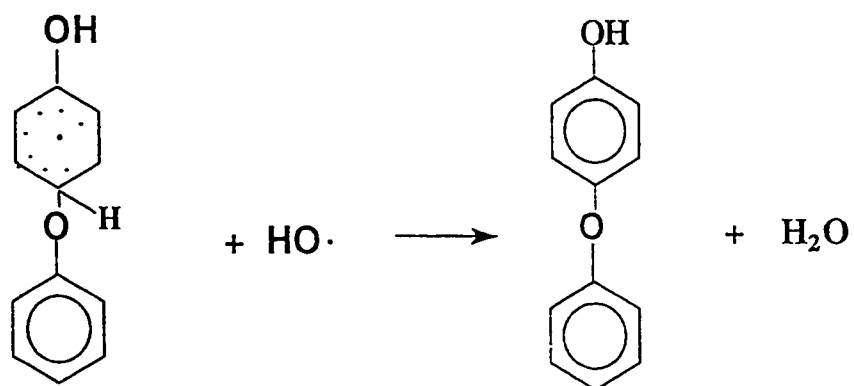
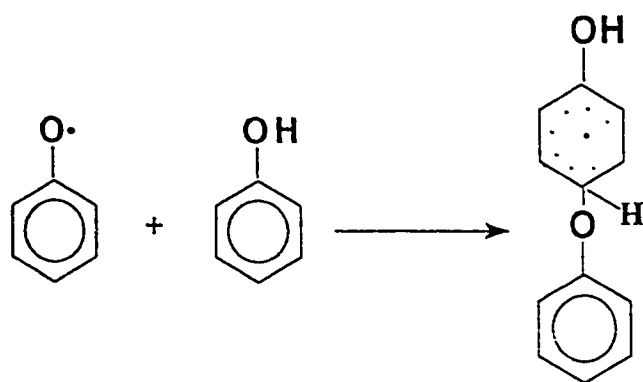
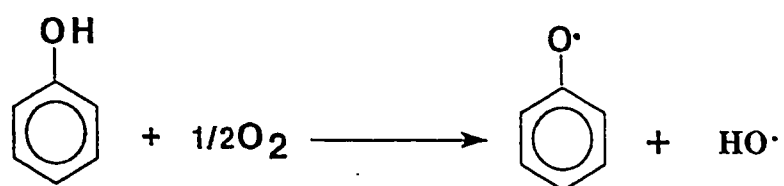
Two free radical mechanisms for the reaction of phenol with oxygen and potassium permanganate are proposed and presented in Schemes 1 and 2, respectively. The two reaction mechanisms produces a final product of the dimer 4-phenoxyphenol which was detected on the carbon surface.

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

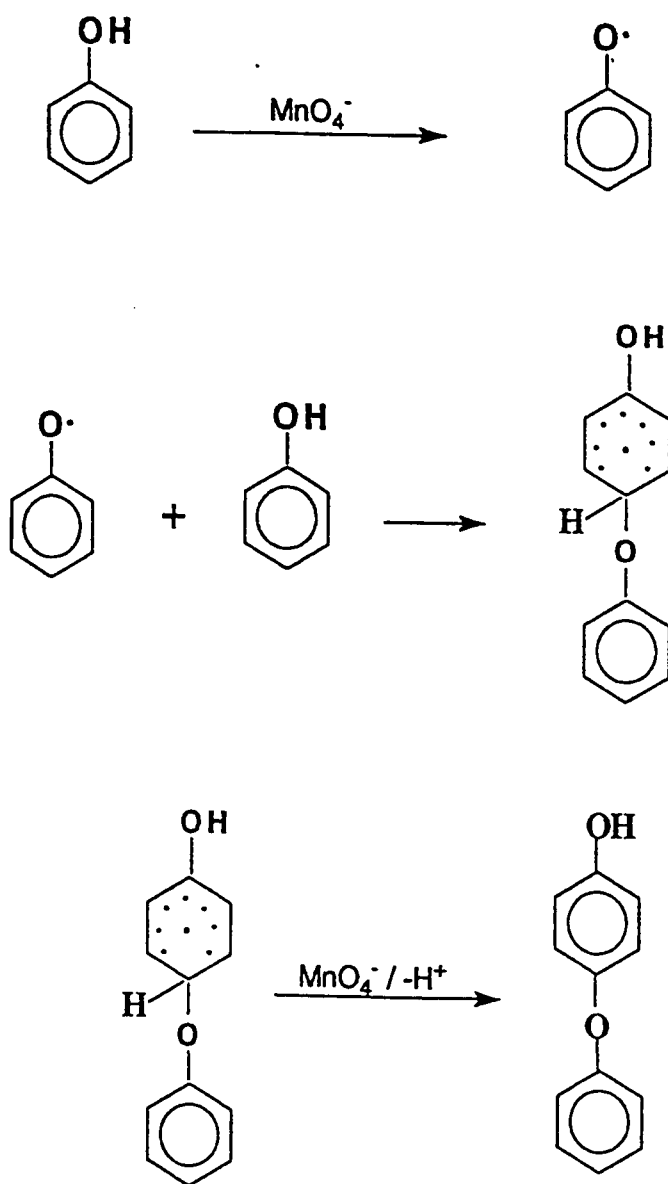


From the previous chemical equation, 1 mg/l of DO consumes 11.75 of phenol, while from the isotherm experiments, the real ratio of oxygen to phenol consumed (difference in uptake) is 1:3.1 and 1:7.8 for Carbon masses of 1000, 500 mg, respectively. This clearly shows that DO is not limiting the telomerization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



Scheme 1. Free Radical Mechanism for the reaction of oxygen with phenol.



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

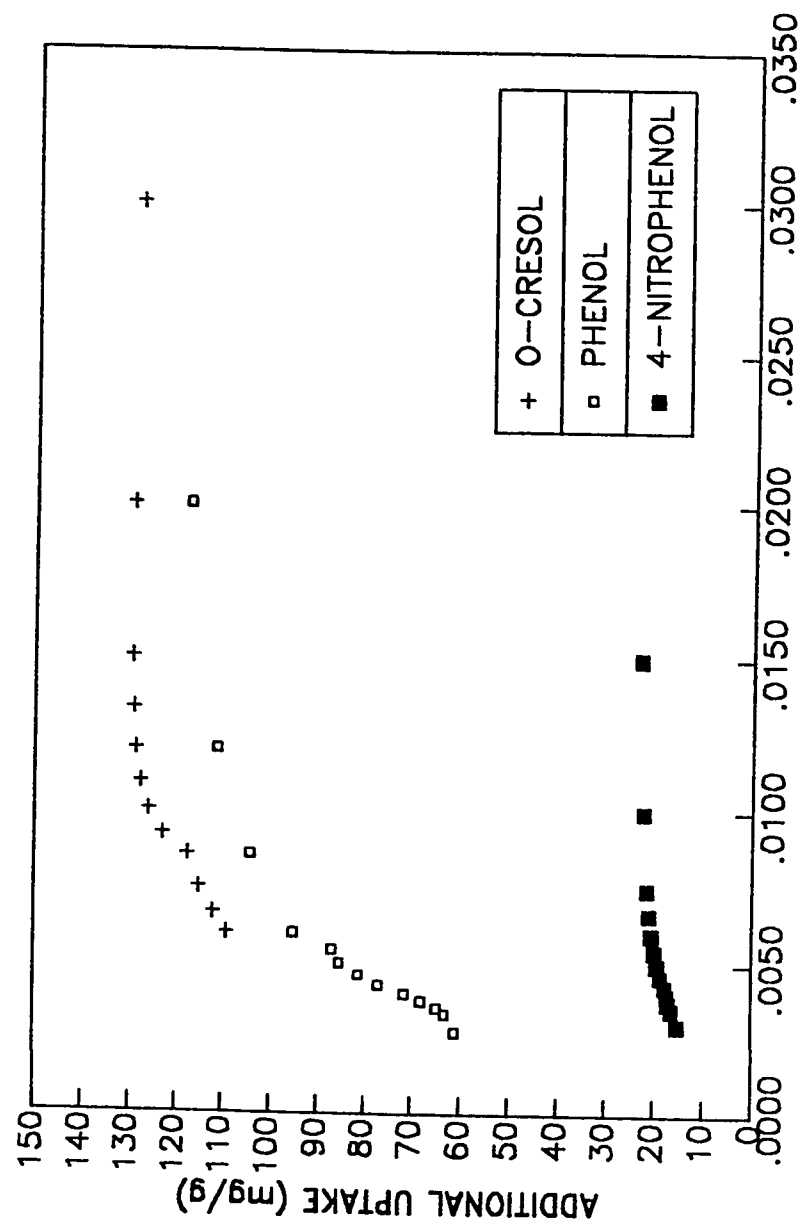


Figure 3.9: Relationship Between Additional Uptake and the Ratio of Initial DO to GAC Mass at T = 21°C and pH of 7.

from data

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 oxidic capacities the aforementioned additional uptake becomes independent of the amount of adsorbate retained under anoxic conditions.

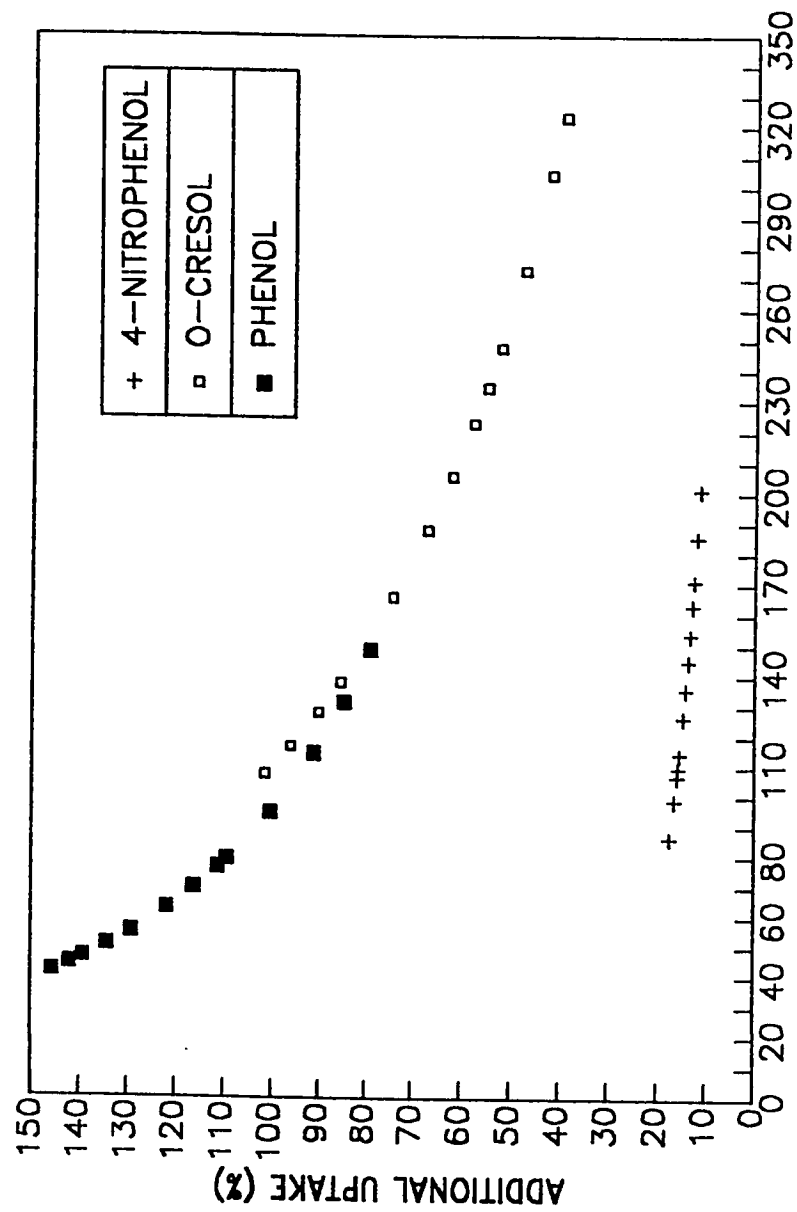


Figure 3.10: Relationship Between Percentage Additional Uptake and the Anoxic Uptake at  $T = 21^{\circ}\text{C}$  and  $\text{pH}$  of 7.

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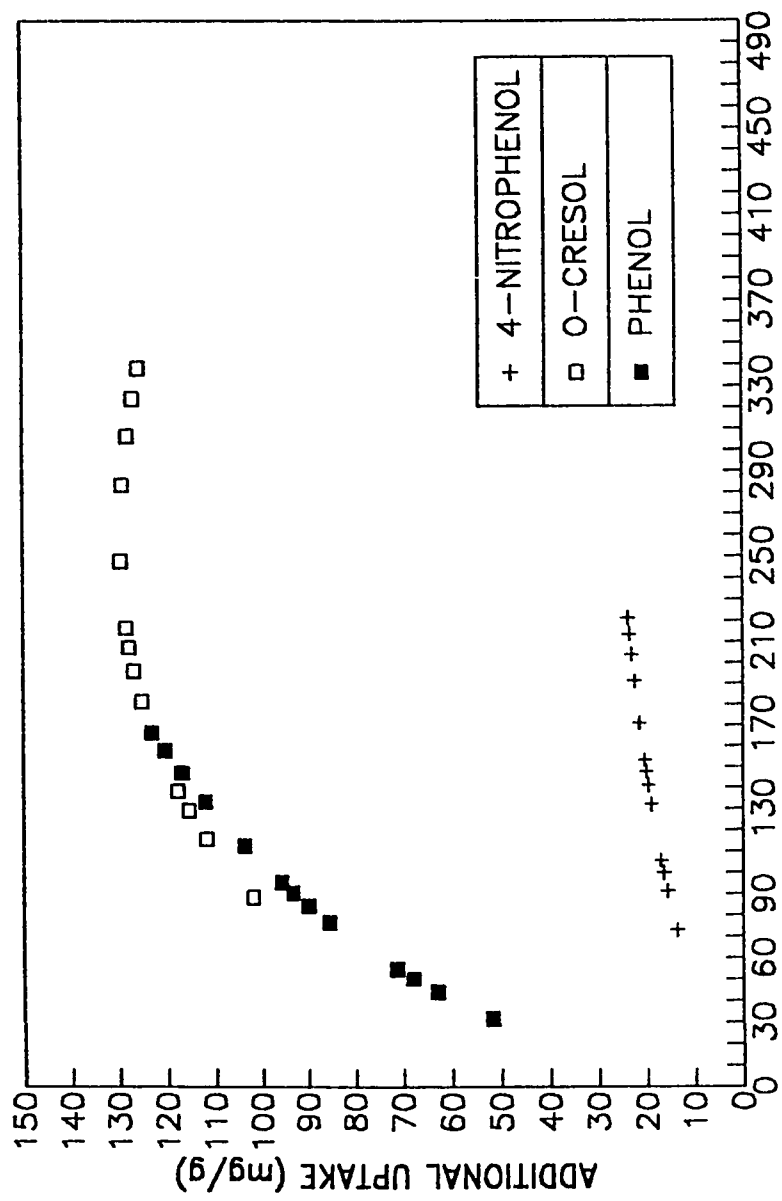


Figure 3.11: Relationship Between Additional Uptake and the Anoxic Uptake at  $T = 21^{\circ}\text{C}$  and pH of 7.

from mad21

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.

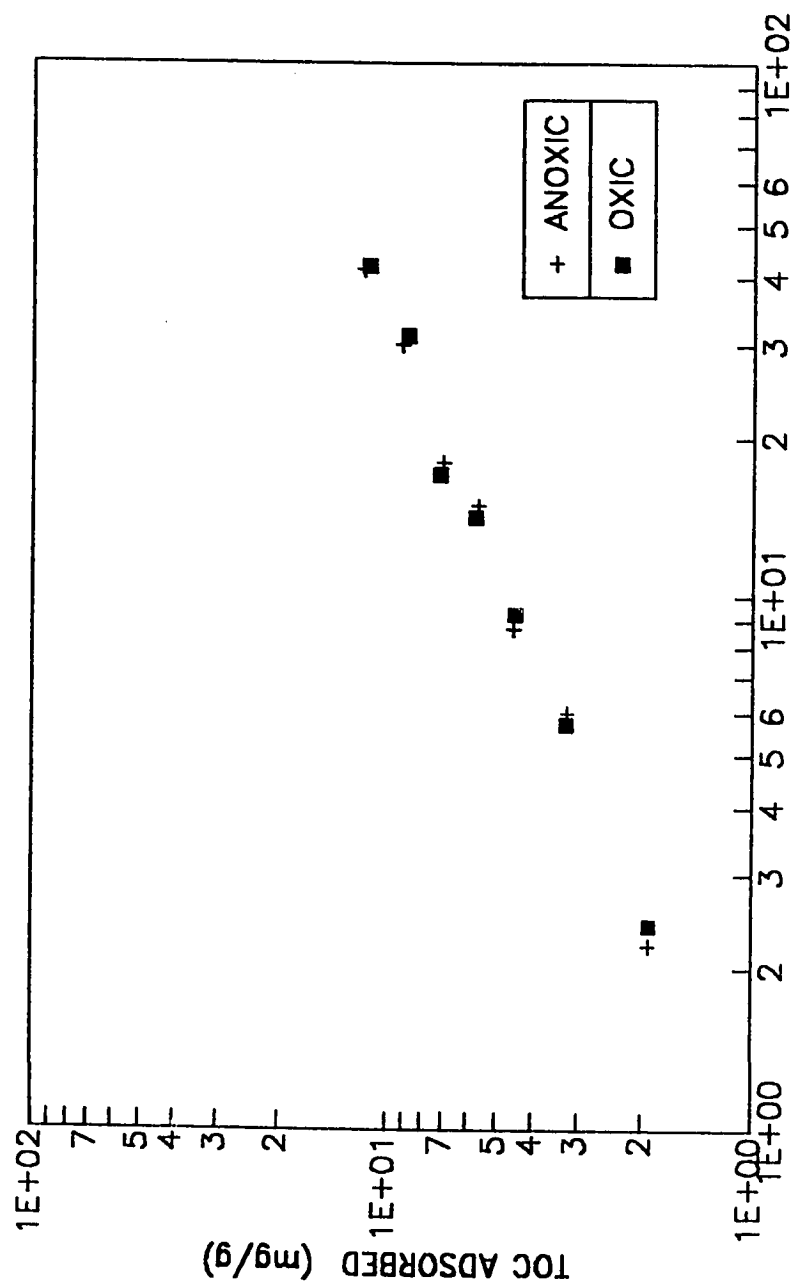


Figure 3.12: Adsorption Isotherm for Chloroform at  $T = 21^{\circ} \text{C}$  and pH of 7.

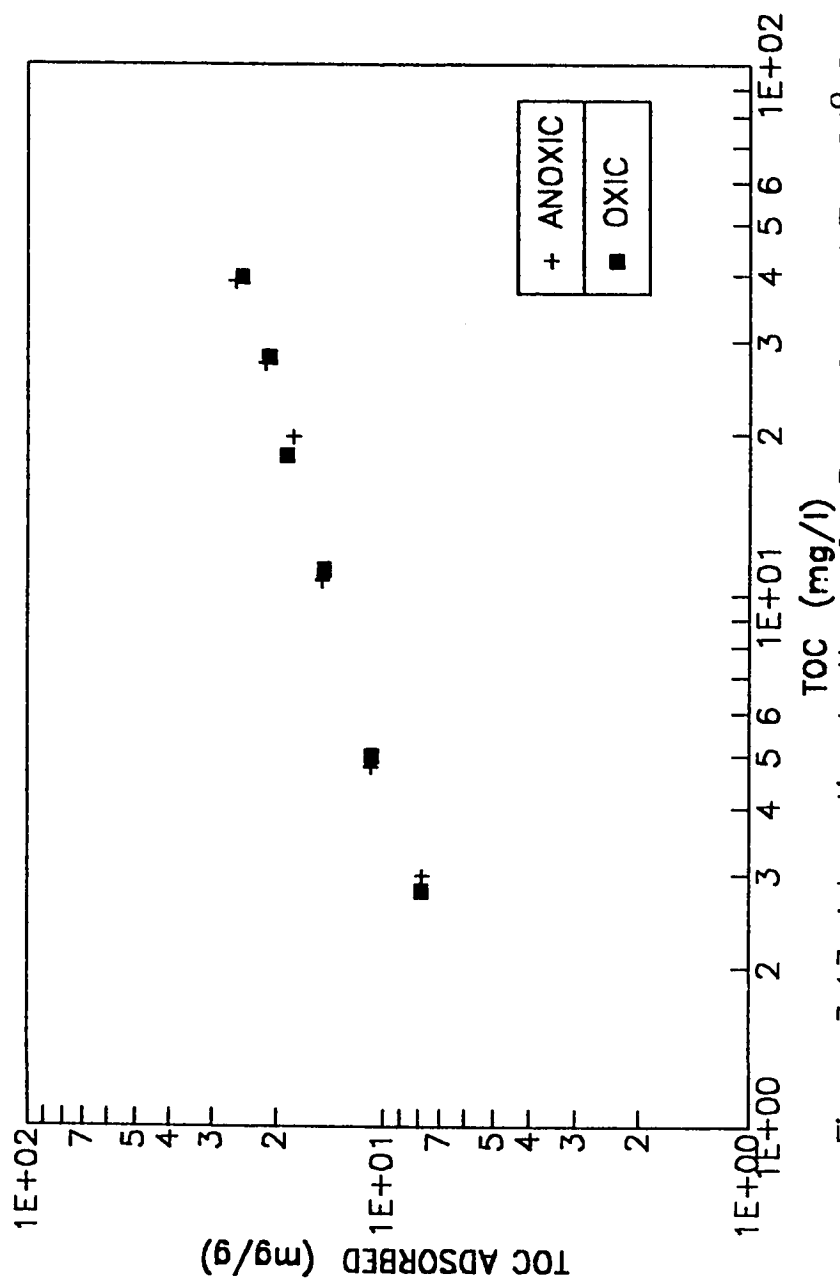
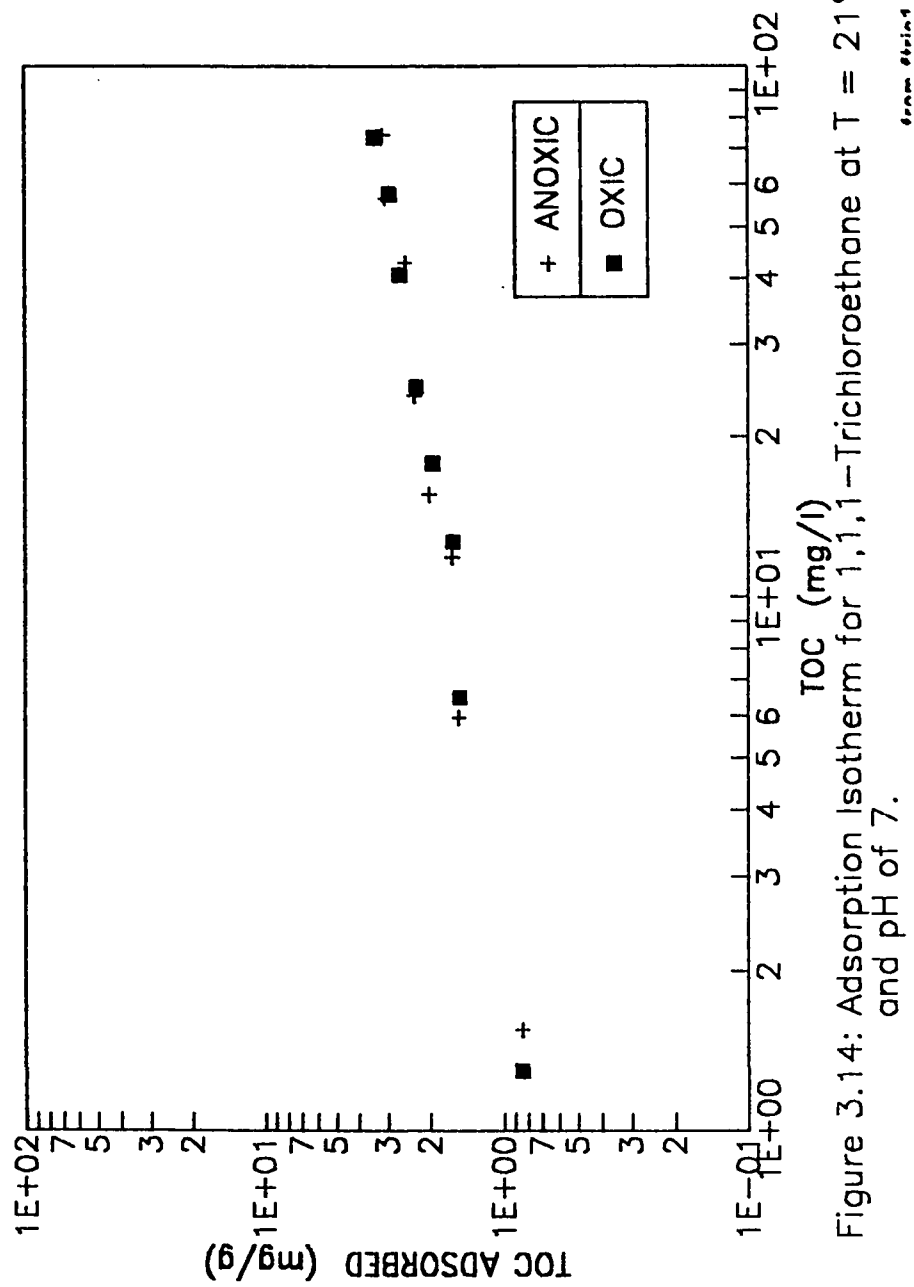


Figure 3.13: Adsorption Isotherm for Bromoform at  $T = 21^{\circ} \text{C}$  and pH of 7.

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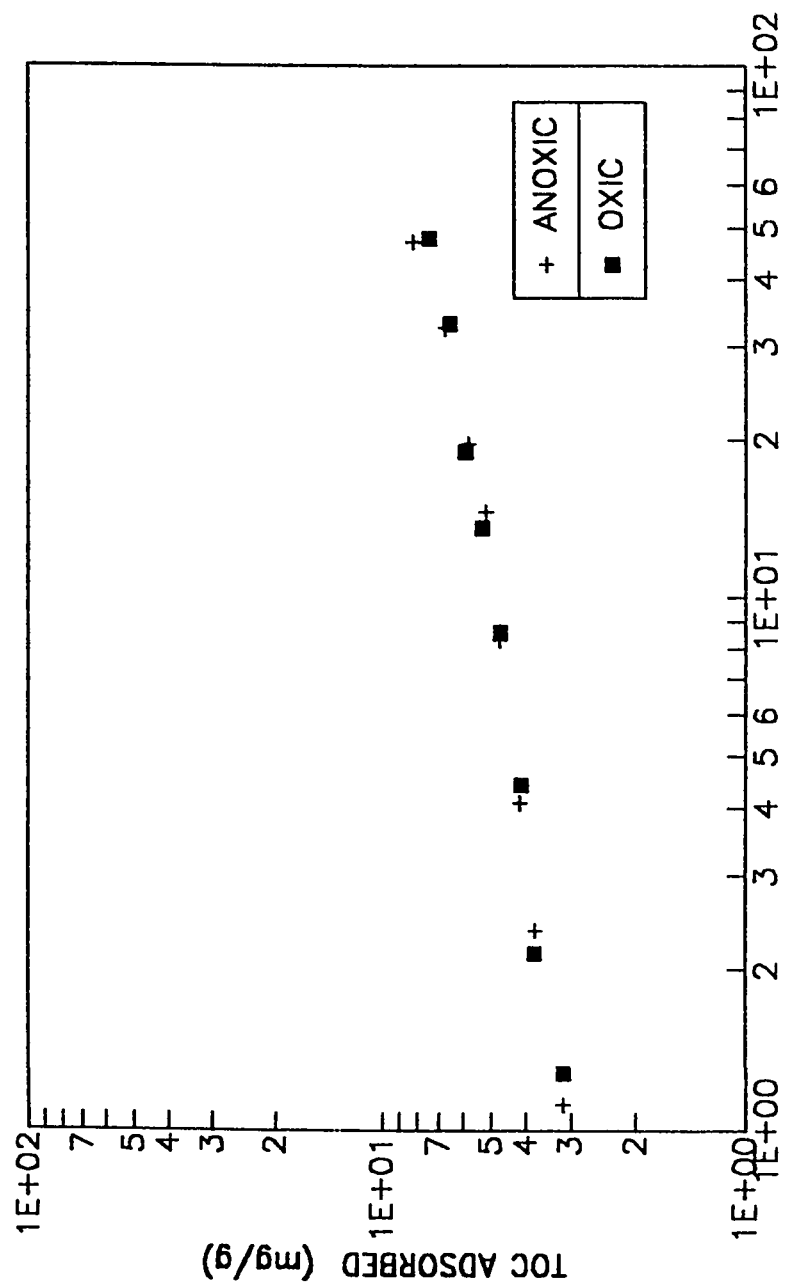


Figure 3.15: Adsorption Isotherm for 1,1,2,2-Tetrachloroethane at  $T = 21^{\circ}\text{C}$  and pH of 7.

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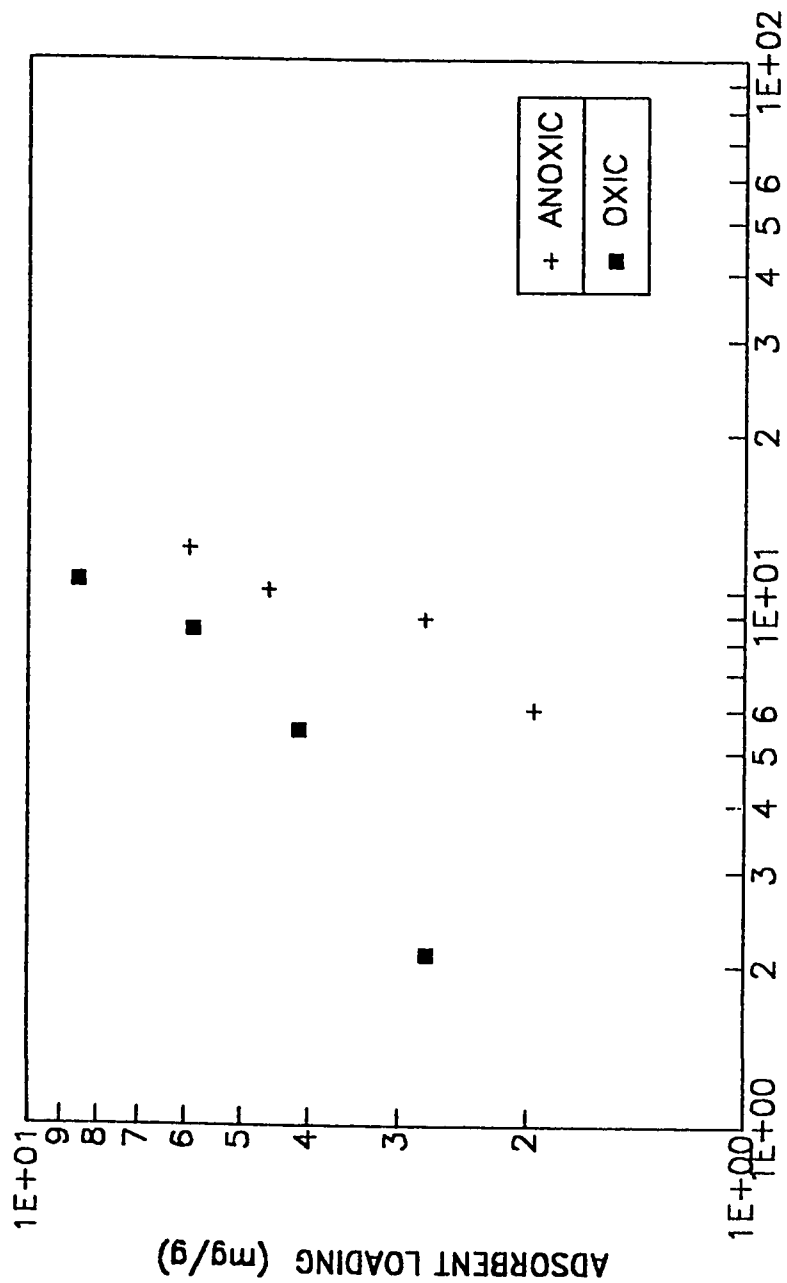


Figure 3.16: Uptakes of TOC for I.W.W, Sample Location 1, at T = 21°C and pH of 7.

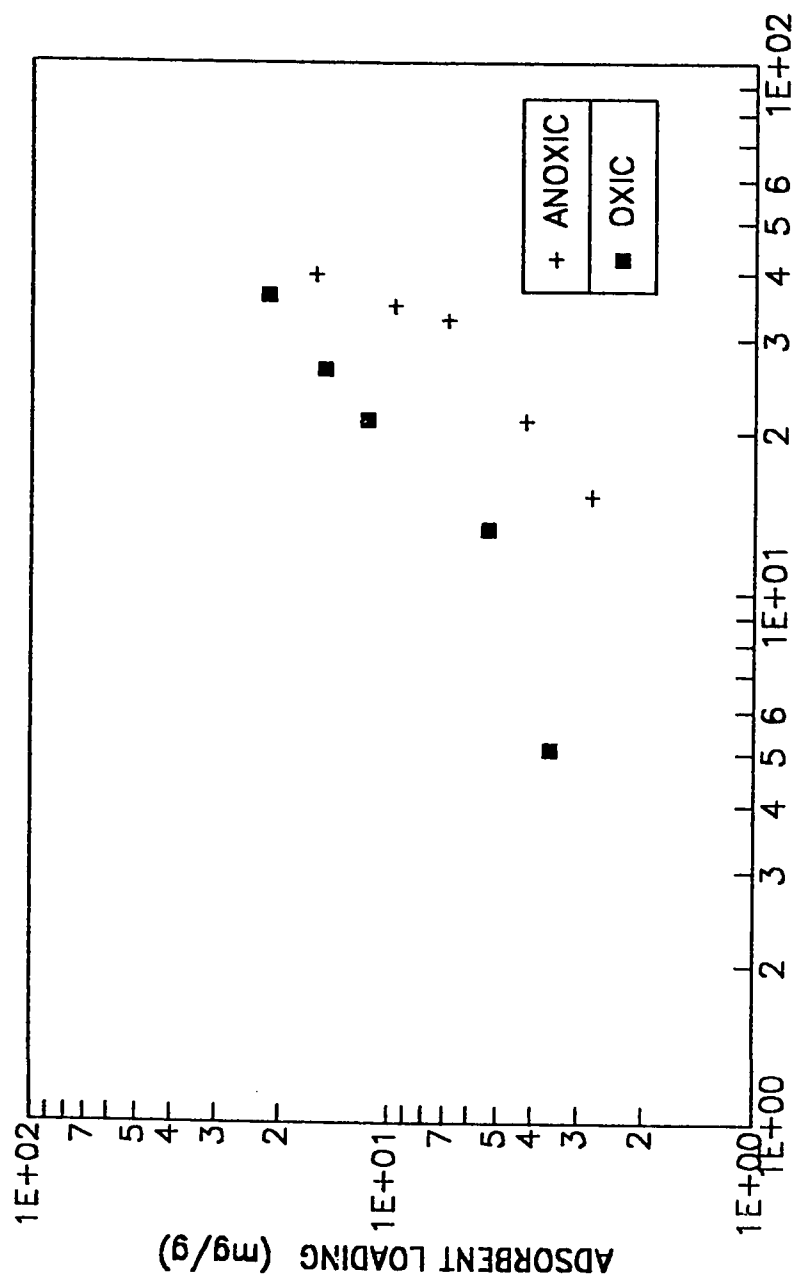


Figure 3.17: Uptakes of TOC for I.W.W, Sample Location 2, at  $T = 21^{\circ}\text{C}$  and pH of 7.

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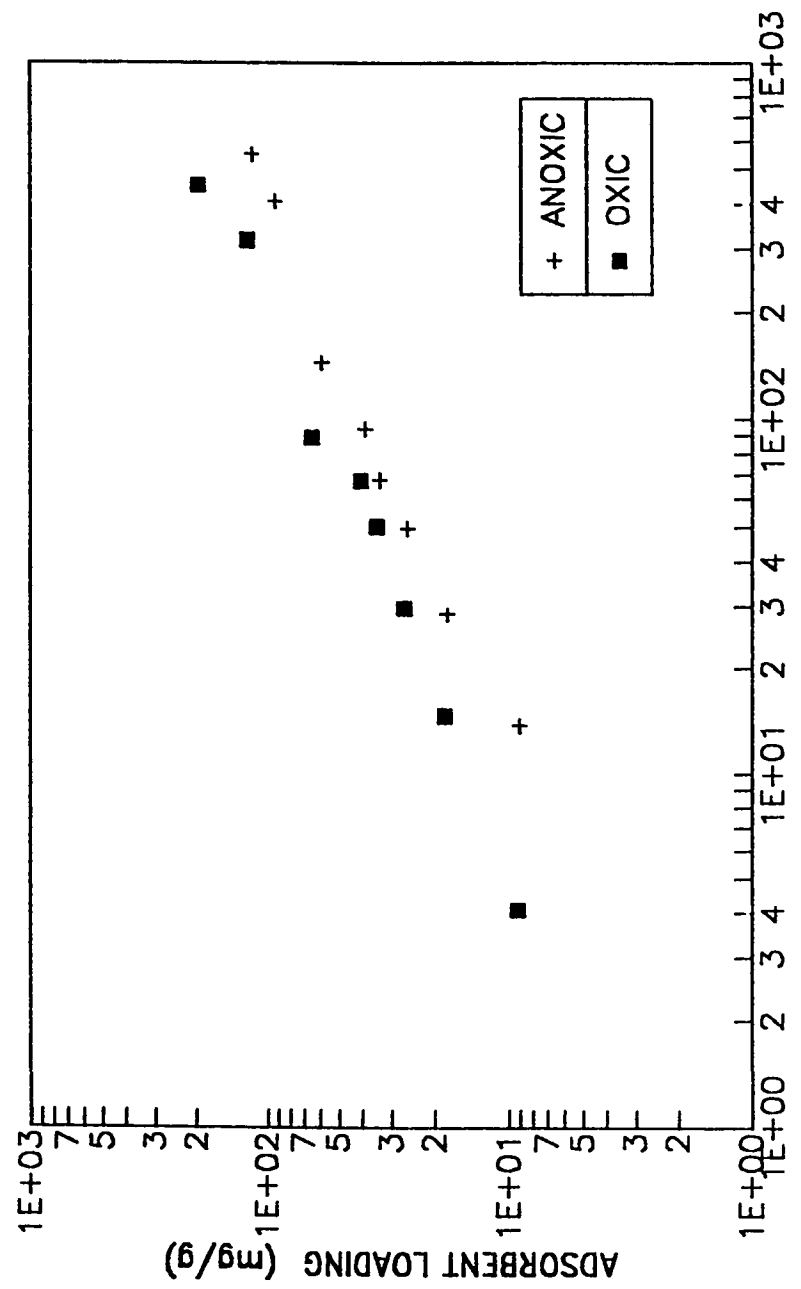


Figure 3.18: Uptakes of TOC for I.W.W, Sample locationon 3, at T = 21° C and pH of 7.

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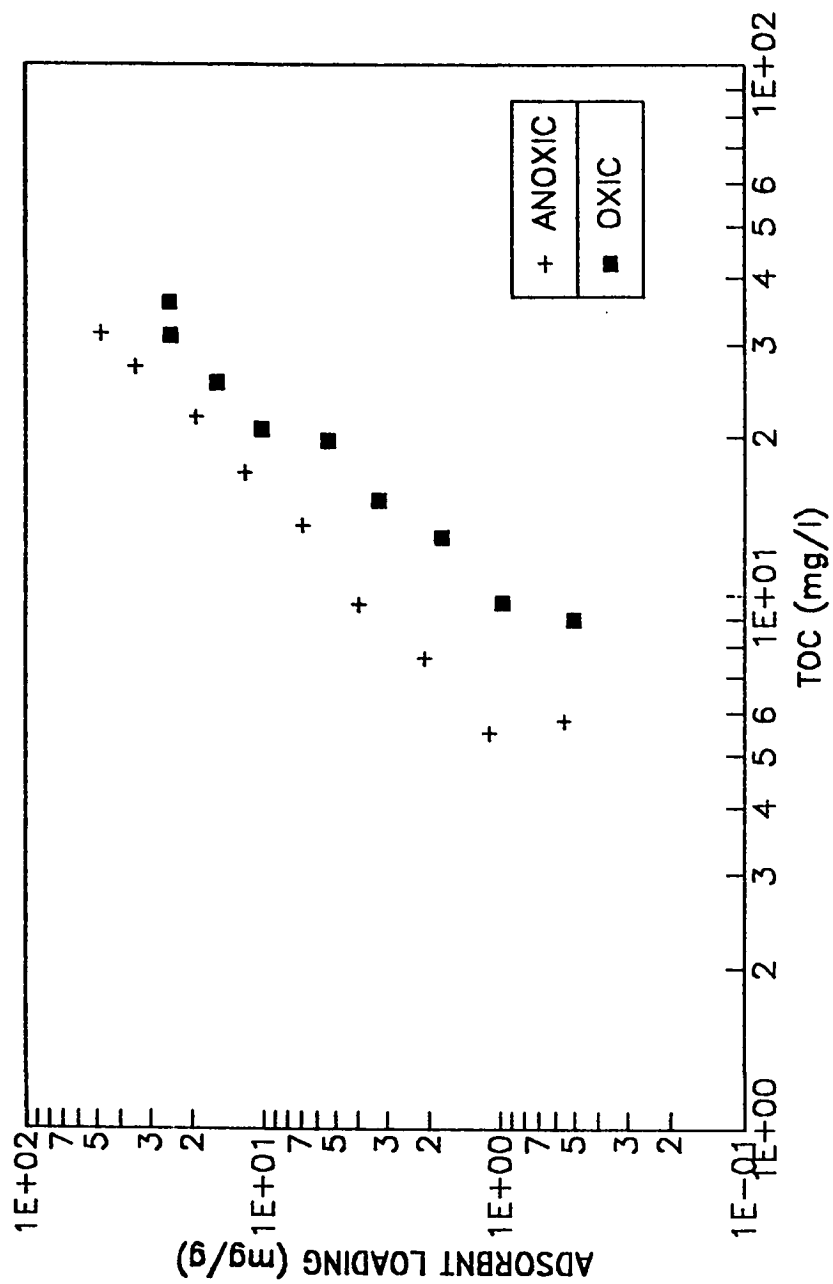


Figure 3.19: Uptakes of TOC for D.W.W at T = 21 °C and pH of 7.

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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) <sup>1/n</sup>	n	R <sup>2</sup>
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<sup>2</sup> 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) <sup>1/n</sup>	1/n	R <sup>2</sup>
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<sup>2</sup> is the coefficient of determination

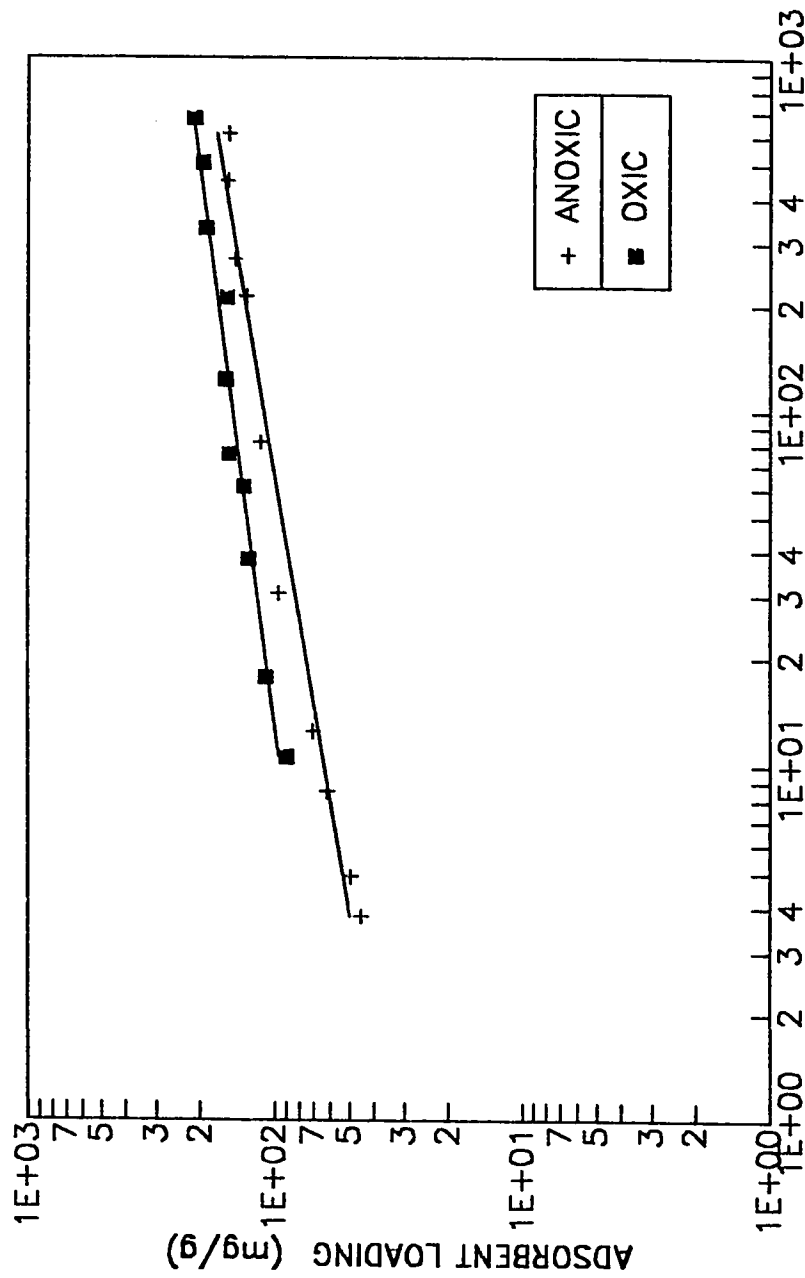


Figure 4.1: Phenol Uptakes at pH 3 and  $T = 21^{\circ}\text{C}$ . Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.

from Table 4.1

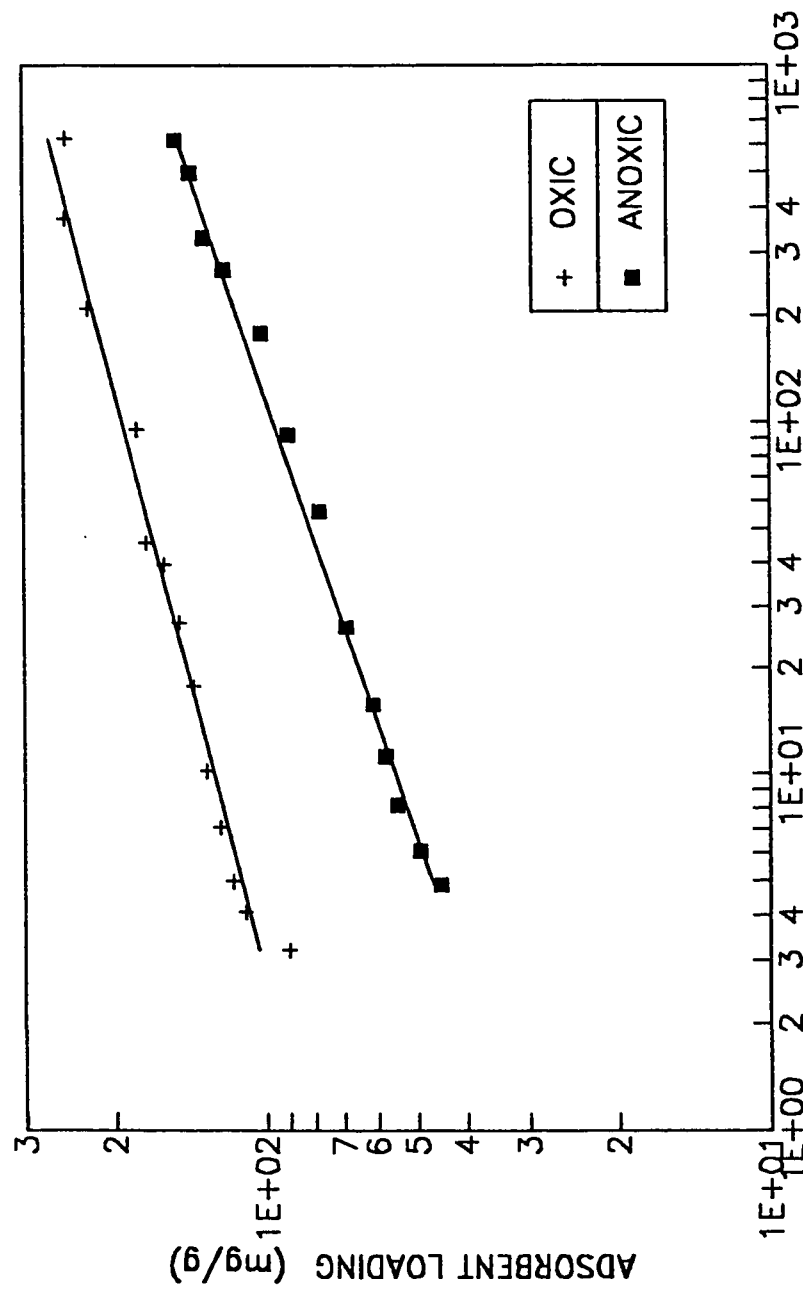


Figure 4.2: Uptakes of Phenol at pH of 7 and  $T = 21^{\circ}\text{C}$  Along with Best Fit Freundlich Curves Using constants Given in Table 4.1.

from 4.1

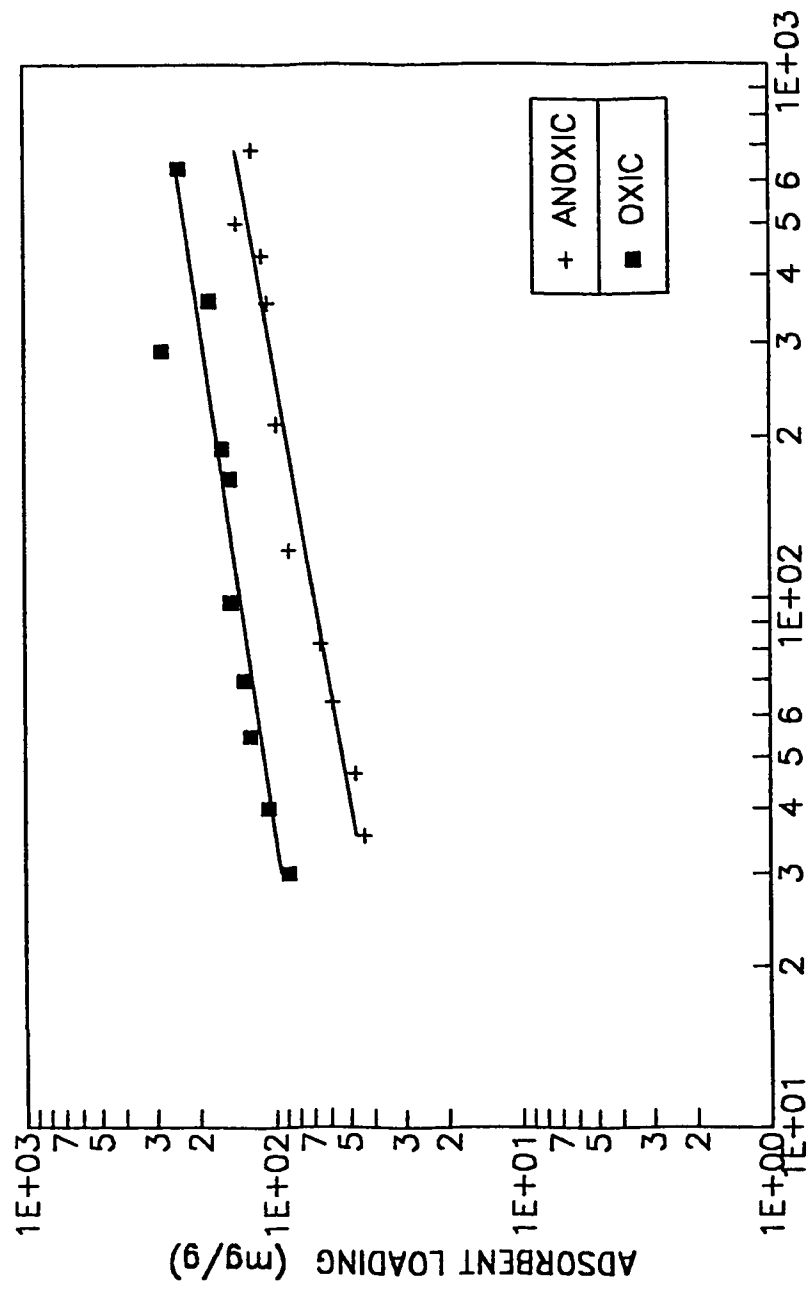


Figure 4.3: Phenol Uptakes at pH 11 and T = 21 °C. Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.

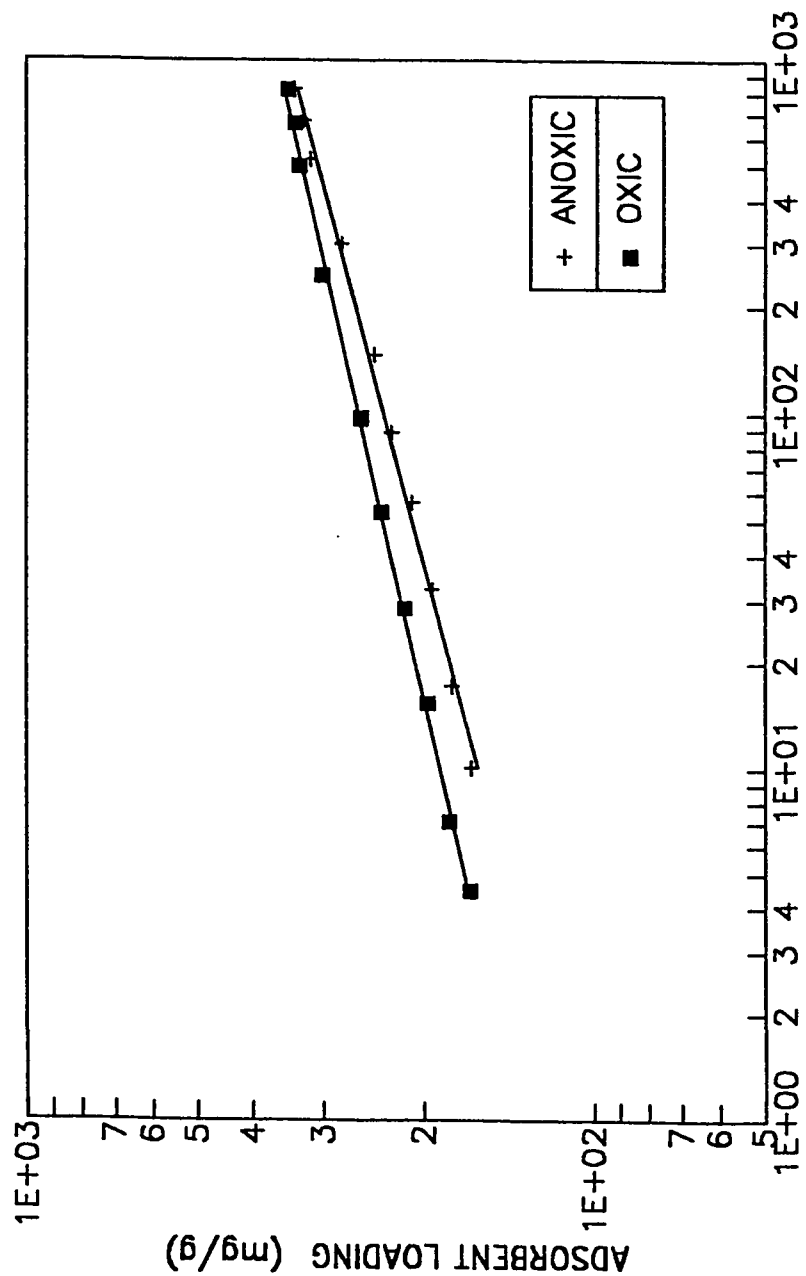


Figure 4.4: o-Cresol Uptakes at pH 3 and T = 21 °C Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.

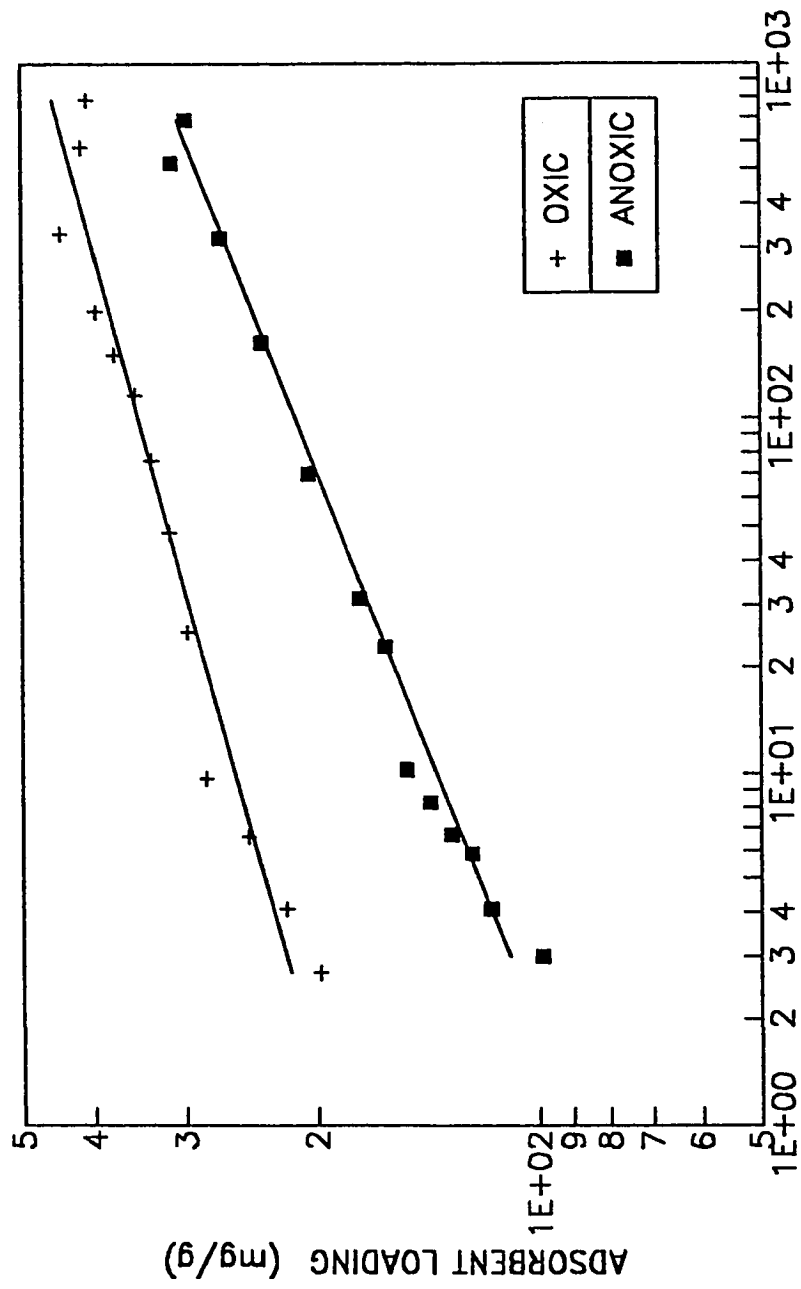


Figure 4.5: Uptakes of o-Cresol at pH of 7 and  $T = 21^{\circ}\text{C}$ . Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.

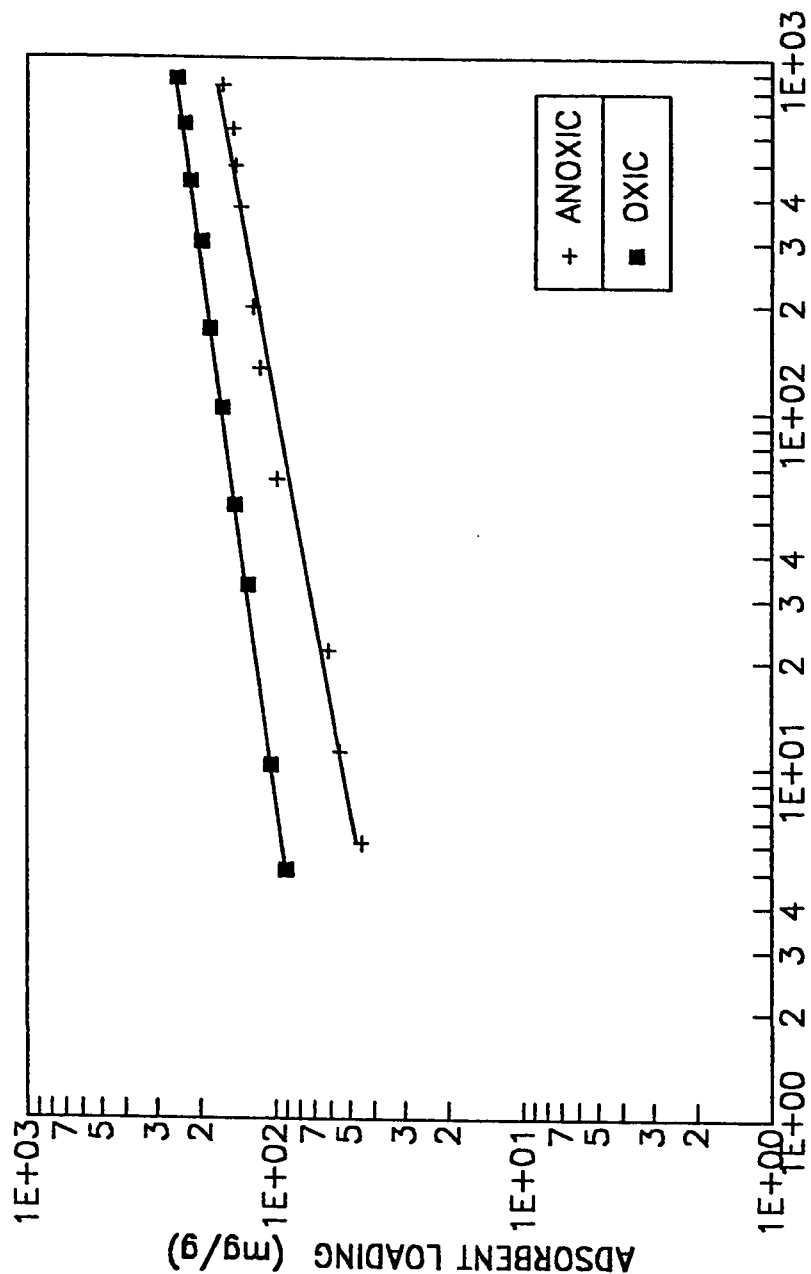


Figure 4.6: Uptakes of o-Cresol at pH 11 and T = 21°C. Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.

gram only

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 pII 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  $pII\ 7 > pII\ 11 > pII\ 3$  for both phenol and o-cresol. Figures 4.9 and 4.10 present the theoretical pC-pII diagrams calculated by the following relation;  $pII = pKa + \text{Log} \{ \text{salt/acid} \}$ . 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 pII variations on adsorption and reaction of the selected phenols. Low pII means abundance of protons in the sorbate solution and completely acid forms of phenol or o-cresol.

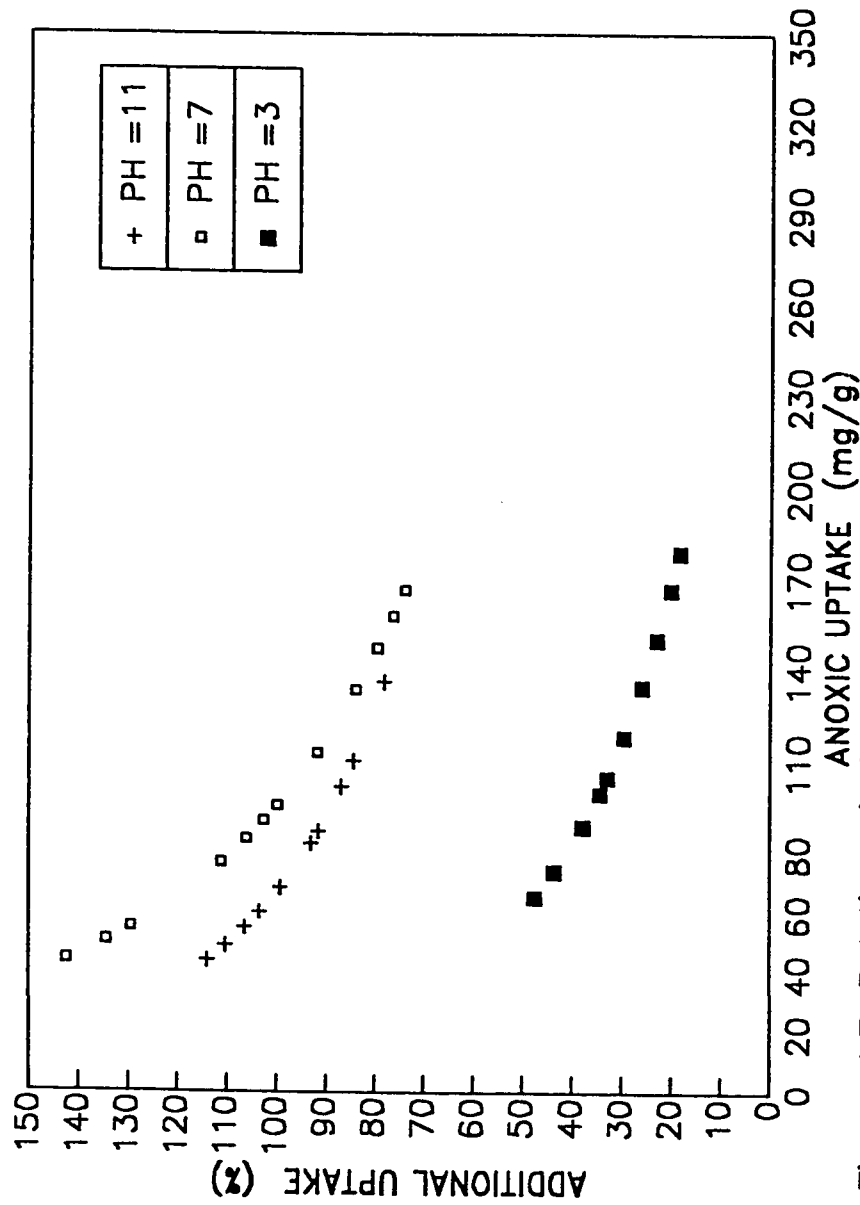


Figure 4.7: Relationship Between the Additional Uptake and the Anoxic Uptake for Phenol at Different pHs and  $T = 21^{\circ}\text{C}$ . *from difnkn'*

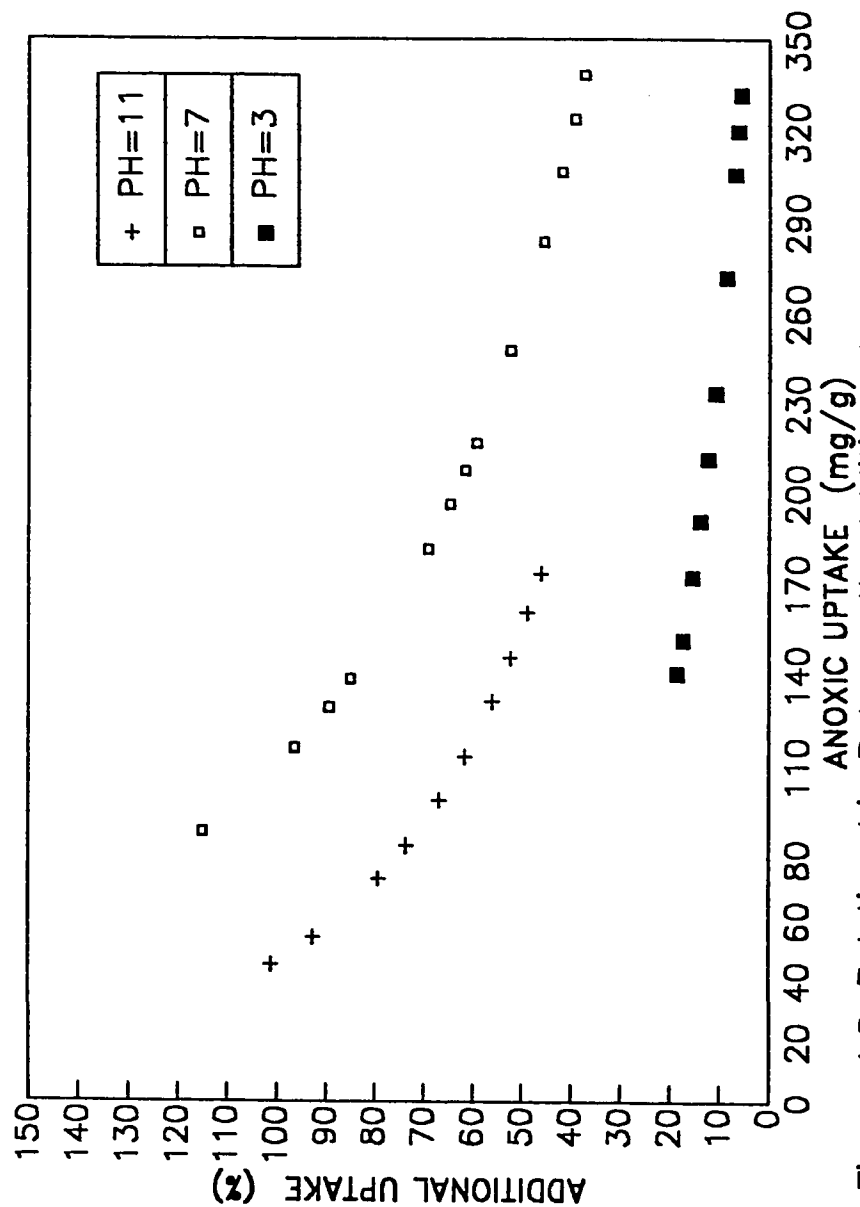


Figure 4.8: Relationship Between the Additional Uptake and the Anoxic Uptake for o-Cresol at Different pHs and T = 21 °C.

from diffusion

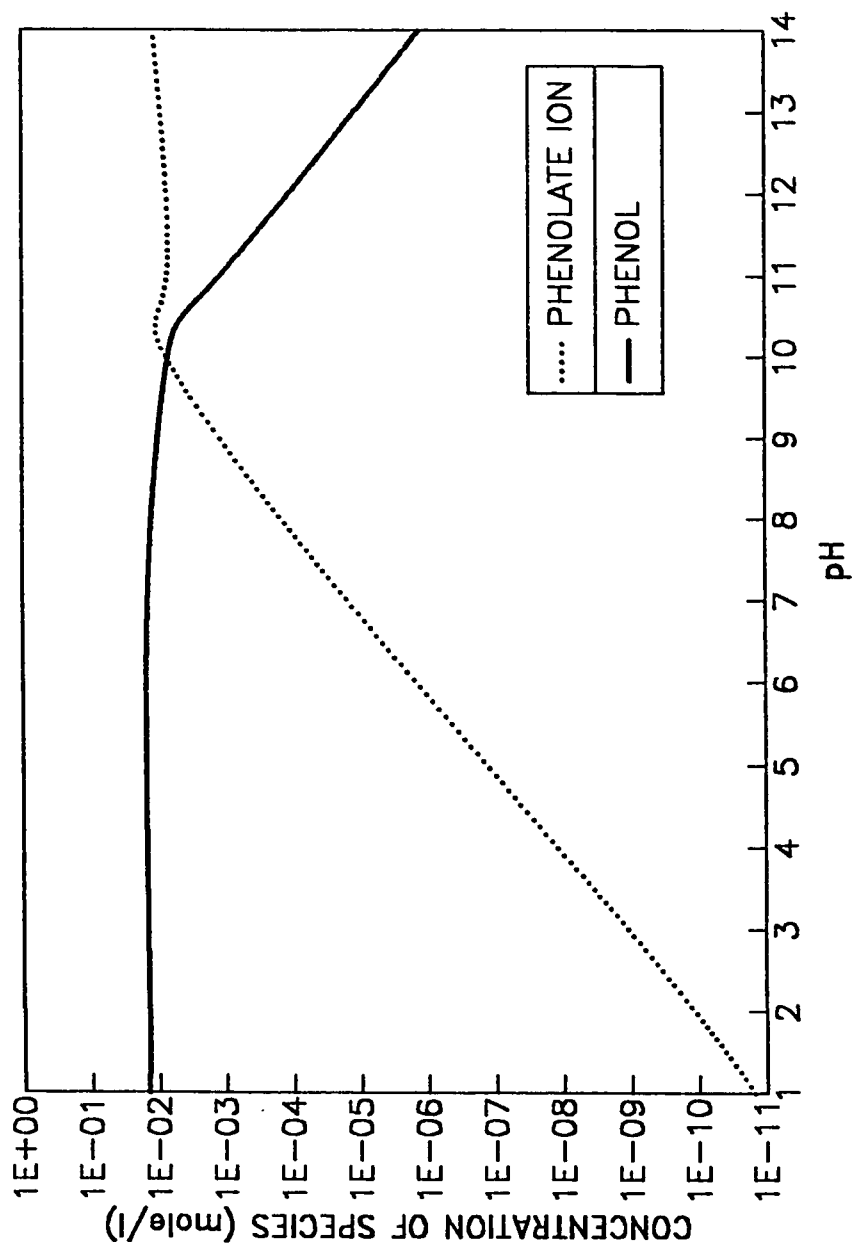


Figure 4.9: pC-pH Diagram for Phenol

B C-BU 1

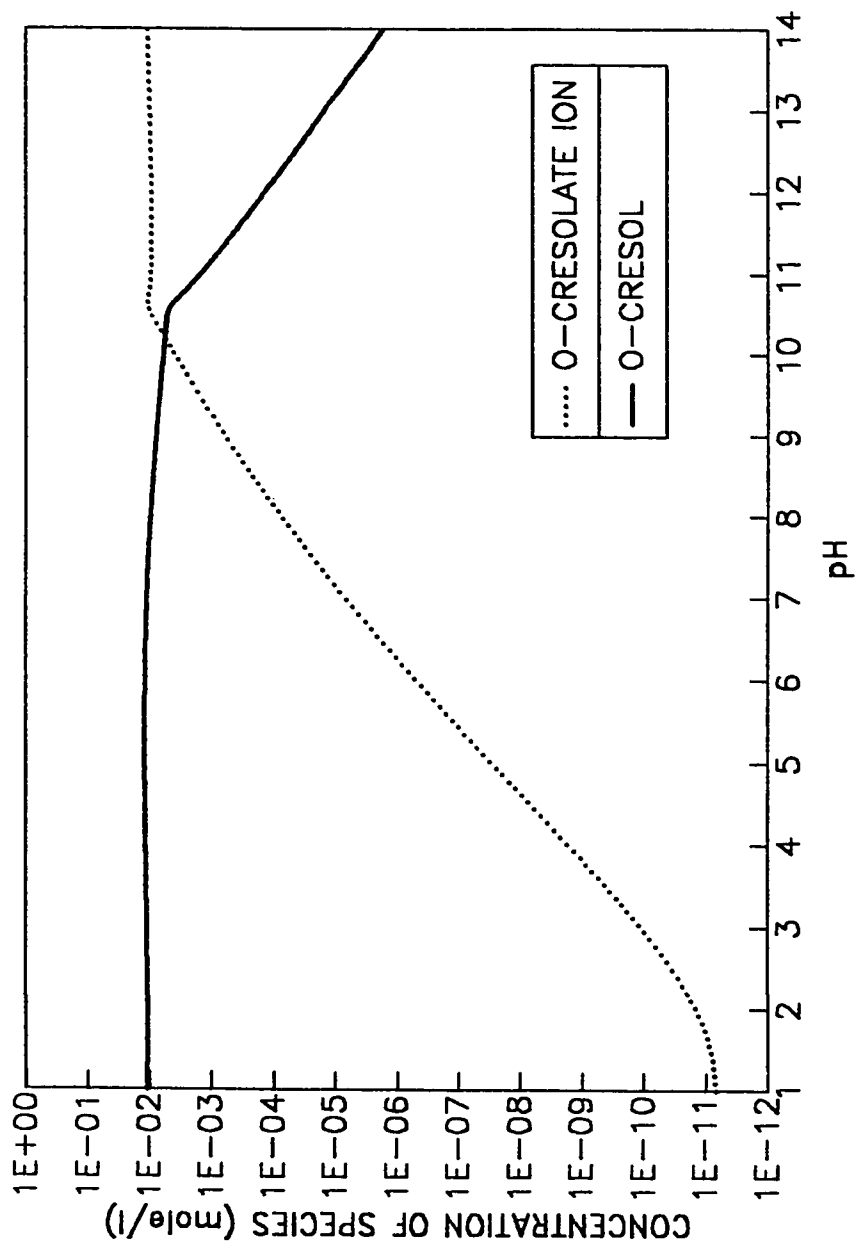


Figure 4.10: pC-pH Diagram for o-Cresol

oC-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  $pK_a$  (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.

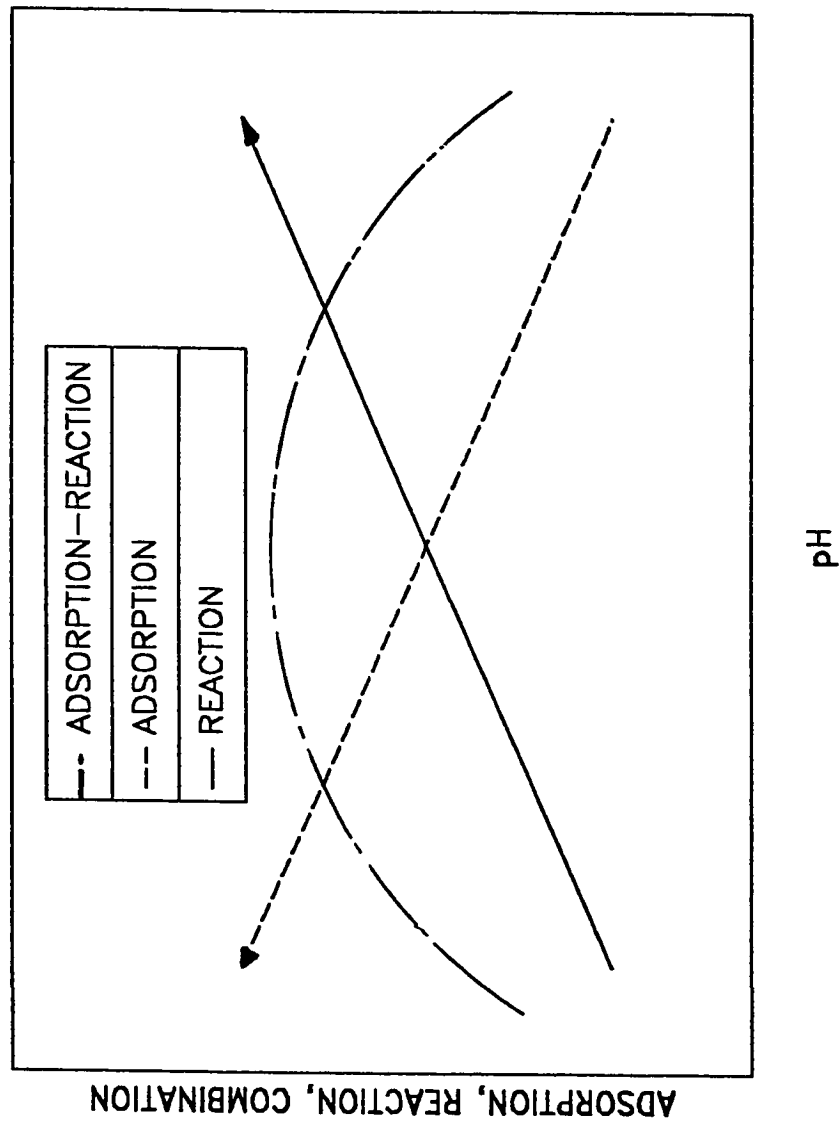


Figure 4.11: Hypothesized Effect of pH on Adsorption-Reaction Combination.

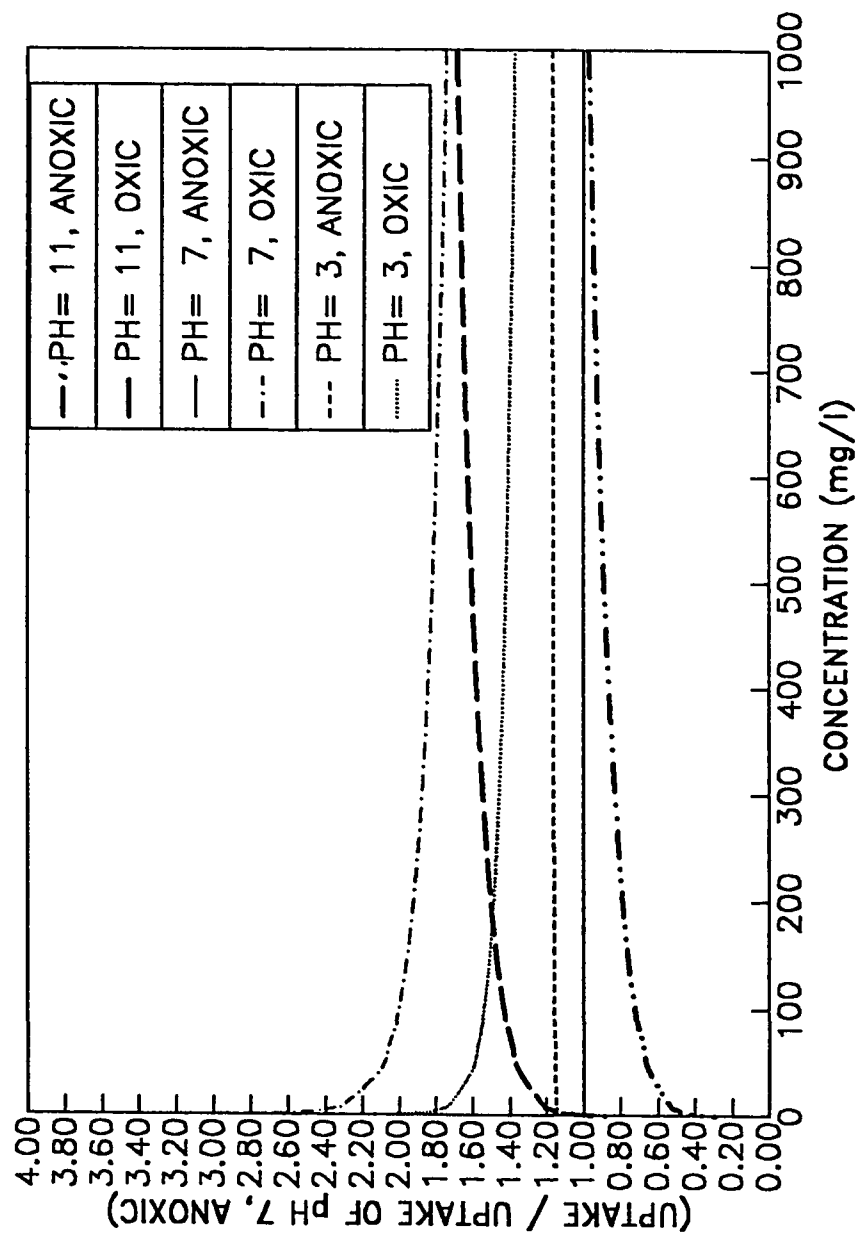


Figure 4.12: Phenol Uptakes at Different pHs Relative to the Uptake at Neutral pH Versus Residual Concentration, at  $T = 21^{\circ}\text{C}$ .

from difab44

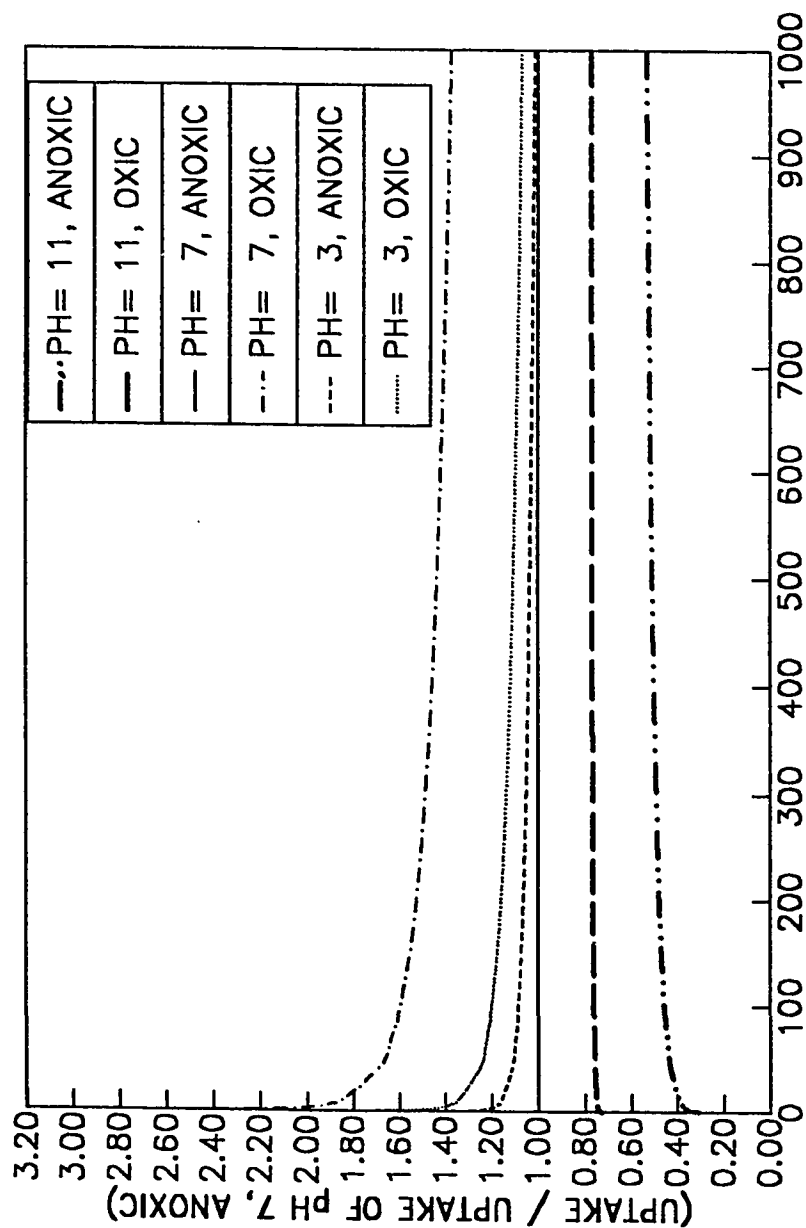


Figure 4.13: o-Cresol Uptakes at different pHs Relative to the Uptake at Neutral pH Versus Residual Concentration, at  $T = 21^{\circ} \text{C}$ .

from data 404

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,  $\Delta q$  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.

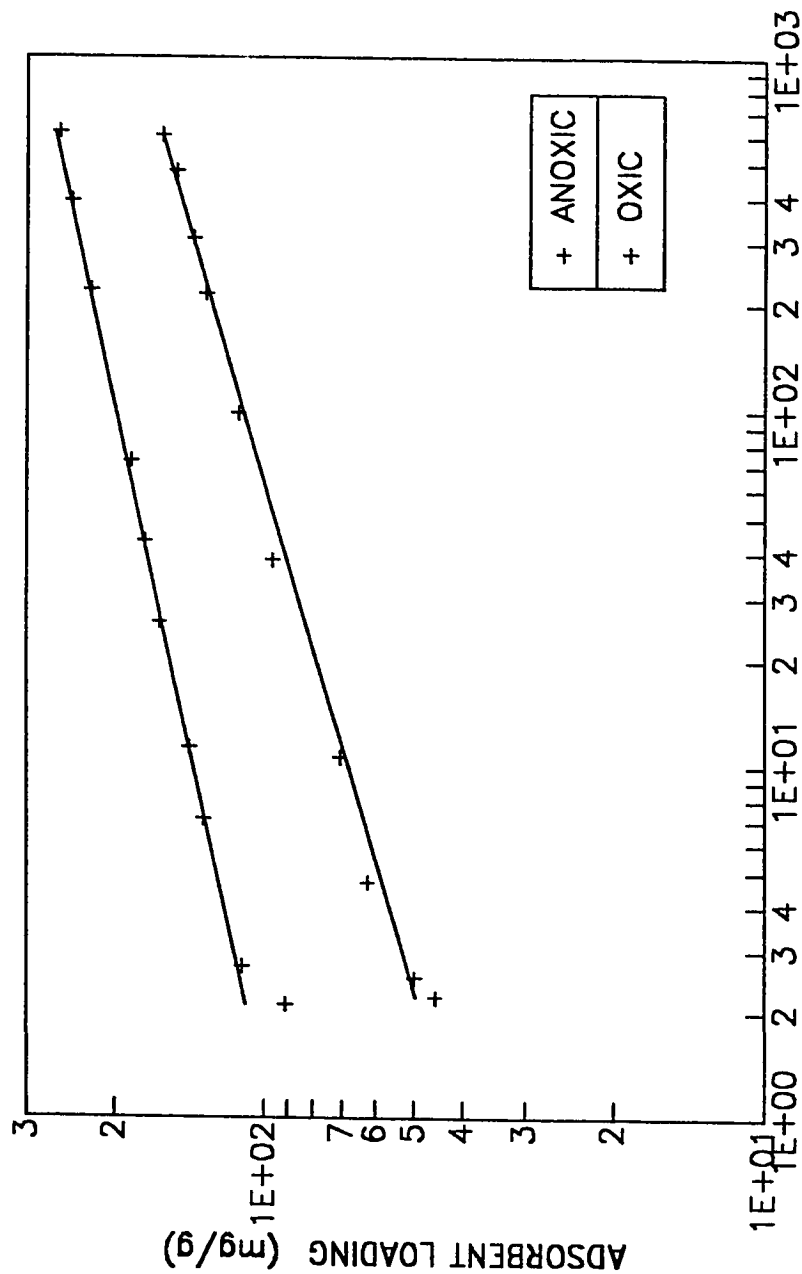


Figure 4.14: Phenol Uptakes at  $T = 8^{\circ}\text{C}$ . and pH of 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.

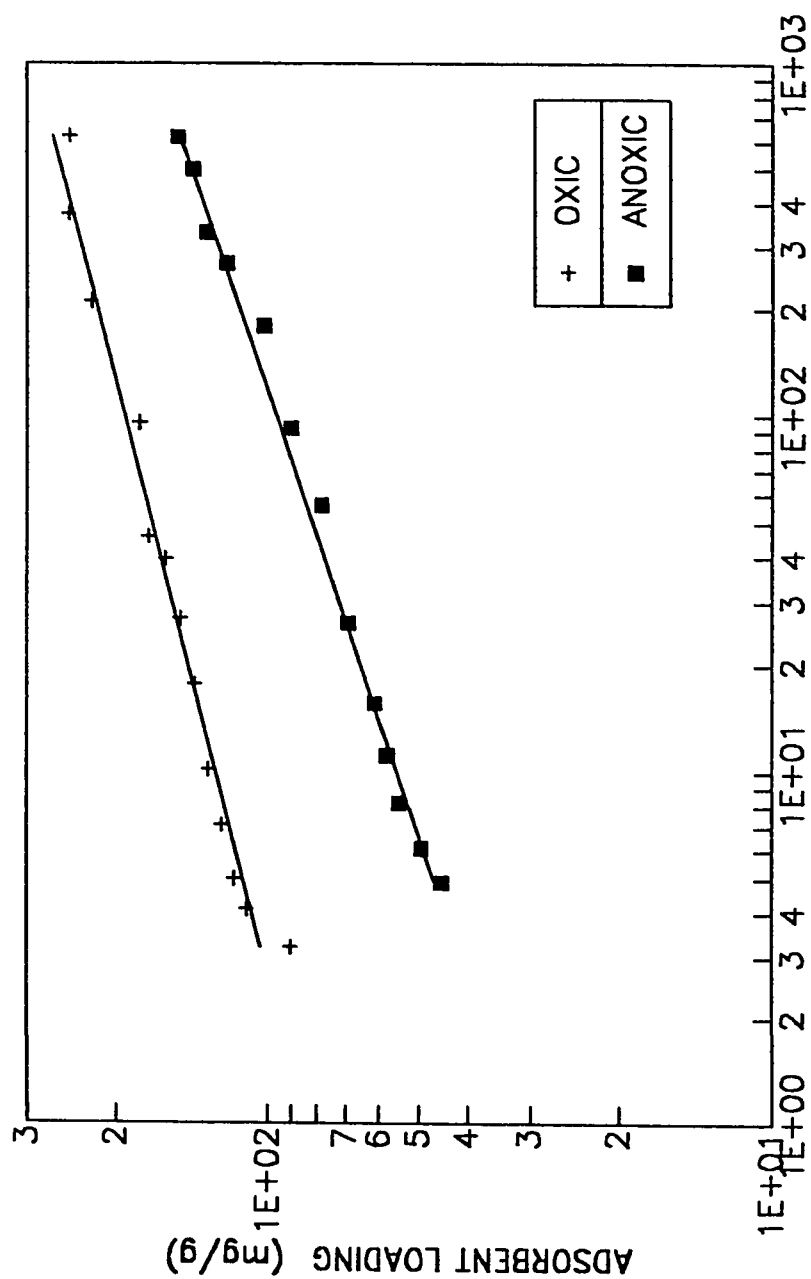


Figure 4.15: Uptakes of Phenol at  $T = 21^{\circ}\text{C}$  and pH of 7 Along with Best Fit Freundlich Curves Using constants Given in Table 4.2.

From Table 4

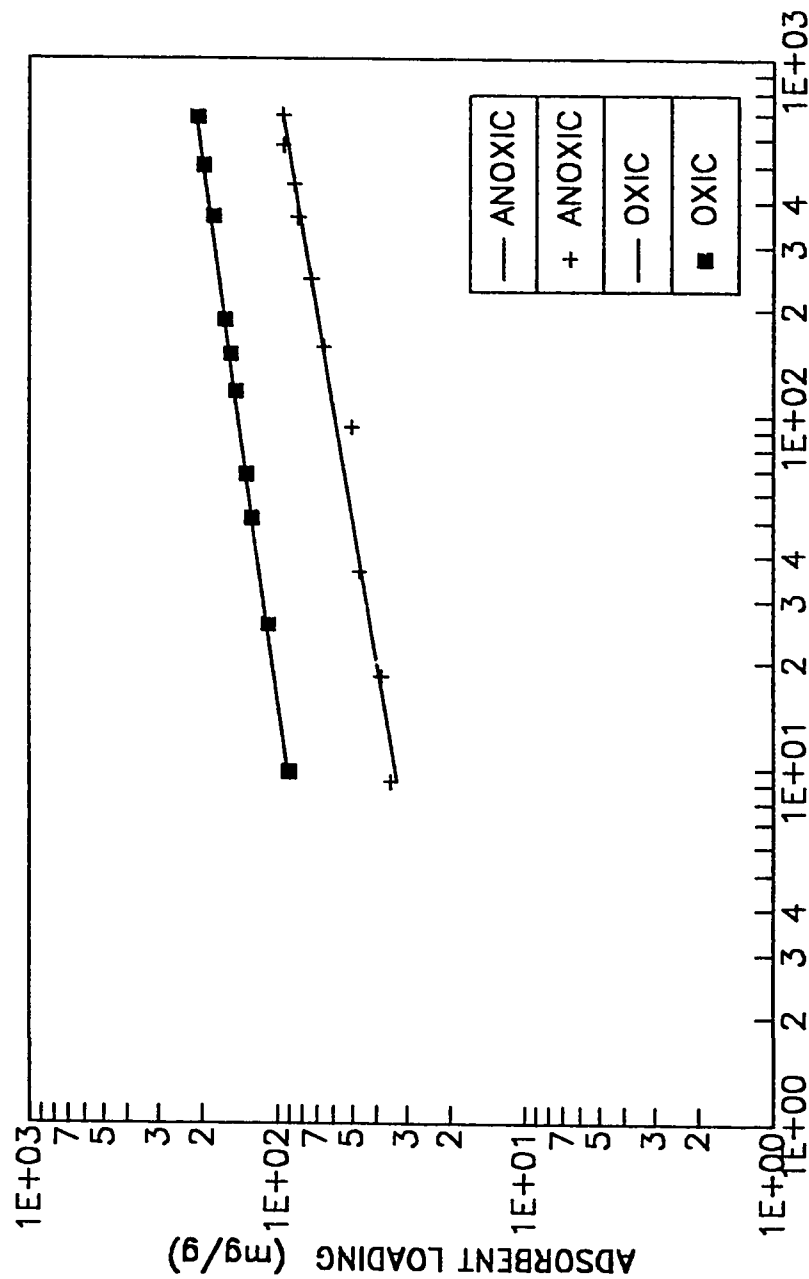


Figure 4.16: Phenol Uptakes at T 35°C. and pH 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.

from table

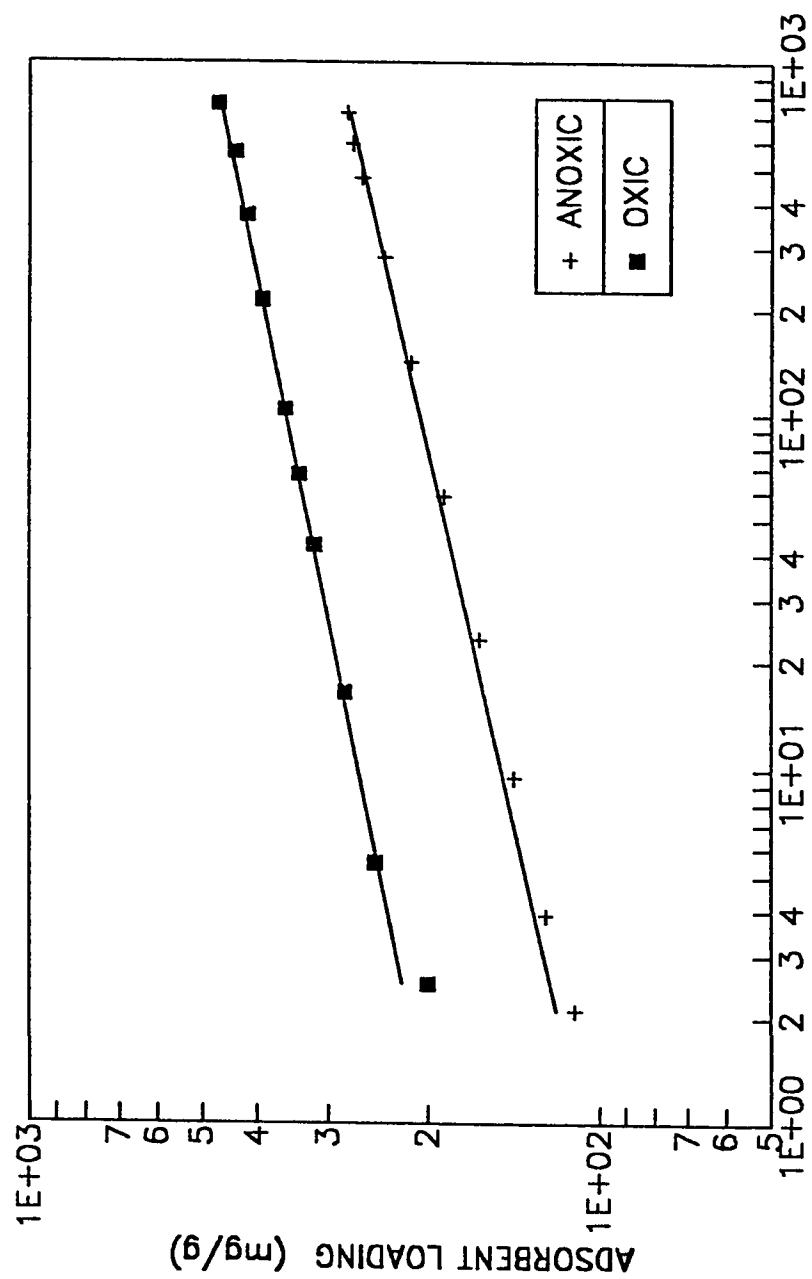


Figure 4.17: o-Cresol Uptakes at  $T = 8^{\circ}\text{C}$ . and pH 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.

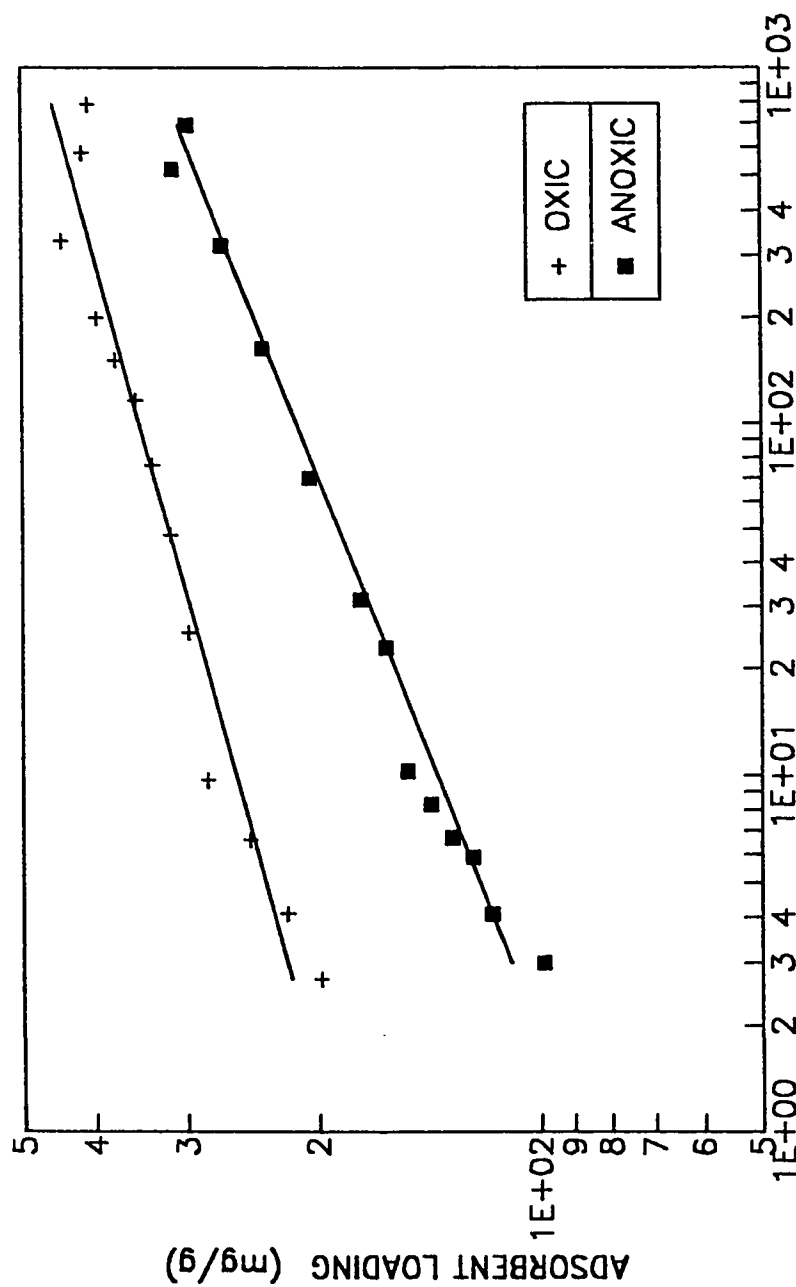


Figure 4.18: o-Cresol Uptakes at  $T = 21^{\circ}\text{C}$ . and pH 7, Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.

from Table 4

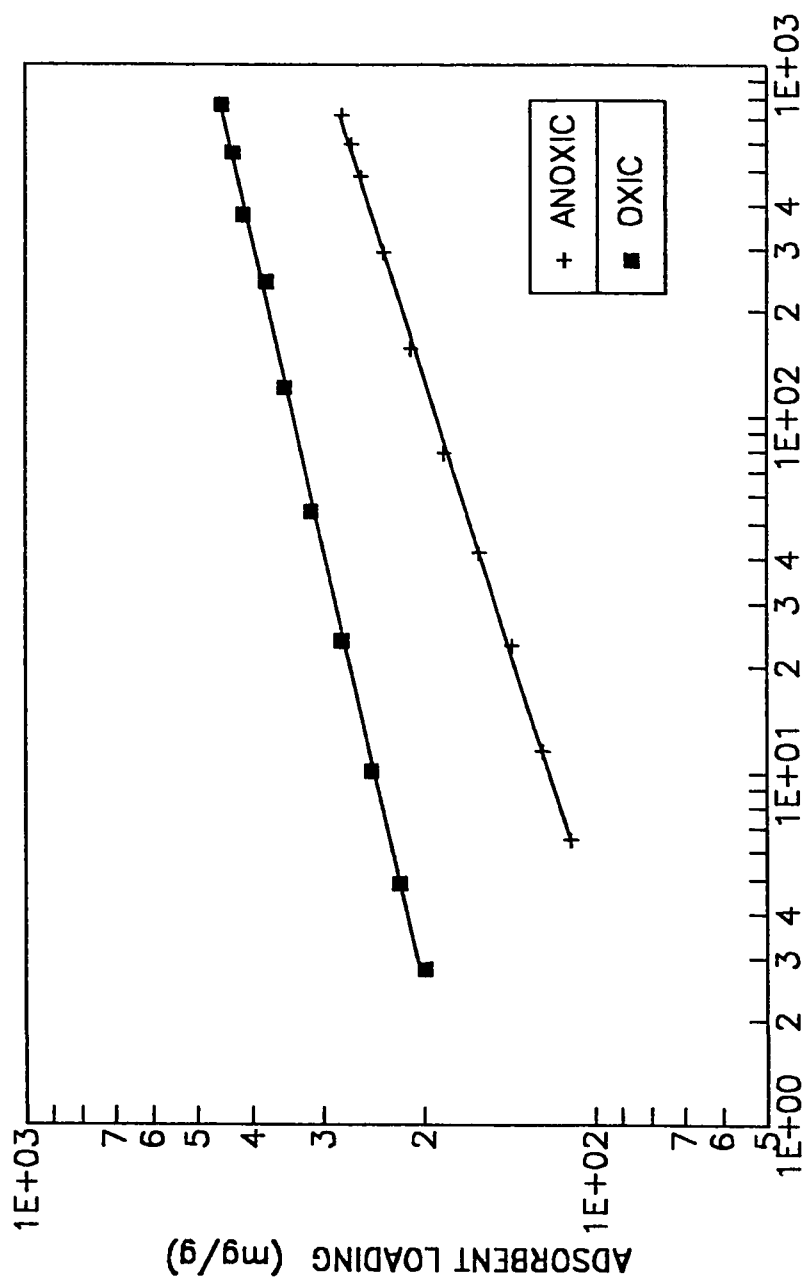


Figure 4.19: o-Cresol Uptakes at  $T = 35^{\circ}\text{C}$ . and pH 7 Along with Best Fit Freundlich Curves Using Constants given in Table 4.2.

from 2005

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  $T = 8^\circ\text{C} < T = 21^\circ\text{C} < T = 35^\circ\text{C}$ . 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) <sup>1/n</sup>	1/n	R <sup>2</sup>
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<sup>2</sup> is the coefficient of determination

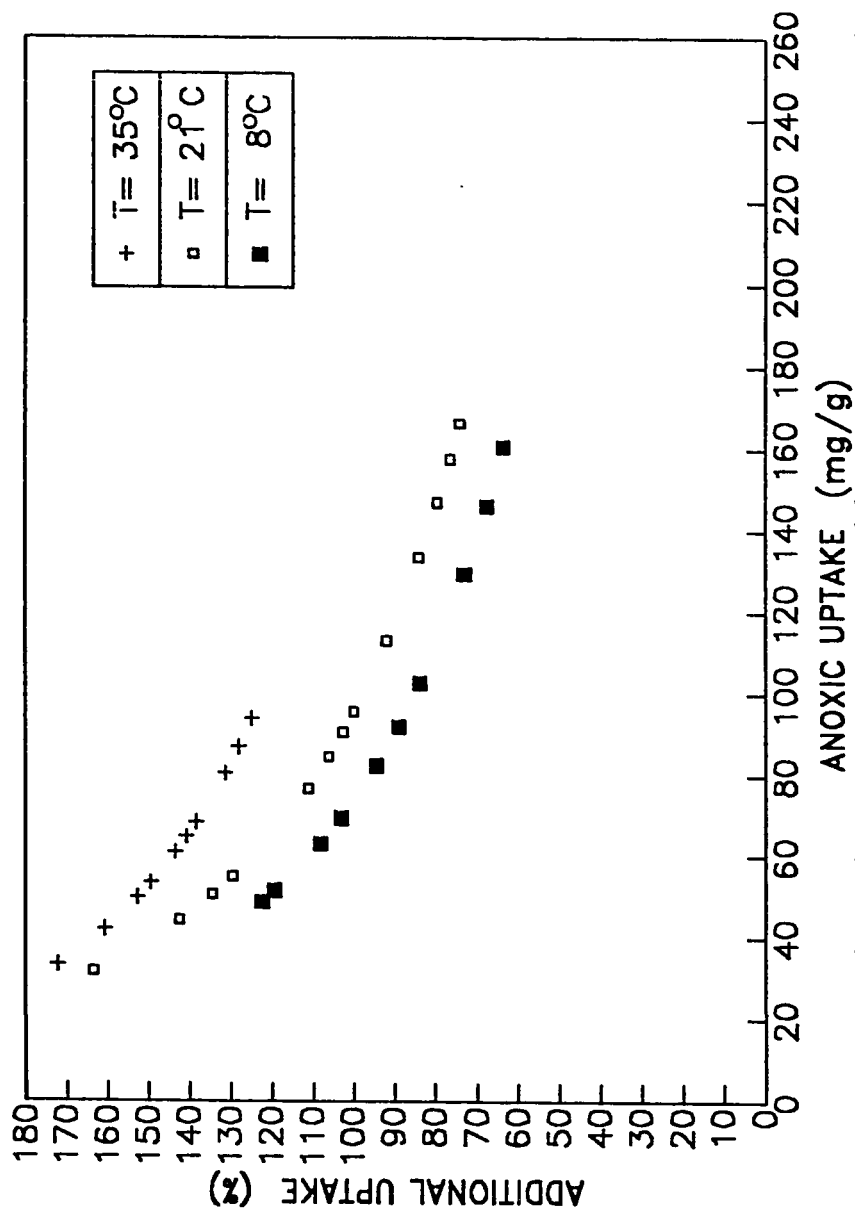


Figure 4.20: Relationship Between the Additional Uptake and the Anoxic Uptake for Phenol at Different Temperatures and pH 7.

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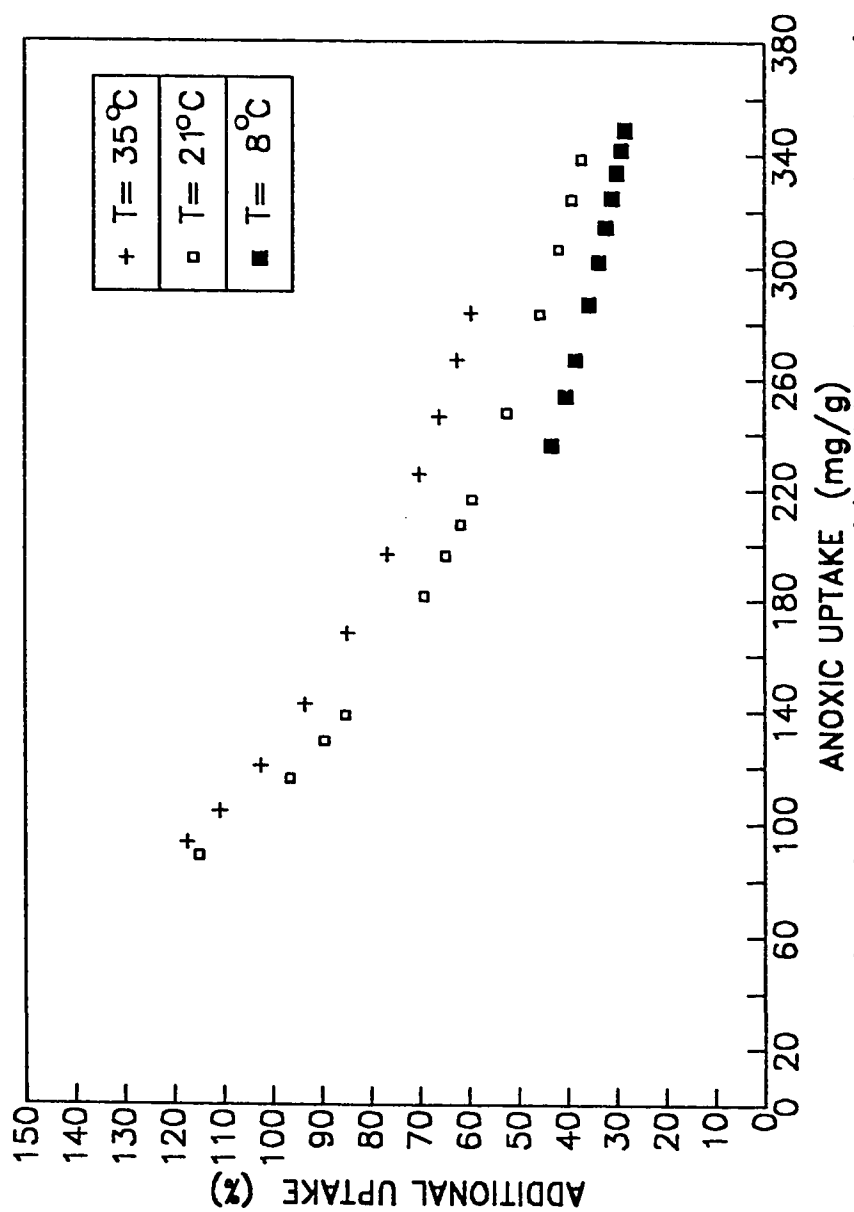


Figure 4.21: Relationship Between the Additional Uptake and the Anoxic Uptake for o-Cresol at Different Temperatures and pH 7.

6-10-10

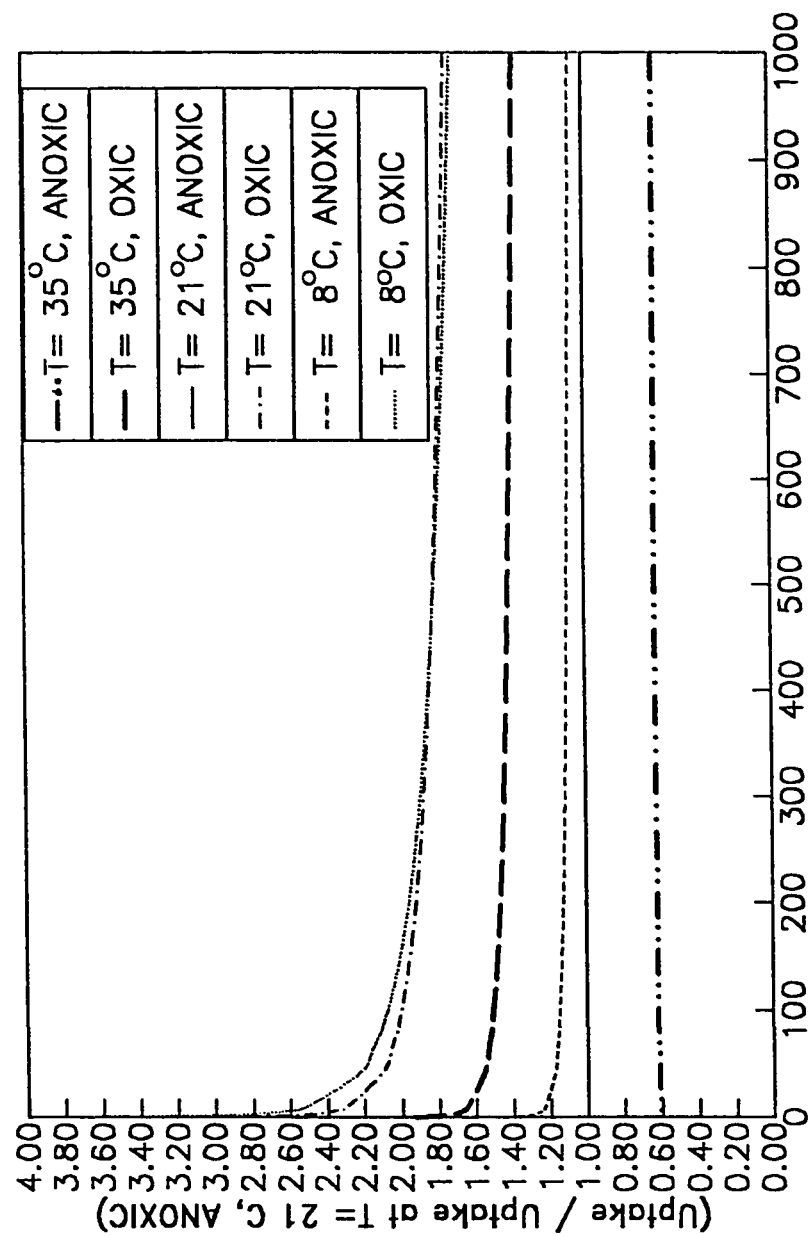


Figure 4.22: Phenol Uptakes at Different Temperatures Relative to the Uptake at Room Temperature Versus Residual Concentration.

from dist. 5

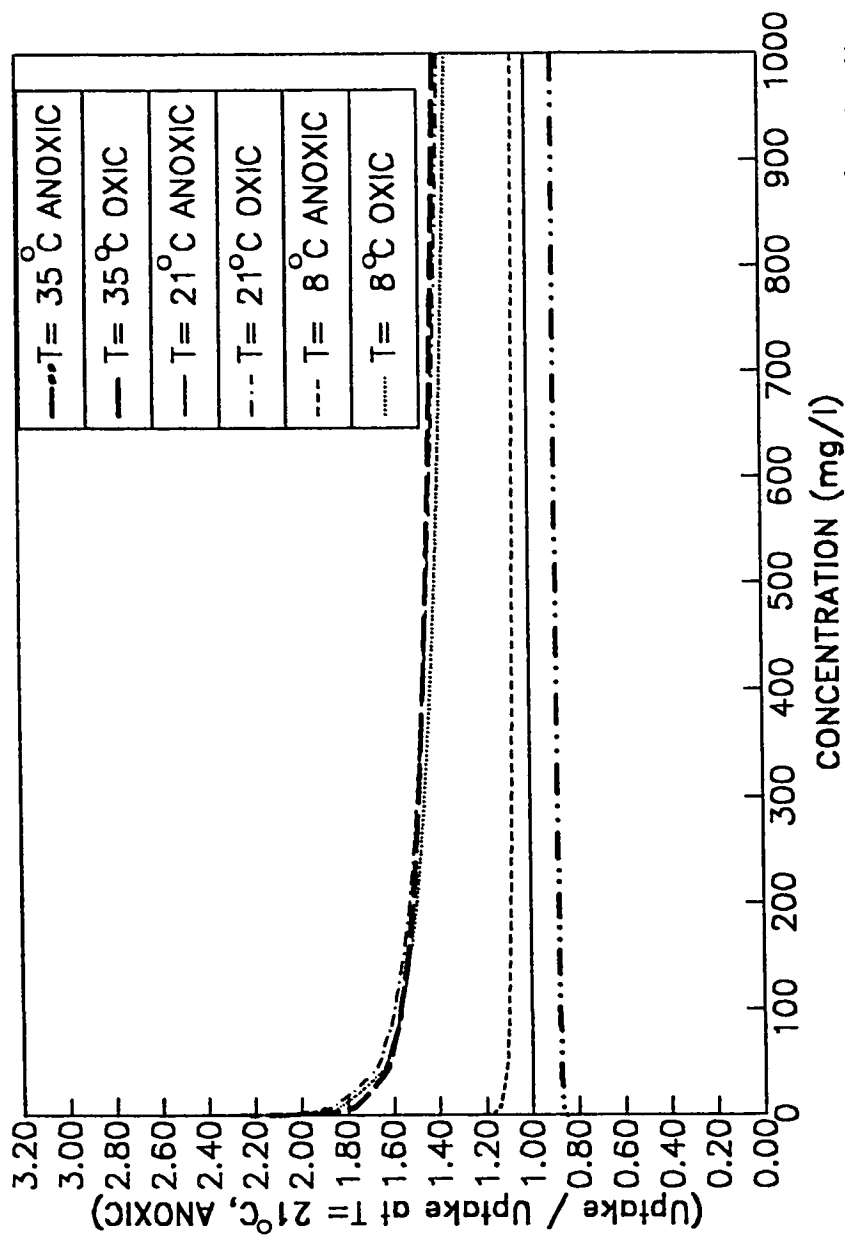


Figure 4.23: o-Cresol Uptakes at Different Temperatures Relative to the Uptake at Room Temperature Versus Residual Concentration.

From JH0001

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:

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

which can linearized as;

$$\log k = k_0 - \frac{\Delta H}{2.3 R_g T} \quad (4.4)$$

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:

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

providing the appropriate constants are used.

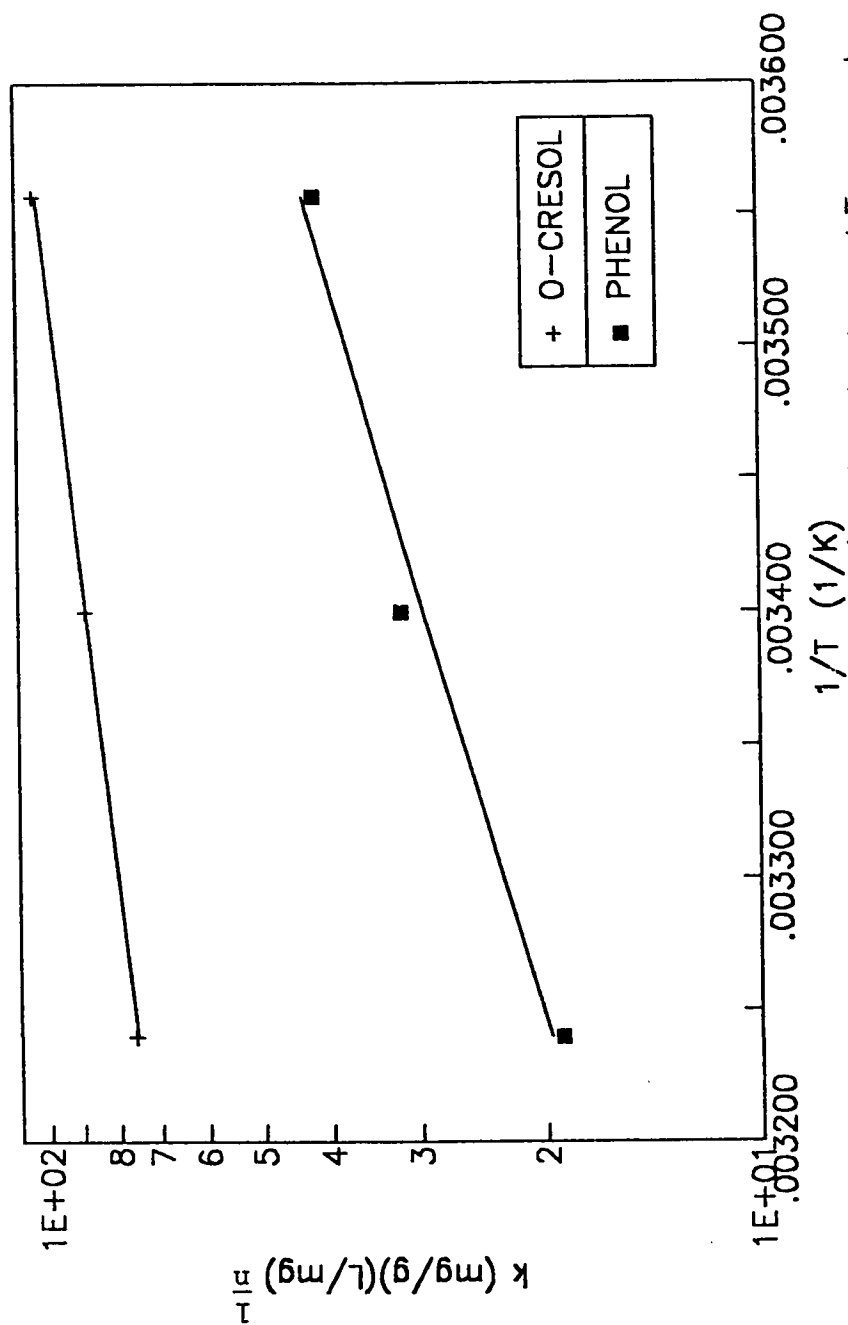


Figure 4.24: Relationship Between Freundlich Constants and Temperature for Phenol and o-Cresol Along with Lines of Best Fit.

FROM ADUUV

## **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 <sup>2</sup>
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<sup>2</sup> is the coefficient of determination

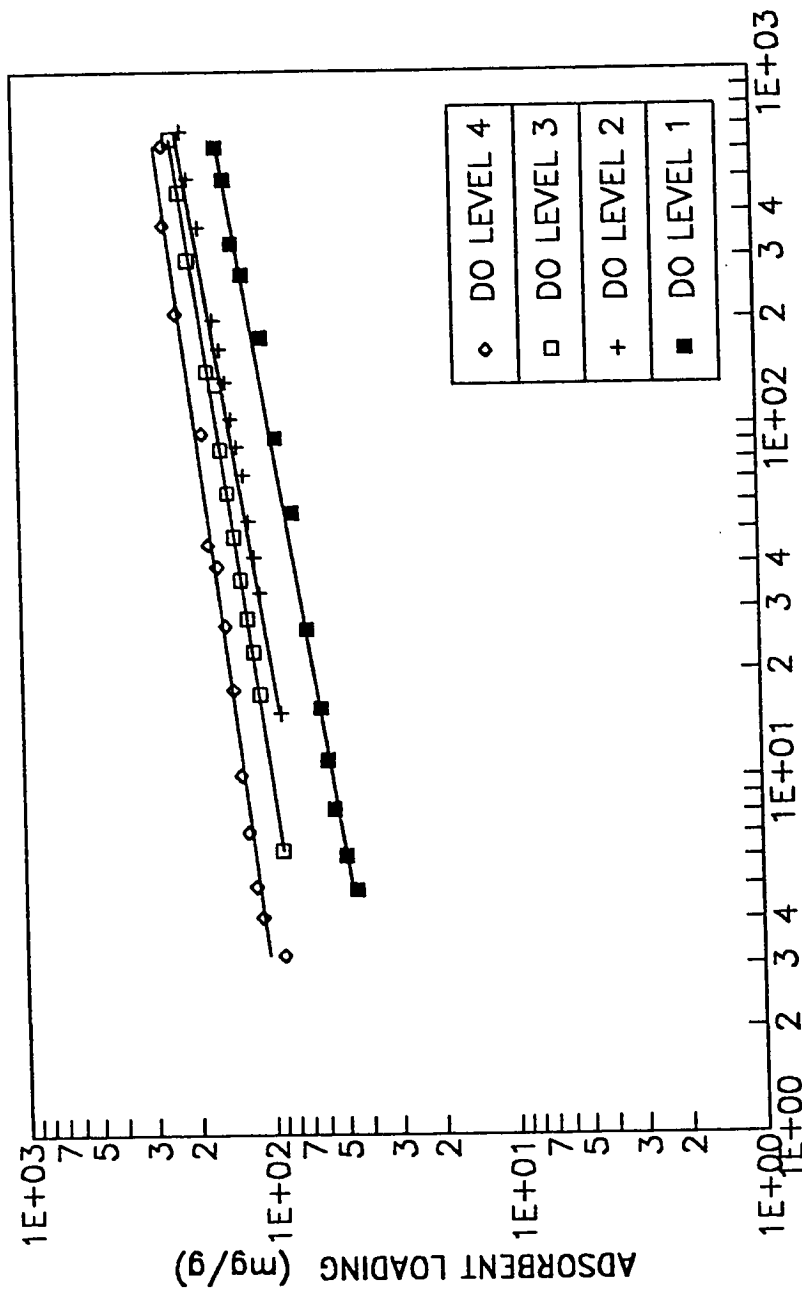


Figure 5.1: Uptakes of Phenol at  $T = 21^\circ\text{C}$ . and pH of 7 Along with Best Fit Freundlich Curves Using constants Given in Table 5.1.

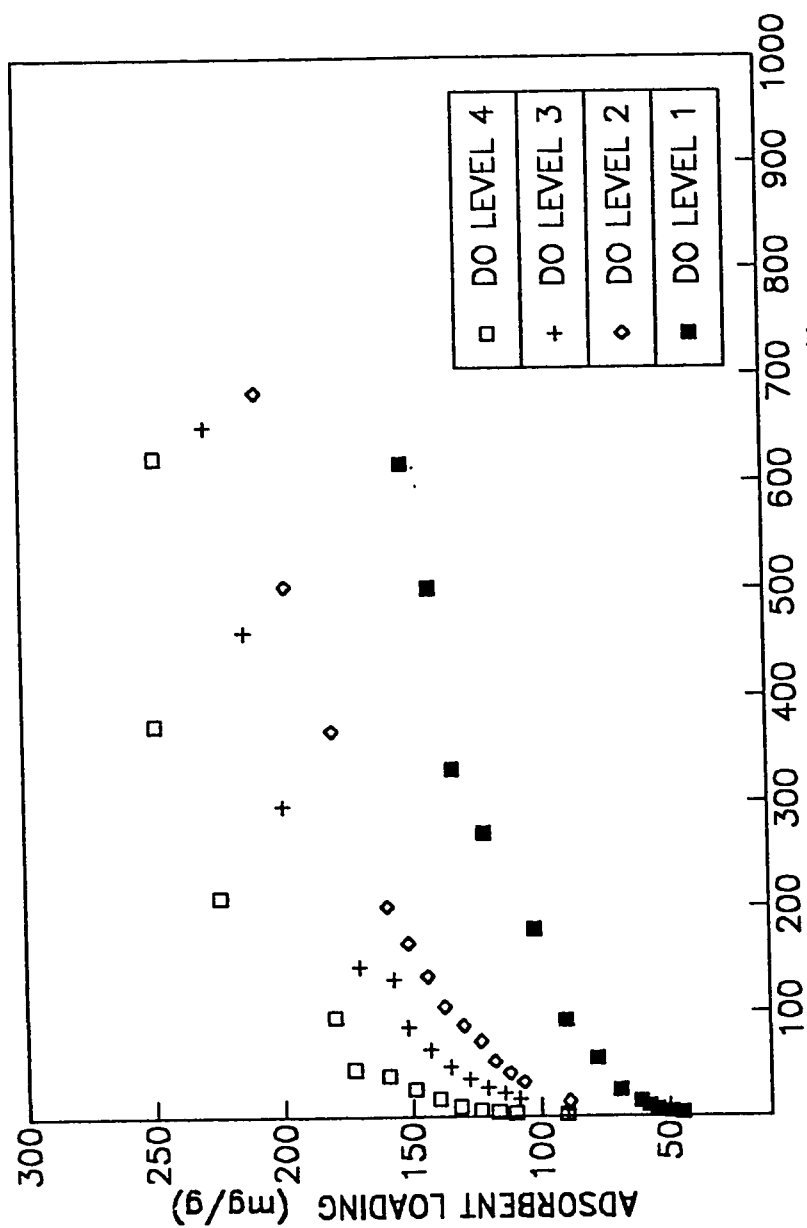


Figure 5.2: Uptakes of Phenol Under Different Oxygen Levels at  $T = 21^{\circ}\text{C}$ . and pH of 7.

from difsan1

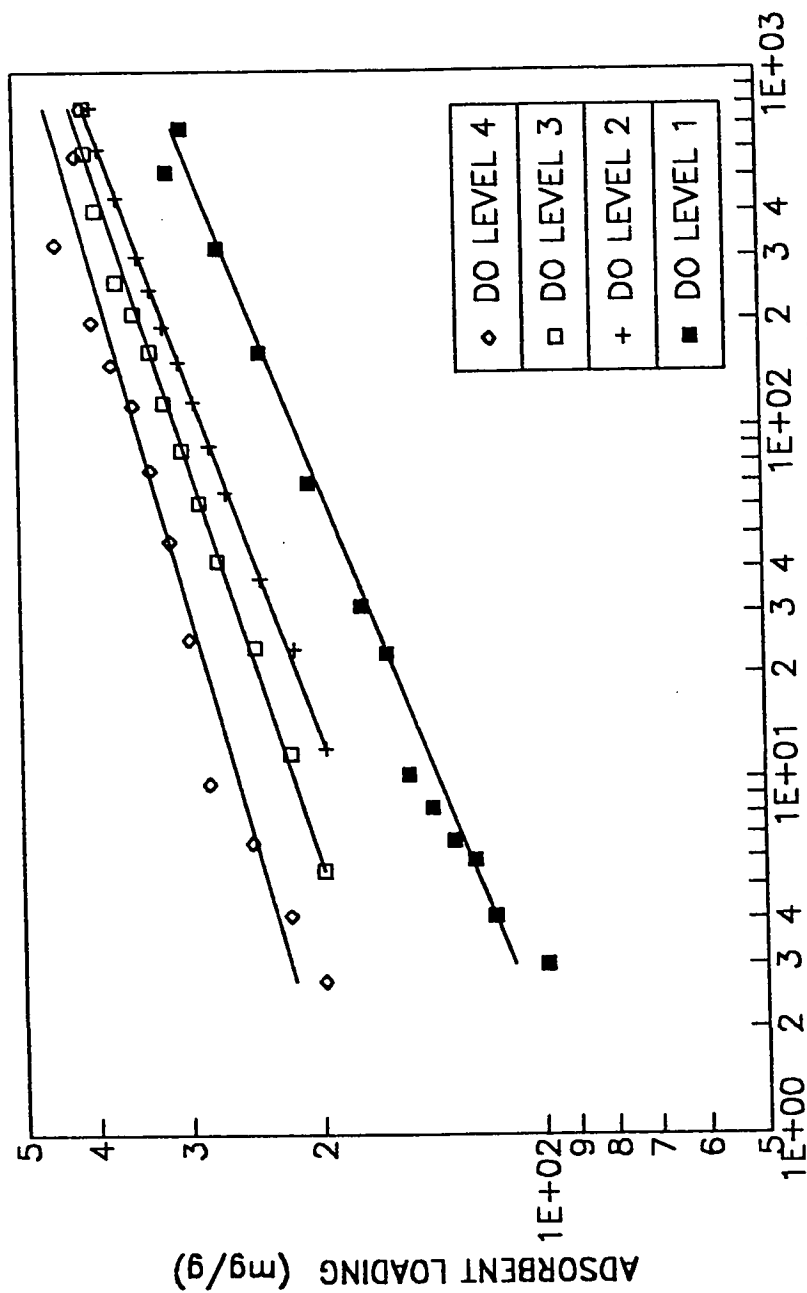


Figure 5.3: Uptakes of o-Cresol at  $T = 21^{\circ}\text{C}$ . and pH of 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 5.1.

from data

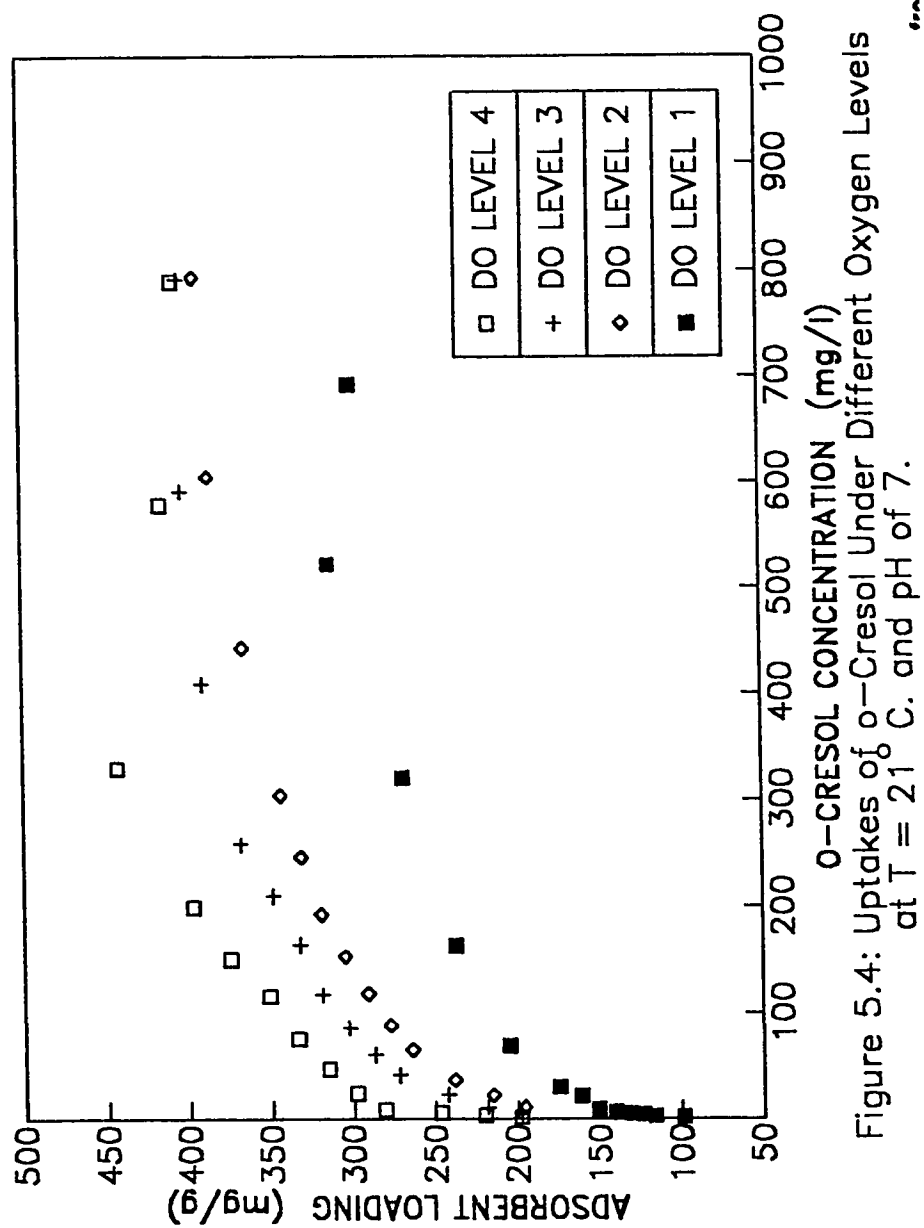


Figure 5.4: Uptakes of o-Cresol Under Different Oxygen Levels at  $T = 21^{\circ}\text{C}$ . and pH of 7.

from diffen

### 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.

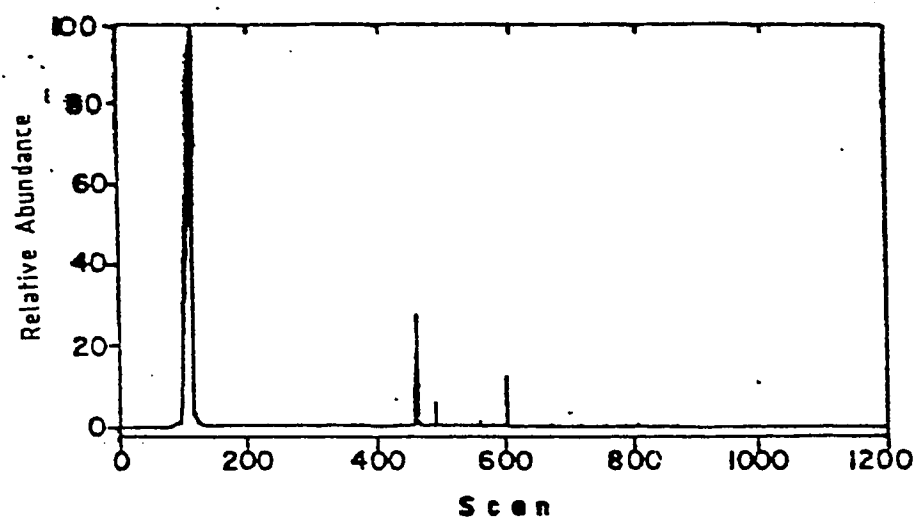


Figure 5.5: GC-MS Total Ion Chromatogram for the Anoxic GAC Sample of o-Cresol

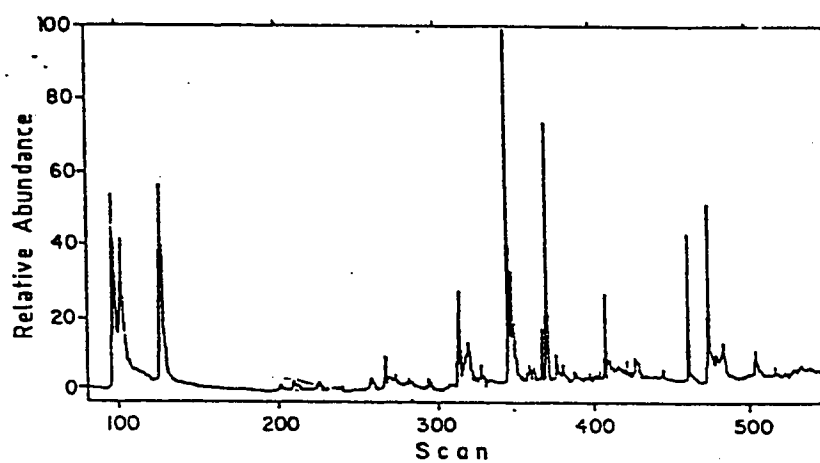


Figure 5.6: GC-MS Total Ion Chromatogram for the "Air Purged" GAC Sample of o-Cresol

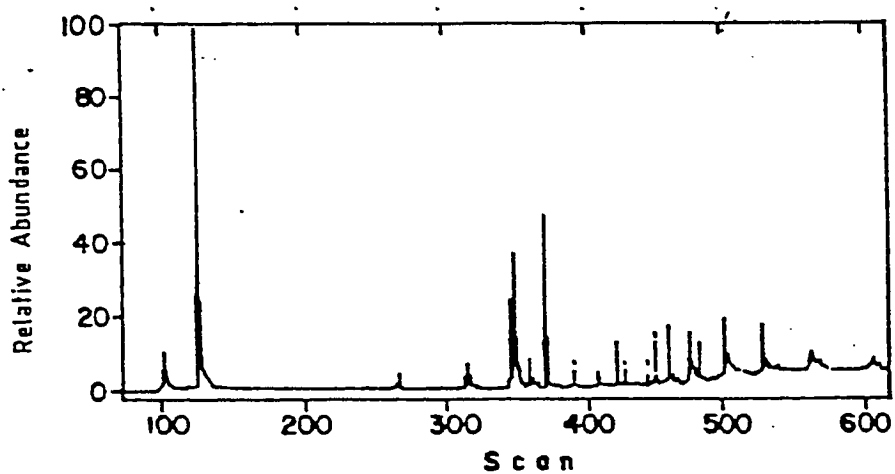


Figure 5.7: GC-MS Total Ion Chromatogram for the Oxidized GAC Sample of o-Cresol

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.

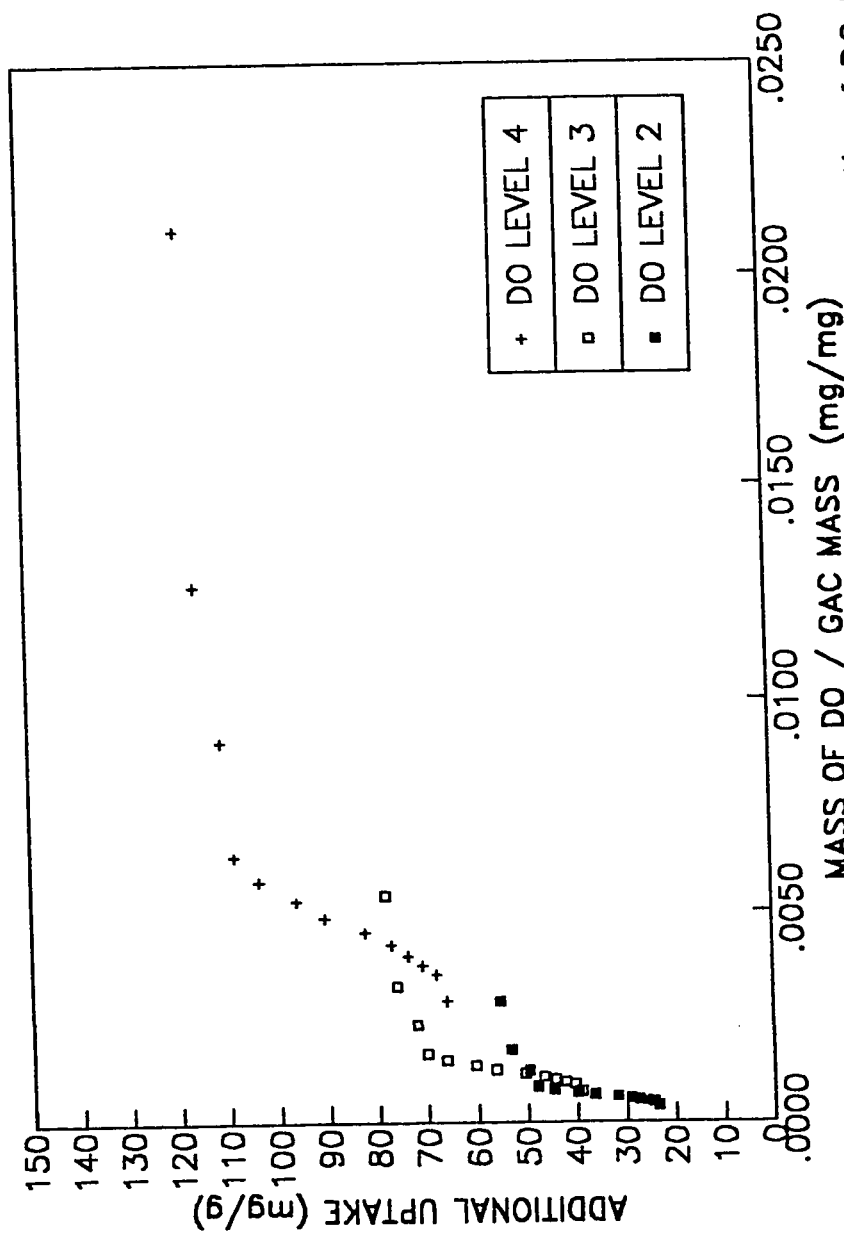


Figure 5.8: Relationship Between Additional Uptake and the Ratio of DO to the GAC Mass for Phenol at  $T = 21^{\circ}\text{C}$ . and pH of 7.

from difm2

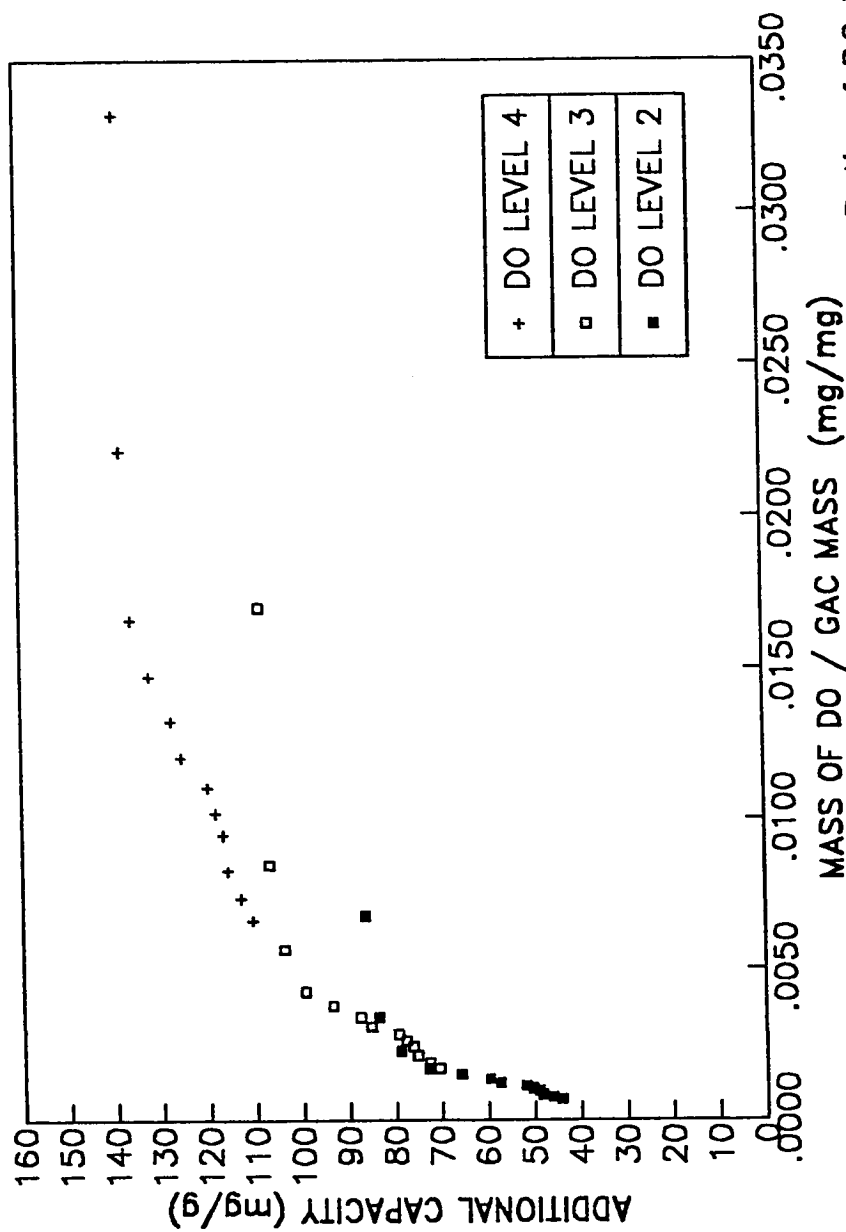


Figure 5.9: Relationship Between Additional Uptake and the Ratio of DO to the GAC Mass for o-Cresol at  $T = 21^{\circ}\text{C}$  and pH of 7.

from difm61

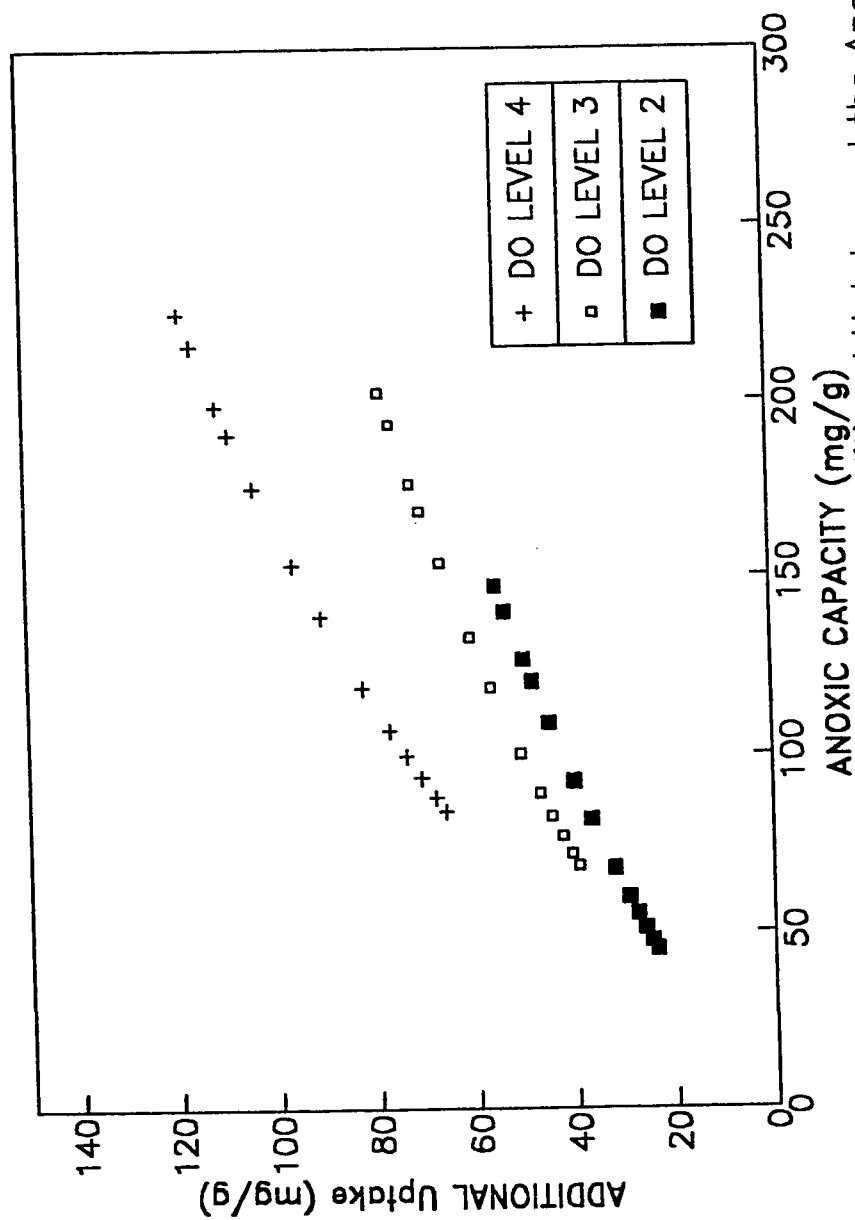


Figure 5.10: Relationship Between the Additional Uptake and the Anoxic Capacity for Phenol at  $T = 21^{\circ}\text{C}$  and pH 7.

from difmnd4

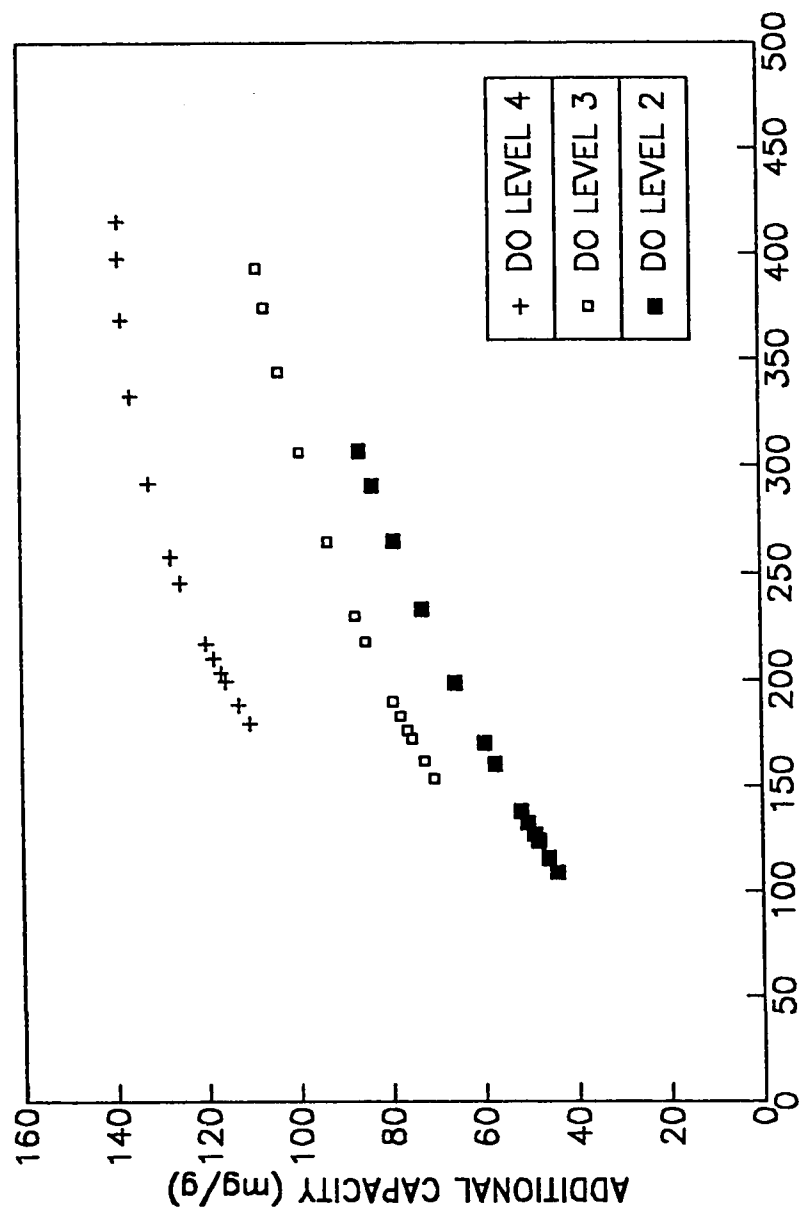


Figure 5.11: Relationship Between the Additional Uptake and the Anoxic Capacity for o-Cresol at T = 21°C and pH 7.  
from difmo4

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

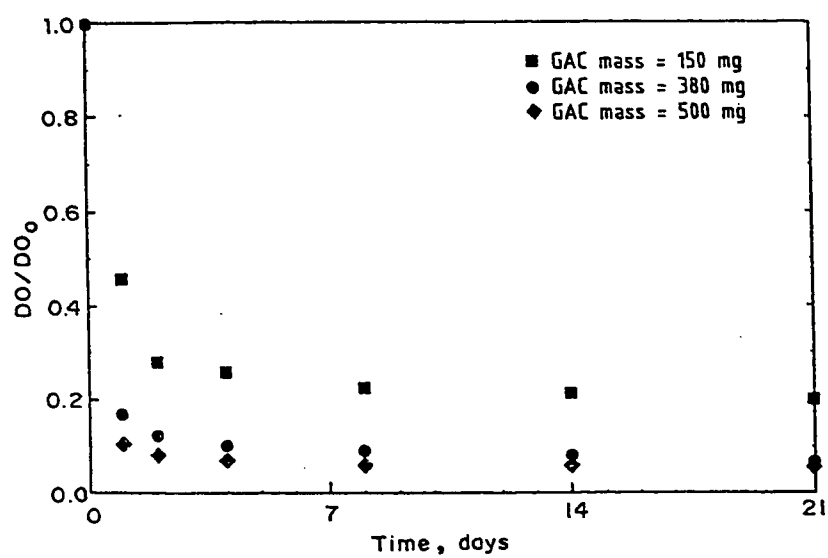


Figure 5.12: Oxygen Uptake with Time.(Ref. 14)

$$\Delta q = M_1 [R_o]^{b_1} \quad (5.1)$$

where,  $\Delta q$  is the change in uptake relative to the anoxic uptake, mg/g.  $R_{\text{sub } o}$  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 oxie uptake was the dependent variable while the anoxic uptake and the GAC mass ratio were the independent variables. The equation took the form:

$$q = q_o + L [q_o]^h [R_o]^d \quad (5.2)$$

where,  $q$  and  $q_o$  are the oxie 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;

$$q = q_o + \{M [R]^{b_1}\} \quad (5.3)$$

while Equation 5.2 can be expressed as;

$$\Delta q = L [q_o]^h [R]^d \quad (5.4)$$

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.

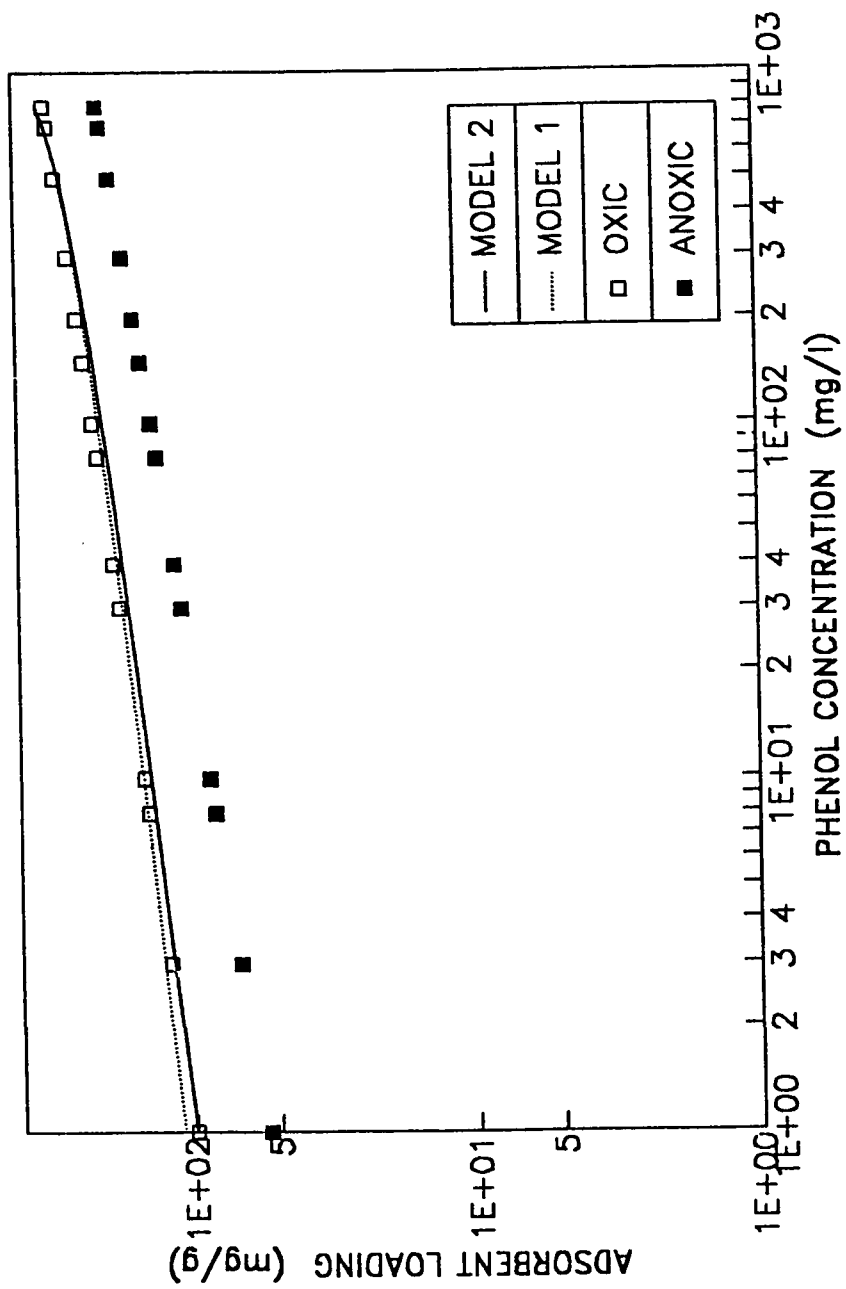


Figure 5.13: Observed and Predicted Phenol Uptakes, Data from Ref. 14.

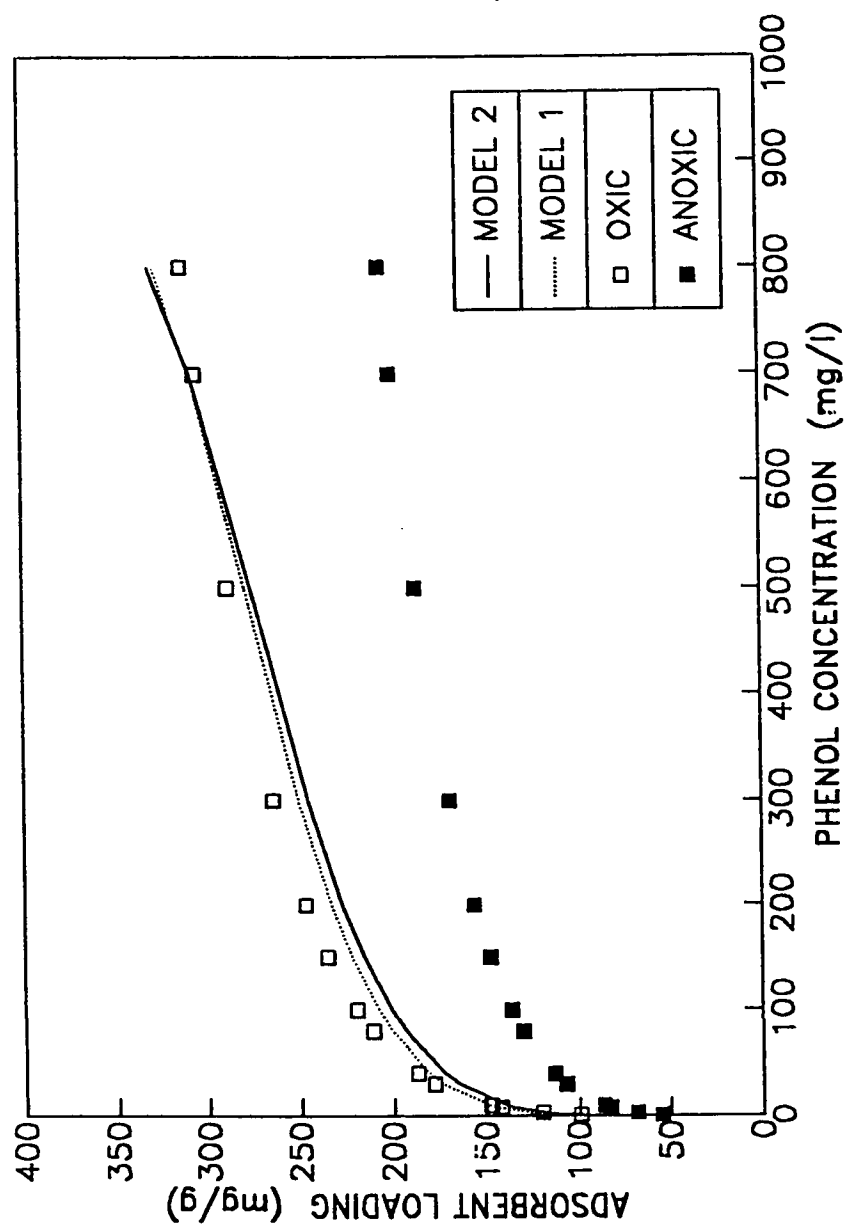


Figure 5.14: Observed and Predicted Phenol Uptakes, Data from Ref. 14.

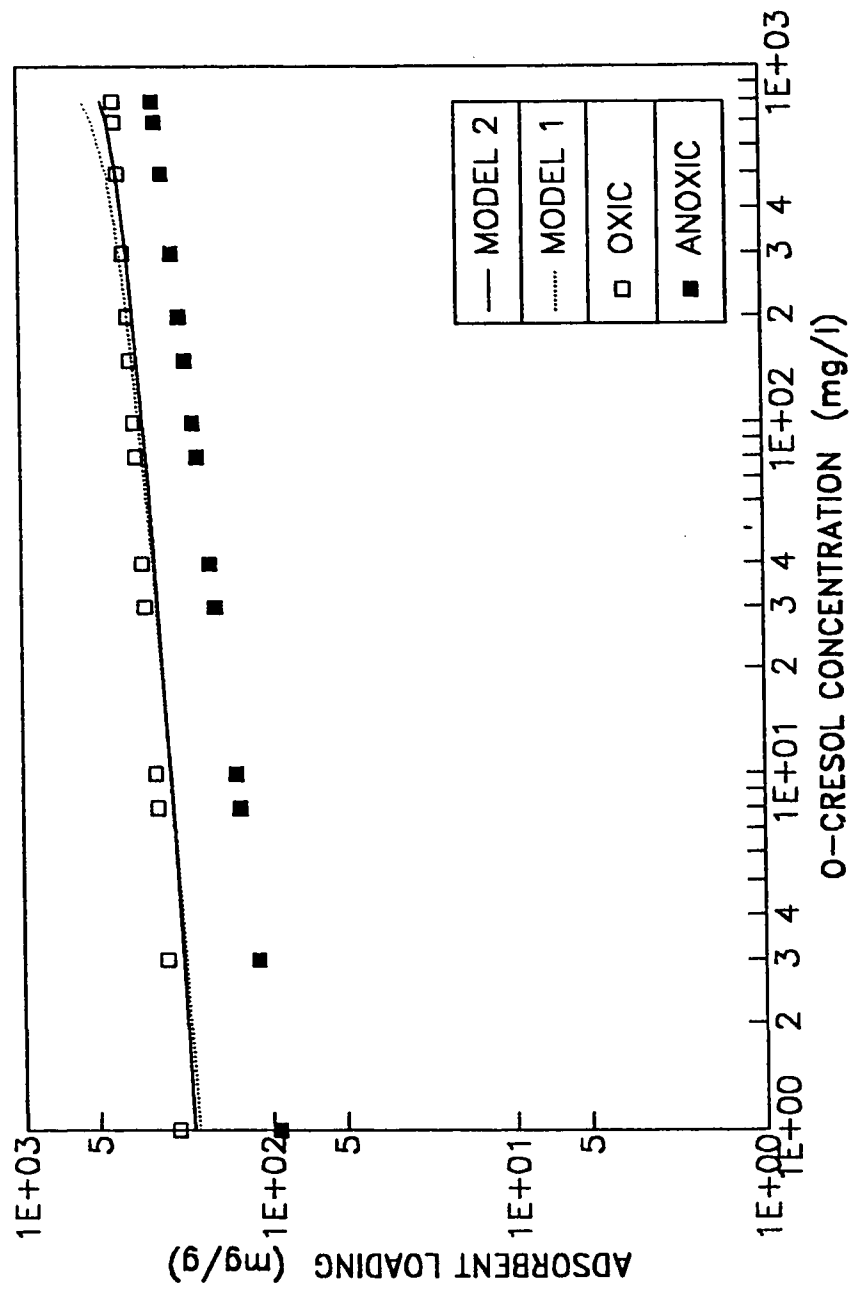


Figure 5.15: Observed and Predicted Uptakes for o-Cresol, Data from Ref. 14.

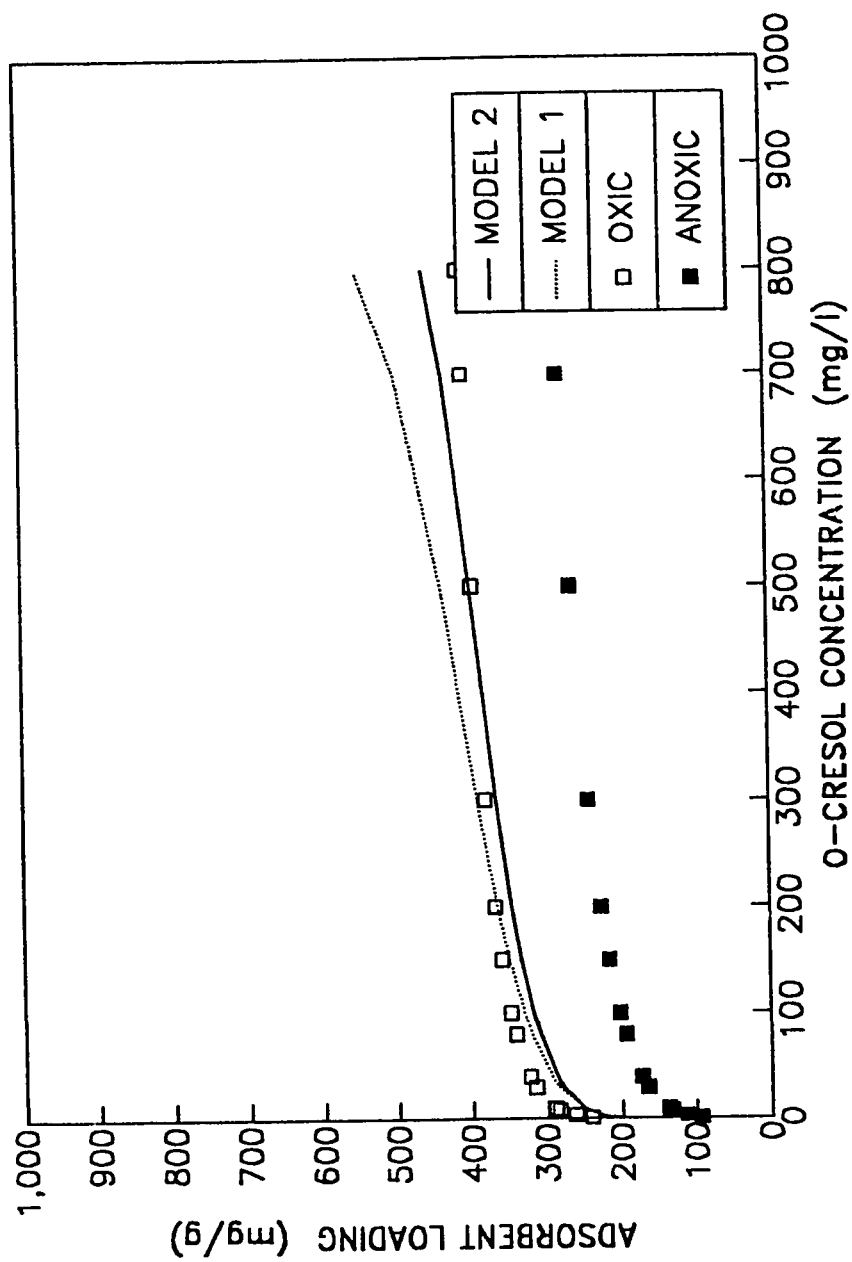


Figure 5.16: Observed and Predicted Uptakes for o-Cresol, Data from Ref. 14.

Using the aforementioned values of  $R$  and the anoxic uptakes given by the anoxic loading the oxie 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 oxie 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 oxie 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 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

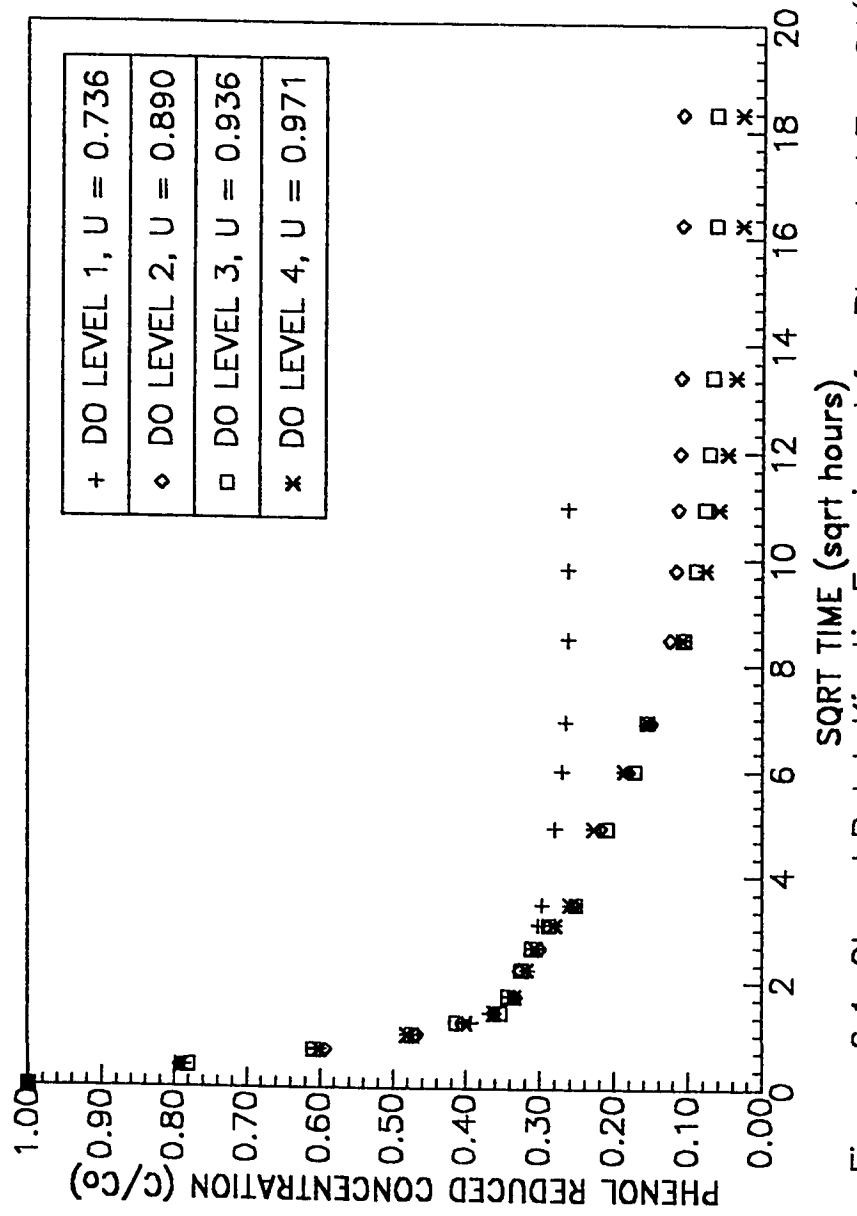


Figure 6.1: Closed Batch Kinetic Experiment for Phenol at T = 21 °C. and pH of 7.

PHKDIFOS

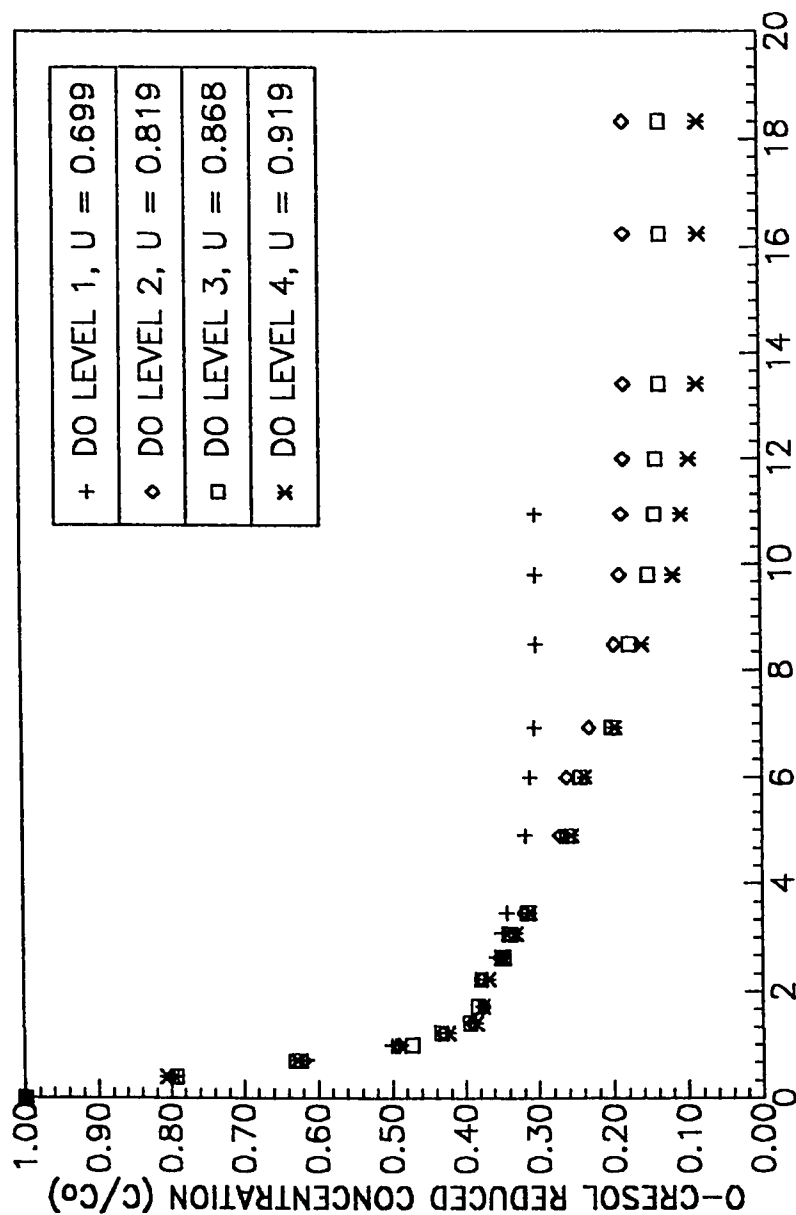


Figure 6.2: Closed Batch Kinetics Experiment for o-Cresol at  $T = 21^{\circ} \text{C}$ . and pH 7.

OC1S

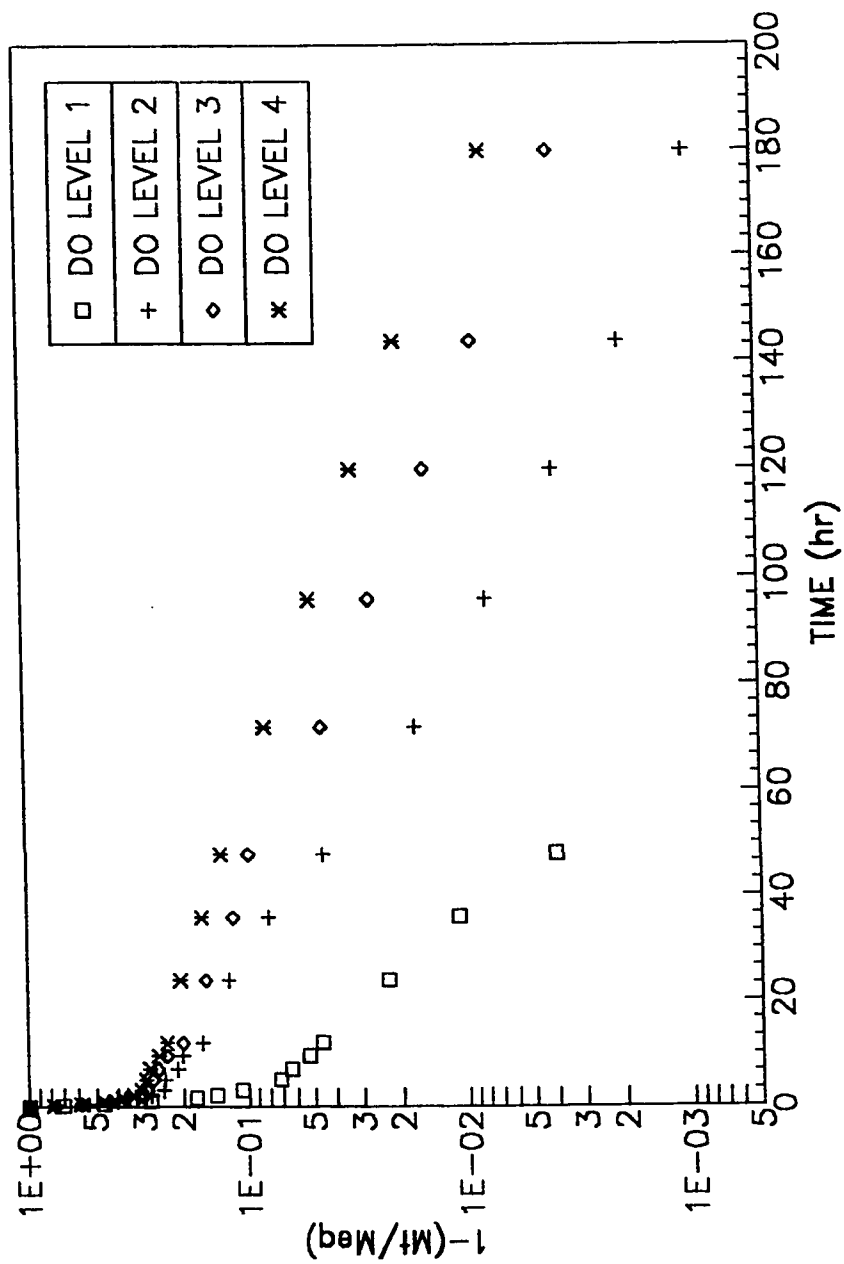


Figure 6.3: Linearized Rate of Phenol Uptake at  $T = 21^{\circ}\text{C}$ . and  $\text{pH}_{\text{from CRANKP}}$

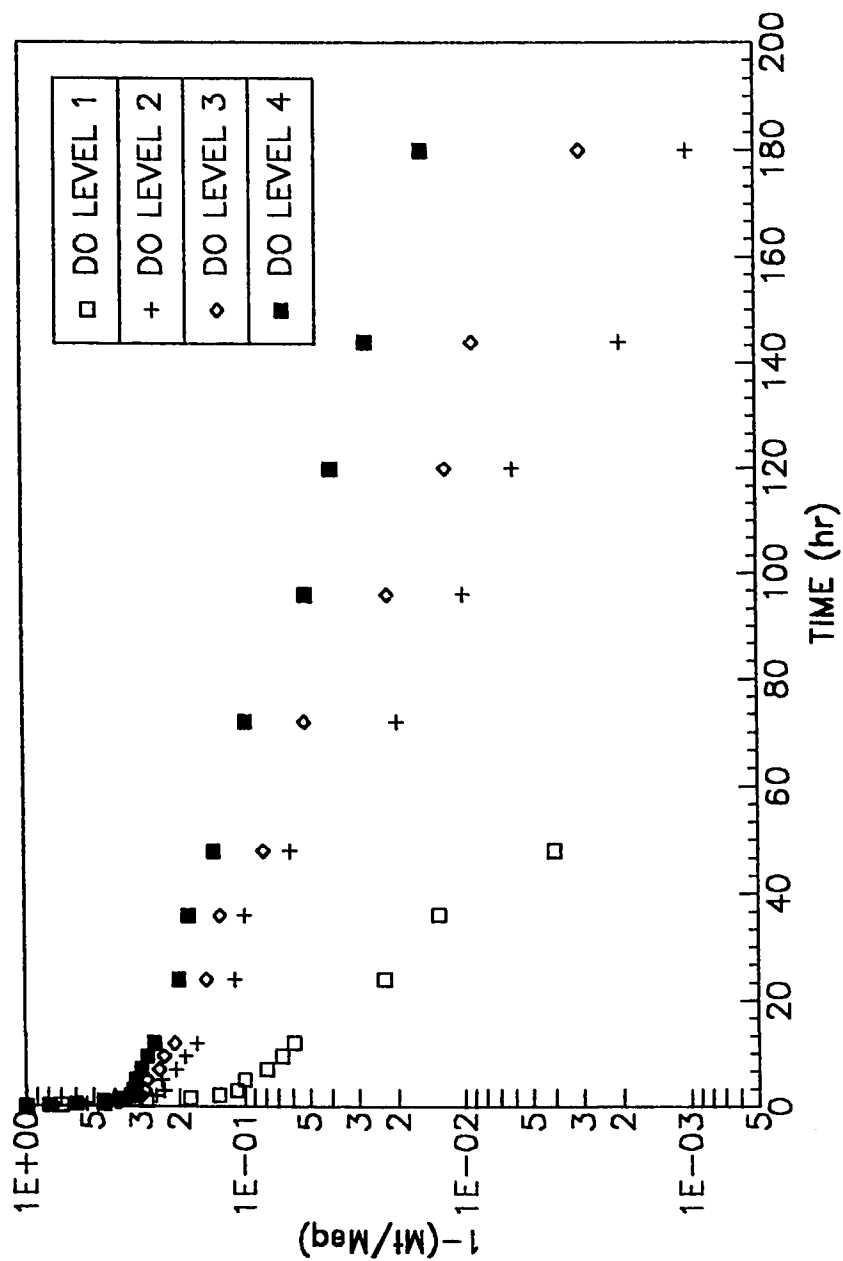


Figure 6.4: Linearized Rate of o-Cresol Uptake at  $T = 21^{\circ}\text{C}$ . and  $\text{pH}_{\text{from 10.1}}$

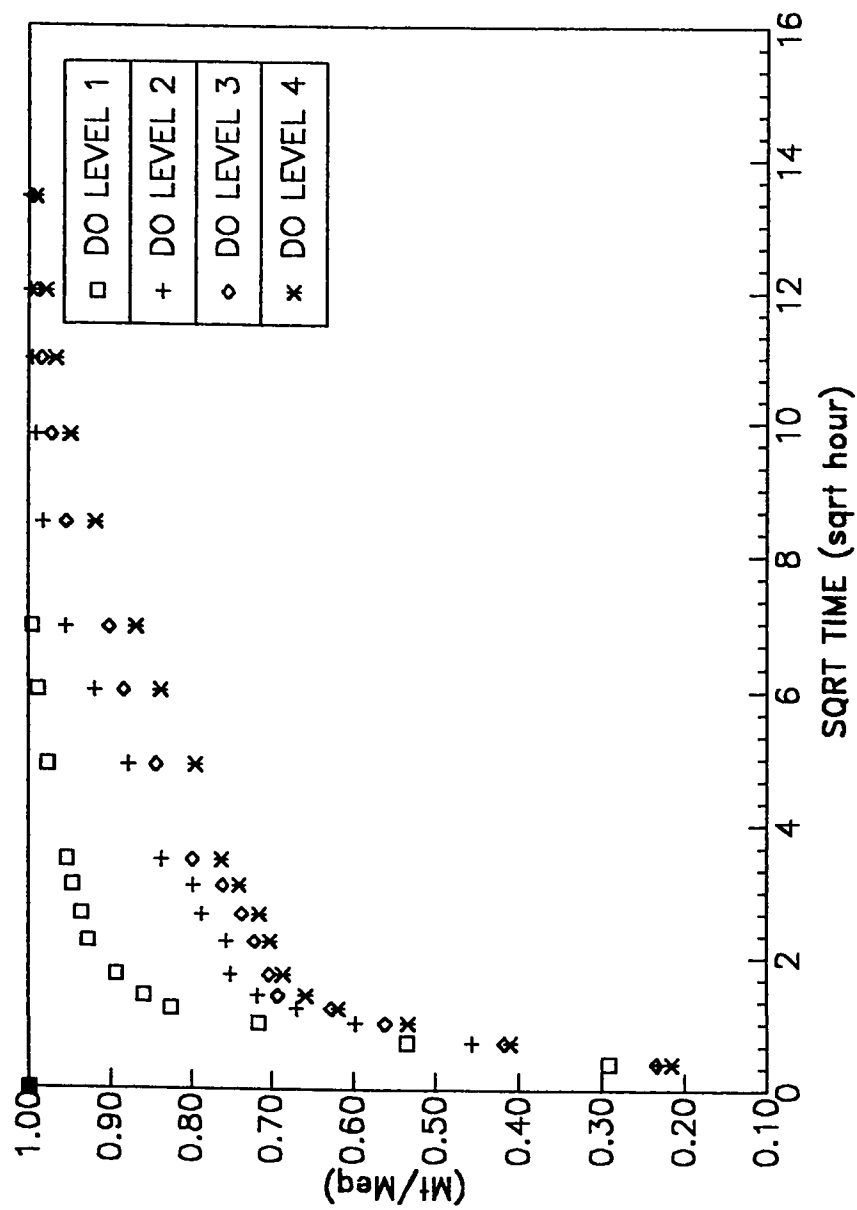


Figure 6.5: Linearized Uptake Rate of Phenol at T = 21° C. and pH of 7

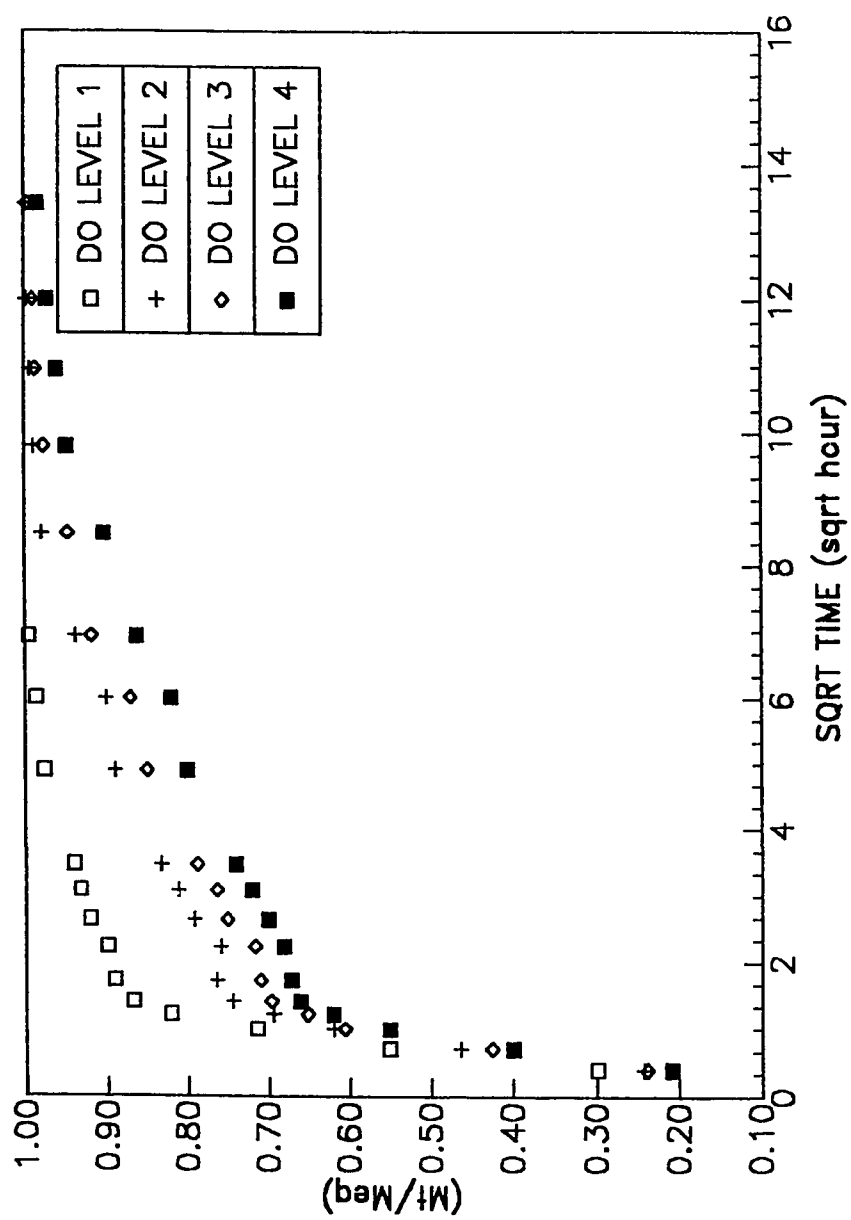


Figure 6.6: Linearized Uptake Rate of o-Cresol at  $T = 21^{\circ}\text{C}$  and  $\text{pH}$  of 7

are masked. As time increase, such differences become more pronounced as a result 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

$$r_i = y_i - v(x, t_i) \quad (6.1)$$

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:

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

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  $c_{\infty}$  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  $\chi^2$  values calculated for the data and from the tables for both phenol and o-cresol. The  $\chi^2$  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  $\chi^2$  values for the anoxic cases were much lower than the oxic ones and the  $\chi^2$  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  $3.53 \times 10^{-8}$  and  $2.41 \times 10^{-8}$  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 <sup>2</sup> /sec	$\chi^2$	$\chi^2_{n,n-0.95}$
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

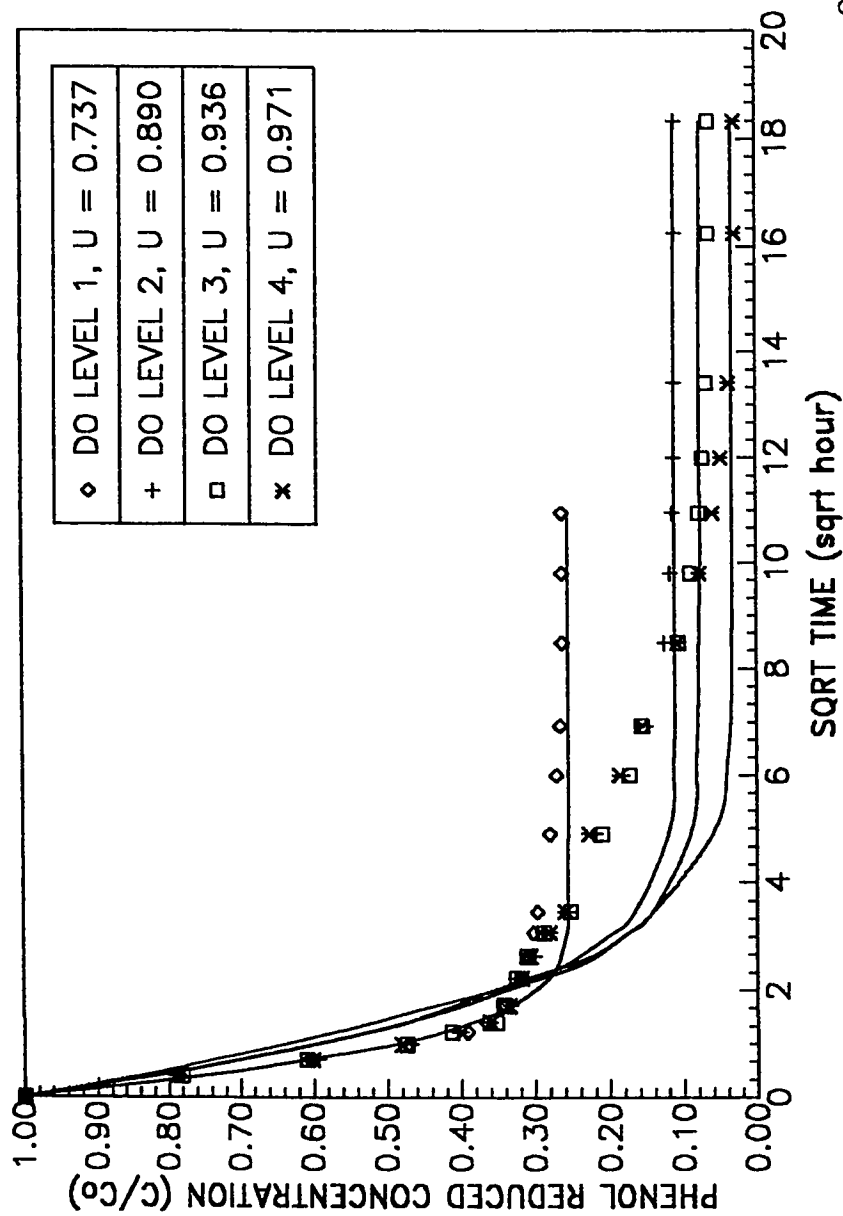


Figure 6.7: Closed Batch Kinetic Experiment for Phenol at  $T = 21^{\circ}\text{C}$ .  
and pH 7 Along with HSDM Predictions.

HSDM1S

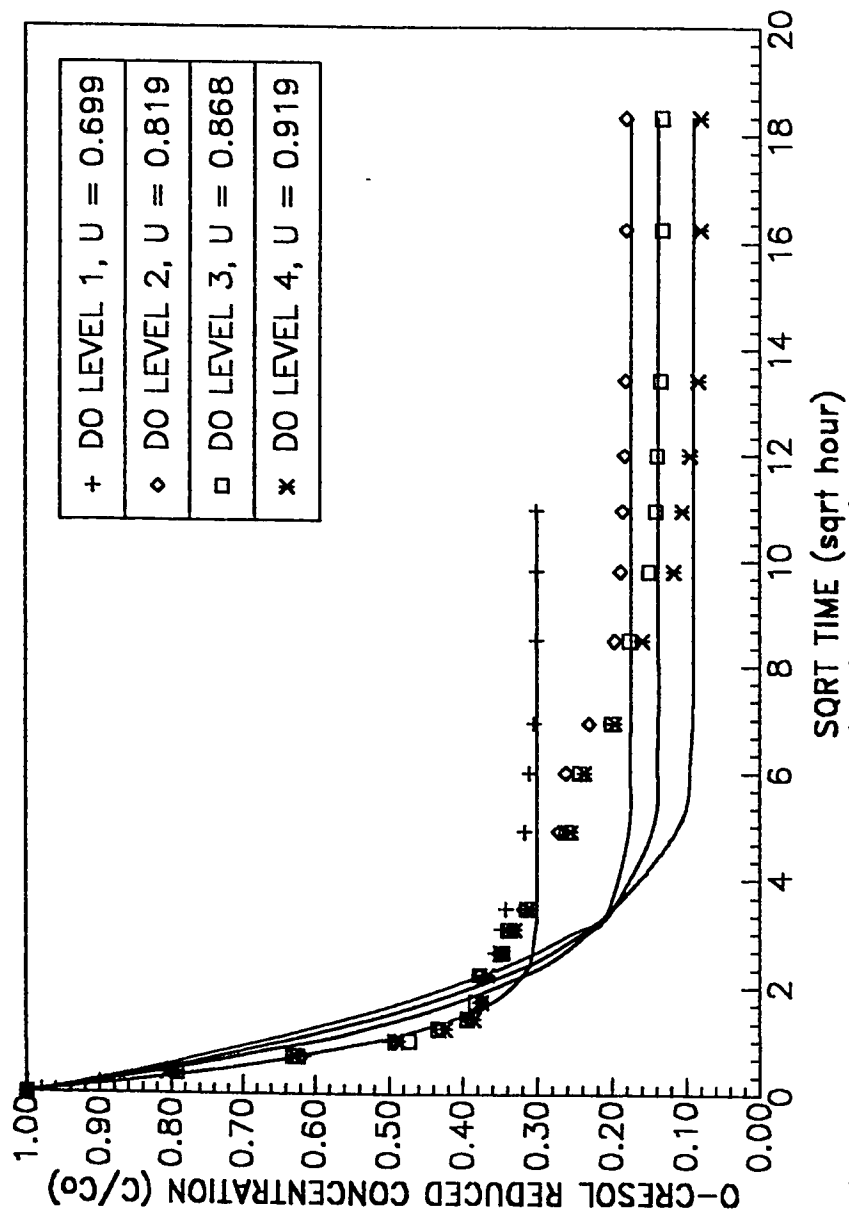


Figure 6.8: Closed Batch Kinetics Experiment for o-Cresol at  $T = 21^\circ \text{C}$ .  
and pH 7 Along with HSDM Predictions.

HSDMO1S

was not always the case for the oxie 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 oxie 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 I (anoxic) and the other levels, while the difference between the diffusivity values in the oxie 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 oxie 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 oxie 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 oxie 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

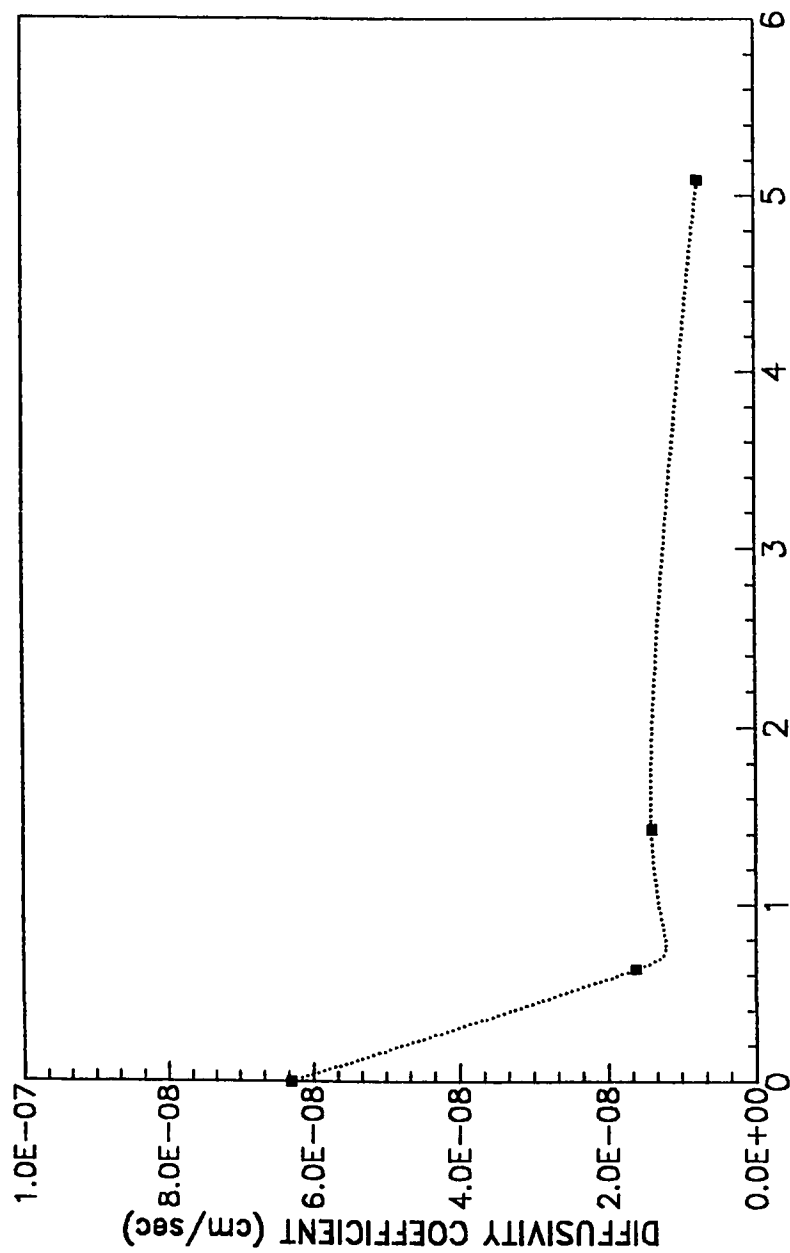


Figure 6.9: Relationship Between the Phenol Apparent Diffusivity (HSDM) and the Ratio of DO to GAC Mass at  $T = 21^{\circ}\text{C}$ . and pH 7. from HDOP

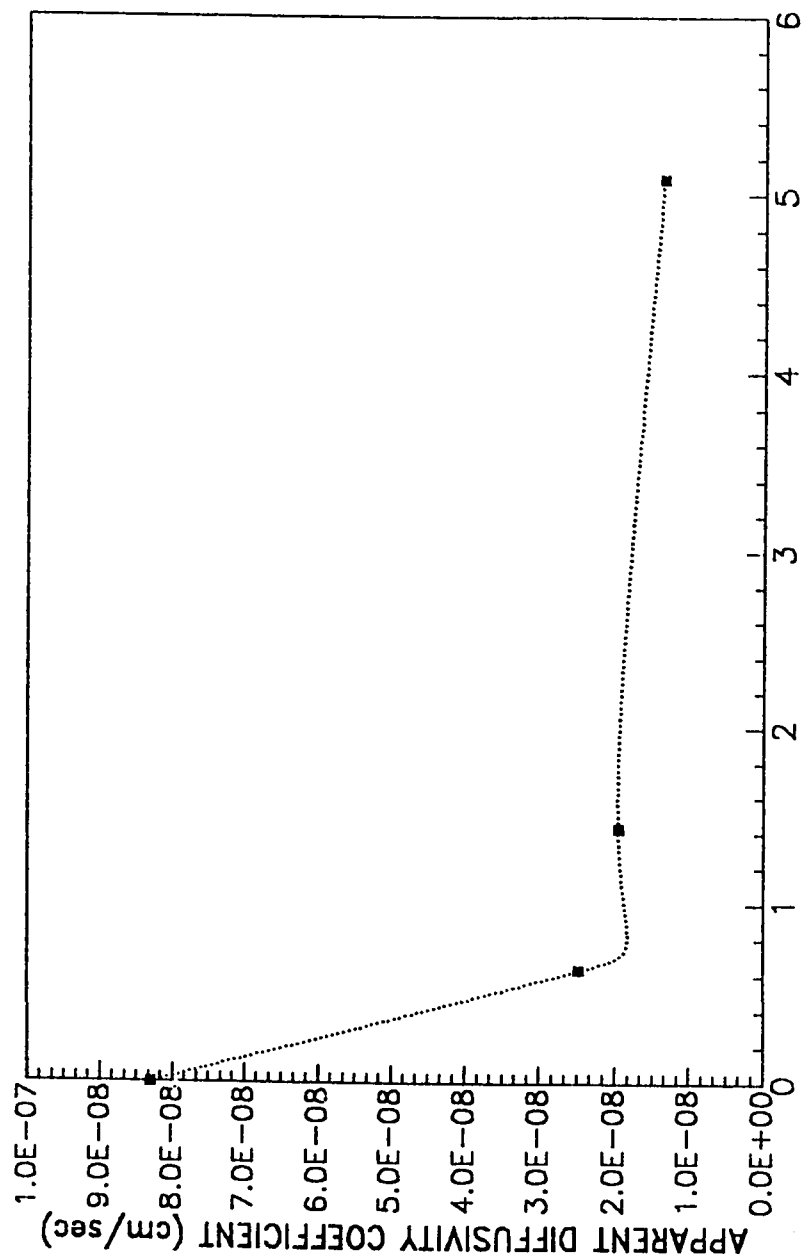


Figure 6.10: Relationship Between the o-Cresol Apparent Diffusivity (HSDM) and the Ratio of DO to GAC Mass at  $T = 21^{\circ}\text{C}$ . and pH 7.

HDOO

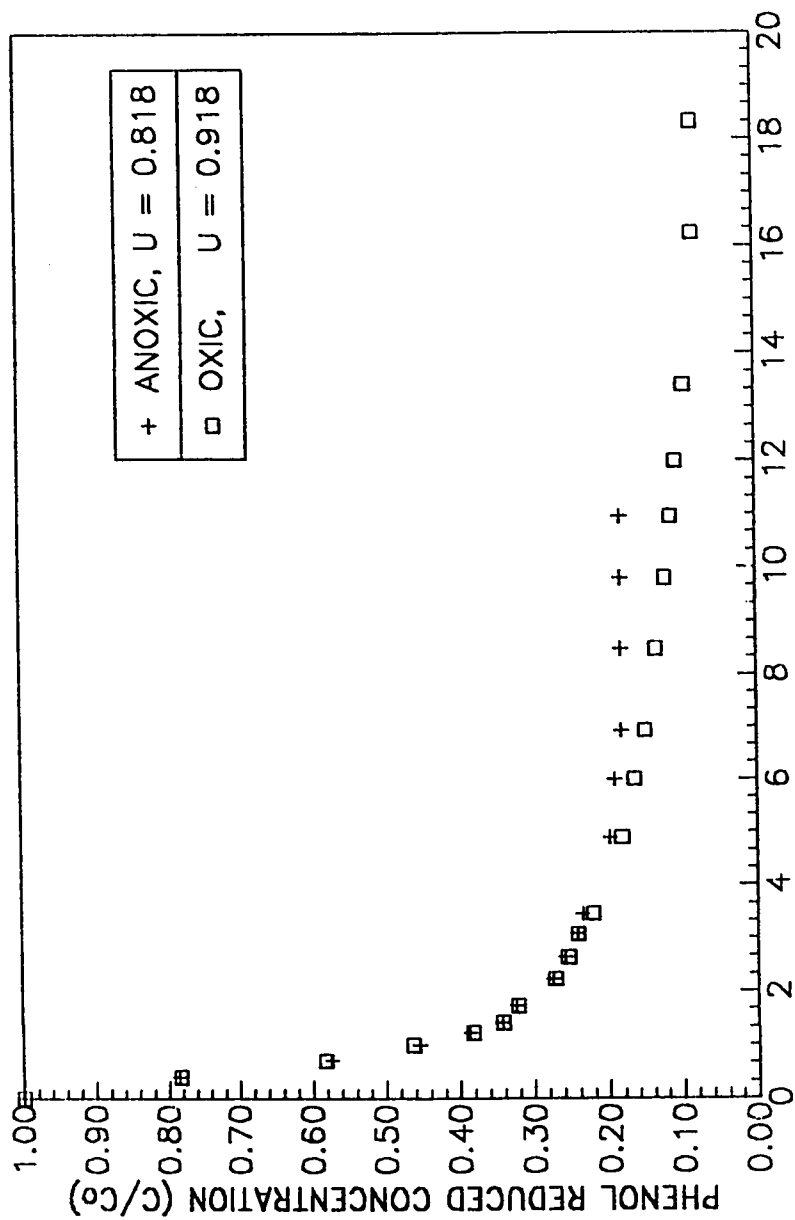


Figure 6.11: Closed Batch Kinetics Experiment for Phenol at pH 3  
and  $T = 21^\circ \text{C}$ .  
from PHK3S

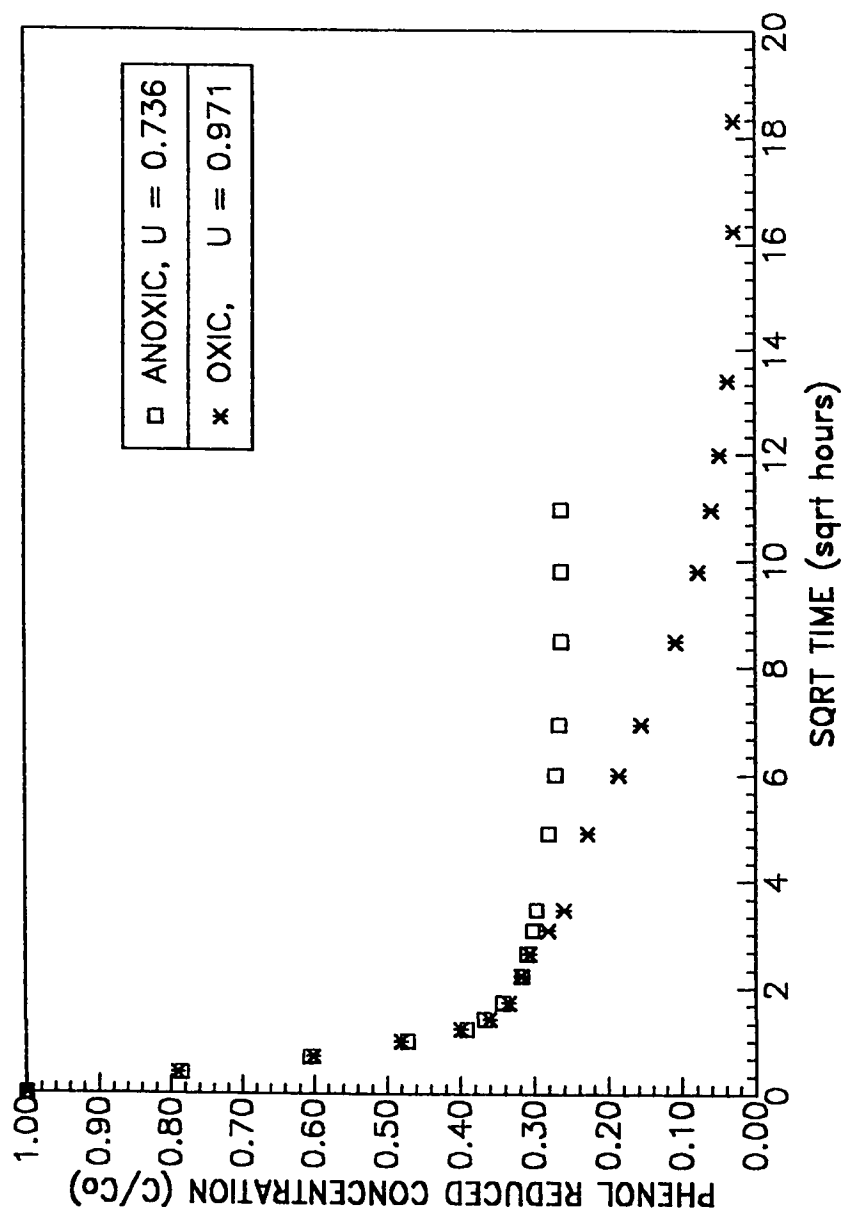


Figure 6.12: Closed Batch Kinetic Experiment for Phenol at pH 7 and  $T = 21^{\circ}\text{C}$ .

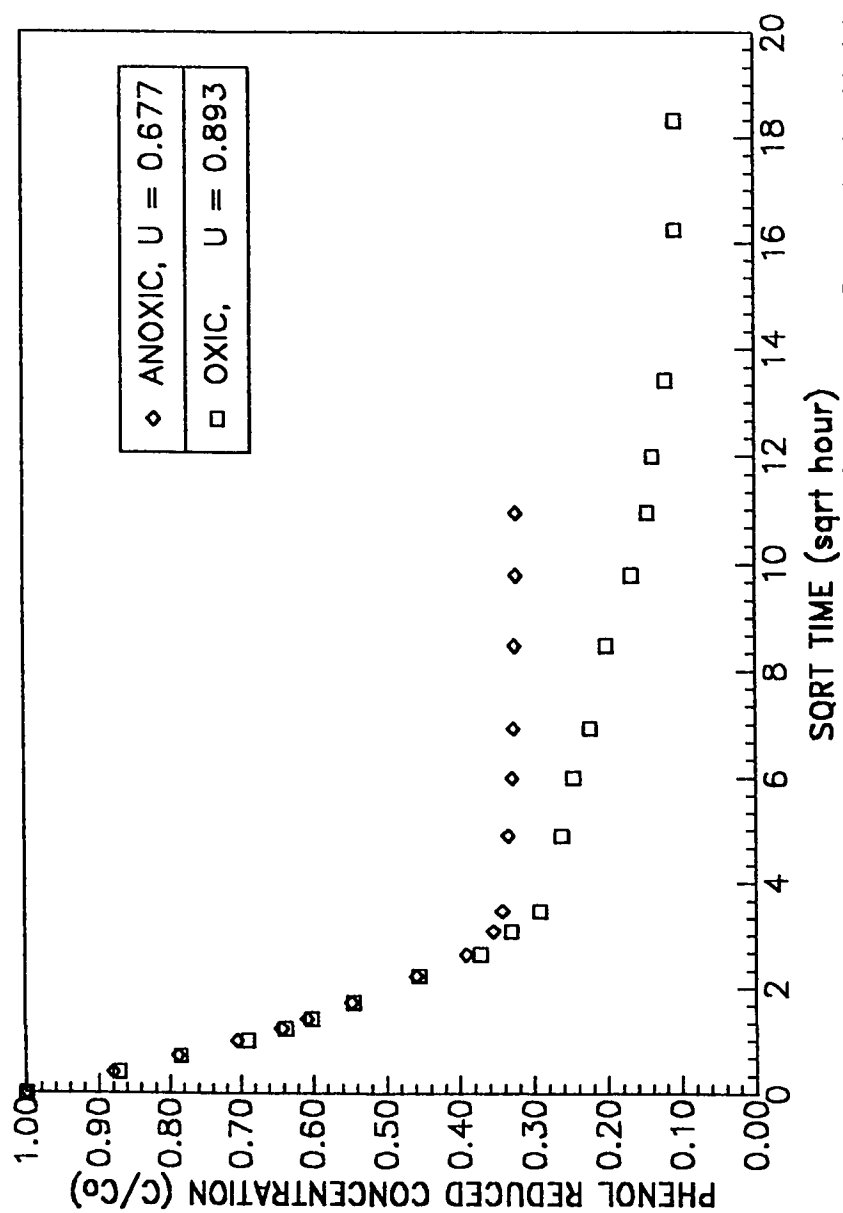


Figure 6.13: Closed Batch Kinetics Experiment for Phenol at pH 11 and  $T = 21^\circ\text{C}$ .

PHK111S

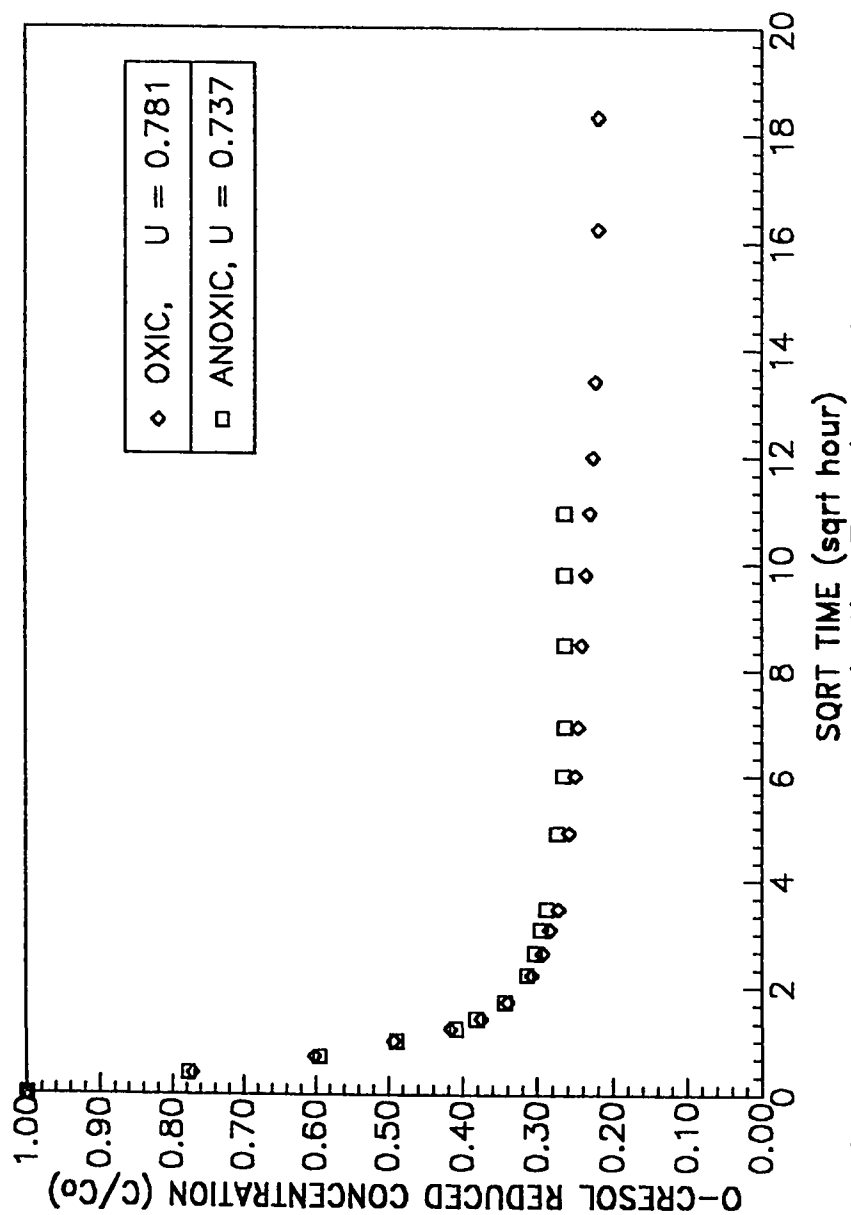


Figure 6.14: Closed Batch Kinetics Experiment for o-Cresol at pH 3 and  $T = 21^\circ \text{C}$ .

OHK3S

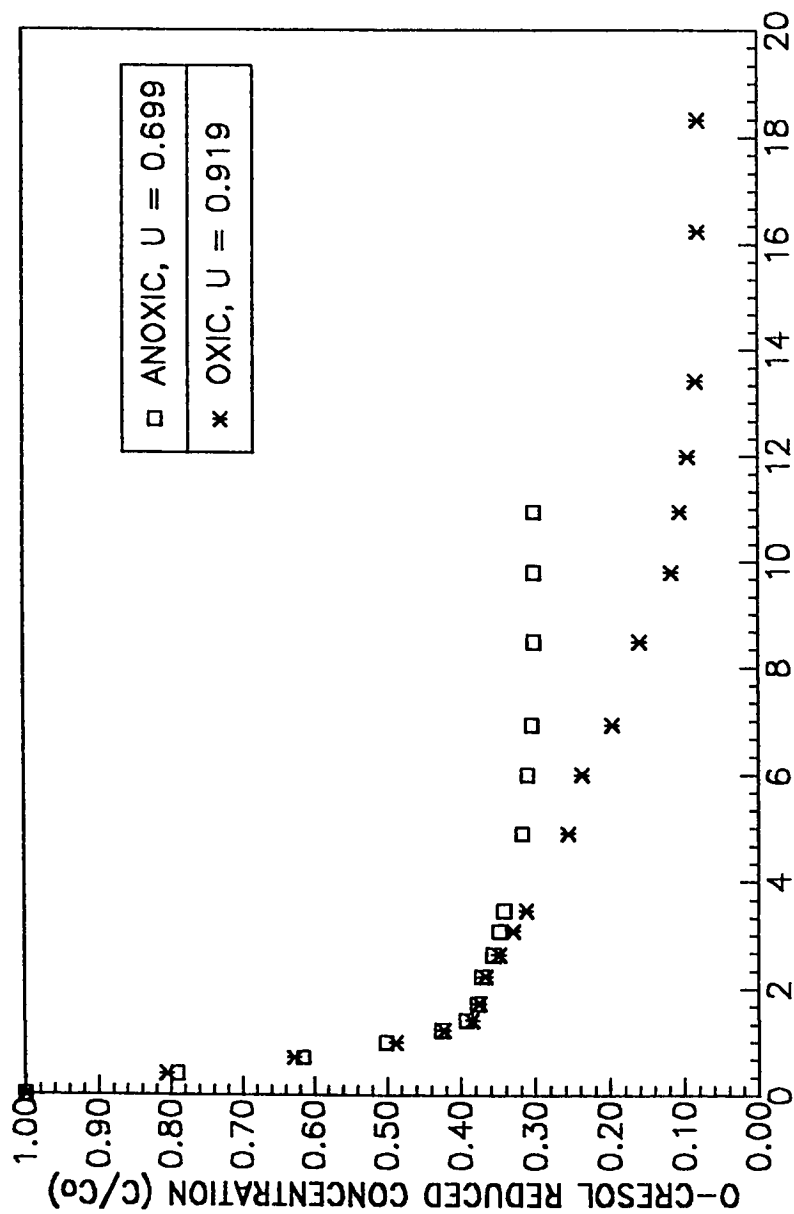


Figure 6.15: Closed Batch Kinetics Experiment for o-Cresol at pH 7 and T = 21° C.

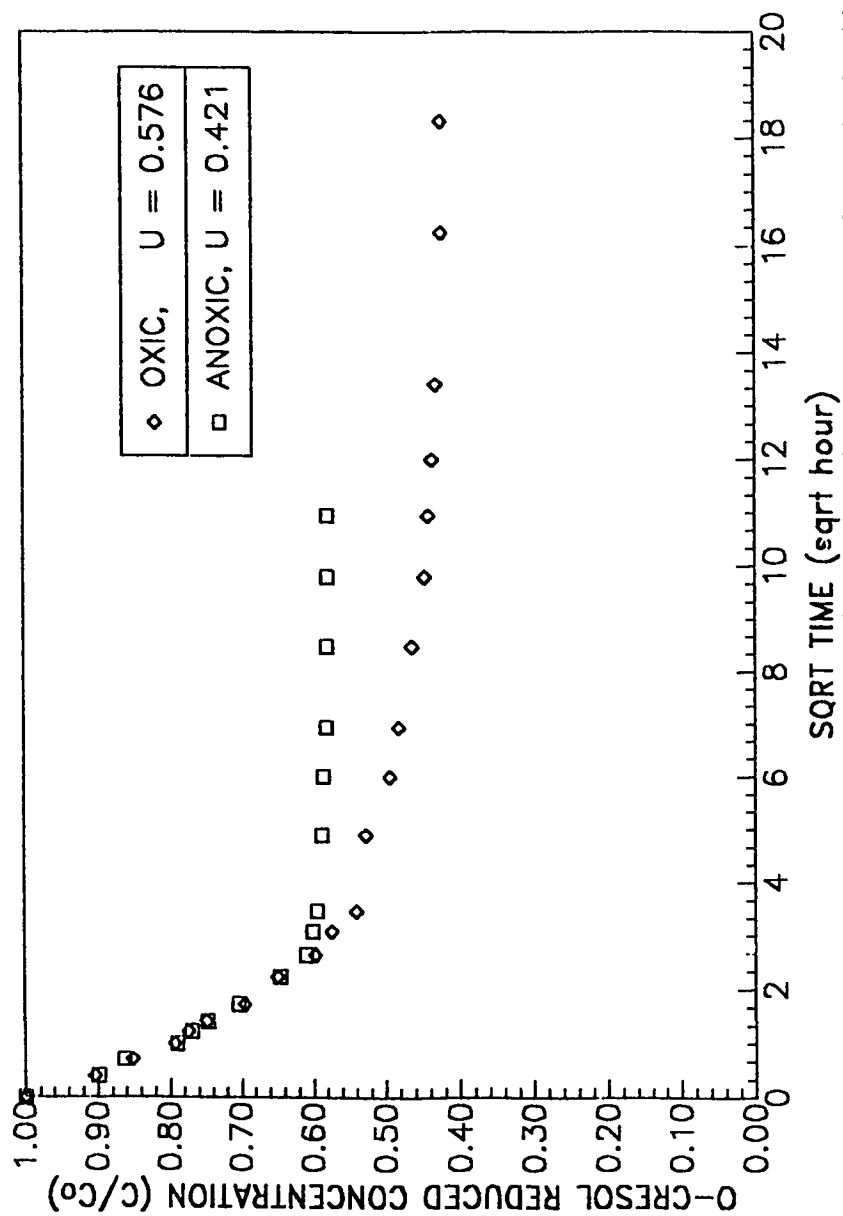


Figure 6.16: Closed Batch Kinetics Experiment for o-Cresol at pH 11 and  $T = 21^{\circ}\text{C}$ .

OHK11S

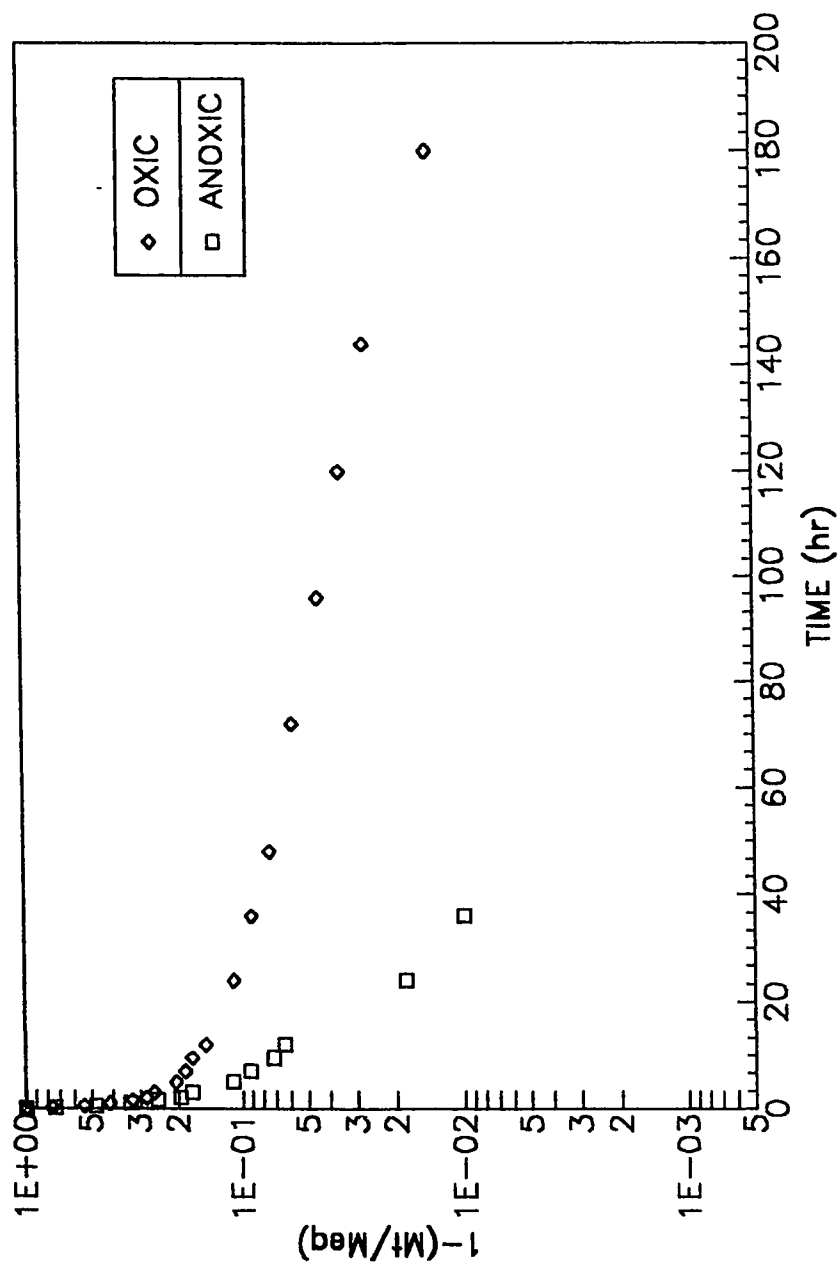


Figure 6.17: Linearized Rate of Phenol Uptake at pH 3 and  $T = 21^\circ\text{C}$

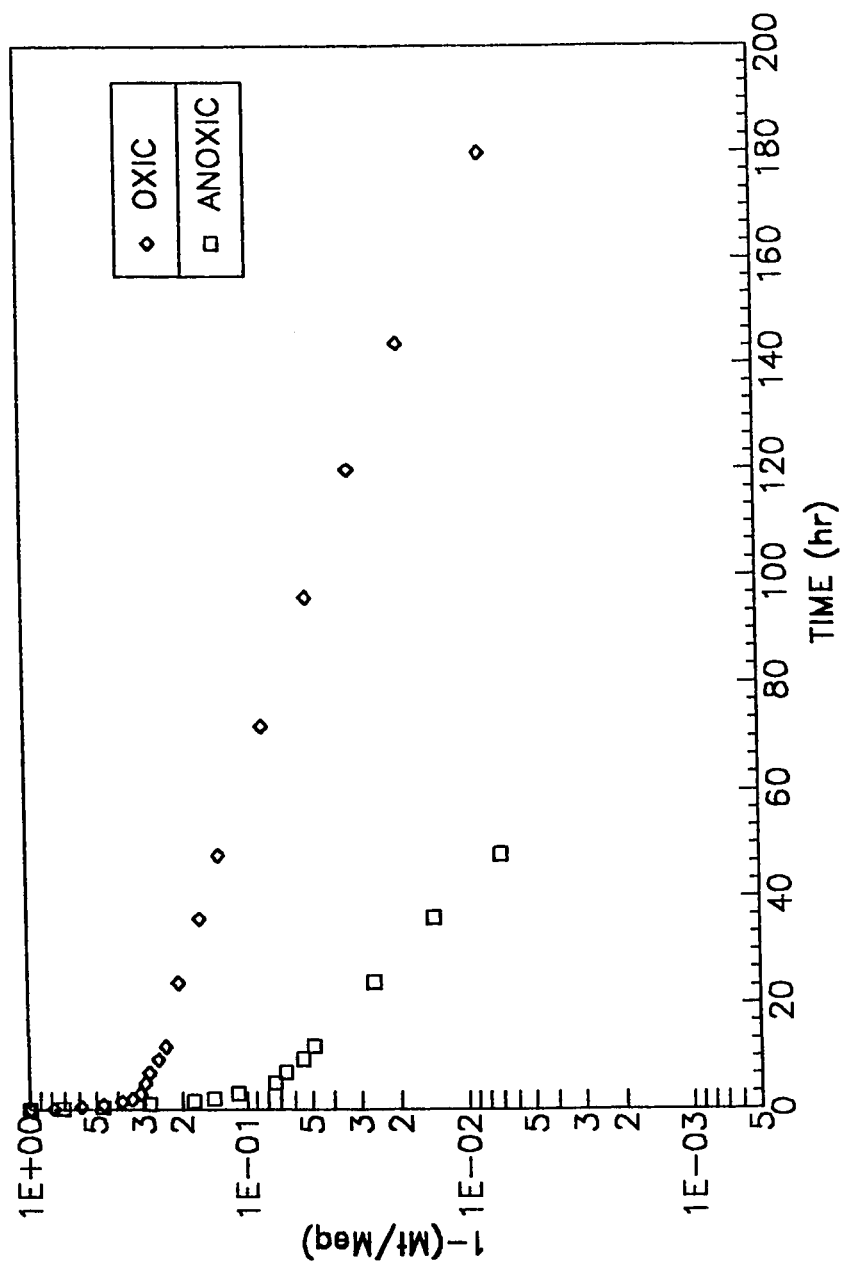


Figure 6.18: Linearized Rate of Phenol Uptake at pH 7 and  $T = 21^\circ\text{C}$  from  $\text{NaOH}$

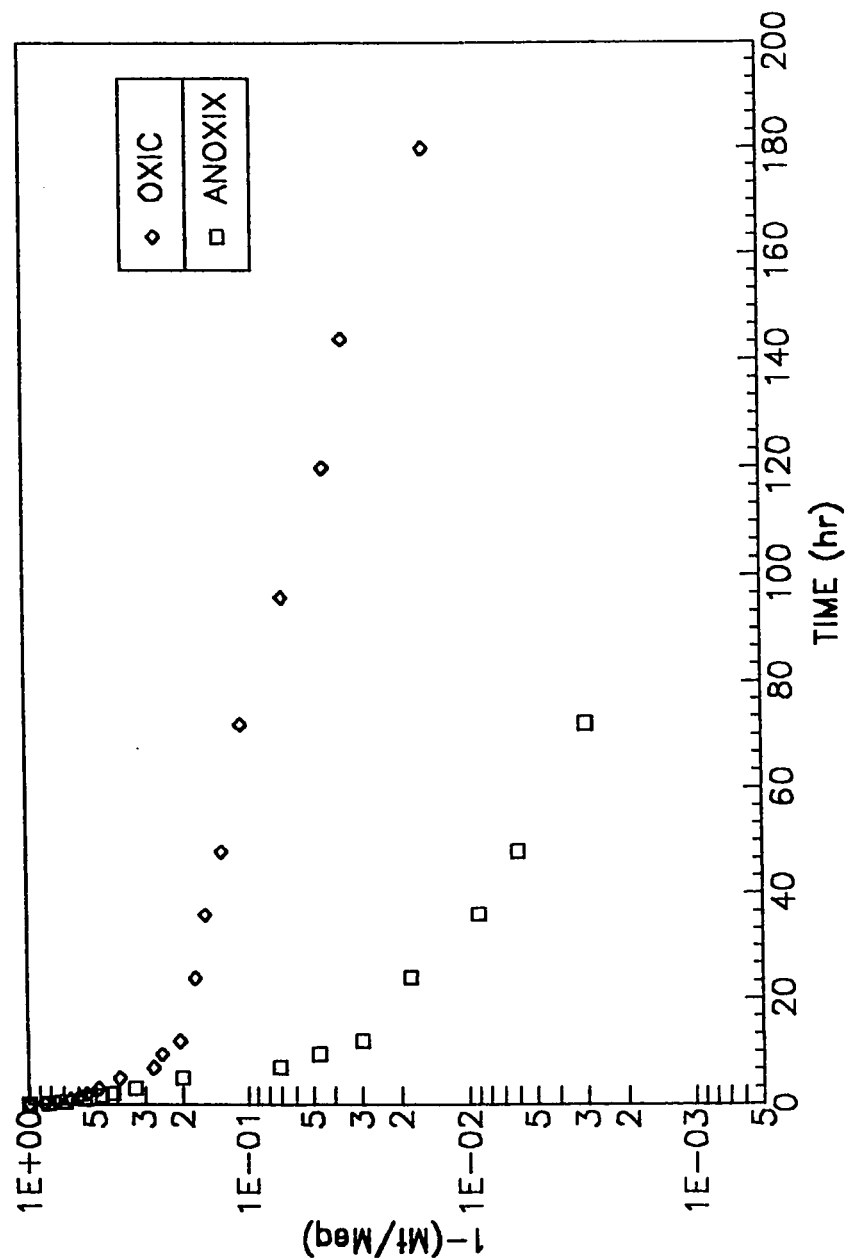


Figure 6.19: Linearized Rate of Phenol Uptake at pH 11 and  $T = 21^\circ\text{C}$  from  $C_{\text{initial}}$

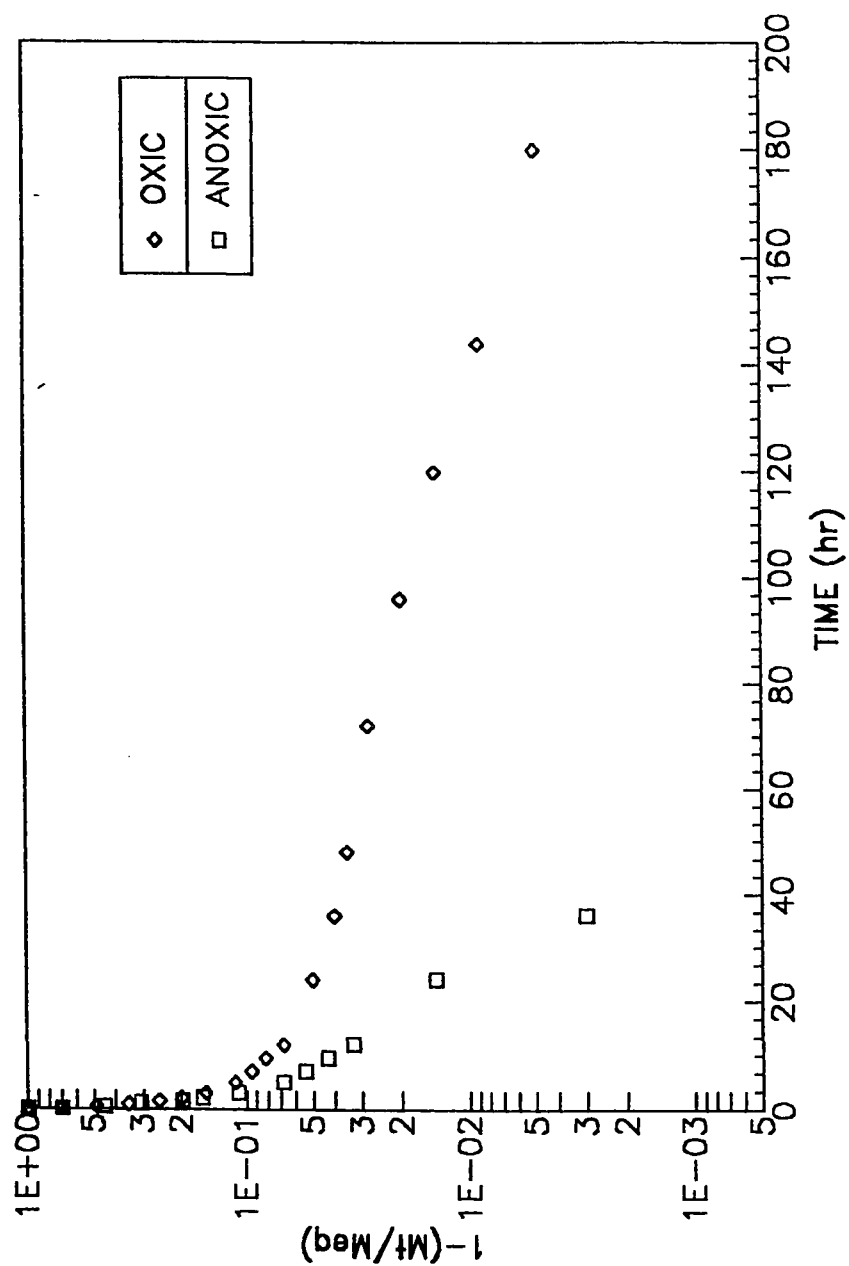


Figure 6.20: Linearized Rate of o-Cresol Uptake at pH 3 and  $T = 21^{\circ}\text{C}$  from  $\text{C}_{60}\text{H}_{12}$

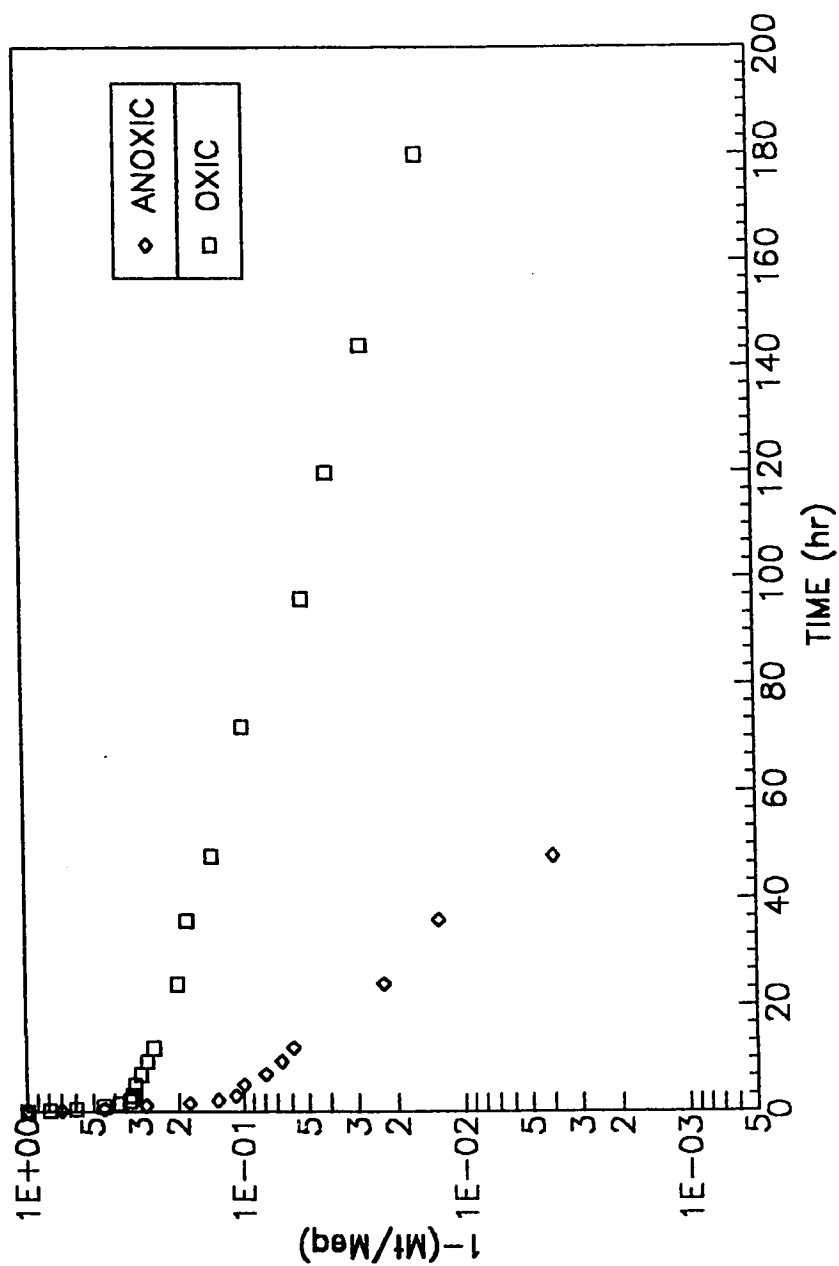


Figure 6.21: Linearized Rate of o-Cresol Uptake at pH 7 and  $T = 21^{\circ}\text{C}$  from 0 to 17

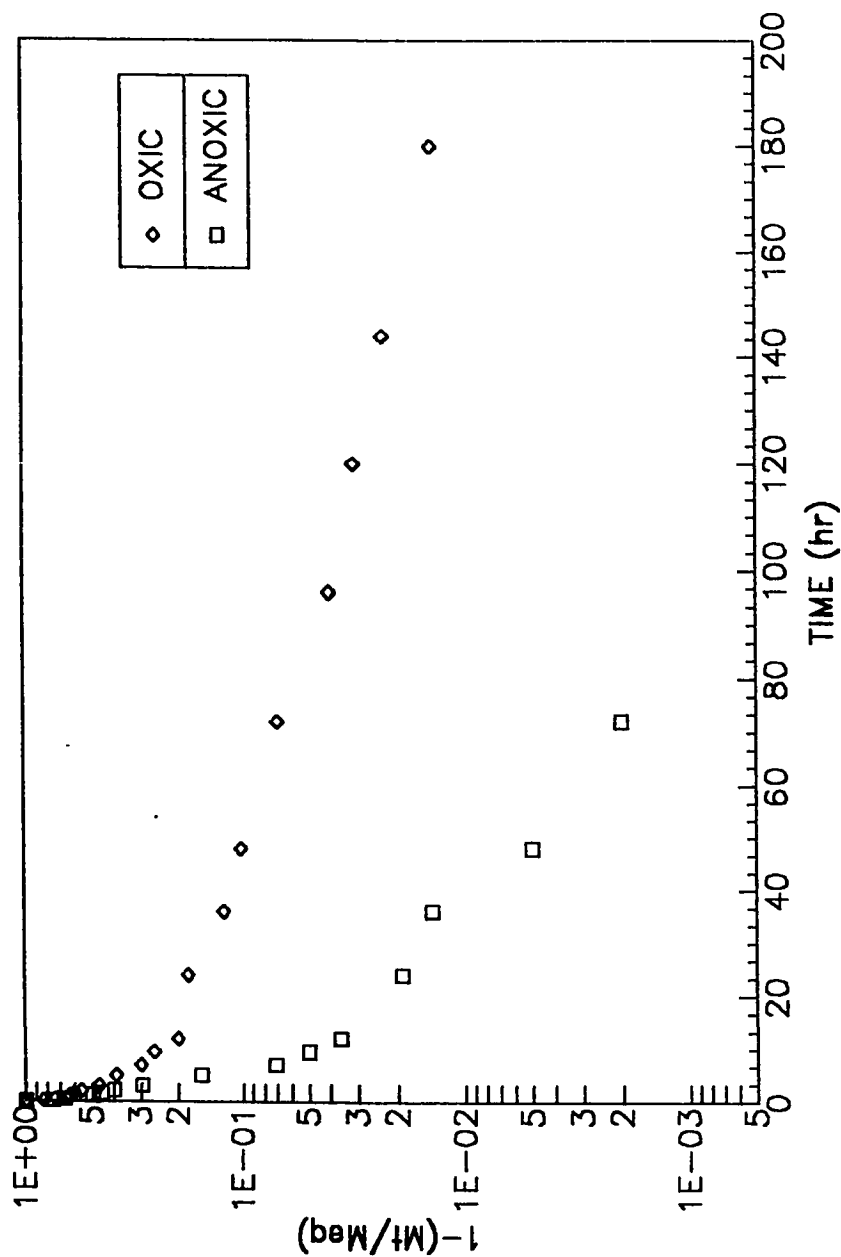


Figure 6.22: Linearized Rate of o-Cresol Uptake at pH 11 and  $T = 21^{\circ}\text{C}$

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 IISDM 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 IISDM 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 IISDM predictions in Figures 6.23-6.28. Those figures depict the good prediction capability IISDM 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  $\chi^2$  values were lower than the table values for both the oxic and anoxic experiment which statistically means that data is fairly predicted by the IISDM 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 <sup>2</sup> /sec	$\chi^2$	$\chi^2_{n.o. 0.95}$
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

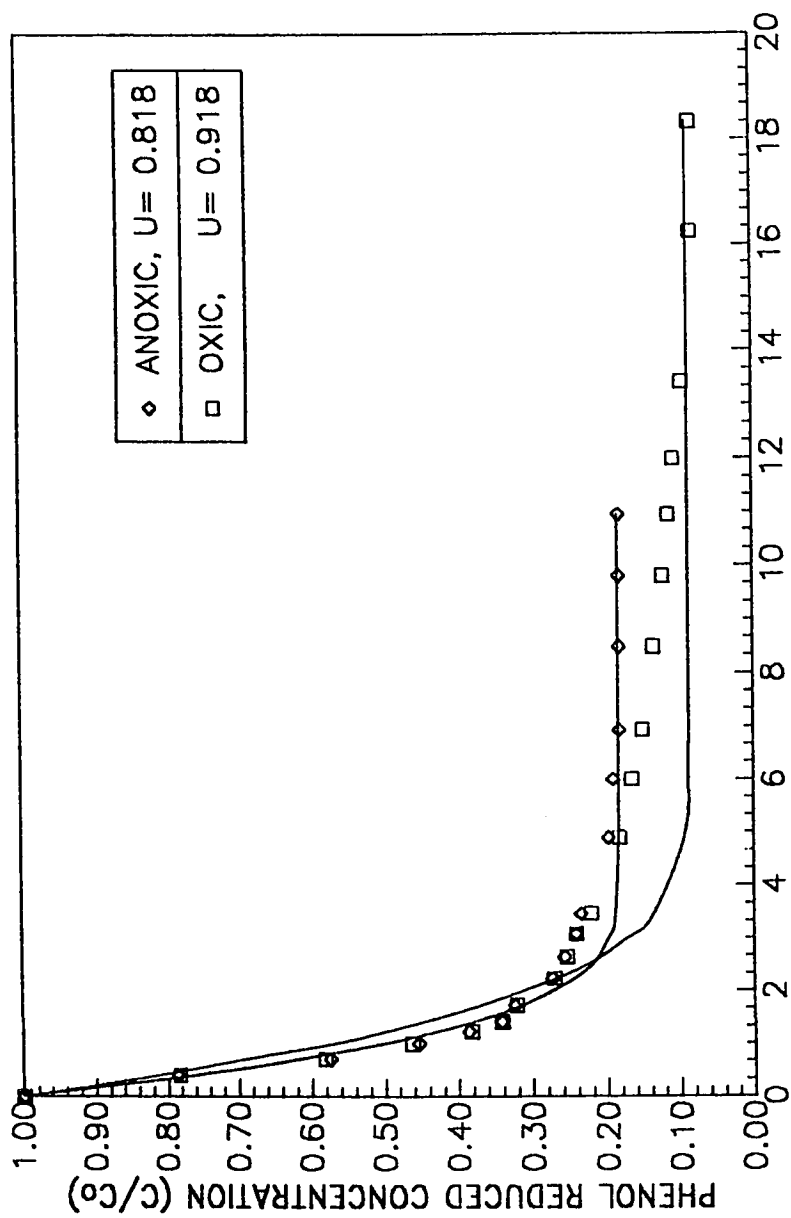


Figure 6.23: Closed Batch Kinetics Experiment for Phenol at pH 3 and  $T = 21^\circ\text{C}$ . Along with HSDM Predictions.

from PHK3MS

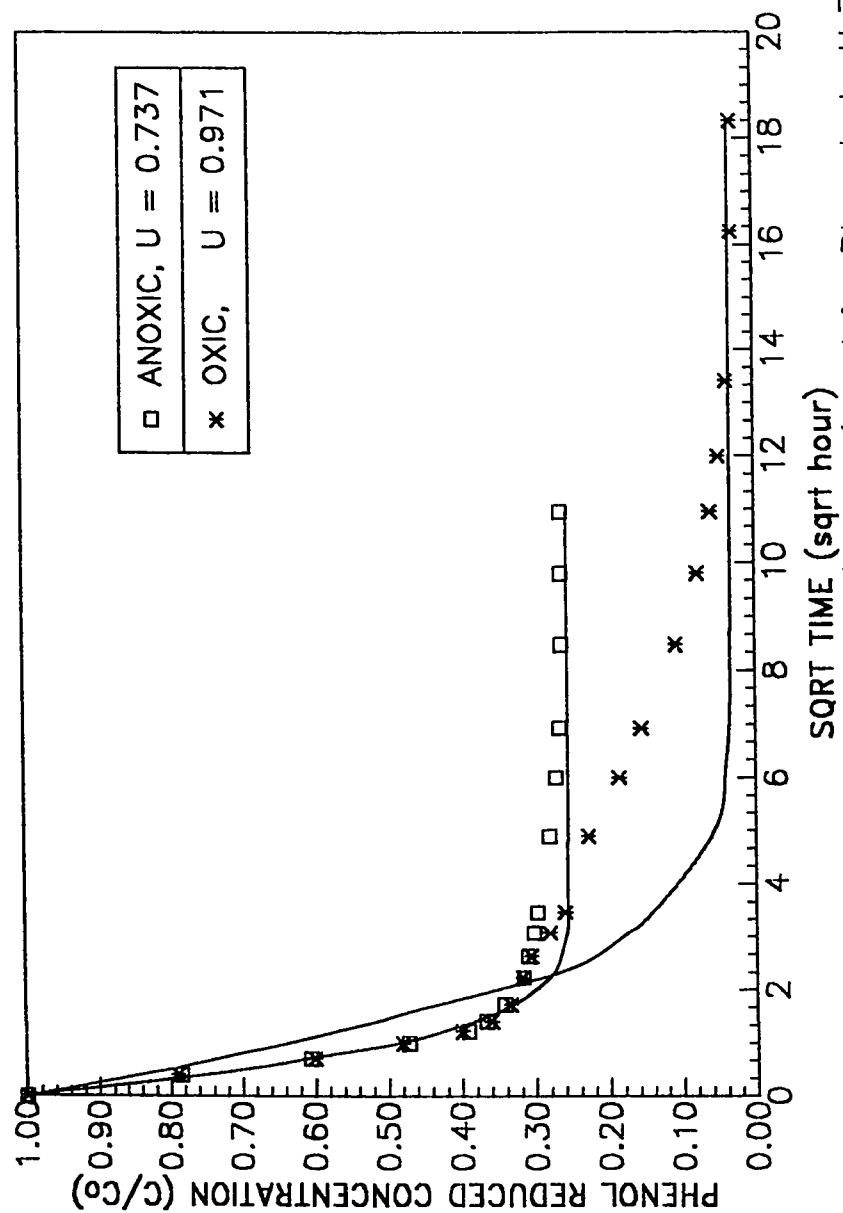


Figure 6.24: Closed Batch Kinetic Experiment for Phenol at pH 7 and  $T = 21^\circ\text{C}$ . Along with HSDM Predictions.

PHK7MS

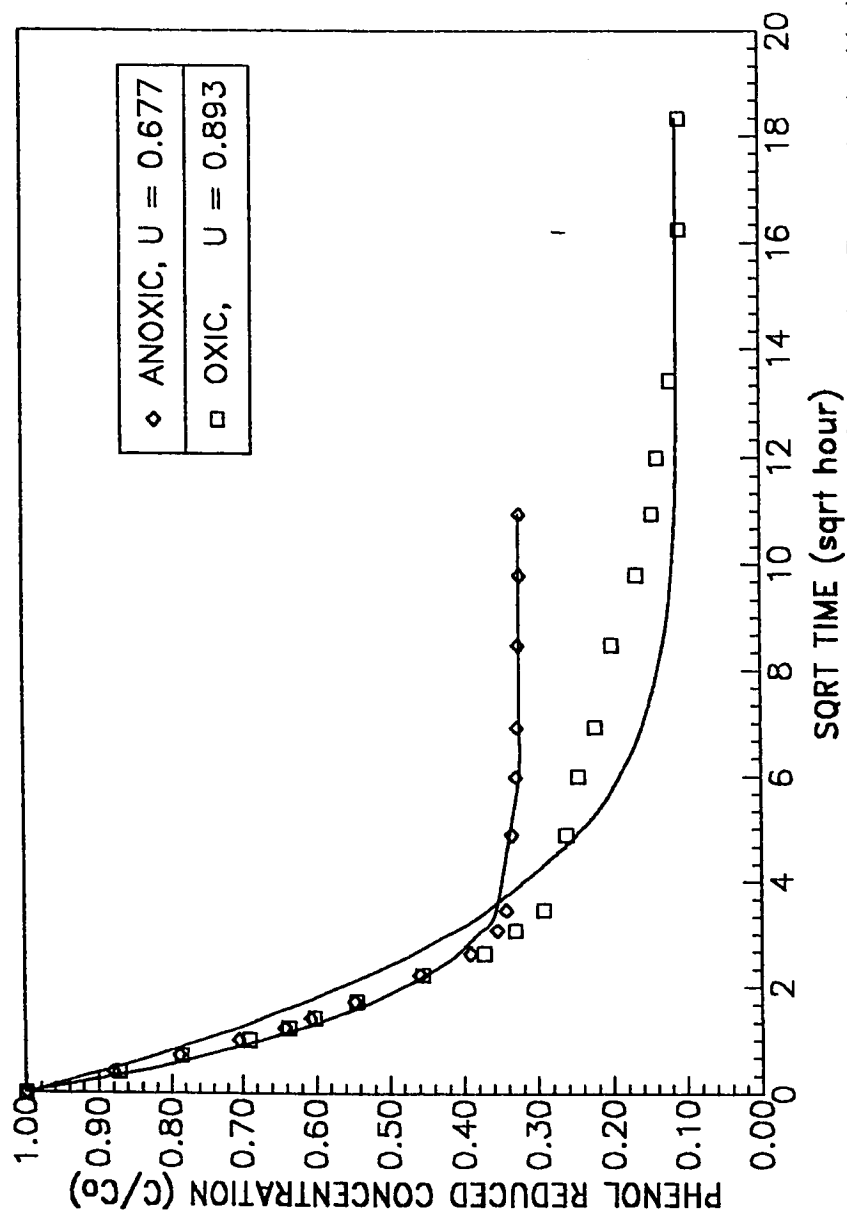


Figure 6.25: Closed Batch Kinetics Experiment for Phenol at pH 11 and  $T = 21^{\circ}\text{C}$ . Along with HSDM Predictions.

PHK11MS

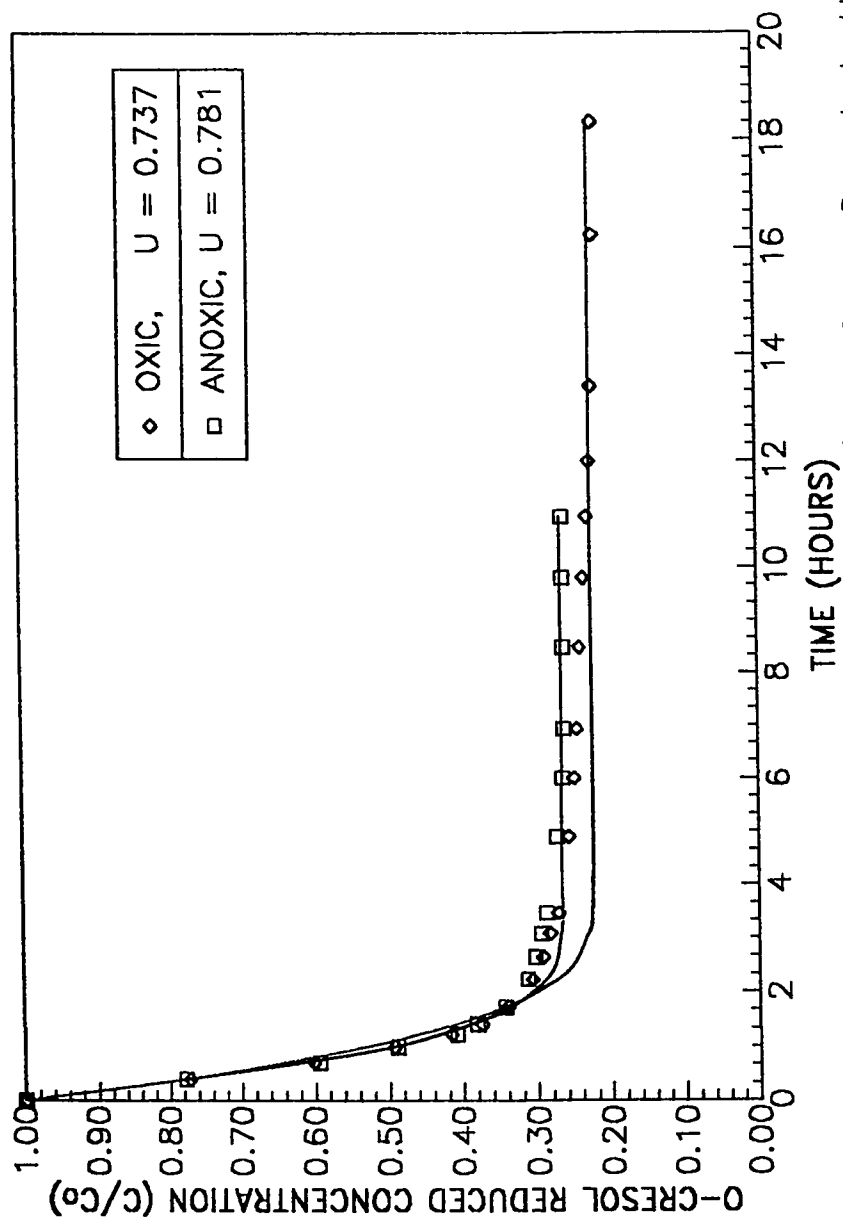


Figure 6.26: Closed Batch Kinetics Experiment for o-Cresol at pH 3 and  $T = 21^\circ\text{C}$ . Along with HSDM Predictions.

OHK3MS

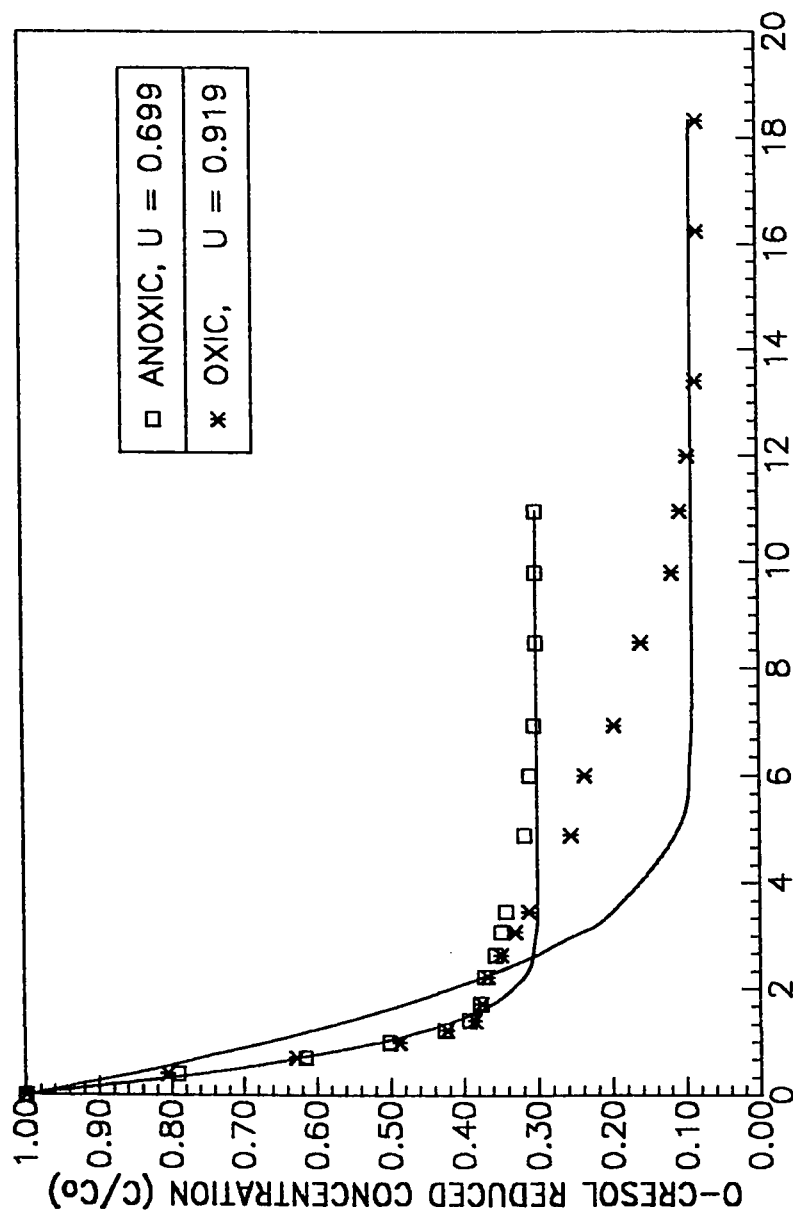


Figure 6.27: Closed Batch Kinetics Experiment for o-Cresol at pH 7 and  $T = 21^\circ\text{C}$ . Along with HSDM Predictions.

ohk7mss

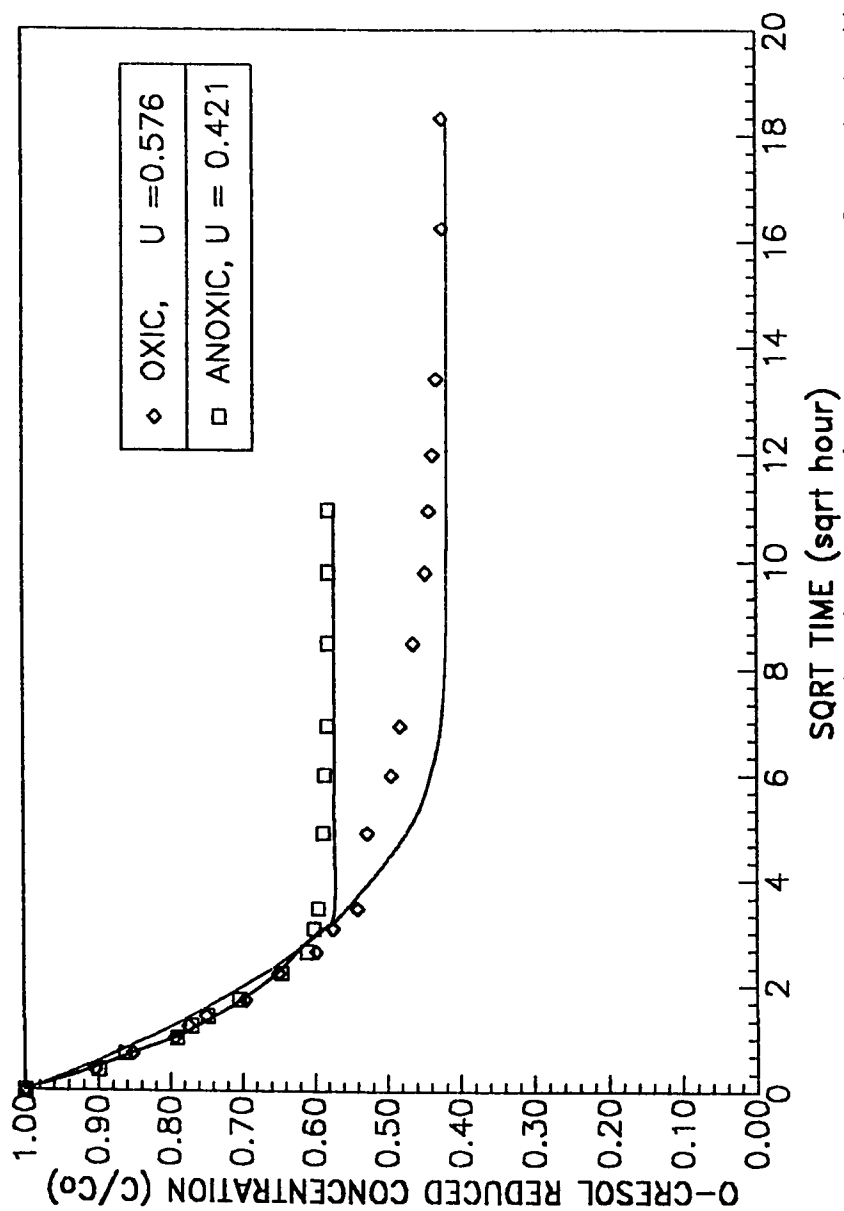


Figure 6.28: Closed Batch Kinetics Experiment for o-Cresol at pH 11 and  $T = 21^\circ \text{C}$ . Along with HSDM Predictions.

OHK11MS

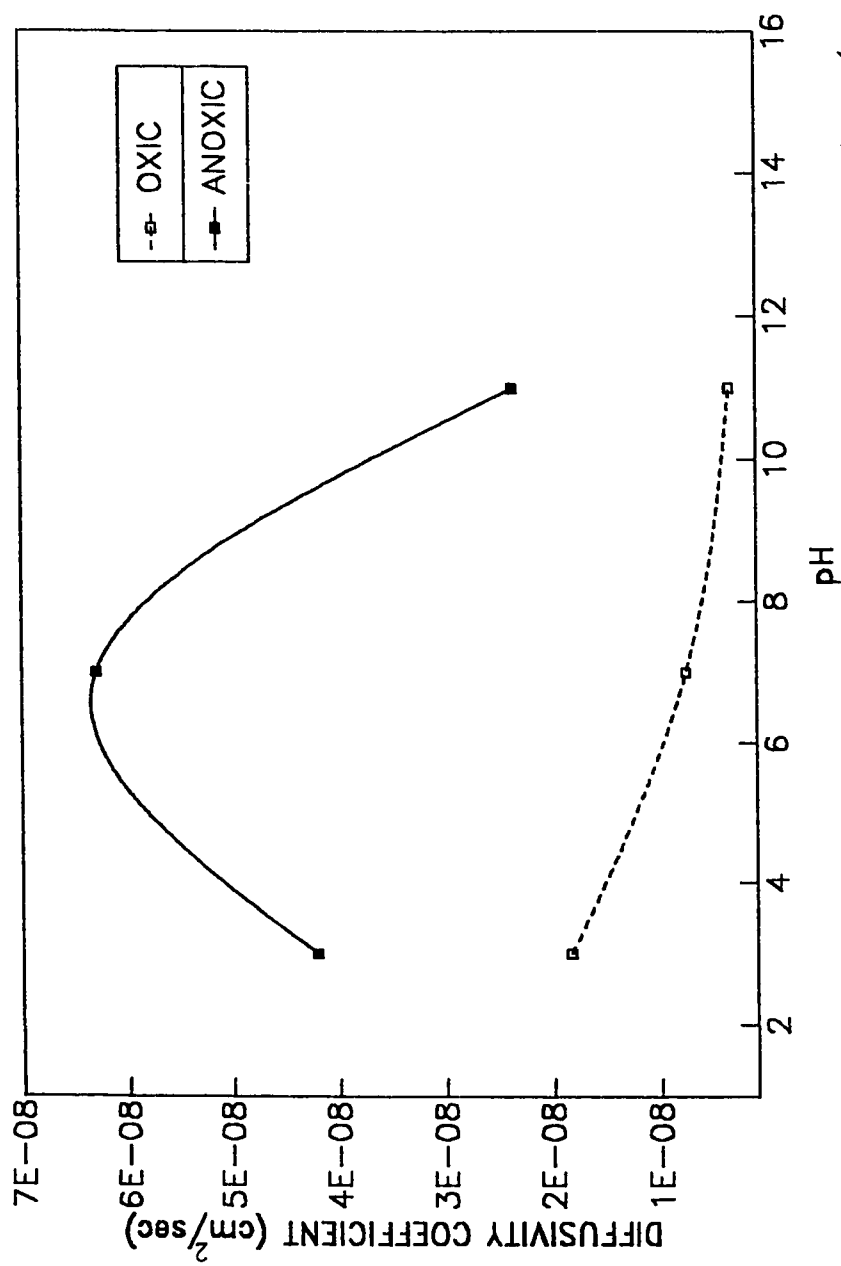


Figure 6.29: Relationship Between Phenol Apparent Diffusivities (HSDM) and pH at  $T = 21^{\circ}\text{C}$ .  
from PPHS

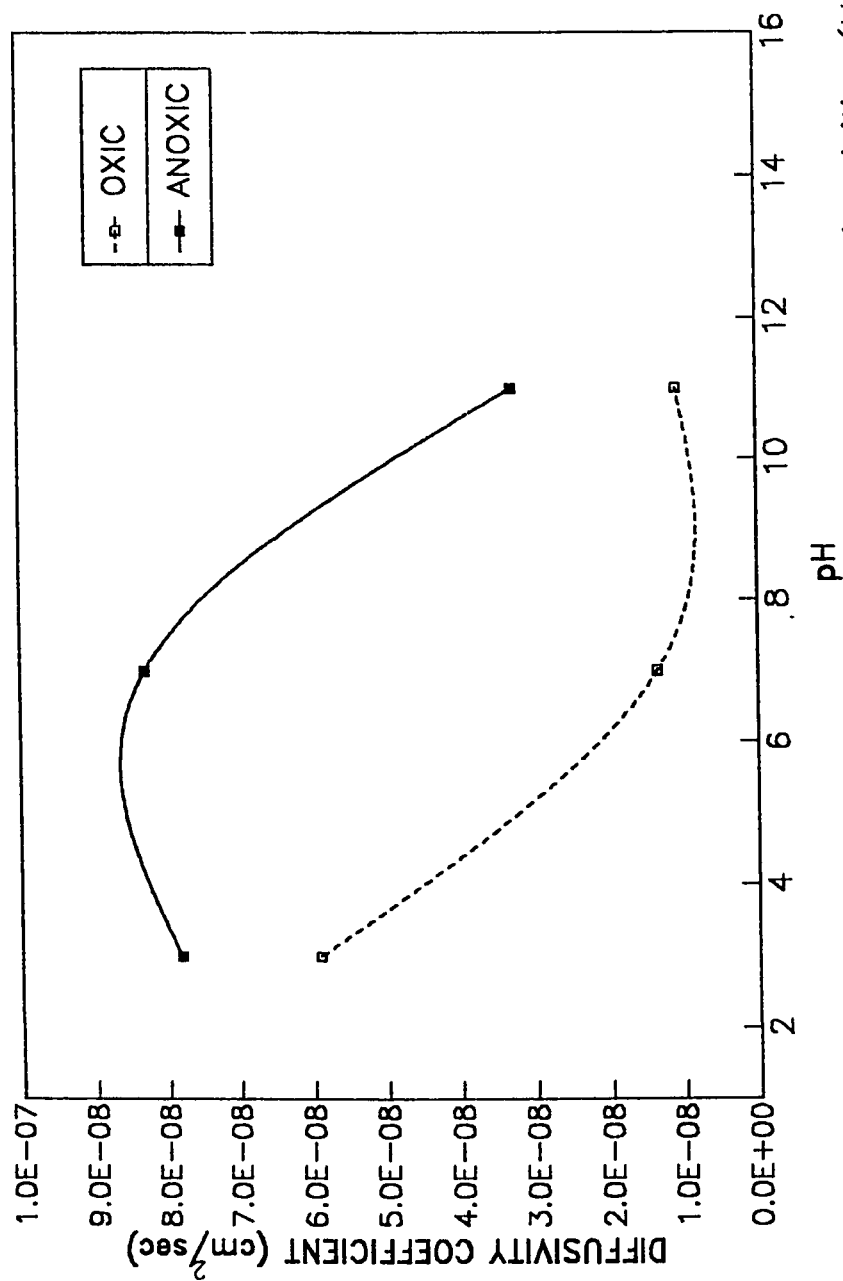


Figure 6.30: Relationship Between o-Cresol Apparent Diffusivities (HSDM) and pH at  $T = 21^{\circ}\text{C}$ .  
from OPHS

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.  $D_L$  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  $D_L$  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  $d_L$  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

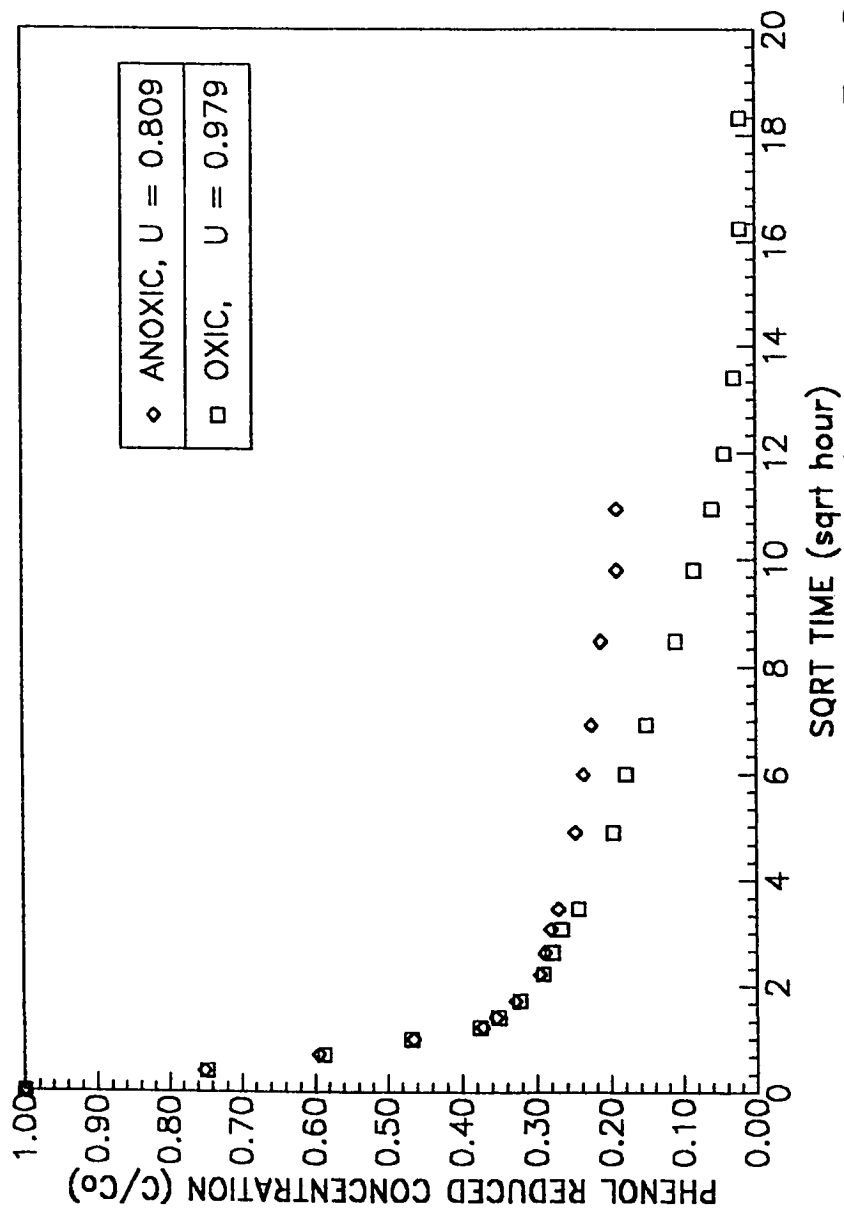


Figure 6.31: Closed Batch Kinetics Experiment for Phenol at  $T = 8^{\circ}\text{C}$ . and pH 7.

PHK8S

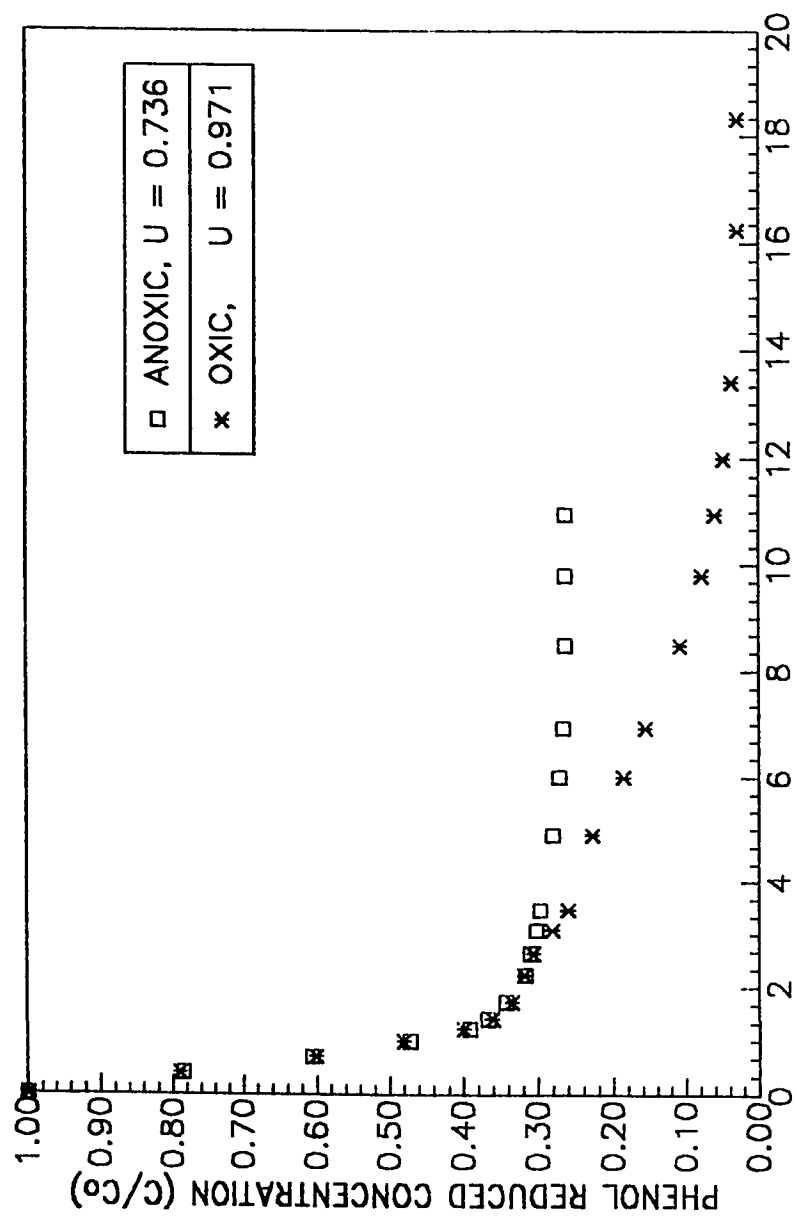


Figure 6.32: Closed Batch Kinetic Experiment for Phenol at  $T = 21^\circ \text{C}$ . and pH 7.

PHK21S

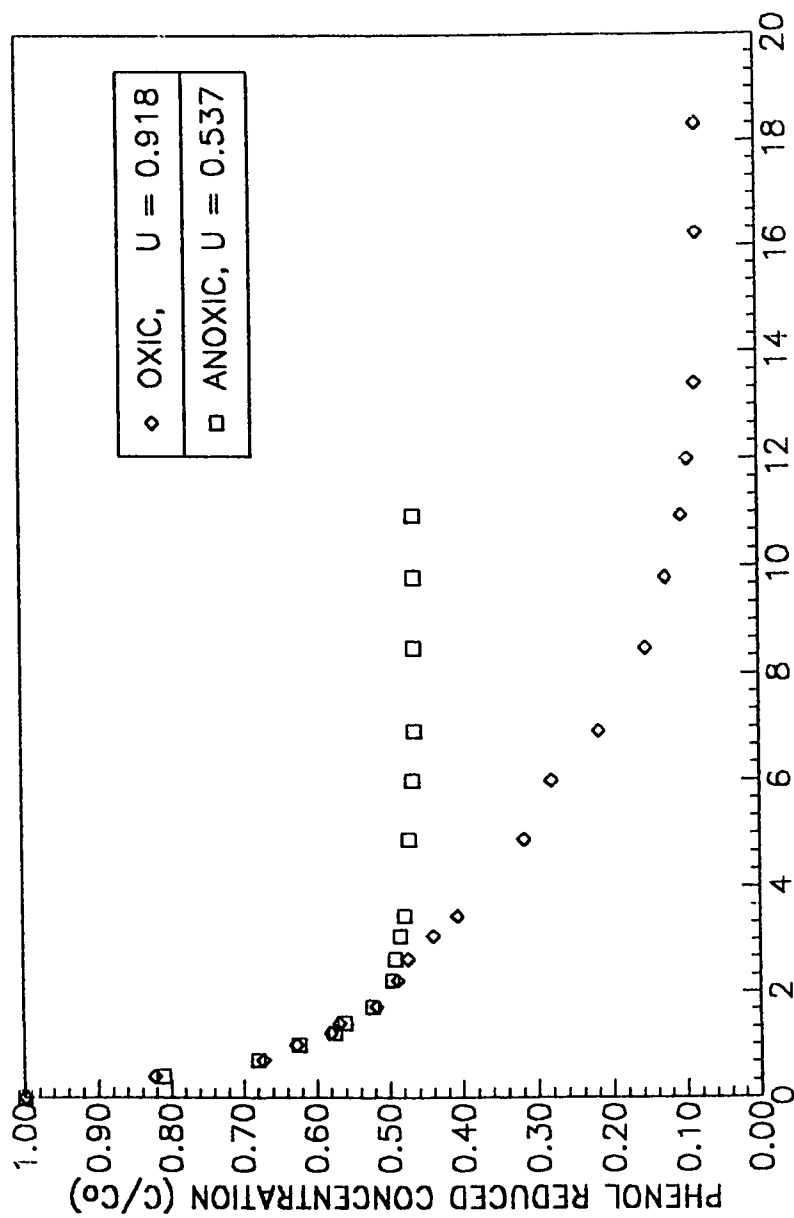


Figure 6.33: Closed Batch Kinetics Experiment for Phenol at  $T = 35^\circ \text{C}$ .  
and pH 7.  
from ohk35S

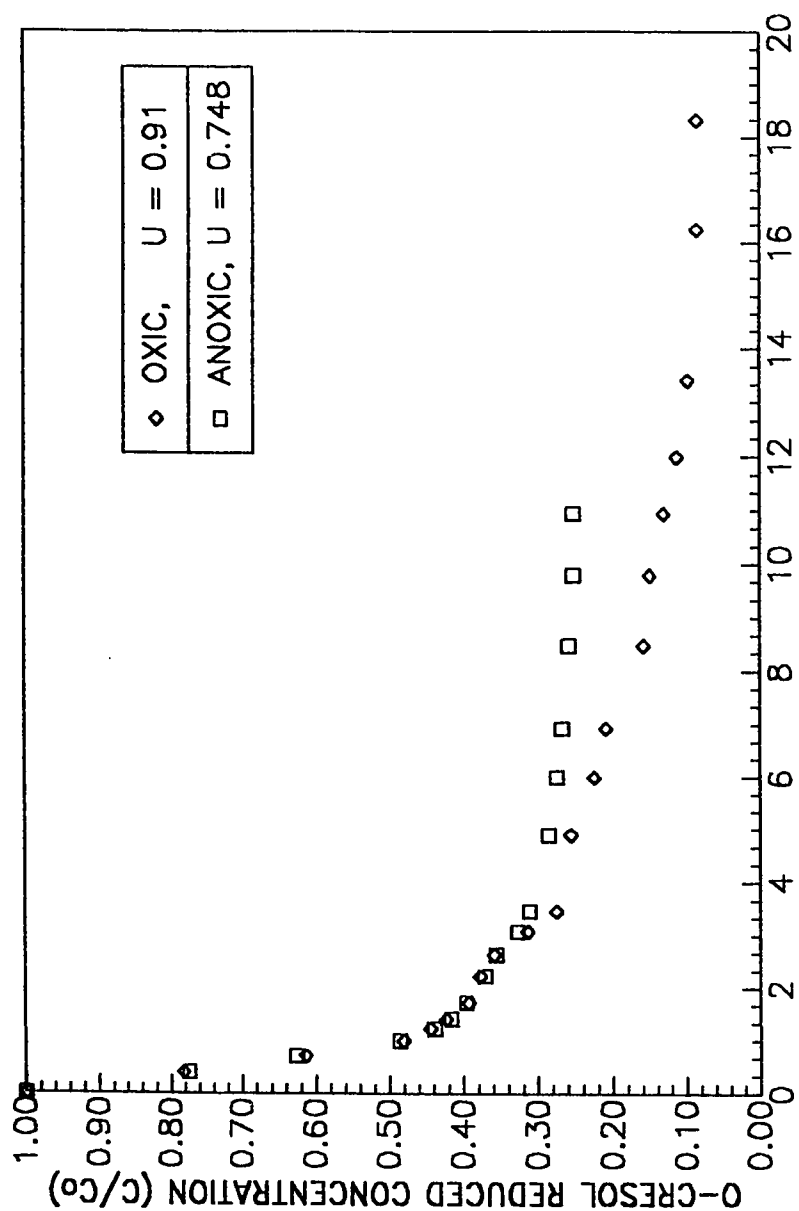


Figure 6.34: Closed Batch Kinetics Experiment for o-Cresol at  $T = 8^\circ \text{C}$ . and pH 7.

01K8S

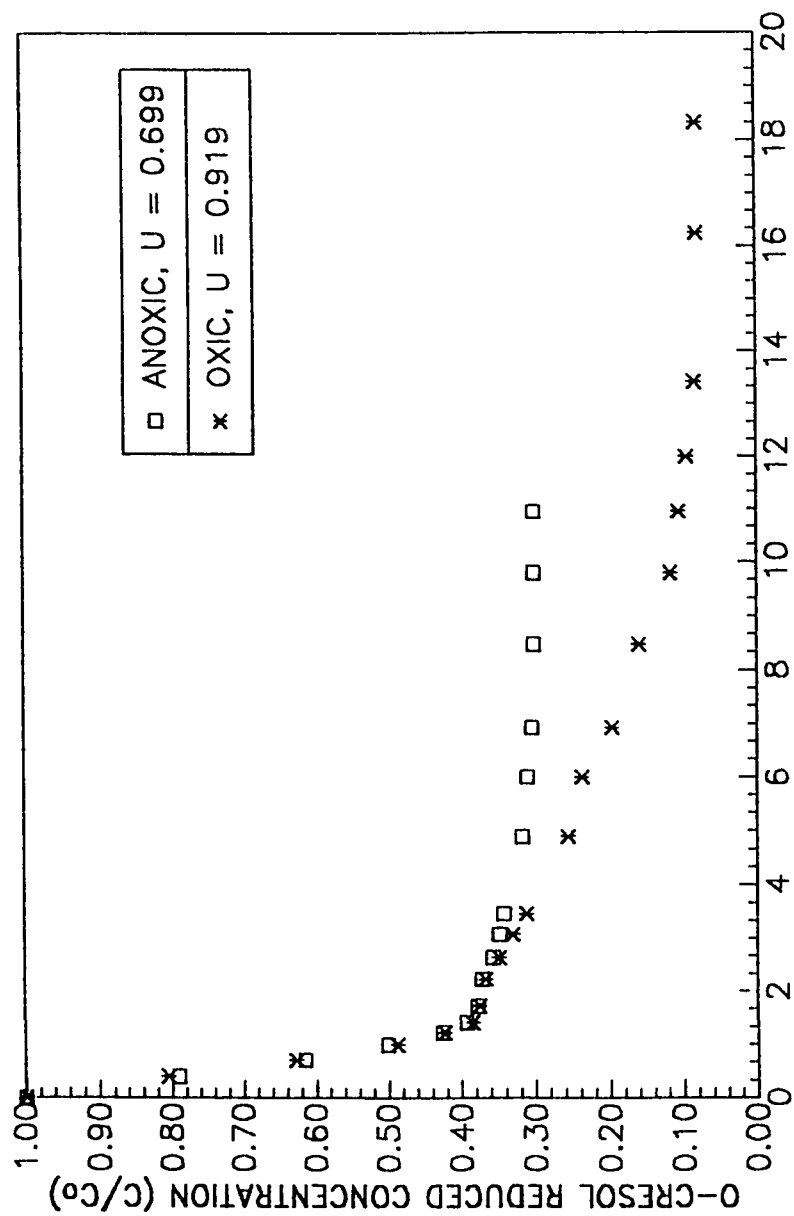


Figure 6.35: Closed Batch Kinetics Experiment for o-Cresol at  $T = 21^\circ \text{C}$ . and pH 7.

OHK215

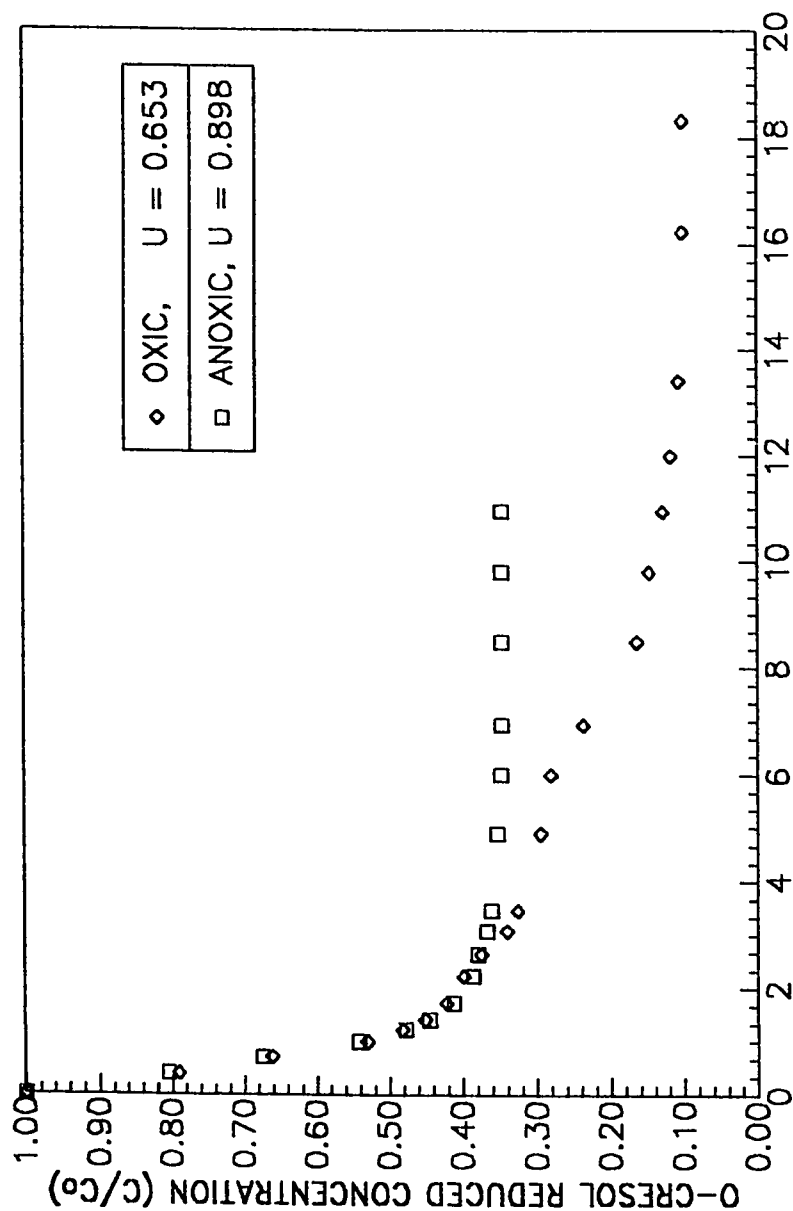


Figure 6.36: Closed Batch Kinetics Experiment for o-Cresol at  $T = 35^\circ\text{C}$ . and PH 7.

OTK35S

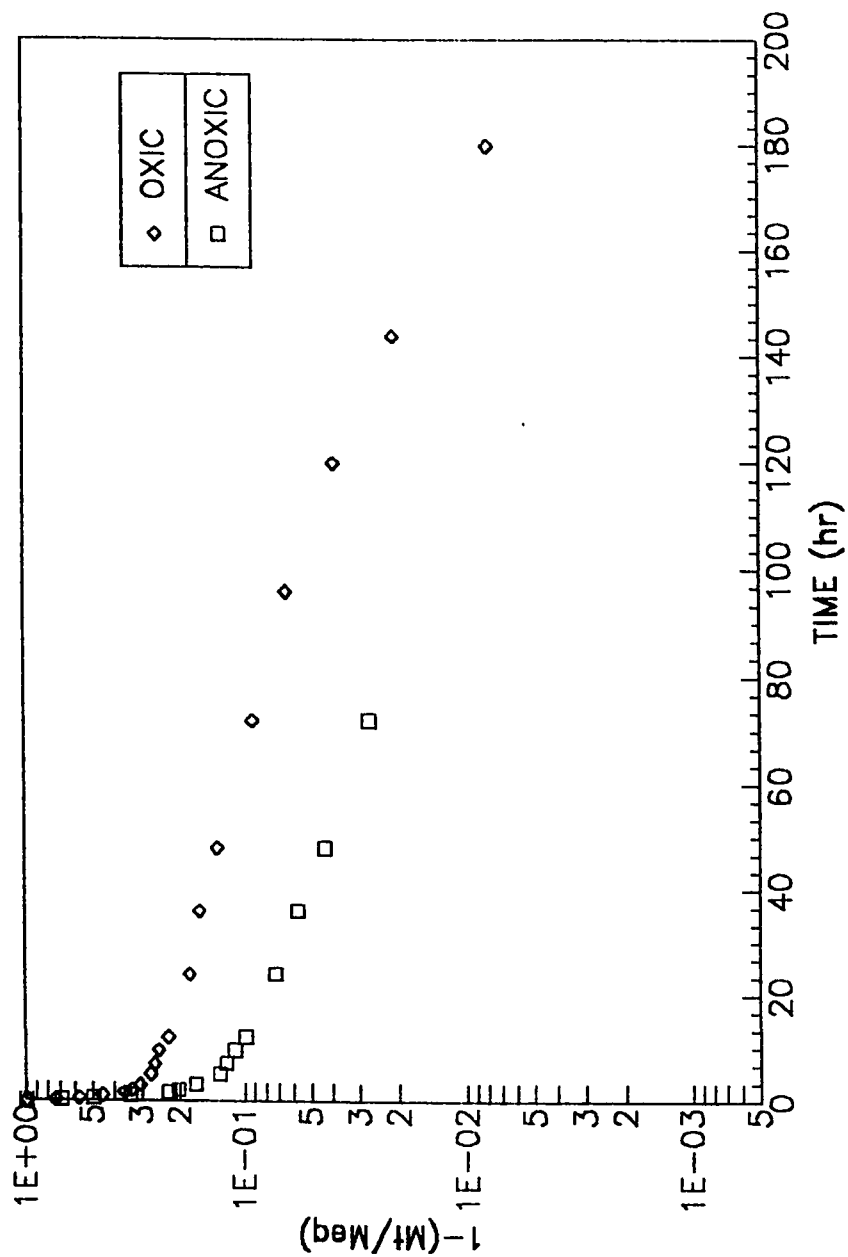


Figure 6.37: Linearized Rate of Phenol Uptake at  $T = 8^\circ \text{C}$ . and  $\text{pH}_{\text{from}} 7.0$

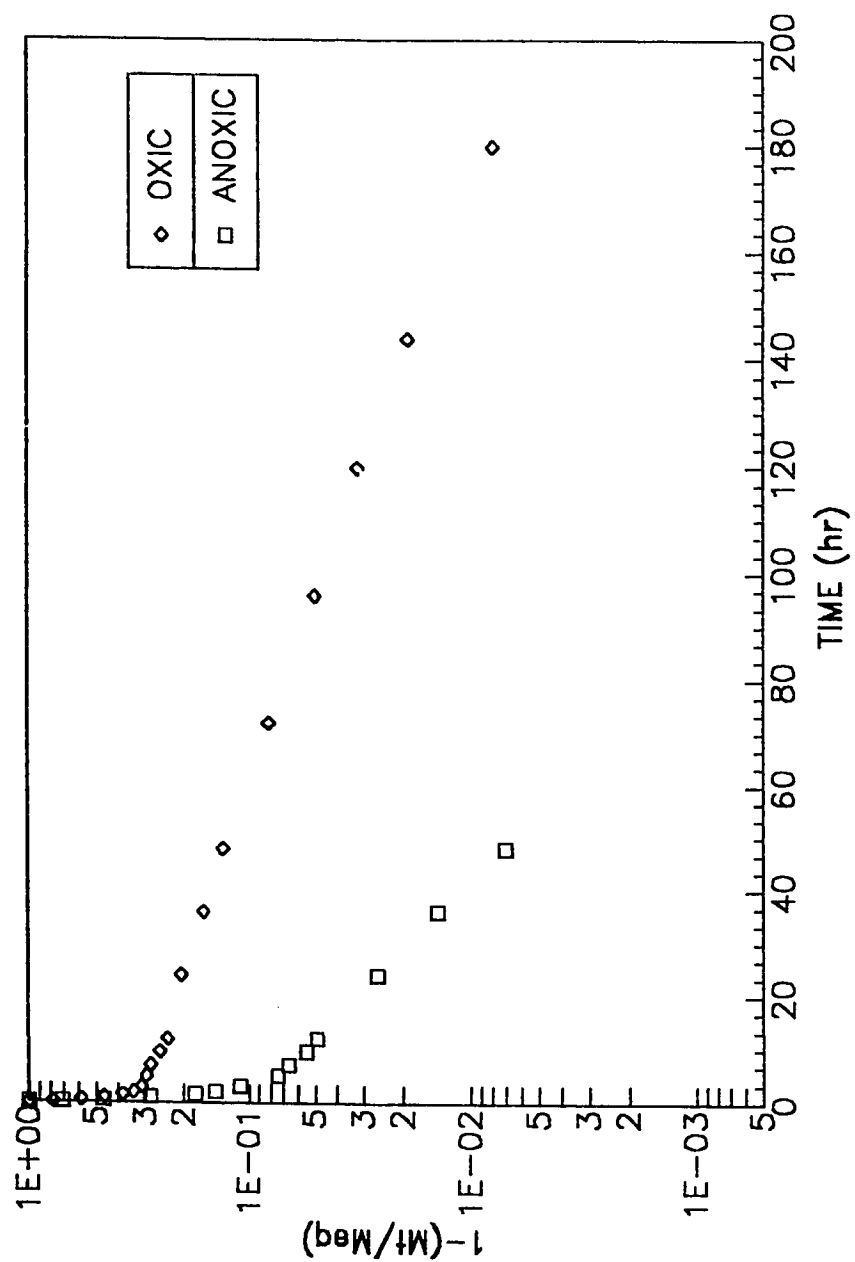


Figure 6.38: Linearized Rate of Phenol Uptake at  $T = 21^{\circ}\text{C}$ . and  $\text{pH}_{\text{from 7.0 to 12.1}}$

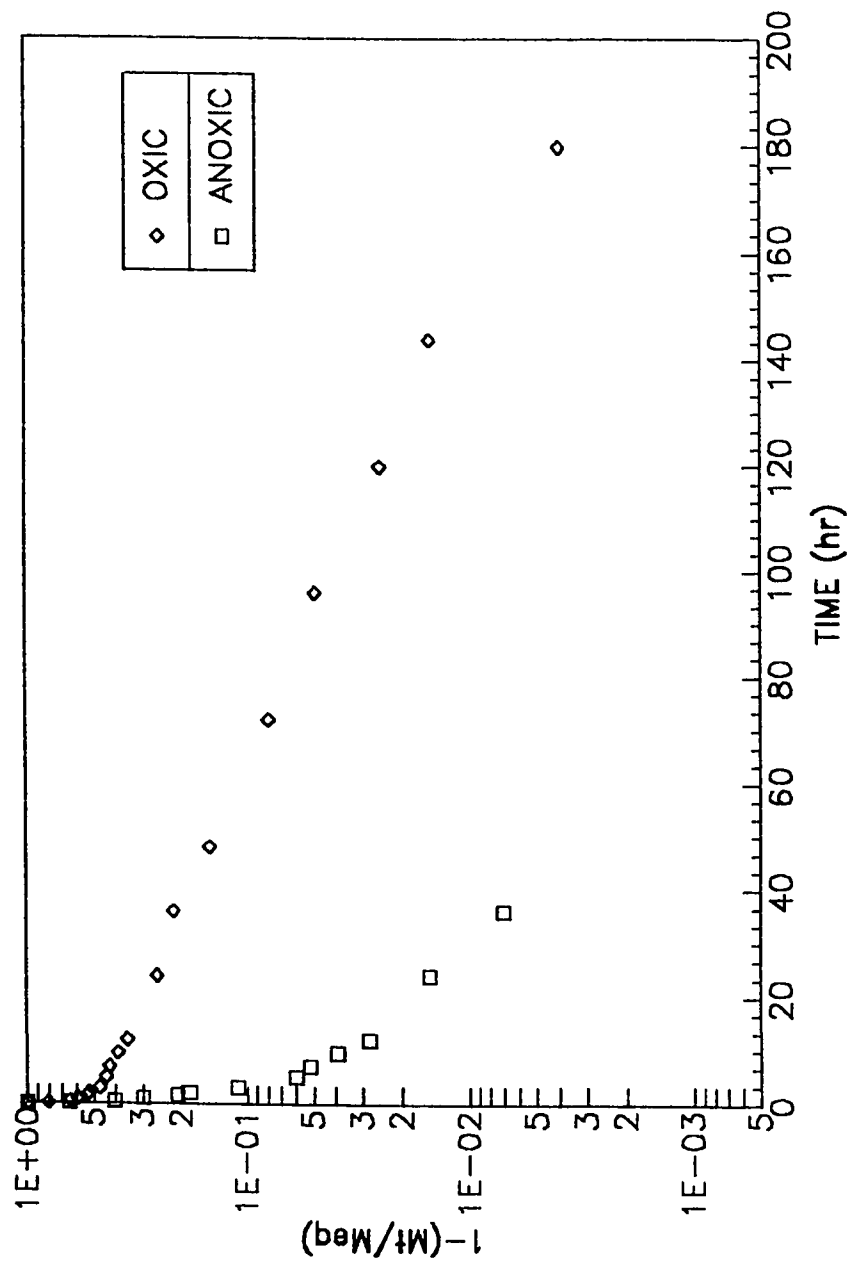


Figure 6.39: Linearized Rate of Phenol Uptake at  $T = 35^{\circ}\text{C}$ . and pH 7

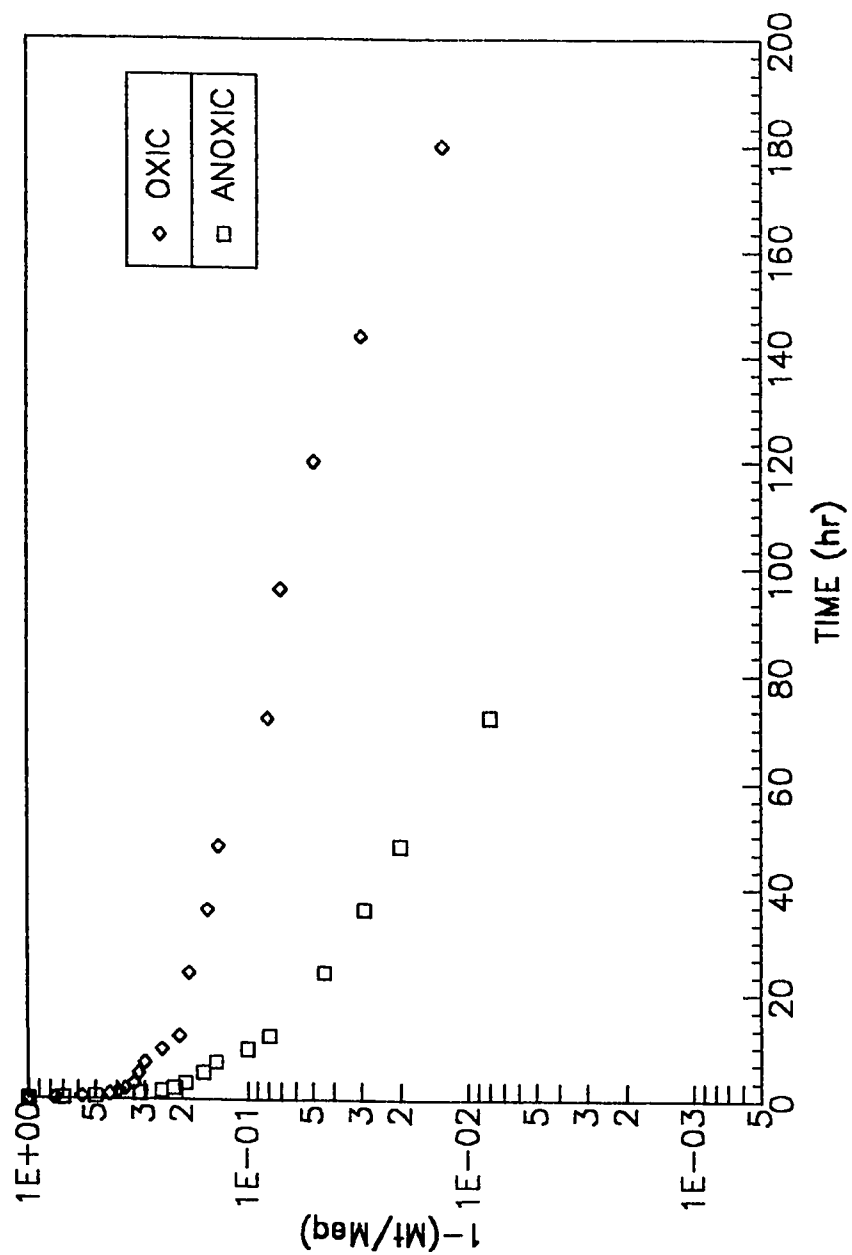


Figure 6.40: Linearized Rate of o-Cresol Uptake at T= 8°C. and pH 7<sub>from OT18</sub>

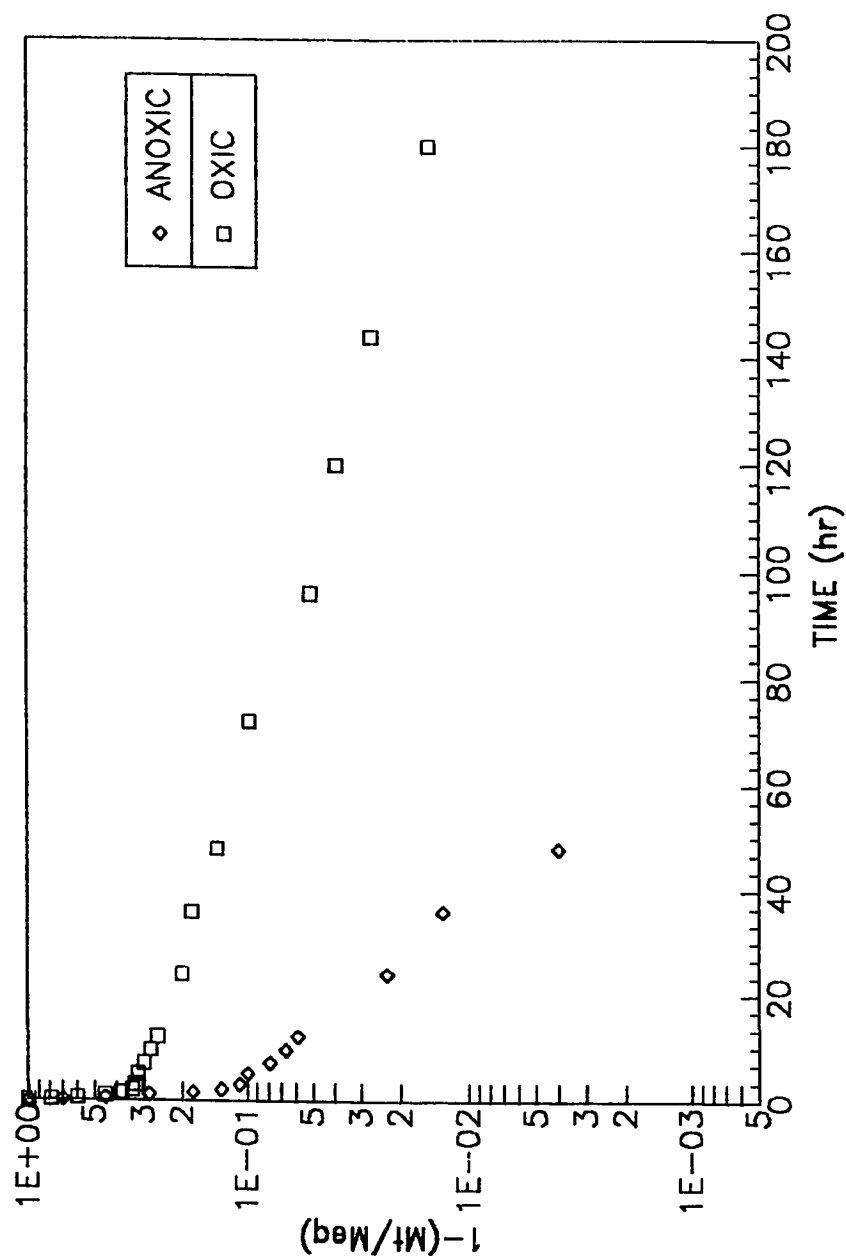


Figure 6.41: Linearized Rate of o-Cresol Uptake  $T = 21^{\circ}\text{C}$ . and pH 7. from OT121

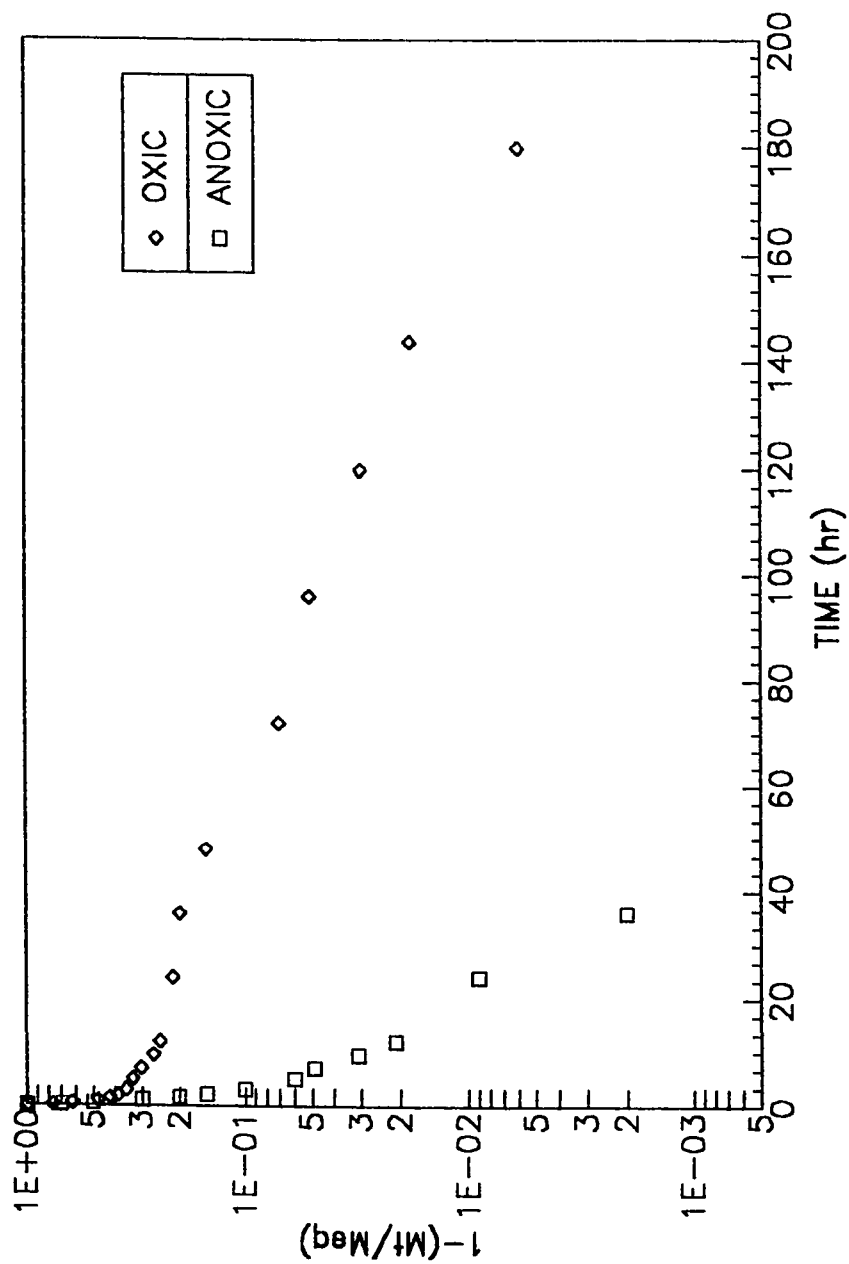


Figure 6.42: Linearized Rate of o-Cresol Uptake at  $T = 35^{\circ}\text{C}$ . and  $\text{pH}_{\text{from OT135}} 7$

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  $\chi^2$  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 <sup>2</sup> /sec	$\chi^2$	$\chi^2_{n,n-0.95}$
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

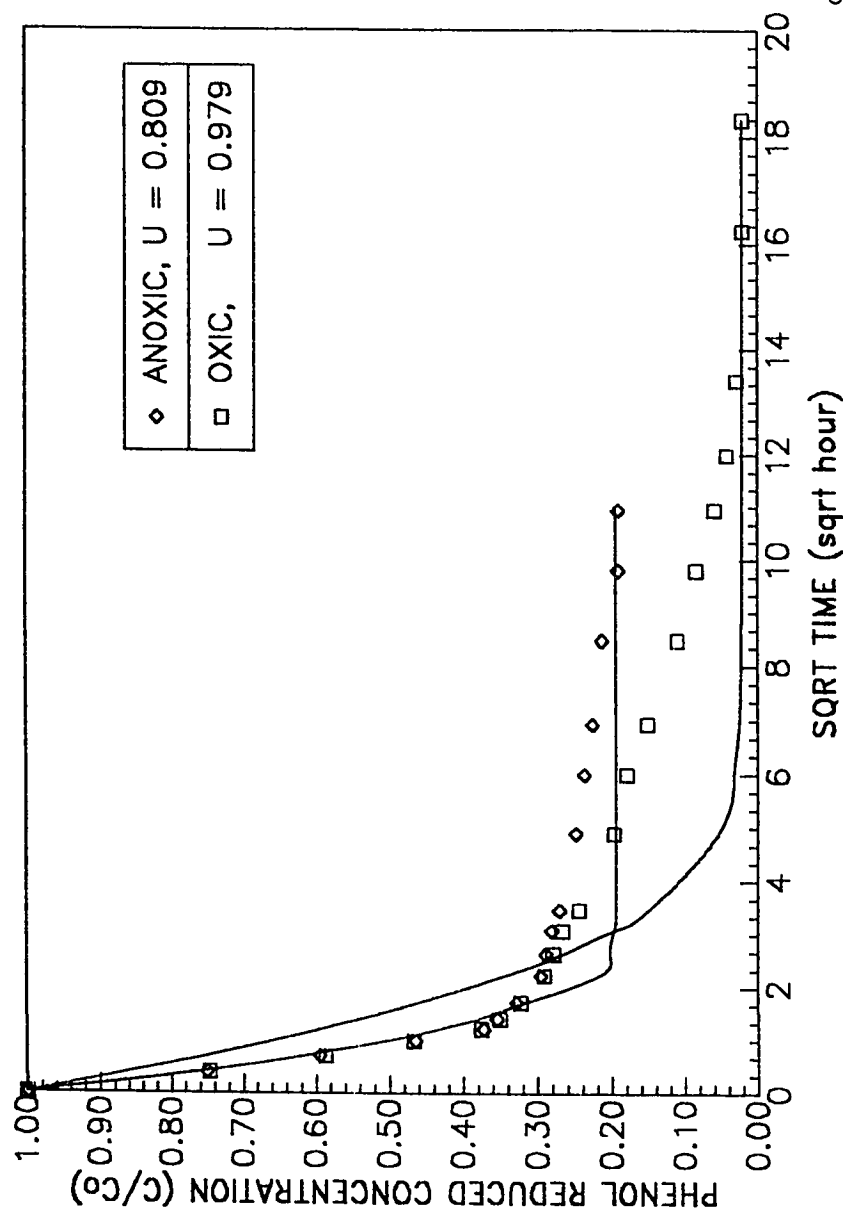


Figure 6.43: Closed Batch Kinetics Experiment for Phenol at  $T = 8^\circ \text{C}$ .  
and pH 7 Along with HSDM Predictions.

PHK8MS

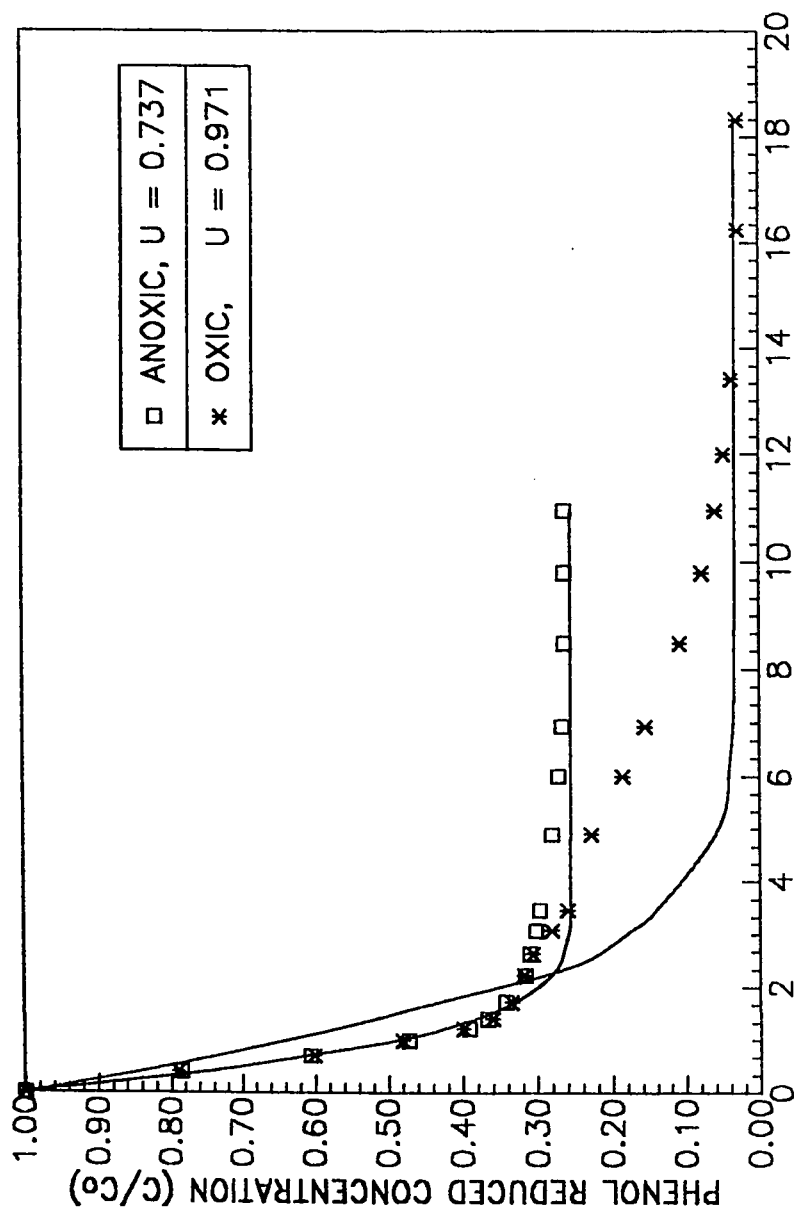


Figure 6.44: Closed Batch Kinetic Experiment for Phenol at  $T = 21^{\circ}\text{C}$ .  
and pH 7 Along with HSDM Predictions.

PHK21MS

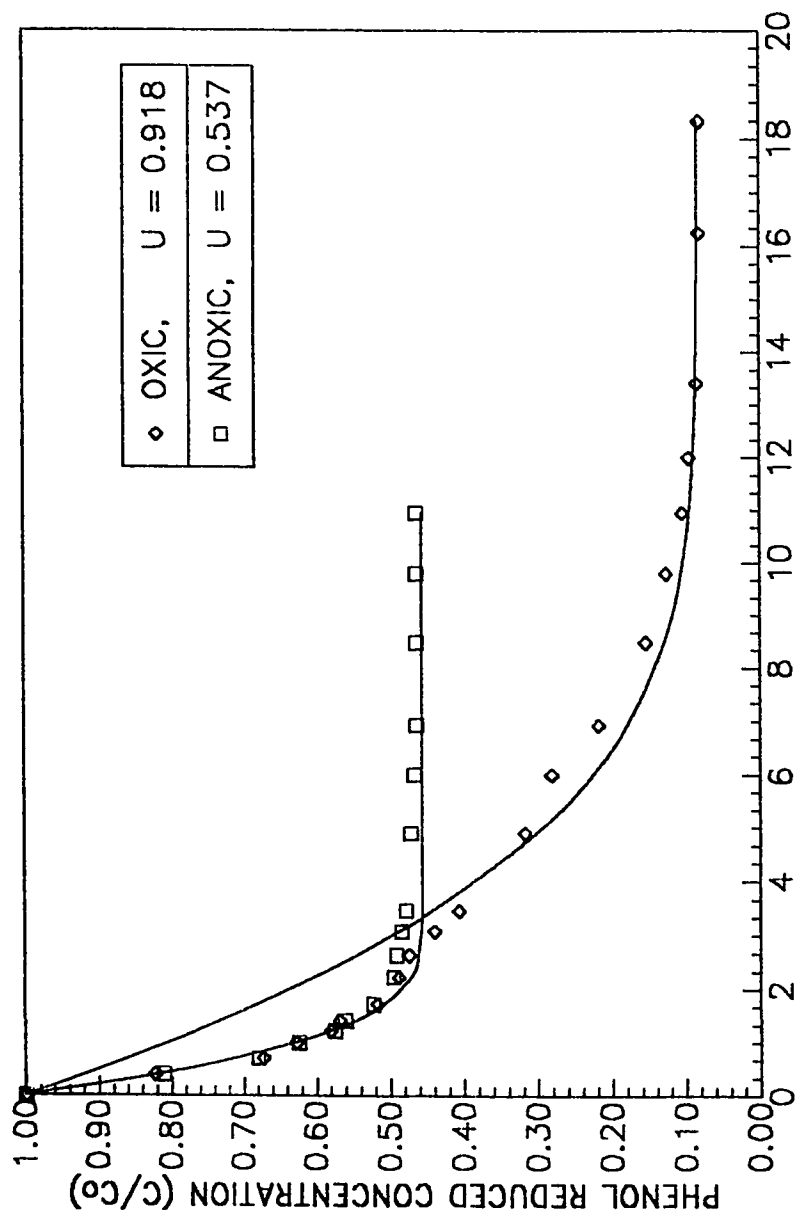


Figure 6.45: Closed Batch Kinetics Experiment for Phenol at  $T = 35^{\circ} \text{C}$ .  
and pH 7 Along with HSDM Prediction.  
from **phk35MS**

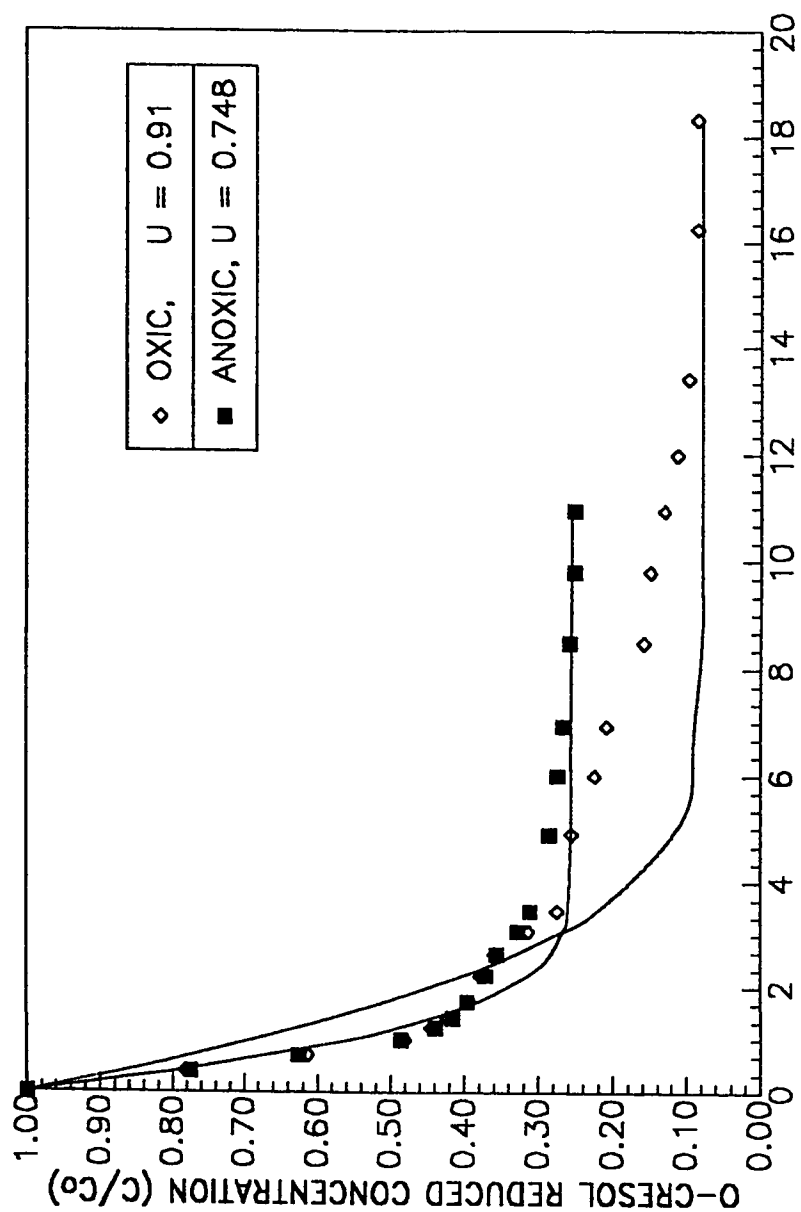


Figure 6.46: Closed Batch Kinetics Experiment for o-Cresol at  $T = 8^\circ \text{C}$ . and pH 7 Along with HSDM Predictions.

OTK3MS

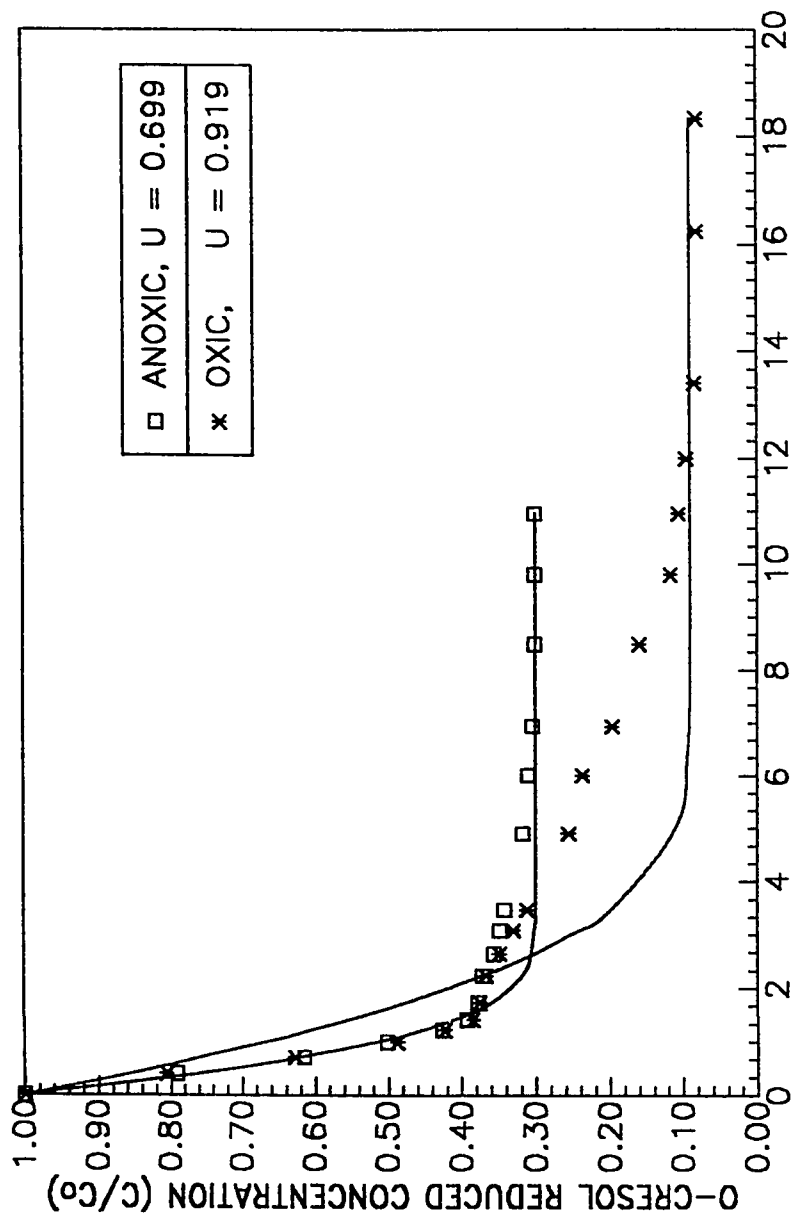


Figure 6.47: Closed Batch Kinetics Experiment for o-Cresol at  $T = 21^\circ \text{C}$ .  
and pH 7 Along with HSDM Predictions.

atk21ms

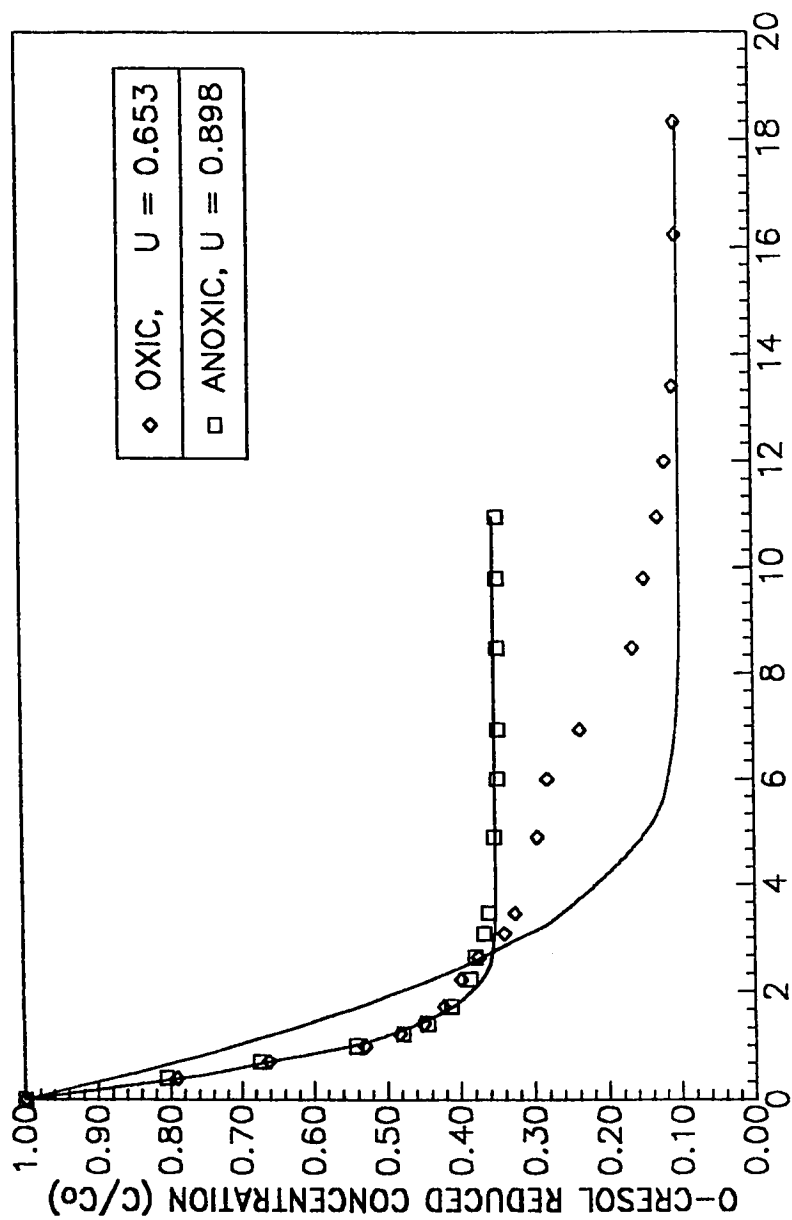


Figure 6.48: Closed Batch Kinetics Experiment for o-Cresol at  $T = 35^{\circ}\text{C}$ .  
and pH 7 Along with HSDM Predictions.

OTK35MS

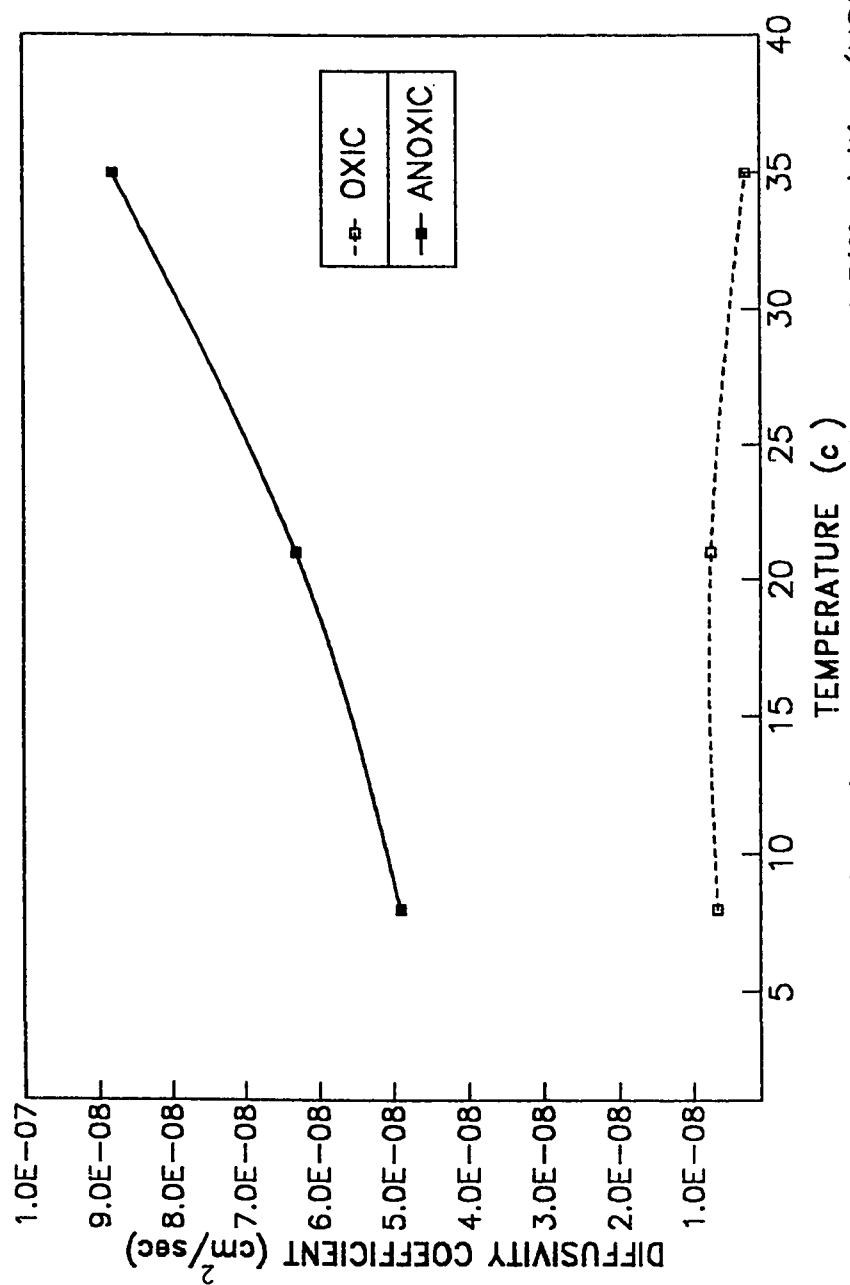


Figure 6.49: Relationship Between Phenol Apparent Diffusivities (HSDM) and Temperature at pH 7.  
from PTHS

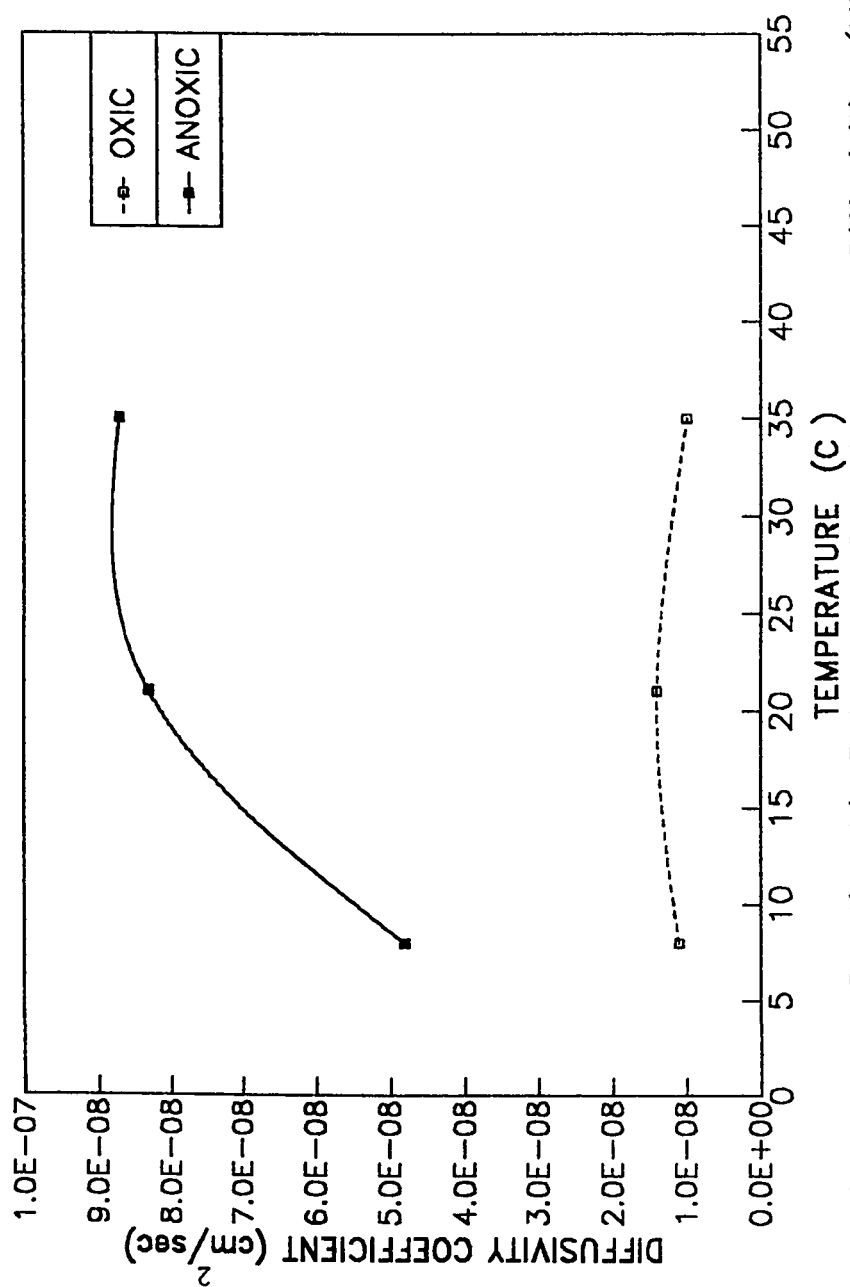


Figure 6.50: Relationship Between o-Cresol Apparent Diffusivities (HSDM) and Temperature at pH 7.  
from OTHS

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:

$$D_s = D_{s0} \exp \frac{-E_a}{R_g T} \quad (6.3)$$

which can linearized as;

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

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.

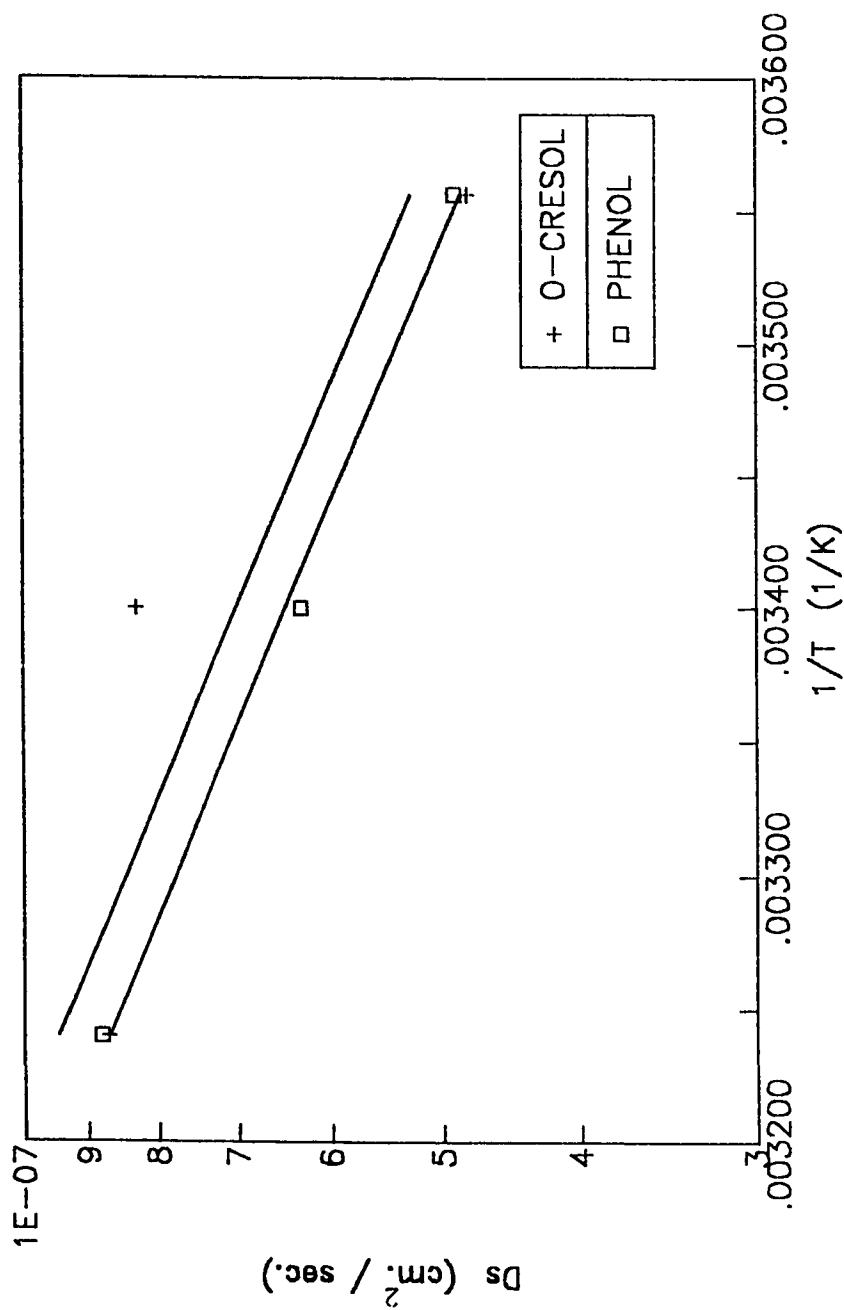


Figure 6.51: Relationship Between Diffusivities and Temperature for Phenol and o-Cresol Along with Lines of Best Fit.

FROM ADIV

### 6.3 Model Formulation

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

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

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.

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

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

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

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:

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

with the same initial and boundary conditions of Equation 6.5

where;

$k_r$  = reaction constant, 1/T, and,

$q_\infty$  = 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:

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

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

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

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

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

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

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

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

where,  $\varphi^2$  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:

$$\text{at } \tau = 0, 0 \leq R \leq 1: Q = 0 \quad (6.11)$$

and the boundary conditions are:

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

$$@ \tau \geq 0, R = 1: \frac{\partial Q}{\partial \tau} = -3 \frac{\partial Q}{\partial R} \quad (6.13)$$

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

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

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

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. In spite 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 ;

$$\frac{2 k_f r}{D_1} = 2 + 1.1 R^{0.6} S^{0.333} \quad (7.1)$$

where,  $k_f$  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:

$$S = \frac{\mu}{\rho_1 D_1} \quad (7.2)$$

$$R = \frac{2 \rho_1 r v}{\mu} \quad (7.3)$$

where,  $\mu$  is viscosity of water = 0.00098 kg.s/m,  $\rho_1$  is density of water = 997.8 kg/m<sup>3</sup>,  $r$

is mean radius of adsorbent particle = 0.00078 m,  $v$  is the superficial velocity = 3.285E-3 m/sec, and  $D_f$  is the diffusivity of the adsorbate in water calculated using the Wilke-Chang equation (65) to be 8.792E-10 m<sup>2</sup>/sec and 7.808E-10 m<sup>2</sup>/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

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

(Reynolds number range of applicability, 0.08-125)

Here,

$$R = \frac{\rho_l r v}{\epsilon \mu} \quad (7.5)$$

where,  $\epsilon$  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) $\text{cm}^2/\text{sec}$	k (Corr. 2) $\text{cm}^2/\text{sec}$
o-cresol	1.72E-03	3.60E-3
phenol	1.86E-03	3.88E-3

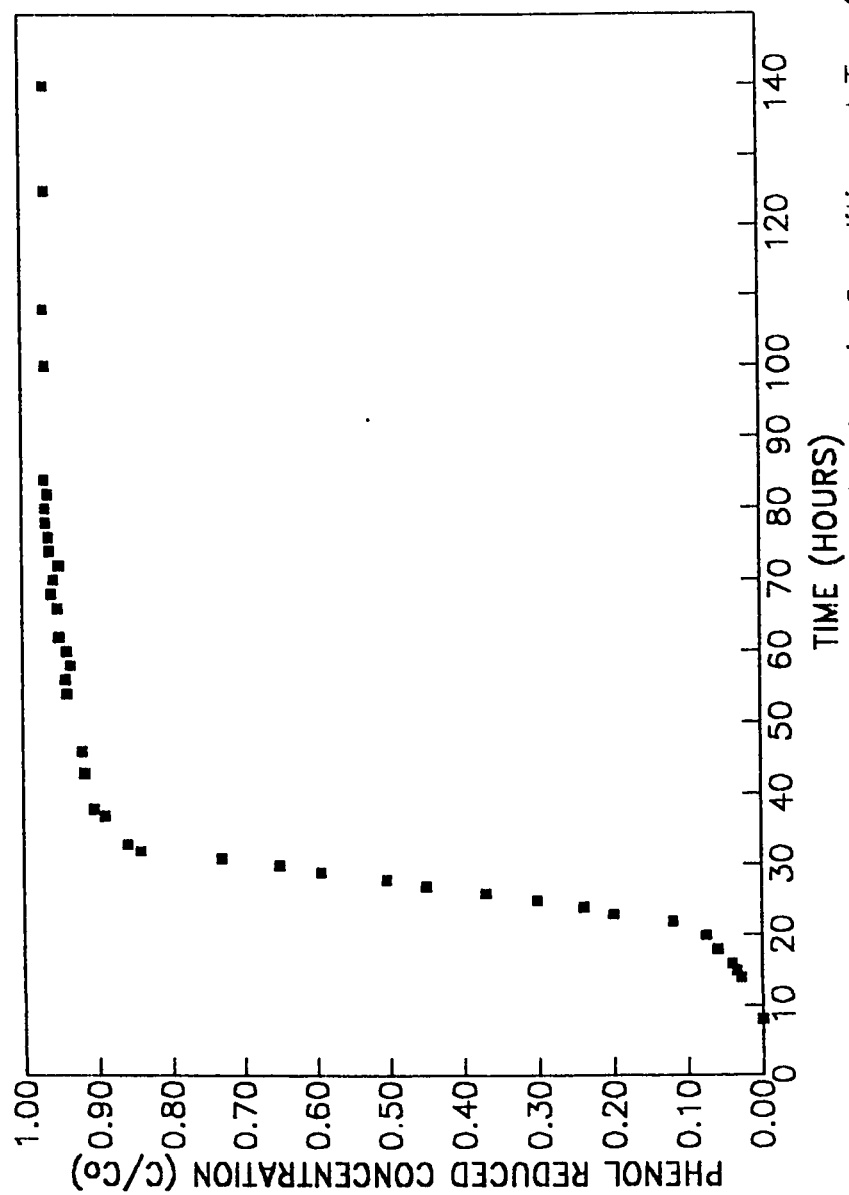


Figure 7.1: Breakthrough of Phenol Under Anoxic Condition at  $T = 21^{\circ} \text{C}$ .  
and pH 7.

PCOLA6

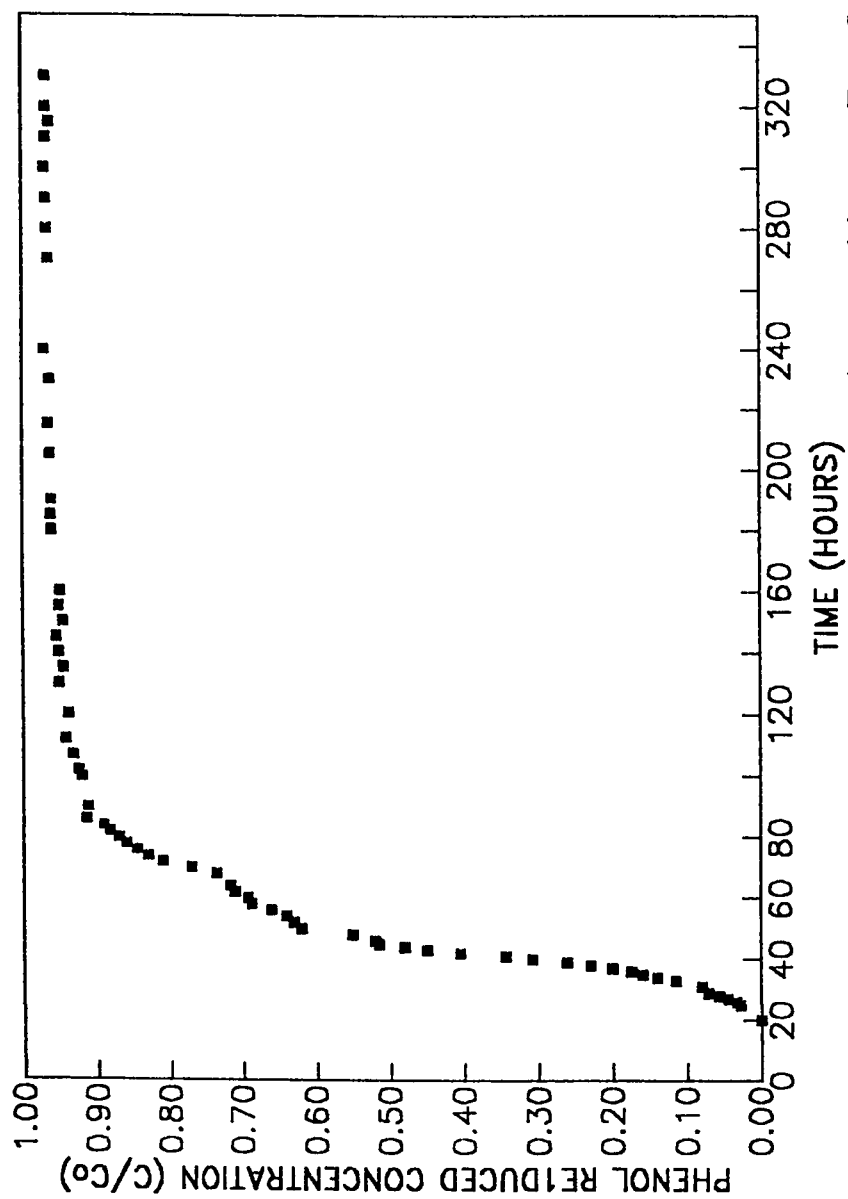


Figure 7.2: Breakthrough of Phenol Under Oxic Condition at  $T = 21^{\circ} \text{C}$ .  
and pH 7.

PCOL06

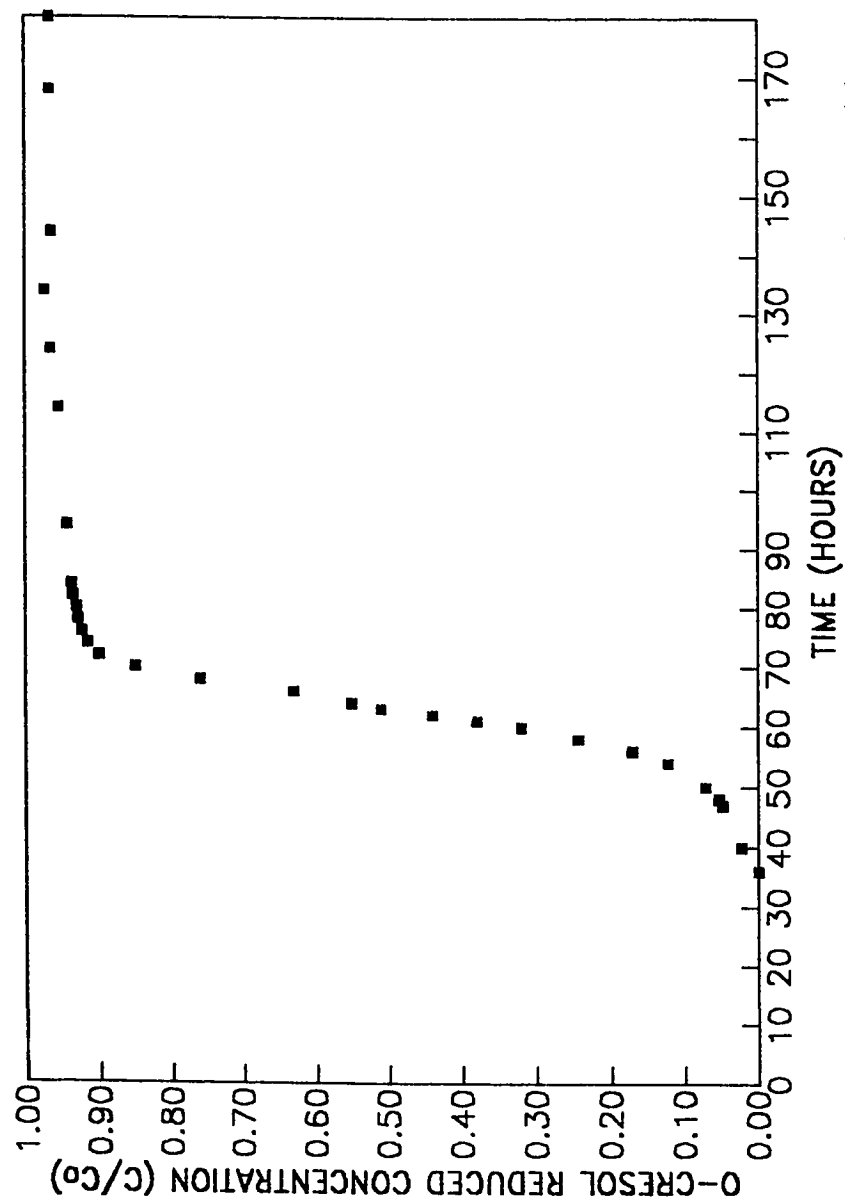


Figure 7.3: Breakthrough of o-Cresol Under Anoxic Condition at  $T = 21^{\circ}\text{C}$ . and pH 7.

OCOLA6

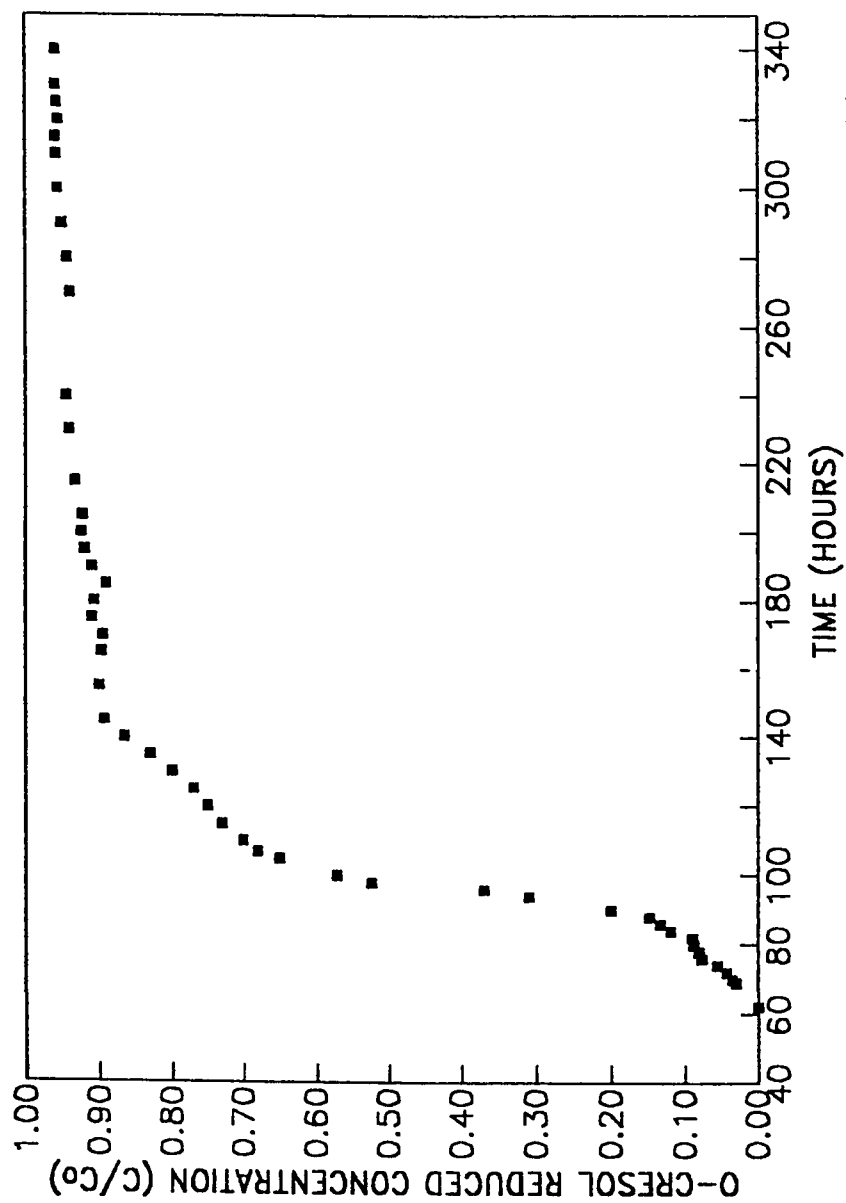


Figure 7.4: Breakthrough of o-Cresol Under Oxic Condition at  $T = 21^{\circ}\text{C}$ . and pH 7.

OC0106

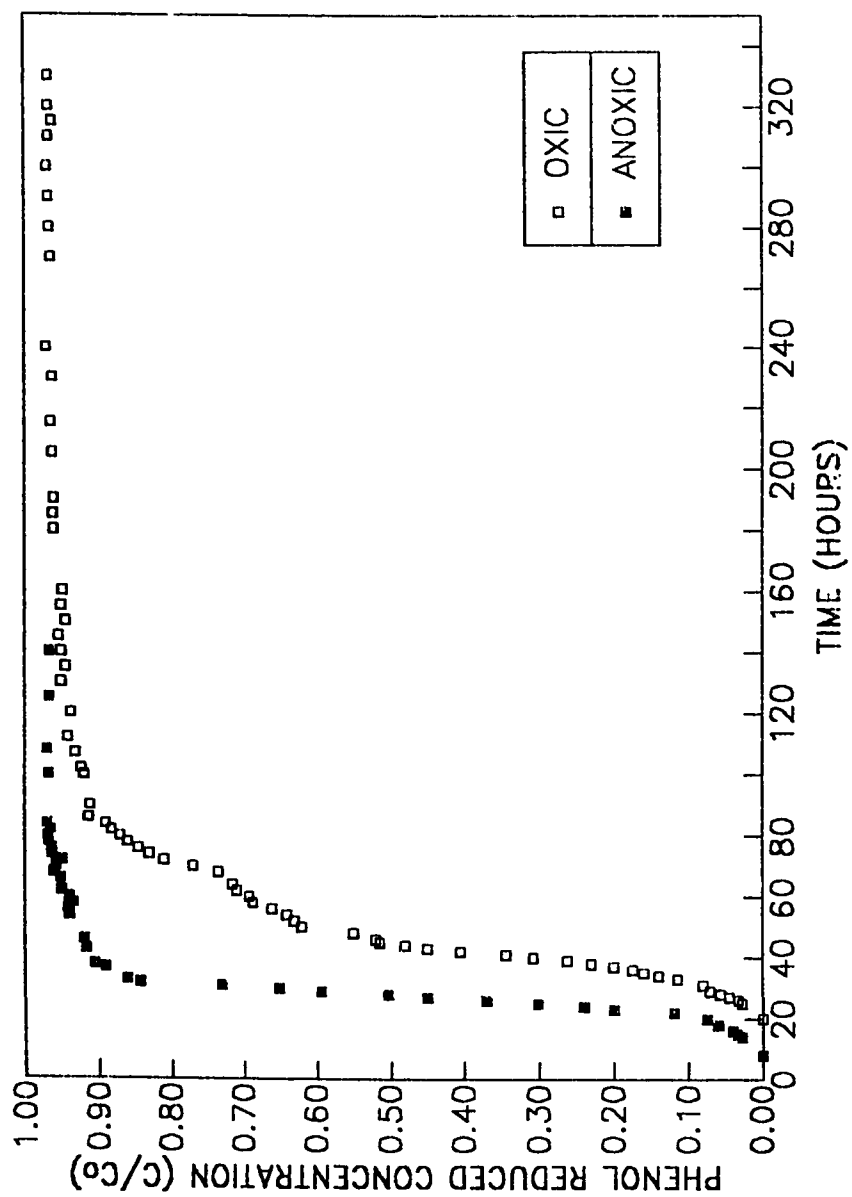


Figure 7.5: Breakthrough Curves for Phenol at  $T = 21^{\circ}\text{C}$  and  $\text{pH } 7.5$

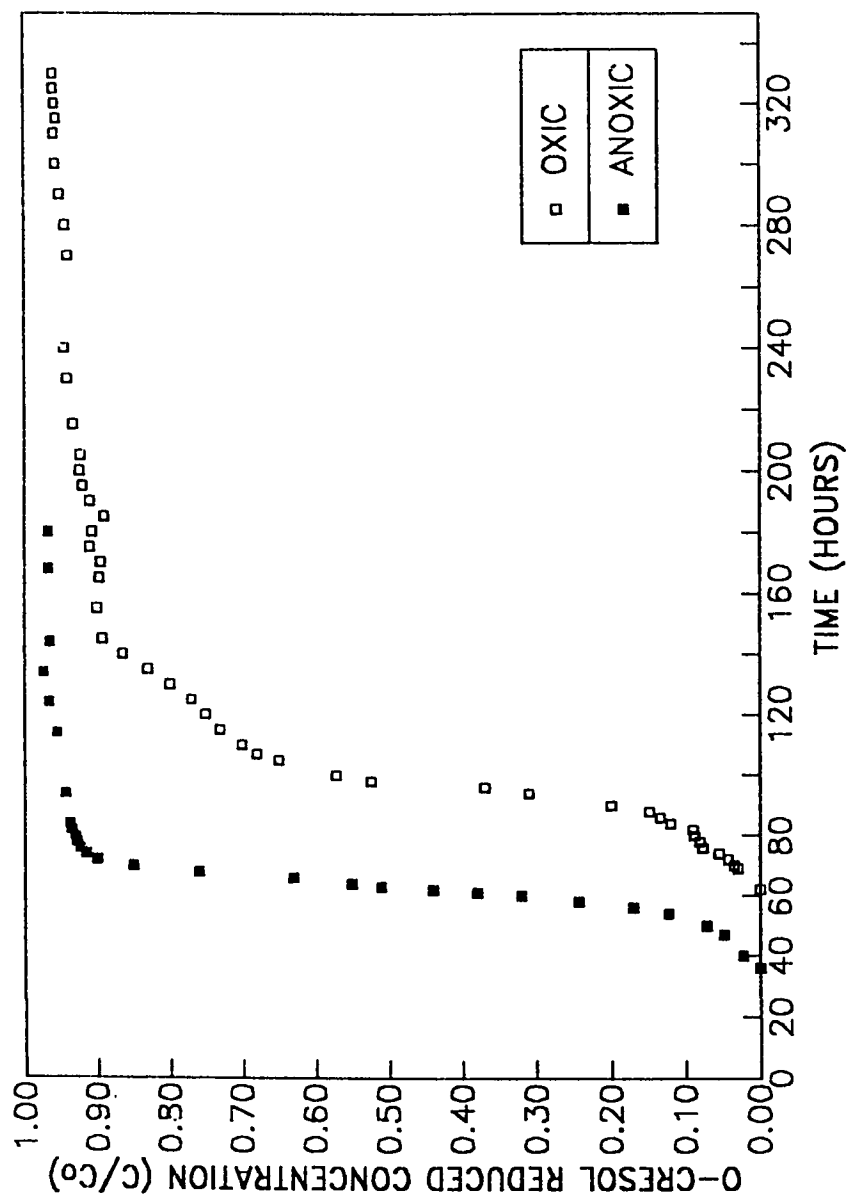


Figure 7.6: Breakthrough Curves for o-Cresol at  $T = 21^{\circ} \text{C}$ . and  $\text{pH}_{0.01}$

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 oxie to anoxic capacities at exhaustion and comparing them to the oxie 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. Oxie 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 Oxidic and Anoxic Conditions.

Compound	Operational Conditions	Iso. Cap. mg/g	Col. Cap. mg/g
o-cresol	oxidic	330.77	295.5
	anoxic	196.60	193.70
phenol	oxidic	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 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

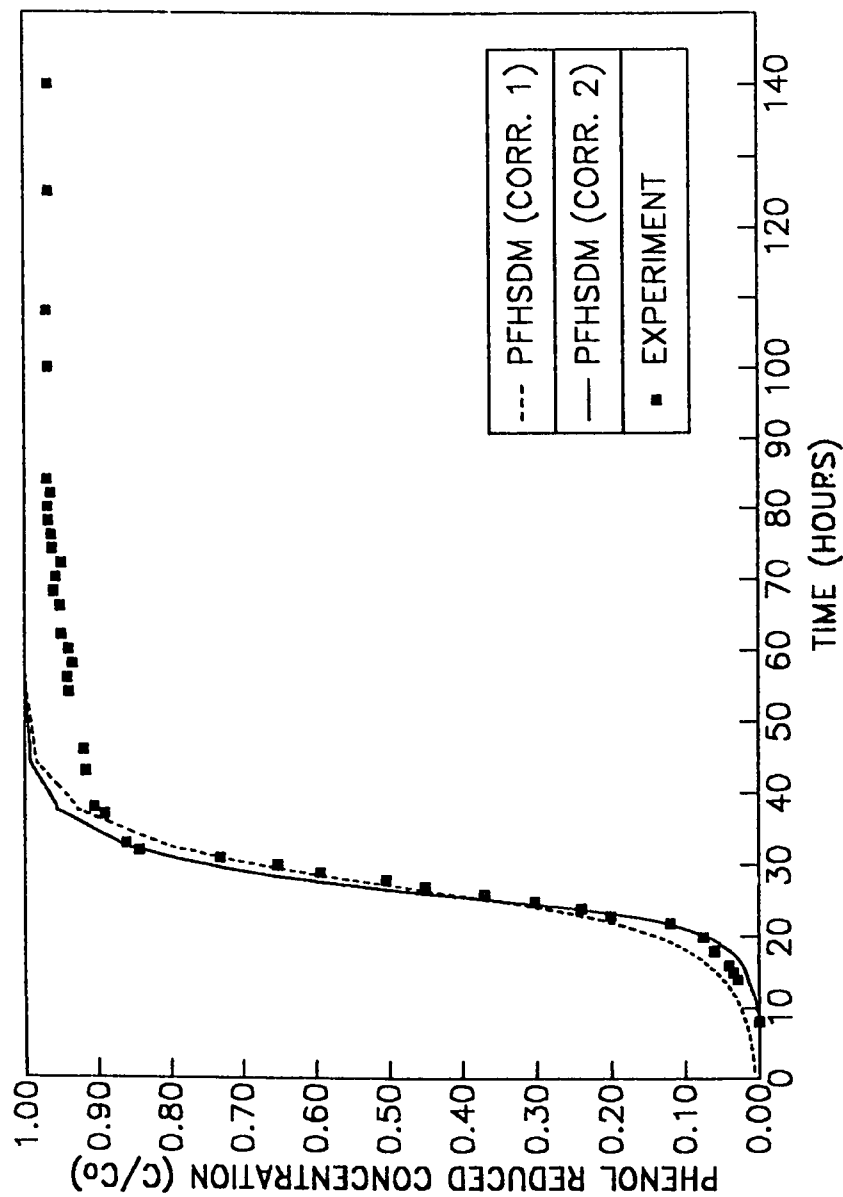


Figure 7.7: Breakthrough of Phenol Under Anoxic Condition at  $T = 21^{\circ}\text{C}$  and pH 7 Along with PFHSDM Predictions.

PCOLAM

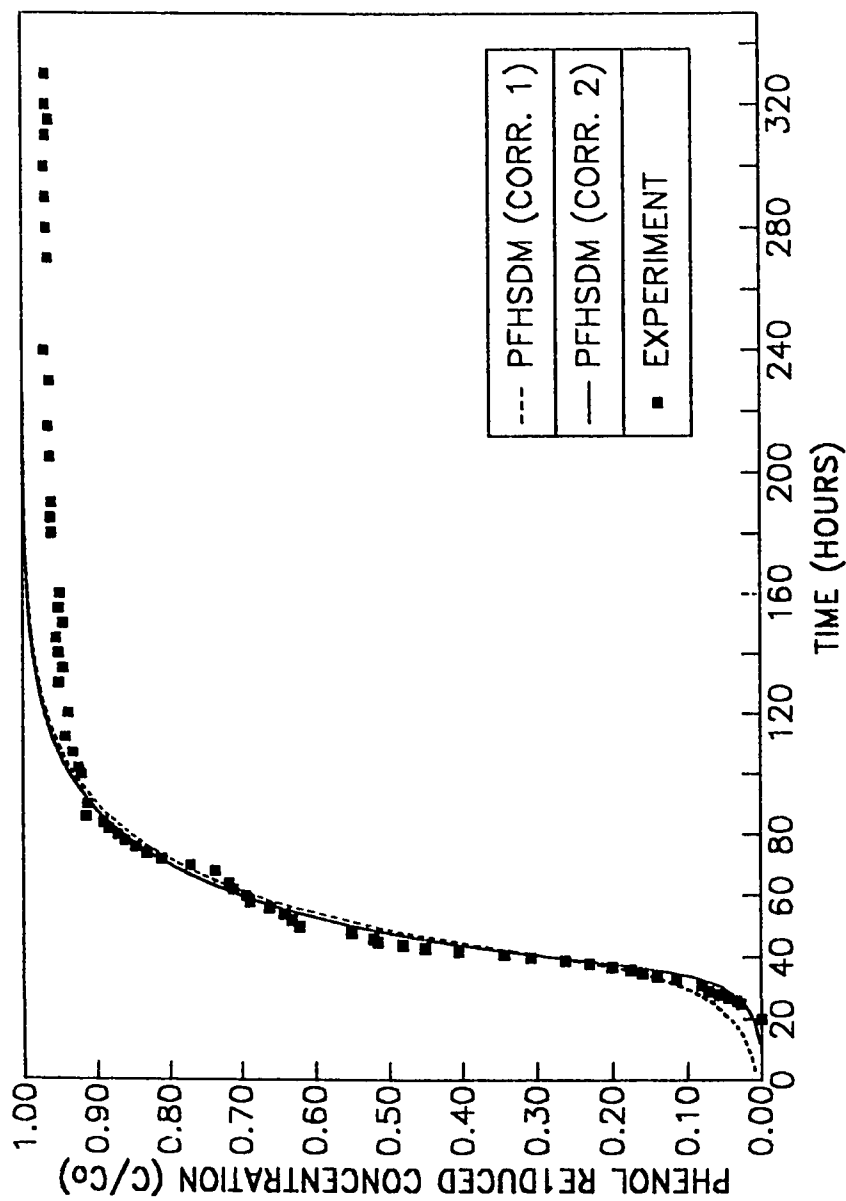


Figure 7.8: Breakthrough of Phenol Under Oxidic Condition at  $T = 21^{\circ}\text{C}$ .  
and pH 7 Along with PFHSDM Predictions.

PCOLM

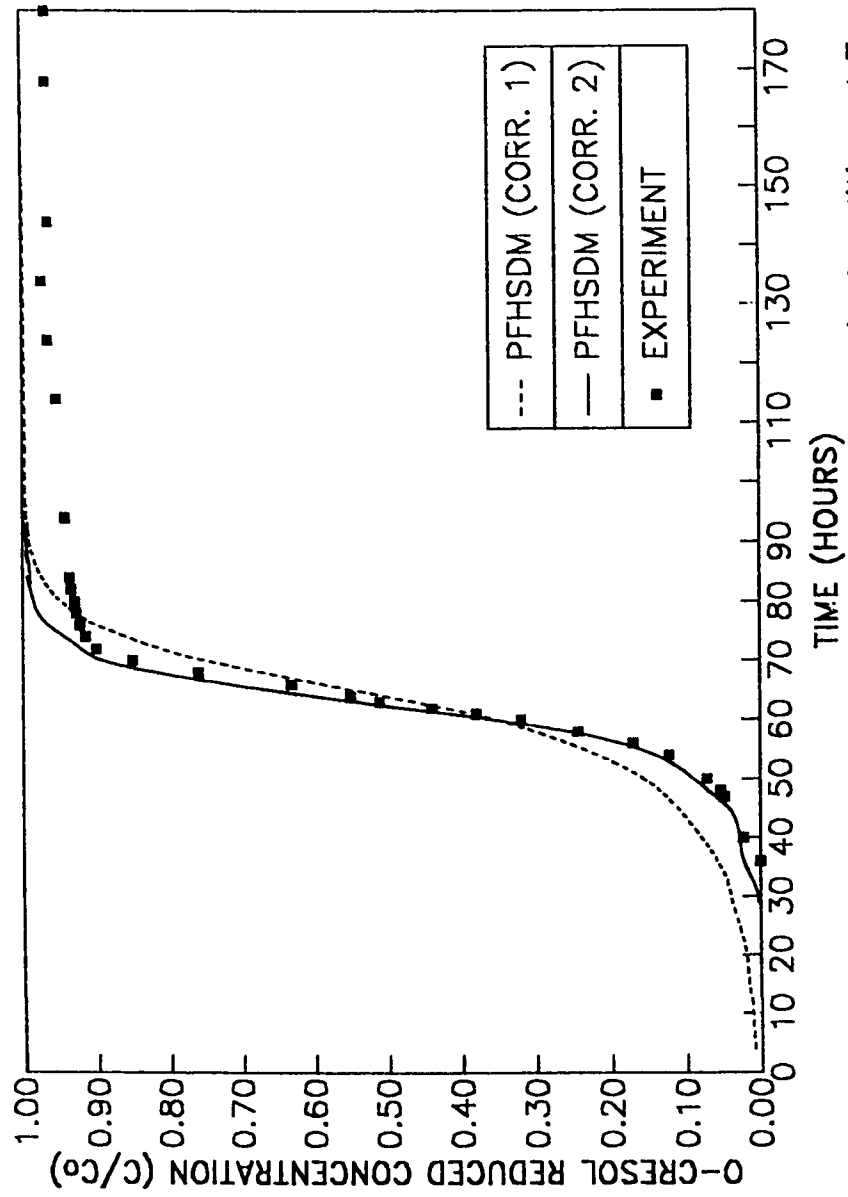


Figure 7.9: Breakthrough of o-Cresol Under Anoxic Condition at  $T = 21^{\circ}\text{C}$ . and pH 7 Along with PFHSDM Predictions.

OCOLAM

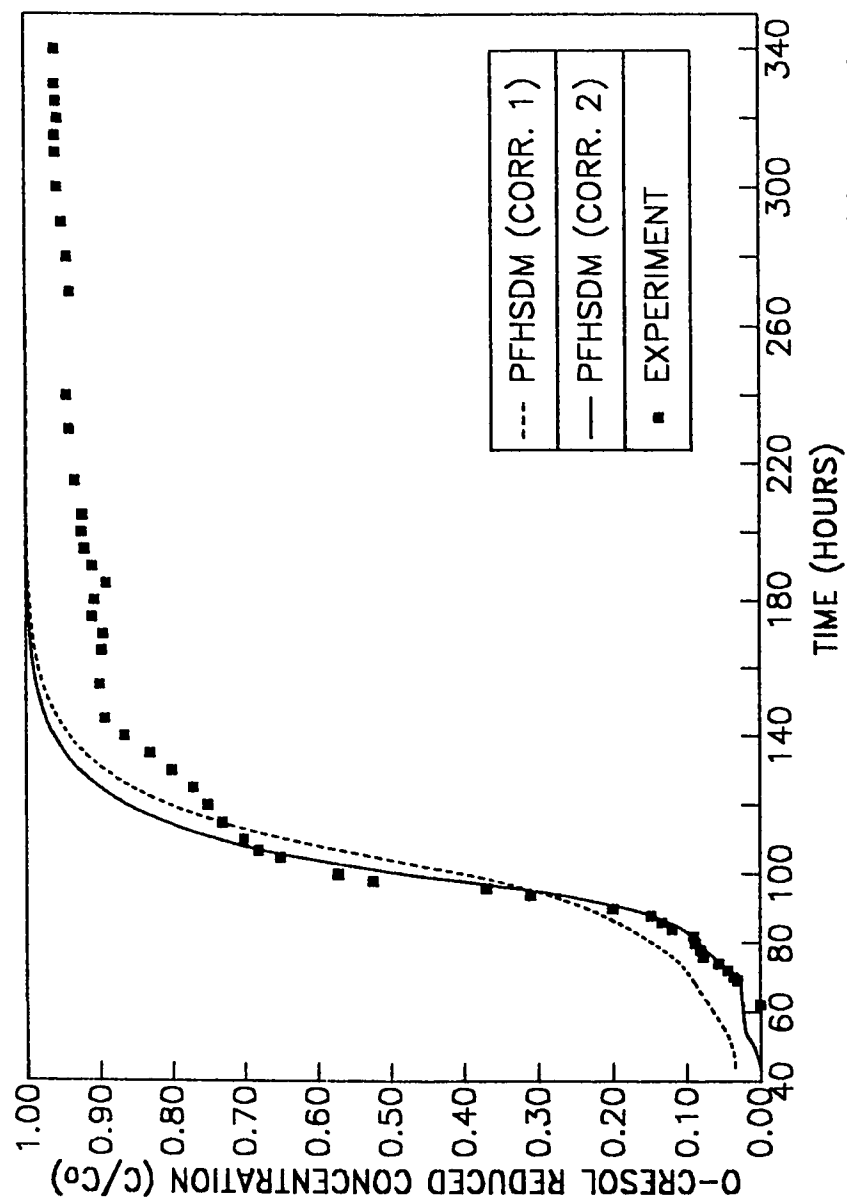


Figure 7.10: Breakthrough of o-Cresol Under Oxidic Conditions at  $T = 21^{\circ}\text{C}$ .  
and pH 7 Along with PFHSDM Predictions.

OCOLM

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 aliphatics. regardless of their chemical and substitutional properties. Testing of actual industrial and domestic wastewater cor-

roboredated 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. Oxidic 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 oxidic 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 studied 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)

Carbon Mass mg	initial DO = 31.1 mg/l		initial DO = 0.0 mg/l	
	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

Carbon Mass mg	initial DO = 30.1 mg/l		initial DO = 0.0 mg/l		
	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		initial		
	TOC mg/l	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

Carbon Mass mg	initial DO = 29.1 mg/l		initial DO = 0.0 mg/l		
	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

Carbon Mass mg	initial DO = 33.6 mg/l		initial DO = 0.0 mg/l		
	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

Carbon Mass mg	initial DO = 6.2 mg/l (normal DO level)		initial DO = 0.0 mg/l		Conc. mg/l
	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

Carbon Mass mg	initial DO = 5.1 mg/l (normal DO level)		initial DO = 0.0 mg/l		Conc. mg/l
	TOC reading	TOC mg/l	TOC reading	TOC 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

Carbon Mass mg	initial DO = 4.9 mg/l (normal DO level)		initial DO = 0.0 mg/l		Conc. mg/l
	TOC reading	TOC mg/l	TOC reading	TOC 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

Carbon Mass mg	initial DO = 5.7 mg/l (normal DO level)		initial DO = 0.0 mg/l		Conc. mg/l
	TOC reading	TOC mg/l	TOC reading	TOC 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)

Carbon Mass mg	initial DO = 30.9 mg/l		initial DO = 0.0 mg/l	
	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°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°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°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  $D_s$ .

PART.COL is the collocation matrices file

YOUR OUTPUT FILE IS HSDM.OUT. FROM THIS FILE GET THE  
FINAL ESTIMATE OF  $D_S$

\*\*\*\*\*

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  $D_S$  ESTIMATE OBTAINED FROM THE  
PROGRAM.

THE OUTPUT FILES ARE TWO: SHSDM.OUT AND OUTPUT.DAT

SHSDM.OUT will give you the final  $D_s$  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 /CO ,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
9000.00D0 /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/cm<sup>3</sup>

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, cm<sup>2</sup>/min

```

PROGRAM HSDM                                HSD00010
C                                             HSD00020
IMPLICIT DOUBLE PRECISION (A-H,O-Z)         HSD00030
C                                             HSD00040
COMMON /CTRL/ IPRC,IPRI,IPO,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
----- HSD00280
SUBROUTINE INPUT                            HSD00290
C                                             HSD00300
IMPLICIT DOUBLE PRECISION (A-H,O-Z)         HSD00310
C                                             HSD00320
COMMON /CTRL/ IPRC,IPRI,IPO,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,IPO                  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

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      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,IPO, 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                                          HSD00850
      SOMETHING IS WRONG HSD00860
      WRITE(*,*) ' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE' HSD00870
      STOP ' ERROR - ALL DONE ' HSD00880
      END IF HSD00890
      IF(ID .EQ. NCP) THEN HSD00900
      IFL1=1 HSD00910
      END IF HSD00920
C                                          HSD00930
C READ IN AND DISTRIBUTE HSD00940
C                                          HSD00950
      IF(IFL1 .NE. 0) THEN HSD00960
C                                          HSD00970
      READ(31,1001) (WP(I),I=1,1D) HSD00980
      DO 2 I=1,1D HSD00990
      READ(31,1001) (BP(I,J),J=1,1D) HSD01000
2 CONTINUE HSD01010
C                                          HSD01020
      IF(IFL1 .EQ. 0) GO TO 10 HSD01030
      IF(IFL1 .EQ. 1) GO TO 11 HSD01040
C                                          HSD01050
      END IF HSD01060
C                                          HSD01070
      IF(IFL1 .EQ. 0) THEN HSD01080
      READ(31,1001) (DUMMY(I),I=1,1D) HSD01090
      DO 6 I=1,1D HSD01100
      READ(31,1001) (DUMMY(J),J=1,1D)

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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,IPO,TOL,METH,MITER HSD01350
COMMON /COL/ NCP,WP(14),BP(14,14)         HSD01360
COMMON /PARM/ CO,QO,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
QO=XK*CO**XN                              HSD01560
C                                          HSD01570
CD=CCONC*QO/CO                            HSD01580
C                                          HSD01590
B1=XKF*RADP*CO                             HSD01600
B2=DS*RHOP*QO*1000.0D0                   HSD01610
BIOT=B1/B2                                HSD01620
C                                          HSD01630
TFAC=DS/(RADP*RADP)                       HSD01640
C                                          HSD01650
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```

      IF(IPRI .EQ. 1) THEN
      WRITE(32,1001) CO,CCONC,CD
      WRITE(32,1004) DS
      WRITE(32,1005) XKF
      WRITE(32,1006) BIOT
      WRITE(32,1007) RADP
      WRITE(32,1008) RHOP
      WRITE(32,1009) XK
      WRITE(32,1010) XN
      WRITE(32,1011) TFAC
C
C      CONTROL PARAMETER
      WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL
      END IF
C
C      FORMAT STATEMENTS
C
1001 FORMAT(2X,'CO      = ',E12.6,/,
      &2X,'CCONC = ',E12.6,/,
      &2X,'CD      = ',E12.6,/)
C
1004 FORMAT(1X,'DS      = ',E12.5)
1005 FORMAT(1X,'XKF     = ',E12.5)
1006 FORMAT(1X,'BIOT    = ',E12.5)
1007 FORMAT(1X,'RADP    = ',E12.5)
1008 FORMAT(1X,'RHOP    = ',E12.5)
1009 FORMAT(1X,'XK      = ',E12.5)
1010 FORMAT(1X,'XN      = ',E12.5)
1011 FORMAT(1X,'TFAC    = ',E12.5)
C
1013 FORMAT(1X,'NTOT =',I4,/,
      & 1X,'TOL      =',E16.6,/,
      & 1X,'METH     =',I4,/,
      & 1X,'MITER    =',I4,/,
      & 1X,'DTINIT   =',E16.6,/,
      & 1X,'DTOUT    =',E16.6,/,
      & 1X,'TFINAL   =',E16.6,/,
      & 1X,'NULL' )
C
      RETURN
      END
C-----
      SUBROUTINE CALCC
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,IPO, TOL,METH,MITER
      COMMON /COL/ NCP,WP(14),BP(14,14)
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,
      &XK,XN,RADP,RHOP,BIOT,CD,TFAC
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
      COMMON /VAR/ Y(15),NTOT
C
      DIMENSION WK(390),IWK(29)
C

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HSD01660
HSD01670
HSD01680
HSD01690
HSD01700
HSD01710
HSD01720
HSD01730
HSD01740
HSD01750
HSD01760
HSD01770
HSD01780
HSD01790
HSD01800
HSD01810
HSD01820
HSD01830
HSD01840
HSD01850
HSD01860
HSD01870
HSD01880
HSD01890
HSD01900
HSD01910
HSD01920
HSD01930
HSD01940
HSD01950
HSD01960
HSD01970
HSD01980
HSD01990
HSD02000
HSD02010
HSD02020
HSD02030
HSD02040
HSD02050
HSD02060
HSD02070
HSD02080
HSD02090
HSD02100
HSD02110
HSD02120
HSD02130
HSD02140
HSD02150
HSD02160
HSD02170
HSD02180
HSD02190
HSD02200

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EXTERNAL FCN,FCNJ	HSD02210
C	HSD02220
N=NTOT	HSD02230
HH=DTINIT	HSD02240
INDEX=1	HSD02250
C	HSD02260
T=0.000	HSD02270
C	HSD02280
ITRY=0	HSD02290
ITRYT=0	HSD02300
TPHYS=0.000	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	HSD02490
WRITE(*,*) (Y(LL),LL=1,NCP)	HSD02500
WRITE(*,2001) ITER,ITRY,T,TPHYS,Y(NTOT)	HSD02510
C	HSD02520
CC	HSD02530
WRITE(32,*) (Y(LL),LL=1,NCP)	HSD02540
WRITE(32,*) ITER,ITRY,T,TPHYS,Y(NTOT)	HSD02550
IF (T/TFAC .LT. TFINAL) GO TO 100	HSD02560
C	HSD02570
WRITE(*,*) 'ITRYT = ',ITRYT	HSD02580
WRITE(32,*) ' 999 999 999 999 999 999 999'	HSD02590
2001 FORMAT(1X,I4,I5,3E12.4)	HSD02600
RETURN	HSD02610
END	HSD02620
C-----	HSD02630
SUBROUTINE FCNJ(N,T,Y,PD)	HSD02640
C	HSD02650
IMPLICIT DOUBLE PRECISION (A-H,O-Z)	HSD02660
C	HSD02670
DIMENSION Y(N),PD(N,N)	HSD02680
C	HSD02690
RETURN	HSD02700
END	HSD02710
C-----	HSD02720
SUBROUTINE FCN(N,T,Y,YPRIME)	HSD02730
C	HSD02740
IMPLICIT DOUBLE PRECISION (A-H,O-Z)	HSD02750
C	
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER	

```

COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ CO,QO,CCONC,DS,XKF,
&XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
C
  DIMENSION Y(N),YPRIME(N)
  DIMENSION BB(14)
C
  ITRY=ITRY+1
C
  NTOT=N
  KK=0
  II=0
C
  N1CP=NCP-1
C
  DO 30 J=1,N1CP
    BB(J)=0.000
30 CONTINUE
  WW=0.000
C
  DO 50 I=1,N1CP
    II=II+1
    LL=0
C
    DO 40 J=1,NCP
      LL=LL+1
      BB(I)=BB(I)+BP(I,J)*Y(LL)
40 CONTINUE
C
C   MASS BALANCE INSIDE PARTICLE (EXCEPT BOUNDARY)
C
  YPRIME(II)=BB(I)
C
  WW=WW+WP(I)*YPRIME(II)
50 CONTINUE
C
C   SOLID-LIQUID INTERFACE
C
  II=II+1
CC
  YPRIME(II) = ((BIOT*(Y(NTOT)-(Y(II)**(1.000/XN)))-WW)/
CC
  &WP(NCP))
C
  IGO=0
C
C   HEAT EQ AT INTERFACE
  BSUM=0.000
  DO 11 KKK=1,NCP
    BSUM=BSUM+BP(NCP,KKK)*Y(KKK)
11 CONTINUE
C
  IF (IGO .EQ. 0) THEN
    IF (Y(II) .LT. 1.0D-15) THEN
CC
      YPRIME(II) = ((BIOT*(Y(NTOT)-Y(II))-WW)/WP(NCP))
CC
      YPRIME(II) = ((BIOT*(Y(NTOT)-0.000)-WW)/WP(NCP))
      YPRIME(II) = (((BIOT*(Y(NTOT)-0.000)-WW)/WP(NCP))+BSUM)*0.5

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C	ELSE	HSD03310
	YPRIME(11) = (((BIOT*(Y(NTOT)-(Y(11)**(1.0D0/XN)))-WW)/	HSD03320
	&WP(NCP))+BSUM)*0.5D0	HSD03330
	END IF	HSD03340
	END IF	HSD03350
		HSD03360
C		HSD03370
C	LIQUID PHASE MASS BALANCE	HSD03380
C		HSD03390
	YPRIME(NTOT)=-3.0D0*CD*(WW+	HSD03400
	&(YPRIME(11)*WP(NCP)))	HSD03410
C		HSD03420
	RETURN	HSD03430
	END	HSD03440
		HSD03450
		HSD03460
		HSD03470
		HSD03480

```
PROGRAM SEARCH                                SHS00010
C                                              SHS00020
INPLICIT DOUBLE PRECISION (A-H,O-Z)          SHS00030
C                                              SHS00040
COMMON /PAR1/ COV(10),CCONCV(10),RADPV(10),RHOPV(10),
&PARV(4,10),NDPV(10),NDSET,IPS(4),ISCALE(4),TM(50,10),
&YM(50,5,10),IDREP(10),NDPSV(10),YF(50,10)   SHS00050
                                              SHS00060
C                                              SHS00070
CHARACTER*80 IFNAME(10)                     SHS00080
C                                              SHS00090
DIMENSION X(4),PARM(4),F(500),XJAC(500,4),XJTJ(10),WORK(103) SHS00100
C                                              SHS00110
EXTERNAL FIND                                SHS00120
C                                              SHS00130
IXJAC=500                                    SHS00140
C                                              SHS00150
OPEN(1,FILE='SHSDM.IN',STATUS='OLD')         SHS00160
OPEN(97,FILE='SHSDM.CTR',STATUS='OLD')       SHS00170
C                                              SHS00180
INPUT SEARCH ROUTINE CONTROL PARAMETER      SHS00190
C                                              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
```

```

      IF(IPS(K) .EQ. 1) THEN
      IPSSUM=IPSSUM+1
      END IF
2 CONTINUE
C
      DO 11 K=1,NDSET
      OPEN(K,FILE=IFNAME(K),STATUS='OLD')
      REWIND(K)
      READ(K,*) NDPV(K),COV(K),IDREP(K)
      DO 22 IP=1,NDPV(K)
      READ(K,*) TM(IP,K),(YM(IP,I,K),I=1,IDREP(K))
22 CONTINUE
      READ(K,*) CCONCV(K)
      READ(K,*) RADPV(K)
      READ(K,*) RHOPV(K)
      READ(K,*) PARV(3,K)
      READ(K,*) PARV(4,K)
      READ(K,*) PARV(1,K)
      READ(K,*) PARV(2,K)
11 CONTINUE
C
C COUNT TOTAL NUMBER OF DATA POINTS
      DO 94 II=1,NDSET
      NDPSV(II)=0
      DO 95 IJ=1,NDPV(II)
      DO 95 JJ=1,IDREP(II)
      IF(YM(IJ,JJ,II) .LE. 1.1D0) THEN
      NDPSV(II)=NDPSV(II)+1
      END IF
95 CONTINUE
94 CONTINUE
C
      M1=0
      DO 211 KK=1,NDSET
      M1=M1+NDPV(KK)
211 CONTINUE
C
      M=0
      DO 21 KK=1,NDSET
      M=M+NDPSV(KK)
21 CONTINUE
C
      WRITE(*,*) ' TOTAL OBSERVATION TIMES :',M1
      WRITE(*,*) ' TOTAL DATA POINTS :',M
      WRITE(*,*) ' YOU ARE SEARCHING FOR ',IPSSUM , ' PARAMETERS'
C
      K=1
      IF(IPS(1) .EQ. 1) THEN
      SCALE=DLOG10(PARV(1,1))
      IF(SCALE .GT. 0.0D0) THEN
      ISCALE(K)=DINT(SCALE)+1
      ELSE
      ISCALE(K)=DINT(SCALE)
      END IF

```

SHS00560  
SHS00570  
SHS00580  
SHS00590  
SHS00600  
SHS00610  
SHS00620  
SHS00630  
SHS00640  
SHS00650  
SHS00660  
SHS00670  
SHS00680  
SHS00690  
SHS00700  
SHS00710  
SHS00720  
SHS00730  
SHS00740  
SHS00750  
SHS00760  
SHS00770  
SHS00780  
SHS00790  
SHS00800  
SHS00810  
SHS00820  
SHS00830  
SHS00840  
SHS00850  
SHS00860  
SHS00870  
SHS00880  
SHS00890  
SHS00900  
SHS00910  
SHS00920  
SHS00930  
SHS00940  
SHS00950  
SHS00960  
SHS00970  
SHS00980  
SHS00990  
SHS01000  
SHS01010  
SHS01020  
SHS01030  
SHS01040  
SHS01050  
SHS01060  
SHS01070  
SHS01080  
SHS01090  
SHS01100

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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
IF TROBLE LIMIT THE PARAMETERS TO	SHS01940
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	SHS02050
LOAD TIME VECTOR FOR THE K'S DATA SET	SHS02060
DO 2 L=1,NDPV(K)	SHS02070
TT(L)=TM(L,K)	SHS02080
2 CONTINUE	SHS02090
C	SHS02100
DO 9 II=1,4	SHS02110
IF(IPS(II) .EQ. 1) THEN	SHS02120
XXV(II)=X(II)*10.0D0**ISCALE(II)	SHS02130
ELSE	SHS02140
XXV(II)=PARV(II,K)	SHS02150
END IF	SHS02160
9 CONTINUE	SHS02170
C	SHS02180
CALL HSDM(COV(K),CCONCV(K),RADPV(K),RHOPV(K),XXV(1),XXV(2)	SHS02190
&,XXV(3),XXV(4),TT,YY,NDPV(K))	SHS02200
C	SHS02200

```

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,IPO,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

```

```

      XK=XK1
      XN=XN1
      XKF=XKF1
      DS=DS1
C
      CALL INIT
C
      CALL CALCC(TT,YY,NDP)
C
      RETURN
C
      END
C-----
      SUBROUTINE INPUT
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
      COMMON /CTRL/ IPRC,IPRI,I PRO,TOL,METH,MITER
      COMMON /COL/ NCP,WP(14),BP(14,14)
      COMMON /PARM/ CO,QO,CCONC,DS,XKF,
&XK,XN,RADP,RHOP,BIOT,CD,TFAC
      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
      COMMON /VAR/ Y(15),NTOT
C
CC      OPEN(30,FILE='SHSDM.CTR',STATUS='OLD')
CC      REWIND (30)
      READ(97,*) IPRC,IPRI,I PRO
C
C      PHYSICAL PARAMETER
C
CC      READ(30,*) CO
CC      READ(30,*) CCONC
CC      READ(30,*) DS
CC      READ(30,*) XKF
CC      READ(30,*) XK
CC      READ(30,*) XN
CC      READ(30,*) RADP
CC      READ(30,*) RHOP
C
C      CONTROL PARAMETER
C
      READ(97,*) NCP
      READ(97,*) TOL,METH,MITER
      READ(97,*) DTINIT
CC      READ(30,*) DTOUT
CC      READ(30,*) TFINAL
CC      READ(30,*) ITMAX
C
      CLOSE (30)
C
      RETURN
      END
C-----
      SUBROUTINE INCOL
C

```

```

SHS02760
SHS02770
SHS02780
SHS02790
SHS02800
SHS02810
SHS02820
SHS02830
SHS02840
SHS02850
SHS02860
SHS02870
SHS02880
SHS02890
SHS02900
SHS02910
SHS02920
SHS02930
SHS02940
SHS02950
SHS02960
SHS02970
SHS02980
SHS02990
SHS03000
SHS03010
SHS03020
SHS03030
SHS03040
SHS03050
SHS03060
SHS03070
SHS03080
SHS03090
SHS03100
SHS03110
SHS03120
SHS03130
SHS03140
SHS03150
SHS03160
SHS03170
SHS03180
SHS03190
SHS03200
SHS03210
SHS03220
SHS03230
SHS03240
SHS03250
SHS03260
SHS03270
SHS03280
SHS03290
SHS03300

```

	IMPLICIT DOUBLE PRECISION (A-H,O-Z)	SHS03310
C		SHS03320
	COMMON /CTRL/ IPRC,IPRI,I PRO,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

FILE: SHSDM      FORTRAN A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DHAIRAN

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)=0.000	SHS04110
11 CONTINUE	SHS04120
C	SHS04130
C LIQUID PHASE	SHS04140
C	SHS04150
Y(NTOT)=1.000	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*1000.000	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,/,
      &2X,'CCONC = ',E12.6,/,
      &2X,'CD    = ',E12.6,/) SHS04470
C                                                     SHS04480
C                                                     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,/,
      & 1X,'TOL    = ',E16.6,/,
      & 1X,'METH   = ',I4,/,
      & 1X,'MITER  = ',I4,/,
      & 1X,'DTINIT = ',E16.6,/,
      & 1X,'DTOUT  = ',E16.6,/,
      & 1X,'TFINAL = ',E16.6,/,
      & 1X,'NULL' ) SHS04600
C                                                     SHS04610
C                                                     SHS04620
C                                                     SHS04630
C                                                     SHS04640
C                                                     SHS04650
C                                                     SHS04660
C                                                     SHS04670
C                                                     SHS04680
C      RETURN                                           SHS04690
      END                                               SHS04700
C-----
C      SUBROUTINE CALCC(TT,YY,NDP)                      SHS04710
C                                                     SHS04720
C                                                     SHS04730
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)              SHS04740
C                                                     SHS04750
C      COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER      SHS04760
C      COMMON /COL/ NCP,WP(14),BP(14,14)               SHS04770
C      COMMON /PARM/ CO,QO,CCONC,DS,XKF,               SHS04780
C      &XK,XN,RADP,RHOP,BIOT,CD,TFAC                   SHS04790
C      COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY    SHS04800
C      COMMON /VAR/ Y(15),NTOT                         SHS04810
C                                                     SHS04820
C      DIMENSION TT(1),YY(1)                            SHS04830
C                                                     SHS04840
C      DIMENSION WK(390),IWK(29)                       SHS04850
C                                                     SHS04860
C      EXTERNAL FCN,FCNJ                                SHS04870
C                                                     SHS04880
C      DO 98 KK=1,NDP                                    SHS04890
C      WRITE(*,*) KK,TT(KK)                             SHS04900
C      98 CONTINUE                                       SHS04910
C                                                     SHS04920
C      N=NTOT                                             SHS04930
C      HH=DTINIT                                          SHS04940
C      INDEX=1                                            SHS04950

```

```

C                                     SHS04960
      T=0.000                                     SHS04970
C                                     SHS04980
      ITRY=0                                     SHS04990
      ITRYT=0                                    SHS05000
      TPHYS=0.000                               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)=1.000                             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

```

Line	Code	Statement	Address
1	C	IMPLICIT DOUBLE PRECISION (A-H,O-Z)	SHS05510
2	C	COMMON /CTRL/ IPRC,IPRI,I PRO,TOL,METH,MITER	SHS05530
3		COMMON /COL/ NCP,WP(14),BP(14,14)	SHS05540
4		COMMON /PARM/ CO,QO,C CONC,DS,XKF,	SHS05550
5		&XK,XN,RADP,RHOP,BIOT,CD,TFAC	SHS05560
6		COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY	SHS05570
7	C	DIMENSION Y(N),YPRIME(N)	SHS05580
8		DIMENSION BB(14)	SHS05590
9	C	ITRY=ITRY+1	SHS05600
10	C	NTOT=N	SHS05610
11		KK=0	SHS05620
12		II=0	SHS05630
13	C	NICP=NCP-1	SHS05640
14	C	DO 30 J=1,NICP	SHS05650
15		BB(J)=0.000	SHS05660
16	30	CONTINUE	SHS05670
17		WW=0.000	SHS05680
18	C	DO 50 I=1,NICP	SHS05690
19		II=II+1	SHS05700
20		LL=0	SHS05710
21	C	DO 40 J=1,NCP	SHS05720
22		LL=LL+1	SHS05730
23		BB(I)=BB(I)+BP(I,J)*Y(LL)	SHS05740
24	40	CONTINUE	SHS05750
25	C	MASS BALANCE INSIDE PARTICLE (EXCEPT BOUNDARY)	SHS05760
26	C	YPRIME(II)=BB(I)	SHS05770
27	C	WW=WW+WP(I)*YPRIME(II)	SHS05780
28	50	CONTINUE	SHS05790
29	C	SOLID-LIQUID INTERFACE	SHS05800
30	C	II=II+1	SHS05810
31	CC	YPRIME(II) = ((BIOT*(Y(NTOT)-(Y(II)**(1.000/XN)))-WW)/	SHS05820
32	CC	&WP(NCP))	SHS05830
33	C	IGO=0	SHS05840
34	C	HEAT EQ AT INTERFACE	SHS05850
35		BSUM=0.000	SHS05860
36		DO 11 KKK=1,NCP	SHS05870
37		BSUM=BSUM+BP(NCP,KKK)*Y(KKK)	SHS05880
38	11	CONTINUE	SHS05890
39	C	IF (IGO.EQ. 0) THEN	SHS05900
40			SHS05910
41			SHS05920
42			SHS05930
43			SHS05940
44			SHS05950
45			SHS05960
46			SHS05970
47			SHS05980
48			SHS05990
49			SHS06000
50			SHS06010
51			SHS06020
52			SHS06030
53			SHS06040
54			SHS06050

	IF(Y(11) .LT. 1.0D-10) THEN	SHS06060
CC	YPRIME(11) = ((BIOT*(Y(NTOT)-Y(11))-WW)/WP(NCP))	SHS06070
CC	YPRIME(11) = ((BIOT*(Y(NTOT)-0.0D0)-WW)/WP(NCP))	SHS06080
	YPRIME(11) = (((BIOT*(Y(NTOT)-0.0D0)-WW)/WP(NCP))+BSUM)*0.5	SHS06090
C		SHS06100
	ELSE	SHS06110
CC	YPRIME(11) = (((BIOT*(Y(NTOT)-(Y(11)**(1.0D0/XN)))-WW)/	SHS06120
	XS=DEXP((1.0D0/XN)*DLOG(Y(11)))	SHS06130
CC	WRITE(*,*) ' XS ,Y(11)',XS,Y(11)	SHS06140
	YPRIME(11) = (((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(11)*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 Flow 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 program 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,N0): 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 redimensioning of DGEARB.for has *
* to be made. *
* The program is also dimensioned to read up to 75 points of varving *
* 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(1) *----- *----- ***
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(1) *----- *----- *----- *----- *----- *
0.0 *6.00000E+03* * * * *

```

vector of new time steps for integration, min.

```

TINC(1) *----- *----- *----- *----- *----- *
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),XN1(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*RHO)               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(1) = 13.26D-05/(((VW*100.00D)**1.14D0)*(VB(1)**5.89D-01 PLU01130
      SC(1) = VW/(DW*DIFL(1))                PLU01140
      END IF                                PLU01150
      IF (KF(1).LE.0.0D0) THEN                PLU01160
      KF(1) = (2.4D0*VS)/((RE**.66D0)*(SC(1)**.58D0))    PLU01170
      ENDIF                                  PLU01180
      IF (PSDFR.LE.0.0D0) THEN                PLU01190
      PSDFR = 0.0D0                          PLU01200
      GO TO 68                               PLU01210
      ELSE                                  PLU01220
      DS(1) = (EPOR*DIFL(1)*CBO(1)*PSDFR)/(1.0D+03*RHO* XK(1)*CBO( PLU01230
      +(1))                                  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,EB PLU01390
      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,EB PLU01410
      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(1) = XK(1)*CBO(1)**XN(1)        PLU01490
          QTE = QTE + QE(1)                 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)*(1.000 - EBED)*1000.000)/(EBED*CBO(I))	PLU01670
EDS(I) = DS(I)*DGS(I)*TAU/(RAD**2.000)	PLU01680
ST(I) = KF(I)*(1.000 - EBED)*TAU/(EBED*RAD)	PLU01690
BIS(I) = ST(I)/EDS(I)	PLU01700
XNI(I) = 1.000/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 = 0.000	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 = 60.000/(TAU*(DGT + 1.000))	PLU02080
TSTEP = DSTEP*TCONV	PLU02090
TTOL = DTOL*TCONV	PLU02100
TOUT = DOUT*TCONV	PLU02110
H0 = DH0*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

PLU02210  
PLU02220  
PLU02230  
PLU02240  
PLU02250  
PLU02260  
PLU02270  
PLU02280  
PLU02290  
PLU02300  
PLU02310  
PLU02320  
PLU02330  
PLU02340  
PLU02350  
PLU02360  
PLU02370  
PLU02380  
PLU02390  
PLU02400  
PLU02410  
PLU02420  
PLU02430  
PLU02440  
PLU02450  
PLU02460  
PLU02470  
PLU02480  
PLU02490  
PLU02500  
PLU02510  
PLU02520  
PLU02530  
PLU02540  
PLU02550  
PLU02560  
PLU02570  
PLU02580  
PLU02590  
PLU02600  
PLU02610  
PLU02620  
PLU02630  
PLU02640  
PLU02650  
PLU02660  
PLU02670  
PLU02680  
PLU02690  
PLU02700  
PLU02710  
PLU02720  
PLU02730  
PLU02740  
PLU02750

```

C
IF ( NDATA .EQ. 0 ) GO TO 90
WRITE(7,109)
CALL OBJFUN ( TDATA,NDATA,ITP )
DO 85 I = 1,NCOMP
  WRITE(7,110) I
  DO 80 J = 1,NDATA
    RES = ((CINT(I,J) - CD(I,J))/CD(I,J))*100.000
    WRITE(7,111) TDATA(J)/TCONV,CD(I,J),CINT(I,J),RES
80  CONTINUE
    WRITE(7,112) NDATA,FMIN(I)
85 CONTINUE
90 STOP

C
C
C      ---- FORMAT BLOCK ----
C
C
2  FORMAT (A)
101 FORMAT(4F20.12)
102 FORMAT(1X,4F20.12)
103 FORMAT(////
+' NUMBER OF RADIAL COLLOCATION POINTS, NC... = ',I15/
+' NUMBER OF AXIAL COLLOCATION POINTS, MC.... = ',I15/
+' TOTAL NO. OF DIFFERENTIAL EQUATIONS, NEQ.. = ',I15/
+' RADIUS OF ADSORBENT PARTICLE, RAD (CM.)... = ',E15.5/
+' MASS OF ADSORBENT, WT (GRAMS)..... = ',E15.5/
+' APPARENT PARTICLE DENSITY, RHOP (GM/CM**3) = ',E15.5/
+' VOID FRACTION OF THE CARBON. EPOR (DIM.) . = ',E15.5/
+' LENGTH OF BED, L (CM.)..... = ',E15.5/
+' VOID FRACTION OF BED, EBED (DIM.)..... = ',E15.5/
+' DIAMETER OF FIXED-BED, DIA, (CM.) ..... = ',E15.5/
+' SURFACE LOADING, SF (GPM/FT**2)..... = ',E15.5/
+' PACKED BED CONTACT TIME, TAU (SEC.)..... = ',E15.5/
+' EMPTY BED CONTACT TIME, EBCT (MIN.)..... = ',E15.5)
1003 FORMAT(/
+' INITIAL INTEGRATION STEP, DHO (MIN.)..... = ',E15.5/
+' INITIAL OUTPUT TIME, DOUT (MIN.)..... = ',E15.5/
+' REYNOLDS NUMBER, RE, (DIM.) ..... = ',E15.5/
+' TEMPERATURE OF WATER, TEMP, (DEG C.) ..... = ',E15.5/
+' DENSITY OF WATER, DW, (GM/CM.CM) ..... = ',E15.5/
+' VISCOSITY OF WATER, VW, (GM/CM-SEC) ..... = ',E15.5/
+' PORE SURFACE DIFFUSION FLUX RATIO, PSDFR . = ',E15.5/)
104 FORMAT(/' PARAMETERS FOR ',A20/
+ 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
C          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/BLOCKC/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  
C  
C  
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| END OF SUBROUTINE ORTHOG |

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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/BLOCKC/STD(3),BEDS(3,7,7),DGI(3),MND,ND,MD,DGI	PLU04180
COMMON MC,NC,NCOMP,N1,DGT,NIN,ISO,CBO(3)	PLU04190
DO 15 K = 1,MC	PLU04200
QTE = 0.000	PLU04210
QTO = 0.000	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. 0.000 .OR. QTO .LE. 0.000 ) THEN	PLU04320
CS(I,K) = 0.000	PLU04330
ELSE	PLU04340
Z1(I) = Z1(I)/QTE	PLU04350
QO(I) = QTO*XN(I)/YM(I)	PLU04360
IF ( XNI(I)*DLOG10(QO(I)) .LT. -20.000 ) THEN	PLU04370
CS(I,K) = 0.000	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(1,K)=(QE(I))*Y0(II)               PLU04470
6     CONTINUE                            PLU04480
      IF(Z(1,K).LE.0.000) THEN            PLU04490
      CS(1,K)=0.000                       PLU04500
      CS(2,K)=0.000                       PLU04510
      CS(3,K)=0.000                       PLU04520
      ELSE                                 PLU04530
      IF(Z(2,K).LE.0.000.AND.Z(1,K).GT.0.000) THEN PLU04540
      CS(1,K)=(Z(1,K)/A1(1))*DEXP(A2(1)*Z(1,K)**A3(1))/CBO(1) PLU04550
      CS(2,K)=0.000                       PLU04560
      CS(3,K)=0.000                       PLU04570
      ELSE                                 PLU04580
      IF(Z(1,K).GT.0.000.AND.Z(2,K).GT.0.000.AND.
+     Z(3,K).LE.0.000) THEN              PLU04590
      ZZ(1)=Z(1,K)                        PLU04600
      ZZ(2)=Z(2,K)                        PLU04610
      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)=0.000                       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 = 1.000                       PLU04840
      ELSE                                 PLU04850
      CINFL = CINF(I,T)                   PLU04860
      ENDIF                                PLU04870
      DO 20 K = 2,MC                      PLU04880
      IF ( CS(I,K) .LE. 0.000 ) THEN      PLU04890
      CBS(I,K) = STD(I)*Y0(IIII + K)     PLU04900
      ELSE                                 PLU04910
      CBS(I,K) = STD(I)*(Y0(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 = 11 + (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)*Y0(KK + M) PLU05020
25      CONTINUE                                     PLU05030
          BB(J,K) = BR(J,K) + BEDS(I,J,NC)*Y0(111 + 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(111+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(111+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)*Y0(1111+M)    PLU05290
50      CONTINUE                                     PLU05300
C                                                    PLU05310
C.....Liquid Phase Mass Balance                        PLU05320
C                                                    PLU05330
          YDOT(1111+K) = -DGI*(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          ----- PLU05430
C          | END OF SUBROUTINE DIFFUN | PLU05440
C          ----- PLU05450
C                                                    PLU05460
C                                                    PLU05470
C          SUBROUTINE OBJFUN ( TD,NDATA,NP ) PLU05480
C          IMPLICIT DOUBLE PRECISION (A-H,O-Z) PLU05490
C          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 TO PLU05580
      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 PLU05740
C PLU05750
C PLU05760
C PLU05770
C PLU05780
C PLU05790
      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-1 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 PLU06050
      | END OF SUBROUTINE PEDERV |

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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),XN1(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

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SUBROUTINE DGEAR (N,TO,H0,Y0,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,H0,Y0,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,JSTART DGE00100
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 Y0(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.0.000) GO TO 400                            DGE00270
IF (N.LE.0) GO TO 410                                  DGE00280
IF ((T-TOUT)*H0.GE.0.000) GO TO 420                    DGE00290
UROUND=.10842D-18                                     DGE00300
DO 10 I=1,N                                             DGE00310
    YMAX(I)=ABS(Y0(I))                                  DGE00320
    IF (YMAX(I).EQ.0.000) YMAX(I)=1.000                 DGE00330
10  Y(I,1)=Y0(I)                                       DGE00340
    NC=N                                                DGE00350
    T=TO                                                DGE00360
    H=H0                                                DGE00370
    IF ((T+H).EQ.T) WRITE (LOUT,15)                   DGE00380
    HMIN=ABS(H0)                                        DGE00390
    HMAX=ABS(TO-TOUT)*10.000                            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)*10.000                         DGE00490
    GO TO 80                                             DGE00500
25  HMAX=ABS(TOUT-TOUTP)*10.000                         DGE00510
    IF ((T-TOUT)*H.GE.0.000) GO TO 500                 DGE00520
    GO TO 85                                             DGE00530
C                                                       DGE00540
30  IF ((T-TOUT)*H.GE.0.000) 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=0.000	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.0.000) GO TO 40	DGE00790
C	DGE00800
CALL INTERP	DGE00810
CALL NGE001 (TOUT,Y,NO,YO)	DGE00820
GO TO 520	DGE00830
85 IF (((T+H)-TOUT)*H.LE.0.000) GO TO 40	DGE00840
IF (ABS(T-TOUT).LE.100.000*UROUND*HMAX) GO TO 500	DGE00850
IF ((T-TOUT)*H.GE.0.000) GO TO 500	DGE00860
H=(TOUT-T)*(1.000-4.000*UROUND)	DGE00870
JSTART=-1	DGE00880
GO TO 40	DGE00890
100 WRITE (LOUT,105) T	DGE00900
110 IF (NHCUT.EQ.10) GO TO 150	DGE00910
NHCUT=NHCUT+1	DGE00920
HMIN=HMIN*.1000	DGE00930
H=H*.1000	DGE00940
WRITE (LOUT,115) H	DGE00950
JSTART=-1	DGE00960
GO TO 40	DGE00970
C	DGE00980
150 WRITE (LOUT,155)	DGE00990
GO TO 500	DGE01000
C	DGE01010
200 WRITE (LOUT,205) T,H	DGE01020
GO TO 500	DGE01030
C	DGE01040
250 WRITE (LOUT,255) T	DGE01050
KFLAG=-2	DGE01060
GO TO 500	DGE01070
C	DGE01080
300 WRITE (LOUT,305) T	DGE01090
GO TO 110	DGE01100
C	

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	DGE01280
CALL INTERP	DGE01290
CALL NGE001 (TOUT,Y,NO,YO)	DGE01300
INDEX=-5	DGE01310
RETURN	DGE01320
C	DGE01330
500 TOUT=T	DGE01340
DO 510 I=1,N	DGE01350
510 YO(I)=Y(I,1)	DGE01360
520 INDEX=KFLAG	DGE01370
TOUTP=TOUT	DGE01380
H0=HUSED	DGE01390
IF (KFLAG.NE.0) H0=H	DGE01400
RETURN	DGE01410
C	DGE01420
15 FORMAT (35H WARNING.. T + H = T ON NEXT STEP.)	DGE01430
105 FORMAT (//35H KFLAG = -1 FROM INTEGRATOR AT T = ,E16.8/39H	DGE01440
1TEST FAILED WITH DABS(H) = HMIN/)	DGE01450
115 FORMAT (24H H HAS BEEN REDUCED TO ,E16.8,26H AND STEP WILLDGE01450	DGE01460
1TRIED//)	DGE01470
155 FORMAT (//44H PROBLEM APPEARS UNSOLVABLE WITH GIVEN INPUT//)DGE01470	DGE01480
205 FORMAT (//35H KFLAG = -2 FROM INTEGRATOR AT T = ,E16.8,5H HDGE01480	DGE01490
1.8/52H THE REQUESTED ERROR IS SMALLER THAN CAN BE HANDLED//DGE01490	DGE01500
255 FORMAT (//37H INTEGRATION HALTED BY DRIVER AT T = ,E16.8/56HDGE01500	DGE01510
1TOO SMALL TO BE ATTAINED FOR THE MACHINE PRECISION/)	DGE01520
305 FORMAT (//35H KFLAG = -3 FROM INTEGRATOR AT T = ,E16.8/45H DGE01520	DGE01530
1TOR CONVERGENCE COULD NOT BE ACHIEVED/)	DGE01540
405 FORMAT (//28H ILLEGAL INPUT.. EPS .LE. 0.//)	DGE01550
415 FORMAT (//25H ILLEGAL INPUT.. N .LE. 0//)	DGE01560
425 FORMAT (//36H ILLEGAL INPUT.. (TO-TOUT)*H .GE. 0.//)	DGE01570
435 FORMAT (//24H ILLEGAL INPUT.. INDEX = ,15//)	DGE01580
445 FORMAT (//44H INDEX = -1 ON INPUT WITH (T-TOUT)*H .GE. 0./4HDGE01580	DGE01590
116.8,9H TOUT =,E16.8,6H H =,E16.8/44H INTERPOLATION WAS DGE01590	DGE01600
2S ON NORMAL RETURN./41H DESIRED PARAMETER CHANGES WERE NOT MDGE01600	DGE01610
END	DGE01620
SUBROUTINE NGE001 (TOUT,Y,NO,YO)	DGE01630
C	DGE01640
C THIS IS CALLED BY "GEAR". IT WAS "INTERP" IN THE DISTRIBUTED VEDGE01640	DGE01650
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,MEQ,MIO,IWEVDGE01870
1    DER,LMAX,IREDQ,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
1    E,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)/OLDLO	DGE02420
OLDLO=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*R1	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

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)=0.000	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,N0,CON,MITER,IER)	DGE02930
IF (IER.NE.0) GO TO 420	DGE02940
GO TO 350	DGE02950
260 R=EL(1)*.1000	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)=1.000	DGE03040
D=.1000*RO-H*(SAVE1(I)-SAVE2(I))	DGE03050
SAVE1(I)=0.000	DGE03060
IF (ABS(RO).LT.UROUND*YMAX(I)) GO TO 280	DGE03070
IF (ABS(D).EQ.0.000) GO TO 420	DGE03080
PW(I)=.1000*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=0.000	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=1.000-R*(1.000-1.000/PW(I))	DGE03270
IF (ABS(D).EQ.0.000) GO TO 440	DGE03280
320 PW(I)=1.000/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(I)*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
1430  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
1460  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
1470  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
1490  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(I1).LE.HMIN*1.000010D0) GO TO 660	DGE03950
IF (KFLAG.LE.-3) GO TO 640	DGE03960
IRED0=2	DGE03970
PR3=1.0D0	DGE03980
GO TO 540	DGE03990
520 PR3=1.0D0	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=1.0D0	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,.074070D0,.0139DGE04720
      $.0021820D0,.00029450D0,.000034920D0,.0000036920D0,.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
      $7.3330D0,10.420D0,13.70D0,1.0D0,1.0D0,1.0D0,1.0D0,1.0D0,1.0D0DGE04770
      $1.0D0,12.0D0,24.0D0,37.890D0,53.330D0,70.080D0,87.970D0,106.DGE04780
      $126.70D0,147.40D0,168.80D0,191.0D0,1.0D0,3.0D0,6.0D0,9.1670DGE04790
      $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)=9.166666666666667D-01	DGE04960
	EL(4)=3.333333333333333D-01	DGE04970
	EL(5)=4.166666666666667D-02	DGE04980
	GO TO 900	DGE04990
105	EL(1)=3.486111111111111D-01	DGE05000
	EL(3)=1.041666666666667D00	DGE05010
	EL(4)=4.861111111111111D-01	DGE05020
	EL(5)=1.041666666666667D-01	DGE05030
	EL(6)=8.333333333333333D-03	DGE05040
	GO TO 900	DGE05050
106	EL(1)=3.298611111111111D-01	DGE05060
	EL(3)=1.141666666666667D00	DGE05070
	EL(4)=0.6250D0	DGE05080
	EL(5)=1.770833333333333D-01	DGE05090
	EL(6)=0.0250D0	DGE05100
	EL(7)=1.388888888888889D-03	DGE05110
	GO TO 900	DGE05120
107	EL(1)=3.1559193121693122D-01	DGE05130
	EL(3)=1.2250D0	DGE05140
	EL(4)=7.518518518518518D-01	DGE05150
	EL(5)=2.552083333333333D-01	DGE05160
	EL(6)=4.861111111111111D-02	DGE05170
	EL(7)=4.861111111111111D-03	DGE05180
	EL(8)=1.388888888888889D-03	DGE05190

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111 EL(1)=2.8018959644393672D-01      DGE05510
    EL(3)=1.4644841269841270D0        DGE05520
    EL(4)=1.17151455026455030D0       DGE05530
    EL(5)=5.7935819003527337D-01      DGE05540
    EL(6)=1.8832286155202822D-01      DGE05550
    EL(7)=4.1430362654320988D-02      DGE05560
    EL(8)=6.2111441798941799D-03      DGE05570
    EL(9)=6.2520667989417989D-04      DGE05580
    EL(10)=4.0417401528512640D-05     DGE05590
    EL(11)=1.5156525573192240D-06     DGE05600
    EL(12)=2.5052108385441719D-08     DGE05610
    GO TO 900                          DGE05620
112 EL(1)=2.7426554003159906D-01      DGE05630
    EL(3)=1.50993867243867240D0       DGE05640
    EL(4)=1.2602711640211640D0       DGE05650
    EL(5)=6.5923418209876543D-01      DGE05660
    EL(6)=2.3045800264550265D-01      DGE05670
    EL(7)=5.5697246105232216D-02     DGE05680
    EL(8)=9.4394841269841270D-03     DGE05690
    EL(9)=1.1192749669312169D-03     DGE05700
    EL(10)=9.0939153439153439D-05     DGE05710
    EL(11)=4.8225308641975309D-06     DGE05720
    EL(12)=1.5031265031265031D-07     DGE05730
    EL(13)=2.0876756987868099D-09     DGE05740
    GO TO 900                          DGE05750
C                                     DGE05760
201 EL(1)=1.0D0                       DGE05770
    GO TO 900                          DGE05780
202 EL(1)=6.6666666666666667D-01      DGE05790
    EL(3)=3.3333333333333333D-01      DGE05800
    GO TO 900                          DGE05810
203 EL(1)=5.4545454545454545D-01      DGE05820
    EL(3)=EL(1)                       DGE05830
    EL(4)=9.0909090909090909D-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)=4.3795620437956204D-01      DGE05910
    EL(3)=8.2116788321167883D-01      DGE05920
    EL(4)=3.1021897810218978D-01      DGE05930
    EL(5)=5.4744525547445255D-02     DGE05940
    EL(6)=3.6496350364963504D-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

```

DOUBLE PRECISION EPSJ,D,RO,YJ,R	DGE06060
DIMENSION Y(N0,6)	DGE06070
COMMON /GEAR1/ T,H,DUMMY(3),UROUND,N,1DUMMY(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,N0)	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

IP(N)=-IP(N)	DGE06610
A(N,K)=A(K,K)	DGE06620
A(K,K)=T	DGE06630
20 IF (T.EQ.0.000) GO TO 80	DGE06640
T=1.000/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.0.000) 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.0.000) 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,XM11,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

```

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C
C
      DIMENSION WK(33),X(3),Y(3),CO(3),QE(N),CF(N),
+XMH1(N),XMK1(N),XMP1(N)
C
      EXTERNAL FCNM
      EXTERNAL FCNJM
C
      READ INITIAL GUESSES FOR ADSORBED PHASE
C
      ADSORBATE CONCENTRATIONS
C
      DO 3 I=1,N
      X(I)=0.5*CE(I)
3      CONTINUE
      NSIG=4
      ITMAX=300
C
      CALL NMAJLS(N,FCNM,FCNJM,NSIG,
&X, FNORM, ITMAX,WK, IER,XMH1,XMK1,XMP1,CE)
C
      IF(IER.NE. 0) THEN
      WRITE(*,*) ' IER = ',IER
      WRITE(*,*) ' X = ', (X(I),I=1,N)
      WRITE(*,*) ' FNORM = ',FNORM
      WRITE(*,*) ' SUBROUTINE IAST MYERS'
      STOP ' something is wrong '
      END IF
C
C
      COMPUTE HYPOTHETICAL LIQUID PHASE CONC'S
      AND THE LIQUID PHASE MOLE FRACTIONS
C
      DO 4 I=1,N
      ARG=XMK1(I)*X(I)**XMP1(I)
      CO(I)=(X(I)/XMH1(I))*DEXP(ARG)
      Y(I)=CE(I)/CO(I)
4      CONTINUE
C
C
      TOTAL CARBON COVERAGE
C
      SUM=0.000
      DO 5 I=1,N
      SUM=SUM+Y(I)/X(I)
5      CONTINUE
      QT=1.000/SUM
C
C
      ADSORBED PHASE ADSORPTION CONCENTRATION
      DO 6 I=1,N
      QE(I)=Y(I)*QT
6      CONTINUE
      RETURN
      END
C-----
      SUBROUTINE FCNM(X,F,XMH1,XMK1,XMP1,CE,N)
C

```

```

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C
      DIMENSION XMH1(N),XMK1(N),XMP1(N),CE(N)
C
      DIMENSION X(N),F(N),H(3),P(3),ARG(3),FR(3),P1(3)
C
      DO 1 I=1,N
        X(I)=DMAX1(X(I),1.0D-20)
1 CONTINUE
C
      DO 2 I=1,N
        H(I)=XMK1(I)*XMP1(I)/(XMP1(I)+1.0D0)
        P(I)=X(I)+H(I)*X(I)**(XMP1(I)+1.0D0)
2 CONTINUE
      DO 3 I=1,N-1
        F(I)=P(I)-P(I+1)
3 CONTINUE
C
      SUM=0.0D0
      DO 4 I=1,N
        ARG(I)=XMK1(I)*X(I)**XMP1(I)
        FR(I)=X(I)/XMH1(I)
        P1(I)=CE(I)/(FR(I)*DEXP(ARG(I)))
        SUM=SUM+P1(I)
4 CONTINUE
      F(N)=SUM-1.0D0
C
      RETURN
      END
C-----
      SUBROUTINE FCNJM(X,FJ,XMH1,XMK1,XMP1,CE,N)
C
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C
      DIMENSION XMH1(N),XMK1(N),XMP1(N),CE(N),F1(3),F2(3)
C
      DIMENSION X(N),FJ(N,N),PR(3),ARG(3),XNOM(3)
C
      DO 1 I=1,N
        X(I)=DMAX1(X(I),1.0D-20)
1 CONTINUE
C
      DO 2 I=1,N
        PR(I)=XMK1(I)*XMP1(I)*X(I)**XMP1(I)
        ARG(I)=XMK1(I)*X(I)**XMP1(I)
        XNOM(I)=-CE(I)*XMH1(I)*(1.0D0+PR(I))
2 CONTINUE
C
      IF (N.EQ.2) THEN
        FJ(1,1)=1.0D0+PR(1)
        FJ(2,1)=XNOM(1)/(X(1)*X(1)*DEXP(ARG(1)))
        FJ(1,2)=-1.0D0-PR(2)
        FJ(2,2)=XNOM(2)/(X(2)*X(2)*DEXP(ARG(2)))
      END IF
      IF (N.EQ.3) THEN

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```

DGE07710
DGE07720
DGE07730
DGE07740
DGE07750
DGE07760
DGE07770
DGE07780
DGE07790
DGE07800
DGE07810
DGE07820
DGE07830
DGE07840
DGE07850
DGE07860
DGE07870
DGE07880
DGE07890
DGE07900
DGE07910
DGE07920
DGE07930
DGE07940
DGE07950
DGE07960
DGE07970
DGE07980
DGE07990
DGE08000
DGE08010
DGE08020
DGE08030
DGE08040
DGE08050
DGE08060
DGE08070
DGE08080
DGE08090
DGE08100
DGE08110
DGE08120
DGE08130
DGE08140
DGE08150
DGE08160
DGE08170
DGE08180
DGE08190
DGE08200
DGE08210
DGE08220
DGE08230
DGE08240
DGE08250

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      FJ(1,1)=1.000+PR(1)
      FJ(2,1)=0.000
      FJ(3,1)=XNOM(1)/(X(1)*DEXP(ARG(1)))
      FJ(1,2)=-1.000-PR(2)
      FJ(2,2)=1.000+PR(2)
      FJ(3,2)=XNOM(2)/(X(2)*DEXP(ARG(2)))
      FJ(1,3)=0.000
      FJ(2,3)=-1.000-PR(3)
      FJ(3,3)=XNOM(3)/(X(3)*DEXP(ARG(3)))
      END IF
C
      RETURN
      END
C-----
      SUBROUTINE IASTMQ(CE, QE, XMH1, XMK1, XMP1, N)
C
C      IAST CALCULATION FOR MYERS ISOTHERMS
C      IF THE SOLID PHASE ADSORBATE
C      CONCENTRATIONS ARE KNOWN
C      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C
      DIMENSION XMH1(N), XMK1(N), XMP1(N), QE(N)
C
      DIMENSION WK(33), X(3)
C
      DIMENSION Y(3), CO(3), CE(N)
C
      EXTERNAL FQNM
      EXTERNAL FQNJM
C      READ INITIAL GUESSES FOR LIQUID PHASE
C      ADSORBATE CONCENTRATIONS
C
      DO 2 I=1, N
      X(I)=0.5*QE(I)
2      CONTINUE
C
      NSIG=4
      ITMAX=1000
C
      CALL NMAJLS(N, FQNM, FQNJM, NSIG,
&X, FNORM, ITMAX, WK, IER, XMH1, XMK1, XMP1, QE)
C
      IF( IER .NE. 0) THEN
      WRITE(*,*) ' IER = ', IER
      WRITE(*,*) ' X = ', (X(I), I=1, N)
      WRITE(*,*) ' FNORM = ', FNORM
      WRITE(*,*) ' SUBROUTINE IAST MYERS'
      STOP ' something is wrong '
      END IF
C
C      COMPUTE HYPOTHETICAL LIQUID PHASE CONC'S
C      AND THE LIQUID PHASE MOLE FRACTIONS
C
      DO 4 I=1, N
      ARG=XMK1(I)*X(I)**XMP1(I)

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DGE08260  
DGE08270  
DGE08280  
DGE08290  
DGE08300  
DGE08310  
DGE08320  
DGE08330  
DGE08340  
DGE08350  
DGE08360  
DGE08370  
DGE08380  
DGE08390  
DGE08400  
DGE08410  
DGE08420  
DGE08430  
DGE08440  
DGE08450  
DGE08460  
DGE08470  
DGE08480  
DGE08490  
DGE08500  
DGE08510  
DGE08520  
DGE08530  
DGE08540  
DGE08550  
DGE08560  
DGE08570  
DGE08580  
DGE08590  
DGE08600  
DGE08610  
DGE08620  
DGE08630  
DGE08640  
DGE08650  
DGE08660  
DGE08670  
DGE08680  
DGE08690  
DGE08700  
DGE08710  
DGE08720  
DGE08730  
DGE08740  
DGE08750  
DGE08760  
DGE08770  
DGE08780  
DGE08790  
DGE08800

```

      CO(I)=(X(I)/XMH1(I))*DEXP(ARG)
4  CONTINUE
C
C   TOTAL CARBON COVERAGE
C
      SUM=0.000
      DO 5 I=1,N
      SUM=SUM+QE(I)
5  CONTINUE
      QT=1.000/SUM
C
C   LIQUID PHASE CONCENTRATION
      DO 6 I=1,N
      CE(I)=QE(I)*CO(I)*QT
6  CONTINUE
      RETURN
      END
C-----
      SUBROUTINE FQNM(X,F,XMH1,XMK1,XMP1,QE,N)
C
C   IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C
      DIMENSION XMH1(N),XMK1(N),XMP1(N),QE(N)
C
      DIMENSION X(N),F(N),H(3),P(3),ARG(3),FR(3),P1(3)
C
      DO 1 I=1,N
      X(I)=DMAX1(X(I),1.0D-20)
1  CONTINUE
C
      DO 2 I=1,N
      H(I)=XMK1(I)*XMP1(I)/(XMP1(I)+1.000)
      P(I)=X(I)+H(I)*X(I)**(XMP1(I)+1.000)
2  CONTINUE
      DO 3 I=1,N-1
      F(I)=P(I)-P(I+1)
3  CONTINUE
C
      SUM=0.000
      DO 4 I=1,N
      P1(I)=QE(I)/X(I)
      SUM=SUM+P1(I)
4  CONTINUE
      F(N)=SUM-1.000
C
      RETURN
      END
C-----
      SUBROUTINE FQNJM(X,FJ,XMH1,XMK1,XMP1,QE,N)
C
C   IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C
      DIMENSION XMH1(N),XMK1(N),XMP1(N),QE(N)
C
      DIMENSION X(N),FJ(N,N),FR(3),F1(3),F2(3)

```

```

DGE08810
DGE08820
DGE08830
DGE08840
DGE08850
DGE08860
DGE08870
DGE08880
DGE08890
DGE08900
DGE08910
DGE08920
DGE08930
DGE08940
DGE08950
DGE08960
DGE08970
DGE08980
DGE08990
DGE09000
DGE09010
DGE09020
DGE09030
DGE09040
DGE09050
DGE09060
DGE09070
DGE09080
DGE09090
DGE09100
DGE09110
DGE09120
DGE09130
DGE09140
DGE09150
DGE09160
DGE09170
DGE09180
DGE09190
DGE09200
DGE09210
DGE09220
DGE09230
DGE09240
DGE09250
DGE09260
DGE09270
DGE09280
DGE09290
DGE09300
DGE09310
DGE09320
DGE09330
DGE09340
DGE09350

```

```

C
DO 1 I=1,N
X(I)=DMAX1(X(I),1.0D-20)
1 CONTINUE
DX=1.80D0*(1.0D-6)**(1.0D0/3.0D0)
C
DO 2 I=1,N
PR(I)=XMK1(I)*XMP1(I)*X(I)**XMP1(I)
2 CONTINUE
C
IF (N.EQ.2) THEN
FJ(1,1)=1.0D0+PR(1)
FJ(2,1)=-QE(1)/X(1)**2.0D0
FJ(1,2)=-1.0D0-PR(2)
FJ(2,2)=-QE(2)/X(2)**2.0D0
END IF
IF (N.EQ.3) THEN
FJ(1,1)=1.0D0+PR(1)
FJ(2,1)=0.0D0
FJ(3,1)=-QE(1)/X(1)**2.0D0
FJ(1,2)=-1.0D0-PR(2)
FJ(2,2)=1.0D0+PR(2)
FJ(3,2)=-QE(2)/X(2)**2.0D0
FJ(1,3)=0.0D0
FJ(2,3)=-1.0D0-PR(3)
FJ(3,3)=-QE(3)/X(3)**2.0D0
END IF
C
RETURN
END
SUBROUTINE NMAJLS(N,FCN,FCNJ,NSIG,X, FNORM, ITMAX,WK, IER
+,XMH1,XMK1,XMP1,CE)
C
C NEWTONS METHOD WITH GLOBALLY CONVERGENCE
C STRATEGY FOR SYSTEM OF NONLINEAR EQUATIONS
C
C N - NUMBER OF NONLINEAR EQUATIONS
C X - UNKNOWN VECTOR
C WK - WORK VECTOR OF LENGTH OF N*(5+2*N)
C FCN - SUBROUTINE FOR FUNCTIONAL EVALUATION
C FCNJ - ANALYTICAL JACOBEAN
C NSIG - SIGNIFICANT DIGITS OF UNKNOWNNS
C FNORM - NORM OF FUNCTION VECTOR
C ITMAX - MAXIMUM ALLOWABLE NUMBER OF ITERATIONS
C IER - 0 - SUCCESSFULL ITERATION
C 100 - NORM NOT SUFFICIENTLY SMALL (OPTIMUM)
C 110 - EXCEEDS MAXIMAL NUMBER OF ITERATIONS
C
C IMPLICIT DOUBLE PRECISION(A-H,I,O-Z)
C
C DIMENSION WK(1),X(N),XMH1(N),XMK1(N),XMP1(N),CE(N)
C
C IER=0
C ITER=0
C

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```

DGE09360
DGE09370
DGE09380
DGE09390
DGE09400
DGE09410
DGE09420
DGE09430
DGE09440
DGE09450
DGE09460
DGE09470
DGE09480
DGE09490
DGE09500
DGE09510
DGE09520
DGE09530
DGE09540
DGE09550
DGE09560
DGE09570
DGE09580
DGE09590
DGE09600
DGE09610
DGE09620
DGE09630
DGE09640
DGE09650
DGE09660
DGE09670
DGE09680
DGE09690
DGE09700
DGE09710
DGE09720
DGE09730
DGE09740
DGE09750
DGE09760
DGE09770
DGE09780
DGE09790
DGE09800
DGE09810
DGE09820
DGE09830
DGE09840
DGE09850
DGE09860
DGE09870
DGE09880
DGE09890
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

	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 1.)	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

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
C	IMPLICIT DOUBLE PRECISION(A-H,O-Z)	DGE11130
C		DGE11140
C	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 $t$
$m_\infty$	mass adsorbed at equilibrium
$n$	Freundlich exponent
$q$	carbon loading
$q_0$	initial capacity
$q_\infty$	capacity at equilibrium
$Q$	dimensionless solid phase concentration in particles.
$\bar{Q}$	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 dissolved 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
$\Delta q$	increase in the carbon uptake
$\epsilon$	bed voidage
$\epsilon_p$	particle porosity
$\mu$	viscosity of water
$\tau$	dimensionless time
$\theta_i$	sphericity
$\varphi$	Thiele modulus

$\rho_i$	density of water
$\rho_r$	density of the carbon particle
$\chi^2$	chi square statistics

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