Effect of dissolved oxygen on activated carbon uptake

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Civil Engineering

September 1993

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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Effect of dissolved oxygen on activated carbon uptake

Abuzaid, Nabil Said Fuad, Ph.D.

King Fahd University of Petroleum and Minerals (Saudi Arabia), 1993
EFFECT OF DISSOLVED OXYGEN ON ACTIVATED CARBON UPTAKE

BY

NABIL SAID FUAD ABUZAID

A Dissertation Presented to the
FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

IN

CIVIL ENGINEERING

July 1993
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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Date: September, 1993
This dissertation is dedicated

to

my parents and my wife
ACKNOWLEDGEMENTS

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

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

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

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

اسم الطالب : نبيل سعيد فؤاد أبو سالم
عنوان الرسالة : تأثير الأكسجين المذاب على قدرة الكربون المنشط.
التخصص : هندسة مدنية (مصادر المياه والبيئة).

بنيت دراسات الحرارة المتساوية على الفينيل والكريستال والتيتانوفيون نسبة 20% زيادة في قدرة الكربون نتيجة لوجود الأكسجين المذاب. وقد تم التوصل إلى نفس هذه الظاهرة عندما استعمل عوامل الأكسدة مثل بور وغيرها من المواد البوليمرية بدلًا من الأكسجين الجزيئي.

بينما إذا الدورة على عدم وجود تأثير يذكر للأكسجين المذاب على درجة الكربون على اتصال المواد الأليفة، وقد أشارت النتائج على سهولة الكمبيوتر كسبب لمشكلة هذه الظاهرة بعد الكشف عن تفاعلات ثلاثية الكرات الفينيل.

بعد استخلاصها من الكمبيوتر في شريحة الأكسجين، وبناءً على ذلك تم إجراء وتقييم لتفاعل لتفاعل لتفاعل فينول الأكسجين وعقار الأكسجين مع الفينول.

وقد أشارت التجارب إلى أن الإضاءة الفيزيائية يزيد عند درجة حرارة معينة في حين أن تفاعلات التصلب زادت عند درجة حرارة عالية ولكن المحوتا المتساوية أظهرت على زيادة في قدرة الكربون، أما بالنسبة لتفاعلات تأثير الحرارة فقد أشارت إلى ازمنة الأكسجين الفيزيائي مع إنتاج مركبات الفينول مع ازمنة الحرارة، وقد وجد أن زيادة فصل الكربون على الامتصاص مركبات الفينول تتزايد مع زيادة الأكسجين المذاب كما تزايد ذلك مركبات الكربن التشاذة. وقد وجد أن كفاءة استرجاع الفينول من الكربون انخفضت في حالة وجود الأكسجين من 20% إلى 25% وأن الفردية الإضافية قادمعت على كمية الأكسجين المذاب وكتلة الكربون.

هذا وقد التوصل إلى توصيات رياضية لربط بين القدرة تحت جو الأكسجين وكلاً من كمية الأكسجين المذاب والقدرة بدون الأكسجين المذاب.

وقد بنيت الأثر الزمني أن عناء الإضاف الظاهر قد قضى مع زيادة كمية الأكسجين المذاب وإحداث ماهية الرطوبة في نسبة الأكسجين الفيزيائي مع زيادة الحرارة والانخفاض في الامتصاص مهتماً مع درجة الحرارة بشكل متناسب، في حين أن التفاعل في الامتصاص في حالة وجود الأكسجين وعندما كانت عند المحوتا المتساوية درجة حرارة 35 درجة مئوية.

وقد تم عمل تدوين رياضي يشتمل على التفاعلات الناتجة عن الأكسجين المذاب مع الامتصاص حيث أظهر أن التفاعل من الدرجة الأولى لا يعتمد على كمية الأكسجين. وقد أثبتت التجارب أن تأثيرات الأكسجين المذاب يؤدي منحنى موجي ميدلي إلى منحنى مختلف كلياً.

الموضوع: التفاعل بين جودة الكربون في حالة تجارب الامتصاص والأمدة قد خلص نهائياً، وقد وجد أن النموذج المعروف به، يمتد قدرة جودة على التطبيق بالنتائج المخبرية.

درجة الدكتوراة في الفلسفة
جامعة الملك عبد الله للعلوم والتقنية
الظهران، المملكة العربية السعودية
بسم الله الرحمن الرحيم

١٩٩٣ م.
Dissertation Abstract

Name: Nabil Said Fuad Ahuzaid
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, values for the oxic cases increase proportionally with temperature and inversely with pH, with the highest difference between oxic and anoxic diffusivities at pH 7 and 35°C.

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

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

Doctor of Philosophy Degree
King Fahd University of Petroleum and Minerals
Dhahran, Saudi Arabia
July 1993
CHAPTER 1

INTRODUCTION

1.1 Introduction

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

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

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

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

1. Establish the dependence 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 CO₂, 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 phenom-
enon 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 molecu-
lar 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 modi-
fied 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 (CO₂ purged). The causes of this enhancement were investi-
gated 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 \((C_e/C_i)\) 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.

Albert 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 adsorpive 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 IISSD 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 IISSD 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 IISSD 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 ($k$ or $D_e$ 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 $D_e$ and plot ($S^2$) versus $D_e$. Estimate $D_e$ where $S^2$ is the lowest ($S^2_{\text{min}}$) which is the best estimate for $D_e$, and calculate the 95% confidence interval for the $D_e$ estimate. Check and ensure that $S_{\text{min}}$ 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 $D_e$ model simulation versus the data.
9. the $D_e$ values required for model simulations are $D_e$ for the best fit and the $D_e$ 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 $k_i$ or $D_e$, 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 $k_i$ if the Biot number $> 100$, should be rejected as inaccurate since at this Biot number only intraparticle mass transport is the dominant factor.

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

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

To reduce the time and expense associated with the pilot-plant studies, several mathematical models have been developed to forecast the impact of process variables on adsorber performance. These fixed-bed adsorber models differ in the way they describe possible combinations of external and internal mass transfer resistances, non-linearity of adsorption isotherms, and axial dispersion. Weber and Chakrovorti (37) and Fritz and Schluender (47) proposed a combination of surface diffusion and pore
diffusion transport, which they assume take place simultaneously. This model is known as the 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 HSDM model for over 100 adsorbate-adsorbent systems which included a number of organics found in drinking water and wastewater treatment (38). Concentration history profiles for complex mixtures such as humic substances, expressed in terms of surrogate parameters such as Total Organic Carbon (TOC), single components with or without background organics, and multicomponent systems have been predicted using the HSDM model (38). Accordingly, the HSDM model can be used as an effective engineering tool for preliminary design purposes and if available to design engineer, it may be used for: 1) to plan the scope of pilot-scale studies, 2) interpret pilot-scale test results, 3) investigate multistage adsorber configuration, and 4) estimate preliminary costs of fixed bed adsorbers (38). Many researchers reported the disagreement between the GAC adsorptive capacities determined from isotherm runs and from column and batch experiments (43,44,45,46). As a result, serious problems were experienced in attempting to use the single-rate HSDM model to predict GAC adsorber breakthrough curves (BTC's) for some adsorbate adsorbent systems. Crittenden and Weber (34) had to adjust the adsorptive capacity of activated carbon as given by the adsorption isotherm in order to fit column breakthrough data. Furthermore, they assumed the ratio of the capacities given by that new pseudo isotherm and the isotherm obtained using the standard batch-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:

\[ q = \frac{Q_bC}{1 + bC} \]  \hspace{1cm} (1.1)

where:

- \( q \) = adsorbed solute, mg/g
\[ C = \text{final liquid phase concentrations of adsorbate in solution, mg/l} \]

\[ Q_i = \text{maximum number of mg adsorbed per gms adsorbent when the surface sites are saturated with adsorbate (i.e., a full monolayer) Langmuir isotherm constants, and} \]

\[ b = \text{empirical equilibrium constant related to the energy or net enthalpy of adsorption with units of inverse concentration.} \]

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

\[ \frac{1}{q} = \frac{1}{Q_i b} \frac{1}{C} + \frac{1}{Q_i} \]  \hspace{1cm} (1.2)

or

\[ \frac{C}{q} = \frac{1}{Q_i b} + \frac{C}{Q_i} \]  \hspace{1cm} (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:

\[ q = kC^{1/n} \]  \hspace{1cm} (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:
\[ q_i = \frac{Q_i b_i C_i}{1 + \sum_{i=0}^{n} b_i C_i} \]  \hspace{1cm} (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, $k_e$, 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:

$$
\frac{\partial \rho}{\partial t} + r_p \frac{\partial C_p}{\partial t} = D_p \left( \frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right)
$$

(1.6)

where;

- $\rho_p$ = density of the carbon particle, M/L$^3$,
- $q$ = carbon loading, M adsorbate/M adsorbent,
- $r_p$ = particle porosity,
- $D_p$ = pore diffusion coefficient, L$^2$/T,
- $C_p$ = pore liquid-phase concentration, M/L$^3$,
- $r$ = distance from the center of the spherical particle, L.

The two boundary conditions for the above equation are:

$$
\text{at } r = 0, t : \frac{\partial C_p}{\partial r} = 0
$$

(1.7)
\[ @ \ r = r_0: \ \ D_p \frac{\partial C_p}{\partial r} = k_f (C - C_s) \] (1.8)

where:

- \( d_p \) = diameter of the spherical GAC particle, \( \text{L} \),
- \( C \) = bulk liquid concentration, \( \text{M/L}^3 \),
- \( C_s \) = adsorbate in the liquid film at the solid-liquid interface, \( \text{M/L}^3 \),
- \( k_f \) = external mass transfer coefficient, \( \text{L/T} \).

The initial condition for Equation 1.7 is

\[ @ \ t = 0, 0 \leq r \leq r_0: \ C_p = 0 \] (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:

\[
\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right)
\]  

(1.10)

where:

\( q \) = carbon loading, M adsorbate/M adsorbent.

\( D_s \) = surface diffusion coefficient assumed independent of concentration, \( \text{m}^2/\text{s} \).

\( r \) = distance from the center of the spherical particle, \( \text{m} \).

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.

\[ @ t = 0, 0 \leq r \leq r_0 : \; q = 0 \]  

(1.11)

\[ @ t \geq 0, r = 0; \; \frac{\partial q}{\partial r} = 0 \]  

(1.12)

\[ @ t \geq 0, r = \frac{r_0}{2}; \; 4\pi r_0^2 \int_0^r (-D_s \frac{\partial q}{\partial r}) \; \text{d}t = V_t (C_0 - C) \]  

(1.13)

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

\[ @ r = \frac{r_0}{2}; \ C_s = f(q_e) \]  \hspace{1cm} (1.14)

1.3.2.3 Packed Bed Kinetics

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

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

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

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

\[ = \frac{Qc_0t}{Mq_e + \varepsilon Vc_0} \]
where;

\[ Q = \text{influent flowrate, } L^3/T \]

\[ C_0 = \text{fluid phase concentration of adsorbate in influent, } M/L^3 \]

\[ t = \text{elapsed time, } T \]

\[ M = \text{total mass of adsorbent in the bed, } M \]

\[ q_e = \text{adsorbent phase concentration at equilibrium with } C_0, \text{ in the fluid phase, } M \]

\[ \varepsilon = \text{ratio of void volume to total bed volume} \]

\[ V = \text{total bed volume, } L^3 \]

The dimensionless solute distribution parameter \( D_\theta \) is defined as

\[ D_\theta = \frac{\text{mass of adsorbate in solid phase at equilibrium}}{\text{mass of adsorbate in liquid phase at equilibrium}} = \frac{\rho \cdot q_e (1 - \varepsilon)}{\varepsilon C_0} \]

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

The dimensionless Biot number, \( B_i \), is defined as:

\[ B_i = \frac{\text{rate of liquid phase mass transfer}}{\text{rate of surface diffusion within the particle}} = \frac{(1 - \varepsilon) k_f r_0}{\varepsilon D_s \theta_i D_\theta} \]

where;

\[ k_f = \text{film transfer coefficient, } L/T \]

\[ D_s = \text{surface diffusion coefficient, } L^2/T \]

\[ \theta_i = \text{sphericity (dimensionless ratio of the surface area of the equivalent volume sphere to the actual surface area of the particle).} \]
\( r_0 = \) particle radius, \( \text{L.} \)

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

\[
St = \frac{k_f \tau (1 - \varepsilon)}{r_0 c_0}
\]

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

The surface diffusion modulus \( E_s \) 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:

\[
E_s = \frac{D_s D_x}{r_0^2} = \frac{St}{B_t}
\]

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

\[
J_s = -D_s p_c \frac{\partial q}{\partial t}
\]

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, \( \text{L.} \)

\( t = \) 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.

\begin{equation}
@ t = 0, 0 \leq r \leq \frac{r_0}{2}: q = 0 \tag{1.11}
\end{equation}

\begin{equation}
@ t \geq 0, r = 0: \frac{\partial q}{\partial r} = 0 \tag{1.12}
\end{equation}

\begin{equation}
@ t \geq 0, (r = r_p, t): \frac{\partial q}{\partial r} = \frac{k_r}{r_p D_0} (C - C_n) \tag{1.15}
\end{equation}

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

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

\begin{equation}
\frac{\partial C}{\partial t} = - V \frac{\partial C}{\partial Z} - \frac{3 (1 - \epsilon_n)}{\epsilon R} k_r (C - C_s) \tag{1.16}
\end{equation}

where,

\( V \) = interstitial velocity

\( Z \) = longitudinal dimension

The initial condition of Equation 1.16 is

\begin{equation}
@ t < \tau, 0 \leq Z \leq L_n: C = 0
\end{equation}

and the boundary condition is

\begin{equation}
@ t \geq 0, Z = 0: C = C_n
\end{equation}
To couple the solid and liquid phase mass balance equations, the surface concentration of adsorbate in the liquid phase $C_{L}(t)$ 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

$$q = KC_{L}^{1/n}$$

The three main equations contain three independent variables, mass throughput $T$, radial position $r$, and axial position $Z$. Dependent variables are liquid phase concentration $C_1(Z, T)$, liquid phase concentration at the exterior surface of the adsorbent $C_2(Z, T)$, 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. Alkylphenolols, 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 these 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.

<table>
<thead>
<tr>
<th>Aliphatics</th>
<th>Alkylphenols</th>
<th>Wastewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>Phenol</td>
<td>domestic</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>1-Methylphenol</td>
<td>petrochemicals</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>2-Nitrophenol</td>
<td></td>
</tr>
<tr>
<td>Tribromomethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Common Name</td>
<td>Structural Formula</td>
</tr>
<tr>
<td>---------------------------</td>
<td>-------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>Methylchloroform</td>
<td><img src="image" alt="Methylchloroform" /></td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td></td>
<td><img src="image" alt="1,1,2,2-Tetrachloroethane" /></td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>Chloroform</td>
<td><img src="image" alt="Trichloromethane" /></td>
</tr>
<tr>
<td>Tribromomethane</td>
<td>Bromoform</td>
<td><img src="image" alt="Tribromomethane" /></td>
</tr>
<tr>
<td>Phenol</td>
<td></td>
<td><img src="image" alt="Phenol" /></td>
</tr>
<tr>
<td>2-Methylphenol</td>
<td>o-Cresol</td>
<td><img src="image" alt="2-Methylphenol" /></td>
</tr>
<tr>
<td>4-Nitrophenol</td>
<td></td>
<td><img src="image" alt="4-Nitrophenol" /></td>
</tr>
</tbody>
</table>

**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 dependence 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

APPARATAS AND EXPERIMENTAL PROCEDURE

2.1 General

2.1.1 Chemicals and Materials

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

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

2.1.2 Apparatus

2.1.2.1 Shakers

Karl Kolb shakers, purchased from Scientific Technical Supplies, West Germany, were used in the loading experiment. The shakers were equipped with temperature control from zero to 100°C and a variable shaking frequency.
Table 2.1 Physical Properties of Filtrasorb-400 Activated Carbon

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Surface Area (N₂ BET Method), m²/g</td>
<td>824</td>
</tr>
<tr>
<td>Bulk Density, g/cm³</td>
<td>0.74</td>
</tr>
<tr>
<td>Particle Density Wetted in Water, gm/cm³</td>
<td>1.3-1.4</td>
</tr>
<tr>
<td>Pore Volume, cm³/gm</td>
<td>0.94</td>
</tr>
<tr>
<td>Effective Size (dₚₐ), cm</td>
<td>0.055-0.065</td>
</tr>
<tr>
<td>Uniformity Coefficient (dₚₐ/dₚₐ)</td>
<td>1.6-2.1</td>
</tr>
<tr>
<td>Particle Size Used in Experiments (dₚₐ), cm</td>
<td>0.156</td>
</tr>
</tbody>
</table>
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/splitless injector at 250°C. The column was DB-1, 25 m x 0.25 mm i.d., with a 0.3 μm film thickness. The carrier gas was Helium at a flow rate of 6 mL/min. The oven temperature was programmed from 50°C to 300°C at 10°C /min with a zero initial time and 5 min. final time. The ion source temperature was 250°C, the emission was 100 μA, and the acceleration voltage was 5 KV.
Figure 2.1: Schematic Diagram of the Kinetics Experimental setup
Figure 2.2: Schematic Diagram of the Columns setup
Data acquisition was carried out with a DS5000 data system. For qualitative analysis of the sample, data were acquired for 30 min. For quantitative analysis of phenol yield, data acquisition was carried out for only 10 min.

2.1.2.5 UV Spectrophotometry

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

2.1.2.6 Total Organic Carbon Analyzer

Beckman 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 KH₂PO₄ 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 adsorbate volatilization, and adsorption of adsorbate onto walls of the container. All bottles were placed in a shaker for a period of 14 days. At the end of the equilibration period, samples were withdrawn from each bottle, filtered through 0.45 μm Millipore filter paper, and analyzed for adsorbate 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 tri bromomethane,
with the following modifications: the purging process was applied to the buffer solution before the addition of the chemicals and the 160-ml bottles were filled completely with the adsorbates to avoid evaporation. Direct measurement of total carbon was done by quickly injecting the sample into a Beckmen Model 915 Total Carbon Analyzer. For each sample, inorganic carbon was measured twice, at the beginning and the end of the equilibration period, to check for the possibility of biological activity. The organic carbon was calculated by subtracting inorganic carbon (if any) from the total carbon. Total Organic Carbon (TOC) measurements of known concentrations of target compounds indicated that the ratio of measured to theoretical TOC was in the range of 0.9-0.97, while the conversion factors between measured TOC and concentrations in mg/l were, 5.92, 7.25, 11.36, and 19.23 for 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloromethane, and tribromomethane, respectively.

2.2.1.3 Wastewater

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

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

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

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

2.2.3 Effect of Different Levels of Dissolved Oxygen

In addition to the oxic and anoxic conditions, two other DO levels were introduced for phenol and o-cresol. Nitrogen was slightly purged until a moderate amount of DO (3-4 mg/l) was achieved. Air was purged so that saturation with air (9.0 mg/l) can be achieved. By this, four levels of DO were achieved and denoted as DO 1
(anoxic), DO 2 (moderate), DO 3 (purged with air), and DO 4 (purged with pure oxygen (oxic)). Each set of bottles included two bottles without activated carbon to serve as blanks to check for sorbate volatilization, and adsorption of sorbate onto walls of the container. All bottles were placed on a shaker at room temperature of about 21°C for a period of 14 days. At the end of the equilibration period, samples were withdrawn from each bottle, treated and analyzed similar to the procedure mentioned above.

2.3 Extraction Experiments

GAC samples used in the anoxic (DO 1) and "pure oxygen purged" (DO 4) phenol solutions and those used in the anoxic, "air purged" (DO 3), and "pure oxygen purged" o-cresol solutions were extracted in a Soxhlet extractor. GAC samples were first extracted for 24 hours with methanol and then with methylene chloride for 3 days following the procedure of Vidic et al. (14). The extracts were dried with anhydrous Na₂SO₄, 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 hatch kinetic experiments under varied temperature, temperatures of 8°C and 35°C were controlled with water circulating from temperature controlled water baths surrounding water jackets. The mixing tanks were connected to the water baths after finishing the purging process and maintaining the the required DO concentration. Samples were taken at predetermined time intervals for concentration measurements until equilibrium, indicated by constant concentration for three consecutive samples, was attained. The cumulative volume of these samples constituted less than 5
percent of the total initial volume in the mixer.

2.5 Column Experiments

Phenol and o-cresol breakthrough curves (BTCs) were obtained under oxic and anoxic conditions using (60 cm long and 2.54 cm I.D.) glass columns charged with 130 g of activated carbon. The influent adsorbate concentrations were maintained at 70 mg/l for all column experiments. The feed solution to the columns was prepared using deionized water buffered similar to the loading experiments in order to keep neutral pH. The activated carbon columns were operated in an upflow mode at a flow rate of 100 ml/min resulting in 0.197 m/min (superficial velocity) at room temperature. The anoxic experiments were performed by purging the feed solution with nitrogen and keeping the solution under a head space of nitrogen. Due to the fact that 144 l. of feed solution was pumped through the column per day it was not possible to completely remove DO from the adsorbate solution and have zero DO content; and hence, DO concentration was in the range of (0.1-0.4) mg/l. The oxic column experiments were performed by purging the adsorbate solution with pure oxygen until saturation was reached and a DO concentration of 30 mg/l was measured. Samples were taken from the effluents for concentration measurements.
Chapter 3

EFFECT OF DISSOLVED OXYGEN ON ACTIVATED CARBON ADSORPTION OF DIFFERENT CHEMICALS

3.1 Introduction

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

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

From the previous work, it was felt that this phenomenon needed more investigation, particularly, because the number of compounds studied was not deemed sufficient to arrive at solid conclusions. Accordingly, in this study, another aromatic compound,
4-nitrophenol, is investigated in addition to phenol and o-cresol. In order to increase understanding of the enhancement nature, oxidizing agents were applied to the phenol solution to investigate their effect on the uptake. Hydrogen peroxide and potassium permanganate were used for this purpose. The adsorption of four aliphatic compounds is also studied, namely, trichloromethane (chloroform), tribromomethane (bromoform), 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane. The aforementioned organic compounds were selected for the purpose of this study because they are common constituents of industrial wastewater effluents, particularly, oil and petrochemicals related industries. The selection was also designed to investigate the dependence of the adsorption enhancement phenomenon, if existent, on the following chemical parameters:

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

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

3.2.1 Adsorption of Aromatics

After the determination of residual concentration of adsorbates, the single-solute isotherms for each of the compounds under study obtained at 21°C were modelled by the Freundlich equation; \( q = ke^{bh} \). 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 \( 4 \)-nitropheno produced 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 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, nitropheno 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 later 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 $T = 21^\circ C$ and pH of 7 Along with Best Fit Freundlich Curves Using constants Given in Table 3.1.
Figure 3.3: Uptakes of o-Cresol at T = 21°C and pH of 7, Along with Best Fit Freundlich Curves Using Constants Given in Table 3.1.
Figure 3.4: Uptakes of 4-Nitrophenol at 21°C and pH of 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 3.1.
phenolics does not. In their work on 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 Oxic GAC Sample of Phenol
3.2.3 Oxidizing Agents

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

Recovery analysis performed on GAC extracts from both isotherms, indicated that only 26% of the adsorbed phenol in the case of hydrogen peroxide and a meager 2.1% in the case of potassium permanganate was extractable. Furthermore, GC-MS analysis of such extracts confirmed the presence of significant quantities of the same dimers and trimers observed in the anoxic 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 (NII₄)₂S₂O₈ 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 $T = 21^\circ$C and pH of 7.
Figure 3.8: Uptakes of Phenol with and without Potassium Permanganate Versus Residual Concentration at $T = 21^\circ C$ 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 show that the researchers who had contradictory results to this study were dealing with another phenomena 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 overall reaction presented in scheme 1 can be shown as

\[ 2 \text{C}_6\text{H}_5\text{OH} + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_{12}\text{O}_2\text{H}_{10} + \text{H}_2\text{O} \]

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 $T = 21^\circ C$ and pH of 7.
Evidently then, at low DO to GAC mass ratio, the enhancement in uptake is limited by the mass of oxygen present in the test environment while at high DO to GAC mass ratio, corresponding to low GAC mass the additional uptake is limited by the mass of GAC or availability of adsorption sites for the telomerization reactions to take place.

Another important parameter that appears to influence this enhancement in uptake under oxic conditions is the adsorbability of the compound as reflected by its retention capacity. The additional uptake attained in the presence of oxygen expressed as a percentage of the anoxic uptake is a decreasing nonlinear function of the anoxic uptake (Figure 3.10). However, such representation of the oxygen-induced enhancement in the uptake of the GAC although readily interpretable in terms of the percentage increase in the extended service life of an adsorber, is misleading since the low anoxic capacities corresponding to high GAC masses and relatively low DO to GAC mass ratio exhibit the highest incremental capacities. To provide more insight into this phenomenon and its dependence on the adsorbability of the pollutant, the actual additional uptake is plotted as a function of the anoxic isotherm uptake in Figure 3.11, since it is directly related to the stoichiometry of the telomerization reactions responsible for this enhancement in view of the limited amount of molecular oxygen and adsorption sites available in the test environment. Figure 3.11 indicates that the additional uptake attained by the presence of oxygen in the test environment is initially an increasing function of the anoxic adsorptive uptake of GAC. Such relationship suggests that the extent of the telomerization taking place on the activated carbon surface is strongly influenced by the retained adsorbate. The data for α-cresol and nitrophenol clearly show that at high oxic capacities the aforementioned additional uptake becomes independent of the amount of adsorbate retained under anoxic conditions.
Figure 3.10: Relationship Between Percentage Additional Uptake and the Anoxic Uptake at $T = 21^\circ C$ and pH of 7.
Figure 3.11: Relationship Between Additional Uptake and the Anoxic Uptake at $T = 21^\circ$ C and pH of 7.
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 $T = 21^\circ C$ and pH of 7.
Figure 3.13: Adsorption Isotherm for Bromoform at T = 21°C and pH of 7.
Figure 3.14: Adsorption Isotherm for 1,1,1-Trichloroethane at $T = 21^\circ C$ and pH of 7.
Figure 3.15: Adsorption Isotherm for 1,1,2,2-Tetrachloroethane at $T = 21^\circ C$ and pH of 7.
Figure 3.16: Uptakes of TOC for I.W.W, Sample Location 1, at $T = 21^\circ C$ and pH of 7.
Figure 3.17: Uptakes of TOC for I.W.W., Sample Location 2, at $T = 21^\circ$C and pH of 7.
Figure 3.18: Uptakes of TOC for I.W.W., Sample location on 3, at
T = 21° C and pH of 7.
Figure 3.19: Uptakes of TOC for D.W.W at $T = 21^\circ C$ and pH of 7.
Biodegradation was discounted as a possible cause for this increase in uptake through monitoring of inorganic carbon. Once again the impact of oxygen on the retention uptake of GAC was more pronounced at low concentrations. Thus in a practical operation of GAC adsorbers which are usually designed to meet stringent effluent criteria, the addition of oxygen to the feed water results in a significant extension of their service life. The reason for the I.W.W response is that the samples contained aromatics which have similar characteristics to the phenolics, while, for the D.W.W, the reason might be the existence of chemicals in the influent stream coming from ARAMCO facilities. Table 3.1 presents the Freundlich model constants for the compounds and waste water samples studied.

To corroborate the findings of this study and to make sure that these differences are not due to experimental errors, statistical analysis was carried out, and the null hypothesis that attributes the differences in uptakes of activated carbon due to the presence of DO to random error was tested. The Analysis of Variance was constructed following the methodology of Montgomery (57), whereby the ratio of the mean squares of the variable of interest (residual concentration) to that of the error is calculated. The F-value is then compared with a corresponding value from a table under the same degrees of freedom as the data and a specified probability of error. The result of the analysis showed that the null hypothesis was strictly rejected.
Table 3.1. Freundlich Model Constants for the Compounds Studied at pH = 7 and a temperature of 21°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Isotherm Type</th>
<th>k (mg/g)(L/mg)^{1/n}</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloroform</td>
<td>oxic</td>
<td>1.09</td>
<td>0.63</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>1.14</td>
<td>0.61</td>
<td>0.99</td>
</tr>
<tr>
<td>bromoform</td>
<td>oxic</td>
<td>5.19</td>
<td>0.43</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>5.33</td>
<td>0.42</td>
<td>0.99</td>
</tr>
<tr>
<td>1,1,1trichloroethane</td>
<td>oxic</td>
<td>0.76</td>
<td>0.34</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>0.77</td>
<td>0.33</td>
<td>0.98</td>
</tr>
<tr>
<td>1,1,2,2tetrachloroethane</td>
<td>oxic</td>
<td>3.01</td>
<td>0.22</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>2.99</td>
<td>0.23</td>
<td>0.97</td>
</tr>
<tr>
<td>D.W.W</td>
<td>oxic</td>
<td>0.016</td>
<td>2.3</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>0.0013</td>
<td>2.9</td>
<td>0.95</td>
</tr>
<tr>
<td>I.W.W loc. 1</td>
<td>oxic</td>
<td>0.26</td>
<td>0.64</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>1.84</td>
<td>0.67</td>
<td>0.94</td>
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<tr>
<td>I.W.W loc. 2</td>
<td>oxic</td>
<td>0.66</td>
<td>0.94</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>0.03</td>
<td>1.65</td>
<td>0.94</td>
</tr>
<tr>
<td>I.W.W loc. 3</td>
<td>oxic</td>
<td>1.58</td>
<td>0.65</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>0.1</td>
<td>1.59</td>
<td>0.95</td>
</tr>
<tr>
<td>o-cresol</td>
<td>oxic</td>
<td>190.4</td>
<td>0.13</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>88.6</td>
<td>0.19</td>
<td>0.98</td>
</tr>
<tr>
<td>phenol</td>
<td>oxic</td>
<td>53.5</td>
<td>0.18</td>
<td>0.97</td>
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<td></td>
<td>anoxic</td>
<td>31.7</td>
<td>0.24</td>
<td>0.99</td>
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<tr>
<td>4-nitrophenol</td>
<td>oxic</td>
<td>87.0</td>
<td>0.15</td>
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<td></td>
<td>anoxic</td>
<td>73.3</td>
<td>0.16</td>
<td>0.94</td>
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</table>

* R² 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: \( q = k \cdot c^{1/n} \).

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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Isotherm Type</th>
<th>k (mg/g)(L/mg)</th>
<th>1/n</th>
<th>1/n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-cresol</td>
<td>oxic, pH 3</td>
<td>134.3</td>
<td>0.14</td>
<td>0.94</td>
<td></td>
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<tr>
<td></td>
<td>anoxic, pH 3</td>
<td>109.6</td>
<td>0.17</td>
<td>0.97</td>
<td></td>
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<td>o-cresol</td>
<td>oxic, pH 7</td>
<td>190.4</td>
<td>0.13</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anoxic, pH 7</td>
<td>88.6</td>
<td>0.19</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>o-cresol</td>
<td>oxic, pH 11</td>
<td>65.4</td>
<td>0.20</td>
<td>0.97</td>
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</tr>
<tr>
<td></td>
<td>anoxic, pH 11</td>
<td>29.4</td>
<td>0.19</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>oxic, pH 3</td>
<td>61.4</td>
<td>0.19</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anoxic, pH 3</td>
<td>36.1</td>
<td>0.24</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>oxic, pH 7</td>
<td>83.5</td>
<td>0.18</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anoxic, pH 7</td>
<td>31.7</td>
<td>0.24</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>oxic, pH 11</td>
<td>32.8</td>
<td>0.31</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anoxic, pH 11</td>
<td>12.5</td>
<td>0.37</td>
<td>0.95</td>
<td></td>
</tr>
</tbody>
</table>

* R² is the coefficient of determination
Figure 4.1: Phenol uptakes at pH 3.0 and T = 21°C. Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.
Figure 4.2: Uptakes of Phenol at pH of 7 and T = 21°C Along with Best Fit Freundlich Curves Using constants Given in Table 4.1.
Figure 4.3: Phenol Uptakes at pH 11 and $T = 21^\circ$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 = 21ºC. Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.
Figure 4.6: Uptakes of o-Cresol at pH 11 and T = 21° C. Along with Best Fit Freundlich Curves Using Constants Given in Table 4.1.
The extraction efficiency of the adsorbates from the GAC was generally lower in the oxic case compared to the anoxic one, thus confirming the findings of Grant and King (13) and Vidic and Suidan (14).

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

Figures 4.7 and 4.8 present the additional uptake as a percentage of the anoxic uptake versus the anoxic uptake for the various pH phenol and o-cresol cases, respectively. From the figures, it is seen that all the curves decrease nonlinearly with increase in the anoxic uptake. The data strongly suggests that at high sorbate concentrations most of the adsorption sites are occupied by the parent compound and thus relatively fewer sites are available for the oxygen-induced telomerization products. It can also be noted that the order of enhancement is pH 7 > pH 11 > pH 3 for both phenol and o-cresol. Figures 4.9 and 4.10 present the theoretical pC-pH diagrams calculated by the following relation; \[ \text{pH} = \text{pK}_a + \log \left( \frac{\text{salt}}{\text{acid}} \right) \]. The salt and acid in the aforementioned equation are the conjugate base and acid. To be able to understand and rationalize the observed trends in Figures 4.7 and 4.8, it is essential to know the consequences of pH variations on adsorption and reaction of the selected phenols. Low pH means abundance of protons in the sorbate solution and completely acid forms of phenol or o-cresol.
Figure 4.7: Relationship Between the Additional Uptake and the Anoxic Uptake for Phenol at Different pHs and $T = 21^\circ$ C.
Figure 4.8: Relationship Between the Additional Uptake and the Anoxic Uptake for o-Cresol at Different pHs and T = 21 C.
Figure 4.9: pC–pH Diagram for Phenol
Figure 4.10: pC–pH Diagram for o-Cresol
pH 7 means neutral solution and mostly acid forms of the compounds, while at pH 11 there are very few protons and the compounds are expected to be in the salt forms. Phenol is expected to ionize more than o-cresol because phenol has a lower pKa (9.96) compared to o-cresol (10.2) (60). Actually, the scanning performed in order to find the optimum wavelength for the spectrophotometric determination of phenol and o-cresol at pH 11 showed that for phenol the wavelength corresponding to maximum absorbance shifted from 270 nm to 288 nm, which is an indication of significant ionization, and hence, formation of phenolate ions, while no change was observed for o-cresol. It can be stated that phenol ionizes more easily than o-cresol which can also be explained by the electron donation property of the methyl group in the case of o-cresol (60). The response of adsorption and chemical reactions to the above solute conditions is as follows: adsorption increases when the number of protons increase (low pH) and vice versa which agrees with the findings of many researchers (17, 18, 19, 22). While, the adsorption of unionized compounds is more than the ionized forms, ions have higher affinity for reaction than unionized compounds (13). Extracts of the carbon used in the oxic pH 3 isotherm were analyzed via GC-MS and found to contain only traces of the dimers and trimers observed in the isotherm extracts at pH 7. The explanation for this finding can best be illustrated graphically. Figure 4.11 illustrates the response of adsorption, reaction, and adsorption-reaction combination to pH variation. In fact, the curve of adsorption-reaction shows that increasing pH has two opposing effects on the phenomenon (i.e. increasing reaction and decreasing adsorption), which yields the trend found in Figures 4.7 and 4.8 for the oxic cases.

The ratio of sorptive uptake at different pH and DO levels to the uptake of the anoxic isotherm at pH 7 versus the residual sorbate concentration is depicted in Figures 4.12 and 4.13.
Figure 4.11: Hypothetized Effect of pH on Adsorption—Reaction Combination.
Figure 4.12: Phenol Uptakes at Different pHs Relative to the Uptake at Neutral pH Versus Residual Concentration, at $T = 21^\circ C$. 

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

from difreb01
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;

$$\Delta q = K_1 [\text{pH} - 10^{-7}]^{-m} C_e^{n_1}$$  \hspace{1cm} (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, \(\text{pH}^+\) 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

$$\frac{1 + K_1 [\text{pH} - 10^{-7}]^{-m} C_e^{n_1}}{K_2^{n_2}}$$  \hspace{1cm} (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 \( C_r \) 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 $T = 8^\circ C$ and pH of 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.
Figure 4.15: Uptakes of Phenol at $T = 21^\circ C$ and pH of 7 Along with Best Fit Freundlich Curves Using constants Given in Table 4.2.
Figure 4.16: Phenol Uptakes at T 35°C and pH 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.
Figure 4.17: α-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 4.1B: o-Cresol Uptakes at T = 21 °C. and pH 7, Along with Best Fit Freundlich Curves Using Constants Given in Table 4.2.
Figure 4.19: o-Cresol Uptakes at T = 35° C. and pH 7 Along with Best Fit Freundlich Curves Using Constants given in Table 4.2.
However, the increase in sorptive uptake was strongly dependent upon temperature. For phenol, the percentage enhancement in sorptive uptake at 1 mg/l residual concentration was 134%, 163%, and 200% at temperatures of 8°C, 21°C, and 35°C, respectively, while for o-cresol, the percentage enhancement in uptake at 1 mg/l residual concentration was 90%, 115%, and 130% at temperatures of 8°C, 21°C, and 35°C, respectively. Table 4.2 lists the Freundlich model constants for the data already shown in the aforementioned Figures. It is noted from the table that the value of 1/n was higher in the case of anoxic compared to oxic isotherms. It is also seen that the value of 1/n reflecting the dependence of the sorptive uptake on the liquid phase concentration increased with temperature. The percentage additional uptake caused by the presence of DO is shown as a function of the anoxic uptake in Figure 4.20 and 4.21 for phenol and o-cresol, respectively. It is apparent that the relative enhancement in uptake is a nonlinearly decreasing function of the anoxic uptake, which can be attributed to sites limitation at high anoxic capacities. It is also noted from Figures 4.20 and 4.21 that the order of percentage enhancement was at T = 8°C < T = 21°C < T = 35°C. Not only do the relative increases depicted in Figures 4.22 and 4.23 suggest that increasing temperatures favor the telomerization reaction but also the actual magnitudes of these incremental capacities point to the same finding which is consistent with the observation of Grant and King (13). An endothermic telomerization reaction would rationalize the observed effects of temperature on adsorption under oxic conditions. However, the differences between the additional capacities at 21° and 35°C are much more pronounced at high anoxic capacities than at low ones, and this is also true between 21° and 8°C. At low anoxic capacities corresponding to low DO to GAC mass ratios, oxygen limitation effects on telomerization become significant, and thus reduction in solubility of oxygen at high temperatures tend to accent such limitation.
Table 4.2. Freundlich Constants for Phenol and o-Cresol at Various Temperatures and pH 7.

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

* \( R^2 \) is the coefficient of determination
Figure 4.20: Relationship Between the Additional Uptake and the Anoxic Uptake for Phenol at Different Temperatures and pH 7.
Figure 4.21: Relationship Between the Additional Uptake and the Anoxic Uptake for o-Cresol at Different Temperatures and pH 7.
Figure 4.22: Phenol Uptakes at Different Temperatures Relative to the Uptake at Room Temperature Versus Residual Concentration.
Figure 4.23: o-Cresol Uptakes at Different Temperatures Relative to the Uptake at Room Temperature Versus Residual Concentration.
These results are contradictory to those of Vidic and Suidan (14) who noted that increasing the temperature from 21°C to 35°C did not have significant effects on the adsorption-enhancement phenomenon attributed to sorbate telomerization.

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

In an attempt to determine the heat of adsorption for phenol and o-cresol, the Arrhenious equation was used. The equation is:
\[ k = k_0 \exp\left(\frac{-\Delta H}{R_a T}\right) \]  

(4.3)

which can linearized as;

\[ \log k = k_0 - \frac{\Delta H}{2.3 R_a T} \]  

(4.4)

where, \( k \) is the Freundlich constant, \( k_0 \) is the intercept, \( R_a \) 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:

\[ q = k_0 \exp\left(-\frac{\Delta H}{R_a T}\right) C^n \]  

(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 ABUK
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;

\[ q = ke^{1/n} \]

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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Isotherm Type</th>
<th>k (mg/g)(L./mg)</th>
<th>1/n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-cresol</td>
<td>anoxic, DO 1</td>
<td>88.6</td>
<td>0.190</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>oxic, DO 2</td>
<td>126.8</td>
<td>0.173</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>oxic, DO 3</td>
<td>151.7</td>
<td>0.154</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>oxic, DO 4</td>
<td>190.4</td>
<td>0.130</td>
<td>0.99</td>
</tr>
<tr>
<td>phenol</td>
<td>anoxic, DO 1</td>
<td>31.7</td>
<td>0.240</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>oxic, DO 2</td>
<td>48.3</td>
<td>0.223</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>oxic, DO 3</td>
<td>61.1</td>
<td>0.203</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>oxic, DO 4</td>
<td>83.5</td>
<td>0.180</td>
<td>0.97</td>
</tr>
</tbody>
</table>

* R² is the coefficient of determination
Figure 5.1: Uptakes of Phenol at $T = 21$ C. and pH of 7 Along with Best Fit Freundlich Curves Using constants Given in Table 5.1.
Figure 5.2: Uptakes of Phenol Under Different Oxygen Levels at $T = 21^\circ C$ and pH of 7.

- DO LEVEL 1
- DO LEVEL 2
- DO LEVEL 3
- DO LEVEL 4

Absorbent Loading (mg/g)

Phenol Concentration (mg/l)
Figure 5.3: Uptakes of o-Cresol at $T = 21^\circ C$ and pH of 7 Along with Best Fit Freundlich Curves Using Constants Given in Table 5.1.
Figure 5.4: Uptakes of o-Cresol Under Different Oxygen Levels at T = 21°C and pH of 7.
5.2.2 Extraction Studies

As mentioned in chapter 3, GC-MS analysis of the extracts of the GAC samples used in the oxic and anoxic phenol experiments resulted in dimers which could be identified as, 2,2-dihydroxy-1,1-biphenyl and 4-phenoxyphenol and a trimer on the GAC used in the oxic loading while only traces of the dimers were detected in the anoxic extracts. However, more work was done in this stage. For o-cresol, the above analysis was performed on the cases of DO levels 1, 3, and 4 (i.e anoxic, "purged with air", and "purged with pure oxygen". Results of the GC-MS scans are presented for the anoxic, "purged with air", and oxic cases in Figures 5.5, 5.6, and 5.7, respectively. It is apparent that the anoxic extracts contained much higher concentration of o-cresol (peak at 120 nm) and trace amounts of the dimers represented by the peaks at scan numbers 342 and 364 relative to the oxygenated samples. Significant amounts of the above two dimers, trimers represented by the peaks at scan numbers 462 and 475, and higher telomers were detected in the two extracts from the partially and fully oxygenated samples. Interestingly, the intensity of the peaks showing such dimers and trimer was higher in DO level 4 sample (DO around 30 mg/l) compared to DO level 3 (DO around 9 mg/l) as shown in Figures 5.6 and 5.7. This telomerization coupled with lower recovery of the original adsorbate explains the results of the loadings presented in Figures 5.1 and 5.3 and Table 5.1. It must be emphasized that no such telomers were found either in the extracts of virgin carbon or in the original stock solutions which suggests that occurrence of telomerization reaction on the activated carbon surface in the presence of molecular oxygen is the reason for the higher oxic uptakes.
Figure 5.5: GC-MS Total Ion Chromatogram for the Anoxic GAC Sample of α-Cresol
Figure 5.6: GC–MS Total Ion Chromatogram for the "Air Purged" GAC Sample of o–Cresol.
Figure 5.7: GC–MS Total Ion Chromatogram for the Oxic GAC Sample of o–Cresol
Since the telomerization was observed to occur on the activated carbon surface, the essential elements for the initiation and progression of such reactions are oxygen, the adsorbate, and reaction sites. For a given adsorbate-adsorbent system at known conditions of pH and temperature, the extent of telomerization is most strongly influenced by two parameters namely the mass of oxygen needed for the reaction and the availability of adsorption sites i.e. mass of GAC. This dual-limitation of the uptake enhancement, attributed to telomerization is best illustrated by Figures 5.8 and 5.9 which shows the additional sorptive uptake attained under oxic conditions versus the DO to GAC mass ratio at the three oxic conditions (DO levels: 2, 3, and 4) for phenol and o-cresol. The data shows that for DO level 2 (lowest amount of oxygen), the increase in the additional uptake relative to the increase in DO to GAC mass was the highest; since the amount of DO was low and thus the ratio of DO to GAC mass was low, the enhancement in uptake is limited by the mass of oxygen present in the test environment. On the other hand, in the case of DO level 4 (highest amount of oxygen), there is almost no effect of DO to GAC mass ratio on the additional uptake after a DO/GAC mass ratio of 0.007 and 0.0117 for phenol and o-cresol, respectively. This can be explained by the sites limitation at this high ratio of DO to GAC mass and hence the additional uptake is limited by the mass of GAC or availability of adsorption sites for the telomerization reaction to take place. Interestingly, and inspite of some scatter, the data of DO level 3 is in between the two trends, in agreement with the plausible explanation given. In fact, the three curves can be taken as one continuous curve reflecting the relation between the additional uptake and the normalized DO contents.
Figure 5.8: Relationship Between Additional Uptake and the Ratio of DO to the GAC Mass for Phenol at $T = 21^\circ C$ and pH of 7.
Figure 5.9: Relationship Between Additional Uptake and the Ratio of DO to the GAC Mass for o-Cresol at $T = 21^\circ$ C. and pH of 7.
Figure 5.10: Relationship Between the Additional Uptake and the Anoxic Capacity for Phenol at $T = 21^\circ C$ and pH 7.
Figure 5.11: Relationship Between the Additional Uptake and the Anoxic Capacity for o-Cresol at $T = 21^\circ$C and pH 7.

DO LEVEL 4
DO LEVEL 3
DO LEVEL 2

ANOXIC CAPACITY (mg/g)

ADDITIONAL CAPACITY (mg/g)
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, 180, 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)
\[ \Delta q = M_1 | R\sub{n} | \sub{b} \]  \hspace{1cm} (5.1) \\

where, \( \Delta q \) is the change in uptake relative to the anoxic uptake, mg g\(^{-1}\). \( R\sub{n} \) is the ratio of DO to GAC mass, \( M_1 \) is the model constant (\( = 827 \) and \( -126 \) 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 anoxic uptake was the dependent variable while the anoxic uptake and the GAC mass ratio were the independent variables. The equation took the form:

\[ q = q_0 + L \cdot |q_0|^{b} |R\sub{n}|^{d} \]  \hspace{1cm} (5.2) \\

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

\[ q = q_0 + (M_1 | R\sub{n}|^b) \]  \hspace{1cm} (5.3) \\

while Equation 5.2 can be expressed as:

\[ \Delta q = L \cdot |q_0|^{b} |R|^{d} \]  \hspace{1cm} (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 5.14: Observed and Predicted Phenol Uptakes. Data from Ref. 14.
Figure 5.15: Observed and Predicted Uptakes for o-Cresol, Data from Ref. 14.
Figure 5.16: Observed and Predicted Uptakes for o-Cresol, Data from Ref. 14.
Using the aforementioned values of R and the anoxic uptakes given by the anoxic loading the oxic loading was predicted by the use of Models 1 and 2. The objective of presenting the data on both logarithmic and linear scales is to clarify the whole range of data, since the logarithmic scale will take care of the low values while the high values will be better illustrated by the linear scale. Figure, 5.13 and 4.14 show that the two models predicted the phenol oxic loading very well while the prediction capability was somewhat weaker in the case of o-cresol as shown in Figures 5.15 and 5.16. This is supported by higher chi-square values in the case of o-cresol prediction compared to that of phenol. The utility of the above models is quite conspicuous, since the oxic loading can be calculated knowing the anoxic loading and the initial DO content.
Chapter 6

KINETICS OF PHENOLICS UPTAKE
BY ACTIVATED CARBON

6.1 Introduction

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

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

6.2.1 Effect of DO Levels

The apparent surface diffusivities for phenol and o-cresol were determined from the batch test data presented in Figures 6.1 and 6.2. It is apparent that rapid uptake of adsorbate, that was independent of the presence of DO in the test environment, occurred during the first 12 hours, followed by a much slower uptake until equilibrium was attained. It is worth noting that equilibrium was attained after only 48 hours in the anoxic batch while taking about 14 days in the oxic batch. Furthermore, the strong dependence of the equilibrium uptake on the DO concentration corroborates the findings of the isotherms discussed earlier. Similar results were observed for phenol at pH 12 by Cooney and Xi (63). The rapid initial uptake is primarily due to physical adsorption of phenol onto activated carbon and the subsequent prolonged uptake is explained by the telomerization reactions which have been reported by Grant and King (13) to be promoted by longer contact times. It is therefore, apparent that telomerization is the rate limiting step in the overall uptake of phenol and o-cresol. The phenol and o-cresol uptake rates in all three batches containing dissolved oxygen were identical for the first two days and remained similar for another day in the two batches containing DO concentrations of 9 and 30 mg/l (DO levels of 3 and 4, respectively) after which time marked differences in uptake were observed. It is conceivable that the rate of diffusion of oxygen, necessary to promote telomerization increases with increasing DO concentrations but it appears that the extent of 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 $T = 21^\circ$C.
and pH of 7.
Figure 6.2: Closed Batch Kinetics Experiment for o-Cresol at $T = 21^\circ$ C. and pH 7.
Figure 6.3: Linearized Rate of Phenol Uptake at $T = 21^\circ C$ and pH of 7.
Figure 6.4: Linearized Rate of o-Cresol Uptake at $T = 21^\circ$C. and pH of 7.
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 $T = 21^\circ$ C. and 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 HISDM to the experimental data (Figures 6.1 and 6.2). The aforementioned procedure had the following statistical criteria

\[ r_i = y_i - v(x,t_i) \]  \hspace{1cm} (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 HISDM. 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:

\[ \text{minimize} = \frac{1}{2} R(x)^T R(x) = \frac{1}{2} \sum_{i=1}^{m} r_i(x)^2 = f(x) \]  \hspace{1cm} (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 \( \log(1 - \frac{m_i}{m_m}) \) 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,

\[ 1 - \frac{m_i}{m_m} = 1 - \frac{c_i - c_m}{c_0 - c_m}. \]
where, $c_i$, and $c_e$ are the initial and equilibrium concentrations, respectively, while $c_i$ 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, $\frac{m_i}{m_e}$ 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 HSIDM 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 HSIDM 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 HSIDM 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 HSIDM predictions for phenol and o-cresol, respectively, Figures 6.7 and 6.8 depict the good prediction capability HSIDM 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 a Temperature of 21°C and pH 7.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Operational Conditions</th>
<th>HSDM (Ds) cm²/sec</th>
<th>$\chi^2$</th>
<th>$\chi^2_{n.o.s.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-cresol</td>
<td>oxic (DO 4)</td>
<td>1.4E-08</td>
<td>0.89</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>oxic (DO 3)</td>
<td>2.0E-08</td>
<td>0.48</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>oxic (DO 2)</td>
<td>2.5E-08</td>
<td>0.36</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic (DO 1)</td>
<td>8.3E-08</td>
<td>0.036</td>
<td>5.7</td>
</tr>
<tr>
<td>phenol</td>
<td>oxic (DO 4)</td>
<td>7.6E-09</td>
<td>2.1</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>oxic (DO 3)</td>
<td>1.4E-08</td>
<td>0.67</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>oxic (DO 2)</td>
<td>1.6E-08</td>
<td>0.36</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic (DO 1)</td>
<td>6.3E-08</td>
<td>0.054</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Figure 6.7: Closed Batch Kinetic Experiment for Phenol at $T = 21^\circ$ C. and pH 7 Along with HSDM Predictions.
Figure 6.8: Closed Batch Kinetics Experiment for o-Cresol at $T = 21^\circ$ C. and pH 7 Along with HSDM Predictions.
was not always the case for the oxic curves. The reason is that the HSDM model is based on physical adsorption assumptions only, and, therefore, does not include any reaction term in the mathematical formulation, however; the diffusivity coefficients calculated for the oxic case, although they do not reflect the nature of the process very well give a way of comparison for the effects of environmental conditions on the telomerization reactions. The diffusivity coefficients found by the HSDM model were plotted against DO to GAC mass ratios in Figures 6.9 and 6.10 for phenol and o-cresol, respectively. The previous Figures clearly indicate that the apparent diffusivity coefficient decreases with increasing DO concentrations. It is also noted that the largest drop in the diffusivity was between the DO level 1 (anoxic) and the other levels, while the difference between the diffusivity values in the oxic levels were not as high. Such decrease in diffusivity, a measure of how fast equilibrium is attained, with increasing DO concentrations, is obviated by the slow telomerization rate controlling the uptake process and resulting in relatively long equilibration time.

6.2.2 Effect of pH Variation

The anoxic and oxic closed batch kinetic experiments for phenol at pH values of 3, 7, and 11 are shown in Figures 6.11, 6.12, and 6.13, respectively, while Figures 6.14, 6.15, and 6.16 represent the o-cresol case. From the aforementioned Figures, it is clear that pH variations affect the kinetics of adsorption presented by the anoxic case as well as the kinetics of adsorption-reaction combination presented by the oxic one. The data in Figures 6.17-6.22 show that the equilibration time for physical adsorption increases with the increase in pH, while, on the other hand, for the oxic case in which telomerization reaction is taking place, the equilibration time is unaffected by the pH variations. However, while at all the pHs equilibrium was attained on the eleventh day of
Figure 6.9: Relationship Between the Phenol Apparent Diffusivity (HSDM) and the Ratio of DO to GAC Mass at $T = 21^\circ$ C. and pH 7.
Figure 6.10: Relationship Between the o-Cresol Apparent Diffusivity (HSDM) and the Ratio of DO to GAC Mass at $T = 21^\circ$ C. and pH 7.
Figure 6.11: Closed Batch Kinetics Experiment for Phenol at pH 3 and $T = 21^\circ C$. from PHK38
Figure 6.12: Closed Batch Kinetic Experiment for Phenol at pH 7 and $T = 21^\circ$ C.
Figure 6.13: Closed Batch Kinetics Experiment for Phenol at pH 11 and $T = 21^\circ C$. 
Figure 6.15: Closed Batch Kinetics Experiment for o-Cresol at pH 7 and T = 21° C.
Figure 6.16: Closed Batch Kinetics Experiment for o-Cresol at pH 11 and T = 21°C.
Figure 6.17: Linearized Rate of Phenol Uptake at pH 3 and T = 21°C.
Figure 6.18: Linearized Rate of Phenol Uptake at pH 7 and $T = 21^\circ_{C}$ from abh17
Figure 6.19: Linearized Rate of Phenol Uptake at pH 11 and $T = 21^\circ C$.
Figure 6.20: Linearized Rate of o-Cresol Uptake at pH 3 and T = 21° C.
Figure 6.21: Linearized Rate of o-Cresol Uptake at pH 7 and $T = 21^\circ C$.
Figure 6.22: Linearized Rate of o-Cresol Uptake at pH 11 and $T = 21^\circ C$.
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 suggest the effect of pH variation on both physical adsorption and reactions. Surface diffusivities ($D_s$) were found by the HSDM model for the three pH values under the oxic and anoxic conditions and are presented in Table 6.2 for both phenol and o-cresol. The HSDM model was used to predict the data presented in the figures of this section; so, the experimental data for phenol and o-cresol under oxic and anoxic conditions at the different pH values are presented again along with the HSDM predictions in Figures 6.23-6.28. Those figures depict the good prediction capability HSDM model has for physical adsorption (oxic curves), while this was not always the case for the anoxic 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 HSDM model.

To be able to analyze the effect of pH on the oxic and anoxic adsorption, $D_s$ values are plotted versus pH for phenol and o-cresol in Figures 6.29 and 6.30, respectively. From the figures it is clear that for the anoxic case (physical adsorption) the highest surface diffusivities were attained at pH 7 and the order of $D_s$ values was at pH 7 < pH 3 < pH 11 which conflicts with the findings of Koh and Chung (23) who observed that the kinetics were increasing with the decrease in pH. For the oxic condition, $D_s$
Table 6.2. Apparent Diffusivities of Phenol and o-Cresol Evaluated by the HSDM Model at Various pHs and temperature of 21°C.

| Compound  | Operational Conditions | HSDM (Ds) cm²/sec | $\chi^2$ | $\chi^2$ 95%  
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>o-cresol</td>
<td>oxic, pH 3</td>
<td>5.9E-08</td>
<td>0.31</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic, pH 3</td>
<td>7.8E-08</td>
<td>0.025</td>
<td>5.7</td>
</tr>
<tr>
<td>o-cresol</td>
<td>oxic, pH 7</td>
<td>1.4E-08</td>
<td>0.89</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic, pH 7</td>
<td>8.3E-08</td>
<td>0.036</td>
<td>5.7</td>
</tr>
<tr>
<td>o-cresol</td>
<td>oxic, pH 11</td>
<td>1.1E-08</td>
<td>0.38</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic, pH 11</td>
<td>3.3E-08</td>
<td>0.0045</td>
<td>5.7</td>
</tr>
<tr>
<td>phenol</td>
<td>oxic, pH 3</td>
<td>1.8E-08</td>
<td>0.4</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic, pH 3</td>
<td>4.2E-08</td>
<td>0.055</td>
<td>5.7</td>
</tr>
<tr>
<td>phenol</td>
<td>oxic, pH 7</td>
<td>7.6E-09</td>
<td>2.07</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic, pH 7</td>
<td>6.3E-08</td>
<td>0.054</td>
<td>5.7</td>
</tr>
<tr>
<td>phenol</td>
<td>oxic, pH 11</td>
<td>3.5E-09</td>
<td>0.21</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic, pH 11</td>
<td>2.4E-08</td>
<td>0.014</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Figure 6.23: Closed Batch Kinetics Experiment for Phenol at pH 3 and $T = 21^\circ C$. Along with HSDM Predictions.
Figure 6.24: Closed Batch Kinetic Experiment for Phenol at pH 7 and $T = 21^\circ C$. Along with HSDM Predictions.
Figure 6.25: Closed Batch Kinetics Experiment for Phenol at pH 11 and T = 21°C. Along with HSDM Predictions.
Figure 6.26: Closed Batch Kinetics Experiment for o-Cresol at pH 3 and $T = 21^\circ$C. Along with HSDM Predictions.
Figure 6.27: Closed Batch Kinetics Experiment for o-Cresol at pH 7 and T = 21°C. Along with HSDM Predictions.
Figure 6.28: Closed Batch Kinetics Experiment for o-Cresol at pH 11 and $T = 21^\circ C$. Along with HSDM Predictions.
Figure 6.29: Relationship Between Phenol Apparent Diffusivities (HSDM) and pH at $T = 21^\circ C$. from PPHS
Figure 6.30: Relationship Between α-Cresol Apparent Diffusivities (HSDM) and pH at $T = 21^\circ$ C.
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, 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, 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, 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 suggest the
Figure 6.31: Closed Batch Kinetics Experiment for Phenol at $T = 8^\circ C.$ and pH 7.
Figure 6.32: Closed Batch Kinetic Experiment for Phenol at $T = 21^\circ$ C. and pH 7.
Figure 6.33: Closed Batch Kinetics Experiment for Phenol at $T = 35^\circ$ C. and pH 7.

from ohk359
Figure 6.34: Closed Batch Kinetics Experiment for \( o\)-Cresol at \( T = 8^\circ C \) and \( \text{pH} 7 \).
Figure 6.35: Closed Batch Kinetics Experiment for o-Cresol at $T = 21^\circ C.$ and pH 7.
Figure 6.36: Closed Batch Kinetics Experiment for o-Cresol at $T = 35^\circ C$ and PH 7.
Figure 6.37: Linearized Rate of Phenol Uptake at $T = 8^\circ C$ and pH 7.
Figure 6.38: Linearized Rate of Phenol Uptake at T = 21°C and pH 7.
Figure 6.39: Linearized Rate of Phenol Uptake at $T = 35^\circ C$. and pH 7.
Figure 6.40: Linearized Rate of o-Cresol Uptake at T= 8°C and pH 7.
Figure 6.41: Linearized Rate of o-Cresol Uptake $T = 21^\circ C$. and pH 7. from OT121
effect of temperature variation on both physical adsorption and reactions. Surface dif-
usions (Dt) were found by the IIIDM 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 χ² 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 IIIDM
model. The IIIDM 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 condi-
tions at the different temperature values were presented again along with the IIIDM
predictions in Figures 6.43-6.48. Like the case in the previous section, the IIIDM
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 experi-
mental and theoretical equilibrium concentrations were similar which is due to the isotherm data provided in the model, the IIIDM has to give lower theoretical concentra-
tion compared to the experimental ones before equilibrium is reached. This happens
because the IIIDM 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 experi-
mental data).

To be able to analyze the effect of temperature on the oxic and anoxic adsorption,
Dt 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 adsorp-
tion), Dt for phenol and o-cresol increasing with temperature. For the oxic condition,
Dt was highest at 21°C. This might be due to the fact that temperature had two oppo-
site 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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Operational Conditions</th>
<th>HSDM (Ds) cm²/sec</th>
<th>χ²</th>
<th>( \chi^2_{n-1, n.o} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-cresol</td>
<td>oxic, T = 8°C</td>
<td>1.1E-08</td>
<td>0.97</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic, T = 8°C</td>
<td>4.8E-08</td>
<td>0.247</td>
<td>5.7</td>
</tr>
<tr>
<td>o-cresol</td>
<td>oxic, T = 21°C</td>
<td>1.4E-08</td>
<td>0.89</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic, T = 21°C</td>
<td>8.3E-08</td>
<td>0.036</td>
<td>5.7</td>
</tr>
<tr>
<td>o-cresol</td>
<td>oxic, T = 35°C</td>
<td>9.9E-09</td>
<td>0.82</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic, T = 35°C</td>
<td>8.7E-08</td>
<td>0.0058</td>
<td>5.7</td>
</tr>
<tr>
<td>phenol</td>
<td>oxic, T = 8°C</td>
<td>6.7E-09</td>
<td>2.7</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>anoxic, T = 8°C</td>
<td>4.9E-08</td>
<td>0.18</td>
<td>5.7</td>
</tr>
<tr>
<td>phenol</td>
<td>oxic, T = 21°C</td>
<td>7.6E-09</td>
<td>2.1</td>
<td>8.05</td>
</tr>
<tr>
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<td>anoxic, T = 21°C</td>
<td>6.3E-08</td>
<td>0.054</td>
<td>5.7</td>
</tr>
<tr>
<td>phenol</td>
<td>oxic, T = 35°C</td>
<td>2.9E-09</td>
<td>0.28</td>
<td>8.05</td>
</tr>
<tr>
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<td>anoxic, T = 35°C</td>
<td>8.8E-08</td>
<td>0.009</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Figure 6.43: Closed Batch Kinetics Experiment for Phenol at T = 8°C and pH 7 Along with HSDM Predictions.

- ANOXIC, U = 0.809
- OXIC, U = 0.979

Phenol Reduced Concentration (C/C₀)

SORT TIME (sqrt hour)
Figure 6.45: Closed Batch Kinetics Experiment for Phenol at $T = 35^\circ$ C. and pH 7 Along with HSDM Prediction.
Figure 6.46: Closed Batch Kinetics Experiment for o-Cresol at $T = 8^\circ C$, and pH 7 Along with HSDM Predictions.
Figure 6.47: Closed Batch Kinetics Experiment for o-Cresol at $T = 21^\circ C$ and pH 7 Along with HSDM Predictions.
Figure 6.48: Closed Batch Kinetics Experiment for o-Cresol at $T = 35^\circ$ C. and pH 7 Along with HSDM Predictions.
Figure 6.49: Relationship Between Phenol Apparent Diffusivities (HSDM) and Temperature at pH 7.
Figure 6.50: Relationship Between α-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 the 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:

$$D_s = D_{so} \exp \left( \frac{-E_a}{R_s T} \right)$$

(6.3)

which can linearized as:

$$\log(D_s) = \log(D_{so}) - \frac{E_a}{2.3 R_s T}$$

(6.4)

where, $D_s$ is the diffusivity coefficient, $D_{so}$ is the intercept, $R_s$ is the universal gas constant = 8.31 J/(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 15335.4 J/mole for phenol and o-cresol, respectively. The close values for $E_a$ in the case of phenol and o-cresol reflects similar responses for the kinetics to temperature variation.
Figure 6.51: Relationship Between Diffusivities and Temperature for Phenol and o-Cresol Along with Lines of Best Fit.
6.3 Model Formulation

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

\[ \frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right) \]  \hspace{1cm} (6.5)

where:

\[ q = \text{carbon loading, M adsorbate/M adsorbent}. \]

\[ D_s = \text{surface diffusion coefficient, L}^2/T. \]

\[ r = \text{distance from the center of the spherical particle, L, and} \]

\[ t = \text{time, T.} \]

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.

\[ @ t = 0, 0 \leq r \leq r_0: \quad q = 0 \]  \hspace{1cm} (6.6)

\[ @ t \geq 0, r = 0: \quad \frac{\partial q}{\partial r} = 0 \]  \hspace{1cm} (6.7)

\[ @ t \geq 0, r = r_0: \quad 4\pi r_0^2 \int_0^t (-D_s \frac{\partial q}{\partial r} \, dt) = V_l \left( C_0 - C \right) \]  \hspace{1cm} (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:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right) - k_r (q - q_\infty)$$  \hspace{1cm} (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:

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

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

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

$$\frac{\partial Q}{\partial \tau} = \frac{\partial Q}{\partial t} \cdot \frac{\partial t}{\partial \tau} = \frac{\partial Q}{\partial t} \cdot \frac{r_0^2}{D_s}$$
\[
\frac{\partial Q}{\partial t} = \frac{\partial Q}{\partial \tau} \cdot \frac{\partial \tau}{\partial t} = \frac{\partial Q}{\partial \tau} \cdot \frac{D_s}{r_0^2} \\
\frac{\partial Q}{\partial \tau} \cdot \frac{D_s}{r_0^2} = \frac{D_s}{r_0^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial Q}{\partial R} \right) - k_r Q \\
\frac{\partial Q}{\partial \tau} = \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial Q}{\partial R} \right) - k_r \left( \frac{r_0^2}{D_s} \right) Q \\
\frac{\partial Q}{\partial \tau} = \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial Q}{\partial R} \right) - \varphi^2 Q \\
(6.10)
\]

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

where, \( \varphi = \sqrt{\frac{k_r r_0^2}{D_s}} \)

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

at \( \varphi = 1 \), both diffusion and reaction have equal importance.

at \( \varphi < 0.1 \), reaction mechanism dominates, and

at \( \varphi \approx 10 \), diffusion mechanism dominates

The initial condition becomes:

\[
(\tau = 0, 0 \leq R \leq 1) : Q = 0 \\
(6.11)
\]

and the boundary conditions are:
\[ @ \tau \geq 0, R = 0: \frac{\partial Q}{\partial R} = 0 \]  
\[ \text{at } \tau \geq 0, R = 1: \frac{\partial Q}{\partial \tau} = -3 \frac{\partial Q}{\partial R} \]  
\[ \text{where, } Q = 3 \int_0^1 Q R^2 dR \]

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

\[ \int_0^1 \frac{\partial Q}{\partial R} dR = -\frac{1}{3} \left( \frac{U}{\alpha - U} + Q \right) \]  
\[ \text{where the total fractional uptake is} \]

\[ U = \frac{C_0 - C_\infty}{C_0} \]

and,

\[ \alpha = \frac{V_s k c_0^{n-1}}{V_l} \]

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

The above differential equations cannot be solved analytically, and a numerical procedure e. g. finite difference or finite element should be used. This is outside the scope of the dissertation, and hence, this effort is recommended for future research.
Chapter 7

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

7.1 Introduction

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

Carbon adsorption can be operated on either a batch or continuous-flow basis. In batch processes the carbon and wastewater are mixed together in a suitable reaction vessel until the concentration of the solute has been reduced to the desired level. Most continuous-flow systems are operated as fixed-bed adsorption columns. Continuous-flow operations have advantages over batch-type operations because rates of adsorption in batches depend upon the concentration of adsorbate in solution, and because they are capable of treating large volumes of wastewaters. Fixed-bed adsorbers may be operated in either the upflow or downflow mode. In downflow systems the carbon can serve for adsorption and for filtration of suspended solids; hence, it is used when the
wastewater contains suspended solids. Upflow columns may be operated either as packed or expanded beds. Packed-beds require a high-quality influent to prevent clogging, whereas expanded beds are capable of handling wastewater high in suspended solids. For the purpose of this study the upflow packed bed system was chosen because the adsorbate solutions did not contain any suspended solids.

The design of fixed bed adsorbers involves estimation of the shape of the breakthrough curve (BTC) and the appearance of the breakpoint. A substantial fraction of the time and expense associated with planning and designing adsorption facilities is involved in predicting or forecasting the operational dynamics of the process. The approach involves the conduction of extensive experimental pilot studies to examine the effect of each system variable. Inspite of the long duration and high costs for such pilot studies, sometimes they fail to predict adsorber behavior. This failure is attributable to difference in the operational characteristics between the experimental and full scale adsorbers. The need for pilot scale column studies stemmed from the lack of a rational design basis utilizing the fundamental adsorptive parameters of GAC (i.e. equilibrium and kinetics). Discrepancies between the isotherm capacities involved in the design and the actual column capacity were always noticed and attributed to irreversibility of the adsorption process, to a decline in the intraparticle diffusivity during the latter part of the breakthrough curve and to the continuously decreasing adsorbate concentration in the liquid phase during an isotherm experiment. Currently, several mathematical models that utilize relatively inexpensive and much less laborious experimentation have been postulated to facilitate scale-up and reduce the cost of adsorber design. Some of these models that have been widely successful in breakthrough prediction of adsorber columns include the pore diffusion model (PDM) and the homogeneous surface diffusion model (HSDM).
It was shown in the previous chapters that dissolved oxygen DO affects equilibrium and kinetics of phenolics adsorption on GAC. In real application, the system condition with regard to DO content can vary appreciably. While, the application of powdered activated carbon in activated sludge processes can provide oxic conditions, anaerobic GAC contactors will result in complete anoxic conditions. In addition, biological activity in fixed bed adsorbers can lead to exhaustion of some of the DO content resulting in different amounts of DO in the adsorber environment. In this chapter, the effect of DO on the BTC's of phenol and o-cresol from GAC will be investigated, and the validity the homogeneous surface diffusion model (HSDM) will be tested.

7.2 Results and Discussion

7.2.1 Determination of External Mass Transfer Coefficients

For phenol and o-cresol, the surface diffusion coefficients have been determined experimentally using closed batch kinetics. The external mass transfer coefficients \( k_1 \) must be evaluated using correlations. The following equation (64) was developed for Reynolds numbers between 3 and 1000:

\[
\frac{2 k_r r}{D_l} = 2 + 1.1 R^{0.6} S^{0.333} \quad (7.1)
\]

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

\[
S = \frac{\mu}{\rho_l D_l} \quad (7.2)
\]

\[
R = \frac{2 \rho_l r V}{\mu} \quad (7.3)
\]

where, \( \mu \) is viscosity of water = 0.00098 kg.s/m, \( \rho_l \) is density of water = 997.8 kg/m³.
is mean radius of adsorbent particle = 0.00078 m, \( v \) is the superficial velocity = 3.285E-3 m/sec, and \( D_t \) is the diffusivity of the adsorbate in water calculated using the Wilke-Chang equation (65) to be 8.792E-10 m^2/sec and 7.808E-10 m^2/sec, for phenol and o-cresol, respectively. The correlation that best matched the experimental column data in a study performed by Crittenden and Weber (34) on phenol was that proposed by Williamson et al. (66) given in

\[
\frac{k_f \rho^{0.55}}{v} = 2.40 \times 10^6 R^{0.66}
\]

(Reynolds number range of applicability, 0.08-125)

Here,

\[
R = \frac{\rho_f \epsilon_v}{\mu}
\]

(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 more 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k$ (Corr. 1) $\text{cm}^2/\text{sec}$</th>
<th>$k$ (Corr. 2) $\text{cm}^2/\text{sec}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-cresol</td>
<td>1.72E-03</td>
<td>3.60E-3</td>
</tr>
<tr>
<td>phenol</td>
<td>1.86E-03</td>
<td>3.88E-3</td>
</tr>
</tbody>
</table>
Figure 7.1: Breakthrough of Phenol Under Anoxic Condition at $T = 21^\circ$ C, and pH 7.
Figure 7.2: Breakthrough of Phenol Under Oxic Condition at $T = 21^\circ$ C. and pH 7.
Figure 7.3: Breakthrough of o-Cresol Under Anoxic Condition at $T = 21^\circ$ C. and pH 7.
Figure 7.4: Breakthrough of o-Cresol Under Oxic Condition at $T = 21^\circ$ C and pH 7.

TIME (HOURS)

o-CRESOL REDUCED CONCENTRATION (C/C₀)
Figure 7.5: Breakthrough Curves for Phenol at $T = 21^\circ$ C. and pH $p\text{CO}_2$. 
Figure 7.6: Breakthrough Curves for o-Cresol at $T = 21^\circ$ C. and $pH_{OCOL}$
anoxic experiments, the initial breakthrough started after 8 hours and 36 hours for phenol and o-cresol, respectively while for the oxic experiments, the corresponding figures were 20 hours and 62 hours. The 50% breakthrough in the anoxic columns occurred after 28 hours and 65 hours for phenol and o-cresol, respectively while for the oxic experiments, the corresponding figures were 50 hours and 100 hours. Finally, column exhaustion characterized by 95% breakthrough capacities occurred in the anoxic column experiments after 50 hours and 93 hours for phenol and o-cresol, respectively while for the oxic experiments, the corresponding figures were 130 hours and 215 hours for phenol and o-cresol respectively. These times were measured from the beginning of the experiment and give a very good indication about the tremendous additional capacity available in the column in the case of oxic conditions compared to the anoxic conditions if any particular effluent (phenolic type) standard is to be achieved. The ratio for those times (oxic/anoxic) for phenol and o-cresol were 2.6 and 2.31 for phenol and o-cresol, respectively. The above figures show that the existence of DO in the adsorbate solution not only prolongs the time needed to reach certain breakthrough point or increase the capacity of the adsorber column but also affect the shape of the BTC resulting in a flatter BTC, which again can be attributed to telomerization reactions rather than pure adsorption in which the BTC is usually sharp and little flattening is expected. Flat BTCs of phenolics from GAC column have also been found by other researches (34,58). The above discussion is applicable to serial column operation in which exhaustion is the criteria for their design. However, in order to investigate the effect of DO on the shape of the early part of the BTC’s interest should be focused on the time between the start of the BTC to the time needed to reach 50% breakthrough capacity. For the anoxic conditions this time was 20 hours and 29 hours for phenol and o-cresol, respectively while for the oxic condition the corresponding figures were 30 hours and 38 hours, hence, the ratio for those times (oxic/anoxic) for phenol and
o-cresol were 1.5 and 1.31 for phenol and o-cresol, respectively. The above figures show that the existence of DO in the adsorbate solution affects the shape of the early BTC resulting in a flatter BTC, and delays the initial breakthrough point which is very important in single column operation in which the adsorber column has to meet an effluent criteria which is usually low; accordingly time to reach the initial breakthrough is the design criteria.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Operational Conditions</th>
<th>Iso. Cap. mg/g</th>
<th>Col. Cap. mg g</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-cresol</td>
<td>oxic</td>
<td>330.77</td>
<td>356.67</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>198.6</td>
<td>207.3</td>
</tr>
<tr>
<td>phenol</td>
<td>oxic</td>
<td>179.39</td>
<td>171.90</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>87.88</td>
<td>94.380</td>
</tr>
</tbody>
</table>
Table 7.3. Isotherm and Column Capacities at 50% BTC for Phenol and o-Cresol Under Oxic and Anoxic Conditions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Operational Conditions</th>
<th>Iso. Cap. mg/g</th>
<th>Col. Cap. mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-cresol</td>
<td>oxic</td>
<td>330.77</td>
<td>295.5</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>196.60</td>
<td>193.70</td>
</tr>
<tr>
<td>phenol</td>
<td>oxic</td>
<td>179.39</td>
<td>148.8</td>
</tr>
<tr>
<td></td>
<td>anoxic</td>
<td>87.88</td>
<td>84.6</td>
</tr>
</tbody>
</table>
previous table with the exception that the listed capacities are those obtained using a square wave passing through the 50 \% breakthrough point. From Table 7.3 it is noted that the for the 50 \% capacity the isotherm and column capacities were very close in the anoxic case and the ratios of column capacities to isotherm capacities were 0.963 and 0.975 for phenol and o-cresol, respectively, while for the oxic condition the corresponding figures were 0.89 and 0.83. This shows some deviation from the square wave in the case of oxic conditions compared to the anoxic conditions. This is expected since under oxic conditions, the column behavior is not only affected by physical adsorption but also by the telomerization reactions.

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

Modeling the BTC’s was performed using the plug-flow homogenous surface diffusion model (PFHSDM). Model predictions for the BTCs were obtained using two sets of independently determined adsorption parameters. The input to the model included adsorption equilibria data described by the Freundlich adsorption isotherm equation for both oxic and anoxic conditions, adsorption kinetic parameters such as surface diffusion coefficients determined from the oxic and anoxic batch experiments, and the external mass transfer coefficient determined from correlations, and physical parameters such as the mass of carbon, length of the column, internal diameter of the column,
molecular weight of the solute, no of compounds in solution, density of carbon, flow-rate of feed solution, initial concentration of sorbate solution, and density of solution, as well as some model related variables such as time for calculation of BTC, accuracy needed, and number of collocation points. The output of the model is the prediction of the BTC with time. It is worth mentioning that while the case under study consisted of single solute and constant influent concentration, the available model is capable of predicting multi-solute adsorption with various influent concentrations. Model predictions, using these two sets of parameters (oxic and anoxic), are shown together with the corresponding experimental BTC's in Figures 7.7-7.10 for phenol and o-cresol, respectively. From these figures it is clear that the PFHSDM model gives very good prediction for the oxic and anoxic conditions especially before tailing, provided that the appropriate parameters, especially, apparent diffusivity are used. This good prediction capability was valid for the cases of film transfer coefficients calculated from both correlations with correlation 2 giving better prediction of the initial BTC's in the all of the cases. As a result, it can be concluded that the use of correlation 2 yields film transfer coefficients that predicts the BTC very well, especially the earlier stage. This supports the finding of Crittenden and Weber (34) who found that correlation 2 best matched their experimental data on adsorption of phenolics. The good predictability the PFHSDM model has for oxic and anoxic conditions conflicts with the findings of Vidic and Suidan (58) who found that only the anoxic parameters would predict the early portion of BTC of the adsorption column operating under oxic conditions. The reason for their findings and hence for this conflict is very obvious, since in their work, they used low mass of carbon (50 g) and relatively high initial o-cresol concentration (200 mg/l) resulting in a rapid BTC which started and finished within 12 hours. This where the intrinsic diffusion controls even with telomerization reactions present, hence, the actual BTC was mostly under anoxic conditions, which was best predicted by the
Figure 7.7: Breakthrough of Phenol Under Anoxic Condition at $T = 21^\circ C$ and pH 7 Along with PFHSDM Predictions.
Figure 7.8: Breakthrough of Phenol Under Oxic Condition at T = 21°C and pH 7 Along with PFHSDM Predictions.
Figure 7.9: Breakthrough of o-Cresol Under Anoxic Condition at $T = 21^\circ C.$ and pH 7 Along with PFHSDM Predictions.
Figure 7.10: Breakthrough of o-Cresol Under Oxic Conditions at T = 21° C. and pH 7 Along with PFHSDM Predictions.
anoxic parameters. However, the oxic condition effects started in the tailing stage resulting in a high portion of the column capacity in the tailing stage. In the case of this study, columns were so designed as to delay BTC's, allowing telomerization reactions to proceed along with physical adsorption right from the beginning of the BTC.

The finding that totally different BTCs as well as different time characteristics are observed under varying levels of DO is extremely important from a practical standpoint. If parallel or short column operation is proposed for design, then the early portion of BTC governs design, while, for series operation or long columns the entire BTC controls the design and number of columns. As has been demonstrated above, the level of DO in the feed wastewater strongly influences both the earlier and later portions of the BTC. Thus, utilizing knowledge of adsorption equilibria and kinetics of diffusion and reaction under ambient DO conditions to design adsorbers so as to prolong adsorber runs sufficiently to permit telomerization, substantially delays times to breakthrough and exhaustion.
Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

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

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

3. The solution pH and temperature appear to strongly influence such chemical reactions. The net effect of pH and temperature on activated carbon adsorption is a combination of their influence on both physical adsorption and chemical reactions. While a pH of 3 was observed to favor physical adsorption, pH of 11 favored oxidation reactions, and the optimal pH for adsorption of phenolics by activated carbon under oxic conditions was pH 7. The anoxic uptake of phenol and o-cresol increased with decreasing temperatures and was highest at the low-
est temperature studied of 8°C. Adsorption enhancement due to telomerization was highest at a temperature of 35°C. Oxidation 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 anoxic 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. \( D_0 \) values for the oxic cases increased proportionally with temperature and inversely with \( \text{pH} \), while the highest difference between oxic and anoxic diffusivities were at \( \text{pH} 7 \) and temperature 35°C.

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

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

8. The finding that totally different BTCs as well as different time characteristics are observed under varying levels of DO is extremely important from a practical standpoint. If parallel column operation is proposed for design, then the early portion of BTC governs design, while, for series operation the entire BTC controls the design and number of columns. As has been demonstrated above, the level of DO in the feed wastewater strongly influences both the earlier and later portions of the BTC. Thus, adsorbers can be designed to take advantage of the simultaneous adsorption-reaction phenomenon to substantially delay times to breakthrough and exhaustion.
9. The HSDM was found to have good prediction capability (before tailing) when the appropriate equilibrium and rate parameters are used and when the telomerization reaction starts with adsorption from the start of the BTC.

8.2 Recommendations for Further Research

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

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

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

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

5. Study of other aromatics, especially, large compounds.
APPENDIX A.1

RAW DATA
APPENDIX A.1.1

RAW DATA FOR THE SCREENING STAGE (isotherms)
Type of experiment: isotherm

Name of solute: 4-nitrophenol

Initial concentration: 1000 mg/l

Volume of solution: 100 ml.

pH: 7

Temperature: 21°C.

Date started: 4/1/1992

Date ended: 18/1/1992

Method of analysis: uv spectrophotometer (318 wavelength)

<table>
<thead>
<tr>
<th>Carbon Mass mg</th>
<th>initial DO = 31.1 mg/l</th>
<th>initial DO = 0.0 mg/l</th>
</tr>
</thead>
<tbody>
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<td>Abs.</td>
<td>Conc. mg/l</td>
</tr>
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<td>1.105</td>
<td>984.5 a</td>
</tr>
<tr>
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<td>1.107</td>
<td>985.0 a</td>
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<td>200.0</td>
<td>0.618</td>
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<tr>
<td>300.0</td>
<td>0.374</td>
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<tr>
<td>400.0</td>
<td>0.227</td>
<td>201.6 b</td>
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<tr>
<td>450.0</td>
<td>0.168</td>
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<td>500.0</td>
<td>1.146</td>
<td>102.0 b</td>
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<td>71.0 b</td>
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<tr>
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<td>46.9 b</td>
</tr>
<tr>
<td>650.0</td>
<td>0.339</td>
<td>30.2 b</td>
</tr>
<tr>
<td>700.0</td>
<td>0.181</td>
<td>16.1</td>
</tr>
<tr>
<td>750.0</td>
<td>0.138</td>
<td>12.3</td>
</tr>
<tr>
<td>800.0</td>
<td>0.118</td>
<td>10.5</td>
</tr>
<tr>
<td>850.0</td>
<td>0.073</td>
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</tr>
<tr>
<td>1000.0</td>
<td>0.031</td>
<td>2.8</td>
</tr>
</tbody>
</table>

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)

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<th>Conc. mg/l</th>
<th>Carbon Mass (mg)</th>
<th>Initial Abs.</th>
<th>Conc. mg/l</th>
</tr>
</thead>
<tbody>
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<td>0.0</td>
<td>1.157</td>
<td>995.5 a</td>
</tr>
<tr>
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<td>990.1 a</td>
<td>0.0</td>
<td>1.153</td>
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</tr>
<tr>
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<td>250.0</td>
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</tr>
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</table>

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)

<table>
<thead>
<tr>
<th>Carbon Mass (mg)</th>
<th>Carbon Mass (mg)</th>
<th>Conc. (mg/l)</th>
<th>Conc. (mg/l)</th>
</tr>
</thead>
<tbody>
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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

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<tr>
<th>Carbon Mass mg</th>
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<th>initial DO = 30.1 mg/l</th>
<th>TOC mg/l</th>
<th>Conc. mg/l</th>
<th>initial DO = 0.0 mg/l</th>
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</thead>
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</table>

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

<table>
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<tr>
<th>Carbon Mass mg</th>
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<th>initial TOC mg/l</th>
<th>initial Conc. mg/l</th>
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<tbody>
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</tr>
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<td>8.2</td>
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</table>

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

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<th>TOC</th>
<th>Conc.</th>
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</thead>
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<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
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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

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<td>240.3</td>
</tr>
<tr>
<td>900.0</td>
<td>19.0</td>
<td>137.8</td>
</tr>
<tr>
<td>1150.0</td>
<td>13.6</td>
<td>98.5</td>
</tr>
<tr>
<td>1450.0</td>
<td>8.6</td>
<td>62.4</td>
</tr>
<tr>
<td>1800.0</td>
<td>4.4</td>
<td>32.1</td>
</tr>
<tr>
<td>2050.0</td>
<td>2.2</td>
<td>15.6</td>
</tr>
<tr>
<td>2500.0</td>
<td>1.3</td>
<td>9.3</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Carbon Mass (mg)</th>
<th>TOC reading</th>
<th>TOC mg/l</th>
<th>Initial DO = 6.2 mg/l</th>
<th>TOC reading</th>
<th>TOC mg/l</th>
<th>Conc. mg/l</th>
</tr>
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<td>41.2</td>
<td></td>
</tr>
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<td>40.5</td>
<td></td>
</tr>
<tr>
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<td>31.5</td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>28.1</td>
<td>31.2</td>
<td></td>
<td>24.5</td>
<td>27.2</td>
<td>a</td>
</tr>
<tr>
<td>100.0</td>
<td>22.9</td>
<td>25.4</td>
<td></td>
<td>19.6</td>
<td>21.8</td>
<td></td>
</tr>
<tr>
<td>200.0</td>
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<td>20.7</td>
<td></td>
<td>15.4</td>
<td>17.1</td>
<td></td>
</tr>
<tr>
<td>400.0</td>
<td>17.7</td>
<td>19.7</td>
<td></td>
<td>12.2</td>
<td>13.6</td>
<td>a</td>
</tr>
<tr>
<td>800.0</td>
<td>13.7</td>
<td>15.2</td>
<td></td>
<td>8.6</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>1600.0</td>
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<td></td>
<td>6.8</td>
<td>7.6</td>
<td></td>
</tr>
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<td>9.7</td>
<td></td>
<td>4.9</td>
<td>5.5</td>
<td>a</td>
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<tr>
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<td>9.0</td>
<td></td>
<td>5.2</td>
<td>5.8</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Carbon Mass mg</th>
<th>TOC reading</th>
<th>TOC mg/l</th>
<th>initial DO = 5.1 mg/l (normal DO level)</th>
<th>initial DO = 0.0 mg/l</th>
</tr>
</thead>
<tbody>
<tr>
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<td>649.2</td>
<td>698.1</td>
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<td>697.5</td>
<td>645.3</td>
<td>693.9 $^a$</td>
</tr>
<tr>
<td>200.0</td>
<td>421.3</td>
<td>453.0</td>
<td>513.2</td>
<td>551.8</td>
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<tr>
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<td>295.8</td>
<td>318.1</td>
<td>379.4</td>
<td>408.0</td>
</tr>
<tr>
<td>1500.0</td>
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<td>89.6</td>
<td>134.5</td>
<td>144.6 $^a$</td>
</tr>
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<td>67.8</td>
<td>87.9</td>
<td>94.5</td>
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<tr>
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<td>46.4</td>
<td>49.9 $^a$</td>
</tr>
<tr>
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<td>14.7</td>
<td>26.6</td>
<td>28.6</td>
</tr>
<tr>
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<td>3.8</td>
<td>4.1</td>
<td>12.8</td>
<td>13.8</td>
</tr>
</tbody>
</table>

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

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

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

<table>
<thead>
<tr>
<th>Carbon Mass (mg)</th>
<th>TOC reading</th>
<th>TOC mg/l</th>
<th>TOC reading</th>
<th>TOC mg/l</th>
<th>Conc. mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
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<td>14.5</td>
<td>15.6</td>
<td>a</td>
</tr>
<tr>
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<td>14.7</td>
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<td>15.0</td>
<td>16.1</td>
<td>a</td>
</tr>
<tr>
<td>100.0</td>
<td>9.8</td>
<td>10.5</td>
<td>11.3</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>200.0</td>
<td>7.9</td>
<td>8.5</td>
<td>9.4</td>
<td>10.1</td>
<td>a</td>
</tr>
<tr>
<td>400.0</td>
<td>5.1</td>
<td>5.5</td>
<td>8.3</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>800.0</td>
<td>2.0</td>
<td>2.1</td>
<td>5.6</td>
<td>6.0</td>
<td>a</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Carbon Mass mg</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
<th>Carbon Mass mg</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
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<td>996.3 a</td>
<td>0.0</td>
<td>1.125</td>
<td>993.1 a</td>
</tr>
<tr>
<td>0.0</td>
<td>1.112</td>
<td>991.1 a</td>
<td>0.0</td>
<td>1.127</td>
<td>995.5 a</td>
</tr>
<tr>
<td>150.0</td>
<td>0.763</td>
<td>675.6 a</td>
<td>250.0</td>
<td>0.690</td>
<td>610.4 a b</td>
</tr>
<tr>
<td>250.0</td>
<td>0.574</td>
<td>505.7 a</td>
<td>350.0</td>
<td>0.509</td>
<td>450.3 a</td>
</tr>
<tr>
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<td>0.305</td>
<td>270.0 a</td>
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<td>0.240</td>
<td>212.3 a</td>
</tr>
<tr>
<td>550.0</td>
<td>0.139</td>
<td>123.2 a</td>
<td>800.0</td>
<td>0.921</td>
<td>81.5 b</td>
</tr>
<tr>
<td>600.0</td>
<td>0.855</td>
<td>75.7</td>
<td>1000.0</td>
<td>0.344</td>
<td>30.4</td>
</tr>
<tr>
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<td>0.692</td>
<td>61.2</td>
<td>1400.0</td>
<td>0.141</td>
<td>12.5</td>
</tr>
<tr>
<td>750.0</td>
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<td>0.096</td>
<td>6.5</td>
</tr>
<tr>
<td>900.0</td>
<td>0.200</td>
<td>17.7</td>
<td>2000.0</td>
<td>0.055</td>
<td>4.9</td>
</tr>
<tr>
<td>1100.0</td>
<td>0.120</td>
<td>10.6</td>
<td>2200.0</td>
<td>0.043</td>
<td>3.8 b</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Carbon Mass (mg)</th>
<th>Abs.</th>
<th>Conc. (mg/l)</th>
<th>Carbon Mass (mg)</th>
<th>Abs.</th>
<th>Conc. (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.159</td>
<td>996.7 a</td>
<td>0.0</td>
<td>1.157</td>
<td>995.5 a</td>
</tr>
<tr>
<td>0.0</td>
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<td>990.1 a</td>
<td>0.0</td>
<td>1.153</td>
<td>991.7 a</td>
</tr>
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<td>250.0</td>
<td>7.179</td>
<td>617.4 a b</td>
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<td>1000.0</td>
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<td>92.7</td>
</tr>
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<td>27.0</td>
<td>1200.0</td>
<td>0.656</td>
<td>56.4</td>
</tr>
<tr>
<td>700.0</td>
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<td>1400.0</td>
<td>0.306</td>
<td>26.3 b</td>
</tr>
<tr>
<td>750.0</td>
<td>0.119</td>
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<td>1600.0</td>
<td>0.183</td>
<td>15.7</td>
</tr>
<tr>
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<td>1700.0</td>
<td>0.130</td>
<td>11.2</td>
</tr>
<tr>
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<td>0.058</td>
<td>5.0</td>
<td>1800.0</td>
<td>0.095</td>
<td>8.2 b</td>
</tr>
<tr>
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<td>2000.0</td>
<td>0.071</td>
<td>6.1</td>
</tr>
<tr>
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<td>2200.0</td>
<td>0.057</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Remarks:

a: 10 dilutions

b: measurements of inorganic carbon before and after the experiment

showed zero difference for biological activity.

Extract 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)

<table>
<thead>
<tr>
<th>Carbon Mass mg</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
<th>Carbon Mass mg</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.109</td>
<td>990.5 a</td>
<td>0.0</td>
<td>1.112</td>
<td>993.3 a</td>
</tr>
<tr>
<td>0.0</td>
<td>1.115</td>
<td>995.7 a</td>
<td>0.0</td>
<td>1.116</td>
<td>996.5 a</td>
</tr>
<tr>
<td>150.0</td>
<td>0.711</td>
<td>635.6 a</td>
<td>250.0</td>
<td>0.772</td>
<td>689.4 a b</td>
</tr>
<tr>
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<td>350.0</td>
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</tr>
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<td>350.0</td>
<td>0.403</td>
<td>360.1 a</td>
<td>500.0</td>
<td>0.489</td>
<td>436.7 a</td>
</tr>
<tr>
<td>500.0</td>
<td>0.213</td>
<td>190.2 a</td>
<td>600.0</td>
<td>0.399</td>
<td>356.6 a b</td>
</tr>
<tr>
<td>550.0</td>
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<td>167.1 a</td>
<td>800.0</td>
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<td>211.3 a</td>
</tr>
<tr>
<td>600.0</td>
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<td>1000.0</td>
<td>0.138</td>
<td>123.1 a</td>
</tr>
<tr>
<td>700.0</td>
<td>0.782</td>
<td>69.8</td>
<td>1400.0</td>
<td>0.916</td>
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</tr>
<tr>
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<td>54.8</td>
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<td>63.4</td>
</tr>
<tr>
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<td>40.1</td>
<td>2000.0</td>
<td>0.522</td>
<td>46.6</td>
</tr>
<tr>
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<td>0.337</td>
<td>30.1</td>
<td>2200.0</td>
<td>0.398</td>
<td>35.5</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Carbon Mass mg</th>
<th>initial DO = 30.9 mg/l</th>
<th>initial DO = 0.0 mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Abs.</td>
<td>Conc. mg/l</td>
</tr>
<tr>
<td>0.0</td>
<td>1.058</td>
<td>998.1 a</td>
</tr>
<tr>
<td>0.0</td>
<td>1.053</td>
<td>992.6 a</td>
</tr>
<tr>
<td>50.0</td>
<td>0.876</td>
<td>825.8 a</td>
</tr>
<tr>
<td>100.0</td>
<td>0.702</td>
<td>662.4 a</td>
</tr>
<tr>
<td>150.0</td>
<td>0.533</td>
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<tr>
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</tr>
<tr>
<td>350.0</td>
<td>1.034</td>
<td>97.5</td>
</tr>
<tr>
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<td>28.6</td>
</tr>
<tr>
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<td>15.4</td>
</tr>
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<td>7.1</td>
</tr>
<tr>
<td>600.0</td>
<td>0.048</td>
<td>4.5</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Carbon Mass mg</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
<th>Carbon Mass mg</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.068 a</td>
<td>987.3</td>
<td>0.0</td>
<td>1.073</td>
<td>992.5 a</td>
</tr>
<tr>
<td>0.0</td>
<td>1.075 a</td>
<td>994.5</td>
<td>0.0</td>
<td>1.072</td>
<td>991.6 a</td>
</tr>
<tr>
<td>50.0</td>
<td>0.854 a</td>
<td>789.900</td>
<td>100.0</td>
<td>0.749</td>
<td>692.9 a</td>
</tr>
<tr>
<td>100.0</td>
<td>0.625 a</td>
<td>578.300</td>
<td>150.0</td>
<td>0.565</td>
<td>522.4 a b</td>
</tr>
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<td>0.347</td>
<td>320.6 a</td>
</tr>
<tr>
<td>200.0</td>
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<td>350.0</td>
<td>0.177</td>
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<tr>
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<td>0.111</td>
<td>10.3</td>
</tr>
<tr>
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<td>700.0</td>
<td>0.090</td>
<td>8.3</td>
</tr>
<tr>
<td>350.0</td>
<td>0.105</td>
<td>9.700</td>
<td>750.0</td>
<td>0.072</td>
<td>6.7</td>
</tr>
<tr>
<td>400.0</td>
<td>0.071</td>
<td>6.600</td>
<td>800.0</td>
<td>0.064</td>
<td>5.9 b</td>
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<td>4.100</td>
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<td>0.044</td>
<td>4.1</td>
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<tr>
<td>500.0</td>
<td>0.029</td>
<td>2.700</td>
<td>1000.0</td>
<td>0.032</td>
<td>3.0</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Carbon Mass (mg)</th>
<th>Abs.</th>
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<th>Carbon Mass (mg)</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
</tr>
</thead>
<tbody>
<tr>
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<td>999.5 a</td>
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<td>0.0</td>
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<td>1002.6 a</td>
<td>0.0</td>
<td>1.075</td>
<td>995.9 a</td>
</tr>
<tr>
<td>50.0</td>
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<td>835.2 a</td>
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<tr>
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<td>0.677</td>
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</tr>
<tr>
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<td>0.531</td>
<td>491.3 a</td>
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<tr>
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<tr>
<td>450.0</td>
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<td>171.6 a</td>
<td>650.0</td>
<td>0.213</td>
<td>196.9 a b</td>
</tr>
<tr>
<td>550.0</td>
<td>1.111</td>
<td>102.9</td>
<td>750.0</td>
<td>0.143</td>
<td>132.6 a</td>
</tr>
<tr>
<td>650.0</td>
<td>0.595</td>
<td>55.1</td>
<td>950.0</td>
<td>0.702</td>
<td>65.0</td>
</tr>
<tr>
<td>750.0</td>
<td>0.355</td>
<td>32.9</td>
<td>1600.0</td>
<td>0.231</td>
<td>21.4</td>
</tr>
<tr>
<td>950.0</td>
<td>0.110</td>
<td>10.2</td>
<td>1800.0</td>
<td>0.120</td>
<td>11.1</td>
</tr>
<tr>
<td>1100.0</td>
<td>0.055</td>
<td>5.100</td>
<td>2200.0</td>
<td>0.066</td>
<td>6.1 b</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Carbon Mass mg</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
<th>Carbon Mass mg</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.097</td>
<td>1004.2 a</td>
<td>0.0</td>
<td>1.094</td>
<td>1001.4 a</td>
</tr>
<tr>
<td>0.0</td>
<td>1.090</td>
<td>997.1 a</td>
<td>0.0</td>
<td>1.085</td>
<td>993.7 a</td>
</tr>
<tr>
<td>150.0</td>
<td>0.668</td>
<td>611.3 a</td>
<td>250.0</td>
<td>0.654</td>
<td>598.3 a</td>
</tr>
<tr>
<td>250.0</td>
<td>0.427</td>
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<td>0.517</td>
<td>473.4 a</td>
</tr>
<tr>
<td>350.0</td>
<td>0.239</td>
<td>218.5 a</td>
<td>500.0</td>
<td>0.335</td>
<td>306.1 a</td>
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<td>500.0</td>
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<td>600.0</td>
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<td>213.4 a</td>
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<td>98.4</td>
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<tr>
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<td>1000.0</td>
<td>0.419</td>
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<tr>
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<td>1400.0</td>
<td>0.116</td>
<td>10.6</td>
</tr>
<tr>
<td>750.0</td>
<td>0.078</td>
<td>7.1</td>
<td>1600.0</td>
<td>0.051</td>
<td>4.7</td>
</tr>
<tr>
<td>900.0</td>
<td>0.030</td>
<td>2.7</td>
<td>2000.0</td>
<td>0.027</td>
<td>2.5 b</td>
</tr>
<tr>
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<td>2.1</td>
<td>2200.0</td>
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</tr>
</tbody>
</table>

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)

<table>
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<th>Carbon Mass (mg)</th>
<th>Abs.</th>
<th>Conc. (mg/l)</th>
<th>Carbon Mass (mg)</th>
<th>Abs.</th>
<th>Conc. (mg/l)</th>
</tr>
</thead>
<tbody>
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<td>0.0</td>
<td>1.157</td>
<td>995.5 a</td>
</tr>
<tr>
<td>0.0</td>
<td>1.152</td>
<td>990.1 a</td>
<td>0.0</td>
<td>1.153</td>
<td>991.7 a</td>
</tr>
<tr>
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<td>1000.0</td>
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<td>92.7</td>
</tr>
<tr>
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<td>56.4</td>
</tr>
<tr>
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<td>15.7</td>
</tr>
<tr>
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<td>11.2</td>
</tr>
<tr>
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<td>8.2 b</td>
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<tr>
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</table>

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)

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<th>Carbon Mass (mg)</th>
<th>Abs.</th>
<th>Conc. (mg/l)</th>
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</thead>
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<td>995.7 a</td>
</tr>
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<td>1000.5 a</td>
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<td>693.5 a</td>
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<td>572.6 a</td>
</tr>
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<tr>
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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)

<table>
<thead>
<tr>
<th>Carbon Mass mg</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
<th>Carbon Mass mg</th>
<th>Abs.</th>
<th>Conc. mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.029</td>
<td>998.3 a</td>
<td>0.0</td>
<td>1.032</td>
<td>1002.2 a</td>
</tr>
<tr>
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<td>0.057</td>
<td>5.5</td>
</tr>
<tr>
<td>400.0</td>
<td>0.057</td>
<td>5.5</td>
<td>800.0</td>
<td>0.027</td>
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<td>2.5</td>
<td>900.0</td>
<td>0.021</td>
<td>2.0 b</td>
</tr>
</tbody>
</table>

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)

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

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)

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

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)

<table>
<thead>
<tr>
<th>carbon mg.</th>
<th>no initial oxygen 0.0 mg/l</th>
<th>initial oxygen exists</th>
<th>3.8 mg/l</th>
<th>8.9 mg/l</th>
<th>31.4 mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Abs. Conc. mg/l</td>
<td>Abs. Conc. mg/l</td>
<td>Abs. Conc. mg/l</td>
<td>Abs. Conc. mg/l</td>
<td>Abs. Conc. mg/l</td>
</tr>
<tr>
<td>0</td>
<td>1.116</td>
<td>997.4a</td>
<td>0.137</td>
<td>994.4a</td>
<td>1.138</td>
</tr>
<tr>
<td>250</td>
<td>.718</td>
<td>617.7a</td>
<td>.683</td>
<td>597.1a</td>
<td>.740</td>
</tr>
<tr>
<td>350</td>
<td>.603</td>
<td>501.3a</td>
<td>.455</td>
<td>398.5a</td>
<td>.379</td>
</tr>
<tr>
<td>500</td>
<td>.385</td>
<td>331.0a</td>
<td>.256</td>
<td>224.3a</td>
<td>.271</td>
</tr>
<tr>
<td>600</td>
<td>.314</td>
<td>270.3a</td>
<td>.928</td>
<td>81.2</td>
<td>1.001</td>
</tr>
<tr>
<td>800</td>
<td>.209</td>
<td>179.4a</td>
<td>.682</td>
<td>59.7</td>
<td>.783</td>
</tr>
<tr>
<td>1000</td>
<td>1.07</td>
<td>92.7</td>
<td>.350</td>
<td>30.6</td>
<td>.519</td>
</tr>
<tr>
<td>1200</td>
<td>0.65</td>
<td>56.4</td>
<td>.393</td>
<td>34.4</td>
<td>.270</td>
</tr>
<tr>
<td>1400</td>
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<td>26.3</td>
<td>.174</td>
<td>15.2</td>
<td>.248</td>
</tr>
<tr>
<td>1600</td>
<td>0.18</td>
<td>15.7 b 750</td>
<td>.141</td>
<td>12.3 b</td>
<td>.093</td>
</tr>
<tr>
<td>1700</td>
<td>0.13</td>
<td>11.2 800</td>
<td>.078</td>
<td>6.8</td>
<td>.069</td>
</tr>
<tr>
<td>1800</td>
<td>0.09</td>
<td>8.2 850</td>
<td>.059</td>
<td>5.2</td>
<td>.067</td>
</tr>
<tr>
<td>2000</td>
<td>0.07</td>
<td>6.1 b 900</td>
<td>.056</td>
<td>4.9 b</td>
<td>.050</td>
</tr>
<tr>
<td>2200</td>
<td>0.05</td>
<td>4.9 1100</td>
<td>.046</td>
<td>4.0</td>
<td>.045</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Carbon mg.</th>
<th>Abs. Conc. mg/l</th>
<th>Carbon mg.</th>
<th>Abs. Conc. mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.157</td>
<td>0</td>
<td>1.133</td>
</tr>
<tr>
<td>0</td>
<td>1.155</td>
<td>0</td>
<td>1.134</td>
</tr>
<tr>
<td>100</td>
<td>.806</td>
<td>50</td>
<td>.871</td>
</tr>
<tr>
<td>150</td>
<td>.607</td>
<td>100</td>
<td>.678</td>
</tr>
<tr>
<td>250</td>
<td>.373</td>
<td>150</td>
<td>.405</td>
</tr>
<tr>
<td>350</td>
<td>.190</td>
<td>200</td>
<td>.200</td>
</tr>
<tr>
<td>450</td>
<td>.817</td>
<td>225</td>
<td>.186</td>
</tr>
<tr>
<td>550</td>
<td>.365</td>
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<td>.158</td>
</tr>
<tr>
<td>600</td>
<td>.266</td>
<td>275</td>
<td>.921</td>
</tr>
<tr>
<td>650</td>
<td>.120</td>
<td>300</td>
<td>.511</td>
</tr>
<tr>
<td>700</td>
<td>.097</td>
<td>325</td>
<td>.195</td>
</tr>
<tr>
<td>750</td>
<td>.078</td>
<td>350</td>
<td>.125</td>
</tr>
<tr>
<td>800</td>
<td>.069</td>
<td>400</td>
<td>.087</td>
</tr>
<tr>
<td>850</td>
<td>.048</td>
<td>450</td>
<td>.051</td>
</tr>
<tr>
<td>1000</td>
<td>.035</td>
<td>500</td>
<td>.035</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbon mg.</th>
<th>Abs. Conc. mg/l</th>
<th>Carbon mg.</th>
<th>Abs. Conc. mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8 mg/l</td>
<td>991.6a</td>
<td>8.9 mg/l</td>
<td>92.8</td>
</tr>
<tr>
<td>31.4 mg/l</td>
<td>993.4a</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.143</td>
<td>996.400</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.895</td>
<td>780.181</td>
<td>0.763</td>
</tr>
<tr>
<td>0.500</td>
<td>0.665</td>
<td>579.905</td>
<td>0.582</td>
</tr>
<tr>
<td>1.000</td>
<td>0.529</td>
<td>461.333</td>
<td>0.463</td>
</tr>
<tr>
<td>1.500</td>
<td>0.438</td>
<td>381.621</td>
<td>0.383</td>
</tr>
<tr>
<td>2.000</td>
<td>0.391</td>
<td>340.769</td>
<td>0.342</td>
</tr>
<tr>
<td>3.000</td>
<td>0.367</td>
<td>319.844</td>
<td>0.321</td>
</tr>
<tr>
<td>5.000</td>
<td>0.310</td>
<td>270.024</td>
<td>0.271</td>
</tr>
<tr>
<td>7.000</td>
<td>0.290</td>
<td>253.086</td>
<td>0.254</td>
</tr>
<tr>
<td>9.500</td>
<td>0.275</td>
<td>240.132</td>
<td>0.241</td>
</tr>
<tr>
<td>12.000</td>
<td>0.251</td>
<td>219.208</td>
<td>0.220</td>
</tr>
<tr>
<td>24.000</td>
<td>0.208</td>
<td>181.345</td>
<td>0.182</td>
</tr>
<tr>
<td>36.000</td>
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<td>164.406</td>
<td>0.165</td>
</tr>
<tr>
<td>48.000</td>
<td>0.171</td>
<td>149.469</td>
<td>0.150</td>
</tr>
<tr>
<td>72.000</td>
<td>0.154</td>
<td>134.514</td>
<td>0.135</td>
</tr>
<tr>
<td>96.000</td>
<td>0.139</td>
<td>121.561</td>
<td>0.122</td>
</tr>
<tr>
<td>120.000</td>
<td>0.130</td>
<td>113.590</td>
<td>0.114</td>
</tr>
<tr>
<td>144.000</td>
<td>0.122</td>
<td>106.615</td>
<td>0.107</td>
</tr>
<tr>
<td>180.000</td>
<td>0.109</td>
<td>94.658</td>
<td>0.095</td>
</tr>
<tr>
<td>264.000</td>
<td>0.040</td>
<td>81.705</td>
<td>0.082</td>
</tr>
<tr>
<td>336.000</td>
<td>0.040</td>
<td>81.705</td>
<td>0.082</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.140</td>
<td>994.000</td>
<td>1.000a b</td>
</tr>
<tr>
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<td>0.786a</td>
</tr>
<tr>
<td>0.500</td>
<td>0.655</td>
<td>571.550</td>
<td>0.575a</td>
</tr>
<tr>
<td>1.083</td>
<td>0.519</td>
<td>452.270</td>
<td>0.455a</td>
</tr>
<tr>
<td>1.503</td>
<td>0.441</td>
<td>384.678</td>
<td>0.387a</td>
</tr>
<tr>
<td>2.083</td>
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<td>0.343a</td>
</tr>
<tr>
<td>3.083</td>
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<td>322.056</td>
<td>0.324a</td>
</tr>
<tr>
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<td>0.274a</td>
</tr>
<tr>
<td>7.083</td>
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<td>0.258a</td>
</tr>
<tr>
<td>9.583</td>
<td>0.276</td>
<td>240.548</td>
<td>0.242a</td>
</tr>
<tr>
<td>12.083</td>
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<td>0.235a</td>
</tr>
<tr>
<td>24.083</td>
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<td>0.198a</td>
</tr>
<tr>
<td>36.083</td>
<td>0.218</td>
<td>189.854</td>
<td>0.191a</td>
</tr>
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<td>48.083</td>
<td>0.207</td>
<td>180.908</td>
<td>0.182a b</td>
</tr>
<tr>
<td>72.083</td>
<td>0.207</td>
<td>180.908</td>
<td>0.182a</td>
</tr>
<tr>
<td>96.083</td>
<td>0.207</td>
<td>180.908</td>
<td>0.182a</td>
</tr>
<tr>
<td>120.083</td>
<td>0.207</td>
<td>180.908</td>
<td>0.182a b</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.120</td>
<td>1001.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
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<td>0.790</td>
</tr>
<tr>
<td>0.500</td>
<td>0.673</td>
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<td>0.601</td>
</tr>
<tr>
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<td>0.481</td>
</tr>
<tr>
<td>1.500</td>
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<td>0.400</td>
</tr>
<tr>
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<td>0.361</td>
</tr>
<tr>
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<td>0.318</td>
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<tr>
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<td>0.306</td>
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<tr>
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<td>0.281</td>
</tr>
<tr>
<td>12.000</td>
<td>0.291</td>
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<td>0.260</td>
</tr>
<tr>
<td>24.000</td>
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<td>0.228</td>
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<tr>
<td>36.000</td>
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<td>0.186</td>
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<td>48.000</td>
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<td>0.156</td>
</tr>
<tr>
<td>72.000</td>
<td>0.121</td>
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<td>0.108</td>
</tr>
<tr>
<td>96.000</td>
<td>0.071</td>
<td>78.078</td>
<td>0.078</td>
</tr>
<tr>
<td>120.000</td>
<td>0.060</td>
<td>60.060</td>
<td>0.060</td>
</tr>
<tr>
<td>144.000</td>
<td>0.048</td>
<td>48.048</td>
<td>0.048</td>
</tr>
<tr>
<td>180.000</td>
<td>0.037</td>
<td>37.037</td>
<td>0.037</td>
</tr>
<tr>
<td>264.000</td>
<td>0.029</td>
<td>29.129</td>
<td>0.029</td>
</tr>
<tr>
<td>336.000</td>
<td>0.029</td>
<td>29.129</td>
<td>0.029</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.122</td>
<td>1002.700</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.880</td>
<td>787.119</td>
<td>0.785</td>
</tr>
<tr>
<td>0.500</td>
<td>0.679</td>
<td>606.633</td>
<td>0.605</td>
</tr>
<tr>
<td>1.083</td>
<td>0.528</td>
<td>472.271</td>
<td>0.471</td>
</tr>
<tr>
<td>1.583</td>
<td>0.437</td>
<td>391.053</td>
<td>0.390</td>
</tr>
<tr>
<td>2.083</td>
<td>0.409</td>
<td>365.985</td>
<td>0.365</td>
</tr>
<tr>
<td>3.083</td>
<td>0.381</td>
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<td>0.340</td>
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<td>0.314</td>
</tr>
<tr>
<td>7.083</td>
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<td>0.300</td>
</tr>
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<td>0.300</td>
</tr>
<tr>
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<td>0.331</td>
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<td>0.295</td>
</tr>
<tr>
<td>24.083</td>
<td>0.316</td>
<td>282.761</td>
<td>0.282</td>
</tr>
<tr>
<td>36.083</td>
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<td>0.278</td>
</tr>
<tr>
<td>48.083</td>
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<td>265.715</td>
<td>0.265</td>
</tr>
<tr>
<td>72.083</td>
<td>0.293</td>
<td>261.705</td>
<td>0.261</td>
</tr>
<tr>
<td>96.083</td>
<td>0.293</td>
<td>261.705</td>
<td>0.261</td>
</tr>
<tr>
<td>120.083</td>
<td>0.293</td>
<td>261.705</td>
<td>0.261</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.099</td>
<td>995.00</td>
<td>1.000 a b</td>
</tr>
<tr>
<td>0.160</td>
<td>0.958</td>
<td>866.645</td>
<td>0.871 a</td>
</tr>
<tr>
<td>0.500</td>
<td>0.863</td>
<td>781.075</td>
<td>0.785 a</td>
</tr>
<tr>
<td>1.000</td>
<td>0.759</td>
<td>686.550</td>
<td>0.690 a</td>
</tr>
<tr>
<td>1.500</td>
<td>0.700</td>
<td>633.815</td>
<td>0.637 a</td>
</tr>
<tr>
<td>2.000</td>
<td>0.661</td>
<td>597.995</td>
<td>0.601 a</td>
</tr>
<tr>
<td>3.000</td>
<td>0.598</td>
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<td>0.544 a</td>
</tr>
<tr>
<td>5.000</td>
<td>0.500</td>
<td>452.725</td>
<td>0.455 a</td>
</tr>
<tr>
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<td>0.387</td>
<td>350.240</td>
<td>0.352 a</td>
</tr>
<tr>
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<td>0.363</td>
<td>288.350</td>
<td>0.330 a</td>
</tr>
<tr>
<td>12.000</td>
<td>0.321</td>
<td>290.540</td>
<td>0.292 a</td>
</tr>
<tr>
<td>24.000</td>
<td>0.288</td>
<td>260.690</td>
<td>0.262 a b</td>
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<tr>
<td>36.000</td>
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<td>0.246 a</td>
</tr>
<tr>
<td>48.000</td>
<td>0.245</td>
<td>221.885</td>
<td>0.223 a</td>
</tr>
<tr>
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<td>0.221</td>
<td>199.995</td>
<td>0.201 a</td>
</tr>
<tr>
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<td>0.184</td>
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<td>0.167 a</td>
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<td>120.000</td>
<td>0.150</td>
<td>144.275</td>
<td>0.145 a</td>
</tr>
<tr>
<td>144.000</td>
<td>0.152</td>
<td>137.310</td>
<td>0.138 a</td>
</tr>
<tr>
<td>180.000</td>
<td>0.132</td>
<td>119.400</td>
<td>0.120 a b</td>
</tr>
<tr>
<td>264.000</td>
<td>0.118</td>
<td>106.465</td>
<td>0.107 a</td>
</tr>
<tr>
<td>336.000</td>
<td>0.118</td>
<td>106.465</td>
<td>0.107 a b</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.097</td>
<td>992.700</td>
<td>1.000 a b</td>
</tr>
<tr>
<td>0.160</td>
<td>0.965</td>
<td>873.576</td>
<td>0.880 a</td>
</tr>
<tr>
<td>0.500</td>
<td>0.865</td>
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<td>0.789 a</td>
</tr>
<tr>
<td>1.083</td>
<td>0.773</td>
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<td>0.643 a</td>
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<td>2.083</td>
<td>0.666</td>
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<td>0.607 a</td>
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<tr>
<td>3.083</td>
<td>0.600</td>
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<tr>
<td>5.083</td>
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<td>0.459 a</td>
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<td>0.407</td>
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<td>0.371 a</td>
</tr>
<tr>
<td>9.583</td>
<td>0.389</td>
<td>352.408</td>
<td>0.355 a</td>
</tr>
<tr>
<td>12.083</td>
<td>0.376</td>
<td>340.496</td>
<td>0.343 a</td>
</tr>
<tr>
<td>24.083</td>
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<td>332.554</td>
<td>0.335 a b</td>
</tr>
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<td>36.083</td>
<td>0.361</td>
<td>326.598</td>
<td>0.329 a</td>
</tr>
<tr>
<td>48.083</td>
<td>0.359</td>
<td>324.613</td>
<td>0.327 a</td>
</tr>
<tr>
<td>72.083</td>
<td>0.356</td>
<td>322.627</td>
<td>0.325 a</td>
</tr>
<tr>
<td>96.083</td>
<td>0.354</td>
<td>320.642</td>
<td>0.323 a</td>
</tr>
<tr>
<td>120.083</td>
<td>0.354</td>
<td>320.642</td>
<td>0.323 a b</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.038</td>
<td>1000.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.802</td>
<td>772.000</td>
<td>0.772</td>
</tr>
<tr>
<td>0.500</td>
<td>0.625</td>
<td>602.000</td>
<td>0.602</td>
</tr>
<tr>
<td>1.000</td>
<td>0.512</td>
<td>493.000</td>
<td>0.493</td>
</tr>
<tr>
<td>1.500</td>
<td>0.433</td>
<td>417.000</td>
<td>0.417</td>
</tr>
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<td>2.000</td>
<td>0.389</td>
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<td>0.375</td>
</tr>
<tr>
<td>3.000</td>
<td>0.353</td>
<td>340.000</td>
<td>0.340</td>
</tr>
<tr>
<td>5.000</td>
<td>0.319</td>
<td>307.000</td>
<td>0.307</td>
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<td>0.393</td>
</tr>
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</tr>
<tr>
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<td>0.372</td>
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<tr>
<td>24.000</td>
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<td>0.258</td>
</tr>
<tr>
<td>36.000</td>
<td>0.260</td>
<td>250.000</td>
<td>0.250</td>
</tr>
<tr>
<td>48.000</td>
<td>0.255</td>
<td>246.000</td>
<td>0.246</td>
</tr>
<tr>
<td>72.000</td>
<td>0.250</td>
<td>241.000</td>
<td>0.241</td>
</tr>
<tr>
<td>96.000</td>
<td>0.244</td>
<td>235.000</td>
<td>0.235</td>
</tr>
<tr>
<td>120.000</td>
<td>0.239</td>
<td>230.000</td>
<td>0.230</td>
</tr>
<tr>
<td>144.000</td>
<td>0.235</td>
<td>226.000</td>
<td>0.226</td>
</tr>
<tr>
<td>180.000</td>
<td>0.232</td>
<td>223.000</td>
<td>0.223</td>
</tr>
<tr>
<td>264.000</td>
<td>0.227</td>
<td>219.000</td>
<td>0.219</td>
</tr>
<tr>
<td>336.000</td>
<td>0.227</td>
<td>219.000</td>
<td>0.219</td>
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</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.038</td>
<td>1000.000</td>
<td>1.000</td>
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<tr>
<td>2.000</td>
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<td>0.778</td>
</tr>
<tr>
<td>1.089</td>
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<td>0.594</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>3.089</td>
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<td>0.343</td>
</tr>
<tr>
<td>5.089</td>
<td>0.325</td>
<td>313.000</td>
<td>0.313</td>
</tr>
<tr>
<td>7.089</td>
<td>0.315</td>
<td>303.000</td>
<td>0.303</td>
</tr>
<tr>
<td>9.589</td>
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<td>0.295</td>
</tr>
<tr>
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<td>0.287</td>
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<tr>
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<td>0.273</td>
</tr>
<tr>
<td>36.089</td>
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</tr>
<tr>
<td>48.089</td>
<td>0.275</td>
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<td>0.265</td>
</tr>
<tr>
<td>72.089</td>
<td>0.273</td>
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<td>0.263</td>
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<tr>
<td>96.089</td>
<td>0.273</td>
<td>263.000</td>
<td>0.263</td>
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<tr>
<td>120.089</td>
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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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.038</td>
<td>1000.00</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.837</td>
<td>806.000</td>
<td>0.806</td>
</tr>
<tr>
<td>0.500</td>
<td>0.652</td>
<td>628.000</td>
<td>0.628</td>
</tr>
<tr>
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<td>0.488</td>
</tr>
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<td>1.500</td>
<td>0.439</td>
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</tr>
<tr>
<td>2.000</td>
<td>0.400</td>
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<td>0.385</td>
</tr>
<tr>
<td>3.000</td>
<td>0.389</td>
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<td>0.375</td>
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<tr>
<td>9.500</td>
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<td>0.330</td>
</tr>
<tr>
<td>12.000</td>
<td>0.324</td>
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<td>0.312</td>
</tr>
<tr>
<td>24.000</td>
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<td>0.256</td>
</tr>
<tr>
<td>36.000</td>
<td>0.246</td>
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<td>0.237</td>
</tr>
<tr>
<td>48.000</td>
<td>0.205</td>
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<td>0.197</td>
</tr>
<tr>
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<td>0.160</td>
</tr>
<tr>
<td>96.000</td>
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<td>0.117</td>
</tr>
<tr>
<td>120.000</td>
<td>0.110</td>
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<td>0.106</td>
</tr>
<tr>
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<td>95.000</td>
<td>0.095</td>
</tr>
<tr>
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<td>84.000</td>
<td>0.084</td>
</tr>
<tr>
<td>264.000</td>
<td>0.084</td>
<td>81.000</td>
<td>0.070</td>
</tr>
<tr>
<td>336.000</td>
<td>0.084</td>
<td>81.000</td>
<td>0.070</td>
</tr>
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</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.042</td>
<td>1000.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.824</td>
<td>791.000</td>
<td>0.791</td>
</tr>
<tr>
<td>0.500</td>
<td>0.641</td>
<td>615.000</td>
<td>0.615</td>
</tr>
<tr>
<td>1.089</td>
<td>0.522</td>
<td>501.000</td>
<td>0.501</td>
</tr>
<tr>
<td>1.589</td>
<td>0.444</td>
<td>426.000</td>
<td>0.426</td>
</tr>
<tr>
<td>2.089</td>
<td>0.409</td>
<td>393.000</td>
<td>0.393</td>
</tr>
<tr>
<td>3.089</td>
<td>0.393</td>
<td>377.000</td>
<td>0.377</td>
</tr>
<tr>
<td>5.089</td>
<td>0.386</td>
<td>371.000</td>
<td>0.371</td>
</tr>
<tr>
<td>7.089</td>
<td>0.371</td>
<td>356.000</td>
<td>0.356</td>
</tr>
<tr>
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<tr>
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<tr>
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<td>48.089</td>
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<tr>
<td>72.089</td>
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<tr>
<td>96.089</td>
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<tr>
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</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.038</td>
<td>1000.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.940</td>
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<td>0.905</td>
</tr>
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<td>0.500</td>
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<td>0.464</td>
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<td>0.424</td>
</tr>
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</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.038</td>
<td>1000.000</td>
<td>1.000</td>
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<tr>
<td>0.160</td>
<td>0.934</td>
<td>899.000</td>
<td>0.899</td>
</tr>
<tr>
<td>0.500</td>
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<td>0.645</td>
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<tr>
<td>7.089</td>
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<tr>
<td>48.089</td>
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<tr>
<td>72.089</td>
<td>0.602</td>
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<td>96.089</td>
<td>0.601</td>
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<td>120.089</td>
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</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.084</td>
<td>994.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.810</td>
<td>742.518</td>
<td>0.747</td>
</tr>
<tr>
<td>0.500</td>
<td>0.636</td>
<td>583.478</td>
<td>0.587</td>
</tr>
<tr>
<td>1.000</td>
<td>0.506</td>
<td>464.198</td>
<td>0.467</td>
</tr>
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<td>0.376</td>
</tr>
<tr>
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<td>0.380</td>
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<td>0.351</td>
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<tr>
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<tr>
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<td>0.291</td>
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<tr>
<td>264.000</td>
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<tr>
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<td>20.874</td>
<td>0.021</td>
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</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.000</td>
<td>1.122</td>
<td>1002.700</td>
<td>1.000</td>
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<td>0.465</td>
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<tr>
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<td>190.427</td>
<td>0.191</td>
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</table>

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: 28.6 gm

Initial oxygen purged (32.3 mg/l)

Temperature: 21°C.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
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<td>0.060</td>
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</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs. (mg/l)</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.122</td>
<td>1002.700</td>
<td>1.000 a b</td>
</tr>
<tr>
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<td>0.304 a</td>
</tr>
<tr>
<td>9.583</td>
<td>0.336</td>
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<td>0.300 a</td>
</tr>
<tr>
<td>12.083</td>
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<td>295.796</td>
<td>0.295 a</td>
</tr>
<tr>
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<td>0.282 a b</td>
</tr>
<tr>
<td>36.083</td>
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<td>278.750</td>
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<td>48.083</td>
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<td>265.715</td>
<td>0.265 a</td>
</tr>
<tr>
<td>72.083</td>
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<td>261.705</td>
<td>0.261 a</td>
</tr>
<tr>
<td>96.083</td>
<td>0.293</td>
<td>261.705</td>
<td>0.261 a</td>
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<tr>
<td>120.083</td>
<td>0.293</td>
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<td>0.261 a b</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
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<tbody>
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<td>0.000</td>
<td>1.080</td>
<td>997.000</td>
<td>1.000</td>
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<tr>
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<td>0.127</td>
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<td>0.096</td>
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<td>81.754</td>
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</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.081</td>
<td>998.000</td>
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</tr>
<tr>
<td>0.160</td>
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<td>0.522</td>
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<td>0.495</td>
</tr>
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<td>0.491</td>
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<td>0.484</td>
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<td>36.083</td>
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<td>0.463</td>
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<tr>
<td>48.083</td>
<td>0.501</td>
<td>462.074</td>
<td>0.463</td>
</tr>
<tr>
<td>72.083</td>
<td>0.501</td>
<td>462.074</td>
<td>0.463</td>
</tr>
<tr>
<td>96.083</td>
<td>0.501</td>
<td>462.074</td>
<td>0.463</td>
</tr>
<tr>
<td>120.083</td>
<td>0.501</td>
<td>462.074</td>
<td>0.463</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>Conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.038</td>
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<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
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<td>0.783</td>
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<tr>
<td>0.500</td>
<td>0.638</td>
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</tr>
<tr>
<td>1.000</td>
<td>0.499</td>
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<td>0.481</td>
</tr>
<tr>
<td>1.500</td>
<td>0.462</td>
<td>445.000</td>
<td>0.445</td>
</tr>
<tr>
<td>2.000</td>
<td>0.439</td>
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<td>0.423</td>
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<tr>
<td>3.000</td>
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<td>0.378</td>
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<td>0.256</td>
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<tr>
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<td>0.159</td>
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<td>0.150</td>
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</tr>
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<tr>
<td>264.000</td>
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<tr>
<td>336.000</td>
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<td>86.000</td>
<td>0.086</td>
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</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs. (mg/l)</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.038</td>
<td>1000.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.100</td>
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<td>0.775</td>
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<td>0.500</td>
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<td>0.626</td>
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<td>1.089</td>
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<td>0.486</td>
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<tr>
<td>1.589</td>
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<td>0.439</td>
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<tr>
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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.

<table>
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<th>Time (Hour)</th>
<th>Abs.</th>
<th>Conc. (c) (mg/l)</th>
<th>c/c0</th>
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<td>1.000</td>
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<tr>
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<td>0.237</td>
</tr>
<tr>
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<td>0.070</td>
</tr>
<tr>
<td>336.000</td>
<td>0.084</td>
<td>81.000</td>
<td>0.070</td>
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</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
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<td>1000.000</td>
<td>1.000</td>
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<td>1.589</td>
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<td>0.426</td>
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<td>2.089</td>
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<td>0.393</td>
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<td>3.089</td>
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</tr>
<tr>
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<td>0.371</td>
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<tr>
<td>7.089</td>
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<td>0.356</td>
</tr>
<tr>
<td>9.589</td>
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<td>0.348</td>
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<tr>
<td>12.089</td>
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<td>0.342</td>
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<tr>
<td>24.089</td>
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<td>0.317</td>
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<tr>
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<tr>
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<tr>
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</tr>
<tr>
<td>120.089</td>
<td>0.314</td>
<td>301.000</td>
<td>0.301</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
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<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.038</td>
<td>1000.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.821</td>
<td>791.000</td>
<td>0.791</td>
</tr>
<tr>
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<td>0.531</td>
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</tr>
<tr>
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</tr>
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<td>0.326</td>
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<tr>
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<td>0.295</td>
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<tr>
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<td>0.281</td>
</tr>
<tr>
<td>48.000</td>
<td>0.246</td>
<td>237.000</td>
<td>0.237</td>
</tr>
<tr>
<td>72.000</td>
<td>0.171</td>
<td>165.000</td>
<td>0.165</td>
</tr>
<tr>
<td>96.000</td>
<td>0.154</td>
<td>148.000</td>
<td>0.148</td>
</tr>
<tr>
<td>120.000</td>
<td>0.134</td>
<td>129.000</td>
<td>0.129</td>
</tr>
<tr>
<td>144.000</td>
<td>0.123</td>
<td>118.000</td>
<td>0.118</td>
</tr>
<tr>
<td>180.000</td>
<td>0.111</td>
<td>107.000</td>
<td>0.107</td>
</tr>
<tr>
<td>264.000</td>
<td>0.106</td>
<td>102.000</td>
<td>0.102</td>
</tr>
<tr>
<td>336.000</td>
<td>0.106</td>
<td>102.000</td>
<td>0.102</td>
</tr>
</tbody>
</table>

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.

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

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.120</td>
<td>1001.000</td>
<td>1.000 a</td>
</tr>
<tr>
<td>0.160</td>
<td>0.885</td>
<td>790.790</td>
<td>0.790 a</td>
</tr>
<tr>
<td>0.500</td>
<td>0.673</td>
<td>601.601</td>
<td>0.601 a</td>
</tr>
<tr>
<td>1.000</td>
<td>0.539</td>
<td>481.481</td>
<td>0.481 a</td>
</tr>
<tr>
<td>1.500</td>
<td>0.448</td>
<td>400.400</td>
<td>0.400 a</td>
</tr>
<tr>
<td>2.000</td>
<td>0.404</td>
<td>361.361</td>
<td>0.361 a</td>
</tr>
<tr>
<td>3.000</td>
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<td>0.334 a</td>
</tr>
<tr>
<td>5.000</td>
<td>0.356</td>
<td>318.318</td>
<td>0.318 a</td>
</tr>
<tr>
<td>7.000</td>
<td>0.343</td>
<td>306.306</td>
<td>0.306 a</td>
</tr>
<tr>
<td>9.500</td>
<td>0.315</td>
<td>281.281</td>
<td>0.281 a</td>
</tr>
<tr>
<td>12.000</td>
<td>0.291</td>
<td>260.260</td>
<td>0.260 a</td>
</tr>
<tr>
<td>24.000</td>
<td>0.255</td>
<td>228.228</td>
<td>0.228 a</td>
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<tr>
<td>36.000</td>
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<td>0.186 a</td>
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<td>48.000</td>
<td>0.175</td>
<td>156.156</td>
<td>0.156 a</td>
</tr>
<tr>
<td>72.000</td>
<td>0.121</td>
<td>108.108</td>
<td>0.108 a</td>
</tr>
<tr>
<td>96.000</td>
<td>0.071</td>
<td>78.078</td>
<td>0.078</td>
</tr>
<tr>
<td>120.000</td>
<td>0.060</td>
<td>60.060</td>
<td>0.060</td>
</tr>
<tr>
<td>144.000</td>
<td>0.048</td>
<td>48.048</td>
<td>0.048</td>
</tr>
<tr>
<td>180.000</td>
<td>0.037</td>
<td>37.037</td>
<td>0.037 b</td>
</tr>
<tr>
<td>264.000</td>
<td>0.029</td>
<td>29.129</td>
<td>0.029 b</td>
</tr>
<tr>
<td>336.000</td>
<td>0.029</td>
<td>29.129</td>
<td>0.029 b</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.120</td>
<td>998.100</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.874</td>
<td>778.586</td>
<td>0.780</td>
</tr>
<tr>
<td>0.500</td>
<td>0.682</td>
<td>607.646</td>
<td>0.609</td>
</tr>
<tr>
<td>1.000</td>
<td>0.531</td>
<td>473.136</td>
<td>0.474</td>
</tr>
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<td>1.500</td>
<td>0.463</td>
<td>412.419</td>
<td>0.413</td>
</tr>
<tr>
<td>2.000</td>
<td>0.395</td>
<td>351.703</td>
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<td>0.383</td>
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<td>0.342</td>
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<td>5.000</td>
<td>0.364</td>
<td>324.614</td>
<td>0.325</td>
</tr>
<tr>
<td>7.000</td>
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<td>0.310</td>
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<tr>
<td>9.500</td>
<td>0.322</td>
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<td>0.288</td>
</tr>
<tr>
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<td>0.252</td>
</tr>
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<td>0.210</td>
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<td>0.156</td>
</tr>
<tr>
<td>72.000</td>
<td>0.119</td>
<td>106.035</td>
<td>0.106</td>
</tr>
<tr>
<td>96.000</td>
<td>0.100</td>
<td>89.221</td>
<td>0.089</td>
</tr>
<tr>
<td>120.000</td>
<td>0.088</td>
<td>78.012</td>
<td>0.078</td>
</tr>
<tr>
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<tr>
<td>264.000</td>
<td>0.071</td>
<td>62.880</td>
<td>0.063</td>
</tr>
<tr>
<td>336.000</td>
<td>0.071</td>
<td>62.880</td>
<td>0.063</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.113</td>
<td>987.000</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.882</td>
<td>790.621</td>
<td>0.793</td>
</tr>
<tr>
<td>0.500</td>
<td>0.660</td>
<td>591.221</td>
<td>0.593</td>
</tr>
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<td>466.596</td>
<td>0.468</td>
</tr>
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<td>0.451</td>
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<td>0.405</td>
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<td>2.000</td>
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<td>0.362</td>
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<td>0.332</td>
</tr>
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<td>326.019</td>
<td>0.327</td>
</tr>
<tr>
<td>7.000</td>
<td>0.334</td>
<td>299.100</td>
<td>0.300</td>
</tr>
<tr>
<td>9.500</td>
<td>0.323</td>
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<td>0.290</td>
</tr>
<tr>
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<td>0.284</td>
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<td>0.255</td>
</tr>
<tr>
<td>24.000</td>
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<td>0.219</td>
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<tr>
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<td>0.167</td>
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<td>0.150</td>
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<td>0.125</td>
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<tr>
<td>96.000</td>
<td>0.130</td>
<td>116.649</td>
<td>0.117</td>
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<tr>
<td>120.000</td>
<td>0.127</td>
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<td>0.114</td>
</tr>
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<td>144.000</td>
<td>0.125</td>
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<td>0.112</td>
</tr>
<tr>
<td>180.000</td>
<td>0.124</td>
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<td>0.111</td>
</tr>
<tr>
<td>264.000</td>
<td>0.122</td>
<td>109.670</td>
<td>0.110</td>
</tr>
<tr>
<td>335.000</td>
<td>0.122</td>
<td>109.670</td>
<td>0.110</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.122</td>
<td>1002.700</td>
<td>1.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.880</td>
<td>787.119</td>
<td>0.785</td>
</tr>
<tr>
<td>0.500</td>
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<td>0.606</td>
</tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>3.083</td>
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<tr>
<td>5.083</td>
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<td>0.316</td>
</tr>
<tr>
<td>7.083</td>
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<td>310.837</td>
<td>0.310</td>
</tr>
<tr>
<td>9.583</td>
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<td>0.302</td>
</tr>
<tr>
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<td>0.297</td>
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<tr>
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</tr>
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<td>0.271</td>
</tr>
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<td>266.718</td>
<td>0.266</td>
</tr>
<tr>
<td>72.000</td>
<td>0.295</td>
<td>263.710</td>
<td>0.263</td>
</tr>
<tr>
<td>96.083</td>
<td>0.295</td>
<td>263.710</td>
<td>0.263</td>
</tr>
<tr>
<td>120.083</td>
<td>0.295</td>
<td>263.710</td>
<td>0.263</td>
</tr>
</tbody>
</table>

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.

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

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: 30/9/1992

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.

<table>
<thead>
<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>conc. (c) (mg/l)</th>
<th>c/c0</th>
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<tbody>
<tr>
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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.

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</table>

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.

<table>
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<th>Time (Hour)</th>
<th>Abs.</th>
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<th>c/c0</th>
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</table>

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.

<table>
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<tr>
<th>Time (Hour)</th>
<th>Abs.</th>
<th>Conc. (C) (mg/l)</th>
<th>C/C0</th>
</tr>
</thead>
<tbody>
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<td>0.072</td>
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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\textdegree}C.

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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.

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<th>C/C0</th>
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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.

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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 of the surface diffusion coefficient Ds.
PART.COL is the collocation matrices file
Your output file is HSDM.OUT. From this file get the final estimate of Ds.

The second step:
Run SHSDM.EXE
This program uses the following input files:
SHSDM.CTR
SHSDM.IN
INPUT.DAT
PART.COL

The only input file you need to adjust is INPUT.DAT. Again the details are shown in the file itself. Here put the Ds estimate obtained from the program.
The output files are two: SHSDM.OUT and OUTPUT.DAT
SHSDM.OUT will give you the final Ds value.
OUTPUT.DAT will give you a table (found at the end of the file) showing the time, EXP C/CO, and PREDICTED C/CO.
0 1 1 /IPRC,IPRI,IPRO DON'T CHANGE
200.98D0 /CD , INITIAL CONC (mg/L)
1.224 /CARBON CONC (g/L)
0.517756D-05 /DS, SURFACE DIFFUSION ESTIMATE (cm^2/min)
0.207473D0 /XKF, FILM TRANSFER ESTIMATE (cm/min)
50.25 /K, FREUNDLICK K PARAMETER (mg/g - mg/l)
0.214 /XN, FREUNDLICK EXPONENET PARAMETER (mg/g - mg/l)
0.050019D0 /RADP, RADUIS OF GAC PARTICLE (cm)
0.74D0 /RHO, DENSITY OF GAC PARTICLE (g/cm^3)
10 /NCP, NUMBER OF COLLOCATION POINTS- DON'T CHANGE
0.1D-04 2 2 /TOL,METH,HITER DON'T CHANGE
1.0D-10 /DTINIT (min) DON'T CHANGE
2.50D0 /DTOUT (min) DELTA TIME OUT
9000.0D0 /TFINAL (min) TOTAL RUN TIME
10000 /ITMAX MAX NUMBER OF ITERATIONS
12 200.98 1 / NUMBER OF DATA POINTS, INITIAL CONCENTRATION, ALWAYS USE
THE THIRD PARAMETER
0.0 1.0 / TIME, MIN C/Co
30.0 0.597
60.0 0.438
90.0 0.356
120.0 0.328
150.0 0.305
180.0 0.293
210.0 0.281
270.0 0.275
390.0 0.262
630.0 0.258
1133.0 0.244
1.2240 /carbon conc ,g/L
0.050019 /particle radius, cm
0.7 /GAC particle density, g/cm3
50.25 /Freundlich k parameter ((q in mg/g) - (C in mg/L))
0.214 /Freundlich n parameter
0.22 /film transfer coefficient cm/min
5.2d-06 /surface diffusion coefficient, cm2/min
PROGRAM HSDM

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

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
COMMON /VAR/ Y(15),NTOT

OPEN(30,FILE='HSDM.IN',STATUS='OLD')
OPEN(31,FILE='PART.COL',STATUS='OLD')
OPEN(32,FILE='HSDM.OUT',STATUS='NEW')

CALL INPUT

CALL INCOL

CALL INIT

CALL CALCC

STOP ' ALL DONE'

END

SUBROUTINE INPUT

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

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,ITTRY
COMMON /VAR/ Y(15),NTOT

READ(30,*) IPRC,IPRI,IPRO

READ(30,*) CO
READ(30,*) CCONC
READ(30,*) DS
READ(30,*) XKF
READ(30,*) XK
READ(30,*) XN.
READ(30,*) RADP
READ(30,*) RHOP

CONTROL PARAMETER

READ(30,*) NCP
READ(30,*) TOL,METH,MITER
READ(30,*) DTINIT
READ(30,*) DTOUT
READ(30,*) TFINAL
READ(30,*) ITMAX
C
RETURN
END
C
SUBROUTINE INCOL
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /FARM/ CO,QO,CCONC,DS,XKF,
&XX,XN,RADP,RHOP,BIOT,CD,TFACT
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
DIMENSION IDL(2)
DIMENSION DUMMY(14)
C
IFL1=0
IFL2=0
10 CONTINUE
C
READ(31,*) ID
IF(ID .EQ. 999) THEN
C
SOMETHING IS WRONG
WRITE(*,*),' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'
STOP ' ERROR - ALL DONE '
END IF
IF(ID .EQ. NCP) THEN
IFL1=1
END IF
C
READ IN AND DISTRIBUTE
C
IF(IFL1 .NE. 0) THEN
C
READ(31,1001) (WP(I),I=1,ID)
DO 2 I=1,ID
READ(31,1001) (BP(I,J),J=1,ID)
2 CONTINUE
C
IF(IFL1 .EQ. 0) GO TO 10
IF(IFL1 .EQ. 1) GO TO 11
C
END IF
C
IF(IFL1 .EQ. 0) THEN
READ(31,1001) (DUMMY(I),I=1,ID)
DO 6 I=1,ID
READ(31,1001) (DUMMY(J),J=1,ID)
6 CONTINUE
6 CONTINUE
   GO TO 10
END IF

11 CONTINUE

WRITE THE MATRIXES
   IF (IPRC EQ 1) THEN
      WRITE(*,'(WEIGHTS')
      WRITE(*,1001) (WP(I), I=1,NCP)
      WRITE(*,'(COLLOCATION MATRIX (B)')
      DO 13 I=1,NCP
          WRITE(*,1001) (BP(I,J), J=1,NCP)
      13 CONTINUE
   END IF

1001 FORMAT (4D20.12)

RETURN
END

C-----------------------------
SUBROUTINE INIT
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ CD,QO,CCONC,DS,XKF,
& XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT

C.
.
.
N=NTOT*NCP+1

C INITIAL CONDITION FOR SOLID PHASE
C
DO 11 I=1,NTOT-1
   Y(I)=0.000
11 CONTINUE

C LIQUID PHASE
C
Y(NTOT)=1.000
C
C COMPUTE DEPENDENT PARAMETERS
C
QO=XK*CO**XN
C
CD=CCONC*Q0/CD
C
B1=XKF*RADP*CO
B2=DS*RHOP*QO*1000.000
BIOT=B1/B2
C
TFAC=DS/(RADP*RADP)
C
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 CONTROL PARAMETER
WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL
END IF

C FORMAT STATEMENTS

1001 FORMAT(2X,'CO ','E12.6,/.','
&2X,'CCONC = ','E12.6,/,','
&2X,'CD = ','E12.6,/)'

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,'METER = ','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)

COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(I4),BP(I4,I4)
COMMON /PARM/ CO,QO,CCONC,DS,XKF,
&XK,XN,RADP,RHOP,BIOT,CO,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(I5),NTOT

C DIMENSION WK(390),IWK(29)

C
EXTERNAL FCN,FCNJ

C

N=NTOT
HH=DINIT
INDEX=1

C

T=0.000
ITRY=0
ITRYT=0
TPHY=0.000
ITER=0

C

WRITE(*,2001) ITER,ITRY,T,TPHY,Y(NTOT)
WRITE(32,*) ITER,ITRY,T,TPHY,Y(NTOT)

C

100 CONTINUE

C

ITER=ITER+1
TEND=T+DTOUT*TFAC

C

ITRY=0
CALL DGEAR(N,FCN,FCNJ,T,HH,Y,TEND,
&TOL,METH,HITER,INDEX,1WK,WK,IER)

C

ITRYT=ITRY+ITRY
T=TEND
TPHY=TFAC

C

WRITE(*,*) (Y(LL),LL=1,NCP)
WRITE(*,2001) ITER,ITRY,T,TPHY,Y(NTOT)

C

WRITE(32,*) (Y(LL),LL=1,NCP)
WRITE(32,*) ITER,ITRY,T,TPHY,Y(NTOT)
IF (T/TFAC LT TFINAL) GO TO 100

C

WRITE(*,*) 'ITRYT = ',ITRY
WRITE(32,*) ' 999 999 999 999 999 999 999'

2001 FORMAT(1X,14,15,3E12.4)
RETURN
END

C-----------------------------------------------
SUBROUTINE FCNJ(N,T,Y,P)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
DIMENSION Y(N),PD(N,N)
C
RETURN
END
C-----------------------------------------------
SUBROUTINE FCN(N,T,Y,YPRIME)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,HITER
COMMON /COL/ NCP, WP(14), BP(14, 14)
COMMON /FARM/ CO, QQ, CCONC, DS, XKF,
&XK, XN, RADP, RHOP, B10T, C0, TFAC
COMMON /WORK/ DTINIT, DTOUT, TFINAL, ITMAX, ITRY

DIMENSION Y(N), YPRIME(N)
DIMENSION BB(14)

C ITRY=ITRY+1
C
NTOT=N
KK=0
II=0

C NICP=NCP-1
C
DO 30 J=1, NICP
BB(J)=0.000
30 CONTINUE
WW=0.000

C DO 50 I=1, NICP
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 MASS BALANCE INSIDE PARTICLE (EXCEPT BOUNDARY)
C
YPRIME(II)=BB(I)
C
WW=WW+WP(I)*YPRIME(II)
50 CONTINUE

C SOLID-LIQUID INTERFACE
C
II=II+1
CC YPRIME(II) = ((BIOT*(Y(NTOT)-(Y(II)***(1.000/XN))))-WW)/
&WP(NCP))
CC
IJO=0
C HEAT EQ AT INTERFACE
HSD03200
BSUM=0.000
DO 11 KKK=1, NCP
BSUM=BSUM+BP(NCP, KKK)*Y(KKK)
11 CONTINUE

C IF (IJO .EQ. 0) THEN
HSD03260
IF(Y(II) .LT. 1.00-15) THEN
HSD03270
CC YPRIME(II) = ((BIOT*(Y(NTOT)-Y(II)))-WW)/WP(NCP))
HSD03280
CC YPRIME(II) = ((BIOT*(Y(NTOT)-0.000)-WW)/WP(NCP))
HSD03290
YPRIME(II) = (((BIOT*(Y(NTOT)-0.000)-WW)/WP(NCP))+BSUM)*0.5HSD03300
C
ELSE
YPRIME(II) = (((BIOT*(Y(NTOT)-(Y(II)**(1.0D0/XN))))-WW)/
&WP(NCP)+BSUM)*0.5D0
END IF
ENDIF

C
LIQUID PHASE MASS BALANCE
C
YPRIME(NTOT)=-3.0D0*CD*(WW+
&(YPRIME(II)*WP(NCP)))
C
RETURN
END
PROGRAM SEARCH

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

COMMON /PAR1/ COV(10),CCONCV(10),RADPV(10),RHOPV(10),
&PARV(10),NPDV(10),NDSET,IPS(4),ISCALE(4),TM(50,10),
&YM(50,5,10),IDREP(10),NDPSV(10),YF(50,10)

CHARACTER*80 IFNAME(10)

DIMENSION X(4),PARM(4),F(500),XJAC(500,4),XJTJ(10),WORK(103)

EXTERNAL FIND

IXJAC=500

OPEN(1,FILE='SHISDM.IN',STATUS='OLD')
OPEN(97,FILE='SHISDM.CTR',STATUS='OLD')

INPUT SEARCH ROUTINE CONTROL PARAMETER
READ(97,*) NSIG
READ(97,*) EPS
READ(97,*) DELTA
READ(97,*) MAXFN
READ(97,*) I0PT
READ(97,*) PARM(1)
READ(97,*) PARM(2)
READ(97,*) PARM(3)
READ(97,*) PARM(4)

K=1

123 CONTINUE
READ(1,1000) IFNAME(K)
IF(IFNAME(K).NE."NULL") THEN

READ IN THE NAME OF THE DATA FILES
NDSET=K
K=K+1
GO TO 123
ELSE

NAME OF OUTPUT FILE
READ(1,1000) IFNAME(K)
END IF

READ(1,*) (IPS(I),I=1,4)

WRITE(*,*) ' YOUR INPUT ',NDSET,' DATA FILE(S):'
DO 1 K=1,NDSET
WRITE(*,*) IFNAME(K)
1 CONTINUE

WRITE(*,*) ' YOUR OUTPUT DATA FILE IS:'
WRITE(*,*) IFNAME(NDSET+1)

IPSUM=0
DO 2 K=1,4
IF(IPS(K) .EQ. 1) THEN
IPSUM=IPSUM+1
END IF
2 CONTINUE

C
DO 11 K=1,NDSET
OPEN(K,FILE=IFNAME(K),STATUS='OLD')
REWRITE(K)
READ(K,*) NDPV(K),COV(K),IDREP(K)
DO 22 IP=1,NDPV(K)
READ(K,*) TM(IP,K),(YM(IP,1,K),I=1,IDREP(K))
11 CONTINUE

22 CONTINUE
READ(K,*) CONCV(K)
READ(K,*) RADPV(K)
READ(K,* ) RHPV(K)
READ(K,*) PARV(3,K)
READ(K,*) PARV(4,K)
READ(K,*) PARV(1,K)
READ(K,*) PARV(2,K)
11 CONTINUE
C
COUNT TOTAL NUMBER OF DATA POINTS
DO 94 JJ=1,NDSET
NDPSV(JJ)=0
DO 95 JJ=1,NDPV(JJ)
DO 95 JJ=1,NDPV(JJ)
IF(YM(IJ,JJ,II) .LE. 1.1D0) THEN
NDPSV(JJ)=NDPSV(JJ)+1
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 ',IPSUM,' 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
X(K) = PARV(1,1)/(10.000**ISCALE(K))
XXX = X(K)*10.000**ISCALE(K)
WRITE(*,*) 'PARAMETER #',K,' = ',XX
K = K+1
END IF

IF(IPS(2).EQ.1) THEN
SCALE = DLOG10(PARV(2,1))
IF(SCALE.GT.0.000) THEN
ISCALE(K) = DINT(SCALE)+1
ELSE
ISCALE(K) = DINT(SCALE)
END IF
X(K) = PARV(2,1)/(10.000**ISCALE(K))
XXX = X(K)*10.000**ISCALE(K)
WRITE(*,*) 'PARAMETER #',K,' = ',XX
K = K+1
END IF

IF(IPS(3).EQ.1) THEN
SCALE = DLOG10(PARV(3,1))
IF(SCALE.GT.0) THEN
ISCALE(K) = DINT(SCALE)+1
ELSE
ISCALE(K) = DINT(SCALE)
END IF
X(K) = PARV(3,1)/(10.000**ISCALE(K))
XXX = X(K)*10.000**ISCALE(K)
WRITE(*,*) 'PARAMETER #',K,' = ',XX
K = K+1
END IF

IF(IPS(4).EQ.1) THEN
SCALE = DLOG10(PARV(4,1))
IF(SCALE.GT.0) THEN
ISCALE(K) = DINT(SCALE)+1
ELSE
ISCALE(K) = DINT(SCALE)
END IF
X(K) = PARV(4,1)/(10.000**ISCALE(K))
XXX = X(K)*10.000**ISCALE(K)
WRITE(*,*) 'PARAMETER #',K,' = ',XX
END IF

CALL TO THE SEARCH ROUTINE
OPEN(NDSET+1,FILE=IFNAME(NDSET+1),STATUS='NEW')
N = IPSUM
CALL ZXSSQ(FIND,M,N,NSIG, EPS,DELTA,MAXFN,IOPT, PARM, X, &SSQ,F,XJAC,IJAC,XJTJ, WORK,INFER,IER)
OUTPUT TO DATA FILE
DO 111 K=1,NDSET
DO 222 IP=1,NDPV(K)
WRITE(NDSET+1,1001) TM(IP,K), (YM(IP,II,K),II=1,1DREP(K)),
& YF(IP,K)
222 CONTINUE
111 CONTINUE

C
1000 FORMAT(A)
1001 FORMAT(2X,6E16.6)
C
STOP ' ALL DONE'
END

C---------------------------------------------------------------
SUBROUTINE FIND(X,M,N,F)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /PAR1/ COV(10),CCONCV(10),RADPV(10),RIOPV(10),
& PARV(10,10),NDPV(10),NDSET,IPS(4),ISCALE(4),TM(50,10),
& YM(50,5,10),IDREP(10),NDSV(10),YF(50,10)
C
DIMENSION X(N),F(500)
DIMENSION TT(50),YY(50)
DIMENSION SSQV(10),XXV(4)
C
DATA ICALL /0/
ICALL=ICALL+1
C
IF TROUBLE LIMIT THE PARAMETERS TO
THE SMALLEST VALUE OF 10D-30
DO 1 KK=1,N
X(KK)=DMAX1(X(KK),1.0D-30)
1 CONTINUE
C
WRITE(*,1000) ICALL,(X(KK)*10.0D0**ISCALE(KK),KK=1,N)
WRITE(NDSET+1,1000) ICALL,(X(KK)*10.0D0**ISCALE(KK),KK=1,N)

C
LL=1
DO 111 K=1,NDSET
LOAD TIME VECTOR FOR THE K'S DATA SET
DO 2 L=1,NDPV(K)
TT(L)=TM(L,K)
2 CONTINUE

C
DO 9 II=1,4
IF(IPS(II).EQ.1) THEN
XXV(II)=X(II)*10.0D0**ISCALE(II)
ELSE
XXV(II)=PARV(II,K)
END IF
9 CONTINUE
C
CALL HSDM(COV(K),CCONCV(K),RADPV(K),RIOPV(K),XXV(1),XXV(2),
& XXV(3),XXV(4),TT,YY,NDPV(K))
C
SHSD1650
SHSD1670
SHSD1680
SHSD1690
SHSD1700
SHSD1710
SHSD1720
SHSD1730
SHSD1740
SHSD1750
SHSD1760
SHSD1770
SHSD1780
SHSD1790
SHSD1800
SHSD1810
SHSD1820
SHSD1830
SHSD1840
SHSD1850
SHSD1860
SHSD1870
SHSD1880
SHSD1890
SHSD1900
SHSD1910
SHSD1920
SHSD1930
SHSD1940
SHSD1950
SHSD1960
SHSD1970
SHSD1980
SHSD1990
SHSD2000
SHSD2010
SHSD2020
SHSD2030
SHSD2040
SHSD2050
SHSD2060
SHSD2070
SHSD2080
SHSD2090
SHSD2100
SHSD2110
SHSD2120
SHSD2130
SHSD2140
SHSD2150
SHSD2160
SHSD2170
SHSD2180
SHSD2190
SHSD2200
C SET UP THE RESIDUAL VECTOR F

SSQV(K)=0.000
DO 3 L=1,NDPV(K)
  YF(L,K)=YY(L)
DO 4 ID=1,IDREP(K)
  IF(YM(L,ID,K) .LE. 1.100) THEN
    CC  WRITE(*,*),LL,F(LL)
    SSQV(K)=SSQV(K)+F(LL)*F(LL)
    LL=LL+1
  END IF
4 CONTINUE
3 CONTINUE
111 CONTINUE
C
WRITE(*,1000) ICALL,(SSQV(I),I=1,NDSET)
WRITE(NDSET+1,1000) ICALL,(SSQV(I),I=1,NDSET)
1000 FORMAT(1X,15,6E16.6)
C
RETURN
END
C----------------------------------------------------------------------------------
SUBROUTINE HSDM(CO1,CCONC1,RADP1,RHOP1,XXF1,DS1,XX1,XN1,
  &TT,YY,NDP)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ CO,QQ,CCONC,DS,XXF,
  &XX1,XN1,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTIN,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
DIMENSION TT(1),YY(1)
C
DATA ICALL /0/
C
OPEN(31,FILE='PART.COL',STATUS='OLD')
OPEN(32,FILE='HSDM.OUT',STATUS='NEW')
C
IF(ICALL .EQ. 0) THEN
  CALL INPUT
  CALL INCOL
  ICALL=1
  END IF
  C
  CO=CO1
  CCONC=CCONC1
  RADP=RADP1
  RHOP=RHOP1
XK=XK1
XN=XN1
XKF=XKF1
DS=DS1

C
CALL INIT
C
CALL CALGC(TT,YY,MDP)
C
RETURN
C
END

C---------------------------------------------
SUBROUTINE INPUT
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
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
COMMON /VAR/ Y(15),NTOT
C
OPEN(30,FILE='SHSOM.CTR',STATUS='OLD')
C
REWIND (30)
READ(97,*),IPRC,IPRI,IPRO
C
PHYSICAL PARAMETER
C
READ(30,*) CO
C
READ(30,*) CCONC
C
READ(30,*) DS
C
READ(30,*) XKF
C
READ(30,*) XK
C
READ(30,*) XN
C
READ(30,*) RADP
C
READ(30,*) RHOP
C
C
CONTROL PARAMETER
C
READ(97,*),NCP
READ(97,*),TOL,METH,MITER
READ(97,*),DTINIT
C
READ(30,*) DTOUT
C
READ(30,*) TFINAL
C
READ(30,*) ITMAX
C
CLOSE (30)
C
RETURN
C
END

C---------------------------------------------
SUBROUTINE INCOL
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

COMMON /CTRL/ IPRC,IPRI,IPRO,IAP,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARAM/ CO,QQ,CCONC,DS,XXF,
&KX,XN,RADP,RHOP,B1OT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT

C

DIMENSION IDL(2)
DIMENSION DUMMY(14)

IFL1=0
IFL2=0
10 CONTINUE

C

READ(31,*1) ID
IF(ID .EQ. 999) THEN

C SOME Thing IS WRONG
WRITE(*,*) ' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'
STOP ' ERROR - ALL DONE '
END IF
IF(ID .EQ. NCP) THEN
IFL1=1
END IF

C

READ in AND Distribute

C

IF(IFL1 .NE. 0) THEN

C

READ(31,1001) (WP(I),I=1,ID)
DO 2 I=1,ID
READ(31,1001) (BP(I,J),J=1,ID)
2 CONTINUE

C

IF(IFL1 .EQ. 0) GO TO 10
IF(IFL1 .EQ. 1) GO TO 11

C

END IF

C

IF(IFL1 .EQ. 0) THEN
READ(31,1001) (DUMMY(I),I=1,ID)
DO 6 I=1,ID
READ(31,1001) (DUMMY(J),J=1,ID)
6 CONTINUE
GO TO 10
END IF

C

WRITE THE MATRIXES

C

IF(IPRC .EQ. 1) THEN
WRITE(*,*) ' WEIGHTS '
WRITE(*,1001) (WP(I),I=1,NCP)
WRITE(*,*) ' COLLOCATION MATRIX (R)' DO 13 I=1,NCP
13 CONTINUE
WRITE(*,1001) (BP(I,J),J=1,NCP)
13 CONTINUE
END IF

C
1001 FORMAT(4D20.12)
C
RETURN
C
END
C

-----------------------------------------------
SUBROUTINE INIT
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,W(14),BP(14,14)
COMMON /PARM/ CQ,Q0,CCONC,DS,XKF,
&XX,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /MIX/ DI,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
NTOT=NCP+1
C
C INITIAL CONDITION FOR SOLID PHASE
C
DO 11 I=1,NTOT-1
  Y(I)=0.000
11 CONTINUE
C
C LIQUID PHASE
C
Y(NTOT)=1.000
C
C COMPUTE DEPENDENT PARAMETERS
C
Q0=XK*CQ**XN
C
CD=CCONC*Q0/Q0
C
B1=XK*RADP*CQ
B2=DS*RHOP*Q0*1000.0D0
BIOT=B1/B2
C
TFAC=DS/(RADP*RADP)
C
IF(IPRI.EQ.1) THEN
  WRITE(32,1001) CO,CCONC,CD
  WRITE(32,1004) DS
  WRITE(32,1005) XK
  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
CONTROL PARAMETER
WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL
END IF

FORMAT STATEMENTS

1001 FORMAT(2X, 'CQ = ', E12.6, '/,
&2X, 'CCONC = ', E12.6, '/,
&2X, 'CD = ', E12.6, '/)

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)

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')

RETURN
END

---------------------------------------------
SUBROUTINE CALCC(TT,YY,NDP)

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP14,BP14,NDP
COMMON /PARM/ CQ,QO,CCONC,DS,XKF,
&XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT

DIMENSION TT(1),YY(1)

DIMENSION WK(390),IWK(29)

EXTERNAL RWC,FNCJ

DO 98 KK=1,NDP
WRITE(*,*) KK,TT(KK)
98 CONTINUE

N=NTOT
HH=DTINIT
INDEX=1
C
T=0.000
C
ITRY=0
ITRYT=0
TPHYS=0.000
ITER=0
C
WRITE(*,*) ITER,ITRY,T,TPHYS,Y(NTOT)
WRITE(32,*), ITER,ITRY,T,TPHYS,Y(NTOT)
C
DO 100 IP=1,NDP
C
ITER=ITER+1
TEND=TT(IP)*TFAC
C
IF(TT(IP) .LE. 0.01) THEN
YY(IP)=1.000
GO TO 100
END IF
C
ITRY=0
CALL DGEAR(N,FCH,FCN,N,HH,Y,TEND,
& TOL,METH,ITER,INDEX,1WK,WK,IER)
C
ITRY=ITRY+ITRY
T=TEND
TPHYS=T/TFAC
C
WRITE(*,*) (Y(LL),LL=1,NCP)
WRITE(*,1000) ITER,ITRY,T,TPHYS,Y(NTOT)
1000 FORMAT(1X,15,15,3E16.6)
C
WRITE(32,*), (Y(LL),LL=1,NCP)
WRITE(32,*), ITER,ITRY,T,TPHYS,Y(NTOT)
C
IF (T/TFAC .LT. TFINAL) GO TO 100
C
YY(IP)=Y(NTOT)
C
100 CONTINUE
C
WRITE(*,*), 'ITRY = ',ITRY
WRITE(32,*), ' 999 999 999 999 999 999 999'
RETURN
END
C-------------------------------
SUBROUTINE FCN(J,N,T,Y,PD)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
DIMENSION Y(N),PD(N,N)
C
RETURN
END
C-------------------------------
SUBROUTINE FCN(3,N,T,Y,YPRIME)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ CO,QO,CONC,DS,XKF,
&XN,RADP,ROHP,BIOT,CO,TFAC
COMMON /WORK/ DTINIT,DOUT,TFINAL,ITMAX,ITRY
C
DIMENSION Y(N),YPRIME(N)
DIMENSION BB(14)
C
ITRY=ITRY+1
C
NTOT=N
KK=0
II=0
C
NCP=NCP-1
C
DO 30 J=1,NCP
BB(J)=0.000
30 CONTINUE
WW=0.000
C
DO 50 I=1,NCP
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
MASS BALANCE INSIDE PARTICLE (EXCEPT BOUNDARY)
C
YPRIME(I)=BB(I)
C
WW=WW+WP(I)*YPRIME(I)
50 CONTINUE
C
SOLID-LIQUID INTERFACE
C
II=II+1
CC
YPRIME(I) = ((BIOT*(Y(NTOT)-(Y(II)**)-(1.000/XN)))-WW)/
CC
&WP(NCP))
C
IGO=0
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(11) .LT. 1.0D-10) THEN
  YPRIME(11) = ((BIOT*(Y(NTOT)-Y(11))/-MM)/WP(NCP))
ELSE
  YPRIME(11) = ((BIOT*(Y(NTOT)-0.0D0)-MM)/WP(NCP))
ENDIF

YPRIME(11) = (((BIOT*(Y(NTOT)-0.0D0)-MM)/WP(NCP)) + BSUM) * 0.5

C
C LIQUID PHASE MASS BALANCE
C
YPRIME(NTOT) = -3.000D0 * CD * (MM + &amp; YPRIME(11) * WP(NCP))
RETURN
END
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 'DGGEAR'.

*********************************************************************************************************
* 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,Y0,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,ND): This subroutine is a dummy subroutine used by GEAR.
* 6- Subroutine MYERS(C0,Q0,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.

* IASTMO: 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 empirical 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 empirical correlations 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 of 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 AUCOL16.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:
  * \( \text{NEQ} = ((\text{NC}+1)\times\text{MC})-1)\times\text{NCOMP} \)
  *
  * where:
    * \( \text{NEQ} \) = number of equations
    * \( \text{NC} \) = number of radial collocation points
    * \( \text{MC} \) = number of axial collocation points
    * \( \text{NCOMP} \) = number of components
  *
  * If more than 147 equations are to be solved the following arrays
    * in the file DGEAR.B FOR must be redimensioned according to the value of
      * \( \text{NEQ} \):
        * \( \text{YMAX}, \text{ERROR}, \text{SAVE1}, \text{SAVE2} \) AND \( \text{IPIV} \)
        * Also the following array must be dimensioned according to \( \text{NEQ} \) squared:
          * \( \text{PW} \).
  *
  * Hence when choosing the number of radial and axial points make sure
    * that \( \text{NEQ} \) does not exceed 147 otherwise redimensioning of DGEAR.B FOR has
      * to be made.
  *
  * The program is also dimensioned to read up to 75 points of varying
    * influent concentrations and 900 TIME STEPS.
### PLUG FLOW HOMOGENEOUS SURFACE DIFFUSION Model DATA FILE

**N.B.:** 1. FOR INTEGER NUMBERS USE TWO FIGURES I.E. IF THE NUMBER IS 0 PUT 0 2. FOR THE E-SPECIFICATION FORMAT USE FIVE DECIMAL PLACES 3. IF THE FREUNDLICH ISOTHERM IS TO BE USED FOR MODEL CAL. PUT UNDER 4. IF THE MYERS ISOTHERM IS TO BE USED FOR MODEL CAL. PUT UNDER ISO 5. WHEN REPLACING A NUMBER IN THE FILE MAKE SURE THE ASTERISKS ARE IN THEIR PLACE.

### BREAKTHROUGH CURVE FOR THE BINARY MIXTURE

### COLLOCATION MATRICES FILES AUCOL=AXIAL, COL=RADIAL

<table>
<thead>
<tr>
<th>Iso</th>
<th>Ncomp</th>
<th>part.radius</th>
<th>particle</th>
<th>PSEDFR</th>
</tr>
</thead>
<tbody>
<tr>
<td>00</td>
<td>0.03</td>
<td>0.154</td>
<td>0.641</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TEMP</th>
<th>W.DENSITY</th>
<th>VICOSITY</th>
<th>APP.DENSITY</th>
<th>LENGTH</th>
<th>FLOW RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9994</td>
<td>0.01206</td>
<td>0.74</td>
<td>20.54</td>
<td>104.7198</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DIA.</th>
<th>MASS OF C</th>
<th>ERROR CRT.</th>
<th>TIME STEP</th>
<th>NCOL</th>
<th>T.TEMP AD.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>120.0</td>
<td>0.00001</td>
<td>1.0000E-05</td>
<td>02</td>
<td>60.0</td>
</tr>
</tbody>
</table>

**TOTAL TIME** **START.TIME** **1STOUT.TIME** **NO.TIME CHANGED**

<table>
<thead>
<tr>
<th>min</th>
<th>min</th>
<th>min</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.88000E+04</td>
<td>0.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**NO. VARYING INF. CONC.** **NO. OF COLUMN DATA**

| 19 | 00 |

**COMPONENT1** **COMPONENT2** **COMPONENT3**

| DCE | TCE | PCE |

**Adsorbates molecular weights**

<table>
<thead>
<tr>
<th>XMT(1)</th>
<th>DMT(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.94</td>
<td>131.39</td>
</tr>
<tr>
<td>165.83</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DS(1)</th>
<th>KF(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.62920E-08</td>
<td>0.36667E-02</td>
</tr>
<tr>
<td>5.27500E-08</td>
<td>3.34970E-08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MOLAL VOL</th>
<th>CB0(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>118.4</td>
<td>1000.0</td>
</tr>
<tr>
<td>140.6</td>
<td>1000.0</td>
</tr>
<tr>
<td>166.5</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fr.(K(1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.544</td>
</tr>
<tr>
<td>159.81</td>
</tr>
<tr>
<td>341.3014</td>
</tr>
</tbody>
</table>

Freundlich K, (mmol/g)/(mmol/L)
<table>
<thead>
<tr>
<th>n(1)</th>
<th>0.587</th>
<th>0.482</th>
<th>0.516</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>MY. H(L/g)</th>
<th>1.81809E+02<em>2.42612E+02</em>1.58575E+03***</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>MY. K *(mmol/g)</th>
<th>3.553</th>
<th>2.1016</th>
<th>3.6443</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>MY. P</th>
<th>0.808</th>
<th>1.2996</th>
<th>0.7476</th>
</tr>
</thead>
</table>

Vector of output time values at which a new time step will be used, min.

<table>
<thead>
<tr>
<th>TIE(1)</th>
<th>0.0</th>
<th>6.00000E+03*</th>
</tr>
</thead>
</table>

Vector of new time steps for integration, min.

<table>
<thead>
<tr>
<th>TINC(1)</th>
<th>60.0</th>
<th>300.0</th>
</tr>
</thead>
</table>

Varying influent conc. values:

<table>
<thead>
<tr>
<th>TIME</th>
<th>COMPONENT1</th>
<th>COMPONENT2</th>
<th>COMPONENT3</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>0.0</th>
<th>97.759</th>
<th>100.475</th>
<th>0.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>780.0</td>
<td>97.04</td>
<td>100.575</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>96.567</td>
<td>99.841</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>95.482</td>
<td>99.187</td>
<td>0.0</td>
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<tr>
<td></td>
<td>95.47</td>
<td>98.184</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>96.849</td>
<td>98.476</td>
<td>0.0</td>
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<tr>
<td></td>
<td>96.961</td>
<td>100.836</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>94.69</td>
<td>99.104</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>96.15</td>
<td>99.5</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>96.139</td>
<td>97.243</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>96.139</td>
<td>97.243</td>
<td>86.363</td>
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<tr>
<td></td>
<td>95.769</td>
<td>96.656</td>
<td>86.304</td>
</tr>
<tr>
<td></td>
<td>97.084</td>
<td>99.006</td>
<td>88.06</td>
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<tr>
<td></td>
<td>95.941</td>
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<td>88.323</td>
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<tr>
<td></td>
<td>96.293</td>
<td>98.701</td>
<td>88.389</td>
</tr>
<tr>
<td></td>
<td>95.135</td>
<td>97.515</td>
<td>86.342</td>
</tr>
<tr>
<td></td>
<td>95.598</td>
<td>104.44</td>
<td>95.011</td>
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<tr>
<td></td>
<td>97.786</td>
<td>102.606</td>
<td>90.963</td>
</tr>
<tr>
<td></td>
<td>96.453</td>
<td>105.116</td>
<td>94.453</td>
</tr>
</tbody>
</table>

*******************************************************************************
SUBJECT: PROGRAM - PLUG.FOR

PROGRAM PLUG

PLUG FLOW HOMOGENEOUS SURFACE DIFFUSION MODEL

C....declaration block

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

DOUBLE PRECISION KF(3),L

CHARACTER*25 CHAR(3),FILEIN,FILEOUT,AUCOL,COL

CHARACTER*80 TITLE

DIMENSION Y0(400),TDATA(75),VB(3),DS(3),

BIS(3),TIE(3),TINC(3),XWT(3),DIFL(3),SC(3)

COMMON/BLOCCA/DS(3),ST(3),EDS(3),BR(7,7)

COMMON/BLOCKB/VM(3),XNI(3),XN(3),WR(7),AZ(18,18),A1(3),A2(3)

*QE(3),XK(3),A1(3)

COMMON/BLOCKC/FMIN(3),TP(900),CP(3,900),CD(3,75),CINT(3,75)

COMMON/BLOCKD/CIN(3,75),TIN(75)

COMMON NC,NC,NCOMP,N1,DGT,NIN,ISO,CBO(3)

DATA INDEX/1/, MF/22/, NSTEPS/900/

WRITE(*,*) 'PLUG DATA'

READ(*,2) FILEIN

OPEN(4,FILE=FILEIN,STATUS='OLD')

WRITE(*,*) 'OUT DATA'

READ(*,2) FILEOUT

OPEN(7,FILE=FILEOUT,STATUS='NEW')

C.....read in data from DATA FILE

READ(4,173) TITLE

READ(4,174) AUCOL,COL

READ(4,175) ISO,NCOMP,RAD,EPOR,PSDFR

READ(4,176) TEMP,DW,VW,RHOP,L,FLRT

READ(4,177) DIA,WT,EPS,DNO,NCOL,DSTEP

READ(4,178) DTOL,DTO,DOUT, NM

READ(4,179) NIN,NDATA

READ(4,180) (CHAR(I), I = 1,NCOMP)

READ(4,181) (XWT(I), I = 1,NCOMP)

READ(4,182) (DS(1), I = 1,NCOMP)

READ(4,182) (KF(I), I = 1,NCOMP)

READ(4,182) (VB(I), I = 1,NCOMP)

READ(4,182) (CBO(I), I = 1,NCOMP)

READ(4,183) (XK(I), I = 1,NCOMP)

READ(4,182) (XN(I), I = 1,NCOMP)

READ(4,182) (A1(I), I = 1,NCOMP)

READ(4,182) (A2(I), I = 1,NCOMP)

READ(4,182) (A3(I), I = 1,NCOMP)

READ(4,187) (TIE(I), I = 1, NM)

READ(4,176) (TINC(I), I = 1, NM)

READ(4,184)

IF (NIN .EQ. 0) GO TO 812

DO 1 J = 1,NIN

READ(4,185) TIN(J), (CIN(I,J), I = 1,NCOMP)

1 CONTINUE

812 IF (NDATA .EQ. 0) GO TO 813

PLU000010

PLU000020

PLU000030

PLU000040

PLU000050

PLU000060

PLU000070

PLU000080

PLU000090

PLU001000

PLU001100

PLU001200

PLU001300

PLU001400

PLU001500

PLU001600

PLU001700

PLU001800

PLU001900

PLU002000

PLU002100

PLU002200

PLU002300

PLU002400

PLU002500

PLU002600

PLU002700

PLU002800

PLU002900

PLU003000

PLU003100

PLU003200

PLU003300

PLU003400

PLU003500

PLU003600

PLU003700

PLU003800

PLU003900

PLU004000

PLU004100

PLU004200

PLU004300

PLU004400

PLU004500

PLU004600

PLU004700

PLU004800

PLU004900

PLU005000

PLU005100

PLU005200

PLU005300

PLU005400

PLU005500
DO 3 J = 1, NDATA
   READ(*,185) TDATA(J), (CD(I,J), I = 1, NCOMP)
3 CONTINUE

C......read in collocation constants

813 OPEN(2, FILE=AUCOL, STATUS='OLD')
OPEN(3, FILE=COL, STATUS='OLD')
READ(3,*) NC
READ(3,101) (WR(J), J = 1, NC)
DO 5 I = 1, NC
   READ(3,101) (BR(I,J), J = 1, NC)
5 CONTINUE
READ(2,*) MC
DO 10 I = 1, MC
   READ(2,101) (AZ(I,J), J = 1, MC)
10 CONTINUE
NEQ = (((NC + 1)*MC - 1)*NCOMP

C......print out collocation constants if NCOL = 1
C......otherwise skip to statement number 25

IF ( NCOL .NE. 1) GO TO 25
WRITE(*,*)
WRITE(*,*) 'RADIAL W VECTOR'
WRITE(*,102) (WR(J), J=1, NC)
WRITE(*,*)
WRITE(*,*) 'RADIAL B MATRIX'
DO 15 I = 1, NC
   WRITE(*,102) (BR(I,J), J = 1, NC)
15 CONTINUE
WRITE(*,*)
WRITE(*,*) 'AXIAL A MATRIX'
DO 20 I = 1, MC
   WRITE(*,102) (AZ(I,J), J = 1, MC)
20 CONTINUE

C......calculate the fixed-bed parameters

25 DO 212, I = 1, NCOMP
   CBO(I) = CBO(I)/XWT(I)
212 CONTINUE

AREA = 3.14159265400*DIA*DIA/4.000
BEDVOL = L*AREA
EBED = 1.000 - WT/(BEDVOL*RHOP)
EBC = BEDVOL/FRLT
TAU = BEDVOL*EBED*60.000/FRLT
SF = .2954238700*FRLT/AREA
VS = FRLT/(60.000*AREA)
IF(PDSR.EQ.0.000) GOTO 69
RE = (2.000*RAD*VS*DWH)/(EBED*VW)
69 DO 68, I = 1, NCOMP
   IF(PDSR.LE.0.000) THEN
   PDSR=0.000
GOTO 68
ELSE
DIFL(1) = 13.260-05/(((W*100.00D0)**1.14D0)*(VR(1)**5.89D-01))
SC(1) = VW/(DW*DIFL(1))
END IF
IF (KF(1).LE.0.00D0) THEN
KF(1) = (2.400*MVS)/((RE**.66D0)*(SC(1)**.58D0))
ENDIF
IF (PSDFR.LE.0.00D0) THEN
PSDFR = 0.00D0
ELSE
GO TO 68
ENDIF
CONTINUE
C
C.....print out fixed bed parameters
WRITE(7,143)
WRITE(*,143)
IF(IS0.EQ.0) THEN
WRITE(7,188)
WRITE(*,188)
ELSE
WRITE(7,189)
WRITE(*,189)
ENDIF
WRITE(7,103) NC, MC, NEQ, RAD, WT, RHOP, EPOR, L, EBED, DIA, SF, TAU, EPL
WRITE(7,1003)DHO, DOUT, RE, TEMP, DW, VW, PSDFR
WRITE(*,103) NC, MC, NEQ, RAD, WT, RHOP, EPOR, L, EBED, DIA, SF, TAU, EPL
WRITE(*,1003)DHO, DOUT, RE, TEMP, DW, VW, PSDFR
C
C.....calculate and print out dimensionless groups
QTE=0.00D0
IF(IS0.EQ.0) THEN
DO 30 I = 1,NCOMP
QE(I) = XK(I)*CBO(I)**XN(I)
QTE = QTE + QE(I)
30 CONTINUE
ELSE
IF(NCOMP.EQ.1) THEN
CALL MYERS(CBO(1),QE(1),1)
QTE=QE(1)
ELSE
IF (NCOMP.EQ.2) THEN
CALL IASTMC(CBO,QE,A1,A2,A3,2)
QTE=QE(1)+QE(2)
ELSE
CALL IASTMC(CBO,QE,A1,A2,A3,3)
QTE=QE(1)+QE(2)+QE(3)
ENDIF
ENDIF
ENDIF
DO 31 I=1,NCOMP
DGS(I) = (RHO*QE(I)*(1.0D0 - EBED)*1000.0D0)/(EBED*COB(I))
EDS(I) = DS(I)*DGS(I)*TAN/(RAD**2.0D0)
ST(I) = KF(I)*(1.0D0 - EBED)*TAN/(EBED*RAD)
BIS(I) = ST(I)/EDS(I)
XNI(I) = 1.0D0/XN(I)
WRITE(7,104) CHAR(I),VB(I),XMT(I),COBI,KX(I),XN(I),D(FL,PLU,01720)
+ KF(I),DS(I),ST(I),DGS(I),BIS(I),EDS(I),SC(I),PLU,01730
WRITE(*,104) CHAR(I),VB(I),XMT(I),COBI,KX(I),XN(I),D(FL,PLU,01740)
+ KF(I),DS(I),ST(I),DGS(I),BIS(I),EDS(I),SC(I),PLU,01750
WRITE(7,190) A1(I),A2(I),A3(I)
WRITE(*,190) A1(I),A2(I),A3(I)
31 CONTINUE

WRITE(7,141)
WRITE(*,141)
WRITE(7,142) (I,CHAR(I), I = 1, NCOMP)
WRITE(*,142) (I,CHAR(I), I = 1, NCOMP)
WRITE(7,106) (I, I = 1, NCOMP)
WRITE(*,106) (I, I = 1, NCOMP)

C.....total solute dist. parameter and bed volumes fed to column

C
DGT = 0.0D0
DO 33 I = 1,NCOMP
DGT = DGT + DGS(I)
33 CONTINUE
BVF = EBED*DGT

C.....calculate equilibrium adsorbent phase concentration fraction

C
DO 35 I = 1,NCOMP
YM(I) = QE(I)/QTE
35 CONTINUE

C.....call subroutine ORTHOG to combine collocation constants

C.....and dimensionless groups and to determine total number

C.....of differential equations being solved for by GEAR

C
CALL ORTHOG ( N )

C.....convert independent variables to dimensionless form

C
TCONV = 60.0D0/(TAN*(DGT + 1.0D0))
TSTEP = DSTEP*TCONV
TTOL = DTOL*TCONV
TOUT = DOUT*TCONV
HO = DHO*TCONV
TO = DTO*TCONV
DO 40 I = 1,NM
TIE(I) = TIE(I)*TCONV
TINC(I) = TINC(I)*TCONV
40 CONTINUE

C.....convert influent and experimental data to dimensionless form

C
PLU,01870
PLU,01880
PLU,01890
PLU,01900
PLU,01910
PLU,01920
PLU,01930
PLU,01940
PLU,01950
PLU,01960
PLU,01970
PLU,01980
PLU,01990
PLU,02000
PLU,02010
PLU,02020
PLU,02030
PLU,02040
PLU,02050
PLU,02060
PLU,02070
PLU,02080
PLU,02090
PLU,02100
PLU,02110
PLU,02120
PLU,02130
PLU,02140
PLU,02150
PLU,02160
PLU,02170
PLU,02180
PLU,02190
PLU,02200
DO 50 J = 1, NDATA
   TDATA(J) = TDATA(J)*TCONV
DO 45 I = 1, NCOMP
   CD(I,J) = CD(I,J)/(CB(I)*XWT(I))
45 CONTINUE
50 CONTINUE
DO 60 J = 1, NIN
   TIN(J) = TIN(J)*TCONV
DO 55 I = 1, NCOMP
   CIN(I,J) = CIN(I,J)/(CB(I)*XWT(I))
55 CONTINUE
60 CONTINUE
C.....Initialize dependent variables
DO 65 I = 1, N
   YO(I) = 0.000
65 CONTINUE
C.....loop for calling GEAR to integrate differential equations
ITP = 0
MA = 1
70 ITP = ITP + 1
   CALL DGEAR (N,T0,H0,Y0,TOUT,EPS,MF,INDEX)
DO 75 I = 1, NCOMP
   CM(I,ITP) = YO(N1*I)
75 CONTINUE
TP(ITP) = TOUT
DOUT = TOUT/TCONV
WRITE(7,150) DOUT,TOUT*BVF,(YO(N1*I)),I=1,N,COMP
WRITE(*,150) DOUT,TOUT*BVF,(YO(N1*I)),I=1,N,COMP
IF (ITP.LT. NSTEPS) THEN
   IF (TOUT.LT. TTOL) THEN
      IF (NM .NE. 0 .AND. TOUT .GE. TIE(MA)) THEN
         TSTEP = TINC(MA)
         IF (MA .EQ. NM) THEN
            NM = 0
         ELSE
            MA = MA + 1
         ENDIF
         ENDFD
         TOUT = TOUT + TSTEP
         IF (TOUT .GT. TTOL) TOUT = TTOL.
         GO TO 70
      ENDIF
   ELSE
      IF (TOUT .NE. TTOL) THEN
         WRITE(6,108) NSTEPS, DOUT
         GO TO 90
      ENDIF
   ENDFD
C.....if experimental data is given call OBJFUN to determine FMIN
C.....for each component and print out results
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
85 CONTINUE
WRITE(7,112) NDATA, FMIN(I)
90 STOP

C

----- FORMAT BLOCK -----

2   FORMAT (A)
101  FORMAT(4F20.12)
102  FORMAT(1X,4F20.12)
103  FORMAT(/"
   ' NUMBER OF RADIAL COLLOCATION POINTS, NC... = ',115/
   ' NUMBER OF AXIAL COLLOCATION POINTS, NC... = ',115/
   ' TOTAL NO. OF DIFFERENTIAL EQUATIONS, N_EQ... = ',115/
   ' RADIUS OF ADSORBENT PARTICLE, RAD (CM)... = ',115.5/
   ' MASS OF ADSORBENT, WT (GRAMS).............. = ',115.5/
   ' APPARENT PARTICLE DENSITY, RHOP (GM/CM**3) = ',115.5/
   ' VOID FRACTION OF THE CARBON, EPOR (DIM.) = ',115.5/
   ' LENGTH OF BED, L (CM)...................... = ',115.5/
   ' VOID FRACTION OF BED, EBED (DIM.)......... = ',115.5/
   ' DIAMETER OF FIXED-BED, DIA, (CM).......... = ',115.5/
   ' SURFACE LOADING, SF (GM/FT**2)............ = ',115.5/
   ' PACKED BED CONTACT TIME, TAU (SEC.)....... = ',115.5/
   ' EMPTY BED CONTACT TIME, EBCT (MIN.)....... = ',115.5/
103  FORMAT(/"
   ' INITIAL INTEGRATION STEP, DIO (MIN.)...... = ',115.5/
   ' INITIAL OUTPUT TIME, DOUT (MIN.)......... = ',115.5/
   ' REYNOLDS NUMBER, RE, (DIM.).............. = ',115.5/
   ' TEMPERATURE OF WATER, TEMP, (DEG C)....... = ',115.5/
   ' DENSITY OF WATER, DW, (GM/CM)............ = ',115.5/
   ' VISCOSITY OF WATER, VW, (GM/CM-SEC)...... = ',115.5/
   ' PORE SURFACE DIFFUSION FLUX RATIO, PSDFR = ',115.5/
104  FORMAT('/" PARAMETERS FOR ',120/
   + 4X,'MOLAL VOLUME AT THE BOILING PT, (CU. CM./CHMOL.) = ',115.5/
   + 4X,'MOLECULAR WEIGHT OF COMPOUND, XWT .......... = ',115.5/
   + 4X,'INITIAL BULK LIQUID-PHASE CONC., (MMOL/L) ....... = ',115.5/
   + 4X,'FREUNDLICH ISO. CAP., XK (MMOL/GM)/(L/MMOL)**XN = ',115.5/
   + 4X,'FREUNDLICH ISOTHERM CONSTANT, XN, (DIM.) ..... = ',115.5/
   + 4X,'LIQUID DIFFUSIVITY, DIFL, (SQ.CM./SEC)........ = ',115.5/
   + 4X,'FILM TRANSFER COEFFICIENT, KF, (CM./SEC) ....... = ',115.5/
   + 4X,'SURFACE DIFFUSION COEFFICIENT, NS, (SQ.CM./SEC) = ',115.5/
   + 4X,'STANTON NUMBER, ST, (DIM.) ............... = ',115.5/
   + 4X,'SOLUTE DISTRIBUTION PARAMETER, DQS, (DIM.) .... = ',115.5/
   + 4X,'BIOT NUMBER, BIS, (DIM.) .................. = ',115.5/
FILE: PLUG FORTRAN A1 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, DIAHRRAN PAGE 339

+ 4X,'DIFFUSIVITY MODULUS, EDS, (DIM.) ............... = ', E1PLU03310
+ 4X,'SCHMIDT NUMBER, SC, (DIM.) ...................... = ', E1PLU03320
190 FORMAT(PLU03330
+ 4X,'MYERS ISOTHERM CONSTANT, H, (l/g).................. = ', E1PLU03330
+ 4X,'MYERS ISOTHERM CONSTANT, K, (MMOL/G)**P............ = ', E1PLU03350
+ 4X,'MYERS ISOTHERM CONSTANT, R, (DIM.) ................. = ', E1PLU03360
141 FORMAT(//20X,'MODEL PREDICTION:',//,5X,'COMPONENT NUMBER', PLU03370
+ 'COMPOUND NAME'/) PLU03380
142 FORMAT(3(13X,11,13X,A20,//)) PLU03390
106 FORMAT(1X,'TIME(min.)',3X,'BED VOLUMES',2X,3(2X,'C(',11,',')/CPLU03600
+ ',')/) 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 = ',13,', 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,G12.5,5X,F9.4,5X,F9.4,6X,F10.5) PLU03490
112 FORMAT(///5X,'FMIN BASED ON',14,2X,'DATA POINTS:', PLU03500
+ 3X,'FMIN = ',F10.6) PLU03510
143 FORMAT(//2X,'PLUG FLOW HOMOGENEOUS SURFACE DIFFUSION MODEL CAPLPLU03520
+ IONS') PLU03530
173 FORMAT(//////,A80) PLU03540
174 FORMAT(///,Z(A11,1X)) PLU03550
175 FORMAT(///,2(12,10X),3(G11.5,1X)) PLU03560
176 FORMAT(///,6(G11.5,1X)) PLU03570
177 FORMAT(///,4(G11.5,1X),12,10X,G11.5,1X) PLU03580
178 FORMAT(///,3(G11.5,1X),12,10X) PLU03590
179 FORMAT(///,2(12,22X)) 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
186 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/DCS(3),ST(3),EDS(3),BR(7,7) PLU03810
COMMON/BLOCKC/STD(3),BDS(3,7,7),DG1(3),MND,ND,MD,DG1 PLU03820
COMMON MC,NC,NCOMP,N1,DGT,NBH,ISO,CBO(3) PLU03830
DIMENSION EDD(3) PLU03840
ND = NC - 1 PLU03850
MD = MC - 1
MND = MC*ND
N1 = MND + MC + MD
N = N1*NCOMP
DO 30 I = 1,NCOMP
   DG1 = 1.000 + DGT
   DG1(I) = 1.000/DGS1(I)
   STD(I) = ST(I)*DG1
   EDD(I) = DG1*DG1(I)*EDS(I)
   DO 20 J = 1,ND
      DO 10 K = 1,NC
         BEds(I,J,K) = EDD(I)*BR(J,K)
      10 CONTINUE
   20 CONTINUE
30 CONTINUE
RETURN
END

-----------------------------
| END OF SUBROUTINE ORTHOG |
-----------------------------

SUBROUTINE DIFFUN ( N,T,YO,YDOT )
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION YO(1),YDOT(1),YM(18),AAM(18),BB(7,18),CS(3,18),
+ Z(3),Z(3),CSS(3),Q0(3),CBS(3,18),Z(3,18)
COMMON/BLOCKA/DGS(3),ST(3),EDS(3),BR(7,7)
COMMON/BLOCKB/YN(3),XN(3),XN(3),WR(7),AZ(18,18),AI(3),AZ(3)
+QE(3),XK(3),A3(3)
COMMON MC,N,NCOMP,N1,DMT,NIH,ISO,CRO(3)
DO 15 K = 1,MC
   QTE = 0.000
   QTO = 0.000
   KK = MND + K
   IF(ISOR.EQ.1) GOTO 12
   DO 5 I = 1,NCOMP
      II = KK + (I-1)*N1
      Z1(I) = YM(I)*Y0(I)
      QTE = QTE + Z1(I)
      QTO = QTO + XN(1)*Z1(I)
   5 CONTINUE
   CONTINUE
DO 10 I = 1,NCOMP
   IF ( QTE .LE. 0.000 .OR. QTO .LE. 0.000 ) THEN
      CS(I,K) = 0.000
   ELSE
      Z1(I) = Z1(I)/QTE
      Q0(I) = QTO*XN(1)/YM(I)
      IF ( XN(1)*QLOK1Q0(I) .LT. -0.000 ) THEN
         CS(I,K) = 0.000
      ELSE
         CS(I,K) = Z1(I) * Q0(I)**XN(1)
      END IF
   END IF
   CONTINUE
END
ENDIF

ENDIF

CONTINUE

GOTO 15

DO 6 I=1,NCOMP

II = KK*(1-1)*NK

Z(I,K) = (QE(I))*Y0(II)

6 CONTINUE

IF(Z(1,K).LE.0.000) THEN

CS(1,K) = 0.000

CS(2,K) = 0.000

CS(3,K) = 0.000

ELSE

IF(Z(2,K).LE.0.000 .AND. .GT.0.000) THEN

CS(1,K) = ((Z(1,K)/A(1))*BEXP(A2(1)*Z(1,K)**A3(1)))/CB0(1)

CS(2,K) = 0.000

CS(3,K) = 0.000

ELSE

IF(Z(1,K).GT.0.000 .AND. Z(2,K).GT.0.000 .AND.

Z(3,K).LE.0.000) THEN

ZZ(1) = Z(1,K)

ZZ(2) = Z(2,K)

CALL IASTMQ(CS,ZZ,A1,A2,A3.2)

CS(1,K) = CS(1)/CB0(1)

CS(2,K) = CS(2)/CB0(2)

CS(3,K) = CS(3)/CB0(3)

ELSE

ZZ(1) = Z(1,K)

ZZ(2) = Z(2,K)

ZZ(3) = Z(3,K)

CALL IASTMQ(CS,ZZ,A1,A2,A3,3)

CS(1,K) = CS(1)/CB0(1)

CS(2,K) = CS(2)/CB0(2)

CS(3,K) = CS(3)/CB0(3)

ENDIF

ENDIF

ENDIF

CONTINUE

DO 60 I = 1,NCOMP

II = (I-1)*NK

II = II + MND

II = II + MD

IF(NIN .EQ. 0) THEN

CINF = 1.000

ELSE

CINF = CINF(I,T)

ENDIF

DO 20 K = 2,MC

IF(CS(I,K).LE.0.000) THEN

CBS(I,K) = STD(I)*Y0(III + K)

ELSE

CBS(I,K) = STD(I)*(Y0(I+K) - CS(I,K))

ENDIF

20 CONTINUE

DO 40 K = 1,MC

CONTINUE
WW(K) = 0.0DO
AAU(K) = 0.0DO
KK = 11 + (K-1)*ND
DO 30 J = 1 , ND
   BB(J,K) = 0.0DO
   DO 25 M = 1 , ND
      BR(J,K) = BB(J,K) + BEDS(I,J,M)*YO(KK + M)
25 CONTINUE
   BB(J,K) = BR(J,K) + BEDS(I,J,NC)*YO(III + K)
30 CONTINUE
   DO 35 J = 1 , ND
      JJ = KK + J
35 CONTINUE
   W(K) = WW(K) + WR(J)*YDOT(JJ)
40 CONTINUE
C......Intraparticle Phase Mass Balance(excluding boundary)
C
   YDOT(JJ) = BB(J,K)
   W(K) = WW(K) + WR(J)*YDOT(JJ)

C......Liquid-Solid Boundary Layer Mass Balance at column entrance
C
   YDOT(III+1) = (STD(I)*DG(I1)*GINFL - CS(I,1))
   + WW(1) / WR(NC)

C
   DO 55 K = 2 , MC
55 CONTINUE
C
C......Liquid-Solid Boundary Layer Mass Balance within column
C
   YDOT(III+K) = (CBS(I,K)*DG(I1) - WW(K)) / WR(NC)

C
   DO 50 M = 2 , MC
      AAU(K) = AAU(K) + AZ(K,M)*YO(III+K)
50 CONTINUE
C
C......Liquid Phase Mass Balance
C
   YDOT(III+K) = -DG1*(AZ(K,1)*GINFL + AAU(K))
   + 3.0DO*CBS(I,K)

C
   55 CONTINUE
60 CONTINUE
RETURN
END

-------------
| END OF SUBROUTINE DIFFUN |
-------------

SUBROUTINE OBJFUN ( TD,NDAT,NP )
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION TD(1)
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) = 0.000 PLU05540
   NP1 = NP - 1 PLU05550
10 DO 5 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 TPLU05580
         CAP = CP(K, I) + ((TD(J) - TP(I))/(TP(I+1) - TP(I)))* PLU05590
            + (CP(K, I+1) - CP(K, I)) PLU05600
         CINT(K, J) = CAP PLU05610
         FMIN(K) = FMIN(K) + ((CAP - CD(K, J))/CD(K, J))**2.000 PLU05620
      GO TO 10 PLU05630
5 CONTINUE PLU05640
10 CONTINUE PLU05650
15 CONTINUE PLU05660
20 CONTINUE PLU05670
RETURN PLU05680
END PLU05690
C

 -----------------------------
| END OF SUBROUTINE OBJFUN |
----------------------------

FUNCTION CINF(I, T)
IMPLICIT DOUBLE PRECISION (A-H, O-Z)
COMMON/BLOCKD/CINF(3, 75), TIN(75)
COMMON MC, NC, NCOMP, N1, DGT, NIN, ISO, CBO(3)
IF (T .LE. TIN(1) ) THEN PLU05790
   CINF = 1.000 PLU05800
ELSE IF (T .GE. TIN(NIN) ) THEN PLU05810
   CINF = CINF(I, NIN) PLU05820
ELSE PLU05830
   J = 1 PLU05840
10 J = J + 1 PLU05850
   IF( T .GE. TIN(J-1) .AND. T .LE. TIN(J) ) THEN PLU05860
      CINF = CINF(I, J-1) + (CINF(I, J) - CINF(I, J-1))*(T-TIN(J-1)) PLU05870
   ELSE IF (J .LT. NIN ) THEN PLU05880
      GO TO 10 PLU05890
ENDIF PLU05890
ENDIF PLU05900
RETURN PLU05910
END PLU05920
SUBROUTINE PEDERV ( N, T, Y, PD, NO ) PLU05930
IMPLICIT DOUBLE PRECISION (A-H, O-Z)
RETURN PLU05940
END PLU05950
C

-------------------------------
| END OF SUBROUTINE PEDERV |
-------------------------------
SUBROUTINE MYERS(CO,Q0,J)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON MC,NC,NCOMP,N4,DGT,N1N,ISO,COBO(3)
COMMON/BLOC KB/YH(3),XN(3),WN(3),WR(7),AZ(18,18),A(3),A2(3)

C                          ------------------------
C
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 30                    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=A2*QEO*A3             PLU06260
F=CO-QEO/A1*DEXP(ARG)      PLU06270
FP=(2.000*DEXP(ARG)+QEO*A2*A3*QEO**2*(A3-1.0))   PLU06280
FSTEP=F/FP                 PLU06290
IF(ABS(F/QEO).GT.EPSMY) THEN
QEO=QEO/FSTEP              PLU06300
IF(QEO.LT.0.0) THEN         PLU06310
QEO=QEO*0.500              PLU06320
GOTO 100                  PLU06330
ENDIF                     PLU06340
QEO=QEO1                  PLU06350
GOTO 100                  PLU06360
ENDIF                     PLU06370
QEO=QEO1                  PLU06380
CE=QEO1/A1*DEXP(A2*QEO1*A3) PLU06390
RETURN                   PLU06400
END
SUBROUTINE DGEAR (N,TO,HO,YO,TOUT,EPS,MF,INDEX) DGE00010
IMPLICIT DOUBLE PRECISION (A-H,O-Z) DGE00020
INTEGER N,MF,INDEX DGE00030
INTEGER NC,MFC,KFLAG,JSTART,IPIV,NSQ,NQUSED,NSTEP,NFE,NJE DGE00040
INTEGER LOUT,1,NO,NHICUT,KGO DGE00050
DOUBLE PRECISION TO,HO,YO,TOUT,EPS DGE00060
DOUBLE PRECISION T,H,HMIN,HMAX,EPSC,UROUND,YMAX,ERROR,SAVE1 DGE00070
DOUBLE PRECISION SAVE2,PW,EPJS,HUSED DGE00080
DOUBLE PRECISION Y,TOUTP,A1,Y1,D DGE00090
COMMON /GVAR1/ T,H,HMIN,HMAX,EPSC,UROUND,NC,MFC,KFLAG,JSTARTDGE00100
COMMON /GVAR2/ YMAX(147) DGE00110
COMMON /GVAR3/ ERROR(147) DGE00120
COMMON /GVAR4/ SAVE1(147) DGE00130
COMMON /GVAR5/ SAVE2(147) DGE00140
COMMON /GVAR6/ PW(21609) DGE00150
COMMON /GVAR7/ IPIV(147) DGE00160
COMMON /GVAR8/ EPSJ,NSQ DGE00170
COMMON /GVAR9/ 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 440 DGE00270
IF (NO.LE.0) GO TO 410 DGE00280
IF (((TO-TOUT)*HO.GE.0.000) GO TO 420 DGE00290
UROUND=1.00822D-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)=YO(I) DGE00340
NC=N DGE00350
T=TO DGE00360
H=HO DGE00370
IF (((T+H).EQ.T) WRITE (LOUT,15) DGE00380
HMIN=ABS(HO) DGE00390
HMAX=ABS((TO-TOUT)*10.000) DGE00400
EPSC=EPS DGE00410
MFC=MF DGE00420
JSTART=0 DGE00430
NO=N DGE00440
NSQ=NO*NO DGE00450
EPSJ=SQRT(UROUND) DGE00460
NHICUT=0 DGE00470
GO TO 50 DGE00480
20  HMAX=ABS((TO-TOUTP)*10.000) DGE00490
   GO TO 80 DGE00500
25  HMAX=ABS((TO-TOUTP)*10.000) DGE00510
   IF (((T-TOUT)*H.LE.0.000) GO TO 500 DGE00520
   GO TO 85 DGE00530
C DGE00540
30  IF (((T-TOUT)*H.LE.0.000) GO TO 440 DGE00550
JSTART=-1
NC=N
EPS=EPS
MF=M

40 IF (((H+T).EQ.T) WRITE (OUT,15)
C
50 CALL NGE002 (Y,Y0)
C
KG0=1-KFLAG
GO TO (60,100,200,300), KGO
C
KFLAG = 0, -1, -2, -3
C
60 CONTINUE
D=0.000
DO 70 I=1,N
    AYI=ABS(Y(I,1))
    YMAX=MAX(YMAX,AYI)
    D=D+(AYI/YMAX)**2
    D=D/(UROUND/EPS)**2
70 IF (D.GT.FLOAT(N)) GO TO 250
IF (INDEX.EQ.3) GO TO 500
IF (INDEX.EQ.2) GO TO 85
80 IF (((T-TOUT)**H.LT.0.000) GO TO 40
C
CALL NGE001 (TOUT,Y,Y0)
GO TO 520
85 IF (((T-TOUT)**H.LE.0.000) GO TO 40
IF (AYI*(T-TOUT)**H.LE.0.000*UROUND) GO TO 500
IF (((T-TOUT)**H.LT.0.000) GO TO 85
H=(TOUT-T)*1.000
JSTART=-1
GO TO 40
100 WRITE (OUT,105) T
110 IF (NHKUT.EQ.10) GO TO 150
    NIHCUT=NHKUT+1
    HMIN=HMIN+.1000
    H=H+.1000
    WRITE (OUT,115) H
    JSTART=-1
    GO TO 40
C
150 WRITE (OUT,155)
GO TO 500
C
200 WRITE (OUT,205) T,H
GO TO 500
C
250 WRITE (OUT,255) T
KFLAG=-2
GO TO 500
C
300 WRITE (OUT,305) T
GO TO 110
C
400 WRITE (LOUT,405) INDEX=-4 RETURN
C
410 WRITE (LOUT,415) INDEX=-4 RETURN
C
420 WRITE (LOUT,425) INDEX=-4 RETURN
C
430 WRITE (LOUT,435) INDEX=-4 RETURN
C
440 WRITE (LOUT,445) T,TOUT,H CALL INTERP
C
CALL NGE001 (TOUT,Y,N0,Y0)
INDEX=-5 RETURN
C
500 TOUT=T DO 510 I=1,N
510 Y0(I)=Y(I,1)
520 INDEX=KFLAG TOUTP=TOUT H0=HUSED IF (KFLAG.NE.0) H0=H RETURN
C
15 FORMAT (35H WARNING.. T + H = T ON NEXT STEP.)
105 FORMAT (//35H KFLAG = -1 FROM INTEGRATOR AT T = ,E16.8/39H
1 TEST FAILED WITH DABS(H) = HMIN//)
115 FORMAT (24H H HAS BEEN REDUCED TO ,E16.8,26H AND STEP WILL DECREASE TO
1 TRIED//)
155 FORMAT (//44H PROBLEM APPEARS UNSOLVABLE WITH GIVEN INPUT//)
205 FORMAT (//35H KFLAG = -2 FROM INTEGRATOR AT T = ,E16.8,5H
2 1.8/52H THE REQUESTED ERROR IS SMALLER THAN CAN BE HANDLED//)
255 FORMAT (//37H INTEGRATION HALTED BY DRIVER AT T = ,E16.8,56H
2 1 TOO SMALL TO BE ATTAINED FOR THE MACHINE PRECISION//)
305 FORMAT (//35H KFLAG = -3 FROM INTEGRATOR AT T = ,E16.8,45H
3 1 TOR CONVERGENCE COULD NOT BE ACHIEVED//)
405 FORMAT (//28H ILLEGAL INPUT.. EPS .LE. 0.//)
415 FORMAT (//25H ILLEGAL INPUT.. N .LE. 0.//)
425 FORMAT (//36H ILLEGAL INPUT.. (T-TOUT)*H .GE. 0.//)
435 FORMAT (//24H ILLEGAL INPUT.. INDEX = ,15//)
445 FORMAT (//44H INDEX = -1 ON INPUT WITH (T-TOUT)*H .GE. 0.//)
116.8,9H TOUT = ,E16.8,6H H = ,E16.8,44H INTERPOLATION WAS DGE01590
2S ON NORMAL RETURN.//4H DESIRED PARAMETER CHANGES WERE NOT MDGE01600
END
SUBROUTINE NGE001 (TOUT,Y,N0,Y0)
C
C THIS IS CALLED BY "GEAR". IT WAS "INTERP" IN THE DISTRIBUTED VEDGE01640
C
DGE01110 DGE01120 DGE01130
DGE01140 DGE01150 DGE01160 DGE01170
DGE01180 DGE01190 DGE01200 DGE01210
DGE01220 DGE01230 DGE01240 DGE01250
DGE01260 DGE01270 DGE01280 DGE01290
DGE01300 DGE01310 DGE01320 DGE01330 DGE01340 DGE01350
DGE01360 DGE01370 DGE01380 DGE01390 DGE01400 DGE01410
DGE01420 DGE01430 DGE01440 DGE01450
DGE01460 DGE01470 DGE01480 DGE01490 DGE01500 DGE01510 DGE01520 DGE01530 DGE01540 DGE01550 DGE01560 DGE01570 DGE01580 DGE01590 DGE01600 DGE01610 DGE01620 DGE01630 DGE01640 DGE01650
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER NO,N,NDUMMY,JSTART,1,L,J
DOUBLE PRECISION TOT,Y,YO,T,H,NDUMMY,S,S1
COMMON /GEAR1/ T,H,NDUMMY(4),N,NDUMMY(2),JSTART
DIMENSION YO(NO), Y(NO,6)
DO 10 I=1,N
10 YO(I)=Y(I,1)
L=JSTART+1
S=(TOT-T)/H
S1=1.000
DO 30 J=2,L
S1=S1*S
DO 20 I=1,N
20 YO(I)=YO(I)+S1*Y(I,J)
30 CONTINUE
RETURN
END

SUBROUTINE NGE002 (Y,NO)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER NO,N,MF,KFLAG,JSTART,IPIV,NUSED,NSTEP,NFE,NJE
INTEGER I,METH,MITER,NO,L,DOUB,MFOLD,NOLD,IRET,MEO,MIO,IWEVDGEO1870
1DER,LMAX,IREDO,J,NSTEPJ,J1,J2,M,IER,NEWQ
DOUBLE PRECISION Y,T,H,HMIN,HMAX,EPS,UPROUND,VMAX,ERROR,SAVE1
DOUBLE PRECISION SAVE2,PW,HUSED
DOUBLE PRECISION EL,OLDLO,TOLD,RMAX,RC,CRATE,EPSOLD,HOLD,FN
1E,EUP,BND,RH,R1,CON,R,HLO,RO,D,PHLO,PR3,D1,ENQ3,ENQ2,PR2,PR1
DOUBLE PRECISION TQ
COMMON /GEAR1/ T,H,HMIN,HMAX,EPS,UPROUND,N,MF,KFLAG,JSTART
COMMON /GEAR2/ VMAX(147)
COMMON /GEAR3/ ERROR(147)
COMMON /GEAR4/ SAVE1(147)
COMMON /GEAR5/ SAVE2(147)
COMMON /GEAR6/ PW(21609)
COMMON /GEAR7/ IPIV(147)
COMMON /GEAR9/ HUSED,NUSED,NSTEP,NFE,NJE
DIMENSION Y(NO,6)
DIMENSION EL(13), TQ(4)
DATA EL(2)/1.000/,OLDLO/1.000/
KFLAG=0
TOLD=T
IF (JSTART.GT.0) GO TO 200
IF (JSTART.NE.0) GO TO 120
CALL DIFFUN (N,T,Y,SAVE1)
DO 110 I=1,N
110 Y(I,1)=H*SAVE1(I)
METH=MF/10
MITER=MF-10*METH
NO=1
L=2
IDOUB=3
RMAX=1.0*04
RC=0.000
CRATE=1.000
EPSOLD=EPS
IIOLD=H
MFOLD=MF
NOLD=N
NSTEP=0
NSTEPJ=0
NFE=1
NJE=0
IRET=1
GO TO 130
120 IF (MF.EQ.MFOLD) GO TO 150
MEO=MEH
MIO=MITER
METH=MF/10
MITER=ME-10*METH
MFOLD=MF
IF (MITER.NE.MIO) IWEVAL=MITER
IF (METH.EQ.MEO) GO TO 150
IDOUB=L+1
IRET=1
GO TO 130
130 CALL NGE003 (METH, NQ, EL, TQ, MAXDER)
LMAX=MAXDER+1
RC=RC*EL(1)/OLDLO
OLDLO=EL(1)
140 FN=FLOAT(N)
EDN=FN*(DBLE(TQ(1))*EPS)**2
E=FN*(DBLE(TQ(2))*EPS)**2
EUP=FN*(DBLE(TQ(3))*EPS)**2
BND=FN*(DBLE(TQ(N))*EPS)**2
GO TO (160,170,200), IRET
150 IF ((EPS.EQ.EPSOLD).AND.(N.EQ.NOLD)) GO TO 160
EPSOLD=EPS
NOLD=N
IRET=1
GO TO 140
160 IF (H.EQ.IIOLD) GO TO 200
RH=H/IIOH
H=IIOH
IREDO=3
GO TO 175
170 RH=DMAX1(RH,HMIN/ABS(H))
175 RH=DMIN1(RH,HMAX/ABS(H),RMAX)
R1=1.000
DO 180 J=2,L
R1=R1*RH
DO 180 I=1,N
180 Y(I,J)=Y(I,J)*R1
H=H*RH
RC=RC*RH
IDOUB=L+1
IF (IREDO.EQ.0) GO TO 690
200 IF (ABS(RC-1.000).GT.0.3000) IWEVAL=MITER
IF (NSTEP.GE.NSTEPJ+20) IWEVAL=MITER
T=T+H
DO 210 J1=1,NQ
DO 210 J2=J1,NQ
J = (NQ+1)*J + 1

DO 210 I = 1, N

210 Y(I,J) = Y(I,J) + Y(I,J+1)

DO 220 M = 1, N

220 ERROR(I) = 0.000

CALL DIFFUN (N, T, Y, SAVE2)

NFE = NFE + 1

IF (T + 1.0) GO TO 290

T = T + 1.0

RC = 1.

NJE = NJE + 1

NSTEP = NSTEP

GO TO (230, 240, 260), MITER

240 NFE = NFE + 1

250 CON = -H*EL(I)

CALL PSET

CALL NCEO04 (Y, NO, CON, MITER, IER)

IF (IER NE 0) GO TO 420

GO TO 350

260 R = EL(I) * 1.000

DO 270 I = 1, N

270 PW(I) = Y(I, 1) + R*I(1, 1, 2)

CALL DIFFUN (N, T, PW, SAVE1)

NFE = NFE + 1

HL0 = H*EL(I)

DO 280 I = 1, N

280 RO = H*SAVE2(I) - Y(I, 2)

PW(I) = 1.000

D = 1.000*RO - H*(SAVE1(I) - SAVE2(I))

SAVE(I) = 0.000

IF (ABS(R).LT. UROUND**YMAX(I)) GO TO 280

IF (ABS(D).EQ.0.000) GO TO 420

PW(I) = D*RO

SAVE(I) = PW(I)*RO

CONTINUE

GO TO 370

290 IF (MITER.NE.0) GO TO (350, 350, 310), MITER

D = 0.000

DO 300 I = 1, N

300 R = H*SAVE2(I) - Y(I, 2)

D = D + (1.000*ERROR(I)/YMAX(I)**2)

SAVE(I) = Y(I, 1) + EL(I)*R

ERROR(I) = R

GO TO 400

C-----------------------------

310 PHLO = HL0

HL0 = H*EL(I)

IF (HL0.EQ. PHLO) GO TO 330

R = HL0/PHLO

DO 320 M = 1, N

320 PW(I) = 1.000/D

330 DO 340 I = 1, N
SAVE1(1)=PW(1)*(H*SAVE2(1)-(Y(1,2)+ERROR(1)))
GO TO 370
DO 360 I=1,N
SAVE1(1)=H*SAVE2(1)-(Y(1,2)+ERROR(1))
C
CALL SOL
CALL NGE006 (N,N0,PF,SAVE1,1P1V)
D=0.000
DO 380 I=1,N
ERROR(1)=ERROR(1)+SAVE1(1)
D=D+SAVE1(1)/YMAX(1)**2
SAVE1(1)=Y(1,1)+EL(1)*ERROR(1)
C
IF (M.NE.0) CRATE=DMAK1(.9000*CRATE,D/D1)
IF ((D*DMIN1(1.000,2.000*CRATE)).LE.BND) GO TO 450
D1=D
M=M+1
IF (M.EQ.3) GO TO 410
CALL DIFFUN (N,T,SAVE1,SAVE2)
GO TO 290
NFE=NFE+2
IF (IWEVAL.EQ.-1) GO TO 440
T=TOLD
RMAX=2.000
DO 430 J=1,NQ
DO 430 J2=1,NQ
J=(NQ+J1)-J2
DO 430 I=1,N
Y(1,J)=Y(1,J)-Y(1,J+1)
IF (ABS(H).LE.HMIN*1.00000100) GO TO 680
RH=.25000
IREDO=1
GO TO 170
IWEVAL=MITER
GO TO 220
IF (MITER.NE.0) IWEVAL=-1
NFE=NFE+M
D=0.000
DO 460 I=1,N
D=D+ERROR(1)/YMAX(1)**2
IF (D.GT.E) GO TO 500
KFLAG=0
IREDO=0
NSTEP=NSTEP+1
HUSED=H
QUSUE=NQ
DO 470 J=1,L
DO 470 I=1,N
Y(1,J)=Y(1,J)+EL(J)*ERROR(1)
IF (IDOUB.EQ.1) GO TO 520
IDOUB=IDOUB+1
IF (IDOUB.GT.1) GO TO 700
IF (L.EQ.LMAX) GO TO 700
DO 490 I=1,N
LMAX=ERROR(1)
C
GO TO 370

GO TO 700
500 KFLAG=KFLAG-1
   T=TOLD
   DO 510 J1=1,NQ
      DO 510 J2=J1,NQ
         J=(NQ*J1)-J2
         DO 510 I=1,N
         510 Y(I,J)=Y(I,J)-Y(I,J+1)
         RMAG=2.0D0
         IF (ABS(Y(I,J)).LE.HMIN*1.00001D0) GO TO 660
         IF (KFLAG.LT.-3) GO TO 640
         IREDO=2
         PR3=1.D20
         GO TO 540
   DO 530 I=1,N
      D1=0.0D0
      DO 530 I=1,N
         530 D1=DI+((ERROR(I)-Y(I,LMAX))/YMAX(I))**2
         ENQ3=.50D0/FLOAT(L+1)
         PR3=((D1/EUP)**ENQ3)*1.40D0+1.4D-06
         ENQ2=.50D0/FLOAT(L)
         PR2=((D/E)**ENQ2)*1.20D0+1.2D-06
         PR1=1.D20
         IF (NP.EQ.1) GO TO 560
         D=0.0D0
         GO TO 550
   DO 550 I=1,N
      D=DI*(Y(I,L)/YMAX(I))**2
      ENQ1=.50D0/FLOAT(NQ)
      PR1=((D/EDN)**ENQ1)*1.30D0+1.3D-06
   560 IF (PR2.LE.PR1) GO TO 570
      IF (PR3.LE.PR1) GO TO 590
      GO TO 580
   570 IF (PR2.GT.PR1) GO TO 580
      NEWQ=NQ
      RH=1.0D0/PR2
      GO TO 620
   580 NEWQ=NQ-1
      RH=1.0D0/PR1
      GO TO 620
   590 NEWQ=L
      RH=1.0D0/PR3
      IF (RH.LT.1.0D0) GO TO 610
      DO 600 I=1,N
      600 Y(I,NEWQ+1)=ERROR(I)*EL(L)/FLOAT(L)
      GO TO 630
   610 IDOUB=10
      GO TO 700
   620 IF ((KFLAG.EQ.0).AND.(RH.LT.1.1D0)) GO TO 610
      IF (NEWQ.EQ.NQ) GO TO 170
   630 NQ=NEWQ
      L=NQ+1
      IRET=2
      GO TO 130
   640 IF (KFLAG.EQ.-7) GO TO 670
RH = .100D0
RH = DMAX1(HMIN/ABS(H), RH)
H = H*RH
CALL DIFFUN (N, T, Y, SAVE1)
NFE = NFE + 1
DO 650 I = 1, N
650 Y(1, 2) = H*SAVE1(1)
IWEVAL = MITER
IDOUB = 10
IF (NQ .EQ. 1) GO TO 200
NQ = 1
L = 2
IRET = 3
GO TO 130
660 KFLAG = -1
GO TO 700
670 KFLAG = 2
GO TO 700
680 KFLAG = 3
GO TO 700
690 RMAX = 10.00D0
700 HOLD = H
JSTART = NQ
RETURN
END
SUBROUTINE NGE03 (METH, NQ, EL, TQ, MAXDER)
IMPLICIT DOUBLE PRECISION (A-H, O-Z)
INTEGER METH, NQ, MAXDER, K
DOUBLE PRECISION EL
DOUBLE PRECISION TQ, PERTST
DIMENSION PERTST(12, 3), EL(13), TQ(4)
DATA PERTST/1.000, 1.000, 2.000, 1.000, 3158000, .07407000, .0139D0/2000
$0021820000, 0002945000, 0003692000, 0003692000, 000352D0\04787000
$1.000, 1.000, 5.000, 1667000, 0.04167000, 1.000, 1.000, 1.000
$1.000, 1.000, 2.000, 12.000, 24.000, 37.89000, 53.33000
$78.97000, 106.9000, 126.7000, 147.4000, 166.8000, 191.000
$2000, 4.000D0, 10.42000, 13.7000, 1.000, 1.000, 1.000, 1.000
$1.000, 12.000, 24.000, 37.89000, 53.33000, 70.08000, 87.97000
$126.7000, 147.4000, 166.8000, 191.000, 1.000, 3.000, 6.000
$12.5000, 1.000, 1.000, 1.000, 1.000, 1.000, 1.000
GO TO (1, 2), METH
1 MAXDER = 12
GO TO (101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112), NQ
2 MAXDER = 5
GO TO (201, 202, 203, 204, 205), NQ
101 EL(1) = 1.000
GO TO 900
102 EL(1) = 0.500D0
GO TO 900
103 EL(1) = 0.166666666666667D0 - 01
EL(3) = 0.7500D0
EL(4) = 1.666666666666667D0 - 01
GO TO 900
104 EL(1) = 0.37500D0
GO TO 900
EL(3)=9.166666666666670-01
EL(4)=3.33333333333330-01
EL(5)=4.166666666666670-02
GO TO 900

105 EL(1)=3.4861111111111110-01
EL(3)=1.04166666666667000
EL(4)=4.861111111111110-01
EL(5)=1.041666666666670-01
EL(6)=8.33333333333330-03
GO TO 900

106 EL(1)=3.2986111111111110-01
EL(3)=1.14166666666667000
EL(4)=0.625000
EL(5)=1.77083333333330-01
EL(6)=0.025000
EL(7)=1.388888888888890-03
GO TO 900

107 EL(1)=3.15591931216931220-01
EL(3)=1.225000
EL(4)=7.51851851851850-01
EL(5)=2.55208333333330-01
EL(6)=4.861111111111110-02
EL(7)=4.861111111111110-03
EL(8)=1.55208333333330-02
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111 EL(1)=2.80189596443936720-01 DGO5510
EL(3)=1.464484126984127000 DGO5520
EL(4)=1.1715145502645503000 DGO5530
EL(5)=5.79358190035273370-01 DGO5540
EL(6)=1.88322861552028220-01 DGO5550
EL(7)=4.14303626543209880-02 DGO5560
EL(8)=6.21114417989417990-03 DGO5570
EL(9)=6.25206679894179890-04 DGO5580
EL(10)=4.04174015285126400-05 DGO5590
EL(11)=1.51565255731922400-06 DGO5600
EL(12)=2.5052108385417190-08 DGO5610
GO TO 900 DGO5620

112 EL(1)=2.74265540031599060-01 DGO5630
EL(3)=1.5099386724386724000 DGO5640
EL(4)=1.2602711640211640000 DGO5650
EL(5)=6.59234182098765430-01 DGO5660
EL(6)=2.30458002645502650-01 DGO5670
EL(7)=5.56972461052322160-02 DGO5680
EL(8)=9.43948412698412700-03 DGO5690
EL(9)=1.11927496693121690-03 DGO5700
EL(10)=9.09391534915349390-05 DGO5710
EL(11)=4.822532886147953090-06 DGO5720
EL(12)=1.50312650312650310-07 DGO5730
EL(13)=2.08767569878680990-09 DGO5740
GO TO 900 DGO5750

C

201 EL(1)=1.000 DGO5770
GO TO 900 DGO5780

202 EL(1)=6.66666666666666670-01 DGO5790
EL(3)=3.3333333333333330-01 DGO5800
GO TO 900 DGO5810

203 EL(1)=5.45454545454545450-01 DGO5820
EL(3)=EL(1) DGO5830
EL(4)=9.09090909090909090-02 DGO5840
GO TO 900 DGO5850

204 EL(1)=0.48000 DGO5860
EL(3)=0.70000 DGO5870
EL(4)=0.20000 DGO5880
EL(5)=0.02000 DGO5890
GO TO 900 DGO5900

205 EL(1)=4.37956204379562040-01 DGO5910
EL(3)=8.21167883211678830-01 DGO5920
EL(4)=3.10218978102189780-01 DGO5930
EL(5)=5.47452554745255500-02 DGO5940
EL(6)=3.64963503649635040-03 DGO5950

C

900 DO 910 K=1,3 DGO5970

910 TQ(K)=PERTST(NQ,METH,K) DGO5980
TQ(4)=.5000*TQ(2)/FLOAT(NQ+2) DGO5990
RETURN DGO6000
END DGO6010
SUBROUTINE NCEOON (Y, NO, CON, MITER, IER) DGO6020
IMPLICIT DOUBLE PRECISION (A-H,O-Z) DGO6030
INTEGER NO,MITER,IER,N,IDUMMY,IPIV,NSQ,1,J1,J DGO6040
DOUBLE PRECISION Y,CON,T,H,DUMMY,IFOUND,YMAX,SAVE1,SAVE2,PW DGO6050
DOUBLE PRECISION EPSJ,D,RO,YJ,R
DIMENSION Y(NO,6)
COMMON /GEAR1/ T,H,DUMMY(3),UROUND,N1,DUMMY(3)
COMMON /GEAR2/ YMAX(I47)
COMMON /GEAR4/ SAVE1(I47)
COMMON /GEAR5/ SAVE2(I47)
COMMON /GEAR6/ PW(21609)
COMMON /GEAR7/ IPIV(I47)
COMMON /GEAR8/ EPSJ,NSQ
IF (MITER.EQ.2) GO TO 20
CALL PEDERV (N,T,Y,PW,N0)
DO 10 I=1,NSQ
10 PW(I)=PW(I)*CON
GO TO 60
20 D=0.000
DO 30 I=1,N
30 D=D+SAVE2(I)**2
R0=ABS(H)*SQR(D)*1.03*UROUND
J1=0
DO 50 J=1,N
YJ=Y(J,1)
R=EPSJ*YMAX(J1)
DGE06060
DGE06070
DGE06080
DGE06090
DGE06100
DGE06110
DGE06120
DGE06130
DGE06140
DGE06150
DGE06160
DGE06170
DGE06180
DGE06190
DGE06200
DGE06210
DGE06220
DGE06230
DGE06240
DGE06250
DGE06260
DGFN3270
I(N)=-I(N)  DGE06610
A(M,K)=A(K,K)  DGE06620
A(K,K)=T  DGE06630
20 IF (T.EQ.0.0D0) GO TO 80  DGE06640
T=1.000/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.0.0D0) GO TO 50  DGE06720
DO 40 I=KP1,N  DGE06730
40 A(I,J)=A(I,J)+A(I,K)*T  DGE06740
50 CONTINUE  DGE06750
60 CONTINUE  DGE06760
70 K=N  DGE06770
IF (A(N,N).EQ.0.0D0) GO TO 80  DGE06780
RETURN  DGE06790
80 IER=K  DGE06800
I(N)=0  DGE06810
RETURN  DGE06820
END  DGE06830

SUBROUTINE DGE066(N,NDIM,A,B,IP)  DGE06840
IMPLICIT DOUBLE PRECISION (A-H,O-Z)  DGE06850
INTEGER N,NDIM,IP,NM1,K,KP1,M1,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 DGE066(N,NDIM,A,B,IP)  DGE07110
C  DGE07120
C LAST 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
C DIMENSION WK(33),X(3),Y(3),CO(3),QE(N),CF(N),
+XMHI(N),XMKI(N),XMP1(N)
C
C EXTERNAL FCNM
C EXTERNAL FCNJM
C
C READ INITIAL GUESSES FOR ADSORBED PHASE
C ADSORBATE CONCENTRATIONS
C
C DO 3 I=1,N
C X(I)=0.5*CE(I)
3 CONTINUE
C NSIG=4
C ITMAX=300
C
C CALL NMAJLS(N,FCNM,FCNJM,NSIG,
&X, FNM, ITMAX, WK, IER, XMHI, XMKI, XMP1, CE)
C
C IF(IER .NE. 0) THEN
C WRITE(*,*) 'IER = ', IER
C WRITE(*,*) 'X = ', (X(I),I=1,N)
C WRITE(*,*) 'FNM = ', FNM
C WRITE(*,*) 'SUBROUTINE IAST HYEARS'
C STOP 'something is wrong'
C END IF
C
C COMPUTE HYPOTHETICAL LIQUID PHASE CONC'S
C AND THE LIQUID PHASE MOLE FRACTIONS
C
C DO 4 I=1,N
C ARG=XMHI(I)*X(I)**XMP1(I)
C CO(I)=(X(I)/XMHI(I))*DEXP(ARG)
C Y(I)=CE(I)/CO(I)
4 CONTINUE
C
C TOTAL CARBON COVERAGE
C
C SUM=0.000
C DO 5 I=1,N
C SUM=SUM+Y(I)/X(I)
5 CONTINUE
C QT=1.000/SUM
C
C ADSORBED PHASE ADSORPTION CONCENTRATION
C DO 6 I=1,N
C QE(I)=Y(I)*QT
6 CONTINUE
C RETURN
C END
C
C---------------------------------------------------------------------
C SUBROUTINE FCNM(X,F,XMHI,XMKI,XMP1,CE,N)
C
IMPLICIT DOUBLE PRECISION(A-H,O-Z)

C DIMENSION XM1(N),XK1(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)=XM1(I)*XMP1(I)/(XMP1(I)+1.0D0)
P(I)=X(I)+H(I)*X(I)**(XMP1(I)+1.0D0)
2 CONTINUE
C
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)=XM1(I)*X(I)**XMP1(I)
FR(I)=X(I)/XM1(I)
P1(I)=CE(I)/(FR(I)*DEXP(ARG(I)))
SUM=SUM+P1(I)
4 CONTINUE
C
F(N)=SUM-1.0D0
C
RETURN
END
C
C-----------------------------------------------------
C SUBROUTINE FCNJM(X,FJ,XM1,XK1,XMP1,CE,N)
C IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C DIMENSION XM1(N),XK1(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)=XM1(I)*XMP1(I)*X(I)**XMP1(I)
ARG(I)=XM1(I)*X(I)**XMP1(I)
XNOM(I)=-CE(I)*XM1(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
C
IF (N.EQ.3) THEN

DE07710
DE07720
DE07730
DE07740
DE07750
DE07760
DE07770
DE07780
DE07790
DE07800
DE07810
DE07820
DE07830
DE07840
DE07850
DE07860
DE07870
DE07880
DE07890
DE07900
DE07910
DE07920
DE07930
DE07940
DE07950
DE07960
DE07970
DE07980
DE07990
DE08000
DE08010
DE08020
DE08030
DE08040
DE08050
DE08060
DE08070
DE08080
DE08090
DE08100
DE08110
DE08120
DE08130
DE08140
DE08150
DE08160
DE08170
DE08180
DE08190
DE08200
DE08210
DE08220
DE08230
DE08240
DE08250
FJ(1,1)=1.000+PR(1)
FJ(2,1)=0.000
FJ(3,1)=XNH1(1)/(X(1)*DEXP(ARG(1)))
FJ(1,2)=-1.000+PR(2)
FJ(2,2)=1.000+PR(2)
FJ(3,2)=XNH1(2)/(X(2)*DEXP(ARG(2)))
FJ(1,3)=0.000
FJ(2,3)=-1.000+PR(3)
FJ(3,3)=XNH1(3)/(X(3)*DEXP(ARG(3)))
END IF
C
RETURN
END

SUBROUTINE IASTMQ(CE,QE,XNH1,XNH2,XMP1,N)
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 XNH1(N),XNH2(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=N
ITMAX=1000
C
CALL NMJL5(N,FQNM,FQNJM,NSIG,
&X,FNORM,ITMAX,WK,IER,XNH1,XNH2,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=XNH1(I)*X(I)**XMP1(I)
DO 68 I=1,N
CO(1)=(X(1)/XMH1(1))*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(1)*QT
6 CONTINUE
RETURN
END

---

SUBROUTINE FQNM(X,F,XMH1,XMK1,XMP1,QE,N)
C
C IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C
C DIMENSION XMH1(N),XMK1(N),XMP1(N),QE(N)
C
C DIMENSION X(N),F(N),H(3),P(3),ARG(3),FR(3),P1(3)
C
C DO 1 I=1,N
X(I)=DMAX1(X(I),1.0D-20)
1 CONTINUE
C
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
C
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

---

SUBROUTINE FQNM(X,FJ,XMH1,XKM1,XMP1,QE,N)
C
C IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C
C DIMENSION XMH1(N),XMK1(N),XMP1(N),QE(N)
C
C DIMENSION X(N),FJ(N,N),FR(3),P1(3),F2(3)
C
C DO 1 I=1,N
C X(1)=DMIN(X(1),1.0D-20)
1 CONTINUE
C DX=1.80D0*(1.0D-6)**(1.0D0/3.0D0)
C DO 2 I=1,N
C PR(I)=XHK1(I)*XMP1(I)**X(1)**XMP1(I)
2 CONTINUE
C IF (N.EQ.2) THEN
C FJ(1,1)=1.00D0+PR(1)
C FJ(2,1)=-QI(1)/X(1)**2.00D0
C FJ(1,2)=-1.00D0-PR(2)
C FJ(2,2)=-QI(2)/X(2)**2.00D0
C END IF
C IF (N.EQ.3) THEN
C FJ(1,1)=1.00D0+PR(1)
C FJ(2,1)=0.00D0
C FJ(3,1)=-QI(1)/X(1)**2.00D0
C FJ(1,2)=-1.00D0-PR(2)
C FJ(2,2)=1.00D0+PR(2)
C FJ(3,2)=-QI(2)/X(2)**2.00D0
C FJ(1,3)=0.00D0
C FJ(2,3)=-1.00D0-PR(3)
C FJ(3,3)=-QI(3)/X(3)**2.00D0
C END IF
C RETURN
C END SUBROUTINE XMAJLS(N,FCN,FCNJ,NSIG,X,FNORM,ITMAX,WK,IER+
C ,XHK1,XMP1,CE)
C NEWTONS METHOD WITH GLOBALLY CONVERGENCE
C STRATEGY FOR SYSTEM OF NONLINEAR EQUATIONS
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 UNKNOWNS
C FNORM - NORM OF FUNCTION VECTOR
C ITMAX - MAXIMUM ALLOWABLE NUMBER OF ITERATIONS
C IER - 0 = SUCCESSFUL ITERATION
C 100 = NORM NOT SUFFICIENTLY SMALL (OPTIMUM)
C 110 = EXCEEDS MAXIMAL NUMBER OF ITERATIONS
C IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C DIMENSION WK(1),X(N),XHK1(N),XMP1(N),CE(N)
C IER=0
C IER=0
C
IFOL=1
IFOU=N
IFJL=N+1
IFJU=N*N
ISL=N+N*N
ISU=N+N*N+N
IXNL=ISU+1
IXNU=ISU+N
IFNL=IXNU+1
IFNU=IXNU+N
IWKGL=IFNU+1

C

1.) FUNCTIONAL EVALUATION AND RES. FUNCTION

CALL FCN(X,WK(IFOL),XMH1,XMK1,XMP1,CE,N)

C

GO=0.000
DO 1 I=IFOL,IFOU
GO=GO+WK(I)*WK(I)
1 CONTINUE
GO=GO*0.5

C

200 CONTINUE

C

ITER=ITER+1

C

II.) CALCULATE JACOBEAN

CALL FCNJ(X,WK(IFJL),XMH1,XMK1,XMP1,CE,N)

C

III.) SOLVE FOR NEWTON STEP

CALL GAUSPI(WK(IFJL),WK(ISL),WK(IFOL),N,WK(IWKGL))

C

IV.) CHECK FOR ACCEPTABILITY

XL=1.0
ITER1=0

C

100 CONTINUE

ITER1=ITER1+1

C

DO 2 I=1,N
WK(I*IXNL+1)=X(I)-XL*WK(ISL+I-1)
2 CONTINUE

C

CALL FCN(WK(I*IXNL),WK(IFNL),XMH1,XMK1,XMP1,CE,N)

C

GN=0.000
DO 3 I=IFNL,IFNU
GN=GN+WK(I)*WK(I)
3 CONTINUE
GN = GN * 0.5DO

A = GN - GO - 1.0D - 04 * XL * 2.0DO * GO

IF(A .GT. 0.0DO) THEN
IF(ITER .GT. 50) THEN
WRITE(*,*) ' Program stalls'
WRITE(*,*) ' try new initial guess'
STOP
END IF
END IF
APPLY FORMULA
XLN = GO / (GN - GO + 2.0 DO)

IF(XLN .LT. 0.1DO * XL) XL = XL * 0.1
IF(XLN .GT. 0.5DO * XL) XL = XL * 0.5
IF(XLN .GE. 0.1 * XL .AND. XLN .LE. 0.5 * XL) THEN
END IF
GO TO 100
END IF

PREPARE TO RETURN TO STEP 1.)

DO 4 I = 1, N
WK(I) = WK(I) + LN + 1 - 1
X(I) = WK(I) * XLN + I - 1
4 CONTINUE
GO = GN

V.) CONVERGENCE TEST

IF(ITER . GT. ITMAX) THEN
WRITE(*,*) ' Iteration stalled or ITMAX too small'
FNORM = 2.0DO * GN
IER = 110
RETURN
END IF

DO 5 I = 1, N
CRIT = DBS(10.0DO**((-NSIG) * X(I)))
IF(DBS(WK(ISL + 1 - 1)) . GT. CRIT) GO TO 200
5 CONTINUE

FNORM = 2.0DO * GN

IF(FNORM .LT. 10.0DO**((-NSIG))) THEN
IER = 0
ELSE
IER = 100
END IF
RETURN
END

SUBROUTINE GAUSPI(A, X, B, N, W)

C
C A - COEFFICIENT MATRIX (UNCHANGED ON RETURN)
C B - CONSTANT VECTOR
C X - SOLUTION VECTOR
C W - WORK VECTOR DIMENSIONED (N,N+1)
C - IN CALLING PROGRAM N*N+1
C C - DIMENSION OF MATRIX
C
C ALGORITHM USES PARTIAL PIVOTING
C BUT DOES NOT CHECK FOR SINGULARITY
C NO ACCURACY CHECK OR ITERATIVE IMPROVEMENT
C OF SOLUTION IS PERFORMED
C
C IMPLICIT DOUBLE PRECISION(A-H,O-Z)
C
C DIMENSION A(N,N),X(N),B(N),W(N,*)
C
DO 1 I=1,N
DO 2 J=1,N
W(1,J)=A(I,J)
2 CONTINUE
W(1,N+1)=B(1)
1 CONTINUE
C
DO 15 KK=1,N-1
C
JP=KK
IP=KK
IJS=KK
JJ=KK
C
C PARTIAL PIVOTING
C
PMAX=DBS(W(IJS,JP))
DO 11 I=IJS+1,N
PCOMP=DBS(W(I,JP))
IF(PMAX.LT.PCOMP) THEN
PMAX=PCOMP
IF(IP.LT.IJS) THEN
DO 12 JJ=JP,N+1
H=W(IJS,JJ)
W(IJS,JJ)=W(IP,JJ)
W(IP,JJ)=H
12 CONTINUE
END IF
11 CONTINUE
C
IF(IP.NE.IJS) THEN
DO 13 JJ=JP,N+1
13 CONTINUE
END IF
C
C TRIANGULATION STEP
C
DO 14 I=IJS+1,N
DO 15 J=JJS+1,N+1
W(1,J)=W(1,J)-W(1,JJS)/W(IJS,JJS)*W(IJS,J)
15 CONTINUE

13 CONTINUE

15 CONTINUE

C

GAUSSIAN ELIMINATION

C

X(N)=W(N,N+1)/W(N,N)

C

DO 16 K1=1,N-1
K=N-K1
SUM=0.0D0
DO 17 J=K+1,N
SUM=SUM+W(K,J)*X(J)

17 CONTINUE

X(K)=(W(K,N+1)-SUM)/W(K,K)

16 CONTINUE

C

RETURN

END

C-----------------------------------------------
NOMENCLATURE

\( b \)  
- equilibrium constant

\( B_t \)  
- Biot number

\( BTC \)  
- breakthrough curve

\( C \)  
- bulk liquid concentration

\( C_h \)  
- 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

\( D_{b} \)  
- 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

\( J_i \)  
- Liquid phase mass flux
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_s$</td>
<td>surface diffusion flux</td>
</tr>
<tr>
<td>GAC</td>
<td>granular activated carbon</td>
</tr>
<tr>
<td>$k_r$</td>
<td>rate constant in Equation 6.5</td>
</tr>
<tr>
<td>$K_{12}$</td>
<td>constants in Equations 4.1 and 4.2</td>
</tr>
<tr>
<td>$k_f$</td>
<td>external mass transfer coefficient</td>
</tr>
<tr>
<td>$K_o$</td>
<td>constant in Equation 4.3</td>
</tr>
<tr>
<td>$k$</td>
<td>Freundlich constant</td>
</tr>
<tr>
<td>$L$</td>
<td>constant in Equations 5.4</td>
</tr>
<tr>
<td>$m$</td>
<td>exponent in Equations 4.1 and 4.2</td>
</tr>
<tr>
<td>$m_i$</td>
<td>mass adsorbed at time $t$</td>
</tr>
<tr>
<td>$m_e$</td>
<td>mass adsorbed at equilibrium</td>
</tr>
<tr>
<td>$n$</td>
<td>Freundlich exponent</td>
</tr>
<tr>
<td>$q$</td>
<td>carbon loading</td>
</tr>
<tr>
<td>$q_0$</td>
<td>initial capacity</td>
</tr>
<tr>
<td>$q_e$</td>
<td>capacity at equilibrium</td>
</tr>
<tr>
<td>$Q$</td>
<td>dimensionless solid phase concentration in particles.</td>
</tr>
<tr>
<td>$Q$</td>
<td>average dimensionless solid phase concentration in particles.</td>
</tr>
<tr>
<td>$Q_l$</td>
<td>Langmuir Constant</td>
</tr>
<tr>
<td>$q^*$</td>
<td>equilibrium solid phase concentration</td>
</tr>
<tr>
<td>$r_i$</td>
<td>measure for the standard deviation in Equation 6.1</td>
</tr>
<tr>
<td>$R$</td>
<td>dimensionless distance from the center of carbon particle</td>
</tr>
<tr>
<td>$R_G$</td>
<td>universal gas constant</td>
</tr>
<tr>
<td>$R_o$</td>
<td>ratio of dissolved oxygen to GAC mass</td>
</tr>
</tbody>
</table>
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

- ΔH  heat of adsorption
Δq  increase in the carbon uptake
e  bed voidage
r_p  particle porosity
μ  viscosity of water
τ  dimensionless time
θ_i  sphericity
ϕ  Thiele modulus
$\rho_t$  
density of water

$\rho_r$  
density of the carbon particle

$\chi^2$  
chi square statistics
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