1986

Prediction of Specific Priority Organics Adsoption on Activated Carbon in Complex Background Mixtures

Eid Abdelmuti Alkhatib
University of Rhode Island

Recommended Citation

Alkhatib, Eid Abdelmuti, "Prediction of Specific Priority Organics Adsoption on Activated Carbon in Complex Background Mixtures" (1986). *Open Access Dissertations.* Paper 603.
https://digitalcommons.uri.edu/oa_diss/603

PREDICTION OF SPECIFIC PRIORITY ORGANICS ADSORPTION ON ACTIVATED CARBON IN COMPLEX BACKGROUND MIXTURES

By

EID ABDELMUTI ALKHATIB

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CIVIL AND ENVIRONMENTAL ENGINEERING

UNIVERSITY OF RHODE ISLAND

1986

DOCTOR OF PHILOSOPHY DISSERTATION

OF

EID ABDELMUTI ALKHATIB

Approved:

Dissertation Committee
Major Professor Leon T. Thiem

Raymond M. Wright

Calvin P. Poon

William R. Wright

A A Nichols

DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND
1986

ABSTRACT

A study was conducted to investigate carbon adsorption of specific priority pollutants, (2,4 Dimethylphenol, Naphthalene, Fluorene, Pyrene, Bis(2-ethylhexyl phthalate) in a complex mixture background, using laboratory and pilot scale reactors for data generation, and various numerical computer models for data evaluation and subsequent prediction. Prediction of adsorption using intra-particle diffusion resistance (surface model and combined surface and pore diffusion model) was more successful using the combined surface and pore diffusion model than by using the surface model alone. Dissolved organic carbon (DOC) was selected as a complex mixture surrogate to evaluate any competitive effect due to individual components in the complex background mixture. Prediction of batch and packed bed adsorption of each of the specific priority organics that were studied was successful when the IAS model was adjusted by evaluating the adsorption equilibrium constants in a complex mixture background. Results from the laboratory scale experiments were verified by a pilot plant study utilizing 4 inch diameter by 3 feet deep carbon contactors with empty bed contact time of 1.75 and 3.75 minutes treating 2,4-dimethylphenol present in a complex mixture background consisting of a domestic secondary treatment effluent.

ACKNOWLEDGEMENTS

This project was funded by the Kuwait Institute for Scientific Research and the Kuwait Environmental Protection Council to whom the author feels deeply indebted. Without the awareness and concern of their directors and staff, this project would not have been made possible.

I wish to express my sincere gratitude to my advisor Dr. Leon T. Thiem for all his support, guidance and supervision throughout this project. I would also like to thank my committee members Dr. Calvin P.C. Poon for his valuable comments and suggestions, Dr. Raymond Wright for his valuable comments, suggestions and all those hours of side meetings we had, and to Dr. William Wright for his review and comments.

Gratitude is extended to Milton and George Huston for all their help in the various stages of project progress as well as in constructing the pilot plant. Their skills and dedication permitted the timely completion of this study.

Appreciation is sincerely expressed to the staff of South Kingstown Wastewater Treatment Facility for their cooperation and help in installing the pilot plant in a safe and secure lucation. My appreciation to Mary Costa and Kevin Fish for their excellent typing and patience in putting up with the quality of my handwriting.

Unending support, patience and encouragement from my wife Fairouz is greatly acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

1.1 Background and Statement of the Problem

A majority of the large-scale industries in Kuwait are located within the Shuaiba Industrial Area (SIA) Complex which consists of three refineries, two chemical fertilizer plants, a liquified petroleum gas plant (LPG), two power and desalination plants, and various small - scale industries.

All of the wastewater that is generated in SIA (about 30,000 m^3/d) is discharged back to the sea with minor in-plant treatment. The available in-plant treatment includes processes such as NH_3 stripping, flue gas desulfurization units, urea hydrolizers, API oil separators and neutralization pits. The main water-wastewater cycle in SIA is shown in Figure 1.1. Treatment of SIA wastewater is a critical issue due to the following.

- The desalination plant water intakes are located in the vicinity of the wastewater outfalls. Several low vapor pressure pollutants that are discharged from the SIA industries to the off-shore waters may carried over during the distillation process that is used to produce drinking water for Kuwait. This is of concern since this distilled water constitutes the major source of drinking water for Kuwait.
- All of the industrial cooling water intakes are located in the vicinity of the wastewater outfalls and as a result

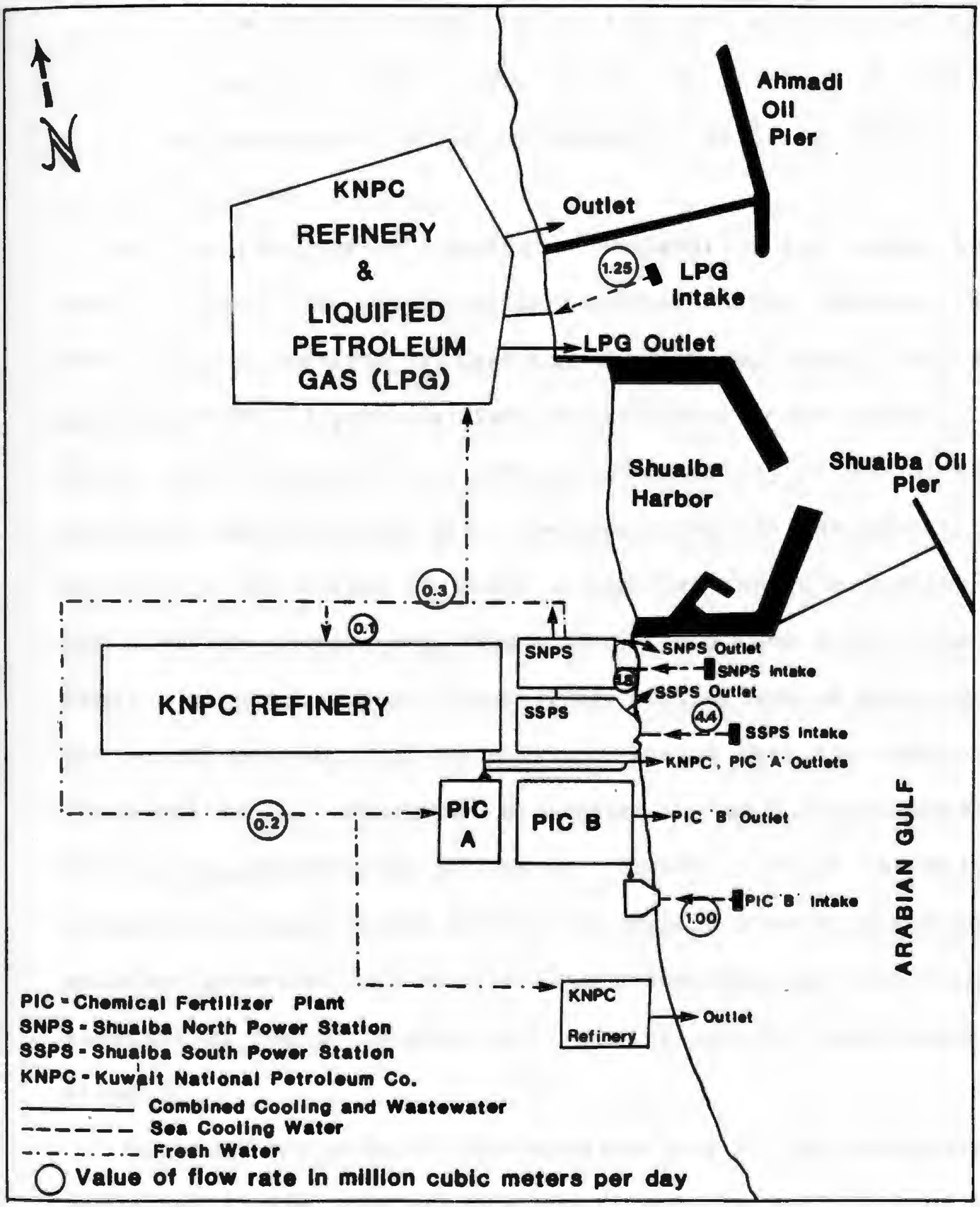


Figure 1-1 Cooling, Freshwater and Wastewater Cycles in SIA

corrosion problems due to waste stream pollutants such as ammonia which corrodes copper - nickel tubes, can occur.

- The major limitation to much needed agriculture in Kuwait is the lack of sufficient and suitable water for irrigation. This has led to the concensus that a non-discharge policy of wastewater needs to be adopted in this area.

With a program of wastewater reclamation and reuse, the treated industrial water can be recycled to the industries, utilized for non-crop irrigation, and can replenish brackish water aquifers. A previous study was conducted by the author[1] in order to investigate the central treatability of all of the wastewater generated from SIA. The study involved the operation of a pilot plant used to model a combined carbon oxidation - nitrification process, employing a continuous flow stirred-tank reactor with recycle and zero sludge wasting mode of operation. The overall conclusion of the study indicated that the combined treatment of SIA industrial wastewater is feasible and adequate for removing conventional pollutants. However, one of the major concerns is the probable presence of organic priority pollutants which are generated by the petroleum industries and can impose substantial health hazards and restrictions on reuse alternatives[2-6].

In order to provide the maximum use of the wastewater generated in SIA with minimum health concern restrictions, a polishing of the effluent derived from the activated sludge treatment system would be essential. This concept of adding treatment units to the conventional secondary treatment sequence provides the model for Best Available Treatment Economically Achievable (BATEA) for this kind of wastewater. Most promising polishing techniques include powder activated carbon (PAC) and granular activated carbon (GAC) processes. The application of this treatment sequence can provide a high quality reclaimed wastewater that can be used for a variety of applications.

1.2 Wastewater Characteristics

A combined petrochemical industrial complex wastewater is expected to contain a variety of priority organic pollutants depending on the nature of the processes. Many of these pollutants are common among the different industrial categories and others are specific. With the lack of information on petrochemical industries wastewater characteristics it is very difficult to establish a criterion for petrochemical wastewater. Petroleum refining industrial wastewater is considered to have the highest levels of organic priority pollutants. Wastewater in the petroleum refining industry is defined as the effluent from an API Separator which is only designed to remove gross concentration of oil and grease.

For the purpose of establishing wastewater characteristics of the petroleum refining industry, literature data were reviewed and supplemented with actual sampling and analysis. The characteristics of petroleum refineries wastewater are presented in Table 1-1. Part of the data were adapted from EPA screening study of 10 petroleum refineries[2,3]. API separator effluent

Table 1.1 Petroleum Refineries Wastewater Characteristics (API Separator Effluent)

	EPA Screening Study[a]										SIA Complex[b]	
Parameter	Refn. -A-	Refn. -C-	Refn. -G-	Refn. -H-	Refn. -I-	Refn. -J-	Refn. -L-	Refn. -N-	Refn. -P-	Refn. -Q-	Refn. KNPC[c]	Refn. KNPC[d]
Conventional pollutants, mg/L												
BOD$_5$	23	117	260	40	66	59	131	101	212	26	210	NA
COD	107	323	840	190	260	177	423	280	537	247	736	NA
TOC	32	71	230	50	81	51	120	103	150	66	NA	NA
TSS	380	28	139	102	39	53	123	85	63	29	NA	NA
Sulfide	8	1.5	27	3.1	0.55	1.4	1.2	6.7	24	0.6	2.5	NA
Oil & Grease	NA	93	99	37	32	77	NA	NA	NA	42	83	NA
NH$_3$-N	12	38	14	6.8	4.3	1.6	1.2	13.3	15	51	3.1	NA
PH	7.2	8.8	10.4	7.9	7.9	8.3	8.3	8.0	10.0	8.6	NA	NA
Metals & inorganics, ug/L												
Arsenic	12	8	5	20	5	3	20	20	20	440	NA	NA
Cadmium	20	1	20	2	20	20	200	20	2	20	7.3	NA
Chromium^{+6}	57	30	0.02	27	NA	23	37	20	73	20	1196	NA
Copper	23	190	8	30	157	25	100	14	6	210	52	NA
Total cyanide	50	430	1300	103	10	10	383	53	63	101	NA	NA
Lead	114	2	181	20	168	60	600	60	20	10	25	NA
Mercury	0.2	3	0.8	0.5	1.2	0.5	1.5	0.5	0.5	2.4	NA	NA
Nickel	50	7	93	5	5	50	500	50	5	50	20	NA
Zinc	NA	690	179	60	100	257	360	603	60	470	NA	NA
Phthalates, ug/l												
Diethyl phthalate	1.3	NA	NA	NA	NA	ND	NA	NA	NA	NA	ND	NA
Bis (2-ethylhexyl) phthalate	NA	290	700	ND	300	180	NA	NA	NA	320	ND	10
Di-n-butylphthalate	0.9	NA	NA	NA	ND	ND	NA	NA	NA	ND	ND	NA
Phenols, ug/l												
Phenol	13	2200	4900	440	390	420	100	NA	NA	60	23	2400
2,4-Dimethylphenol	NA	NA	NA	175	NA	ND	100	71	NA	NA	47	1000
2,4-Dichlorophenol	NA	NA	NA	ND	NA	NA	NA	NA	NA	NA	NA	NA
Aromatics, ug/l												
Benzene	100	417	409	NA	NA	NA	100	100	1100	894	NA	NA
Ethylbenzene	100	38	NA	NA	NA	NA	100	100	28	NA	NA	NA
Toluene	100	NA	96	NA	NA	NA	100	100	655	107	NA	NA
Polycyclic aromatic, ug/l												
Naphthalene	NA	950	1100	NA	290	ND	500	302	3200	NA	20	160
Anthracene	5	190	1100	NA	NA	30	230	140	660	NA	ND	NA
Chrysene	NA	NA	40	NA	NA	30	20	6	NA	NA	ND	6
Pyrene	NA	NA	40	NA	NA	30	ND	16	NA	NA	ND	10
Fluorene	NA	NA	NA	NA	NA	ND	270	NA	NA	NA	ND	16
Halogenated aliphatics, ug/l												
Chloroform	5	ND	NA	NA	NA	NA	10	15	100	6	NA	NA
Methylene Chloride	100	3	293	NA	NA	NA	100	100	1600	4	NA	NA
Tetrachloroethylene	50	NA	NA	NA	NA	NA	NA	NA	ND	NA	NA	NA

a: Adapted from references (2,3) (averages of 24-hr. composite samples on 3 consecutive days).
b: Shuaiba Industrial Area Complex (Studied Area).
c: Analyzed for the purpose of this study (Average of three 24-hr. composite samples).
d: Adapted from reference (4).
NA: Not analyzed.
ND: Not detected.
Refn.: Refinery

samples were collected in 24 hour composites on three consecutive days and analyzed for the presence of the 129 priority pollutants, and other conventional parameters. Table 1-1 also includes the results of analysis performed on one of SIA major refineries (KNPC-Shuaiba). Three 24-hour composite samples of the API separator effluent were analyzed for priority pollutants over a one month period of time.

1.3 Selection of Representative Priority Organics

Based on the data presented in Table 1, the representative priority organics of refinery wastewater which were selected for use in this study were:

1. Bis(2-ethylhexyl)phthalate
2. 2,4- Dimethylphenol
3. Naphthalene
4. Pyrene
5. Fluroene

The reasons for their selection are the following:

1. These compounds are potential health hazards and exhibit toxic, carcinogenic or mutagenic properties.
2. The selected compounds have been measured in most of the surveyed refineries including the SAA refineries.
3. Compounds selected were representative of the major chemical groups within the priority organics compounds typically found in refinery wastes.

4. Volatile priority pollutants were excluded since significant removals would be expected to occur by treatment processes preceeding GAC adsorption such as dissolved air flotation.

1.4 Objectives of the Study

Most of the research previously conducted or activated carbon adsorption has focussed on the adsorption of a single solute or a multi-solute mixture of known composition. Within the past few years the adsorption of specific organics present in unknown background composition has begun to be studied. These studies only considered ground water which was contaminated with volatile organics. Compared to the types and levels of organic chemicals present in a refinery wastewater the groundwater background organic chemical composition is close to that of a pure water. The performance of models developed for predicting carbon adsorption of individual solutes in the presence of a relatively contaminated water such as a refinery wastewater need to be examined. Accordingly the objectives of this research project are the following:

1. Evaluate the adsorption isotherm parameters of the following compounds; 1) 2,4,dimethylphenol, 2) napthalene, 3) fluorene, 4) pyrene and 5) bis(2-ethylhexyl) phthalate. The isotherm parameters will be determined first as single solutes and then as multi-solutes in both an ultrapure water background and in a typical complex wastewater background. Several isotherm models will be used for fitting the

experimental data including the Langmuir, Freundlich, three parameter, Singer and Yen and the Polanyi model.

2. Examine the fundamental relationships between the adsorptive behavior of the selected priority organics and their major physico-chemical properties.
3. Test the efficacy of the Ideal Adsorbed Solution Theory (IAST) to predict the competitive interaction of the selected priority organics in an ultrapure water background and in complex wastewater backgrounds of varying strengths.
4. Determine the basic adsorption transport parameters including the film transfer coefficient and the intraparticle diffusion coefficients in various background solvent mixtures.
5. Verify the batch surface diffusion (HSDM) and batch pore surface diffusion (PSDM) models by using predetermined adsorption transport parameters including: 1) Plug
6. Verify and compare four packed bed adsorption models including: 1) Plug Homogenous Surface Diffusion Model (PHSDM), 2) Plug Pore and Surface Diffusion Model (PPSDM), 3) Dispersed Flow Homogenous Surface Diffusion Model (DFHSDM), and 4) Dispersed Flow Pore Surface Diffusion Model (DFPSDM).
7. Validate the selected adsorption model predictions by use of a pilot plant treating secondary wastewater spiked with a selected priority organic compound.

GENERAL CONSIDERATIONS AND LITERATURE REVIEW

2.1 General Considerations

Within the past few decades adsorption has evolved as an effective technology for the treatment of water and industrial wastewater to control the release of hazardous organic chemicals. Accordingly there has been an extensive volume of research undertaken by various investigators on the subject of adsorption by activated carbon. In this section the literature review is specific for carbon adsorption research areas relating directly to this study. For a more comprehensive review of adsorption by activated carbon and the principles of adsorption and diffusion, the reader is referred to Weber[10], Cherimisinoff and Ellerbusch[11], McGuire and Suffet[12,13], Slejko[14], Ruthven[15], Cussler[16], and specifically the list of references that complement their work.

In determining the applicability of adsorption to removal of specific contaminants there are two basic factors to be considered, the first is the adsorption capacity available on the carbon, and the second is the contact time required for removing a particular adsorbate. Both factors are influenced by certain properties of adsorbent, adsorbate and solute. It is rather difficult to distinguish the effect of an individual carbon property on adsorbant-absorbate affinity. However, the carbon properties may be looked at as a qualitative indicator of the intensity of adsorption in a particular system.

2.1.1 Adsorbent Related Properties

The raw material, activation process and the post activation conditions are factors that influence the surface chemistry of activated carbon which in turn is important in determining its activity or capacity or adsorption. The majority of the surface area of the carbon is comprised of non-polar basal planes that support physical adsorption. Physical adsorption is governed by Van der Waals forces which are comprised of London dispersion and electrostatic forces. A small portion of the surface area is comprised of heterogenous edges of carbon planes to which carbon-oxygen functional groups are attached. These functional groups enable the activated carbon to undergo halogenation, hydrogenation and oxidation. Commercial carbons typically have surface areas in the range from 650 to 1500 m^2/gm. This is usually measured by a nitrogen adsorption method referred to as BET and the measured surface area values are close to another measurement called the carbon iodine number. An increasing surface area results in greater carbon adsorption capacity. Although the total carbon surface area could reach a value as high as 2500 m^2/gm, the surface area to adsorption capacity relationship is true only up to a carbon surface area of about 1500 m^2/gm[17]. At and above this level, any increased area is only produced by means of very fine pores (<1nm) that are only able to accommodate very small organic molecules.

Pore structure can influence both adsorption capacity and adsorption rate. The pore volume of activated carbon range from

0.5 to 1.5 cc/gm. Experimental studies of pore-size distribution indicate that pore volume is not uniformly distributed over pore radius. Keinath[18] who has reviewed the literature on pore size distribution, reported that bimodal and trimodal distributions of pore size are possible. In a bimodal distribution he reported values for two peaks at 10 and 1000Å. The effective capacity of activated carbon depends on both the distribution of volume with pore size and the distribution of the molecular sizes of adsorbates. Pore structures influence the overall rate of mass transfer within the carbon because the migration of adsorbate molecules to the carbon surface and the subsequent transfer across the surface film occur rapidly relative to the transport within the internal pore structure to the final adsorption sites[19].

Carbon particle size is also another physical property that can influence the surface area which in turn effects the capacity and affinity of the carbon. As the size of carbon particles increase, the available surface area per unit mass of carbon is substantially decreased. The effect of carbon particle size on the breakthrough characteristics of the adsorption of some phenolic compounds was studied by Zogorski and Faust[21]. They reported that the time for initial breakthrough increases with the decrease of carbon size down to 25 x 30 US sieve number. Smaller carbon particle diameters will not change the time for initial breakthrough. Their observations were in agreement with an earlier study by Weber and Keinath[21]. Many researchers[13] argue the point that based on the limited research in this area there is not a clear relationship between grain size and breakthrough characteristics. Weber[13] has determined that the adsorption rate is either dependent upon the inverse of the diameter or dependent upon some higher power aproaching second-order dependency if the controlling rate step is intraparticle.

2.1.2 Adsorbate Related Properties

Molecular volume, structure branching, solubility and polarity are the most significant physical properties of adsorbates that can influence adsorption behavior. In a complex mixture of organic adsorbates, it would be extremely difficult to quality and quantify a general explanation on the effects of interacted behavior of the various adsorbates on the extend of adsorption. There has been an extensive amount of research to attempt basic relationships, however, these studies are specific to individual solvents and solutes. Al-Bahrani and Martin[22] conducted a study on the effect of the molecular structure of selected solutes on the activated carbon adsorption by using a liquid chromatography technique and by attaching different functional groups to a Benezene ring. These researchers concluded that the carbon capacity for the adsorption of the polycyclic compounds was higher than that for the corresponding monocyclic compounds. They also observed a general tendency of an increase in adsorption capacity with an increase in molecular weight, however, they did not attribute the adsorption increase to the decrease in solubility and explained this observation by correlation with an increase in the molecular volume. In their study they used the dipole moment of a molecule as a measure of polarity and found no correlation between the solute polarity and the carbon capacity for the compounds studied[23]. Although adsorbate polarity is related to aqueous solubility, for organic molecules of essentially equal solubility, adsorptive capacity is enhanced for the least polar molecules. Giusti et al.[16] studied the adsorption of 93 organic compounds representing 10 different functional groups found in petrochemical wastewater. Their study indicated that adsorptive capacity increased with the decrease of solubility and this trend held for each functional group as well as between the different groups. In their study they measured the strength of adsorption of each functional group and ranked increasing trend of amenability to them in order of weakest adsorbed to highest adsorbed as follows: polynuclear aromatics, undissociated organic acids, aldehydes, alcohols, esters, ketones and glycols.

A common finding between Morris and Weber[24], Giusti et al[23] and al-Bahrani and Martin[22] was that an increase of branching within the carbon skeleton of the adsorbates will decrease their carbon adsorptive capacity. Such behavior could be attributed to a restriction on diffusion by the smaller pore size. Yen and Singer[25] studied the adsorption of a homologous series of phenol compounds. The researchers observed that the substituent functional groups significantly affects the carbon adsorption characteristics. However, the position of the substitution did not relate to adsorption characteristics.

2.1.3 Solvent Related Properties

The three most significant aqueous properties which have a particular impact on adsorption mechanism are: Temperature, its pH, and the background complexity (presence of other competing adsorbates). An increase in the solvent temperature will decrease the adsorption capacity. This is due to the fact that adsorption reactions are exothermic. However, the rate of adsorpton will increase with an increase in temperature. This is due primarily to the increased rate of diffusion of the adsorbate molecules. Therefore, temperature is important in batch systems, but is of less consequence in continuous flow systems because of the difference in adsorption kinetics.

Under appropriate pH ranges many organics may dissociate into ionic species, and this can affect adsorbability. Similarly there are some adsorbates that have affinity for H^+ or OH^- ions the adsorption of which can directly effect the solution pH and therefore the adsorbate solubility and the carbon adsorption capacity. Ward and Getzin[26] observed that a decrease in the solution pH will increase the adsorptive capacity of carbon for aromatic acids and the carbon adsorptive capacity will reach a maximum when $pH = pK_a$. These findings were in agreement with the work of Murin and Snoeyink[27] who investigated substituted phenols and humic acids. Coughlin and Ezra[28] noted a pH dependence on adsorption of non-ionizable species such as alcohol. They explained this adsorption pH dependence on the occurrence of hydrogen ion neutralization of the surface oxides on the carbon which prior to neutralization acted to block the micropores available for adsorption.

A major influence on adsorption is the complexity of the solvent background in terms of other adsorbable compounds. This is of great importance particularly when dealing with complex organic background solvents such as a refinery wastewater. The adsorbates present in the wastewater will compete for adsorption sites. The degree of adsorption inhibition of competing adsorbates is related to the relative size and affinities as well as the relative concentration of each of the competing solutes. Since physical adsorption is a reversible process, the lesser affinity adsorbates tend to be displaced by the higher affinity adsorbates. The desorption of lesser affinity adsorbates can cause a deterioration of the effluent quality in packed bed adsorption systems and is called the chromatographic effect.

The relative concentration of adsorbate species has an effect on competition for adsorption sites. Murin and Snoeynik[27] studied the competitive adsorpton of di and trichlorophenols by applying the Langmuir isotherm model in a range of concentration between 15 - 105 μM/L. They observed an increase in competition with the increase of competitive compound concentration. Martin and Al-Bahrani[30] studied the effect of competitive adsorption in batch and packed column systems. For selected organics they concluded that the competitive effects became more pronounced with the increase in the number of solutes in solution. Fritz et al[29] in an experimental study using a single and bisolute batch system, observed an increase in the effect of the external mass transfer resistance on the adsorption process as the initial adsorbate concentration decreased. This indicates that diffusion in the adsorbed phase is a major contributor to intraparticle mass transport. Similar observations were obtained when Merk et al.[31] investigated fixed bed systems.

The competitive effect that is due to the relative molecular size may also be attributed to the retardation of adsorbate transport by a blockage blocking of the pore structure. In the presence of high and low molecular size adsorbates the larger size molecule may block the pore structure and prevent the passage of the smaller sized molecule even if the latter has a higher diffusion rate. the majority of adsorption competition occurs on the non-specific sites. However there are some sites which are very specific for adsorbates (ionic species). For the carbon adsorption sites which are specific for adsorbates (ionic species) competitive adsorption effects are not significant and adsorption is highly pH dependent.

2.2 Equilibria and Adsorption Isotherms

Adsorption equilibria reflect the condition when the adsorbate in the solution is in a dynamic equilibria with that at the surface of the adsorbent. At this point there is a thermodynamically defined distribution of the adsorbate between the two phases. The distribution ratio of adsorbate between the two phases is expressed by q_e/C_e where q_e is the amount of adsorbate per unit mass of adsorbent and C_e is the equilibrium concentration of adsorbate remaining in the solution. This ratio is a function of adsorbate concentration, the affinity of the adsorbate to the absorbent and the competition between different adsorbates. A single solute plot of q_e versus C_e is referred to as an adsorption isotherm. Such isotherms can have different shapes as shown in Figure 2-2. Adsorption isotherm data are essential for evaluation of carbon adsorption capacity and for predictive modeling for analysis and design of adsorption systems.

In Figure 2-1, the linear relationship shown by the middle isotherm is commonly referred to as Henry's law which is valid at sufficient low concentrations such that all molecules on the adsorbent surface are isolated from their nearest neighbors. The Henry's constant may be expressed in terms of concentration or pressure. In terms of concentration the relationship is:

$$q_e = K_h C_e \qquad (2\text{-}1)$$

where q_e = solid concentration of adsorbate

C_e = concentration of adsorbate in solution

K_h = Henry's constant

The temperature dependence of Henry's constant obeys the Van't Hoff relationship:

$$\frac{d\ln K_h}{dT} = \frac{\Delta U_o}{RT^2} \qquad (2\text{-}3)$$

where ΔU_o = the difference in internal energy between the adsorbed and the dissolved adsorbate in solution

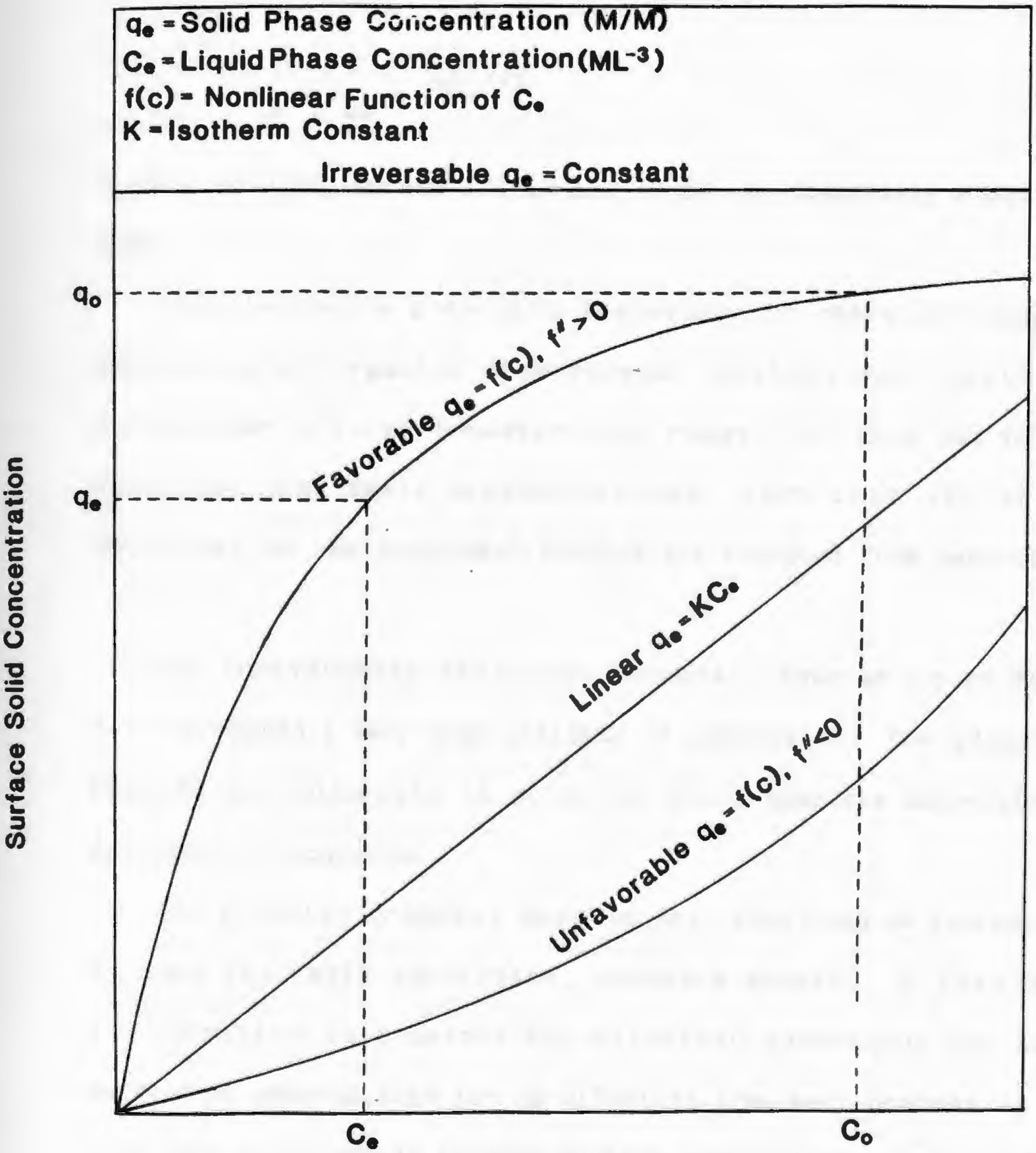


Figure 2-1 Equilibrium Phase Distribution System

T = absolute temperature

R = gas constant

By neglecting the differences in heat capacity between the solid and liquid phases, Eq. (2-2) may be integrated to yield:

$$K_h = K_{ho}\, e^{-\Delta U_o/RT} \qquad (2\text{-}3)$$

A plot of $l_n K_h$ versus 1/T in Eq. (2-3) is essentially a straight line.

Henry's Law is generally inadequate in characterizing the adsorption of organics from aqueous solution onto activated carbon over a large concentration range, and this law is only validated over small concentrations, such that all of the molecules on the adsorbent surface are isolated from each other.

The irreversible distribution curve shown at top of Figure 2-1 represents a very high affinity of adsorbate. The adsorbent removes all adsorbate in solution until complete saturation of adsorbent is achieved.

The priority organics used in this study can be represented by many favorable adsorption, isotherm models. A favorable distribution is required for effective adsorption but not a sufficient prerequisite for an effective treatment process as the time for equilibrium becomes another controlling factor that can limit adsorption feasibility.

2.2.1 Modifications to the Langmuir Model

The Langmuir isotherm is the simplest theoretical model which is extensively applied in adsorption studies. The model was originally developed by Langmuir[33] for a single gas adsorbate. It is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate on the adsorbent surface, all sites are energetically equivalent, and there is no interaction between adsorbate molecules on the neighboring sites. For a solid-liquid system the Langmuir model takes the following form:

$$q_e = \frac{q_m\, b\, C_e}{1 + b\, C_e} \qquad (2\text{-}4)$$

This relationship can be expressed in the linear form:

$$\frac{C_e}{q_e} = \frac{1}{b\, q_m} + \frac{C_e}{q_m} \qquad (2\text{-}5)$$

where q_m = Langmuir monolayer solid phase concentration, M/M

b = Constant related to net enthalpy (ΔH)

The Langmuir model was successfully applied in many carbon adsorption studies including studies by Mattson et al.[34] and Weber et al.[35] both studies utilized the Langmuir model only over a limited range of concentration. At higher concentrations when the effect of molecular interaction becomes pronounced the model deviates from the measured data. Deviations can also occur due to the heterogeneity of sites on the carbon.

The measurement of the surface area of micropore adsorbents presented a major obstacle to the early researchers of carbon adsorption. By knowing the adsorbate molecular size and experimentally determining the monolayer saturation limit it would seem possible to accurately predict the extent of adsorption. However even with advances in surface area measurement in physical adsorption the formation of second and subsequent layers of adsorbed adsorbate may commence at concentrations below that which are required to saturate one layer. Brunauer et al.[36] solved this problem by modifying the monolayer Langmuir model and expanding it to a multilayer model which is known as the BET model. The basic assumption in this expanded adsorption model is that any adsorbate layer need not be complete before subsequent layers can form. The BET model takes the form:

$$q_e = \frac{B\, C_e q_m}{(C_e - C_c)\,[1+(B-1)\,(C_e/C_c)]} \qquad (2\text{-}6)$$

where B = BET energy constant

C_c = saturation concentration (solubility limit)

BET Model reduces to the Langmuir model in the concentration ranges where $C_e \ll C_c$.

The Langmuir model may be easily extended to binary or multicomponent systems. The resulting expression for the isotherm is:

$$q_{ei} = \frac{q_{mi}\ b_i\ C_{ei}}{1 + \sum_{j=1}^{N} b_j C_{ej}} \qquad (2\text{-}7)$$

where the subscript i corresponds to species i and C_{ej} is the equilibrium concentration of all of the adsorbing species in solution. This extension is merely mathematical and lacks experimental verification.

Further modifications to the Langmuir model were suggested by Jain & Snoeyink[37]. Their modifications are based on the assumption that a certain amount of adsorption may occur without competition. Further, it was assumed that the number of sites for which there was no competition was equal to $(q_{m1}-q_{m2})$ where $q_{m1} > q_{m2}$. For this case they proposed the following relationships:

$$q_{e1} = \frac{(q_{m1} - q_{m2})\ b_1\ C_{e1}}{1 + b_1\ C_{e1}} + \frac{q_{m2}\ b_1\ C_{e1}}{1 + b_1\ C_{ei} + b_2\ C_{e2}} \qquad (2\text{-}8)$$

$$q_{e2} = \frac{q_{m2}\ b_2\ C_{e2}}{1 + b_1\ C_{e1} + b_2\ C_{e2}} \qquad (2\text{-}9)$$

However, these equations were tested only for binary system and their utility for multi-systems is not clear. When $q_{m1} = q_{m2}$ the proposed model is the same as the extended model shown in equation (2-7).

2.2.2 Modifications to the Freundlich Model

The Freundlich model has been used in an extensive number of studies to evaluate carbon adsorption including Thiem et al.[38]. Freundlich[39] found that adsorption equilibrium can be described more accurately by this relationship:

$$q_e = KC_e^{1/Nf} \qquad (2\text{-}10)$$

where K and $1/N_f$ are defined as Freundlich constants. This expression can be linearized to yield the form:

$$l_n\, q_e = l_n\, K + 1/N_f \ln C_e \qquad (2\text{-}11)$$

According to Weber[40] the value of "K" can be taken as a relative indicator of adsorption capacity, while $1/N_f$ is indicative of the energy of adsorption. The Freundlich isotherm is different from the Langmuir and BET models in that there is an assumption of a heterogeneous surface energy and number of different adsorption sites on the carbon. The basic disadvantage of the Freundlich model is that the model is not applicable at low adsorbate concentrations, i.e. it does not reduce to Henry's Law. Also at high adsorbate concentration the model does not compare with predictions from the Langmuir model. The applicability of the Freundlich model is restricted to a limited concentration range. An empirical multi-solute extension of the Freundlich model for more than one solute was proposed by Fritz and Schluender[41] as:

$$q_{ei} = \frac{a_{io} C_{ei}^{b_{io}}}{1 + \sum_{j=1}^{N} a_{ij} C_{ej}^{b_{ij}}} \tag{2-12}$$

where a_{io}, a_{ij}, b_{io}, and b_{ij} are isotherm constants determined by the best fit of multi-solute data, C_{ei} is the equilibrium concentration of species i in solution and N is the number of adsorbates in the system.

2.2.3 Three Parameters Model

As an attempt to overcome the limited concentration application range of Langmuir and Freundlich models, Radke and Prausnitz[42] developed a three-parameter model that combines both Langmuir and Freundlich models. This model has the following relationship:

$$q_e = \frac{\alpha C_e}{1 + \beta C_e^{\gamma}} \tag{2-13}$$

where, α, β, γ can be estimated mathematically by fitting experimental data. As was intended originally by Radke and Prausnitz the model reduces to the Langmuir isotherm at $\alpha = 1$, to Henry's Law at low concentrations approaching zero, and to the Freundlich model at high concentrations. Mathew[43] extended Eq. (2-13) to predict multicomponent equilibria and used the extended equation to predict the equilibrium data of the Radke-Prausnitz study[42]. Mathew also compared the three models of Jain and Snozyink[37], Radke and Prausnitz[42], and the three parameter equations to the extended form of equation 2-13. His observations on two component mixtures indicated that the extended form of equation 2-13 gave the best of the studied models prediction. Mathew's extended three parameter model is

$$q_{ei} = \frac{\alpha_i C_{ei}}{\sum_i^N 1 + \beta_i C_{ei}^{\gamma_i}} \qquad (2\text{-}14)$$

Singer and Yen[25,47] developed a three parameter model by modifying the original Freundlich model (equation 2-10) at a lower concentration as follows:

1. Take the logarithm of both sides of the equation and rearrange

$$\log C_e = Nf\ (\log q_e - \log K) \qquad (2\text{-}15)$$

2. Establish a third parameter q_x such that when $q_e \geq q_x$, the Freundlich equation (2-15) is valid and when $q_e < q_x$ the relationship becomes:

$$\log C_e = \log (q_e/q_x) - \frac{1}{\mathrm{Ln}10} (Nf-1)(1-q_e/q_x) + Nf \log q_x - \log K \qquad (2\text{-}16)$$

Equation (2-16), for $q_e \leq q_x$, was obtained by forcing the Freundlich equation to meet thermodynamic requirement at infinite dilution (Henry's Law), i.e., that $(d\log C_e/d\log q_e) = 1$. The parameters K, N_f and q_x are determined statistically by best-fitting the model to the experimental data. The model showed a better prediction of single solute data at lower concentrations than the original Freundlich model did.

2.2.4. Ideal Adsorbed Solution Theory (IAS)

IAS model was first developed by Myers & Prausnitz[44] to calculate the adsorption equilibria for compounds in a mixture of gases, using data only from single-solute isotherms. The basic idea lies in the recognition that in an ideal solution the partial pressure of an adsorbate is given by the product of its mole fraction in the adsorbed phase and the pressure exert as pure adsorbed at the same temperature and spreading pressure as these of the mixture. The IAS model was later extended by Radke and Prausnitz[45] to account for adsorption equilibrium in solution. The IAS model proved reliable for these systms in which the solute adsorption loading is moderate. For higher loadings a relaxation of the theory to allow for single solute-solute interactions on the surface of the adsorbent is required. Many researchers[46-48] have used the IAS model successfully in its original form.

IAS Model is based on the thermodynamic equivalence of the spreading pressure for each adsorbate at equilibrium. The adsorbent is considered to be thermodynamically inert; i.e., the change in a thermodynamic property of the adsorbent during adsorption is assumed to be negligible as compared to the change in the same property of the adsorbate. The IAS model also assumed that the adsorbent possesses a temperature - invariant area which is the same for all adsorbates and the Gibbs definition of adsorption applies.

Thermodynamic

The fundamental thermodynamic equations representing the combined first and second laws may be written in four equivalent ways: 1) internal energy, 2) enthalpy, 3) Helmholtz free energy, and 4) Gibbs free energy. For an adsorbed phase the Helmholtz free energy in two dimensions designated by superscript "a" can be written as:

$$dH^a = - S^a dT + \sigma dA + \sum_i \mu_i^a dn_i^a + \mu_s^a dn_s^a \qquad (2\text{-}17)$$

where subscripts i and s represent solute and solvent respectively, σ is the interfacial tension, μ_i is the chemical potential, n_i is the number of moles adsorbed on the solid surface, A is the area of solution-solid interface, S is the entropy and T is the absolute temperature.

By Euler's theorem, Eq. (2-17) can be integrated to give

$$H^a = \sigma A + \sum_i \mu_i^a n_i^a + \mu_s^a n_s^a \qquad (2\text{-}18)$$

Taking the differential of H^a in Eq. (2-18) gives

$$dH^a = \sigma dA + A d\sigma + \sum_i \mu_i^a dn_i^a + \sum_i n_i^a d\mu_i^a$$

$$+ \mu_s^a \, dn_s^a + n_s^a \, d\mu_s^a \qquad (2\text{-}19)$$

Comparing Eq. (2-17) with Eq. (2-19) results in the Gibbs isothermal equation

$$-Ad\sigma = \sum_i n_i^a \, d\mu_i^a + n_s^a \, d\mu_s^a \qquad \text{(Constant T)} \qquad (2\text{-}20)$$

At equilibrium, the chemical potentials of the adsorbed phase and liquid phase are equal. If C_i and C_s are the bulk liquid concentration of solute i and solvent S in moles per unit volume, the isothermal Gibbs-Duhem equation can be written as

$$\sum_i C_i \, d\mu_i^a + C_s \, d\mu_s^a = 0 \qquad \text{(Constant T)} \qquad (2\text{-}21)$$

Combining Eq. (2-21) and Eq. (2-20) give

$$-Ad\sigma = \sum_i \left(n_i^a - \frac{C_i}{C_s} n_s^a\right) d\mu_i^a \qquad (2\text{-}22)$$

In dilute solutions the quantity $(n_i^a - N_s^a C_i/C_s)$ can be related to n_i^m, the quantity adsorbed (an experimentally measured quantity), by the equation:

$$n_i^m = V\Delta C_i = (n_i^a - \frac{C_i}{C_s} n_s^a) \qquad (2\text{-}23)$$

where V is the total volume of solution and ΔC_i is the decrease in the solute concentration. Accordingly the desired equation which is valid over the solute concentration range of interest is obtained by substituting equation (2-21) into Equation (2-20).

$$-A\ d\sigma = A\ d\pi = \sum_i n_i^m\ d\mu_i^a \qquad (2\text{-}24)$$

where the summation is over the solute species only. The spreading pressure π is defined as the difference between the interfacial tension of pure solvent-solid interface and that of the solution-solid interface at same temperature.

$$\pi = \sigma_{\text{pure solvent-solid}} - \sigma_{\text{solution-solid}} \qquad (2\text{-}25)$$

The difference between q_{ei} as used previously and n_i^m is that q_{ei} is for a specified adsorbent weight, while n_i^m is for unspecified amount of adsorbent.

The adsorbed phase fugacity $(f_i^a)^{49}$ is defined as

$$d\mu_i^a = RT\ \ d\ln f_i^a \qquad (2\text{-}26)$$

and

$$\lim_{\pi \to 0} \frac{f_i^{a}}{Z_i \pi} = 1 \qquad (2\text{-}27)$$

where Z_i, the adsorbed-phase mole fraction is defined by

$$Z_i = \frac{n_i^{m}}{\sum_i n_i^{m}} = \frac{n_i^{m}}{n_T^{m}} \qquad (2\text{-}28)$$

The adsorbed-phase fugacity is two-dimensional and has the same units as the spreading pressure π. Henry's Law for adsorption, results from the substitution of equations (2-26), (2-27) and (2-28) with Equation (2-24).

Ideal Adsorbed Phase

Radke & Prausnitz[45] proposed that when solute is adsorbed simultaneously from dilute solutions at constant temperature and spreading pressure, then the fugacity f_i^a is proportional to the mole fraction Z_i

$$f_i^{a}(T, \pi, Z_i) = Z_i f_i^{ao}(T, \pi) \qquad (2\text{-}29)$$

where f_i^{ao} is the fugacity that a single solute i exerts during adsorption from dilute solution at the same temperature and spreading pressure. The superscript "0" denotes single-solute adsorption. Equation (2-29) becomes exact as $Z_i \to 1$. Substituting Equation (2-28) into equation (2-24) gives:

$$A\, d\pi = \sum_i Z_i\, n_T^m\, d\mu_i^a \qquad (2\text{-}30)$$

Rearranging and factoring out the total moles adsorbed, n_T^m, gives:

$$\frac{A}{n_T^m} = \sum_i Z_i \left(\frac{\partial \mu_i^a}{\partial \pi}\right)_{T,Z_i} \qquad (2\text{-}31)$$

For an ideal adsorbed phase, equation (2-24), equation (2-26), and equation (2-29) gives:

$$\left(\frac{\partial \mu_i^a}{\partial \pi}\right)_{T,Z_i} = \left(\frac{\partial \mu_i^{ao}}{\partial \pi}\right)_T = \frac{A}{n_i^{mo}} \qquad (2\text{-}32)$$

substituting equation (2-32) into equation (2-31) finally yields:

$$\frac{1}{n_T^m} = \sum_i \frac{Z_i}{n_i^{mo}} \quad (\text{constant } T,\pi) \qquad (2\text{-}32)$$

Equation (2-32) provides one of the two relationships of the IAS theory for calculating multi-solute equilibria. The second relationship results from considering the equilibria between the adsorbed and liquid phases.

Phase Equilibria

If a mixture of solutes is in equilibrium with an adsorbent, the chemical potential of solute i in the adsorbed phase is equal to that in the liquid phase "l"

$$\mu_i^a = \mu_i^l \tag{2-33}$$

The value of μ_i^a depends on T, π, and the adsorbate composition as measured by the mole fraction Z_i. To calculate the chemical potential, the integral form of equation (2-26) can be derived and substituted into the ideality assumption of equation (2-29)

$$\mu_i^a\ (T,\pi,Z_i) = \mu_i^{ao}(T,\pi) + RT\ \mathrm{Ln}\ Z_i \tag{2-34}$$

For single-solute adsorption the intensive variables T and π fix the concentration C_io in the dilute liquid phase. Thus by substituting μ_i^{ao} in equation (2-34) the following equation is derived:

$$\mu_i^{ao} = \mu_i^{lo}\ [T, C_i^o(\pi)] = \mu_i^{l\#}(T) + RT\ \mathrm{Ln}\ C_i^o\ (\pi) \tag{2-35}$$

where the superscript "#" denotes the ideal dilute solution (Henry's Law) standard state of the liquid phase. The activity coefficient is considered = 1. The concentration $C_i^o(\pi)$ refers to solute i when that solute adsorbs singly from a solution at the same T and π as that of the mixture.

In a dilute liquid mixture at constant temperature, μ_i^l is a function only of C_i, the concentration of solute i, in that mixture. Therefore, the right hand side of equation (2-35) becomes

$$\mu_i^{l}(T,C_i) = \mu_i^{l\#}(T) + RT\,\mathrm{Ln}\,C_i \tag{2-36}$$

Equations (2-33) to (2-36) lead to the second relationship of the IAS Model for calculating multi-solute equilbria

$$C_i = C_i^o(\pi)\cdot Z_i \tag{2-37}$$

Evaluation of Spreading Pressure (π)

In order to use Equation (2-32) to (2-37), π values must be known for the various singly-adsorbing solutes in the mixture. The π values can be evaluated from equation (2-24) by

$$\pi(C_i^o) = \frac{RT}{A}\int_o^{C_i^o}\frac{N_i^m}{C_i}\,dc_i \tag{2-38}$$

According to Radke and Prausnitz[45], experimental single-solute isotherms are required for calculating π values. The isotherms can be constructed by plotting a curve of n_i^{mo}/C_i^o as a function of C_i^o. The area under the isotherm curve determines π. In this method, experimental data must be available over the range of loading from zero to n_i^{mo} in order to calculate π accurately. To reduce the error in determining π, Kidnay and Myers[50] recommended integration of the curve $d\ln C_i^o/d\mathrm{Ln}\, n_i^{mo}$.

Yen and Singer[41] introduced an improved method of calculation which allowed for equilibrium concentration to be calculated independent of experimental observation as originally required by Radke and Prausnitz[45]. They used Kidnay and Myers[50] method for evaluating the spreading pressure (π) and used their modified Freundlich three parameter model to utilize the single solute isotherm as input for calculation. They also substituted for all invariant adsorptive terms the corresponding solid phase concentration. The following set of equations describes the sequence in their calculating method.

- The spreading pressure per unit weight of adsorbent can be obtained by substituting q_i^o and q_i in place of n_i^{mo} and n_i^m. Subsequently the spreading pressure according to Kidnay and Myers[50] can be given by

$$\pi(q_i^o, wt = 1) = \frac{RT}{A} \int_o^{q_i^o} \frac{d \log C_i}{d \log q_i} \, d\, q_i \qquad (2\text{-}39)$$

- The IAS theory is based on the equivalence of spreading pressure for all the components in the mixture i.e., $\pi_1 = \pi_2 = \ldots = \pi_n$. Therefore by canceling the common factor RT/A, Eq. (2-39) can be represented for mixtures as

$$\int_o^{q_1^o} \frac{d \log C_1}{d \log q_1} \, dq_1 = \int_o^{q_2^o} \frac{d \log C_2}{d \log q_2} \, dq_2 = \ldots =$$

$$\int_o^{q_i^o} \frac{d \log C_i}{d \log q_i} \, dq_i = \int_o^{q_n^o} \frac{d \log C_n}{d \log q_n} \, dq_n \qquad (2\text{-}40)$$

- The equilibrium relationships Eq. (2-37) for each solute, are written:

$$C_i = C_i^o \, Z_i \qquad (2\text{-}41)$$

- The adsorbed-phase fraction can be represented by definition of Z_i as

$$\sum_{i=1}^{N} Z_i = 1 \qquad (2\text{-}42)$$

- The quantities of q_i^o can be obtained from single solute isotherms, and can assume any of previously defined mathematical forms

$$q_i^o = f(C_i^o) \qquad (2\text{-}43)$$

- Total q_T can be calculated from Eq. (2-32)

$$\frac{1}{q_T} = \sum_{i=1}^{N} \frac{Z_i}{q_i^o} \qquad (2\text{-}44)$$

- The adsorption of each solute in a mixture can then be calculated from Eq. (2-28)

$$q_i = Z_i \, q_T \qquad (2\text{-}45)$$

- If the activated carbon dosage is represented by m

$$q_i = \frac{(C_i^o - C_i)}{m} \qquad (2\text{-}46)$$

The equations (2-40) to (2-46) constitute a set of simultaneous equations from which the IAS Model calculations can be made. There are a total of (5N+1) equations. The initial concentrations of each solute C_i^o, the applied carbon dosage m, and the functional adsorption relationship Eq. (2-43) are known.

The unknown variables C_i, q_i, Z_i, C_i^o, q_i^o and q_T comprise a total set of (5N+1) unknowns. With (5N+1) independent equations and (5N+1) unknowns, there should be a unique solution to these equations. Yen and Singer[51] solved these equations using their modified Freundlich three-parameter model. They successfully tested their numerical solution for predicting the adsorption of phenols on activated carbon. Crittenden et al.[52] also used the IAS model for predicting multicomponent adsorption equilibria in a mixture of six volatile organic compounds in ultrapure water background. Instead of using the modified Freudlich three-parameter model Crittenden et al. used the conventional Freundlich model.

2.2.5 Multicomponent Equilibria of Complex Mixtures

Industrial wastewater is composed of a very complex background mixture of organics and inorganics. In order to apply the existing predictive adsorption modeling techniques it would be essential to identify and quantify all adsorbing species which are present. This is usually a very expensive and difficult task to achieve. Recently a few studies were directed at predicting the competitive equilibrium interaction between individual components and unknown mixtures. Frick and Sontheimer[8] tested the importance of competition due to dissolved organic carbon (DOC) background. They used underground water to determine the background effect of multisolute mixture. Their method for quantifying the effects of a complex background involved characterizing the multisolute mixture as a solution of three compounds with defined adsorption properties (well, intermediate and weakly adsorbed). Crittenden et al[7] studied the prediction of multicomponent adsorption equilibria for volatile organics in background mixtures of unknown composition. The researchers accomplished this by using the theoretical components in the IAS calculations to account for the competitive effects of the unknown mixture. To date their are no studies which consider the complex mixture background that characterize secondary wastewater effluents or raw industrial wastewater.

2.3. Kinetics of Adsorption

Adsorption equilibrium is considered to be the most important factor for evaluating the feasibility of using activated carbon. If enough time is allowed equilibrium will be achieved. However, for engineering applications, the rate of adsorption is a primary concern. Several distinct resistances to mass transfer may limit the adsorption rate and without detailed analysis coupled with subsequent experimental measurements, it is not always obvious which resistance is the rate limiting step. Associated with activated carbon adsorption, whether in a finite batch system or in a packed bed, there are two major rate limiting steps which include film transfer resistance and effective intraparticle resistance. Intraparticle resistance is divided into surface diffusion and pore diffusion.

2.3.1. Film Transfer Resistance

The simplest theory that describes interfacial mass transfer is called the film theory. In this theory a hydrodynamic film surrounds the activated carbon pellet so that transfer of adsorbate occurs through the film. A mass balance with the assumption of a linear driving force across the film yields the following equation:

$$\frac{\partial q}{\partial t} = k_f\, a(C-C_s) = \frac{3\, k_f}{R}\,(C-C_s) \qquad (2\text{-}47)$$

in which q = Adsorbed phase concentration over the particle.

C, C_s = Bulk and surface adsorbate concentration

a = External surface area per unit particle volume (= 3/R for spherical particle)

k_f = Mass transfer coefficient

R = Radius of pellet

The significance of the film transfer resistance can be evaluated by considering the ratio of internal-to-external gradients defined by Biot number (Bi).

$$Bi = \frac{k_f R}{3 D_s \varepsilon_p} \qquad (2\text{-}48)$$

Nerentricks[53], and Roberts and York[54] have discovered that the value of D_s determined from a batch reactor study is not significantly affected by the external film resistance if the Biot number larger than 60 is maintained. The batch rate study used to experimentally measure D_s is usually conducted in completely mixed reactor or Carberry reactor with enough mixing power to provide a Biot number not less than 100. According to Haznd et al.[55] a Biot number larger than 100 will substantially reduce the external resistance which allows for an accurate determination of D_s. The appropriate dimensionless group characterizing film tranfer is the Sherwood number (Sh) (ratio of mass transfer velocity to molecular diffusion velocity) defined by:

$$Sh = \frac{2\ k_f R}{D_L} \qquad (2\text{-}49)$$

in which D_L = molecular diffusivity, L/T^2, and the remaining parameters defined previously. For a dilute solution, the empirical correlation of Wilke and Chang[56] has been extensively used in the literature for calculating the D_L value. The molal volume parameter at the normal boiling point included in this correlation can be estimated using a technique discussed by Treybal[57]. By analogy with the Nusselt number in heat transfer, it can be experimentally concluded that the limiting value of the Sherwood number approaches 2 at very low Reynolds number. At higher Reynolds numbers convective effects become significant and a correlation of the form $Sh = f(S, R_N)$ is expected. Such correlations are widely applied in mass transfer studies and available for both completely mixed batch reactors and packed beds[58-62]. There has been much debate in the literature as to whether the low-velocity limit of the Sherwood number approaching 2 which is derived for an isolated sphere is applicable to a packed bed. This issue was reviewed by Wakao and Funazkri[63]. They corrected the earlier correlations for axial dispersion and developed a correlation applicable to Reynold numbers ranging between 3-10,000. Their reevaluation of gas-phase data was considerably higher than those obtained under the assumption of zero fluid effective dispersion coefficient.

Levenspiel[58] presented an analytical solution that includes dispersion for calculating the film transfer coefficient from the immediate breakthrough concentration in a minicolumn study. In a similar approach Weber and Liu[59] developed a method for evaluating both k_f and D_s simultaneously in minicolumn such that the column is sufficiently short not to contain the wavefront of sorbent-sorbate system.

2.3.2 Intraparticle Transfer Resistance

Intraparticle resistance is a lump-sum term reflecting the influence of the overall diffusion mechanisms most likely to occur in the activated carbon pellet. Intraparticle resistance involves both surface diffusion and pore diffusion which act dynamically in parallel. Pore diffusion involves migration of molecules through the pores in the liquid phase toward the center of a carbon pellet. Therefore, pore size distribution, tortuosity and branching are important factors in the pore diffusion mechanism. Surface diffusion occurs in the solid phase i.e. the molecules migrate by jumping between the adsorption sites. Both pore and surface diffusion can describe the intraparticle mass transfer dynamics. However, a number of investigations[64-67] have indicated that surface diffusion generally predominates. The conclusions reached from other studies were that pore diffusion was a limiting factor[68-71].j Some researchers advocated the use of an overall effective diffusion coefficient without the need for differentiation[72].

The mathematical description of adsorpton on a spherical carbon pellet, taking into account pore diffusion and a constant radial effective pore diffusion coefficient was developed by a number of investigators[73,74].

$$\epsilon_p \frac{\partial C_p}{\partial t} + (1-\epsilon_p)\rho_s \frac{\partial q}{\partial t} = \frac{\epsilon_p}{r^2} \frac{\partial}{\partial r} \{r^2 D_p \frac{\partial C_p}{\partial r}\} \qquad (2\text{-}50)$$

where ϵ_p = Intraparticle void

C_p = Adsorbate concentration in the pore void

ρ_s = Particle density including pore voids

q = Solid phase concentration

t = Time

r = Radial coordinates

D_p = Pore diffusion coefficient

R_p = Pore radius

C = Solute concentration in bulk solution

Initial and boundary conditons are as follows:

$C_p = 0$ and $q = 0$ at $t = 0$ (for all r)

$$- D_p \frac{\partial C_p}{\partial r}\Big|_{r=R_p} = k_f \, (C - C_p\big|_{r=R_p}) \qquad (2\text{-}51)$$

$$\frac{\partial C_p}{\partial r}\Big|_{r=0} = 0 \text{ (for all t)} \qquad (2\text{-}52)$$

With this model, the pore diffusion only occurs within intraparticle pore voids and adsorbing on vacant pore wall sites. Adsorbed molecules can resume pore diffusion only by first desorbing.

For the case of surface diffusion where surface flux predominates and pore flux can be neglected a material balance on a spherical particle with constant effective surface diffusion coefficient will yield:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} [r^2 \frac{\partial q}{\partial r}] \qquad (2\text{-}53)$$

The corresponding initial and boundary condition are

$$q = 0 \text{ at } t = 0 \ (0 < r < R) \qquad (2\text{-}54)$$

$$\frac{\partial q}{\partial r} \Big|_{r=0} = 0 \qquad (2\text{-}55)$$

$$\frac{3k_f}{R} (C-C_s) = D_s(q)\rho_s \frac{\partial q}{\partial r} \Big|_{r=R} \qquad (2\text{-}56)$$

where $D_s(q)$ = Surface diffusion coefficient as a function of the solid phase uptake

C_s = Adsorbate concentration at the interface of the carbon particle M/L^3

The previous mathematical relationships discussed the kinetics of adsorption of a single spherical particle exposed to a solute concentration at the particle's external surface. These mathematical relationships can be used to describe adsorption in completely mixed batch reactors. For more practical engineering applications, the prediction of breakthrough curves from the basic kinetics of equilibrium data is a prerequisite, since it provides the right approach for evaluating the dynamic capacity of packed beds.

The differential liquid phase mass balance equation for an adsorption column and for spherical adsorbent particle within such a column can provide the mathematical distribution to describe the dynamic behavior of a packed bed. If the flow pattern can be reprresented as an axially dispersed plug flow the main balance will yield:

$$- D_e \frac{\partial^2 C}{\partial z^2} + \frac{V_a}{\varepsilon} \frac{\partial C}{\partial z} + \rho_a(1-\varepsilon) \frac{\partial q}{\partial t} + \frac{\partial C}{\partial t} = 0 \qquad (2.57)$$

The equilibrium relationship is expressed by the Freundlich isotherm

$$q_s = K\, C_s^{1/Nf} \qquad (2.58)$$

Initial and boundary conditions

$$C = C_o + \left(\frac{\varepsilon D_e}{V_a}\right) \frac{\partial c}{\partial z} \quad \text{at } z = 0 \qquad (2\text{-}59)$$

$$\frac{\partial c}{\partial Z} = 0 \qquad \text{at } z = L \qquad (2\text{-}60)$$

$$\frac{\partial q}{\partial r} = 0 \qquad \text{at } r = 0 \tag{2-61}$$

$$\frac{\partial q}{\partial r} = \frac{k_f}{D_s \rho_s} (C-C_s) \text{ at } r = R \tag{2-62}$$

$$q = 0 \qquad \text{at } t = 0 \tag{2-63}$$

$$C = 0 \qquad \text{at } t = 0 \tag{2-64}$$

where

D_e = Dispersion coefficient

Z = Longitudinal distance in packed bed

ε = Bed void fraction

1/Nf = Exponent of Freundlich isotherm

V_a = Approach velocity

q_s = Solid phase concentration at the particle, M/M-C

In a plug flow system, the axial dispersion is neglected so that the term $-D_e\ \partial^2 C/\partial Z^2$ can be dropped, reducing equation (2-57) to a first-order hyperbolic equation.

$$\frac{V_a}{\varepsilon} \frac{\partial C}{\partial z} + (\rho_s \frac{1-\varepsilon}{\varepsilon}) \frac{\partial q}{\partial t} + \frac{\partial C}{\partial t} = 0 \tag{2-65}$$

The following dimensionless transform may be performed for simplification.

$$\bar{r} = r/R \tag{2-66}$$

$$\bar{q} = q/q_o \tag{2-67}$$

$$\bar{C} = C/C_o \tag{2-68}$$

$$\bar{t} = t/(\tau D_g) \tag{2-69}$$

$$D_g = \frac{q_o \rho_s \, (1-\varepsilon)}{C_o \varepsilon} = \text{solute distribution parameter} \tag{2-70}$$

$$Nd = \frac{D_s D_g \tau}{R^2} = \text{surface diffusion modulus} \tag{2-71}$$

$$P_e = \frac{V_a L}{\varepsilon D_e} = \text{Peclet number} \tag{2-72}$$

$$Sh = \frac{k_f R}{D_g D_s} \left(\frac{1-\varepsilon}{\varepsilon}\right) = \text{Modified Sherwood number} \tag{2-73}$$

$$St' = \frac{3(1-\varepsilon)}{R\varepsilon} (k_f \tau) = \text{Modified Stanton number} \tag{2-74}$$

where

C_o = Initial liquid phase concentration, mM/g-C

q_o = Solid phase concentration in equilibrium to C, mM/g-C

τ = Bed retention time

L = Column length

The solid phase mass balance equation becomes

$$\frac{\partial \bar{q}}{\partial \bar{t}} = Nd \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left(\bar{r}^2 \frac{\partial \bar{q}}{\partial \bar{r}} \right) \tag{2-75}$$

The liquid phase mass balance equation becomes

$$- \frac{1}{Pe} \frac{\partial^2 \bar{C}}{\partial \bar{z}^2} + \frac{\partial \bar{C}}{\partial \bar{z}} + \frac{\partial \bar{q}}{\partial \bar{t}} + \frac{1}{D_g} \frac{\partial \bar{C}}{\partial \bar{t}} = 0 \tag{2-76}$$

and the Freundlich isotherm becomes

$$\bar{q}_s = \bar{C}_s^{\,1/Nf} \tag{2-77}$$

$$\frac{\partial \bar{q}}{\partial \bar{t}} = 3 \frac{\partial}{\partial \bar{t}} \left(\int_0^1 \overline{q r^2} \, d\bar{r} \right) \tag{2-78}$$

The transformed initial and boundary conditions are

$$\bar{C} = 1 + \frac{1}{P_e} \frac{\partial \bar{C}}{\partial \bar{z}} \qquad \text{at } \bar{z} = 0 \tag{2-79}$$

$$\bar{C}_0 = f(\bar{t}) \qquad \text{at } \bar{z} = 0 \tag{2-80}$$

$$\frac{\partial \bar{C}}{\partial \bar{z}} = 0 \qquad \text{at } \bar{z} = 1 \tag{2-81}$$

$$\frac{\partial \bar{q}}{\partial \bar{r}} = 0 \qquad \text{at } \bar{r} = 0 \tag{2-82}$$

$$\frac{\partial \bar{q}}{\partial \bar{r}} = Sh \, (\bar{C} - \bar{C}_s) \qquad \text{at } \bar{r} = 1 \tag{2-83}$$

$$\bar{q}\ (\bar{r},\bar{z}) = 0 \qquad \text{at } \bar{t} = 0 \qquad (2\text{-}84)$$

$$\bar{C}\ (\bar{z}) = 0 \qquad \text{at } \bar{t} = 0 \qquad (2\text{-}85)$$

Equations (2-75) through (2-85), along with the Freundlich exponent 1/Nf, and the dimensionless groups, D_g, P_e, Sh and N_d represent the dynamics of the breakthrough curves. The parameters D_g and Nf are experimentally calculated from the isotherm studies. P_e is calculated from empirical relationships, and k_f can be calculated as discussed previously. The remaining coefficient required for evaluating Sh and Nd is the effective surface diffusion D_s which is usually obtained from batch rate studies as discussed by many researchers (Liu et al[75], Furusawa et al.[76], Mathews et al.[77], and Suzuki and Kawazoe[78-80]. The procedure used in this study for evaluating D_s along with the polynomial empirical equation that describes solutions to the homogenous surface diffusion model batch reactor is presented by Hand et al[55].

2.4 Development of Predictive Models

Predictive mathematical models can save substantial efforts in the initial planning stages of full-scale GAC treatment design. The successful models should be able, once provided with the necessary input data, to predict the breakthrough curve characteristics of specific compound(s) of interest, as well as the impact of process variables on the process performance so that the optimum scheme can be identified. Batch reactor models and packed bed models that have been applied in this study were developed at Michigan Technological University[81] and modified over a period of 12 years. The models were tested on multicomponent mixtures in clean background water. No attempt has been made to test these models for adsorption prediction in complex background mixtures or to verify them on large scale pilot plants treating complex wastewater prior to this study.

2.4.1 Batch Reactor Predictive Models

The batch reactor predictive models were developed, based on two intraparticle diffusion resistances. The first resistance, homogeneous surface diffusion resistance, is modeled by BHSDM. The PSDM model considers that the pore and surface diffusion resistances act in parallel. Both numerical models include the following assumptions:

1. External fluid film resistances exist.
2. No surface diffusion interaction between adsorbate
3. Local equilibrium exists at the absorbent surface
4. The multicompoent equilibrium theory described by the Ideal Adsorbed Solution (IAS) Theory with the Freundlich isotherm is used to represent the single solute isotherm capacity.

The flow diagram[81] for the batch reactor predictive model for both BHSDM and BPSDM is shown in Figure 2-2.

2.4.2. Packed Bed Predictive Models

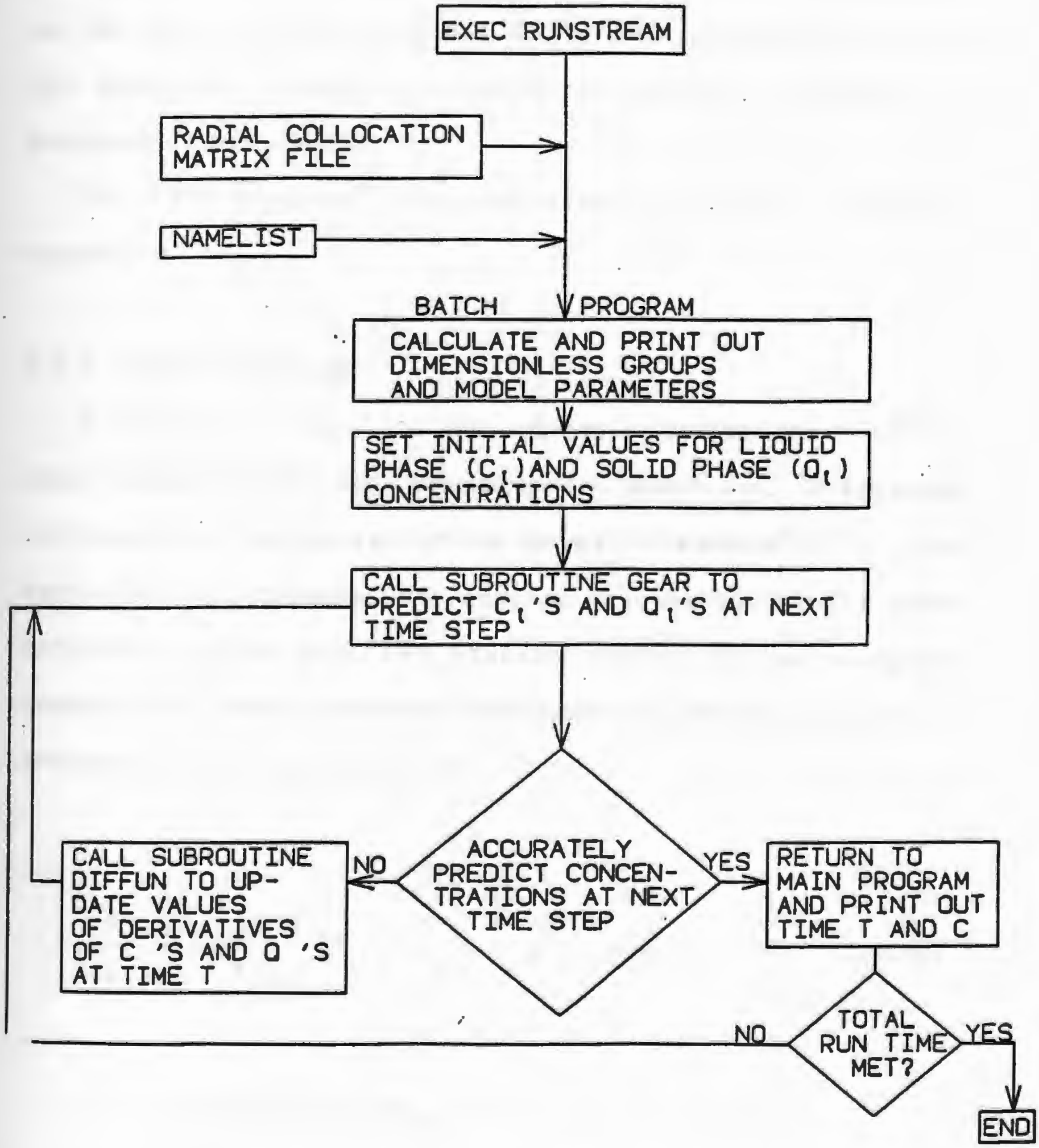


Figure 2-2 Flow Diagram for Batch Programs

Similar to batch models, the packed bed predictive models incorporate either homogenous surface diffusion mechanism or homongenous and pore diffusion mechanism acting in parallel. They also involves two flow schemes. The first flow scheme is plug flow where the axial dispersion term $-D_e \partial^2 C/\partial z^2$ is neglected and the second flow is a scheme dispersed flow scheme in which the dispersion term is included in the axial transport of adsorbate in the bed.

The flow diagram[81] for the packed bed model is shown in Figure 2-3.

2.4.3 Numeric Solution

Orthogonal collocation was applied by Crittenden et al[82] to solve dynamic breakthrough equations in a packed bed. Orthogonal collocation is explained in detail elsewere[83-86]. The application of orthogonal collocation to equation (2-76) after introducing the modified Stanton number and including the assumption of zero dispersion coefficient will result in a set of ordinary differential equations

$$\frac{d\bar{C}_l}{d\bar{t}} = - D_g \sum_{k=2}^{M+2} A^u_{l,k} \bar{C}_k - D_g A^u_l f(\bar{t}) \qquad (2\text{-}86)$$

$$- D_g St (\bar{C}_l - \bar{C}_{s,l})$$

in which l represent a collocation point in the axial direction and A^u represents a collocation constants matrix for the first

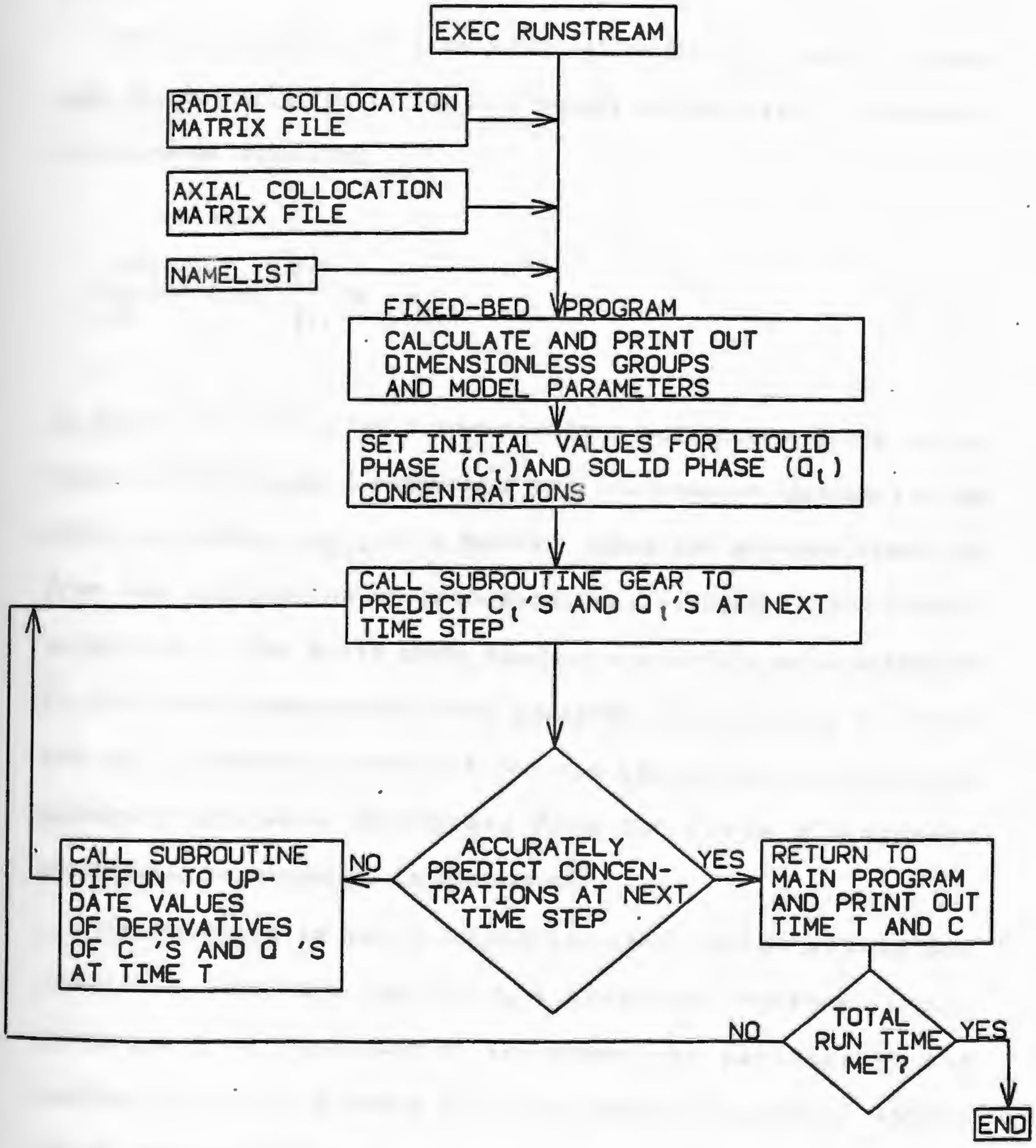


Figure 2-3 Flow Diagram for Fixed-Bed Programs

order derivatives which were determined from the roots of unsymmetric shifted Legendre polynomial as discussed in Finlayson[84]. The equation is valid for $l = 2$ to $M + 2$, where M is the number of internal collocation points in the axial direction.

The application of orthogonal collocation to the solid phase mass balance equation (2-75) will result in this set of ordinary differential equations

$$\frac{d\bar{q}_{i,l}}{d\bar{t}} = Nd \sum_{j=1}^{N+1} B_{i,j}\bar{q}_{j,l} \qquad (2\text{-}87)$$

in which the subscript i represents a collocation point in the radial direction and l represents the collocation points in the axial direction. $q_{j,l}$ is a matrix. Since the unknowns resulting from the application of orthogonal collocation in the radial direction in the solid phase equation and in the axial direction in the liquid phase equationare included. The matrix B is the set of collocation constants for the Laplacian with spherical geometry and were determined from the roots of Legendre polynomials as discussed in Finlayson[84].

The equation is valid for collocation points within the adsorbent particle (not at the exterior boundary) i.e. i increases from the center of the adsorbent particle to the surface ($i = 1$ to N where N is the number of points). Another set of boundary condition applied

$$St' (\bar{C} - \bar{C}_s) = \frac{\partial}{\partial \bar{t}} \int_0^1 \bar{q}\, \bar{r}^2\, d\bar{r} \qquad (2\text{-}88)$$

where St = St/3α

α = y/x, ratio of solid mole fraction to liquid phase mole fraction.

The resulting orthogonal collocation equation involve the adsorbent phase surface concentration is:

$$\frac{d\bar{q}_{N+1,l}}{d\bar{t}} = \frac{St'}{W_{N+1}} (\bar{C}_l - \bar{C}_{s,l}) - \sum_{j=1}^{N} \frac{W_j}{W_{N+1}} \frac{d\bar{q}_{j,l}}{d\bar{t}} \qquad (2\text{-}89)$$

in which the subscript $_{N+1}$ refer to the adsorbent phase concentration at the surface. The weighing factors, W_j which are used for integration are determined from the roots of the symmetric Legendre polynumericals[84]. The above equation is valid throughout the bed or from l = 1 to M + 2.

To couple the liquid phase and solid phase mass balances the Freundich equation or Langmuir equation may be used.

The numerical computer solution requires a data file that includes the various variable values and collocation files. For batch models, one collocation file for the radial dependence is required as where for the packed bed models two collocation files, one for the radial dependence and the other for axial dependence, are required. For example, the location of orthogonal collocation points for 4 axial and 3 radial points is shown in Figure 2-4.

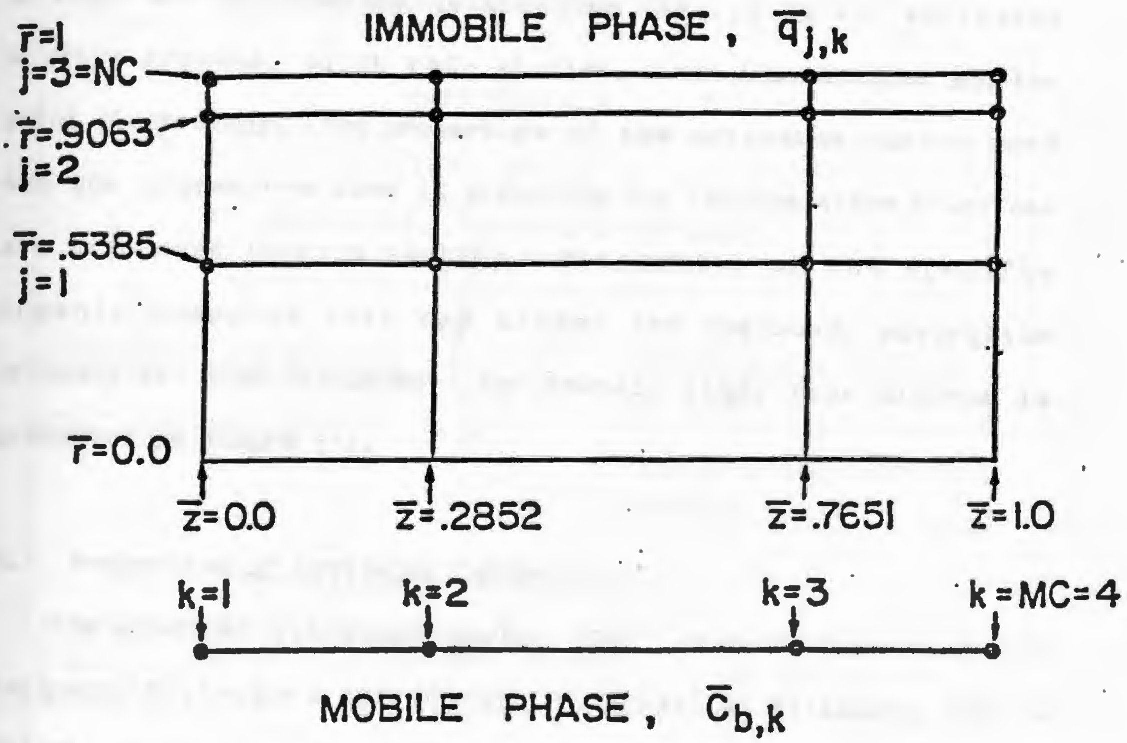


Figure 2-4 Location of Orthogonal Collocation Points for 4 Axial and 3 Radial Points

EXPERIMENTAL, MATERIALS, EQUIPMENT AND METHODS

Contained within this section are the experimental and analytical methodologies that were used to conduct the various laboratory tests performed including the single solute isotherm, mixed component isotherms both in ultra pure water background and in a complex unknown mixture background of secondary wastewater effluent and petrochemical wastewater treated by the activated sludtge process, batch rate studies, minicolumn studies and the pilot plant study. The properties of the activated carbon used and the procedures used in preparing the various sizes fractions are discussed in this section. Properties of the specific organic compound that may affect the compounds adsorption affinity are also discussed. The overall study flow diagram is presented in Figure 3-1.

3.1 Properties of Activated Carbon

The granular activated carbon (GAC) used in this study is Calgon's Filtrasorb 400 (Calgon Corporation, Pittsburg, PA); a bituminous based carbon activated with an oxygen-nitrogen mixture. Table 3-1 presents Filtrsorb 400's major properties as adopted from the manufacturer's data. One of the important properties of GAC that is usually not considered in presenting the activated carbon specifications is the pore radii and their distribution. Since the molecular weight of the adsorbate affects the affinity of adsorption through surface attraction, higher molecular weight compounds possess a higher surface attraction. However, this may

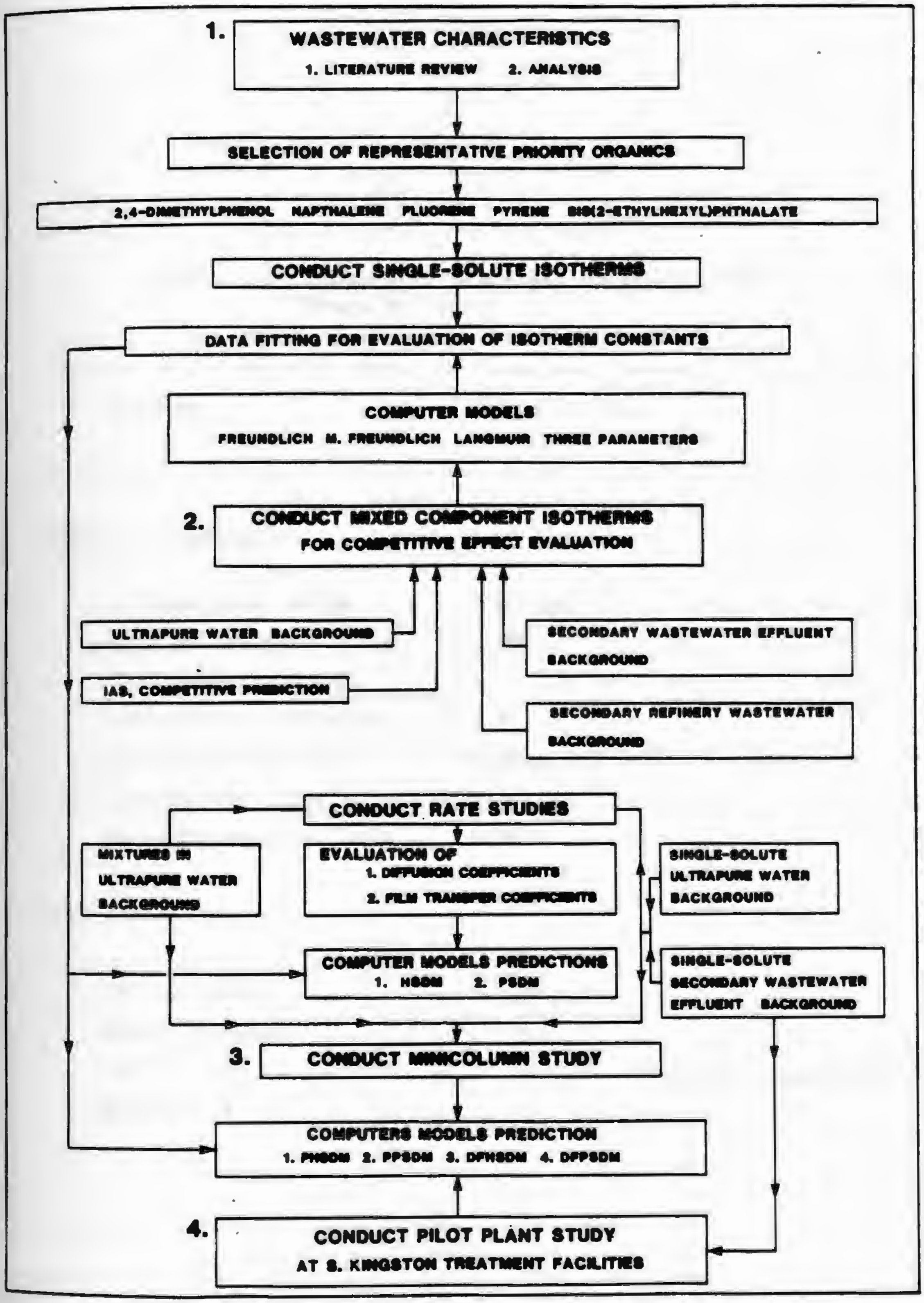


Figure 3-1 Flow Diagram for the Study

Table 3.1. Properties of Calgon Filtrasorb-400 Granular Carbon

Property	Calgon F-400 (12x40)	
Physical Properties		
Surface Area, m^2/gm	950-1050	
Apparent Density, g/cc	0.803	
Real Density, g/cc	2.1	
Uniformity Coefficient	1.8	
Effective Size, mm	0.55-0.65	
Pore Volume, cc/g	0.85	
Particle density, cc/g	1.4^{o}	
Specifications		
Iodine Number	1,000	
Abrasion Number	75	
Ash %	0.5	Mineral Constituent
Moisture %	2	

hold only while the compound molecule is smaller than the pore size of the carbon. The major part of the pore surface area exists in pores ranging from 10Å to 1000Å thus the adsorption of molecules larger than 1000Å in size are hindered since there are few pores in this range. Keinath[87], who has reviewed the literature on pore-size measurements, indicated that a bimodal distribution of pore sizes are possible in commercial activated carbons. Scholten[88] showed a trimodal distribution. Keinath and Scholten pore size distributions for activated carbon are illustrated in Figure 3-2, (a,b). Substantial variations in the predominant pore size distribution can be observed in the two curves. Keinath reports a majority of the pores occur around 1000Å, while Scholten shows the majority of pores around 100Å. Such variation can substantially affect adsorption particularly in a mixed component background. the impact of pore size distribution on organic adsorpability is a very difficult subject to evaluate because of the complexity of interaction with other variables.

3.2 Properties of Specific Organics

All chemicals were ultra pure grades and were obtained from Aldrich Chemical Company. Table 3-2 presents the physical properties of the specific priority organics used in this study. Such properties may reflect the adsorption affinity of the organic compound or can be used for relative comparison between each other. Molal volume at the normal boiling point was calculated for the organic compounds based on the atomic volumes

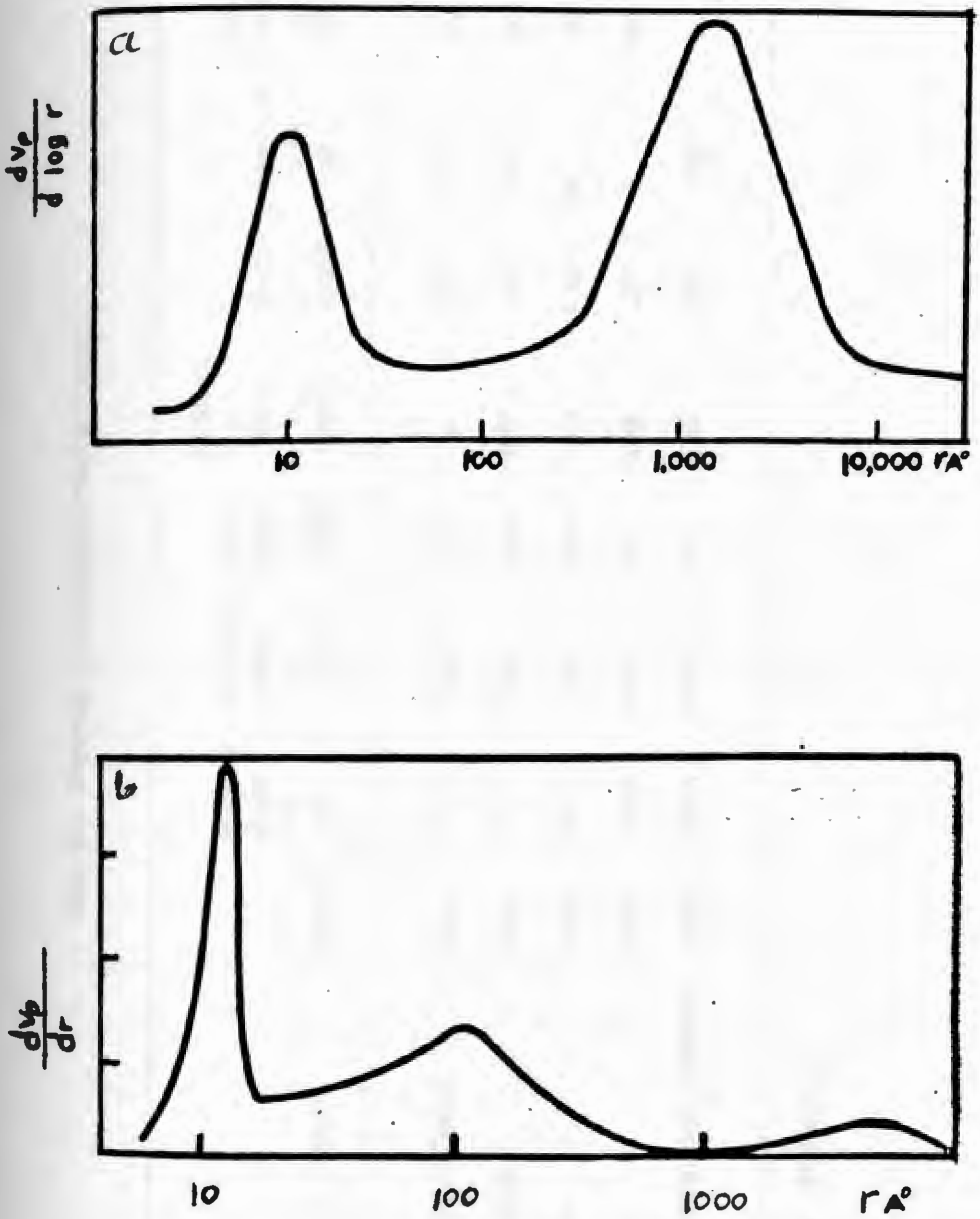


Figure 3-2 Pore Size Distribution for Activated Carbon

Table 3-2. Properties of the Selected Priority Organics

Compound	Formula	Molecular Weight M_w (g)	Molecular Volume M_v $(A^o)^3$	Molal Volume V_m (Cm^3/M)	Solubility in Water C_c (mg/L)	Density ρ (g/Cm^3)	Refractive Index nD	Melting Point M_p (°C)
2,4 - Dimethylphenol	$C_8H_{10}O$	122.16	210.3	126.6	4200	0.965	1.542	26
Naphthalene	$C_{10}H_8$	128.11	183.2	110.3	32.83	1.162	1.400	81
Fluorene	$C_{13}H_{10}$	166.21	229.5	138.2	1.453	1.203	NA	116
Pyrene	$C_{16}H_{10}$	202.24	264.3	159.1	0.098	1.271	NA	156
Bis (2-Ethylhexyl) phthalate	$C_{24}H_{38}O_4$	390.54	661.3	398.1	0.489	0.981	1.485	-50

NA = Not Available

of the compound's element components as described by Treybal[57]. The properties of density, refractive index and melting points were obtained from the CRC Hand Book of Chemistry and Physics[89]. Molecular volumes were calculated from the equation:

$$M_v = \frac{M_w \times 10^{24}}{N \times \rho} \qquad (3\text{-}1)$$

where M_v = Molecular volume, $(A^{o})^3$

M_w = Molecular weight, g

N = Avogadoros number

ρ = Density of compound, g/cm^3

10^{24} = conversion factor of cm^3 60 $(\text{Å})^3$

Solubility of the compounds were determined experimentally during the various phases of analysis conducted in this study except for the solubility of compound 2,4-Dimethylphenol which taken was from reference 90.

3.3 Methods of Analysis

For all the experiments conducted in this study, a uniform analytical procedure was strictly followed. All samples were collected in 190 ml head free bottles with teflon lined caps and kept in the refrigerator for no longer than 24 hours until analysis.

EPA[91] Method 625 - Base/Neutral and Acid/Neutral procedure was followed for the analysis of all specific organics of interest. Due to the limited volumes produced in many experiments smaller volumes of samples were collected and analyzed (150 ml) rather than 1000 ml as specified in EPA method. Therefore, only a micro Kuderna Danish (45 ml) concentrator was needed for extract concentrations. A separatory funnel extraction by methylene chloride at pH>11 was first conducted on the sample for extracting the base-neutral extractable compounds, naphthalene, fluorene, pyrene, and bis (2-ethylhexyl) phthalate, then and extraction was conducted at pH < 2 for 2,4-dimethylphenol. It was noticed that in the prior base-neutral extraction the recovery of 2,4-dimethylphenol by as much as 20%. Therefore, the final concentration of 2,4-dimethylphenol combined both fractions extracted by acid-neutral and base-neutral steps. The final extract was then passed through a solvent rinsed drying column containing about 12 cm^3 of anhydrous sodium sulfate to remove all traces of water. The dried extract was then transfered to the micro Kuderna-Danish concentrator, for concentration in a water bath at 65°C down to a final volume of 1 ml.

The GC analysis of the base-neutral and acid extractables was performed using a Tracor Model 565 LSC-2 gas chromatograph equipped with split-splitless injection pore and connected to a Spectra-Physics SP-4270 integrator. The identification of the specific organics tested as well as their concentration was based on their retention times and peak area which have been determined experimentally by the analysis of standard reference materials. The gas chromatograph operating conditions are presented in Table 3-3. Quality control ampule samples as received from the EPA

Table 3-3. Gas Chromatograph Operating Conditions and Specific Organic Compound Retention Times

Property	Condition
Injection procedure	Spitless Mode
Initial temperature	$50^{o}c$
Initial time	2 min.
Temperature programing rate	10^{o}/min.
Final temperature	$250^{o}C$
Temperature of injection port	$220^{o}C$
Temperature of FID	$300^{o}C$
Pressure	20 PSI
Chromatographic Column	
Length	30 meter
I.D.	0.5mm
Phase	SE-54
Film Thickness	1.00 Microns
Retention times	
2,4-Dimethylphenol	6.1 minutes
Naphthalene	6.5 minutes
Fluorene	12.4 minutes
Pyrene	18.4 minutes
Bis(2-Ethylhexyl)phthalate	22.8 minutes

Laboratory at Cincinnatti were used to verify the accuracy of analysis.

Dissolved organic carbon analysis (DOC) was performed using O.I.C. TOC instrument Model 700. The samples generated in the isotherm studies with an ultrapure background water were allowed to stand for one hour to settle the carbon particles before being analyzed for DOC. Samples which contained suspended solids that were present in the secondary wastewater treatment facility effluent were filtered by using medium grade filters before DOC measurements. The optimum conditions of the oxidant sodium persulfate volume, digestion reaction time and purging time were determined to achieve maximum DOC conversion. After the operating conditions were set the TOC instrument was calibrated using potassium hydrogen phthalate and all parameters kept constant during the period of the study.

3.4 Preparation of Activated Carbon

All the different size grades of activated carbon used in this study were prepared from representative samples of F-400 GAC (12 x 40 U.S. sieve number). The fine GAC 50 x 60 U.S. sieve number used for minicolumn studies and the powdered activated carbon 200 x 325 U.S. sieve number used in the isotherm studies were prepared by successive crushing and sieving of GAC as described in Appendix A. The various size grades of carbon were then washed with ultrapure distilled water to remove the fines, dried overnight at 105°C and then stored in air tight dark bottles for further reuse.

3.5 Isotherm Study Procedure

A bottle point isotherm procedure was used to conduct all equilibrium studies. The steps followed are presented in Appendix A. An equilibrium time of 6 days was found to be sufficiently long to reach the total capacity of activated carbon. Carbon dosages generally ranged from 0.27 - 187.8 mg/L. The initial liquid-phase concentrations were obtained by running blanks with no carbon added, along with the samples. So any losses by adsorption on the glass walls or any other unaccounted for losses can be accounted for. All isotherm studies were conducted at temperatures between 20-22^{o}C and at a pH of 6.6-7.0. The solutions were buffered with a 10^{-3} M phosphate buffer. Conventional roto-shakers were found to be unsatisfactory in providing good mixing, particularly when the isotherm bottles were completely filled. Therefore, a rotating contactor was designed and built in the URI department of civil and environmental engineering workshop. The contactor was designed to hold up to 40 bottles arranged in a vertical position. By adjusting the rotating speed, continuous settling of the activated carbon particles can be maintained which allows contact mixing through the whole volume of water in the bottle. A photograph of the contactor is shown in Figure 3-3.

3.6 Batch Rate Study Procedure

Adsorption rate tests to measure the effective intraparticle surface diffusion (D_S) were conducted in a 8.8 L Bellco flask

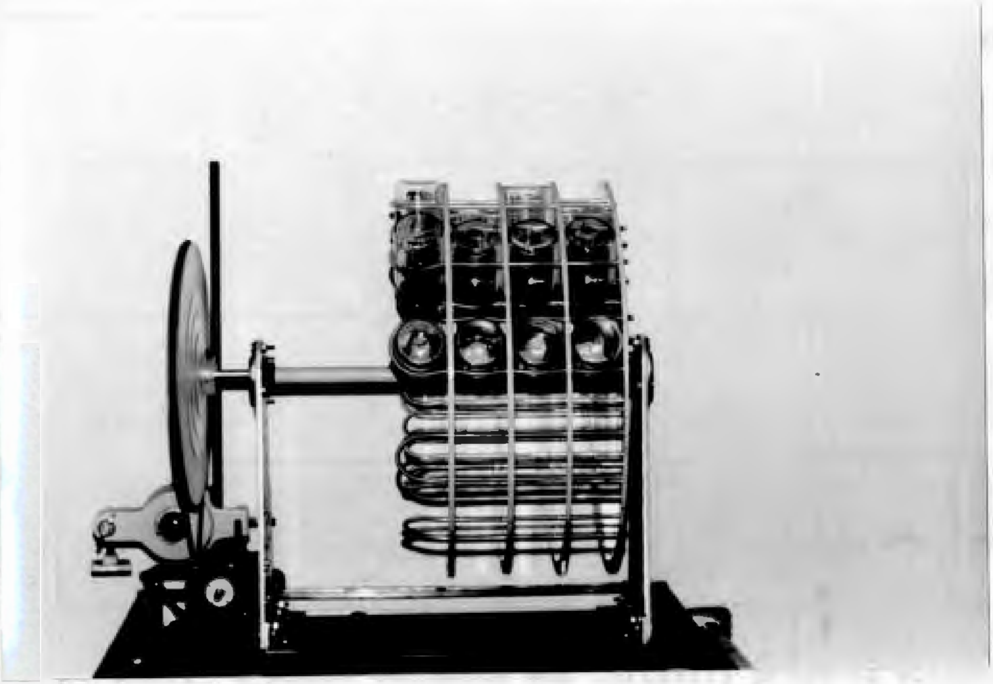


Figure 3-3. Photograph of the rotating contactor used in the isotherm study.

glassspinner operated as a completely mixed batch reactor. The reactor wass covered with a teflon lined plastic lid. Two baffles of 4.5 cm width extended from the reactor lid to 8 cm from the reactor bottom to minimize vortexing. Mixing was provided by a rheostatic controlled stirrer with a 44 cm^2 plexiglass semi-circular paddle area. The paddle rotational speed was maintained at 950 rpm for all the rate studies. Biot numbers were calculated in the reactor and maintained not less than 100. A sensitivity analysis on the effective diffusion coefficient showed that a ± 20% error in the D_s value did not affect the breakthrough chaacteristics. The power dissipated in the reactor was measured by a strobe light in conjunction with a torque meter using the equation

$$P = T\omega \qquad (3\text{-}2)$$

where P = power

T = torque

ω = angular velocity

The pH of the solution was initially adjusted to 7. The pH was measured after each sampling and only varied within the range of ± 0.2 pH unit. A blank solution was initially prepared without the addition of carbon, and allowed to agitate until an equilibrium concentration was reached. The compounds 2,4-dimethylphenol and fluorene did not vary with time, however, naphthalene reached an equilibrium initial concentration after 26 hours. The Freundlich isotherm was used to calculate the required 50 x 60 mesh carbon dosage to achieve a 50% reduction in the initial solute concentration. This calculated carbon mass was then introduced into the reactor at t=0. Samples were then periodically withdrawn until equilibrium was reached, and then the samples were analyzed for solute concentration as described before. The total volume of all samples withdrawn was less than 15% of the reactor capacity.

3.7 Minicolumn Study Procedure

The minicolumn studies were conducted in 1 cm ID glass columns. In order to support the carbon in the column, a 1 cm perforated teflon plug that fits exactly was first placed at the bottom of the column. A fine stainless steel mesh was then placed on top of the teflon plug. The preweighted amount of fine GAC (50x60) was packed in the column in slurry form, the carbon then thoroughly wetted until all the void spaces were filled with water. Another perforated teflon plug and fine stainless steel mesh assembly was then placed on top of the carbon bed and maintained in position by a tightly fitted O-ring. Such an arrangement insured a uniform distribution of flow and a fixed, carbon packed bed length and allowed for an up-flow mode of operation.

The solution was introduced to a 20 liter glass bottle and kept mixing for a period of time until an equilibrium with the initial concentrations was achieved. Another make-up batch was equilibrated similary and set aside to replace the empty batch as needed. pH was adjusted and maintained between 6.9-7.1 for all runs. The solution was introduced to the column by parastaltic pump proceeded by a glass wool filter to collect any undissolved organics. Influent samples were collected at the sampling point just at the bottom of the column. When two columns were run in parallel, the parastaltic pump was equipped with a double head arrangement which provided a constant and equal flow for both columns. A photograph of the minicolumn setup is shown in Figure 3-4.

3.8 Pilot Plant Study Procedure

The pilot plant study was conducted at the South Kingstown Wastewater Treatment Facility in Rhode Island. The influent to the pilot plant was obtained from the full-scale plant secondary clarifier, before chlorination. A submersible pump was installed just below the wastewater overflow at the clarifier weir. The pilot plant was composed of the following units.

1. Dual media filter 6 inches ID by 6 feet high, packed from bottom to top by 6 inches of gravel, 18 inches of filtration sand and 12 inches of 12 x 25 US sieve number anthracite with 1.4 uniformity coefficient and 0.61 sphericity.
2. Two GAC packed bed arranged in parallel (4 inches ID by 6 feet height). The two columns were filled with equal amounts of F-400 (12 x 30 U.S. sieve number). The carbon was supported on 6 inches of gravel resting on a stainless steel mesh. Sieve analysis on the GAC indicated that the effective size of carbon was 0.122 cm.

The tubing, valves and fittings were all made of 3/4 and 1/2 inches PVC. The valving was arranged so that influent grab

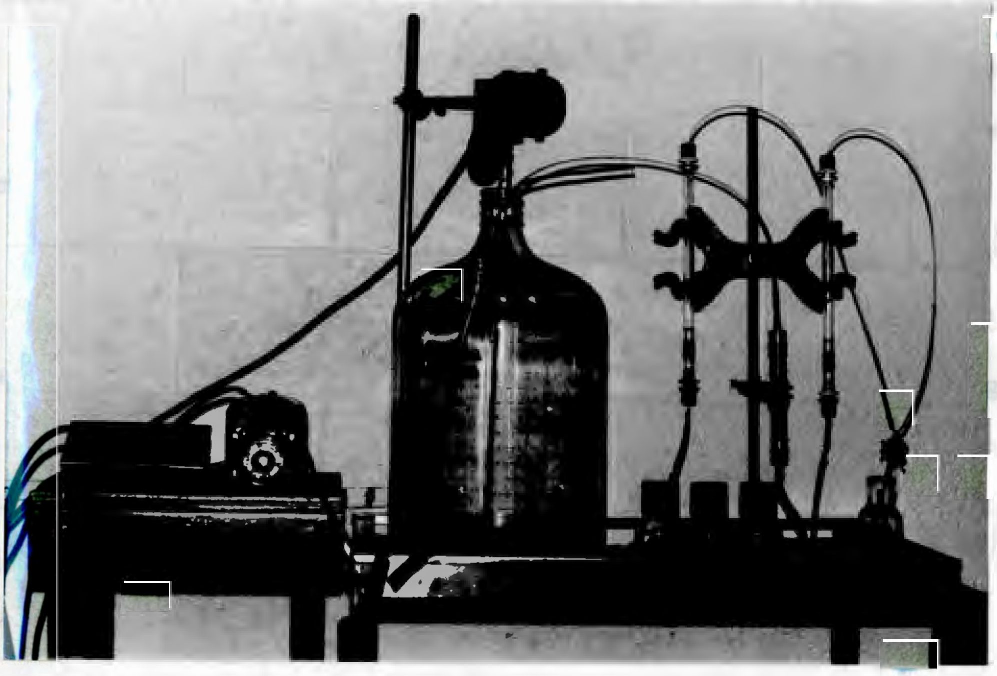


Figure 3-4. Photograph of minicolumn setup

samples could be collected in between the sand filter and GAC column No. I, and the effluent samples of GAC columns No. I and No. II. Two influent flow meters were installed, the first is between the sand filter and columns No. I to measure the total flow and the second between column No. I and No. II to measure the influent flow to column No. II. The difference in flow between the two flowmeters represents the flow in column No. I.

A high concentration of 2,4-dimethylphenol was prepared in a 50 liter Nalgene mix tank. The required flow rate that provided the designed influent concentration was continuously applied via the parastaltic pump at a point before the first flowmeter. The sand filter was backwashed by non-chlorinated drinking water. The effluent wastewater after passing through the sand filter was used for backwashing both GAC columns. This pilot plant arrangement substantially reduced the frequency of backwashing the GAC column. A schematic of the pilot plant is shown in Figure 3-5 and photographs of the pilot plant and the full-scale secondary clarifier are shown in Figures 3-6 and 3-7.

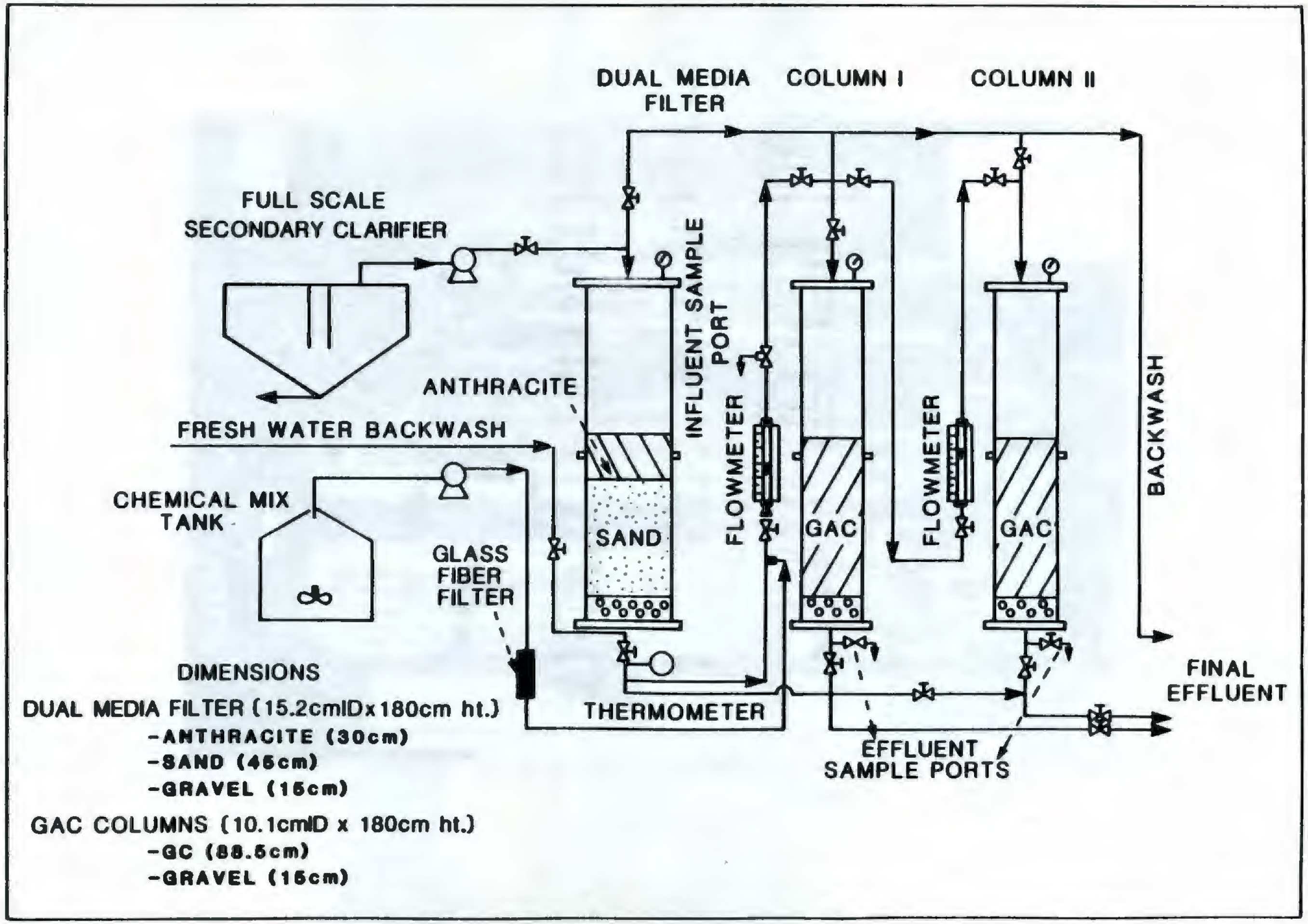


Figure 3-5 Schematic of the Pilot Plant

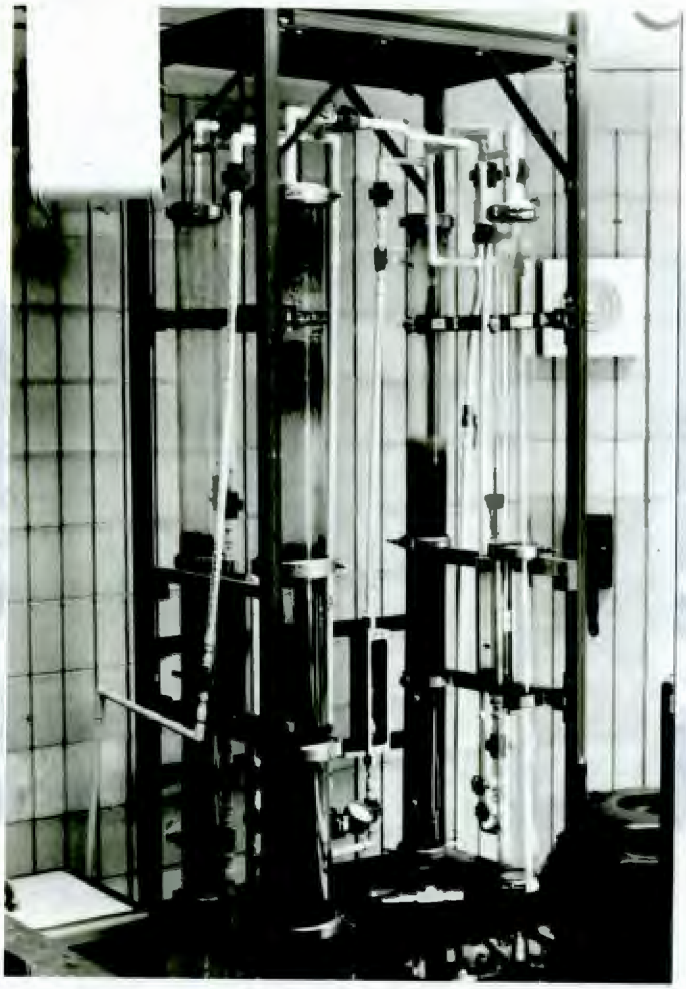


Figure 3-6. Photograph of pilot plant

Figure 3-7 Photograph of the Secondary Clarifier

RESULTS AND DISCUSSION

4.1 Single-Solute Adsorption Studies

In the design of an adsorption system, it is necessary to have a quantitative description of the equilibrium relationship between adsorption capacity and the adsorbate concentration remaining in the solute for a particular system. However, different mixtures can behave remarkably different because of the effects of background solvent constituents which are not identified. An adsorption isotherm study is the most practical approach to characterizing the adsorption relationship. By performing a single-solute adsorption isotherm in ultrapure water background the competitive background effects can be eliminated. By next performing the adsorption isotherms in a mixture of complex background wastewater the competition effect due to background can be isolated.

For this study, adsorption isotherms were conducted at a pH of 6.8 and a temperature of 22°C which are typical secondarywastewater effluent characteristics in summer, the time planned for running the verification step using the pilot plant. The pH can affect the results of isotherm study in various ways: 1) There is a close relationship between adsorbability and solubility. The less soluble a material is, the more likely that this material will be adsorbed. 2) The pH of the liquid will affect the dispersibility of the pulvarized carbon suspension. At pH levels below 7, a carbon suspension tends to agglomerate into larger flocs which will enhance settling and filtration of the carbon particles.

The time required to achieve isotherm equilibrium has been reported differently in various research studies. An equilibrium time as low as 2 hours, at 22°C was reported by Dobbs and Cohen[90]. By increasing the equilibrium time to about 2 days only increased the equilibrium capacity by 10 percent. The temperature at which the isotherm is conducted also appears to affect the equilibrium time[52], with the decrease of temperature, the equilibrium time required to achieve the same percentage of equilibrium will increase. This is attributed to the decrease in the rate of diffusion into the carbon pellet. Due to the difficulty in reproducing the initial adsorbate concentration in different background mixtures, it was necessary to allow for a longer equilibrium time than normal. Crittenden et al.[52] demonstrated that isotherm results do not depend on the initial adsorbate concentration if adequate equilibrium times are allowed. Consequently, the equilibrium time considered in this study is 6 days and this time proved satisfactory for all the isotherm tests conducted. Equilibrium uptake appears to be independent of particle size. This has been verified experimentally for the adsorption of many organic compounds[52]. Therefore, the equilibrium isotherm study was conducted using pulvarized activated carbon 200 x 325 U.S. mesh number. The pulvarized carbon used was obtained by crushing 12 x 40 U.S. mesh number granular carbon as described previously. The same carbon stock was used for preparing the pulvarized carbon and for the pilot plant study, so similarity was maintained for other GAC parameters.

The single solute data for each of the compounds studied were fitted by four isotherm models: Conventional Freudlich model, Modified Freundlich model (Singer and Yen)[51], Langmuir model and the three parameters model (Radke-Prausnitz)[42]. The mathematical relationships which describe these models have been discussed and explained in section 2. The calculated best fit parameters for each of the single solute compounds along with the corresponding correlation coefficients are listed in Table 4-1 and Table 4-2 for the Freundlich, modified Freundlich, Langmuir and three parameters models respectively.

Figures 4-1 through 4-5 show the log-log plots of the single-solute isotherms for all of the selected organic compounds with their raw data presented in Appendix B, table B-1 through table B-5. Within the range of the concentrations tested, the Modified Freundlich model and the three parameters model compared extremely well for all of the compounds. R-square values indicate that both the modified Freundlich and the three parameters models fit the data better than the Freundlich and Langmuir models. For the case of 2,4-dimethylphenol where the lowest R-square values were calculated, the three parameters model showed a slightly better fit than the Modified Freundlich model.

The variation in slope (1/Nf values) could lead to substantial differences if the isotherm parameters are used outside of the concentration range in which they are determined. For the compounds fluorene, pyrene, naphthalene and bis(2-ethylhexyl)phthalate the range of concentration tested

Table 4-1. Single Solute Freundlich and Modified Freundlich Isotherm Adsorption Parameters of the Selected Priority Organic Compounds

		Freundlich			Modified Freundlich			
Compound	No. of Observations	Nf	K	R**2	Nf	log q_x	log K	R**2
2,4-Dimethylphenol	7	3.334	0.039	0.786	5.009	-2.482	-1.792	0.82
Naphthalene	8	2.926	0.1007	0.986	3.034	-2.998	-1.051	0.987
Fluorene	6	2.384	0.560	0.987	2.412	-2.972	-0.275	0.987
Pyrene	6	2.592	0.646	0.951	2.591	-3.324	-1.898	0.951
Bis (2-Ethylhexyl)phthalate	6	1.812	0.435	0.987	1.988	-4.197	-0.679	0.990

R**2 = R - Square Best Fit

Model Input Units: C_e in (M/L) and q_e in (M/g-C)

Table 4.2. Single Solute Langmuir and Three Parameters Model Isotherm Adsorption Parameters of the Selected Priority Organic Compounds

		Langmuir Model			Three Parameters Model (Radke - Prausnitz)			
Compound	No. of Observations	Q	b	R**2	α	β	ρ	R**2
2,4-Dimethylphenol	7	0.275E-2	9.1883E5	0.817	0.3298E3	0.5247E5	0.9059	0.833
Naphthalene	8	0.263E-2	9.3386E5	0.919	0.9547E4	0.1425E6	0.6983	0.996
Fluorene	6	0.296E-2	2.1631E6	0.951	0.2156E5	0.9906E5	0.6577	0.994
Pyrene	6	0.139E-2	7.8657E7	0.879	-0.1112E6	-0.3178E5	0.5013	0.986
Bis (2-Ethylhexyl)phthalate	6	0.131E-3	1.1061E7	0.967	0.4087E4	0.2635E5	0.5246	0.989

R**2 = R - Square Best Fit.

Model Input Units: C_e in (M/L) and q_e in (M/g-C)

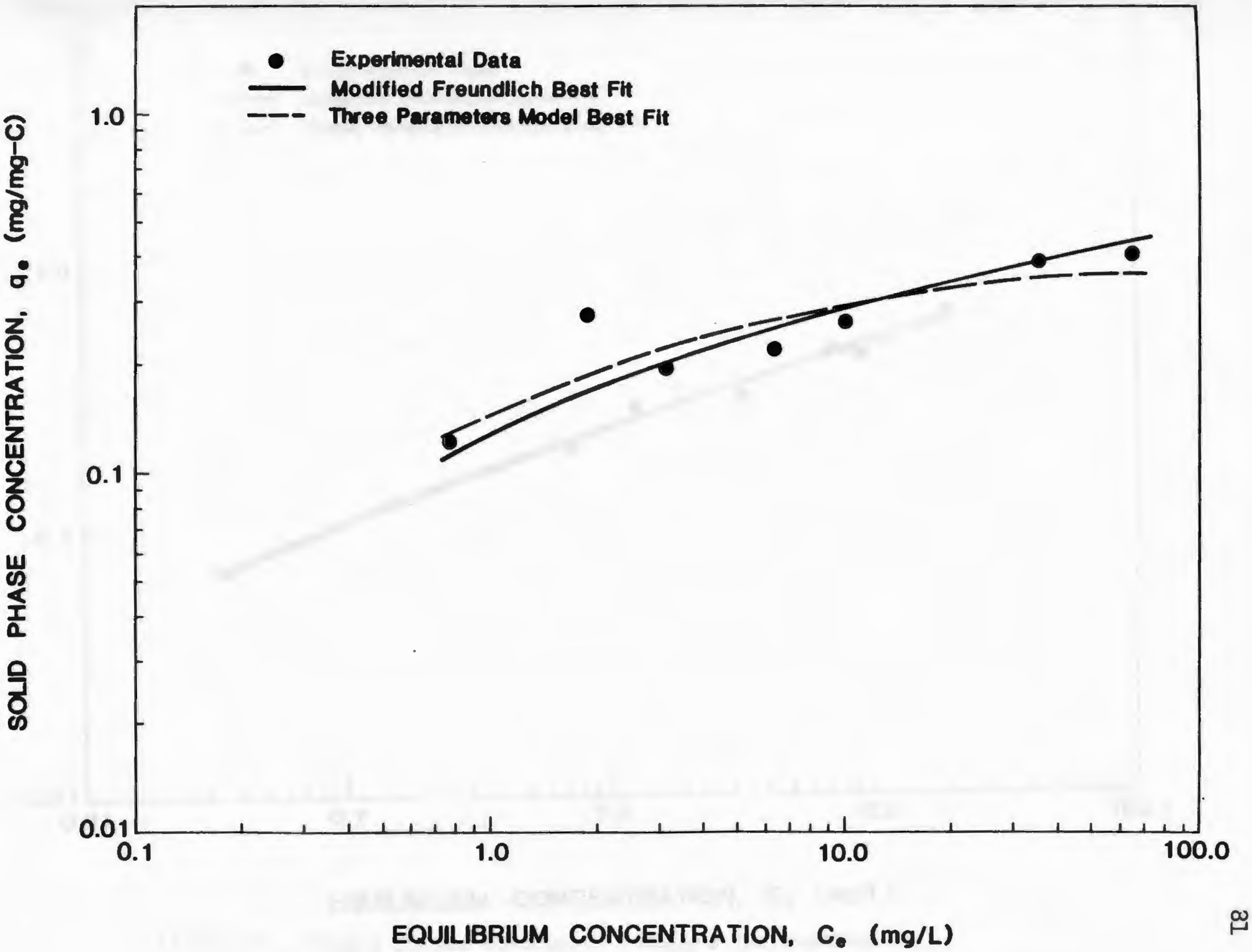


Figure 4-1 Single Solute Adsorption Isotherm for 2,4-Dimethylphenol

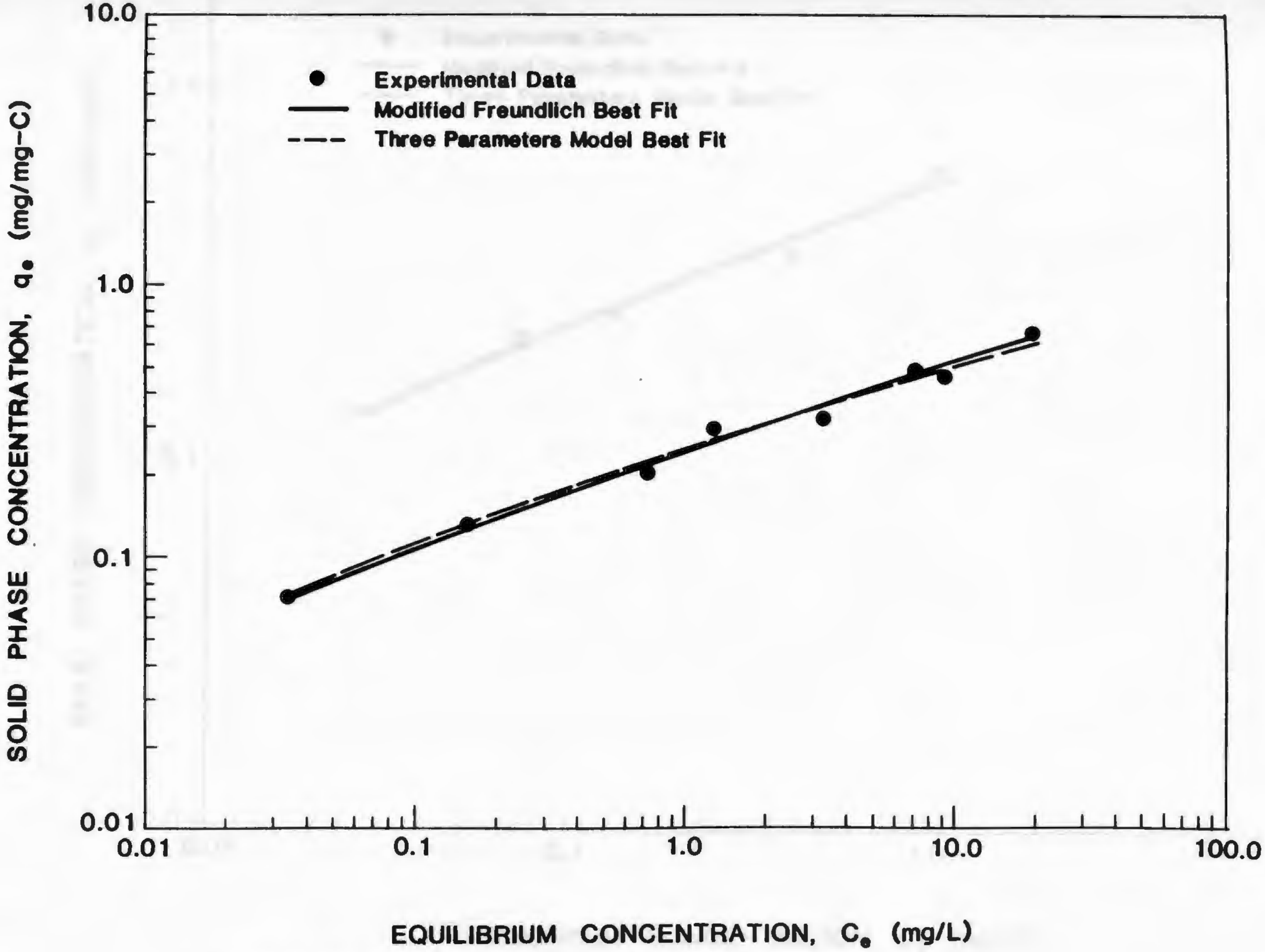
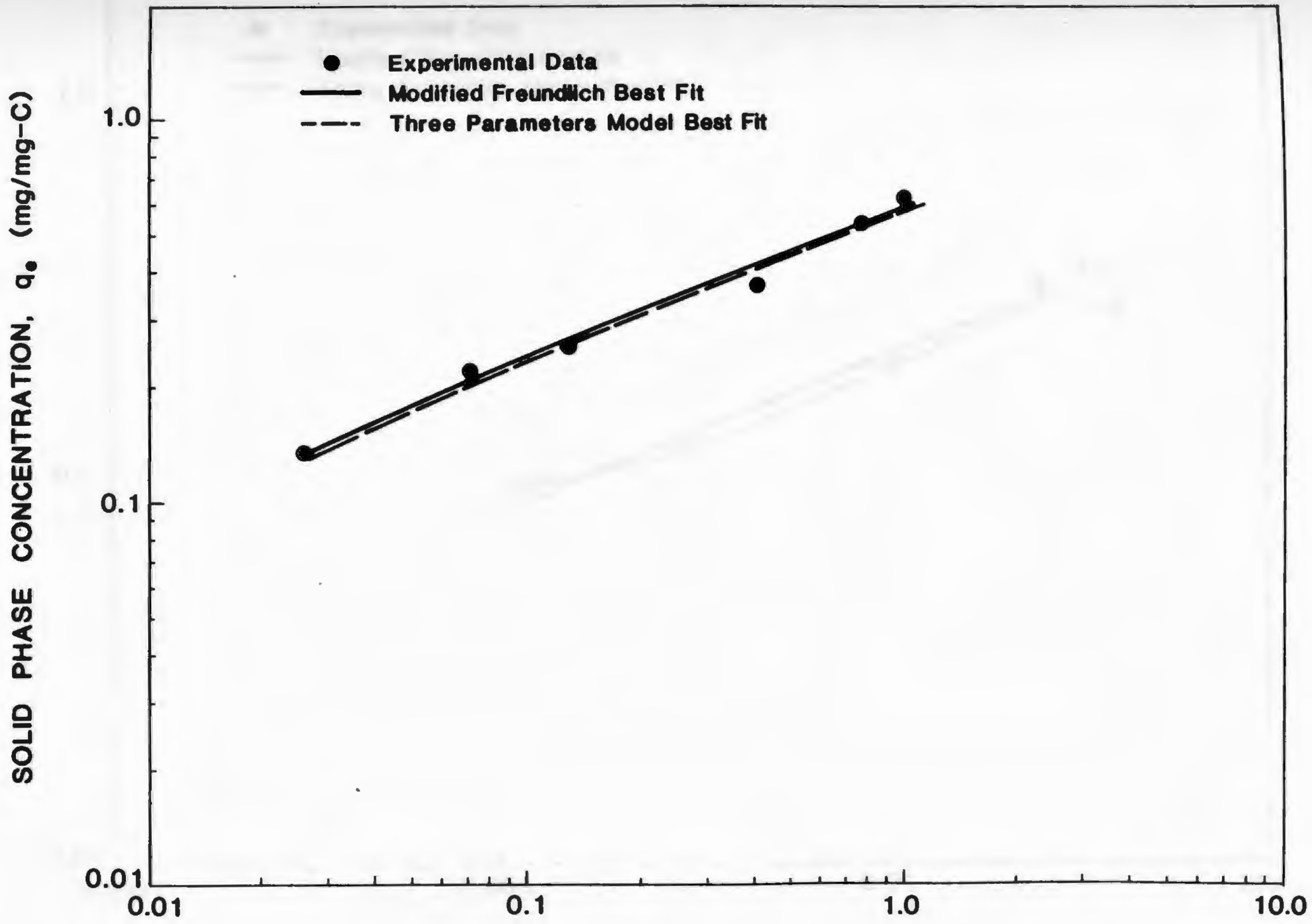


Figure 4-2 Single Solute Adsorption Isotherm for Naphthalene



EQUILIBRIUM CONCENTRATION, C_e (mg/L)

Figure 4-3 Single Solute Adsorption Isotherm for Fluorene

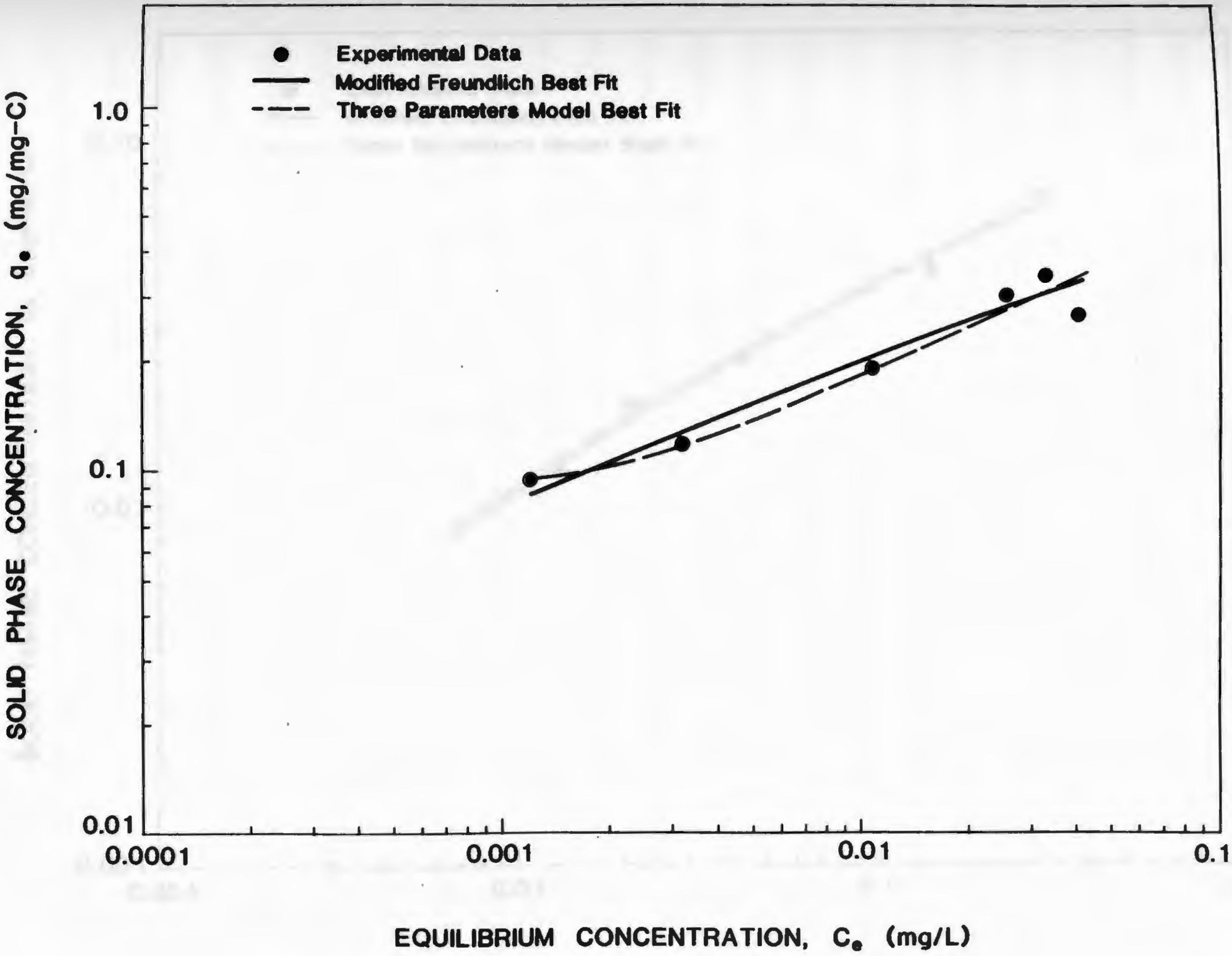


Figure 4-4 Single Solute Adsorption Isotherm for Pyrene

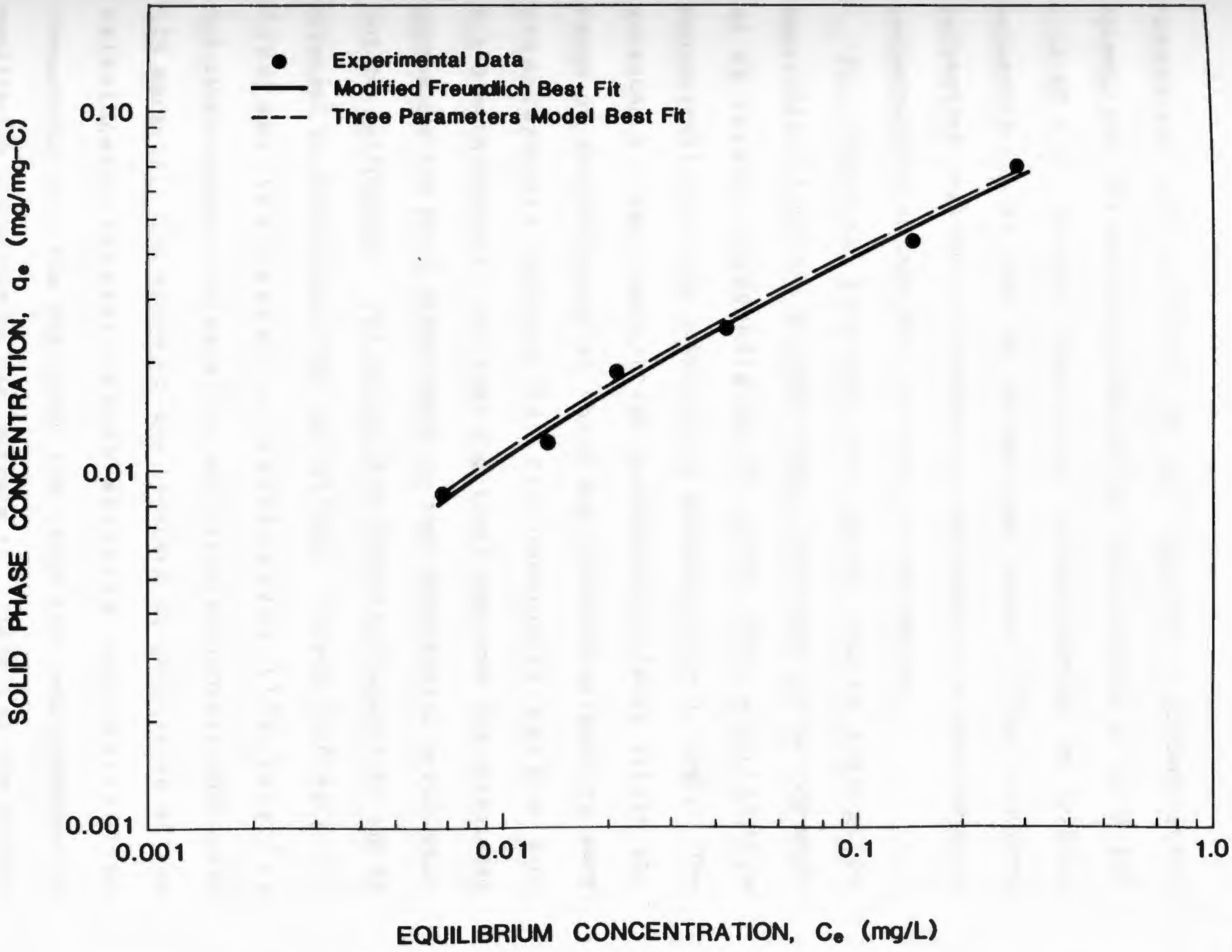


Figure 4-5 Single Solute Adsorption Isotherm for Bis(2-ethylhexyl)phthalate

ranged as high as 80-95% of their saturation concentration values, i.e. the maximum solubility for the compound at 22°C and a pH of 6.6. For the compound 2,4-dimethylphenol an initial concentration as high as 108 mg/L was tested. The isotherm parameters that were calculated are applicable to a wide range of concentrations of that could be found in wastewater.

For comparison purposes, the single solute adsorption capacities of all the selected organic compounds can be expressed as mg organic compound/gram of carbon when equilibrium concentration of the compound is assumed to be 0.1 mg/l. The selected 0.1 mg/l equilibrium concentration falls within the range of concentration at which the isotherm parameters were predetermined, except for the compounds pyrene and 2,4-dimethylphenol, but even for these compounds the calculated parameters are still close enough so that substantial error will not be introduced. The calculated adsorption capacities can be arranged in decending order as follows: Pyrene (346 mg/g-C), fluorene (231 mg/g-C), naphthalene (102 mg/g-C), 2,4-dimethylphenol (69 mg/g-C), and bis(2-ethylhexyl)phthalate (39 mg/g-C). The slope of the isotherm is indicative of the relationship between carbon affinity and equilibrium concentration. The shallower the slope the less dependent on equilibrium concentration the isotherm is. Observing the slopes of the isotherms of the five organic compounds tested, their dependency on the equilibrium concentration can be ranked in decreasing order as: bis(2-ethylhexyl) phthalalte, fluorene, pyrene, naphthalene and 2,4-dimethylphenol. In an attempt to correlate the adsorption capacity of the compound with some of its physical properties, the molecular volume and the solubility of the compound were considered. Apart from bis(2-ethylhexyl) phthalate the ranking of the compound adsorption capacities in decreasing order follow the increase in their solubilities. Considering the molecular volume, bis(2-ethyhlhexyl) phthalate has the largest molecular volume and showed the lowest adsorption capacity. For the rest of the compounds which had somewhat similar molecular volumes, no correlation between the molecular volumes and the adsorption capacity is indicated.

Another attempt was made to quantitatively evaluate the single solute isotherm by using the Dubinin-Polayi theory[92-94]. This adsorption theory assumes that the adsorbed species within the activated carbon pellet behave as a liquid, although due to the effect of the force field of the adsorbent, the properties of this liquid phase is different from the properties of the bulk liquid. The adsorption potential ε, is referred to as the difference in free energy between the adsorbed phase and the saturated liquid sorbate at the same temperature and can be calculated by:

$$\varepsilon = RT \ln (C_c/C_e) \qquad (4\text{-}1)$$

where C_c = Saturation concentration of solute, mg/L

C_e = Equilibrium concentration, mg/L

R = Gas constant, 8.3144 Joules/deg. mole.

T = Absolute temperature, ^{o}K

For a given adsorbent - adsorbate system there is a unique temperature independent relationship which is referred to as the characteristic curve and often approximated by the Gaussian expression:

$$W = W_o e^{-K_a \varepsilon^2} \qquad (4\text{-}2)$$

where W = solid phase loading of adsorbate in Cm^3 adsorbate/100 g-C

W_o = Maximum solid phase loading of adsorbent in cm^3 adsorbate/100 g-C.

K_a = adsorption energy constant, Mole/K.Joul.

The solid phase loading of adsorbate, W can be estimated by the following relationship.

$$W = q \cdot V_m \cdot 100/M_w \qquad (4\text{-}3)$$

where q = Solid phase concentration, g/g-C

V_m = Molal volume, cm^3/mole

M_w = Molecular weight, g

Taking the logarithm of equation (4-2) a linear relationship can be derived and by linear regression analysis, the values W_o and K_a can be calculated as quantitative fitting parameters.

The resulting constant for the selected organic compounds along with the correlation coefficient of the best fit are listed in Table 4-3. The correlation value indicates a good linearity for all the compounds within the range of concentration tested. However the validity of the outcome of this theory depends on various factors which include: 1) Reliability of solubility data varies considerably in the literature, e.g. the solubility of pyrene and fluorene were found to be 40-60 percent less than the reported ones under the same testing conditions and the bis(2-ethylhexyl) phthalate solubility was reported[90] to be 50 mg/ℓ while no more than 0.48 mg/L saturation solubility was achieved in this study. 2) The mathematical expression of the characteristic curve of equation (4-2) does not reduce to Henry's Law in the low concentration limit. This is a theoretical requirement for any thermodynamically consistent physical isotherm. This factor, however, is irrelevant in this study as the single-solute isotherms of fluorene, pyrene and bis(2-ethylhexyl) phlthlate were tested at concentrations which approached their saturation solubility, and for the single-solute isotherms of 2,4-dimethylphenol and naphthelene, moderate concentration range were tested. Based on Dubinin-Polanyi potential theory, the calculated maximum adsorption capacities (W_o) can be arranged in decending order in the following manner: 2,4-dimethylphenol (0.557 g/g-C), fluorene (0.522 g/g-C) Naphthalene (0.481 g/g-C), pyrene (0.336 g/g-C) and bis(2-ethylhexyl) phthalate (0.057 g/g-C). This order is not comparable with the order resulting from the Freundlich model.

Table 4-3. Dubinin - Polanyi Isotherm Constants for the Selected Priority Organics

Compound	Solid Phase Loading, W_0 (cm^3/100g-C)	Adsorption Constant K_a (Mole/K.Joul)	R**2
2,4 Dimethylphenol	57.8	0.0031	0.79
Naphthalene	41.4	0.0073	0.94
Fluorene	43.4	0.0154	0.92
Pyrene	26.4	0.0098	0.67
Bis(2-Ethylhexyl) phthalate	5.8	0.0183	0.96

Another isotherm analysis approach adopted by Manes[93,94] and based also on Polanyi's theory was considered for isotherm analysis in this study. The difference between Dubinin-Polany's approach and Polany's approach as adopted by Manes is that Manes does not linerize the equation and uses the abscissa to plot the quotient of ε/V_m. He called this curve a correlation curve. In order to predict the correlation curve of certain compounds, Manes and Hofer[95] introduced the refractive index "n", as another physical property of the organic compound. So the correlation curve is a predictive approach when the refractive index is the physical property that controls it. The equation suggested by Mane and Hofer can be expressed as:

$$\frac{RT/V_{mi} \text{Ln } C_{ci}/C_{ei}}{RT/V_{mr} \text{Ln } C_{cr}/C_{er}} = \frac{(nD_i^2 - 1)/(nD_i^2 + 2)}{(nD_r^2 - 1)/(nD_r^2 + 2)} \qquad (4\text{-}4)$$

The subscript "i" denotes the compound of interest and subscript "r" denotes the reference compound. The left hand side of the equation is the potential energy over the molal volume. In order to apply this analysis method on the isotherm tests conducted, the refractive index and isotherm data for each compound is needed. The refractive indices were obtained from the CRC Handbook of Chemistry and Physics[89] and found only for some of the compounds.

The correlation curve developed for 2,4-dimethylphenol is shown in Figure 4-6. The solid line is the visual fit line for the experimental data points. An attempt was made to predict

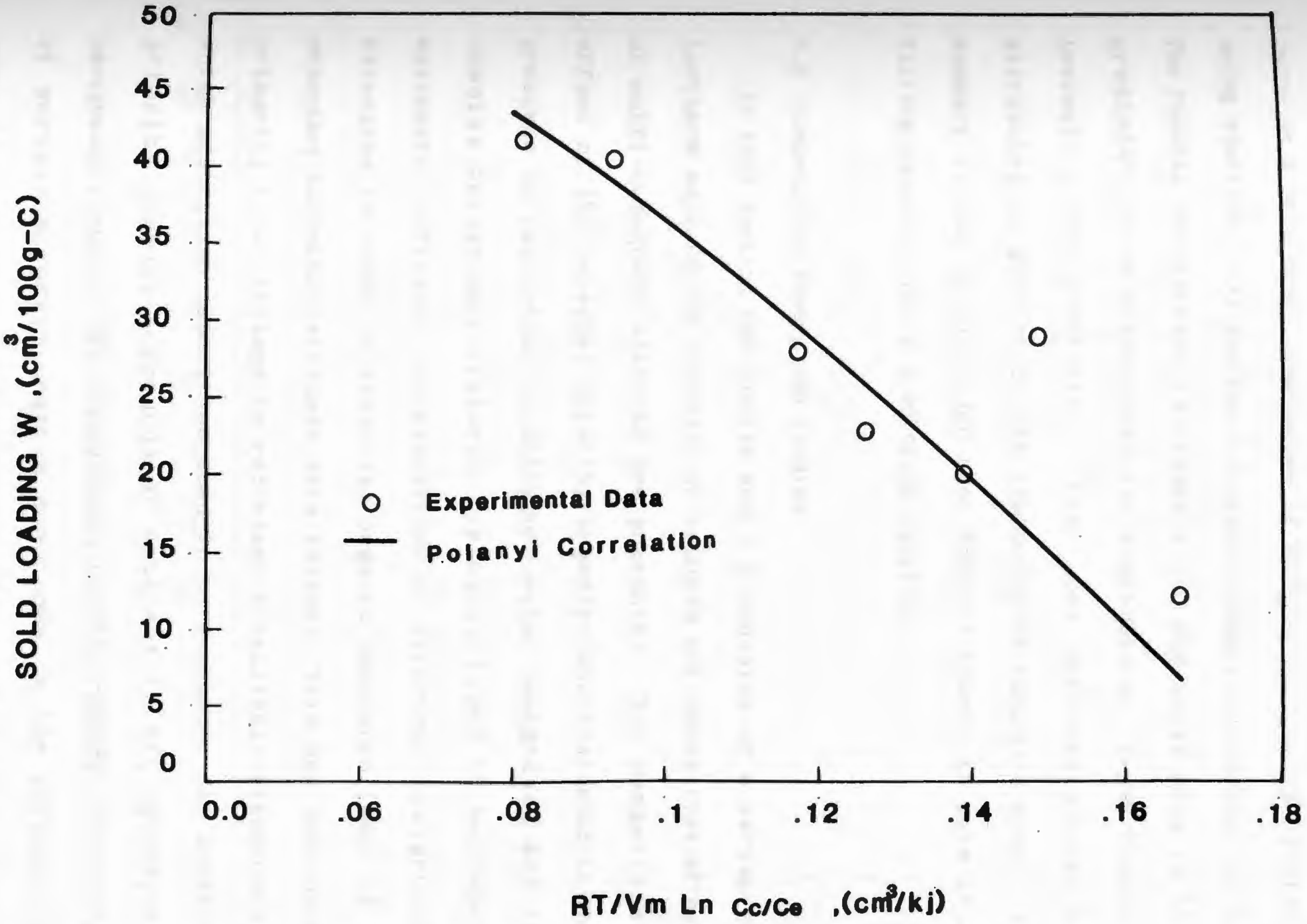


Figure 4-6 Polanyi Correlation Curve for 2,4-Dimethylphenol

naphthelene isotherm using the 2,4-dimethylphenol correlation curve as a reference. New values of $RT/V_m \ln C_c/C_e$ were obtained using equation (4-4) and the 2,4-dimethylphenol correlation curve. The results are plotted in Figure 4-7. The solid line is the predicted correlation curve for naphthalene. These results indicate a poor prediction. This poor correlation can be attributed in general to the limitation of Polanyi's model. In summary it can be concluded that Polanyi theory is more of a fitting equation than a predictive equation.

4.2 Competitive Adsorption Studies

In this section the results and a discussion of a series of isotherm experiments conducted to evaluate the competitive effect of multi-component mixtures are presented. The competitive effect of the selected priority organics was evaluated in the presence of each other in ultrapure water background and in complex background mixtures typically found in secondary wastewater effluent. An evaluation of different background strengths in terms of dissolved organic compounds (DOC) of a secondary wastewater effluent were tested. This has been done primarily in an attempt to represent a realistic situation in which adsorption capacities need to be evaluated for certain priority organic compounds of interest in highly complex background mixture. EPA regulations currently require monitoring of certain priority organic compounds in the effluent of wastewater treatment facilities. The ultimate goal is to reduce the levels of the compounds either through pretreatment treatment

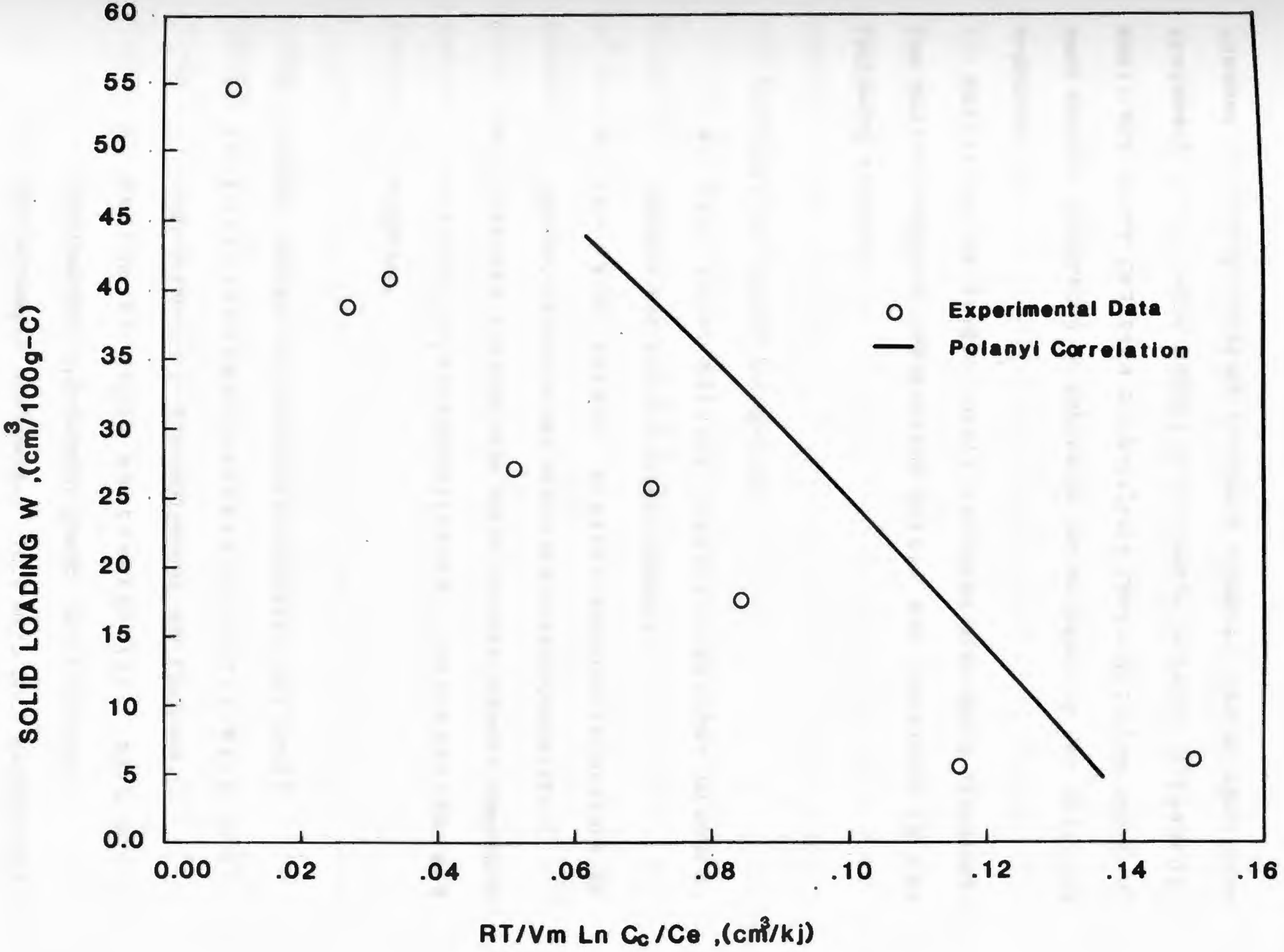


Figure 4-7 Prediction of Naphthalene Isotherm Using Polanyi Correlation Curve for 2,4-Dimethylphenol

schemes or through in-plant treatment schemes. Carbon adsorption treatment is a viable solution to remove organic compounds. Until now there has been no available research on the impact of such complex background on activated carbon capacity for priority organics.

Utilizing the single solute isotherms previously discussed, the multi-component competition effect was examined in the following sequence:

1. Ultra-pure water background
    a. High water soluble organic compounds mixture, naphthalene and 2,4-dimethylphenol.
    b. Low water soluble organic compounds mixture of pyrene, fluorene and bis(2-ethylhexyl)phthalate.
    c. Combined low and high water soluble organic compounds mixture, 2,4-dimethylphenol, naphthalene and fluorene.

2. Complex background (secondary wastewater effluent)
    a. Full strength wastewater (27.3 mg/L DOC), naphthalene, 2,4-dimethylphenol and fluorene.
    b. Medium strength wastewater (19.1 mg/L DOC), naphthalene, 2,4-dimethylphenol and fluorene.
    c. Low strength wastewater (10.1 mg/L DOC) naphthalene, 2,4-dimethylphenol and fluorene

3. Complex background (activated sludge pilot plant effluent treating refinery wastewater), naphthalene, 2,4-dimethylphenol and fluorene.

Ideal adsorption solution theory (IAS) was tested to predict the competitive interaction for each of the previously mentioned mixture combinations. The mathematical formulation that explains the IAS is discussed in section 2. The Singer and Yen[51] modifications for solving the IAS equations were used to predict the competitive interaction.

IAS theory was successfully applied for prediction of multicomponent adsorption equilibria in many studies[7,42,52]. All of these studies considered only a multicomponent mixture adsorption in an ultrapure background. The applicability of IAS in a complex background mixture of unknown composition has never been tested. One of the objectives of this study is to evaluate this applicability.

Statistical analysis of IAS predicted and observed experimental data was evaluated for each of the above combinations using statistical analysis system (SAS) software. Statistical values were obtained through the following formulations.

1. Relative Error (RE)

Mathematically defined as

$$RE = \frac{|\overline{X} - \overline{C}|}{\overline{X}} \tag{4-5}$$

This simple comparison between observed and predicted values is very rough and the statistics in it cannot recognize the variabiity of data. However, this relationship can provide some measure of the model adequacy when other statistical parameters such as the media and standard deviation of the relative sample are evaluated.

2. Root Mean Square Error (RMSE)

Mathematically defined as

$$RMSE = \sqrt{\frac{\sum(X_i - C_i)^2}{N}} \tag{4-6}$$

This type of analysis provides a direct measure of model error. The main disadvantage of this test is that it does not readily lend itself to pooling across variables to assess overall model credibility.

3. Analysis of Variance in Linear Regression.

According to Bethea et al.[96], the proposed functional relationship between the observed and predicted data is

$$Y = \beta_o + \beta_1 X + E \tag{4-7}$$

where Y and X are the observed and predicted values, respectively E is a random error, and the parameters β_0 and β_1 are the regression coefficients. The means square due to error, $MS_E=SS_E/(n-2)$, is an unbiased estimator for σ^2 because the expected $MS_E = \sigma^2$ regardless of whether or not the hypothesis H_O: $\beta_1 = 0$ is true. It can be shown that the expected value of the mean square due to regression $MS_R = SS_R/1$, is a biased estimator for σ^2 unless $\beta_1 = 0$. This can be shown by

$$\begin{aligned} E(MS_R) &= E(SS_R/1) \\ &= \sigma^2 + \beta_1^2 \sum(X_i-\overline{X})>\sigma^2 \end{aligned} \tag{4-8}$$

These two expected mean squares suggest the use of the ratio

$$F = MS_R/MSE \tag{4-9}$$

in testing H_O: $\beta_1 = 0$. This ratio has an F-distribution with $\nu_1=1$ and $\nu_2 = n-2$ degrees of freedom if H_o: $\beta_1 = 0$ is true. Thus to test H_o: $\beta_1 = 0$ H_O is rejected if $F>F_{1,n-2,1-\alpha}$. Since MS_R and MS_E both estimate σ^2 under H_O: $\beta_1 = 0$, H_O is also rejected if F is significantly larger than 1 since the expected $MS_R>\sigma^2$ when H_O:$\beta_1 = 0$ is not true. H_o: $\beta_1 = 0$ can also be tested by using T $= (\beta_1 - 0)/S\beta_i$ and the t-statistic with n-2 degrees of freedom. It can be shown that T^2 is an F- statistics with 1 and n-2 degrees of freedom so that using F is equivalent to using T or T^2. Theoretically a value for $\beta_1 = 1$ can be considered which is the slope of the regression line. In order to test whether or not the proposed β_1 is valid, the T statistics in the equation:

$$T = \frac{\hat{\beta}_1 - \beta_1}{S_{\hat{\beta}_1}} \qquad (4\text{-}10)$$

By checking that the value of T is less than the tabular of $T_{1,n,0.95}$, the hypothesis that $\beta_1 = 1$ can be accepted or rejected within 95% probability.

The following method which was developed by Leggel and Williams[97] was used in comparing the various models tested in this study. Their method is specific for evaluating a model's reliability or comparing between models. A reliability index k was defined which can be determined from set $x_1, x_2, \ldots, x_n$ of model prediction and a corresponding set $y_1, y_2, \ldots, y_n$ of observations. Applying their method one can express model predictibility as an "accurate within a factor of k," that is, the closer k is to one the better the model predictability is. A measure of k means that all model prediction observations fall within 1/k and k times the corresponding observed values. The reliability index was evaluated by two approaches. The geometric index (k_g) is a measure of the tangent of the angles θ_i which falls between a line from the origin to (x_i, y_i) and the 45^o line which represents a perfect fit. The statistical index k_s which is based on a measure of the distribution of the random variables whose values are a possible observed value corresponding to a predicted value.

4.2.1 Competitive Adsorption in Ultrapure Water Background

The competitive interaction of the preselected priority organics was examined in three combination sets based on their solubility in water (high, low and higha nd low solubilities combined). This approach is reasonable since for many compounds the solubility of the compound may indicate its adsorbability, that is the lower the solubility of a compound the higher its adsorbability. This general observation is confirmed by the results of the single-solute study discussed previously. However, there are other factors such as a compound's molecular weight, polarity, refractive index and others which can influence a compound's adsorption on carbon.

In order to test the competition prediction by the IAS model using the modified Freundlich isotherm parameters, a bottle point isotherm study was conducted for each of the prementioned sets. The raw data are presented in Appendix C in Table C-1 to Table C-3. The predicted values of the IAS Model and the experimental data are plotted as shown in Figures 4-8 to Figure 4-10. It can be observed clearly from these figures that the IAS model with the modified Singer and Yen calculation gives a very good prediction for the three solubility groups that were tested.

The model prediction worked very well over the entire range of concentrations tested. Such good agreement is attributed to the influence of the Singer and Yen modification which allowed for the isotherm parameters to be fitted down to concentrations approaching zero. The Singer and Yen modification was required

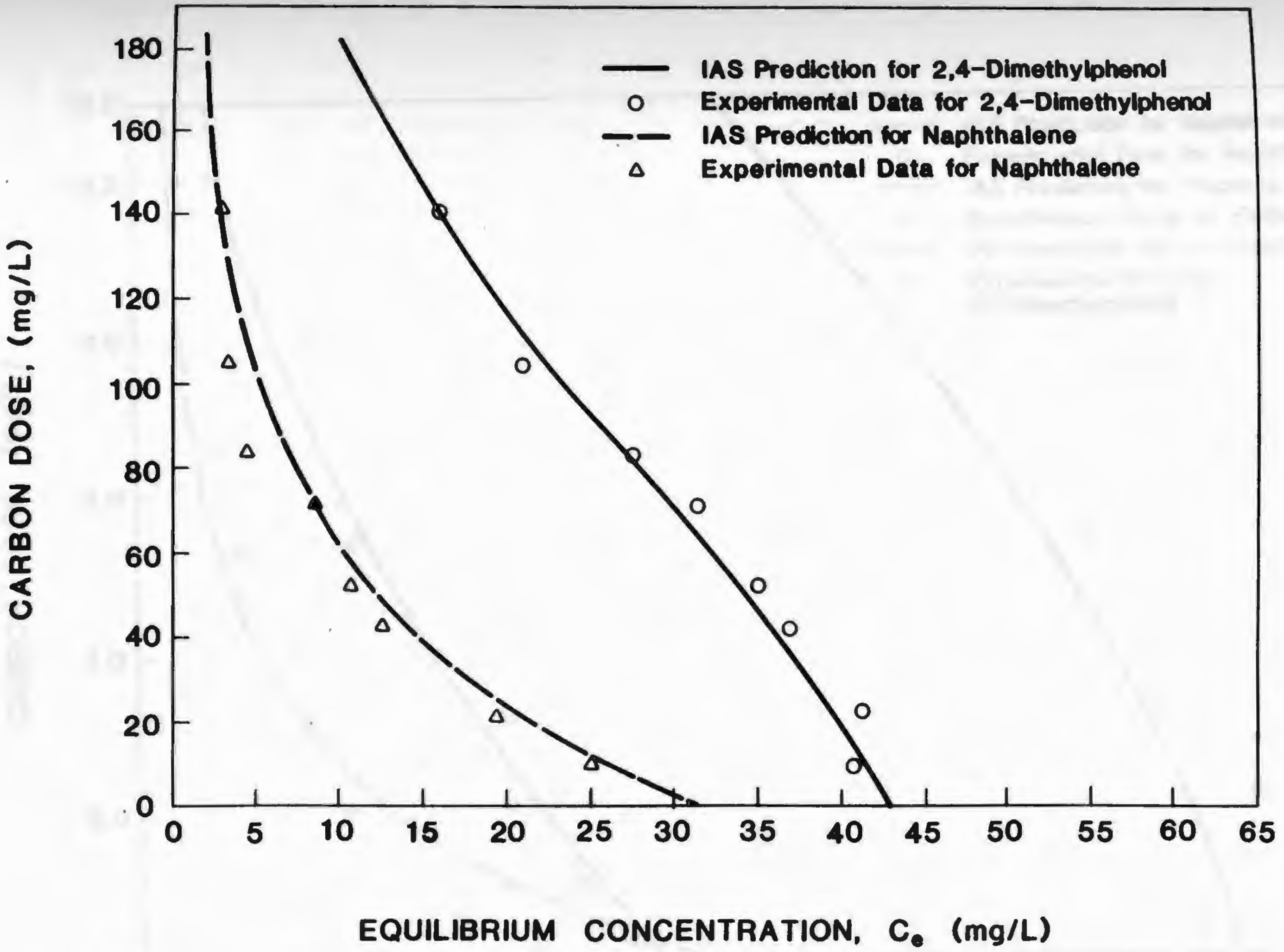


Figure 4-8 IAS Prediction of Mixed Component Mixture in Ultrapure Water Background (2,4-Dimethylphenol-Naphthalene)

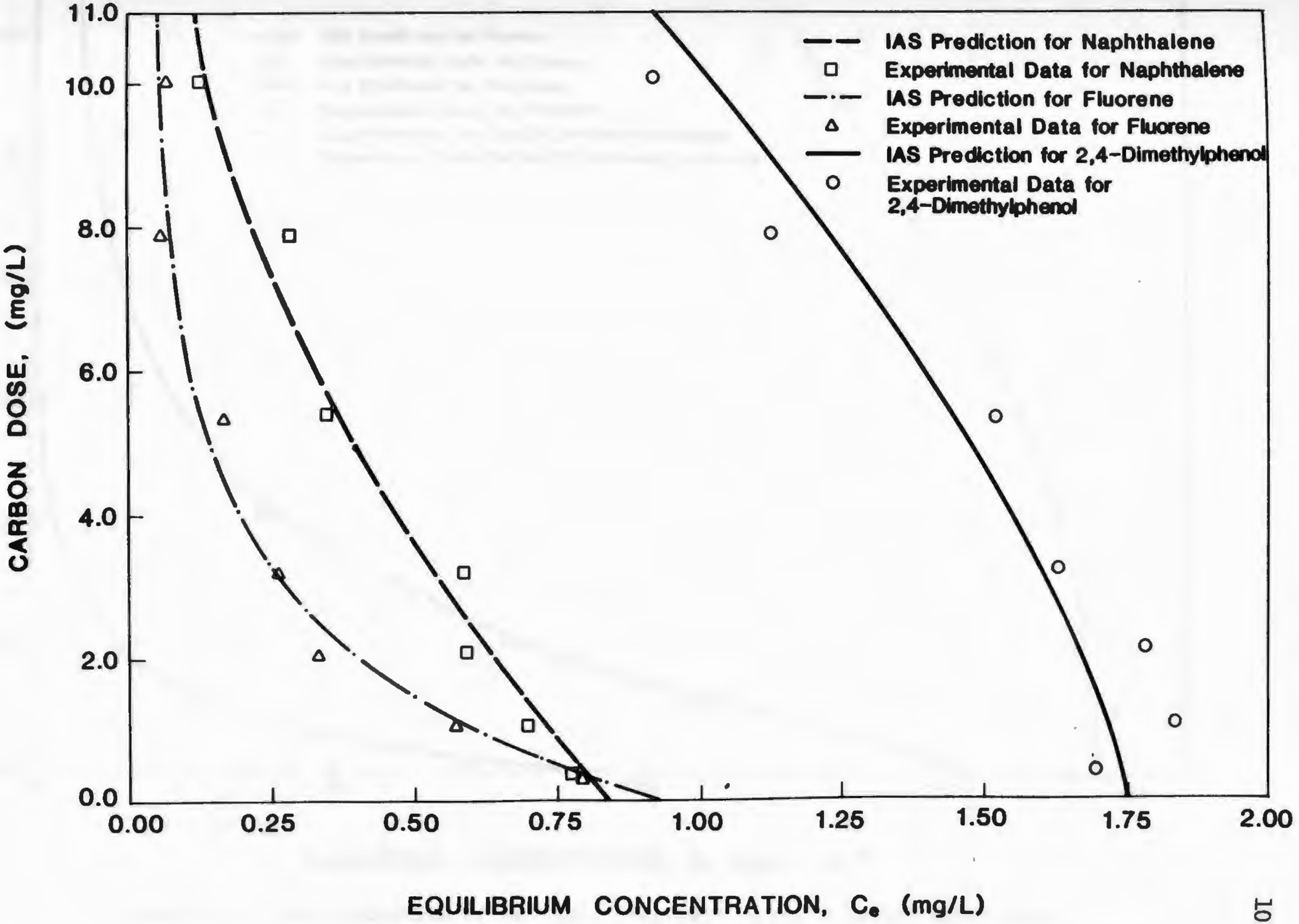


Figure 4-9 IAS Prediction of Multiple Component Mixture in Ultrapure Water Background (2,4-Dimethylphenol- Fluorene-Naphthalene)

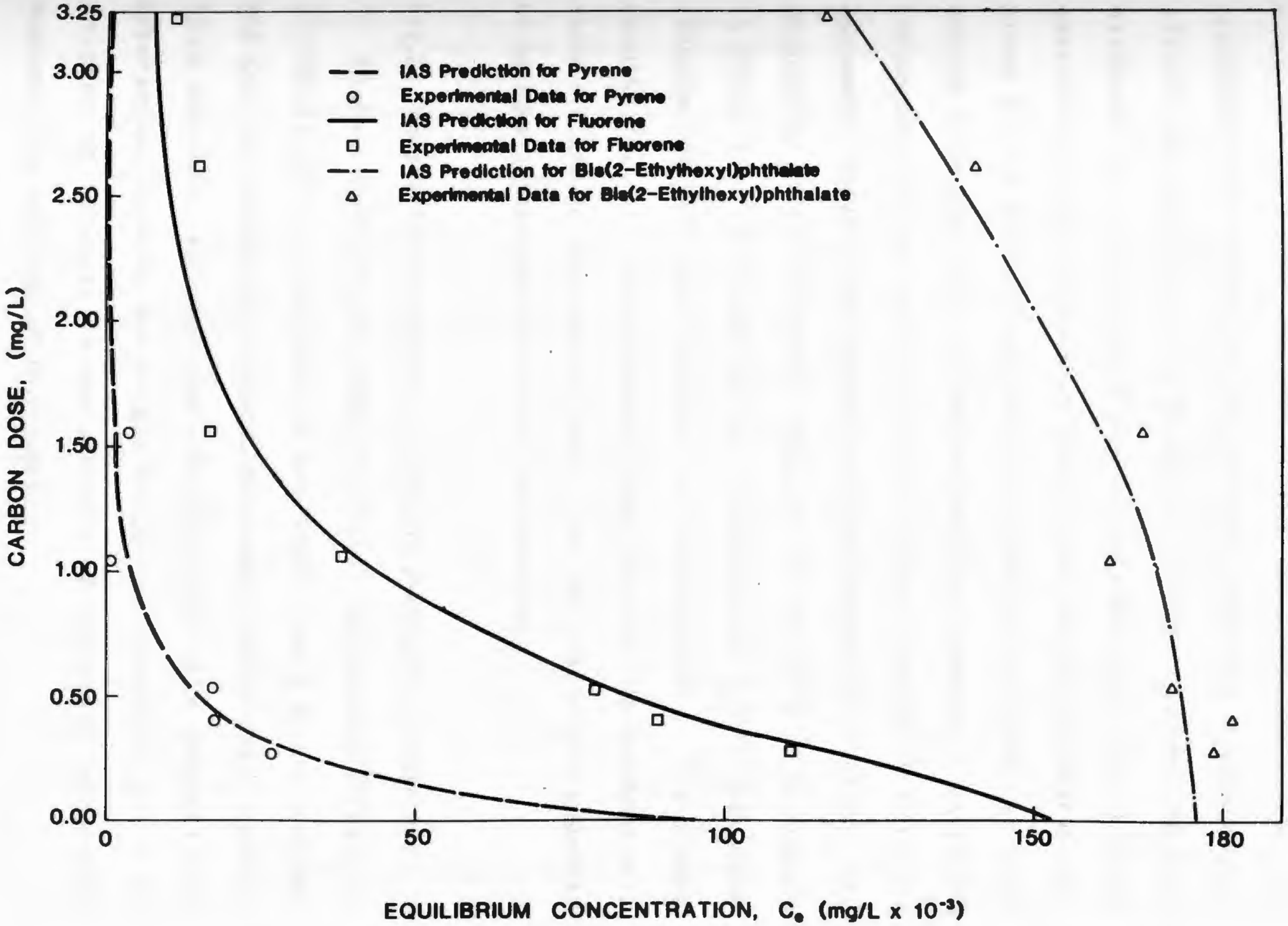


Figure 4-10 IAS Prediction of Multiple Component Mixture in Ultrapure Water Background (Pyrene-Fluorene-Bis 2-Ethylhexyl) phthalate

since the compounds that were studied had low solubilities. The precision of the single solute isotherm data can substantially affect IAS prediction. Within the three studied isotherm mixtures in an ultrapure water background, there were considerable differences in the initial solute concentrations. Since a long equilibrium time of 6 days was allowed, initial solute concentration variations were not expected to influence the accuracy of the results. This is supported again by the good agreement between IAS prediction and experimental data. The statistical linear regression analysis of the data is presented in Table 4-4. R-square values ranged between 0.878-0.994 which indicate the very good behavior of the IAS model. The t-test results fell into the acceptance limit for both the hypothesis of slope = 1 and an intercept of zero. The IAS prediction appeared to be equally accurate for all of the mixtures.

4.2.2 Competitive Adsorption in Complex Wastewater Background

In this part of the study the total background effect in a complex mixture composition was treated as a single compound and was represented by the dissolved organic carbon (DOC) content. This approach allowed the evaluation of the competitive interaction between any single solute or specific group of solutes of interest in the presence of a complex background mixture. The rational of this approach:

1. The evaluation of adsorption capacity and the diffusion rate of specific compounds in the presence of a complex background is

Table 4-4. Statistical Linear Regression Testing of IAS Theory Prediction Versus Observed in Ultrapure Water Background

Group	Compound	No. of Points	R-Square	Root MSE	F-Value	Estimate Intercept	T For $H_0:\beta_0=0$	STD Error of Estimate Intercept	Estimate Slope	T For $H_0:\beta_1=1$	STD Error of Estimate Slope
High Water Soluble Compounds	Naphthalene	8	0.992	0.814	698.0	0.783	1.54	0.509	1.019	0.487	0.039
	2,4-Dimethylphenol	8	0.986	1.107	435.4	0.900	0.61	1.487	0.951	-1.066	0.046
Low Water Soluble Compounds	Pyrene	5	0.929	3.593	66.0	0.201	0.11	1.843	1.103	0.762	0.136
	Fluorene	7	0.992	4.381	626.3	-3.117	-1.10	2.823	1.111	2.504	0.044
	Bis(2-Ethylhexyl) Phthalate	7	0.931	6.147	67.2	32.827	2.11	15.569	0.795	-2.115	0.097
Combined High-Low Water Soluble Compounds	2,4-Dimethylphenol	7	0.969	0.071	189.4	0.200	2.21	0.090	0.854	-2.357	0.062
	Naphthalene	7	0.878	0.104	43.3	-0.017	-0.23	0.075	0.989	-0.075	0.150
	Fluorene	7	0.994	0.023	1006.3	0.011	0.96	0.0119	0.986	-0.441	0.031

Statistical Values Obtained by SAS General Linear Models Procedure of great importance for actual process design for wastewater treatment.

2. Due to cost constraints and the present limitations in analytical methodology it is almost impossible to completely identify the composition of a wastewater.
3. The use of a fictive or surrogate background component like DOC can permit the use of available isotherm predictive models without the necessity of a major alternation.
4. The selection of a DOC parameter to represent the lump-sum background effect is significant for the following reasons: 1) DOC is easy to measure and insensitive to interferences commonly present in a complex wastewater, 2) only organic compounds have high affinity for activated carbon, therefore the presence of any other inorganic compounds such as heavy metals which are generally less adsorbable will not have a significant competitive background effect on adsorption in comparison to the DOC component.

The general procedure followed for conducting the isotherm tests was discussed previously in Section 3. However, a more detailed explanation of the procedures will be discussed in the following paragraph. The full-strength secondary wastewater effluent was collected as a composite sample on three consecutive days from the South Kingstown Wastewater Treatment Facility. The characteristics of wastewater effluents from secondary wastewater treatment facilities are consistent in composition within a narrow range. A very high portion of the DOC background is generally composed of humic substances, proteins, carbohydrate and microbial cells and lysis compounds. Prior to use the full-strength wastewwater was filtered to remove suspended solids and the three batches of different strength wastewaters were prepared by dilution with ultrapure water. Constants masses of 2,4-dimethylphenol, naphthalene and fluorene were dissolved in 20 ml of methylene chloride and introduced into each batch prior to buffering. Three days of constant mixing was utilized to allow for evaporating methylene chloride. The wastewater was then filtered through glass wool to remove any particles of undissolved organics and any remaining suspended solids before introduction into the isotherm bottles. Although this preparatory procedure was consistant for all wastewater batches a fixed initial concentration of the three compounds was not achieved. This was attributed to possible complexing of the organics during mixing. The effect of the variation of the initial concentrations of the specific compounds was minimal relative to the much higher total DOC concentration in the background of the mixture. Due to the potential presence of microorganisms in the wastewater, there exists the potential for biodegradation of some of the specific compounds which might affect the results of the isotherm study. However, the six days of equilibrium time which were allowed was too short to acclamate the microorganisms. Control samples for each group studied which contained no activated carbon were used to exclude any effects resulting from biodegradation and/or complexing.

An overall isotherm for the DOC background in secondary wastewater was evaluated. This isotherm related the total residual concentration of DOC to the solid phase loading. The results of this experiment are shown in Figure 4-11 and the corresponding raw data is presented in Appendix C Table C-4. The graph in Figure 4-11 presents a different kind of isotherm to that which is normally found. The curving downward of the isotherm line indicates that there is a nonadsorbable fraction of the DOC present in the wastewater background. Even with the addition of higher amount of carbon, there is still no substantial reduction of the DOC equilibrium concentration. The nonadsorbable fraction is indicated by the intersection of the graph with the x axis. For the secondary wastewater which was evaluated the fraction of the nonadsorbable compound is equivalent to about 50% of the total DOC. In order to evaluate the isotherm constants for the adsorbable fraction of the total DOC, the Freundlich and modified Freundlich models were fitted to the rising part of the curve (drawn in a solid line). The isotherm parameters calculated by use of the Freundlich and modified Freundlich models are presented in Table 4-5. These data indicate a much lower adsorption capacity of DOC parameters as compared to any of the selected priority organics tests.

Theoretically the competition effect due to the presence of low adsorbable compounds is weak in comparison to the competitive effect of resulting from strongly adsorpable compounds. However as will be shown later a very high competitive effect can still be induced. The competition between the strongly adsorbed and

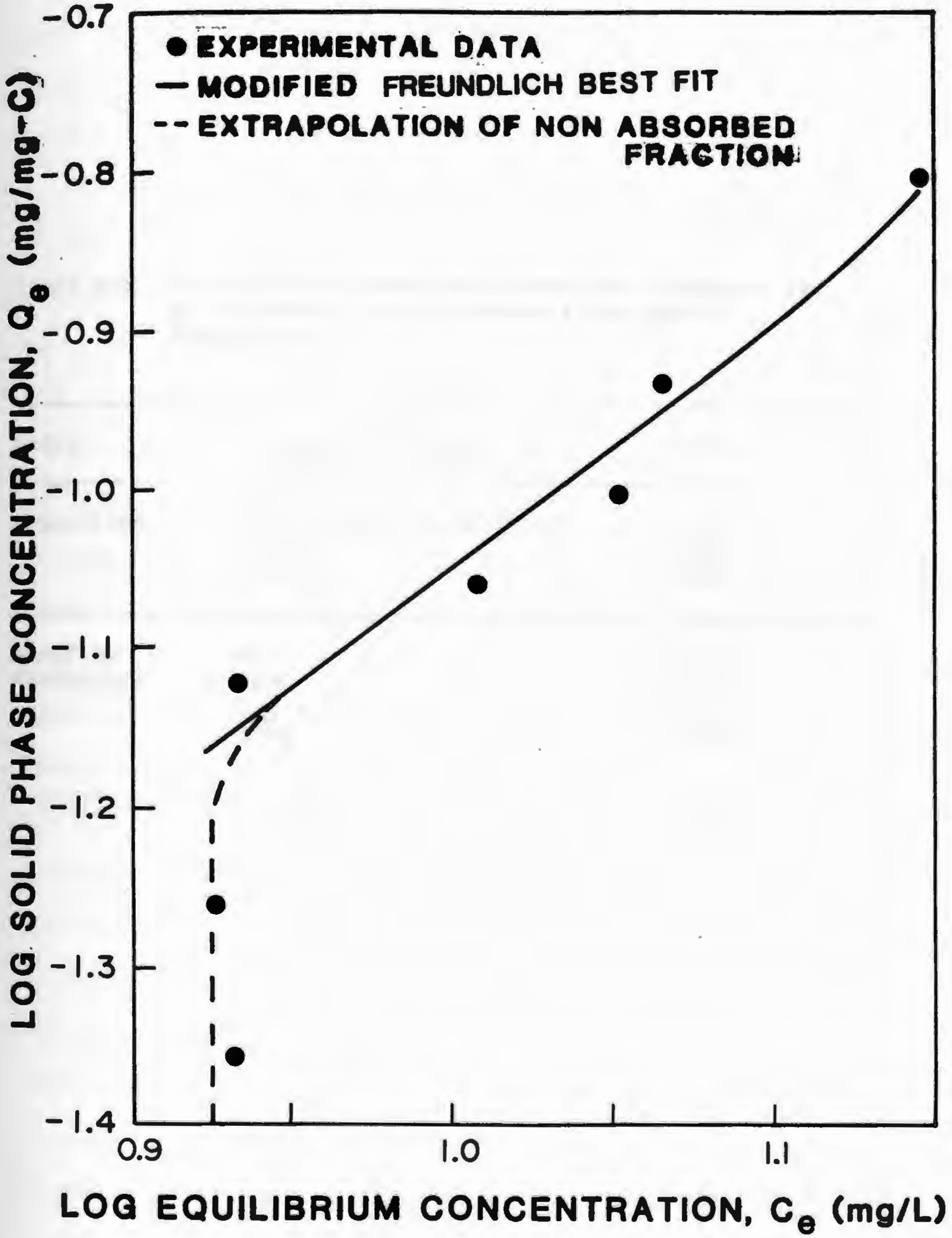


Figure 4-11 Adsorption Isotherm of DOC Background in Secondary Wastewater Effluent

Table 4-5. Freundlich and Modified Freundlich Parameters for DOC Parameter in the Secondary Wastewater Background

Model	Isotherm Constant	Value
Freundlich	K, (µM./g) (L/µM.)**1/Nf	0.224
	1/Nf	0.667
	R**2	0.970
Modified Freundlich	Nf	0.521
	logK	3.749
	log q_x	-1.961
	R**2	0.941

weakly adsorbed DOC lump-sum parameter is not site preferential. Molecular volume is another important factor in the adsorption process. Retardation of adsorption of the strongly adsorbed compounds can occur by the presence of high molecular volume compounds in the background mixture as was the case with the secondary wastewater effluent background.

The results of the IAS prediction and the experimental data of the specific priority organics 2,4-dimethylphenol and naphthalene isotherms in different DOC strengths of secondary effluent wastewater background are shown in Figure 4-12 to Figure 4-14 and their corresponding raw data are presented in Appendix C, Table C-5 to Table C-7. A close observation of these figures show that the IAS model underpredicts the experimental results indicating an increase of positive displacement with the increase of DOC background concentration. Also, there is a minimum dose of 3.5-5.5 mg/ℓ of activated carbon which is required before any measureable adsorption of the specific priority organics can be detected. Such behavior indicates that the DOC background actually retards the adsorption of the more strongly adsorbed compound rather than preferentially competing with them on the adsorption sites. Similiar results were obtained when the effluent of the activated sludge pilot plant treating petroleum refinery wastewater was tested as shown in Figure 4-15 with the corresponding raw data in Appendix C, Table C-8. In an attempt to quantify the retardation factor with the increase of the DOC background concentration, the experimental data above the minimum activated carbon dosage previously discussed was fitted with the

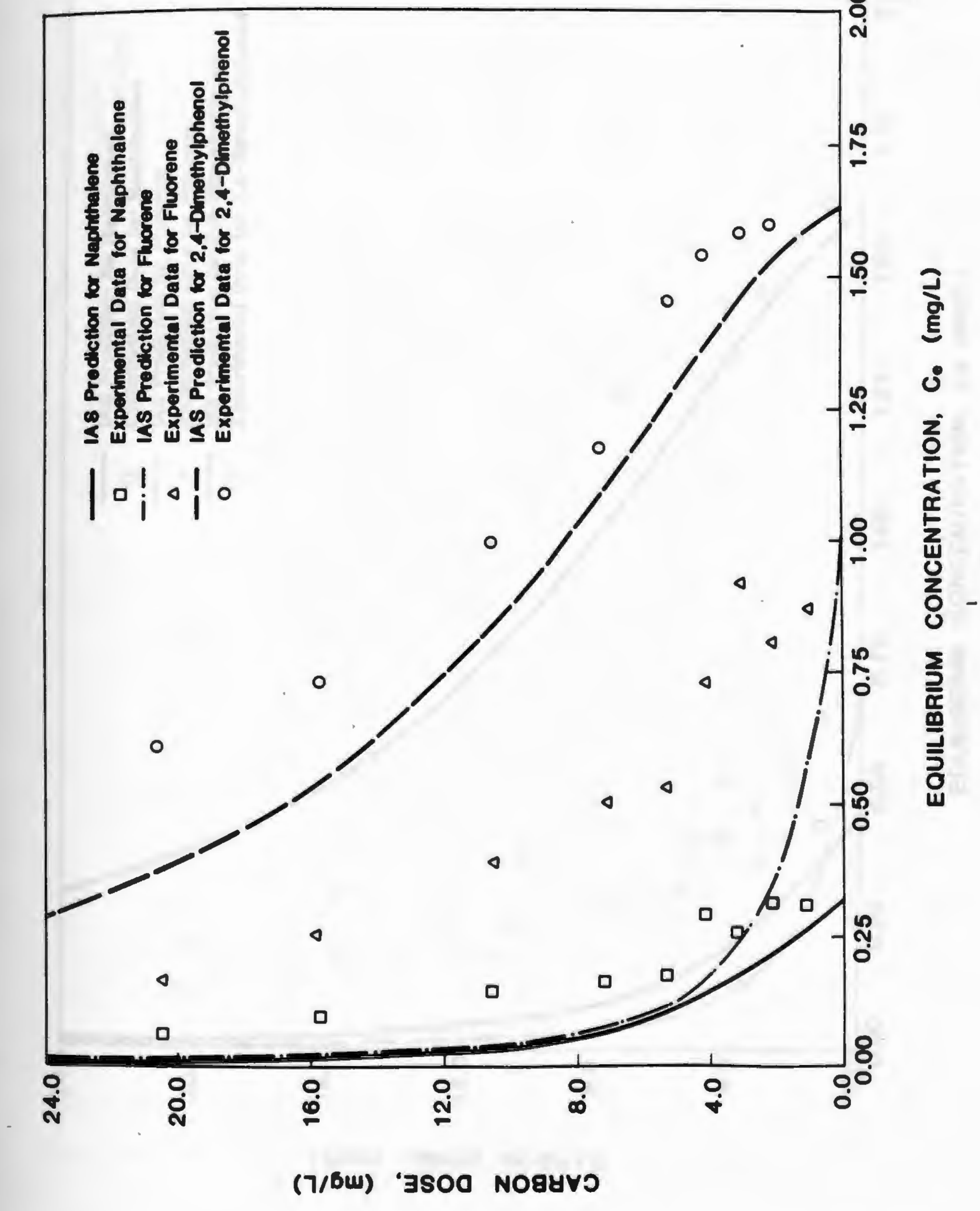


Figure 4-12 IAS Prediction in Complex Background Mixture (10.1 mg/l DOC) - Secondary Wastewater Effluent

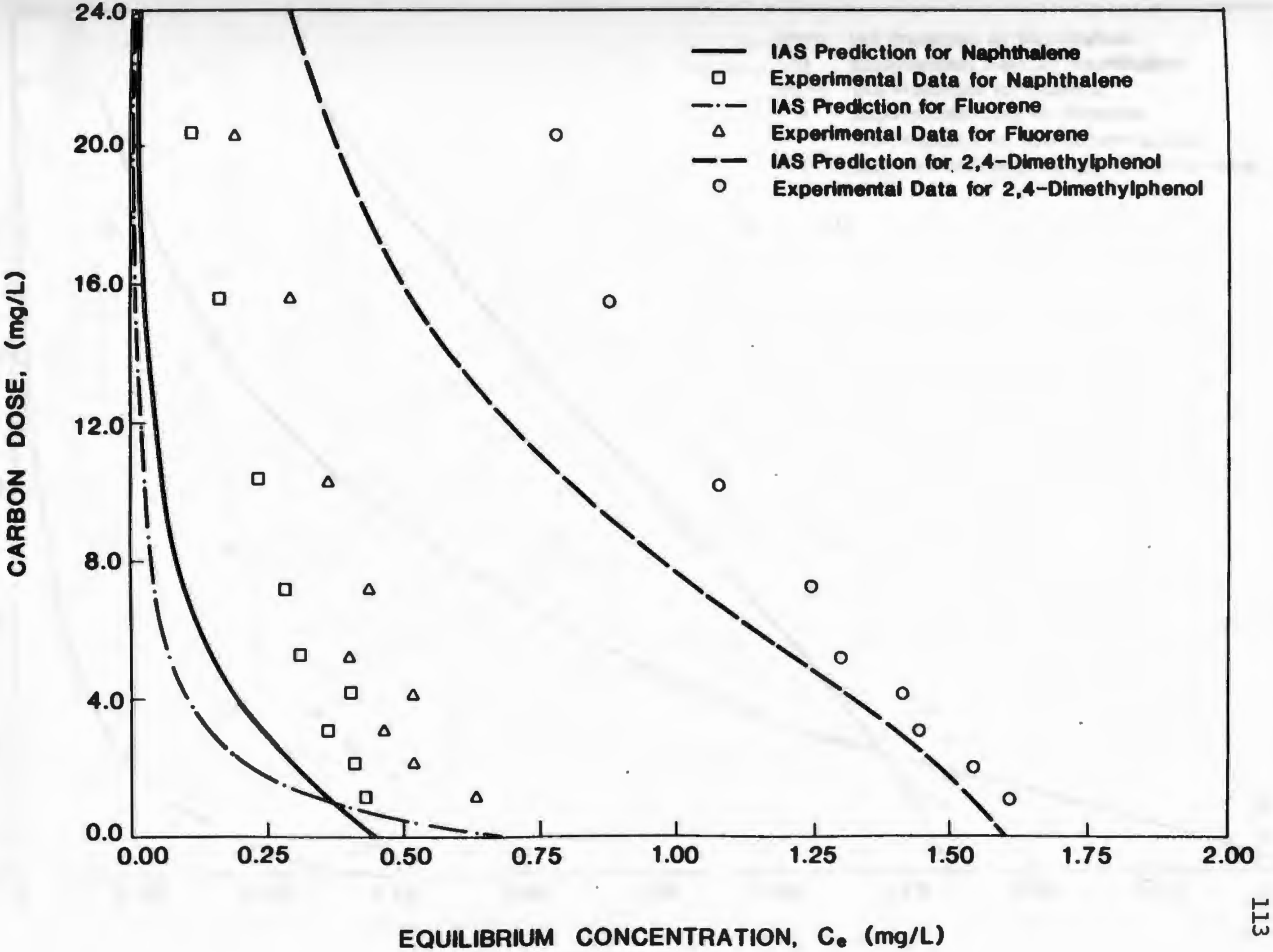


Figure 4-13 IAS Prediction in Complex Background Mixture (19.1 mg/l DOC) - Secondary Wastewater Effluent

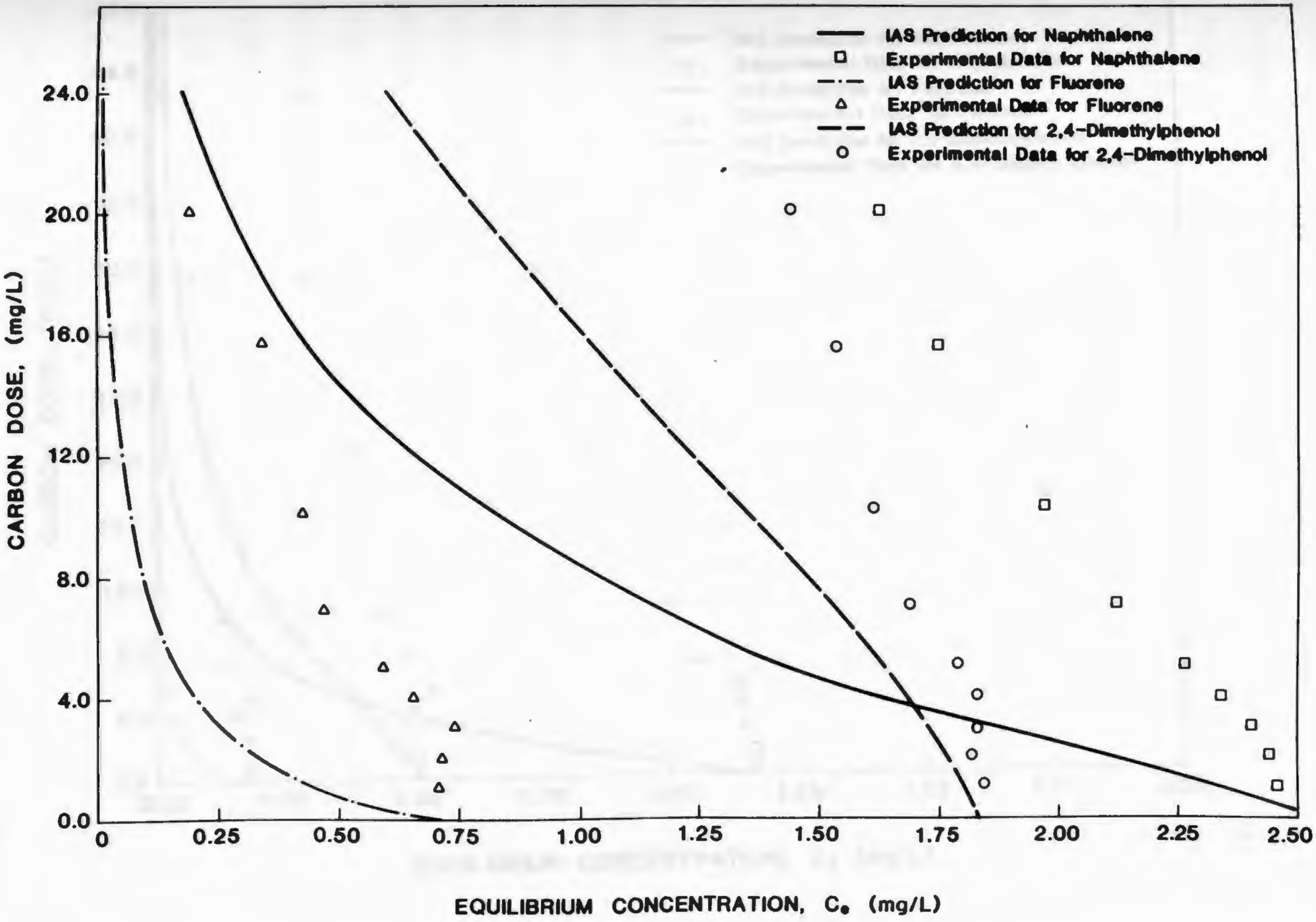


Figure 4-14 IAS Prediction in Complex Background Mixture (27.3 mg/l DOC) - Secondary Wastewater Effluent

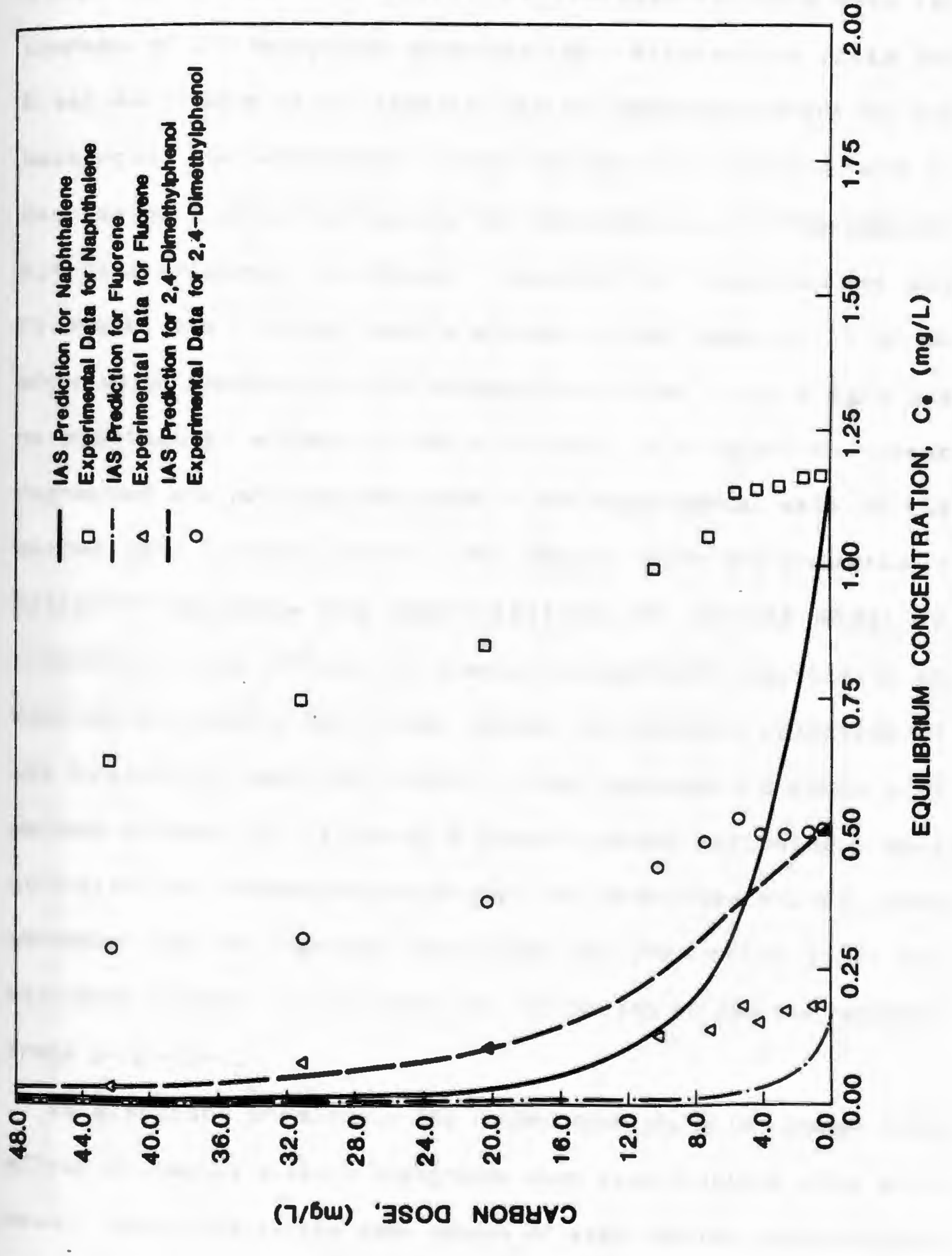


Figure 4-15 IAS Prediction in Complex Background Effluent (18.1 mg/l DOC) - Secondary Treated Refinery Wastewater Effluent

Freundlich and modified Freundlich model. The calculated isotherm parameters are presented in Table 4-6. The Freundlich isotherm parameter K indicates decrease in value with the increase of DOC background concentration. Figure 4-16 plots the K values of each of the studied specific compounds versus the DOC background concentration. This indicates a clear trend of decreasing K with increasing DOC concentration for the compound 2,4-dimethylphenol is shown. However for naphthalene and fluorene, the K values reach a minimum in the range of 125 to 146 after which lowering the DOC concentration from 19 to 10 mg/L has no substantial affect on the K values. A statistical linear regression analysis was performed on the experimental data of the competitive isotherm study. The results which are presented in Table 4-7 indicate the unsuitability of the IAS model in predicting the effect of complex background competition on adsorption. Most of the T test values indicated a rejection of the hypothesis that the slope = 1 and intercept = 0 within a 95 percent probability. Although R-square values indicated a good correlation between experimental and predicted values, this parameter does not indicate how close the prediction is to the measured values. It is more an indication of how the relative trend progresses.

As discussed previously IAS failed predicting the competitive effect of complex mixture background when single solute data were used. Justified by the same amount of experimental work required for both single solute and complex mixtures isotherm parameters evaluation, the isotherm parameters for the organic compounds in

Table 4-6. Measured Mixed Component Isotherm Constants in Various Wastewater Background

Isotherm Constants	2,4 Dimethylphenol				Naphthalene				Fluorene			
	DOCI	DOCII	DOCIII	REF	DOCI	DOCII	DOCIII	REF	DOCI	DOCII	DOCIII	REF
K,(M./g)(L/M.)**1/Nf	0.687	0.206	0.043	0.535	14.390	0.011	1.368	0.067	0.005	0.0102	0.209	0.246
K,(µM./g)(L/µM.)**1/Nf	31.49	170.04	254.15	28.80	38.44	140.64	127.06	40.15	146.50	125.50	246.26	35.04
1/Nf	0.649	0.3763	0.3124	0.5124	0.8758	0.2916	0.5309	0.5030	0.2248	0.2899	0.4822	0.4765
NFSY	1.351	1.9269	2.8684	1.4399	1.0796	3.1738	1.4990	1.8402	3.7940	3.1273	2.0479	1.5810
FSY	-0.163	-0.7838	-1.5317	-9.4558	1.0841	-1.9643	0.1360	-1.1670	-2.2642	-1.9908	-0.6803	-0.6083
Log(q_x)	-3.806	-3.4163	-3.2955	-4.2728	-3.3564	-3.8807	-4.0426	-4.0401	-3.8105	-3.8722	-3.6047	-4.7022

DOCI = Secondary treatment facility effluent (DOC = 27.3 mg/l)
DOCII = Secondary treatment facility effluent (DOC = 19.1 mg/l)
DOCIII = Secondary treatment facility effluent (DOC = 10.1 mg/l)
REF = Secondary treated refinery wastewater effluent (DOC = 18.1 mg/l)
Constants Equations: are presented previously
NFSY = Nf in modified Freundlich Model
FSY = log K in modified Freundlich Model
log(q_x) = Modified Freundlich Parameter

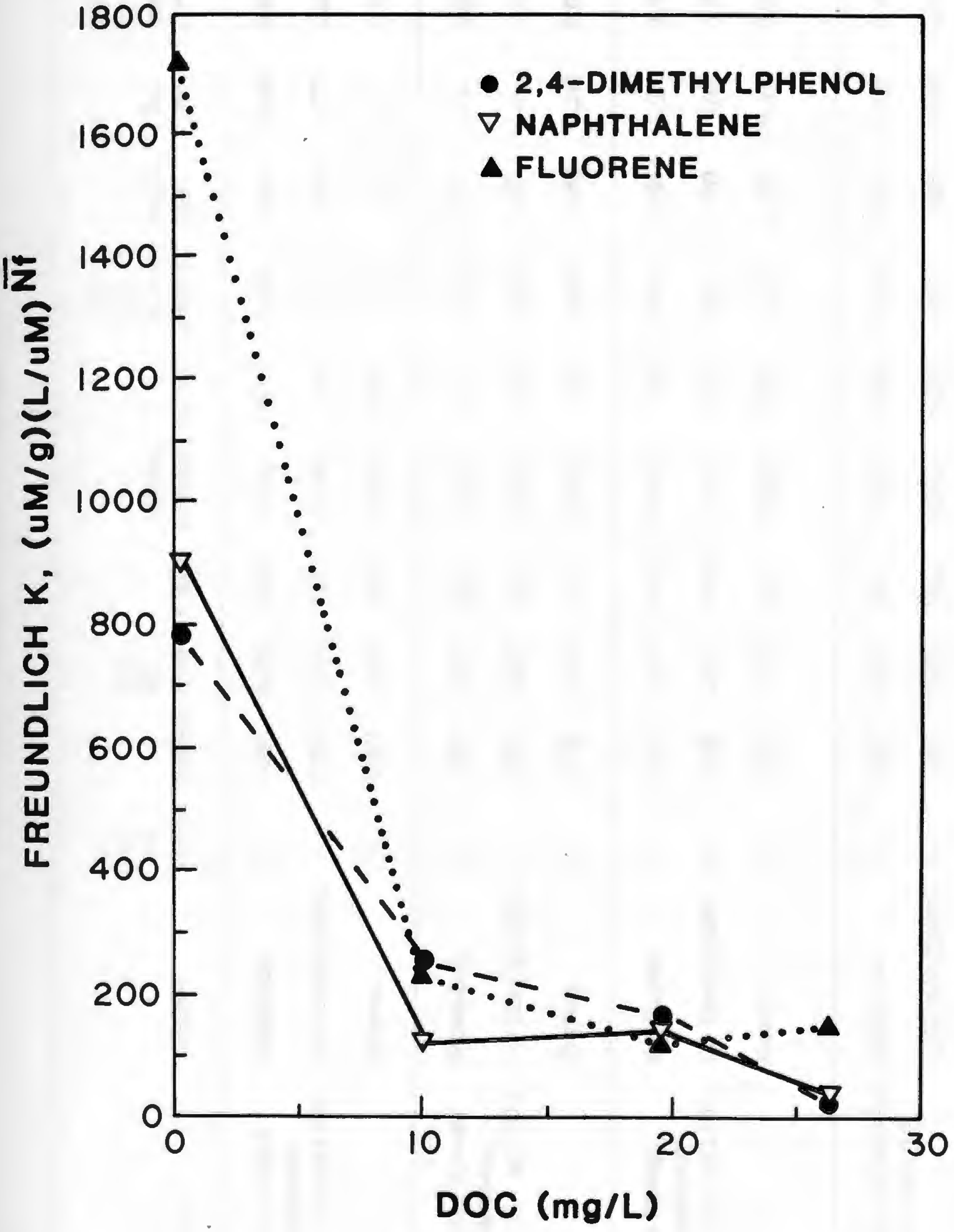


Figure 4-16 Variation of Freundlich Isotherm Parameter "K" in Different Strengths of Complex Mixture Background

Table 4-7. Linear Regression Analysis of IAS Theory Prediction for Mixed Component in Different Strengths of Complex Mixture Background

Group	Compound	No. of Points	R-Square	Root MSE Error	F-Value	Estimate Intercept	T For $H_0:\beta_0=0$	STD Error of Estimate Intercept	Estimate Slope	T For $H_0:\beta_1=1$	STD Error of Estimate Slope
Full Strength Wastewater (27.3 mg/l DOC)	Naphthalene	6	0.991	0.058	459.8	-3.007	-16.15	0.186	1.970	10.66	0.091
	2,4-Dimethylphenol	6	0.947	0.093	71.1	-2.399	-5.42	0.443	2.256	4.70	0.268
	Fluorene	6	0.937	0.019	59.8	-0.074	-3.20	0.023	0.391	-12.17	0.051
Medium Strength Wastewater (19.1 mg/l DOC)	Naphthalene	6	0.920	0.021	46.2	-0.057	-2.51	0.0226	0.577	-4.98	0.085
	2,4-Dimethylphenol	6	0.977	0.067	167.5	-0.324	-3.35	0.096	1.084	1.004	0.084
	Fluorene	6	0.745	0.020	11.7	-0.057	-1.88	0.030	0.2699	-9.248	0.079
Low Strength Wastewater (10.1 mg/l DOC)	Naphthalene	6	0.918	0.016	44.8	-0.028	-1.83	0.015	0.594	-4.579	0.089
	2,4-Dimethylphenol	6	0.986	0.053	279.4	-0.221	-3.13	0.071	1.040	0.646	0.062
	Fluorene	6	0.930	0.018	53.1	-0.050	-2.74	0.018	0.286	-18.308	0.039
Refinery Wastewater (18.1 mg/L DOC)	Naphthalene	6	0.671	0.087	8.2	-0.381	-2.06	0.185	0.574	-2.132	0.201
	2,4-Dimethylphenol	6	0.979	0.024	182.1	-0.433	-9.20	0.047	1.528	4.663	0.113
	Fluorene	6	0.943	0.018	66.4	-0.047	-3.87	0.012	0.567	-6.232	0.067

Statistical Values Obtained by SAS General Linear Models Procedure complex mixture were used in the IAS Model. The IAS prediction and experimental data using multi-solute isotherm constants are presented in Appendix C, TAble C-9 to Table C-11. A substantial improvement in the IAS predicability occurred using the multi-solute isotherm constants as shown in Appendix C table C-9 to C-11. The use of Freundlich isotherm constants derived from complex mixture data has been evaluated for predictions in the batch rate study, the minicolumn study and the pilot plant study.

4.3 Batch Rate Studies

- Determination of Batch Rate Mass Transport Coefficients

For each of the specific organic compounds studied, the pore diffusion and the film transfer coefficients which are used in the models tested for predicting adsorption breakthrough curves must be determined. Wilke and Chang[56] developed an empirical correlation for Calculating the molecular diffusion coefficients of organic compounds in dilute solutions. They found that the molecular diffusion of certain compounds is a function of its molal volume, molecular weight of solvent, temperature, and the viscosity of the solvent. They expressed the correlation for molecular diffusion in water solvent by the equation:

$$D_L = \frac{7.4 \times 10^{-8} (\phi M_w)^{0.5} \; T}{\mu \; V_m^{0.6}} \qquad (4\text{-}11)$$

where D_L = Molecular diffusion of the compound, cm^2/sec

M_w = Molecular weight of the solvent, g

μ = Solution viscosity, centipoise

T = Temperature, ^{o}K

ϕ = Association factor for solvent and equal to 2.6 for water

V_m = Molal volume of solute at normal boiling point, $cm^3/mole$

If the molal volume is not known, it can be calculated according to the procedure described by Treybal[57].

The film transfer coefficient in a completely mixed batch reactor used in rate studies was calculated according to the empirical relationship described by Letterman et al.[98] in the form below:

$$\frac{2k_f R}{D_L} = 2 + 0.64 \left[(R_N)^6\right]^{0.197} S^{0.33} \qquad (4\text{-}12)$$

where k_f = Film transfer coefficient, cm/sec

D_L = Molecular diffusion coefficient, cm^2/sec

R = Radius of activated carbon pellet, cm

S = Dimensionless Schmidt's number

R_N = Dimensionless Reynold's number

The dimensionless S and R_N are defined in the following equations

$$S = \frac{\mu}{\rho_L D_L} \qquad (4\text{-}13)$$

$$R_N = \frac{(2R)^{2/3}\ P_s^{1/6}}{\left(\frac{\mu}{\rho_L}\right)^{1/2}} \qquad (4\text{-}14)$$

in which μ = Viscosity, Kg/cm sec

ρ_L = Density of water, Kg/cm^3

P_s = Specific power, cm^2/sec^3

The pore diffusion coefficient (D_p) was set equal to the molecular diffusion coefficient (D_L) times the void fraction of the activated carbon (ε_p).

$$Dp = D_L * \varepsilon p \qquad (4\text{-}15)$$

Based on the manufacturer's data ε_p is considered equal to 0.64 for activated carbon type F-400.

The previously discussed coefficients were calculated for each of the compounds studied. Their values are presented in Table 4-8.

The effective surface diffusion coefficients, D_s, were determined experimentally from completely mixed batch rate studies according to Hand et al.[55] The procedure used is described in Section 3 of this report. The experiments were performed in the following sequence and the rationale for their selection is discussed accordingly.

1. Mixed Component Batch Rate Study in Ultrapure Water Background

Table 4-8. Results of Batch Mass Transport Coefficients in Ultrapure Water Background

Compound	Film Transfer k_f (cm/sec)	Molecular Diffusion D_L (cm^2/sec)	Pore Diffusion D_p (cm^2/sec)	Surface Diffusion D_s (cm^2/sec)
2,4-Dimethylphenol	$1.304\text{x}10^{-2}$	$0.758\text{x}10^{-5}$	$0.485\text{x}10^{-5}$	$4.450\text{x}10^{-11}$
Naphthelene	$1.330\text{x}10^{-2}$	$0.757\text{x}10^{-5}$	$0.484\text{x}10^{-5}$	$3.369\text{x}10^{-11}$
Fluorene	$1.190\text{x}10^{-2}$	$0.633\text{x}10^{-5}$	$0.404\text{x}10^{-5}$	$1.985\text{x}10^{-11}$

The effective surface diffusion coefficients for the compounds 2,4-dimethylphenol, naphthalene and fluorene were determined in three separate batch runs in the presence of each other in ultrapure water background. The required carbon dosage to achieve a 50% removal was calculated based on the initial concentration of the compound in which the D_S value was to be determined disregarding the presence of the other compounds. With this sequence of experimentation any effect on the D_S evaluation due to the competitive effect by the other compounds is now accounted for. The experimental data analysis for calculating the D_S values for each of the studied compounds is presented in Appendix D, Table D-1 to Table D-3. The homogeneous surface diffusion model (HSDM) and the pore and homogeneous surface diffusion model (PSDM) were both used to predict the mixed component batch rate data as shown in Figure 4-17 to Figure 4-19. The corresponding raw data are presented in Appendix D Table D-4 to Table D-6. For each compound, HSDM substantially underpredicted the rate of diffusion. Such behavior was expected as the input data for the model considered only one compound while experimentally the other two compounds were present. The D_S values were calculated based on the experimental data so these values actually reflect the experimental behavior of the system. However, the deviation of the HSDM model prediction may theoretically reflect the competition effect of the other compounds. The PSDM model gave a better prediction of the rate of diffusion by allowing for the diffusion of the compound through the intersticial liquid in the pore which again

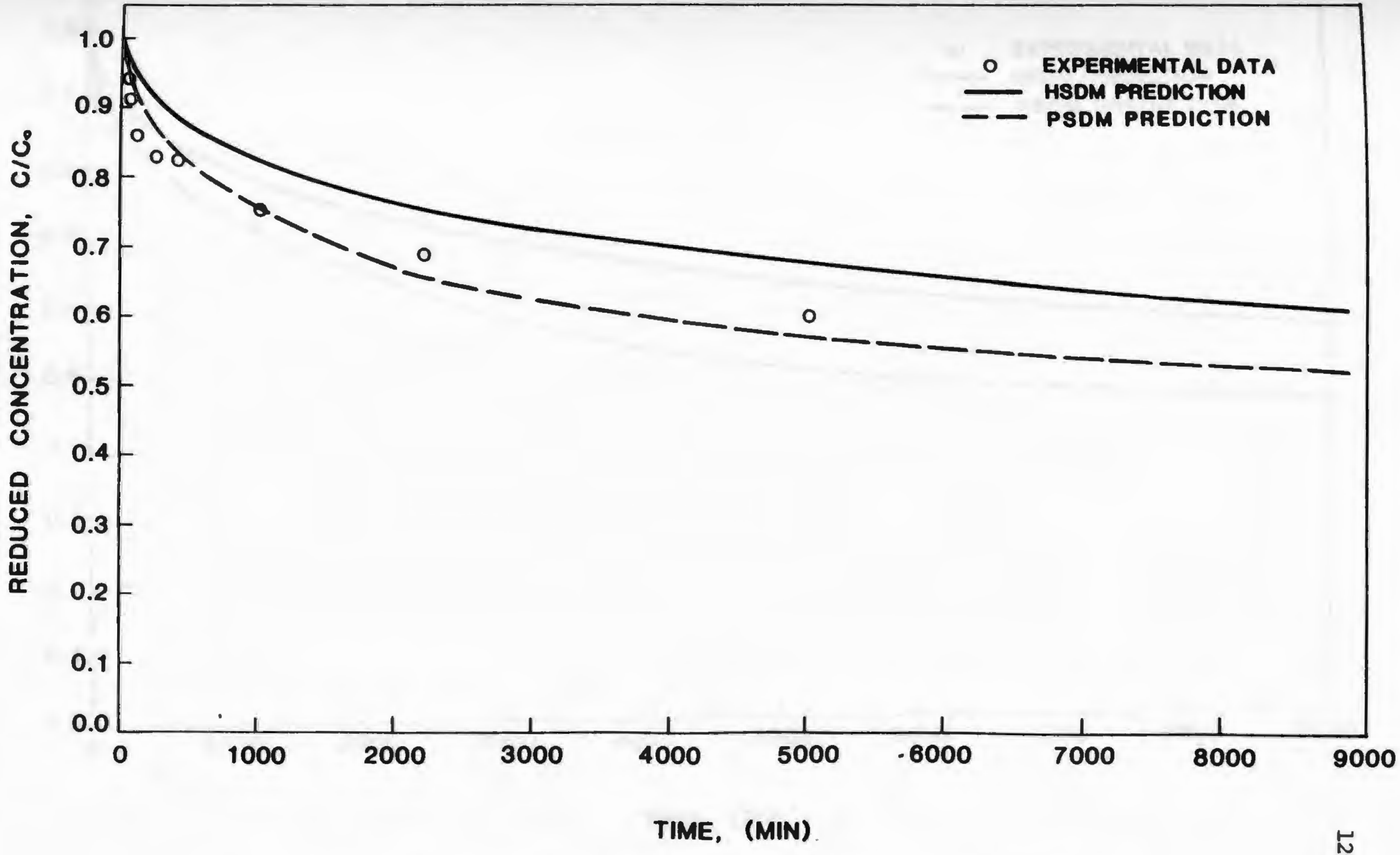


Figure 4-17 Multiple Component Batch Rate Study for 2,4-Dimethylphenol in Ultrapure Water Background

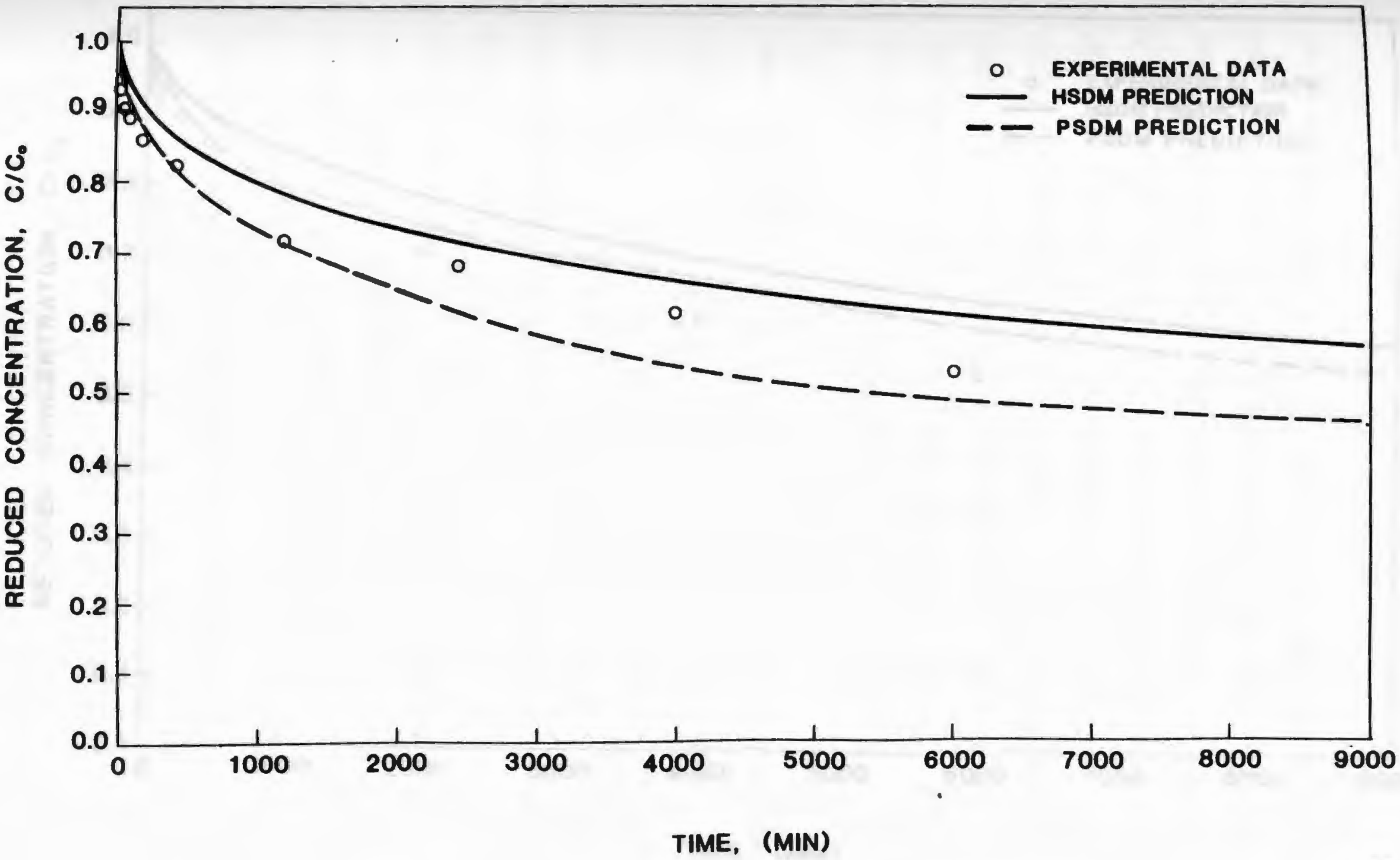


Figure 4-18 Multiple Component Batch Rate Study for Naphthalene in Ultrapure Water Background

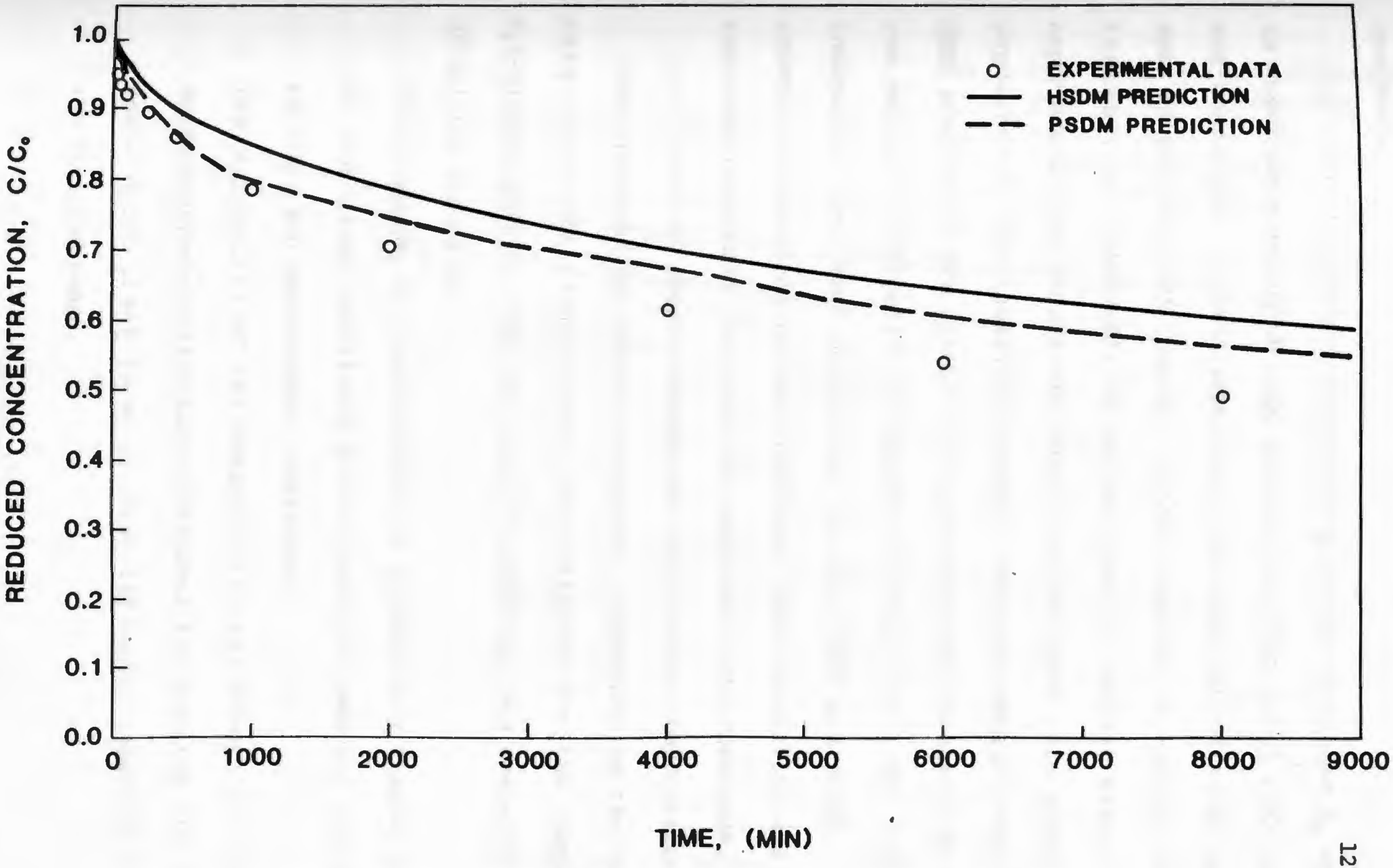


Figure 4-19 Multiple Component Batch Rate Study for Fluorene in Ultrapure Water Background

illustrates the importance of pore diffusion in the adsorption phenomena.

In order to evaluate the validity of the calculated D_s values in mixed component batch rate studies, another batch rate study was conducted. In this experiment, the required activated carbon dose to achieve a 50% removal of the compound no longer holds. Instead, an intermediate carbon dose to achieve measurable experimental data points was selected and a batch rate study was conducted as previously discussed. The experimental, PHSDM and HSDM predictions are plotted in Figure 4-20 and the corresponding raw data are presented in Appendix D Table D-7. The results indicate a very good prediction by both PSDM and HSDM. The extent of variation between HSDM and PSDM prediction was much less than previously indicated for each one of the compounds.

2. Effect of Complex Background on Diffusion Coefficients

The effect of the complex background composition on the batch rate diffusion coefficient was evaluated for the compound 2,4-dimethylphenol. The rationale of selecting this compound out of all the others is:

- The compound is representative of a chemically similar group of wide range substituted phenols that are commonly found in refinery and petrochemical wastewater.
- The solubility of the compound is high enough so a high concentration solution can be prepared for spiking the full scale pilot plant to an produce influent concentration in the required range.

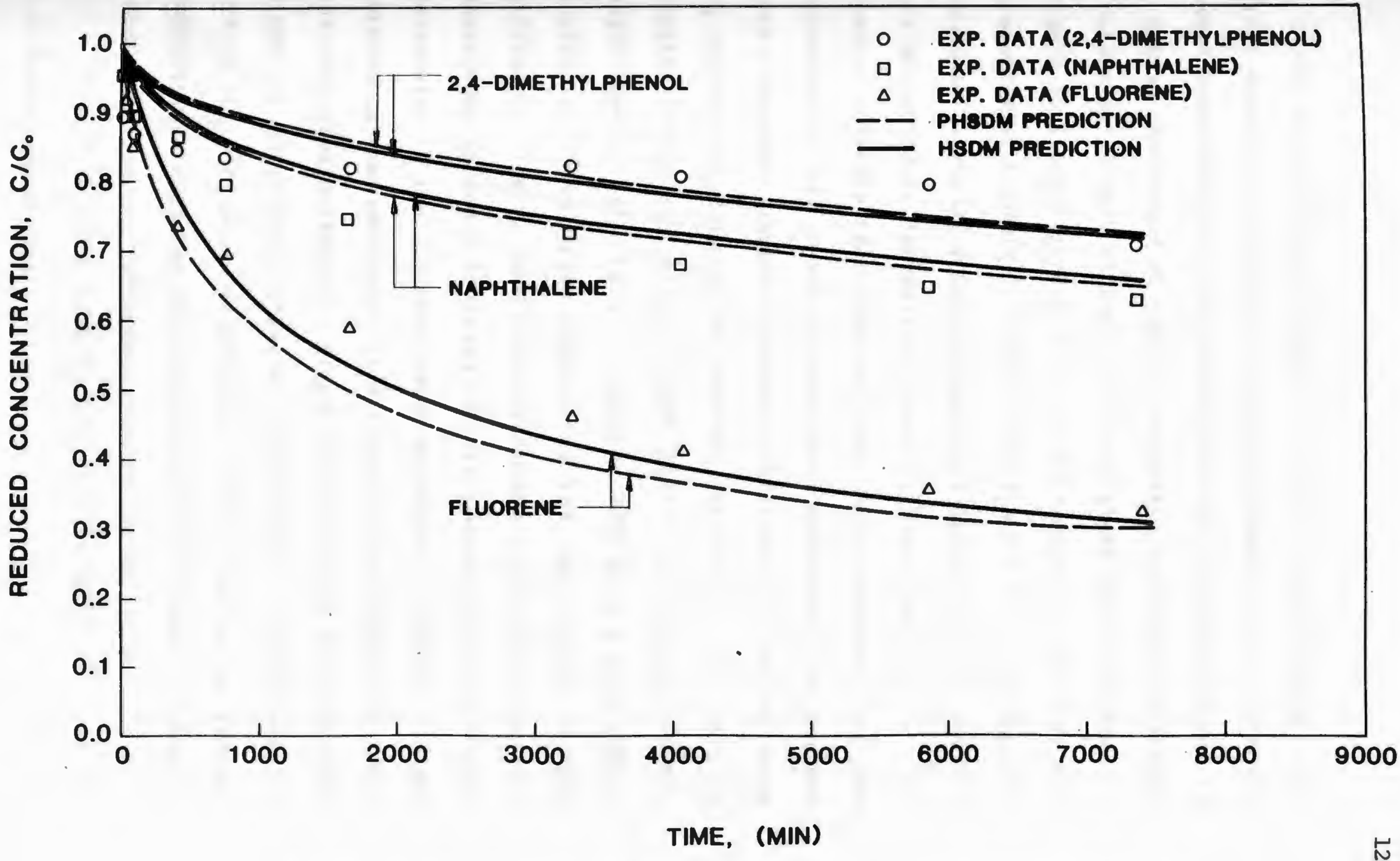


Figure 4-20 Multiple Component Batch Rate Study in Ultrapure Water Background

Two single component batch rate studies were conducted. The first experiment included 2,4-dimethylphenol in an ultrapure water background and the second included 2,4-dimethylphenol in a complex background of typical secondary wastewater effluent containing 20 mg/L of DOC. The rate study data are shown in Figure 4-21 and Figure 4-22. The corresponding raw data are presented in Appendix D, Table D-8 and Table D-9. D_s values were calculated using the procedure described before and the results are presented in Appendix D, Table D-10 and Table D-11. The results indicate that HSDM and PSDM both underpredicted the experimental data in the ultrapure water background. For the case with a secondary treatment wastewater effluent background using D_s values and Freundlich isotherm parameters calculated in complex background mixture HSDM still underpredicted the experimental rate data. However, PSDM gave a much better prediction which again emphasizes the importance of pore diffusion. The D_s coefficient calculated in the complex mixture background showed a decrease of 41% compared to the value calculated in the ultrapure water background. There is no clear relation between adsorbability defined by the Freundlich model and effective diffusion. Higher adsorbability does not mean higher the effective diffusion coefficients. The decrease of effective diffusion coefficient due to complex background composition indicates the presence of the retardation factor which slows down the diffusion within the carbon pellet.

4.4 Minicolumn Studies

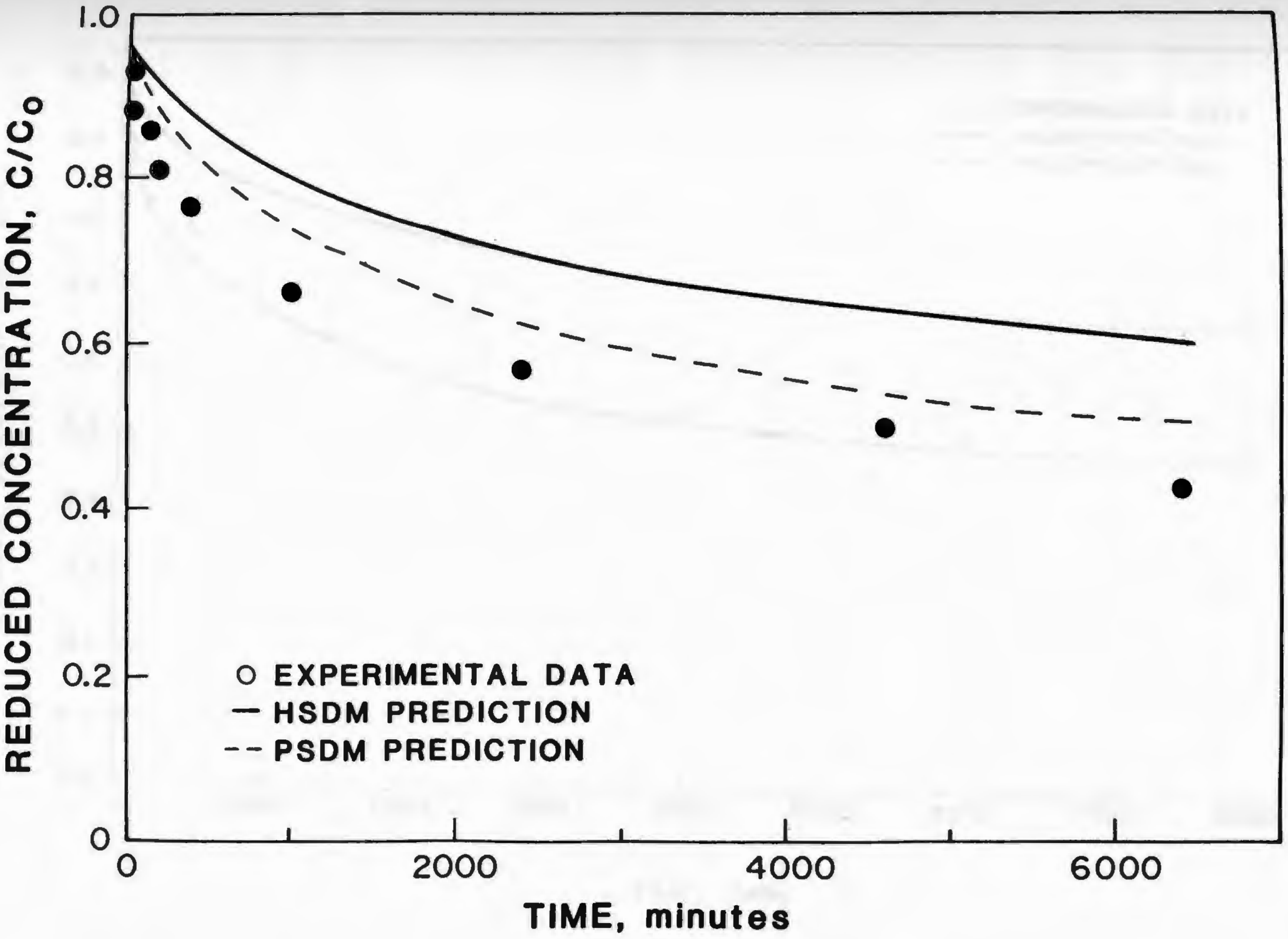


Figure 4-21 Single-Solute Batch Rate Study for 2,4-Dimethylphenol in Ultrapure Water Background

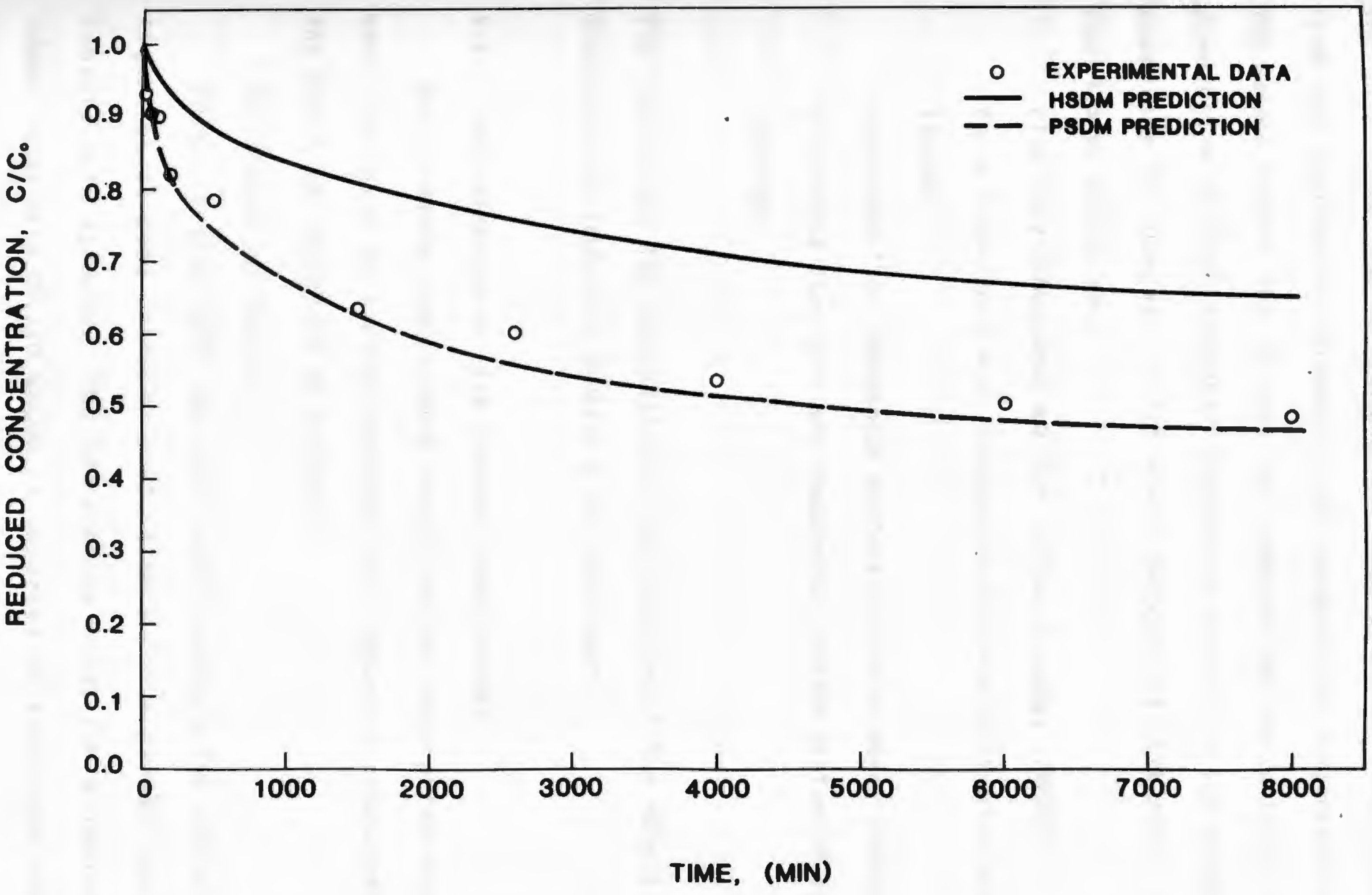


Figure 4-22 Single-Solute Batch Rate Study for 2,4-Dimethylphenol in Complex Mixture Background

The minicolumn study was conducted for two main reasons. The first reason was to evaluate the film transfer coefficients from the spontaneous breakthrough dimensionless concentrations. The second reason was to test and compare the validity of the prediction of four computer adsorption models on the specific compounds of interest in different background mixtures. The four tested models were:

- Plug flow homogenous surface diffusion model (PHSDM)
- Plug flow pore and homogenous surface diffusion model (PPSDM)
- Dispersed flow homogenous surface diffusion model (DFHSDM)
- Dispersed flow pore and homogenous surface diffusion model (DFPSDM)

The theory and the mathematical formulation of the models are discussed previously in Section 2 of this report.

4.4.1. Determination of Film Transfer Coefficients

Film transfer coefficients in a fixed bed adsorption column were evaluated by various methods using empirical relationships and analytical solutions as follows:

- Williamson Correlation

This correlation[62] was developed originally for evaluating liquid-phase mass transfer coefficients for a packed bed of benzoic acid spheres. The correlation holds for a Reynold's number range of 0.08-120 which is expected in activated carbon adsorption column applications. The equation which describes this correlation is:

$$\frac{k_f}{V_s} S^{0.58} = 2.4 R_N^{-0.66} \quad (4\text{-}16)$$

where V_S = superficial velocity in column, cm/sec. The rest of the parameters are defined previously.

- Wakao and Funazkri Correlation

This correlation[63] was developed for evaluating the effect of dispersion coefficients in dilute solution and applied extensively for estimating film transfer coefficients in packed bed differential columns. The correlation is applicable for Reynold's number in the range of 3-10,000. the equation which describes this correlation is:

$$\frac{2\ k_f\ R}{D_L} = 2 + 1.1\ R_N^{0.6}\ S^{0.33} \quad (4\text{-}17)$$

All the parameters in this correlation are defined previously

- Analytical Solution

Levenspiel[58] discussed an analytical solution for the determination of film transfer coefficient from the spontaneous breakthrough concentration in a minicolumn. He included dispersion terms in this solution:

$$C/C_o = \frac{4a \exp(P_e/2)}{(1+a)^2 \exp(a\ P_e/2) - (1-a)^2 \exp(-a\ P_e/2)} \qquad (4\text{-}18)$$

where P_e = Peclet number = $V_s L/D_e \varepsilon$ (4-19)

St = Stanton number = $k_f L(1-\varepsilon)/R\ V_s$ (4-20)

$a = (1+12\ St/P_e)^{0.5}$

The dispersion coefficient, D_e is estimated by the correlation proposed by Fried[99].

$$D_e = D_L \left(0.67 + 1.15\ (V_s R/\varepsilon\ D_L)^{1.2}\right) \qquad (4\text{-}21)$$

All these parameters are defined previously.

The results of the calculated packed column film transfer coefficients for 2,4-dimethylphenol, naphthalene and fluorene are presented in Table 4-9 along with other diffusion coefficients.

4.4.2 Results of Multiple Component Mixtures in Ultrapure Water

A Minicolumn fixed component study was conducted in ultrapure water background. The operating conditions of the columnn as well as the diffusion, isotherms and film transfer coefficients required for predicting each minicolumn run are presented in Table 4-10. A hydraulic load of 9.2 gpm/ft^2 was selected which is acceptable for full scale plant applications. This provides an empty bed contact time (EBCT) of 0.039 minutes. The four prediction models were tested for predicting the

Table 4-9. Packed Bed Transfer Coefficients

Compound	Film Transfer Coefficient, k_f (Cm/sec.)			Dispersion Coefficient	Pore Diffusion Coefficient	Molecular Diffusion
	Williamson Correlation	Wakao & Fanazkri Correlation	Analytical Soln*	D_e (Cm^2/sec.)	D_p (Cm^2/sec.)	D_L (Cm^2/sec.)
2,4-Dimethylphenol	7.578×10^{-3}	6.880×10^{-3}	8.030×10^{-3}	0.1588	0.484×10^{-5}	0.758×10^{-5}
Naphthalene	7.583×10^{-3}	6.901×10^{-3}	7.379×10^{-3}	0.1589	0.485×10^{-5}	0.757×10^{-5}
Fluorene	6.507×10^{-3}	5.759×10^{-3}	8.310×10^{-3}	0.1646	0.405×10^{-5}	0.633×10^{-5}

*Spontaneous Backthrough Concentration (C/C_o), 2,4-Dimethylphenol = 0.197, Naphthalene = 0.223, Fluorene = 0.188

Table 4-10. Operation Characteristics of the Mixed Component Minicolumn Study in Ultrapure Water Background

Parameter	2,4-Dimethylphenol	Naphthalene	Fluorene
K (μM./g)(L/μM.)**NF	788.5	907.9	1,721.4
1/Nf	0.236	0.334	0.414
D_s , (cm^2/s.)	4.450×10^{-11}	3.369×10^{-11}	1.990×10^{-11}
k_f , (cm/s.)	7.578×10^{-3}	7.583×10^{-3}	6.505×10^{-3}
D_p , (cm^2/s.)	0.485×10^{-5}	0.485×10^{-5}	0.405×10^{-5}
D_e , (cm^2/s.)	0.1588	0.1589	0.1646
Hydraulic Load, (gpm/ft^2)	9.2		
Column Diameter, (cm)	1.0		
Column Length, (cm)	1.48		
Carbon Type	F - 400		
Particle Radius, (cm)	0.0181		
Bed Volume, (cm^3)	1.162		
Carbon Apparent Density, (g/cm^3)	0.8034		
Carbon Void	0.640		
Avg. pH	7.0		
Temperature, (^{o}C)	25		
Run Time, (hr.)	83.3		

experimental data. Raw data are presented in Appendix E Table E-1 Table E-3. The results which are plotted in Figure 4-23 to 4-25 show that PPSDM and DFPSDM models predicted the data better than both DFHSDM and PHSDM. The results also show that pore diffusion is the most influential factor in the adsorption of the four packed column predictions. The dispersion magnitude in the packed bed depends on two factors which are the Reynold's number and the concentration profile through the particle. If adsorption within the activated carbon is strong and rapid, the concentration profile through the particle becomes asymmetric which leads to an additional contribution to axial dispersion. This effect is only important at low Reynold's number since at high Reynold values there is a sufficient turbulent mix to ensure a uniform boundary concentration around the individual activated carbon particles. Based on the previous discussion and experimental results, PPSDM is considered the model of choice for this study. To substantiate its validity, its predictive capability was evaluated by statistical linear regression and its sensitivity was evaluated for the major mass transfer coefficients and isotherm constants. The results of the statistical linear regression tests are presented in Table 4-11. The R-square, STD ERR and Root MSE values indicate a very good ability of PPSDM to predict the experimental data. However, the t-test theory indicated in all cases of intercept and slope a rejection outcome within 90% probability. The experimental data does not follow a pure normal distribution. By using C/C_0 which is less than one in all cases, very small standard error values

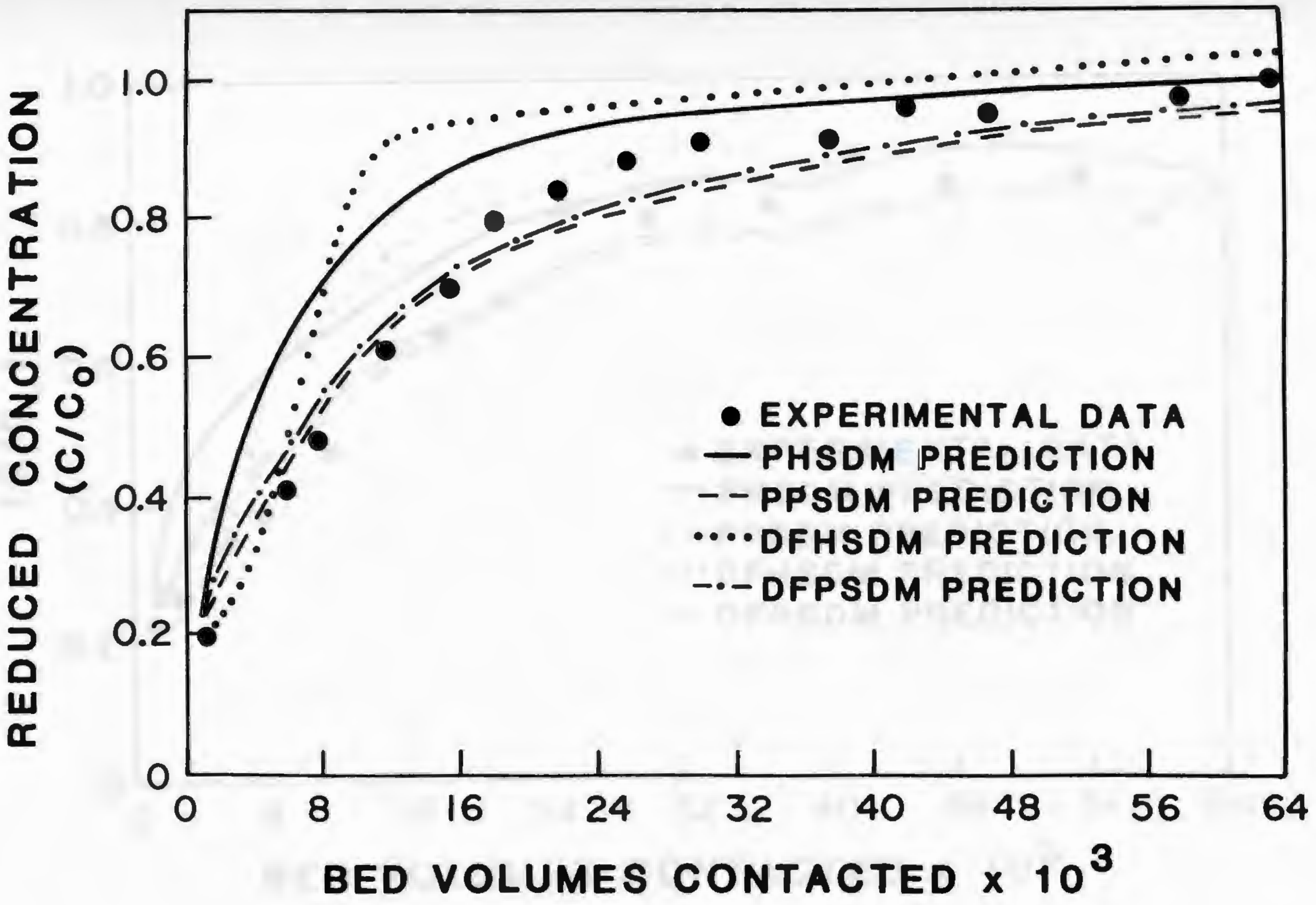


Figure 4-23 Mixed Component Minicolumn Breakthrogh of 2,4-Dimethylphenol in Ultrapure Water Background

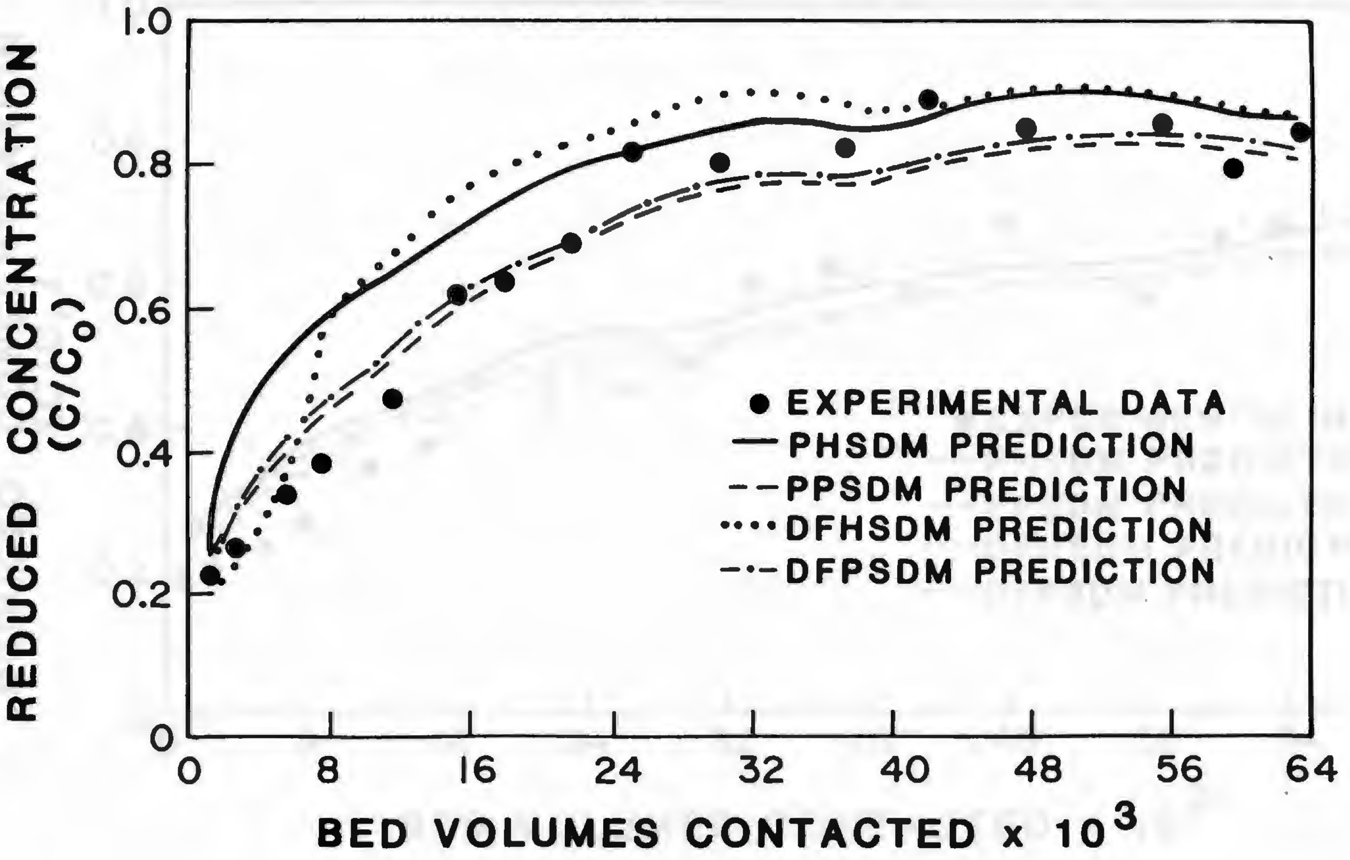


Figure 4-24 Mixed Component Minicolumn Breakthrough of Naphthalene in Ultrapure Water Background

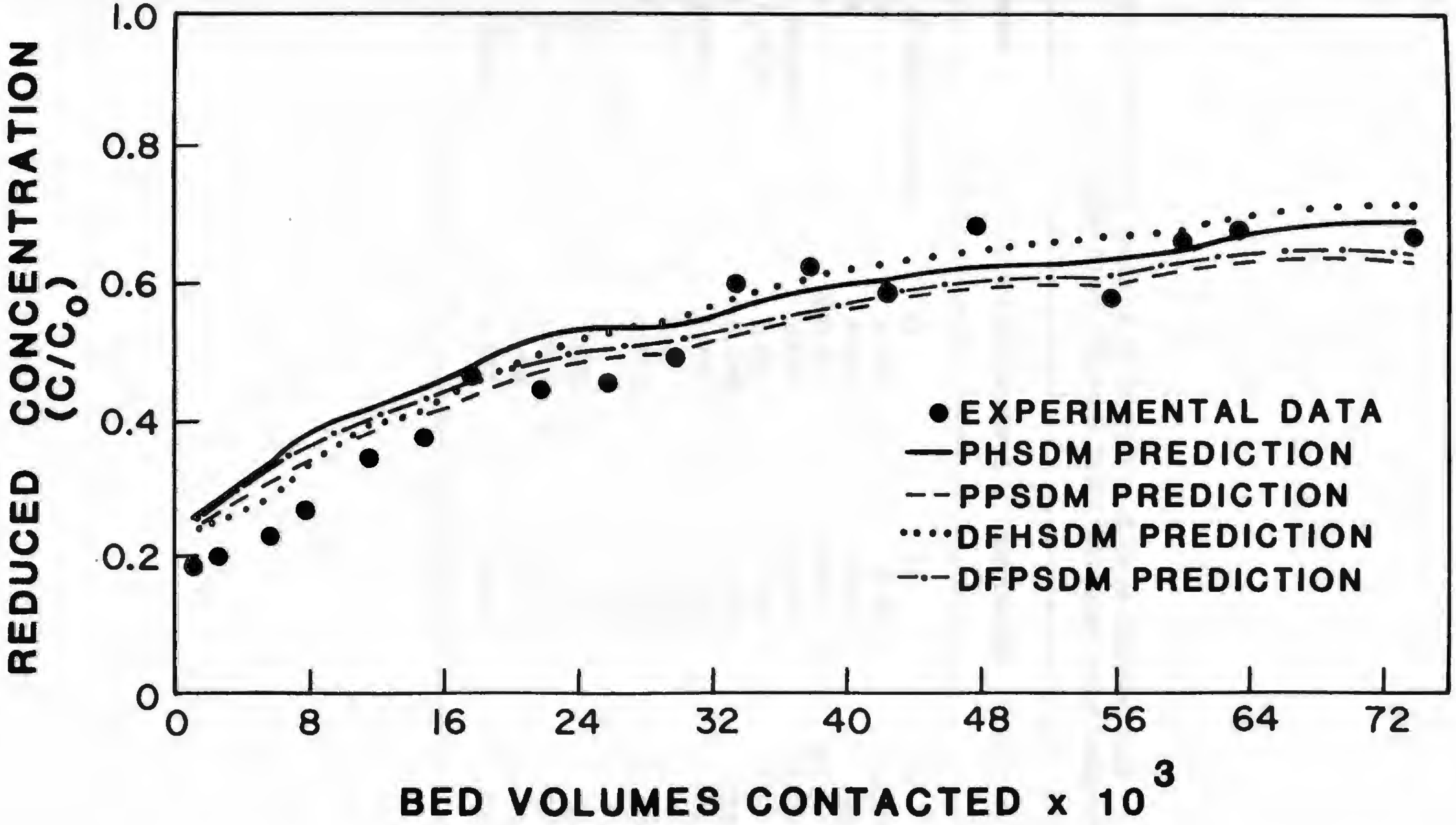


Figure 4-25 Mixed Component Minicolumn Breakthrough of Fluorene in Ultrapure Water Background

Table 4-11. Statistical Analysis of PPSDM Prediction vs.Observed Data in MiniColumn Mixed Component Study (Ultrapure Water Backgrtound)

Parameter	2,4-Dimethylphenol	Naphthalene	Fluorene
Number of observations	15	16	18
R-square	0.997	0.971	0.959
Root MSE	0.020	0.034	0.026
F-value	1890.6	464.6	376.5
Intept. Estimated	0.077	0.115	0.135
T. for $H_0:\beta_0=0$	5.03	4.44	7.20
STD ERR	0.0153	0.0258	0.0187
Slope Estimate	0.865	0.812	0.714
T for $H_0:\beta_1=1$	-6.78	-4.99	-7.77
STD ERR	0.0199	0.0377	0.368
Reliability Index			
Kg	1.079	1.111	1.158
sum Sq	0.022	0.044	0.097
K_s	1.079	1.111	1.159
Sum Sq	0.087	0.178	0.392

are produced which in turn can give high t-test values that more likely will fail this test. The reliability index procedure as discussed in Section 3 can give a much better basis of comparison. The procedure discussed in section 3 was originally designed for correlating various models for the same type of data sets and its application in this kind of study is more appropriate. The closer the K_g and K_s values are to one the better correlation will be. The results of the reliability index parameters are presented in Table 4-11. The values of K_s and K_g ranged from 1.079 - 1.159 which indicate a very good prediction of PPSDM for the three organic compounds tested.

The sensitivity of the PPSDM prediction of the minicolumn study was tested for various diffusion coefficients and isotherm constants by varying their values ± 50%. Experimental procedure error as well as the error of the empirical relationships used for evaluating these constants are expected to be in the range of ± 20%. Plots of the deviation from PPSDM prediction in the mixed component minicolumn study in ultrapure water are shown in Figure 4-26 toi Figure 4-28. The results indicate that in general, by increasing the constant values the PPSDM will under predit and by decreasing the constants values the PPSDM will overpredict. The XK coefficient which is a measure of the Freundlich isotherm carbon capacity showed the highest deviation followed by XN, D_p and D_s. The film transfer coefficient k_f showed the highest deviation in the initial stage of the breakthrough curve behavior and then the course tampered to less deviation than D_s as the break through curve progressed. To further measure the

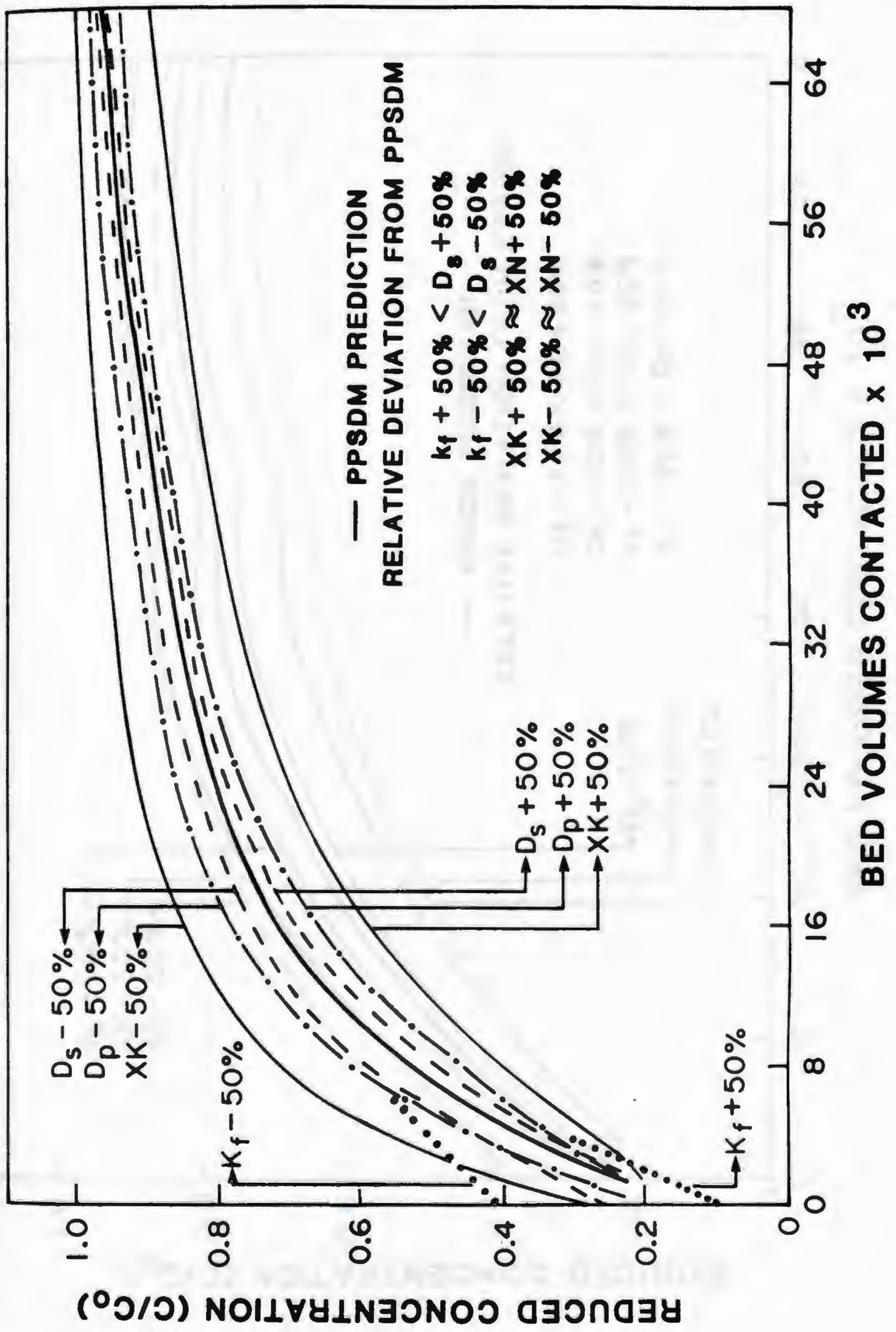


Figure 4-26 Sensitivity of PPSDM Prediction for Multiple Component Minicolumn Study of 2,4-Dimethylphenol in Ultrapure Water Background

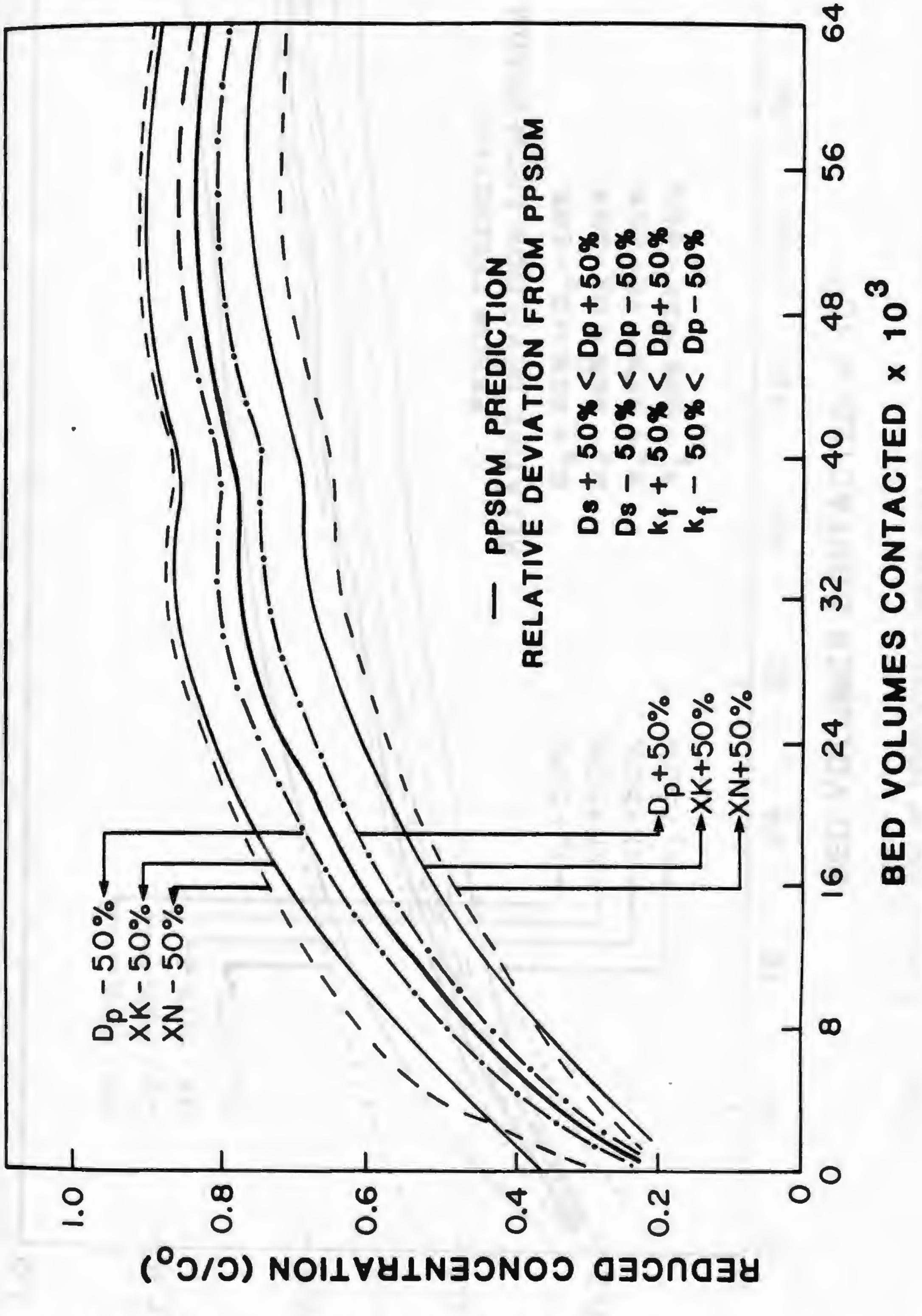


Figure 4-27 Sensitivity of PPSDM Prediction of Multiple Component Minicolumn Study of Naphthalene in Ultrapure Water Background

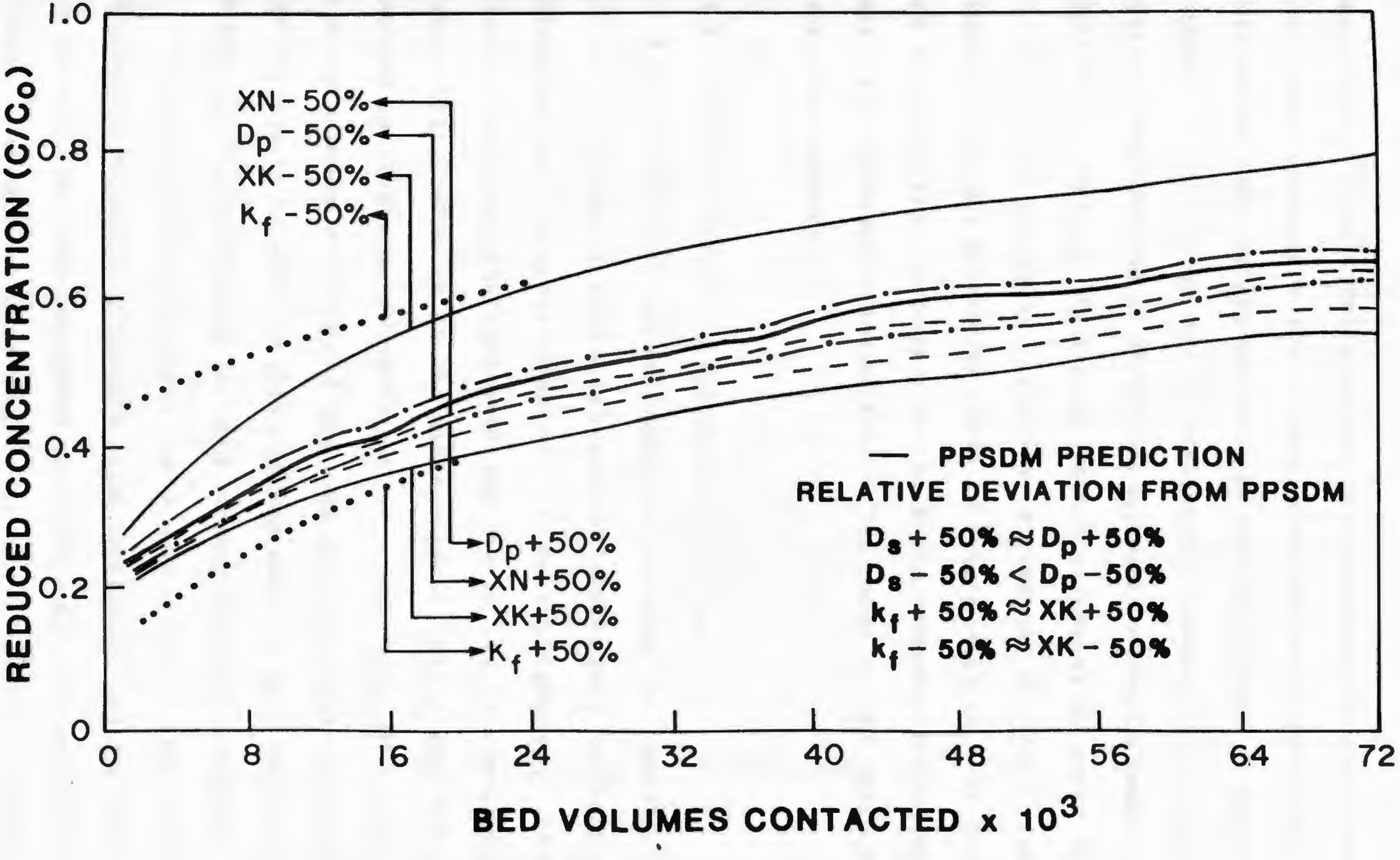


Figure 4-28 Sensitivity of PPSDM Prediction of Multiple Component Study of Fluorene in Ultrapure Water Background

sensitivity of the model a Monte-Carlo approach in which the model input constants are randomly withdrawn from normal distribution would be appropriate. By running the model X number of times, the certainty can be evaluated. However due to the relative long CPU time of PPSDM this approach becomes unfeasable. Therefore, to lump-sum the maximum possible cumulative error of all the model constants, each was incremented by ±20%. The results of this are plotted as shown in Figure 4-29 to 4-31 for each of the organic compound in the mixed component minicolumn study. All experimental values fall in the range of the maximum ± 20% error boundary.

4.4.3 Background Effects on Minicolumn Prediction

A minicolumn study was conducted to evaluate the impact of DOC in a complex mixture background (secondary effluent wastewater) on the prediction of 2,4-dimethylphenol. The selection of 2,4-dimethylphenol was due to its intermediate adsorbability relative to the other organic compounds. This compound is also a major constituent of a large group of phenols which characterize refinery and petrochemical wastewater and the high solubility in water of this compound makes it much easier to achieve feasable pilot plant influent concentrations by spiking.

Two minicolumn studies were conducted, one with 2,4-dimethylphenol in ultrapure water background, and the other in a secondary effluent background with a 20.4 mg/L concentration of DOC. The operational characteristics as well as the specifications of both minicolumns are exactly similar and are

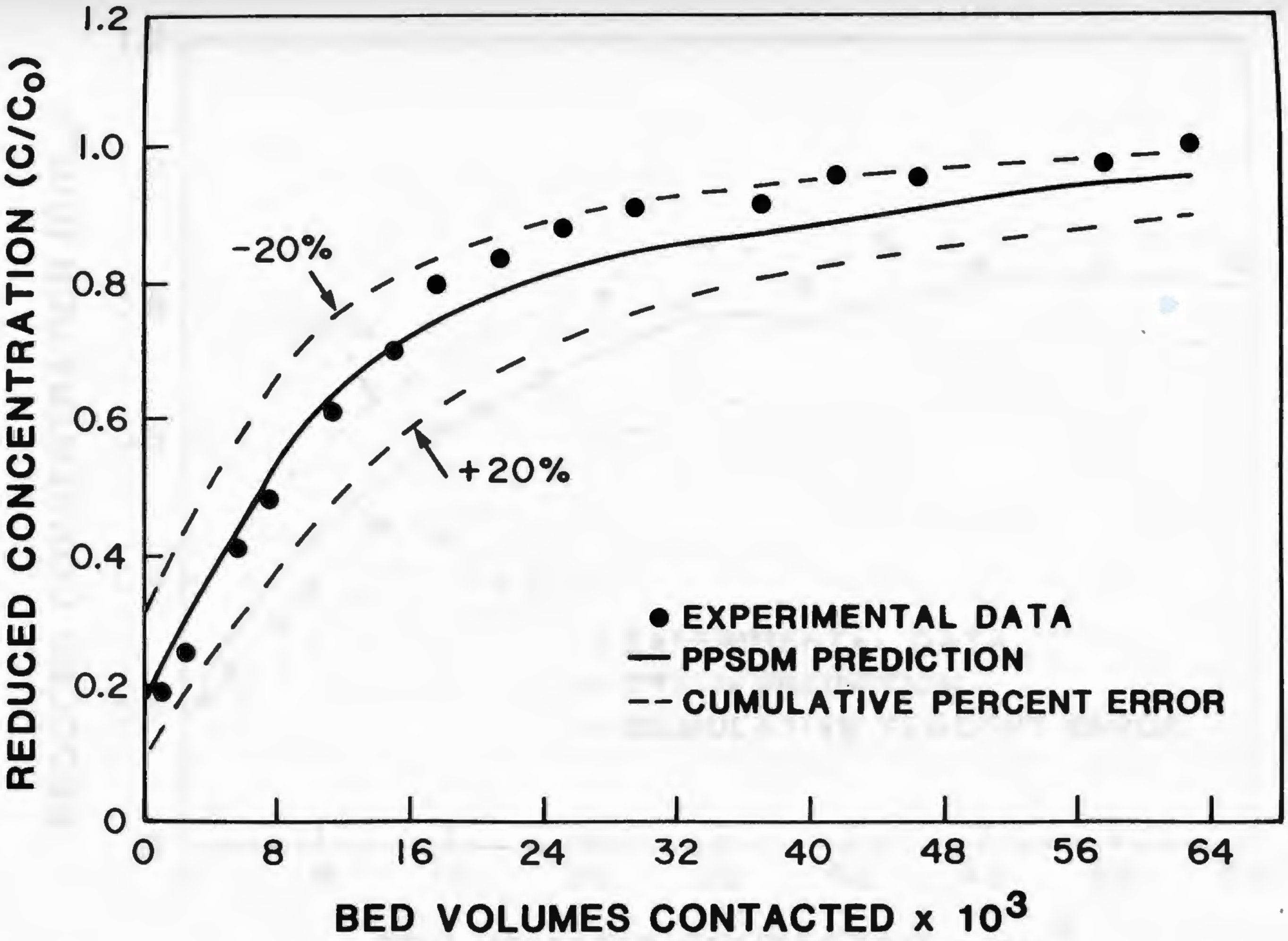


Figure 4-29 PPSDM Prediction for Assumed Maximum 20% Cumulative Error in Model Constants for 2,4-Dimethylphenol

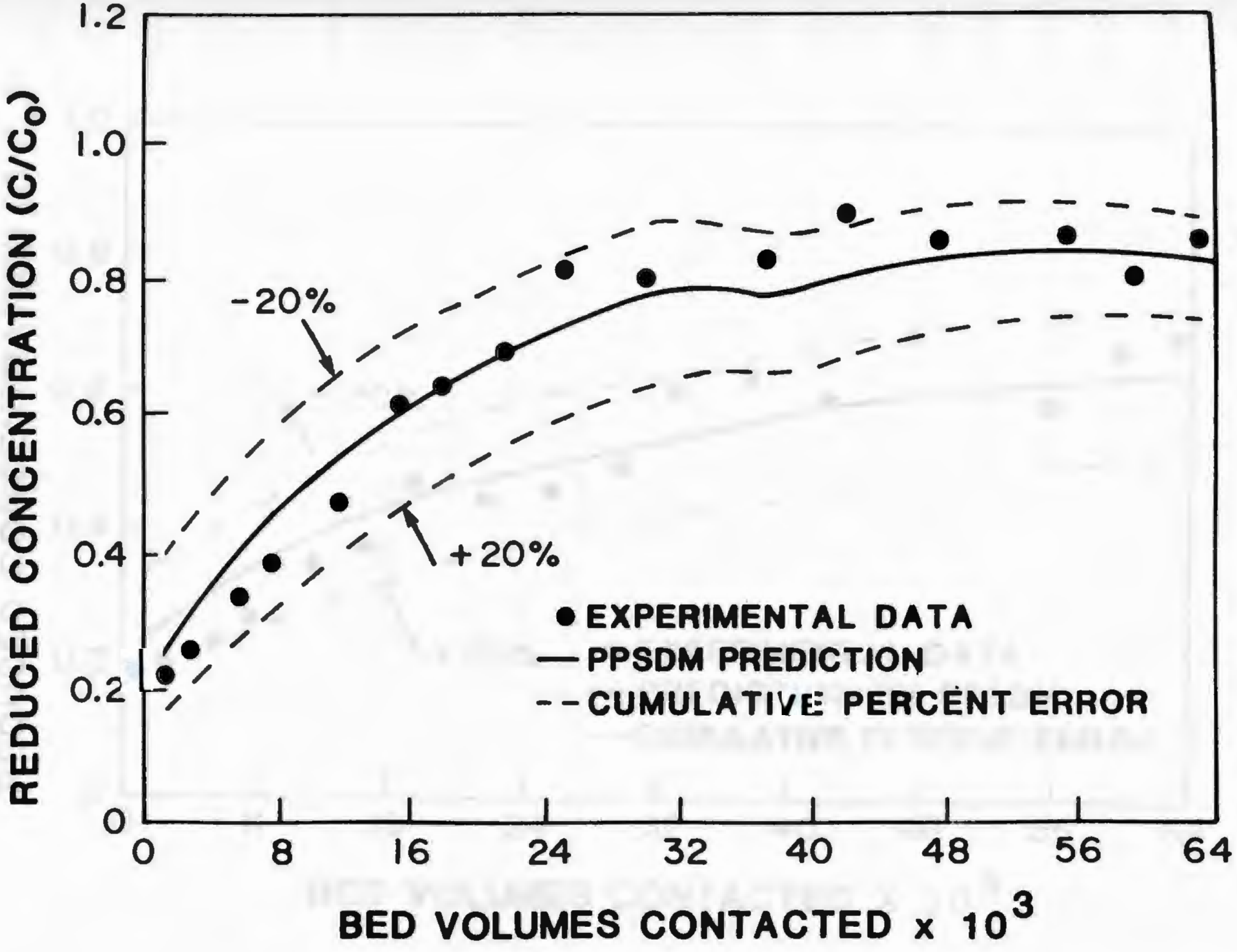


Figure 4-30 PPSDM Prediction for Assumed Maximum 20% Cumulative Error in Model Constants for Naphthalene

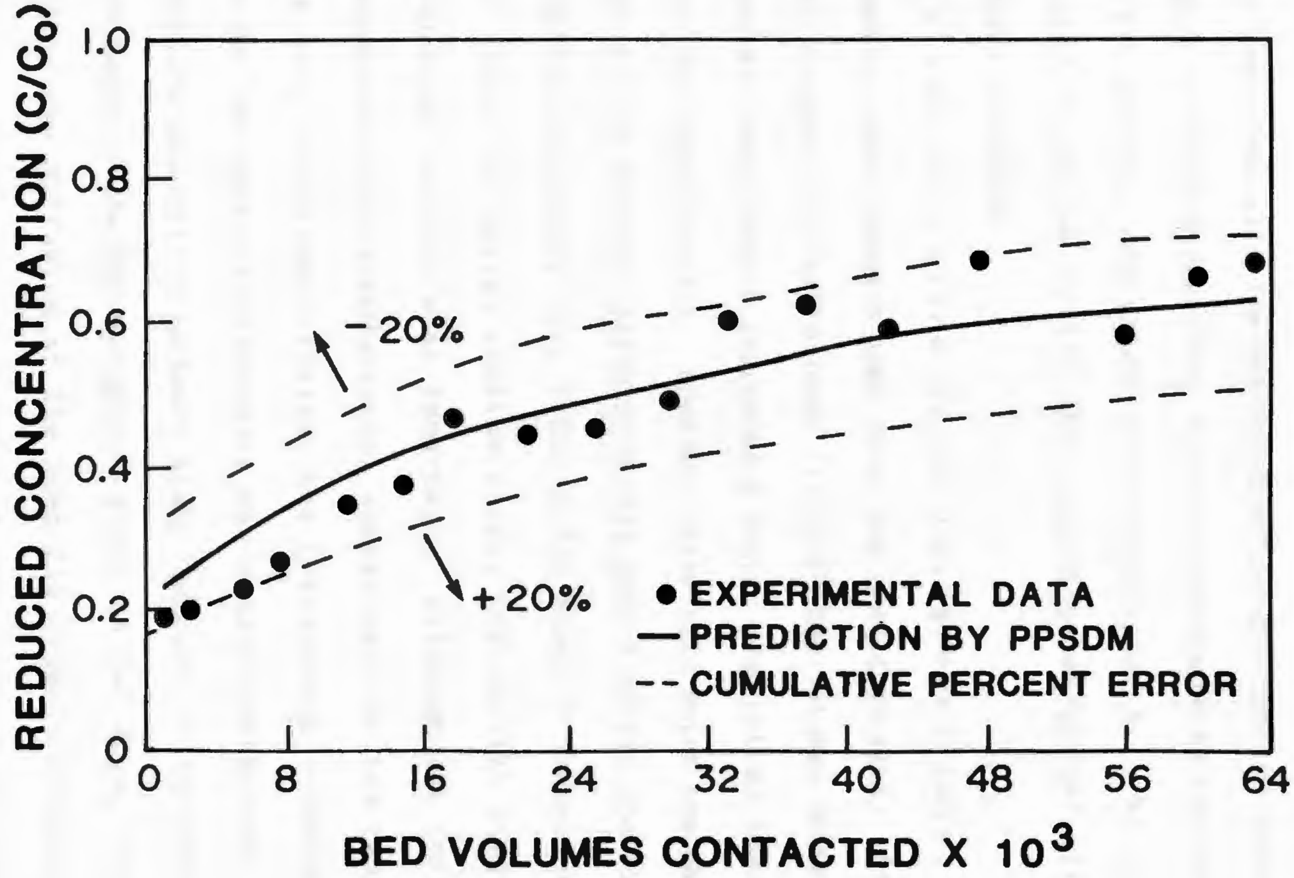


Figure 4-31 PPSDM Prediction for Assumed Maximum 20% Cumulative Error in Model Constants for Fluorene

presented in Table 4-12. As for the case of the mixed component minicolumn study, PHSDM, PPSDM, DFHSDM and DFPSDM were used to predict the breakthrough curve characteristics. The experimental data in comparison with the predicted values are plotted as shown in Figure 4-32 and Figure 4-33 with the corresponding raw data in Tables E-4 and E-5. The values of the constants, K, 1/Nf and D_s were used relative to the corresponding background mixture previously estimated.

In the ultrapure water background case, the 2,4-dimethylphenol breakthrough curve was predicted well. At the initial stages of breakthrough ($<15x10^3$ bed volumes contacted) the pore diffusion models indicated a better prediction than the surface diffusion models. However, after this point the pattern changed and the surface diffusion models gave a better prediction. Pore diffusion models will still be the model of choice in this study. Since for design consideration, the initial stages of breakthrough are the most important. Although the influent concentration of 2,4-dimethylphenol varied only in the range of 10% in both minicolumn studies, the breakthrough occurred much faster for the case with secondary wastewater background. The competitive adsorption isotherm study (section 2) indicated that the influence of the DOC background acted in two ways, first by retarding the diffusion of the specific organic compounds and second by reducing the capacity of the activated crbon as represented by the Freundlich constant K. Such observations are confirmed by the minicolumn study. By observing Figure 4-33, it can be visually observed that pore diffusion models gave a better

Table 4-12. Operation Characteristics of Single-Solute 2,4-Dimethylphenol Minicolumn Study in Different Water Background

Parameter	Ultra Pure Water Background	Secondary Effluent Background (avg. DOC = 20.4 mg/L)
K,(uM./g)(L/uM.)**1/N_f	788.5	170.0
1/N_f	0.2357	0.3763
D_s,(cm^2/sec)	5.930×10^{-11}	3.158×10^{-11}
k_f, (cm/sec)	7.578×10^{-3}	7.578×10^{-3}
D_p,(cm^2/sec)	0.485×10^{-5}	0.485×10^{-5}
D_e,(cm^2/sec)	0.1588	0.1588
Hydraulic Load, (gpm/ft^2)	10.9	
Column Diameter, (cm)	1.0	
Bed Length, (cm)	2.35	
Carbon type	F-400	
Particle Radius, (cm)	0.0181	
Bed Volume, (cm^3)	1.846	
EBCT, (min.)	0.052	
Carbon Apparent Density, (g/cm^3)	0.8034	
Carbon Void	0.64	
Avg. pH	7.1	
Temperature, (°C)	22	

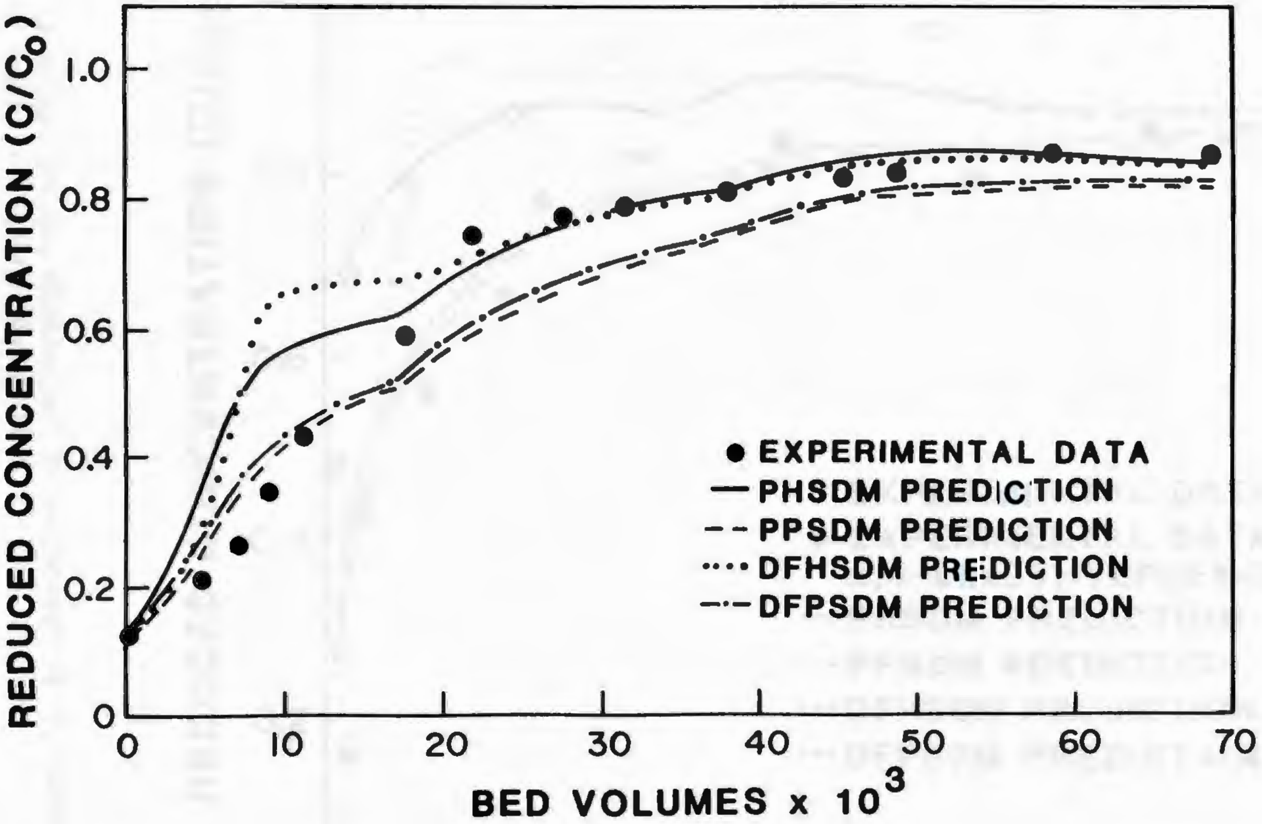


Figure 4-32 Single-Solute Minicolumn Breakthrough of 2,4-Dimethylphenol in Ultrapure Water Background

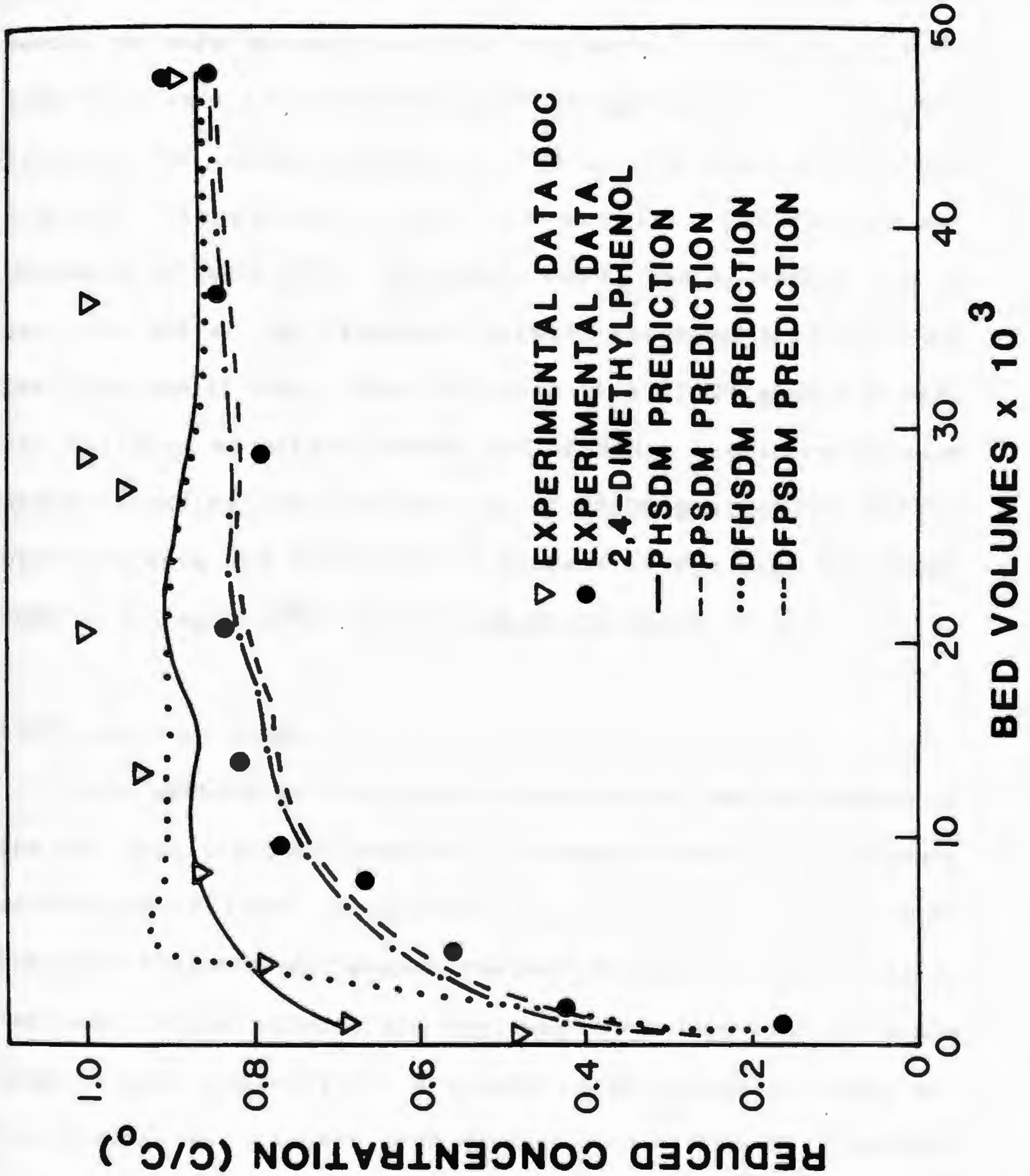


Figure 4-33 Single-Solute Minicolumn Breakthrough of 2,4-Dimethylphenol in Complex Mixture Background

prediction than surface diffusion models. For statistical support of this conclusion, the reliability index analysis was applied to the results of prediction of the four used models versus the experimental results of the minicolumn study of 2,4-dimethylphenol in ultrapure water background. This study was selected for comparison purposes as it visually showed the highest discrepancy of the four models. The results are presented in table 4-13. The closer the K_g and K_s values are to one, the better the agreement between the model prediction and the experimental data. This indicates that PPSDM gave the best fit followed by DFPSDM, PHSDM and DFHSDM. Linear regression analysis and reliability indices of PPSDM prediction versus observed data are presented in Table 4-14 for both minicolumn runs in ultrapure water and in complex mixture.

4.5 Pilot Plant Study

This section of the study investigates the performance of the GAC pilot plant for treating 2,4-dimethylphenol in secondary wastewater effluent background. The pilot plant was located in the South Kingstown Wastewater Treatment Facility in Rhode Island. Influent to the pilot plant was pumped through the full-scale plant secondary clarifier. A schematic of the pilot plant and its specifications have been discussed in section 2. The pilot plant consists of a dual media filter for suspended solids removal, followed by two identical GAC packed bed columns arranged in parallel and containing F-400 12x30 U.S. mesh number. The flow to the packed beds was set to provide an average EBCT of

Table 4-13. Reliability Index Analysis for Various Models Prediction vs. Experimental Data of 2,4-Dimethylphenol (Ultrapure Water Background)

Parameter	PPSDM	PHSDM	PFHSDM	DFPSDM
K_g	1.159	1.332	1.339	1.174
SUM SQ.	0.065	0.243	0.252	0.077
K_s	1.159	1.339	1.346	1.175
SUM SQ.	0.262	1.024	1.062	0.312
NO. OBSERVATIONS	12	12	12	12

Table 4-14. Statistical Analysis of PPSDM Prerdiction Versus Observed Data of 2,4-Dimethylphenol Minicolumn Study

Parameter	Ultra pure water Background	Secondary Wastewater Effluent Background
Number of observation	12	11
R-Square	0.963	0.983
Root MSE	0.0498	0.0235
F-Value	258.2	533.2
Intcpt. Estimated	0.083	0.147
T. for $H_0:\beta_1 = 0$	2.47	5.830
STD ERR	0.033	0.025
Reliability Index		
K_g	1.159	1.133
SUM SQ.	0.065	0.043
K_s	1.159	1.135
SUM SQ	0.262	0.175

3.56 and 1.75 minutes for column I and II respectively. The pilot plant flow was 1.3 gal/minute and the hydraulic load to column I was set to 6.1 gpm/ft^2 and column 12.4 gpm/ft^2.

The pilot plant backwash system was arranged in a way to provide clean water for the dual sand filter and to use the actual wastewater passing through the sand filter to backwash the GAC columns. This sequence provided minimum disturbance of the GAC beds and reduced the backwash frequency of the sand filter to once every 24 hours and the GAC column to once every two to three days.

During the study period, the influent pH ranged from 6.8-7.0 and the influent temperature ranged from 17.8-18.9^{o}C. The pilot plant influent BOD$_5$ which is the effluent of the full-scale treatment facility ranged from 9-15 mg/L. The influent DOC concentration averaged 20.34 mg/L with a standard deviation of 2.47. By observing the breakthrough curves data, it can be seen that the nonadsorpable fraction of DOC approached 50% for both EBCTs tested which confirm again that the nonadsorpable fraction is truly nonadsorbable organics and not merely slowly adsorbed compounds and thus a function of EBCT.

The pilot plant study served three major purposes, the first was to test the predictability of the minicolumn's verified PPSDM and DFPSDM in a much larger scale pilot plant subjected to an actual wastewater characteristic conditions. The second objective was to evaluate the influence of EBCT on model prediction. The third objective was to compare the performance of the minicolumn study to a much larger pilot plant in an attempt to evaluate parameters that may influence up-scaling considerations required for full-scale design of carbon packed bed treatment facilities.

Figure 4-34 and Figure 4-35 present the predicted breakthrough curves along with the experimental data of 2,4-dimethylphenol and the experimental DOC breakthrough in Columns I and II. Operation characteristics are presented in Table 4-15. Since the two columns are arranged in parallel with the same amount and type of carbon, any variation of the characteristics of breakthrough curves ars attributed directly to the influence of EBCT. The variation of the influent suspended solid concentration produced an unaccounted for head loss in the sand filter. Therefore it was difficult to maintain a constant flow to the GAC columns which in turn caused a variable influent concentration of 2,4-dimethylphenol. Influent concentration variations are plotted on these figures as C_0/C where C is the average concentration through the pilot plant operation period. DOC breakthrough curves indicate an immediate breakthrough at C/C_0 equal to 0.52 for both EBCT. This indicates that 48 percent of the total DOC concentration is nonadsorpable. Total breakthrough occurred after 6500 and 10,000 bed volumes respectively for columns II and I which is, somewhat equivalent to their EBCT ratio. The results which are plotted in Figure 4-34 and Figure 4-35, shows that the prediction by DFPSDM and PPSDM are practically equivalent which indicates that the dispersion coefficient is insignificant in this pilot plant study.1 For the case of the EBCT of 1.75 minutes both models

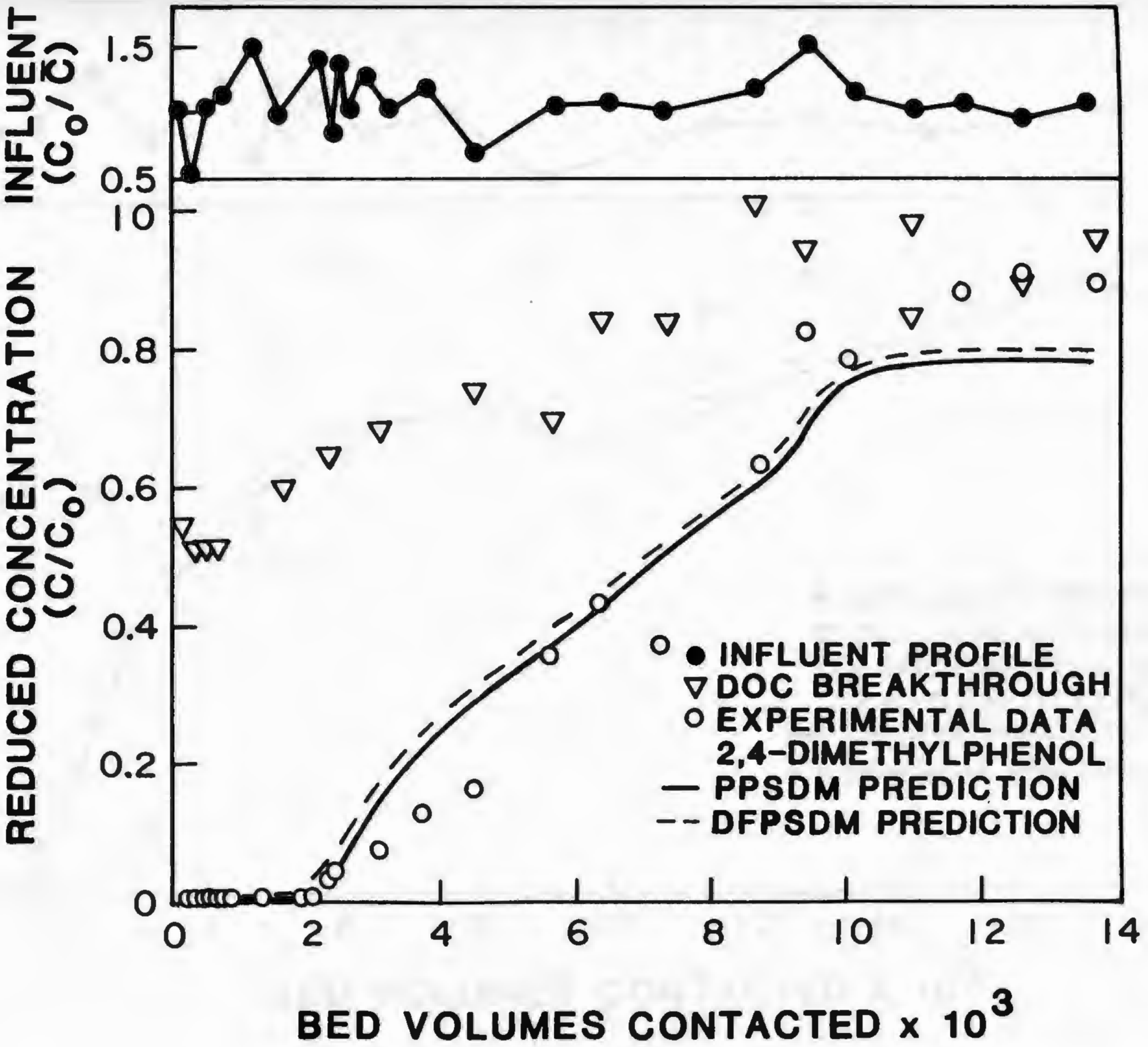


Figure 4-34 Pilot Plant (Column I) Breakthrough for 2,4-Dimethylphenol in South Kingstown Wastewater Treatment Facility Effluent

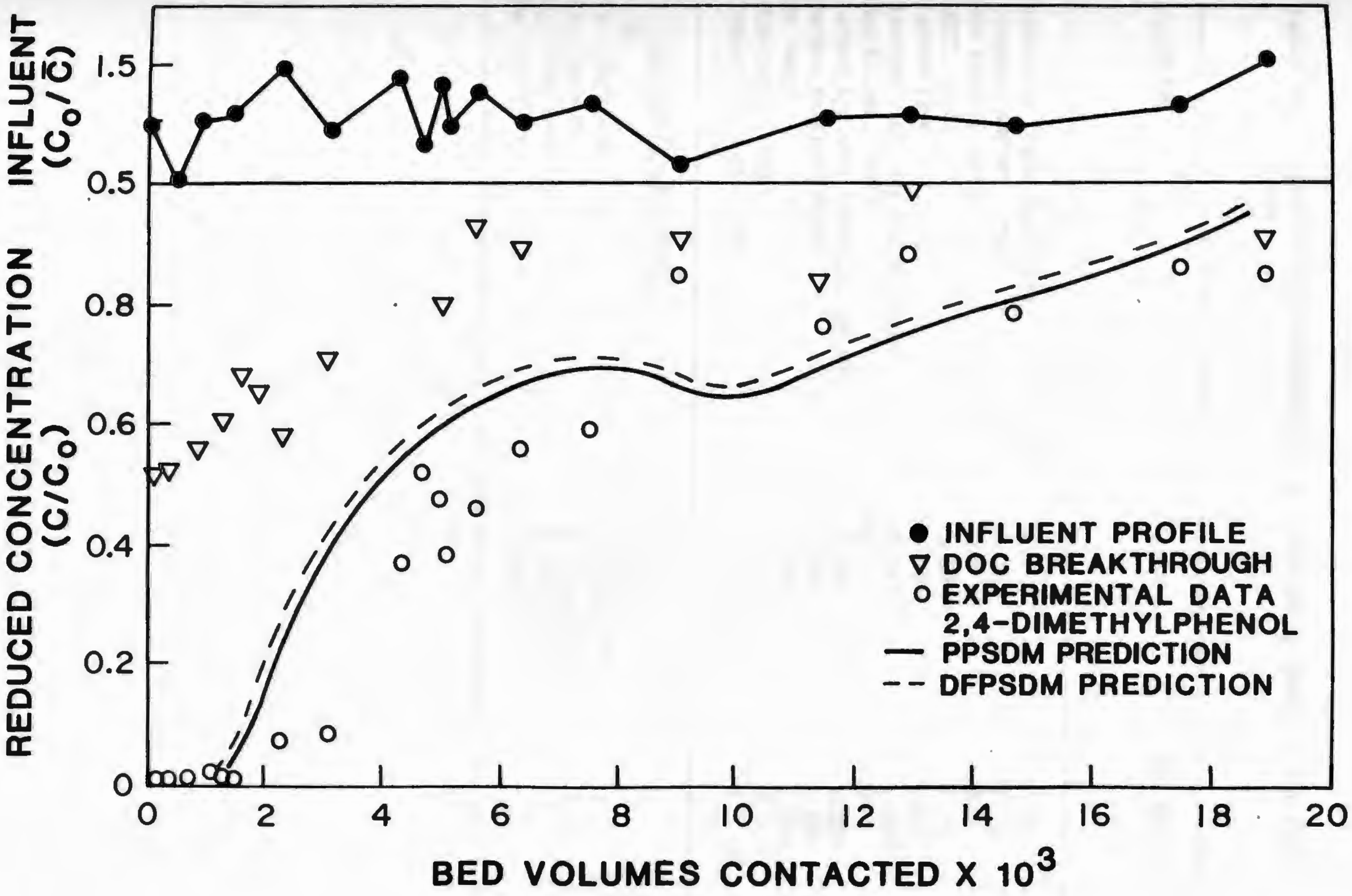


Figure 4-35 Pilot Plant (Column II) Breakthrough for 2,4-Dimethylphenol in South Kingstown Wastewater Treatment Facility Effluent

Table 4-15. Operation Characteristics of 2,4-Dimethylphenol Pilot Plant Study.

Parameter	Column I	Column II
Hydraulic Load, (gpm/ft^2)	6.1	12.4
Column Diameter, (cm)	10.16	10.16
Bed Length, (cm)	88.5	88.5
EBCT, (min)	3.56	1.75
Carbon Type	F-400	F-400
Average Particle Radius, (cm)	0.062	0.062
Bed Volume, (cm^2)	7175	7175
Carbon Apparent Density, (g/cm^3)	0.803	0.803
Carbon Particle Void	0.64	0.64
pH Range	6.8-7.0	6.8-7.0
BOD$_5$ Range, (mg/L)	9-15	9-15
Temperture Range (C^o)	17.8-18.9	17.8-18.9
K, (μM./g) (L/μM.)**1/N$_f$	170.0	
1/N$_f$	0.3763	
D$_s$, (cm^2/sec)	3.158×10^{-11}	
k$_f$, (cm/sec)	7.578×10^{-3}	
D$_p$, (cm^2/sec)	0.485×10^{-5}	
D$_e$, (cm^2/sec)	0.1588	

predicted the effluent profile of 2,4-dimethylphenol fairly well. In the case of 3.56 minutes EBCT, a much better effluent profile prediction was produced. Statistical analysis of observed versus predicted results are presented in Table 4-16. As observed in the minicolumn statistical analysis, the obtained values of T tests in both models falls off the acceptance boundaries with 90% probability. However, the reliability index Kg recorded 1.38 and 1.63 for the prediction of PPSDM and DFPSDM, respectively. Both models overpredicted the experimental data particularly at the initial stages of breakthrough curve progress. This indicates that the contribution of the pore diffusion coefficient is experimentally higher than the calculated one. Increasing the pore diffusion coefficient value will give a better prediction as previously shown in the sensitivity analysis of the minicolumn study. The better prediction obtained in the case of the higher EBCT study verify this observation. The increase of contact time adsorbate molecules allows them to diffuse deeper into the pores of carbon pellets. The raw data of the pilot plant study are presented in Appendix F Table F-1 and Table F-2.

Table 4-16. Statistical Analysis of 2,4-Dimethylphenol Predicted vs. Observed in Pilot Plant Study

Statistical parameters	COLUMN I		COLUMN II	
	PPSDM	DFPSDM	PPSDM	DFPSDM
No. of observations	15	15	17	17
R-SQR	0.96	0.96	0.77	0.78
Root MSE	0.06	0.06	0.10	0.10
F-Value	298.9	308.1	51.5	52.7
Intcpt	0.10	0.11	0.29	0.30
T for Ho: $\beta_0=0$	3.72	4.12	4.78	5.01
STD ERR	0.027	0.026	0.061	0.059
Slope	0.78	0.77	0.66	0.66
T for Ho: $\beta_1=1$	-4.84	-5.31	-3.63	-3.78
STD ERR.	0.045	0.044	0.093	0.091
Reliability Index				
K_g	1.38	1.44	1.63	1.64
Sum Sq.	0.39	0.49	0.97	0.99
K_s	1.65	1.45	1.73	1.75
Sum Sq.	1.65	2.10	5.15	5.33

CONCLUSIONS

Based on the results of this study, the principal conclusion of this research are summarized as follows:

1. Among the four single-solute isotherm models tested, the Modified Freundlich and the three parameter's model provided the best fit to the experimental data. The isotherm parameters calculated are applicable to a wide range of the studied organics concentrations that can reach as high as 80-95% of the saturation concentration of fluorene, pyrene, naphthalene and bis(2-Ethylhexyl)phthalate and up to 65 mg/l for 2,4-dimethylphenol.
2. The calculated adsorption capacities can be arranged in decending order as follows: pyrene, fluorene, naphthalene, 2,4-dimethylphenol and bis(2-ethylhexyl) phthalate. Apart from the compound bis(2-ethylhexyl) phthalate, an increase in adsorption capacity was observed compared to the decrease in solubility of the compound in water. The deviation of bis(2-ethylhexyl) phthalate was attributed to its relative high molecular volume, however, there was no correlation between adsorption capacities and molecular volumes among the rest of the compounds.
3. Dubinin-Polanyi adsorption isotherm worked well for fitting isotherm data. However it was unsuccessful as a predictive model when tested in a bi-solute system.

This is attributed to: lack of good solubility data and lack of good physical property data which could characterize adsorption behavior.

4. IAS prediction using single-solute isotherm parameters worked very well in evaluating the competitive interactions for multi-component mixtures in an ultrapure water background. However, the theory was unsuccessful when tested for prediction on multi-component mixture in complex wastewater background. Considerable improvement in the IAS prediction was achieved when the single-solute isotherm parameters were replaced by a new set of isotherm parameters calculated from complex background mixture isotherms.
5. The selection of a fictive or surrogate parameter such as DOC is one choice for evaluating the competitive effect in a complex mixture background.
6. The calculated effective diffusion coefficient "D_S" in ultrapure water background and in a complex mixture background indicated that there was a substantial decrease in "D_S" values which were evaluated in the complex mixture. This emphasizes the impact of the DOC parameter on the intraparticle diffusion rate.
7. For batch systems, HSDM underpredicted the experimental data for all of the compounds tested. However, PSDM gave a much better prediction which emphasizes the importance of pore diffusion as a controlling factor in both an ultrapure water background and a complex

mixture background. Similar results were concluded for packed bed systems. Among the four models tested (PHSDM, PPSDM, DFHSDM, DFPSDM) PPSDM and DFPSDM gave the best predictions.

8. The competition between the strongly adsorbed compounds studied and the weakly adsorbed lumped DOC background in secondary wastewater effluent is not site preferential. Retardation of adsorption of the strongly adsorbed compound may occur.

RECOMMENDATIONS

Based on the work that has been conducted in this study outlined below are several areas that require further research effort:

1. The relative importance of GAC adsorption and biodegradation in the removal of priority organics needs further assessment. So far there are no available prediction models that include both biodegradation and adsorption interactions. Based on observations from this study the biodegradation rate kinetics may be evaluated by successively exhausting and bio-regenerating the activated carbon in a packed bed. For example, if the carbon is exhausted and then the process is shut off for a certain time the difference in carbon capacity can be directly related to biodegration. By successive exhaustion and bio-regeneration at different time intervals the rate of bio-degradation can be evaluted.
2. The deviation of the IAS prediction should be evaluated in various background mixtures other than secondary wastewater effluent. For example various raw sewage and industrial wastewater combinations can be evaluated. The impact of different strengths of the DOC fictive parameter on the deviation of IAS prediction is a worthwhile consideration.

3. It is recommended that the impact of different strengths of DOC fictive parameter in complex background mixture on the diffusion rate coefficients be evaluated for other than secondary wastewater effluent.

REFERENCES

1. Alkhatib, E.A., "Treatment of High Ammonia Refinery Wastewater for Reuse". A Master's Thesis submitted to the State University of New York at Buffalo, (1982).

2. U.S. Environmental Protection Agency, "Draft Development Document including the Data Base for the Review of Effluent Limitations Guidelines (BATEA), New Source Performance Standards, and Pretreatment Standards for the Petroleum Refining Point Source Category." Washington, D.C., March, (1978).

3. U.S. Environmental Protection Agency, "Development Document for Proposed Effluent Limitations Guidelines, New Source Performance Standards, and Pretreatment Standards for the Petroleum Refining Point Source Category." EPA 440/1-79/014-b, Washington, D.C., Dec., (1979).

4. Shunbo, F., Literathy, P., Abdilly, F., and Al-Ali, M., "Study of Micropollutants in Industrial Effluent Discharges in the Shuaiba Industrial Area." Kuwait Institute for Scientific Research, Kuwait, Sept., (1983).

5. Chapman, P.M., Romberg, P.G., Vigers, G.A., "Design of Monitoring Studies for Priority Pollutants." JWPCF, Vol. 54, No. 3, 1982, p. 292.

6. Basso, M., Nolan, T., Shaw, J.,"Evaluation of EPA Analytical Protocols for Measurement of Priority Pollutants in Refinery Wastewaters," presented at WPCF Conference, Detroit, Michigan, Oct., 1981.

7. Crittenden, J.C., Luft, P., Hand, D.W., and Friedman, G., "Prediction of Multicomponent Adsorption Equilibria in Background Mixtures of Unknown Composition." Manuscript accepted for publication in Water Research, (1985).

8. Frick, B.R. and Sonthiemer, H., "Treatment of Water by Granular Activated Carbon." Amer. Chemical Soc. Books, Washington, D.C., Advances in Chemistry, Series, No. 202, 1983, p. 247.

9. Crittenden, J.C., P.J. Luft, D.W. Hand, and G. Friedman, "Prediction of Fixed Bed Adsorption Removal of Known Organics and Total Organic Halogen in Computing Background Mixtures of Unknown Composition," Proceeding of the 1984 National Conference of Environmental Engineering, Sponsored by ASCE, Los Angeles, CA (1984).

10. Weber, W. J., Jr., Physicochemical Processes for Water Quality Control, Wiley-Interscience, New York, (1972).

11. Cherimisinoff, P.N., and Ellerbusch, F., ed. Carbon Adsorption Handbook, Ann Arbor Science Publishers, Inc., Ann Arbor, (1978).

12. McGuire, M.J., and Suffet, I.H., ed. Activated Carbon Adsorption of Organics from the Aqueous Phase, Vol. 1 and 2, Ann Arbor Science Publishers Inc., Ann Arbor, (1980).

13. McGuire, M.J., and Suffet, I.H., ed. Treatment of Water by Granular Activated Carbon, Advances in Chemistry Series, 202, American Chemical Society, Washington, D.C., (1983).

14. Slejko, F.L., ed. Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application, Marcel Dekker, Inc., New York, (1985).

15. Ruthven, D.M., Principles of Adsorption and Adsorption Processes, John Wiley and Sons, Inc. New York, 1984.

16. Cussler, E.L., Diffusion: Mass Transfer in Fluid Systems, Cambridge University Press, Cambridge, 1984.

17. Johnson, R.L., Lowes, F.J., Jr., Smith, R.M., and Powers, T.J., "Evaluation of the Use of Activated Carbons and Chemical Regeneration in Treatment of Wastewaters. Public Health Service Publication No. 999-WP-12, 1964.

18. Keinath, T.M., "Mathematical Modeling of Heterogeneous Sorption in Continuous Contactors for Wastewater Decontamination." Final Report, Contract No. DADA-17-72-C-2034, Clemson University, S.C. (1973).

19. Zanitch, R.T. and Stenzel, M.H., Economics of Granular Activated Carbon Water and Wastewater Treatment Systems, in Carbon Adsorption Handbook, P.N. Cheremisinoff S., R. Ellerbugeh, Eds., Ann Arbor Science Publishers, Ann Arbor, Michigan, 1978.

20. Zogorski, J.S., and Faust, S.S., "Operational Parameters for Optimum Removal of Phenolic Compounds from Polluted Waters by Columns of Activated Carbon." American Institute of Chemical Engineers Symposium Series Water I. Physical, Chemical Wastewater Treatment, 73 (166): 54 (1976).

21. Weber, W.J., and Keinath, L.M., "Mass Transfer of Purgeable Pollutants from Dilute Aqueous Solution in Fluidized Bed Adsorbers." Chemical Engineering Progress Symposium Series - Physical Adsorption Processes and Principles, 74 (63): (1967).

22. Al-Bahrani, K.S., and Martin, J.R., "Adsorption Studies Using Gas-Liquid Chromatography - I. Effect of Molecular Structure." Water Research, 10, (1976).

23. Giusti, D.kM., Conway, R.A. and Lawson, C.T., "Activated Carbon Adsorption of Petrochemicals", Jour. WPCF, 46, (1974).

24. Morris, J.C. and Weber, W.J., Jr., "Adsorption of Biochemically Resistant Materials from Solution, Part II." U.S. Public Health Service, AWTR-16, Report 999-WR-33 (1966).

25. Singer, P.C. and Yen, C.Y., "Adsorption of Alkylphenols by Activated Carbon", Chapt. 8 in Activated Carbon Adsorption of Organics from Aqueous Phase, Vol. 1, ed. by I.H. Suffet and M.J. McGuire, Ann Arbor Science Publishers, Inc., Ann Arbor, MI (1980).

26. Ward, T.M., and Getzen, F.W., "Influence of pH on the Adsorption of Aromatic Acids on Activated Carbon." Environmental Science and Technology, Vol. 4, No. 1, (1970).

27. Murin, C.J., and Snoeyink, V.L., "Competitive Adsorption of 2,4-Dichlorophenol and 2,4,6-Trichorophenol in the Nanomolar to Micromolar Concentration Range." Environmental Science and Technology, Vol. 13, No. 3, (1979).

28. Coughlin, R.W., and Ezra, F.S., "Role of Surface Acidity in the Adsorption of Organic Pollutants on the Surface of Carbon." Environmental Science and Technology, Vol. 2, No. 4, (1968).

29. Fritz, W., Merk, W., and Shlunder, E.U., "Competitative Adsorption of Two Dissolved Organics onto Activated Carbon - II," Chemical Engineering Science, Vol. 36, 1981, p. 731.

30. Martin, R.J. and Al-Bahrani, K.S., "Adsorption Studies Using Gas-Liquid Chromatography - II. Competitive Adsorption Water Research, Vol. 11, 1977, p. 991.

31. Merk, W., Fritz, W., and Shlunder, E.U., "Competitative Adsorption of Two Dissolved Organics Onto Activated Carbon - III." Chemical Engineering Science, Vol. 36, 1981, p. 743.

32. Weber, W.J., Jr., "Evolution of a Technology," Journal of the Sanitary Engineering Division, ASCE, Vol. 110, No. 5, Oct. (1984).

33. Langmuir, I., "The Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum," J. Amer. Chem. Soc., 40, 1361, (1918).

34. Mattson, J.S., Mark, H.B., Jr., Malbin, M.D., Weber, W.J., Jr., and Crittenden, J.C., "Surface Chemistry of Active Carbon: Specific Adsorption of Phenols", J. Colloid Interface Sci., 31, 116, (1969).

35. Weber, W.J., Jr., and Morris, J.C., "Kinetic of Adsorption on Carbon from Solution," J. San. Eng. Div. of ASCE, SA2, 31 (1963).

36. Brunauer, S., Emmett, P.H., and Teller, E., "Adsorption of Gases in Multimolecular Layers," Jour. Am. Chem. Soc., 60, 309 (1938).

37. Jain, J.S., and Snoeyink, V.L., "Adsorption from Bisolute Systems on Active Carbon," JWPCF, Vol. 45, 1973, p. 2463.

38. Thiem, L.T., Badorek, D.L., Johari, A., and Alkhatib, E., "Adsorption of Synthetic Organic Shock Loadings", manuscript accepted for publication in ASCE, 1986.

39. Freundlich, H., Colloid and Capillary Chemistry, Matheum and Co., Ltd., London, (1926).

40. Weber, W.J., Jr., Physicochemical Processes for Water Quality Control, Wiley-Interscience, New York, (1972).

41. Fritz, W., and Schluender, J.M., "Simultaneous Adsorption Equilibria of Organic Solutes in Dilute Aqueous Solution of Activated Carbon", Chem. Eng. Sci., 29, 1974, p. 1279.

42. Radke, C.J., and Prausnitz, J.M., "Adsorption of Organic Solutes from Dilute Aqueous Solution by Activated Carbon", Ind. Eng. Chem. Fund., 11, 1972, p. 445.

43. Mathews, A., Mathematical Modeling of Multicomponent Adsorption in Batch Reactors, Thesis, University of Michigan (1975).

44. Myers, A.L. and Prausnitz, J.M., "Thermodynamic of Mixed-Gas Adsorption", Jour. AIChE, Vol. 11, No. 1, p. 121.

45. Radke, C.J., and Prausnitz, J.M., "Thermodynamics of Multi-Solute Adsorption from Dilute Liquid Solutions," Jour. AIChE, Vol. 18, No. 4, pp. 761 (1972).

46. Jossens, L., Prausnitz, J.M., Fritz, W., Schlunder, E.U. and Myers, A.L., "Thermodynamics of Multi-Solute Adsorption from Dilute Aqueous Solutions," Chem. Eng. Sci., Vol. 33, 1978, p. 1097.

47. Myers, A.L., and Zolandz, R.R., "Effect of pH on Multi-Component Adsorption from Dilute Aqueous Solution", Chapter 12 in Vol. 1 Reference 12.

48. Frye, W.H., "Predictions of Competitive Adsorption: Observations of Anomalous Behavior in Specific Bi - and Tri-Solute Systems", Ph.D. Dissertation, University of Massachusetts at Amherst, 1980.

49. Rowley, H.H., and Innes, W.B., J. Phys. Chem., Vol. 46, 1942, p. 548.

50. Kidnay, A.J. and Myers, A.L., "A Simplified Method for the Prediction of Multicomponent Adsorption Equilibria from Single Gas Isotherms", Jour. AIChE, Vol. 12, No. 5, 1966, p. 981.

51. Yen, C.Y., and Singer, P.C., "Competitive Adsorption of Phenols on Activated Carbon", Journal of the Sanitary Engineering Division, ASCE, Vol. 110, No. 5, Oct. (1984).

52. Crittenden, J.C., Luft, P., Hand, D.W., Oravitz, J., Loper, S.W. and Metin, A., "Prediction of Multicomponent Adsorption Equilibria Using Ideal Adsorbed Solution Theory", Manuscript Submitted to Environmental Science and Technology, January 26th, 1984.

53. Neretnieks, I., "Analysis of Some Adsorption Experiments with Activated Carbon," Chemical Engineering Science, Vol. 31, 1976, p. 1029.

54. Roberts, P.V. and York, R.Y., "The Adsorption of Normal Paraffins from Binary Liquid Solutions by Molecular Sieve 5A Adsorbent, "Industrial Engineering of Chemical Process Design Development Vol. 6, No. 4, 1967, p. 516.

55. Hand, D.W., Crittenden, J.C. and Thacker, E.W., "User-Oriented Batch Reactor Solutions to the Homogeneous Surface Diffusion Model," ASCE, Vol. 109, No. EE2, 1983, p. 82.

56. Wilke, C.R., and Chang, P., "Correlation of Diffusion Coefficients in Dilute Solutions," American Institute of Chemical Engineering Journal, Vol. 1, 1955, p. 264.

57. Treybal, R.E., Mass Transfer Operation, 3rd ed., McGraw-Hill, N.Y., 1980.

58. Levenspiel, O., Chemical Reaction Engineering, John Wiley and Sons, New York, N.Y., 1972.

59. Weber, W.J., Jr., and Liu, K.T., "Determination of Mass Transport Parameters for Fixed-Bed Adsorbers," Chemical Engineering Communication, Vol. 6, 1980, p. 49.

60. Sherwood, T., Pigford, R., Wilke, C., Mass Transfer, McGraw-Hill Book Co., Inc. New York, N.Y., 1975.

61. Hobler, T., Mass Transfer and Absorbers, Pergamon Press, New York, N.Y., 1966.

62. Williamson, J.E., Bazaire, K.E., and Geankoplis, C.J., "Liquid Phase Mass Transfer at Low Renyalds Numbers," I&EC Fundamentals Vol. 2, No. 2, 1963, p. 126.

63. Wakao, N. and Funozkri, T., "Effect of Fluid Dispersion Coefficients on Particle-to-Fluid Mass Transfer Coefficients in Packed Beds," Chemical Engineering Science Vol. 33, 1978, p. 1375.

64. Weber, W.S., Jr., Crittenden, J.C., "Madam I-A Numeric Method for Design of Adsorption Systems," JWPCF Vol. 47, No. 5, 1975, p. 924.

65. Crittenden, J.C. and Weber, W.J., Jr., "Predictive Model for Design of Fixed-Bed Adsorbers: Single Component Model Verification," ASCE, EE3, 1978.

66. Famularo, J., Muller, J.A., and Pannu, A.S., "Prediction of Carbon Column Performance from Pure-Solute Data," JWPCF, Vol. 52, No. 7, 1980, p. 2019.

67. Crittenden, J.C., Hand, D.W. and Thacker, W.E., "Simplified Models for Design of Fixed-Bed Adsorption Systems," ASCE, JEE, Vol. 110, No. 2, 1984, p. 440.

68. Weber, W.J., Jr., and Rumer, R.R., "Intraparticle Transport of Sulfonated Alkylbenzenes in Porous Solid: Diffusion with Nonlinear Adsorption," Water Resources Res. Vol. 1, 1965, p. 361.

69. Dedrick, R.L., and Beckmann, R.B., "Kinetics of Adsorption by Activated Carbon from Dilute Aqueous Solution," AIChE Symp. Ser. No. 74, 1967.

70. Furusawa, T., and Smith, J.M., "Fluid-Particle and Intraparticle Mass Transport in Slurries," Ind. Eng. Chem. Fundamentals, Vol. 12, 1973, p. 197.

71. Weber, T.W. and Chakravorti, R.K., "Pore and Solid Diffusion Models for Fixed-Bed Adsorbers," AIChE Journal, Vol. 20, No. 2, 1974, p. 228.

72. Frederick, S.C., Roberts, P.V., "Activated Carbon Sorption of DOC from Wastewater," ASCE, Vol. 108, No. EE4, 1982, p. 766.

73. Crittenden, J.C., "Mathematic Modeling of Fixed Bed Adsorbers Dynamic-Single Component and Multicomponent," Thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Civil Engineering, Water Resources Engineering), University of Michigan, (1976).

74. Neretnicks, I., "Adsorption in Finite Bath and Countercurrent Flow with Systems having a Nonlinear Isotherm," Chemical Engineering Science, Vol. 31, 1976, p. 107.

75. Liu, K.T. and Weber, W.J., Jr., "Characterization of Mass Transfer Parameters for Adsorber Modeling and Design", WPCF Journal, Vol. 53, No. 10, 1981, p. 1541.

76. Furusawa, T., and Smith, J.M., "Fluid-Particle and Intraparticle Mass Transport Rates in Slurries," Ind. Eng. Chem. Fundam., Vol. 12, 1973, p. 197.

77. Mathews, A.P., and Weber, W.J., Jr., "Effect of External Mass Transfer and Intraparticle Diffusion on Adsorption Rates in Slurries Reactor," Amer. Inst. Chem. Engr. Symp. Ser., Vol. 73, 1977, p. 91.

78. Suzuki, M. and Kawazoe, K., "Batch Measurement of Adsorption Rate in an Agitated Tank," Journal of Chemical Engineering of Japan, Vol. 7, No. 5, 1974, p. 346.

79. Suzuki, M., and Kawazoe, K., "Effective Surface Diffusion Coefficients of Volatile Organics on Activated Carbon During Adsorption from Aqueous Solution," Journal of Chemical Engineering of Japan, Vol. 8, No. 5, 1975, p. 379.

80. Suzuki, M. and Kawazoe, K., "Concentration Decay in a Batch Adsorption Tank," Seisan-Kenkyu, Vol. 26, No. 7, 1974, p. 29.

81. Hand, D.W., Friedman, G. and Crittenden, J., "User Manual for Executing the Batch and Fixed Bed HSDM and PSDM Computer Algorithms," Michigan Technological University Houghton, Michigan, 1985.

82. Crittenden, J.C., Wong, B.W.C., Thacker, W.E., Snoeyink, V.L., and Hinrichs, B.L., "Mathematical Model of Sequential Loading in Fixed-Bed Adsorbers," JWPCF, Vol. 52, No. 11, 1980, p. 2780.

83. Villadsen, J.V. and Stewart, W.E., "Solution of Boundary-Value Problems by Orthogonal Collocation." Chem. Eng. Sci. (G.B.), Vol. 22, 1967, p. 1483.

84. Finlayson, B.A., <u>The Method of Weighted Residuals and Variational Principles</u>, Academic Press, New York, N.Y. 1972.

85. Villadsen and Michelsen, <u>Solution of Differential Equation Models by Polynomial Approximation</u>. Prentice-Hall, Englewood Cliffs, N.J., 1978.

86. Stroud and Secrest, <u>Gaussian Quadrature Formulas</u>, Prentice-Hall, Englewood Cliffs, N.J., 1966.

87. Keinath, T.M., "Mathematical Modeling of Heterogeneous Sorption in Continuous Contactors for Wastewater Decontamination". Final Report, Contract No. DADA-17-72-C-2034, Clemson University, S.C., 1977.

88. Scholen, J.J.F., Porous Carbon Solids, Academic Press, London and New York, 1967, p. 237.

89. CRC Handbook of Chemistry and Physics, 61st Edition, CRC Press, Inc., 1980-1981.

90. Dobbs, R.A. and Cohen, J.M., "Carbon Adsorption Isotherms for Toxic Organics," EPA-600/8-80-023, 1980.

91. Environmental Protection Agency, Federal Register, Part VIII, 40 CFR Part 136, Oct., 1984.

92. Polanyi, M., "Adsorption of Gases (vapors) by a Solid Nonvolatile Adsorbent," Verh. Dent. Physik. Ges. 18:55 (1916); "Adsorption from Solutions of Substances of Limited Solubility," Z. Physik 2:111, (1920).

93. Manes, M., "The Polanyi Adsorption Potential Theory and its Applications to Adsorption from Water Solution onto Activated Carbon." Activated Carbon Adsorption of Organics from the Aqueous Phase, Vol. 1, Editors Suffet, I. and McGuire, M., 1980.

94. Manes, M., and Greenbank, M., "Adsorption of Multicomponent Liquids from Water Onto Activated Carbon: Convenient Estimation Methods," Treatment of Water by Granular Activated Carbon, Advances in Chemistry Series 202, Editors McGuire, M., and Suffet, I., 1983.

95. Manes, M. and Hofer, L.J.E., "Application of the Polanyi Adsorption Potential Theory to Adsorption from Solutions on Activated Carbon," J. Phys. Chem. Vol. 73, 1969, p. 584.

96. Bethea, R.M., Duran, B.S., and Soullion, T.L., Statistical Methods for Engineers and Scientists, Marcel Dekker, Inc., New York, N.Y., 1985.

97. Leggett, R.W., and Williams, L.R., "A Reliability Index for Models," Ecological Modeling, Vol. 13, 1981, p. 303.

98. Letterman, R.D., Quon, J.E. and Gemmel, R.S., "Film Transport Coefficient in Agitated Suspensions of Activated Carbon," JWPCF, Vol. 46, No. 11, 1974, p. 2537.

99. Fried, J.J., Combarnous, N.A., in V.T. Chow ed., Advances in Hydroscience, Academic Press, New York, N.Y., 1971.

NOTATION

Roman Symbol	Description and Units
A	Area of solution - solid interface
a_{io}	Freundlich isotherm constant for multi-solute system
a	External surface area/unit volume
B	BET Energy Constant (dimensionless)
b	Langmuir model constant related to net enthally
b_{io}	Isotherm constnat (dimensionless)
b_{ij}	Isotherm constant (dimensionless)
Bi	Biot number = $k_f R/3D_s \varepsilon$ (dimsionless)
C	Bulk solution concentration (M/L^3)
C_c	Saturation concentration (M/L^3)
C_e	Equilibrium concentration (M/L^3)
C_i	Solute i bulk liquid concentration in Gibbs-Duhem
C_o	Influent concentration in packed bed and concentration at $t = o$ in batch system (M/L^3)
C_p	Adsorpate concentration in particle pore void (M/L^3)
C_s	Solvent concentration in Gibbs-Duhem equation ($Mole/L^3$)
C_s	Fluid phase concentration near surfaceparticle (M/L^3)
D_e	Dispersion coefficient (L^2/T)
D_g	Solute distribution parameter $q_e \rho_s (1-\varepsilon)/C_o \varepsilon$ (dimensionless)
D_L	Molecular diffusivity (L^2/T)
D_p	Pore diffusion coefficient(L^2/T)
D_s	Surface diffusion coefficient (L^2/T)
$f(c)$	Solid phase concentration as a function of liquid phase concentration (M/M)
f_i	Fugacity of adsorbate i in mixture (M/T^2)

FSY	Constant i Singer-Yen modified Freundlich model
H	Helmholtz energy of the adsorbed phase (ML^2/T^3), kcal/Mole)
K	Freundlich isotherm constant, β,M. Freundlich Constant
K_a	Adsorption energy constant in polanyi model (Mole/K.Joul)
K_f	Liquid film mass transfer (L/T)
K_g	Geometrical reliability index (dimensionless)
K_h	Henry's coefficient
K_{ho}	Henry's coefficient referenced to temperature T_o
K_s	Statistical reliability index (dimensinless)
L	Packed bed length (L)
m	Carbon dosage (M/L^3)
M_p	Melting point OC
M_w	Molecular weight (g)
M_v	Molecular volume $((\AA)^3)$
nD	Refractive index
Nd	Surface diffusion modulus $D_s D_g \tau/R^2$ (dimensionless)
1/Nf	Freundlich isotherm and modified Freundlich constant (dimensionless)
n_i	Number of moles of solute i in solution
n_s	Number of moles adsorbed on surface
n_T	Total number of moles
P	Power dissipated in batch reactor (ML^2/l^3)
P_e	Peclet number $V_a L/\varepsilon D_e$ (dimensionless)
P_s	Specific power (L^2/T^3)
q_e	Adsorbent phase concentration in equilibrium (M/M)
q_m	Langmuir monolayer saturation constant (M/M)
q_s	Solid phase concentration at particle surface (M/M)

q_x	Singer-Yen model constant
R	Adsorbent radius (L)
R	Gas constant (Joules/Deg. Mole)
r	Radial coordinate (L)
R_N	Reynold number (dimensionless)
R_p	Radius of intraparticle pore (L)
S	Entropy
$\underline{S}$	Schmidt number $\mu/\rho_L D_L$ (dimensionless)
Sh	Sherwood number 2 $k_f R/D_L$ (dimensionless)
St	Stanton number
St	Modified Stanton number $St/3^oC$ (dimensionless)
T	Absolute temperature (^oK)
t	time (T)
T	Torque
ΔU_o	Difference in internal energy between adsorbed and disolved phases (ML^2/T^2)
V_a	Approach velocity in carbon bed (L/T)
V_m	Molal volume (L^3/Mole)
V_p	Adsorbent pore volume ($(A^o)^3$)
V_s	Superficial velocity in column = V_a (L/T)
W_o	Maximum solid phase loading in Polanyi model (L^3/M)
XK	Denote Freundlich constant in adsorption models
Z	Longitudinal coordinate in packed bed (L)
Z_i	Adsorbed-phase mole fraction

GREEK

α	Isotherm constant in three parameters model
β	Isotherm constant in three parameters model

B_1	Slope constant in linear regression
B_o	Intercept constant in linear regression
ε	Bed void fraction (dimensionless)
ε	Adsorption potential in Polanyi model (L^3/K•Joul)
ε_p	Intraparticle void fraction (dimensionless)
μ	Liquid viscosity (M/L•T)
μ_i	Chemical potential of solute (kcal/mde, ML^2/T^2)
μ_s	Chemical potential of solvent (Kcal/mole, ML^2/T^2)
π	spreading pressure = difference in interfacial tension of pure solvent and solid interface (M/T^2)
ρ_a	Apparent density (M/L^3)
ρ_l	Fluid density (M/L^3)
ρ_s	Density of the solid including pore voids (M/L^3)
ρ	Density of compound (M/L^3)
σ	Interfacial tension
τ	Hydraulic residence time (T)
ω	Angular velocity
ϕ	Association factor of solvent = 2.6 for water

SUBSCRIPT

i	Denote solute i
r	Denote reference component in polanyi model
s	Denote solvent
T	Denote total amount

SUPERSCRIPT

a	Denote adsorbed phase
ℓ	Denote liquid phase
m	Denote unspecified amount of adsorbent

o	Denote single-solute adsorption
#	Denote ideal dilute solution (Henry's Law)
-	Denote dimensionless symbol
Λ	Denote estimated value in t-test distribution

ABBREVIATIOANS

DAF	Dissolved Air Flotation
DFHSDM	Dispersed Flow Homogenous Surface Diffusion Model
DFPSDM	Dispersed Flow Pore Surface Diffusion Model
DOC	Dissolved Organic Carbon
GAC	Granular Activated Carbon
HSDM	Batch Homogenous Surface Diffusion Model
IAS	Ideal Adsorption Theory
KNPC	Kuwait National Petroleum Company
LPG	Liquified Petroleum Gas
MS_R	Mean Square Error
PAC	Powdered Activated Carbon
PHSDM	Plug Flow Homogenous Surface Diffusion Model
PPSDM	Plug Flow Pore and Surface Diffusion Model
PSDM	Batch Pore and Surface Diffusion Model
RE	Relative Error
RMSE	Relative Mean Square Error
SIA	Shuaiba Industrial Area - Kuwait
SS_R	Sum of Squares Due to Regression
T	Student-t-Test

APPENDIX A

- Preparation of Activated Carbon
- Procedures for Conducting Isotherm Studies

Appendix A Methodology for Carbon Preparation and Bottle Point Isotherm Studies

The following procedures were applied for conducting all adsorption isotherm experiments performed in this study. The methodology emphasized reducing the possibility of contamination by external sources of trace organics and the elimination of any substantial microorganism activity.

I. Cleaning procedure

All glassware used in the isotherm studies was cleaned from any trace organics according to the following procedure:

a. All glassware was washed with a free phosphate laboratory cleaning agent.

b. The washed classware was then rinsed with ultra pure water which was prepared in the following manner:

1. Distilled water produced using Wheaton autostill - 5 distillation unit.
2. The distilled water was passed through activated carbon column to remove traces of organics.
3. The organic free water was then filtered using millipore membrane filter (size 0.45 μ) to remove microorganisms.

II. Preparation of powdered activated carbon

As the time to equilibrium is dependent on activated carbon particle size, powdered activated carbon was used to conduct all isotherm studies. The powdered activated carbon (PAC) was prepared from representative granular activated carbon (GAC) used in the mini column and pilot plant studies.

a. Procedure for washing GAC

1. The GAC was placed in clean 500 ml glass beakers one third full of carbon and washed with ultrapure water while stirring until all scum and fine materials were removed.
2. The extra water in the beakers was decanted and the wet carbon dried over night at 105°C.
3. The dried carbon was put in a dessicator for two hours. The dessicated carbon was then transferred to a clean bottle and stored airtight for future use.

b. Crushing GAC

a. A ball mill was used for crushing the GAC. All the equipment used for crushing the GAC was first cleaned in accordance with glass cleaning procedure described in section 1.

1. A reasonable portion of the washed GAC was placed in the ball mill and allowed to crush for 30 minutes.
2. The crushed carbon was sieved through U.S. No. 200 and 325 sieves for a period of 20 minutes.
3. The carbon retained on the 325 mesh screen was collected and steps 1 and 2 were repeated on the portion of carbon retained on the 200 mesh screen.
4. Steps 1,2,3 were repeated in sequence until enogh PAC was collected.

c. Procedure for washing PAC

1. The PAC produced in the previous section was placed in isotherm bottles up to the one-third mark.
2. The remaining volume was then filled with ultra pure water and shaken for a few minutes. Then centrifuged for 20 minutes.
3. The supernatant was poured off to remove any remaining fines produced during crushing.

An airtight dark bottle was dried overnight at 105°C.

5. The dried bottle was then dessicated for 20 minutes.
6. The PAC was then placed in the airtight bottles and stored in the dark for further usage.

III. Conducting Isotherm Studies

a. Determination of Carbon Dosages

The procedure described below presents the determination of carbon dosages using the Freundlich isotherm model. The equations can be modified to incorporate any other isotherm model required.

1. The initial solute concentration can be calculated considering the highest solid phase concentration required q and the optimum balance accuracy available. The equation used is:

$$C_O = Ce + qM/V$$

2. Range of carbon dosages can be determined based on the accuracy of the instrument available for

measuring solute concentration Ce, and the accuracy of the balance available.

$$M = V(Co - Ce)/q$$

b. Solution Preparation

1. The required volume of ultra pure water and/or the background water was placed in a suitable size glass container.
2. The water matrix was buffered using a 10-3 M phosphate buffer. (1 mL of potassium monobasic phosphate solution per liter of water). pH was adjusted to the required pH using 1N NaOH or 1N H_2SO_4.
3. A stock solution of the required priority organics was prepared in ultra pure methylene chloride solvent.
4. The stock solution was spiked in excess of the initial concentration required in the water matrix with the volume not to exceed 1% of the total volume. Continuum mixing was maintained in the container using a magnetic stirrer, until all methylene chloride evaporates.

c. The solution was filtered through a glass wool filter to remove any suspended solids or any organics containing undissolved particles.

d. The carbon dosages were added to each isotherm bottle except the blank bottles. The bottles were then filled with the prepared solution by siphoning from the solution container until there was no headspace and tightly capped.

e. The bottles were then placed on the rotating contactor to reach equilibrium for 6 days.

APPENDIX B

Single-Solute Isotherm Data

Table B-1. Single Solute Isotherm Data for 2,4-Dimethylphenol

Initial Conc. C_o (mg/L)	Carbon Dose (mg/L)	Equilibrium Conc. C_e (mg/L)	Solid phase Conc. q_e (mg/mg-C)	C_e (M/L)	q_e (M/g-C)
108.810	111.10	64.097	0.402	0.5247E-3	0.3294E-2
108.810	187.80	35.411	0.391	0.2898E-3	0.2898E-2
19.649	37.10	10.007	0.260	0.8192E-4	0.2128E-2
19.649	60.80	6.279	0.220	0.5140E-4	0.1801E-2
19.649	84.10	3.139	0.196	0.2570E-4	0.1608E-2
3.910	7.20	1.930	0.275	0.1580E-4	0.2247E-2
3.910	26.20	0.770	0.120	0.6300E-5	0.9823E-3

Test Characteristics:

Adsorbed type = Activated Carbon F-400
Adsorbent size = Powder, 200 x 325 U.S. Sieve No.
pH = 6.8, Buffered
Temperature = 22°C
Equilibrium period = 6 days
Compound M.W. = 122.16

Table B-2. Single Solute Isotherm Data for Naphthalene

Initial Conc. C_o (mg/l)	Carbon Dose (mg/l)	Equilibrium Conc. C_e (mg/l)	Solid Phase Concentration q_e (mg/mg-C)	C_e (M./L)	q_e (M./g-C)
32.666	21.06	19.288	0.635	0.1505E-3	0.4956E-2
32.666	52.63	9.248	0.615	0.7216E-4	0.3472E-2
32.666	105.26	1.290	0.298	0.1009E-4	0.2326E-2
8.035	2.11	7.032	0.476	0.5487E-4	0.3717E-2
8.035	15.27	3.214	0.316	0.2505E-4	0.2469E-2
8.035	35.76	0.732	0.204	0.5712E-5	0.1593E-2
1.520	21.06	0.034	0.070	0.2708E-6	0.5501E-3
1.520	10.53	0.157	0.129	0.1222E-5	0.1011E-2

Test Characteristics:

Adsorbent type = Activated carbon F=400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.8, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Compound M.W. = 128.16

Table B-3. Single Solute Isotherm Data for Fluorene

Initial Conc. C_o (mg/l)	Carbon Dose (mg/l)	Equilibrium Conc. C_e (mg/l)	Solid Phase Concentration q_e (mg/mg-C)	C_e (M/L)	q_e (M/g-C)
1.353	0.52	1.013	0.650	0.6097E-5	0.3917E-2
1.353	1.05	0.787	0.540	0.4733E-5	0.3247E-2
1.353	3.16	0.133	0.270	0.8020E-6	0.1625E-2
1.353	10.10	0.027	0.131	0.1606E-6	0.7904E-3
1.187	1.93	0.410	0.368	0.2467E-5	0.2215E-2
1.187	5.26	0.072	0.212	0.4332E-6	0.1275E-2

Test Characteristics:

Adsorbent type = Activated carbon F-400
Adsorbent size = Powder, 200x325 U.S. Sieve No.
pH = 6.8, Buffered
Temperature = 22°C
Equilibrium period = 6 days
Compound M.W. = 166.21

Table B-4. Single Solute Isotherm Data for Pyrene

Initial Conc.	Carbon Dose	Equilibrium Conc.	Solid Phase Concentration		
C_o (mg/l)	(mg/l)	C_e (mg/l)	q_e (mg/mg-C)	C_e (M/L)	q_e (M/g-C)
0.0693	0.105	0.0400	0.2791	0.1978E-6	0.1340E-2
0.0415	0.052	0.0253	0.3115	0.1251E-6	0.1540E-2
0.0415	0.078	0.0213	0.2590	0.1053E-6	0.1281E-2
0.0415	0.160	0.0106	0.1931	0.5240E-7	0.9548E-3
0.0415	0.320	0.0312	0.1260	0.1540E-7	0.5934E-3
0.0415	0.420	0.0012	0.0960	0.5900E-8	0.4747E-3

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.8, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Compound M.W. = 202.24

Table B-5. Single Solute Isotherm Data for Bis (2-Ethylhexyl) phthalate

Initial Conc. C_o (mg/l)	Carbon Dose (mg/l)	Equilibrium Conc. C_e (mg/l)	Solid Phase Concentration q_e (mg/mg-C)	C_e (M/L)	q_e (M/g-C)
0.4733	2.72	0.2827	0.0701	0.7238E-6	0.1798E-3
0.4733	7.52	0.1467	0.0434	0.3756E-6	0.140E-3
0.4733	16.40	0.0423	0.0263	0.1083E-6	0.6730E-4
0.4733	38.33	0.0133	0.0120	0.3410E-7	0.3070E-4
0.0333	0.63	0.0213	0.0191	0.5450E-7	0.4880E-4
0.0333	3.15	0.0066	0.0085	0.1690E-7	0.2170E-4

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.8, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Compound M.W. = 390.56

APPENDIX C

Competitive Adsorption Data

- Ultrapure Water Background
- Complex Mixture Background

Table C-1. Data for Competitive Adsorption of Naphthalene and 2,4-Dimethylphenol in Ultrapure Water Background

	Carbon Dose	Equilibrium Concentration, C_e (mg/l)			
		Naphthalene		2,4-Dimethylphenol	
No.	(mg/l)	Experimental	IAS* Prediction	Experimental	IAS* Prediction
1	0.00	31.86	-	42.83	-
2	140.1	2.80	2.62	16.21	15.84
3	105.3	3.22	4.48	21.88	22.92
4	84.2	4.80	6.82	27.08	26.81
5	73.5	8.50	8.43	31.14	29.54
6	52.7	10.73	11.68	35.02	33.91
7	42.1	12.51	14.00	37.67	36.02
8	21.0	19.45	20.95	41.80	39.95
9	10.5	25.13	26.08	40.82	41.61

*IAS = Ideal Adsorption Solution Prediction

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Power, 200x325 U.S. Sieve No.

pH = 6.8, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Table C-2. Data for Competitive Adsorption of 2,4-Dimethylphenol, Naphthalene and Fluorene in Ultra Pure Water Background

		Equilibrium Concentration, C_e (mg/l)					
	Carbon Dose	2,4-Dimethylphenol		Naphthalene		Fluorene	
No.	(mg/l)	Experimental	IAS* Prediction	Experimental	IAS* Prediction	Experimental	IAS* Prediction
1	0.00	1.7591	-	0.8330	-	0.9640	-
2	15.75	0.6832	0.7064	0.0789	0.0708	0.09173	0.0250
3	10.53	0.9232	1.0360	0.1364	0.1493	0.0604	0.0519
4	7.90	1.1243	1.2390	0.2834	0.2301	0.0574	0.0823
5	5.30	1.5145	1.4460	0.3486	0.3641	0.1594	0.1444
6	3.20	1.6324	1.6000	0.5782	0.5296	0.2493	0.2582
7	2.10	1.7832	1.6680	0.5926	0.6364	0.3287	0.3773
8	1.05	1.8320	1.7220	0.6964	0.7418	0.5748	0.5808
9	0.42	1.6984	1.7460	0.7848	0.7996	0.7942	0.7805
10	0.21	-	1.7530	-	0.8169	-	0.8662

*IAS = Ideal Adsorption Solution Prediction

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.8, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Table C-3. Data for Competitive Adsorption of Pyrene, Fluorene and Bis(2-Ethylhexyl) Phthalate in Ultra Pure Water Background

	Carbon Dose	Equilibrium Concentration, C_e (μg/l)					
		Pyrene		Fluorene		Bis(2-ethylhexyl)phthalate	
No.	(μg/l)	Experimental	IAS* Prediction	Experimental	IAS* Prediction	Experimental	IAS* Prediction
1	0.000	95.8	-	153.0	-	179.9	-
2	3200	ND	0.346	13.4	7.268	108.5	121.800
3	2610	ND	0.516	15.3	9.874	141.2	136.700
4	1550	3.6	1.621	16.4	22.560	167.2	161.300
5	1050	ND	3.868	38.2	40.490	16.2	169.300
6	520	17.2	13.940	77.8	83.900	171.6	174.000
7	420	17.4	18.960	88.8	96.250	182.2	174.600
8	260	26.5	33.060	110.5	118.300	178.4	175.300

*IAS = Ideal Adsorption Solution Prediction

ND = Not Detected

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.8, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Table C-4. Isotherm Data of Dissolved Organic Compounds (DOC) in Typical Secondary Wastewater Treatment Facility Effluent

Carbon Dose mg/L	Equilibrium Conc. C_e (mg/l)	Solid Phase Conc. q_e (mg/mg-C)	C_e (M./L)	q_e (M./g-c)
0.00	16.51	-	-	-
15.8	14.02	0.158	0.1168E-2	0.1314E-1
42.1	11.58	0.117	0.9649E-3	0.9750E-2
52.5	11.30	0.099	0.9415E-3	0.8258E-2
73.5	10.18	0.086	0.8412E-3	0.7175E-2
106.0	8.60	0.075	0.7164E-3	0.6276E-2
146.7	8.61	0.054		
182.0	8.64	0.043		

Test Characteristics:

Adsorbent Type = Activated Carbon F-400

Adsorbent Size = Powder, 200x325 U.S. Sieve No.

pH = 6.9, Buffered

Temperature = 22°C

Equilibrium period = 6 days

DOC = Dissolved organic carbon

Table C-5. Data for Competitive Adsorption of 2,4-Dimethylphenol. Naphthalene and Fluorene in 10.1 mg/l DOC Background (Kingston Treatment Facility Effluent)

		Equilibrium Concentration, C_e (mg/l)					
	Carbon Dose	2,4-Dimethylphenol		Naphthalene		Fluorene	
No.	(mg/l)	Experimental	IAS* Prediction	Experimental	IAS* Prediction	Experimental	IAS* Prediction
1	0.00	1.6267	-	0.3028	-	1.0132	-
2	20.60	0.6132	0.3717	0.0634	0.0103	0.1623	0.0116
3	15.75	0.7238	0.5370	0.0932	0.0179	0.2582	0.0193
4	10.53	0.9950	0.8310	0.1348	0.0389	0.3813	0.0404
5	7.30	1.1750	1.0840	0.1523	0.0706	0.4953	0.0745
6	5.30	1.4583	1.2610	0.1834	0.1078	0.5288	0.1206
7	4.21	1.5456	1.3580	0.2974	0.1376	0.7345	0.1653
8	3.16	1.5753	1.4460	0.2538	0.1745	0.9218	0.2353
9	2.05	1.6013	1.5280	0.3175	0.2211	0.8033	0.3651
10	1.05	1.5863	1.5870	0.2913	0.2652	0.8625	0.5830

*IAS = Ideal Adsorption Solution Prediction

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.9, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Type of Wastewater = Secondary effluent with 10.1 mg/l DOC

Table C-6. Data for Competitive Adsorption of 2,4-Dimethyl Phenol, Naphthalene and Fluorene in 19.1 mg/c DOC Background (Kingston Treatment Facilty Effluent)

		Equilibrium Concentration, C_e (mg/l)					
	Carbon Dose	2,4-Dimethylphenol		Naphthalene		Fluorene	
No.	(mg/l)	Experimental	IAS* Prediction	Experimental	IAS* Prediction	Experimental	IAS* Prediction
1	0.00	1.5933	-	0.4399	-	0.6533	-
2	20.60	0.6037	0.3485	0.0927	0.0139	0.1936	0.0070
3	15.75	0.7503	0.5025	0.0155	0.0239	0.2867	0.0116
4	10.53	1.1237	0.7833	0.2208	0.0516	0.3713	0.0242
5	7.30	1.2526	1.1030	0.2706	0.0937	0.4482	0.0443
6	5.30	1.4133	1.2050	0.3041	0.1433	0.4014	0.0712
7	4.21	1.4825	1.3010	0.4123	0.1835	0.5110	0.0971
8	3.16	1.4468	1.3920	0.4662	0.2347	0.4663	0.1376
9	2.05	1.5375	1.4790	0.4688	0.3028	0.5163	0.2138
10	1.05	1.6014	1.5450	0.4303	0.3730	0.6288	0.3489

*IAS = Ideal Adsorption Solution Prediction

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.9, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Type of Wastewater = Secondary effluent with 19.01 mg/l DOC

Table C-7. Data for Competitive Adsorption of 2,4-Dimethylphenol, Naphthalene and Fluorene in 27.3 mg/l DOC Background (Kingston Treatment Facility Effluent)

		Equilibrium Concentration, C_e (mg/l)					
		2,4-Dimethylphenol		Naphthalene		Fluorene	
No.	Carbon Dose (mg/l)	Experimental	IAS* Prediction	Experimental	IAS* Prediction	Experimental	IAS* Prediction
1	0.00	1.8330	-	2.5375	-	0.72001	-
2	20.60	1.4798	0.7765	1.6253	0.2532	0.1889	0.0204
3	15.75	1.5251	1.0200	1.7483	0.4251	0.3066	0.0337
4	10.53	1.6125	1.3260	1.9625	0.7792	0.4122	0.0647
5	7.30	1.6813	1.5140	2.1253	1.1480	0.4849	0.1059
6	5.30	1.8124	1.6210	2.2613	1.4570	0.5937	0.1526
7	4.21	1.8205	1.6750	2.3388	1.6530	0.6568	0.1919
8	3.16	1.8274	1.7220	2.4038	1.8610	0.7467	0.2465
9	2.05	1.8167	1.7670	2.4513	2.0970	0.7234	0.3352
10	1.05	1.8443	1.8030	2.4613	2.3170	0.7198	0.4677

*IAS = Ideal Adsorption Solution Prediction

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.9, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Type of Wastewater = Secondary effluent with 27.3 mg/l DOC

Table C-8. Data for Competitive Adsorption of 2,4-Dimethylphenol, Naphthalene and Fluorene in Treated Refinery Wastewater Background

No.	Carbon Dose (mg/l)	Equilibrium Concentration, C_e (mg/l)					
		2,4-Dimethylphenol		Naphthalene		Fluorene	
		Experimental	IAS* Prediction	Experimental	IAS* Prediction	Experimental	IAS* Prediction
1	0.00	0.5065	-	1.1330	-	0.1800	-
2	42.10	0.2934	0.0348	0.6414	0.0797	0.0441	0.0010
3	31.51	0.3146	0.0521	0.7508	0.0129	0.0682	0.0008
4	20.60	0.3738	0.0967	0.8504	0.0285	0.0982	0.0016
5	10.53	0.4379	0.2374	0.9834	0.1172	0.1214	0.0061
6	7.30	0.4863	0.3245	1.0888	0.2314	0.1354	0.0119
7	5.30	0.5339	0.3831	1.1700	0.3647	0.1692	0.0197
8	4.21	0.5018	0.4139	1.1295	0.4688	0.1583	0.2690
9	3.16	0.5028	0.4418	1.3245	0.5956	0.1813	0.0378
10	1.05	0.5040	0.4888	1.2845	0.9342	0.1789	0.9137
11	0.53	0.5136	0.4982	1.3438	1.0320	0.1805	0.1236

*IAS = Ideal Adsorption Solution Prediction

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.9, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Type of Wastewater = Secondary effluent with 18.1 mg/l DOD

Table C-9. IAS Prediction of Competitive Adsorption in 10.1 mg/l DOC Concentration Background Using Competitive Isotherm Parameters

No.	Carbon Dose (mg/l)	Equilibrium Concentration, C_e (mg/l)					
		2,4-Dimethylphenol		Naphthalene		Fluorene	
		Experimental	IAS* Prediction	Experimental	IAS* Prediction	Experimental	IAS* Prediction
1	0.00	1.6767	-	0.3028	-	1.0133	-
2	20.60	0.6132	0.7713	0.0634	0.1559	0.1623	0.3440
3	15.75	0.7238	0.9428	0.0932	0.1828	0.2582	0.4404
4	10.53	0.9950	1.1440	0.1348	0.2145	0.3813	0.5700
5	7.30	1.1750	1.2830	0.1523	0.2380	0.4953	0.6740
6	5.30	1.4563	1.3730	0.1864	0.2538	0.5288	0.7507
7	4.21	1.5456	1.4240	0.2974	0.2630	0.7345	0.7964
8	3.16	1.5753	1.4740	0.2538	0.2723	0.9218	0.8440
9	2.05	1.6013	1.5270	0.3175	0.2825	0.8033	0.8990

*IAS = Ideal Adsorption Solution Prediction

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.9, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Type of Wastewater = Secondary effluent with 10.1 mg/l DOC

Table C-10. IAS Prediction of Competitive Adsorption in 19.1 mg/l DOC Concentration Background Using Competitive Isotherm Parameters

		Equilibrium Concentration, C_e (mg/l)					
	Carbon Dose	2,4-Dimethylphenol		Naphthalene		Fluorene	
No.	(mg/l)	Experimental	IAS* Prediction	Experimental	IAS* Prediction	Experimental	IAS* Prediction
1	0.00	1.5933	-	0.4399	-	0.6533	-
2	20.60	0.6038	0.8495	0.0927	0.2256	0.1936	0.4103
3	15.75	0.7502	0.9530	0.1545	0.2693	0.2807	0.4678
4	10.53	1.1238	1.0730	0.2308	0.3194	0.3713	0.5278
5	7.30	1.2526	1.1570	0.2706	0.3537	0.4482	0.5661
6	5.30	1.4133	1.2130	0.3043	0.3767	0.4013	0.5900
7	4.21	1.4825	1.2450	0.4123	0.3889	0.5110	0.6030
8	3.10	1.5375	1.2770	0.4662	0.4012	0.4663	0.6156
9	2.05	1.6014	1.3120	0.4688	0.4145	0.5163	0.6289

*IAS = Ideal Adsorption Solution Prediction

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.9, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Type of Wastewater = Secondary effluent with 19.1 mg/l DOC

Table C-11. IAS Prediction of Competitive Adsorption in 27.3 mg/l DOC Concentration Background Using Competitive Isotherm Parameters

		Equilibrium Concentration, C_e (mg/l)					
	Carbon Dose	2,4-Dimethylphenol		Naphthalene		Fluorene	
No.	(mg/l)	Experimental	IAS* Prediction	Experimental	IAS* Prediction	Experimental	IAS* Prediction
1	0.00	1.8331	-	2.5375	-	0.7200	-
2	20.60	1.4398	1.6180	1.6253	1.8920	0.1889	0.2455
3	15.75	1.5251	1.674	1.7483	2.0330	0.3066	0.3259
4	10.53	1.6125	1.728	1.9625	2.1850	0.4122	0.4293
5	7.30	1.6813	1.7610	2.1257	2.2860	0.4849	0.5060
6	5.30	1.8124	1.7810	2.2613	2.3520	0.5437	0.5583
7	4.21	1.8274	1.7910	2.3388	2.3880	0.6569	0.5884
8	3.16	1.8167	1.8020	2.4038	2.4240	0.7468	0.6180
9	2.05	1.8443	1.8130	2.4513	2.4630	0.7235	0.6512

*IAS = Ideal Adsorption Solution Prediction

Test Characteristics:

Adsorbent type = Activated carbon F-400

Adsorbent size = Powder, 200x325 U.S. Sieve No.

pH = 6.9, Buffered

Temperature = 22°C

Equilibrium period = 6 days

Type of Wastewater = Secondary effluent with 27.3 mg/l DOC

APPENDIX D

Batch Rate Study Data

- Ultrapure Water Background
- Complex Mixture Background

Page 208 is missing.

Table D-2. Experimental Data Analysis Mixed Component of Naphthalene Batch Rate Study (Ultrapure Water Background

Mixing time (min)	Measured Conc. C (mg/L)	Dimensionless Conc. $\bar{C}$	Model Calculated Dimensionless times $\bar{t}$	Calculated Surface Diffusion Coefficient D_s (cm^2/sec)
32	4.535	0.933	3.941×10^{-4}	6.724×10^{-11}
60	4.389	0.903	6.192×10^{-4}	5.635×10^{-11}
90	4.287	0.882	8.321×10^{-4}	5.048×10^{-11}
180	4.176	0.859	1.129×10^{-3}	3.425×10^{-11}
450	3.952	0.813	1.967×10^{-3}	2.387×10^{-11}
1200	3.476	0.715	5.169×10^{-3}	2.352×10^{-11}
2400	3.344	0.688	6.450×10^{-3}	1.468×10^{-11}
4000	2.922	0.601	1.183×10^{-2}	1.615×10^{-11}
6000	2.542	0.523	1.828×10^{-2}	1.664×10^{-11}

*Reference Hand W.D. et al.
Activated carbon particle radius = 0.0181 cm
Initial concentrations: = 4.8611 mg/l of Naphthalene
= 3.0149 mg/l of 2,4-Dimethylphenol
= 0.7612 mg/l of Fluorene

Calculated D_s (Avg.) = 3.369×10^{-11} cm^2/sec

1n$\bar{t}$. = $-1.14297 - 9.14255\,\bar{C} + 13.2808(\bar{C})^2 - 11.982(\bar{C})^3$

$D_s = \bar{t}\,R^2/t$

Table D-3. Experimental Data Analysis of Mixed Component Fluorene Batch Rate Study (Ultrapure Water Background)

Mixing time t (min.)	Measured Conc. C (mg/l)	Dimensionless Conc. $\bar{C}$	Model Calculated Dimensionless time $\bar{t}$	Calculated Surface Diffusion Coefficient D_s (cm^2/sec)
30	0.938	0.953	2.520×10^{-4}	4.587×10^{-11}
60	0.923	0.938	3.200×10^{-4}	2.917×10^{-11}
90	0.907	0.922	4.087×10^{-4}	2.470×10^{-11}
180	0.871	0.885	6.938×10^{-4}	2.110×10^{-11}
440	0.844	0.858	9.895×10^{-4}	1.230×10^{-11}
1000	0.769	0.782	2.364×10^{-3}	1.291×10^{-11}
2000	0.694	0.705	4.828×10^{-3}	1.318×10^{-11}
4000	0.607	0.617	9.238×10^{-3}	1.261×10^{-11}
6000	0.534	0.543	1.435×10^{-2}	1.307×10^{-11}
8000	0.483	0.491	1.879×10^{-2}	1.282×10^{-11}

*Reference Hand, W.D. et al.
Activated Carbon Particle size = 0.0181 cm
Initial Concentrations = 0.9834 mg/l of Fluorene
= 3.2870 mg/l of 2,4-Dimethylphenol
= 3.8307mg/l of Naphthalene

Calculated D_s (Avg.)= 1.985×10^{-11} cm^2/sec

$$\ln\bar{t} = -1.19429 - 9.1582\,\bar{C} + 12.896\,(\bar{C})^2 - 11.6176\,(\bar{C})^3$$

$$D_s = \bar{t}\,R^2/t$$

Table D-4. Prediction of mixed Component Batch Rate Models for 2,4-Dimethylphenol in an Ultrapure Water Background

No.	Time (min)	Reduced Concentration, C/C^o Experimental	Prediction HSDM*	Prediction PSDM*
1	32	0.935	0.973	0.968
2	60	0.912	0.959	0.947
3	90	0.88	0.949	0.929
4	180	0.85	0.925	0.891
5	260	0.827	0.909	0.869
6	405	0.823	0.889	0.837
7	1000	0.748	0.830	0.749
8	2300	0.680	0.761	0.659
9	5000	0.600	0.671	0.559

*HSDM = Homogenous Surface Diffusion Model
*PSDM = Pore and Surface Diffusion Model
Reactor Volume = 8800 ml, weight of carbon = 0.088 gm
Carbon size = 40 x 50 mesh number,
Initial concentrations: = 26.78 µM./L of 2,4-Dimethylphenol
= 24.36 µM./L of Naphthalene
= 4.76 µM./L of Fluorene

Table D-5. Mixed Component Batch Rate Models for Naphthalene in an Ultrapure Water Background

		Reduced Concentration, C/C^o		
No.	Time (min)	Experimental	Prediction HSDM*	Prediction PSDM*
1	32	0.933	0.969	0.965
2	60	0.103	0.950	0.943
3	90	0.882	0.945	0.924
4	180	0.859	0.917	0.881
5	450	0.813	0.867	0.810
6	1200	0.715	0.791	0.701
7	2400	0.68	0.720	0.611
8	4000	0.601	0.658	0.542
9	6000	0.523	0.605	0.490

*HSDM = Homogenous Surface Diffusion Model
*PSDM = Pore and Surface Diffusion Model
Reactor Volume = 8800 ml, weight of carbon = 0.0918 gm,
Carbon size = 40 x 50 mesh number,
Initial concentrations: = 37.93 µM./L of Naphthalene
= 24.68 µM./L of 2,4-Dimethylphenol
= 4.58 µM./L of Fluorene

Table D-6. Prediction of Mixed Compound Batch Rate Models for Fluorene in ultrapure an Water Background

No.	Time (Min.)	Reduced Concentration, C/C_0 Experimental	Prediction HSDM*	Prediction PSDM*
1	30	0.953	0.992	0.992
2	60	0.938	0.984	0.985
3	90	0.922	0.977	0.979
4	180	0.885	0.960	0.960
5	440	0.858	0.919	0.917
6	1000	0.787	0.859	0.851
7	2000	0.705	0.790	0.764
8	4000	0.617	0.703	0.682
9	6000	0.543	0.644	0.621
10	8000	0.491	0.603	0.576

*HSDM = Homogenous Surface Diffusion MOdel
*PSDM = Pore and Surface Diffusion Model
Reactor volume = 8800 ml, weight of carbon = 0.015 gm
Carbon size = 40x50 mesh number,
Initial Concentrations: = 5.92 µM./L of Fluorene
= 26.89 µM./L of 2,4-Dimethylphenol
= 29.89 µM./L of Naphthalene

Table D-7. Mixture Component Batch Rate Models Prediction for 2,4 Dimethylphenol, Naphthalene and Flurene in an Ultrapure Water Background

		Reduced Concentration, C/C_0								
No	Time (min)	2,4-Dimethylphenol			Naphthalene			Flurene		
		Exp.	HSDM	PHSDM	Exp.	HSDM	PHSDM	EXP.	HSDM	PHSDM
1	30	0.889	0.979	0.979	0.945	0.976	0.975	0.909	0.967	0.964
2	90	0.858	0.964	0.965	0.888	0.957	0.955	0.858	0.921	0.905
3	400	0.837	0.922	0.925	0.848	0.900	0.898	0.733	0.775	0.724
4	750	0.824	0.896	0.898	0.789	0.865	0.863	0.688	0.676	0.623
5	1660	0.813	0.851	0.853	0.741	0.807	0.805	0.585	0.537	0.497
6	3280	0.813	0.799	0.800	0.715	0.745	0.743	0.466	0.421	0.397
7	4050	0.804	0.781	0.782	0.666	0.724	0.722	0.409	0.389	0.369
8	5860	0.789	0.746	0.747	0.636	0.685	0.680	0.352	01.337	0.324
9	7320	0.747	0.724	0.724	0.617	0.661	0.659	0.318	0.310	0.299
10	9860	0.727	0.694	0.694	0.607	0.629	0.628	0.301	0.277	0.270

HSDM = Homogenous Surfice Diffusion Model
PHSDM = Pore and Surface Diffusion Model
Reactor Volume = 8800 ml, carbon weight = 0.0744 gm,
Carbon Size = 40x50 mesh number,
Initial Concentrations: = 22.81 μM./L of 2,4-Dimethylphenol
= 9.52 μM./L of Naphthalene
= 1.76 μM./L of Flurene

Table D-8. Experimental Data Analysis of Single-Solute 2,4-Dimethylphenol Batch Rate Study (Ultrapure Water Background)

Mixing time t (min.)	Measured Conc. C (mg/l)	Dimensionless Conc. $\bar{C}$	Model Calculated Dimensionless time $\bar{t}$	Calculated Surface Diffusion Coefficient D_s (cm^2/sec)
30	2.429	0.928	5.380x10-4	$9.791\text{x}10^{-11}$
70	2.303	0.880	$1.097\text{x}10^{-3}$	$8.556\text{x}10^{-11}$
120	2.245	0.858	$1.475\text{x}10^{-3}$	$6.710\text{x}10^{-11}$
220	2.133	0.811	$2.614\text{x}10^{-3}$	$6.489\text{x}10^{-11}$
400	2.002	0.765	$4.259\text{x}10^{-3}$	$5.814\text{x}10^{-11}$
1000	1.727	0.660	$1.033\text{x}10^{-3}$	$5.639\text{x}10^{-11}$
2400	1.479	0.565	$1.860\text{x}10^{-2}$	$4.231\text{x}10^{-11}$
4600	1.290	0.493	$2.646\text{x}10^{-2}$	$3.141\text{x}10^{-11}$
6400	1.107	0.423	$3.557\text{x}10^{-2}$	$3.034\text{x}10^{-11}$

*Reference Hand, W.D. et al.

Activated Carbon Particle Radius = 0.0181 cm

Initial Concentrations = 2.618 mg/L of 2.4 Dimethylphenol

Calculated D_s (Avg.) $5.930\text{x}10^{-11}$ cm^2/sec

$\ln \bar{t} = -1.02388 - 9.21408\bar{C} + 14.2349(\bar{C})^2 - 12.8098\ (\bar{C})^3$

$D_s \ = \bar{t}\, R^2/t$

Table D-9. Experimental Data Analysis of Single-Solute 2,4-Dimethylphenol Batch Rate Study in Complex Mixture Background (20.7 mg/l DOC)

Mixing time (min)	Measured Conc. C (mg/L)	Dimensionless Conc. $\bar{C}$	Model Calculated Dimensionless times* $\bar{t}$	Calculated Surface Diffusion Coefficient D_s (cm^2/sec)
30	2.753	0.951	$2.953\text{x}10^{-4}$	$5.375\text{x}10^{-11}$
70	2.643	0.913	$5.347\text{x}10^{-4}$	$4.170\text{x}10^{-11}$
120	2.582	0.892	$7.244\text{x}10^{-4}$	$3.296\text{x}10^{-11}$
240	2.385	0.824	$1.734\text{x}10^{-3}$	$3.949\text{x}10^{-11}$
500	2.264	0.782	$2.757\text{x}10^{-3}$	$3.005\text{x}10^{-11}$
1500	1.835	0.634	$9.565\text{x}10^{-3}$	$3.482\text{x}10^{-11}$
2600	1.725	0.590	$1.219\text{x}10^{-2}$	$2.562\text{x}10^{-11}$
4000	1.543	0.533	$1.737\text{x}10^{-2}$	$2.371\text{x}10^{-11}$
6000	1.456	0.503	$2.019\text{x}10^{-2}$	$1.838\text{x}10^{-11}$
8000	1.392	0.481	$2.243\text{x}10^{-2}$	$1.531\text{x}10^{-11}$

*Reference Hand W.D. et al.

Activated carbon particle radius = 0.0181 cm

Initial concentration: = 2.8949 mg/l of 2,4-Dimethylphenol

Calculated D_s (Avg) = $3.1579\text{x}10^{-11}$ cm^2/sec

$\ln\bar{t} = 1.14297 - 9.14255C + 13.2803(C) - 11.982(C)^3$

$D_s = \bar{t}\,R^2/t$

Table D-10. Single-Solute Batch Rate Models Prediction for 2,4-Dimethylphenol in Ultrapure Water Background

No.	Time (min)	Reduced Concentration, C/C_o Experimental	Prediction HSDM*	Prediction PSDM*
1	30	0.928	0.970	0.967
2	70	0.880	0.950	0.939
3	120	0.858	0.930	0.912
4	220	0.811	0.903	0.874
5	400	0.765	0.869	0.829
6	1000	0.660	0.799	0.736
7	2400	0.565	0.708	0.629
8	4600	0.493	0.629	0.545
9	6400	0.423	0.580	0.506

*HSDM = Homogenous Surface Diffusion Model
*PSDM = Pore and Homogenous Surface Diffusion Model
Reactor Volume = 8800 ml, weight of carbon = 0.079 gm
Initial Concentration = 21.42 μM./L

Table D-11. Single-Solute Batch Rate Models Prediction for 2,4-Dimethylphenol in a Complex Mixture Background

		Reduced Concentration		
No.	Time (min)	Experimental	Prediction HSDM*	Prediction PSDM*
1	30	0.951	0.970	0.940
2	70	0.913	0.957	0.897
3	120	0.892	0.943	0.866
4	240	0.824	0.918	0.812
5	500	0.782	0.883	0.741
6	1500	0.634	0.809	0.615
7	2600	0.596	0.759	0.554
8	4000	0.533	0.715	0.511
9	6000	0.503	0.674	0.482
10	8000	0.481	0.637	0.471

*HSDM = Homogenous Surface Diffusion Model
*PSDM = Pore and Surface Diffusion Model
Reactor Volume = 8800 ml, weight of carbon = 0.265 gm,
Carbon size = 40 x 50 mesh number, Carbon type = F-400,
Initial concentrations: = 23.68 μM./L of 2,4-Dimethylphenol
DOC in background water = 20.68 mg/L

APPENDIX E

Minicolumn Study Data

- Mixed Components in Ultrapure Water Background
- Single-Solute in Ultrapure Water Background
- Single-Solute in Complex Mixture Background

Table E-1. Mixed Component Minicolumn Study of 2,4-Dimethylphenol (Ultrapure Water Background)

Time (min.)	Bed Volumes Contacted	Influent Conc. (μM./L)	Exp. Effluent Conc. (μM./L)	Reduced Conc., C/C_o				
				Exp.	Prediction PHSDM	Prediction PPSDM	Prediction DFHSDM	Prediction DFHSDM
0.0	0.0	16.75	-	-	-	-	-	-
40	1015	16.75	3.17	0.147	0.250	0.227	0.206	0.253
100	2538	-	4.18	0.261	0.428	0.305	0.232	0.326
220	5583	-	6.60	0.412	0.618	0.435	0.475	0.446
300	7614	16.92	8.22	0.486	0.693	0.517	0.711	0.522
460	11674	-	10.37	0.614	0.804	0.642	0.911	0.643
560	14212	17.46	12.31	0.705	0.850	0.691	0.932	0.691
700	17765	-	13.86	0.794	0.886	0.737	0.946	0.733
860	21826	17.79	14.91	0.838	0.919	0.782	0.956	0.7851
1000	25379	-	15.67	0.881	0.935	0.812	0.962	0.810
1180	29947	17.65	16.13	0.914	0.942	0.844	0.966	0.848
1320	33500	-	-	-	0.956	0.863	0.967	0.865
1480	37561	17.86	16.24	0.901	0.965	0.881	0.968	0.880
1680	42636	-	17.00	0.952	0.979	0.901	0.979	0.904
1880	47712	17.86	17.02	0.953	0.990	0.918	0.989	0.921
2200	55833	-	-	-	0.993	0.932	0.989	0.930
2320	58879	17.86	17.82	1.00	0.999	0.944	0.992	-
2500	63447	17.86	17.82	1.00	0.999	0.944	0.992	-
2900	73598	18.01	-	-	1.025	0.975	1.021	-
3600	91363	17.93	-	-	1.022	0.990	1.016	-
4200	106591	18.11	-	-	1.034	1.009	1.032	-
5000	126894	17.92	-	-	1.032	1.013	1.029	-

PHSDM = plug flow homogenous surface diffusion model
PPPSDM = plug flow pore and homogenous surface diffusion model
DFHSDM = dispersed flow homogenous surface diffusion model
DFPSDM = dispersed flow pore and homogenous surface diffusion model
Operation characteristics: Flow = 29.5 ml/min., temp.= 25°C
Avg. pH = 7.0, column I.D. = 1.0 cm,
Carbon bed volume = 1.1624 cm^3,
Carbon weight = 0.55 gm, carbon type = F-400
Mesh size = 40 x 50 U.S. sieve No.
$D_s = 4.45 \times 10^{-11}$ cm^2/sec, $k_f = 7.578 \times 10^{-3}$ cm/sec, $D_p = 0.484 \times 10^{-5}$ Cm^2/sec. $D_e = 0.1588$ cm^2/sec.
XK = 788.5, XN = 0.2357

Table E-2. Mixed Component Minicolumn Study of Naphthalene (Ultrapure Water Background)

Time (Min.)	Bed Volume Contacted	Influent Conc. (μM./L)	Exp. Effluent Conc. (μM./L)	Reduced Concentration, C/C_o				
				Exp.	Prediction PHSDM	Prediction PPSDM	Prediction DFHSDM	Prediction DFPSDM
0.0	0	11.41	—	—	—	—	—	—
40	1,015	11.41	2.32	0.223	0.268	0.246	0.208	0.227
100	2,538	—	2.72	0.261	0.428	0.321	0.239	0.342
220	5,583	—	4.49	0.341	0.547	0.412	0.424	0.424
300	7,614	10.37	3.64	0.388	0.585	0.462	0.568	0.469
460	11,674	—	4.45	0.474	0.645	0.535	0.670	0.539
560	14,212	10.20	8.70	0.615	0.699	0.587	0.748	0.593
700	17,765	—	9.07	0.641	0.756	0.635	0.795	0.634
860	21,826	11.33	8.53	0.692	0.90	0.675	0.827	0.681
1,000	25,379	—	10.07	0.817	0.823	0.717	0.858	0.719
1,180	29,947	12.32	9.91	0.809	0.852	0.773	0.900	0.773
1,320	33,500	—	—	—	0.869	0.780	0.901	0.780
1,480	37,561	11.12	9.25	0.832	0.849	0.772	0.882	0.774
1,680	42,636	—	9.89	0.890	0.869	0.796	0.886	0.799
1,880	47,712	11.92	10.20	0.856	0.900	0.828	0.908	0.828
2,200	55,833	—	10.25	0.860	0.891	0.831	0.901	0.830
2,320	58,879	11.18	8.94	0.801	0.882	0.827	0.892	—
2,500	63,447	10.89	9.30	0.854	0.870	0.820	0.876	—
2,400	73,598	12.42	—	—	0.958	0.900	0.946	—
3,600	91,363	11.78	—	—	0.952	0.912	0.953	—
4,200	106,591	11.58	—	—	0.946	0.915	0.942	—
5,000	126,498	10.97	—	—	0.913	0.893	0.908	—

PHSDM = Plug Flow Homogeneous Surface Diffusion Model
PPSDM = Plug Flow Pore and Homogeneous Surface Diffusion Model
DFHSDM = Dispersed Flow Homogeneous Surface Diffusion Model
DFDSDM = Dispersed Flow Pore and Homogenous Surface Diffusion Model
Operation Characteristics: Flow = 29.5 ml/min., Temp. = 25°C
Ave. pH = 7.0, Column I.D. = 1.0 cm
Carbon Bed Volume = 1.1624 cm^3
Carbon Weight = 0.55 gm, Carbon Type
F-400, Mesh Size = 40 x 50 U.S. Sieve No.

D_s = 3.369×10^{-11} Cm^2/sec., K_f = 7.583×10^{-3} Cm/sec, Dp = 0.4850×10^{-5} Cm^2/sec.
D_e = 0.1589 Cm^2/sec., XK = 907.9, XN = 0.3369

Table E-3. Mixed Component Minicolumn Study of Fluorene (Ultrapure Water Background)

Time (min.)	Bed Volume Contacted	Influent Conc. (μM./L)	Exp. Effluent Conc. (μM./L)	Reduced Conc., C/C_0				
				Exp.	Prediction PHSDM	Prediction PPSDM	Prediction DFHSDM	Prediction DFHSDM
0.0	0.0	2.87						
40	1015	2.73	0.51	0.188	0.250	0.247	0.241	0.261
100	2538	-	0.55	0.208	0.287	0.268	0.257	0.293
220	5583	-	0.63	0.231	0.342	0.313	0.298	0.336
300	7614	2.84	0.76	0.269	0.375	0.338	0.333	0.360
460	11674	-	0.99	0.350	0.419	0.386	0.394	0.407
560	14214	3.01	1.07	0.378	0.442	0.407	0.412	0.427
700	17765	-	1.42	0.471	0.481	0.439	0.401	0.446
860	21826	3.13	1.41	0.450	0.517	0.475	0.505	0.485
1000	25379	-	1.41	0.451	0.531	0.491	0.528	0.508
1180	29947	3.01	1.49	0.495	0.540	0.507	0.553	0.518
1320	33500	-	1.81	0.601	0.565	0.526	0.578	0.530
1480	37561	3.12	1.95	0.625	0.587	0.548	0.604	0.551
1680	42636	-	1.86	0.595	0.607	0.567	0.628	0.571
1880	47712	3.10	2.11	0.681	0.623	0.583	0.649	0.584
2200	55833	-	1.83	0.592	0.639	0.600	0.669	0.610
2320	58879	3.03	2.01	0.665	0.643	0.605	0.674	
2500	63447	3.27	2.22	0.690	0.673	0.635	0.703	
2900	73598	3.08	-	0.672	0.690	0.651	0.720	
3600	91363	3.05	-	-	0.713	0.678	0.739	
4200	106591	3.15	-	-	0.748	0.713	0.767	
5000	126498	3.23	-	-	0.786	0.752	0.798	

PHSDM = plug flow homogenous surface diffusion model
PPSDM = plug flow pore and homogenous surface diffusion model
DFHSDM = Dispersed flow homogenous surface diffusion model
DFPSDM = dispersed flow pore and homogenous surface diffusion model
Operation characteristics: Flow = 29.5 ml/min, temp: 25°C, Avg. pH = 7.0,
Carbon I.D. = 1.0 cm, carbon bed volume = 1.1624cm^3,
Carbon weight = 0.55 gm, carbon type = F-400,
Mesh size = 40 x 50 U.S. Sieve No.
$D_s = 1.990\times10^{-11}$ cm^2/sec, $K_f = 6.505 \times 10^{-3}$ cm/sec, $D_p = 0.4048\times10^{-5}$ cm^2/sec,
$D_e = 0.1646$ cm^2/sec, XK = 1721.4 , XN = 0.414

Table E-4. Single-Solute Minicolumn Study for 2,4-Dimethylphenol (Ultrapure Water Background)

Time (Min.)	Bed Volume Fed	Influent Conc. (μm/L)	Exp. Effluent Conc. (μm/L)	Reduced Concentration, C/C_0				
				Exp.	Prediction PHSDM	Prediction PPSDM	Prediction DFHSDM	Prediction DFPSDM
0.0	0	22.85	—	—	—	—	—	—
20	379	—	2.58	0.113	0.107	0.107	0.119	0.126
260	4,930	—	4.91	0.215	0.381	0.270	0.295	0.283
380	7,206	22.37	5.99	0.268	0.504	0.364	0.509	0.372
460	8,723	22.53	—	—	0.550	0.409	0.628	0.414
480	9,102	21.55	7.43	0.345	0.548	0.410	0.639	0.414
620	11,757	—	—	0.441	0.581	0.455	0.662	0.458
920	17,446	20.33	—	—	0.624	0.519	0.655	0.520
1,060	20,101	21.78	—	—	0.684	0.574	0.691	0.574
1,160	21,997	—	16.12	0.740	0.709	0.603	0.719	0.664
1,460	27,686	—	16.88	0.775	0.760	0.668	0.760	0.668
1,660	31,478	22.51	—	—	0.787	0.702	0.783	0.702
1,670	31,668	—	17.48	0.789	—	—	—	—
1,980	37,547	22.61	—	—	0.816	0.741	0.808	0.741
2,000	37,926	—	18.59	0.822	0.817	0.744	0.809	0.743
2,400	45,511	23.34	—	—	0.865	0.797	0.855	0.796
2,420	45,890	—	19.54	0.877	0.866	0.799	0.857	0.799
2,560	48,505	—	19.72	0.845	0.868	0.809	0.861	0.807
3,000	56,899	22.69	—	—	0.867	0.821	0.859	0.820
3,100	58,785	—	19.72	0.869	0.866	0.823	0.858	0.822
3,600	68,267	21.95	—	—	0.855	0.824	0.848	0.823
3,620	68,646	—	18.88	0.860	0.855	0.824	0.848	0.823
4,000	75,852	—	—	—	0.861	0.833	0.855	0.832

PHSDM = Plug Flow Homogeneous Surface Diffusion Model
PPSDM = Plug Flow Pore and Homogeneous Surface Diffusion Model
DFHSDM = Dispersed Flow Homogeneous Surface Diffusion Model
DFDSDM = Dispersed Flow Pore and Homogenous Surface Diffusion Model

Operation Characteristics: Flow = 35 ml/min., Temp. = 25°C
Ave. pH = 7.1, Column I.D. = 1.0 cm
Carbon Bed Volume = 1.8457 cm3
Carbon Weight = 0.85 gm, Carbon Type = F-400, Mesh Size = 40 x 50 U.S. Sieve No.

D_S = 5.92×10^{-11} Cm^2/sec., K_F = 7.578×10^{-3} Cm/sec, Dp = 0.4846×10^{-5} Cm^2/sec.
D_e = 0.1508 Cm2/sec., XK = 788.5, XN = 0.2357

Table E-5. Single-Solute Minicolumn Study for 2,4-Dimethylphenol in Complex Mixture Background (20.4 mg/l DOC)

		Influent		Effluent		Reduced Concentration, C/C_o				
Time (min.)	Bed Volumes Contacted	DOC (mg/L)	2-4 Dim. (mg/L)	DOC (mg/L)	2-4 Dim. (mg/L)	Exp.	Pred. PHSDM	Pred. PPSDM	Pred. BFHSDM	Pred. DFPSDM
0.0	0.0	21.80	2.667	12.68	-	-	-	-	-	-
40	758	-	2.658	15.25	0.584	0.219	0.709	0.321	0.179	0.335
100	1896	21.25	-	-	1.123	0.421	0.761	0.452	0.549	0.459
220	4172	-	2.633	18.92	1.486	0.564	0.824	0.623	0.923	0.625
340	6447	20.6	-	-	-	-	0.854	0.676	0.923	0.678
400	7585	19.40	2.605	17.02	1.732	0.665	0.863	0.701	0.920	0.701
500	9860	-	-	17.19	1.995	0.766	0.880	0.745	0.920	0.745
700	13273	20.3	2.601	19.30	2.261	0.817	0.895	0.785	0.921	0.786
720	13652	19.97	2.50	18.78	2.050	0.819	0.873	0.775	0.911	0.774
900	17065	19.93	-	-	-	-	0.887	0.794	0.902	0.794
1060	20099	-	2.598	20.88	2.695	0.845	0.908	0.823	0.920	0.823
1420	26925	20.31	-	19.39	-	-	0.877	0.825	0.886	0.824
1520	28821	21.00	2.441	21.11	1.860	0.800	0.867	0.821	0.874	0.820
1920	36400	19.34	2.448	19.47	1.853	0.850	0.873	0.834	0.875	0.833
2500	47403	20.95	2.470	18.78	2.096	0.918	0.888	0.859	0.887	0.858

Operation characteristics: Flow = 35 ml/min, Temp = 25°C
Column I.D. = 1.0 cm, carbon bed
Volume = 1.8457 cm^3, carbon weight = 0.85 gm
Carbon type = F-400, Mesh size = 40 x 50

DOC = Dissolved Organic Carbon
PHSDM = Plug Flow Homogenous Surface Diffusion Model
PPSDM = Plug Flow Pore and Homogenous Surface Diffusion Model
DFHSDM = Dispersed Flow Homogenous Surface Diffusion Model
DFPSDM = Dispersed Flow Pore and Surface Diffusion Model
$D_s = 3.158 \times 10^{-11}$ cm^2/sec, $k_f = 7.578 \times 10^{-3}$ cm/sec, $D_p = 0.4846 \times 10^{-5}$ cm^2/sec
$D_e = 0.1588$ cm^2/sec, XK = 170.04, XN = 0.3763

APPENDIX F

Pilot Plant Study at South Kingstown Wastewater Treatment Facility

- Data for Column (I)

- Data for Column (II)

Table F-1. Pilot Plant Column (I) Data for Single-Solute 2,4-Dimethylphenol in a Complex Mixture Background

	Bed	Influent		Effluent		Reduced Concentration, C/C_o		
Time (min.)	Volumes Contacted	DOC (mg/l)	2,4-Dim. (mg/l)	DOC (mg/l)	2,4-Dim. (mg/l)	Exp.	Pred. PPSDM	Pred. DFPSDM
0.0	0.0	20.10	2.51	---	---	---	---	---
390	115	19.18	1.21	10.62	ND	ND	ND	ND
815	230	19.97	1.18	---	ND	ND	ND	ND
1,580	460	---	2.61	---	ND	ND	ND	ND
1,925	546	---	2.23	---	ND	ND	ND	ND
2,310	661	25.88	2.23	13.34	ND	ND	ND	ND
2,680	776	31.0	2.72	16.20	ND	ND	ND	ND
3,310	948	23.04	---	12.07	ND	ND	ND	ND
3,965	1,149	---	3.73	---	ND	ND	ND	ND
5,290	1,523	12.24	2.33	7.47	ND	ND	ND	ND
7,430	2,126	---	3.42	---	ND	ND	ND	ND
8,075	2,327	---	2.03	---	ND	ND	0.02	0.03
8,480	2,442	30.27	3.40	13.30	0.11	0.03	0.04	0.05
8,780	2,528	---	2.47	---	0.10	0.04	0.05	0.06
9,570	2,758	27.52	3.17	---	---	---	0.09	0.10
10,890	3,132	25.34	2.50	17.43	0.18	0.07	0.15	0.16
12,920	3,706	---	2.95	---	0.38	0.13	0.23	0.24
15,540	4,453	21.50	1.73	15.80	0.29	0.17	0.32	0.32
19,600	5,631	15.80	2.63	10.90	0.93	0.35	0.37	0.37
21,980	6,293	21.89	2.70	18.60	1.17	0.43	0.43	0.43
25,200	7,240	17.85	2.53	15.10	0.93	0.37	0.51	0.51
29,920	8,591	20.01	2.93	20.40	1.86	0.63	0.60	0.60
32,590	9,367	23.18	3.86	21.78	3.23	0.83	0.69	0.69
34,840	9,999	21.47	2.86	21.50	2.26	0.779	0.78	0.78
38,020	10,918	15.30	2.57	14.80	2.21	0.86	0.78	0.78
40,280	11,579	---	2.63	---	2.34	0.89	0.78	0.78
43,570	12,527	18.10	2.45	16.52	2.25	0.92	0.78	0.78
47,330	13,590	19.25	2.70	18.73	2.43	0.90	0.79	0.79
58,200	16,693	---	---	---	---	---	0.88	0.88
62,700	18,015	---	---	---	---	---	0.91	0.91

Operation Characteristics: Column I.D. = 10.16 cm, Carbon bed Vol. = 7171 Cm^3,
Flow = 2015 ml/min., Carbon wt. = 2.794 kg
Mesh Size = 12x30, wt. avg. particle radius = 0.0618Cm,
Carbon type = F-400

DOC = Dissolved Organic Carbon
ND = Not Detected
- = Not Analysed
D_s = 3.158×10^{-11} Cm^2/sec., $k_f = 7.528\times10^{-3}$ Cm/sec., $D_p = 0.4846\times10^{-5}$ Cm^2/sec.
D_e = 0.344 Cm^2/sec., XK = 170.04, XN = 0.3763

Table F-2. Pilot Plant Column (II) Data for Single-Solute 2,4-Dimethylphenol in Complex Mixture Background

	Bed	Influent		Effluent		Reduced Concentration, C/C_o		
Time (min.)	Volumes Contacted	DOC (mg/l)	2,4-Dim. (mg/l)	DOC (mg/l)	2,4-Dim. (mg/l)	Exp.	Pred. PPSDM	Pred. DFPSDM
0.0	0.0	20.1	2.51	---	---	---	---	---
390	234	19.18	1.21	9.90	ND	ND	ND	ND
815	467	19.97	1.18	10.52	ND	ND	ND	ND
1,580	935	24.51	2.61	13.81	ND	ND	ND	ND
1,925	1,110	---	2.23	---	0.06	0.02	ND	ND
2,310	1,344	25.88	2.23	15.78	---	ND	0.02	0.02
2,680	1,577	31.0	2.72	21.1	0.03	ND	0.05	0.06
3,310	1,928	23.04	---	15.01	---	---	0.13	0.13
3,965	2,337	---	3.73	13.45	0.27	0.07	0.26	0.27
5,290	3,096	12.24	2.33	8.60	0.19	0.08	0.41	0.42
7,430	4,323	---	3.42	---	1.25	0.37	0.55	0.55
8,075	4,732	---	2.03	---	1.07	0.52	0.58	0.58
8,480	4,966	20.27	3.40	16.10	1.61	0.47	0.57	0.58
8,780	5,141	---	2.47	---	0.93	0.38	0.60	0.60
9,570	5,608	27.52	3.17	25.64	1.47	0.46	0.62	0.63
10,890	6,368	25.34	2.50	22.56	1.40	0.56	0.67	0.67
12,920	7,536	---	2.95	---	1.73	0.59	0.70	0.70
15,540	9,054	21.50	1.73	19.50	1.47	0.85	0.64	0.65
19,600	11,450	15.80	2.63	13.10	2.01	0.76	0.69	0.69
21,980	12,852	21.89	2.70	21.78	2.41	0.89	0.77	0.78
25,200	14,721	17.85	2.53	13.50	1.97	0.78	0.81	0.81
29,920	17,467	20.01	2.93	17.06	2.53	0.86	0.90	0.90
32,590	19,045	23.18	3.86	20.53	3.24	0.85	1.08	1.08
34,840	20,330	21.47	2.86	---	---	---	1.08	1.07
38,020	22,199	15.30	2.57	---	2.29	0.89	0.97	0.97
40,280	23,543	---	2.63	---	---	---	0.95	0.95
43,570	25,470	18.10	2.45	17.9	2.11	0.86	0.92	0.92
47,330	27,632	19.25	2.70	---	---	---	0.95	0.95

Operation Characteristics: Column I.D. = 10.16 cm, Carbon bed Vol. = 7175 Cm^3,
Flow = 4097 ml/min., Carbon wt. = 2.794 kg
Mesh Size = 12x30, wt. avg. particle radius = 0.0618Cm,
Carbon type = F-400

DOC = Dissolved Organic Carbon
ND = Not Detected
\- = Not Analysed
D_s = 3.158×10^{-11} Cm^2/sec., $k_f = 7.578\times10^{-3}$ Cm/sec., $D_p = 0.4846\times10^{-5}$ Cm^2/sec.
D_e = 0.793 Cm^2/sec., XK = 170.04, XN = 0.3763

BIBLIOGRAPHY

Al-Bahrani, K.S., and Martin, J.R., "Adsorption Studies Using Gas-Liquid Chromatography - I. Effect of Molecular Structure." Water Research, 10, (1976).

Alkhatib, E.A., "Treatment of High Ammonia Refinery Wastewater for Reuse". A Master's Thesis submitted to the State University of New York at Buffalo, (1982).

Basso, M., Nolan, T., Shaw, J., "Evaluation of EPA Analytical Protocols for Measurement of Priority Pollutants in Refinery Wastewaters," presented at WPCF Conference, Detroit, Michigan, Oct., 1981.

Bethea, R.M., Duran, B.S., and Soullion, T.L., Statistical Methods for Engineers and Scientists, Marcel Dekker, Inc., New York, N.Y., 1985.

Brunauer, S., Emmett, P.H., and Teller, E., "Adsorption of Gases in Multimolecular Layers," Jour. Am. Chem. Soc., 60, 309 (1938).

Chapman, P.M., Romberg, P.G., Vigers, G.A., "Design of Monitoring Studies for Priority Pollutants." JWPCF, Vol. 54, No. 3, 1982, p. 292.

Cherimisinoff, P.N., and Ellerbusch, F., ed. Carbon Adsorption Handbook, Ann Arbor Science Publishers, Inc., Ann Arbor, (1978).

Coughlin, R.W., and Ezra, F.S., "Role of Surface Acidity in the Adsorption of Organic Pollutants on the Surface of Carbon." Environmental Science and Technology, Vol. 2, No. 4, (1968).

CRC Handbook of Chemistry and Physics, 61st Edition, CRC Press, Inc., 1980-1981.

Crittenden, J.C., "Mathematic Modeling of Fixed Bed Adsorbers Dynamic-Single Component and Multicomponent," Thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Civil Engineering, Water Resources Engineering), University of Michigan, (1976).

Crittenden, J.C., Hand, D.W. and Thacker, W.E., "Simplified Models for Design of Fixed-Bed Adsorption Systems," ASCE, JEE, Vol. 110, No. 2, 1984, p. 440.

Crittenden, J.C., Luft, P., Hand, D.W., and Friedman, G., "Prediction of Multicomponent Adsorption Equilibria in Background Mixtures of Unknown Composition." Manuscript accepted for publication in Water Research, (1985).

Crittenden, J.C., P.J. Luft, D.W. Hand, and G. Friedman, "Prediction of Fixed Bed Adsorption Removal of Known Organics and Total Organic Halogen in Computing Background Mixtures of Unknown Composition," Proceeding of the 1984 National Conference of Environmental Engineering, Sponsored by ASCE, Los Angeles, CA (1984).

Crittenden, J.C., Luft, P., Hand, D.W., Oravitz, J., Loper, S.W. and Metin, A., "Prediction of Multicomponent Adsorption Equilibria Using Ideal Adsorbed Solution Theory", Manuscript Submitted to Environmental Science and Technology, January 26th, 1984.

Crittenden, J.C. and Weber, W.J., Jr., "Predictive Model for Design of Fixed-Bed Adsorbers: Single Component Model Verification," ASCE, EE3, 1978.

Crittenden, J.C., Wong, B.W.C., Thacker, W.E., Snoeyink, V.L., and Hinrichs, B.L., "Mathematical Model of Sequential Loading in Fixed-Bed Adsorbers," JWPCF, Vol. 52, No. 11, 1980, p. 2780.

Cussler, E.L., <u>Diffusion: Mass Transfer in Fluid Systems</u>, Cambridge University Press, Cambridge, 1984.

Dedrick, R.L., and Beckmann, R.B., "Kinetics of Adsorption by Activated Carbon from Dilute Aqueous Solution," AIChE Symp. Ser. No. 74, 1967.

Dobbs, R.A. and Cohen, J.M., "Carbon Adsorption Isotherms for Toxic Organics," EPA-600/8-80-023, 1980.

Environmental Protection Agency, Federal Register, Part VIII, 40 CFR Part 136, Oct., 1984.

Famularo, J., Muller, J.A., and Pannu, A.S., "Prediction of Carbon Column Performance from Pure-Solute Data," JWPCF, Vol. 52, No. 7, 1980, p. 2019.

Finlayson, B.A., <u>The Method of Weighted Residuals and Variational Principles</u>, Academic Press, New York, N.Y. 1972.

Frederick, S.C., Roberts, P.V., "Activated Carbon Sorption of DOC from Wastewater," ASCE, Vol. 108, No. EE4, 1982, p. 766.

Freundlich, H., <u>Colloid and Capillary Chemistry</u>, Matheum and Co., Ltd., London, (1926).

Frick, B.R. and Sonthiemer, H., "Treatment of Water by Granular Activated Carbon." Amer. Chemical Soc. Books, Washington, D.C., Advances in Chemistry, Series, No. 202, 1983, p. 247.

Fried, J.J., Combarnous, N.A., in V.T. Chow ed., Advances in Hydroscience, Academic Press, New York, N.Y., 1971.

Fritz, W., Merk, W., and Shlunder, E.U., "Competitative Adsorption of Two Dissolved Organics onto Activated Carbon - II," Chemical Engineering Science, Vol. 36, 1981, p. 731.

Fritz, W., and Schluender, J.M., "Simultaneous Adsorption Equilibria of Organic Solutes in Dilute Aqueous Solution of Activated Carbon", Chem. Eng. Sci., 29, 1974, p. 1279.

Frye, W.H., "Predictions of Competitive Adsorption: Observations of Anomalous Behavior in Specific Bi - and Tri-Solute Systems", Ph.D. Dissertation, University of Massachusetts at Amherst, 1980.

Furusawa, T., and Smith, J.M., "Fluid-Particle and Intraparticle Mass Transport in Slurries," Ind. Eng. Chem. Fundamentals, Vol. 12, 1973, p. 197.

Giusti, D.kM., Conway, R.A. and Lawson, C.T., "Activated Carbon Adsorption of Petrochemicals", Jour. WPCF, 46, (1974).

Hand, D.W., Crittenden, J.C. and Thacker, E.W., "User-Oriented Batch Reactor Solutions to the Homogeneous Surface Diffusion Model," ASCE, Vol. 109, No. EE2, 1983, p. 82.

Hand, D.W., Friedman, G. and Crittenden, J., "User Manual for Executing the Batch and Fixed Bed HSDM and PSDM Computer Algorithms," Michigan Technological University Houghton, Michigan, 1985.

Hobler, T., Mass Transfer and Absorbers, Pergamon Press, New York, N.Y., 1966.

Jain, J.S., and Snoeyink, V.L., "Adsorption from Bisolute Systems on Active Carbon," JWPCF, Vol. 45, 1973, p. 2463.

Johnson, R.L., Lowes, F.J., Jr., Smith, R.M., and Powers, T.J., "Evaluation of the Use of Activated Carbons and Chemical Regeneration in Treatment of Wastewaters. Public Health Service Publication No. 999-WP-12, 1964.

Jossens, L., Prausnitz, J.M., Fritz, W., Schlunder, E.U. and Myers, A.L., "Thermodynamics of Multi-Solute Adsorption from Dilute Aqueous Solutions," Chem. Eng. Sci., Vol. 33, 1978, p. 1097.

Keinath, T.M., "Mathematical Modeling of Heterogeneous Sorption in Continuous Contactors for Wastewater Decontamination." Final Report, Contract No. DADA-17-72-C-2034, Clemson University, S.C. (1973).

Kidnay, A.J. and Myers, A.L., "A Simplified Method for the Prediction of Multicomponent Adsorption Equilibria from Single Gas Isotherms", Jour. AIChE, Vol. 12, No. 5, 1966, p. 981.

Langmuir, I., "The Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum," J. Amer. Chem. Soc., 40, 1361, (1918).

Leggett, R.W., and Williams, L.R., "A Reliability Index for Models," Ecological Modeling, Vol. 13, 1981, p. 303.

Letterman, R.D., Quon, J.E. and Gemmel, R.S., "Film Transport Coefficient in Agitated Suspensions of Activated Carbon," JWPCF, Vol. 46, No. 11, 1974, p. 2537.

Levenspiel, O., Chemical Reaction Engineering, John Wiley and Sons, New York, N.Y., 1972.

Liu, K.T. and Weber, W.J., Jr., "Characterization of Mass Transfer Parameters for Adsorber Modeling and Design", WPCF Journal, Vol. 53, No. 10, 1981, p. 1541.

Manes, M., "The Polanyi Adsorption Potential Theory and its Applications to Adsorption from Water Solution onto Activated Carbon." Activated Carbon Adsorption of Organics from the Aqueous Phase, Vol. 1, Editors Suffet, I. and McGuire, M., 1980.

Manes, M., and Greenbank, M., "Adsorption of Multicomponent Liquids from Water Onto Activated Carbon: Convenient Estimation Methods," Treatment of Water by Granular Activated Carbon, Advances in Chemistry Series 202, Editors McGuire, M., and Suffet, I., 1983.

Manes, M. and Hofer, L.J.E., "Application of the Polanyi Adsorption Potential Theory to Adsorption from Solutions on Activated Carbon," J. Phys. Chem. Vol. 73, 1969, p. 584.

Martin, R.J. and Al-Bahrani, K.S., "Adsorption Studies Using Gas-Liquid Chromatography - II. Competitive Adsorption Water Research, Vol. 11, 1977, p. 991.

Myers, A.L., and Zolandz, R.R., "Effect of pH on Multi-Component Adsorption from Dilute Aqueous Solution", Chapter 12 in Vol. 1 Reference 12.

Mathews, A., Mathematical Modeling of Multicomponent Adsorption in Batch Reactors, Thesis, University of Michigan (1975).

Mathews, A.P., and Weber, W.J., Jr., "Effect of External Mass Transfer and Intraparticle Diffusion on Adsorption Rates in

Slurries Reactor," Amer. Inst. Chem. Engr. Symp. Ser., Vol. 73, 1977, p. 91.

Mattson, J.S., Mark, H.B., Jr., Malbin, M.D., Weber, W.J., Jr., and Crittenden, J.C., "Surface Chemistry of Active Carbon: Specific Adsorption of Phenols", J. Colloid Interface Sci., 31, 116, (1969).

McGuire, M.J., and Suffet, I.H., ed. Activated Carbon Adsorption of Organics from the Aqueous Phase, Vol. 1 and 2, Ann Arbor Science Publishers Inc., Ann Arbor, (1980).

McGuire, M.J., and Suffet, I.H., ed. Treatment of Water by Granular Activated Carbon, Advances in Chemistry Series, 202, American Chemical Society, Washington, D.C., (1983).

Merk, W., Fritz, W., and Shlunder, E.U., "Competitative Adsorption of Two Dissolved Organics Onto Activated Carbon - III." Chemical Engineering Science, Vol. 36, 1981, p. 743.

Morris, J.C. and Weber, W.J., Jr., "Adsorption of Biochemically Resistant Materials from Solution, Part II." U.S. Public Health Service, AWTR-16, Report 999-WR-33 (1966).

Murin, C.J., and Snoeyink, V.L., "Competitive Adsorption of 2,4-Dichlorophenol and 2,4,6-Trichorophenol in the Nanomolar to Micromolar Concentration Range." Environmental Science and Technology, Vol. 13, No. 3, (1979).

Myers, A.L. and Prausnitz, J.M., "Thermodynamic of Mixed-Gas Adsorption", Jour. AIChE, Vol. 11, No. 1, p. 121.

Neretnieks, I., "Analysis of Some Adsorption Experiments with Activated Carbon," Chemical Engineering Science, Vol. 31, 1976, p. 1029.

Neretnicks, I., "Adsorption in Finite Bath and Countercurrent Flow with Systems having a Nonlinear Isotherm," Chemical Engineering Science, Vol. 31, 1976, p. 107.

Polanyi, M., "Adsorption of Gases (vapors) by a Solid Nonvolatile Adsorbent," Verh. Dent. Physik. Ges. 18:55 (1916); "Adsorption from Solutions of Substances of Limited Solubility," Z. Physik 2:111, (1920).

Radke, C.J., and Prausnitz, J.M., "Thermodynamics of Multi-Solute Adsorption from Dilute Liquid Solutions," Jour. AIChE, Vol. 18, No. 4, pp. 761 (1972).

Radke, C.J., and Prausnitz, J.M., "Adsorption of Organic Solutes from Dilute Aqueous Solution by Activated Carbon", Ind. Eng. Chem. Fund., 11, 1972, p. 445.

Roberts, P.V. and York, R.Y., "The Adsorption of Normal Paraffins from Binary Liquid Solutions by Molecular Sieve 5A Adsorbent, "Industrial Engineering of Chemical Process Design Development Vol. 6, No. 4, 1967, p. 516.

Rowley, H.H., and Innes, W.B., J. Phys. Chem., Vol. 46, 1942, p. 548.

Ruthven, D.M., Principles of Adsorption and Adsorption Processes, John Wiley and Sons, Inc. New York, 1984.

Scholen, J.J.F., Porous Carbon Solids, Academic Press, London and New York, 1967, p. 237.

Sherwood, T., Pigford, R., Wilke, C., Mass Transfer, McGraw-Hill Book Co., Inc. New York, N.Y., 1975.

Shunbo, F., Literathy, P., Abdilly, F., and Al-Ali, M., "Study of Micropollutants in Industrial Effluent Discharges in the Shuaiba Industrial Area." Kuwait Institute for Scientific Research, Kuwait, Sept., (1983).

Singer, P.C. and Yen, C.Y., "Adsorption of Alkylphenols by Activated Carbon", Chapt. 8 in Activated Carbon Adsorption of Organics from Aqueous Phase, Vol. 1, ed. by I.H. Suffet and M.J. McGuire, Ann Arbor Science Publishers, Inc., Ann Arbor, MI (1980).

Slejko, F.L., ed. Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application, Marcel Dekker, Inc., New York, (1985).

Suzuki, M. and Kawazoe, K., "Batch Measurement of Adsorption Rate in an Agitated Tank," Journal of Chemical Engineering of Japan, Vol. 7, No. 5, 1974, p. 346.

Suzuki, M. and Kawazoe, K., "Concentration Decay in a Batch Adsorption Tank," Seisan-Kenkyu, Vol. 26, No. 7, 1974, p. 29.

Suzuki, M., and Kawazoe, K., "Effective Surface Diffusion Coefficients of Volatile Organics on Activated Carbon During Adsorption from Aqueous Solution," Journal of Chemical Engineering of Japan, Vol. 8, No. 5, 1975, p. 379.

Stroud and Secrest, Gaussian Quadrature Formulas, Prentice-Hall, Englewood Cliffs, N.J., 1966.

Thiem, L.T., Badorek, D.L., Johari, A., and Alkhatib, E., "Adsorption of Synthetic Organic Shock Loadings", manuscript accepted for publication in ASCE, 1986.

Treybal, R.E., Mass Transfer Operation, 3rd ed., McGraw-Hill, N.Y., 1980.

U.S. Environmental Protection Agency, "Development Document for Proposed Effluent Limitations Guidelines, New Source Performance Standards, and Pretreatment Standards for the Petroleum Refining Point Source Category." EPA 440/1-79/014-b, Washington, D.C., Dec., (1979).

U.S. Environmental Protection Agency, "Draft Development Document including the Data Base for the Review of Effluent Limitations Guidelines (BATEA), New Source Performance Standards, and Pretreatment Standards for the Petroleum Refining Point Source Category." Washington, D.C., March, (1978).

Villadsen and Michelsen, Solution of Differential Equation Models by Polynomial Approximation. Prentice-Hall, Englewood Cliffs, N.J., 1978.

Villadsen, J.V. and Stewart, W.E., "Solution of Boundary-Value Problems by Orthogonal Collocation." Chem. Eng. Sci. (G.B.), Vol. 22, 1967, p. 1483.

Wakao, N. and Funozkri, T., "Effect of Fluid Dispersion Coefficients on Particle-to-Fluid Mass Transfer Coefficients in Packed Beds," Chemical Engineering Science Vol. 33, 1978, p. 1375.

Ward, T.M., and Getzen, F.W., "Influence of pH on the Adsorption of Aromatic Acids on Activated Carbon." Environmental Science and Technology, Vol. 4, No. 1, (1970).

Weber, T.W. and Chakravorti, R.K., "Pore and Solid Diffusion Models for Fixed-Bed Adsorbers," AIChE Journal, Vol. 20, No. 2, 1974, p. 228.

Weber, W.J., Jr., Physicochemical Processes for Water Quality Control, Wiley-Interscience, New York, (1972).

Weber, W.J., Jr., "Evolution of a Technology," Journal of the Sanitary Engineering Division, ASCE, Vol. 110, No. 5, Oct. (1984).

Weber, W. J., Jr., Physicochemical Processes for Water Quality Control, Wiley-Interscience, New York, (1972).

Weber, W.S., Jr., Crittenden, J.C., "Madam I-A Numeric Method for Design of Adsorption Systems," JWPCF Vol. 47, No. 5, 1975, p. 924.

Weber, W.J., and Keinath, L.M., "Mass Transfer of Purgeable Pollutants from Dilute Aqueous Solution in Fluidized Bed Adsorbers." Chemical Engineering Progress Symposium Series - Physical Adsorption Processes and Principles, 74 (63): (1967).

Weber, W.J., Jr., and Liu, K.T., "Determination of Mass Transport Parameters for Fixed-Bed Adsorbers," Chemical Engineering Communication, Vol. 6, 1980, p. 49.

Weber, W.J., Jr., and Morris, J.C., "Kinetic of Adsorption on Carbon from Solution," J. San. Eng. Div. of ASCE, SA2, 31 (1963).

Weber, W.J., Jr., and Rumer, R.R., "Intraparticle Transport of Sulfonated Alkylbenzenes in Porous Solid: Diffusion with Nonlinear Adsorption," Water Resources Res. Vol. 1, 1965, p. 361.

Williamson, J.E., Bazaire, K.E., and Geankopl is, C.J., "Liquid Phase Mass Transfer at Low Renyalds Numbers," I&EC Fundamentals Vol. 2, No. 2, 1963, p. 126.

Wilke, C.R., and Chang, P., "Correlation of Diffusion Coefficients in Dilute Solutions," American Institute of Chemical Engineering Journal, Vol. 1, 1955, p. 264.

Yen, C.Y., and Singer, P.C., "Competitive Adsorption of Phenols on Activated Carbon", Journal of the Sanitary Engineering Division, ASCE, Vol. 110, No. 5, Oct. (1984).

Zanitch, R.T. and Stenzel, M.H., Economics of Granular Activated Carbon Water and Wastewater Treatment Systems, in <u>Carbon Adsorption Handbook</u>, P.N. Cheremisinoff S., R. Ellerbugeh, Eds., Ann Arbor Science Publishers, Ann Arbor, Michigan, 1978.

Zogorski, J.S., and Faust, S.S., "Operational Parameters for Optimum Removal of Phenolic Compounds from Polluted Waters by Columns of Activated Carbon." American Institute of Chemical Engineers Symposium Series Water I. Physical, Chemical Wastewater Treatment, 73 (166): 54 (1976).