

## AN ABSTRACT OF THE THESIS OF

Maoyu Yang for the degree of Doctor of Philosophy in Civil Engineering  
presented on May 21, 1993.

Title: Adsorption of Chlorophenols on Granular Activated Carbon

Abstract approved: \_\_\_\_\_ **Signature redacted for privacy.**

Dr. Peter O. Nelson

Studies were undertaken of the adsorption of chlorinated phenols from aqueous solution on granular activated carbon (Filtrisorb-400, 30x40 mesh). Single-component equilibrium adsorption data on the eight compounds in two concentration ranges at pH 7.0 fit the Langmuir equation better than the Freundlich equation. The adsorptive capacities at pH 7.0 increase from pentachlorophenol to trichlorophenols and are fairly constant from trichlorophenols to monochlorophenols. Equilibrium studies were performed at various temperatures at pH 7.0. The adsorption process was found to be exothermic for pentachlorophenol and 2,4,6-trichlorophenol, and endothermic for 2,4-dichlorophenol and 4-chlorophenol.

Equilibrium measurements were also conducted for 2,4,5-trichlorophenol, 2,4-dichlorophenol, and 4-chlorophenol over a wide pH range. A surface complexation model was proposed to describe the effect of pH on adsorption equilibria of chlorophenols on activated carbon. Activated carbon surface functional sites are divided into acidic groups and basic groups with which molecular and ionized forms of chlorophenols interact, respectively, to form two neutral surface complexes, of which the complex of basic groups is more substantial and more stable than that of acidic groups. The simulations of the model are in excellent agreement with the experimental data.

Batch kinetics studies were conducted of the adsorption of chlorinated phenols on granular activated carbon. The external film diffusion model, linear-driving-force approximation, and surface reaction kinetics model were employed to fit the adsorption

kinetics data of chlorophenols. The results show that the surface reaction model best describes both the short-term and long-term kinetics, while the external film diffusion model describes the short-term kinetics data very well and the linear-driving-force approximation improved its performance for the long-term kinetics. The mass transfer coefficient was found to increase from more chlorinated compounds to less chlorinated compounds. Two-component adsorption kinetics experiments revealed that the adsorption of chlorophenols on activated carbon is to some extent an irreversible process and non-ideal competition between two components exists.

Multicomponent adsorption equilibria of chlorophenols on granular activated carbon was investigated in the micromolar equilibrium concentration range. The Langmuir competitive and Ideal Adsorbed Solution (IAS) models were tested for their performances on the three binary systems of pentachlorophenol/2,4,6-trichlorophenol, 2,4,6-trichlorophenol/2,4-dichlorophenol, and 2,4-dichlorophenol/4-chlorophenol, and the tertiary system of 2,4,6-trichlorophenol/2,4-dichlorophenol/4-chlorophenol, and found to fail to predict the two-component adsorption equilibria of the former two binary systems and the tertiary system. A new prediction method and a modification of the IAS model, both based on thermodynamic considerations, were proposed. The required parameters are the single-component Langmuir isotherm constants and initial concentrations for each component. The proposed new method and the modification of the IAS model were found to significantly improve the accuracy of the predictions of two-component adsorption equilibria of chlorophenols. This new method also performs much better than the Langmuir competitive and IAS models in the three-component system.

Studies were also conducted on the desorption equilibria and kinetics of chlorophenols. The results indicate that the Langmuir equation fits both adsorption and desorption equilibrium data better than the Freundlich equation and the degree of the irreversibility of adsorption increases from 4-chlorophenol to pentachlorophenol. A linear-driving-force desorption rate equation was proposed, which describes the desorption kinetic data very well. The desorption mass transfer coefficients were found to increase from pentachlorophenol to 4-chlorophenol.

# Adsorption of Chlorophenols on Granular Activated Carbon

by

Maoyu Yang

A THESIS

submitted to

Oregon State University

in partial fulfillment of  
the requirements for the  
degree of

Doctor of Philosophy

Completed May 21, 1993

Commencement June 1994

## ACKNOWLEDGMENTS

I am especially thankful to my major professor, Dr. Peter O. Nelson, for his encouragement, guidance and support throughout the course of this study. I would like to express my deep gratitude to Dr. Kenneth J. Williamson for all the support he gave me.

I would also like to acknowledge other members of my committee, Dr. Sandra L. Woods, Dr. Jonathan D. Istok and Dr. Robert Lawrence for their valuable and thoughtful suggestions. Special thanks to Ann Kimmerling for her generosity and help. Thanks to all my family members.

## TABLE OF CONTENTS

|           |   |     |
|-----------|---|-----|
| Chapter 1 | INTRODUCTION  | 1   |
| Chapter 2 | BACKGROUND  | 4   |
|           | Model Isotherms for Single-Component Adsorption                     | 4   |
|           | Prediction Methods for Multicomponent Adsorption Equilibria         | 7   |
|           | Surface Complexation Modeling                                       | 15  |
|           | Kinetic Models  | 17  |
| Chapter 3 | SINGLE-COMPONENT ADSORPTION EQUILIBRIA OF<br>CHLOROPHENOLS          | 23  |
|           | Materials and Methods   | 23  |
|           | Results and Discussion  | 26  |
|           | Conclusions   | 56  |
| Chapter 4 | ADSORPTION KINETICS OF CHLOROPHENOLS                                | 58  |
|           | Materials and Methods   | 58  |
|           | Results and Discussion  | 58  |
|           | Conclusions   | 84  |
| Chapter 5 | MULTICOMPONENT ADSORPTION EQUILIBRIA OF<br>CHLOROPHENOLS            | 86  |
|           | A New Method for Predicting Multicomponent Adsorption<br>Equilibria | 86  |
|           | Modification of IAS Model   | 95  |
|           | Results and Discussion  | 97  |
|           | Conclusions   | 124 |
| Chapter 6 | DESORPTION EQUILIBRIUM AND KINETICS OF<br>CHLOROPHENOLS             | 125 |
|           | Introduction  | 125 |
|           | Materials and Methods   | 126 |

|  |     |
|--|-----|
| Results and Discussion                                   | 127 |
| Conclusions  | 138 |
| Chapter 7 SUMMARY AND CONCLUSIONS                        | 140 |
| BIBLIOGRAPHY   | 145 |
| APPENDICES   | 151 |
| Appendix A. Computer Program for IAS Model               | 151 |
| Appendix B. Computer Program for Modified IAS Model      | 153 |
| Appendix C. FITEQL Input and Output (2,4,5-TCP)          | 155 |
| Appendix D. Single-Component Adsorption Equilibrium Data | 161 |
| Appendix E. Adsorption Kinetics Data                     | 189 |
| Appendix F. Multicomponent Adsorption Equilibrium Data   | 195 |
| Appendix G. Desorption Equilibrium and Kinetics Data     | 199 |

## LIST OF FIGURES

|             |   |    |
|-------------|---|----|
| Figure 3.1  | Langmuir isotherms for adsorption of PCP, 2,4,6-TCP and 3,4-DCP (higher concentration range)                  | 28 |
| Figure 3.2  | Langmuir isotherms for adsorption of PCP, 2,4,6-TCP and 3,4-DCP (lower concentration range)                   | 29 |
| Figure 3.3  | Langmuir isotherms for adsorption of 2,4,5-TCP at different pH  | 31 |
| Figure 3.4  | Effect of phosphate on adsorption of 2,4,5-TCP as a function of pH and optimum surface complexation model fit | 40 |
| Figure 3.5  | Amounts adsorbed of 4-CP and 2,4-DCP as a function of pH and optimum surface complexation model fits          | 41 |
| Figure 3.6  | Calculated surface speciation of activated carbon (0.5 g/l) in the presence of 1.525 mmol/l 2,4,5-TCP         | 42 |
| Figure 3.7  | Effect of dissolved organic matter on adsorption equilibrium  | 46 |
| Figure 3.8  | Langmuir isotherms for adsorption of PCP at various temperatures  | 47 |
| Figure 3.9  | Langmuir isotherms for adsorption of 2,4,6-TCP at various temperatures  | 48 |
| Figure 3.10 | Langmuir isotherms for adsorption of 2,4-DCP at various temperatures  | 49 |
| Figure 3.11 | Langmuir isotherms for adsorption of 4-CP at various temperatures   | 50 |
| Figure 3.12 | Effect of temperature on adsorption of 2,4-DCP  | 51 |
| Figure 4.1  | Effect of stirring speeds on adsorption rate of 2,4,6-TCP   | 59 |
| Figure 4.2  | Effect of pH on adsorption rate of 2,4,5-TCP  | 60 |
| Figure 4.3  | Comparison of kinetic models for adsorption of 2,4-DCP  | 63 |
| Figure 4.4  | Comparison of kinetic models for adsorption of 4-CP   | 64 |
| Figure 4.5  | Changes of 2,4-DCP concentration with time and predictions of surface reaction model                          | 66 |
| Figure 4.6  | Changes of 2,4-DCP concentration with time and predictions of external film diffusion model                   | 67 |

|             |  |     |
|-------------|--|-----|
| Figure 4.7  | Changes of 2,4,6-TCP concentration with time and predictions of surface reaction model                                     | 68  |
| Figure 4.8  | Changes of 2,4,6-TCP concentration with time and predictions of external film diffusion model                              | 69  |
| Figure 4.9  | Comparison of kinetic models for adsorption of 2,4-DCP (high initial concentration)  | 72  |
| Figure 4.10 | Comparison of kinetic models for adsorption of 2,4,6-TCP (long term)   | 73  |
| Figure 4.11 | Comparison of kinetic models for adsorption of PCP (long term)   | 74  |
| Figure 4.12 | Interruption test for adsorption of 2,4,6-TCP  | 75  |
| Figure 4.13 | Sensitivity analysis: $K_a$ parameter  | 78  |
| Figure 4.14 | Sensitivity analysis: $Q$ parameter  | 79  |
| Figure 4.15 | Sensitivity analysis: $b$ parameter  | 80  |
| Figure 4.16 | Changes of 2,4,6-TCP and 2,4-DCP concentrations with time in batch reactor (two components were introduced simultaneously) | 81  |
| Figure 4.17 | Changes of 2,4,6-TCP and 2,4-DCP concentrations with time in batch reactor (2,4,6-TCP was introduced 10 hours earlier)     | 82  |
| Figure 4.18 | Changes of 2,4,6-TCP and 2,4-DCP concentrations with time in batch reactor (2,4-DCP was introduced 10 hours earlier)       | 83  |
| Figure 5.1  | Flow diagram of computations for modified IAS model  | 96  |
| Figure 5.2  | Adsorption equilibria of PCP in the presence of TCP<br>(Initial concentrations: PCP, 0.580 mmol/l; TCP, 0.138 mmol/l)      | 112 |
| Figure 5.3  | Adsorption equilibria of TCP in the presence of PCP<br>(Initial concentrations: PCP, 0.580 mmol/l; TCP, 0.138 mmol/l)      | 113 |
| Figure 5.4  | Adsorption equilibria of PCP in the presence of TCP<br>(Initial concentrations: PCP, 0.478 mmol/l; TCP, 0.276 mmol/l)      | 114 |
| Figure 5.5  | Adsorption equilibria of TCP in the presence of PCP<br>(Initial concentrations: PCP, 0.478 mmol/l; TCP, 0.276 mmol/l)      | 115 |
| Figure 5.6  | Langmuir isotherms of TCP in the presence of DCP   | 116 |
| Figure 5.7  | 2,4,5-TCP/2,4-DCP two-component adsorption as a function of pH and optimum surface complexation model fits                 | 122 |

|            |  |     |
|------------|--|-----|
| Figure 5.8 | 2,4,5-TCP/2,4-DCP two-component adsorption as a function of pH and separate SCM fits to each component adsorption data | 123 |
| Figure 6.1 | Langmuir isotherms for adsorption and desorption of PCP  | 129 |
| Figure 6.2 | Langmuir isotherms for adsorption and desorption of 2,4-DCP  | 130 |
| Figure 6.3 | Langmuir isotherms for adsorption and desorption of 4-CP   | 131 |
| Figure 6.4 | Changes of PCP concentration with time during desorption and predictions of desorption kinetic rate equation           | 135 |
| Figure 6.5 | Changes of 2,4-DCP concentration with time during desorption and predictions of desorption kinetic rate equation       | 136 |
| Figure 6.6 | Changes of 4-CP concentration with time during desorption and predictions of desorption kinetic rate equation          | 137 |

## LIST OF TABLES

|           |   |     |
|-----------|---|-----|
| Table 3.1 | pKa Values for Chlorophenols  | 24  |
| Table 3.2 | Adsorption Constants for Chlorophenols at pH 7.0  | 30  |
| Table 3.3 | Effect of pH on Langmuir Constants for 2,4,5-TCP  | 32  |
| Table 3.4 | Surface Complexation and Aqueous Reactions in Activated Carbon/2,4,5-Trichlorophenol System             | 37  |
| Table 3.5 | Best Estimates for Chlorophenol/Carbon Surface Complexation Constants                                   | 37  |
| Table 3.6 | Langmuir Parameters for Adsorption of Chlorophenols as a Function of Temperature and Heat of Adsorption | 52  |
| Table 3.7 | Reproducibility for Analytical Measurements   | 53  |
| Table 3.8 | Standard Deviations and 95% Confidence Intervals for Langmuir Parameters                                | 54  |
| Table 3.9 | Blank Test Results  | 55  |
| Table 4.1 | Mass Transfer Coefficients for Three Chlorophenols  | 70  |
| Table 5.1 | Two-Component (PCP/2,4,6-TCP) Adsorption  | 100 |
| Table 5.2 | Two-Component (2,4,6-TCP/2,4-DCP) Adsorption  | 103 |
| Table 5.3 | Two-Component (2,4-DCP/4-CP) Adsorption   | 106 |
| Table 5.4 | Three-Component (2,4,6-TCP/2,4-DCP/4-CP) Adsorption   | 109 |
| Table 5.5 | Best Estimates for 2,4,5-TCP/2,4-DCP Two-Component Surface Complexation Constants                       | 120 |
| Table 5.6 | Best Estimates for Conditional Surface Complexation Constants (2,4,5-TCP/2,4-DCP System)                | 121 |
| Table 6.1 | Comparison of Langmuir and Freundlich Constants for Adsorption and Desorption of Three Compounds        | 132 |
| Table 6.2 | Single-Solute Desorption Irreversibility  | 132 |
| Table 6.3 | Desorption Kinetic Parameters   | 138 |

# Adsorption of Chlorophenols on Granular Activated Carbon

## Chapter 1 INTRODUCTION

Chlorinated phenols are of environmental concern due to anthropogenic inputs from industrial wastes, degradation of chlorinated pesticides, and use of pentachlorophenol as a wood preservative. Chlorophenols in the nanomolar to micromolar concentration range also form during municipal water purification *via* the phenol-chlorine reaction. Chlorophenol removal is necessary because chlorophenols are odor-producing and some have been found to be carcinogenic. 2-Chlorophenol, 2,4-dichlorophenol, and 2,6-dichlorophenol are the major odor-causing species and produce detectable odor at the 2 and 3  $\mu\text{g/l}$  levels.

Adsorption is a fundamental process for separating inorganic and organic contaminants from waters and wastewaters. Activated carbon remains the principal adsorbent in full-scale treatment. At present, the applications of activated carbon adsorption in water treatment in the United States are predominantly traditional taste and odor control. However, activated carbon adsorption is increasingly being considered for removal of synthetic organic chemicals, color-forming organics, and disinfection by-products and their naturally occurring precursors. It has been found that the chlorophenols can be strongly adsorbed by activated carbon and will not break through conventional

granular activated carbon (GAC) columns for years (Montgomery, 1985). It is expected that the application of activated carbon to control contamination of drinking water by toxic or carcinogenic compounds at low concentrations will increase.

The recent concerns with the removal of chlorinated phenols have focused attention on the biodegradation of these compounds on activated carbon (Speitel et al., 1989). The highly chlorinated phenols, i.e., tetra- and pentachlorophenol, can be degraded anaerobically and various lower chlorinated phenols, i.e., tri-, di- and monochlorophenol, will be formed as their metabolites (Nicholson et al., 1990). Biodegradation and adsorption will occur simultaneously in these systems. Therefore, it is of significance to investigate the adsorption behavior of various chlorophenols on granular activated carbon.

Both kinetics and thermodynamics or equilibrium are important to the process of activated carbon adsorption. The chlorophenols can partially or totally ionize in aqueous solution and pH will play an important role in activated carbon adsorption. The objectives of this thesis are:

(1) to investigate equilibrium characteristics of activated carbon adsorption of chlorinated phenols and to determine the isotherm parameters for single-component systems;

(2) to develop and verify a surface complexation model for describing the effect of pH on equilibrium adsorption of organic electrolytes on activated carbon;

(3) to investigate competitive adsorption equilibrium characteristics of chlorophenols in multicomponent systems;

(4) to develop and verify a non-ideal competitive model for predicting

multicomponent adsorption equilibria of chlorophenols;

(5) to modify the Ideal Adsorbed Solution (IAS) model and to verify the modified IAS model for predicting multicomponent adsorption equilibria of chlorophenols;

(6) to investigate the adsorption kinetics of chlorophenols and to determine which kinetic model can best describe the kinetic processes of chlorophenol adsorption;

(7) to investigate the desorption equilibrium and kinetics of chlorophenols on activated carbon;

(8) to investigate the influence of pH on adsorption equilibrium and kinetics of chlorophenols;

(9) to investigate the influence of temperature on adsorption equilibrium of chlorophenols.

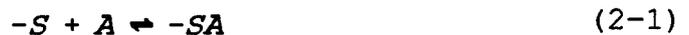
## Chapter 2 BACKGROUND

### Model Isotherms for Single-Component Adsorption

In this context, single-component actually means one contaminant component in aqueous solution. The solvent (water) is simply assumed to be inert, the adsorption of the contaminant component is assumed to be unaffected by the water, and therefore, the system is treated as a single-component system.

To represent the equilibrium relation for single-component adsorption, a number of model isotherms reported in the literature will be reviewed.

**Langmuir Isotherm.** Langmuir adsorption isotherm describes equilibrium between surface and solution as a reversible chemical equilibrium between species (Langmuir, 1918). The adsorbent surface is considered to be made up of fixed individual sites where molecules of adsorbate may be chemically bound. Denote an unoccupied surface site as  $-S$  and the adsorbate in dilute solution as species  $A$ , with concentration  $C$ , and consider the reaction between the two to form occupied sites ( $-SA$ ):



Assume that this reaction has a fixed free energy of adsorption equal to  $\Delta G_a^0$  that is not dependent on the extent of adsorption and not affected by interaction among sites. Each site is assumed to be capable of binding at most one molecule of adsorbate; the Langmuir

model allows accumulation only up to a monolayer.

If  $Q$  is the maximum number of moles adsorbed per mass adsorbent when the surface sites are saturated with adsorbate (i.e., a full monolayer), and  $q$  is the number of moles of adsorbate per mass adsorbent at equilibrium. According to the law of mass action, we have

$$b = \frac{[-SA]}{[-S][A]} = \frac{q}{(Q - q)C} \quad (2-2)$$

where  $b = \exp(-\Delta G_a^0/RT)$ , an equilibrium constant and  $C$  is equilibrium concentration in solution. The rearrangement of equation 2-2 leads to

$$q = \frac{QbC}{1 + bC} \quad (2-3)$$

Correspondence of experimental data to the Langmuir equation does not mean that the stated assumptions are valid for the particular system being studied, because departure from the assumptions can have a canceling effect. An advantage of this model is that it can approach Henry's law at low concentrations. The constants in the Langmuir equation can be determined by plotting  $C/q$  versus  $C$  and making use of equation 2-3 rewritten as

$$\frac{C}{q} = \frac{1}{Qb} + \frac{C}{Q} \quad (3-4)$$

**BET Isotherm.** The BET adsorption isotherm (Brunauer et al., 1938) extends the Langmuir model from a monolayer to several molecular layers. This isotherm has the form

$$\frac{q}{Q} = \frac{BC}{(C_s - C) [1 + (B - 1) \frac{C}{C_s}]} \quad (2-5)$$

Where  $B$  is a dimensionless constant related to the difference in free energy between adsorbate on the first and successive layers and  $C_s$  is the saturation concentration of the adsorbate in solution.

**Freundlich Isotherm.** The Langmuir and BET models incorporate an assumption that the energy of adsorption is the same for all surface sites and not dependent on degree of coverage. In reality, the energy of adsorption may vary because real surfaces are heterogeneous. The Freundlich adsorption isotherm (Freundlich, 1926) attempts to account for this. The Freundlich isotherm has the form

$$q = K C^n \quad (2-6)$$

$q$  and  $C$  are the equilibrium solid- and solution-phase concentrations of solute;  $K$  and  $n$  are empirical constants, which can be evaluated by plotting  $\log q$  versus  $\log C$ . A potential disadvantage of this model is that it does not approach Henry's law at low concentrations.

**Langmuir-Freundlich Isotherm.** Sips (1948) modified the Langmuir isotherm by the introduction of a power law expression of Freundlich form:

$$q = \frac{QbC^n}{1 + bC^n} \quad (2-7)$$

which reduces to the Freundlich type for low concentration and exhibits saturation for high concentration. This isotherm contains three parameters.

**Toth Isotherm.** Toth (Toth, 1971; Jossens and Prausnitz, 1978) has considered only adsorption of gases but his ideas can be extended to adsorption of solutes from dilute aqueous solution. Toth isotherm has the form

$$q = \frac{QC}{(b + C^M)^{1/M}} \quad (2-8)$$

which contains three parameters. Toth equation reduces to Henry's law at very low concentrations and exhibits saturation at high concentrations.

### **Prediction Methods for Multicomponent Adsorption Equilibria**

Polluted water usually contains more than one contaminant. Multicomponent adsorption involves competition to occupy the limited adsorbent surface available and the interactions between different adsorbates. A number of methods have been developed that aim at predicting multicomponent adsorption equilibria using data from single-component adsorption isotherms. For simple systems considerable successes have been achieved but

there is still no established method with universal proven applicability, and this problem remains one of the more challenging obstacles to the development of improved methods of process design (Ruthven, 1984).

**Multicomponent Langmuir Isotherm.** A common model for predicting adsorption equilibria in multicomponent systems is the Langmuir model for competitive adsorption, which was first developed by Butler and Ockrent (1930). This model is based on the same assumptions as the Langmuir model for single adsorbates. Assuming, as did Langmuir, that the rate of adsorption of a species at equilibrium is equal to its rate of desorption, the equation

$$q_i = \frac{Q_i b_i C_i}{1 + \sum_{i=1}^n b_i C_i} \quad (2-9)$$

was developed, in which  $Q_i$  and  $b_i$  are the Langmuir constants determined from the single-solute adsorption isotherm of species  $i$ . Because of its mathematical simplicity, this model is widely used (Hsieh et al., 1977; Crittenden et al., 1980; Murin and Snoeyink, 1979).

Broughton (1948) observed that the extension of the Langmuir theory to adsorption from binary adsorbate systems is thermodynamically consistent only in the special case where  $Q_1 = Q_2$ . However, Young and Crowell (1962) have pointed out that thermodynamic consistency is of secondary importance if the equation provides the correct analytical description of the adsorption phenomena.

**Modified Multicomponent Langmuir Isotherm.** Jain and Snoeyink (1973) have noted

that if the Langmuir model for competitive adsorption satisfactorily predicts the extent of adsorption from a bisolute system when  $Q_1 \neq Q_2$ , it is probably because there is competition for all available sites. They have proposed a model which can be used to predict the extent of adsorption of each species from a bisolute solution if a portion of the adsorption occurs without competition. The model was based on the hypothesis that adsorption without competition occurs when  $Q_1 \neq Q_2$ . Further, it was assumed that the number of sites for which there was no competition was equal to the quantity  $(Q_1 - Q_2)$ , where  $Q_1 > Q_2$ . On this basis, the following equations were proposed:

$$q_1 = \frac{(Q_1 - Q_2) b_1 C_1}{1 + b_1 C_1} + \frac{Q_2 b_1 C_1}{1 + b_1 C_1 + b_2 C_2} \quad (2-10)$$

$$q_2 = \frac{Q_2 b_2 C_2}{1 + b_1 C_1 + b_2 C_2} \quad (2-11)$$

The first term on the right side of equation 2-10 is the Langmuir expression for the number of moles of species 1 that adsorb without competition on the surface area proportional to  $(Q_1 - Q_2)$ . The second term represents the number of moles of species 1 adsorbed on the surface area proportional to  $Q_2$  under competition with species 2 and is based on the Langmuir model for competitive adsorption. The number of moles of species 2 adsorbed on surface area proportional to  $Q_2$  under competition with species 1 can be calculated from equation 2-11.

**Multicomponent Langmuir-Freundlich Isotherm.** The Sips equation (eqn 2-7) may be easily extended to binary or multicomponent systems (Ruthven 1984; Yu and Neretnieks, 1990). The resulting expression for the isotherm is

$$q_i = \frac{Q_i b_i C_i^{n_i}}{1 + \sum b_i C_i^{n_i}} \quad (2-12)$$

The simple formula makes this method very attractive. Although not thermodynamically consistent, this expression has been shown to provide a reasonably good empirical correlation of binary equilibrium data for a number of simple gases on molecular sieve adsorbents (Yon and Turnock, 1971) and is widely used for design purposes (Maurer, 1980). However, because of the lack of a proper theoretical foundation this approach should be treated with caution.

**Ideal Adsorbed Solution (IAS) Model.** The most common model for describing adsorption equilibrium in multicomponent systems is the Ideal Adsorbed Solution (IAS) model, which was developed by Radke and Prausnitz (Radke and Prausnitz, 1972). This model relies upon the assumption that the adsorbed phase forms an ideal solution and hence the name Ideal Adsorbed Solution (IAS) model has been adopted. The following part should only be a summary of the main equations and assumptions of this theory.

Equation 2-13 used within this theory relates the concentration of solute  $i$  in the mixture,  $C_i$ , to a corresponding concentration of this solute in a single solute system,  $C_i^0$ :

$$C_i(\Pi, T, Z_i) = Z_i C_i^0(\Pi, T) \quad (2-13)$$

Here,  $Z_i$  represents the mole fraction of surface coverage by component  $i$ ,  $\pi$ , the spreading pressure on the surface and  $T$ , the absolute temperature. The spreading pressure defines the lowering of surface tension at the adsorbate-solution interface:

$$\Pi = \gamma^0 - \gamma \quad (2-14)$$

$\gamma^0$  is the surface tension of the pure solvent (water) and  $\gamma$  the surface tension created by the mixture of solvent and solutes.

Equation 2-13 holds only when  $\pi$  and  $T$  in the mixture are the same as those in the respective single-solute systems.

Spreading pressure can be related to the characteristic adsorption equilibria of each single solute system according to:

$$\Pi_i = \frac{RT}{A} \int_0^{c_i^0} q_i^0 \frac{dc_i^0}{c_i^0} \quad (2-15)$$

In equation 2-15,  $R$  is the universal gas constant,  $A$ , the surface area per unit weight,  $C_i^0$ , the liquid-phase concentration of species  $i$  in single-solute systems which gives the same spreading pressure as that of the mixture and  $q_i^0$ , the solid-phase loading corresponding to  $C_i^0$ .

Equivalence of the spreading pressures of all the solutes in the mixture gives

$$\int_0^{c_1^0} q_1^0 \frac{dc_1^0}{c_1^0} = \int_0^{c_2^0} q_2^0 \frac{dc_2^0}{c_2^0} = \int_0^{c_3^0} q_3^0 \frac{dc_3^0}{c_3^0} = \dots \quad (2-16)$$

The relations between  $q_i^0$  and  $C_i^0$  are given by the single solute adsorption isotherm:

$$q_i^0 = f_i(C_i^0) \quad (2-17)$$

Combining the IAS theory with the Gibbs equation for isothermal adsorption gives the relationship necessary for equilibrium calculations:

$$\frac{1}{q_T} = \sum_i^n \frac{Z_i}{q_i^0} \quad (2-18)$$

Other two equations required for IAS model calculations are

$$\sum_i^n Z_i = 1 \quad (2-19)$$

$$q_i = Z_i q_T \quad (2-20)$$

Equations 2-13, 2-16, 2-17, 2-18, 2-19 and 2-20 constitute a set of simultaneous equations from which the IAS model calculation can be made.

This model has received widespread use in multisolute adsorption research for a variety of reasons (Jossens and Prausnitz, 1978; Yu and Neretnieks, 1990; Yen and Singer, 1984; Crittenden et al., 1985a; Crittenden et al., 1985b; Smith and Weber, 1988; Weber and Smith, 1987; Fritz and Schlunder, 1981). Besides the fact that application of

IAS model necessitates only single-solute data, the model is flexible in that multicomponent calculations can be performed using several different single-solute isotherm relationships. In addition, this model has a solid theoretical foundation, providing a useful understanding of the thermodynamic approach to adsorption. In this regard it is similar to the Gibbs adsorption equation upon which it is based. This is in contrast to the Langmuir competitive model, which is founded on the same limiting assumptions as the single-solute Langmuir model (i.e., monolayer adsorption and a homogeneous adsorbent surface).

However, Radke and Prausnitz (1972) have pointed out that the IAS model for predicting multisolute adsorption is most reliable for those systems where solute adsorption loading is moderate. If solute adsorption loading is large, the deviations of the predictions from experimentally observed data may be significant. Similar to the Langmuir and other multisolute equilibria models, the IAS model predicts that the adsorbate more favorably adsorbed in single-solute solutions also adsorbs to a greater extent when in competition at equimolar concentration. This is true only when adsorption is reversible and competition for adsorption sites is ideal. The criterion of ideal competition implies that the adsorbent is homogeneous with respect to adsorption sites and that the sites are equally accessible. However, activated carbon cannot be considered homogeneous because of its extensive microporous structure and the occurrence of different functional groups on the activated carbon surface. An ideal competition assumption, therefore, is invalid. Many researchers (Grant and King, 1990; Yonge et al., 1985; Snoeyink et al., 1969) have also shown that the adsorption of some compounds,

such as phenolic compounds, are highly irreversible. This implies that it is difficult to replace each other once one of the components is prior adsorbed on activated carbon. It is evident that adsorption kinetics will affect the multicomponent adsorption if the adsorption rates of components are not proportional to their respective adsorptive capacities. Consequently, IAS and other existing multisolute equilibria models will fail to accurately predict solid-phase loadings under system conditions that exhibit significant non-ideal, that is, unequal competition and irreversible adsorption effects (Thacker et al., 1984; Smith and Weber, 1988; Yonge and Keinath, 1986).

**Modifications of IAS Model.** A number of attempts have been made to modify the IAS model to improve its accuracy and to reduce computational efforts. Using the IAS model, DiGiano et al. (1978) derived a simplified competitive equilibrium adsorption model (SCAM). This model, which is based on the Freundlich isotherm, assumes the single-solute isotherms of all the components are equal and it utilizes average isotherm constants when this assumption is not valid. The IAS equations have been reduced to a single expression:

$$q_i = K' \frac{n'-1}{n'} [K_i C_i^{n_i}]^{\frac{1}{n'}} \left[ \sum_{i=1}^N \left( \frac{K_i}{K'} C_i^{n_i} \right)^{\frac{1}{n'}} \right]^{(n'-1)} \quad (2-21)$$

where  $q_i$  is the solid-phase equilibrium concentration of solute  $i$ ;  $n_i$  and  $K_i$ , the empirical Freundlich constants for single solute  $i$ ;  $C_i$ , the liquid-phase equilibrium concentration of solute  $i$ ;  $n'$ , the average value of  $n_i$ ; and  $K'$ , the average value of  $K_i$ .

This model significantly simplifies the computations of the IAS model, although it does not improve its accuracy (Yonge and Keinath, 1986; Wilmanski and Brèemen, 1990).

One popularized approach to modify the IAS model is to incorporate an empirical coefficient,  $R_i$ , into equation 2-20 to more accurately describe experimental equilibria (Thacker et al., 1984; Smith and Weber, 1988; Yonge and Keinath, 1986; Speitel et al., 1989):

$$Q_i = R_i Z_i Q_T \quad (2-22)$$

The modification factors,  $R_i$ , are determined from multisolute equilibrium data with a minimization procedure. This modification provides a significantly better description of the data. This improvement, however, is the result of parameters that are determined from the multisolute data itself.

### Surface Complexation Modeling

In the past quarter century there has been increasing interest in the sorption properties and surface chemistry of hydrous oxides. Common hydrous oxides, such as those of iron, aluminum, manganese, and silicon, can sorb a large number of chemical species. Experimental sorption data have been described by various empirical means, including partition coefficients, isotherm equations, and conditional equilibrium sorption constants. Much effort has been also invested in the development of theoretical models of the oxide/water interface. This work has been conducted to gain understanding of the

sorption mechanisms involved, describe the available data in an efficient manner, and enable prediction of sorption.

Schindler, Stumm, and coworkers (Schindler and Kamber, 1968; Schindler and Gamsjager, 1972; Stumm et al., 1970; Huang and Stumm, 1973) proposed new ways of describing surface charge development and sorption models that embody the central features of the well-known electric-double-layer (EDL) theory but emphasize chemical reactions of sorbing ions with surface functional groups: the *surface complexation approach*. In this approach, sorbing ions are considered to react chemically with specific surface hydroxyl groups after coming through the interfacial electric field at the surface. The electric field, which may be positive or negative, results from a positive or negative surface charge caused by the chemical reactions at the surface.

The reactions with surface hydroxyl groups are considered analogous to the formation of soluble complexes and are described by mass law equations. However, the corresponding equilibrium constants are not, in fact, constant. What distinguishes surface reactions from reactions among (monomeric) solutes is the variable electrostatic energy of interaction caused by the variable charge on the surface. These electrostatic effects are taken into account by applying a coulombic correction factor, derived from EDL theory, to the equilibrium constants of the surface complexation reactions.

Surface complexation models have been widely applied to hydrous oxides/inorganics or organics systems, while very few studies have been conducted to apply the surface complexation models to activated carbon/inorganics systems. In order to gain better insight into the mechanism of cadmium removal, Huang and Ostovic (1978)

have characterized the surface properties of activated carbon in terms of its surface acidity and hydroxo group. The association between cadmium ions and activated carbon was interpreted and described by a surface complexation model. No studies were found that applied surface complexation models to activated carbon/organics systems.

### Kinetic Models

To properly interpret the kinetic experimental data, it is necessary to determine for the experimental system which of the steps in the adsorption process governs the overall adsorption rate. The process of adsorption of an organic compound by a porous adsorbent can be categorized as three consecutive steps. The first step is transport of solute across the boundary layer or surface film to the exterior surface of the adsorbent particle. The second step is transport of solute within the pores of the adsorbent particle, from the exterior of the particle to the interior surfaces of the particle. Similarly, solute may be transported along surfaces of pore walls. The final step is the physical or chemical binding of solute to the interior surface of the adsorbent.

*External Film Diffusion Model.* If external film diffusion is the rate-controlling step, the rate equation (Wermeulen, 1958; Kuo et al., 1987) can be expressed by

$$\frac{dq}{dt} = \frac{K_f a}{M} (C - C^*) \quad (2-23)$$

where  $K_f a$  is the mass transfer coefficient;  $C$ , the adsorbate concentration in bulk liquid-phase;  $C^*$ , the adsorbate concentration of the liquid that is in equilibrium with the solid-

phase concentration  $q$ ; and  $M$ , the carbon dosage.

Assuming the adsorption isotherm can be expressed by the Langmuir equation, i.e.,  $q = QbC^*/(1 + bC^*)$ , and taking advantage of the mass balance  $q = (C_0 - C)/M$  where  $C_0$  is the initial adsorbate concentration, equation 23 can be changed to

$$-\frac{dC}{dt} = K_r a \left( C - \frac{C_0 - C}{b[QM - (C_0 - C)]} \right) \quad (2-23')$$

Usually, external transport is the rate-limiting step in systems which have: (a) poor mixing; (b) dilute concentration of adsorbate; (c) small particle sizes of adsorbent; and (d) high affinity of adsorbate for adsorbent (Zogorski et al., 1976). Some experiments conducted at low concentrations have shown that film diffusion solely controls the adsorption kinetics of low molecular weight substances (Fritz et al., 1981; Merk et al., 1981).

***Internal Surface Diffusion Model.*** The adsorbate can diffuse by two mechanisms within the adsorbent, pore and surface diffusions. For pore diffusion, the adsorbate is transported within the pore fluid. For surface diffusion, the adsorbate continues to move along the surface of the adsorbent to available adsorption sites as long as it has enough energy to leave its present site. Investigations (Brecher et al., 1967; Furusawa and Smith, 1973; Komiyama and Smith, 1974) have demonstrated that surface diffusion is the dominant mechanism, so the contribution of pore diffusion is neglected. Many researchers (Crittenden and Weber, 1978a; Crittenden and Weber, 1978b; Crittenden et al., 1980; van Vliet and Weber, 1981; Wu and Gschwend, 1986; Traegner and Suidan, 1989) have used

the surface diffusion model for describing the kinetic data or for design of adsorbers.

The partial differential equation for this model is written in spherical coordinates as:

$$\frac{\partial q(r, t)}{\partial t} = D_s \left( \frac{\partial^2 q(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial q(r, t)}{\partial r} \right) \quad (2-24)$$

in which  $q(r, t)$  represents the solid-phase concentration along the inner surface of the particle;  $r$ , the radial coordinate with an origin at the center of the particle; and  $D_s$ , the surface diffusion coefficient. The magnitude of  $D_s$  is a measure of how fast the molecules diffuse inside the carbon particle and therefore sets a time scale for the adsorption process. Two boundary conditions and one initial condition have to be specified in order to obtain a unique solution to equation 2-24. Initially the particle is free of adsorbate, i.e.:

$$q(r, t=0) = 0 \quad (2-25)$$

The boundary condition at the center of the particle is:

$$\frac{\partial q(r=0, t)}{\partial r} = 0 \quad (2-26)$$

i.e., no adsorbate flux across the center. Finally, the continuity of flux at the solid-liquid interface has to be satisfied:

$$\rho_p D_s \frac{\partial q(r=d_p/2, t)}{\partial r} = K_f (C_b - C_s) \quad (2-27)$$

with  $C_b$  and  $C_s$  denoting the bulk liquid and solid-liquid interface adsorbate concentrations, respectively;  $d_p$ , the particle diameter; and  $\rho_p$ , the apparent density of the carbon particle. This boundary condition contains the second important kinetic parameter  $K_f$ , which represents the liquid film mass transfer coefficient. The parameter  $K_f$  is a measure for how fast the molecules diffuse across the stagnant liquid film layer. It is assumed that local equilibrium occurs at the exterior carbon surface.

The average carbon loading, which is only a function of time, is given by:

$$q_{avg} = \frac{3}{(d_p/2)^3} \int_0^{d_p/2} q(r, t) r^2 dr \quad (2-28)$$

**Linear-Driving-Force Approximation.** The surface diffusion model (eqn 2-24) is usually approximated by the linear-driving-force relation (Vermeulen, 1958; Kuo et al., 1987):

$$\frac{dq}{dt} = K_p a (q^* - q) \quad (2-29)$$

where  $K_p a$  ( $= 60 D_s/d_p^2$ ) is the mass transfer coefficient and  $q^*$  is the solid-phase concentration in equilibrium with the instantaneous fluid-phase concentration outside the particle.

If adsorption isotherm can be expressed by the Langmuir equation, i.e.,  $q^* = QbC/(1 + bC)$  and mass balance  $q = (C_0 - C)/M$  is used, equation 2-29 becomes:

$$-\frac{dC}{dt} = K_p a \left( \frac{MQbC}{1 + bC} + C - C_0 \right) \quad (2-29')$$

**Surface Reaction Model.** For the case in which surface reaction is the rate-controlling step, the rate of adsorption can be expressed as (Vermeulen, 1958; Kuo et al., 1987)

$$\frac{dq}{dt} = K_a \left[ C(Q - q) - \frac{q}{b} \right] \quad (2-30)$$

where  $K_a$  is the surface reaction rate constant, and  $Q$  and  $b$  are the Langmuir adsorptive capacity and equilibrium constant, respectively. Using the mass balance  $q = (C_0 - C)/M$ , the above equation changes to

$$-\frac{dC}{dt} = K_a \left[ C(QM - C_0 + C) - \frac{1}{b} (C_0 - C) \right] \quad (3-30')$$

The adsorption process can be pictured as one in which molecules leave solution and are held on the solid surface by chemical and physical binding. If the bonds that form between the adsorbate and adsorbent are very strong, the process is almost always irreversible, and chemical adsorption or chemisorption is said to have occurred. On the other hand, if the bonds that are formed are very weak, as is characteristic of bonds formed by the dispersion interactions or hydrogen bonding, physical adsorption is said to have occurred. The molecules adsorbed by this means are easily removed, or desorbed, by a change in the solution concentration of the adsorbate, and for this reason, the process

is said to be reversible. There is a difference in the activation energy of adsorption reaction between physisorption and chemisorption. For chemical bonding, activation energy is higher than 10 kcal/mole, and for dispersion interactions and hydrogen bonding, it ranges from 2 to 10 kcal/mole.

Kuo et al. (1987) showed that the rate of the adsorption of dissolved organics from *in situ* tar sand by-product waters could be described by the surface reaction kinetics, i.e., equation 3-30. Grant and King (Grant and King, 1990) found that the oxidative coupling of phenolic compounds on carbon surfaces was a plausible explanation for irreversible adsorption. Their data indicated that a chemical reaction occurred and that the phenolate ion was more reactive than phenol. Because chemical reaction is slow compared to physisorption, surface reaction kinetics may control the adsorption process.

## Chapter 3 SINGLE-COMPONENT ADSORPTION EQUILIBRIA OF CHLOROPHENOLS

### Materials and Methods

**Chemicals.** Eight chlorinated phenols were studied, pentachlorophenol (PCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,4,5-trichlorophenol (2,4,5-TCP), 2,4-dichlorophenol (2,4-DCP), 3,4-dichlorophenol (3,4-DCP), 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP). The pKa values for these compounds are given in Table 3-1. Aqueous solutions of each chlorinated phenol were prepared by dissolving it in glass-distilled, deionized water, having varying concentrations of 100 to 300 mg/l. Preliminary studies indicated that in the neutral pH range (6.5 to 7.5), a 5 mM phosphate ( $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ ) buffer could maintain the pH of solution with adsorbate concentration of less than 300 mg/l within 0.2 unit fluctuation during adsorption. A 5 mM phosphate buffer was included in all subsequent experiments, unless noted otherwise. Using low concentration of phosphate aims at minimizing its influence on the adsorption of chlorophenols. The pH of each solution was adjusted with minimum amounts of HCl and NaOH solutions.

**Activated Carbon.** The adsorbent used throughout this study was Calgon Filtrasorb-400 activated carbon, the properties of which are described elsewhere (Montgomery, 1985). The carbon received from the manufacturer was ground in an analytical mill and sieved

to yield a 30 x40 mesh size (0.59 - 0.42 mm). After sieving, the carbon was washed with glass-distilled, deionized water to remove all fines, dried overnight in an oven at 105°C, and stored in an air-tight desiccator until use.

**Table 3.1 pKa Values for Chlorophenols**

| Compound                  | pKa                                    |
|---------------------------|--|
| Pentachlorophenol         | 5.25 <sup>a</sup><br>4.74 <sup>b</sup> |
| 2,3,4,6-Tetrachlorophenol | 5.40 <sup>a</sup>                      |
| 2,4,6-Trichlorophenol     | 6.15 <sup>a</sup><br>5.99 <sup>b</sup> |
| 2,4,5-Trichlorophenol     | 6.94 <sup>a</sup>                      |
| 2,4-Dichlorophenol        | 7.85 <sup>a</sup>                      |
| 4-Chlorophenol            | 9.18 <sup>c</sup>                      |
| 2-Chlorophenol            | 8.49 <sup>c</sup><br>8.52 <sup>b</sup> |

<sup>a</sup> after Schellenberg et al. (1984)

<sup>b</sup> after Westall et al. (1985)

<sup>c</sup> after CRC Handbook of Chem. Phys. (1990-1991)

**Equilibrium Studies.** Batch studies were used to obtain the equilibrium data. 40-ml portions of aqueous solution with the desired pH and adsorbate concentration were placed in 40-ml Teflon tubes containing accurately weighed amounts of carbon. Then the tubes were continuously shaken in a shaker bath for 6 days. This equilibration time was determined from preliminary kinetic studies. The temperature was kept constant at 30°C

for all experiments, except for studies on the effect of temperature. After adsorption equilibrium was reached, the equilibrium concentration was measured and the extent of adsorption was calculated. If the desired solution pH was outside the phosphate buffering region (pH 6.5-7.5) and the acidic and basic buffering region (pH < 4 and pH > 10 ), occasionally it was necessary to adjust pH during the equilibration period to maintain the desired pH. The final pH was measured.

**Analytical Techniques.** 5-ml aliquots were used for analysis of chlorophenols. The samples were first acetylated and then extracted into hexane. Each sample was added to 45 ml of glass-distilled water in a 150-ml separatory funnel using a 5-ml volumetric pipette. 50  $\mu$ l of internal standard (either 2,4,6-tribromophenol for 2,4,5-trichlorophenol, or 2,6-dibromophenol for other chlorophenols) was added using a 50- $\mu$ l syringe. After one ml of a 0.73 g/ml solution of potassium carbonate and one ml of acetic anhydride were added, the funnel was shaken for exactly two minutes. The complete acetylation reaction would take about two hours, after which 5 ml of hexane was added using a dedicated 5-ml volumetric pipette and again the funnel was shaken for another two minutes. After 30 minutes, the water layer was drained and the hexane layer was withdrawn using a new pasteur pipette and transferred to a 2-ml amber glass vial with Teflon-lined cap, which was stored in a refrigerator until gas chromatograph analysis was conducted.

Using an autosampler, 1  $\mu$ l of hexane solution was injected into a Hewlett Packard Model 5890A Gas Chromatograph equipped with a  $^{63}$  Ni electron capture detector (ECD) and 30 m by 0.323 mm i.d. DB-5 fused-silica capillary column (J+W Scientific, Orangeville, CA). Helium (5 psi) was used as the carrier gas and a 95% argon/5%

methane mixture was used as the ECD auxiliary gas. The detector temperature was set at 320°C and injector temperature was 250°C. The samples were run using a temperature program as follows: an initial oven temperature of 45°C was held for 2 minutes, increased by 15°C/min to 150°C, and then by 5°C/min to a final temperature of 215°C that was held for 5 minutes.

## Results and Discussion

*Isotherms of Chlorophenols at pH 7.* Equilibrium adsorption data at pH 7.0 for all compounds fitted the Langmuir equation,  $q = QbC/(1 + bC)$ . The constants in the Langmuir equation were determined by plotting  $C/q$  versus  $C$  and making use of the above equation rewritten as a linearized form,  $C/q = 1/(Qb) + C/Q$ . Representative Langmuir plots of PCP, 2,4,6-TCP, and 3,4-DCP for high and low concentration ranges are shown in Figures 3.1 and 3.2, respectively. The Freundlich equation ( $q = k C^n$ ) was also used to fit the data, and the empirical constants  $k$  and  $n$  were evaluated by plotting  $\log q$  versus  $\log C$ . The values of  $Q$ ,  $b$ ,  $k$ , and  $n$  are given in Table 3.2, together with the linear regression correlation coefficients. The values of R-squared indicate that except 4-CP for high concentration range, the Langmuir equation fitted the equilibrium data much better than the Freundlich equation. This suggests a monolayer coverage of the accessible sites on the surface of the carbon. Except for PCP, the Freundlich equation better describes the equilibrium data in the high concentration range than in the low concentration range. The adsorption constants are concentration-dependent, because there are significant differences in the magnitudes of the constants between the two

concentration ranges. The higher concentration range has a larger  $Q$  and smaller  $b$ ,  $k$  and  $n$ . Noteworthy also is the fact that the Langmuir adsorptive capacities ( $Q$ ) increase from pentachlorophenol to trichlorophenols and do not change significantly from trichlorophenols to monochlorophenols. For molecular species, the more chlorinated a chlorophenol, the less soluble in water or more hydrophobic, and then the more adsorptive the compound. A comparison of the pKa values of the compounds reveals that at pH 7 the percentage of neutral molecules in all species increases from pentachlorophenol to monochlorophenols. The dominant species is the ionized form for pentachlorophenol and the molecular form for monochlorophenols, respectively. The adsorptive capacity for the neutral molecules is larger than that for the ionized forms. It is the combination of two factors, chlorination level and dissociation extent, that results in such a change of the adsorptive capacities for chlorophenols. In addition, from the comparisons of adsorption constants between 2,4,5-TCP and 2,4,6-TCP, 2,4-DCP and 3,4-DCP, and 4-CP and 2-CP, it can be deduced that the position of chlorine on the phenyl ring has no influence on the adsorption of chlorophenols.

***Isotherms of 2,4,5-TCP at Various pH Values.*** Isotherms for adsorption of 2,4,5-TCP at pH values of  $4.15 \pm 0.2$ ,  $5.22 \pm 0.1$ ,  $6.58 \pm 0.01$ ,  $8.17 \pm 0.2$ ,  $9.3 \pm 0.2$ ,  $10.25 \pm 0.1$  were determined. Representative isotherms are presented in Figure 3.3. The solid lines shown in Figure 3.3 represent the Langmuir plots of best fit. There are only slight differences between the isotherms for pH  $4.15 \pm 0.2$  and pH  $5.22 \pm 0.1$ , but significant differences exist for other pH values. Similar results have been observed by Snoeyink et al. (1969).

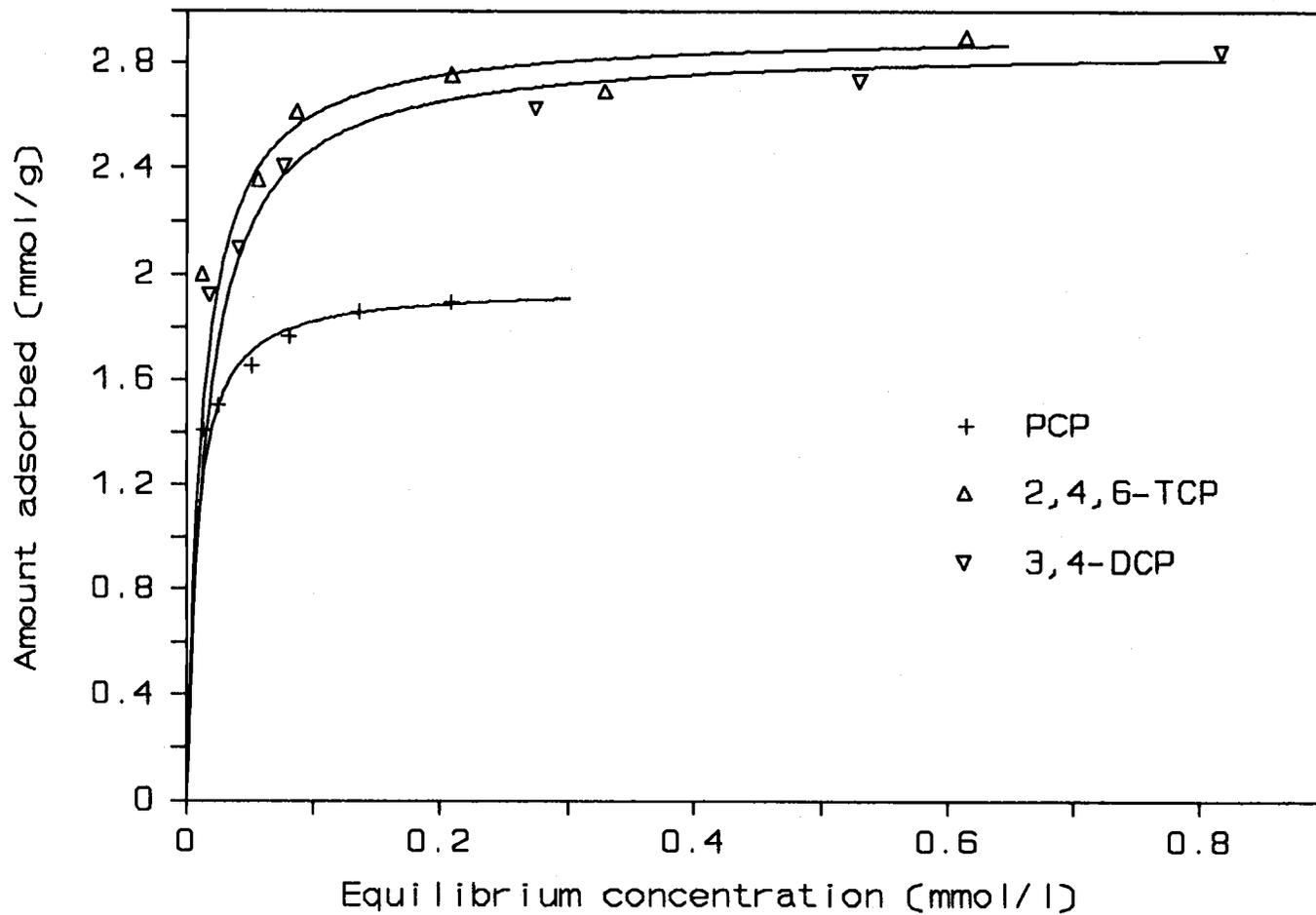


Figure 3.1 Langmuir isotherms for adsorption of PCP, 2,4,6-TCP and 3,4-DCP (higher concentration range)

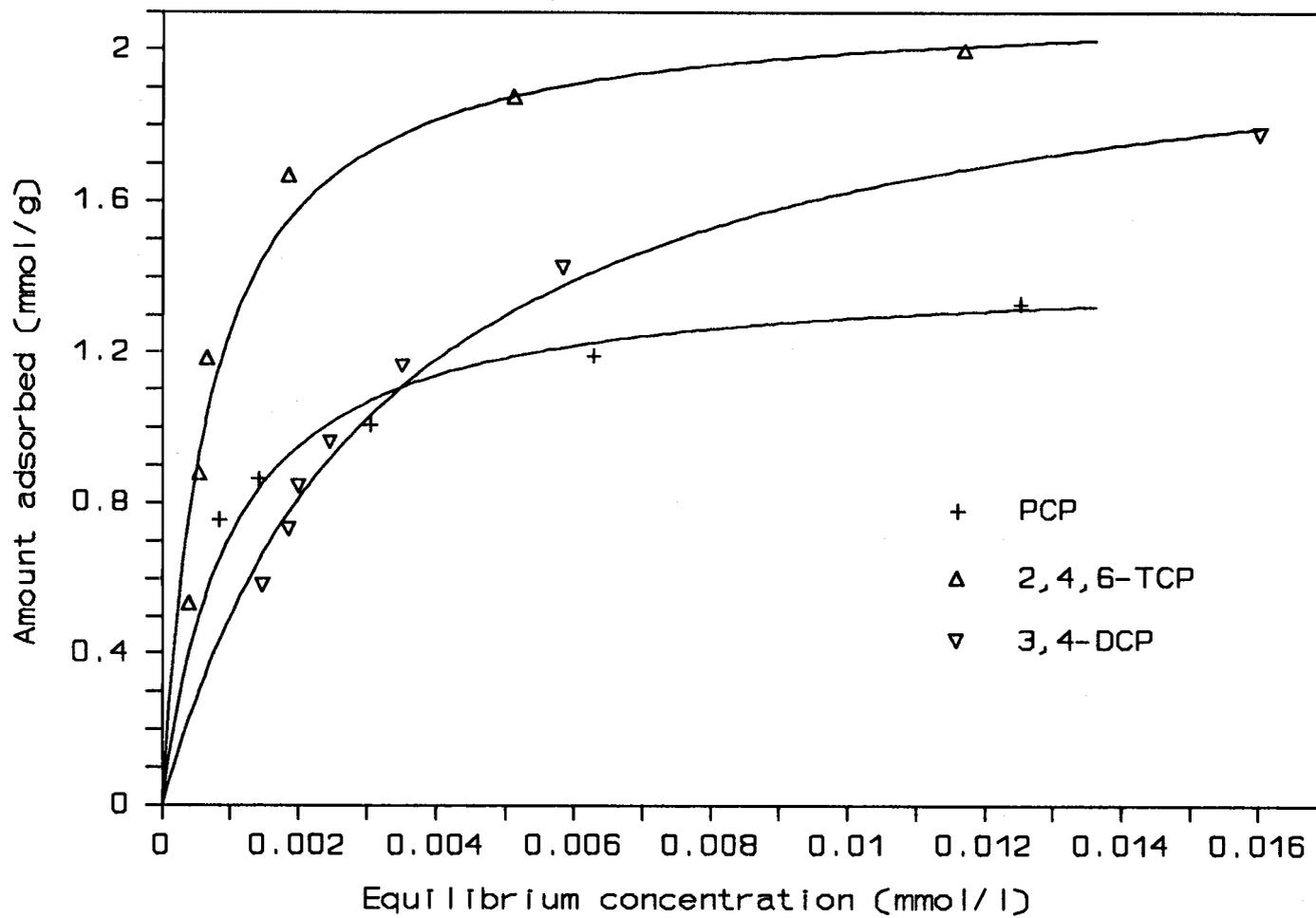


Figure 3.2 Langmuir isotherms for adsorption of PCP, 2,4,6-TCP and 3,4-DCP (lower concentration range)

**Table 3.2 Adsorption Constants for Chlorophenols at pH 7**

| Adsorbate        | Concentration Range<br>10 <sup>-3</sup> mmol/l | Langmuir    |             |                | Freundlich |       |                |
|------------------|--|-------------|-------------|----------------|------------|-------|----------------|
|                  |  | Q<br>mmol/g | b<br>l/mmol | R <sup>2</sup> | K          | n     | R <sup>2</sup> |
| PCP              | 0.843-12.53                                    | 1.419       | 1012.3      | 0.998          | 3.397      | 0.210 | 0.996          |
|                  | 13.2-208.4                                     | 1.954       | 135.6       | 1.000          | 2.308      | 0.114 | 0.987          |
| 2,3,4,6-<br>TeCP | 0.317-5.55                                     | 1.473       | 2874.2      | 0.998          | 3.956      | 0.195 | 0.956          |
|                  | 5.55-492.9                                     | 2.211       | 91.69       | 0.998          | 2.360      | 0.098 | 0.983          |
| 2,4,6-<br>TCP    | 0.39-11.70                                     | 2.135       | 1350.5      | 0.997          | 10.27      | 0.328 | 0.769          |
|                  | 11.70-614.4                                    | 2.920       | 82.35       | 0.999          | 3.090      | 0.092 | 0.928          |
| 2,4,5-<br>TCP    | 0.157-10.33                                    | 1.943       | 1979.9      | 0.999          | 8.999      | 0.304 | 0.911          |
|                  | 2.60-171.2                                     | 2.628       | 250.3       | 0.999          | 3.176      | 0.116 | 0.997          |
| 2,4-DCP          | 0.712-15.52                                    | 2.014       | 1007.9      | 0.998          | 5.583      | 0.243 | 0.866          |
|                  | 15.83-960.7                                    | 2.911       | 43.85       | 0.998          | 2.896      | 0.090 | 0.980          |
| 3,4-DCP          | 1.47-16.01                                     | 2.166       | 299.4       | 0.995          | 12.51      | 0.442 | 0.900          |
|                  | 17.3-816.4                                     | 2.867       | 62.89       | 0.999          | 2.949      | 0.100 | 0.964          |
| 4-CP             | 2.06-23.42                                     | 1.810       | 300.8       | 0.997          | 5.038      | 0.297 | 0.992          |
|                  | 20.15-781.9                                    | 3.090       | 17.04       | 0.988          | 3.087      | 0.208 | 0.993          |
| 2-CP             | 1.90-21.86                                     | 1.939       | 504.3       | 0.994          | 3.708      | 0.190 | 0.978          |
|                  | 21.86-791.3                                    | 3.132       | 31.85       | 0.998          | 3.208      | 0.145 | 0.990          |

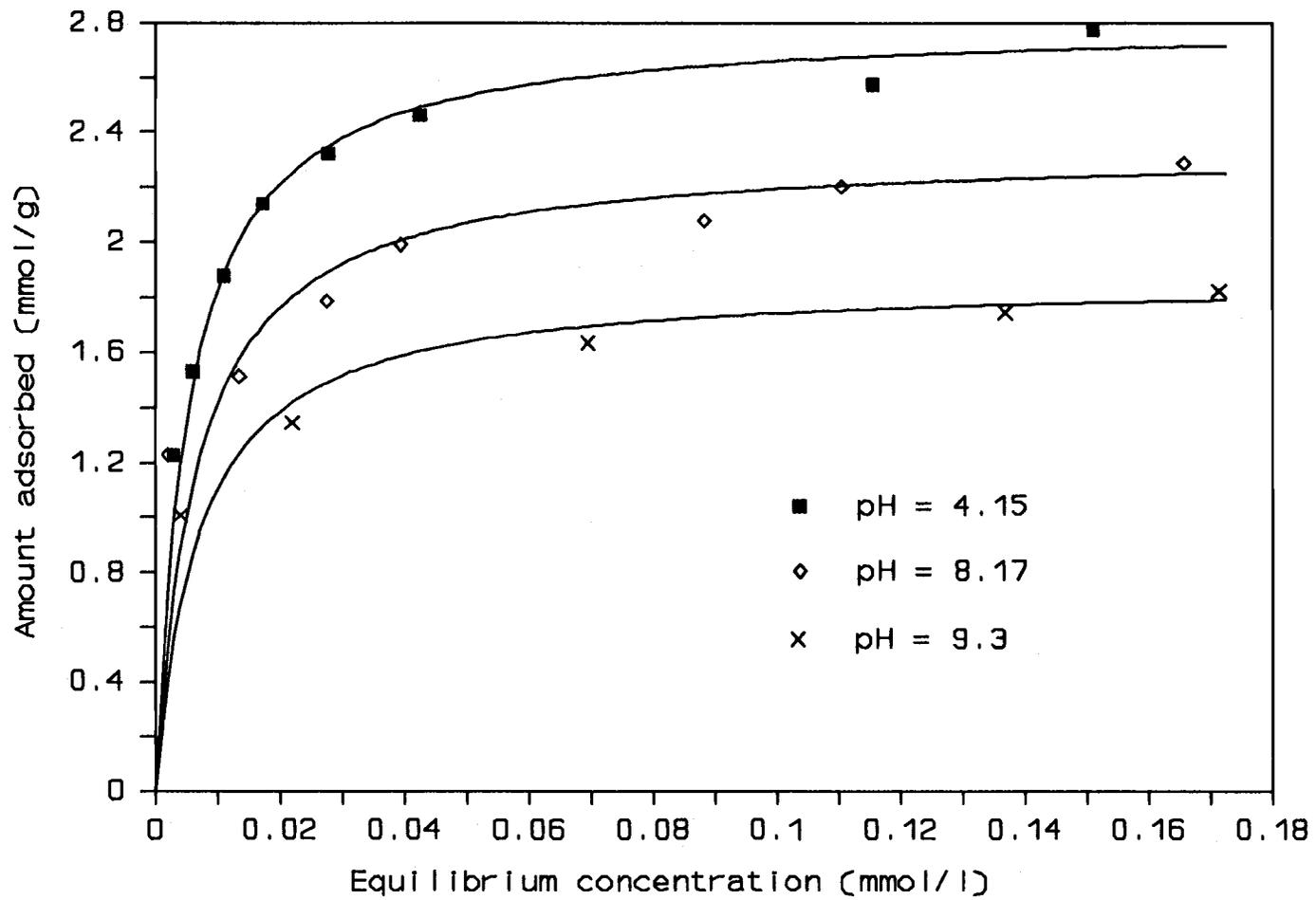


Figure 3.3 Langmuir isotherms for adsorption of 2,4,5-TCP at different pH

Langmuir constants  $Q$  and  $b$  for 2,4,5-TCP at different pH values were determined by regressing the isotherm data using the linearized form of the Langmuir equation. To minimize the effect of concentration range on the magnitude of the constants, only data within close concentration range for various pH values (except pH  $10.25 \pm 0.1$ ) were used. A summary of Langmuir capacity,  $Q$ , and constant,  $b$ , at various pH values, plus the concentration range within which the data were obtained, are given in Table 3.3.

Several observations are evident from Table 3.3. The magnitude of  $b$  is fairly constant among the various pH values with close concentration ranges. However, it decreases significantly for pH  $10.25 \pm 0.1$ , which can be attributed to the much higher concentration range. Decreasing pH value below the compound's pKa (6.94) appears to have no subsequent influence on the adsorptive capacity of 2,4,5-TCP. But a linear decrease in the adsorptive capacity of the compound occurs at pH values greater than its pKa.

**Table 3.3 Effect of pH on Langmuir Constants for 2,4,5-TCP**

| PH    | Q(mmol/g) | b(l/mmol) | Concentration Range (mmol/l) |
|-------|-----------|-----------|------------------------------|
| 4.15  | 2.798     | 189.0     | 0.00293-0.151                |
| 5.22  | 2.846     | 216.1     | 0.00227-0.141                |
| 6.58  | 2.743     | 188.9     | 0.00200-0.128                |
| 8.17  | 2.334     | 154.9     | 0.00185-0.166                |
| 9.30  | 1.861     | 147.0     | 0.00387-0.171                |
| 10.25 | 1.643     | 50.35     | 0.0295-0.249                 |

**Surface Complexation Model.** For the purposes of simplicity, activated carbon surface functional groups can be divided into two generalized types (Jankowska et al., 1991; Muller et al., 1980): acidic groups which may undergo neutralization by bases and basic groups which may be neutralized by acids. Carboxyl, phenolic, quinonoid, and normal lactone are the principal types of acidic surface functional groups, while usually structures corresponding to chromene or pyrone-like structures, are attributed to the basic group. The surface ionization reaction are therefore expressed by



where  $\equiv AH$  and  $\equiv A^-$  represent neutral and negatively charged surface acidic groups,  $\equiv BH^+$  and  $\equiv B$  represent positively charged and neutral basic groups,  $K_a^{intr}$  and  $K_b^{intr}$  are intrinsic equilibrium constants, and  $H_s^+$  denotes a proton at the carbon surface. The mass law equations corresponding to reactions 3-1 and 3-2 are

$$K_a^{intr} = \frac{[\equiv A^-] [H^+]_s}{[\equiv AH]} \quad (3-3)$$

$$K_b^{intr} = \frac{[\equiv B] [H^+]_s}{[\equiv BH^+]} \quad (3-4)$$

The concentration of protons at some location,  $i$ , in the electrical double layer is related to the bulk concentration by the Boltzmann distribution (Davis et al., 1978; Muller et al., 1980), e. g.,

$$[H^+]_i = [H^+] \exp\left(\frac{-F\Psi}{RT}\right) \quad (3-5)$$

where  $\Psi$  is the surface potential,  $F$  is the Faraday's constant,  $R$  is the gas constant, and  $T$  is the absolute temperature.

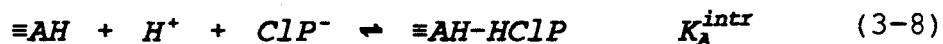
Hence

$$K_a^{intr} = \frac{[\equiv A^-] [H^+] \exp(-F\Psi/RT)}{[\equiv AH]} \quad (3-6)$$

and

$$K_b^{intr} = \frac{[\equiv B] [H^+] \exp(-F\Psi/RT)}{[\equiv BH^+]} \quad (3-7)$$

In the presence of chlorophenols, the following surface complexation reactions can be proposed:



where HCIP and CIP<sup>-</sup> represent molecular and ionized forms of chlorophenol,  $K_A^{intr}$  and  $K_B^{intr}$  represent intrinsic equilibrium surface complexation constants, and  $\equiv\text{AH-HCIP}$  and  $\equiv\text{BH-CIP}$  are surface complexes.

The concentrations of CIP<sup>-</sup> in the electrical double layer are expressed in terms of the Boltzmann distribution, e. g.,

$$[\text{CIP}^-]_i = [\text{CIP}^-] \exp(F\psi/RT) \quad (3-10)$$

Thus, the mass law equations corresponding to reactions 8 and 9 are

$$K_A^{intr} = \frac{[\equiv\text{AH-HCIP}]}{[\equiv\text{AH}] [\text{H}^+] [\text{CIP}^-]} \quad (3-11)$$

$$K_B^{intr} = \frac{[\equiv\text{BH-CIP}]}{[\equiv\text{BH}^+] [\text{CIP}^-] \exp(F\psi/RT)} \quad (3-12)$$

The formation of the surface complexes,  $\equiv\text{AH-HCIP}$  and  $\equiv\text{BH-CIP}$  readjusts the acid-base equilibrium and affects the surface charge. The formation of  $\equiv\text{BH-CIP}$  serves to directly decrease (make more negative) the surface charge and hence the surface potential. The net surface charge density, in coulombs per square meter, is given by

$$\sigma = \frac{F}{AS} ([\equiv\text{BH}^+] - [\equiv\text{A}^-]) \quad (3-13)$$

where A is the specific surface area (m<sup>2</sup>/g) and S the solid (carbon) concentration (g/l).

To specify the influence of the excess surface charge density on the formation of

surface complexes, we require an estimate of the surface potential. According to the Gouy-Chapman theory (for a symmetrical electrolyte with valence  $Z$ ), the surface charge density  $\sigma$  is related to the surface potential  $\Psi$  (in volts) by

$$\sigma = \sqrt{8\epsilon RTI} \sinh \frac{ZF\Psi}{2RT} \quad (3-14)$$

where  $\epsilon$  is the bulk permittivity of water and  $I$  the ionic strength.

Table 3.4 summarizes the surface complexation and aqueous reactions and corresponding equilibrium constants for activated carbon/2,4,5-TCP system. The two surface complexation constants,  $K_A^{intr}$  and  $K_B^{intr}$ , and total concentrations of acidic and basic groups can be extracted from adsorption data via the nonlinear regression program FITEQL (Westall, 1982). These constants and concentrations can in turn be used to simulate the adsorption data. The two properties of the electrical double layer, specific surface area and interface capacitance are assigned, respectively, 941 m<sup>2</sup>/g (after Huang and Ostovic, 1978) and 1.2 F/m<sup>2</sup> (Westall, 1982; Davis et al., 1978).

The optimal surface complexation constants for 2,4,5-TCP, 2,4-DCP and 4-CP are given in Table 3.5, together with overall variances (SOS/DF), which are the main indicator of the goodness of fit in the output from FITEQL. Westall (1982) notes that values of variance between 0.1 and 20 indicate a reasonably good fit. The three values of variances are all in close proximity to 1, indicating that the proposed model is very successful in fitting the adsorption data (Westall, 1982; Dzombak and Morel, 1990).

**Table 3.4 Surface Complexation and Aqueous Reactions in Activated Carbon/2,4,5-Trichlorophenol System**

|  |                                    |
|--|------------------------------------|
| Surface complexation reactions             | log K <sup>intr</sup>              |
| $\equiv A^- + H^+ = \equiv AH$             | 7.78 <sup>a</sup>                  |
| $\equiv B + H^+ = \equiv BH^+$             | 5.70 <sup>a</sup>                  |
| $\equiv AH + H^+ + ClP^- = \equiv AH-HClP$ | log K <sub>A</sub> <sup>intr</sup> |
| $\equiv BH^+ + ClP^- = \equiv BH-ClP$      | log K <sub>B</sub> <sup>intr</sup> |
| Aqueous reactions                          | log K                              |
| $HClP = H^+ + ClP^-$                       | -6.94                              |
| $H_2O = H^+ + OH^-$                        | -14.0                              |

<sup>a</sup> after Huang and Ostovic (1978)

**Table 3.5 Best Estimates for Chlorophenol/Carbon Surface Complexation Constants**

| Adsorbate | log K <sub>A</sub> <sup>intr</sup> | log K <sub>B</sub> <sup>intr</sup> | SOS/DF |
|-----------|------------------------------------|------------------------------------|--------|
| 2,4,5-TCP | 21.48                              | 16.65                              | 2.28   |
| 2,4-DCP   | 25.19                              | 13.05                              | 0.38   |
| 4-CP      | 27.41                              | 16.68                              | 1.41   |

Equilibrium measurements were made for adsorption of 2,4,5-TCP from solutions at pH range of 4 to 10 with phosphate (Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>) concentrations of zero

and 5 mM. The solutions with or without phosphate contained the same initial 2,4,5-TCP concentrations of 1.525 mmol/l and the same carbon dosages were used. This implies that for the two systems with and without phosphate, the equilibrium concentrations are essentially identical if the amounts adsorbed are very close to each other, and therefore, the equilibrium data are highly comparable because the influence of concentration range on adsorption is eliminated. The data shown in Figure 3.4 indicate that no phosphate effect can be observed in whole pH range studied for any of these systems. It seems to be a reasonable explanation that phosphate is a too weak adsorbate to compete with chlorophenol. Some investigators have reported similar results for systems with salts of low concentration. Zogorski et al. (1976) noted that 0.05 M phosphate buffer exhibited no discernible influence on the rate of adsorption of 2,4-dichlorophenol and 2,4-dinitrophenol, whether in an undissociated or dissociated form. Snoeyink et al. (1969) studied the effect of NaCl on the adsorption of phenol and p-nitrophenol (PNP) and found no distinguishable differences in capacity for NaCl concentrations of zero and 0.01 M at pH 2.0 and pH 10.0. However, they have observed a significant increase in capacity at lower surface coverage for the PNP system with 1.0 M NaCl at pH 10.0. This has been explained by the formation of ion pairing of the cation with the PNP anion, which would have the effect of increasing adsorptive capacity because the ion pair would behave more like the acid form of the PNP, or the reduction of repulsive forces between the adsorbed anions, which allows more molecules on the surface at lower solution concentrations.

The curve in Figure 3.4 represents the optimum fit of the surface complexation model to both sets of 2,4,5-TCP adsorption data obtained from the solutions with and

without phosphate. Figure 3.5 shows 2,4-DCP and 4-CP adsorption data as a function of pH (without phosphate) and the optimum surface complexation model fits. Similar to the relationship between adsorptive capacity and equilibrium pH for 2,4,5-TCP (Table 3.3), no subsequent influence on adsorption is observed for decreasing pH value below the compounds' pKa values, while marked decrease in amounts adsorbed occurs as pH increases above the pKa values. The two figures demonstrate that the proposed surface complexation model can describe very well the adsorption data of chlorophenols on activated carbon.

Figure 3.6 gives surface speciation of activated carbon in 2,4,5-TCP solution calculated as a function of pH with the surface complexation model. Total concentrations of basic and acidic groups derived from adsorption data with the optimization procedure are respectively 0.926 and 0.443 mmol/l (equivalent to 1.853 and 0.886 mmol/g), indicating that basic sites are about twice as many as acidic sites. Site saturation is essentially attained below pH 9.21 for basic groups. Surface complex of basic groups ( $\equiv\text{BH-CIP}$ ) is relatively stable as pH increases. However, surface complex of acidic groups ( $\equiv\text{AH-HCIP}$ ) is very susceptible to the change of pH and site saturation occurs only at pH 4.19. These imply that the electrostatic interaction between positively charged basic groups ( $\equiv\text{BH}^+$ ) and negatively charged chlorophenolate ion ( $\text{CIP}^-$ ), leading to the formation of the complex of basic groups, is more important and stronger than the interaction between neutral acidic groups ( $\equiv\text{AH}$ ) and neutral molecular chlorophenol ( $\text{HCIP}$ ).

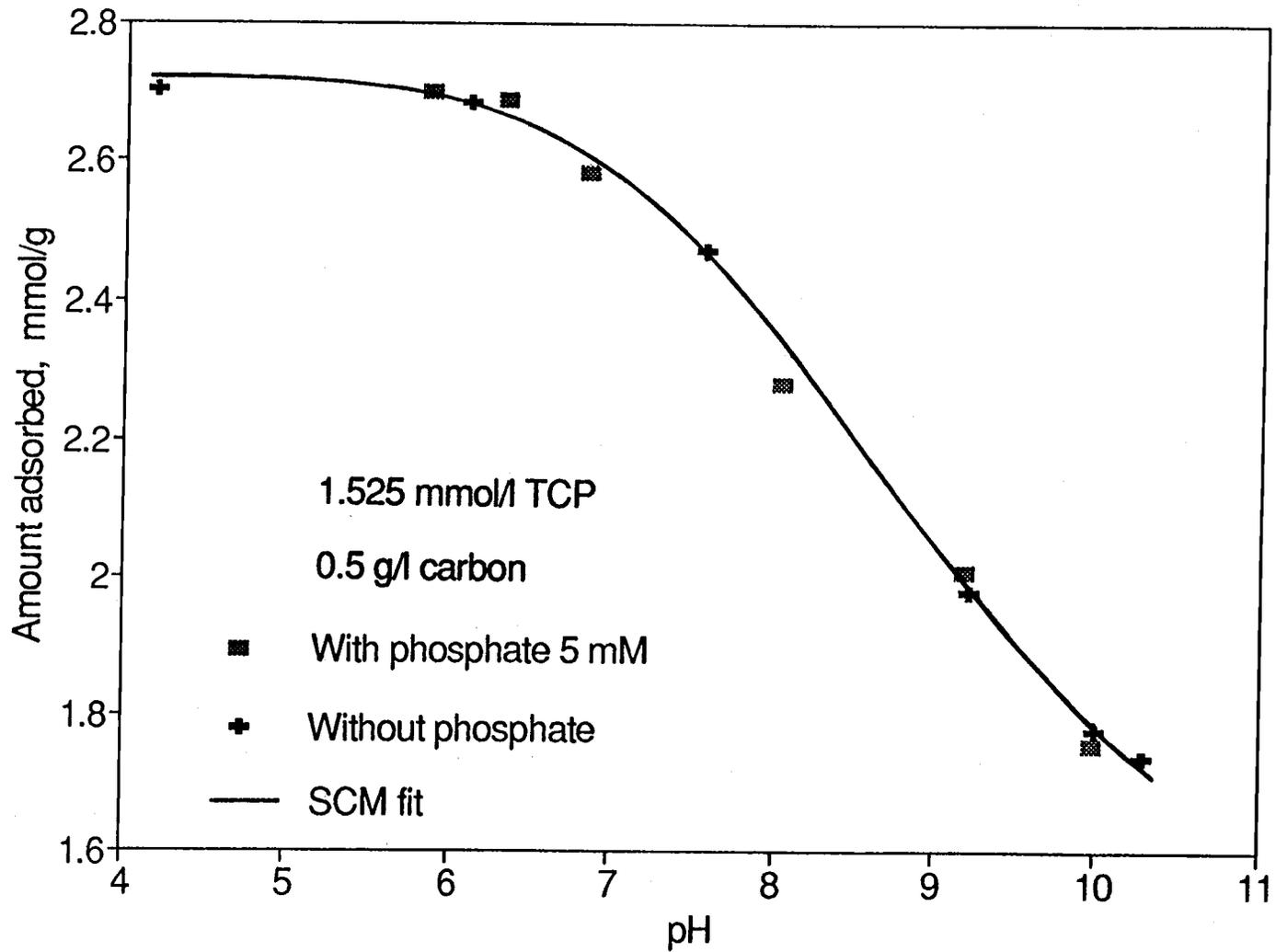


Figure 3.4 Effect of phosphate on adsorption of 2,4,5-TCP as a function of pH and optimum surface complexation model fit

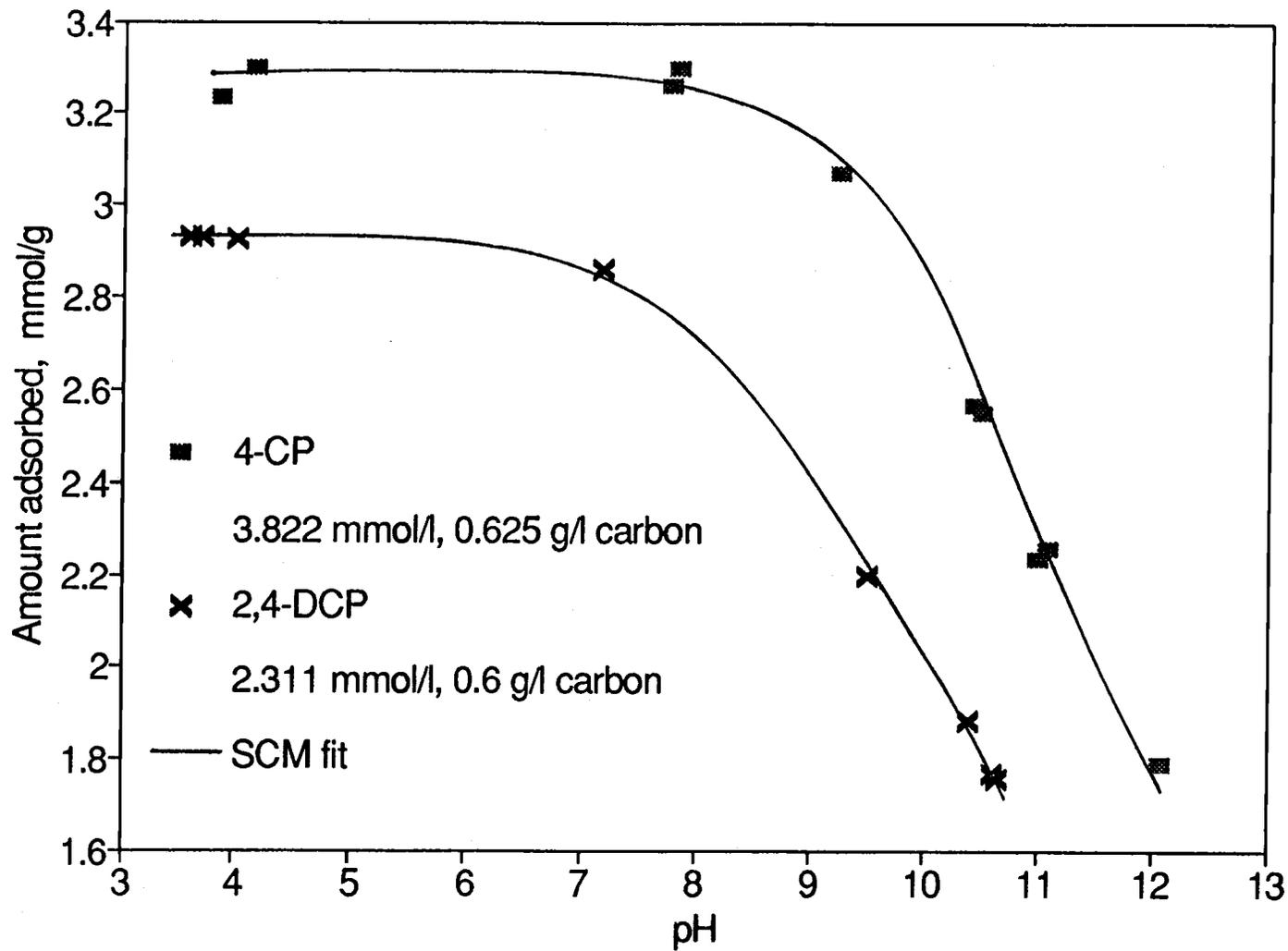


Figure 3.5 Amounts adsorbed of 4-CP and 2,4-DCP as a function of pH and optimum surface complexation model fits

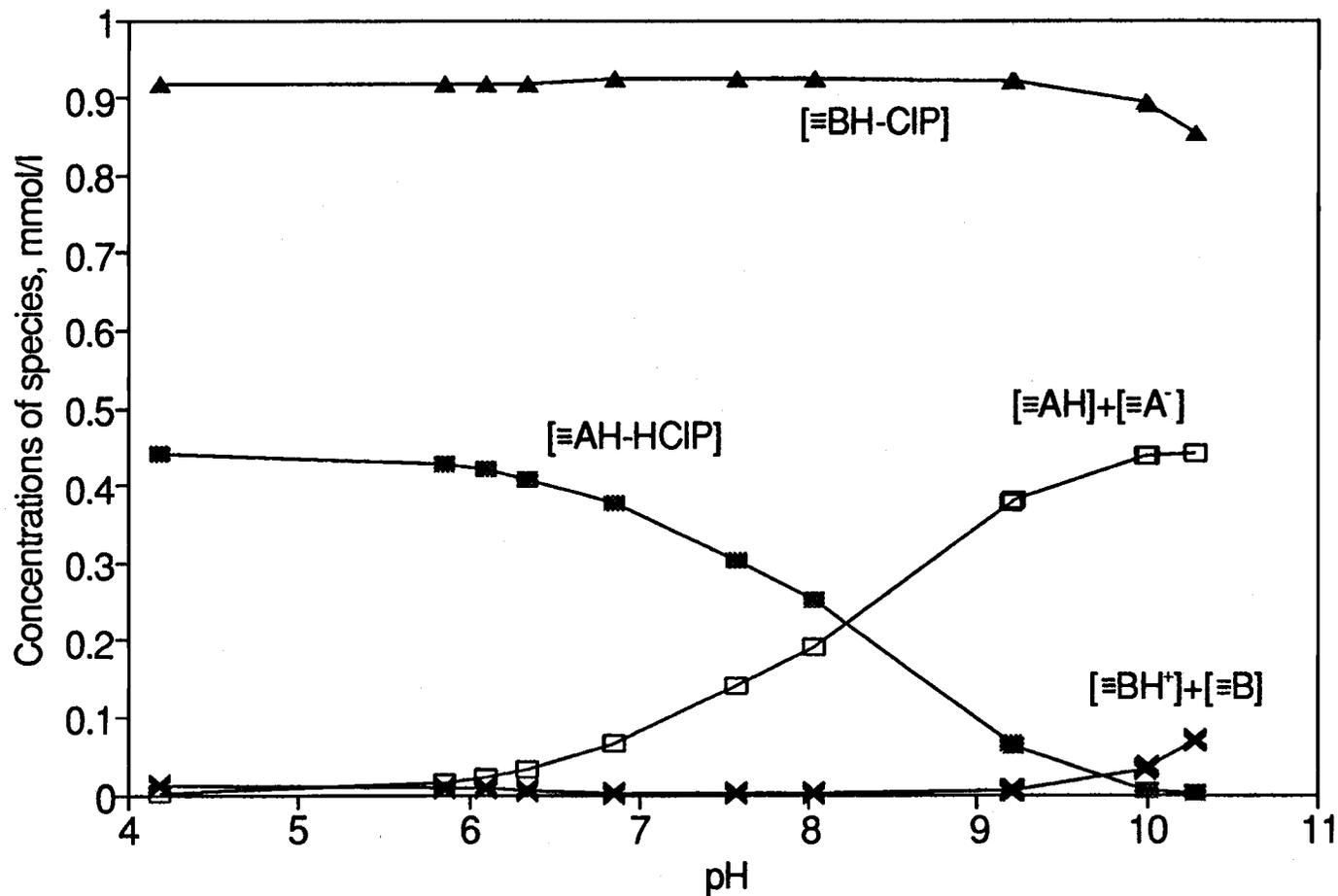


Figure 3.6 Calculated surface speciation of activated carbon (0.5 g/l) in the presence of 1.525 mmol/l 2,4,5-TCP (  $[\equiv\text{BH-CIP}] + [\equiv\text{BH}^+] + [\equiv\text{B}] = 0.926 \text{ mmol/l}$ ,  $[\equiv\text{AH-HCIP}] + [\equiv\text{AH}] + [\equiv\text{A}^-] = 0.443 \text{ mmol/l}$ )

Some investigators have given an insight into the mechanisms of adsorption of phenolic compounds on activated carbon. It is suggested that the chlorophenols are adsorbed with the phenyl ring parallel to the surface of the adsorbent and interaction is between the  $\pi$ -electron system of the phenyl ring and the aromatic surface structure (Coughlin and Ezra, 1968) of the carbon. In addition, Mattson et al.(1970) substantiate the presence of significant numbers of carbonyl and carboxyl functional groups on the surfaces of activated carbon using infrared internal reflectance spectrophotometric techniques. Chlorophenols may be adsorbed at the carbonyl oxygens on the activated carbon surface according to a donor-acceptor complexation mechanism. The carbonyl oxygen acts as the electron donor and the aromatic ring of the solute acts as the electron acceptor. The functional groups containing oxygen, such as phenolic, carbonyl, carboxyl, lactone, and quinone (Boehm, 1964) may also offer adsorptive sites for hydrogen bonding of the phenolic protons, particularly at low pH levels where the chlorophenols are predominantly in molecular form. From this study, these likely mechanisms seem applicable only to the interaction between neutral chlorophenol molecules and neutral acidic sites. The electrostatic bonding of chlorophenolate ions with positively charged basic sites may be more substantial for adsorption of chlorophenols on activated carbon.

***Effect of Dissolved Organic Matter on Adsorption Equilibrium.*** Figure 3.7 shows the effect of background dissolved organic matter (DOM) on adsorption equilibrium of 3,4-DCP. Background solution containing DOM (acetate and its metabolites) was collected from biodegradation reactor and prefiltered through a glass fiber filter prior to use to remove suspended particles. The results indicate that the presence of 5 mg/l (as TOC) of

background DOM reduces the Langmuir adsorptive capacity about 13%. The precise mechanisms responsible for reduction by DOM of target compound adsorption are not readily apparent. DOM may alter such solution properties as solubility and hydrophobicity and, therefore, adsorption characteristics. Direct competition for adsorption sites between target compounds and the adsorbing components of the background DOM is certainly another potential mechanism for reduction of the adsorptive capacity.

*Effect of Temperature on Adsorption Equilibrium.* Equilibrium studies were performed at various temperatures at pH 7.0. The data obtained from these studies are plotted in Figures 3.8 -3.11. There are two patterns for the effect of temperature on the adsorption of chlorophenols on granular activated carbon. For PCP and 2,4,6-TCP, the amount adsorbed, for a given equilibrium concentration is seen to increase with decreasing temperature, and therefore, the adsorption is an exothermic process. Contrary to these results, for 2,4-DCP and 4-CP, an increase in temperature resulted in increased adsorption, and the adsorption reaction is endothermic. The parameters of the Langmuir equation for each isotherm of these four compounds have been computed and are tabulated in Table 3.6.

The change in the heat content of a system in which adsorption occurs, that is, the total amount of heat evolved in the adsorption of a definite quantity of solute on adsorbent, is termed the heat of adsorption,  $\Delta H$ . The differential heats of adsorption for the four chlorophenols have been determined using the values of  $Q$ , computed from the Langmuir equation, corresponding to the selected temperatures and the Van't Hoff-Arrhenius equation in the form (Weber and Morris, 1964):

$$\Delta H = 2.3R \frac{T_1 T_2}{T_2 - T_1} (\log Q_2 - \log Q_1) \quad (3-1)$$

An example computation of adsorption heat for 2,4-DCP is demonstrated here. The logarithms of  $Q$  for the data of 2,4-DCP from Table 3.4 are plotted *versus* the reciprocal of kelvin temperature in Figure 3.12. From this plot the slope,  $-\Delta H/(2.3R)$ , has been taken and  $\Delta H$  has been computed as follows:

$$\Delta H = -2.3 (1.986) (-269.4) = 1233 \text{ cal./mole}$$

The heats of adsorption for the four compounds are also included in Table 3.6.

Temperature effects on adsorption equilibrium generally are not significant, particularly over the range of temperature encountered in water and waste waters. This fact is shown by Figures 3.8 - 3.11 and the values of isotherm parameters in Table 3.6 (except for 2,4,6-TCP). In practical operations, variation of temperature will be small relative to that which has been imposed on the experimental systems. The observed temperature-dependence is undoubtedly the net effect of temperature on the adsorbate-adsorbent bonds, the solvent-adsorbent bonds, the adsorbate-adsorbate interactions, and the solvent-adsorbate interactions. The solvent-adsorbent bond is important because adsorption of a solute molecule probably involves concomitant displacement of solvent molecules from the surface. Snoeyink et al. (1969) reported that the reaction of acid with coconut-shell carbon is endothermic. Grant and King (1990) reported that the adsorption of phenol on Filtrasorb-100 activated carbon is endothermic, an observation that is consistent with the temperature-dependence of 2,4-DCP and 4-CP adsorption, and

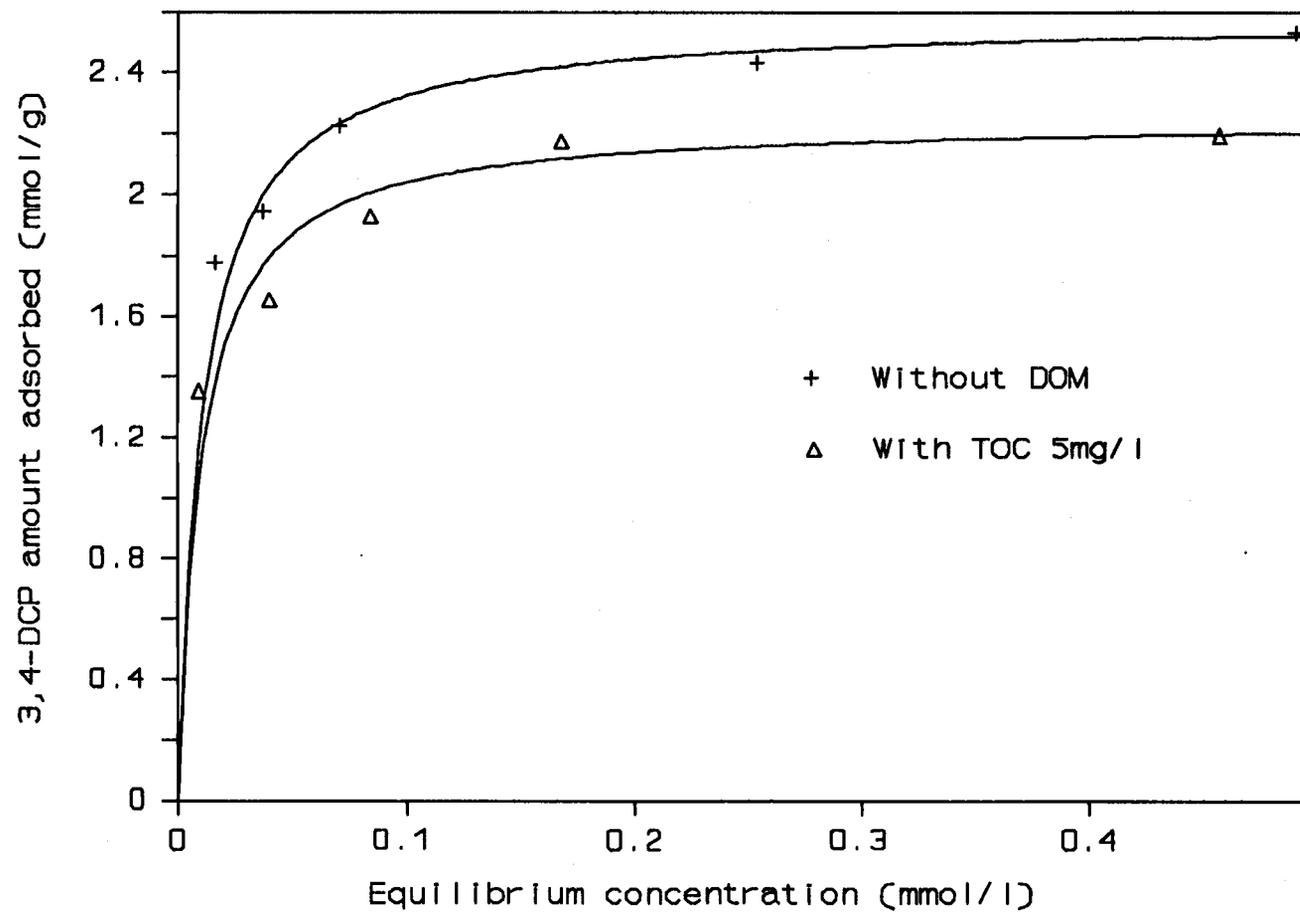


Figure 3.7 Effect of dissolved organic matter on adsorption equilibrium

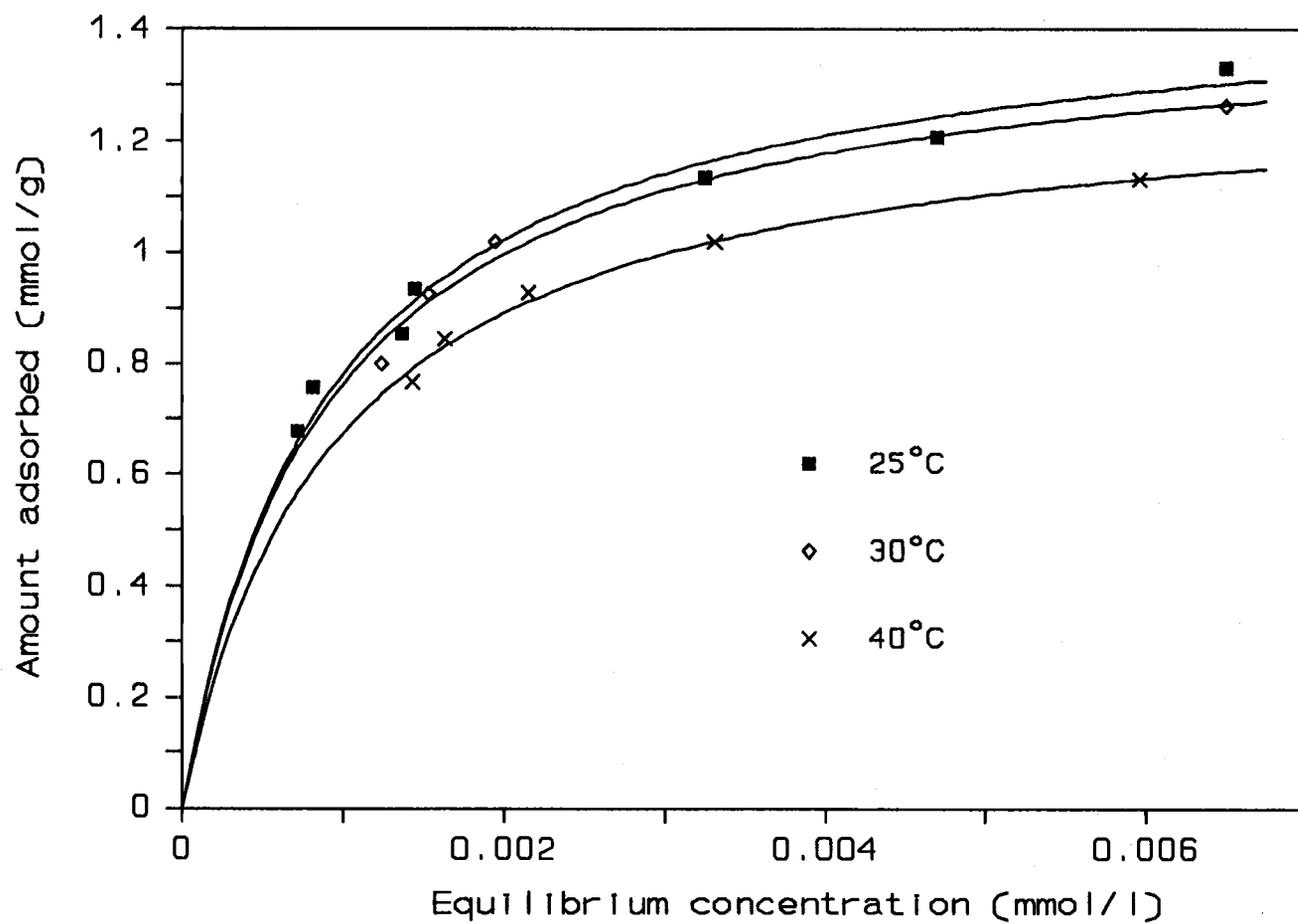


Figure 3.8 Langmuir isotherms for adsorption of PCP at various temperatures

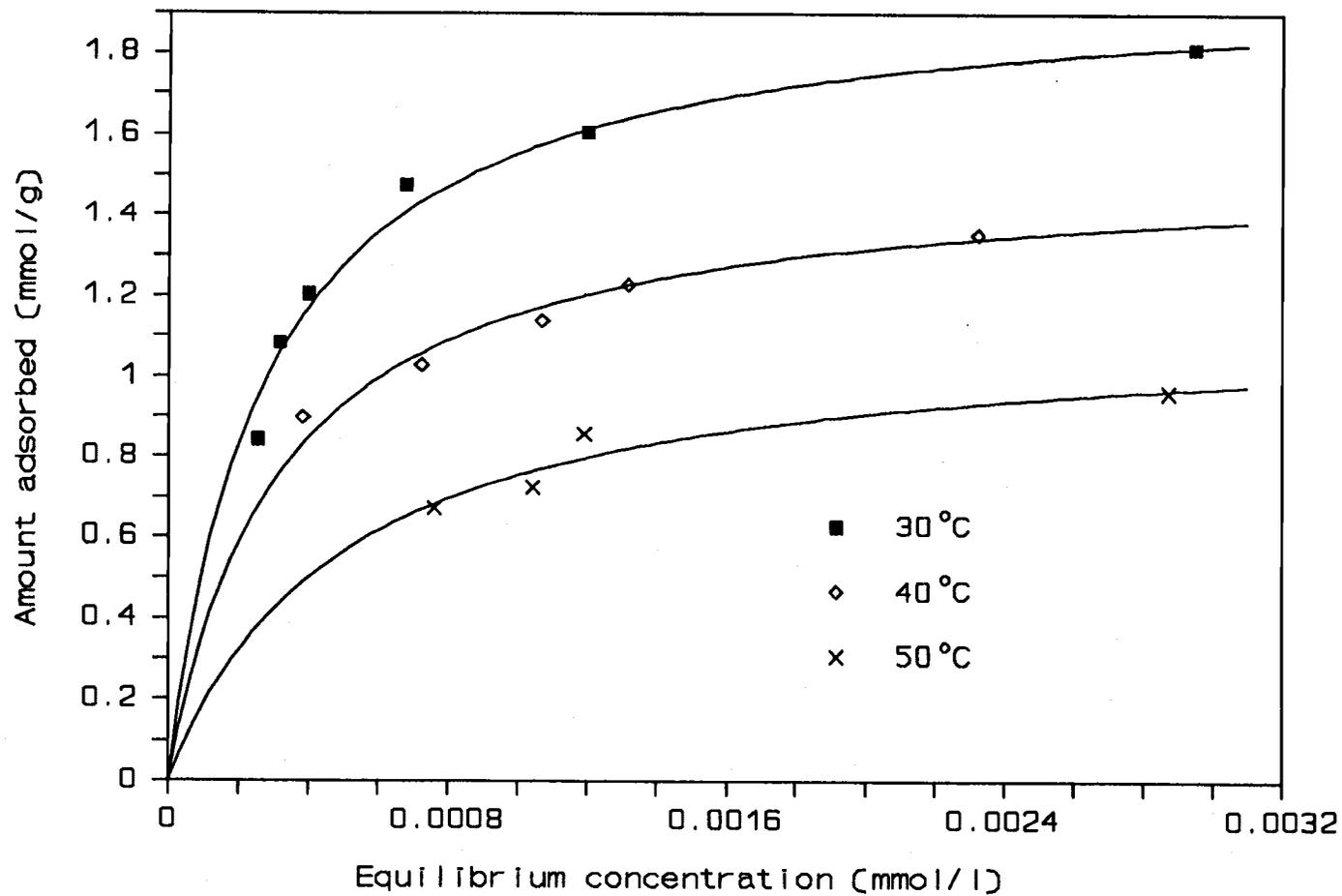


Figure 3.9 Langmuir isotherms for adsorption of 2,4,6-TCP at various temperatures

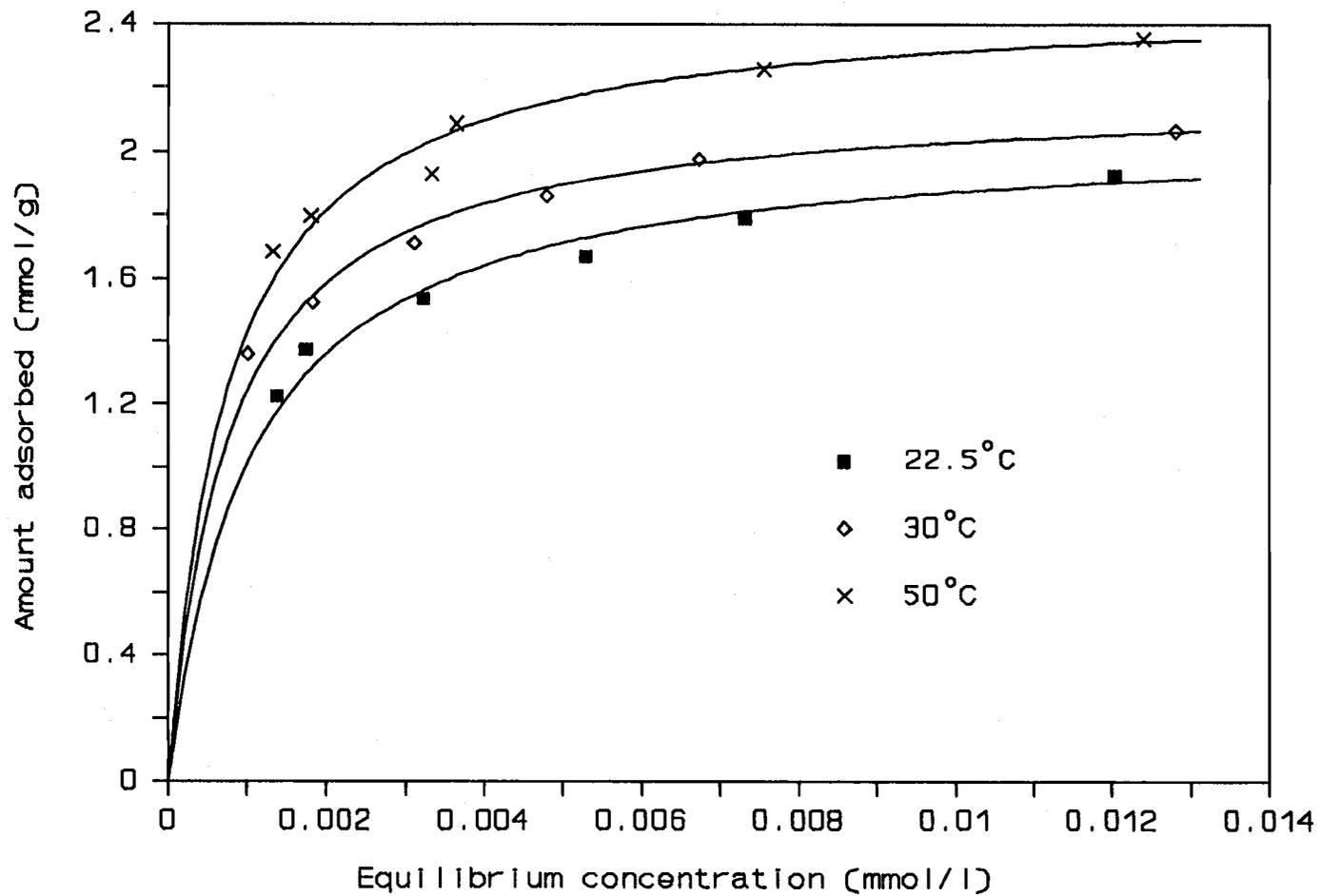


Figure 3.10 Langmuir isotherms for adsorption of 2,4-DCP at various temperatures

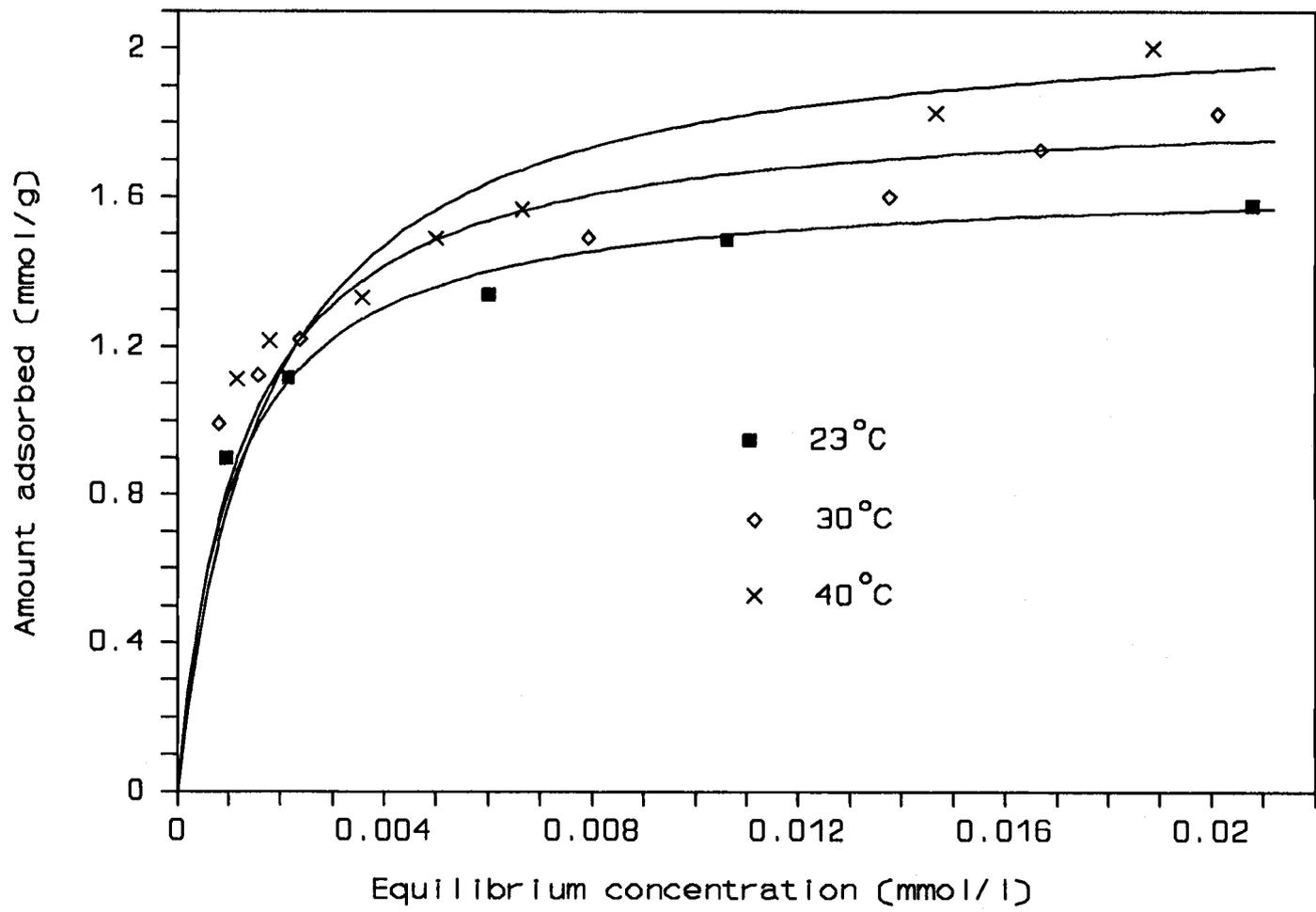


Figure 3.11 Langmuir isotherms for adsorption of 4-CP at various temperatures

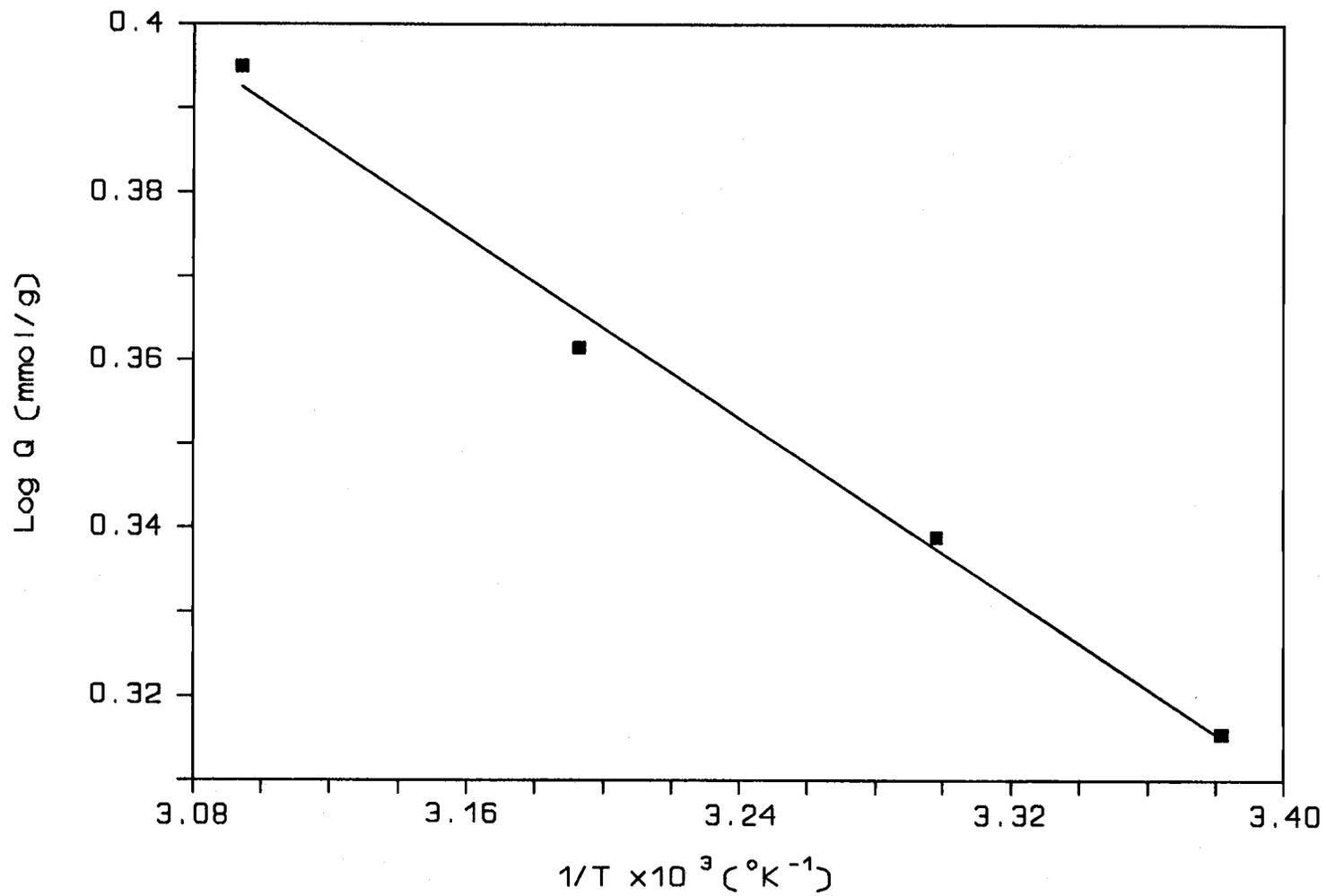


Figure 3.12 Effect of temperature on adsorption of 2,4-DCP

**Table 3.6 Langmuir Parameters for Adsorption of Chlorophenols as a Function of Temperature and Heat of Adsorption**

| Adsorbate | Temperature<br>°C | Q<br>mmol/g | b<br>l/mmol | $\Delta H$<br>cal/mole |
|-----------|-------------------|-------------|-------------|------------------------|
| PCP       | 25                | 1.483       | 1112.9      |                        |
|           | 30                | 1.438       | 1130.3      | -1565                  |
|           | 40                | 1.310       | 1063.8      |                        |
| 2,4,6-TCP | 30                | 1.986       | 3585.4      |                        |
|           | 40                | 1.527       | 3108.6      | -5426                  |
|           | 50                | 1.137       | 1964.4      |                        |
| 2,4-DCP   | 22.5              | 2.067       | 962.0       |                        |
|           | 30                | 2.182       | 1327.8      | 1233                   |
|           | 40                | 2.299       | 1712.8      |                        |
|           | 50                | 2.483       | 1358.7      |                        |
| 4-CP      | 23                | 1.647       | 946.1       |                        |
|           | 30                | 1.856       | 800.0       | 2672                   |
|           | 40                | 2.110       | 574.4       |                        |

regarded this phenomenon as evidence for the occurrence of a chemical reaction. At pH 7.0, predominant species are anionic for PCP and 2,4,6-TCP, and neutral for 2,4-DCP and 4-CP. This might explain the adsorption being exothermic for the former, and endothermic for the latter. However, the total process and realistic mechanism are very

complex, and the effect of temperature on adsorption equilibria is difficult to interpret.

**Reproducibility of Measurements.** Six identical and independent analytical measurements including acetylation, extraction and gas chromatography were performed for a 2,4-DCP solution sample of 0.026 mmol/l. The ratios of area of 2,4-DCP peak to that of internal standard and standard deviations have been calculated and are given in Table 3.7.

**Table 3.7 Reproducibility for Analytical Measurements**

| Ratio of areas | Standard deviation | Coefficient of variation (%) |
|----------------|--------------------|------------------------------|
| 0.04804        |                    |                              |
| 0.04808        |                    |                              |
| 0.04798        | 0.00036            | 0.75                         |
| 0.04802        |                    |                              |
| 0.04800        |                    |                              |
| 0.04891        |                    |                              |

From the small relative standard deviation it can be concluded that the reproducibility of analytical measurements is very good and the error resulting from analytical procedures is minor.

To provide an estimate of experimental error for the isotherm parameters, five isotherms for adsorption of 2,4-DCP have been independently obtained from the bottle

**Table 3.8 Standard Deviations and 95% Confidence Intervals for Langmuir Parameters**

|                              | Q<br>mmol/g       | b<br>l/mmol       |
|------------------------------|-------------------|-------------------|
| Langmuir parameters          | 2.3439            | 1249.3            |
|                              | 2.3564            | 1193.0            |
|                              | 2.3428            | 1132.3            |
|                              | 2.3421            | 1225.4            |
|                              | 2.2473            | 1195.7            |
| Means                        | 2.3265            | 1199.1            |
| Standard deviations          | 0.0447            | 43.9              |
| Coefficient of variation (%) | 2.05              | 3.66              |
| 95% confidence intervals     | 2.2710<br>-2.3820 | 1144.6<br>-1253.6 |

experiments, in which the same stock solution was used and for each isotherm each bottle was dosed with a definite amount of carbon. Table 3.8 shows the standard deviations and 95% confidence intervals for the Langmuir parameters. The errors may result from

experimental procedures, such as pipetting of solution and weighing of carbon, but most of them may be attributed to the heterogeneity of activated carbon.

**Blank Test.** Blank tests have been conducted with PCP, 2,4-DCP and 4-CP of 0.5 mmol/l at 30 and 40°C, and the results are given in Table 3.9. From the table, the ratios of peak areas for chlorophenols and internal standard at 30 and 40°C are very close to those of controls, and thus the effects of biodegradation and volatilization can be neglected.

**Table 3.9 Blank Test Results**

| Adsorbate | Temperature<br>°C | Ratio of Areas |
|-----------|-------------------|----------------|
| PCP       | control           | 0.846          |
|           | 30                | 0.844          |
|           | 40                | 0.868          |
| 2,4-DCP   | control           | 0.150          |
|           | 30                | 0.153          |
|           | 40                | 0.149          |
| 4-CP      | control           | 0.0222         |
|           | 30                | 0.0229         |
|           | 40                | 0.0224         |

## Conclusions

Studies were undertaken of the adsorption of chlorinated phenols from aqueous solution on granular activated carbon. Single-component equilibrium adsorption data on the eight compounds in two concentration ranges at pH 7.0 fit the Langmuir equation better than the Freundlich equation, while the Freundlich equation improves its performance in high concentration range. There are pronounced differences in the magnitudes of the constants between the two concentration ranges, and thus the adsorption constants are concentration-dependent. The adsorptive capacities at pH 7.0 increase from pentachlorophenol to trichlorophenols and are fairly constant from trichlorophenols to monochlorophenols. The position of chlorine on the phenyl ring has no influence on the adsorption of chlorophenols. No effect of phosphate on the adsorption was observed in the pH range of 4 - 10. The presence of background dissolved organic matter could reduce the adsorptive capacity of chlorophenols. Equilibrium studies were performed at various temperatures at pH 7.0. The adsorption process was found to be exothermic for pentachlorophenol and 2,4,6-trichlorophenol, and endothermic for 2,4-dichlorophenol and 4-chlorophenol. Different dissociation extents of these compounds seem to be responsible for such temperature effects.

Equilibrium measurements were also conducted for 2,4,5-trichlorophenol, 2,4-dichlorophenol, and 4-chlorophenol over a wide pH range. No subsequent influence on adsorption is observed for decreasing pH values below the compounds' pKa values, while marked decrease in amounts adsorbed occurs as pH increases above the pKa values. A

surface complexation model has been proposed to describe the effect of pH on adsorption equilibria of chlorophenols on activated carbon. Activated carbon surface functional sites are divided into acidic groups and basic groups which may be neutralized by bases or acids. Molecular and ionized forms of chlorophenols interact, respectively, with these two kinds of surface groups to form two neutral surface complexes, of which the complex of basic groups is more substantial and more stable than that of acidic groups. The simulations of the model are in excellent agreement with the experimental data.

## Chapter 4 ADSORPTION KINETICS OF CHLOROPHENOLS

### Materials and Methods

***Kinetic studies.*** Batch kinetic experiments were conducted by using a 3-liter glass reactor. The solution was stirred with a two-blade stirring rod attached to a motor. The temperature of the adsorbate solution was kept constant at 30°C during the experiment by placing the reactor in a constant temperature chamber. A 5 mM phosphate buffer was included in all experiments. At appropriate intervals, solution samples (2 to 8 ml) were withdrawn for analysis.

### Results and Discussion

***Effect of Stirring Speed on Adsorption Rate.*** Three stirring speeds of approximately 200, 400 and 800 rpm have been tried to see the effect of stirring speed on adsorption rate. Kinetic studies with 2,4,6-trichlorophenol indicated that the rate of adsorption was independent of stirring for a shaft speed greater than 400 rpm, as shown in Figure 4.1. Since too vigorous stirring could cause a severe attrition of carbon, all subsequent kinetic experiments were conducted at a stirring speed of 600 rpm.

***Effect of pH on Adsorption Rate.*** Figure 4.2 shows the effect of solution pH on the observed rate of adsorption of 2,4,5-TCP by granular activated carbon. Because the pKa of 2,4,5-TCP is 6.94, essentially all species are present in the neutral form at pH 3.95 or

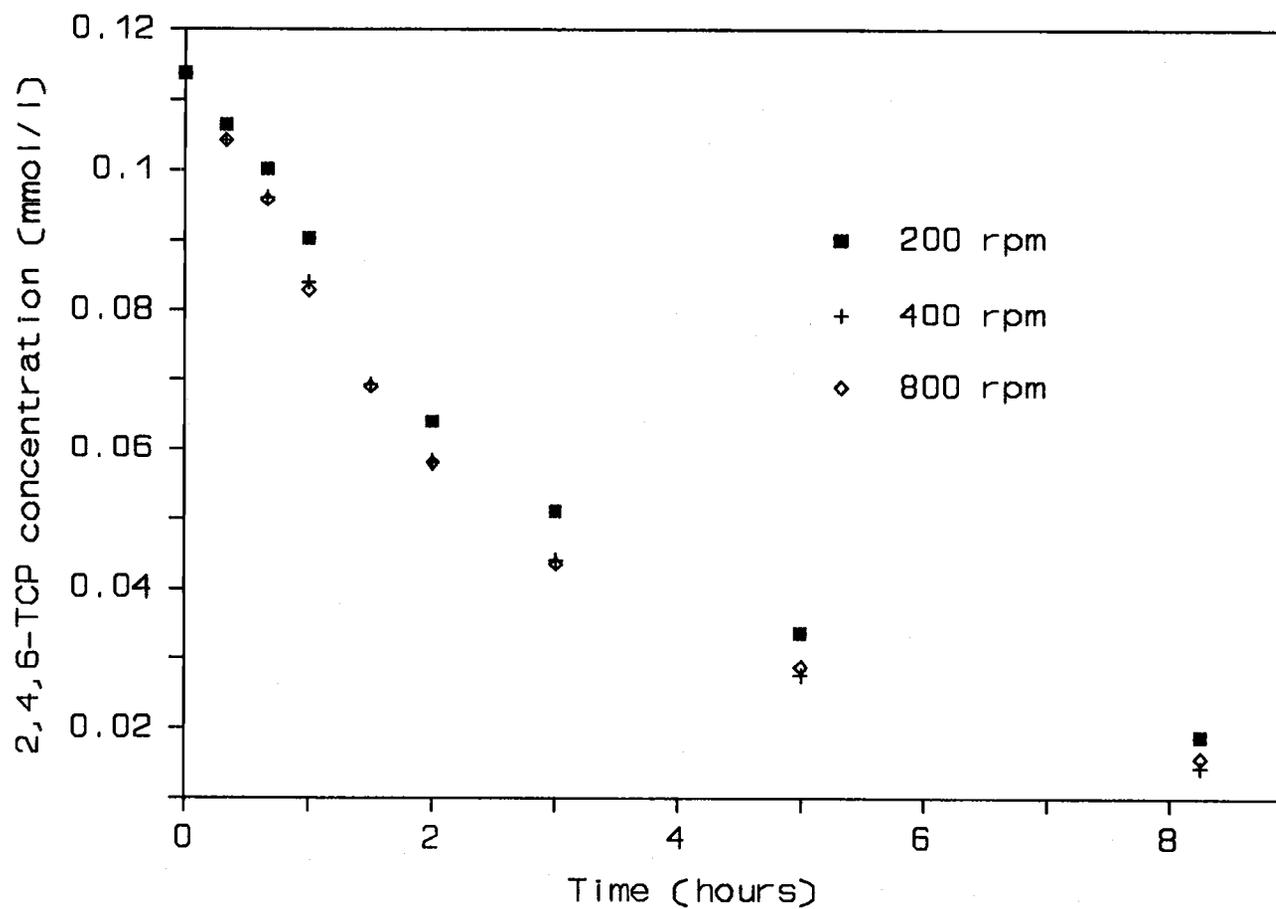


Figure 4.1 Effect of stirring speeds on adsorption rate of 2,4,6-TCP

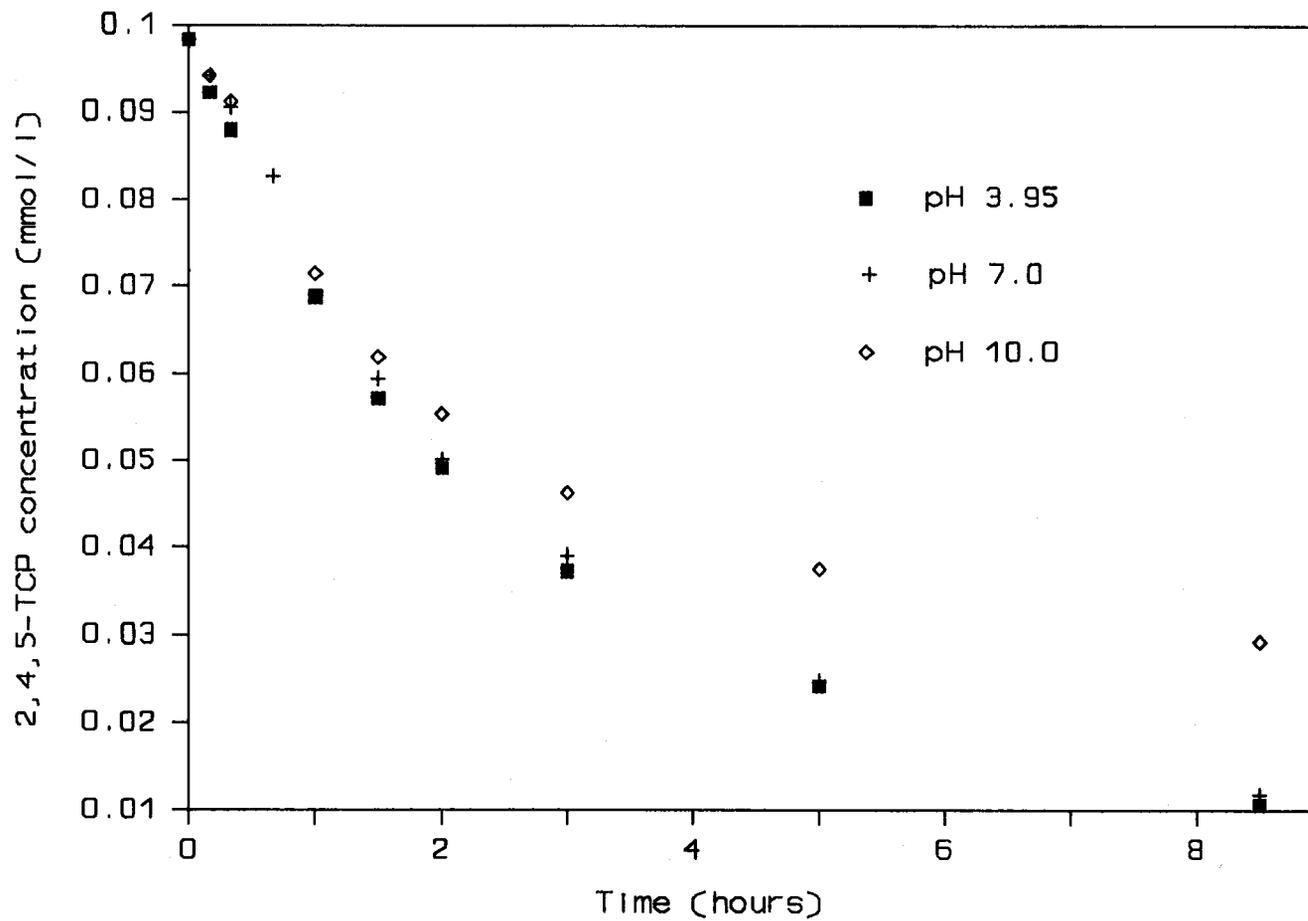
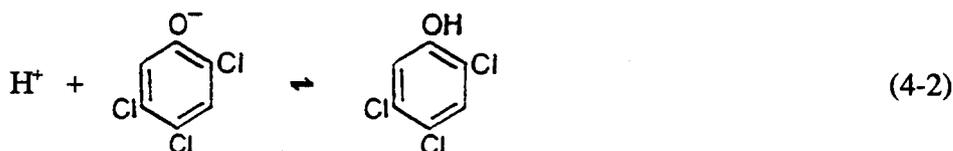


Figure 4.2 Effect of pH on adsorption rate of 2,4,5-TCP

in the ionized form at pH 10.0, both forms being approximately equal at pH 7.0. The rate of adsorption of 2,4,5-TCP at pH 10.0 is slower than that at pH 3.95 and 7.0, and there is only a slight difference between the adsorption rates for pH 3.95 and 7.0. Similar kinetic behavior was reported for the adsorption of alkylbenzenesulfonic acids and phenols (Weber and Morris, 1963; Zogorski et al., 1976). The uncharged molecular species of 2,4,5-TCP may be adsorbed by the carbon, which bears net negative charges, more rapidly than the negatively charged ionic species. At higher pH, both the repulsive forces between the adsorbate anion and the carbon surface, and between the adsorbed species themselves, would tend to reduce the adsorption rate. Thus, the adsorption rate of chlorophenols in acidic solutions is much higher than that in basic solutions.

That the adsorption rates for pH 3.95 and 7.0 are essentially identical may be explained by the existence of the following chemical equilibria in the solution:



Because of the rapidity of acid-base reactions, these two equilibria can be reached nearly instantaneously. Even though the molecular species of 2,4,5-TCP at pH 7.0 accounts for only 47%, most species adsorbed by GAC can be the molecular 2,4,5-TCP, due to the

proton donation by the phosphate buffer.

**Adsorption Kinetics.** Figures 4.3 and 4.4 shows the typical data from short-term kinetic studies on the adsorption of 2,4-DCP and 4-CP by 30x40 mesh Filtrasorb-400 granular activated carbon as a function of time, and the curves predicted by the external film diffusion model (eqn 2-23), linear-driving-force approximation (eqn 2-29), and surface reaction kinetics (eqn 2-30). Adsorption is indicated by the decreasing concentration of solute remaining in solution. The curves are all the best fits to the data with the R-squared values of 0.999, 0.981, and 0.999 for the external film diffusion model, linear-driving-force approximation, and surface reaction kinetics for 2,4-DCP, and 0.993, 0.983, and 0.998 for these three models for 4-CP, respectively. The required Langmuir isotherm constants are given in Table 3.2. It is evident from the R-squared values that while both the surface reaction kinetics and the external film diffusion model appear to describe the kinetic data very well, surface reaction kinetics fits the data a little better than external film diffusion model.

The performances of the models are compared using statistical techniques. This comparison was achieved by calculating both the sum of the squares of the errors (SSE) and the square of the correlation coefficient (R-SQUARE). In mathematical forms these quantities are

$$SSE = \sum ( \hat{C}_i - C_i )^2 \quad (4-3)$$

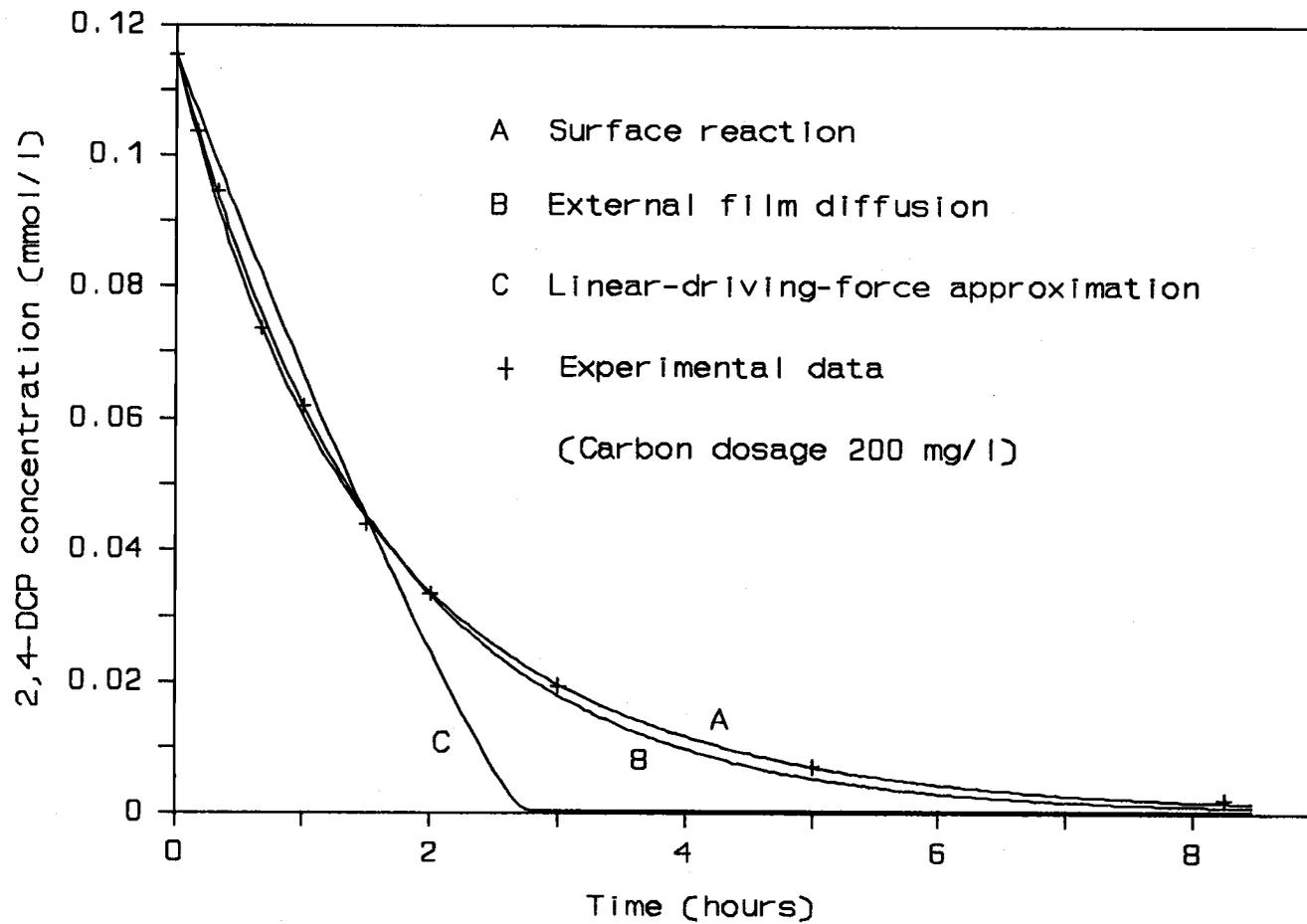


Figure 4.3 Comparison of kinetic models for adsorption of 2,4-DCP

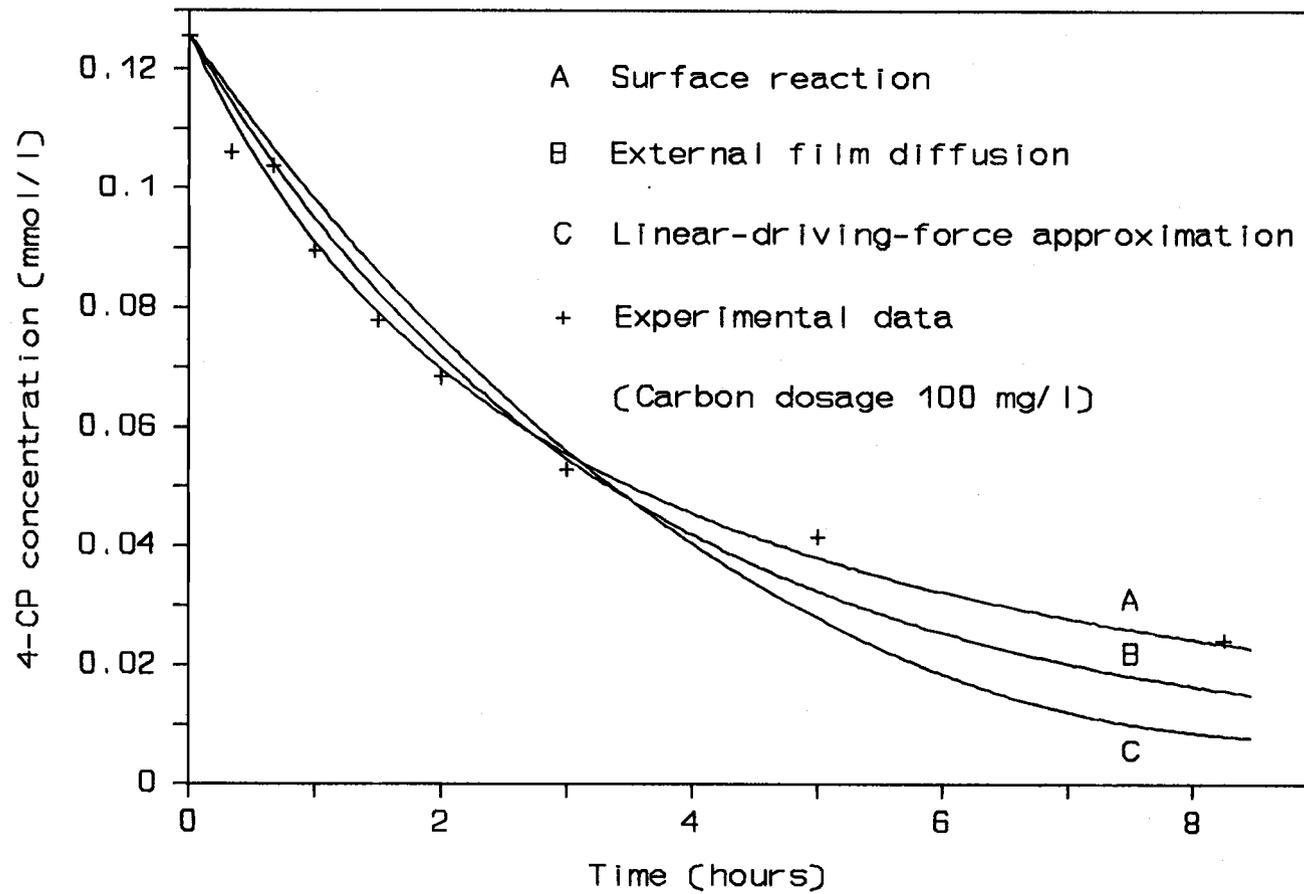


Figure 4.4 Comparison of kinetic models for adsorption of 4-CP

in which  $C_i$  = the experimentally determined concentration of kinetic data point  $i$ , and  $\hat{C}_i$  = the predicted concentration; and

$$R-SQUARE = \frac{\sum C_i^2 - SSE}{\sum C_i^2} \quad (4-4)$$

Figures 4.5 - 4.8 show the adsorption kinetic data of 2,4-DCP and 2,4,6-TCP at different adsorbate concentrations and different carbon dosages, and their respective best fit curves predicted by the surface reaction kinetics and external film diffusion models. Mass transfer coefficients and corresponding R-square values for these two models are summarized in Table 4.1. Mass transfer coefficients for the surface reaction kinetics varied slightly with initial adsorbate concentration and carbon dosage. They varied directly with initial concentration and inversely with carbon dosage. However, mass transfer coefficients for the external film diffusion model are very close to each other for all the cases if carbon dosage is not included in the rate expression. It can be seen that except for 2,4-DCP at the carbon dosage of 100 mg/l the R-square values for the surface reaction kinetics are all higher than those for the external film diffusion model for these three chlorophenols.

In Table 4.1 two observations are made. The external film diffusion model improved its performance on the 2,4,6-TCP and 2,4-DCP systems when the initial adsorbate concentration decreased to about one-fifth. The R-squared values are highest among these three cases for both adsorbates and almost the same as those of the surface

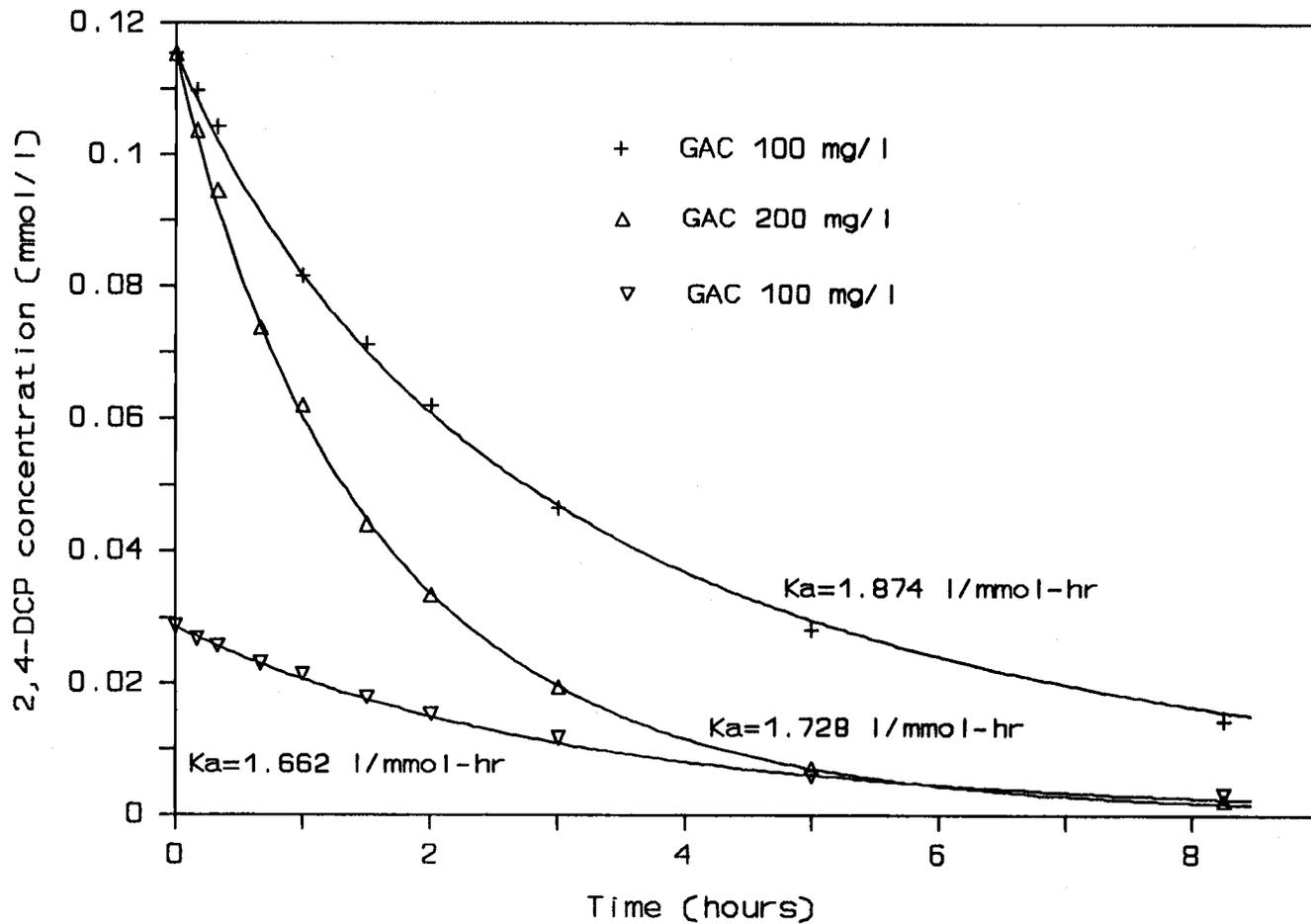


Figure 4.5 Changes of 2,4-DCP concentration with time and predictions of surface reaction model

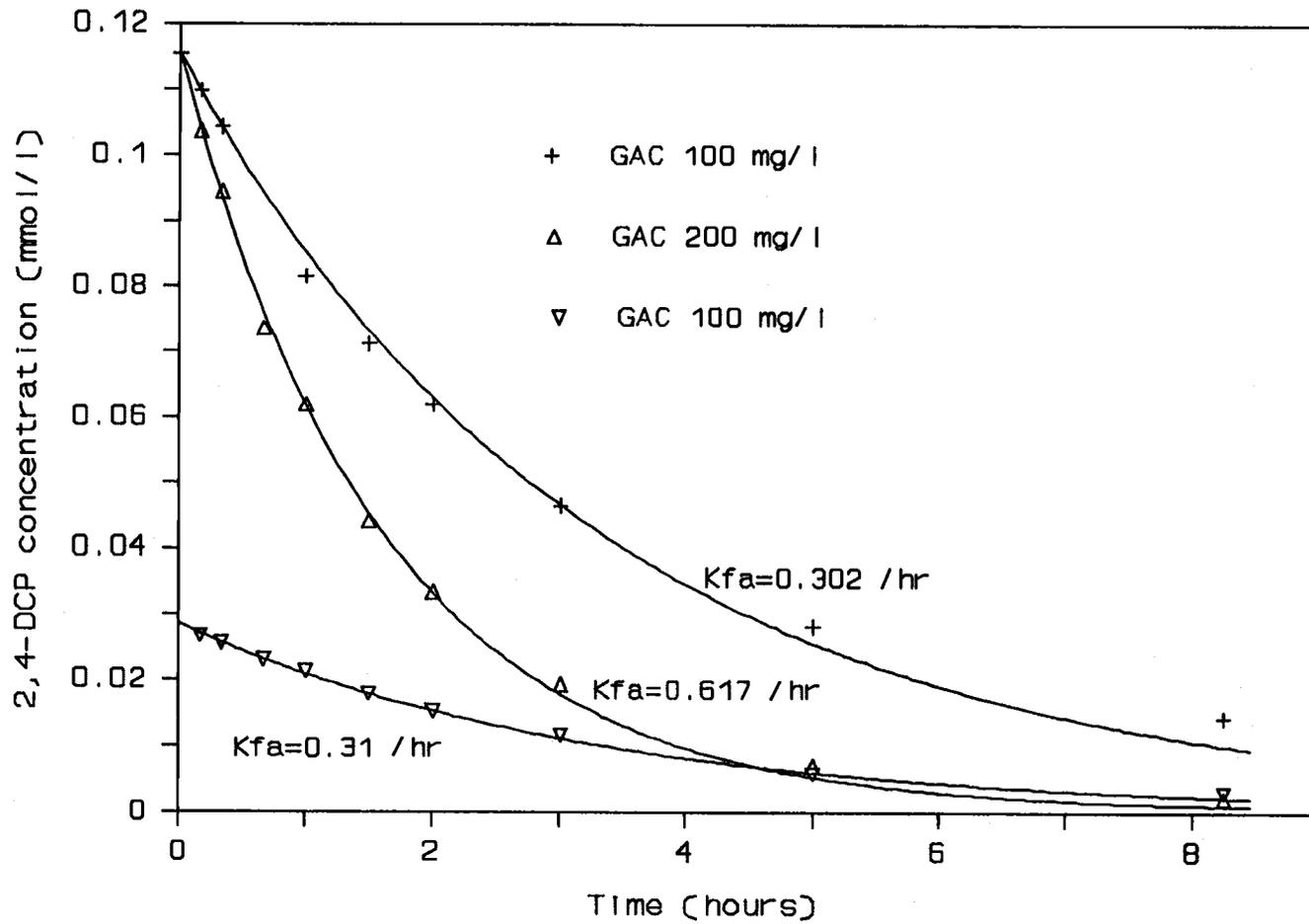


Figure 4.6 Changes of 2,4-DCP concentration with time and predictions of external film diffusion model

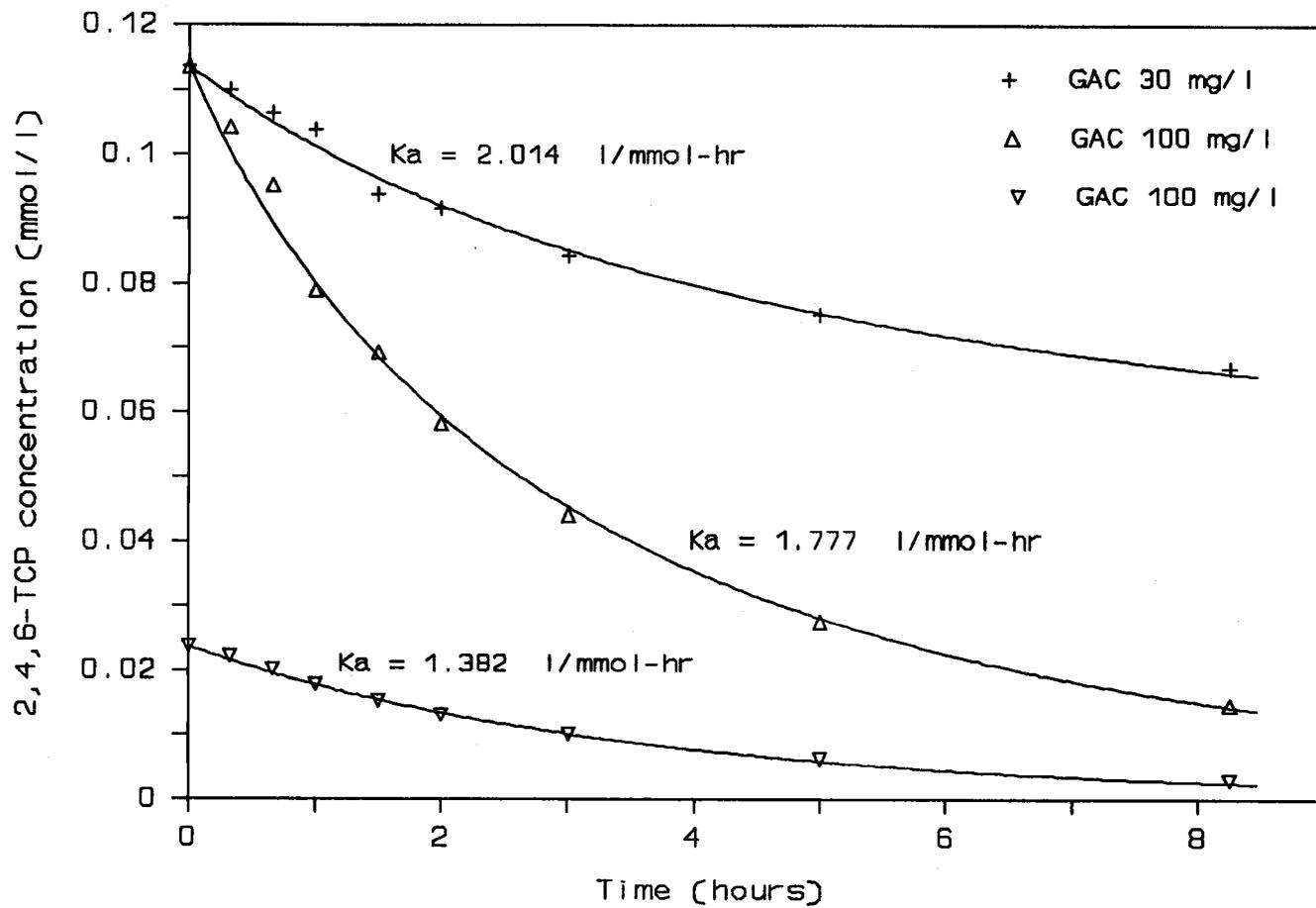


Figure 4.7 Changes of 2,4,6-TCP concentration with time and predictions of surface reaction model

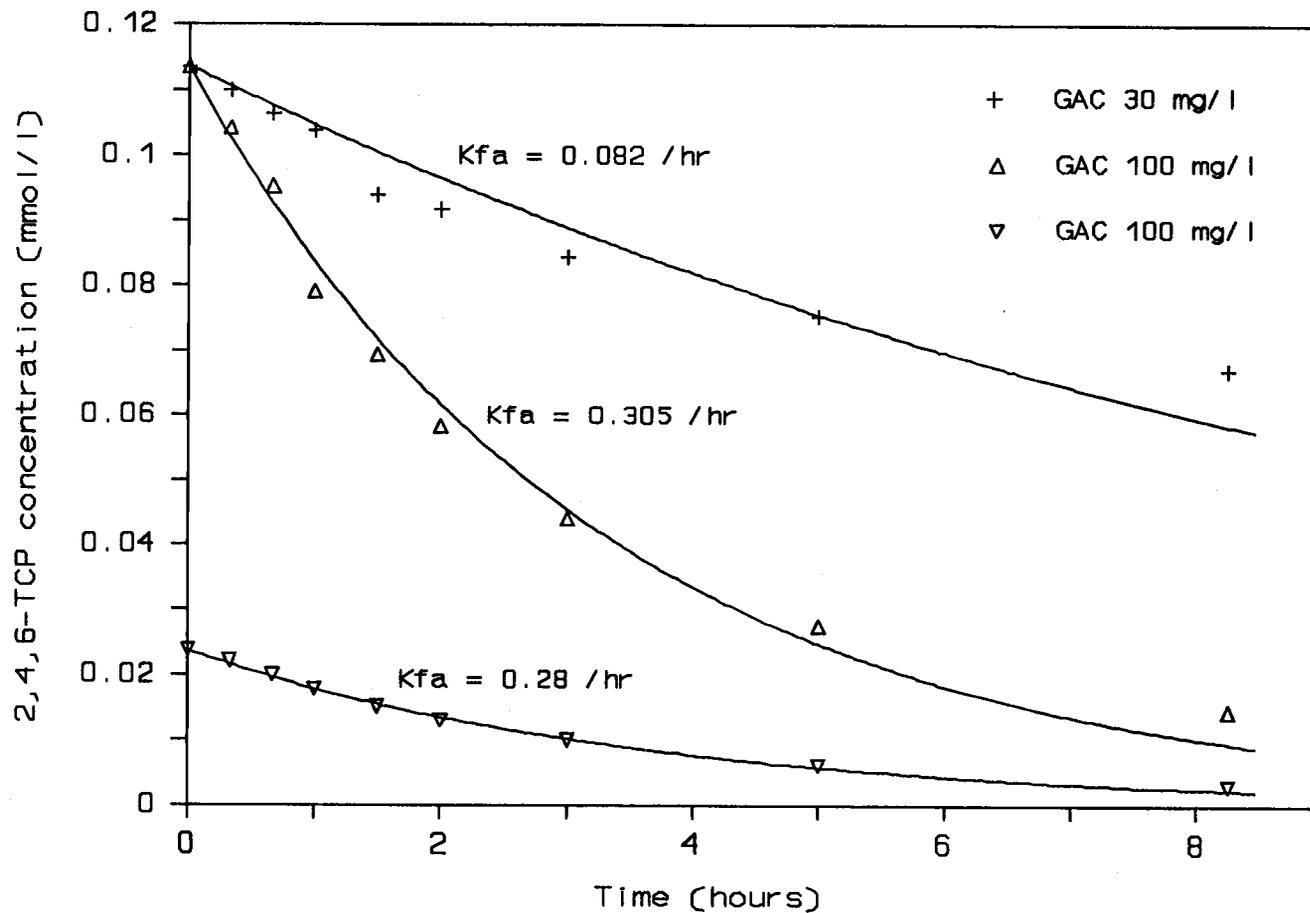


Figure 4.8 Changes of 2,4,6-TCP concentration with time and predictions of external film diffusion model

**Table 4.1 Mass Transfer Coefficients for Three Chlorophenols**

| Adsorbate | Init.conc.<br>mmol/l | Carbon dosage<br>mg/l | Surface reaction           |                | External diffusion     |                |
|-----------|----------------------|-----------------------|----------------------------|----------------|------------------------|----------------|
|           |                      |                       | K <sub>a</sub><br>l/mmol-h | R <sup>2</sup> | K <sub>p</sub><br>1/hr | R <sup>2</sup> |
| 2,4,6-TCP | 0.1136               | 30                    | 2.014                      | 1.000          | 0.082                  | 0.997          |
|           | 0.1136               | 100                   | 1.777                      | 0.998          | 0.305                  | 0.997          |
|           | 0.0238               | 100                   | 1.382                      | 0.999          | 0.280                  | 0.999          |
| 2,4-DCP   | 0.1154               | 100                   | 1.874                      | 1.000          | 0.302                  | 0.998          |
|           | 0.1154               | 200                   | 1.728                      | 0.999          | 0.617                  | 0.999          |
|           | 0.0287               | 100                   | 1.662                      | 0.999          | 0.310                  | 0.999          |
| 4-CP      | 0.1257               | 100                   | 1.980                      | 0.998          | 0.280                  | 0.993          |

reaction kinetics. This implies that the external transport resistance increases as adsorbate concentration decreases. Also, at the same carbon dosage (100 mg/l) and approximately the same initial adsorbate concentrations, the mass transfer coefficient for the surface reaction kinetics increases from 1.777 l/mmol-hr for 2,4,6-TCP to 1.874 l/mmol-hr for 2,4-DCP and 1.980 l/mmol-hr for 4-CP. This means that at pH 7.0, the order in which adsorption equilibrium is attained will be first 4-CP, then 2,4-DCP and finally 2,4,6-TCP. This implies that the more chlorinated a chlorophenol, the slower it reaches adsorption

equilibrium. Decreasing dissociation extent from 4-CP to 2,4,6-TCP may account for this observation.

A high initial adsorbate concentration study on the adsorption kinetics of 2,4-DCP and two long-term studies on the adsorption kinetics of 2,4,6-TCP and PCP have also been performed, as shown in Figures 4.9, 4.10 and 4.11, respectively. It is seen from the figures that surface reaction kinetics still best describe the kinetic data of these three experiments. Noteworthy also is the observation that the linear-driving-force approximation has improved its performance and the external film diffusion model has become the worst for the long-term kinetics.

The distinction between external diffusion or surface reaction and intraparticle diffusion controlled processes can be made by performing an interruption test. This test has been used by Zogorski et al. (1976) and Weber and Morris (1963). In an interruption test, the adsorbent is removed from the adsorbate solution for a period and then reimmersed. When concentration gradients are present, the pause gives time for the gradients to level off within the pores of the adsorbent. When intraparticle diffusion is the rate-limiting step, the rate of removal immediately after reimmersion is greater than the rate prior to interruption. The interruption period has no influence on the rate of adsorption after reimmersion when external transport or surface reaction is rate limiting. Thus, the interruption test is a simple test for determining if large concentration gradients exist within the pores of the adsorbent.

A interruption test was conducted with 2,4,6-TCP to help define the nature of the rate-limiting step in the adsorption process of chlorophenols. After 3 hours from the

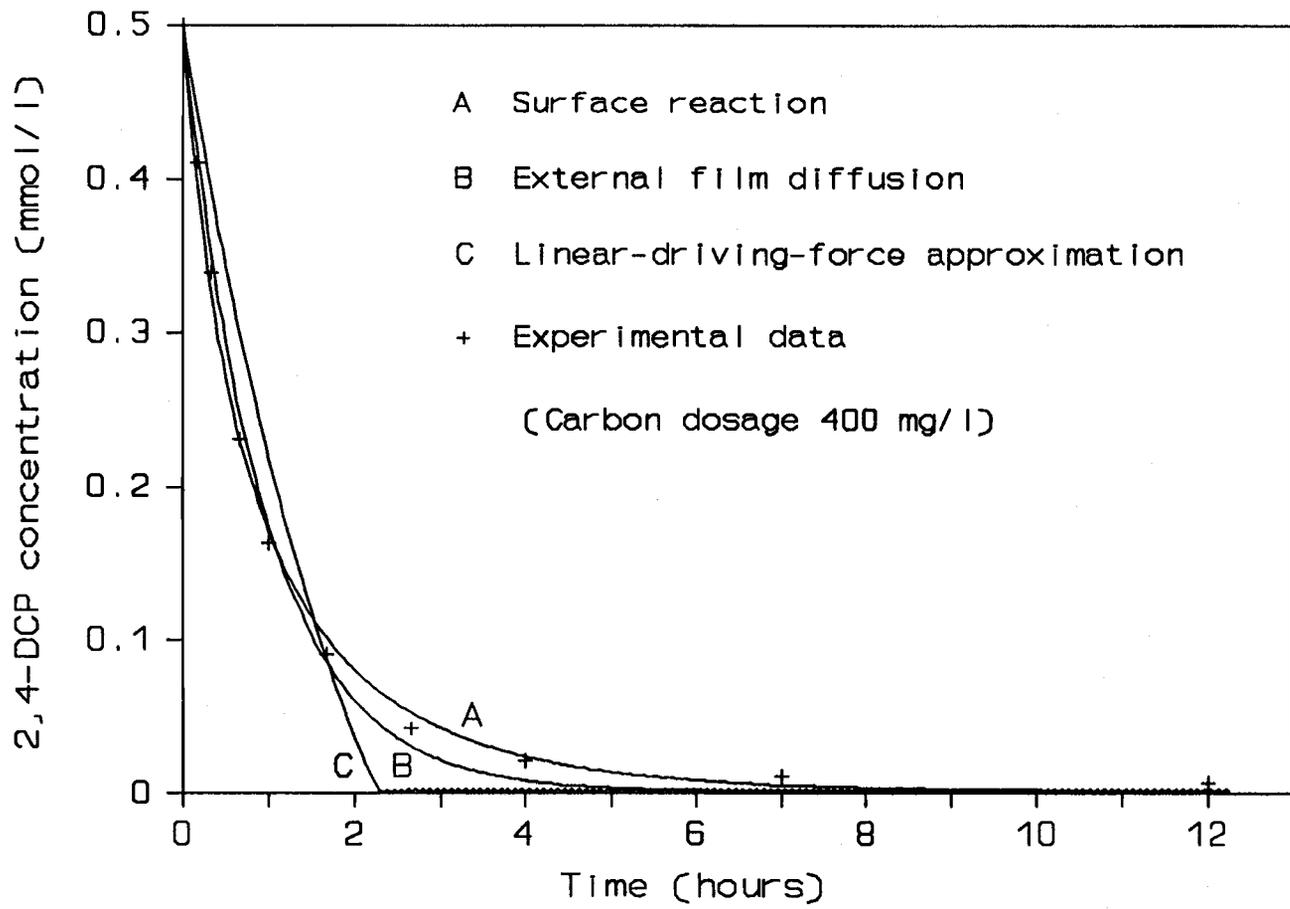


Figure 4.9 Comparison of kinetic models for adsorption of 2,4-DCP (high initial concentration)

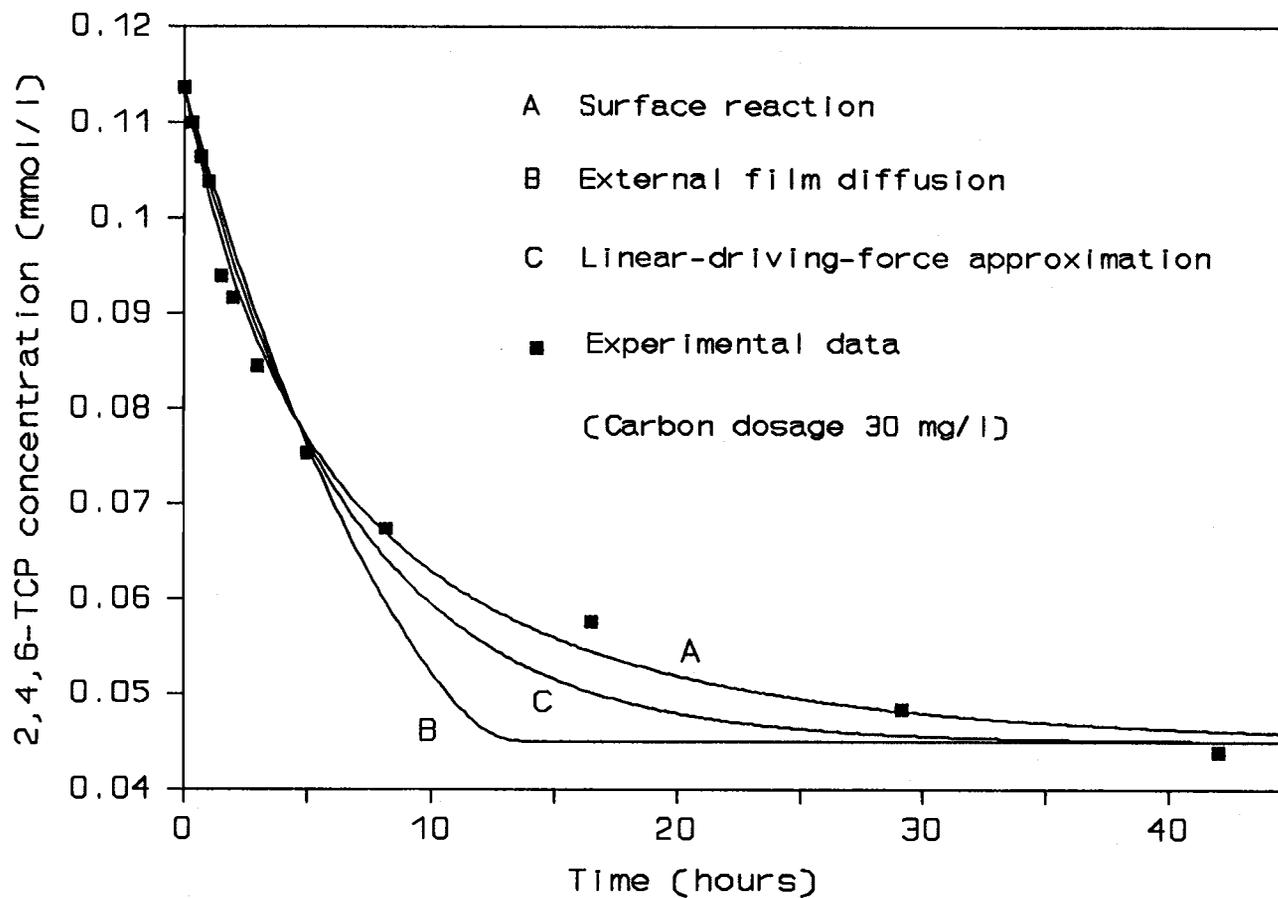


Figure 4.10 Comparison of kinetic models for adsorption of 2,4,6-TCP (long term)

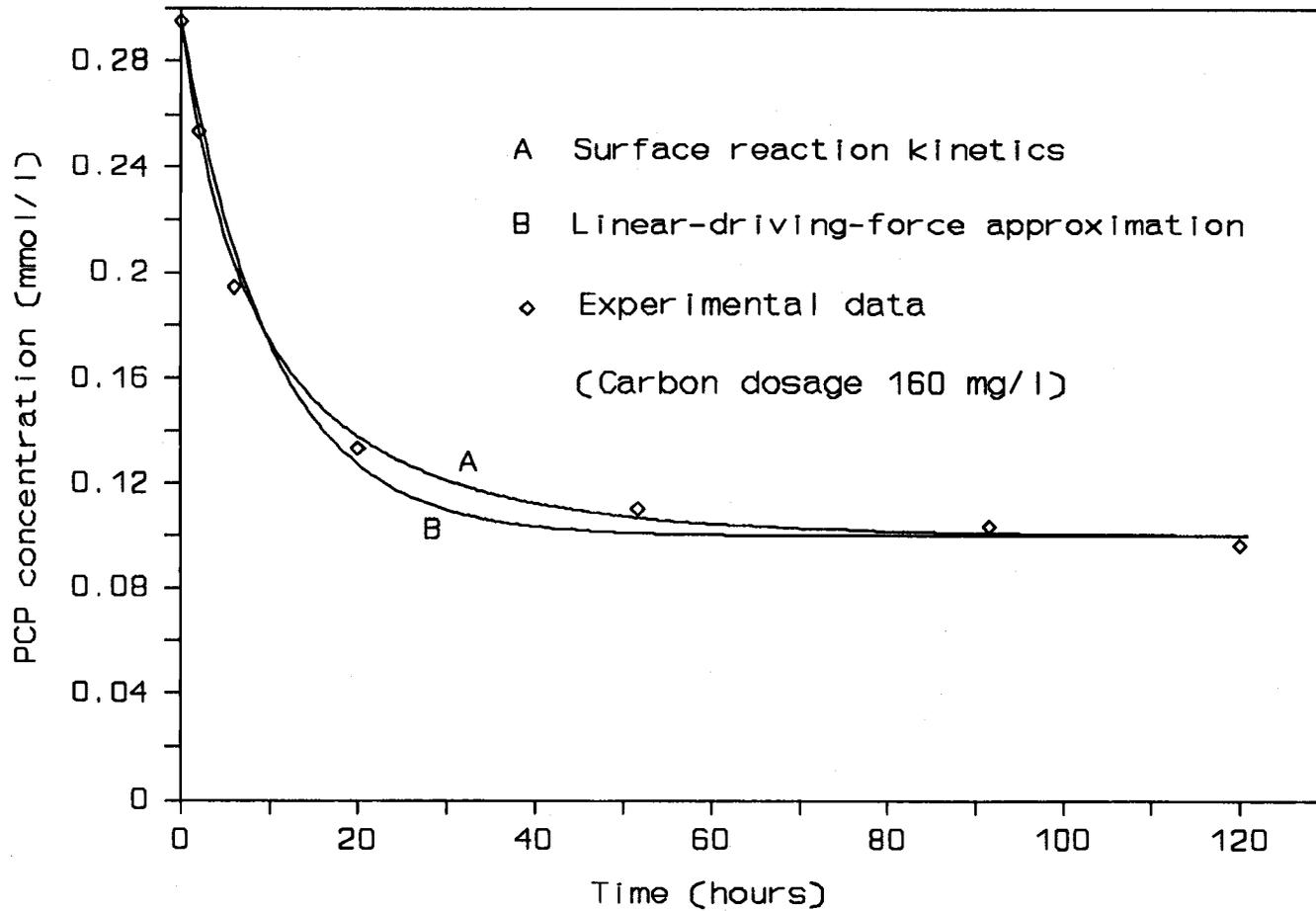


Figure 4.11 Comparison of kinetic models for adsorption of PCP (long term)

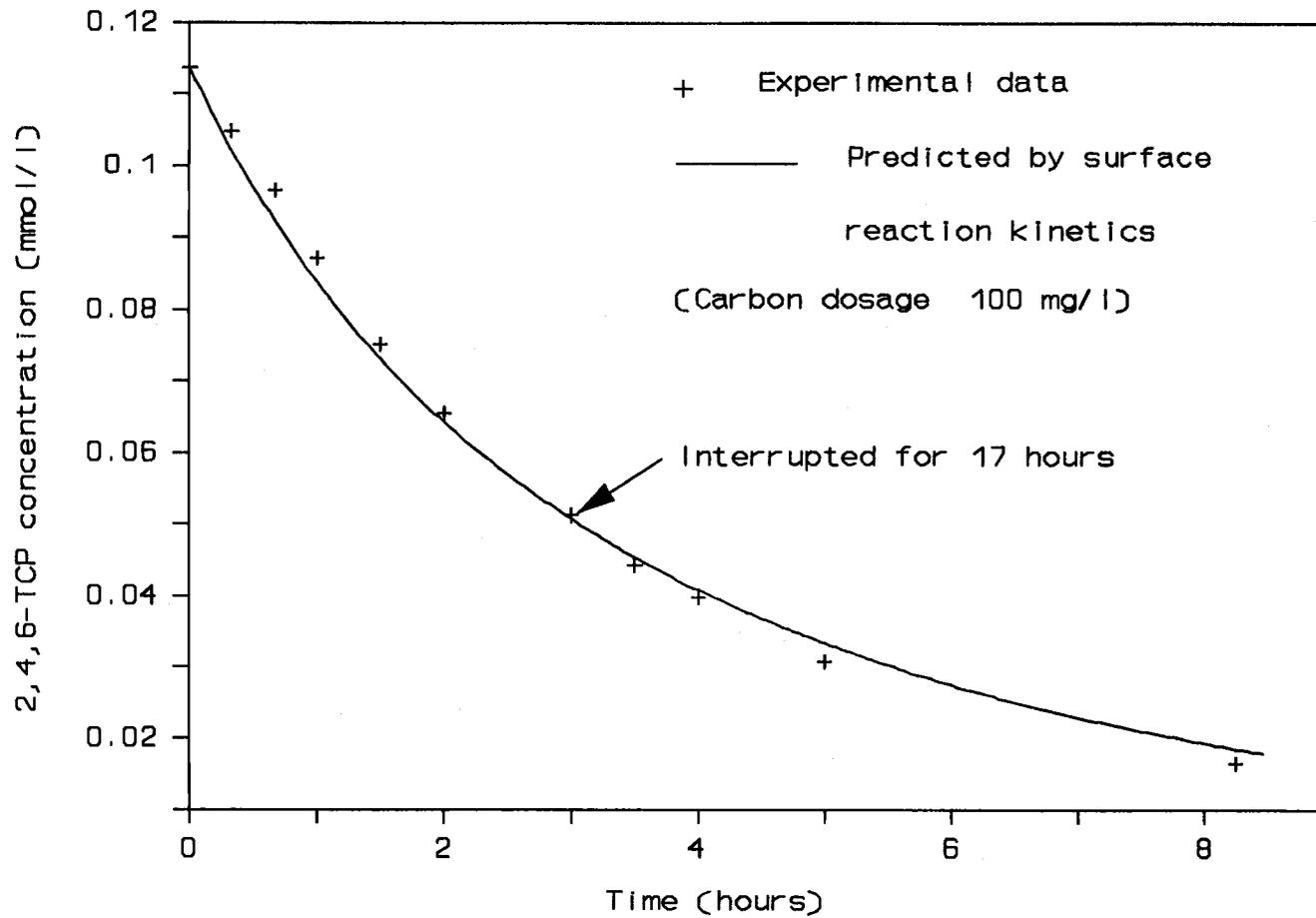


Figure 4.12 Interruption test for adsorption of 2,4,6-TCP

starting of the kinetic experiment, the adsorbate solution was decanted, and the adsorbent was left in the reactor with a few milliliters of solution. The experiment started again 17 hours later. The results of this interruption test are shown in Figure 4.12, in which the concentration of 2,4,6-TCP remaining in solution is plotted against accumulated immersion time. The figure also indicates that surface reaction kinetics can fit the experimental data over the entire kinetic process. The rate of adsorption of 2,4,6-TCP appears not to be limited by internal diffusion. This observation is based on the lack of influence of the interruption period on the concentration profile after reimmersion.

Several characteristics of the adsorbent, adsorbate, and solution phase are of importance in determining the rate-limiting step. These factors include the particle size of the adsorbent, concentration of adsorbate, degree of mixing, interaction of adsorbate with adsorbent, and mass transfer coefficients in each individual adsorption step. Usually, external film transport is the rate-limiting step in systems which have dilute concentration of adsorbate and small particle sizes of adsorbent. In contrast, the intraparticle step limits the overall transfer for those systems which have large particle sizes of adsorbent and high concentration of adsorbate. Surface reaction controls the overall adsorption process for systems in which surface reaction is a chemical reaction because it is usually slow compared to physisorption. It can be concluded from the above kinetic results that both the external film diffusion model and the surface reaction kinetics model fit the kinetic data, but surface reaction kinetics is better. Several researchers (Mattson et al., 1969a; Mattson et al., 1969b; Grant and King, 1990) have indicated the formation of charge-transfer complexes between phenolic compounds and carbon surface functional groups,

or an oxidative coupling reaction of phenolic compounds on the carbon surface. As shown in chapter 3, the adsorption equilibrium of chlorophenols on activated carbon can be described very well by the proposed surface complexation model, in which molecular and ionized forms of chlorophenols interact respectively with acidic and basic surface functional groups to form two neutral surface complexes, of which the complex of basic groups is more substantial and more stable than that of acidic groups. Thus, chemisorption appears to be the most reasonable explanation for the kinetic characteristics of the adsorption of chlorophenols on activated carbon.

**Sensitivity Analysis.** An understanding of the relative importance of each parameter in the surface reaction kinetics model can be seen from the sensitivity analysis presented in Figures 13, 14 and 15, where typical chlorophenol kinetics parameters have been used in the simulations. As shown in Figures 13 and 14, the surface reaction kinetics model is very sensitive to the parameters  $K_a$  and  $Q$ . This gives an indication of the necessity of obtaining accurate Langmuir adsorptive capacity. Figure 15 shows that the effect of Langmuir constant  $b$  on kinetic process is very small.

**Two-component Adsorption Kinetic Process.** The experiments have been performed to verify that the adsorption of chlorophenols on activated carbon is to some extent an irreversible process and non-ideal competition between two components exists. In kinetic studies with 2,4-DCP and 2,4,6-TCP, two adsorbates were introduced simultaneously or one of two was added 10 hours later. The duration of the experiments is 6 days, which is the same as the equilibration time for equilibrium studies, and the results are given in Figures 4.16 - 4.18. It can be seen that the final concentrations are always lower for

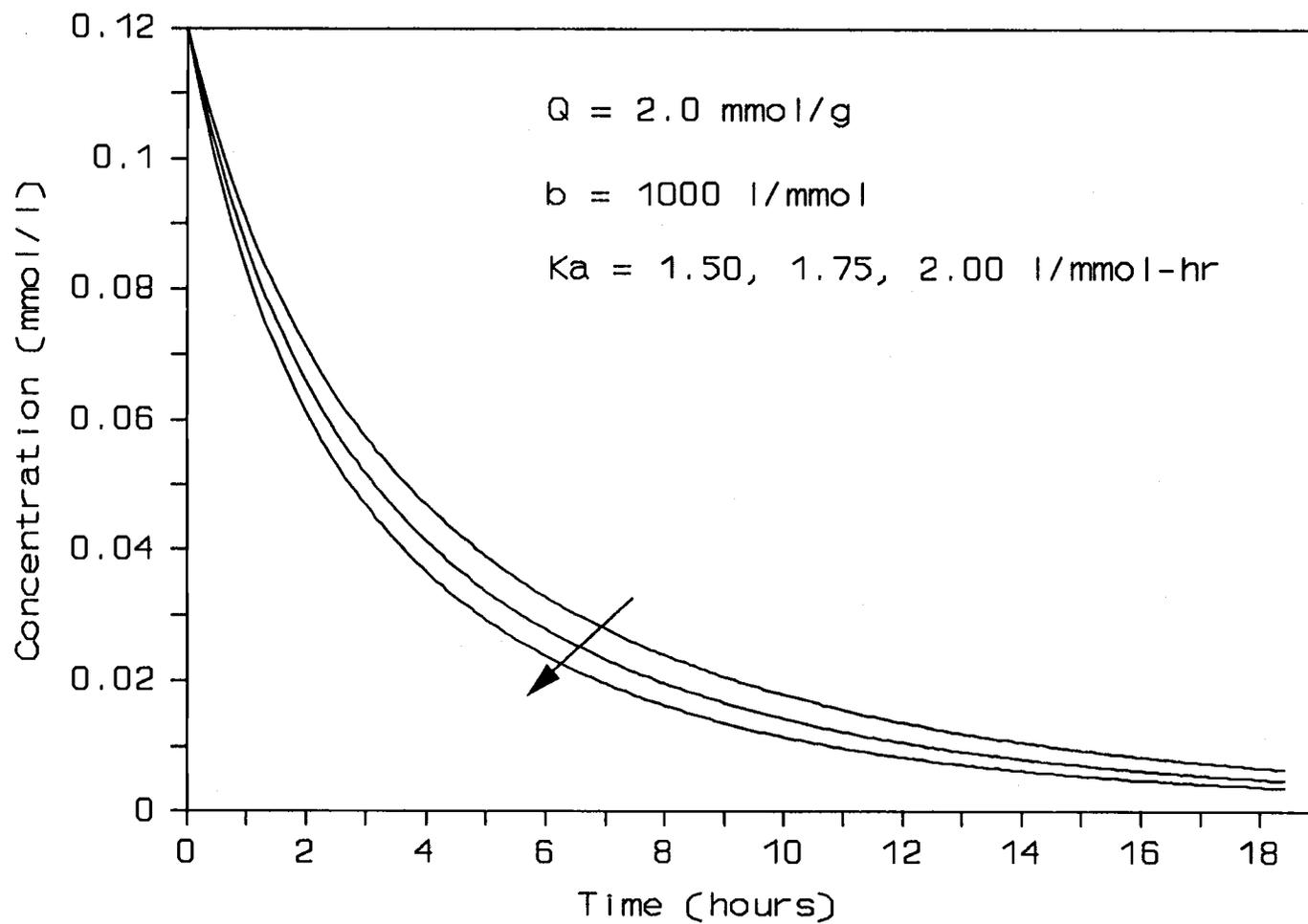


Figure 4.13 Sensitivity analysis: Ka parameter

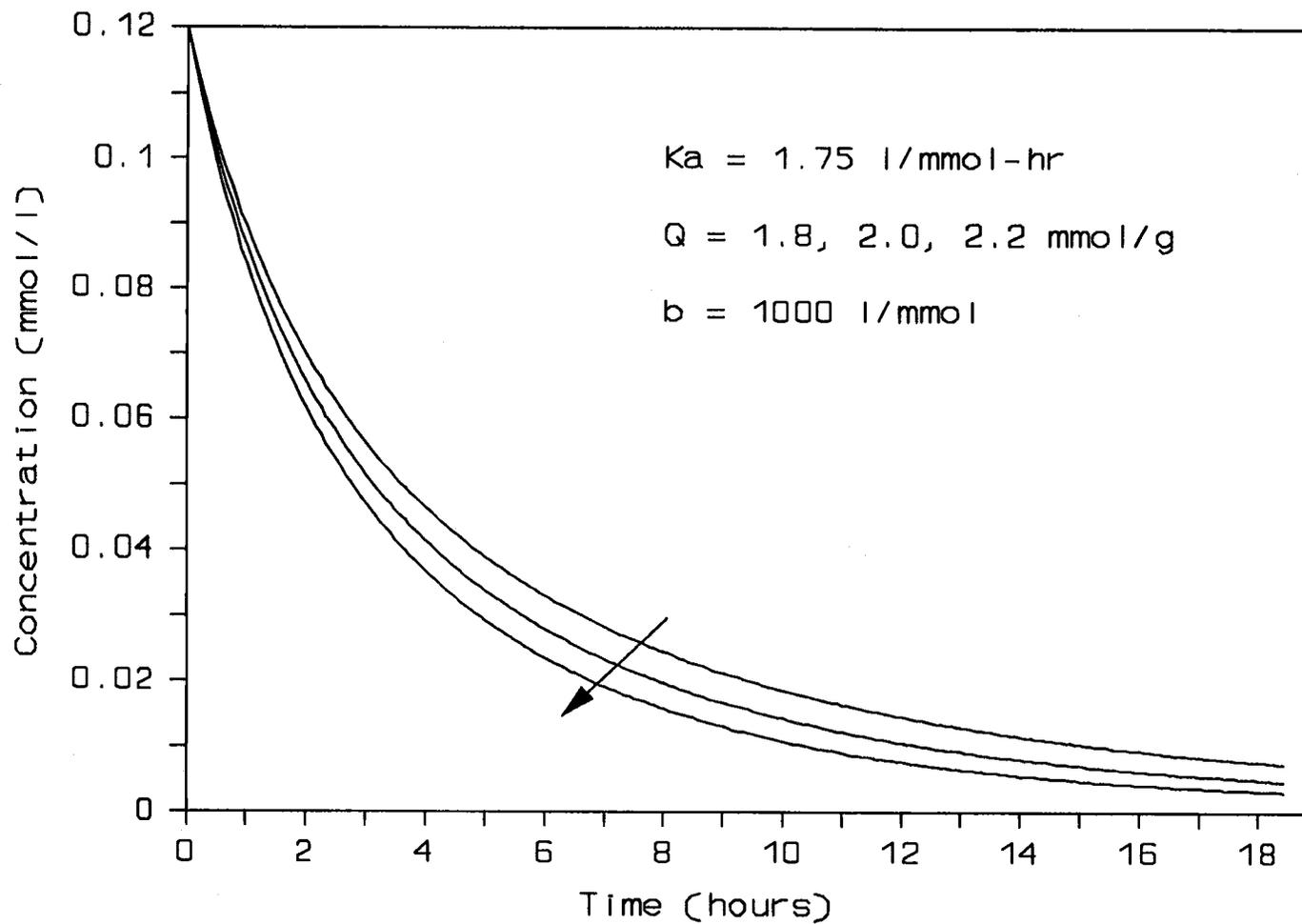


Figure 4.14 Sensitivity analysis: Q parameter

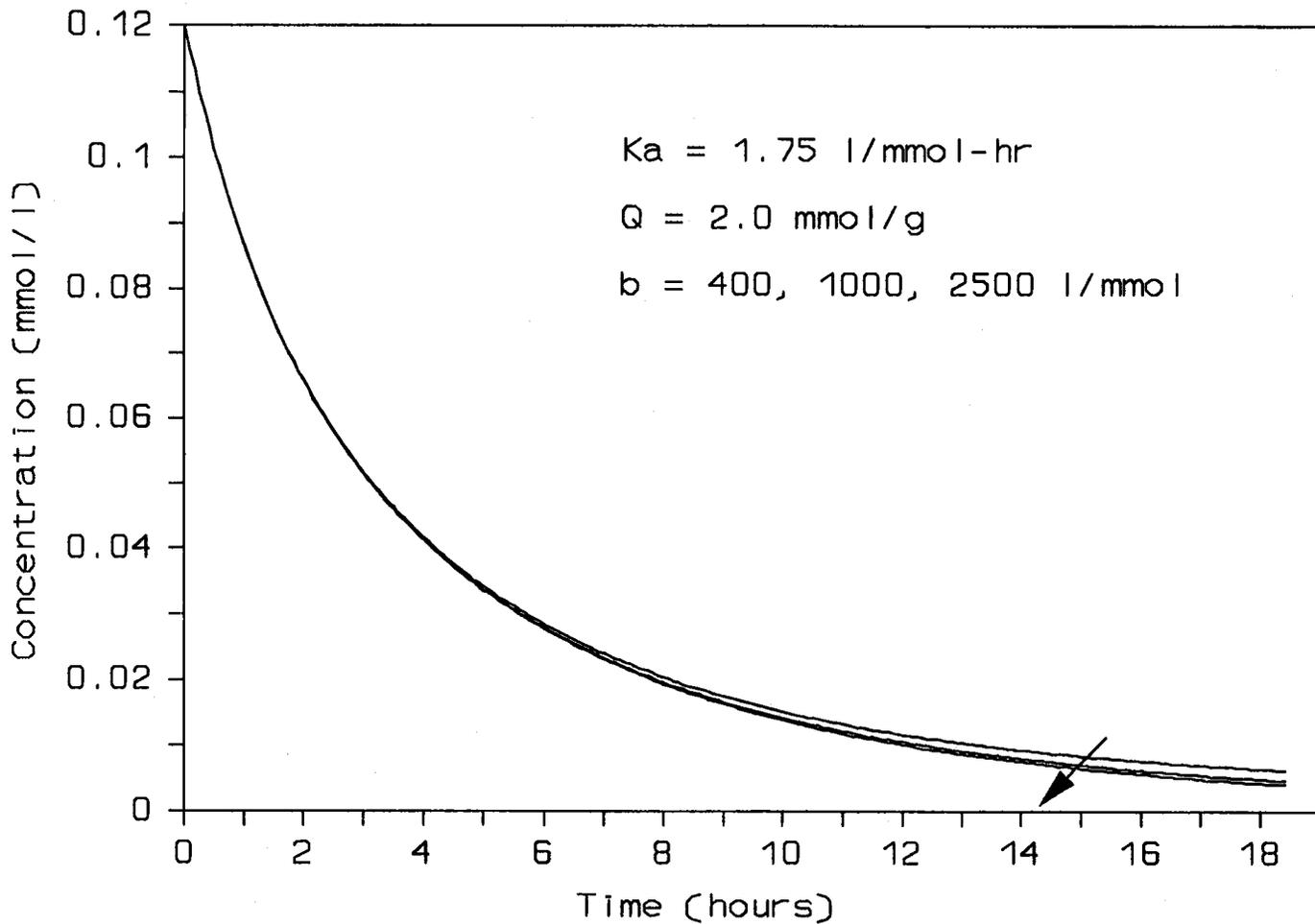


Figure 4.15 Sensitivity analysis: b parameter

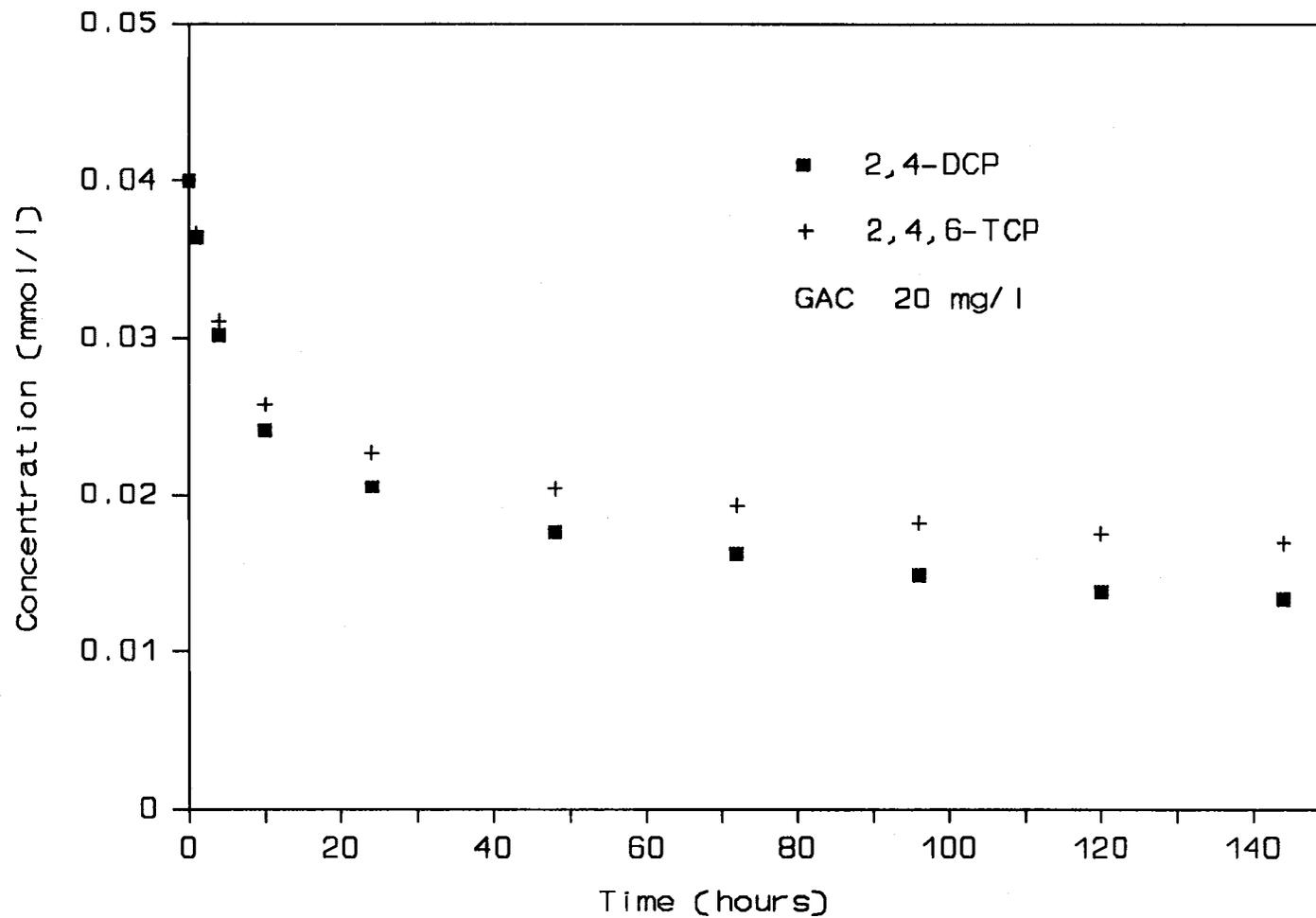


Figure 4.16 Changes of 2,4,6-TCP and 2,4-DCP concentrations with time in batch reactor (two components were introduced simultaneously)

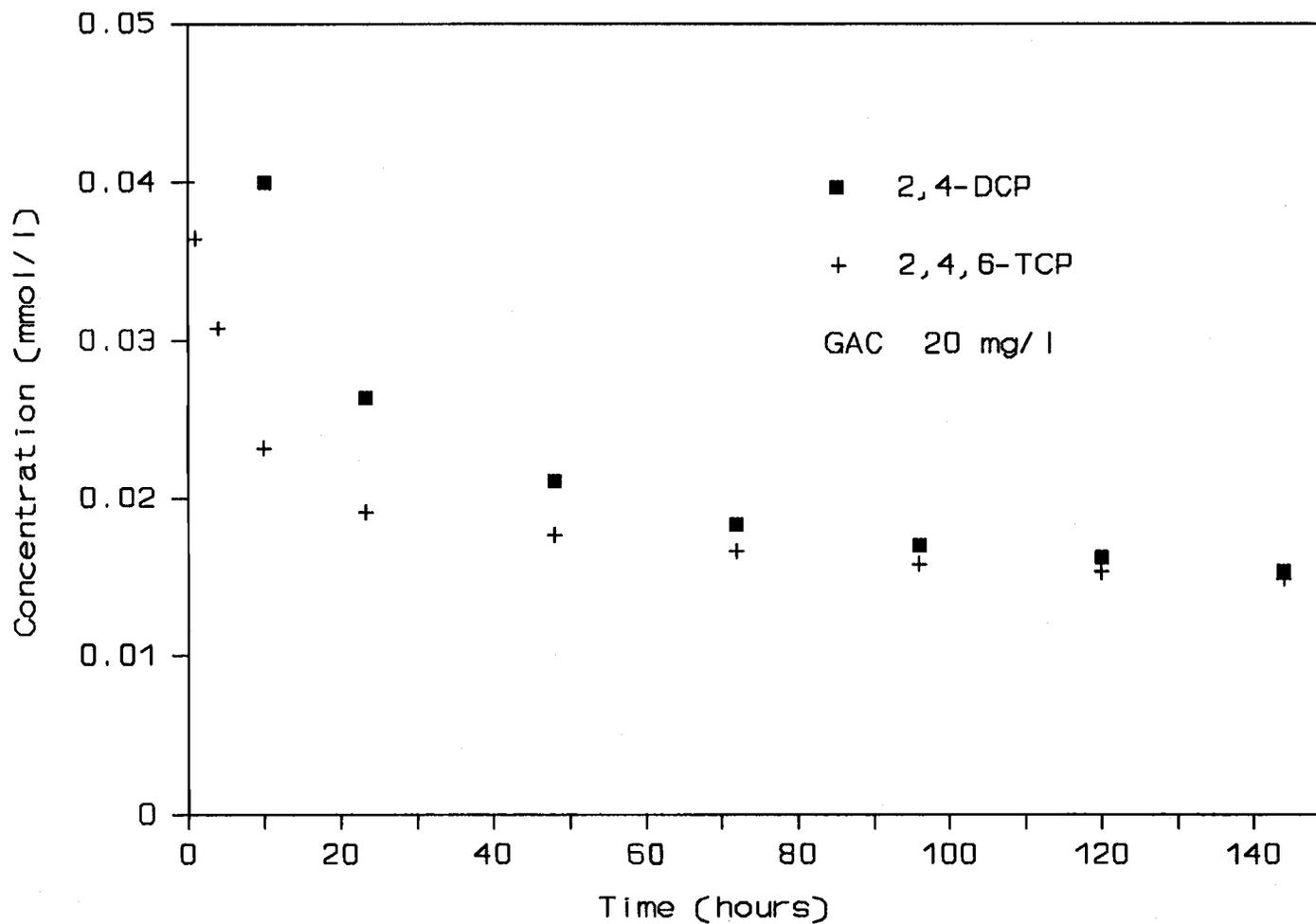


Figure 4.17 Changes of 2,4,6-TCP and 2,4-DCP concentrations with time in batch reactor (2,4,6-TCP was introduced 10 hours earlier)

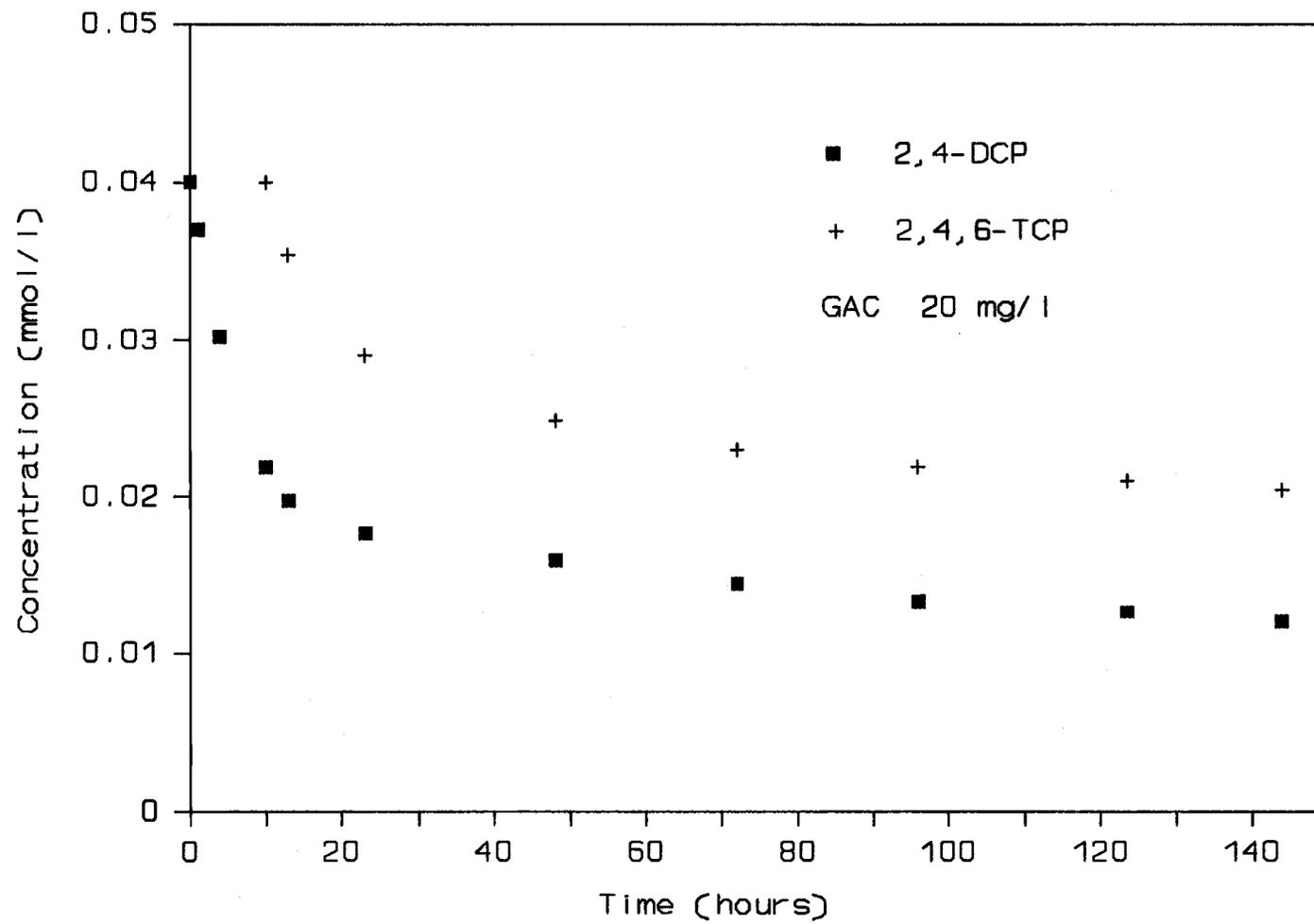


Figure 4.18 Changes of 2,4,6-TCP and 2,4-DCP concentrations with time in batch reactor (2,4-DCP was introduced 10 hours earlier)

adsorbates added later and higher for adsorbates added earlier as compared with the respective concentrations of adsorbates in simultaneously introduced system. The difference of 10 hours contact time in a total 144 hours could not result in so significant a disparity in final concentration. It must be due to the irreversibility of adsorption, that is, that molecular or anionic species of earlier added chlorophenol preferentially occupy higher-energy active sites on the carbon surface and some of them cannot be replaced by later added species. In another sense, the preferential adsorption can be said to occur in systems of simultaneously introduced two components if the adsorption rates of components are not proportional to their respective adsorptive capacities. From Figure 4.16 this disproportion of adsorption rates with adsorptive capacities is seen to exist in 2,4-DCP/2,4,6-TCP system because the adsorption rate of 2,4-DCP is higher than that of 2,4,6-TCP while the adsorptive capacity for 2,4-DCP is lower than that for 2,4,6-TCP. This may explain why the Langmuir, IAS and other existing multicomponent equilibrium models fail to predict solid-phase loadings in systems of chlorophenols.

## **Conclusions**

Batch kinetics studies were conducted of the adsorption of chlorinated phenols on granular activated carbon. pH played an important role in the adsorption kinetics of chlorophenols at pH values above the pKa values of the compounds, while little influence on adsorption rate was observed if pH was decreased below the pKa values. The external film diffusion model, the linear-driving-force approximation, and the surface reaction kinetics model have been employed to fit the adsorption kinetics data of chlorophenols.

The results show that the surface reaction model best describes both short-term and long-term kinetics, while the external film diffusion model describes the short-term kinetics data very well and the linear-driving-force approximation improves its performance for the long-term kinetics. The interruption test also indicates that the rate of adsorption is not limited by internal surface diffusion. The mass transfer coefficient increases from more chlorinated compounds to less chlorinated compounds, which implies that the more chloro groups in a chlorophenol, the slower it reaches adsorption equilibrium. The two-component adsorption kinetics experiments have revealed that the adsorption of chlorophenols on activated carbon is to some extent irreversible and that non-ideal competition between two components exists. Chemisorption appears to be the most reasonable explanation for the kinetics characteristics of the adsorption of chlorophenols on activated carbon.

## Chapter 5 MULTICOMPONENT ADSORPTION EQUILIBRIA OF CHLOROPHENOLS

### **A New Method for Predicting Multicomponent Adsorption Equilibria**

It has been pointed out that the Langmuir competitive model, IAS model, and other existing multicomponent equilibria models fail to predict solid-phase loadings under system conditions that exhibit significant irreversible adsorption effects and non-ideal competition. As we can see from the previous and following chapters, chlorophenols show a very high affinity for activated carbon, the adsorption process is highly irreversible, and thus these systems are non-ideal. It seems impossible for a model to accurately predict multicomponent adsorption equilibria in non-ideal systems if the model does not use other parameters in addition to single-component isotherm constants. From the view point of thermodynamics, all liquid- and solid-phase solutions can be treated as a non-ideal solution while an ideal solution is merely a particular case of non-ideal solutions. The derivation of the proposed prediction method will start with the fundamentals of solution thermodynamics.

Let us consider in detail adsorption on a adsorbent surface from a binary liquid mixture. We can assume that at adsorption equilibrium we have two binary solutions (two phases): the solid or surface solution and the bulk solution. At thermodynamic equilibrium:

$$\mu_1^s = \mu_1 \quad , \quad \mu_2^s = \mu_2 \quad (5-1)$$

where  $\mu_1^s$  and  $\mu_2^s$  are the chemical potentials of components 1 and 2, respectively, in the surface solution, and  $\mu_1$  and  $\mu_2$  are the corresponding chemical potentials in the bulk solution.

Adopting the thermodynamic description of adsorption equilibria used by Fu et al. (1948) we can rewrite equilibria (eqn 5-1) in the form:

$$\mu_1^{0,s} + RT \ln x_1^s f_1^s = \mu_1^0 + RT \ln x_1 f_1 \quad (5-2)$$

$$\mu_2^{0,s} + RT \ln x_2^s f_2^s = \mu_2^0 + RT \ln x_2 f_2 \quad (5-3)$$

where  $\mu_1^{0,s}$  and  $\mu_2^{0,s}$  are the standard chemical potentials of components 1 and 2 in the surface solution,  $\mu_1^0$  and  $\mu_2^0$  are those in the bulk solution,  $x_i^s$  and  $x_i$ , and  $f_i^s$  and  $f_i$  are accordingly the mole fractions and the activity coefficients of the respective components in the surface and bulk solutions. Of course, the standard chemical potentials of the components depends on the reference system used.

From equations 5-2 and 5-3 we get

$$\frac{x_1^s}{x_1} = \frac{f_1}{f_1^s} \exp \left[ -\frac{1}{RT} (\mu_1^{0,s} - \mu_1^0) \right] \quad (5-4)$$

$$\frac{x_2^s}{x_2} = \frac{f_2}{f_2^s} \exp \left[ -\frac{1}{RT} (\mu_2^{0,s} - \mu_2^0) \right] \quad (5-5)$$

Dividing equation 5-4 by equation 5-5, side by side, we get:

$$\frac{x_1^s x_2}{x_1 x_2^s} = \frac{f_1 f_2^s}{f_1^s f_2} \exp \left\{ -\frac{1}{RT} [(\mu_1^{0,s} - \mu_1^0) - (\mu_2^{0,s} - \mu_2^0)] \right\} \quad (5-6)$$

Let us denote:

$$\alpha = \frac{x_1^s x_2}{x_1 x_2^s} \quad (5-7)$$

$$D = \frac{f_1 f_2^s}{f_1^s f_2} \quad (5-8)$$

$$K = \exp \left\{ -\frac{1}{RT} [(\mu_1^{0,s} - \mu_1^0) - (\mu_2^{0,s} - \mu_2^0)] \right\} \quad (5-9)$$

Using the notations 5-7, 5-8 and 5-9, we can write equation 5-6 in the form:

$$\frac{x_1^s x_2^s}{x_1 x_2} = DK = \alpha \quad (5-10)$$

Since  $x_1^s = q_1 / (q_1 + q_2)$ ,  $x_2^s = q_2 / (q_1 + q_2)$ ,  $x_1 = C_1 / (C_1 + C_2)$ , and  $x_2 = C_2 / (C_1 + C_2)$ , we have:

$$\frac{q_1 C_2}{q_2 C_1} = DK = \alpha^1 \quad (5-11)$$

where  $q_1$  and  $q_2$  are the amounts adsorbed, and  $C_1$  and  $C_2$  are the equilibrium concentrations for components 1 and 2, respectively. The quantity  $\alpha$  is known as the distribution coefficient or distribution function.  $K$  is a function only of temperature. At a given temperature,  $K$  is a constant. When adsorption takes place from an ideal solution and the surface solution is also ideal, then  $D = 1$ , and:

$$\frac{q_1 C_2}{q_2 C_1} = K = \alpha = \text{constant} \quad (5-12)$$

In case of adsorption from a non-ideal solution, the value of  $D$ , and therefore the

---

<sup>1</sup> From the Langmuir competitive model (eqn 2-9), we have:

$$\frac{q_1 C_2}{q_2 C_1} = \frac{Q_1 b_1}{Q_2 b_2} = \text{constant}$$

Hence it is not surprising that the Langmuir competitive model holds only in ideal systems.

value of  $\alpha$ , vary with the concentrations of components 1 and 2 in the surface and bulk solutions.

Now, consider two-component competitive adsorption from another aspect. The two-component adsorption can be described as the following competitive reactions:



in which  $-S$  represents the unoccupied surface sites, and  $SA$  and  $SB$  represent the surface sites occupied by components  $A$  and  $B$ , respectively.

Denote single-component adsorptive capacities of components  $A$  and  $B$  as  $Q_1$  and  $Q_2$ , and single-component adsorption constants as  $b_1$  and  $b_2$ , respectively. Applying the law of mass action to the single-component system, for component 1 we have

$q_1 = b_1 C_1 (Q_1 - q_1)$ , which, after rearrangement, leads to the single-component Langmuir equation. For a two-component system in which component 1 is the dominantly adsorbed component, the following equation can be obtained from a mass balance:

$$q_1 = b_1 C_1 (Q_1 - q_1) - f q_2
 \tag{5-14}$$

where  $f = Q_1 / Q_2$ , a factor for converting  $q_2$  into  $q_1$ . The first term on the left side would represent the amount adsorbed for component 1, if single-component adsorption took place, and the second term represents correction to the amount adsorbed due to

competition from  $q_2$ . The difference between the two terms produces the real solid-loading for component 1,  $q_1$ . Combining equations 5-11 and 5-14, and solving for  $q_1$ , we get

$$q_1 = \frac{Q_1 b_1 C_1}{1 + b_1 C_1 + \frac{Q_1 C_2}{Q_2 C_1 \alpha}} \quad (5-15)$$

which we call a Langmuir-type equation. Equations 5-11 and 5-15 can be used to calculate  $q_1$  and  $q_2$  if  $A$  is the dominantly adsorbed component and  $\alpha$  is known from two-component adsorption data.

Similarly, if component  $B$  is the dominantly adsorbed component, we have

$$q_2 = b_2 C_2 (Q_2 - q_2) - \frac{q_1}{f} \quad (5-16)$$

From equations 5-11 and 5-16, we also get

$$q_2 = \frac{Q_2 b_2 C_2}{1 + b_2 C_2 + \frac{Q_2 C_1 \alpha}{Q_1 C_2}} \quad (5-17)$$

which is a Langmuir-type equation, too. Equations 5-11 and 5-17 can also be used to calculate  $q_2$  and  $q_1$  if  $B$  is the dominantly adsorbed component and  $\alpha$  is known. The ratio of  $q_1$  and  $q_2$ , that is, which component is dominantly adsorbed, may be estimated

from the initial and equilibrium concentrations of components.

If  $\alpha$  is unknown, however, we can not use the above equations for calculation.

From the mass balance, we have

$$q_1 = \frac{C_{1,0} - C_1}{M} \quad , \quad q_2 = \frac{C_{2,0} - C_2}{M} \quad (5-18)$$

where  $M$  is the carbon dosage, and  $C_{1,0}$  and  $C_{2,0}$  are the initial concentrations of components  $A$  and  $B$ , respectively. From equation 5-18, we have

$$\frac{q_1}{q_2} = \frac{C_{1,0} - C_1}{C_{2,0} - C_2} \quad (5-19)$$

Substitution of equation 5-19 into equation 5-11 leads to

$$\frac{(C_{1,0} - C_1) C_2}{(C_{2,0} - C_2) C_1} = \alpha$$

Hence, equations 5-15 and 5-17 change to:

$$q_1 = \frac{Q_1 b_1 C_1}{1 + b_1 C_1 + \frac{Q_1}{Q_2} \frac{C_{2,0} - C_2}{C_{1,0} - C_1}} \quad (5-20)$$

$$q_2 = \frac{Q_2 b_2 C_2}{1 + b_2 C_2 + \frac{Q_2}{Q_1} \frac{C_{1,0} - C_1}{C_{2,0} - C_2}} \quad (5-21)$$

In practice, we can use equations 5-19 and 5-20 or 5-19 and 5-21 for calculations of two-component adsorption equilibria. The conversion factor,  $f$ , which is incorporated in equations 5-15, 5-17, 5-20 and 5-21, can be  $Q_1 b_1 C_1 (1 + b_2 C_2) / \{Q_2 b_2 C_2 (1 + b_1 C_1)\}$ , instead of  $Q_1/Q_2$ . But this will increase the complexity of calculations, even though sometimes it may improve the prediction results. This prediction method can also be readily extended to three- or more component system.

For three-component adsorption, we have the mass balance equations 5-19 and

$$\frac{q_1}{q_3} = \frac{C_{1,0} - C_1}{C_{3,0} - C_3} \quad (5-22)$$

Assume component 1 is the dominant adsorbed component. According to the law of mass action and the mass balance, we have

$$q_1 = b_1 C_1 (Q_1 - q_1) - \frac{Q_1}{Q_2} q_2 - \frac{Q_1}{Q_3} q_3 \quad (5-23)$$

From equations 5-19, 5-22 and 5-23, we have

$$q_1 = \frac{Q_1 b_1 C_1}{1 + b_1 C_1 + \frac{Q_1}{Q_2} \frac{C_{2,0} - C_2}{C_{1,0} - C_1} + \frac{Q_1}{Q_3} \frac{C_{3,0} - C_3}{C_{1,0} - C_1}} \quad (5-24)$$

When component 1 is the dominant adsorbed component, equations 5-19, 5-22 and 5-24 can be used to calculate  $q_1$ ,  $q_2$  and  $q_3$ .

If component 2 is the dominant adsorbed component, we can use equation 5-19 and the following for calculations:

$$\frac{q_2}{q_3} = \frac{C_{2,0} - C_2}{C_{3,0} - C_3} \quad (5-25)$$

$$q_2 = \frac{Q_2 b_2 C_2}{1 + b_2 C_2 + \frac{Q_2}{Q_1} \frac{C_{1,0} - C_1}{C_{2,0} - C_2} + \frac{Q_2}{Q_3} \frac{C_{3,0} - C_3}{C_{2,0} - C_2}} \quad (5-26)$$

If component 3 is the dominant adsorbed component, equations 5-22, 5-25 and the following can be used:

$$q_3 = \frac{Q_3 b_3 C_3}{1 + b_3 C_3 + \frac{Q_3}{Q_1} \frac{C_{1,0} - C_1}{C_{3,0} - C_3} + \frac{Q_3}{Q_2} \frac{C_{2,0} - C_2}{C_{3,0} - C_3}} \quad (5-27)$$

### Modification of IAS Model

Because of the influence of non-ideal competition and irreversibility of multicomponent adsorption, the spreading pressures of the components may not be equal. To take this into account, we multiply either side of the spreading pressure equivalence equation by a factor  $F$  for the two component system:

$$F \int_0^{C_1^0} q_1^0 \frac{dC_1^0}{C_1^0} = \int_0^{C_2^0} q_2^0 \frac{dC_2^0}{C_2^0} \quad (5-28)$$

where  $C_i^0$  is the liquid-phase concentration of species  $i$  in single-component systems which gives the same spreading pressure as that of the mixture and  $q_i^0$ , the solid-phase loading corresponding to  $C_i^0$ .

If the relations between  $q_i$  and  $C_i$  can be expressed by the Langmuir isotherm, i.e.,  $q_1 = Q_1 b_1 C_1 / (1 + b_1 C_1)$  and  $q_2 = Q_2 b_2 C_2 / (1 + b_2 C_2)$ , integration of equation 5-28 gives

$$F Q_1 \ln(1 + b_1 C_1^0) = Q_2 \ln(1 + b_2 C_2^0) \quad (5-29)$$

$F$  can be determined by testing whether equation 5-11,  $q_1 C_2 / (q_2 C_1) = \alpha$ , if  $\alpha$  is known, or equation 5-19,  $q_1 / q_2 = (C_{0,1} - C_1) / (C_{0,2} - C_2)$ , if  $\alpha$  is unknown, is satisfied.

The other equations required for calculation are

$$C_i(\Pi, T, Z_i) = Z_i C_i^0(\Pi, T) \quad (2-13)$$

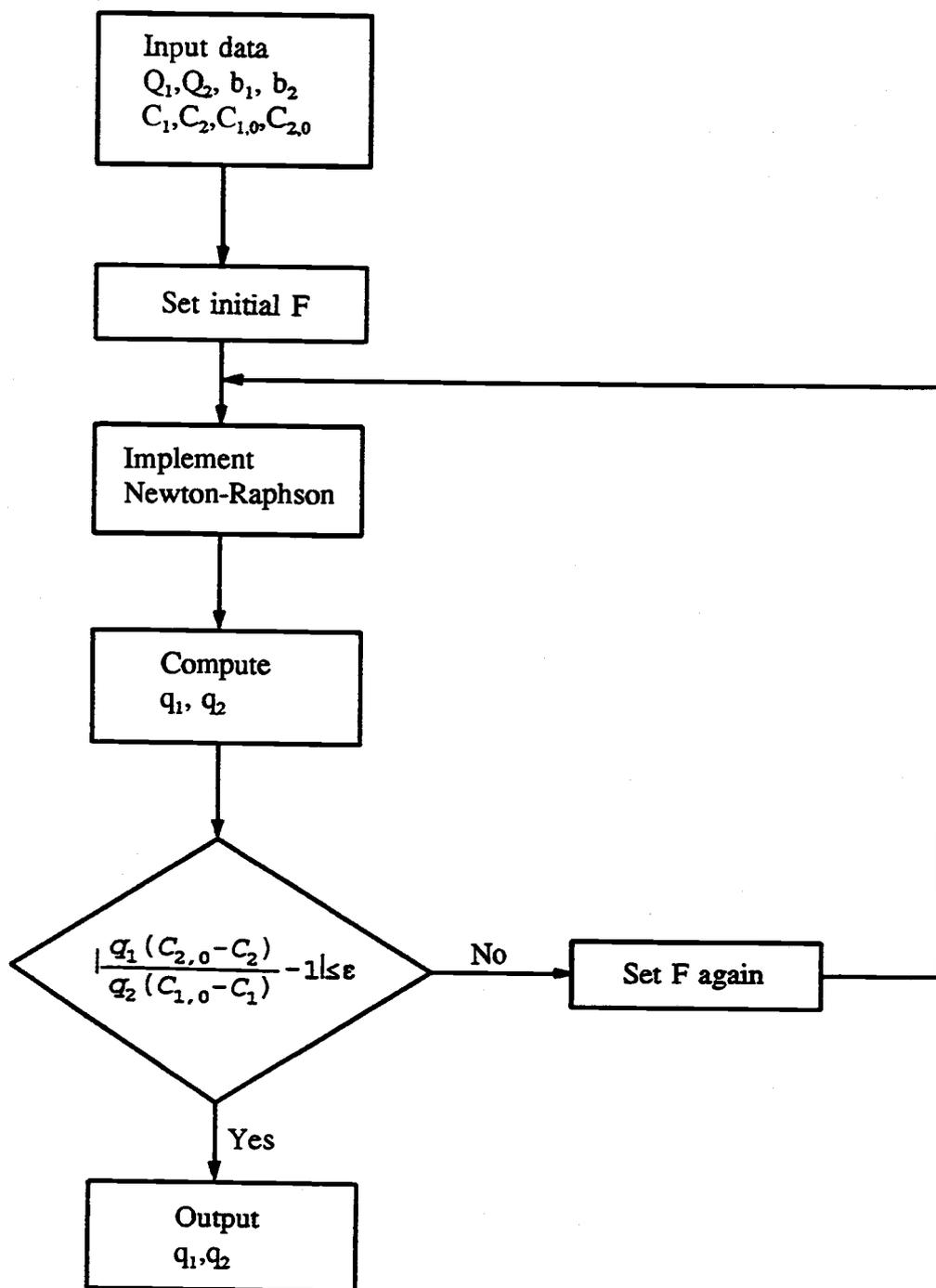


Figure 5.1 Flow diagram of computations for modified IAS model

$$\frac{1}{Q_T} = \sum_1^n \frac{Z_i}{Q_i^0} \quad (2-18)$$

$$\sum_1^n Z_i = 1 \quad (2-19)$$

$$Q_i = Z_i Q_T \quad (2-20)$$

This modified IAS method can be solved by implementing a Newton-Raphson algorithm. The flow diagram of the computation is given in Figure 5-1. It can also be extended to three- or more component system, but the complexity of computations may increase considerably.

## Results and Discussion

***Multicomponent Adsorption Equilibria at pH 7.*** Two-component adsorption equilibrium data for PCP/2,4,6-TCP, 2,4,6-TCP/2,4-DCP and 2,4-DCP/4-CP systems of different initial concentration ratios, together with the prediction results of the various models, are given in Tables 5.1, 5.2 and 5.3, respectively. Typical experimental data and prediction results of various models are also shown in Figures 5.2 - 5.5. To reduce systematic errors, single-component Langmuir isotherms were measured each time two-component adsorption was conducted for each system, and only data within the

concentration range from which most two-component adsorption equilibrium data are obtained were used for extraction of the isotherms constants. The data in Table 5.1 and 5.2 show that the predictions of the Langmuir competitive and IAS models are close to each other, and except for 2,4,6-TCP of case 1 (with  $C_{0,TCP} = 0.822$  mmol/l and  $C_{0,DCP} = 0.247$  mmol/l) in Table 5.2, for which both are close to the experimental values with sums of relative deviations of 73.3% and 81.1%, respectively, both deviate from the experimental values to relatively large extents. The predictions of 2,4,6-TCP adsorption from the PCP/2,4,6-TCP and 2,4,6-TCP/2,4-DCP systems are always higher than the respective observed values, and those of PCP and 2,4-DCP adsorption from these two systems are always lower than the observed values. These facts imply that the Langmuir competitive and IAS models predict that the adsorbate more favorably adsorbed in single-component solutions also adsorbs to a greater extent when in competition with another compound. But this is true only when adsorption is reversible and competition for adsorption sites is ideal. The ideal competition implies that the adsorbent is homogeneous with respect to adsorption sites and that the sites are equally accessible. However, activated carbon cannot be considered homogeneous because of its extensive microporous structure and the occurrence of different functional groups on the activated carbon surface. An ideal competition assumption, therefore, is invalid. Many researchers (Grant and King, 1990; Yonge et al., 1985; Snoeyink et al., 1969) have also shown that the adsorption of some compounds, such as phenolics, are highly irreversible. Our experimental results of adsorption and desorption equilibria for the four compounds revealed that PCP and 2,4,6-TCP are adsorbed on activated carbon much more irreversibly than 2,4-DCP and 4-CP.

This may explain why the Langmuir competitive and IAS models failed to accurately predict solid-phase loadings in PCP/2,4,6-TCP and 2,4,6-TCP/2,4-DCP solutions and their predictions are significantly improved for the 2,4-DCP/4-CP system (Table 5.3).

It is noteworthy that the new method significantly improves the predictions for the PCP/2,4,6-TCP and 2,4,6-TCP/2,4-DCP systems. The relative deviations between the predicted values of the new method and the experimental values are much lower than those for the Langmuir competitive and IAS models. In all situations equilibrium adsorbate concentrations are very small compared to the initial concentrations. Since in cases 1 and 2 of Table 5.1 the initial PCP concentrations are higher than 2,4,6-TCP and a higher solid-phase loading can be expected for PCP than 2,4,6-TCP, we apply the Langmuir-type equation to PCP. For the same reason, we use the Langmuir-type equation to predict the adsorption of 2,4,6-TCP in the last case (with  $C_{0,PCP} = 0.205$  mmol/l and  $C_{0,TCP} = 0.645$  mmol/l). Similarly, for the 2,4,6-TCP/2,4-DCP system, we apply the Langmuir-type equation to 2,4,6-TCP in case 1 and to 2,4-DCP in cases 2 and 3. For most points of cases 1 and 3 in the 2,4,6-TCP/2,4-DCP system, the relative deviations are within 10%. It may be concluded from this fact that the new prediction method is the most successful in predicting the adsorption from a two-component system in which one of two components is dominantly adsorbed. It is evident that the improvements made by the new method must be attributed to the thermodynamic condition (equation 5-11) which is imposed on the two-component adsorption equilibria. Additionally, except for some situations, such as case 1 of PCP/2,4,6-TCP system, the  $\alpha$  (distribution coefficient) values are fairly constant within each case, even though they change to some extent from case

**Table 5.1 Two-Component (PCP/2,4,6-TCP) Adsorption\***

$Q_{PCP} = 1.3607 \text{ mmol/g}$      $b_{PCP} = 581.43 \text{ l/mmol}$

(Concentration range: 0.000904 - 0.01324 mmol/l)

$Q_{TCP} = 2.4035 \text{ mmol/g}$      $b_{TCP} = 1793.4 \text{ l/mmol}$

(Concentration range: 0.000276 - 0.01437 mmol/l)

Case 1.  $C_{0,PCP} = 0.580 \text{ mmol/l}$      $C_{0,TCP} = 0.138 \text{ mmol/l}$

**Pentachlorophenol**

| $C_{eq,PCP}$<br>$\mu\text{mol/l}$ | $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $q_{obsd}$<br>$\text{mmol/g}$ | Langmuir               |          | IAS Model              |          | $\alpha$ | Equation 5-20          |          | Modified IAS Model |                        |          |
|-----------------------------------|-----------------------------------|-------------------------------|------------------------|----------|------------------------|----------|----------|------------------------|----------|--------------------|------------------------|----------|
|                                   |                                   |                               | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% |          | $q$<br>$\text{mmol/g}$ | $R$<br>% | $F$                | $q$<br>$\text{mmol/g}$ | $R$<br>% |
| 0.989                             | 0.109                             | 0.392                         | 0.442                  | 12.8     | 0.417                  | 6.38     | 0.465    | 0.458                  | 16.8     | 2.302              | 0.509                  | 29.8     |
| 1.058                             | 0.135                             | 0.469                         | 0.450                  | 4.05     | 0.420                  | 10.4     | 0.539    | 0.478                  | 1.92     | 2.540              | 0.533                  | 13.6     |
| 1.297                             | 0.208                             | 0.529                         | 0.482                  | 8.88     | 0.435                  | 17.8     | 0.675    | 0.543                  | 2.65     | 2.866              | 0.598                  | 13.0     |
| 1.638                             | 0.229                             | 0.715                         | 0.548                  | 23.4     | 0.492                  | 31.2     | 0.588    | 0.621                  | 13.1     | 2.589              | 0.655                  | 8.39     |
| 1.877                             | 0.459                             | 0.804                         | 0.510                  | 36.6     | 0.416                  | 48.3     | 1.027    | 0.667                  | 17.0     | 3.437              | 0.714                  | 11.2     |
| 7.168                             | 2.067                             | 1.020                         | 0.639                  | 37.4     | 0.366                  | 64.1     | 1.215    | 1.070                  | 4.90     | 2.926              | 1.019                  | 0.00     |
| 14.47                             | 4.185                             | 1.127                         | 0.677                  | 39.9     | 0.298                  | 73.6     | 1.222    | 1.199                  | 6.39     | 2.680              | 1.103                  | 2.13     |
| sum of R, %                       |                                   |                               |                        | 163      |                        | 252      |          |                        | 62.8     |                    |                        | 78.1     |

**2,4,6-Trichlorophenol**

| $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $C_{eq,PCP}$<br>$\mu\text{mol/l}$ | $q_{obsd}$<br>$\text{mmol/g}$ | Langmuir               |          | IAS Model              |          | Equation 5-19          |          | Modified IAS Model     |          |      |
|-----------------------------------|-----------------------------------|-------------------------------|------------------------|----------|------------------------|----------|------------------------|----------|------------------------|----------|------|
|                                   |                                   |                               | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% |      |
| 0.109                             | 0.989                             | 0.093                         | 0.267                  | 187      | 0.294                  | 216      | 0.109                  | 17.2     | 0.121                  | 30.1     |      |
| 0.135                             | 1.058                             | 0.111                         | 0.315                  | 184      | 0.349                  | 214      | 0.114                  | 2.70     | 0.127                  | 14.4     |      |
| 0.208                             | 1.297                             | 0.126                         | 0.422                  | 235      | 0.479                  | 280      | 0.129                  | 2.38     | 0.143                  | 13.5     |      |
| 0.229                             | 1.638                             | 0.145                         | 0.419                  | 189      | 0.487                  | 236      | 0.148                  | 2.07     | 0.159                  | 9.66     |      |
| 0.459                             | 1.877                             | 0.191                         | 0.679                  | 255      | 0.800                  | 319      | 0.159                  | 16.8     | 0.170                  | 11.0     |      |
| 2.067                             | 7.168                             | 0.242                         | 1.004                  | 315      | 1.421                  | 487      | 0.254                  | 4.96     | 0.242                  | 0.00     |      |
| 4.185                             | 14.47                             | 0.267                         | 1.066                  | 299      | 1.678                  | 528      | 0.284                  | 6.37     | 0.261                  | 2.25     |      |
| sum of R, %                       |                                   |                               |                        | 1664     |                        | 2280     |                        | 52.5     |                        |          | 80.9 |

**Table 5.1 (continued)**

Case 2.  $C_{0,PCP} = 0.478$  mmol/l     $C_{0,TCP} = 0.276$  mmol/l

**Pentachlorophenol**

| $C_{eq,PCP}$<br>$\mu\text{mol/l}$ | $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $q_{obsd}$<br>mmol/g | Langmuir    |        |       | IAS Model   |        |          | Equation 5-20 |        | Modified IAS Model |             |        |
|-----------------------------------|-----------------------------------|----------------------|-------------|--------|-------|-------------|--------|----------|---------------|--------|--------------------|-------------|--------|
|                                   |                                   |                      | q<br>mmol/g | R<br>% |       | q<br>mmol/g | R<br>% | $\alpha$ | q<br>mmol/g   | R<br>% | F                  | q<br>mmol/g | R<br>% |
| 2.205                             | 1.735                             | 0.734                | 0.323       | 56.0   | 0.176 | 76.0        | 1.364  | 0.669    | 8.86          | 3.595  | 0.732              | 0.27        |        |
| 3.618                             | 3.237                             | 0.792                | 0.321       | 59.5   | 0.132 | 83.3        | 1.554  | 0.835    | 5.43          | 3.414  | 0.826              | 4.29        |        |
| 3.891                             | 3.412                             | 0.844                | 0.328       | 61.1   | 0.132 | 84.4        | 1.523  | 0.858    | 1.66          | 3.345  | 0.837              | 0.83        |        |
| 9.079                             | 8.426                             | 0.921                | 0.336       | 63.5   | 0.081 | 91.2        | 1.624  | 1.088    | 18.1          | 2.971  | 0.937              | 1.74        |        |
| 11.98                             | 8.932                             | 0.976                | 0.395       | 43.0   | 0.096 | 90.2        | 1.299  | 1.143    | 17.1          | 2.708  | 0.956              | 2.05        |        |
| 16.35                             | 12.71                             | 1.036                | 0.388       | 59.5   | 0.075 | 92.8        | 1.361  | 1.194    | 15.3          | 2.650  | 0.975              | 5.89        |        |
| sum of R, %                       |                                   |                      |             | 343    |       | 518         |        |          | 66.5          |        |                    | 15.1        |        |

**2,4,6-Trichlorophenol**

| $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $C_{eq,PCP}$<br>$\mu\text{mol/l}$ | $q_{obsd}$<br>mmol/g | Langmuir    |        |       | IAS Model   |        |       | Equation 5-19 |        | Modified IAS Model |        |
|-----------------------------------|-----------------------------------|----------------------|-------------|--------|-------|-------------|--------|-------|---------------|--------|--------------------|--------|
|                                   |                                   |                      | q<br>mmol/g | R<br>% |       | q<br>mmol/g | R<br>% |       | q<br>mmol/g   | R<br>% | q<br>mmol/g        | R<br>% |
| 1.735                             | 2.205                             | 0.422                | 1.387       | 229    | 1.604 | 280         |        | 0.386 | 8.53          | 0.423  | 0.24               |        |
| 3.237                             | 3.618                             | 0.455                | 1.566       | 244    | 1.863 | 309         |        | 0.481 | 5.71          | 0.476  | 4.62               |        |
| 3.412                             | 3.891                             | 0.485                | 1.568       | 223    | 1.878 | 287         |        | 0.494 | 1.86          | 0.482  | 0.62               |        |
| 8.426                             | 9.079                             | 0.522                | 1.698       | 225    | 2.124 | 307         |        | 0.622 | 19.2          | 0.536  | 2.68               |        |
| 8.932                             | 11.98                             | 0.554                | 1.605       | 190    | 2.107 | 280         |        | 0.656 | 18.4          | 0.549  | 0.90               |        |
| 12.71                             | 16.35                             | 0.586                | 1.645       | 181    | 2.178 | 272         |        | 0.682 | 16.4          | 0.557  | 5.12               |        |
| sum of R, %                       |                                   |                      |             | 1292   |       | 1735        |        |       | 70.1          |        |                    | 14.2   |

**Table 5.1 (continued)**

Case 3.  $C_{0,PCP} = 0.205$  mmol/l     $C_{0,TCP} = 0.645$  mmol/l

**Pentachlorophenol**

| $C_{eq,PCP}$<br>μmol/l | $C_{eq,TCP}$<br>μmol/l | $q_{obsd}$<br>mmol/g | Langmuir    |        | IAS Model   |        | $\alpha$ | Equation 5-19 |        | Modified IAS Model |             |        |
|------------------------|------------------------|----------------------|-------------|--------|-------------|--------|----------|---------------|--------|--------------------|-------------|--------|
|                        |                        |                      | q<br>mmol/g | R<br>% | q<br>mmol/g | R<br>% |          | q<br>mmol/g   | R<br>% | F                  | q<br>mmol/g | R<br>% |
| 0.083                  | 0.436                  | 0.270                | 0.036       | 86.7   | 0.028       | 89.6   | 1.664    | 0.255         | 5.56   | 6.853              | 0.143       | 47.0   |
| 0.136                  | 0.838                  | 0.299                | 0.042       | 86.0   | 0.028       | 90.6   | 1.946    | 0.375         | 25.4   | 6.799              | 0.202       | 32.4   |
| 0.209                  | 1.105                  | 0.331                | 0.054       | 83.7   | 0.032       | 90.3   | 1.674    | 0.427         | 29.0   | 5.557              | 0.250       | 24.5   |
| 0.248                  | 2.085                  | 0.372                | 0.040       | 89.2   | 0.018       | 95.2   | 2.668    | 0.540         | 45.2   | 6.711              | 0.283       | 23.9   |
| 0.583                  | 4.521                  | 0.387                | 0.049       | 87.3   | 0.015       | 96.1   | 2.471    | 0.643         | 66.1   | 4.956              | 0.372       | 3.88   |
| 0.887                  | 7.781                  | 0.403                | 0.045       | 88.8   | 0.010       | 97.5   | 2.807    | 0.692         | 71.7   | 4.595              | 0.408       | 1.24   |
| 1.088                  | 9.439                  | 0.429                | 0.046       | 89.3   | 0.009       | 97.9   | 2.780    | 0.706         | 64.6   | 4.339              | 0.421       | 1.86   |
| sum of R, %            |                        |                      |             | 611    |             | 657    |          |               | 308    |                    |             | 135    |

**2,4,6-Trichlorophenol**

| $C_{eq,TCP}$<br>μmol/l | $C_{eq,PCP}$<br>μmol/l | $q_{obsd}$<br>mmol/g | Langmuir    |        | IAS Model   |        | Equation 5-20 |        | Modified IAS Model |        |     |
|------------------------|------------------------|----------------------|-------------|--------|-------------|--------|---------------|--------|--------------------|--------|-----|
|                        |                        |                      | q<br>mmol/g | R<br>% | q<br>mmol/g | R<br>% | q<br>mmol/g   | R<br>% | q<br>mmol/g        | R<br>% |     |
| 0.436                  | 0.083                  | 0.850                | 1.027       | 20.8   | 1.036       | 21.9   | 0.802         | 5.65   | 0.451              | 46.9   |     |
| 0.838                  | 0.136                  | 0.940                | 1.399       | 48.8   | 1.418       | 50.9   | 1.179         | 25.4   | 0.637              | 32.2   |     |
| 1.105                  | 0.209                  | 1.042                | 1.535       | 47.3   | 1.564       | 50.1   | 1.344         | 29.0   | 0.786              | 24.6   |     |
| 2.085                  | 0.248                  | 1.168                | 1.840       | 57.5   | 1.873       | 60.4   | 1.695         | 45.1   | 0.889              | 23.9   |     |
| 4.521                  | 0.583                  | 1.213                | 2.063       | 70.1   | 2.118       | 74.6   | 2.015         | 66.1   | 1.168              | 3.71   |     |
| 7.781                  | 0.887                  | 1.261                | 2.168       | 71.9   | 2.227       | 76.6   | 2.161         | 71.4   | 1.275              | 1.11   |     |
| 9.439                  | 1.088                  | 1.337                | 2.192       | 63.9   | 2.255       | 68.7   | 2.200         | 64.5   | 1.315              | 1.65   |     |
| sum of R, %            |                        |                      |             | 380    |             | 403    |               | 307    |                    |        | 134 |

\*  $C_{eq}$  = equilibrium concentration,  $C_0$  = initial concentration,  $q_{obsd}$  = observed amount adsorbed, Langmuir = Langmuir Competitive Model (equation 2-9), R = relative deviation ( $|q_{obsd} - q_{pred}|/q_{obsd}$ ),  $\alpha$  = distribution coefficient ( $q_{PCP}C_{TCP}/(q_{TCP}C_{PCP})$ ), F = Modified factor (on the PCP side of equation 5-22)

**Table 5.2 Two-Component (2,4,6-TCP/2,4-DCP) Adsorption\***

$Q_{TCP} = 2.1079 \text{ mmol/g}$      $b_{TCP} = 2564.4 \text{ l/mmol}$

(Concentration range: 0.000143 - 0.00838 mmol/l)

$Q_{DCP} = 1.8959 \text{ mmol/g}$      $b_{DCP} = 2313.4 \text{ l/mmol}$

(Concentration range: 0.000371 - 0.00873 mmol/l)

Case 1.  $C_{0,TCP} = 0.822 \text{ mmol/l}$      $C_{0,DCP} = 0.247 \text{ mmol/l}$

**2,4,6-Trichlorophenol**

| $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $C_{eq,DCP}$<br>$\mu\text{mol/l}$ | $q_{obsd}$<br>$\text{mmol/g}$ | Langmuir               |             | IAS Model              |             | $\alpha$ | Equation 5-20          |             | Modified IAS Model     |             |
|-----------------------------------|-----------------------------------|-------------------------------|------------------------|-------------|------------------------|-------------|----------|------------------------|-------------|------------------------|-------------|
|                                   |                                   |                               | $q$<br>$\text{mmol/g}$ | $R$<br>$\%$ | $q$<br>$\text{mmol/g}$ | $R$<br>$\%$ |          | $q$<br>$\text{mmol/g}$ | $R$<br>$\%$ | $q$<br>$\text{mmol/g}$ | $R$<br>$\%$ |
| 0.243                             | 0.043                             | 0.652                         | 0.762                  | 16.9        | 0.766                  | 17.5        | 0.600    | 0.671                  | 2.97        | 0.630                  | 3.29        |
| 0.426                             | 0.045                             | 0.782                         | 1.048                  | 33.9        | 1.053                  | 34.6        | 0.358    | 0.949                  | 21.3        | 0.758                  | 3.07        |
| 1.129                             | 0.114                             | 1.379                         | 1.467                  | 6.43        | 1.478                  | 7.23        | 0.336    | 1.443                  | 4.67        | 1.113                  | 19.3        |
| 1.300                             | 0.129                             | 1.498                         | 1.517                  | 1.23        | 1.529                  | 2.08        | 0.331    | 1.505                  | 0.48        | 1.155                  | 22.9        |
| 1.962                             | 0.185                             | 1.561                         | 1.642                  | 5.15        | 1.658                  | 6.17        | 0.313    | 1.666                  | 6.70        | 1.263                  | 19.1        |
| 2.318                             | 0.194                             | 1.647                         | 1.694                  | 2.91        | 1.711                  | 3.90        | 0.279    | 1.721                  | 4.53        | 1.288                  | 21.8        |
| 4.310                             | 0.377                             | 1.730                         | 1.802                  | 4.19        | 1.826                  | 5.57        | 0.290    | 1.881                  | 8.71        | 1.410                  | 18.5        |
| 5.503                             | 0.495                             | 1.784                         | 1.830                  | 2.56        | 1.857                  | 4.09        | 0.298    | 1.926                  | 7.94        | 1.445                  | 19.0        |
| sum of R, %                       |                                   |                               |                        | 73.3        |                        | 81.1        |          |                        | 57.3        |                        | 127         |

**2,4-Dichlorophenol**

| $C_{eq,DCP}$<br>$\mu\text{mol/l}$ | $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $q_{obsd}$<br>$\text{mmol/g}$ | Langmuir               |             | IAS Model              |             | Equation 5-19          |             | Modified IAS Model |                        |             |
|-----------------------------------|-----------------------------------|-------------------------------|------------------------|-------------|------------------------|-------------|------------------------|-------------|--------------------|------------------------|-------------|
|                                   |                                   |                               | $q$<br>$\text{mmol/g}$ | $R$<br>$\%$ | $q$<br>$\text{mmol/g}$ | $R$<br>$\%$ | $q$<br>$\text{mmol/g}$ | $R$<br>$\%$ | F                  | $q$<br>$\text{mmol/g}$ | $R$<br>$\%$ |
| 0.043                             | 0.243                             | 0.196                         | 0.112                  | 43.0        | 0.106                  | 45.7        | 0.202                  | 3.08        | 1.844              | 0.190                  | 3.25        |
| 0.045                             | 0.426                             | 0.235                         | 0.092                  | 61.1        | 0.086                  | 63.5        | 0.286                  | 21.3        | 2.644              | 0.228                  | 3.14        |
| 0.114                             | 1.129                             | 0.415                         | 0.121                  | 71.0        | 0.110                  | 73.6        | 0.435                  | 4.63        | 2.282              | 0.335                  | 19.3        |
| 0.129                             | 1.300                             | 0.451                         | 0.123                  | 72.8        | 0.111                  | 75.5        | 0.453                  | 0.46        | 2.247              | 0.348                  | 23.0        |
| 0.185                             | 1.962                             | 0.470                         | 0.126                  | 73.3        | 0.111                  | 76.4        | 0.502                  | 6.78        | 2.146              | 0.380                  | 19.1        |
| 0.194                             | 2.318                             | 0.497                         | 0.115                  | 76.8        | 0.100                  | 79.8        | 0.518                  | 4.47        | 2.236              | 0.388                  | 21.9        |
| 0.377                             | 4.310                             | 0.522                         | 0.128                  | 75.5        | 0.106                  | 79.7        | 0.568                  | 8.77        | 1.948              | 0.426                  | 18.4        |
| 0.495                             | 5.503                             | 0.539                         | 0.134                  | 75.2        | 0.109                  | 79.9        | 0.582                  | 7.95        | 1.851              | 0.437                  | 19.0        |
| sum of R, %                       |                                   |                               |                        | 549         |                        | 574         |                        | 57.5        |                    |                        | 127         |

**Table 5.2 (continued)**

Case 2.  $C_{0,TCP} = 0.513$  mmol/l     $C_{0,DCP} = 0.618$  mmol/l

**2,4,6-Trichlorophenol**

| $C_{eq,TCP}$<br>μmol/l | $C_{eq,DCP}$<br>μmol/l | $q_{obsd}$<br>mmol/g | Langmuir      |        | IAS Model     |        | $\alpha$ | Equation 5-19 |        | Modified IAS Model |        |
|------------------------|------------------------|----------------------|---------------|--------|---------------|--------|----------|---------------|--------|--------------------|--------|
|                        |                        |                      | $q$<br>mmol/g | R<br>% | $q$<br>mmol/g | R<br>% |          | $q$<br>mmol/g | R<br>% | $q$<br>mmol/g      | R<br>% |
| 0.852                  | 0.467                  | 0.770                | 1.079         | 40.1   | 1.113         | 44.4   | 0.455    | 0.602         | 21.9   | 0.653              | 15.2   |
| 3.414                  | 1.445                  | 0.887                | 1.409         | 58.9   | 1.481         | 66.9   | 0.350    | 1.030         | 16.2   | 0.806              | 9.16   |
| 3.974                  | 1.504                  | 0.979                | 1.464         | 49.5   | 1.536         | 56.8   | 0.313    | 1.043         | 6.52   | 0.810              | 17.3   |
| 6.087                  | 2.206                  | 1.025                | 1.515         | 47.9   | 1.600         | 56.2   | 0.298    | 1.164         | 13.6   | 0.835              | 18.5   |
| 9.545                  | 3.463                  | 1.078                | 1.541         | 43.0   | 1.641         | 52.3   | 0.297    | 1.277         | 18.5   | 0.854              | 20.8   |
| sum of R, %            |                        |                      |               | 239    | 277           |        |          | 76.6          |        | 80.9               |        |

**2,4-Dichlorophenol**

| $C_{eq,DCP}$<br>μmol/l | $C_{eq,TCP}$<br>μmol/l | $q_{obsd}$<br>mmol/g | Langmuir      |        | IAS Model     |        | Equation 5-20 |        | Modified IAS Model |               |        |
|------------------------|------------------------|----------------------|---------------|--------|---------------|--------|---------------|--------|--------------------|---------------|--------|
|                        |                        |                      | $q$<br>mmol/g | R<br>% | $q$<br>mmol/g | R<br>% | $q$<br>mmol/g | R<br>% | F                  | $q$<br>mmol/g | R<br>% |
| 0.467                  | 0.852                  | 0.929                | 0.481         | 48.3   | 0.449         | 51.7   | 0.725         | 21.9   | 1.795              | 0.788         | 15.2   |
| 1.445                  | 3.414                  | 1.073                | 0.484         | 54.9   | 0.418         | 61.0   | 1.246         | 16.2   | 1.708              | 0.974         | 9.16   |
| 1.504                  | 3.974                  | 1.186                | 0.450         | 62.1   | 0.384         | 67.7   | 1.263         | 6.48   | 1.760              | 0.981         | 17.3   |
| 2.206                  | 6.087                  | 1.245                | 0.446         | 64.2   | 0.368         | 70.4   | 1.414         | 13.6   | 1.702              | 1.014         | 18.5   |
| 3.463                  | 9.545                  | 1.315                | 0.454         | 65.5   | 0.362         | 72.5   | 1.558         | 18.5   | 1.625              | 1.042         | 20.8   |
| sum of R, %            |                        |                      |               | 295    | 323           |        |               | 76.6   |                    | 81.0          |        |

**Table 5.2 (continued)**

Case 3.  $C_{0,TCP} = 0.206$  mmol/l  $C_{0,DCP} = 0.989$  mmol/l

**2,4,6-Trichlorophenol**

| $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $C_{eq,DCP}$<br>$\mu\text{mol/l}$ | $q_{obsd}$<br>mmol/g | Langmuir    |        |             | IAS Model |             | $\alpha$ | Equation 5-19 |             | Modified IAS Model |  |
|-----------------------------------|-----------------------------------|----------------------|-------------|--------|-------------|-----------|-------------|----------|---------------|-------------|--------------------|--|
|                                   |                                   |                      | q<br>mmol/g | R<br>% | q<br>mmol/g | R<br>%    | q<br>mmol/g |          | R<br>%        | q<br>mmol/g | R<br>%             |  |
| 0.101                             | 0.448                             | 0.191                | 0.239       | 25.3   | 0.247       | 29.4      | 0.916       | 0.184    | 3.73          | 0.187       | 2.21               |  |
| 0.108                             | 0.579                             | 0.235                | 0.224       | 4.75   | 0.234       | 0.65      | 1.109       | 0.209    | 11.2          | 0.205       | 12.8               |  |
| 0.203                             | 1.091                             | 0.270                | 0.271       | 0.39   | 0.291       | 7.77      | 1.117       | 0.268    | 0.87          | 0.250       | 7.51               |  |
| 0.450                             | 2.129                             | 0.306                | 0.344       | 12.5   | 0.381       | 24.6      | 0.981       | 0.317    | 3.77          | 0.285       | 6.82               |  |
| 0.793                             | 3.504                             | 0.345                | 0.385       | 11.5   | 0.439       | 27.1      | 0.917       | 0.343    | 0.54          | 0.302       | 12.7               |  |
| 1.870                             | 7.138                             | 0.381                | 0.453       | 19.0   | 0.539       | 41.5      | 0.791       | 0.367    | 3.70          | 0.316       | 17.0               |  |
| 2.444                             | 9.026                             | 0.402                | 0.469       | 16.7   | 0.566       | 40.8      | 0.765       | 0.372    | 7.62          | 0.319       | 20.7               |  |
| sum of R, %                       |                                   |                      |             | 90.1   |             | 172       |             |          | 31.4          |             | 79.7               |  |

**2,4-Dichlorophenol**

| $C_{eq,DCP}$<br>$\mu\text{mol/l}$ | $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $q_{obsd}$<br>mmol/g | Langmuir    |        |             | IAS Model |             | Equation 5-20 |       | Modified IAS Model |        |  |
|-----------------------------------|-----------------------------------|----------------------|-------------|--------|-------------|-----------|-------------|---------------|-------|--------------------|--------|--|
|                                   |                                   |                      | q<br>mmol/g | R<br>% | q<br>mmol/g | R<br>%    | q<br>mmol/g | R<br>%        | F     | q<br>mmol/g        | R<br>% |  |
| 0.448                             | 0.101                             | 0.920                | 0.856       | 6.90   | 0.847       | 7.90      | 0.885       | 3.80          | 1.258 | 0.899              | 2.30   |  |
| 0.579                             | 0.108                             | 1.133                | 0.971       | 14.3   | 0.960       | 15.3      | 1.006       | 11.2          | 1.108 | 0.987              | 12.9   |  |
| 1.091                             | 0.203                             | 1.300                | 1.183       | 9.00   | 1.164       | 10.5      | 1.290       | 0.82          | 1.107 | 1.202              | 7.54   |  |
| 2.129                             | 0.450                             | 1.474                | 1.319       | 10.5   | 1.284       | 12.9      | 1.528       | 3.67          | 1.171 | 1.371              | 6.98   |  |
| 3.504                             | 0.793                             | 1.664                | 1.379       | 17.1   | 1.330       | 20.1      | 1.654       | 0.60          | 1.193 | 1.453              | 12.7   |  |
| 7.138                             | 1.870                             | 1.836                | 1.403       | 23.6   | 1.325       | 27.8      | 1.769       | 3.66          | 1.230 | 1.525              | 16.9   |  |
| 9.026                             | 2.444                             | 1.941                | 1.406       | 27.5   | 1.318       | 32.1      | 1.794       | 7.57          | 1.234 | 1.540              | 20.7   |  |
| sum of R, %                       |                                   |                      |             | 109    |             | 127       |             | 31.4          |       | 80.0               |        |  |

\*  $C_{eq}$  = equilibrium concentration,  $C_0$  = initial concentration,  $q_{obsd}$  = observed amount adsorbed, Langmuir = Langmuir Competitive Model (equation 2-9), R = relative deviation ( $|q_{obsd} - q_{pred}|/q_{obsd}$ ),  $\alpha$  = distribution coefficient ( $q_{TCP}C_{DCP}/(q_{DCP}C_{TCP})$ ), F = Modified factor (on the DCP side of equation 5-22)

**Table 5.3 Two-Component (2,4-DCP/4-CP) Adsorption<sup>a</sup>**

$Q_{DCP} = 1.9640 \text{ mmol/g}$       $b_{DCP} = 1898.01 \text{ l/mmol}$

(Concentration range: 0.000371 - 0.0155 mmol/l)

$Q_{CP} = 2.0677 \text{ mmol/g}$       $b_{CP} = 191.67 \text{ l/mmol}$

(Concentration range: 0.00206 - 0.0725 mmol/l)

Case 1.  $C_{0,DCP} = 0.740 \text{ mmol/l}$       $C_{0,CP} = 0.248 \text{ mmol/l}$

**2,4-Dichlorophenol**

| $C_{eq,DCP}$<br>μmol/l | $C_{eq,CP}$<br>μmol/l | $q_{obsd}$<br>mmol/g | Langmuir    |        | IAS Model   |        | $\alpha$ | Equation 5-20 |        | Modified IAS Model |             |        |
|------------------------|-----------------------|----------------------|-------------|--------|-------------|--------|----------|---------------|--------|--------------------|-------------|--------|
|                        |                       |                      | q<br>mmol/g | R<br>% | q<br>mmol/g | R<br>% |          | q<br>mmol/g   | R<br>% | F                  | q<br>mmol/g | R<br>% |
| 0.802                  | 3.403                 | 1.048                | 0.942       | 10.1   | 0.932       | 11.1   | 12.84    | 1.054         | 0.58   | 1.224              | 1.019       | 2.82   |
| 1.256                  | 5.161                 | 1.206                | 1.071       | 11.2   | 1.056       | 12.4   | 12.52    | 1.267         | 5.08   | 1.186              | 1.151       | 4.52   |
| 3.020                  | 11.71                 | 1.397                | 1.254       | 10.2   | 1.227       | 12.1   | 12.10    | 1.600         | 14.5   | 1.140              | 1.337       | 4.32   |
| 6.784                  | 23.27                 | 1.629                | 1.379       | 15.3   | 1.341       | 17.7   | 11.21    | 1.785         | 9.59   | 1.095              | 1.438       | 11.7   |
| 13.86                  | 41.84                 | 1.827                | 1.463       | 19.9   | 1.415       | 22.5   | 10.65    | 1.874         | 2.58   | 1.073              | 1.503       | 17.7   |
| sum of R, %            |                       |                      |             | 66.7   | 75.8        |        |          | 32.3          | 41.1   |                    |             |        |

**4-Chlorophenol**

| $C_{eq,CP}$<br>μmol/l | $C_{eq,DCP}$<br>μmol/l | $q_{obsd}$<br>mmol/g | Langmuir    |        | IAS Model   |        | Equation 5-19 |        | Modified IAS Model |        |
|-----------------------|------------------------|----------------------|-------------|--------|-------------|--------|---------------|--------|--------------------|--------|
|                       |                        |                      | q<br>mmol/g | R<br>% | q<br>mmol/g | R<br>% | q<br>mmol/g   | R<br>% | q<br>mmol/g        | R<br>% |
| 3.403                 | 0.802                  | 0.346                | 0.425       | 22.6   | 0.435       | 25.7   | 0.348         | 0.60   | 0.337              | 2.65   |
| 5.161                 | 1.256                  | 0.396                | 0.468       | 18.2   | 0.483       | 22.0   | 0.416         | 5.12   | 0.379              | 4.33   |
| 11.71                 | 3.020                  | 0.447                | 0.517       | 15.5   | 0.545       | 21.8   | 0.512         | 14.5   | 0.428              | 4.26   |
| 23.27                 | 6.784                  | 0.498                | 0.503       | 0.91   | 0.543       | 8.98   | 0.546         | 9.66   | 0.440              | 11.6   |
| 41.84                 | 13.86                  | 0.518                | 0.469       | 9.36   | 0.520       | 0.35   | 0.531         | 2.59   | 0.427              | 17.5   |
| sum of R, %           |                        |                      |             | 66.6   | 78.8        |        |               | 32.5   | 40.3               |        |

**Table 5.3 (continued)**

Case 2.  $C_{0,DCP} = 0.493$  mmol/l     $C_{0,CP} = 0.495$  mmol/l

**2,4-Dichlorophenol**

| $C_{eq,DCP}$<br>μmol/l | $C_{eq,CP}$<br>μmol/l | $Q_{obsd}$<br>mmol/g | Langmuir    |        | IAS Model   |        | $\alpha$ | Equation 5-20 |        | Modified IAS Model |             |        |
|------------------------|-----------------------|----------------------|-------------|--------|-------------|--------|----------|---------------|--------|--------------------|-------------|--------|
|                        |                       |                      | q<br>mmol/g | R<br>% | q<br>mmol/g | R<br>% |          | q<br>mmol/g   | R<br>% | F                  | q<br>mmol/g | R<br>% |
| 0.405                  | 3.875                 | 0.646                | 0.602       | 6.79   | 0.594       | 8.04   | 9.586    | 0.557         | 13.7   | 1.029              | 0.607       | 6.02   |
| 0.896                  | 8.678                 | 0.819                | 0.766       | 6.50   | 0.748       | 8.68   | 9.806    | 0.919         | 12.2   | 1.046              | 0.781       | 4.68   |
| 1.374                  | 12.87                 | 0.909                | 0.844       | 7.23   | 0.819       | 9.93   | 9.555    | 1.129         | 24.2   | 1.034              | 0.849       | 6.63   |
| 3.864                  | 33.81                 | 1.112                | 0.972       | 12.6   | 0.928       | 16.6   | 9.295    | 1.561         | 40.3   | 1.030              | 0.967       | 13.1   |
| 7.020                  | 61.87                 | 1.249                | 1.000       | 19.9   | 0.941       | 24.6   | 9.904    | 1.725         | 38.2   | 1.053              | 1.024       | 18.0   |
| sum of R, %            |                       |                      |             | 50.0   |             | 67.9   |          |               | 129    |                    |             | 48.4   |

**4-Chlorophenol**

| $C_{eq,CP}$<br>μmol/l | $C_{eq,DCP}$<br>μmol/l | $Q_{obsd}$<br>mmol/g | Langmuir    |        | IAS Model   |        | Equation 5-19 |        | Modified IAS Model |        |      |
|-----------------------|------------------------|----------------------|-------------|--------|-------------|--------|---------------|--------|--------------------|--------|------|
|                       |                        |                      | q<br>mmol/g | R<br>% | q<br>mmol/g | R<br>% | q<br>mmol/g   | R<br>% | q<br>mmol/g        | R<br>% |      |
| 3.875                 | 0.405                  | 0.643                | 0.611       | 5.02   | 0.619       | 3.73   | 0.555         | 13.8   | 0.606              | 5.81   |      |
| 8.678                 | 0.896                  | 0.808                | 0.788       | 2.55   | 0.806       | 0.27   | 0.907         | 12.1   | 0.772              | 4.49   |      |
| 12.87                 | 1.374                  | 0.891                | 0.839       | 5.79   | 0.865       | 2.93   | 1.106         | 24.1   | 0.834              | 6.41   |      |
| 33.81                 | 3.864                  | 1.047                | 0.904       | 13.6   | 0.951       | 9.19   | 1.470         | 40.3   | 0.910              | 13.1   |      |
| 61.87                 | 7.020                  | 1.111                | 0.936       | 15.7   | 0.997       | 10.2   | 1.535         | 38.2   | 0.911              | 18.0   |      |
| sum of R, %           |                        |                      |             | 42.7   |             | 26.3   |               | 129    |                    |        | 47.8 |

**Table 5.3 (continued)**

Case 3.  $C_{0,DCP} = 0.239$  mmol/l  $C_{0,CP} = 0.750$  mmol/l

2,4-Dichlorophenol

| $C_{eq,DCP}$<br>μmol/l | $C_{eq,CP}$<br>μmol/l | $q_{obsd}$<br>mmol/g | Langmuir      |        | IAS Model     |        | $\alpha$ | Equation 5-19 |        | Modified IAS Model |               |        |
|------------------------|-----------------------|----------------------|---------------|--------|---------------|--------|----------|---------------|--------|--------------------|---------------|--------|
|                        |                       |                      | $q$<br>mmol/g | R<br>% | $q$<br>mmol/g | R<br>% |          | $q$<br>mmol/g | R<br>% | F                  | $q$<br>mmol/g | R<br>% |
| 0.251                  | 7.855                 | 0.318                | 0.315         | 1.01   | 0.307         | 3.49   | 10.03    | 0.352         | 10.7   | 1.059              | 0.330         | 3.71   |
| 0.672                  | 20.50                 | 0.459                | 0.404         | 12.0   | 0.386         | 15.9   | 9.967    | 0.503         | 9.59   | 1.054              | 0.421         | 8.28   |
| 1.209                  | 34.34                 | 0.518                | 0.457         | 11.8   | 0.430         | 17.0   | 9.439    | 0.570         | 10.0   | 1.033              | 0.457         | 11.7   |
| 3.020                  | 64.94                 | 0.570                | 0.587         | 2.98   | 0.544         | 4.56   | 7.410    | 0.642         | 12.6   | 0.961              | 0.495         | 13.2   |
| sum of R, %            |                       |                      |               | 27.8   | 41.0          |        |          | 42.9          |        | 36.9               |               |        |

4-Chlorophenol

| $C_{eq,CP}$<br>μmol/l | $C_{eq,DCP}$<br>μmol/l | $q_{obsd}$<br>mmol/g | Langmuir      |        | IAS Model     |        | Equation 5-20 |        | Modified IAS Model |        |
|-----------------------|------------------------|----------------------|---------------|--------|---------------|--------|---------------|--------|--------------------|--------|
|                       |                        |                      | $q$<br>mmol/g | R<br>% | $q$<br>mmol/g | R<br>% | $q$<br>mmol/g | R<br>% | $q$<br>mmol/g      | R<br>% |
| 7.855                 | 0.251                  | 0.989                | 1.043         | 5.49   | 1.052         | 6.32   | 1.094         | 10.7   | 1.028              | 3.89   |
| 20.50                 | 0.672                  | 1.403                | 1.309         | 6.70   | 1.328         | 5.35   | 1.541         | 9.84   | 1.292              | 7.91   |
| 34.34                 | 1.209                  | 1.558                | 1.378         | 11.6   | 1.406         | 9.76   | 1.716         | 10.1   | 1.377              | 11.6   |
| 64.94                 | 3.020                  | 1.655                | 1.342         | 18.9   | 1.387         | 16.2   | 1.864         | 12.6   | 1.437              | 13.2   |
| sum of R, %           |                        |                      |               | 42.7   | 37.6          |        | 43.2          |        | 36.6               |        |

\*  $C_{eq}$  = equilibrium concentration,  $C_0$  = initial concentration,  $q_{obsd}$  = observed amount adsorbed, Langmuir = Langmuir Competitive Model (equation 2-9), R = relative deviation ( $|q_{obsd} - q_{pred}|/q_{obsd}$ ),  $\alpha$  = distribution coefficient ( $q_{DCP}C_{CP}/(q_{CP}C_{DCP})$ ), F = modified factor (on the DCP side of equation 5-20)

**Table 5.4 Three-Component (2,4,6-TCP/2,4-DCP/4-CP) Adsorption<sup>a</sup>**

$Q_{TCP} = 2.1079 \text{ mmol/g}$      $b_{TCP} = 2564.4 \text{ l/mmol}$     (Concentration range: 0.000143 - 0.00838 mmol/l)  
 $Q_{DCP} = 1.8959 \text{ mmol/g}$      $b_{DCP} = 2313.4 \text{ l/mmol}$     (Concentration range: 0.000371 - 0.00873 mmol/l)  
 $Q_{CP} = 2.0677 \text{ mmol/g}$      $b_{CP} = 191.67 \text{ l/mmol}$     (Concentration range: 0.00206 - 0.0725 mmol/l)

Case 1.  $C_{0,TCP} = 0.165 \text{ mmol/l}$      $C_{0,DCP} = 0.615 \text{ mmol/l}$      $C_{0,CP} = 0.257 \text{ mmol/l}$

2,4,6-Trichlorophenol

| $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $C_{eq,DCP}$<br>$\mu\text{mol/l}$ | $C_{eq,CP}$<br>$\mu\text{mol/l}$ | $Q_{obsd}$<br>$\text{mmol/g}$ | Langmuir               |          | IAS Model              |          | Equation 5-19          |          |
|-----------------------------------|-----------------------------------|----------------------------------|-------------------------------|------------------------|----------|------------------------|----------|------------------------|----------|
|                                   |                                   |                                  |                               | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% |
| 0.147                             | 0.506                             | 1.401                            | 0.215                         | 0.282                  | 31.1     | 0.294                  | 36.7     | 0.213                  | 0.94     |
| 0.304                             | 0.871                             | 2.669                            | 0.251                         | 0.382                  | 52.0     | 0.404                  | 61.0     | 0.281                  | 12.0     |
| 1.043                             | 2.927                             | 12.06                            | 0.327                         | 0.442                  | 35.1     | 0.493                  | 50.8     | 0.409                  | 25.1     |
| 2.107                             | 5.682                             | 24.51                            | 0.359                         | 0.470                  | 30.8     | 0.540                  | 50.4     | 0.451                  | 25.5     |
| sum of R, %                       |                                   |                                  |                               |                        |          | 149                    | 198.9    | 63.5                   |          |

2,4-Dichlorophenol

| $C_{eq,DCP}$<br>$\mu\text{mol/l}$ | $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $C_{eq,CP}$<br>$\mu\text{mol/l}$ | $Q_{obsd}$<br>$\text{mmol/g}$ | Langmuir               |          | IAS Model              |          | Equation 5-26          |          |
|-----------------------------------|-----------------------------------|----------------------------------|-------------------------------|------------------------|----------|------------------------|----------|------------------------|----------|
|                                   |                                   |                                  |                               | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% |
| 0.506                             | 0.147                             | 1.401                            | 0.804                         | 0.788                  | 1.92     | 0.771                  | 4.10     | 0.795                  | 1.12     |
| 0.871                             | 0.304                             | 2.669                            | 0.938                         | 0.887                  | 5.41     | 0.856                  | 8.74     | 1.051                  | 12.0     |
| 2.927                             | 1.043                             | 12.06                            | 1.225                         | 1.006                  | 17.8     | 0.933                  | 23.8     | 1.532                  | 25.1     |
| 5.682                             | 2.107                             | 24.51                            | 1.347                         | 1.028                  | 23.7     | 0.926                  | 31.3     | 1.691                  | 25.5     |
| sum of R, %                       |                                   |                                  |                               |                        |          | 48.8                   | 67.9     | 63.7                   |          |

Table 5.4 (continued)

4-Chlorophenol

| $C_{eq,CP}$<br>$\mu\text{mol/l}$ | $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $C_{eq,DCP}$<br>$\mu\text{mol/l}$ | $Q_{obsd}$<br>$\text{mmol/g}$ | Langmuir               |          | IAS Model              |          | Equation 5-25          |          |
|----------------------------------|-----------------------------------|-----------------------------------|-------------------------------|------------------------|----------|------------------------|----------|------------------------|----------|
|                                  |                                   |                                   |                               | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% |
| 1.401                            | 0.147                             | 0.506                             | 0.334                         | 0.197                  | 41.1     | 0.203                  | 39.2     | 0.331                  | 0.90     |
| 2.669                            | 0.304                             | 0.871                             | 0.388                         | 0.246                  | 36.8     | 0.256                  | 34.0     | 0.435                  | 12.0     |
| 12.06                            | 1.043                             | 2.927                             | 0.490                         | 0.375                  | 23.6     | 0.403                  | 17.8     | 0.613                  | 25.1     |
| 24.51                            | 2.107                             | 5.682                             | 0.514                         | 0.401                  | 22.1     | 0.441                  | 14.2     | 0.645                  | 25.5     |
| sum of R, %                      |                                   |                                   |                               |                        | 123.6    | 105.2                  | 63.5     |                        |          |

Case 2.  $C_{0,TCP} = 0.137 \text{ mmol/l}$      $C_{0,DCP} = 0.128 \text{ mmol/l}$      $C_{0,CP} = 0.771 \text{ mmol/l}$

2,4,6-Trichlorophenol

| $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $C_{eq,DCP}$<br>$\mu\text{mol/l}$ | $C_{eq,CP}$<br>$\mu\text{mol/l}$ | $Q_{obsd}$<br>$\text{mmol/g}$ | Langmuir               |          | IAS Model              |          | Equation 5-22          |          |
|-----------------------------------|-----------------------------------|----------------------------------|-------------------------------|------------------------|----------|------------------------|----------|------------------------|----------|
|                                   |                                   |                                  |                               | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% |
| 0.0113                            | 0.142                             | 5.353                            | 0.181                         | 0.0256                 | 85.8     | 0.0261                 | 85.6     | 0.159                  | 12.1     |
| 0.202                             | 0.232                             | 9.725                            | 0.209                         | 0.278                  | 33.0     | 0.284                  | 35.9     | 0.215                  | 2.81     |
| 0.679                             | 0.681                             | 31.59                            | 0.268                         | 0.354                  | 32.2     | 0.371                  | 38.4     | 0.311                  | 16.3     |
| 1.109                             | 1.289                             | 42.01                            | 0.293                         | 0.403                  | 37.7     | 0.429                  | 46.4     | 0.330                  | 12.6     |
| 1.656                             | 1.595                             | 65.98                            | 0.325                         | 0.415                  | 27.8     | 0.443                  | 36.3     | 0.358                  | 10.3     |
| sum of R, %                       |                                   |                                  |                               |                        | 216.5    | 242.6                  | 54.1     |                        |          |

2,4-Dichlorophenol

| $C_{eq,DCP}$<br>$\mu\text{mol/l}$ | $C_{eq,TCP}$<br>$\mu\text{mol/l}$ | $C_{eq,CP}$<br>$\mu\text{mol/l}$ | $Q_{obsd}$<br>$\text{mmol/g}$ | Langmuir               |          | IAS Model              |          | Equation 5-25          |          |
|-----------------------------------|-----------------------------------|----------------------------------|-------------------------------|------------------------|----------|------------------------|----------|------------------------|----------|
|                                   |                                   |                                  |                               | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% | $q$<br>$\text{mmol/g}$ | $R$<br>% |
| 0.142                             | 0.0113                            | 5.353                            | 0.169                         | 0.262                  | 55.4     | 0.253                  | 49.7     | 0.149                  | 11.7     |
| 0.232                             | 0.202                             | 9.725                            | 0.195                         | 0.260                  | 32.9     | 0.242                  | 24.1     | 0.201                  | 2.81     |
| 0.681                             | 0.679                             | 31.59                            | 0.250                         | 0.288                  | 15.2     | 0.254                  | 1.60     | 0.291                  | 16.3     |
| 1.289                             | 1.109                             | 42.01                            | 0.273                         | 0.380                  | 39.2     | 0.329                  | 20.5     | 0.308                  | 12.6     |
| 1.595                             | 1.656                             | 65.98                            | 0.303                         | 0.324                  | 6.86     | 0.272                  | 10.2     | 0.335                  | 10.3     |
| sum of R, %                       |                                   |                                  |                               |                        | 149.6    | 106.1                  | 53.7     |                        |          |

Table 5.4 (continued)

4-Chlorophenol

| C <sub>eq,CP</sub><br>μmol/l | C <sub>eq,TCP</sub><br>μmol/l | C <sub>eq,DCP</sub><br>μmol/l | Q <sub>obsd</sub><br>mmol/g | Langmuir    |        | IAS Model   |        | Equation 5-27 |        |
|------------------------------|-------------------------------|-------------------------------|-----------------------------|-------------|--------|-------------|--------|---------------|--------|
|                              |                               |                               |                             | q<br>mmol/g | R<br>% | q<br>mmol/g | R<br>% | q<br>mmol/g   | R<br>% |
| 5.353                        | 0.0113                        | 0.142                         | 1.008                       | 0.890       | 11.8   | 0.899       | 10.8   | 0.890         | 11.8   |
| 9.725                        | 0.202                         | 0.232                         | 1.163                       | 0.984       | 15.4   | 0.996       | 14.4   | 1.196         | 2.79   |
| 31.59                        | 0.679                         | 0.681                         | 1.451                       | 1.207       | 16.8   | 1.227       | 15.4   | 1.686         | 16.2   |
| 42.01                        | 1.109                         | 1.289                         | 1.569                       | 1.119       | 28.7   | 1.148       | 26.8   | 1.767         | 12.6   |
| 65.98                        | 1.656                         | 1.595                         | 1.690                       | 1.212       | 28.3   | 1.240       | 26.6   | 1.864         | 10.3   |
| sum of R, %                  |                               |                               |                             |             | 101    |             | 94     |               | 53.7   |

\* C<sub>eq</sub> = equilibrium concentration, C<sub>0</sub> = initial concentration, Q<sub>obsd</sub> = observed amount adsorbed, Langmuir = Langmuir Competitive Model (equation 2-9), R = relative deviation ( $|Q_{obsd} - Q_{pred}|/Q_{obsd}$ )

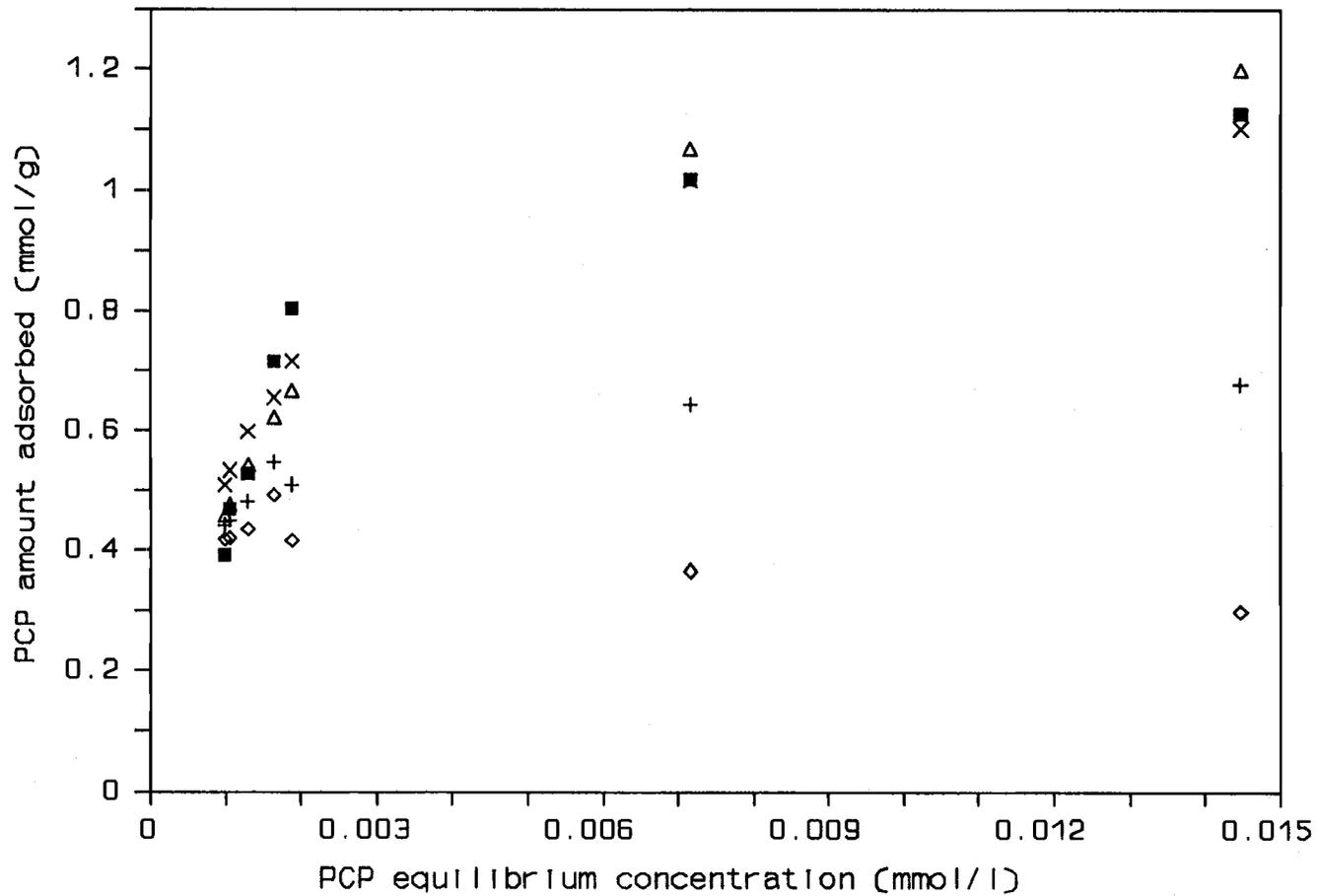


Figure 5.2 Adsorption equilibria of PCP in the presence of TCP  
 (Initial concentrations: PCP, 0.580 mmol/l; TCP, 0.138 mmol/l)  
 ■ Experimental data; + Langmuir; ◇ IAS; △ New method; x Modified IAS

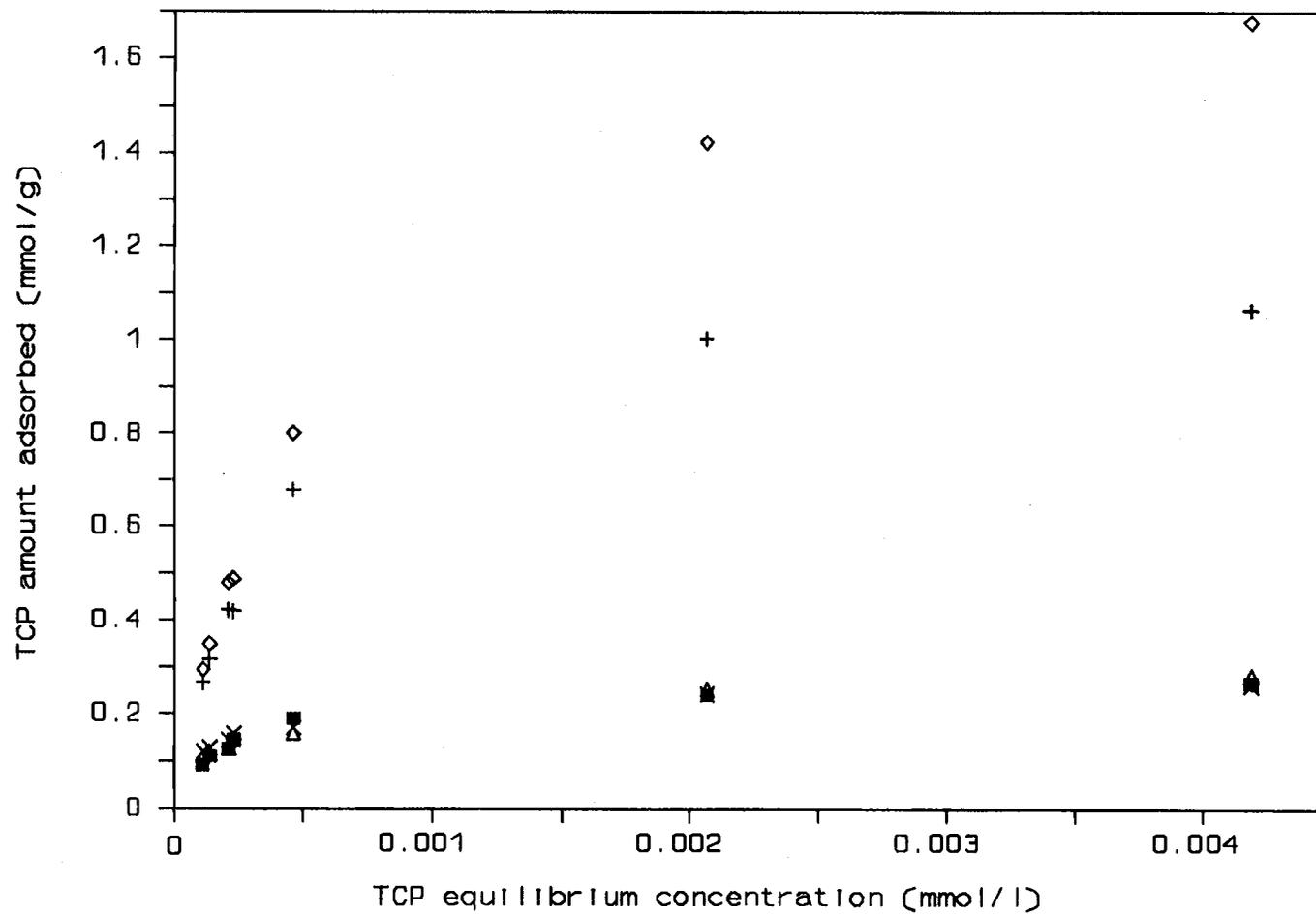


Figure 5.3 Adsorption equilibria of TCP in the presence of PCP  
 (Initial concentrations: PCP, 0.580 mmol/l; TCP, 0.138 mmol/l)  
 ■ Experimental data; + Langmuir; ◇ IAS; △ New method; × Modified IAS

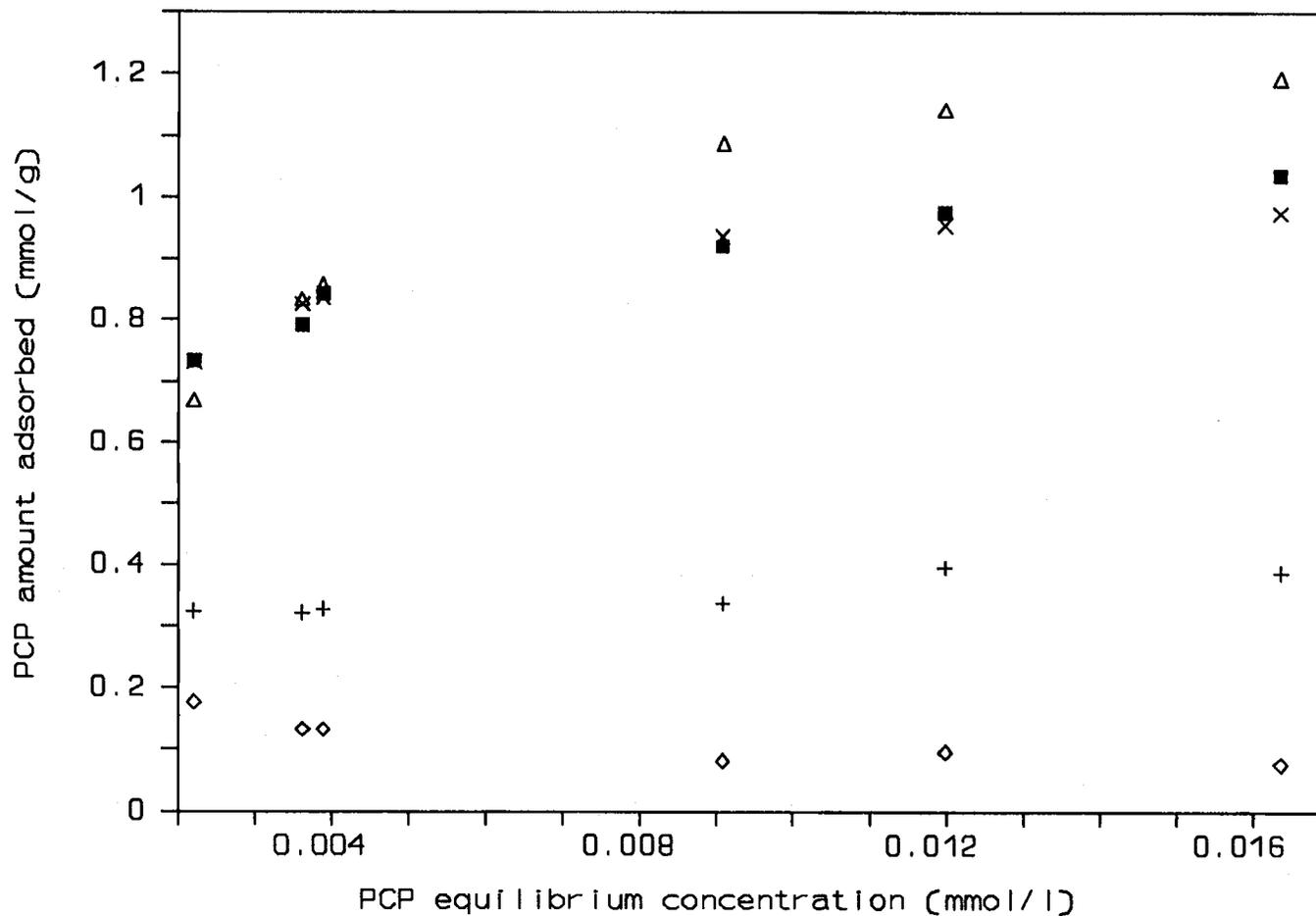


Figure 5.4 Adsorption equilibria of PCP in the presence of TCP

(Initial concentrations: PCP, 0.478 mmol/l; TCP, 0.276 mmol/l)

■ Experimental data; + Langmuir; ◇ IAS; △ New method; × Modified IAS

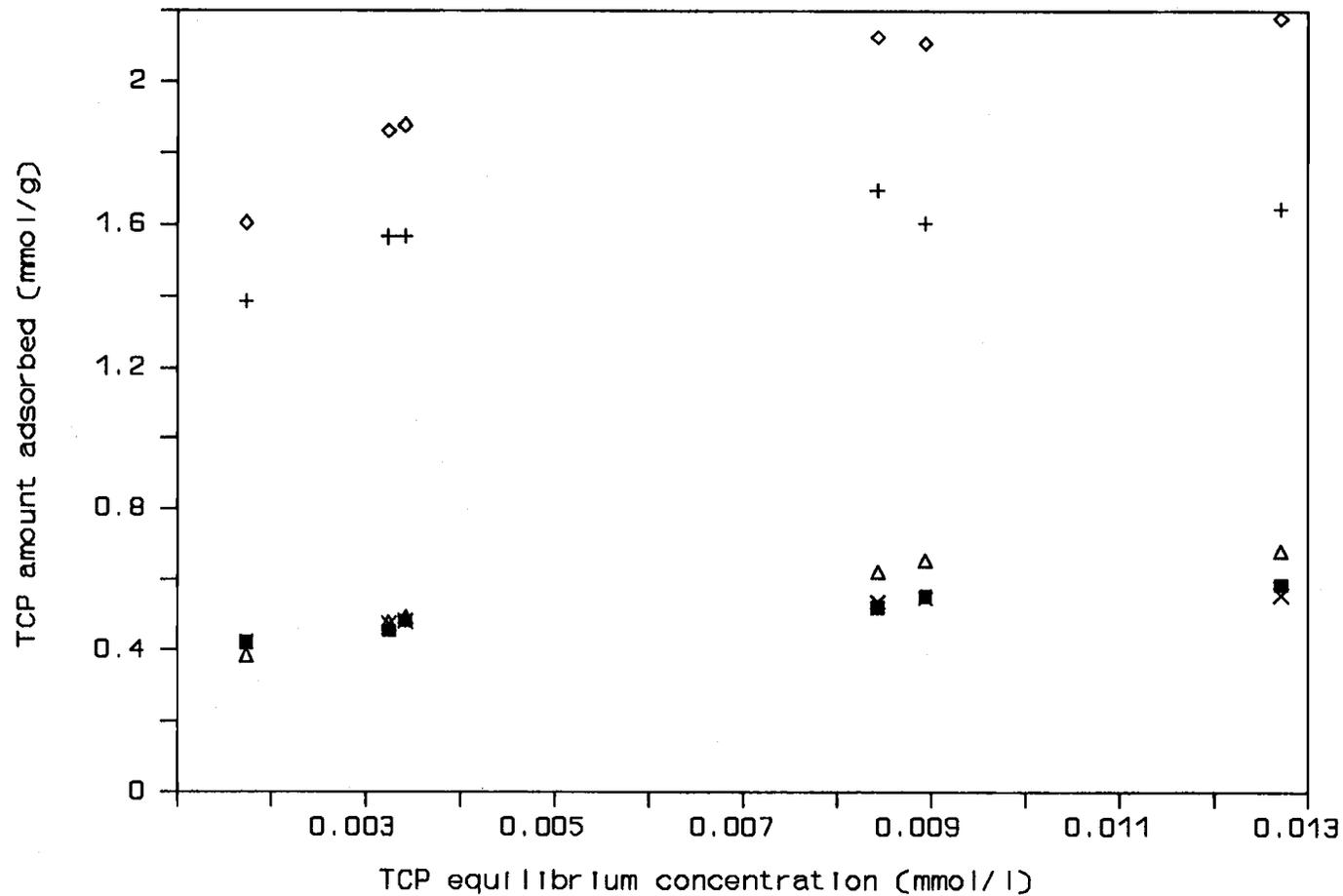


Figure 5.5 Adsorption equilibria of TCP in the presence of PCP  
 (Initial concentrations: PCP, 0.478 mmol/l; TCP, 0.276 mmol/l)  
 ■ Experimental data; + Langmuir; ◇ IAS; △ New method; × Modified IAS

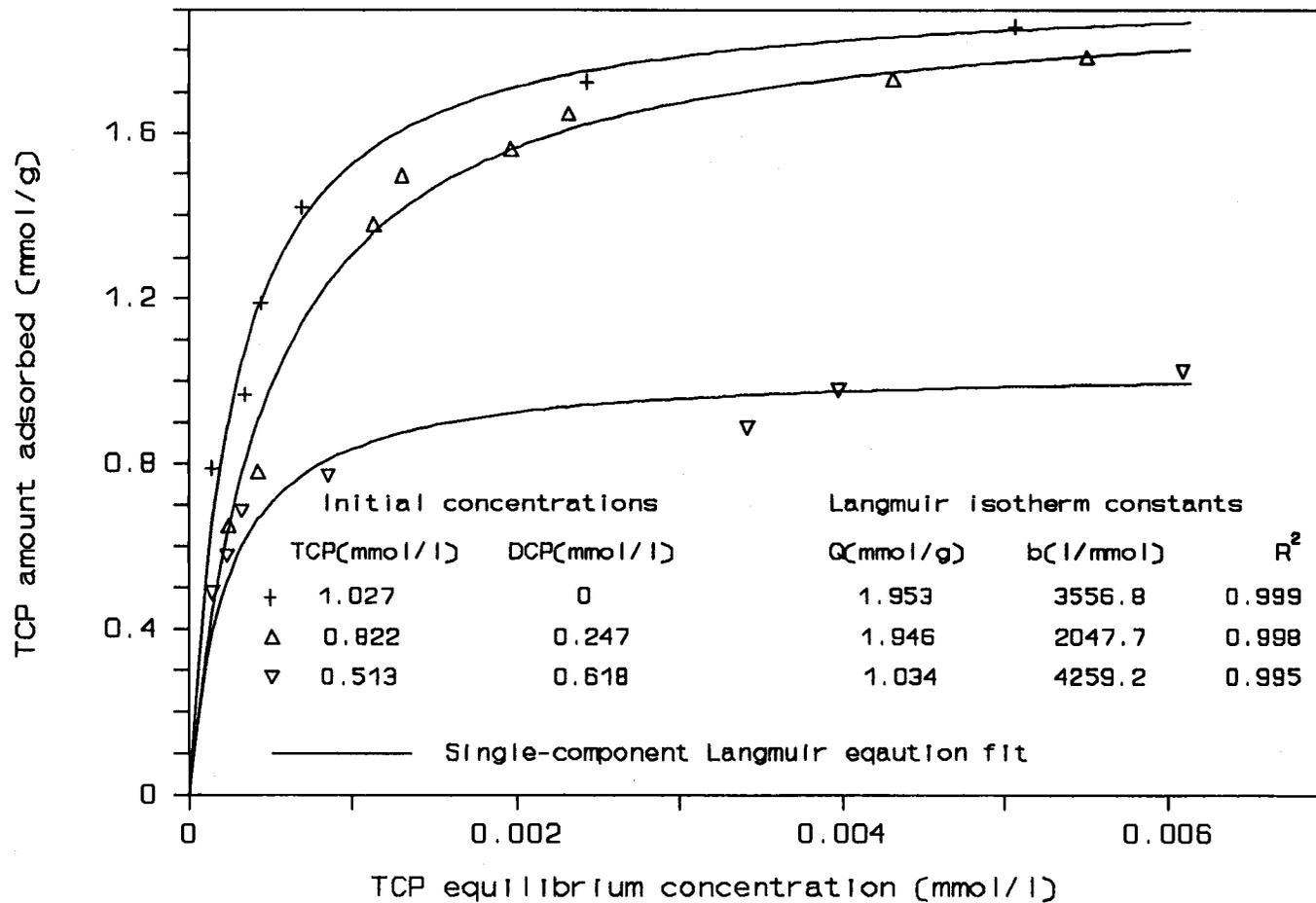


Figure 5.6 Langmuir isotherms of TCP in the presence of DCP

to case. For a wastewater, if the concentration ratio of two contaminants does not change remarkably and the  $\alpha$  value is prior determined, we can use the Langmuir-type equations 5-15 or 5-17 without resorting to the initial concentrations of two components. The simplicity and higher accuracy may make this method very attractive.

The modified IAS model also significantly improves the accuracy of the predictions for two-component adsorption. The relative deviations are relatively low compared to those of the Langmuir competitive and IAS models. In some cases, such as cases 2 and 3 of PCP/2,4,6-TCP system and case 2 of 2,4-DCP/4-CP system, it is better than the new method. This may be explained by that the modified IAS model uses all the single-component isotherm constants of both components while the new method only uses three isotherm constants. The  $F$  values are fairly constant within each case, even though they change to some extent from case to case. As mentioned above, we can use the modified IAS model to predict the two-component adsorption equilibria without knowing the initial concentrations of two components if  $\alpha$  or  $F$  is known. Values of  $F$  greater than 1 are indications of the influence of irreversibility and non-ideal competition of two-component adsorption.

Table 5.3 shows that the Langmuir competitive and IAS models predict the 2,4-DCP/4-CP two component adsorption equilibria very well. The reason for this may be that the adsorption of 2,4-DCP and 4-CP on activated carbon is fairly reversible. The new method predicts the solid loadings better than the Langmuir competitive and IAS models in case 1 and worse than these two models in case 2, while the predictions of these three models for case 3 are very close. Responsible for higher deviations of the predictions of

the new method in case 2 may be much higher concentration range of 2,4-DCP single-component isotherm data than that of 2,4-DCP two-component equilibrium data. The modified IAS model improves the accuracy of the predictions for all cases, and thus is the most successful among the four models tested for this system. The values of the modification factor  $F$  are very close to 1, which indicates that the competition between 2,4-DCP and 4-CP is basically ideal.

Table 5.4 shows three component adsorption equilibrium data for the 2,4,6-TCP/2,4-DCP/4-CP system. Similar to two component systems, the performances of the Langmuir competitive and IAS models are essentially identical for the three-component system. The relative deviations between the predicted values of the new method and experimental values are relatively low in comparison with those for the Langmuir competitive and IAS models. The proposed new method appears to be the best of the three models. This implies that the new method based on thermodynamic consideration of two-component adsorption equilibria can be successfully extended to three-component system.

The important thing to note is that even though the new method and modified IAS model presented in this thesis use initial concentrations in addition to single-component isotherm constants, they still require fewer parameters than the widely used IAS modification shown in equation 2-22, in which the modification factors,  $R_i$ , are determined from multicomponent equilibrium data with a statistical technique. From the mass balance expression  $q = (C_o - C)/M$ , one can see that to calculate the solid-phase loading  $q$ , carbon dosage  $M$  must be used in addition to initial concentration  $C_o$ .

For multicomponent adsorption conducted with the same two-component solution but varying carbon dosages, the equilibrium data of each component conform to single-component adsorption isotherms. The equilibrium data of each component in all cases of three systems can be described by single-component Langmuir equation. From Figure 5.6 which is just such an example, it can be seen that when 2,4,6-TCP is the dominantly adsorbed component, the Langmuir capacity is almost the same as single-component adsorption capacity but the adsorption constant becomes smaller, and if 2,4-DCP is the dominant adsorbed component both capacity and constant for 2,4,6-TCP change. This can be explained by equations 5-11, 5-15 and 5-17. For the case in which 2,4,6-TCP is the dominant adsorbed component, we use the Langmuir-type equation (eqn 5-15) to predict 2,4,6-TCP adsorption equilibrium. The term  $Q_1 C_2 / (Q_2 C_1 \alpha)$ , which is equivalent to  $Q_1 q_2 / (Q_2 q_1)$  or  $Q_1 (C_{0,2} - C_2) / (Q_2 (C_{0,1} - C_1))$ , in equation 5-15, is almost constant. Hence the Langmuir-type equation can be changed to the single-component Langmuir equation, and  $Q$  remains the same but  $b$  decreases. For the case in which 2,4-DCP is the dominant adsorbed component, equation 5-11 is used to predict the 2,4,6-TCP adsorption equilibrium. Substitution of equation 5-17 into equation 5-11 and rearrangement lead to

$$q_1 = \frac{Q_2 b_2 \alpha C_1}{1 + \frac{Q_2 q_1}{Q_1 q_2} + b_2 \alpha \frac{q_2}{q_1} C_1} \quad (5-30)$$

which can also be treated as a Langmuir equation because the terms  $\alpha$ ,  $1 + Q_2 q_1 / (Q_1 q_2)$  and  $b_2 \alpha q_2 / q_1$  are basically constant. In this case, both  $Q$  and  $b$  change:  $Q$  decreases and

b may decrease or increase.

**Multicomponent Adsorption Equilibria at Various pH Values.** Two-component adsorption was conducted for the 2,4,5-TCP/2,4-DCP system at various pH values. Figure 5.7 gives 2,4,5-TCP and 2,4-DCP equilibrium adsorption data and the surface complexation model fits, and Table 5.5 summarizes the surface complexation constants and overall variance. For convergence of optimization procedure, only two complexation constants ( $K_A^{\text{intr}}$  for 2,4-DCP and  $K_B^{\text{intr}}$  for 2,4,5-TCP) were extracted using FITEQL, whereas the other two complexation constants ( $K_A^{\text{intr}}$  for 2,4,5-TCP and  $K_B^{\text{intr}}$  for 2,4-DCP) were fixed. Both 2,4,5-TCP and 2,4-DCP adsorption data follow the same patterns as in single-component adsorption, although the presence of competing species decreases the respective solid-phase loadings. The constants provide good simulation of 2,4-DCP

**Table 5.5 Best Estimates for 2,4,5-TCP/2,4-DCP Two-Component Surface Complexation Constants**

| Adsorbate | $\log K_A^{\text{intr}}$ | $\log K_B^{\text{intr}}$ | SOS/DF |
|-----------|--------------------------|--------------------------|--------|
| 2,4,5-TCP | 21.48 <sup>a</sup>       | 14.58                    | 42.3   |
| 2,4-DCP   | 24.12                    | 13.05 <sup>a</sup>       |        |

<sup>a</sup> from Table 3.5

**Table 5.6 Best Estimates for Conditional Surface Complexation Constants (2,4,5-TCP/2,4-DCP System)**

| Adsorbate | $\log K_A^{\text{intr}}$ | $\log K_B^{\text{intr}}$ | SOS/DF |
|-----------|--------------------------|--------------------------|--------|
| 2,4,5-TCP | 24.86                    | 12.14                    | 2.32   |
| 2,4-DCP   | 20.34                    | 15.05                    | 0.99   |

adsorption but underestimate below pH 4.5 and overestimate within pH 7.4 - 8.2 2,4,5-TCP adsorption with about 10% deviations. Compared to the four multicomponent adsorption models tested in this chapter, the Langmuir competitive model, the IAS model, the proposed new method, and the modified IAS model, the surface complexation model performs very well in predicting two-component adsorption equilibria of chlorophenols/activated carbon system.

As shown in Figure 5.8, 2,4,5-TCP and 2,4-DCP adsorption data can separately excellently be fitted by the surface complexation model. Since the adsorption equilibria of each component were attained in the presence of the other component, the constants extracted from optimization procedure are called "conditional surface complexation constants". Table 5.6 gives the conditional surface complexation constants, which are somewhat different in magnitude from those of single-component adsorption. In effect, the conditional surface complexation constants are not supposed to be equal to the surface complexation constants obtained from single-component adsorption data.

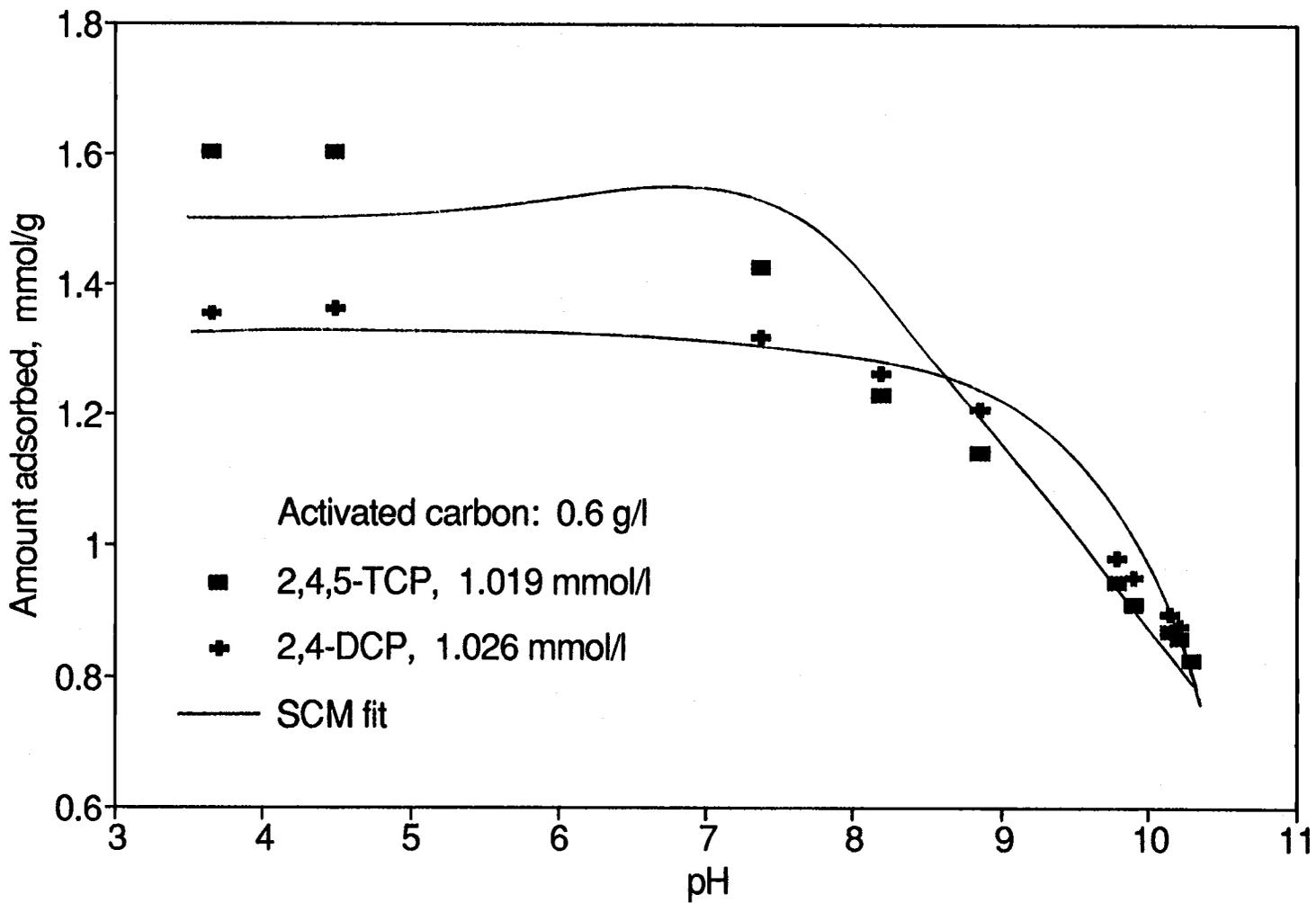


Figure 5.7 2,4,5-TCP/2,4-DCP two-component adsorption as a function of pH and optimum surface complexation model fits

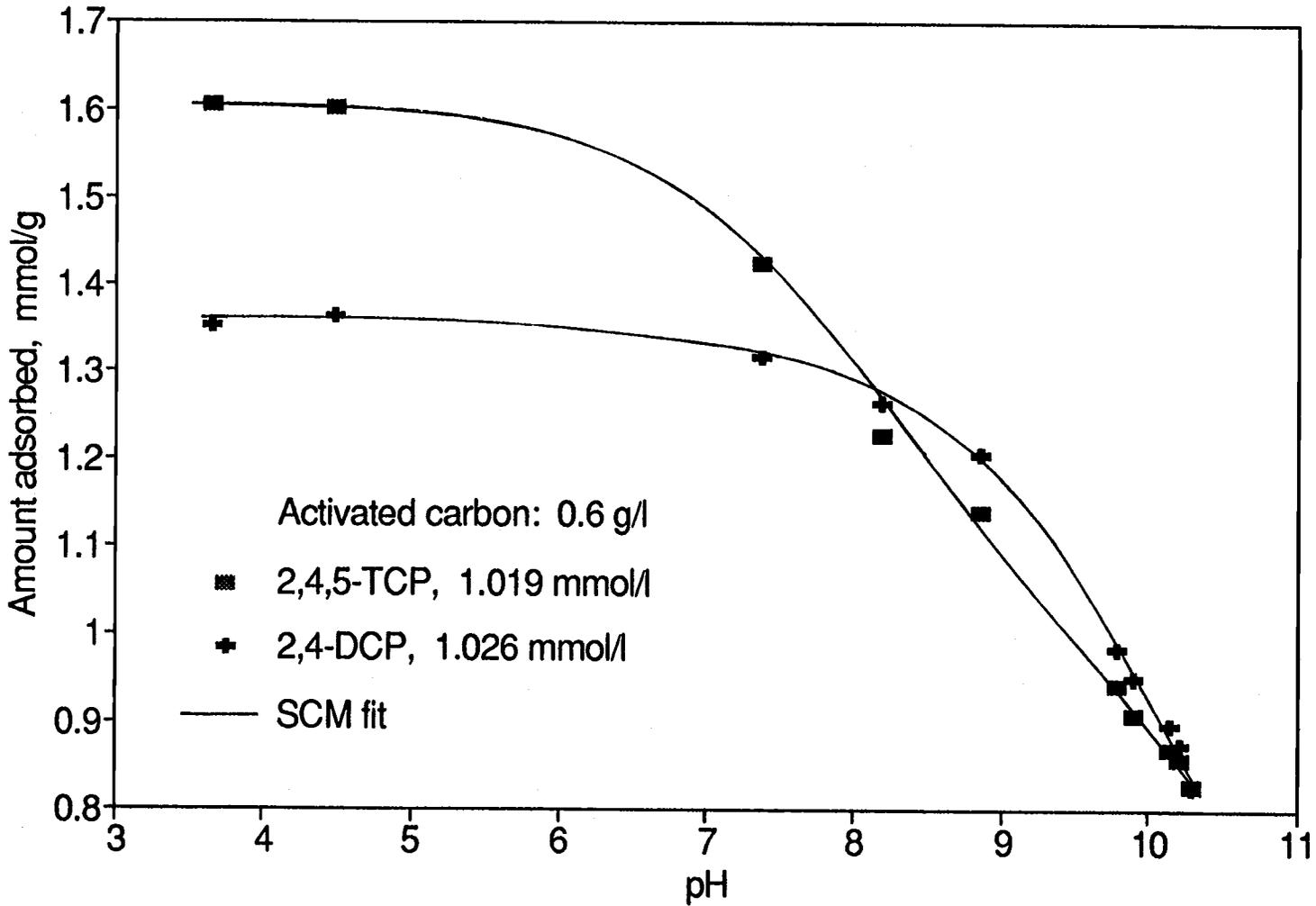


Figure 5.8 2,4,5-TCP/2,4-DCP two-component adsorption as a function of pH and separate SCM fits to each component adsorption data

## Conclusions

Two- and three- component adsorption equilibria of chlorophenols on granular activated carbon were investigated in the micromolar equilibrium concentration range. The Langmuir competitive and Ideal Adsorbed Solution (IAS) models were tested for their performances on the three binary systems of pentachlorophenol/2,4,6-trichlorophenol, 2,4,6-trichlorophenol/2,4-dichlorophenol, and 2,4-dichlorophenol/4-chlorophenol, and the tertiary system of 2,4,6-trichlorophenol/2,4-dichlorophenol/4-chlorophenol, and found to fail to predict the two-component adsorption equilibria of the former two binary systems and the tertiary system. A new prediction method and a modification of the IAS model, both based on thermodynamic considerations, have been proposed. The required parameters are the single-component Langmuir isotherm constants and initial concentrations for each component. The proposed new method and the modified IAS model were found to significantly improve the accuracy of the predictions of two-component adsorption equilibria of chlorophenols. The new method also performs much better than the Langmuir competitive and IAS models in the three-component system. The observation that the equilibrium data of each component in two-component systems can be described by single-component adsorption isotherms has also been explained by rearranging the equations of the new method. 2,4,5-TCP/2,4-DCP two-component adsorption equilibria at various pH values were described by the surface complexation model with as high as 10% deviation at some points, while the separate SCM fits to each component are in excellent agreement with the adsorption data.

## Chapter 6 DESORPTION EQUILIBRIUM AND KINETICS OF CHLOROPHENOLS

### Introduction

In recent years, the failures of multicomponent adsorption equilibrium models in predicting solid-phase loadings have been reported for a large number of activated carbon-organic compound systems (Thacker et al., 1984; Smith and Weber, 1988; Yonge and Keinath, 1986). This is because these models assume that both liquid- and solid-phase solutions are ideal and thus ideal competition occurs. Many systems, however, cannot be dealt with as ideal ones because of high liquid- and/or solid-phase adsorbate concentrations (Radke and Prausnitz, 1992) or strong interaction between adsorbates and activated carbon. The latter frequently bring about irreversibility of adsorption, which seems an important reason for deviations of multicomponent adsorption from ideal competition. Yonge et al. (1985) showed that the degree of irreversibility was as high as 85 - 97% for certain phenolic compounds and postulated high-energy bonding (chemisorption) to be the cause of strong irreversibility.

It has been shown in chapter 3 that chlorophenols can be favorably adsorbed by activated carbon and the adsorptive capacities are fairly high. Thus chlorophenols are compounds which have a very strong affinity with activated carbon. Chapter 5 has demonstrated that the Langmuir competitive and IAS models fail to accurately predict solid-phase loadings on activated carbon for most systems. These facts imply that the

chlorophenols-activated carbon systems are not ideal and the irreversibility of adsorption must be taken into account. Investigations have been conducted on desorption equilibria and kinetics in order to gain a more complete understanding of single-component adsorption irreversibility. This chapter presents desorption equilibrium and kinetic data and proposes a desorption rate equation.

### **Materials and Methods**

*Desorption Kinetics.* Batch desorption kinetic experiments were conducted for PCP, 2,4-DCP and 4-CP. The experimental protocol consisted of equilibrating a 300 mg GAC sample at a initial liquid-phase adsorbate concentration of approximately 2 mM. A larger mass of GAC was used so as to minimize the effects of unintentional loss of GAC which could occur during the desorption procedure and to result in a detectable adsorbate concentration during the operation of desorption kinetics. Following equilibration, the liquid and solid phases were separated by using an all-glass Millipore filtration unit designed to hold 47-mm diameter disks. The GAC retained on the glass-fiber filters was rinsed back into the reactor with 3 liters of adsorbate free buffer solution agitated as previously described. 2 - 5 ml solution samples were withdrawn at appropriate intervals. Preliminary experiments were performed to determine if a significant quantity of GAC remained on the filters following this rinse procedure. This was done by drying the filters, following the rinse procedure, at 105°C to a constant weight and comparing this weight to the tare weight of the filters. Less than 3 mg of carbon was found to adhere to the filters.

**Desorption Equilibrium.** Single-solute desorption isotherms were developed to determine the extent of single-solute irreversible adsorption for the three compounds. The adsorption isotherm data were first generated by using the procedure described previously. Following equilibration, the solution was decanted and the GAC and tube wall were washed with deionized, double-distilled water. These processes were completed very carefully and quickly to avoid any loss of GAC and any detectable desorption. 40-ml portions of deionized, double-distilled water with 5 mM phosphate buffer and pH 7.0 were pipetted into the tubes containing equilibrated GAC. The tubes were then shaken for 6 days. From kinetic results, no considerable desorption was observed after 2 days. This indicates that a 6-day equilibration period was sufficient for the attainment of equilibrium in the desorption isotherm studies. The equilibrium solid-phase loading on the GAC was calculated after desorption using

$$q = \frac{q_0 m - CV}{m} \quad (6-1)$$

where  $q_0$  = equilibrium solid-phase loading after the initial adsorption step (moles per gram),  $m$  = mass of GAC in the tubes (grams),  $C$  = equilibrium liquid-phase adsorbate concentration after desorption (moles per liter),  $V$  = volume of solution (liters), and  $q$  = equilibrium solid-phase loading after desorption (moles per gram).

## Results and Discussion

**Desorption Equilibrium.** The adsorption and desorption isotherms are shown in

Figures 6.1 - 6.3. The fact that adsorption isotherms all lie below the respective desorption isotherms implies the occurrence of irreversible adsorption, since the two isotherms should coincide for completely reversible adsorption. The Langmuir and Freundlich constants for these adsorption and desorption isotherms are tabulated in Table 6.1. The adsorptive capacities are seen to be lower than the desorption capacities for all these three compounds. The data listed in Table 6.2 summarize the relative degree of irreversibility for the three adsorbates. Percent irreversibility is defined as  $1 - C_d/C_a$ , where  $C_d$  and  $C_a$  represent desorption and adsorption equilibrium liquid-phase concentrations at the same solid-phase loading, respectively. The results from this definition are comparable between components at given adsorbate concentrations, although they are different from this concentration to the other. The data at 0.02 mmol/l adsorption equilibrium concentration were used for the calculation. These data indicate that the degree of irreversibility increases from 4-CP to PCP.

On the basis of the findings of Mattson et al. (1969a), which indicated the formation of charge-transfer complexes between adsorbates and activated carbon surface functional groups, chemisorption appears to be the most logical explanation for irreversible adsorption. Depending on the type of surface functional groups as well as the type of adsorbate, a sufficiently strong bond that resists desorption can be formed. The degree of irreversibility then would be directly related to the number of high-energy (chemisorption) bonds. That fraction of adsorption that was reversible would then likely be that fraction of adsorption that occurred as a result of van der Waals forces and/or weaker charge-transfer complexes that occur at other adsorption sites on the activated

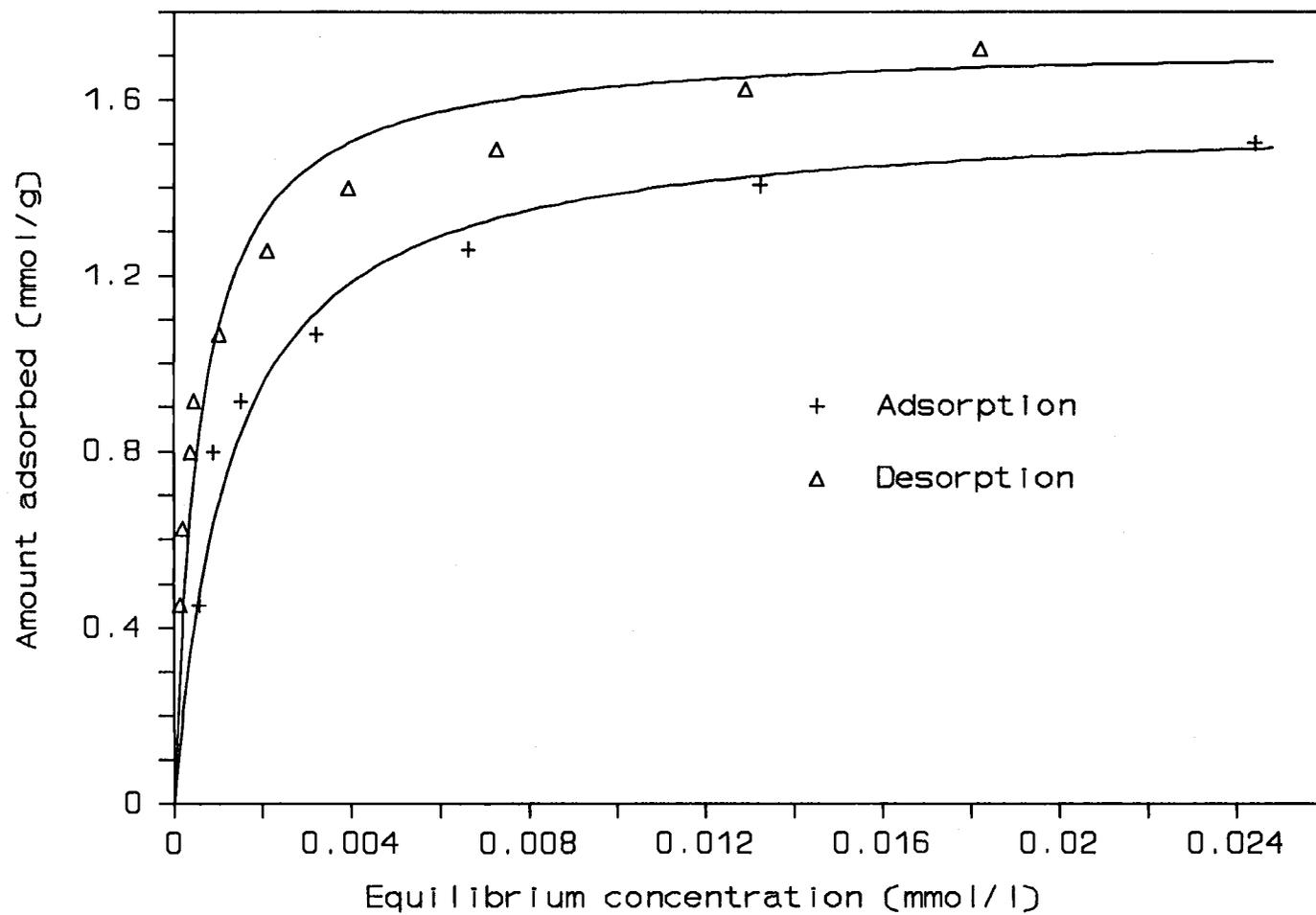


Figure 6.1 Langmuir isotherms for adsorption and desorption of PCP

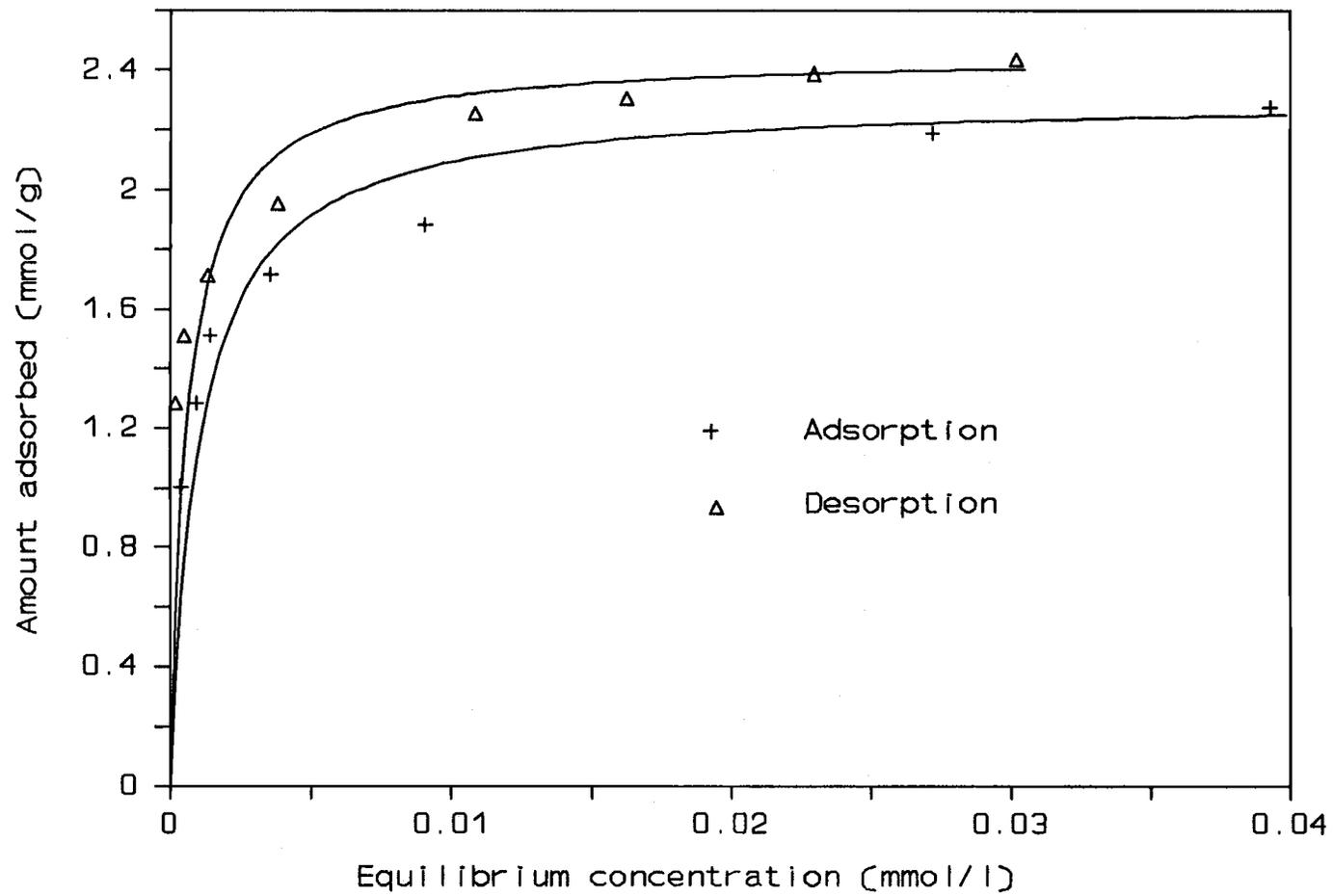


Figure 6.2 Langmuir isotherms for adsorption and desorption of 2,4-DCP

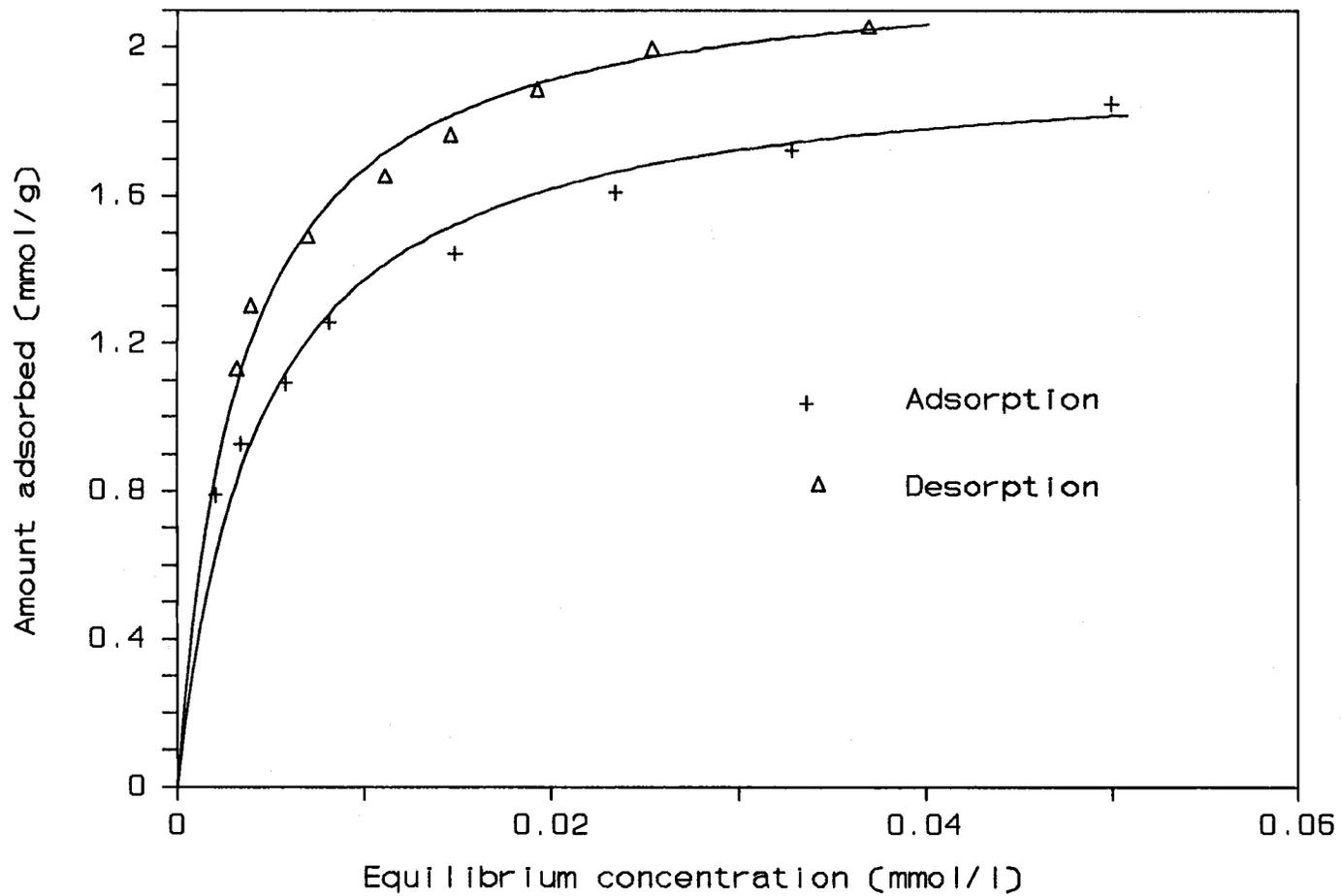


Figure 6.3 Langmuir isotherms for adsorption and desorption of 4-CP

**Table 6.1 Comparison of Langmuir and Freundlich Constants for Adsorption and Desorption of Three Compounds**

| Adsorbate | Conc. range<br>10 <sup>-3</sup> mmol/l | Langmuir    |             |                | Freundlich |       |                |       |
|-----------|--|-------------|-------------|----------------|------------|-------|----------------|-------|
|           |  | Q<br>mmol/g | b<br>l/mmol | R <sup>2</sup> | K          | n     | R <sup>2</sup> |       |
| PCP       | Ads <sup>a</sup>                       | 0.574-24.44 | 1.569       | 768.1          | 0.999      | 4.622 | 0.271          | 0.845 |
|           | Des <sup>b</sup>                       | 0.122-18.23 | 1.729       | 1678.3         | 0.997      | 4.886 | 0.236          | 0.925 |
| 2,4-DCP   | Ads                                    | 0.385-39.27 | 2.310       | 965.1          | 0.999      | 4.053 | 0.164          | 0.950 |
|           | Des                                    | 0.182-30.19 | 2.452       | 1664.0         | 0.999      | 3.870 | 0.125          | 0.994 |
| 4-CP      | Ads                                    | 2.06-50.00  | 1.977       | 226.4          | 0.997      | 4.369 | 0.270          | 0.986 |
|           | Des                                    | 3.16-37.00  | 2.234       | 298.0          | 0.999      | 4.744 | 0.238          | 0.972 |

<sup>a</sup> Adsorption

<sup>b</sup> Desorption

**Table 6.2 Single-Solute Desorption Irreversibility**

| Adsorbate | Irreversibility, % |
|-----------|--------------------|
| PCP       | 83                 |
| 2,4-DCP   | 74                 |
| 4-CP      | 56                 |

carbon surface.

Grant and King (1990) found that most of the adsorption of phenol at pH 12.1 was irreversible and irreversible uptakes at pH 1.8 were much lower than those at higher pH values. They also found that irreversible adsorption of phenolic compounds on carbon surfaces was caused by oxidative coupling. From the pKa values of chlorophenols, it can be known that most species are present in ionized forms for PCP and in molecular forms for 4-CP. That phenolate ions were more reactive than phenols seems to be responsible for that the degree of irreversibility of adsorption increases from 4-CP to PCP.

The interaction of the aromatic ring with the surface of the activated carbon may give another plausible explanation for the change of the degree of adsorption irreversibility from 4-CP to PCP. It is well known that the electron density of an aromatic ring is strongly influenced by the nature of the substituent. A chloro group acts as a strong electron withdrawing group in reducing the overall electron density in the pi-system of the ring. Thus, chloro-substituted aromatic compounds act as acceptors in donor-acceptor complexes (i. e., charge-transfer complexes), and the aromatic compounds with more chloro groups form stronger complexes with a given donor than the compounds with fewer chloro groups. This may explain why the adsorption of PCP is most irreversible and that of 4-CP is least irreversible.

***Desorption Kinetics.*** The desorption rate can be observed from the desorption kinetic data to decrease as desorption propagates and finally (approximately 3 - 4 days) becomes so small that equilibrium can be considered to be reached. The desorption of all three compounds followed a biphasic pattern: a fast desorption phase following by a slow

phase. The fast phase lasted only a few hours for 4-CP, about 1 day for 2,4-DCP, and 2 days for PCP. If the difference between actual solid-phase loading and solid-phase loading that is in equilibrium with the instantaneous liquid-phase concentration outside the particle is the driving force for desorption, the desorption rate equation can be expressed by

$$-\frac{dq}{dt} = k_d \left( q - \frac{Q_d b_d C}{1 + b_d C} \right) \quad (6-2)$$

where  $k_d$  is the mass transfer coefficient;  $Q_d$  and  $b_d$ , the Langmuir constants for desorption isotherm; and  $C$ , the adsorbate concentration in the bulk liquid-phase. The term  $Q_d b_d C / (1 + b_d C)$  represents the solid-phase loading in equilibrium with  $C$ .

Using the mass balance  $q = q_0 - C/M$ , where  $q_0$  is the initial solid-phase loading and  $M$  is the carbon dosage, equation (6-2) can be changed to

$$\frac{dC}{dt} = k_d \left( q_0 M - C - \frac{Q_d b_d C M}{1 + b_d C} \right) \quad (6-3)$$

Figures 6.4 - 6.6 show the typical desorption kinetic data and curves fitted by equation (6-2) for PCP, 2,4-DCP and 4-CP. Table 6.3 summarizes the parameters used for fitting, and the R-square values. The Langmuir isotherm constants for desorption are obtained from the desorption isotherms shown in Figures 6.1 - 6.3. It is evident that the desorption kinetic model (equation 6-2) can describe the desorption kinetic data very well. Noteworthy is the fact that 4-CP reached desorption equilibrium most rapidly while PCP slowest. The increases in desorption mass transfer coefficient  $k_d$  from PCP to 4-CP are

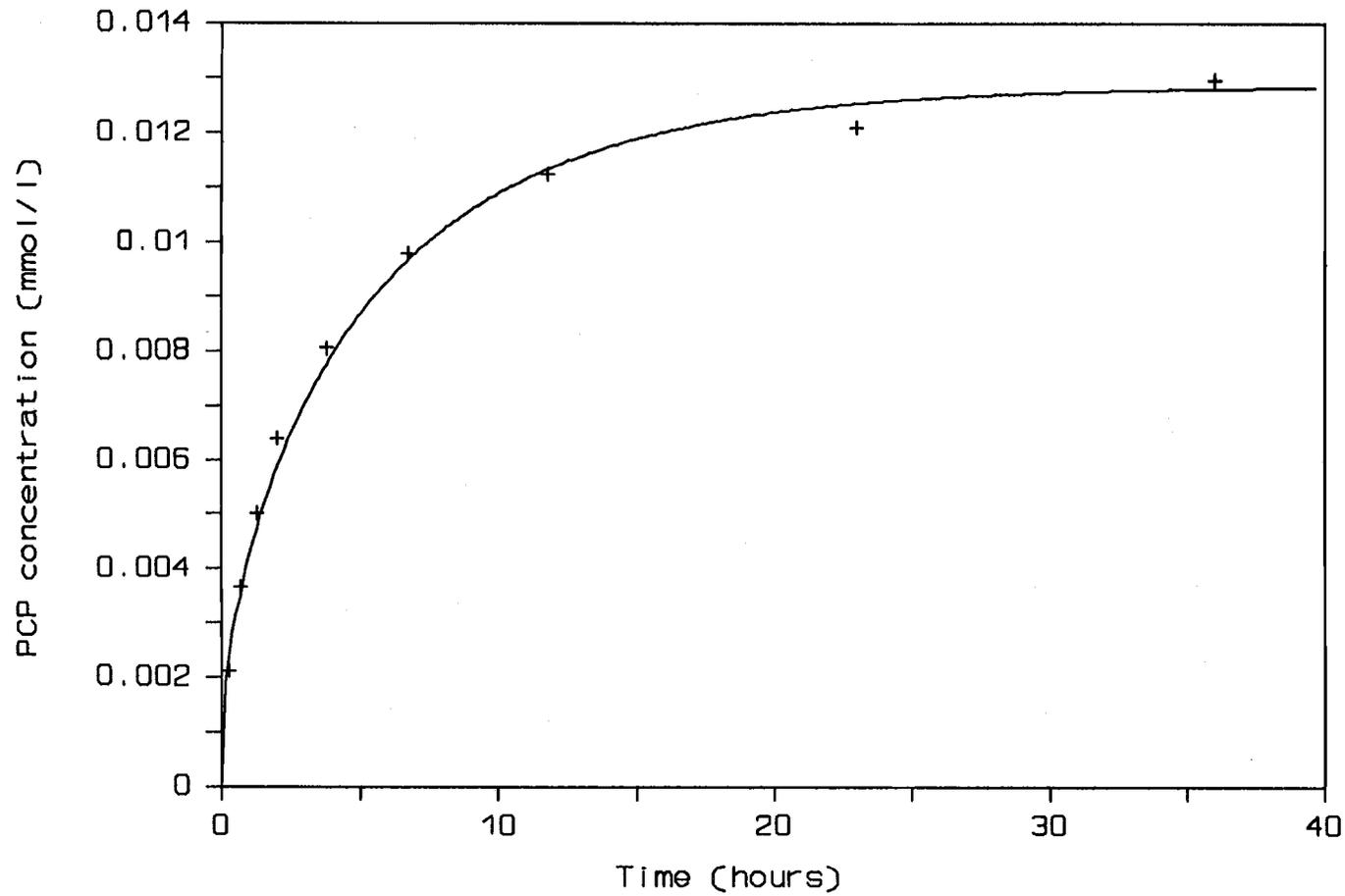


Figure 6.4 Changes of PCP concentration with time during desorption and predictions of desorption kinetic rate equation

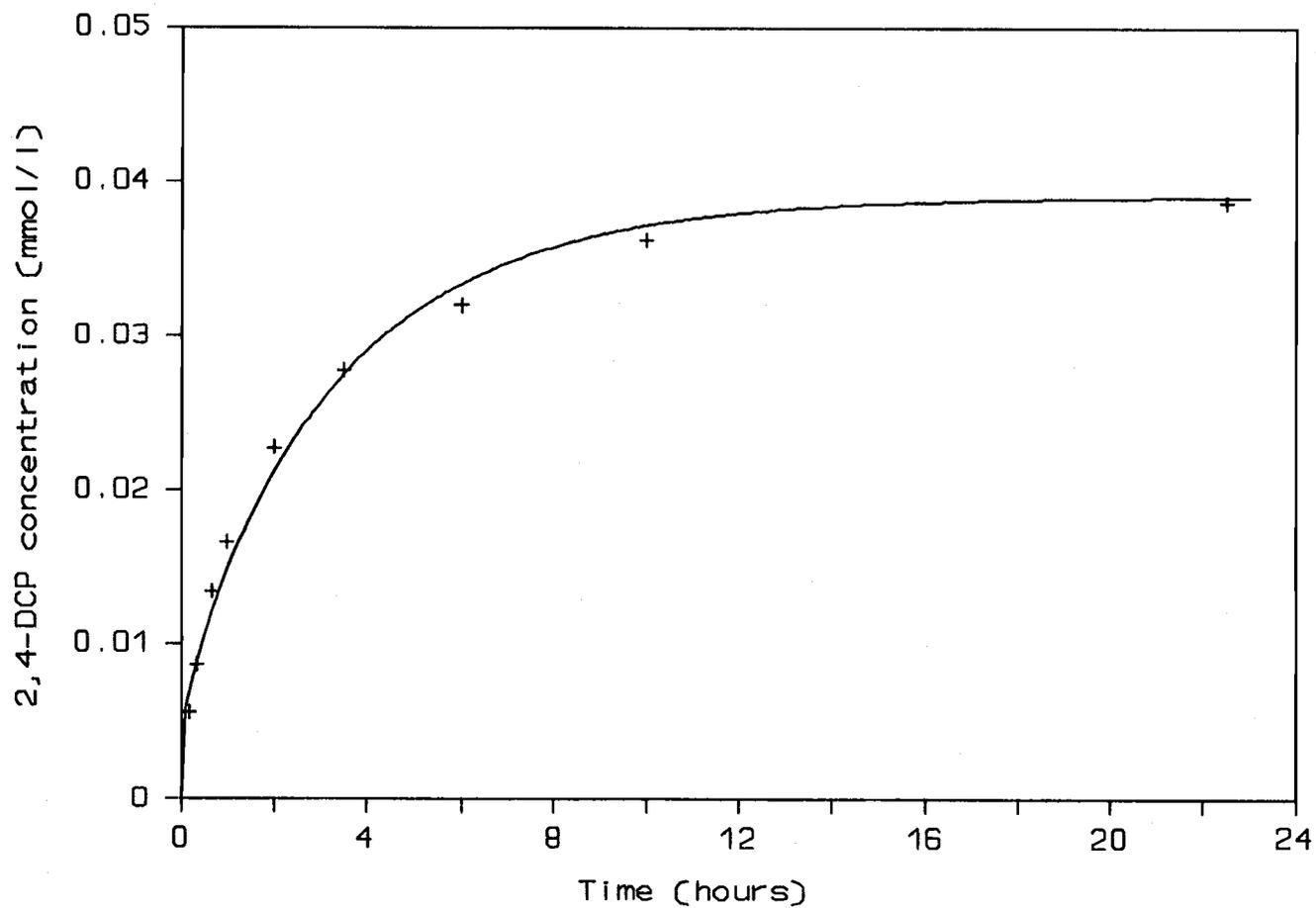


Figure 6.5 Changes of 2,4-DCP concentration with time during desorption and predictions of desorption kinetic rate equation

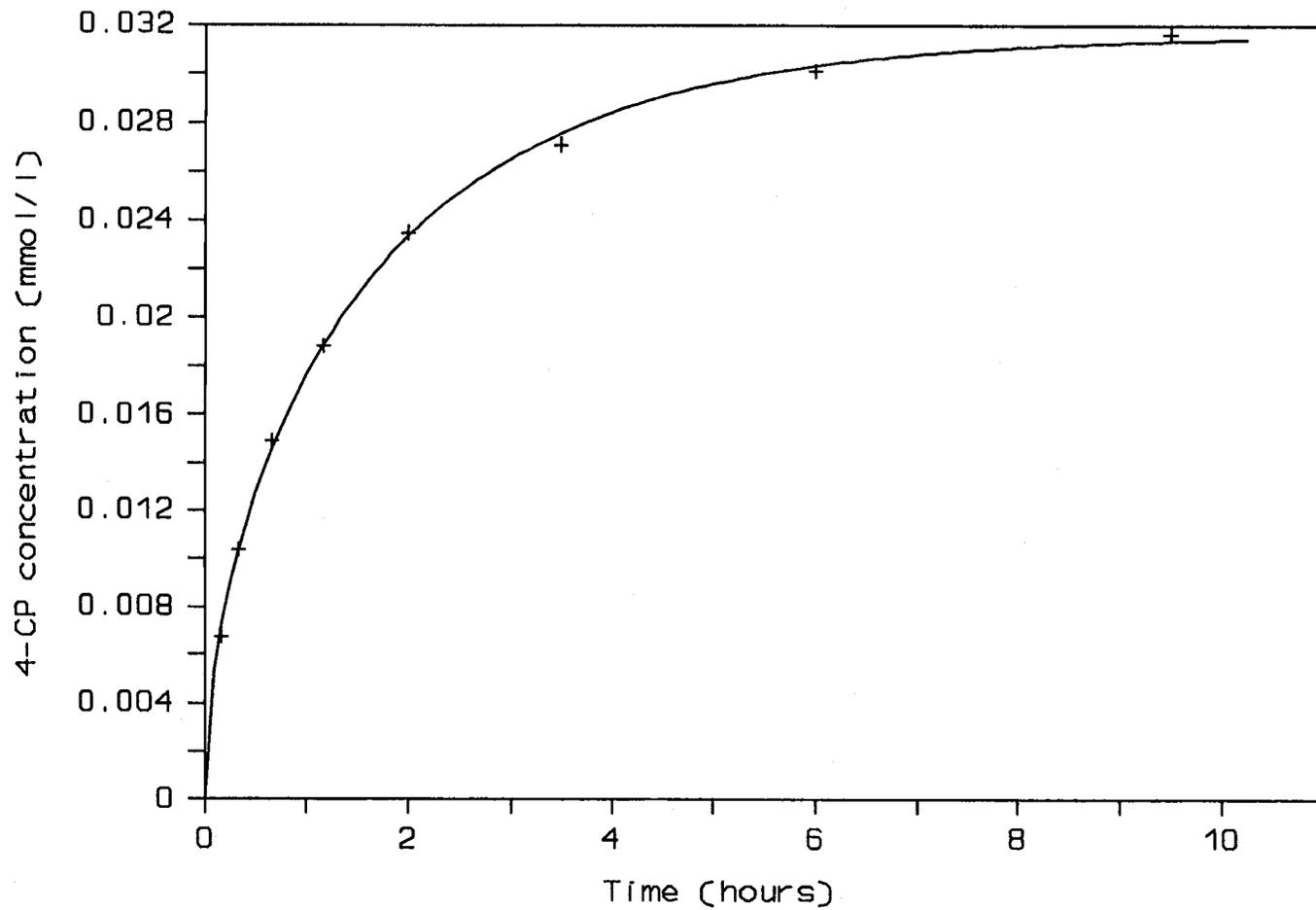


Figure 6.6 Changes of 4-CP concentration with time during desorption and predictions of desorption kinetic rate equation

**Table 6.3 Desorption Kinetic Parameters**

| Adsorbate | $Q_d$<br>mmol/g | $b_d$<br>l/mmol | $q_0$<br>mmol/g | M<br>g/l | $k_d$<br>1/hr | $R^2$ |
|-----------|-----------------|-----------------|-----------------|----------|---------------|-------|
| PCP       | 1.729           | 1678.3          | 1.781           | 0.1      | 0.087         | 0.999 |
| 2,4-DCP   | 2.452           | 1664.0          | 2.805           | 0.1      | 0.250         | 0.998 |
| 4-CP      | 2.234           | 298.0           | 2.336           | 0.1      | 0.270         | 1.000 |

consistent with this phenomenon. This order is identical with the one for the changes of adsorption mass transfer coefficient. It is not unexpected that the less chlorinated a chlorophenol, the faster it reaches both adsorption and desorption equilibria. The difference in the strength of the interaction between these three chlorophenols and activated carbon may be again responsible for the changes of desorption rates.

### Conclusions

Studies were conducted on the desorption equilibria and kinetics of chlorophenols. The results indicate that the Langmuir equation fits both adsorption and desorption equilibrium data better than the Freundlich equation and the degree of the irreversibility of adsorption increases from 4-chlorophenol to pentachlorophenol. A desorption rate equation has been proposed which describes the desorption kinetics data very well. The desorption mass transfer coefficients were found to increase from pentachlorophenol to

4-chlorophenol. The more chlorinated a chlorophenol, the slower and more irreversible is its desorption process. The differences in the strength of interaction between chlorophenols and activated carbon may be responsible for the changes of adsorption irreversibility and desorption rate.

## Chapter 7 SUMMARY AND CONCLUSIONS

A number of single-component adsorption equilibrium models have been developed in the past decades, while the Langmuir and Freundlich equations can satisfactorily fit equilibrium data for most systems. Existent adsorption kinetics models, the external film diffusion model, internal surface diffusion model, linear-driving-force approximation, or surface reaction kinetics model, have been shown to successfully describe adsorption kinetics processes. Considerable achievements have also been made in prediction of multicomponent adsorption equilibria for simple systems, but it remains a very challenging task to accurately predict multicomponent adsorption equilibria under non-ideal competitive conditions. Little effort has been given to desorption mechanisms and kinetics, especially for systems like chlorophenols, which show a very high affinity for activated carbon.

Studies were undertaken of the adsorption of chlorinated phenols from aqueous solution on granular activated carbon. Single-component equilibrium adsorption data on the eight compounds in two concentration ranges at pH 7.0 fit the Langmuir equation better than the Freundlich equation, while the Freundlich equation exhibits improved performance in higher concentration ranges. There are pronounced differences in the magnitudes of the constants between the two concentration ranges, and thus the adsorption constants are concentration-dependent. The adsorptive capacities at pH 7.0 increase from

pentachlorophenol to trichlorophenols and are fairly constant from trichlorophenols to monochlorophenols. No effect of phosphate on the adsorption was observed in the pH range of 4 - 10. The presence of background dissolved organic matter could reduce the adsorptive capacity of chlorophenols. Equilibrium studies were performed at various temperatures at pH 7.0. The adsorption process was found to be exothermic for pentachlorophenol and 2,4,6-trichlorophenol, and endothermic for 2,4-dichlorophenol and 4-chlorophenol.

Equilibrium measurements were also conducted for 2,4,5-trichlorophenol, 2,4-dichlorophenol, and 4-chlorophenol over a wide pH range. No subsequent influence on adsorption is observed for decreasing pH values below the compounds' pKa values, while marked decrease in amounts adsorbed occurs as pH increases above the pKa values. A surface complexation model (SCM) has been proposed to describe the effect of pH on adsorption equilibria of chlorophenols on activated carbon. Activated carbon surface functional sites are divided into acidic groups and basic groups which may be neutralized by bases or acids. Molecular and ionized forms of chlorophenols interact, respectively, with these two kinds of surface groups to form two neutral surface complexes, of which the complex of basic groups is more substantial and more stable than that of acidic groups. The simulations of the model are in excellent agreement with the experimental data.

Batch kinetics studies were conducted of the adsorption of chlorinated phenols on granular activated carbon. pH played an important role in the adsorption kinetics of chlorophenols at pH values above the pKa values of the compounds, while little influence

on adsorption rate was observed if pH was decreased below the pKa values. The external film diffusion model, the linear-driving-force approximation, and the surface reaction kinetics model have been employed to fit the adsorption kinetics data of chlorophenols. The surface reaction model best describes both short-term and long-term kinetics, while the external film diffusion model describes the short-term kinetics data very well and the linear-driving-force approximation exhibits improved performance for the long-term kinetics. The interruption test also indicates that the rate of adsorption is not limited by internal surface diffusion. The mass transfer coefficient increases from more chlorinated compounds to less chlorinated compounds, which implies that the more chloro groups in a chlorophenol, the slower it reaches adsorption equilibrium. The two-component adsorption kinetic experiments have revealed that the adsorption of chlorophenols on activated carbon is to some extent irreversible and that non-ideal competition between two components exists.

Two- and three- component adsorption equilibria of chlorophenols on granular activated carbon were investigated in the micromolar equilibrium concentration range. The Langmuir competitive and Ideal Adsorbed Solution (IAS) models were tested for their performances on the three binary systems of pentachlorophenol/2,4,6-trichlorophenol, 2,4,6-trichlorophenol/2,4-dichlorophenol, and 2,4-dichlorophenol/4-chlorophenol, and the tertiary system of 2,4,6-trichlorophenol/2,4-dichlorophenol/4-chlorophenol, and found to fail to predict the two-component adsorption equilibria of the former two binary systems and the tertiary system. A new prediction method and a modification of the IAS model, both based on thermodynamic considerations, have been proposed. The required

parameters are the single-component Langmuir isotherm constants and initial concentrations for each component. The proposed new method and the modified IAS model were found to significantly improve the accuracy of the predictions of two-component adsorption equilibria of chlorophenols. The new method also performs much better than the Langmuir competitive and IAS models in the three-component system. 2,4,5-TCP/2,4-DCP two-component adsorption equilibria at various pH values were described by the surface complexation model with as high as 10% deviation at some points, and the separate SCM fits to each component are in excellent agreement with the adsorption data.

Studies were conducted on the desorption equilibria and kinetics of chlorophenols. The Langmuir equation fits both adsorption and desorption equilibrium data better than the Freundlich equation and the degree of the irreversibility of adsorption increases from 4-chlorophenol to pentachlorophenol. A linear-driving-force desorption rate equation has been proposed which describes the desorption kinetics data very well. The desorption mass transfer coefficients were found to increase from pentachlorophenol to 4-chlorophenol. The more chlorinated a chlorophenol, the slower and more irreversible is its desorption process. The differences in the strength of interaction between chlorophenols and activated carbon may be responsible for the changes of adsorption irreversibility and desorption rate.

In summary, the following important conclusions can be drawn for the adsorption of chlorinated phenols on granular activated carbon:

- (1) The Langmuir equation fits single-component equilibrium adsorption data

better than the Freundlich equation;

(2) The adsorptive capacities at pH 7.0 increase from PCP to TCP and are fairly constant from TCP to CP;

(3) The proposed surface complexation model describes very well the experimental data for the effect of pH on adsorption equilibria;

(4) The adsorption process is exothermic for PCP and 2,4,6-TCP, and endothermic for 2,4-DCP and 4-CP;

(5) The surface reaction model best describes kinetics adsorption data;

(6) The mass transfer coefficient increases from 2,4,6-TCP to 4-CP;

(7) The adsorption process is to some extent irreversible;

(8) Multicomponent adsorption is non-ideal, and the Langmuir competitive and IAS models fail to predict the adsorption equilibria of PCP-TCP, TCP-DCP and PCP-TCP-CP systems;

(9) The proposed new method and the modified IAS model significantly improve the accuracy of the predictions of multicomponent adsorption equilibria;

(10) The Langmuir equation fits desorption equilibrium data better than the Freundlich equation;

(11) The degree of the irreversibility of adsorption increases from 4-CP to PCP;

(12) The proposed desorption rate equation describes desorption kinetics data very well;

(13) The desorption mass transfer coefficient increases from PCP to 4-CP.

## BIBLIOGRAPHY

- Boehm H. P. (1964) Chemical identification of surface groups. *Advan. Catalysis*. **16**, 179-274.
- Brecher L. E., Frantz D.C. and Kostecki J.A. (1967) Combined diffusion in batch adsorption systems displaying BET isotherms: Part II. *AIChE Symp. Ser.* **63**, 25-30.
- Broughton D.B. (1948) Adsorption isotherms for binary gas mixtures. *Ind. Eng. Chem.* **40**, 1506.
- Brunauer S., Emmet P. H. and Teller E. (1938) Adsorption of gases in multimolecular layers. *J. Amer. Chem. Soc.* **60**, 309-319.
- Butler J. A. V. and Ockrent C. (1930) Studies in electrocapillarity. III. *J. Phys. Chem.* **34**, 2841-2859.
- Coughlin R. W. and Ezra F. S. (1968) Role of surface acidity in the adsorption of organic pollutants on the surface of carbon. *Environ. Sci. Technol.* **2**, 291-297.
- CRC Handbook of Chemistry and Physics (1990-1991). pp.8-36, 71st edition.
- Crittenden J. C., Luft P., Hand D. W., Oravitz J. L., Loper S. W. and Ari M. (1985a) Prediction of multicomponent adsorption equilibria using ideal adsorbed solution theory. *Environ. Sci. Technol.* **19**, 1037-1043.
- Crittenden J. C., Luft P. and Hand D. W. (1985b) Prediction of multicomponent adsorption equilibria in background mixtures of unknown composition. *Water Res.* **19**, 1537-1548.
- Crittenden J. C. and Weber W. J., Jr. (1978a) Predictive model for design of fixed-bed adsorbers: Parameter estimation and model development. *J. Environ. Eng. Div.* **104**, 185-197.

- Crittenden J. C. and Weber W. J., Jr. (1978b) Model for design of multicomponent adsorption systems. *J. Environ. Eng. Div.* **104**, 1175-1195.
- Crittenden J. C., Wong B. W. C., Thacker W. E., Snoeyink V. L. and Hinrichs R. L. (1980) Mathematical model of sequential loading in fixed-bed adsorbers. *J. Water Pollut. Control Fed.* **52**, 2780-2792.
- Davis J. A., James R. O. and Leckie J. O. (1978) Surface ionization and complexation at the oxide/water interface. 1. Computation of electrical double layer properties in simple electrolytes. *J. Colloid Interface Sci.*, **63**, 480-490.
- DiGiano F. A., Baldauf G. and Sontheimer H. (1978) A simplified competitive equilibrium adsorption model. *Chem. Eng. Sci.* **33**, 1667-1673.
- Dzombak D. A. and Morel F. M. M. (1990) Surface complexation modeling. Wiley-Interscience, New York.
- Elton G. A. H. (1954) *J. Chem. Soc.* 2958.
- Freundlich H. (1926) Colloid and Capillary Chemistry, Methuen, London
- Fritz W. and Schlunder E. U. (1981) Competitive adsorption of two dissolved organics onto activated carbon: I. Adsorption equilibria. *Chem. Eng. Sci.* **36**, 721-730.
- Fritz W., Merk W. and Schlunder E. U. (1981) Competitive adsorption of two dissolved organics onto activated carbon: II. Adsorption kinetics in batch reactors. *Chem. Eng. Sci.* **36**, 731-741.
- Fu Y., Hansen R. S. and Bartell F. E. (1948) Thermodynamics of adsorption from solution. I. *J. Phys. Chem.* **52**, 374-386.
- Furusawa T. and Smith J. M. (1973) Fluid-particle and intraparticle mass transport rates in slurries. *Ind. Eng. Chem. Fund.* **12**, 197-203.
- Grant T. M. and King C. J. (1990) Mechanism of irreversible adsorption of phenolic compounds by activated carbons. *Ind. Eng. Chem. Res.* **29**, 264-271.
- Hsieh J. S. C., Turian R. M. and Tien C. (1977) Multicomponent liquid phase adsorption in fixed bed. *AIChE J.* **23**, 263-275.
- Huang C. P. and Ostovic F. B. (1978) Removal of Cadmium (II) by activated carbon

- adsorption. *J. Environ. Eng. Div., ASCE* **104 (EES)**, 863-878.
- Huang C. P. and Stumm W. (1973) Specific adsorption of cations on hydrous  $\gamma\text{-Al}_2\text{O}_3$ . *J. Colloid Interface Sci.*, **43**, 409-420.
- Jain J. S. and Snoeyink V. L. (1973) Adsorption from bisolute systems on activated carbon. *J. Water Pollut. Control Fed.* **45**, 2463-2479.
- Jankowska H., Swiatkowski A. and Choma J. (1991) Activated carbon. pp.82-85. Ellis Horwood Series in Physical Chemistry.
- Jossens L. and Prausnitz J. M. (1978) Thermodynamics of multi-solute adsorption from dilute aqueous solutions. *Chem. Eng. Sci.* **33**, 1097-1106.
- Komiyama H. and Smith J. M. (1974) Surface diffusion on liquid filled pores. *AIChE J.* **20**, 1110.
- Kuo J. F., Fedram E. O., Hines A. L. and McTernan W. F. (1987) Kinetics of adsorption of organics from water produced during *in situ* tar sands experiments. *Chem. Eng. Comm.* **50**, 201-211.
- Langmuir I. (1918) The adsorption of gases on plane surfaces of glass, mica, and platinum. *J. Amer. Chem. Soc.* **40**, 1362-1402.
- Mattson J. S., Mark H.B., Jr., Malbin M. N., Weber W. J., Jr. and Crittenden J. C. (1969a) Surface chemistry of active carbon: Specific adsorption of phenols. *J. Colloid Interface Sci.* **31**, 116-130.
- Mattson J. S., Mark H.B., Jr. and Weber W. J., Jr. (1969b) Identification of surface functional groups on active carbon by infrared internal reflection spectrophotometric. *Anal. Chem.* **41**, 355-358.
- Mattson J. S., Lee L., Mark H. B., Jr. and Weber W. J., Jr. (1970) Surface oxides of activated carbon: Internal reflectance spectroscopic examination of activated sugar carbons. *J. Colloid Interface Sci.* **33**, 284-293.
- Maurer R. T. (1980) *ACS Symp. Ser.* **135**, 73.
- Merk W., Fritz W. and Schlunder E. U. (1981) Competitive adsorption of two dissolved organics onto activated carbon: III. Adsorption kinetics in fixed beds. *Chem. Eng. Sci.* **36**, 743-754.

- Montgomery J. M., Consulting Engineers, Inc. (1985) Water Treatment Principles and Design. pp.183-184. Wiley-Interscience, New York.
- Muller G., Radke C. J. and Prausnitz J. M. (1980) Adsorption of weak organic electrolytes from aqueous solution on activated carbon. *J. Phys. Chem.*, **84**, 367-376.
- Murin C. J. and Snoeyink V. L. (1979) Competitive adsorption of 2,4-dichlorophenol and 2,4,6-trichlorophenol in the nanomolar to micromolar concentration range. *Environ. Sci. Technol.* **13**, 305-311.
- Nicholson D. K., Woods S. L., Istok J. D. and Peek D. C. (1992) Reductive dechlorination of chlorophenols by a pentachlorophenol-acclimated methanogenic consortium. *Appl. Environ. Microbiol.* **58**, 2280-2286.
- Radke C. J. and Prausnitz J. M. (1972) Thermodynamics of multi-solute adsorption from dilute liquid solutions. *AIChE J.* **18**, 761-768.
- Ruthven D. M. (1984) Principles of Adsorption and Adsorption Processes. John Wiley & Sons, New York.
- Schellenberg K., Leuenberger C. and Schwarzenbach R. P. (1984) Sorption of chlorophenols by natural sediments and aquifer materials. *Environ. Sci. Technol.* **18**, 652-657.
- Schindler P. W. and Gamsjager H. (1972) Acid-base reactions of the TiO<sub>2</sub> (Anatase) - Water interface and the point of zero charge of TiO<sub>2</sub> suspensions. *Kolloid Z. Z. Polymere*, **250**, 759-763.
- Schindler P. W. and Kamber H. R. (1968) Die aciditat von silanolgruppen. *Helv. Chim. Acta*, **51**, 1781-1786.
- Sips R. (1948) On the structure of a catalyst surface. *J. Chem. Phys.* **16**, 490-494.
- Smith E. H. and Weber W. J., Jr. (1988) Modeling activated carbon adsorption of target organic compounds from leachate-contaminated groundwaters. *Environ. Sci. Technol.* **22**, 213-321.
- Snoeyink V. L., Weber W. J., Jr. and Mark H. B., Jr. (1969) Sorption of phenol and nitrophenol by active carbon. *Environ. Sci. Technol.* **3**, 918-926.

- Speitel G. E., Jr., Lu C. J., Turakhia M. and Zhu X. J. (1989a) Biodegradation of trace concentrations of substituted phenols in granular activated carbon columns. *Environ. Sci. Technol.* **23**, 68-74.
- Speitel G. E., Jr., Lu C. J., Zhu X. J. and Turakhia M. H. (1989b) Biodegradation and adsorption of a bisolute mixture in GAC columns. *J. Water Pollut. Control Fed.* **61**, 221-229.
- Stumm W., Huang C. P. and Jenkins S. R. (1970) Specific chemical interactions affecting the stability of dispersed systems. *Croat. Chem. Acta*, **42**, 223-244.
- Thacker W. E., Crittenden J. C. and Snoeyink V. L. (1984) Modeling of adsorber performance: Variable influent concentration and comparison of adsorbents. *J. Water Pollut. Control Fed.* **56**, 243-250.
- Toth J. (1971) State equations of the solid-gas interface layers. *Acta Chim. Acad. Sci. Hung.* **69**, 311.
- Traegner U. K. and Suidan M. T. (1989) Evaluation of surface and film diffusion coefficients for carbon adsorption. *Water Res.* **23**, 267-273.
- van Vliet B. M. and Weber W. J., Jr. (1981) Comparative performance of synthetic adsorbents and activated carbon for specific compound removal from wastewaters. *J. Water Pollut. Control Fed.* **53**, 1585-1598.
- Weber W. J., Jr. and Morris J. C. (1963) Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Amer. Soc. Civil Eng.* **89**, 31-59.
- Weber W. J., Jr. and Morris J. C. (1964) Equilibrium and capacities for adsorption on carbon. *J. Sanit. Eng. Div. Amer. Soc. Civil Eng.* **90**, 79-107.
- Weber W. J., Jr. and Smith E. H. (1987) Simulation and design models for adsorption processes. *Environ. Sci. Technol.* **21**, 1040-1050.
- Wermeulen T. (1958) Separation by adsorption methods. *Adv. in Chem. Eng.* **2**, 163-165.
- Westall J. FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants from Experimental Data. Department of Chemistry, Oregon State University, Corvallis, OR, 1982; Report 82-01.

- Westall J. C., Leuenberger C., Schwarzenbach R. P. (1985) Influence of pH and ionic strength on the aqueous-nonaqueous distribution of chlorinated phenols. *Environ. Sci. Technol.* **19**, 193-198.
- Wilmanski K. and Breemen A. N. (1990) Competitive adsorption of trichloroethylene and humic substances from groundwater on activated carbon. *Water Res.* **24**, 773-779.
- Wu S. C. and Gschwend P. M. (1986) Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environ. Sci. Technol.* **20**, 717-725.
- Yen C. Y. and Singer P. C. (1984) Competitive adsorption of phenols on activated carbon. *J. Environ. Eng.* **110**, 976-989.
- Yon C. M. and Turnock P. H. (1971) Multicomponent adsorption equilibria on molecular sieves. *AIChE Symp. Ser.* **67**, 75-83.
- Yonge D. R. and Keinath T. M. (1986) The effects of non-ideal competition on multi-component adsorption equilibria. *J. Water Pollut. Control Fed.* **58**, 77-81.
- Yonge D. R., Keinath T. M., Poznanska K. and Jiang Z. P. (1985) Single-solute irreversible adsorption on granular activated carbon. *Environ. Sci. Technol.* **19**, 690-694.
- Young D. M. and Crowell A. D. (1962) Physical Adsorption of Gases: Chapter 11. The adsorption of gas mixtures. Butterworths, Inc., Washington, D. C.
- Yu J. W. and Neretnieks I. (1990) Single-component and multicomponent adsorption equilibria on activated carbon of methycyclohexane, toluene, and isobutyl methyl ketone. *Ind. Eng. Chem. Res.* **29**, 220-231.
- Zogorski J. S., Faust S. D. and Haas J. H., Jr. (1976) The kinetics of adsorption of phenols by granular activated carbon. *J. Colloid Interface Sci.* **55**, 329-341.

## APPENDICES

### Appendix A Computer Program for IAS Model

```

REM THIS PROGRAM SOLVES IDEAL ADSORBED SOLUTION
REM (IAS) MODEL FOR TWO COMPONENT SYSTEM.
REM NEWTON-RAPHSON METHOD IS USED. LANGMUIR ISOTHERM
REM PARAMETERS NEED TO BE INPUTTED.
PRINT "HOW MANY DATA POINTS";
INPUT N
DIM Q(2), B(2), C01(N), C02(N), C1(N), C2(N), X01(N)
DIM X02(N), X1(N), X2(N), Z1(N), Z2(N)
REM INPUT LANGMUIR ISOTHERM PARAMETERS FOR EACH OF
REM COMPONENTS
PRINT "ADSORPTIVE CAPACITY (COMPONENT 1)";
INPUT Q(1)
PRINT "ADSORPTIVE CAPACITY (COMPONENT 2)";
INPUT Q(2)
PRINT "CONSTANT B (COMPONENT 1)";
INPUT B(1)
PRINT "CONSTANT B (COMPONENT 2)";
INPUT B(2)
REM INPUT EXPERIMENTAL DATA POINTS (CONCENTRATIONS)
PRINT "C1"
FOR I = 1 TO N
    INPUT C1(I)
NEXT I
PRINT "C2"
FOR I = 1 TO N
    INPUT C2(I)
NEXT I
REM COMPUTATION FOR IAS
DEF FNA (X) = Q(1) * LOG(1 + B(1) * X) - Q(2)
    * LOG(1 + B(2) * X * C2(I) / (X - C1(I)))
DEF FNB (X) = Q(1) * B(1) / (1 + B(1) * X) + Q(2) * B(2)
    * C1(I) * C2(I) / ((X + B(2) * C2(I) * X - C1(I))
    * (X - C1(I)))
FOR I = 1 TO N
    X1 = C1(I) * 1.02
10    X2 = X1 - FNA(X1) / FNB(X1)
    RESIDUE = ABS(X1 - X2)
    IF RESIDUE < .000001 THEN 20
    X1 = X2
    GOTO 10
20    C01(I) = X2
    C02(I) = C01(I) * C2(I) / (C01(I) - C1(I))
    Z1(I) = C1(I) / C01(I)
    Z2(I) = C2(I) / C02(I)
    X01(I) = Q(1) * B(1) * C01(I) / (1 + B(1) * C01(I))
    X02(I) = Q(2) * B(2) * C02(I) / (1 + B(2) * C02(I))

```

```

      X1(I) = Z1(I) / (Z1(I) / X01(I) + Z2(I) / X02(I))
      X2(I) = Z2(I) / (Z1(I) / X01(I) + Z2(I) / X02(I))
NEXT I
REM OUTPUT COMPUTATIONAL RESULTS
OPEN "A:DC1.IAS" FOR OUTPUT AS #1
PRINT TAB(5); "C1"; TAB(14); "C2"; TAB(22); "C01";
      TAB(31); "C02"; TAB(41); "Z1"; TAB(50); "Z2";
      TAB(58); "X1"; TAB(67); "X2"
PRINT #1, TAB(5); "C1"; TAB(14); "C2"; TAB(22); "C01";
      TAB(31); "C02"; TAB(41); "Z1"; TAB(50); "Z2";
      TAB(58); "X1"; TAB(67); "X2"
PRINT
FOR I = 1 TO N
  PRINT USING "###.#### "; C1(I); C2(I); C01(I);
      C02(I); Z1(I); Z2(I); X1(I); X2(I)
  PRINT #1, USING "###.#### "; C1(I); C2(I); C01(I);
      C02(I); Z1(I); Z2(I); X1(I); X2(I)
NEXT I
CLOSE #1
END

```

## Appendix B Computer Program for Modified IAS Model

```

REM THIS PROGRAM SOLVES MODIFIED IDEAL ADSORBED
REM SOLUTION (IAS) MODEL FOR TWO COMPONENT SYSTEM.
REM NEWTON-RAPHSON METHOD IS USED. LANGMUIR ISOTHERM
REM PARAMETERS AND INITIAL LIQUID-PHASE
REM CONCENTRATIONS NEED TO BE INPUTTED.
PRINT "HOW MANY DATA POINTS";
INPUT N
DIM Q(2), B(2), C01(N), C02(N), C1(N), C2(N), X01(N)
DIM X02(N), X1(N), X2(N), Z1(N), Z2(N), F(N)
REM INPUT LANGMUIR ISOTHERM PARAMETERS FOR EACH OF
REM OMPONENTS
PRINT "ADSORPTIVE CAPACITY (COMPONENT 1)";
INPUT Q(1)
PRINT "ADSORPTIVE CAPACITY (COMPONENT 2)";
INPUT Q(2)
PRINT "CONSTANT B (COMPONENT 1)";
INPUT B(1)
PRINT "CONSTANT B (COMPONENT 2)";
INPUT B(2)
REM INPUT EXPERIMENTAL DATA POINTS (CONCENTRATIONS)
PRINT "INITIAL CONCENTRATION (COMPONENT 1)";
INPUT CI1
PRINT "INITIAL CONCENTRATION (COMPONENT 2)";
INPUT CI2
PRINT "C1"
FOR I = 1 TO N
    INPUT C1(I)
NEXT I
PRINT "C2"
FOR I = 1 TO N
    INPUT C2(I)
NEXT I
REM COMPUTATION FOR MODIFIED IAS
DEF FNA (X) = Q(1) * LOG(1 + B(1) * X) - F(I) * Q(2)
    * LOG(1 + B(2) * X * C2(I) / (X - C1(I)))
DEF FNB (X) = Q(1) * B(1) / (1 + B(1) * X) + F(I) * Q(2)
    * B(2) * C1(I) * C2(I) / ((X + B(2) * C2(I) * X
    - C1(I)) * (X - C1(I)))
FOR I = 1 TO N
    F(I) = 1
    J = 0
    W2 = 0
    a = (CI1 - C1(I)) * C2(I) / ((CI2 - C2(I)) * C1(I))
5    X1 = C1(I) * 1.02
10   X2 = X1 - FNA(X1) / FNB(X1)
    RESIDUE = ABS(X1 - X2)

```

```

IF RESIDUE < .0000001 THEN 20
X1 = X2
GOTO 10
20 C01(I) = X2
C02(I) = C01(I) * C2(I) / (C01(I) - C1(I))
Z1(I) = C1(I) / C01(I)
Z2(I) = C2(I) / C02(I)
X01(I) = Q(1) * B(1) * C01(I) / (1 + B(1) * C01(I))
X02(I) = Q(2) * B(2) * C02(I) / (1 + B(2) * C02(I))
X1(I) = Z1(I) / (Z1(I) / X01(I) + Z2(I) / X02(I))
X2(I) = Z2(I) / (Z1(I) / X01(I) + Z2(I) / X02(I))
K = X1(I) * C2(I) / (X2(I) * C1(I))
IF ABS(a / K - 1) < .005 THEN 30
W = ABS(a / K - 1)
J = J + 1
IF J = 1 THEN W1 = W
IF J = 2 THEN W2 = W
IF W2 > W1 THEN 25
F(I) = F(I) + .001
PRINT F(I)
GOTO 5
25 F(I) = F(I) - .001
PRINT F(I)
GOTO 5
30 NEXT I
REM OUTPUT COMPUTATIONAL RESULTS
OPEN "A:DC1.MIA" FOR OUTPUT AS #1
PRINT TAB(5); "C1"; TAB(13); "C2"; TAB(20); "C01";
TAB(28); "C02"; TAB(37); "Z1"; TAB(45); "Z2";
TAB(52); "X1"; TAB(60); "X2"; TAB(68); "F"
PRINT #1, TAB(5); "C1"; TAB(13); "C2"; TAB(20); "C01";
TAB(28); "C02"; TAB(37); "Z1"; TAB(45); "Z2";
TAB(52); "X1"; TAB(60); "X2"; TAB(69); "F"
PRINT
FOR I = 1 TO N
PRINT USING "###.#### "; C1(I); C2(I); C01(I);
C02(I); Z1(I); Z2(I); X1(I); X2(I); F(I)
PRINT #1, USING "###.#### "; C1(I); C2(I); C01(I);
C02(I); Z1(I); Z2(I); X1(I); X2(I); F(I)
NEXT I
CLOSE #1
END

```

Appendix C FITEQL Input and Output (2,4,5-TCP)

```

1
1
1
1
1
1
40
3
1      2      1
00004 -3.0  1.00E-3  HA
00006 -3.0  1.00E-3  B
00160 -1.0  0.00E00  PSI
00011  0.0  0.00E00  XClP
00001  0.0  0.00E00  H+
00008  0.0  0.00E00  ClP-

00001  0.0      01 01
00002 -14.0     01 -1
00003  7.78    04 01 160 01  01 01
00004  0.0     04 01
00005  5.7     06 01 160 01  01 01
00006  0.0     06 01
00007  6.94    01 01  08 01
00008  0.0     08 01
00009 10.0     04 01  01 02  08 01  11 01
00010 15.0     06 01 160 -1  01 01  08 01  11 01

1.2    941.0  0.5
      2
      009
      010
      004
      006
      12      1      2      0
      011

0.001352
0.001350
0.001342
0.001344
0.001293
0.001237
0.001141
0.001004
0.000989
0.000878
0.000888
0.000868
      001
-4.19
-5.86
-6.11
-6.35
-6.85
-7.57
-8.04
-9.19
-9.21
-9.98
-10.00
-10.28

```

008  
-3.763  
-3.758  
-3.738  
-3.742  
-3.634  
-3.541  
-3.416  
-3.283  
-3.271  
-3.189  
-3.196  
-3.183  
00 00

## INPUT DATA FOR VERIFICATION

## CHEMICAL EQUILIBRIUM PROBLEM

| ID  | X        | LOGX  | T        | GROUP   | NAME |
|-----|----------|-------|----------|---------|------|
| 4   | 1.00E-03 | -3.00 | 1.00E-03 | I -T    | HA   |
| 6   | 1.00E-03 | -3.00 | 1.00E-03 | I -T    | B    |
| 160 | 1.00E-01 | -1.00 | 0.00E-01 | I -T    | PSI  |
| 11  | 1.00E+00 | 0.00  | 0.00E-01 | II -T,X | XC1P |
| 1   | 1.00E+00 | 0.00  | 0.00E-01 | III-X   | H+   |
| 8   | 1.00E+00 | 0.00  | 0.00E-01 | III-X   | ClP- |

| ID | LOGK   | 4    | 6    | 160   | 11   | 1     | 8    |
|----|--------|------|------|-------|------|-------|------|
| 1  | 0.00   | 0.00 | 0.00 | 0.00  | 0.00 | 1.00  | 0.00 |
| 2  | -14.00 | 0.00 | 0.00 | 0.00  | 0.00 | -1.00 | 0.00 |
| 3  | 7.78   | 1.00 | 0.00 | 1.00  | 0.00 | 1.00  | 0.00 |
| 4  | 0.00   | 1.00 | 0.00 | 0.00  | 0.00 | 0.00  | 0.00 |
| 5  | 5.70   | 0.00 | 1.00 | 1.00  | 0.00 | 1.00  | 0.00 |
| 6  | 0.00   | 0.00 | 1.00 | 0.00  | 0.00 | 0.00  | 0.00 |
| 7  | 6.94   | 0.00 | 0.00 | 0.00  | 0.00 | 1.00  | 1.00 |
| 8  | 0.00   | 0.00 | 0.00 | 0.00  | 0.00 | 0.00  | 1.00 |
| 9  | 10.00  | 1.00 | 0.00 | 0.00  | 1.00 | 2.00  | 1.00 |
| 10 | 15.00  | 0.00 | 1.00 | -1.00 | 1.00 | 1.00  | 1.00 |

SURFACE PROPERTIES:  $C(F/M^{**2}) = 1.200$      $S(M^{**2}/G) = 941.0$   
 $A(G/L) = 0.5$

## PARAMETERS FOR OPTIMIZATION:

LOG K FOR SPECIES:                    9            10  
T FOR COMPONENTS:                    4            6

## INPUT DATA FOR VERIFICATION

## SERIAL DATA AND ESTIMATED STANDARD DEVIATION

## TOTAL CONCENTRATION FOR COMPONENT:

|    | 11        |
|----|-----------|
| 1  | 1.352E-03 |
| 2  | 1.350E-03 |
| 3  | 1.342E-03 |
| 4  | 1.344E-03 |
| 5  | 1.293E-03 |
| 6  | 1.237E-03 |
| 7  | 1.141E-03 |
| 8  | 1.004E-03 |
| 9  | 9.890E-04 |
| 10 | 8.780E-04 |
| 11 | 8.880E-04 |
| 12 | 8.680E-04 |

## LOG FREE CONCENTRATION FOR COMPONENT:

|    | 1      | 8     |
|----|--------|-------|
| 1  | -4.19  | -3.76 |
| 2  | -5.86  | -3.76 |
| 3  | -6.11  | -3.74 |
| 4  | -6.35  | -3.74 |
| 5  | -6.85  | -3.63 |
| 6  | -7.57  | -3.54 |
| 7  | -8.04  | -3.42 |
| 8  | -9.19  | -3.28 |
| 9  | -9.21  | -3.27 |
| 10 | -9.98  | -3.19 |
| 11 | -10.00 | -3.20 |
| 12 | -10.28 | -3.18 |

## STANDARD DEVIATION OF FREE CONCENTRATION:

|           |   |          |        |          |           |
|-----------|---|----------|--------|----------|-----------|
| COMPONENT | 1 | RELATIVE | 0.0230 | ABSOLUTE | 0.000E-01 |
| COMPONENT | 8 | RELATIVE | 0.0230 | ABSOLUTE | 0.000E-01 |

## STANDARD DEVIATION OF TOTAL CONCENTRATION:

|           |    |          |        |          |           |
|-----------|----|----------|--------|----------|-----------|
| COMPONENT | 11 | RELATIVE | 0.0100 | ABSOLUTE | 1.000E-06 |
|-----------|----|----------|--------|----------|-----------|

## VALUES OF ADJUSTABLE PARAMETERS AT EACH ITERATION: LOG K, T, LOG X

| I  | V(Y): SOS/DF | 9         | 10        | 4         | 6         |
|----|--------------|-----------|-----------|-----------|-----------|
| 0  | 5.950E+02    | 1.000E+01 | 1.500E+01 | 1.000E-03 | 1.000E-03 |
| 1  | 1.300E+02    | 1.461E+01 | 1.572E+01 | 1.000E-04 | 1.281E-03 |
| 2  | 3.306E+02    | 1.851E+01 | 1.603E+01 | 1.000E-05 | 1.884E-03 |
| 3  | 1.547E+02    | 1.929E+01 | 1.503E+01 | 4.080E-04 | 1.292E-03 |
| 4  | 1.724E+02    | 2.013E+01 | 1.544E+01 | 6.284E-05 | 1.324E-03 |
| 5  | 6.074E+01    | 2.138E+01 | 1.572E+01 | 8.342E-05 | 1.339E-03 |
| 6  | 9.540E+01    | 2.227E+01 | 1.581E+01 | 4.494E-04 | 8.342E-04 |
| 7  | 4.594E+01    | 2.127E+01 | 1.634E+01 | 4.622E-04 | 8.642E-04 |
| 8  | 2.532E+00    | 2.142E+01 | 1.654E+01 | 4.403E-04 | 9.320E-04 |
| 9  | 2.291E+00    | 2.146E+01 | 1.660E+01 | 4.413E-04 | 9.301E-04 |
| 10 | 2.283E+00    | 2.147E+01 | 1.663E+01 | 4.425E-04 | 9.277E-04 |
| 11 | 2.282E+00    | 2.148E+01 | 1.664E+01 | 4.429E-04 | 9.268E-04 |
| 12 | 2.282E+00    | 2.148E+01 | 1.664E+01 | 4.430E-04 | 9.265E-04 |
| 13 | 2.282E+00    | 2.148E+01 | 1.664E+01 | 4.431E-04 | 9.264E-04 |
| 14 | 2.282E+00    | 2.148E+01 | 1.665E+01 | 4.431E-04 | 9.264E-04 |
| 15 | 2.283E+00    | 2.148E+01 | 1.665E+01 | 4.431E-04 | 9.264E-04 |

\*\*\*\*\* OPTIMIZATION PROCEDURE CONVERGED

|    |           |           |           |           |           |
|----|-----------|-----------|-----------|-----------|-----------|
| 15 | 2.283E+00 | 2.148E+01 | 1.665E+01 | 4.431E-04 | 9.264E-04 |
|----|-----------|-----------|-----------|-----------|-----------|

## DESCRIPTION OF CHEMICAL EQUILIBRIUM: ELECTROSTATICS

|    | T(SIGMA)   | LOG X(PSI) | SIGMA(C/M**2) | PSI(V)  |
|----|------------|------------|---------------|---------|
| 1  | -9.055E-04 | 2.616      | -0.1857       | -0.1547 |
| 2  | -8.949E-04 | 2.585      | -0.1835       | -0.1529 |
| 3  | -8.887E-04 | 2.568      | -0.1823       | -0.1519 |
| 4  | -8.779E-04 | 2.536      | -0.1800       | -0.1500 |
| 5  | -8.520E-04 | 2.461      | -0.1747       | -0.1456 |
| 6  | -7.819E-04 | 2.259      | -0.1603       | -0.1336 |
| 7  | -7.345E-04 | 2.122      | -0.1506       | -0.1255 |
| 8  | -6.429E-04 | 1.857      | -0.1319       | -0.1099 |
| 9  | -6.442E-04 | 1.861      | -0.1321       | -0.1101 |
| 10 | -7.104E-04 | 2.052      | -0.1457       | -0.1214 |
| 11 | -7.117E-04 | 2.056      | -0.1460       | -0.1216 |
| 12 | -7.282E-04 | 2.104      | -0.1493       | -0.1244 |

## DESCRIPTION OF CHEMICAL EQUILIBRIUM: -LOG C

|    | 1     | 2    | 3    | 4     | 5    | 6    | 7    | 8    | 9    | 10   |
|----|-------|------|------|-------|------|------|------|------|------|------|
| 1  | 4.19  | 9.81 | 6.48 | 12.69 | 4.99 | 9.11 | 1.01 | 3.76 | 3.35 | 3.04 |
| 2  | 5.86  | 8.14 | 4.86 | 9.37  | 5.05 | 7.48 | 2.68 | 3.76 | 3.37 | 3.04 |
| 3  | 6.11  | 7.89 | 4.66 | 8.89  | 5.11 | 7.27 | 2.91 | 3.74 | 3.38 | 3.04 |
| 4  | 6.35  | 7.65 | 4.46 | 8.42  | 5.17 | 7.05 | 3.15 | 3.74 | 3.39 | 3.04 |
| 5  | 6.85  | 7.15 | 4.18 | 7.57  | 5.42 | 6.74 | 3.54 | 3.63 | 3.42 | 3.04 |
| 6  | 7.57  | 6.43 | 3.85 | 6.32  | 5.92 | 6.31 | 4.17 | 3.54 | 3.52 | 3.03 |
| 7  | 8.04  | 5.96 | 3.72 | 5.58  | 6.32 | 6.10 | 4.52 | 3.42 | 3.60 | 3.03 |
| 8  | 9.19  | 4.81 | 3.55 | 4.00  | 6.98 | 5.35 | 5.53 | 3.28 | 4.19 | 3.04 |
| 9  | 9.21  | 4.79 | 3.56 | 3.99  | 6.99 | 5.34 | 5.54 | 3.27 | 4.20 | 3.04 |
| 10 | 9.98  | 4.02 | 3.74 | 3.59  | 6.70 | 4.47 | 6.23 | 3.19 | 5.26 | 3.05 |
| 11 | 10.00 | 4.00 | 3.75 | 3.59  | 6.69 | 4.44 | 6.26 | 3.20 | 5.30 | 3.05 |
| 12 | 10.28 | 3.72 | 3.90 | 3.50  | 6.62 | 4.15 | 6.52 | 3.18 | 5.77 | 3.07 |

## DESCRIPTION OF CHEMICAL EQUILIBRIUM: C (MOL/L)

|    | 1         | 2         | 3         | 4         | 5         | 6         |
|----|-----------|-----------|-----------|-----------|-----------|-----------|
| 1  | 6.457E-05 | 1.549E-10 | 3.295E-07 | 2.051E-13 | 1.027E-05 | 7.683E-10 |
| 2  | 1.380E-06 | 7.244E-09 | 1.377E-05 | 4.301E-10 | 8.829E-06 | 3.316E-08 |
| 3  | 7.762E-07 | 1.288E-08 | 2.201E-05 | 1.274E-09 | 7.777E-06 | 5.411E-08 |
| 4  | 4.467E-07 | 2.239E-08 | 3.482E-05 | 3.765E-09 | 6.798E-06 | 8.837E-08 |
| 5  | 1.413E-07 | 7.079E-08 | 6.665E-05 | 2.707E-08 | 3.770E-06 | 1.841E-07 |
| 6  | 2.692E-08 | 3.715E-07 | 1.416E-04 | 4.812E-07 | 1.200E-06 | 4.902E-07 |
| 7  | 9.120E-09 | 1.096E-06 | 1.902E-04 | 2.614E-06 | 4.791E-07 | 7.919E-07 |
| 8  | 6.457E-10 | 1.549E-05 | 2.787E-04 | 9.949E-05 | 1.040E-07 | 4.464E-06 |
| 9  | 6.166E-10 | 1.622E-05 | 2.774E-04 | 1.028E-04 | 1.028E-07 | 4.584E-06 |
| 10 | 1.047E-10 | 9.550E-05 | 1.820E-04 | 2.557E-04 | 1.990E-07 | 3.362E-05 |
| 11 | 1.000E-10 | 1.000E-04 | 1.782E-04 | 2.599E-04 | 2.053E-07 | 3.600E-05 |
| 12 | 5.248E-11 | 1.905E-04 | 1.264E-04 | 3.150E-04 | 2.381E-07 | 7.131E-05 |

|    | 7         | 8         | 9         | 10         |
|----|-----------|-----------|-----------|------------|
| 1  | 9.705E-02 | 1.726E-04 | 4.428E-04 | 9.161E-04  |
| 2  | 2.099E-03 | 1.746E-04 | 4.293E-04 | 9.175E-04  |
| 3  | 1.236E-03 | 1.828E-04 | 4.211E-04 | 9.185E-04  |
| 4  | 7.047E-04 | 1.811E-04 | 4.083E-04 | 9.195E-04  |
| 5  | 2.858E-04 | 2.323E-04 | 3.764E-04 | 9.225E-04  |
| 6  | 6.745E-05 | 2.877E-04 | 3.010E-04 | 9.247E-04  |
| 7  | 3.048E-05 | 3.837E-04 | 2.503E-04 | 9.251E-04  |
| 8  | 2.931E-06 | 5.212E-04 | 6.487E-05 | 9.218E-04  |
| 9  | 2.877E-06 | 5.358E-04 | 6.286E-05 | 9.217E-04  |
| 10 | 5.902E-07 | 6.471E-04 | 5.444E-06 | 8.926E-04  |
| 11 | 5.546E-07 | 6.368E-04 | 4.967E-06 | 8.902E-04  |
| 12 | 2.999E-07 | 6.561E-04 | 1.708E-06 | 8.548E-04? |

## Appendix D Single-Component Adsorption Equilibrium Data

### Effect of Phosphate at Various pH Values

Initial 2,4,5-TCP concentration: 301 mg/l

Carbon dosage: 20 mg/40 ml

| pH    | phosphate (5 mM) |              | no phosphate |              |
|-------|------------------|--------------|--------------|--------------|
|       | q<br>mmol/g      | Ce<br>mmol/l | q<br>mmol/g  | Ce<br>mmol/l |
| 4.19  |                  |              | 2.704        | 0.1724       |
| 5.86  | 2.699            | 0.1747       |              |              |
| 6.11  |                  |              | 2.683        | 0.1829       |
| 6.35  | 2.687            | 0.1812       |              |              |
| 6.85  | 2.585            | 0.2324       |              |              |
| 7.57  |                  |              | 2.473        | 0.288        |
| 8.04  | 2.281            | 0.3839       |              |              |
| 9.19  | 2.007            | 0.521        |              |              |
| 9.21  |                  |              | 1.978        | 0.5353       |
| 9.98  | 1.755            | 0.6468       |              |              |
| 10    |                  |              | 1.776        | 0.6364       |
| 10.28 |                  |              | 1.736        | 0.6562       |

## Effect of pH on Adsorption of 2,4-DCP and 4-CP

| PH    | 2,4-DCP     |              | 4-CP        |              |
|-------|-------------|--------------|-------------|--------------|
|       | q<br>mmol/g | Ce<br>mmol/l | q<br>mmol/g | Ce<br>mmol/l |
| 3.6   | 2.93        | 0.824        |             |              |
| 3.71  | 2.93        | 0.8459       |             |              |
| 3.86  |             |              | 3.237       | 2.115        |
| 4.01  | 2.924       | 0.6887       |             |              |
| 4.17  |             |              | 3.297       | 2.031        |
| 7.18  | 2.862       | 0.5432       |             |              |
| 7.77  |             |              | 3.263       | 2.011        |
| 7.82  |             |              | 3.301       | 1.95         |
| 9.25  |             |              | 3.07        | 1.945        |
| 9.51  | 2.199       | 0.9261       |             |              |
| 10.39 | 1.879       | 0.9958       |             |              |
| 10.46 |             |              | 2.562       | 2.047        |
| 10.48 |             |              | 2.549       | 2.037        |
| 10.61 | 1.769       | 0.9292       |             |              |
| 10.67 | 1.757       | 1.02         |             |              |
| 11    |             |              | 2.237       | 2.074        |
| 11.11 |             |              | 2.258       | 2.036        |
| 12.07 |             |              | 1.786       | 2.112        |

## PCP Isotherm Data at pH 7.0

| Ce<br>mg/l | q<br>mg/g | Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|------------|-----------|--------------|-------------|----------|----------|----------|
| 0.225      | 201.5     | 0.000843     | 0.755726    | 0.001115 | -3.07417 | -0.12163 |
| 0.379      | 230.5     | 0.001423     | 0.864614    | 0.001645 | -2.84678 | -0.06317 |
| 0.811      | 267       | 0.003041     | 1.009001    | 0.003013 | -2.51698 | 0.003891 |
| 1.67       | 317.3     | 0.00628      | 1.190252    | 0.005276 | -2.20204 | 0.075638 |
| 3.34       | 354.5     | 0.012527     | 1.32986     | 0.009419 | -1.90215 | 0.123805 |
| 3.53       | 389.6     | 0.013249     | 1.406583    | 0.009419 | -1.87781 | 0.148165 |
| 6.51       | 415.9     | 0.024441     | 1.501535    | 0.016277 | -1.61188 | 0.176535 |
| 13.55      | 457.7     | 0.050869     | 1.652446    | 0.030784 | -1.29354 | 0.218127 |
| 21.35      | 488.7     | 0.080149     | 1.764366    | 0.045426 | -1.09610 | 0.246588 |
| 36.12      | 514.4     | 0.135603     | 1.857152    | 0.073016 | -0.86773 | 0.268847 |
| 55.5       | 524.16    | 0.208388     | 1.892389    | 0.110119 | -0.68112 | 0.277010 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000696 |
| Std Err of Y Est    | 0.000181 |
| R Squared           | 0.997846 |
| No. of Observations | 5        |
| Degrees of Freedom  | 3        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.704563 |
| Std Err of Coef. | 0.018895 |

|     |          |
|-----|----------|
| Q = | 1.419318 |
| b = | 1012.303 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.003775 |
| Std Err of Y Est    | 0.000830 |
| R Squared           | 0.999620 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.511778 |
| Std Err of Coef. | 0.004983 |

|     |          |
|-----|----------|
| Q = | 1.953968 |
| b = | 135.5526 |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.531087 |
| Std Err of Y Est    | 0.007609 |
| R Squared           | 0.995633 |
| No. of Observations | 5        |
| Degrees of Freedom  | 3        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.210244 |
| Std Err of Coef. | 0.008038 |

|     |          |
|-----|----------|
| K = | 3.396933 |
| n = | 0.210244 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.363306 |
| Std Err of Y Est    | 0.006653 |
| R Squared           | 0.986742 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.113697 |
| Std Err of Coef. | 0.006589 |

|     |          |
|-----|----------|
| K = | 2.308373 |
| n = | 0.113697 |

## 2,3,4,6-TeCP Isotherm Data at pH 7.0

| Ce<br>mg/l | q<br>mg/g | Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|------------|-----------|--------------|-------------|----------|----------|----------|
| 0.074      | 178.2     | 0.000319     | 0.768500    | 0.000415 | -3.49603 | -0.11435 |
| 0.119      | 218       | 0.000513     | 0.940141    | 0.000545 | -3.28971 | -0.02680 |
| 0.221      | 248.6     | 0.000953     | 1.072106    | 0.000888 | -3.02087 | 0.030237 |
| 0.592      | 283.4     | 0.002553     | 1.222183    | 0.002088 | -2.59294 | 0.087136 |
| 1.29       | 325.7     | 0.005563     | 1.404605    | 0.003960 | -2.25467 | 0.147554 |
| 1.29       | 325.7     | 0.005563     | 1.404605    | 0.003960 | -2.25467 | 0.147554 |
| 4.47       | 370.7     | 0.019277     | 1.598671    | 0.012058 | -1.71495 | 0.203759 |
| 13.64      | 420.5     | 0.058823     | 1.813437    | 0.032437 | -1.23044 | 0.258502 |
| 22.22      | 452       | 0.095825     | 1.949284    | 0.049159 | -1.01851 | 0.289875 |
| 60.72      | 465.8     | 0.261859     | 2.008797    | 0.130356 | -0.58193 | 0.302936 |
| 89.54      | 495.8     | 0.386148     | 2.138174    | 0.180597 | -0.41324 | 0.330043 |
| 114.29     | 512       | 0.492884     | 2.208038    | 0.223222 | -0.30725 | 0.344006 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000236 |
| Std Err of Y Est    | 0.000081 |
| R Squared           | 0.997740 |
| No. of Observations | 5        |
| Degrees of Freedom  | 3        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.678595 |
| Std Err of Coef. | 0.018646 |

|     |          |
|-----|----------|
| Q = | 1.473632 |
| b = | 2874.171 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.004933 |
| Std Err of Y Est    | 0.004186 |
| R Squared           | 0.998096 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.452336 |
| Std Err of Coef. | 0.008834 |

|     |          |
|-----|----------|
| Q = | 2.210741 |
| b = | 91.68653 |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.597243 |
| Std Err of Y Est    | 0.024490 |
| R Squared           | 0.956126 |
| No. of Observations | 5        |
| Degrees of Freedom  | 3        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.195332 |
| Std Err of Coef. | 0.024157 |

|     |          |
|-----|----------|
| K = | 3.955879 |
| n = | 0.195332 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.372990 |
| Std Err of Y Est    | 0.010127 |
| R Squared           | 0.982934 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.097627 |
| Std Err of Coef. | 0.005752 |

|     |          |
|-----|----------|
| K = | 2.360427 |
| n = | 0.097627 |

## 2,4,6-TCP Isotherm Data at pH 7.0

| Ce<br>mg/l | q<br>mg/g | Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|------------|-----------|--------------|-------------|----------|----------|----------|
| 0.077      | 105.6     | 0.000390     | 0.534873    | 0.000729 | -3.40892 | -0.27174 |
| 0.105      | 173.7     | 0.000531     | 0.879805    | 0.000604 | -3.27422 | -0.05561 |
| 0.126      | 234.2     | 0.000638     | 1.186243    | 0.000538 | -3.19504 | 0.074173 |
| 0.363      | 329.5     | 0.001838     | 1.668945    | 0.001101 | -2.73550 | 0.222442 |
| 1.01       | 370.3     | 0.005115     | 1.875601    | 0.002727 | -2.29109 | 0.273140 |
| 2.31       | 394.8     | 0.011700     | 1.999696    | 0.005851 | -1.93180 | 0.300963 |
| 2.31       | 394.8     | 0.011700     | 1.999696    | 0.005851 | -1.93180 | 0.300963 |
| 11.13      | 465.5     | 0.056374     | 2.357797    | 0.023909 | -1.24891 | 0.372506 |
| 17.01      | 516.6     | 0.086157     | 2.616623    | 0.032926 | -1.06470 | 0.417741 |
| 41.06      | 543.9     | 0.207972     | 2.754900    | 0.075491 | -0.68199 | 0.440105 |
| 64.89      | 532.2     | 0.328673     | 2.695638    | 0.121927 | -0.48323 | 0.430661 |
| 121.3      | 572.6     | 0.614394     | 2.900268    | 0.211840 | -0.21155 | 0.462438 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000346 |
| Std Err of Y Est    | 0.000126 |
| R Squared           | 0.997083 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.468492 |
| Std Err of Coef. | 0.012667 |

|     |          |
|-----|----------|
| Q = | 2.134508 |
| b = | 1350.473 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.004158 |
| Std Err of Y Est    | 0.003189 |
| R Squared           | 0.998644 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.342455 |
| Std Err of Coef. | 0.006309 |

|     |          |
|-----|----------|
| Q = | 2.920090 |
| b = | 82.35189 |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 1.011691 |
| Std Err of Y Est    | 0.119733 |
| R Squared           | 0.768680 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.328260 |
| Std Err of Coef. | 0.090037 |

|     |          |
|-----|----------|
| K = | 10.27286 |
| n = | 0.328260 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.489994 |
| Std Err of Y Est    | 0.017651 |
| R Squared           | 0.927649 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.091698 |
| Std Err of Coef. | 0.012804 |

|     |          |
|-----|----------|
| K = | 3.090258 |
| n = | 0.091698 |

## 2,4,5-TCP Isotherm Data at pH 7.0

| Ce<br>mg/l | q<br>mg/g | Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|------------|-----------|--------------|-------------|----------|----------|----------|
| 0.031      | 100.6     | 0.000157     | 0.509547    | 0.000308 | -3.80405 | -0.29281 |
| 0.047      | 147.1     | 0.000238     | 0.745074    | 0.000319 | -3.62331 | -0.12780 |
| 0.054      | 132.6     | 0.000273     | 0.671630    | 0.000407 | -3.56301 | -0.17286 |
| 0.074      | 170.4     | 0.000374     | 0.863090    | 0.000434 | -3.42618 | -0.06394 |
| 0.095      | 189.6     | 0.000481     | 0.960340    | 0.000501 | -3.31768 | -0.01757 |
| 0.202      | 234.3     | 0.001023     | 1.186749    | 0.000862 | -2.99006 | 0.074359 |
| 0.266      | 273.2     | 0.001347     | 1.383781    | 0.000973 | -2.87053 | 0.141067 |
| 0.514      | 314.6     | 0.002603     | 1.593476    | 0.001633 | -2.58445 | 0.202345 |
| 2.04       | 366.8     | 0.010332     | 1.857873    | 0.005561 | -1.98578 | 0.269016 |
| 0.514      | 314.6     | 0.002603     | 1.593476    | 0.001633 | -2.58445 | 0.202345 |
| 2.04       | 366.8     | 0.010332     | 1.857873    | 0.005561 | -1.98578 | 0.269016 |
| 5.37       | 420.3     | 0.027199     | 2.128855    | 0.012776 | -1.56543 | 0.328146 |
| 33.8       | 508       | 0.171199     | 2.573063    | 0.066535 | -0.76649 | 0.410450 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000259 |
| Std Err of Y Est    | 0.000043 |
| R Squared           | 0.999425 |
| No. of Observations | 9        |
| Degrees of Freedom  | 7        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.514639 |
| Std Err of Coef. | 0.004662 |

|     |          |
|-----|----------|
| Q = | 1.943109 |
| b = | 1979.875 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.001520 |
| Std Err of Y Est    | 0.000899 |
| R Squared           | 0.999411 |
| No. of Observations | 4        |
| Degrees of Freedom  | 2        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.380562 |
| Std Err of Coef. | 0.006529 |

|     |          |
|-----|----------|
| Q = | 2.627691 |
| b = | 250.3250 |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.954205 |
| Std Err of Y Est    | 0.059246 |
| R Squared           | 0.910676 |
| No. of Observations | 9        |
| Degrees of Freedom  | 7        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.304492 |
| Std Err of Coef. | 0.036043 |

|     |          |
|-----|----------|
| K = | 8.999234 |
| n = | 0.304492 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.501937 |
| Std Err of Y Est    | 0.005989 |
| R Squared           | 0.996941 |
| No. of Observations | 4        |
| Degrees of Freedom  | 2        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.115585 |
| Std Err of Coef. | 0.004526 |

|     |          |
|-----|----------|
| K = | 3.176415 |
| n = | 0.115585 |

## 2,4-DCP Isotherm Data at pH 7.0

| Ce<br>mg/l | q<br>mg/g | Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|------------|-----------|--------------|-------------|----------|----------|----------|
| 0.116      | 139.3     | 0.000711     | 0.854706    | 0.000832 | -3.14767 | -0.06818 |
| 0.169      | 158.2     | 0.001036     | 0.970671    | 0.001068 | -2.98424 | -0.01292 |
| 0.202      | 223.2     | 0.001239     | 1.369493    | 0.000905 | -2.90678 | 0.136559 |
| 0.956      | 270       | 0.005865     | 1.656644    | 0.003540 | -2.23167 | 0.219229 |
| 1.27       | 283.4     | 0.007792     | 1.738863    | 0.004481 | -2.10833 | 0.240265 |
| 2.53       | 312.2     | 0.015523     | 1.915572    | 0.008103 | -1.80901 | 0.282298 |
| 2.58       | 318.4     | 0.015830     | 1.953613    | 0.008103 | -1.80051 | 0.290838 |
| 10.11      | 375.8     | 0.062032     | 2.305804    | 0.026902 | -1.20738 | 0.362822 |
| 10.57      | 375.2     | 0.064854     | 2.302122    | 0.028171 | -1.18805 | 0.362128 |
| 43.1       | 408.3     | 0.264449     | 2.505215    | 0.105559 | -0.57765 | 0.398845 |
| 66.4       | 430.5     | 0.407411     | 2.641428    | 0.154239 | -0.38996 | 0.421838 |
| 90.7       | 454       | 0.556510     | 2.785617    | 0.199779 | -0.25452 | 0.444921 |
| 156.6      | 469.9     | 0.960854     | 2.883175    | 0.333262 | -0.01734 | 0.459871 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000492 |
| Std Err of Y Est    | 0.000147 |
| R Squared           | 0.997886 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.496604 |
| Std Err of Coef. | 0.011427 |

|     |          |
|-----|----------|
| Q = | 2.013674 |
| b = | 1007.900 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.007834 |
| Std Err of Y Est    | 0.005415 |
| R Squared           | 0.998229 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.343566 |
| Std Err of Coef. | 0.006471 |

|     |          |
|-----|----------|
| Q = | 2.910647 |
| b = | 43.85290 |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.746829 |
| Std Err of Y Est    | 0.058743 |
| R Squared           | 0.866008 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.242546 |
| Std Err of Coef. | 0.047702 |

|     |          |
|-----|----------|
| K = | 5.582505 |
| n = | 0.242546 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.461740 |
| Std Err of Y Est    | 0.009004 |
| R Squared           | 0.980048 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.090318 |
| Std Err of Coef. | 0.005763 |

|     |          |
|-----|----------|
| K = | 2.895615 |
| n = | 0.090318 |

## 3,4-DCP Isotherm Data at pH 7.0

| Ce<br>mg/l | q<br>mg/g | Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|------------|-----------|--------------|-------------|----------|----------|----------|
| 0.24       | 95        | 0.001472     | 0.582893    | 0.002526 | -2.83192 | -0.23441 |
| 0.302      | 119       | 0.001852     | 0.730150    | 0.002537 | -2.73212 | -0.13658 |
| 0.325      | 137.6     | 0.001994     | 0.844275    | 0.002361 | -2.70025 | -0.07351 |
| 0.4        | 156.8     | 0.002454     | 0.962081    | 0.002551 | -2.61007 | -0.01678 |
| 0.57       | 189.6     | 0.003497     | 1.163332    | 0.003006 | -2.45625 | 0.065704 |
| 0.95       | 232.3     | 0.005828     | 1.425328    | 0.004089 | -2.23441 | 0.153914 |
| 2.61       | 289.8     | 0.016014     | 1.778132    | 0.009006 | -1.79549 | 0.249964 |
| 2.82       | 313       | 0.017302     | 1.920481    | 0.009009 | -1.76188 | 0.283410 |
| 6.57       | 342.3     | 0.040311     | 2.100257    | 0.019193 | -1.39456 | 0.322272 |
| 12.42      | 391.9     | 0.076205     | 2.404589    | 0.031691 | -1.11801 | 0.381040 |
| 44.7       | 428.3     | 0.274266     | 2.627929    | 0.104366 | -0.56182 | 0.419613 |
| 86.4       | 445.5     | 0.530126     | 2.733464    | 0.193939 | -0.27562 | 0.436713 |
| 133.1      | 463.4     | 0.816664     | 2.843293    | 0.287224 | -0.08795 | 0.453821 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.001541 |
| Std Err of Y Est    | 0.000192 |
| R Squared           | 0.994623 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.461608 |
| Std Err of Coef. | 0.015177 |

|     |          |
|-----|----------|
| Q = | 2.166337 |
| b = | 299.3787 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.005546 |
| Std Err of Y Est    | 0.003128 |
| R Squared           | 0.999378 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.348825 |
| Std Err of Coef. | 0.004348 |

|     |          |
|-----|----------|
| Q = | 2.866766 |
| b = | 62.88925 |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 1.097391 |
| Std Err of Y Est    | 0.058202 |
| R Squared           | 0.900232 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.442005 |
| Std Err of Coef. | 0.065805 |

|     |          |
|-----|----------|
| K = | 12.51387 |
| n = | 0.442005 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.469702 |
| Std Err of Y Est    | 0.014295 |
| R Squared           | 0.964227 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.100260 |
| Std Err of Coef. | 0.009655 |

|     |          |
|-----|----------|
| K = | 2.949187 |
| n = | 0.100260 |

## 4-DCP Isotherm Data at pH 7.0

| Ce<br>mg/l | q<br>mg/g | Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|------------|-----------|--------------|-------------|----------|----------|----------|
| 0.264      | 101.4     | 0.002053     | 0.788920    | 0.002603 | -2.68740 | -0.10296 |
| 0.439      | 119.2     | 0.003415     | 0.927409    | 0.003682 | -2.46653 | -0.03272 |
| 0.743      | 140.4     | 0.005780     | 1.092351    | 0.005292 | -2.23801 | 0.038362 |
| 1.04       | 161.6     | 0.008091     | 1.257294    | 0.006435 | -2.09197 | 0.099436 |
| 1.89       | 185.5     | 0.014704     | 1.443242    | 0.010188 | -1.83254 | 0.159339 |
| 3.01       | 206.8     | 0.023418     | 1.608962    | 0.014555 | -1.63043 | 0.206546 |
| 2.59       | 175.3     | 0.020150     | 1.363883    | 0.014774 | -1.69570 | 0.134777 |
| 5.95       | 210       | 0.046292     | 1.633859    | 0.028333 | -1.33448 | 0.213214 |
| 10         | 236.8     | 0.077802     | 1.842371    | 0.042229 | -1.10900 | 0.265377 |
| 18.8       | 265.9     | 0.146269     | 2.068777    | 0.070703 | -0.83484 | 0.315713 |
| 29.9       | 294.7     | 0.232630     | 2.292849    | 0.101459 | -0.63333 | 0.360375 |
| 53.1       | 315.9     | 0.413133     | 2.457791    | 0.168091 | -0.38390 | 0.390545 |
| 73.9       | 350       | 0.574963     | 2.723099    | 0.211142 | -0.24036 | 0.435063 |
| 100.5      | 390.7     | 0.781918     | 3.039757    | 0.257230 | -0.10683 | 0.482838 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.001836 |
| Std Err of Y Est    | 0.000283 |
| R Squared           | 0.996800 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.552359 |
| Std Err of Coef. | 0.015647 |

|     |          |
|-----|----------|
| Q = | 1.810415 |
| b = | 300.8365 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.018987 |
| Std Err of Y Est    | 0.010916 |
| R Squared           | 0.987500 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.323599 |
| Std Err of Coef. | 0.014863 |

|     |          |
|-----|----------|
| Q = | 3.090240 |
| b = | 17.04283 |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.702295 |
| Std Err of Y Est    | 0.011531 |
| R Squared           | 0.992236 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.297042 |
| Std Err of Coef. | 0.013137 |

|     |          |
|-----|----------|
| K = | 5.038427 |
| n = | 0.297042 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.489496 |
| Std Err of Y Est    | 0.010662 |
| R Squared           | 0.992811 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.207946 |
| Std Err of Coef. | 0.007223 |

|     |          |
|-----|----------|
| K = | 3.086714 |
| n = | 0.207946 |

## 2-DCP Isotherm Data at pH 7.0

| Ce<br>mg/l | q<br>mg/g | Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|------------|-----------|--------------|-------------|----------|----------|----------|
| 0.244      | 145.9     | 0.001898     | 1.135143    | 0.001672 | -2.72161 | 0.055050 |
| 0.437      | 163       | 0.003399     | 1.268186    | 0.002680 | -2.46852 | 0.103183 |
| 1.05       | 182.7     | 0.008169     | 1.421458    | 0.005747 | -2.08781 | 0.152734 |
| 1.36       | 206.3     | 0.010581     | 1.605072    | 0.006592 | -1.97546 | 0.205494 |
| 2.81       | 232.4     | 0.021862     | 1.808138    | 0.012091 | -1.66029 | 0.257231 |
| 2.81       | 232.4     | 0.021862     | 1.808138    | 0.012091 | -1.66029 | 0.257231 |
| 4.76       | 259.3     | 0.037034     | 2.017427    | 0.018357 | -1.43139 | 0.304798 |
| 13.82      | 295.5     | 0.107523     | 2.299074    | 0.046768 | -0.96849 | 0.361552 |
| 22.5       | 331.8     | 0.175056     | 2.581498    | 0.067811 | -0.75682 | 0.411871 |
| 47.9       | 350.4     | 0.372675     | 2.726211    | 0.136700 | -0.42866 | 0.435559 |
| 62.7       | 373.3     | 0.487823     | 2.904380    | 0.167961 | -0.31173 | 0.463053 |
| 77.4       | 385.4     | 0.602194     | 2.998521    | 0.200830 | -0.22026 | 0.476907 |
| 101.7      | 393.6     | 0.791254     | 3.062320    | 0.258384 | -0.10168 | 0.486050 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.001022 |
| Std Err of Y Est    | 0.000380 |
| R Squared           | 0.993514 |
| No. of Observations | 5        |
| Degrees of Freedom  | 3        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.515604 |
| Std Err of Coef. | 0.024052 |

|     |          |
|-----|----------|
| Q = | 1.939472 |
| b = | 504.3157 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.010023 |
| Std Err of Y Est    | 0.004655 |
| R Squared           | 0.997758 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.319298 |
| Std Err of Coef. | 0.006179 |

|     |          |
|-----|----------|
| Q = | 3.131861 |
| b = | 31.85469 |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.569159 |
| Std Err of Y Est    | 0.013616 |
| R Squared           | 0.978341 |
| No. of Observations | 5        |
| Degrees of Freedom  | 3        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.189862 |
| Std Err of Coef. | 0.016309 |

|     |          |
|-----|----------|
| K = | 3.708172 |
| n = | 0.189862 |

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.506249 |
| Std Err of Y Est    | 0.008880 |
| R Squared           | 0.990465 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.145079 |
| Std Err of Coef. | 0.005811 |

|     |          |
|-----|----------|
| K = | 3.208114 |
| n = | 0.145079 |

## 2,4,5-TCP Isotherms at Various pH Values

| pH = 4.15 |       |          | Regression Output:  |                 |
|-----------|-------|----------|---------------------|-----------------|
| Ce        | q     | Ce/q     | Constant            | 0.001891        |
| 0.578     | 242.3 | 0.002385 | Std Err of Y Est    | 0.000936        |
| 1.17      | 302.2 | 0.003871 | R Squared           | 0.998107        |
| 2.16      | 370.8 | 0.005825 | No. of Observations | 8               |
| 3.39      | 422.5 | 0.008023 | Degrees of Freedom  | 6               |
| 5.47      | 458.4 | 0.011932 | X Coefficient(s)    | 0.001810        |
| 8.37      | 485.6 | 0.017236 | Std Err of Coef.    | 0.000032        |
| 22.8      | 507.9 | 0.044890 | Q =                 | 552.3619 mg/g   |
| 29.8      | 547.2 | 0.054459 | or                  | 2.797760 mmol/g |
|           |       |          | b =                 | 0.957304 l/mg   |
|           |       |          | or                  | 189.0006 l/mmol |

| pH = 5.22 |       |          | Regression Output:  |                 |
|-----------|-------|----------|---------------------|-----------------|
| Ce        | q     | Ce/q     | Constant            | 0.001626        |
| 0.448     | 241.4 | 0.001855 | Std Err of Y Est    | 0.000671        |
| 0.675     | 302   | 0.002235 | R Squared           | 0.998652        |
| 1.38      | 377.5 | 0.003655 | No. of Observations | 8               |
| 3.84      | 427.9 | 0.008974 | Degrees of Freedom  | 6               |
| 4.86      | 457.5 | 0.010622 | X Coefficient(s)    | 0.001780        |
| 9.38      | 488   | 0.019221 | Std Err of Coef.    | 0.000026        |
| 15.3      | 521.4 | 0.029344 | Q =                 | 561.7905 mg/g   |
| 27.9      | 551   | 0.050635 | or                  | 2.845517 mmol/g |
|           |       |          | b =                 | 1.094642 l/mg   |
|           |       |          | or                  | 216.1152 l/mmol |

| pH = 6.58 |       |          | Regression Output:  |                 |
|-----------|-------|----------|---------------------|-----------------|
| Ce        | q     | Ce/q     | Constant            | 0.001930        |
| 0.394     | 241.9 | 0.001628 | Std Err of Y Est    | 0.000966        |
| 1.05      | 301.6 | 0.003481 | R Squared           | 0.996816        |
| 1.4       | 361.7 | 0.003870 | No. of Observations | 8               |
| 5.07      | 412.9 | 0.012279 | Degrees of Freedom  | 6               |
| 5.91      | 440.7 | 0.013410 | X Coefficient(s)    | 0.001846        |
| 11.3      | 467.4 | 0.024176 | Std Err of Coef.    | 0.000042        |
| 14.5      | 504.6 | 0.028735 | Q =                 | 541.4717 mg/g   |
| 25.3      | 529.7 | 0.047762 | or                  | 2.742600 mmol/g |
|           |       |          | b =                 | 0.956760 l/mg   |
|           |       |          | or                  | 188.8932 l/mmol |

pH = 8.17

Regression Output:

| Ce    | q     | Ce/q     | Constant | Std Err of Y Est | R Squared | No. of Observations | Degrees of Freedom | X Coefficient(s) | Std Err of Coef. |
|-------|-------|----------|----------|------------------|-----------|---------------------|--------------------|------------------|------------------|
| 0.365 | 242.4 | 0.001505 | 0.002765 | 0.001432         | 0.997400  | 7                   | 5                  | 0.002169         | 0.000049         |
| 2.62  | 298.5 | 0.008777 |          |                  |           |                     |                    |                  |                  |
| 5.4   | 352.7 | 0.015310 |          |                  |           |                     |                    |                  |                  |
| 7.77  | 392.9 | 0.019776 |          |                  |           |                     |                    |                  |                  |
| 17.4  | 410   | 0.042439 |          |                  |           |                     |                    |                  |                  |
| 21.8  | 434.9 | 0.050126 |          |                  |           |                     |                    |                  |                  |
| 32.7  | 451.2 | 0.072473 |          |                  |           |                     |                    |                  |                  |

Q = 460.8999 mg/g  
 or 2.334498 mmol/g  
 b = 0.784558 l/mg  
 or 154.8954 l/mmol

pH = 9.3

Regression Output:

| Ce    | q     | Ce/q     | Constant | Std Err of Y Est | R Squared | No. of Observations | Degrees of Freedom | X Coefficient(s) | Std Err of Coef. |
|-------|-------|----------|----------|------------------|-----------|---------------------|--------------------|------------------|------------------|
| 0.765 | 198.8 | 0.003848 | 0.003656 | 0.001890         | 0.998220  | 5                   | 3                  | 0.002722         | 0.000066         |
| 4.31  | 265.9 | 0.016209 |          |                  |           |                     |                    |                  |                  |
| 13.7  | 322.8 | 0.042441 |          |                  |           |                     |                    |                  |                  |
| 27    | 344.4 | 0.078397 |          |                  |           |                     |                    |                  |                  |
| 33.8  | 359.5 | 0.094019 |          |                  |           |                     |                    |                  |                  |

Q = 367.3288 mg/g  
 or 1.860552 mmol/g  
 b = 0.744483 l/mg  
 or 146.9834 l/mmol

pH = 10.25

Regression Output:

| Ce   | q     | Ce/q     | Constant | Std Err of Y Est | R Squared | No. of Observations | Degrees of Freedom | X Coefficient(s) | Std Err of Coef. |
|------|-------|----------|----------|------------------|-----------|---------------------|--------------------|------------------|------------------|
| 5.83 | 196.7 | 0.029639 | 0.012088 | 0.001127         | 0.999747  | 4                   | 2                  | 0.003083         | 0.000034         |
| 15.8 | 255.1 | 0.061936 |          |                  |           |                     |                    |                  |                  |
| 29.5 | 289.1 | 0.102040 |          |                  |           |                     |                    |                  |                  |
| 49.2 | 299.9 | 0.164054 |          |                  |           |                     |                    |                  |                  |

Q = 324.3579 mg/g  
 or 1.642900 mmol/g  
 b = 0.255046 l/mg  
 or 50.35374 l/mmol

Comparison of 3,4-DCP Isotherms  
with and without DOM

| Without DOM |          |          |
|-------------|----------|----------|
| Ce          | q        | Ce/q     |
| 0.016014    | 1.778132 | 0.009006 |
| 0.037305    | 1.944410 | 0.019185 |
| 0.070560    | 2.226653 | 0.031689 |
| 0.254018    | 2.433427 | 0.104387 |
| 0.490857    | 2.530985 | 0.193939 |

Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.004177 |
| Std Err of Y Est    | 0.001341 |
| R Squared           | 0.999777 |
| No. of Observations | 5        |
| Degrees of Freedom  | 3        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.388280 |
| Std Err of Coef. | 0.003341 |

|     |          |
|-----|----------|
| Q = | 2.575460 |
| b = | 92.94793 |

| With DOM |          |          |
|----------|----------|----------|
| Ce       | q        | Ce/q     |
| 0.008774 | 1.352313 | 0.006488 |
| 0.040066 | 1.652349 | 0.024248 |
| 0.084672 | 1.926003 | 0.043963 |
| 0.167505 | 2.175727 | 0.076988 |
| 0.457111 | 2.195361 | 0.208216 |

Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.004507 |
| Std Err of Y Est    | 0.002223 |
| R Squared           | 0.999428 |
| No. of Observations | 5        |
| Degrees of Freedom  | 3        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.445000 |
| Std Err of Coef. | 0.006146 |

|     |          |
|-----|----------|
| Q = | 2.247188 |
| b = | 98.73054 |

## Effect of Temperature on PCP Adsorption

| 25 C         |             |          | Regression Output:  |          |
|--------------|-------------|----------|---------------------|----------|
| Ce<br>mmol/l | q<br>mmol/g | Ce/q     | Constant            | 0.000606 |
| 0.000714     | 0.676936    | 0.001056 | Std Err of Y Est    | 0.000093 |
| 0.000812     | 0.756724    | 0.001073 | R Squared           | 0.996778 |
| 0.001368     | 0.852759    | 0.001604 | No. of Observations | 7        |
| 0.001444     | 0.933269    | 0.001547 | Degrees of Freedom  | 5        |
| 0.003249     | 1.134364    | 0.002864 | X Coefficient(s)    | 0.674468 |
| 0.004693     | 1.208376    | 0.003884 | Std Err of Coef.    | 0.017148 |
| 0.006498     | 1.331849    | 0.004879 |                     |          |
|              |             |          | Q =                 | 1.482648 |
|              |             |          | b =                 | 1112.944 |

| 30 C         |             |          | Regression Output:  |          |
|--------------|-------------|----------|---------------------|----------|
| Ce<br>mmol/l | q<br>mmol/g | Ce/q     | Constant            | 0.000615 |
| 0.001238     | 0.798243    | 0.001551 | Std Err of Y Est    | 0.000070 |
| 0.001530     | 0.924604    | 0.001655 | R Squared           | 0.998879 |
| 0.001938     | 1.019195    | 0.001902 | No. of Observations | 4        |
| 0.006498     | 1.263614    | 0.005142 | Degrees of Freedom  | 2        |
|              |             |          | X Coefficient(s)    | 0.695277 |
|              |             |          | Std Err of Coef.    | 0.016467 |
|              |             |          | Q =                 | 1.438273 |
|              |             |          | b =                 | 1130.338 |

| 40 C         |             |          | Regression Output:  |          |
|--------------|-------------|----------|---------------------|----------|
| Ce<br>mmol/l | q<br>mmol/g | Ce/q     | Constant            | 0.000717 |
| 0.001426     | 0.765750    | 0.001862 | Std Err of Y Est    | 0.000043 |
| 0.001631     | 0.843372    | 0.001934 | R Squared           | 0.999304 |
| 0.002148     | 0.926771    | 0.002317 | No. of Observations | 5        |
| 0.003310     | 1.017390    | 0.003254 | Degrees of Freedom  | 3        |
| 0.005957     | 1.130393    | 0.005269 | X Coefficient(s)    | 0.763491 |
|              |             |          | Std Err of Coef.    | 0.011630 |
|              |             |          | Q =                 | 1.309772 |
|              |             |          | b =                 | 1063.809 |

| T(K)  | Q       | LOG Q    | Regression Output:  |                  |
|-------|---------|----------|---------------------|------------------|
| 298.2 | 1.48265 | 0.171038 | Constant            | -0.97337         |
| 303.2 | 1.43827 | 0.157840 | Std Err of Y Est    | 0.004292         |
| 313.2 | 1.30977 | 0.117195 | R Squared           | 0.988301         |
|       |         |          | No. of Observations | 3                |
|       |         |          | Degrees of Freedom  | 1                |
|       |         |          | X Coefficient(s)    | 341.9399         |
|       |         |          | Std Err of Coef.    | 37.20210         |
|       |         |          | Reaction Heat =     | -1564.73 cal/mol |

## Effect of Temperature on 2,4,6-TCP Adsorption

30 C

| Ce       | q        | Ce/q     | Regression Output:  |          |
|----------|----------|----------|---------------------|----------|
| mmol/l   | mmol/g   |          | Constant            | 0.000140 |
| 0.000253 | 0.843168 | 0.000300 | Std Err of Y Est    | 0.000020 |
| 0.000319 | 1.082577 | 0.000294 | R Squared           | 0.998735 |
| 0.000400 | 1.205152 | 0.000332 | No. of Observations | 6        |
| 0.000678 | 1.475966 | 0.000459 | Degrees of Freedom  | 4        |
| 0.001200 | 1.605632 | 0.000747 | X Coefficient(s)    | 0.503472 |
| 0.002947 | 1.810937 | 0.001627 | Std Err of Coef.    | 0.008955 |
|          |          |          | Q=                  | 1.986203 |
|          |          |          | b=                  | 3585.369 |

40 C

| Ce       | q        | Ce/q     | Regression Output:  |          |
|----------|----------|----------|---------------------|----------|
| mmol/l   | mmol/g   |          | Constant            | 0.000210 |
| 0.000384 | 0.896857 | 0.000429 | Std Err of Y Est    | 0.000028 |
| 0.000724 | 1.028212 | 0.000704 | R Squared           | 0.997362 |
| 0.001068 | 1.137956 | 0.000939 | No. of Observations | 5        |
| 0.001316 | 1.228114 | 0.001072 | Degrees of Freedom  | 3        |
| 0.002324 | 1.351027 | 0.001720 | X Coefficient(s)    | 0.655060 |
|          |          |          | Std Err of Coef.    | 0.019449 |
|          |          |          | Q=                  | 1.526576 |
|          |          |          | b=                  | 3108.558 |

50 C

| Ce       | q        | Ce/q     | Regression Output:  |          |
|----------|----------|----------|---------------------|----------|
| mmol/l   | mmol/g   |          | Constant            | 0.000447 |
| 0.00076  | 0.67     | 0.001134 | Std Err of Y Est    | 0.000092 |
| 0.001043 | 0.723969 | 0.001441 | R Squared           | 0.991941 |
| 0.001190 | 0.856337 | 0.001389 | No. of Observations | 4        |
| 0.002871 | 0.962028 | 0.002985 | Degrees of Freedom  | 2        |
|          |          |          | X Coefficient(s)    | 0.879645 |
|          |          |          | Std Err of Coef.    | 0.056064 |
|          |          |          | Q=                  | 1.136821 |
|          |          |          | b=                  | 1964.430 |

| T (K) | Q      | Log Q    | Regression Output:  |                  |
|-------|--------|----------|---------------------|------------------|
| 323.2 | 1.1368 | 0.055684 | Constant            | -3.61101         |
| 313.2 | 1.5266 | 0.183725 | Std Err of Y Est    | 0.008768         |
| 303.2 | 1.9862 | 0.298022 | R Squared           | 0.997384         |
|       |        |          | No. of Observations | 3                |
|       |        |          | Degrees of Freedom  | 1                |
|       |        |          | X Coefficient(s)    | 1186.271         |
|       |        |          | Std Err of Coef.    | 60.74584         |
|       |        |          | Reaction Heat =     | -5425.71 cal/mol |

## Effect of Temperature on 2,4-DCP Adsorption

22.5 C

| Ce       | q        | Ce/q     | Regression Output:  |          |
|----------|----------|----------|---------------------|----------|
| mmol/l   | mmol/g   |          | Constant            | 0.000502 |
| 0.001374 | 1.225374 | 0.001121 | Std Err of Y Est    | 0.000084 |
| 0.001740 | 1.372867 | 0.001267 | R Squared           | 0.998524 |
| 0.003227 | 1.536290 | 0.002100 | No. of Observations | 6        |
| 0.005286 | 1.669034 | 0.003167 | Degrees of Freedom  | 4        |
| 0.007315 | 1.788799 | 0.004089 | X Coefficient(s)    | 0.483681 |
| 0.012035 | 1.924492 | 0.006253 | Std Err of Coef.    | 0.009296 |
|          |          |          | Q=                  | 2.067478 |
|          |          |          | b=                  | 962.0086 |

30 C

| Ce       | q        | Ce/q     | Regression Output:  |          |
|----------|----------|----------|---------------------|----------|
| mmol/l   | mmol/g   |          | Constant            | 0.000345 |
| 0.001002 | 1.359298 | 0.000737 | Std Err of Y Est    | 0.000047 |
| 0.001823 | 1.523900 | 0.001196 | R Squared           | 0.999533 |
| 0.003109 | 1.710922 | 0.001817 | No. of Observations | 6        |
| 0.004790 | 1.857825 | 0.002578 | Degrees of Freedom  | 4        |
| 0.006725 | 1.977000 | 0.003401 | X Coefficient(s)    | 0.458226 |
| 0.012802 | 2.064316 | 0.006201 | Std Err of Coef.    | 0.004947 |
|          |          |          | Q=                  | 2.182328 |
|          |          |          | b=                  | 1327.798 |

40 C

| Ce       | q        | Ce/q     | Regression Output:  |          |
|----------|----------|----------|---------------------|----------|
| mmol/l   | mmol/g   |          | Constant            | 0.000253 |
| 0.000743 | 1.529800 | 0.000485 | Std Err of Y Est    | 0.000100 |
| 0.001634 | 1.701482 | 0.000960 | R Squared           | 0.996369 |
| 0.002247 | 1.815347 | 0.001238 | No. of Observations | 6        |
| 0.004831 | 1.957531 | 0.002468 | Degrees of Freedom  | 4        |
| 0.006666 | 2.057236 | 0.003240 | X Coefficient(s)    | 0.435020 |
| 0.009675 | 2.222429 | 0.004353 | Std Err of Coef.    | 0.013130 |
|          |          |          | Q=                  | 2.298744 |
|          |          |          | b=                  | 1712.834 |

50 C

|          |          |          | Regression Output:  |          |
|----------|----------|----------|---------------------|----------|
| Ce       | q        | Ce/q     | Constant            | 0.000296 |
| mmol/l   | mmol/g   |          | Std Err of Y Est    | 0.000051 |
| 0.001327 | 1.684963 | 0.000787 | R Squared           | 0.999267 |
| 0.001805 | 1.797058 | 0.001004 | No. of Observations | 6        |
| 0.003327 | 1.929802 | 0.001724 | Degrees of Freedom  | 4        |
| 0.003640 | 2.087325 | 0.001743 | X Coefficient (s)   | 0.402773 |
| 0.007551 | 2.255467 | 0.003348 | Std Err of Coef.    | 0.005452 |
| 0.012389 | 2.351043 | 0.005269 |                     |          |
|          |          |          | Q=                  | 2.482785 |
|          |          |          | b=                  | 1358.731 |

| T (K) | Q       | Log Q    | Regression Output:  |          |
|-------|---------|----------|---------------------|----------|
| 295.7 | 2.06748 | 0.315441 | Constant            | 1.226138 |
| 303.2 | 2.18233 | 0.338920 | Std Err of Y Est    | 0.003705 |
| 313.2 | 2.29874 | 0.361489 | R Squared           | 0.992016 |
| 323.2 | 2.48279 | 0.394939 | No. of Observations | 4        |
|       |         |          | Degrees of Freedom  | 2        |
|       |         |          | X Coefficient (s)   | -269.437 |
|       |         |          | Std Err of Coef.    | 17.09201 |
|       |         |          | Reaction Heat=      | 1232.962 |

## Effect of Temperature on 4-CP Adsorption

|          |          |          | Regression Output:  |              |
|----------|----------|----------|---------------------|--------------|
| Ce       | 23 C     | Ce/q     | Constant            | 0.000641     |
| mmol/l   | q        |          | Std Err of Y Est    | 0.000155     |
|          | mmol/g   |          | R Squared           | 0.999235     |
| 0.000957 | 0.898473 | 0.001065 | No. of Observations | 5            |
| 0.002147 | 1.114675 | 0.001926 | Degrees of Freedom  | 3            |
| 0.006007 | 1.339106 | 0.004486 |                     |              |
| 0.010623 | 1.485735 | 0.007150 | X Coefficient(s)    | 0.607245     |
| 0.020797 | 1.576255 | 0.013194 | Std Err of Coef.    | 0.009698     |
|          |          |          |                     | Q = 1.646780 |
|          |          |          |                     | b = 946.1319 |

|          |          |          | Regression Output:  |              |
|----------|----------|----------|---------------------|--------------|
| Ce       | 30 C     | Ce/q     | Constant            | 0.000673     |
| mmol/l   | q        |          | Std Err of Y Est    | 0.000381     |
|          | mmol/g   |          | R Squared           | 0.993305     |
| 0.000815 | 0.990490 | 0.000823 | No. of Observations | 7            |
| 0.001578 | 1.121408 | 0.001407 | Degrees of Freedom  | 5            |
| 0.002371 | 1.218661 | 0.001945 |                     |              |
| 0.007929 | 1.490223 | 0.005321 | X Coefficient(s)    | 0.538766     |
| 0.013765 | 1.600195 | 0.008602 | Std Err of Coef.    | 0.019780     |
| 0.016682 | 1.726624 | 0.009662 |                     |              |
| 0.020124 | 1.823130 | 0.011038 |                     |              |
|          |          |          |                     | Q = 1.856090 |
|          |          |          |                     | b = 799.9947 |

|          |          |          | Regression Output:  |              |
|----------|----------|----------|---------------------|--------------|
| Ce       | 40 C     | Ce/q     | Constant            | 0.000825     |
| mmol/l   | q        |          | Std Err of Y Est    | 0.000301     |
|          | mmol/g   |          | R Squared           | 0.992705     |
| 0.001167 | 1.112431 | 0.001049 | No. of Observations | 7            |
| 0.001795 | 1.215669 | 0.001476 | Degrees of Freedom  | 5            |
| 0.003583 | 1.329381 | 0.002695 |                     |              |
| 0.004997 | 1.488727 | 0.003356 | X Coefficient(s)    | 0.473988     |
| 0.006650 | 1.567278 | 0.004243 | Std Err of Coef.    | 0.018170     |
| 0.014662 | 1.824626 | 0.008036 |                     |              |
| 0.018852 | 1.999682 | 0.009427 |                     |              |
|          |          |          |                     | Q = 2.109756 |
|          |          |          |                     | b = 574.4293 |

| T(K)  | Q      | LOG Q    | Regression Output:  |                  |
|-------|--------|----------|---------------------|------------------|
| 296.2 | 1.6468 | 0.216640 | Constant            | 2.190101         |
| 303.2 | 1.8561 | 0.268601 | Std Err of Y Est    | 0.005038         |
| 313.2 | 2.1098 | 0.324241 | R Squared           | 0.995617         |
|       |        |          | No. of Observations | 3                |
|       |        |          | Degrees of Freedom  | 1                |
|       |        |          | X Coefficient(s)    | -583.841         |
|       |        |          | Std Err of Coef.    | 38.73691         |
|       |        |          | Reaction Heat =     | 2671.694 cal/mol |

## Reproducibility of 2,4-DCP Isotherm Measurements

| (1)      |          |          | Regression Output:  |          |
|----------|----------|----------|---------------------|----------|
| Ce       | q        | Ce/q     | Constant            |          |
| 0.000495 | 1.203545 | 0.000411 | Std Err of Y Est    | 0.000341 |
| 0.000938 | 1.371687 | 0.000683 | R Squared           | 0.000119 |
| 0.001268 | 1.512101 | 0.000838 | No. of Observations | 0.998561 |
| 0.002218 | 1.696173 | 0.001307 | Degrees of Freedom  | 9        |
| 0.003840 | 1.844846 | 0.002081 |                     | 7        |
| 0.004725 | 1.943961 | 0.002430 | X Coefficient(s)    | 0.426636 |
| 0.007374 | 2.060776 | 0.003578 | Std Err of Coef.    | 0.006120 |
| 0.016106 | 2.191750 | 0.007348 |                     |          |
| 0.019351 | 2.298535 | 0.008418 |                     |          |
|          |          |          | Q =                 | 2.343913 |
|          |          |          | b =                 | 1249.300 |

| (2)      |          |          | Regression Output:  |          |
|----------|----------|----------|---------------------|----------|
| Ce       | q        | Ce/q     | Constant            |          |
| 0.000535 | 1.214754 | 0.000440 | Std Err of Y Est    | 0.000355 |
| 0.000896 | 1.360478 | 0.000659 | R Squared           | 0.000133 |
| 0.001185 | 1.512691 | 0.000783 | No. of Observations | 0.998029 |
| 0.002053 | 1.696763 | 0.001210 | Degrees of Freedom  | 9        |
| 0.003887 | 1.844846 | 0.002107 |                     | 7        |
| 0.005646 | 1.942782 | 0.002906 | X Coefficient(s)    | 0.424376 |
| 0.009085 | 2.057826 | 0.004415 | Std Err of Coef.    | 0.007127 |
| 0.011091 | 2.200600 | 0.005040 |                     |          |
| 0.020649 | 2.296176 | 0.008992 |                     |          |
|          |          |          | Q =                 | 2.356400 |
|          |          |          | b =                 | 1192.977 |

| (3)      |          |          | Regression Output:  |          |
|----------|----------|----------|---------------------|----------|
| Ce       | q        | Ce/q     | Constant            |          |
| 0.000584 | 1.217704 | 0.000480 | Std Err of Y Est    | 0.000376 |
| 0.000737 | 1.375227 | 0.000536 | R Squared           | 0.000119 |
| 0.002047 | 1.511511 | 0.001354 | No. of Observations | 0.998806 |
| 0.002123 | 1.696173 | 0.001252 | Degrees of Freedom  | 9        |
| 0.003651 | 1.838356 | 0.001986 |                     | 7        |
| 0.005787 | 1.942192 | 0.002979 | X Coefficient(s)    | 0.426841 |
| 0.008082 | 2.059596 | 0.003924 | Std Err of Coef.    | 0.005576 |
| 0.013982 | 2.185851 | 0.006396 |                     |          |
| 0.023421 | 2.280246 | 0.010271 |                     |          |
|          |          |          | Q =                 | 2.342790 |
|          |          |          | b =                 | 1132.337 |

(4) Regression Output:

| Ce       | q        | Ce/q     | Constant            |          |
|----------|----------|----------|---------------------|----------|
| 0.000491 | 1.213575 | 0.000404 | Std Err of Y Est    | 0.000348 |
| 0.000825 | 1.345729 | 0.000613 | R Squared           | 0.000126 |
| 0.001280 | 1.512101 | 0.000846 | No. of Observations | 0.998311 |
| 0.002230 | 1.702072 | 0.001310 | Degrees of Freedom  | 9        |
| 0.003657 | 1.844846 | 0.001982 |                     | 7        |
| 0.005415 | 1.935702 | 0.002797 | X Coefficient(s)    | 0.426972 |
| 0.009085 | 2.057826 | 0.004415 | Std Err of Coef.    | 0.006637 |
| 0.013038 | 2.197060 | 0.005934 |                     |          |
| 0.020295 | 2.286146 | 0.008877 |                     |          |

Q = 2.342069  
b = 1225.393

(5) Regression Output:

| Ce       | q        | Ce/q     | Constant            |          |
|----------|----------|----------|---------------------|----------|
| 0.000666 | 1.217704 | 0.000547 | Std Err of Y Est    | 0.000372 |
| 0.001002 | 1.359298 | 0.000737 | R Squared           | 0.000103 |
| 0.001823 | 1.523900 | 0.001196 | No. of Observations | 0.998990 |
| 0.003109 | 1.710922 | 0.001817 | Degrees of Freedom  | 8        |
| 0.004790 | 1.857825 | 0.002578 |                     | 6        |
| 0.006725 | 1.977000 | 0.003401 | X Coefficient(s)    | 0.444969 |
| 0.012802 | 2.063726 | 0.006203 | Std Err of Coef.    | 0.005775 |
| 0.020000 | 2.185261 | 0.009152 |                     |          |

Q = 2.247345  
b = 1195.702

## Appendix E Adsorption Kinetics Data

### Effect of Stirring Speed on Adsorption Rate

Carbon dosage: 100 mg/l

| Time, hr | 2,4,6-TCP concentration (mg/l) |         |         |
|----------|--------------------------------|---------|---------|
|          | 200 rpm                        | 400 rpm | 800 rpm |
| 0        | 22.44                          | 22.42   | 22.44   |
| 0.3333   | 21.02                          | 20.58   | 20.58   |
| 0.6666   | 19.75                          | 18.97   | 18.91   |
| 1        | 17.84                          | 16.57   | 16.36   |
| 1.5      |                                | 13.69   | 13.62   |
| 2        | 12.64                          | 11.5    | 11.47   |
| 3        | 10.07                          | 8.69    | 8.6     |
| 5        | 6.62                           | 5.45    | 5.69    |
| 8.25     | 3.75                           | 2.87    | 3.12    |

### Effect of pH on Adsorption Rate

Carbon dosage: 100 mg/l

| Time, hr | 2,4,5-TCP concentration (mg/l) |        |         |
|----------|--------------------------------|--------|---------|
|          | pH 3.95                        | pH 7.0 | pH 10.0 |
| 0        | 19.4                           | 19.4   | 19.4    |
| 0.1666   | 18.21                          | 18.6   | 18.6    |
| 0.3333   | 17.37                          | 17.9   | 18      |
| 0.6666   |                                | 16.33  |         |
| 1        | 13.58                          |        | 14.1    |
| 1.5      | 11.29                          | 11.74  | 12.23   |
| 2        | 9.71                           | 9.9    | 10.94   |
| 3        | 7.36                           | 7.71   | 9.14    |
| 5        | 4.78                           | 4.87   | 7.4     |
| 8.5      | 2.09                           | 2.33   | 5.78    |

## 2,4-DCP Kinetics Data

| 2,4-DCP concentration (mmol/l) |         |         |         |
|--------------------------------|---------|---------|---------|
| Carbon                         | 0.1 g/l | 0.2 g/l | 0.1 g/l |
| Time, hr                       |         |         |         |
| 0                              | 0.1154  | 0.1154  | 0.02865 |
| 0.1666                         | 0.1098  | 0.1037  | 0.02675 |
| 0.3333                         | 0.1043  | 0.0945  | 0.02559 |
| 0.6666                         |         | 0.0736  | 0.02307 |
| 1                              | 0.0816  | 0.062   | 0.02135 |
| 1.5                            | 0.0712  | 0.044   | 0.01792 |
| 2                              | 0.062   | 0.0334  | 0.01528 |
| 3                              | 0.0465  | 0.0194  | 0.01172 |
| 5                              | 0.0282  | 0.0072  | 0.00589 |
| 8.25                           | 0.0144  | 0.0022  | 0.00301 |

## 2,4,6-TCP Kinetics Data

| 2,4,6-TCP concentration (mmol/l) |          |         |         |
|----------------------------------|----------|---------|---------|
| Carbon                           | 0.03 g/l | 0.1 g/l | 0.1 g/l |
| Time, hr                         |          |         |         |
| 0                                | 0.1136   | 0.1136  | 0.02376 |
| 0.3333                           | 0.1100   | 0.1042  | 0.02208 |
| 0.6666                           | 0.1064   | 0.0952  | 0.02011 |
| 1                                | 0.1037   | 0.079   | 0.01778 |
| 1.5                              | 0.0939   | 0.0693  | 0.01514 |
| 2                                | 0.0916   | 0.0582  | 0.01302 |
| 3                                | 0.0844   | 0.044   | 0.01003 |
| 5                                | 0.0752   | 0.0276  | 0.00618 |
| 8.25                             | 0.0670   | 0.0145  | 0.00294 |

## 4-CP Kinetics Data

Carbon dosage: 100 mg/l

| Time,hr | 4-CP concentration (mmol/l) |
|---------|-----------------------------|
| 0       | 0.1257                      |
| 0.3333  | 0.1061                      |
| 0.6666  | 0.1039                      |
| 1       | 0.0896                      |
| 1.5     | 0.078                       |
| 2       | 0.0685                      |
| 3       | 0.0528                      |
| 5       | 0.0414                      |
| 8.25    | 0.0242                      |

## 2,4-DCP Kinetics Data (High Initial Concentration)

Carbon dosage: 400 mg/l

| Time,hr | 2,4-DCP concentration (mmol/l) |
|---------|--------------------------------|
| 0       | 0.5                            |
| 0.1666  | 0.411                          |
| 0.3333  | 0.34                           |
| 0.6666  | 0.231                          |
| 1       | 0.163                          |
| 1.666   | 0.0906                         |
| 2.666   | 0.042                          |
| 4       | 0.0214                         |
| 7       | 0.0111                         |
| 12      | 0.0073                         |

## 2,4,6-TCP Kinetics Data (Long Term)

Carbon dosage: 30 mg/l

| Time, hr | 2,4,6-TCP concentration (mmol/l) |
|----------|----------------------------------|
| 0        | 0.1136                           |
| 0.3333   | 0.11                             |
| 0.6666   | 0.1064                           |
| 1        | 0.1037                           |
| 1.5      | 0.0939                           |
| 2        | 0.0916                           |
| 3        | 0.0844                           |
| 5        | 0.0752                           |
| 8.166    | 0.0674                           |
| 16.5     | 0.0576                           |
| 29.16    | 0.0483                           |
| 42       | 0.044                            |

## PCP Kinetics Data (Long Term)

Carbon dosage: 160 mg/l

| Time, hr | PCP concentration (mmol/l) |
|----------|----------------------------|
| 0        | 0.2951                     |
| 2        | 0.2534                     |
| 6        | 0.1945                     |
| 20       | 0.1333                     |
| 51.6     | 0.1104                     |
| 91.6     | 0.1036                     |
| 120      | 0.0965                     |

## Interruption Test

Carbon dosage: 100 mg/l

| Time, hr | 2,4,6-TCP concentration (mmol/l) |
|----------|----------------------------------|
| 0        | 0.1136                           |
| 0.3333   | 0.1049                           |
| 0.6666   | 0.0965                           |
| 1        | 0.0873                           |
| 1.5      | 0.0751                           |
| 2        | 0.0656                           |
| 3        | 0.0513 (interrupted)             |
| 3.5      | 0.0444                           |
| 4        | 0.0398                           |
| 5        | 0.0309                           |
| 8.25     | 0.0165                           |

## Irreversibility Test

Carbon dosage: 20 mg/l

| Time, hr | concentration (mmol/l) |           |
|----------|------------------------|-----------|
|          | 2,4-DCP                | 2,4,6-TCP |
| 0        | 0.04                   | 0.04      |
| 1        | 0.0364                 | 0.0366    |
| 4        | 0.0302                 | 0.0311    |
| 10       | 0.0241                 | 0.0258    |
| 24       | 0.0205                 | 0.0227    |
| 48       | 0.0176                 | 0.0204    |
| 72       | 0.0162                 | 0.0193    |
| 96       | 0.0149                 | 0.0182    |
| 120      | 0.0138                 | 0.0175    |
| 144      | 0.0133                 | 0.0169    |

## Irreversibility Test (Continued)

Carbon dosage: 20 mg/l

| Time, hr | concentration (mmol/l) |           |
|----------|------------------------|-----------|
|          | 2,4-DCP                | 2,4,6-TCP |
| 0        |                        | 0.04      |
| 1        |                        | 0.0365    |
| 4        |                        | 0.0308    |
| 10       | 0.04                   | 0.0232    |
| 23.25    | 0.0264                 | 0.0191    |
| 48       | 0.0211                 | 0.0176    |
| 72       | 0.0183                 | 0.0166    |
| 96       | 0.017                  | 0.0158    |
| 120      | 0.0162                 | 0.0153    |
| 144      | 0.0153                 | 0.0149    |

Carbon dosage: 20 mg/l

| Time, hr | concentration (mmol/l) |           |
|----------|------------------------|-----------|
|          | 2,4-DCP                | 2,4,6-TCP |
| 0        | 0.04                   |           |
| 1        | 0.037                  |           |
| 4        | 0.0302                 |           |
| 10       | 0.0219                 | 0.04      |
| 13       | 0.0197                 | 0.0354    |
| 23       | 0.0176                 | 0.029     |
| 48       | 0.0159                 | 0.0249    |
| 72       | 0.0144                 | 0.023     |
| 96       | 0.0133                 | 0.0219    |
| 123.5    | 0.0126                 | 0.021     |
| 144      | 0.012                  | 0.0204    |

## Appendix F Multicomponent Adsorption Equilibrium Data

### Single-Component Adsorption Isotherm Constants for PCP/2,4,6-TCP System

| PCP          |             |          |
|--------------|-------------|----------|
| Ce<br>mmol/l | q<br>mmol/g | Ce/q     |
| 0.000904     | 0.380935    | 0.002374 |
| 0.001536     | 0.645815    | 0.002378 |
| 0.002082     | 0.809999    | 0.00257  |
| 0.003379     | 0.955752    | 0.003535 |
| 0.005802     | 1.068735    | 0.005429 |
| 0.013243     | 1.192983    | 0.011101 |

#### Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.001264 |
| Std Err of Y Est    | 0.000280 |
| R Squared           | 0.994586 |
| No. of Observations | 6        |
| Degrees of Freedom  | 4        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.734929 |
| Std Err of Coef. | 0.027110 |

$$Q = 1.3607 \text{ mmol/g}$$

$$b = 581.43 \text{ l/mmol}$$

#### 2,4,6-TCP

| Ce<br>mmol/l | q<br>mmol/g | Ce/q     |
|--------------|-------------|----------|
| 0.000276     | 1.101426    | 0.000250 |
| 0.000437     | 1.225750    | 0.000356 |
| 0.000782     | 1.498805    | 0.000522 |
| 0.000888     | 1.582609    | 0.000561 |
| 0.002841     | 1.830798    | 0.001551 |
| 0.005111     | 2.016825    | 0.002534 |
| 0.014366     | 2.344214    | 0.006128 |

#### Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000232 |
| Std Err of Y Est    | 0.000119 |
| R Squared           | 0.997334 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.416059 |
| Std Err of Coef. | 0.009619 |

$$Q = 2.4035 \text{ mmol/g}$$

$$b = 1793.4 \text{ l/mmol}$$

Single-Component Adsorption Isotherm Constants  
for 2,4,6-TCP/2,4-DCP System

2,4,6-TCP

| Ce<br>mmol/l | q<br>mmol/g | Ce/q     |
|--------------|-------------|----------|
| 0.000143     | 0.790932    | 0.000181 |
| 0.000344     | 0.968210    | 0.000356 |
| 0.000441     | 1.189808    | 0.000370 |
| 0.000691     | 1.420172    | 0.000486 |
| 0.002435     | 1.724077    | 0.001412 |
| 0.005065     | 1.857523    | 0.002726 |
| 0.005503     | 1.954441    | 0.002815 |
| 0.008376     | 2.069867    | 0.004047 |

Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000185 |
| Std Err of Y Est    | 0.000085 |
| R Squared           | 0.997085 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.474411 |
| Std Err of Coef. | 0.010471 |

$$Q = 2.1079 \text{ mmol/g}$$

$$b = 2564.4 \text{ l/mmol}$$

2,4-DCP

| Ce<br>mmol/l | q<br>mmol/g | Ce/q     |
|--------------|-------------|----------|
| 0.000371     | 0.965786    | 0.000384 |
| 0.000890     | 1.235994    | 0.000720 |
| 0.001356     | 1.453104    | 0.000933 |
| 0.003433     | 1.649565    | 0.002081 |
| 0.008731     | 1.812397    | 0.004817 |

Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000228 |
| Std Err of Y Est    | 0.000037 |
| R Squared           | 0.999676 |
| No. of Observations | 5        |
| Degrees of Freedom  | 3        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.527446 |
| Std Err of Coef. | 0.005474 |

$$Q = 1.8959 \text{ mmol/g}$$

$$b = 2313.4 \text{ l/mmol}$$

Single-Component Adsorption Isotherm Constants  
for 2,4-DCP/4-CP System

2,4-DCP

| Ce       | q        | Regression Output:  |          |
|----------|----------|---------------------|----------|
| mmol/l   | mmol/g   | Constant            | 0.000268 |
| 0.000371 | 0.965786 | Std Err of Y Est    | 0.000080 |
| 0.00089  | 1.235994 | R Squared           | 0.999447 |
| 0.001356 | 1.453104 | No. of Observations | 6        |
| 0.003433 | 1.649565 | Degrees of Freedom  | 4        |
| 0.008731 | 1.812397 |                     |          |
| 0.015523 | 1.915572 | X Coefficient(s)    | 0.509170 |
|          |          | Std Err of Coef.    | 0.005986 |

Q = 1.963977 mmol/g  
b = 1898.014 l/mmol

4-CP

| Ce       | q        | Regression Output:  |          |
|----------|----------|---------------------|----------|
| mmol/l   | mmol/g   | Constant            | 0.002523 |
| 0.002057 | 0.789250 | Std Err of Y Est    | 0.000662 |
| 0.003418 | 0.927649 | R Squared           | 0.997204 |
| 0.005782 | 1.092232 | No. of Observations | 9        |
| 0.008079 | 1.257563 | Degrees of Freedom  | 7        |
| 0.014737 | 1.443093 |                     |          |
| 0.023415 | 1.609172 | X Coefficient(s)    | 0.483625 |
| 0.032841 | 1.722884 | Std Err of Coef.    | 0.009678 |
| 0.049973 | 1.850061 |                     |          |
| 0.072491 | 1.971254 |                     |          |

Q = 2.067715 mmol/g  
b = 191.6730 l/mmol

2,4,5-TCP/2,4-DCP Two-Component Adsorption at Various pH Values

Initial concentrations: 2,4,5-T 2,4,5-TCP, 1.019 mmol/l;  
2,4-DCP, 1.026 mmol/l. Carbon dosage, 24 mg/40 ml.

| pH    | 2,4,5-TCP    |             | 2,4-DCP      |             |
|-------|--------------|-------------|--------------|-------------|
|       | Ce<br>mmol/l | q<br>mmol/g | Ce<br>mmol/l | q<br>mmol/g |
| 3.66  | 0.0494       | 1.604       | 0.2019       | 1.354       |
| 4.49  | 0.0533       | 1.603       | 0.2044       | 1.363       |
| 7.37  | 0.1637       | 1.426       | 0.2359       | 1.317       |
| 8.19  | 0.2786       | 1.229       | 0.2595       | 1.262       |
| 8.85  | 0.3413       | 1.139       | 0.3088       | 1.205       |
| 9.79  | 0.4493       | 0.942       | 0.4311       | 0.983       |
| 9.91  | 0.4759       | 0.909       | 0.4583       | 0.95        |
| 10.14 | 0.492        | 0.868       | 0.4821       | 0.895       |
| 10.22 | 0.5016       | 0.859       | 0.4987       | 0.875       |
| 10.3  | 0.5188       | 0.827       | 0.5273       | 0.824       |

## Appendix G Desorption Equilibrium and Kinetics Data

## PCP Adsorption and Desorption Isotherms

## Adsorption

| Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|--------------|-------------|----------|----------|----------|
| 0.000574     | 0.452012    | 0.001269 | -3.24105 | -0.34484 |
| 0.000891     | 0.799326    | 0.001115 | -3.04975 | -0.09727 |
| 0.001505     | 0.914495    | 0.001646 | -2.82231 | -0.03881 |
| 0.003216     | 1.067212    | 0.003014 | -2.49257 | 0.028251 |
| 0.006643     | 1.258921    | 0.005276 | -2.17763 | 0.099998 |
| 0.013249     | 1.406583    | 0.009419 | -1.87778 | 0.148165 |
| 0.024441     | 1.501535    | 0.016277 | -1.61186 | 0.176535 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000830 |
| Std Err of Y Est    | 0.000203 |
| R Squared           | 0.998908 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.637544 |
| Std Err of Coef. | 0.009426 |

$$Q = 1.568518 \text{ mmol/g}$$

$$b = 768.1136 \text{ l/mmol}$$

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.664858 |
| Std Err of Y Est    | 0.077470 |
| R Squared           | 0.845072 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.271059 |
| Std Err of Coef. | 0.051903 |

$$K = 4.622305$$

$$n = 0.271059$$

## Desorption

| Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|--------------|-------------|----------|----------|----------|
| 0.000122     | 0.452012    | 0.000271 | -3.91097 | -0.34484 |
| 0.000176     | 0.624947    | 0.000283 | -3.75225 | -0.20415 |
| 0.000364     | 0.798965    | 0.000456 | -3.43813 | -0.09747 |
| 0.000436     | 0.914134    | 0.000477 | -3.35966 | -0.03898 |
| 0.001018     | 1.065768    | 0.000955 | -2.99220 | 0.027662 |
| 0.002112     | 1.255671    | 0.001682 | -2.67529 | 0.098876 |
| 0.003935     | 1.399362    | 0.002812 | -2.40502 | 0.145930 |
| 0.007256     | 1.487454    | 0.004878 | -2.13925 | 0.172443 |
| 0.012888     | 1.623564    | 0.007938 | -1.88978 | 0.210469 |
| 0.018232     | 1.719237    | 0.010604 | -1.73916 | 0.235335 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000344 |
| Std Err of Y Est    | 0.000205 |
| R Squared           | 0.997182 |
| No. of Observations | 10       |
| Degrees of Freedom  | 8        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.578264 |
| Std Err of Coef. | 0.010868 |

|     |                 |
|-----|-----------------|
| Q = | 1.729311 mmol/g |
| b = | 1678.327 l/mmol |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.688989 |
| Std Err of Y Est    | 0.055398 |
| R Squared           | 0.925297 |
| No. of Observations | 10       |
| Degrees of Freedom  | 8        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.236191 |
| Std Err of Coef. | 0.023727 |

|     |          |
|-----|----------|
| K = | 4.886406 |
| n = | 0.236191 |

## 2,4-DCP Adsorption and Desorption Isotherms

## Adsorption

| Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|--------------|-------------|----------|----------|----------|
| 0.000385     | 1.004417    | 0.000384 | -3.41348 | 0.001914 |
| 0.000926     | 1.285433    | 0.000720 | -3.03315 | 0.109049 |
| 0.001411     | 1.511228    | 0.000933 | -2.85040 | 0.179330 |
| 0.003570     | 1.715547    | 0.002081 | -2.44721 | 0.234402 |
| 0.009080     | 1.884893    | 0.004817 | -2.04187 | 0.275286 |
| 0.027181     | 2.189225    | 0.012415 | -1.56573 | 0.340290 |
| 0.039268     | 2.281261    | 0.017213 | -1.40595 | 0.358175 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000448 |
| Std Err of Y Est    | 0.000275 |
| R Squared           | 0.998574 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.432961 |
| Std Err of Coef. | 0.007314 |

|    |          |        |
|----|----------|--------|
| Q= | 2.309673 | mmol/g |
| b= | 965.1070 | l/mmol |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.607820 |
| Std Err of Y Est    | 0.031305 |
| R Squared           | 0.950052 |
| No. of Observations | 7        |
| Degrees of Freedom  | 5        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.164478 |
| Std Err of Coef. | 0.016865 |

|     |          |
|-----|----------|
| K = | 4.053407 |
| n = | 0.164478 |

## Desorption

| Ce       | q        | Ce/q     | LOG Ce   | LOG q    |
|----------|----------|----------|----------|----------|
| mmol/l   | mmol/g   |          |          |          |
| 0.000182 | 1.285433 | 0.000141 | -3.73937 | 0.109049 |
| 0.000511 | 1.510614 | 0.000338 | -3.29096 | 0.179153 |
| 0.001325 | 1.713707 | 0.000773 | -2.87768 | 0.233936 |
| 0.003810 | 1.954546 | 0.001949 | -2.41904 | 0.291046 |
| 0.010860 | 2.257013 | 0.004811 | -1.96416 | 0.353534 |
| 0.016259 | 2.306417 | 0.007049 | -1.78888 | 0.362938 |
| 0.022947 | 2.388023 | 0.009609 | -1.63926 | 0.378038 |
| 0.030187 | 2.435881 | 0.012392 | -1.52016 | 0.386656 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.000245 |
| Std Err of Y Est    | 0.000154 |
| R Squared           | 0.999054 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                   |          |
|-------------------|----------|
| X Coefficient (s) | 0.407814 |
| Std Err of Coef.  | 0.005123 |

|    |          |        |
|----|----------|--------|
| Q= | 2.452093 | mmol/g |
| b= | 1664.044 | l/mmol |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.587661 |
| Std Err of Y Est    | 0.008905 |
| R Squared           | 0.993616 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                   |          |
|-------------------|----------|
| X Coefficient (s) | 0.125103 |
| Std Err of Coef.  | 0.004093 |

|     |          |
|-----|----------|
| K = | 3.869563 |
| n = | 0.125103 |

## 4-CP Adsorption and Desorption Isotherms

## Adsorption

| Ce<br>mmol/l | q<br>mmol/g | Ce/q     | LOG Ce   | LOG q    |
|--------------|-------------|----------|----------|----------|
| 0.002057     | 0.789250    | 0.002606 | -2.68670 | -0.10278 |
| 0.003418     | 0.927649    | 0.003685 | -2.46612 | -0.03261 |
| 0.005782     | 1.092232    | 0.005294 | -2.23785 | 0.038315 |
| 0.008079     | 1.257563    | 0.006424 | -2.09261 | 0.099529 |
| 0.014737     | 1.443093    | 0.010212 | -1.83157 | 0.159294 |
| 0.023415     | 1.609172    | 0.014551 | -1.63049 | 0.206602 |
| 0.032841     | 1.722884    | 0.019062 | -1.48357 | 0.236256 |
| 0.049973     | 1.850061    | 0.027011 | -1.30126 | 0.267186 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.002234 |
| Std Err of Y Est    | 0.000473 |
| R Squared           | 0.997367 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.505869 |
| Std Err of Coef. | 0.010609 |

|    |                 |
|----|-----------------|
| Q= | 1.976796 mmol/g |
| b= | 226.4387 l/mmol |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.640400 |
| Std Err of Y Est    | 0.016656 |
| R Squared           | 0.986495 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                  |          |
|------------------|----------|
| X Coefficient(s) | 0.270271 |
| Std Err of Coef. | 0.012909 |

|     |          |
|-----|----------|
| K = | 4.369185 |
| n = | 0.270271 |

## Desorption

| Ce       | q        | Ce/q     | LOG Ce   | LOG q    |
|----------|----------|----------|----------|----------|
| mmol/l   | mmol/g   |          |          |          |
| 0.003158 | 1.132031 | 0.002790 | -2.50047 | 0.053858 |
| 0.003913 | 1.302419 | 0.003004 | -2.40743 | 0.114750 |
| 0.006955 | 1.490702 | 0.004665 | -2.15766 | 0.173390 |
| 0.011125 | 1.654866 | 0.006723 | -1.95366 | 0.218762 |
| 0.014549 | 1.765346 | 0.008241 | -1.83716 | 0.246829 |
| 0.019217 | 1.885941 | 0.010189 | -1.71630 | 0.275528 |
| 0.025363 | 1.995643 | 0.012709 | -1.59578 | 0.300082 |
| 0.036956 | 2.056329 | 0.017972 | -1.43231 | 0.313092 |

## Langmuir Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.001502 |
| Std Err of Y Est    | 0.000193 |
| R Squared           | 0.998826 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                   |          |
|-------------------|----------|
| X Coefficient (s) | 0.447687 |
| Std Err of Coef.  | 0.006264 |

|    |                 |
|----|-----------------|
| Q= | 2.233700 mmol/g |
| b= | 297.9786 l/mmol |

## Freundlich Constants

## Regression Output:

|                     |          |
|---------------------|----------|
| Constant            | 0.676124 |
| Std Err of Y Est    | 0.016712 |
| R Squared           | 0.971706 |
| No. of Observations | 8        |
| Degrees of Freedom  | 6        |

|                   |          |
|-------------------|----------|
| X Coefficient (s) | 0.237980 |
| Std Err of Coef.  | 0.016578 |

|     |          |
|-----|----------|
| K = | 4.743777 |
| n = | 0.237980 |

## Desorption Kinetics Data

## PCP

(Initial loading: 1.781 mmol/g)

| Time, hr | Conc., mmol/l |
|----------|---------------|
| 0        | 0             |
| 0.25     | 0.002119      |
| 0.666666 | 0.003646      |
| 1.25     | 0.005018      |
| 2        | 0.006390      |
| 3.75     | 0.008051      |
| 6.75     | 0.009783      |
| 11.75    | 0.011228      |
| 23       | 0.012094      |
| 36       | 0.012961      |

## 2,4-DCP

(Initial loading: 2.805 mmol/g)

| Time, hr | Conc., mmol/l |
|----------|---------------|
| 0        | 0             |
| 0.166666 | 0.005583      |
| 0.333333 | 0.008651      |
| 0.666666 | 0.013437      |
| 1        | 0.016566      |
| 2        | 0.022763      |
| 3.5      | 0.027794      |
| 6        | 0.032028      |
| 10       | 0.03626       |
| 22.5     | 0.03866       |

## 4-CP

(Initial loading: 2.336 mmol/g)

| Time, hr | Conc., mmol/l |
|----------|---------------|
| 0        | 0             |
| 0.166666 | 0.006747      |
| 0.333333 | 0.010397      |
| 0.666666 | 0.014924      |
| 1.166666 | 0.018814      |
| 2        | 0.023482      |
| 3.5      | 0.027089      |
| 6        | 0.030130      |
| 9.5      | 0.031616      |