

MODIFICATION OF A MATHEMATICAL MODEL TO
TAKE INTO ACCOUNT PARTICLE SIZE DISTRIBUTION
IN FIXED BED CARBON ADSORPTION SYSTEMS

by

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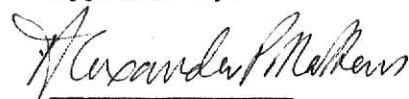
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NOTATIONS

A_{lp}^u	element of collocation matrix A^u for the first derivative, unsymmetrical geometry
B_{ji}	element of collocation matrix B for the second derivative, spherical geometry
C	solution concentration (M/L^3)
C_o	initial or influent concentration (M/L^3)
C_s	solution concentration at external surface of particle (M/L^3)
$\bar{C}$	reduced solution concentration, C/C_o
$\bar{C}_K$	$\bar{C}$ at axial collocation point K
$\bar{C}_1$	$\bar{C}$ at axial collocation point 1
$\bar{C}_s$	reduced solution concentration at particle surface, C_s/C_o
$\bar{C}_{sk}$	$\bar{C}_s$ at axial collocation point K
$\bar{C}_{s1}$	$\bar{C}_s$ at axial collocation point 1
D_g	solute distribution parameter
E_d	surface diffusion modulus
K	Freundlich isotherm constant (L^n/MM^{n-1})
K_1	Linear isotherm constant (L/M)
K_f	film transfer coefficient (L/T)
L_b	bed length (L)
M'	number of axial collocation points
n	Freundlich isotherm exponent
N_D	number of data points
N'	number of radial collocation points
q	surface concentrations (M/M)
q_e	surface concentration in equilibrium with C_o (M/M)

q_s	surface concentration at external surface of particle (M/M)
$\bar{q}$	reduced surface concentration, q/q_e
$\bar{q}_i$	$\bar{q}$ at radial collocation point i
$\bar{q}_{ik}$	$\bar{q}$ at radial collocation point i and axial collocation point K
$\bar{q}_1$	$\bar{q}$ at radial collocation point 1
$\bar{q}_{N'+1}$	$\bar{q}$ at radial collocation point $N'+1$
$\bar{q}_{N'+1,k}$	$\bar{q}$ at radial collocation point $N'+1$ and axial collocation point K
$\bar{q}_s$	reduced surface concentration at particle surface, q_s/q_e
r	radial distance (L)
$\bar{r}$	reduced radial distance, r/R
R	particle radius (L)
Sh	Sherwood number
St	Stanton number
t	time (T)
T'	throughput
v	interstitial velocity (L/T)
v_s	superficial velocity or flow rate (L/T)
W_1	element of collocation vector W
$W_{N'+1}$	element of collocation vector W
Z	axial distance (L)
Z/L_b	reduced axial distance, Z/L_b
b	porosity of fixed bed
θ	dimensionless time
ρ	apparent density of particle (M/L ³)

Chapter 1

INTRODUCTION

1.1 General discussion of the problem

The removal of organic compounds is an important step in any water or wastewater treatment systems. Because of widespread use of pesticides, there is a potential for contamination of drinking water. Generally, this is of concern in the of surface waters due to the influence of runoff. But these pesticides form only a few of the more than 700 organic compounds identified in drinking water supplies (Sanks, 1980). Domestic wastewater and the effluents of various industries using variety of organic chemicals in their chemical processes are the other sources of organic chemicals entering the water bodies. A number of these organic chemicals pose potentially hazardous conditions to human, animal as well as aquatic life. Hence, there is a need to regulate the release of these organics to the environment and find systems to effectively remove these from water.

A list of some of the most harmful chemicals has been developed by the Environmental Protection Agency (EPA). For its part, the congress also has passed regulatory acts such as; Federal Water Pollution Control Act (Public law 92-500), Toxic Substance Control Act (Public law 92-500), Resource Conservation and Recovery Act (Public

law 92-580, section 300), Safe Drinking Water Act (Public law 93-523) and Clean Water Act (Public law 95-217, section 53(a)).

The list developed by EPA has 129 pollutants termed as 'priority pollutants'. Those pollutants are included in the priority pollutants list which: (1) occur frequently in water, (2) are chemically stable, (3) are produced in sizable amounts, and (4) can be analyzed with available methods.

Of these organic pollutants, phenolic compounds are important from the toxicity point of view. They represent one of the most objectionable chemical families because of the taste and odor they impart to water. Even a small dose as low as 5 g/l, will impart taste and odor to drinking water (Lanouette, 1977). Even though a substituted phenol, e.g., parachlorophenol, is not actually listed in the list of priority pollutants, it is part of the chlorophenol family included in the list. This chlorophenol family includes pentachlorophenol, 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol.

These chlorophenols are readily soluble in water and some of the industries that have chlorophenols in their wastewater are textile, ink, metal finishing, steam electric, leather tanning and finishing.

The compound 2,4-dichlorophenol has demonstrated toxicity to certain microorganisms, plants and aquatic species and has demonstrated teratogenicity in non-human mammals. Pentachlorophenol is a widely used registered biocide in the leather industry. Several bioassays have shown that pentachlorophenol is lethal to various species of aquatic life at a concentration of about 200 g/l.

Pentachlorophenol exhibits a weak mutagenic activity. In non-human mammals, the sublethal effects of poisoning include pathological and histopathological changes in the kidneys, liver, spleen, lungs and brain (EPA Development Document for Effluent Limitation series). In human, the results of pentachlorophenol poisoning can range from elevated blood pressure and rapid respiration to coma and death. For the protection of human health, the ambient water concentration of pentachlorophenol should be no greater than 140 $\mu\text{g/l}$.

Phthalate esters are synthetic compounds used primarily as plasticizers. Phthalic acid esters are extensively used in polyvinyl chloride plastics manufacturing and on a smaller scale as pesticide carrier, in formulation for cosmetics, fragrances, industrial oils and insect repellents.

The phthalate esters have a pleasant smell and are very sparingly soluble in water. A few of the industries that have phthalate esters in their wastewater are metal finishing, steam electric, leather tanning and finishing.

Of the phthalate esters appearing in the priority pollutants list, recent studies have produced suggestive but not conclusive evidence that dimethyl phthalate has a cancer liability. Available data show that adverse effects on aquatic life occur at phthalate ester concentrations as low as 3 $\mu\text{g/l}$. Phthalate esters can harm both aquatic and terrestrial organisms at low concentrations. The compounds exhibit teratogenic and mutagenic effects under certain laboratory conditions. Phthalate esters have also been found to have a low order of toxicity. Orally administered phthalate esters generally produce

enlarging of the liver and kidney and atrophy of the testes in laboratory animals. Specific esters produced enlargement of heart and brain and degeneration of central nervous system tissue. For protection of human health from the toxic properties of dimethyl phthalate ingested through water and contaminated aquatic organisms, the ambient water criteria is determined to be 160 $\mu\text{g/l}$.

The occurrence of maximum concentrations of a chlorophenol and dimethyl phthalate in raw wastewater and secondary effluent of various industries are listed in Tables 1.1 and 1.2 respectively.

Conventional methods of water and wastewater treatment include chemical clarification (coagulation, flocculation and sedimentation), filtration, biodegradation and chlorination or ozone treatment. By using these methods, the effluent of a wastewater plant has been found to contain a BOD of 1-2 mg/l and COD of 25-45 mg/l (Culp et al., 1978). However, if activated carbon adsorption is incorporated in the system, BOD reduces to 0-1 mg/l and COD to 5-15 mg/l (Culp et al., 1978). Though drinking water standards have not been set for many organic compounds due to lack of data, in the case of trihalomethanes, for example, 100 $\mu\text{g/l}$ is likely to be accepted as maximum contamination level, (Sanks, 1980). Therefore, selected treatment systems should be able to remove organic chemicals to very low values, of order less than 1 mg/l. Activated carbon adsorption has been found to be very useful and reliable method for this removal in treatment systems. Use of activated carbon has recently been finding a large scope in treatment systems, when dealing with low concentrations of organics in particular.

TABLE 1.1
Maximum Concentrations Reported of Chlorophenols in Industrial Effluents

Industry type	Raw wastewater ($\mu\text{g/l}$)	Secondary effluent ($\mu\text{g/l}$)
Ink formulating	1300	--
Timber products processing	306	--
Textile mills	940	15
Leather tanning and finishing	6,200	1,700
Paint formulating	4,900	3,700
Gum and Wood chemicals	47	--
Pulp, Paper and Paperboard	1,200	1,400
Metal finishing (coils subcategory)	50,000	--

Source: EPA Development Document for Effluent Limitation series

TABLE 1.2
Maximum Concentrations Reported of Dimethyl Phthalate in the
Industrial Effluents

Industry type	Raw wastewater ($\mu\text{g/l}$)	Secondary effluent ($\mu\text{g/l}$)
Ink formulating	10	--
Petroleum refining	--	In traces
Textile mills	14	1
Leather tanning and finishing	118	77
Paint formulating	--	219
Metal finishing	1200	--

Source: EPA Development Document for Effluent Limitation Series.

When activated carbon is used following biological treatment, it is referred to as advanced or tertiary treatment. However, it can also be a central part of a physical-chemical treatment system. Activated carbon adsorption has been found to be a very effective and economical method to remove undesirable organics from dilute solutions. This process has also been found to remove organics from water and wastewater present at very low concentrations which can not be removed by the conventional treatment systems.

From the importance of this process, for maximum economy, the performance of the carbon to adsorb organics from water or wastewater has to be carefully evaluated. Two general criteria for such an evaluation are (EPA, 1973; Culp et al., 1978):

- (1) Determination of equilibrium capacity of carbon or, maximum capacity of carbon to remove a particular organic.
- (2) Determination of adsorption rate to determine the time taken to reach equilibrium capacity.

An isotherm, even though helpful in determining the capacity of the carbon, does not take into account the adsorption kinetics. Since plant scale use of activated carbon involves a dynamic system, the rates of adsorption are as important as the equilibrium adsorption properties. The rate determinations can be best made by dynamic pilot tests (Culp et al., 1978). These dynamic tests include operation of adsorption columns. As a result, a breakthrough curve is obtained for each test. These breakthrough curves can be used for such purposes as:

- (1) to compare the performance of two or more adsorbents to remove a particular organic and
- (2) to determine the minimum contact time

required to produce the desired quality of carbon column effluent. Since operation of such columns is time consuming and expensive, different mathematical models have been prepared by many researchers (Crittenden, 1976; Hinrichs, 1975; Balzli et al., 1978).

All of these models are based on the same size of particles in the adsorption column. Use of a single diameter of particles is the drawback of these models since, in the operation of adsorption columns on a plant scale, carbon is used as a mixture of different sizes as supplied by the manufacturer. Therefore, the predictions of these models will be of little help in understanding the actual breakthrough curve of the column. A model will be more useful if it takes into account the different sizes of carbon present in the column. An effort has been made in this research to evaluate and predict the effect of particle size distribution, on the breakthrough profiles from the adsorption columns.

1.2 Objectives and scope of the study

The objectives of the research presented herein are:

- (1) To establish adsorption isotherms for dimethyl phthalate and parachlorophenol.
- (2) To assess the performance of an adsorption model to predict adsorption rates from single and multicomponent system.
- (3) To assess the performance of a fixed bed model to predict breakthrough curves from column studies.

The scope of this research is:

- (1) To establish adsorption equilibria as well as the kinetics of dimethyl phthalate and parachlorophenol adsorption:

- (i) Single solute and multisolute equilibrium studies were conducted to obtain parameters of isotherms.
 - (ii) Kinetic studies were conducted to determine different transport parameters. Adsorption rates were developed for single and multisolute system with different carbon sizes and their doses.
- (2) Column studies were conducted with different sizes of carbon put together and the results of a mathematical fixed bed model were tested to compare the experimental results, and thus to show the validity of the model to predict the breakthrough curves of an adsorption column.

Chapter 2

REVIEW OF RELATED LITERATURE

2.1 Adsorption Equilibrium

An adsorption isotherm is an expression of the equilibrium between the concentration of an adsorbate on the adsorbent surface and the concentration in the solution. Adsorption isotherms can be classified as to whether they describe the adsorption phenomenon of a single solute, or competitive adsorption of two or more solutes. However, single solute isotherms have been applied to evaluate the isotherms of complex mixtures. This usually is expressed as a single parameter such as chemical oxygen demand (COD) and total organic carbon (TOC). There are many isotherm equations available to describe the equilibrium data.

2.1.1 Single solute equilibrium models

Generally, single solute equilibrium data can be well described by one or more isotherms equations. These isotherm equations, when fitted with experimental data, yield parameters useful in evaluating particular adsorption process.

Two of the simplest equations used to describe adsorption phenomenon onto activated carbon are,

$$q = K_r \quad \text{Irreversible isotherm}$$

and

$$q = K_L C \quad \text{Linear isotherm}$$

The surface concentration is denoted by q , the solution concentration by C and K_r , K_L are the isotherm constants. The equilibrium data of a very strongly adsorbing species may sometimes be approximated by the irreversible isotherm, while the linear isotherm may approximate the equilibrium data most likely at low concentrations.

Two non-linear equations, Freundlich and Langmuir isotherms have been popularly used by investigators to describe their equilibrium data. The Freundlich isotherm (Freundlich, 1926) is expressed as:

$$q = KC^n$$

or $\log q = \log K + n \log C$

A plot of the quantity adsorbed at equilibrium, q , against equilibrium concentration, C , on log-log scale gives a straight line, from which the parameters K and n are easily obtained. Although it may have a theoretical basis in the case of heterogeneous adsorbents (Adamson, 1976), the Freundlich isotherm is basically empirical. The Langmuir isotherm (Langmuir, 1918) is given by:

$$q = QbC/1+bC$$

The constant, Q , is the monolayer saturation surface concentration. The isotherm has a theoretical base that assumes only a monolayer adsorption, constant energy of adsorption and no migration of solute molecules on plane the of the adsorbent surface.

Two convenient linear forms of Langmuir equation are

$$C/q = 1/Qb + C/Q$$

or

$$1/q = 1/Q + (1/Qb)(1/C)$$

The Langmuir equation reduces to the linear isotherm at low solution concentrations.

Sweeney et al. (1982) have suggested a different approach for evaluating adsorption isotherm parameters. It assumes the amount of adsorbent as the independent variable and the final concentration as the dependent variable. The equation given is:

$$C^2 + (1/b - C_o - C_n + Q^o X)C + C_o C_n - C_o / b - Q^o C_n X = 0$$

For Langmuir isotherm

$$(C - C_o)(C - C_n)^{-1/n} + K_F X = 0$$

For Freundlich isotherm

In the case of adsorption by activated carbon in aqueous systems, neither the Freundlich nor Langmuir equations may describe the data satisfactorily over a range of the concentrations of interest. Therefore, an empirical equation with three parameters has been proposed (Redlich and Peterson, 1959; Radke and Prausnitz, 1972; and Mathews and Weber, 1977).

$$q = AC / (1 + BC^\beta)$$

$$\beta < 1$$

At high concentrations this equation becomes the Freundlich isotherm, and at low concentration, it reduces to a linear isotherm, and when $\beta = 1$, it becomes the Langmuir isotherm. The three parameters A, B and β have to be determined by statistical fit of the equation to the experimental data.

Another three parameter model recently presented by Jossens et al. (1978) is

$$C = q/H \exp(Fq^p)$$

or

$$\ln C = \ln q - \ln H + Kq_e^p$$

It expresses solution concentration as a function of surface concentration. The constant p is such that $0 < p < 1$ and it is related to the distribution of energy sites on the surface. H and F are constants which are functions of temperature only. The isotherm is developed using thermodynamics for the adsorption of dilute solutes on heterogeneous surfaces.

Another type of isotherm expressing the solution concentration as a function of surface concentration is one suggested by van Vliet and Weber (1979,1980). The equation given is

$$C = a_1 q (a_2 q^{a_3} + a_4)$$

where $a_1, a_2, \dots, a_4$ are the coefficients determined by a

nonlinear curve fitting technique to minimize the sum of squares of residuals between experimental and predicted values.

Another three parameter equation is suggested by Newman and used by Radke and Prausnitz (1972) is:

$$q = [(1 + AC) + k(1 + BC^k)] / [(1 + AC) + (1 + BC^k)]^2$$

But this equation does not seem to provide an adequate fit to p-cresol and p-chlorophenol experimental data.

The Polanyi adsorption potential theory (Adamson, 1976; Manes and Hofer, 1969), originally developed for gas phase adsorption, has recently been applied to the adsorption of solutes from a liquid phase. According to this theory, there is a potential field within the range of the attractive forces, i.e., adsorptive space, of a solid surface. Points of equal potential, E_p , are connected to form an equipotential surface so that this surface and the solid surface enclose a volume, U . A plot of U versus E_p is termed the characteristic curve and is dependent on adsorbent nature, but independent of temperature. The adsorption potential is expressed as

$$\epsilon_s = RT \ln(C_s/C)$$

where C_s and C are the saturated and the equilibrium concentrations, and ϵ_s is the adsorption potential of adsorbent adsorbing as a vapor. It is also noted that adsorption of a solid solute would have to be

accompanied by the desorption of an equal volume of solvent. The equation then becomes:

$$RT \ln(C_s/C) = \epsilon_{s1} = \epsilon_s - \epsilon_1 (V_s/V_1)$$

where, ϵ_1 is the adsorption potential of the solvent and V_s and V_1 are the molar volumes of solute and solvent. The authors also note that, the schematic plots of volume adsorbed against adsorption potential of solute, solvent and solute from solution collapse to one single curve by application of a single abscissa factor. The deviations from unity of the scale factor required to make two such curves coincide is a measure of the extent to which the adsorption potential deviates from proportionality to the molar volume. However, this plot is curvilinear and it is not possible to obtain a mathematical expression from the theory. Therefore, the data would need to be fitted to other mathematical equation to use in a kinetic model.

2.1.2 Multisolute equilibrium models

The most commonly employed model to describe adsorption equilibrium in a multisolute system, till recently, has been the Langmuir model for competitive adsorption derived by Butler and Ockrent(1930), Markham and Benton (1931). This model is based on the same assumptions as the Langmuir model for single solute systems. It was given as

$$q_i = Q_i b_i C_i / (1 + \sum_{j=1}^k b_j C_j)$$

The surface concentration q_i of adsorbate i is expressed as a function of the solution concentrations of all k adsorbates in the mixture. The parameters Q_i , b_i are obtained from the single solute system.

Schay et al. (1957) have modified the Langmuir competitive equation by the use of interaction terms to describe the equilibrium data better. Their model is

$$q_i = (a_i b_i / \eta_i) / [1 + \sum_{j=1}^k (b_j C_j / \eta_j)]$$

where η_i , the interaction term for each solute, is evaluated by correlating the model to multisolute experimental data.

Jain and Snoeyink (1973) have introduced a bisolute model which is also a modification of the Langmuir competitive adsorption model; it applies to those systems where $Q_1 \neq Q_2$ and some adsorption occurs without competition under this condition. It is not a completely competitive model in the sense that it assumes competition for the number of sites equal to $Q_1 - Q_2$ ($Q_1 > Q_2$), and only solute 1 is received in these areas. For remaining sites, however, the solutes compete. The former case is assumed to be due to either chemical specificity or molecular exclusion. The model is

$$q_1 = [(Q_1 - Q_2) b_1 C_1 / (1 + b_1 C_1)] + [(Q_2 b_1 C_1) / (1 + b_1 C_1 + b_2 C_2)]$$

$$q_2 = (Q_2 b_2 C_2) / (1 + b_1 C_1 + b_2 C_2)$$

where

q_1, q_2 = amount of solute 1 and 2 adsorbed per unit weight of adsorbent at equilibrium concentrations C_1 and C_2

respectively.

Q_1, Q_2 = Monolayer capacities for q_1 and q_2 , respectively that are obtained from single solute isotherm.

Sheindorf et al. (1981) have proposed a Freundlich type multicomponent isotherm. It assumes that an exponential distribution of adsorption energies exists for each component. The pre-exponential coefficient and exponents of monocomponent isotherms are parameters of multicomponent isotherm. The isotherm is of the form

$$q_i = K_i C_i \left(\sum_{j=1}^k a_{ij} C_j \right)^{n_i - 1}$$

where a_{ij} are the competition coefficients.

Mathews(1975) has extended the three parameter isotherm to multisolute adsorption by

$$q_i = A_i C_i / (1 + \sum_j B_j C_j^{\beta_j})$$

The constants are evaluated from a single solute system, which is described by a three parameter isotherm. For multisolute systems not adequately described by this equation, Mathews has proposed the use of interaction terms as done by Schay et al.(1957). The equation then given is

$$q_i = [A_i(C_i/\eta_i)] / \left[\sum_{j=1}^k 1 + B_j(C_j/\eta_j) \right]$$

The interaction coefficients η_i , are calculated by the correlation of mixture equilibrium data.

Fritz and Schlünder (1974) have proposed a general empirical multisolute model:

$$Y_i = a_{i0} X_i^{b_{i0}} / C_i + \sum_{j=1}^k a_{ij} X_j^{b_{ij}}$$

Y_i and X_i are the surface concentrations and the solution concentrations respectively. The other values are constants for the system. For $b_{i0} = b_{ij} = C_i$, the model reduces to the Langmuir competitive model or the Mathews multisolute extension of a three parameter isotherm. Few of the constants used may need multisolute equilibrium data for their calculation. With only one solute present and equating C_1 equal to zero, the equation reduces to the Freundlich equation. The equation for solute two in a bisolute system is then given as:

$$Y_2 = a_{20} X_2^{b_{20}} / (X_2^{b_{22}} + a_{21} X_1^{b_{21}})$$

By rearranging the terms, a plot of $X_2^{b_{22} + b_{22}/Y_2}$ against $X_2^{b_{22}}$ gives a straight line. The slope is equal to $1/a_2$ and intercepts are equal to $(a_{21}/a_2) X_1^{b_{21}}$ for varied X_1 . If the intercepts (multiplied by a_2) are plotted on a log-log scale against

concentration of solute one, a straight line is obtained and a_{21} and b_{21} can be determined.

A three parameter isotherm model proposed by Redlich and Peterson (1959) is given as

$$q_i = A_i C_i / (1 + \sum_{j=1}^k B_j C_j^{g_j})$$

where A, B, g are three empirical coefficients. The value of g lies between 0 and 1.

The ideal adsorbed solution model (IAS model) has been developed from dilute solution thermodynamics by Radke and Prausnitz (1972A) using the method of Myres and Prausnitz (1965) for gas mixtures. Use of single solute isotherms is made to predict multisolute equilibria.

The single solute isotherm need not be any specific isotherm. The model assumptions are:

- (1) the adsorbent is thermodynamically inert.
- (2) the available specific surface area is identical for all adsorbates.
- (3) the solution is dilute.
- (4) the adsorbed phase forms an ideal solution.

This model, however suffers from some drawbacks, such as:

- (1) in order to calculate spreading pressures accurately, very low concentration data - generally of the order below $5 \times 10^{-5} M$ - is required for single solute systems and

(2) For strongly adsorbed solutes, prediction is not in good agreement, and at high surface loadings the assumption of ideal adsorption solution may fail.

To simplify the calculations involved in the IAS model, Fritz and Schlüder (1981) have represented the single solute data with several Freundlich isotherms. In order to have good representation, the Freundlich curve fitted to data is replaced by a stepped curve as:

$$Y_i = a_{ik} X^b$$

Each step is of the height $1/b_{ik}$. These Freundlich isotherms are used in an empirical bisolute extension of the Freundlich isotherm suggested by the authors which is given as:

$$Y_1 = a_1 X_1^{b_1 + b_{12}} / X_1^{b_{12}} + a_{12} X_2^{b_{12}} \left(\lim_{X_2 \rightarrow 0} Y_1 = a_1 X_1^{b_1} \right)$$

$$Y_2 = a_2 X_2^{b_2 + b_{21}} / X_2^{b_{21}} + a_{21} X_1^{b_{21}} \left(\lim_{X_1 \rightarrow 0} Y_2 = a_2 X_2^{b_2} \right)$$

The constants a_1 , b_1 , a_2 , b_2 are determined by Freundlich isotherms for each solute and the others by bisolute data correlation. This greatly simplifies the calculation of spreading pressure without any loss of accuracy.

DiGiano et al. (1978) have proposed another model, denoted as the simplified IAS model. Although empirical originally, predictions are in good agreement with the predictions of the IAS model at low concentrations. The results, however may be different from that of the

IAS model, at higher concentrations. If the single solute equilibrium is expressed by the Langmuir isotherm, then the simplified model is identical to the competitive Langmuir isotherm, provided that the monolayer coverage value Q for all species is same. If the single solute equilibrium is expressed by the Freundlich isotherm, the simplified model gives the following equations to determine the surface loading of each species in a multisolute system.

$$q_i = Qb_i C_i / (1 + \sum_{j=1}^N b_j C_j)$$

$$q_i = K_i' (n_i' - 1) / n_i' (K_i C_i^{n_i'})^{1/n_i'} \left[\sum_{j=1}^N (K_j / K_i') C_j^{n_j'} \right]^{1/n_i'}$$

where n_i , K_i are Freundlich constants.

and $n' = \sum_{i=1}^N n_i / N$, $K' = (\prod_{i=1}^N K_i)^{1/N}$

Rosene and Manes (1976) have proposed a multisolute model based on the Polanyi adsorption theory and thermodynamics. For the bisolute case the authors developed a graphical technique to predict the surface concentration q_1 and q_2 , knowing solution concentrations C_1 and C_2 . However, the conversion of the graphical technique to a system of describing equations is tedious and not too clear. The model in general is difficult to use.

2.2 Adsorption kinetics

Adsorption kinetics involves determination of the rate of adsorption on the adsorbent. The rate of adsorption is determined by one or more diffusional steps. Those diffusional steps are:

(1) mass transfer from flowing phase to the external surfaces of the adsorbent through the liquid film surrounding the particle (film

transfer) (2) intraparticle diffusion and (3) reaction at the phase boundaries (reaction resistance). The intraparticle diffusion is further divided into pore diffusion and solid phase diffusion. Solid phase diffusion is a result of the concentration gradient within the individual adsorbent particle in a mobile adsorbed layer covering the internal pore surfaces of a porous solid. Pore diffusion is the fluid phase transport through a network of fluid filled pores inside the particle. The slowest of these three steps will be the rate controlling step. The reaction step is usually very fast and generally therefore is neglected as the rate controlling step.

2.2.1 Single solute batch modeling

Several models have been developed taking into account one or a combination of different rate processes. There also have been attempts to simplify these rate processes by different assumptions. Those included are:

An overall or effective reaction rate expression - (Thomas, 1944; Hiester and Vermeulen, 1952; Keinath and Weber, 1968).

A linear or quadratic driving force approximation for intraparticle diffusion - (Glueckauf and Coates, 1947; Vermeulen, 1953; Vassiliou and Dranoff, 1962; Hall et al., 1966; Cooney and Strusi, 1972; Hsieh et al., 1977).

A linear or irreversible isotherm - (Boyd et al., 1947; Edeskuty and Amundson, 1952a, 1952b; Rosen, 1952; Tien and Thodes, 1960; Masamune and Smith, 1965; Huang and Li, 1973; Suzuki and Kawazoe, 1974a).

Film transfer as the only rate controlling factor - (Garipey and Zwiebel, 1971; Zwiebel et al., 1972; Kyte, 1973; Keinath, 1977).

These models produce results which may not be sufficiently accurate. Other models derived have more flexibility and more wide acceptability as being more realistic.

Weber and Rumer (1965) proposed a model considering pore diffusion, cylindrical particle shape and the Langmuir isotherm for benzenesulfonates. Snoeyink and Weber (1968) proposed a similar model considering spherical shape of particles.

Suzuki and Kawazoe (1974b) proposed a model which considered surface diffusion as the rate controlling step. The diffusivities found for fifteen different organics were correlated to the ratio of boiling point of the solute to the adsorption temperature.

Neretnieks (1976a) presented and solved equations for pore, surface and combined diffusion along with film transfer considerations. The isotherms used were of Freundlich and Langmuir forms.

DiGiano and Weber (1973) have considered film resistance, pore diffusion and Langmuir isotherm in their infinite batch model to describe the data of p-nitrophenol and 2,4-dinitrophenol with activated carbon. The infinite batch model was selected to avoid imposing a mathematically difficult boundary condition. An infinite batch system is one in which a boundary condition of constant concentration of solute in solution is implied. It was found that the anionic forms of the solute did not diffuse as rapidly as in their

neutral forms.

2.2.2 Single solute modeling for fixed beds

To save both time and money, several models have been developed using rate processes described earlier to predict the breakthrough curves of fixed beds.

Morton and Murril (1967) and Stuart and Camp (1973) used fixed bed models which account for film and surface diffusion and a nonlinear isotherm. They showed that the experimental data fitted to the model well. A similar model, but with axial dispersion also, was used by Colwell and Dranoff (1969) to show that it described the experimental data satisfactorily.

Wheeler and Middleman (1970) proposed a model which incorporated three types of resistances. Intraparticle transport was described by surface diffusion and the surface reaction was assumed to obey Michaelis-Menton kinetics. Particle to fluid convective mass transfer was also considered.

Chakravorti and Weber (1975) accounted for film resistance, surface diffusion, a nonlinear isotherm and axial dispersion in their fixed bed model. However, the batch model did not fit the experimental data very well. This was thought to be due to ignoring the film resistance.

* (Peel and Benedeck (1980) developed a model based on the knowledge of the internal structure of activated carbon. The model divides the carbon particles into two regions, macropores and micropores.) Relatively rapid diffusion and adsorption occurs in macropores and rest of it occurs in the micropores till the equilibrium is reached.

The model equations considered film transfer, surface diffusion in the macropores, and linear transport into the micropores. The model predicts the column performance fairly but not more accurately than other models.

2.2.3 Single solute fixed bed models with two or more adsorbents

Many researchers have tried to use different adsorbents rather than only one type of adsorbent to compare their performances, by fitting their models to the data. Smith et al. (1959) studied the adsorption of 2,4-dichlorophenol on four activated carbons of different types. They tried to correlate the kinetics to the carbon characteristics, such as, pore size distribution and surface area. A relationship was apparent between the adsorption rate and micropores in the adsorbent (less than about 250 Å radius of pore).

Suzuki and Kawazoe (1974a) have proposed a model for the adsorption of 2-dodecyl benzene sulfonate on four different types of activated carbons, assuming a rectangular (irreversible) isotherm.

Spahn and Schlünder (1975) determined pore diffusivities for twelve different carbons. They could not, however, find any relationship between pore diffusivities and either total pore volume or micropore volume (pore radius less than or equal to 1000 Å) or macropores volume (pore radii greater than or equal to 1000 Å). They used an irreversible isotherm.

Westermarck (1975) modeled four carbons. The water used was treated by sedimentation, biological oxidation and coagulation with alum. It was further filtered to remove suspended solids. The contaminants were measured as chemical oxygen demand. The experimental

data was corrected for nonadsorbable and extremely adsorbable compounds by varying values of the isotherm constant in the linear isotherm, and the pore diffusivity. The film transfer coefficients were estimated from other fixed bed experiments.

Hölzel et al. (1979) found a fairly linear relationship between the surface diffusivities for p-nitrophenol and the pore volume of the activated carbons. The p-nitrophenol exhibited a higher diffusivity in a carbon with larger pore volume.

Van Vliet and Weber (1979) used two activated carbons and eight synthetic (carbonaceous and polymeric) adsorbents to study the adsorption of p-chlorophenol and p-toluenesulfonate. The adsorbents differed widely in capacity, film transfer coefficients and surface diffusivity values. The film transfer coefficients for the synthetic adsorbents could not be estimated accurately by using values from the literature. They, therefore, incorporated particle shape and a surface topography factor in film transfer coefficients.

Lee et al. (1980) developed a model to predict adsorption of humic substances on different carbons. The model predicted correctly the fixed bed performance by using film transfer coefficients and surface diffusivities independent of fixed bed experimental data. They also showed that the use of alum coagulation before adsorption changed the performance of the carbons and increased service times of all the carbons.

2.2.4 Multisolute modeling for batch systems

Mathews (1975) applied a homogeneous solid phase diffusion model for single solute and bisolute adsorption in a finite batch reactor.

The three parameter isotherm of Radke and Prausnitz was extended for a bisolute system using bisolute equilibrium data. Film transfer coefficients and surface diffusivities were estimated by a parameter search technique to fit single solute rate data and these values were used to predict bisolute fixed bed experiments. Runs with a mixture of phenol and p-toluene sulfonate were predicted well but data from phenol and p-bromophenol were not predicted so well. The mixture of phenol and dodecyl benzene sulfonate was predicted poorly by the model. This was thought to be due to solute-solute interaction affecting the kinetics. A change in film transfer coefficients but same diffusivities made the model predict better results.

Liapis and Rippin (1978) presented a model with general equations describing multisolute adsorption in a finite batch reactor. The equations included film and intraparticle resistance. Intraparticle resistance was due to pore, surface, or combined diffusion. Numerical solutions of bisolute adsorption with pore or surface diffusion were given for the case of independently diffusing solutes. A solute was assumed to diffuse within the adsorbent either independently of concentration of solution or with the dependence on the other solutes. The experimental data for 2-butanol and t-amyl alcohol adsorbed on activated carbon was tested against the prediction of the model. The single solute data was described by the Freundlich equation, while bisolute data was described by the Fritz and Schlünder equations. Film transfer coefficients were calculated from literature and surface diffusivities were calculated by trial and error fit of the models to the experimental data. Both models described adsorption data very

well. They also found that the pore diffusivity happened to decrease with increasing starting concentration.

Adsorption of several phenolic compounds on activated carbon was used by Fritz et al. (1980) to develop their model for single solute and bisolute systems. The Freundlich equation was used to describe single solute data while bisolute data was described by the IAS theory or Fritz-Schlünder equation. Both film transfer and intraparticle transport were incorporated in the model. They found an interesting fact that for low concentrations of the order $1 \times 10^{-4} \text{M}$, a simple film resistance model predicted well. At higher concentrations, intraparticle transport had to be taken into account. The predictions were found to deviate from the experimental data and were thought to be due to diffusional interactions between the solutes. The surface diffusion model was modified by the introduction of an extended form of Fick's first law such that the diffusion of each solute was a function of concentration gradients of both solutes. This seemed to improve the predictions.

2.2.5 Multisolute modeling for fixed beds

Crittenden (1976) and Crittenden and Weber (1978a, 1978b, 1978c) have studied single solute and bisolute adsorption of the same solutes and adsorbent as used by Mathews (1975). They used the homogeneous solid diffusion model including film resistance. The influent concentration was varied 20%. The surface diffusivities were calculated from single solute batch experiments while film transfer coefficients were calculated from the data in the literature. The model successfully described the single solute data from fixed beds but

not from bisolute fixed bed experiments. The discrepancies observed were thought to be due to (1) experimental data scatter, (2) poor equilibrium description, and (3) failure of the assumption of independent diffusion of solutes. They also noted that for a mixture with adsorbates having rate parameters of considerable magnitude, the best statistical fit of the model to the data occurred when lower single solute values of film transfer coefficient and surface diffusivities were assumed to apply to both solutes.

Liapis and Rippin (1978) have proposed another fixed bed model which includes film resistance, pore diffusion and axial dispersion. The model incorporates diffusivities from batch experiments, and the predictions for two alcohols were found to be in good agreement with the experimental results. The model, however, failed to describe the overshoot of the weaker adsorbed species. Also, an increase in the bed length was observed to induce a larger displacement of this species.

Crittenden et al. (1980) studied the adsorption of p-nitrophenol and p-bromophenol on a duolite A-7 resin with a model that incorporated homogeneous solid diffusion and film transfer as resistance steps. The film transfer coefficients were estimated from the literature. The equilibrium data were described by the Langmuir competitive isotherm. The surface diffusivities were calculated by fitting the model to experimental fixed bed data for the simultaneous feeding of the two solutes. Good agreement was observed between the prediction of the model and the experimental bed runs data for sequential feeding of the two solutes. The discrepancies observed were

thought to be due to capacity changes during regeneration of the resin between the runs.

Famularo et al. (1980) developed a microcore/macroshe11 model representing diffusion through an adsorbent having a bimodal pore size distribution. An adsorbent particle was divided into two regions, a spherical core with micropores enclosed by an annular shell with macropores. A linear force was assumed to be the driving factor for transport through each region. Film resistance was also incorporated. Kinetic parameters were determined for phenol and p-nitrophenol with carbon as adsorbent, by single solute batch tests and isotherms determined previously. A drawback of this model seems to be that instead of two parameters as required by other conventional models, this model needs four parameters.

Thacker et al. (1981) studied adsorption of 3,5-dimethyl phenol, 3,5-dichlorophenol, and Rhodamine 6G on four different activated carbons and a coal gasification char. One carbon was pretreated with aqueous chlorine to evaluate the effect of chlorine pretreatment on adsorption. The film transfer and homogeneous surface diffusion were the mass transfer steps incorporated into the model. The single solute data was fitted to Freundlich and Myres isotherm whereas the bisolute data was described by the IAS model. The surface diffusivities were estimated from the best statistical fit to the experimental batch tests. The film transfer coefficients were calculated from the literature. The model predicts very well for single and bisolute bed studies of adsorption, desorption and sustained step changes in the

influent concentration.

2.3 Size of carbon particles

Morris and Weber (1964,1964A) reported that the rate of the adsorption correlated with inverse of square of the diameter of carbon particles. Their observation was based on rate of adsorption of 3-dodecyl benzene sulfonate (DBS) and alkyl benzene sulfonate (ABS). They also found adsorption capacity was affected by carbon size.

Dedrick and Beckmann (1967) and Martin and Al Baharani (1978) found an inverse relationship between rate of adsorption and carbon particle radius. These researchers and Letterman et al. (1974) did not find any relationship between adsorption capacity and size of particle.

It follows from these results that the smaller the size of the particle, the faster will be the adsorption. This makes the use of the smaller particles desirable in plant-scale operations. However, due to the large pressure drop caused by small particles, they are not used in plant-scale operation. As far as adsorption capacity is concerned, effect of the particle size on it is not so clear yet and it may depend up on the respective carbon-solute systems under study. Peel (1980) has suggested that for a range of sizes of activated carbon, the differences in the activation process could affect the adsorption capacity.

Chapter 3

EXPERIMENTAL MATERIALS AND METHODS

3.1 Materials

3.1.1 Solutes

The solutes used in this study were: dimethyl phthalate (DMP) and parachlorophenol (PCP). The characteristics of each solute are given in Table 3.1.

Both reagents were obtained from J. T. Baker Chemical Co., (Phillisberg, N.J.). DMP was obtained in liquid form and PCP was obtained in crystal form. DMP has very low solubility in water whereas PCP is readily soluble.

All stock solutions were prepared with deionized, pure water. The system used to obtain this water was SYBRON/BARNSTEAD NANOPURE system. In this system, distilled water is passed through ultra pure and organic removal filters. This water is further passed through a set of four filters, 1 organic, 2 ultrapure and 1 micron filter. Stock solutions were prepared and diluted to desired concentration with appropriate dilution water about two hours before the start of the experiment. All experiments were initiated within three hours after the appropriate solutions were made.

TABLE 3.1
Solutes and Their Properties

	Dimethyl phthalate	Parachlorophenol
Supplier	J.T. Baker Chemical Co.	J.T. Baker Chemical Co.
Grade	Baker TM	Baker TM
Formula	$C_6H_4-1,2(COOCH_3)_2$	C_6H_4OHC1
Molecular Weight	194.2	128.5
pK_a	--	9.18
Melting Point,°C	0-2	42-44
Solubility in 100 gms water	0.4	2.70

TABLE 3.2
Properties of Activated Carbon

Manufacturer	Carborundum Co., N.Y.
U. S. Mesh size	12 x 40
Raw material	Bituminous coal
Physical properties:	
Surface area, m ² /g	1000-1100
Apparent density, gm/cc	0.47
Particle density wetted in water, gm/cc	1.35
Backwashed and drained density, lb/ft ³	25
Effective size, mm	0.60
Uniformity coefficient	1.9 or less

3.1.2 Adsorbent

The adsorbent used in this study is granular activated carbon. (Carborundum Co., N.Y.). The properties of carbon are listed in Table

3.2.

The various sizes of carbon used in the column studies were obtained by mechanically sieving with a RO-TAP testing sieve shaker (Tyler industrial products).

3.2 Methods

3.2.1 Analytical methods

The solution concentrations of DMP and PCP were analyzed by ultraviolet-light-absorption spectrophotometry with a Bausch and Lomb spectronic 710 spectrophotometer. Initial tests were made to determine the wavelengths of maximum absorption for DMP and PCP. After these wavelengths of maximum absorption were established, several standard solutions of DMP and PCP were prepared. These standard solutions were used to obtain a calibration chart for each solute at its wavelength of maximum absorbance. Table 3.3 lists the wavelengths selected and the respective molar absorptivities.

DMP was analyzed at a wavelength of 230 nm and PCP was analyzed at a wavelength of 279 nm. Mixtures of DMP and PCP were analyzed at wavelengths of 240 nm and 279 nm.

Experiments were also carried out for a bisolute system and the Friedel's method (1951) was used to compute individual concentrations. The Friedel's method is based on the assumption that the absorbance measured in a mixture is the sum of the absorbance of each compound at that wavelength. A set of equations developed at each wavelength is

TABLE 3.3
Molar Absorptivities of Solutes

Solute	Wave length (NM)		
	230	240	279
	Molar absorptivities (l/mole-cm)		
Dimethyl phthalate	8108.19	5962.05	1308.49
Parachlorophenol	--	467.07	1500.00

used as follows:

$$A_{240} = \epsilon_{DMP1} C_{DMP} + \epsilon_{PCP1} C_{PCP}$$

$$A_{279} = \epsilon_{DMP2} C_{DMP} + \epsilon_{PCP1} C_{PCP}$$

where

A_{240} , A_{279} = Total absorbance at 240 nm and 279 nm

C_{DMP} , C_{PCP} = Concentrations of DMP and PCP respectively

ϵ_{DMP1} , ϵ_{PCP1} = Molar absorptivities of DMP and PCP at
wavelength 240 nm.

ϵ_{DMP2} , ϵ_{PCP2} = Molar absorptivities of DMP and PCP at
wavelength 240 NM.

C_{DMP} and C_{PCP} were found by solving these two simultaneous equations.

Tests were also carried out to note whether stirring and filtering through glass fiber filters produced any change in the absorbance of DMP, PCP and the mixture of them. Single solute and bisolute solutions of known concentrations were stirred at the designated speed of 600 rpm in the equipment designed for rate studies for two hours ~ as in the rate study. This did not produce any change in the concentration of the solutes. A solution of known concentration of each solute was filtered through glass fiber filters - intended to be used in the equilibrium studies. This also did not produce any change in the absorbance of any solute.

3.2.2 Particle size distribution

The granular activated carbon was sieved through a series of U. S. standard sieves nos. 12 to 40 to collect eight different fractions of carbon to be used in the fixed bed experiments. The

particle size distribution of the carbon supplied by the manufacturer is shown in Table 3.4.

The average diameter of the particle was calculated in three different ways.

(1) Geometric mean :- The geometric mean diameter of the carbon particles was found by finding the geometric mean of upper and lower sieve sizes used to get that particular size fraction.

(2) Log-mean :- Each of the eight size fractions collected by sieving was subjected to image analysis to find the particle size distribution in that particular fraction. An image analyser by Bausch and Lomb was used. Image analysis gives the horizontal distance between the two points of the longest curve on the surface of the particle in the position at analysis.. The results of image analysis were plotted on log-probability paper as diameter against cumulative of fractions. The 50% value on the graph was used as log-mean diameter. The log-probability graphs of the eight fractions are given in the appendix.

(3) Sauter mean :- The sauter mean diameter of a particle is defined as

$$d_p = \sum d_{pi}^3 \Delta x_i / \sum d_{pi}^2 \Delta x_i$$

d_{pi} and Δx_i are the diameter of a particular size fraction and its number percentage in the size distribution respectively. Table 3.5 lists all three diameters of a size fraction in carbon supplied by the manufacturer.

TABLE 3.4
Particle Size Distribution in Supplied Carbon

Sieve size	Percent fraction
#12-14	9.4
#14-16	21.0
#16-18	17.6
#18-20	20.0
#20-25	14.5
#25-30	9.8
#30-35	4.6
#35-40	3.1

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DOCUMENT(S) IS OF
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TABLE 3.5
Carbon Size Fractions and Their Diameters

Size fraction (sieve no.)	Geometric mean(cm)	Log-mean (cm)	Sauter mean (cm)
#12-#14	1539×10^{-4}	1786×10^{-4}	1979.99×10^{-4}
#14-#16	1290×10^{-4}	1540×10^{-4}	1733.87×10^{-4}
#16-#18	1091×10^{-4}	1315×10^{-4}	1497.59×10^{-4}
#18-#20	917×10^{-4}	1200×10^{-4}	1337.33×10^{-4}
#20-#25	772×10^{-4}	920×10^{-4}	1070.77×10^{-4}
#25-#30	647×10^{-4}	805×10^{-4}	936.58×10^{-4}
#30-#35	543×10^{-4}	760×10^{-4}	873.41×10^{-4}
#35-#40	458×10^{-4}	560×10^{-4}	708.14×10^{-4}

3.2.3 Equilibrium experiments

Equilibrium studies to determine the capacity of carbon at various solution concentrations were carried out by standard bottle-point method. The method consists of allowing a solution of known initial concentration to come into contact with different amounts of carbon doses until an equilibrium is reached. Carbon for equilibrium studies was prepared by washing carbon samples several times with deionized water to remove fines. The samples were then dried in an oven at 120° C for sufficient time for carbon to attain constant weight. Fine carbon was used, in order to reduce the time required to reach equilibrium. Some of the carbon was ground in a blender and then sieved to obtain 200/230 (passing through sieve number 200 but retained on sieve number 230) size fraction. For this experiment, 180 ml Teflon round-shaped flasks and 125 ml conical glass flasks were used. The flasks were thoroughly washed, cleaned and dried at temperature of either 120°C (for glass flasks) or at 70°C (for Teflon flasks).

Different amounts of fine carbon were added carefully to the marked flasks. To each flask, 100 ml of solution of known concentration was added. The bottles were tightly closed and sealed to make sure they were air-tight. Each isotherm was developed with at least two starting concentrations. The bottles were then placed in controlled environment incubator shaker (Labline Instruments, Ill.) and the contents were mixed at the desired temperature. Two to three bottles containing the solution were used without any carbon to serve as blanks. These blanks served as a check on possible biological

degradation or adsorption on glass or teflon. Several solutions with the same amounts of carbon were also made to determine when equilibrium is reached.

In the case of DMP, equilibrium was reached in about five days while in the case of PCP it took about six days to reach equilibrium. After it was made sure that the equilibrium was reached, the samples were filtered through glass fiber filter (Gelman Science Co.) to remove the carbon. The filtrate was then analyzed for the remaining concentration. The amount that was adsorbed was calculated from the difference between the concentration in the blank solution samples and those that were filtered.

The surface concentration in equilibrium with solution concentration, Q_e (mmoles/gm or mg/gm) was then computed from experimental data using equation

$$Q_e = (C_o - C_e)W$$

where

C_o is solution concentration in blank sample (mmoles/l or mg/l)

C_e is final equilibrium solution concentration (mmoles/l or mg/l)

W is the dose of the carbon (gm/l)

3.2.4 Batch kinetic experiments

The carbon for batch kinetic experiments was prepared by sieving desired size fractions. These fractions were washed separately several times with deionized water to remove fines. The samples were then

dried in an oven at 120° C for sufficient time for the carbon to attain constant weight. The different dried samples were then stored in polythene bags in an incubator at constant temperature. The studies for rate of adsorption were carried out in a 4.5-liter glass jar. It was covered at top by a plexiglass cover. Four thin rectangular plexiglass plates of size 21.5cm x 1.5cm x 0.9cm each were attached to the cover to serve as baffles. The depth of each baffle from the bottom was about 3cm. The solution was stirred by a four-blade impeller. Generally, for all experiments a speed of 600 rpm was used. But if the carbon particles were found to settle at this speed, a higher speed of 800 rpm was used. The speeds were controlled by a variable speed transformer unit. All the kinetic experiments were conducted at room temperature using deionized water.

The procedure for each experiment involved preparing and placing three liters of solution of desired concentration in the glass jar. Then the solution was stirred for a while to reach equilibrium within the vessel. A predetermined amount of solution was withdrawn and analyzed to determine initial concentration. After that, a carefully weighed amount of carbon of predetermined size was added to the vessel and rapidly agitated. At selected intervals of time, a sample was withdrawn from the vessel and analyzed for concentration. The samples were collected by a pipet with teflon filter attached to make sure no fine particles of carbon were removed with the sample. The graphs of C/C_0 against time were plotted.

3.2.5 Fixed bed experiments

The experimental setup selected for the fixed bed experiments

shown in Fig. 1. The experiments were carried out in a 5-cm inner diameter plexiglass tube. The bed of carbon was supported on two pieces of 140-mesh size, brass screen. The carbon for the fixed bed studies was prepared by sieving different size fractions of carbon and washing each fraction by tap water several times to remove fines. The samples were then dried in an oven at 120° C for sufficient time for the carbon to attain constant weight. Dried samples were then stored in polythene bags in an incubator at constant temperature.

The column was fed with tap water from a tank in which constant head was maintained by overflow. The water added to this tank was first passed through a three foot filter column packed with activated carbon. A variable flow masterflex pump was used to force the water into the column at the desired flow rate. The solution was made at a much higher concentration than used in the experiment and its flow was adjusted so as to have proper dilution to the desired concentration in the system.

Predetermined amounts of different sizes of carbons were weighed separately and mixed in a large beaker. The entire amount of carbon was then added to the column, which was about half filled with water. The entire bed was then fluidized so that particles were arranged in the order of smaller particles at top and larger particles at bottom of the column. When the bed was fluidized, the column was tapped lightly to remove any trapped air bubbles. To avoid radial and axial dispersion, the ratio of column diameter to average particle diameter was 26.3 or greater while the ratio of bed length to average particle

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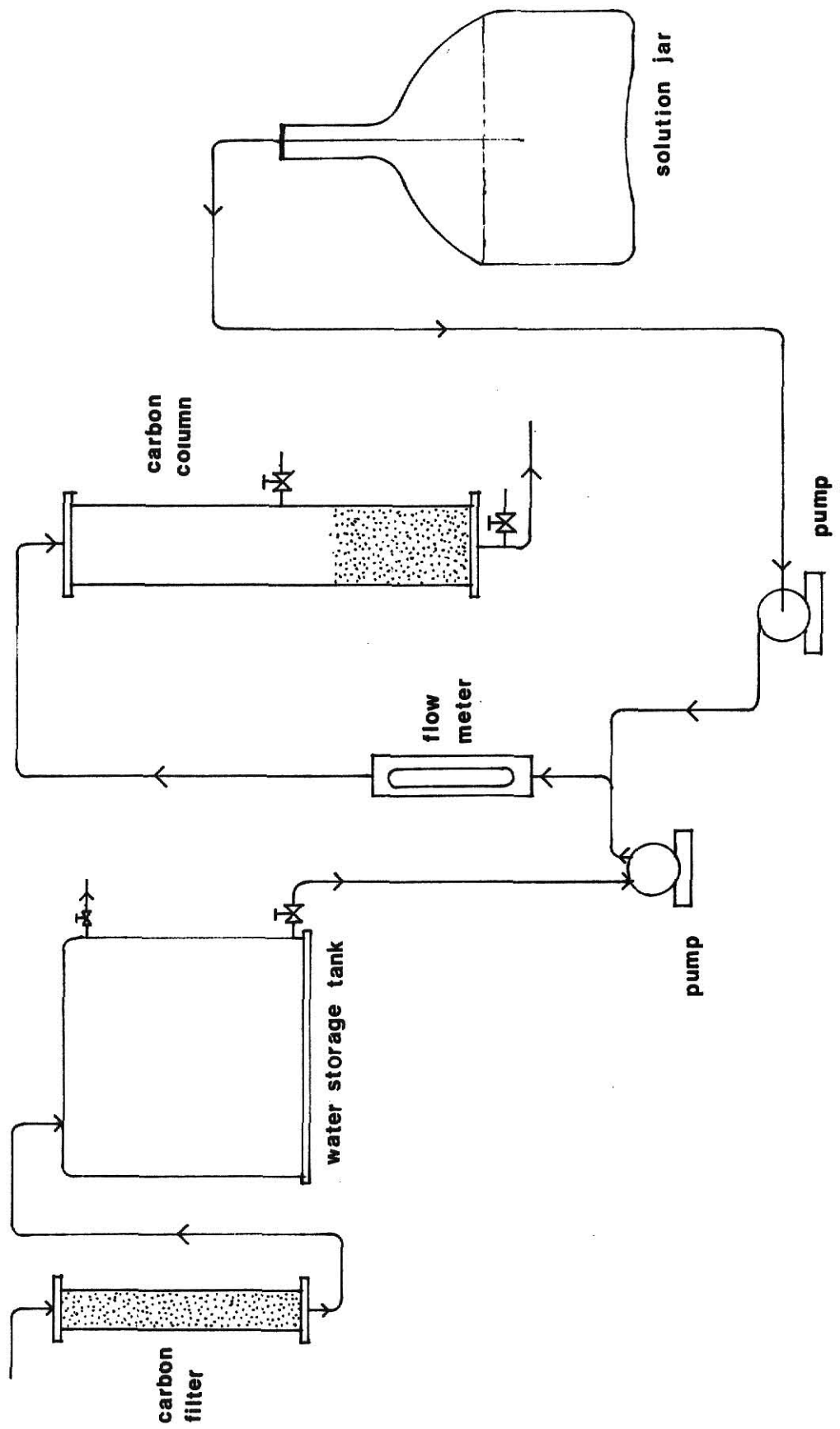


Fig. 3.1. Set up for fixed bed experiments [schematic].

diameter was 100 or greater, as used by Thacker et al., 1981. The column was operated in the downflow direction and flow rates were varied from 500 ml/min to 800 ml/min. Effluent samples were collected at regular intervals and analyzed for concentration. Influent was also checked frequently to make sure there was no variation in the influent concentration. Graphs of C/C_0 against time were plotted for each run.

Chapter 4

KINETIC MODEL AND ITS MODIFICATION

As described earlier, film transfer, surface diffusion and pore diffusion are the important rate controlling steps in an adsorption phenomenon. Depending upon the conditions, one or more of these will control the rate. The pore diffusion and homogeneous solid diffusion are two parallel processes and therefore, the (faster) of the two will control the rate of intraparticle transport. In addition to these processes, the equilibrium relationship is also important and the isotherm shape has been found to influence the shape of a breakthrough curve (Chakravorti and Weber, 1974).

It is desirable that a model be capable of accounting for both film transfer and intraparticle transport. The mass-balance equation on an adsorbent particle gives (Thacker et al., 1981):

$$\epsilon_p \frac{\partial C}{\partial t} + \frac{\partial q}{\partial t} = D_s / r^2 \frac{\partial}{\partial r} (r^2 \frac{\partial s}{\partial r}) + D_p / r^2 \frac{\partial}{\partial r} (r^2 \frac{\partial C}{\partial r})$$

The first term on the left-hand side of the equation represents the rate of accumulation of solute in the fluid in pores and the second term gives the rate of accumulation on the surface of the particle. Here, ϵ_p is the porosity, C , the solution concentration, q , the surface concentration, D_s , the surface diffusivity

coefficient, D_p , the pore diffusivity coefficient, and r , the radial distance. The first term on the right-hand side gives the rate of homogeneous solid diffusion while the second term is the rate of pore diffusion. To simplify the solution, generally only one of the intraparticle diffusion is considered important. So if the homogeneous solid diffusion is considered important and the fluid phase accumulation term is neglected, since the surface concentration is greater than the concentration in the pore fluid for small values of ξ_p , the equation reduces to

$$\partial q / \partial t = D_s r^2 \partial / \partial r (r^2 \partial q / \partial r)$$

This equation was developed by Rosen (1952). The film transfer can be taken into account in the diffusion model by appropriate boundary conditions. In case of only homogeneous solid diffusion, this condition is obtained by equating the rate of mass transfer through the surface film to the rate of change of average concentration of the particle and is expressed as

$$R^2 K_f (C - C_s) / \rho = \partial / \partial t \int_0^R q r^2 dr$$

The model equations selected for modification in this research are developed and solved by Thacker et al. (1981). They incorporate the homogeneous solid diffusion equation of Rosen (1952). The homogeneous solid diffusion and film transfer are the two steps of transport considered to develop model equations. The model equations are solved

by the orthogonal collocation method and according to the authors, it is more economical method to solve the differential equations compared to the finite differences method.

4.1 Model description

The model is based on following assumptions:

- (1) the rate of adsorption is diffusion limited, i.e., local equilibrium exists at the external surface of an adsorbent particle.
- (2) liquid-diffusion resistance occurs at the external surface and can be described as film transfer.
- (3) an adsorbent particle is a homogeneous solid.
- (4) an adsorbent particle is spherically shaped.
- (5) flow in the fixed bed is plug-flow.

The fixed bed model for a single solute is given below:

$$\partial q / \partial t = D_s / r^2 \partial / \partial r (r^2 \partial q / \partial r) \quad (1)$$

$$@ t = 0, 0 \leq r \leq R : q = 0 \quad (2)$$

$$@ t \geq 0, r = 0 : \partial q / \partial r = 0 \quad (3)$$

$$@ t \geq 0, r = R : R^2 k_f (C - C_s) / \rho = \partial / \partial t \int_0^R q r^2 dr \quad (4)$$

$$@ r = R : C_s = f(q_s) \quad (5)$$

$$\partial C / \partial t = -v \partial C / \partial Z - [3(1 - \epsilon_s) / \epsilon_s R] k_f (C - C_s) \quad (6)$$

$$@ t = 0, 0 \leq Z \leq L_b : C = 0 \quad (7)$$

$$@ t \geq 0, Z = 0 : C = C_0 \quad (8)$$

The first equation is the Rosen (1952) equation. It gives the rate of solute accumulation on the surface of the adsorbent particle

through homogeneous solid diffusion. The surface diffusivity is D_s , r , the radial distance, and q , the surface concentration. Equation 2 applies the initial condition that at time zero, the surface concentration at any radial distance inside the particle is zero, whereas equation 3 implies that at any time greater than zero, the concentration gradient at the center of the particle is zero. The radius of the particle R . Equation 4 gives the mass-balance equation on the adsorbent particle. The rate of mass transfer through the surface film is equal to the rate at which the average concentration of particle changes. The film transfer coefficient is k_f , C_s , the solution concentration at the external surface of particle and ρ is the apparent density of particle. Equation 5 is the isotherm relation between the surface and solution concentration of the solute with q_s as the surface concentration at the external surface of particle. Equations 6, 7, and 8 apply to the fixed bed condition. Equation 6 gives the mass balance of the solute at any point in the bed. The rate of change in the concentration of solute is equal to sum of convective change in the concentration inside the bed and rate of mass transfer through the film to the solid surface. Here, v is the superstitial velocity in fixed bed, ϵ_B , the porosity of bed, and Z , the axial distance inside the bed. Equation 7 applies the initial condition to the bed that at time zero, the solution concentration inside the bed is zero whereas equation 8 implies that at any time greater than zero, the solution concentration at the entrance to the bed is equal to the initial concentration. L_b and C_0 are the length of bed and initial solution concentration respectively.

Above equations are transformed into non-dimensional form by introducing following variables:

$$\bar{r} = r/R$$

$$\bar{q} = q/q_e$$

$$\bar{q}_s = q_s/q_e$$

$$\bar{C} = C/C_o$$

$$\bar{C}_s = C_s/C_o$$

$$\bar{Z} = Z/L_b$$

$$\Upsilon = L_b/\nu$$

$$D_g = q_e(1-\epsilon_s)/C_o$$

$$T' = t / \Upsilon D_g$$

$$E_d = D_s D_g \Upsilon / r^2$$

$$S_t = K_f \Upsilon (1-\epsilon_s)/R$$

The non-dimensional fixed bed model then becomes:

$$\partial \bar{q} / \partial T' = E_d / r^2 \partial / \partial r (r^2 \partial \bar{q} / \partial \bar{r}) \quad (9)$$

$$@ T' = 0; 0 < \bar{r} < 1 : \bar{q} = 0 \quad (10)$$

$$@ T' > 0 : \bar{r} = 0 : \partial \bar{q} / \partial \bar{r} = 0 \quad (11)$$

$$@ T' > 0; \bar{r} = 1 : S_t (\bar{C} - \bar{C}_s) = \partial / \partial r \int_0^1 \bar{q} \bar{r}^2 dr \quad (12)$$

$$@ \bar{r} = 1 : \bar{C}_s = f(\bar{q}_s) \quad (13)$$

$$\partial \bar{C} / \partial T' = -D_g \partial \bar{C} / \partial \bar{Z} - 3 D_g S_t (\bar{C} - \bar{C}_s) \quad (14)$$

$$@ T' = 0; 0 \leq \bar{Z} \leq 1 : \bar{C} = 0 \quad (15)$$

$$@ T' \geq 0; \bar{Z} = 0 : \bar{C} = f(T') \quad (16)$$

4.2 Model solution

Generally in the case of a non-linear isotherm, the differential equations in an adsorption model are solved using numerical methods. Most popular of those methods seems to be the finite-differences method, however, the orthogonal collocation method has also been successfully used. (Liapis and Rippin, 1977; Crittenden et al., 1980). The present model also uses the orthogonal collocation method to solve the differential equations numerically.

The collocation method presents one of the several other weighted residual methods. In this method, the unknown solution of a differential equation is approximated by a trial function. This trial function has constants and/or functions such that, when this trial solution is substituted into the differential equation, the residual is forced to zero at collocation points. The orthogonal collocation is a special case of the collocation method, in that, the trial functions are a set of orthogonal polynomials and the collocation points are the roots of these polynomials. By the application of orthogonal collocation, the partial differential equations are reduced to first order ordinary differential equations.

The current problem is an initial value problem with respect to time, and when the orthogonal collocation method is applied to the non-dimensional, fixed bed equations presented before, the following set of equations is obtained:

$$d\bar{q}_{ik}/dT' = E_d \sum_{j=1}^{N'+1} B_{ij} \bar{q}_{jk} \quad \text{for } i = 1, 2, 3, \dots, N' \\ k = 1, 2, 3, \dots, M'+2$$

$$@ T' = 0 : \bar{q}_{ik} = 0$$

$$d\bar{q}_{N'+1}/dT' = 1/W_{N'+1} \left[\sum_{j=1}^{N'} W_j d\bar{q}_{jk}/dT' + S_t (\bar{C}_k - \bar{C}_{sk}) \right]$$

for $k = 1, 2, 3, \dots, M'+2$

$$@ T' = 0 : \bar{q}_{N'+1,k} = 0$$

$$\bar{C}_{sk} = f(\bar{q}_{N'+1,k})$$

$$d\bar{C}/dT' = -D_g \sum_{p=1}^{M'+2} A_{lp}^u \bar{C}_p - 3D_g S_t (\bar{C}_l - \bar{C}_{sl})$$

for $l = 2, 3, 4, \dots, M'+2$

$$@ T' = 0 : \bar{C}_l = 0$$

Here N' is the number of internal collocation points along the particle radius and the matrices B and W are the associated collocation constants, for spherical geometry. These constants are calculated from the polynomials listed by Stroud and Secrest (1966) and the method is outlined by Finlayson (1972). Point 1 is at the center of the particle and point $N'+1$ is at the surface of the particle. The number of internal collocation points along the axial direction of bed is M' . The axial collocation point 1 is at the entrance of the bed and point $M'+2$ is at the exit from the bed. The matrix A^u is a set of collocation constants for axial direction and these constants have been developed with roots to the orthogonal polynomials for unsymmetric geometry (Finlayson, 1972) with the procedure given by Finlayson (1972). The resulting ordinary differential equations are solved by the computer subroutine GEAR (Gear, 1976; Hindmarsh, 1974). This subroutine utilizes Adam's predictor-corrector method for numerical integration.

The authors of the computer program (Thacker et al., 1981) have

tested numerical solution of the differential equations by this method with another model where analytical solution was available. They found close agreement between the orthogonal collocation solution of that model and the analytical solution. This confirmed the fact that orthogonal collocation method is a reliable and accurate numerical method.

4.3 Model modification

The modification of the model is based on treating the whole bed as a series of small beds, or layers, containing one particular size of carbon. Thus the whole bed becomes a series of beds with smaller particles at top and larger particles at the bottom of the column. This is accomplished by fluidizing the bed first, before starting the column experiment. Since weight of the carbon in each small bed can be known once we know the particle size distribution of the different particles, the length of each bed can be estimated as:

$$\text{Bedl} = (\text{Wt(I)} / \text{Total wt})L$$

where

Wt(I) = weight of the I^{th} fraction

Bedl = length of the respective small bed

L = total length of the bed

As the first bed becomes saturated, effluent becomes the influent for the next bed, at respective times. This series of effluent becoming influent to the next bed continues to the last bed, the effluent of which is the final effluent of the bed.

The original computer program takes into account sustained changes in the influent concentrations. This change is taken into

account by calculating all the intermediate influent concentrations between two consecutive changes in influent concentrations by linear interpolation over the time period over which this change takes place. This fact is utilized in the modification. All the effluents of a layer at various times are stored as a vector and are used as varying influents to the next bed, changing at the same period of time at which they were stored. If the influent to the bed does not change during an experiment, this storage vector will be zero for the top layer.

The only additional data required for this modified model than the original model is:

- (1) distribution of various particle size fractions
- (2) radii of these particle fractions and,
- (3) film transfer coefficients for these different sizes.

4.4 Estimation of Kinetic data for the model

The single solute equilibrium constants were determined by fitting a Freundlich isotherm to the equilibrium data. The curved portion of the data near small concentrations was represented by a linear isotherm. The constants obtained from the three parameter isotherm equation were used to estimate the surface diffusivity values by the best statistical fit to the single solute batch rate data. These surface diffusivity values were used in the fixed bed model. Since the hydrodynamic conditions in the fixed bed experiments and batch rate studies were different, the film transfer coefficients estimated from trial and error were not used.

A correlation suggested by Dwivedi and Upadhyay(1977) was used to estimate the film transfer coefficients for different sizes of carbon particles for fixed bed conditions. The correlation used is given as

$$\begin{aligned} \epsilon J_d &= 1.1068 N_{Re}^{-0.72} & \text{for } N_{Re} < 10 \\ \epsilon J_d &= 0.4548 N_{Re}^{-0.4069} & \text{for } N_{Re} > 10 \\ J_d &= (k_f/u) N_{Sc}^{2/3} \end{aligned}$$

where

ϵ = porosity of the bed

J_d = mass transfer factor

N_{Re} = Reynolds number $(D_p G/\mu)$

k_f = film transfer coefficient

u = superficial fluid velocity (G/ρ)

N_{Sc} = Schmidt number $(\mu/\rho D_L)$

The molecular diffusivities, D_L , were calculated from the equation of Wilke and Chang (1955), which is given as:

$$D_L \mu/T = 7.4 \times 10^{-8} (XM)^{0.5} / V_o^{0.6}$$

where

μ = solution viscosity, centipoise

T = absolute temperature, °K

X = association parameter

M = molecular weight of the solvent

V_o = molal volume of the solute at normal boiling point

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Equilibrium Studies

5.1.1 Single solute isotherm for dimethyl phthalate

A total number of three isotherms were carried out in this study for each DMP And PCP. Out of these three, two were conducted using deionized distilled water at 24° C and 17° C respectively, and one was conducted using tap water at 17° C. The reason were that during fixed bed studies, the temperature of tap water used was 17° C and since the capacity of the carbon is known to change with temperature. Also, the pH of tap water was found to be 8.99, the hardness was 120 ppm and alkalinity was about 60-70 ppm.

The three parameter equation given below was utilized to describe the data.

$$q = AC / (1 + BC^{\beta}), \quad \beta < 1$$

The experimental data and predicted values are listed in Figs. 5.1 to 5.3. The estimation of isotherm parameters was done by using a nonlinear-parameter-estimation-computer program (Mathews,1975). The program computes the parameters A, B and β by using the principal axis

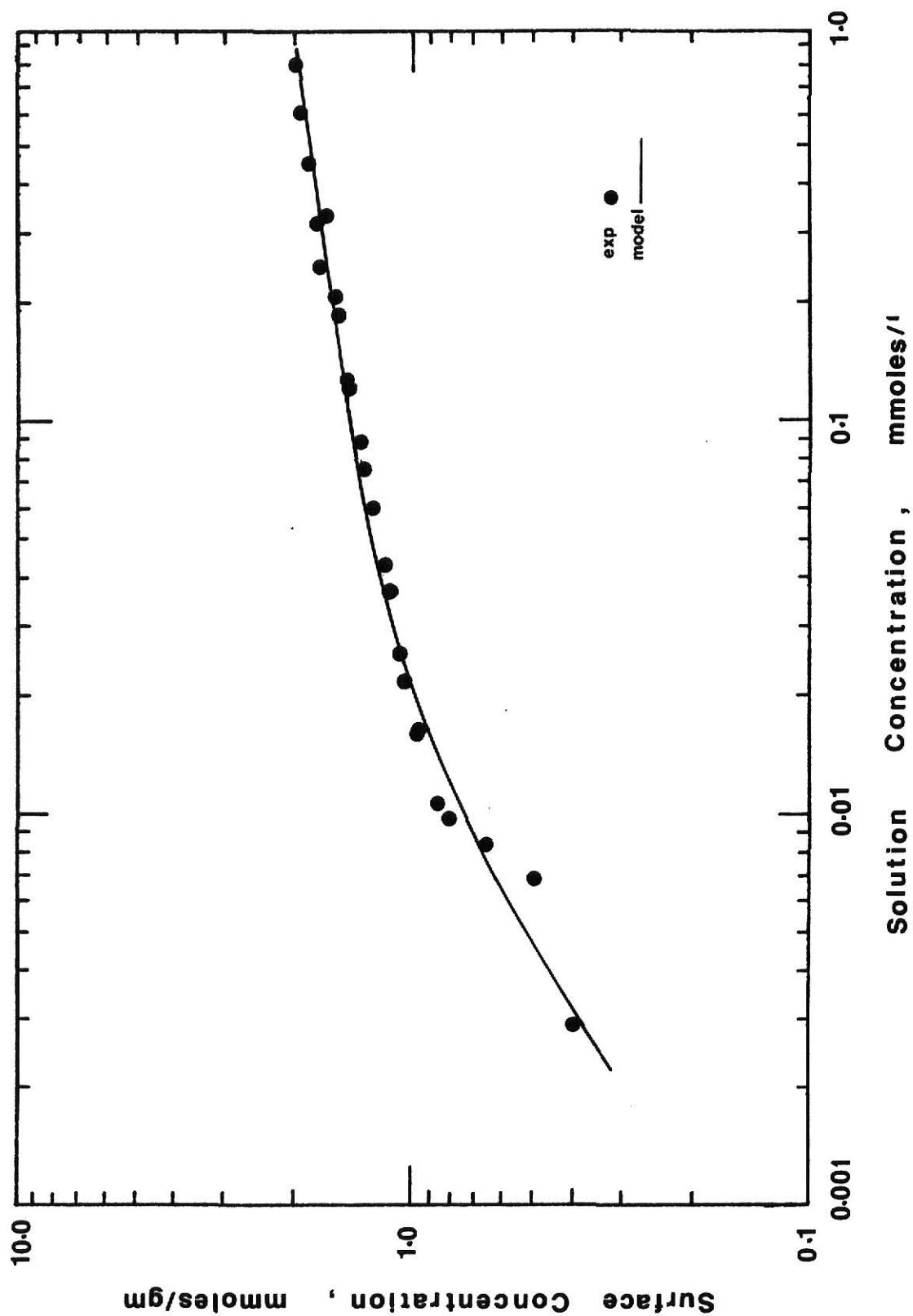


Fig. 5.1. Adsorption isotherm for DMP at 24°C.

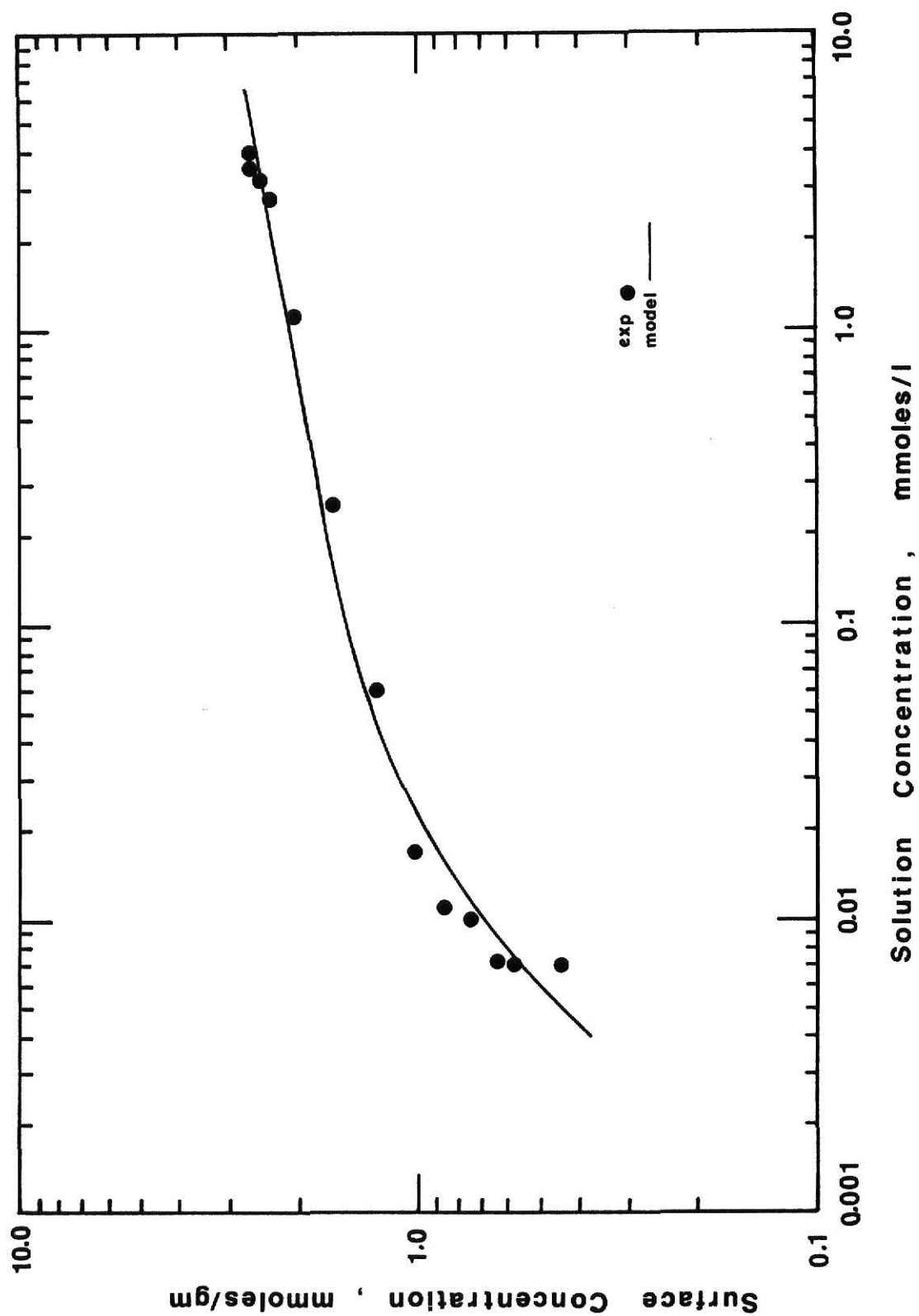


Fig. 5.2. Adsorption isotherm for DMP at 17°C.

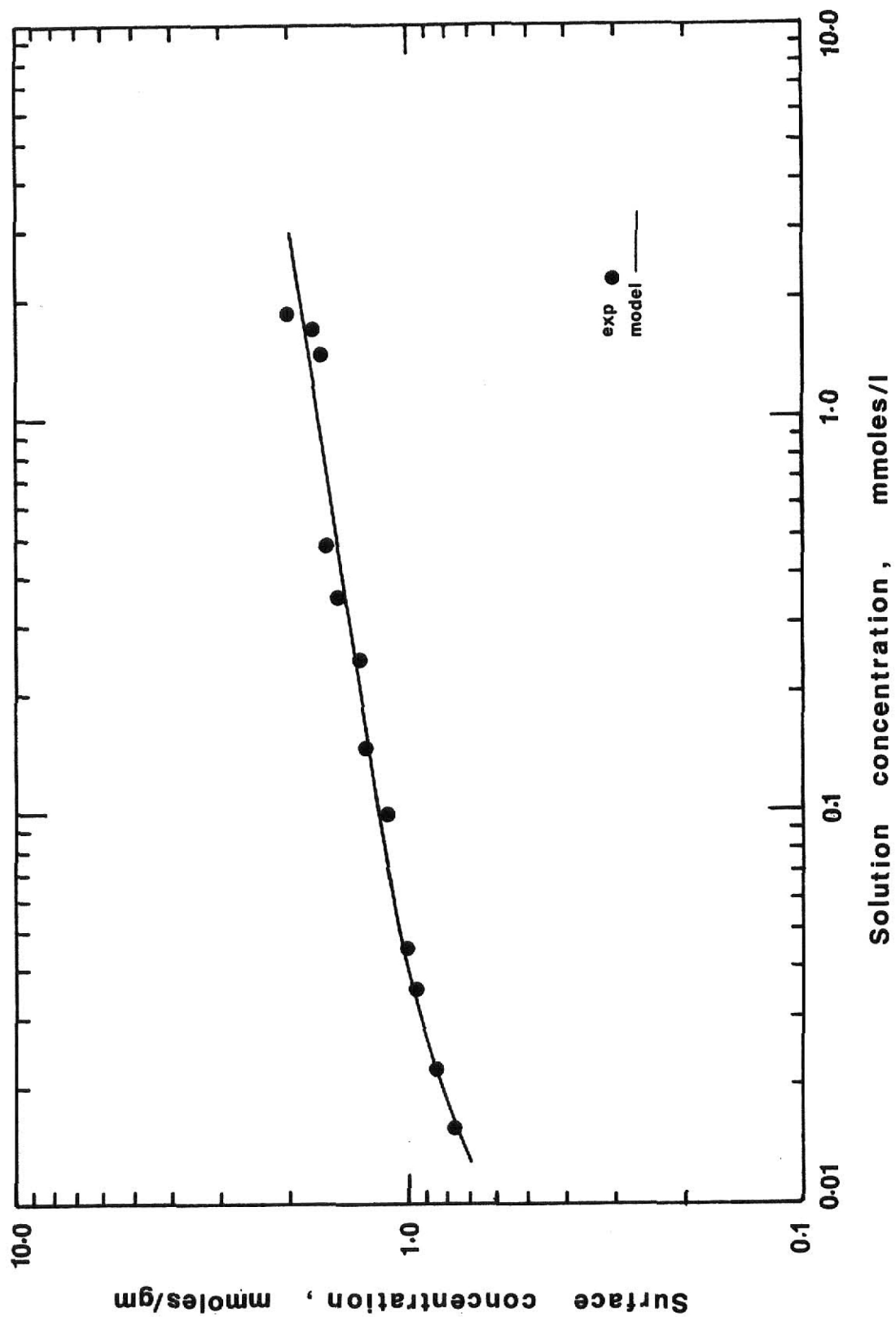


Fig.5.3. Adsorption isotherm for DMP at 17°C with tap water.

method and minimization of sum of squares of residuals between the experimental and predicted values.

From Figs. 5.1 and 5.2, the curves seem to remain as a straight line up to about a concentration of 7×10^{-5} M. Then they start curving downwards. As far as temperature is concerned, in this case, it does not appear to affect the capacity of the carbon by any appreciable amount. Both isotherms show about the same amount of solute adsorbed over a range of 10^{-6} to 10^{-3} M. The necessity of carrying out an isotherm in tap water arose due to the fact that the fixed bed mathematical model consistently showed more adsorption when parameters of isotherm at 17° C were used. As fixed bed experiments suggested, the tap water isotherm is much more flatter and at the same time adsorbs less. (Fig.5.3). The tap water isotherm runs more or less parallel to the previous two isotherms but on the downward side. The difference in adsorption seems to be of the order of 16 % at a concentration of 10^{-3} M. This lower adsorption of DMP on carbon in tap water could be possibly due to other complex species present in the tap water which have stronger affinity and are very strongly adsorbed than DMP. The pH of tap water could also be affecting the capacity of the carbon. The model seems to give a good fit of the data. In the figures shown, lines show the prediction whereas solid symbols present experimental data. The three parameters of the isotherms are listed in Table 5.1.

5.1.2 Single solute equilibrium isotherms for parachlorophenol

Figures 5.4 to 5.6 show the isotherms values - predicted and experimental - for parachlorophenol. As compared to DMP, PCP isotherms

are much more flatter and are almost straight up to a concentration of 1.7×10^{-5} M. After this point, they become slightly curved downward. The temperature seems to affect PCP more than DMP. The adsorption is reduced from temperature 24° C to 17° C. This difference in capacity at 10^{-3} M is about 22 %. Actually as temperature of solution reduces, the adsorption capacity of carbon increases. In this case, however, it is seen to decrease with the lower temperature. One possible reason is of biological activity. Even though the blanks showed no difference, presence of carbon in other bottles may have enhanced this activity. The pH also could probably be affecting the capacity as in case of DMP. This fact is opposite of normal adsorption. It is difficult to explain and needs further investigation. Use of tap water further reduces the capacity of carbon as can be seen from Fig. 5.6. This isotherm is almost a straight line. The difference in capacities at 10^{-3} M is about 19 % from distilled water isotherm at 17° C. The difference in capacities at the same temperature but different waters can again be attributed to one or more complex species present in tap water which have stronger affinity and are more strongly adsorbed than PCP. The model in this case also seems to give a good fit to the data.

The parameters of the three isotherms are given in Table 5.2. Comparing overall adsorption for both DMP and PCP, it is seen that for the same concentration, the capacity of carbon for PCP is more than DMP. This could also be possible due to the smaller molecules of PCP compared to DMP.

TABLE 5.1
Three Parameter Isotherm Constants for Dimethyl Phthalate

Isotherm	A	B	β
At 24° C	197.63	97.22	0.885
At 17° C	139.88	64.39	0.889
At 17° C (Tap water)	212.29	123.44	0.872

TABLE 5.2
Three Parameter Isotherm Constants for Parachlorophenol

Isotherm	A	B	β
At 24° C	121.86	38.15	0.916
At 17° C	96.01	36.16	0.848
At 17° C (Tap water)	4574.00	2105.97	0.889

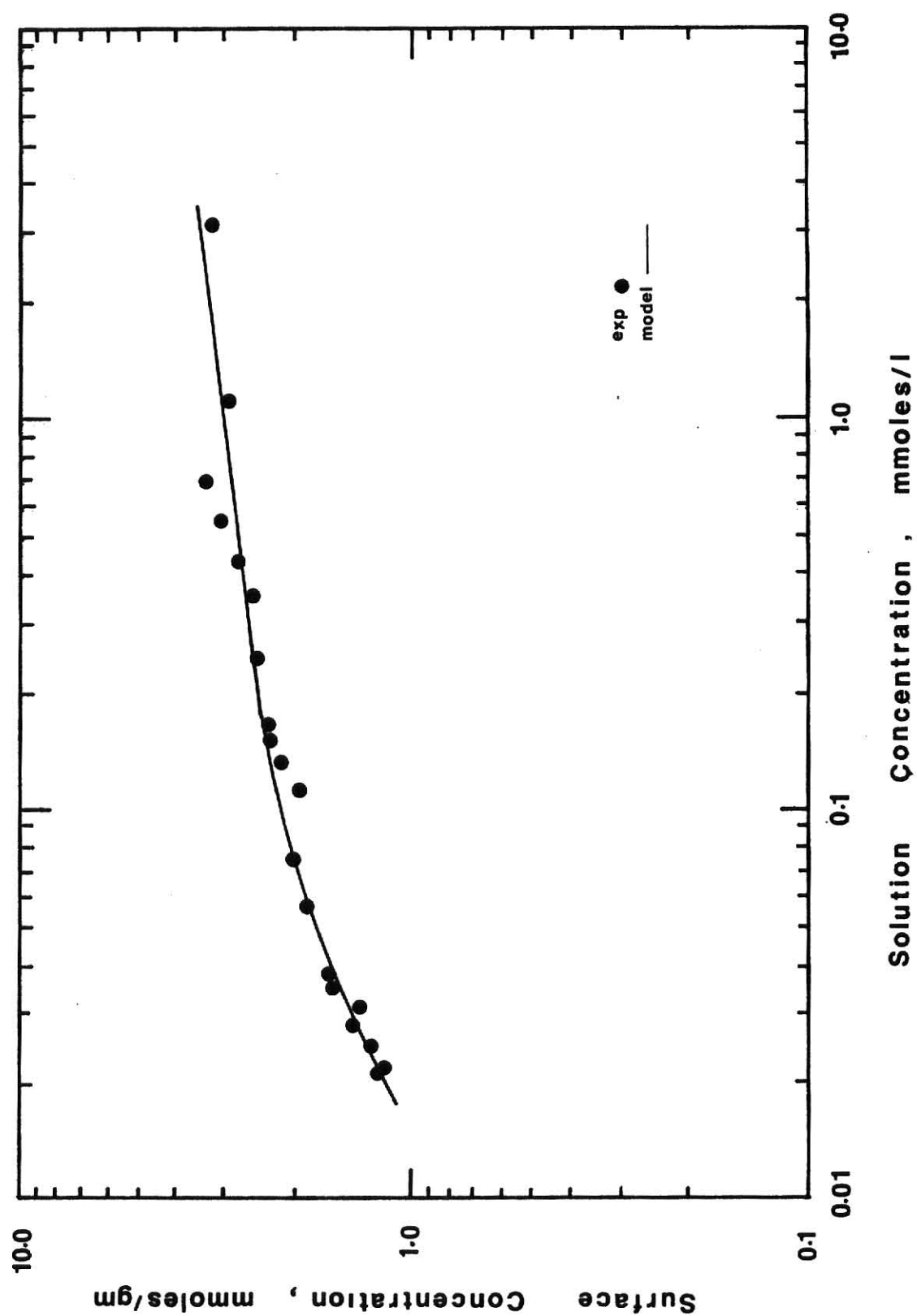


Fig. 5.4. Adsorption isotherm for PCP at 24°C.

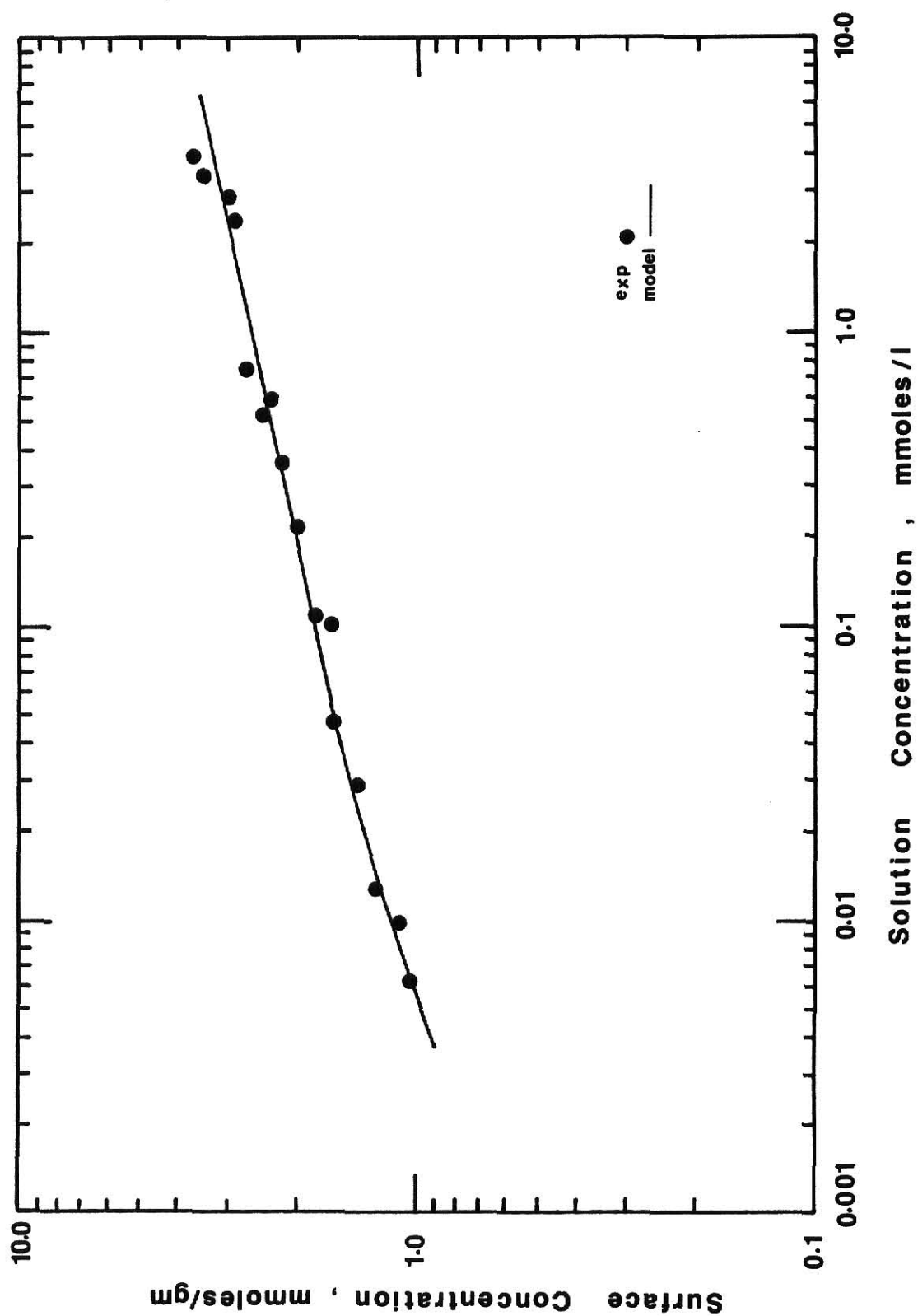


Fig. 5.5. Adsorption Isotherm for PCP at 17°C.

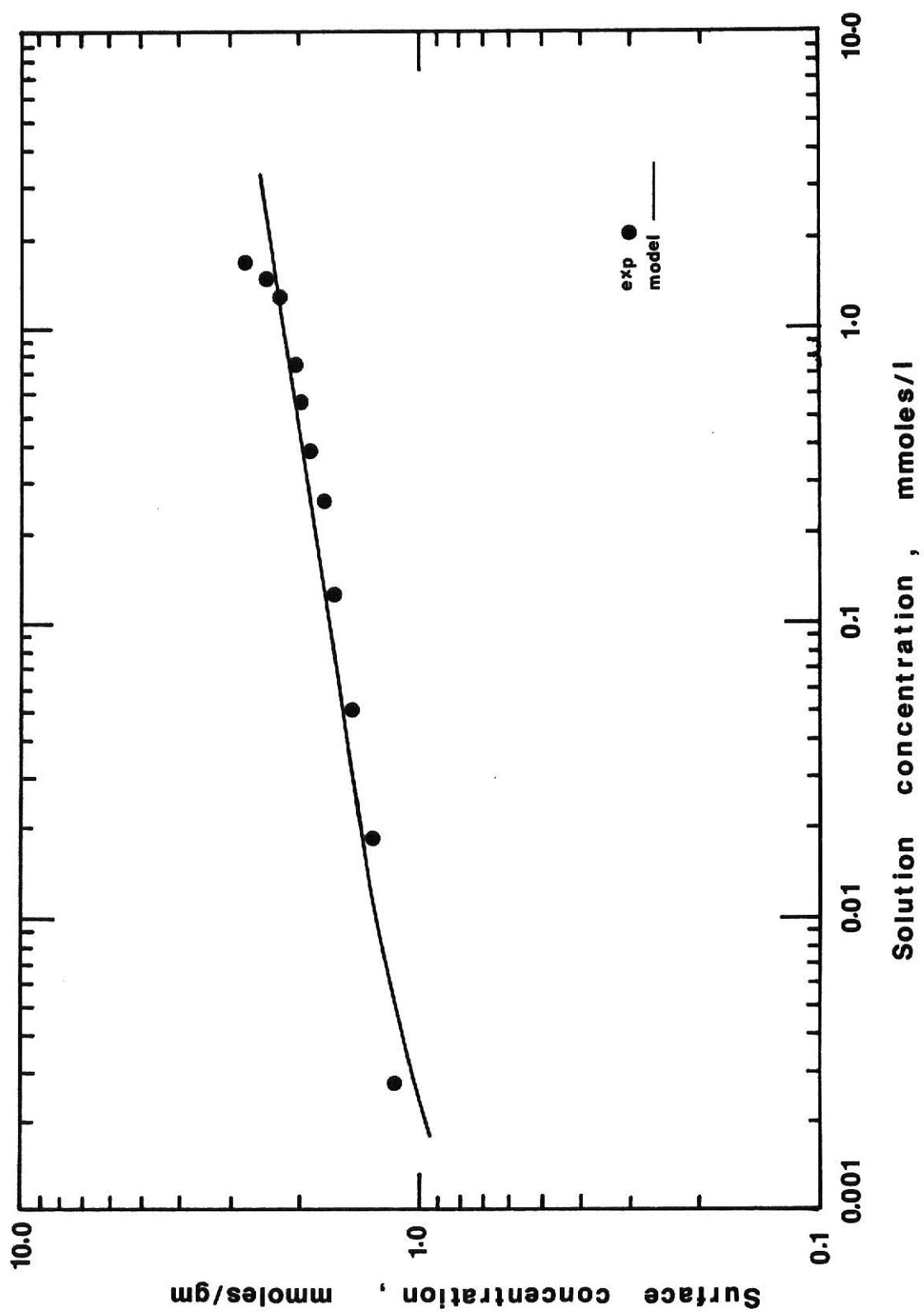


Fig. 5.6. Adsorption isotherm for PCP at 17°C with tap water.

5.1.3 Solubility of solutes

Figures 5.7 and 5.8 show the plot of q against C/C_{sol} . This should improve the predictions by elimination of one more variable - solubility. Significant improvements were, however, not noted.

5.1.4 Bisolute systems with Dimethyl phthalate and Parachlorophenol

Two models were selected, in this study, to describe the bisolute system of DMP and PCP. Those were:

1. Mathews (1975) model given as

$$q_i = A_i(C_i/\eta_i) / (1 + \sum_{j=1}^k B_j(C_j/\eta_j)^{\beta_j})$$

2. Prausnitz model (IAS model)

Both models use the data of single solute equilibrium. The comparison of predictions of both models and experimental values are given in Tables 5.3 and 5.4. The isotherm data has been collected at 24°C.

The interaction terms η_i used in the Mathews' model are obtained from mixture equilibrium data using A_i , B_i and β_i developed for each solute. From Table 5.3, it can be seen that the surface concentrations prediction by this model are generally smaller than experimental values. At higher concentrations of PCP, and also of DMP, the surface concentration predictions are poor. In the case of DMP however, at low concentrations, the predictions are in better agreements but still on the lower side. But the PCP values predicted are still too low.

Table 5.4 shows the results of Prausnitz's model. Model predictions are very poor compared to Mathews' model predictions. However, Prausnitz's model seems to predict that PCP is adsorbed more strongly than DMP which is evident from individual isotherms.

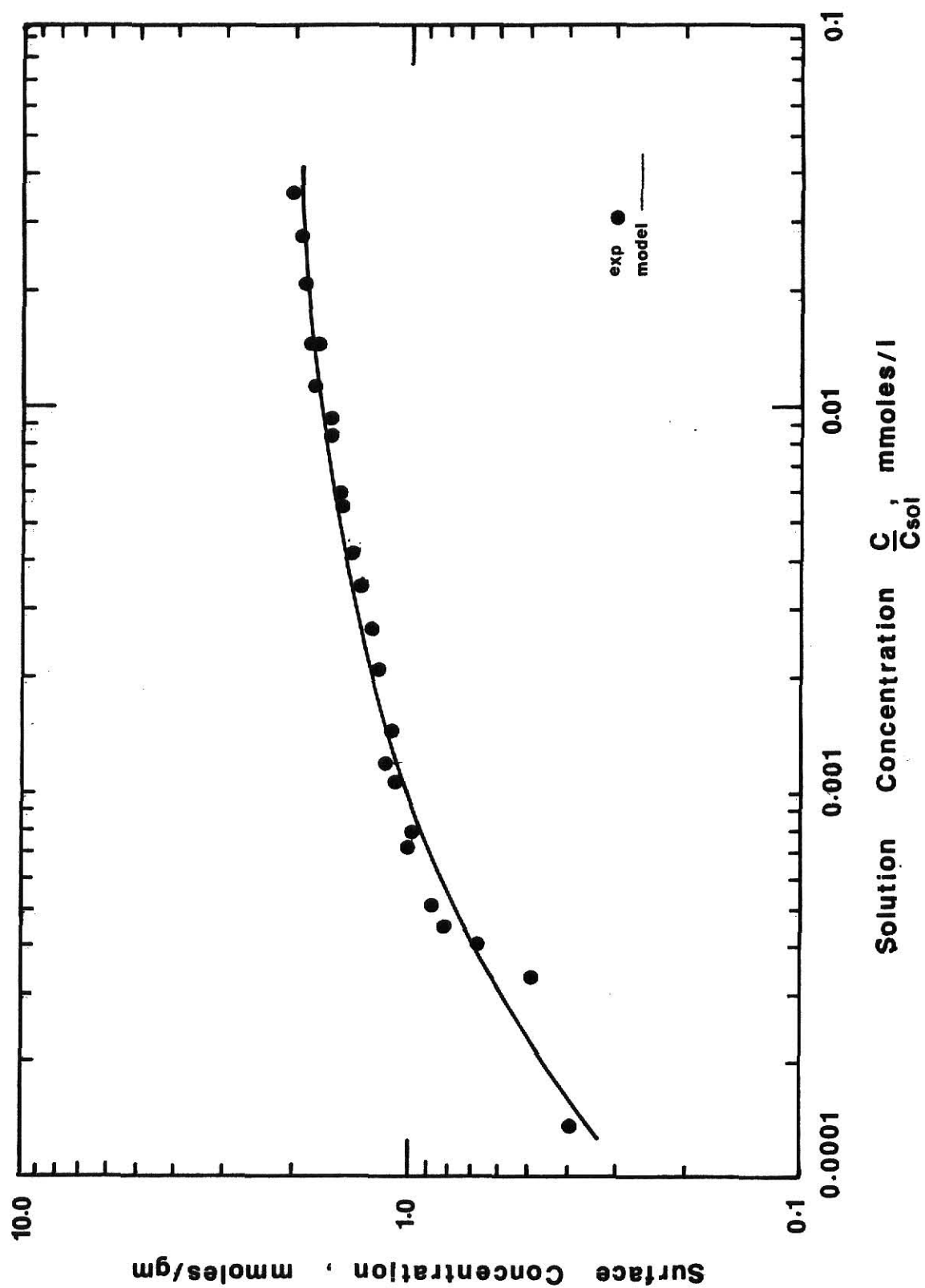


Fig. 5.7. Adsorption isotherm for $(\frac{C}{C_{sol} DMP})$ at $24^{\circ} C$.

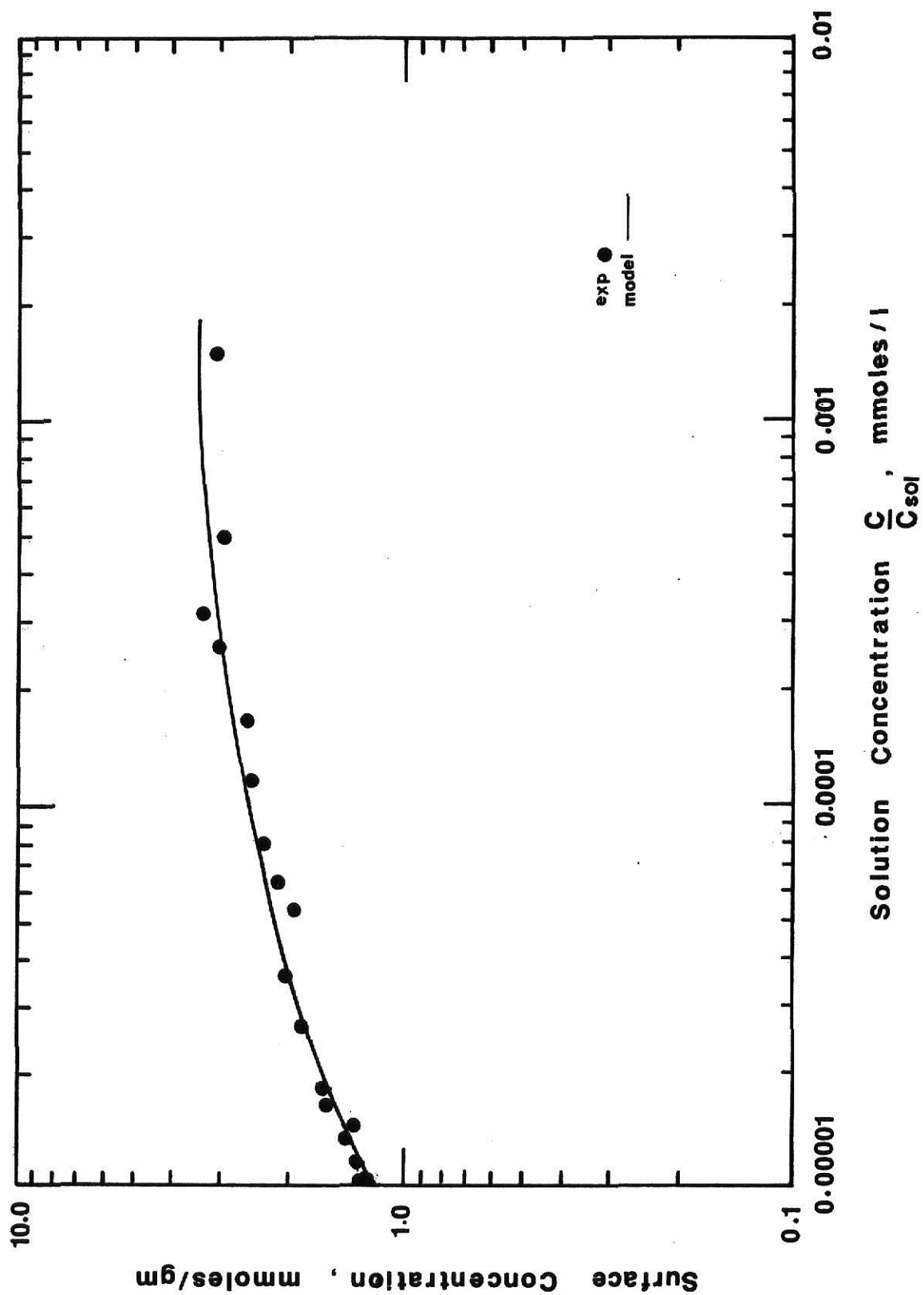


Fig. 5.8. Adsorption isotherm for $(\frac{C}{C_{sol}})_{PCP}$ at 24°C.

TABLE 5.3
Bisolute Equilibrium for DMP and PCP by Mathews' Equilibrium Model *

C_{DMP} mmoles/l	C_{PCP} mmoles/l	EXP		Model		EXP		Model	
		q_{DMP}	mmoles/gm	q_{DMP}	mmoles/gm	q_{PCP}	mmoles/gm	q_{PCP}	mmoles/gm
7.660	7.496	2.340	1.795	2.500	1.045				
5.870	5.720	2.065	1.750	2.140	1.014				
4.290	4.300	1.900	1.684	1.900	1.004				
2.800	2.760	1.800	1.620	1.800	9.498 x 10 ⁻¹				
1.630	1.760	1.674	1.497	1.648	9.618 x 10 ⁻¹				
8.730 x 10 ⁻¹	9.910 x 10 ⁻¹	1.520	1.385	1.500	9.351 x 10 ⁻¹				
8.170 x 10 ⁻¹	8.370 x 10 ⁻¹	1.830	1.412	1.630	8.608 x 10 ⁻¹				
7.000 x 10 ⁻¹	7.620 x 10 ⁻¹	1.500	1.368	1.190	8.857 x 10 ⁻¹				
5.590 x 10 ⁻¹	6.180 x 10 ⁻¹	1.470	1.329	1.270	8.743 x 10 ⁻¹				
4.660 x 10 ⁻¹	5.350 x 10 ⁻¹	1.340	1.290	1.160	8.810 x 10 ⁻¹				
4.400 x 10 ⁻¹	5.260 x 10 ⁻¹	1.366	1.268	1.350	9.016 x 10 ⁻¹				
3.470 x 10 ⁻¹	3.910 x 10 ⁻¹	1.310	1.254	1.220	8.405 x 10 ⁻¹				
2.580 x 10 ⁻¹	2.990 x 10 ⁻¹	1.240	1.202	1.170	8.287 x 10 ⁻¹				
2.330 x 10 ⁻¹	2.830 x 10 ⁻¹	1.220	1.173	1.215	8.472 x 10 ⁻¹				
2.120 x 10 ⁻¹	2.440 x 10 ⁻¹	1.130	1.176	1.080	8.050 x 10 ⁻¹				
1.170 x 10 ⁻¹	1.530 x 10 ⁻¹	1.100	1.051	1.060	8.173 x 10 ⁻¹				
1.130 x 10 ⁻¹	1.540 x 10 ⁻¹	1.098	1.034	1.090	8.380 x 10 ⁻¹				
7.560 x 10 ⁻²	9.910 x 10 ⁻²	1.030	9.837 x 10 ⁻¹	1.000	7.671 x 10 ⁻¹				
6.600 x 10 ⁻²	9.900 x 10 ⁻²	9.900 x 10 ⁻¹	9.270 x 10 ⁻¹	9.900 x 10 ⁻¹	8.272 x 10 ⁻¹				
5.320 x 10 ⁻²	1.040 x 10 ⁻¹	9.470 x 10 ⁻¹	8.238 x 10 ⁻¹	8.960 x 10 ⁻¹	9.580 x 10 ⁻¹				
1.926 x 10 ⁻²	4.958 x 10 ⁻²	7.846 x 10 ⁻¹	6.100 x 10 ⁻¹	7.603 x 10 ⁻¹	9.341 x 10 ⁻¹				
8.854 x 10 ⁻³	2.099 x 10 ⁻²	6.661 x 10 ⁻¹	4.959 x 10 ⁻¹	6.527 x 10 ⁻¹	6.993 x 10 ⁻¹				
7.027 x 10 ⁻³	1.949 x 10 ⁻²	5.674 x 10 ⁻¹	4.350 x 10 ⁻¹	5.603 x 10 ⁻¹	7.178 x 10 ⁻¹				
4.714 x 10 ⁻³	1.476 x 10 ⁻²	4.976 x 10 ⁻¹	3.556 x 10 ⁻¹	4.926 x 10 ⁻¹	6.623 x 10 ⁻¹				
3.852 x 10 ⁻³	1.077 x 10 ⁻²	4.427 x 10 ⁻¹	3.321 x 10 ⁻¹	4.367 x 10 ⁻¹	5.521 x 10 ⁻¹				

TABLE 5.3 (continued)

C_{DMP}	C_{PCP}	EXP q_{DMP}	Model q_{DMP}	EXP q_{PCP}	Model q_{PCP}
	mmoles/l	mmoles/gm		mmoles/gm	
2.568×10^{-3}	7.035×10^{-3}	3.616×10^{-1}	2.671×10^{-1}	3.611×10^{-1}	4.352×10^{-1}
2.266×10^{-3}	7.041×10^{-3}	3.991×10^{-1}	2.420×10^{-1}	3.972×10^{-1}	4.473×10^{-1}
2.158×10^{-3}	8.421×10^{-3}	3.326×10^{-1}	2.242×10^{-1}	3.305×10^{-1}	5.205×10^{-1}

$$* q = \frac{A_i(C_i/n_i)}{1 + \sum_{j=1}^K B_j(C_j/n_j)} \beta_j$$

TABLE 5.4

Bisolute Equilibrium for DMP and PCP by Prausnitz Equilibrium Model

C_{DMP}	C_{PCD}	EXP	Model	Modified	EXP	Model	Modified
		q_{DMP}	q_{DMP}	q_{DMP}	q_{PCP}	q_{PCP}	q_{PCP}
mmoles/l		mmoles/gm		mmoles/gm		mmoles/gm	
7.660	7.496	2.340	5.081×10^{-1}	1.2023	2.500	3.215	1.976
5.870	5.720	2.065	5.221×10^{-1}	1.235	2.140	3.103	1.907
4.290	4.300	1.900	5.272×10^{-1}	1.247	1.900	2.996	1.841
2.800	2.760	1.800	5.497×10^{-1}	1.300	1.800	2.817	1.731
1.630	1.760	1.674	5.347×10^{-1}	1.265	1.648	2.677	1.645
8.730	9.910×10^{-1}	1.520	5.505×10^{-1}	1.302	1.500	2.458	1.510
8.170	8.370×10^{-1}	1.830	6.061×10^{-1}	1.434	1.630	2.333	1.434
7.000	7.620×10^{-1}	1.500	5.867×10^{-1}	1.388	1.190	2.322	1.427
5.590	6.180×10^{-1}	1.470	5.949×10^{-1}	1.407	1.270	2.236	1.374
4.660	5.350×10^{-1}	1.340	5.833×10^{-1}	1.380	1.160	2.198	1.351
4.400	5.260×10^{-1}	1.366	5.681×10^{-1}	1.344	1.350	2.209	1.357
3.470	3.910×10^{-1}	1.310	6.196×10^{-1}	1.466	1.220	2.038	1.252
2.580	2.990×10^{-1}	1.240	6.254×10^{-1}	1.479	1.170	1.929	1.185
2.330	2.830×10^{-1}	1.220	6.095×10^{-1}	1.442	1.215	1.926	1.184
2.120	2.440×10^{-1}	1.130	6.363×10^{-1}	1.505	1.080	1.838	1.300
1.170	1.530×10^{-1}	1.100	6.156×10^{-1}	1.456	1.060	1.674	1.029
1.130	1.540×10^{-1}	1.098	3.992×10^{-1}	1.417	1.090	1.696	1.042
7.560	9.910×10^{-2}	1.030	6.260×10^{-1}	1.481	1.000	1.479	9.088×10^{-1}
6.600	9.900×10^{-2}	9.900	5.754×10^{-1}	1.361	9.900×10^{-1}	1.532	9.414×10^{-1}
5.320	1.040×10^{-1}	9.470	4.808×10^{-1}	1.137	8.960	1.658	1.019
1.926	4.958×10^{-2}	7.846	4.041×10^{-1}	9.562×10^{-1}	7.603×10^{-1}	1.392	8.554×10^{-1}
8.854	2.099×10^{-2}	6.661	3.849×10^{-1}	9.108×10^{-1}	6.527×10^{-1}	9.675×10^{-1}	5.945×10^{-1}
4.714	1.476×10^{-2}	4.976	2.865×10^{-1}	6.779×10^{-1}	4.926×10^{-1}	8.893×10^{-1}	5.465×10^{-1}
3.852	1.077×10^{-3}	4.427	2.822×10^{-1}	6.677×10^{-1}	4.367×10^{-1}	7.360×10^{-1}	4.522×10^{-1}
2.266	7.041×10^{-3}	3.991	2.061×10^{-1}	4.877×10^{-1}	3.972×10^{-1}	5.978×10^{-1}	3.673×10^{-1}
2.158	8.421×10^{-3}	3.326	1.960×10^{-1}	4.638×10^{-1}	3.305×10^{-1}	6.651×10^{-1}	4.087×10^{-1}

 $R_{DMP} = 2.3662$, $R_{PCP} = 0.6145$

The predictions are far lower for DMP and far higher for PCP. Thacker et al. (1981) have noticed that in the case of Prausnitz's model, the ratios of experimental solution concentration values to the predicted solution concentration values were moderately constant. When the experimental values were multiplied by these ratios, they obtained better prediction using these modified values. Here, however only in case PCP, the ratios of experimental surface concentration values to the predicted surface concentration values were moderately constant. There was no such consistency in ratios in the case of DMP. Nevertheless, the average of such all ratios is used to find modified surface concentration values.

$$\text{Modified } q_{\text{DMP}} = R_{\text{DMP}} q_{\text{DMP}}$$

$$\text{Modified } q_{\text{PCP}} = R_{\text{PCP}} q_{\text{PCP}}$$

R_{DMP} was found to be equal to 2.3662 while R_{PCP} was equal to 0.6145. This seems to improve the results as seen from Table 5.4.

The discrepancy between the experimental and predicted values is difficult to explain. The possibilities of inaccurate predictions by IAS theory are given as (Radke and Prausnitz, 1972a):

(1) Inaccurate spreading pressure integrations due to lack of single solute data at low concentrations ranges. Both DMP and PCP have been reduced to concentrations of the order of less than $5 \times 10^{-5} \text{ M}$ in their isotherms. However, PCP does not seem to have such low concentrations as found in bisolute equilibrium. This could possibly be one of the reasons that the deviations seem to be unreasonably high.

(2) The failure of the assumption of an ideal adsorbed solution

due to a dense surface coverage.

As stated by Thacker et al. (1981), a value of R less than one means the spreading pressure is less than the expected by the model. In other words, the interfacial tension has not been lowered as much as would be expected by the theory. The R values, however, depend on the adsorbent. Another possible reason could be solute-solute reaction on the carbon surface.

Figures 5.9 and 5.10 are the plots of $q_{\text{exp}}/q_{\text{calc}}$ against the solution concentration using Mathews' model and Prausnitz's model respectively. In Fig. 5.9, the Mathews' equilibrium model is seen to predict well. The values for DMP are between 10% whereas the Prausnitz model values are scattered over up to 1/5 times the experimental values. For PCP, the Mathews equilibrium model seems to give values about 1/2 times the experimental values. Prausnitz model values, even though deviated from unity, form a band near 0.6 value. When multiplied by this value, the predictions are seen to improve as indicated by the modified values in Table 5.4.

5.2 Batch kinetic studies

Adsorption rate studies were performed to gather the kinetic data of surface diffusion coefficient and batch film transfer coefficient. The rate studies were done for single solute as well as bisolute systems.

5.2.1 Single solute rate study

Since fixed bed experiments use various size fractions of carbon, the rate studies were conducted using carbon size fractions of #12-14, #18-20, #30-35 and #35-40. Studies were also carried out using a

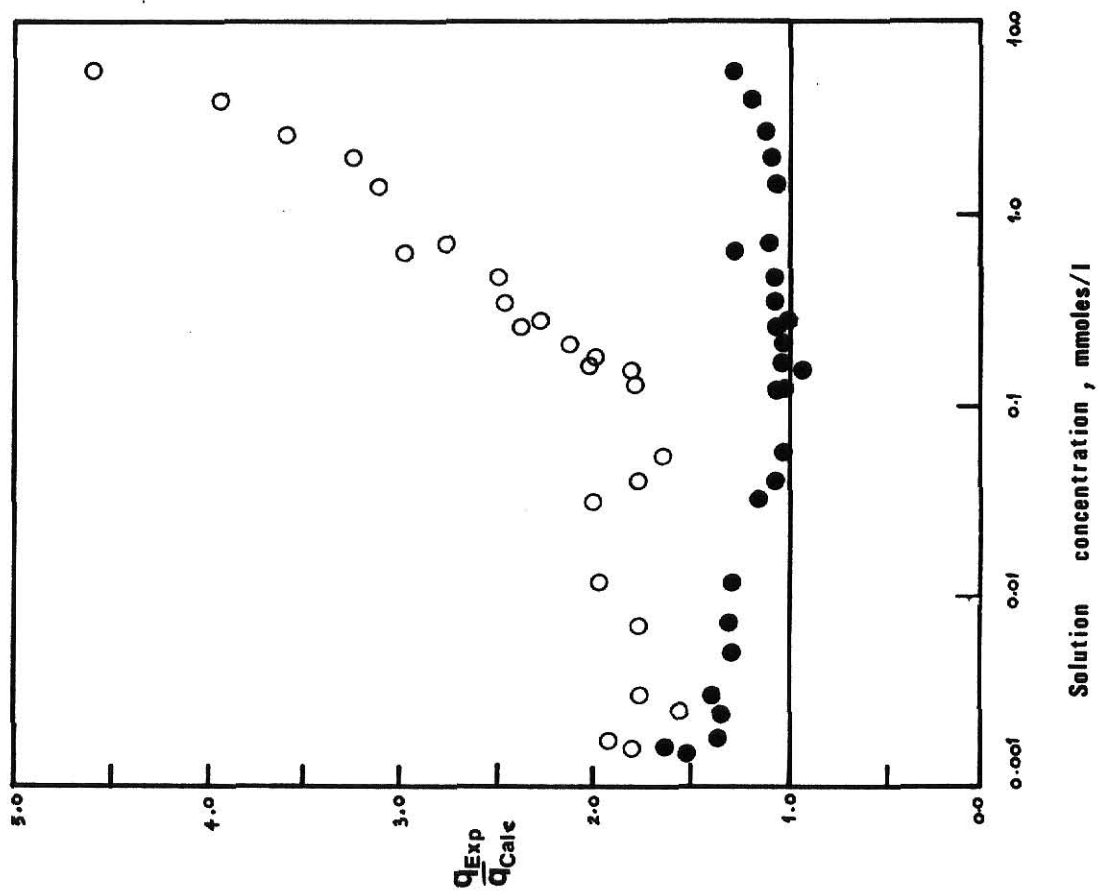


Fig. 5.9. DMP in bisolute isotherm.

● Mathews model ,

○ Prausnitz model

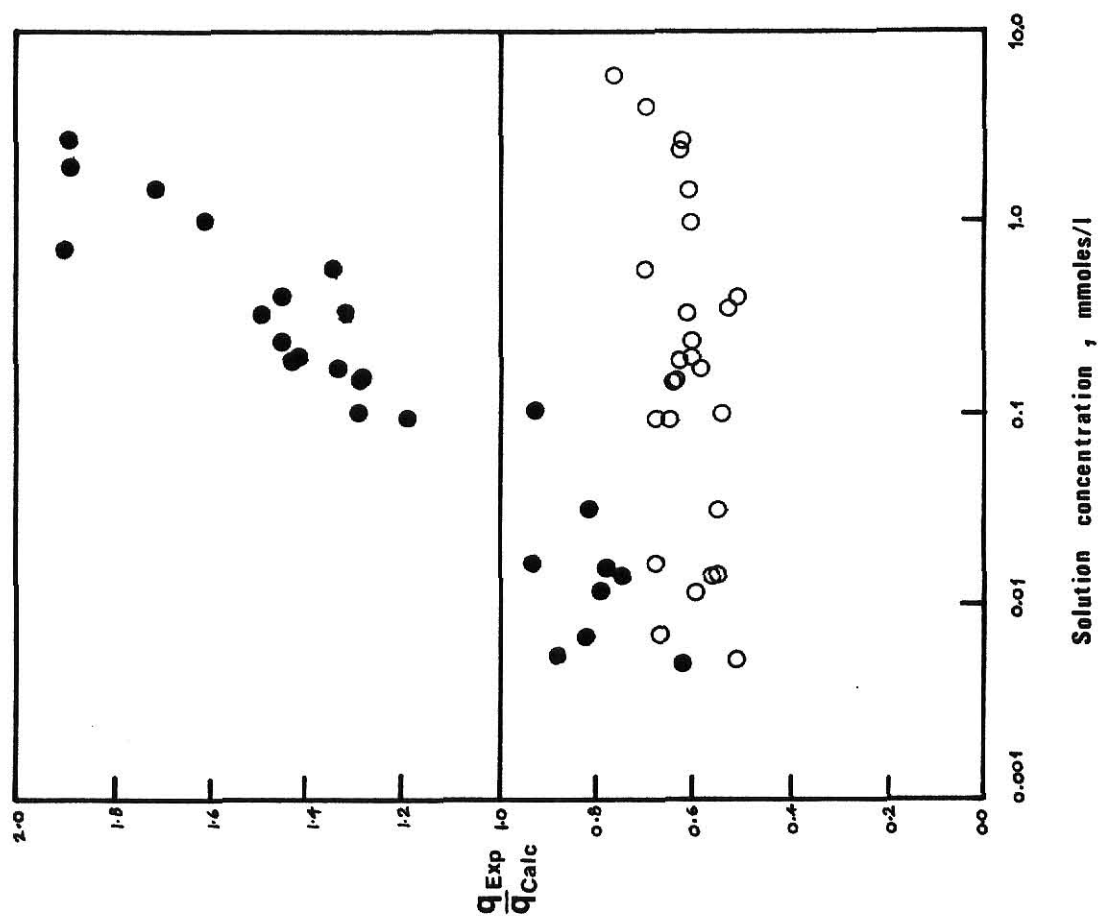


Fig. 5.10. PCP in bisolute isotherm.

● Mathews model ,

○ Prausnitz model

mixture of particles of sizes #13-20 and #30-35. The surface diffusivities and batch film transfer coefficients of single solute system were estimated by the computer program written by Mathews (1975). For size #12-14, a speed of 800rpm was used. For other sizes a speed of 600 was used. Figures 5.11 to 5.20 show the predicted and experimental values for different sizes of carbon particles. This prediction is plotted using log-mean diameter of the particle. As before, the line represents predicted values and solid symbols indicate experimental values.

Figures 5.11 to 5.15 show that the model gives an excellent fit with the experimental data of DMP. The values of surface diffusivities and batch film transfer coefficients for various sizes of carbon and DMP are listed in Table 5.6.

In the case of PCP, in Figs. 5.16 and 5.19, the experimental points are slightly below the predicted curve during the initial period and slightly higher near the end of the period. This could possibly due to the carbon fines formed during stirring by collision of particles and fines adsorbing more solute a little faster. For smaller particles, however, from Figs. 5.18 to 5.20 the predictions fit very well. The values of surface diffusivities and batch film transfer coefficients for various sizes of carbon and PCP are given in Table 5.9 for log-mean diameter.

Ideally, since the pore structure of all carbons is same, surface diffusion coefficient should not change for different particle sizes. The difference in surface diffusivities is possibly mainly due to the different amounts of fines formed during stirring.

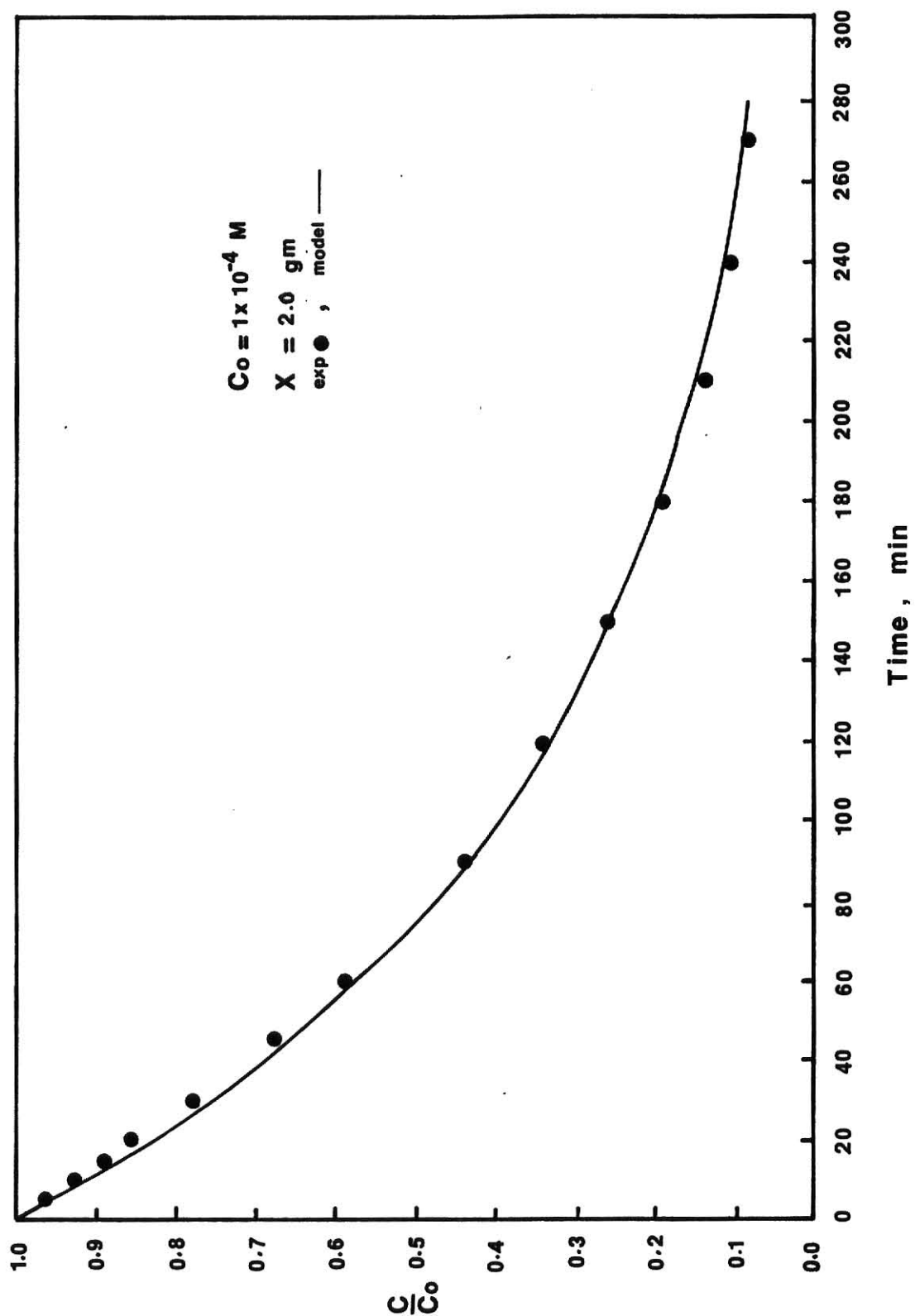


Fig. 5-11. Adsorption rate for DMP for carbon size #12/14.

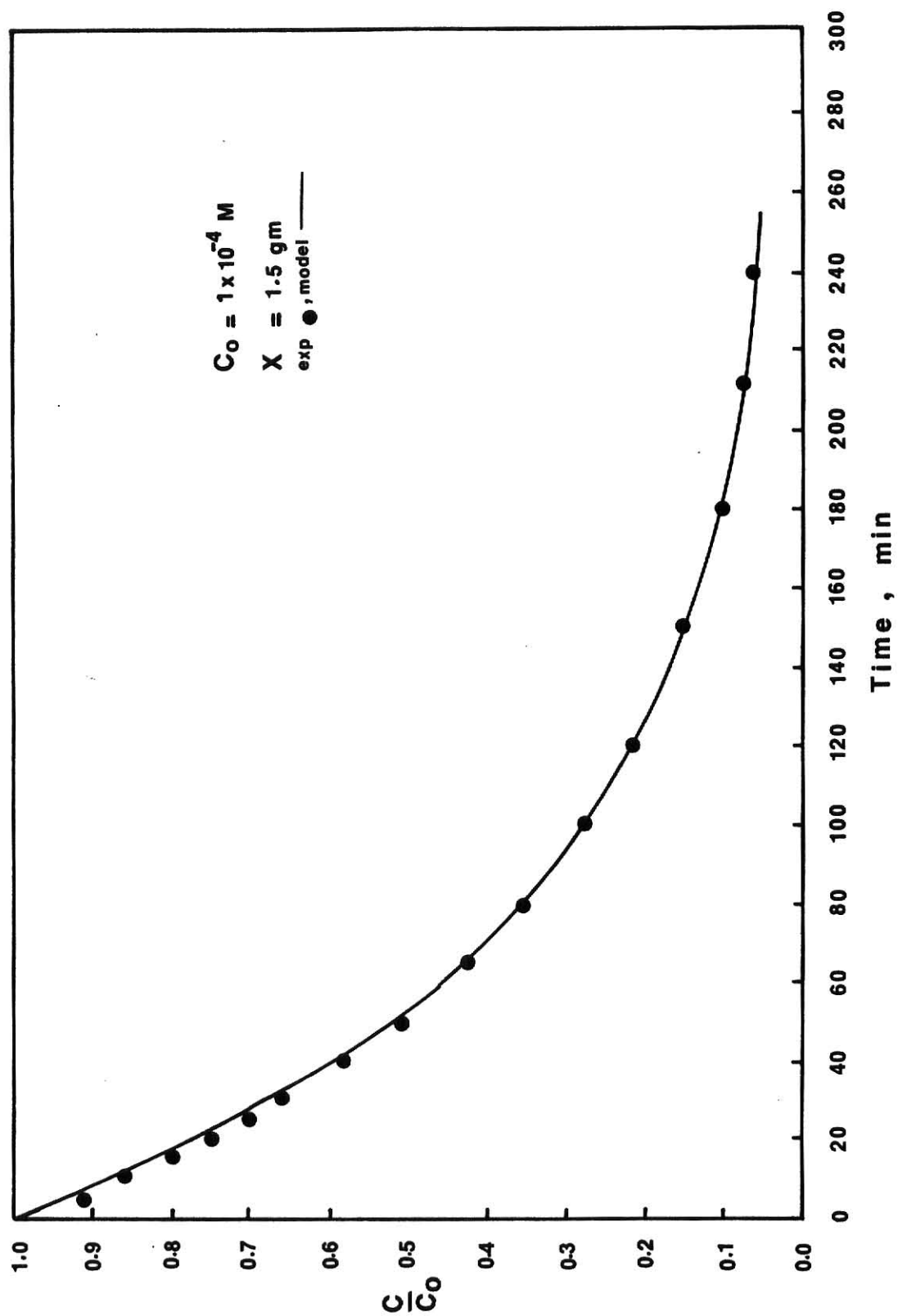


Fig. 5-12. Adsorption rate for DMP for carbon size #18/20.

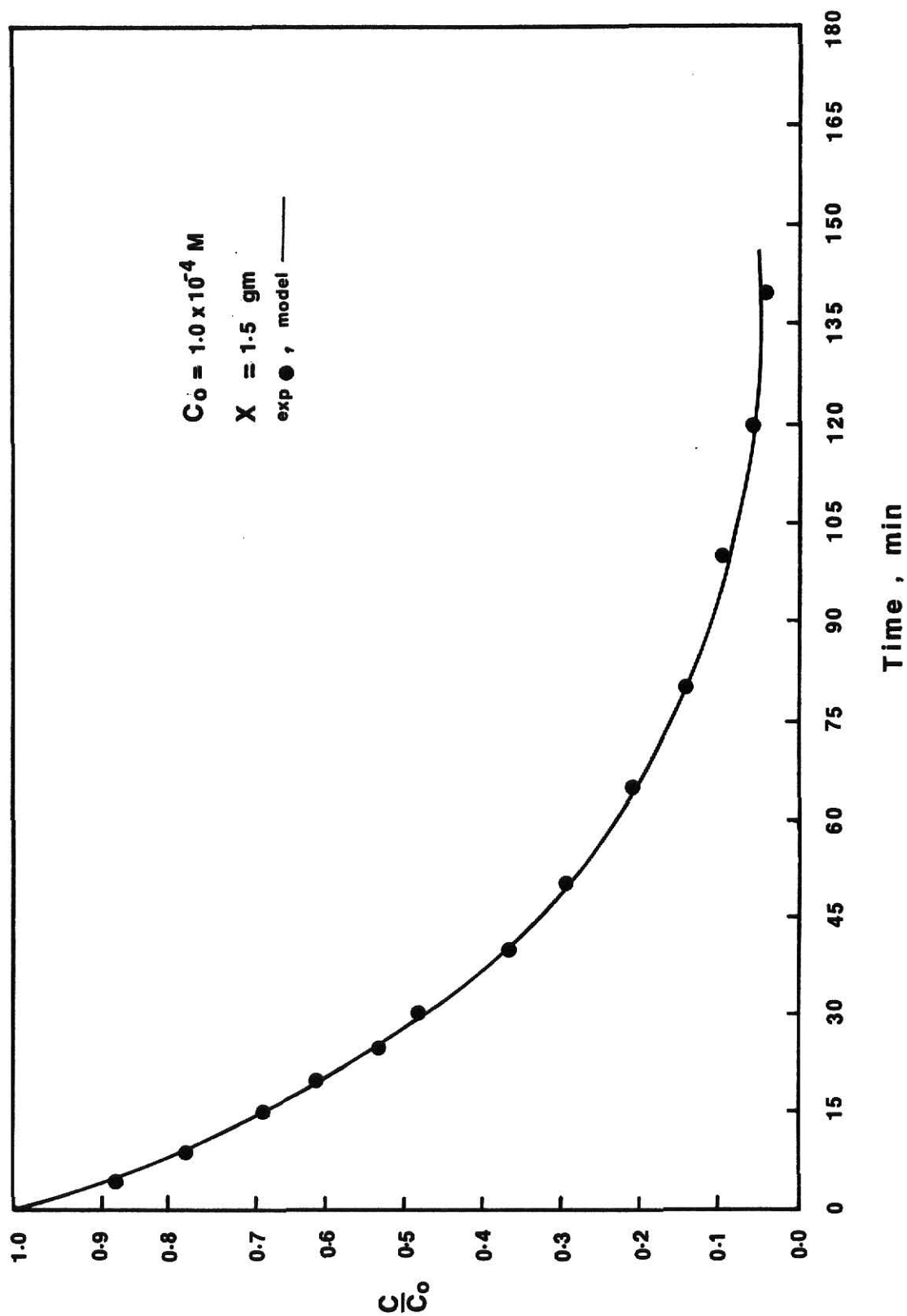


Fig. 5.13. Adsorption rate for DMP for carbon size #30/35.

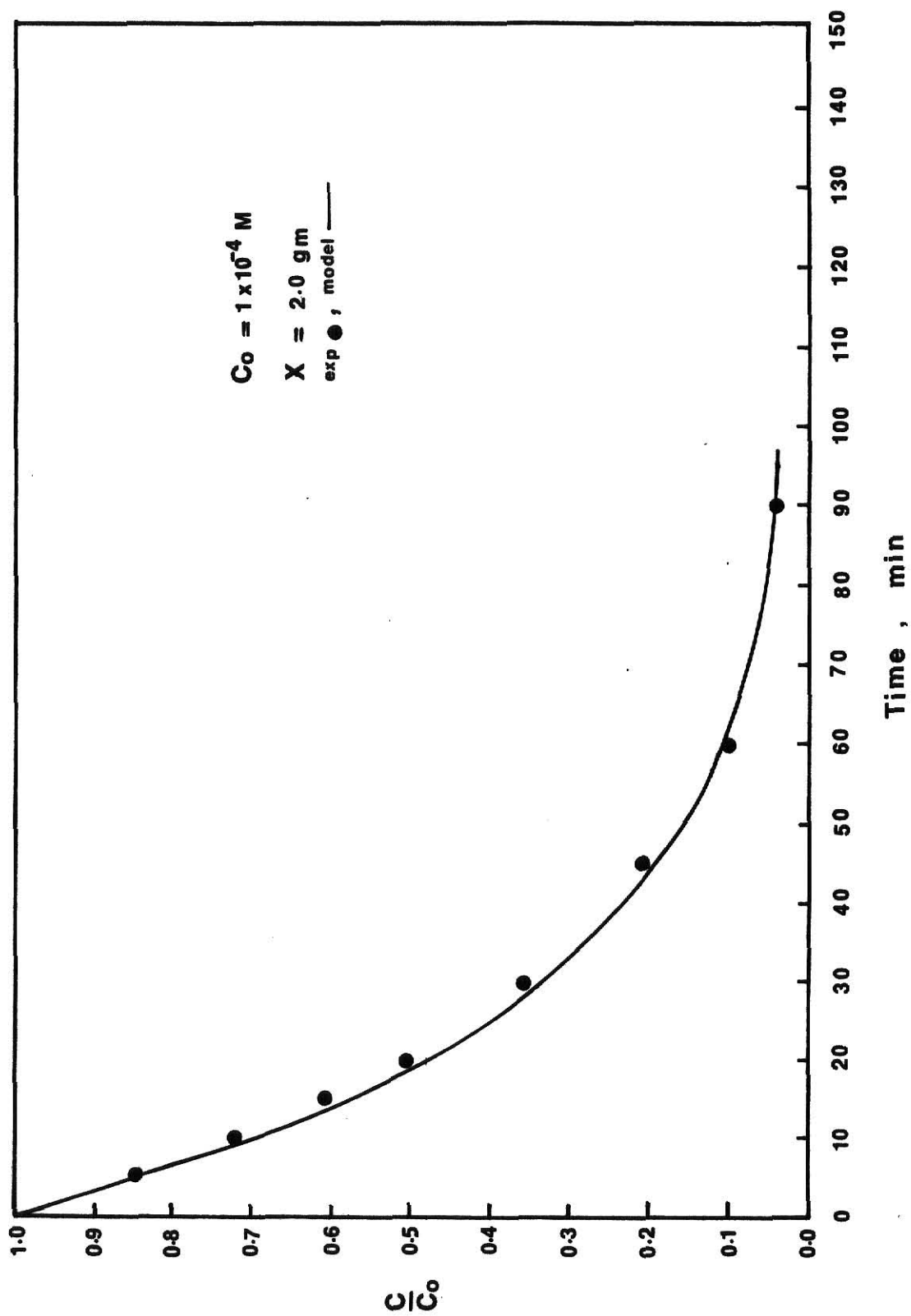


Fig. 5.14. Adsorption rate for DMP for carbon size #35/40.

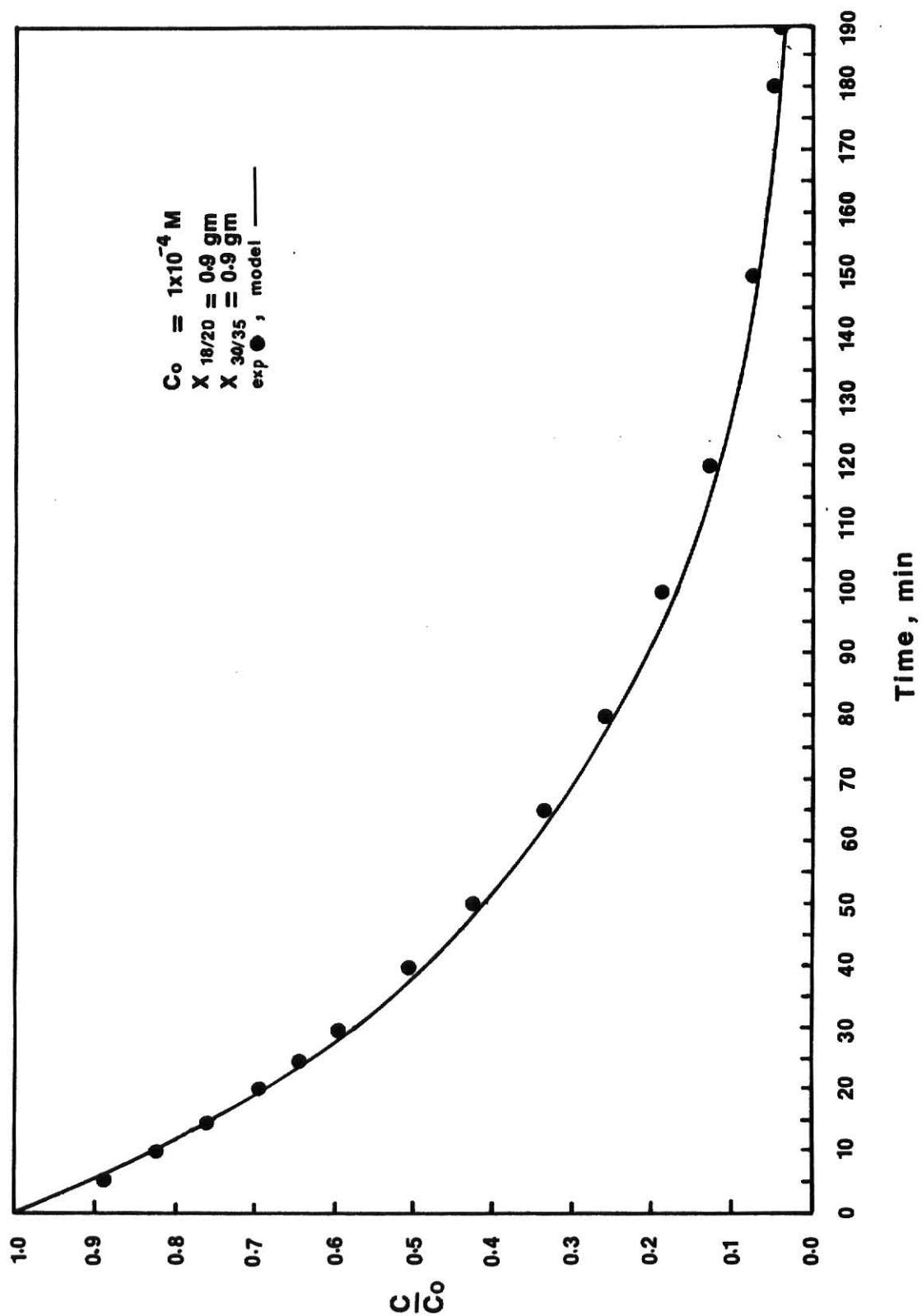


Fig. 5.15. Adsorption rate for DMP for carbon # (18/20+30/35).

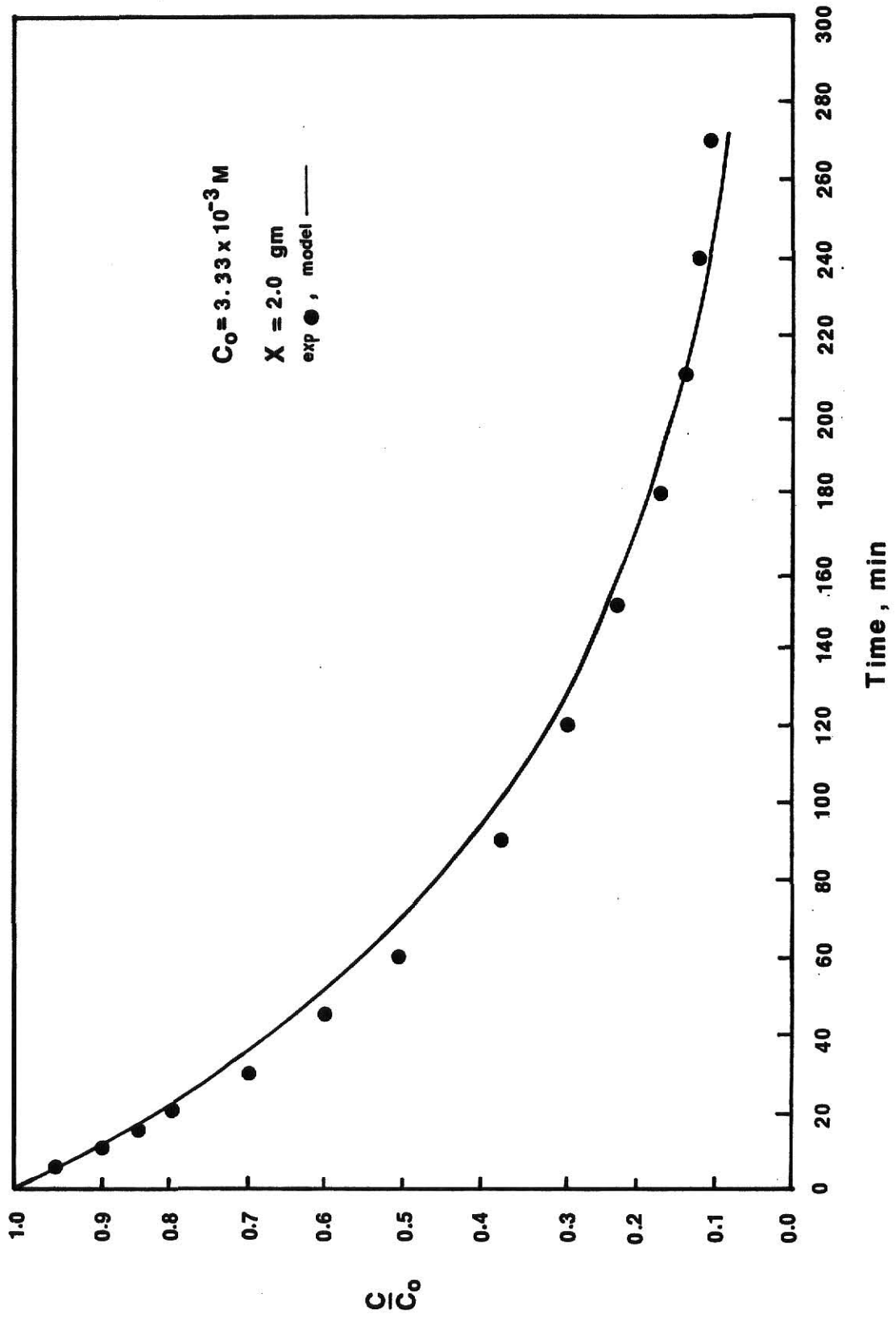


Fig. 5.16. Adsorption rate for PCP for carbon size #12/14.

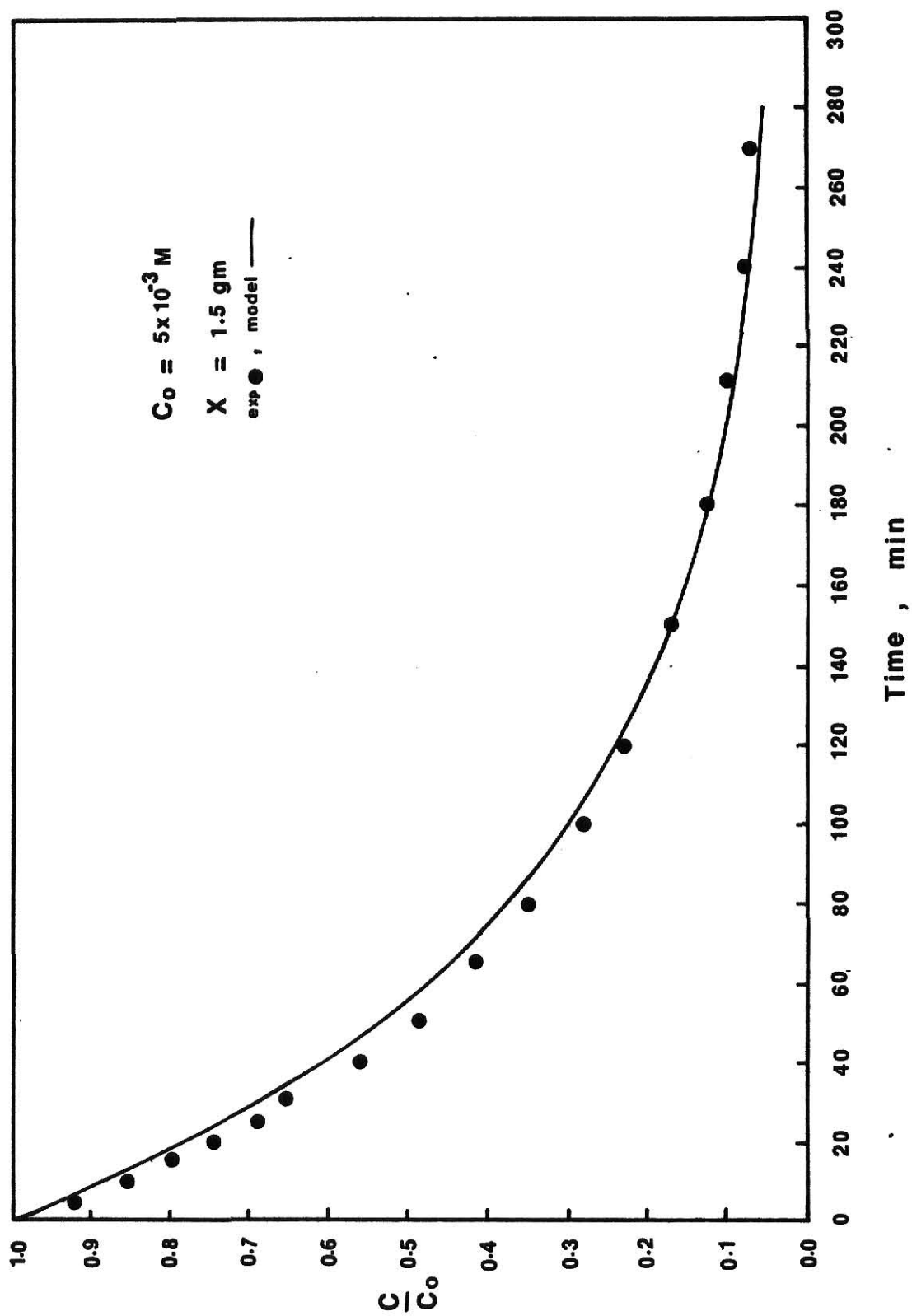


Fig. 5-17. Adsorption rate for PCP for carbon size #18/20.

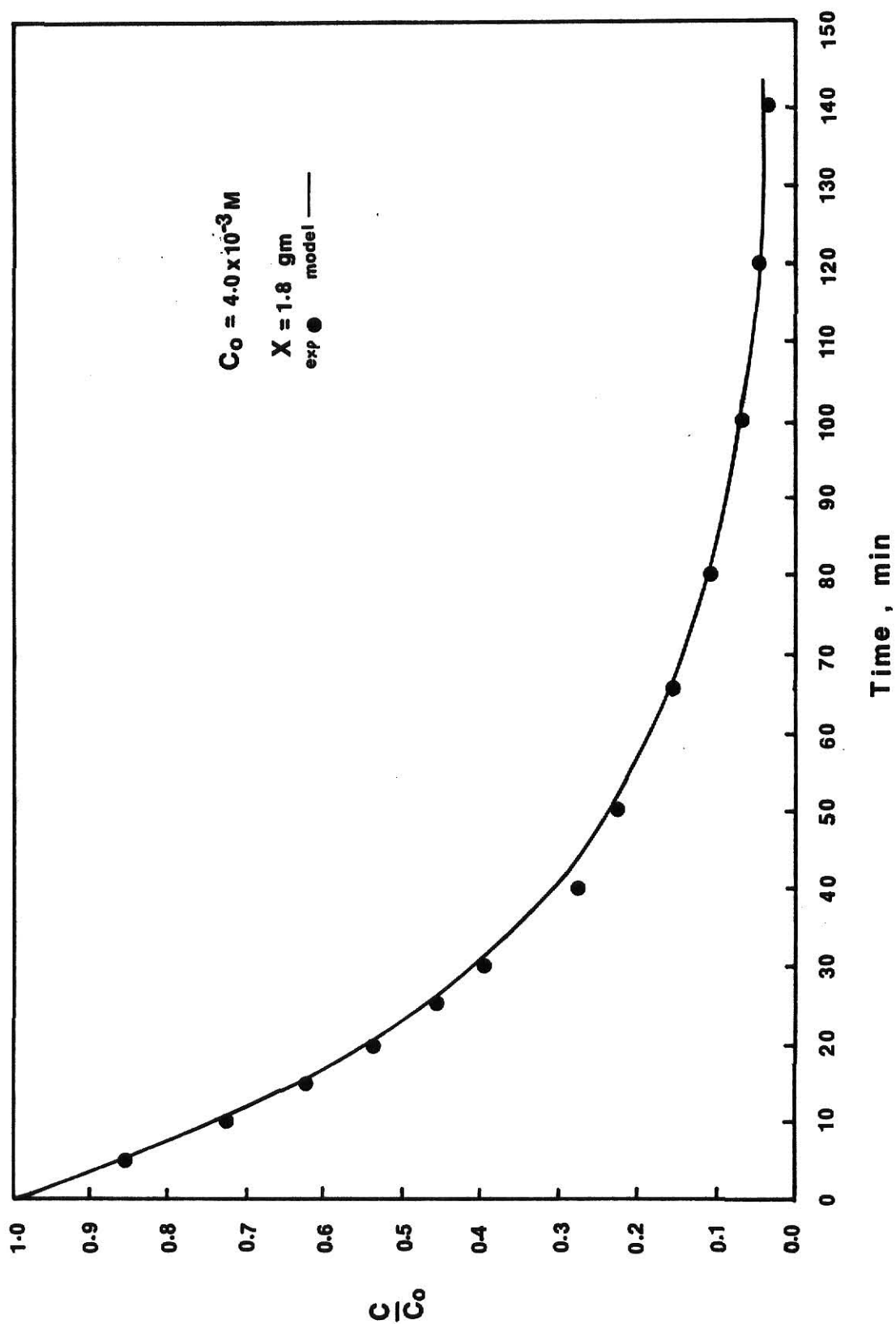


Fig. 5.18. Adsorption rate for PCP for carbon size #30/35.

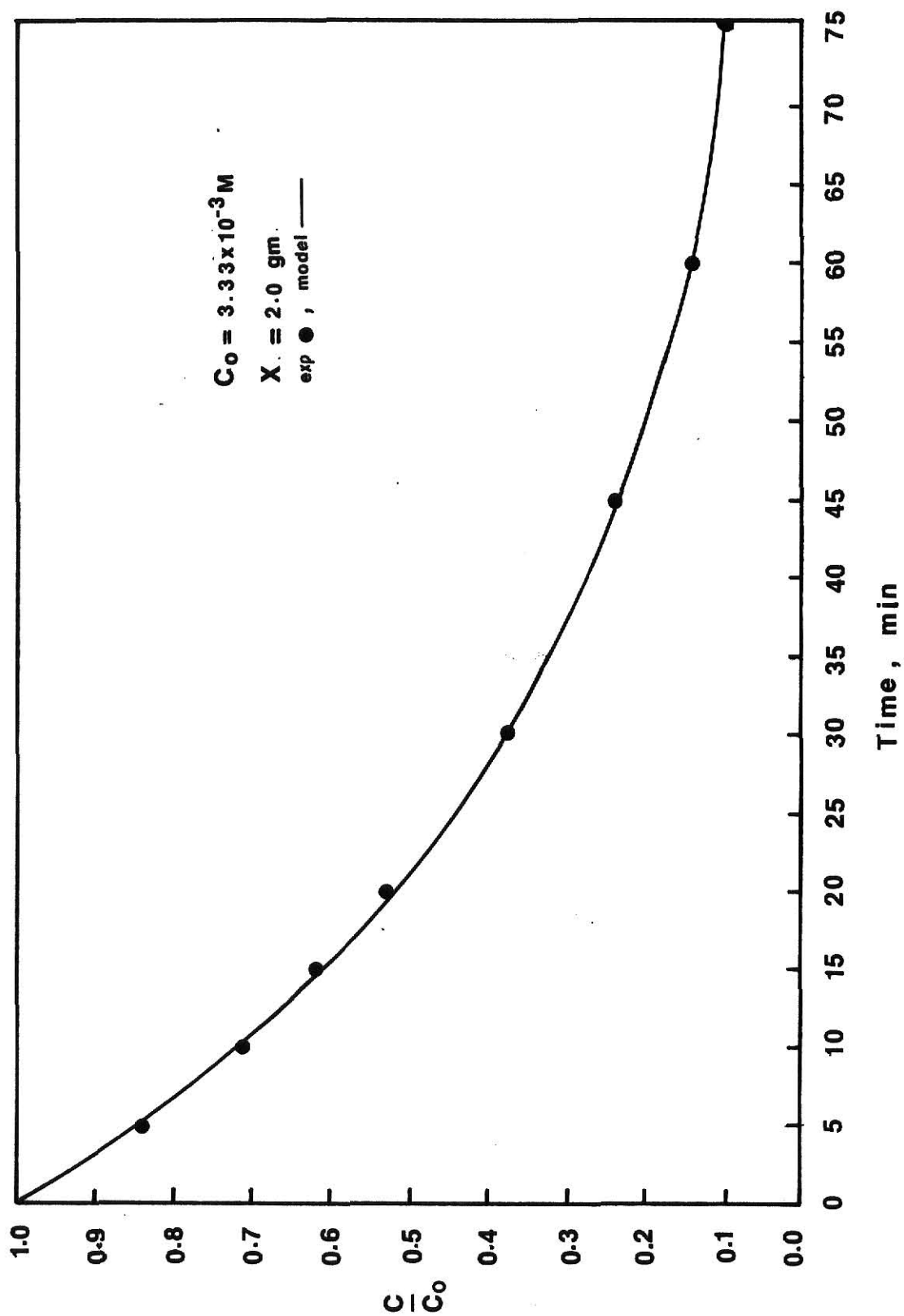


Fig. 5.19. Adsorption rate for PCP for carbon size #35/40.

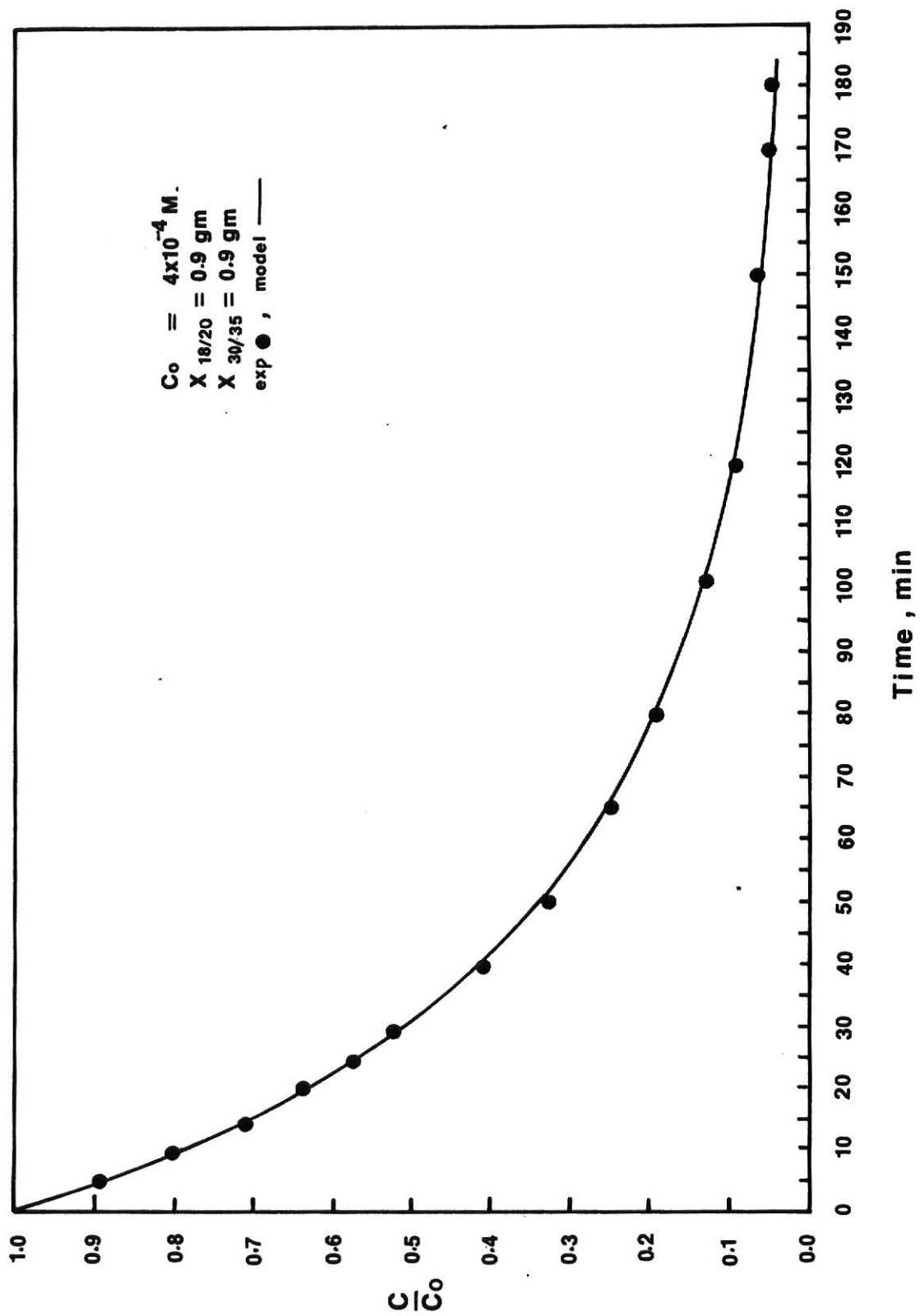


Fig. 5.20. Adsorption rate for PCP for carbon #18/20+30/35).

Tables 5.5, 5.7, 5.8 and 5.10 list the surface diffusivities and batch film transfer coefficients for the geometric mean and the sauter mean diameter of particles, for DMP and PCP respectively.

5.2.2 Bisolute rate studies

Bisolute studies were carried out for two sizes of carbon, #18-20 and #30-35 and a mixture of these two sizes. Both rates were predicted by using the computer program written by Mathews (1975). The equilibrium model data of both Mathews and Prausnitz were used in the computer program separately. Figures 5.21 to 5.23 show the results with Mathews equilibrium model and Figs. 5.24 to 5.26 show the results with Prausnitz equilibrium model using log-mean diameter.

Mathews' equilibrium data uses interaction coefficients found from his equilibrium model for bisolute systems. For DMP the coefficient was 20.08 and for PCP it was 22.31. From the Figs. 5.19 to 5.21, it is seen that the model does not give a good fit at all. Even though the faster of two species DMP has been predicted correctly according to the experimental values, the predicted values are too high. This is probably due to interaction of DMP and PCP on the surface of carbon. Another reason for poor predictions may be the inadequate correlation of the mixture equilibrium data.

On the other hand, Figs. 5.24 to 5.26 show a fairly good prediction. In Figs. 5.25 and 5.26, however, equilibrium of PCP is predicted faster than DMP, contrary to Fig. 5.24. Also the portion near equilibrium is not described very well. But for a large part of the curve, both results agree impressively. In particular, DMP seems to have been described better than PCP at both carbon sizes. The fact

TABLE 5.5
Surface Diffusivities and Batch Film Transfer Coefficients
for Dimethyl Phthalate (Geometric mean diameter)

Sieve size	Surface Diffusivities	Batch Film Transfer Coefficients
#12-14	3.331×10^{-8}	3.688×10^{-3}
#18-20	3.426×10^{-8}	4.149×10^{-3}
#30-35	4.247×10^{-8}	4.691×10^{-3}
#35-40	2.094×10^{-8}	4.424×10^{-3}
(#18-20 + #30-35)	3.902×10^{-8}	3.658×10^{-3}

TABLE 5.6
Surface Diffusivities and Batch Film Transfer Coefficients
for Dimethyl phthalate (Log-mean diameter)

Sieve size	Surface Diffusivities	Batch Film Transfer Coefficients
#12-14	4.127×10^{-8}	4.311×10^{-3}
#18-20	5.077×10^{-8}	5.483×10^{-3}
#30-35	5.982×10^{-8}	6.586×10^{-3}
#35-40	4.873×10^{-8}	5.383×10^{-3}
(#18-20 + 30-35)	4.997×10^{-8}	5.564×10^{-3}

TABLE 5.7
Surface Diffusivities and Batch Film Transfer Coefficients
for Dimethyl Phthalate (Sauter mean diameter)

Sieve Size	Surface Diffusivities	Batch Film Transfer Coefficients
#12-14	6.378×10^{-8}	5.294×10^{-3}
#18-20	7.456×10^{-8}	6.705×10^{-3}
#30-35	9.528×10^{-8}	8.304×10^{-3}
#35-40	8.072×10^{-8}	7.480×10^{-3}
(#18-20 +#30-35)	9.974×10^{-8}	6.269×10^{-3}

TABLE 5.8
Surface Diffusivities and Batch Film Transfer Coefficients
for Parachlorophenol (Geometric mean diameter)

Sieve size	Surface Diffusivities	Batch Film Transfer Coefficients
#12-14	1.749×10^{-8}	4.083×10^{-3}
#18-20	2.532×10^{-8}	3.971×10^{-3}
#30-35	1.110×10^{-8}	4.813×10^{-3}
#35-40	1.429×10^{-8}	4.954×10^{-3}
(#18-20 +#30-35)	8.655×10^{-9}	4.499×10^{-3}

TABLE 5.9
Surface Diffusivities and Batch Film Transfer Coefficients
for Parachlorophenol (Log-mean diameter)

Sieve size	Surface Diffusivities	Batch Film Transfer Coefficients
#12-14	2.201×10^{-8}	4.772×10^{-3}
#18-20	3.690×10^{-8}	5.345×10^{-3}
#30-35	1.951×10^{-8}	6.674×10^{-3}
#35-40	1.519×10^{-8}	4.397×10^{-3}
(#18-20 + #30-35)	1.287×10^{-8}	7.166×10^{-3}

TABLE 5.10
Surface Diffusivities and Batch Film Transfer Coefficients
for Parachlorophenol (Sauter mean diameter)

Sieve size	Surface Diffusivities	Batch Film Transfer Coefficients
#12-14	1.559×10^{-8}	6.105×10^{-3}
#18-20	2.361×10^{-8}	7.069×10^{-3}
#30-35	1.502×10^{-8}	9.207×10^{-3}
#35-40	3.337×10^{-8}	6.815×10^{-3}
(#18-20 + 30-35)	1.527×10^{-8}	8.203×10^{-3}

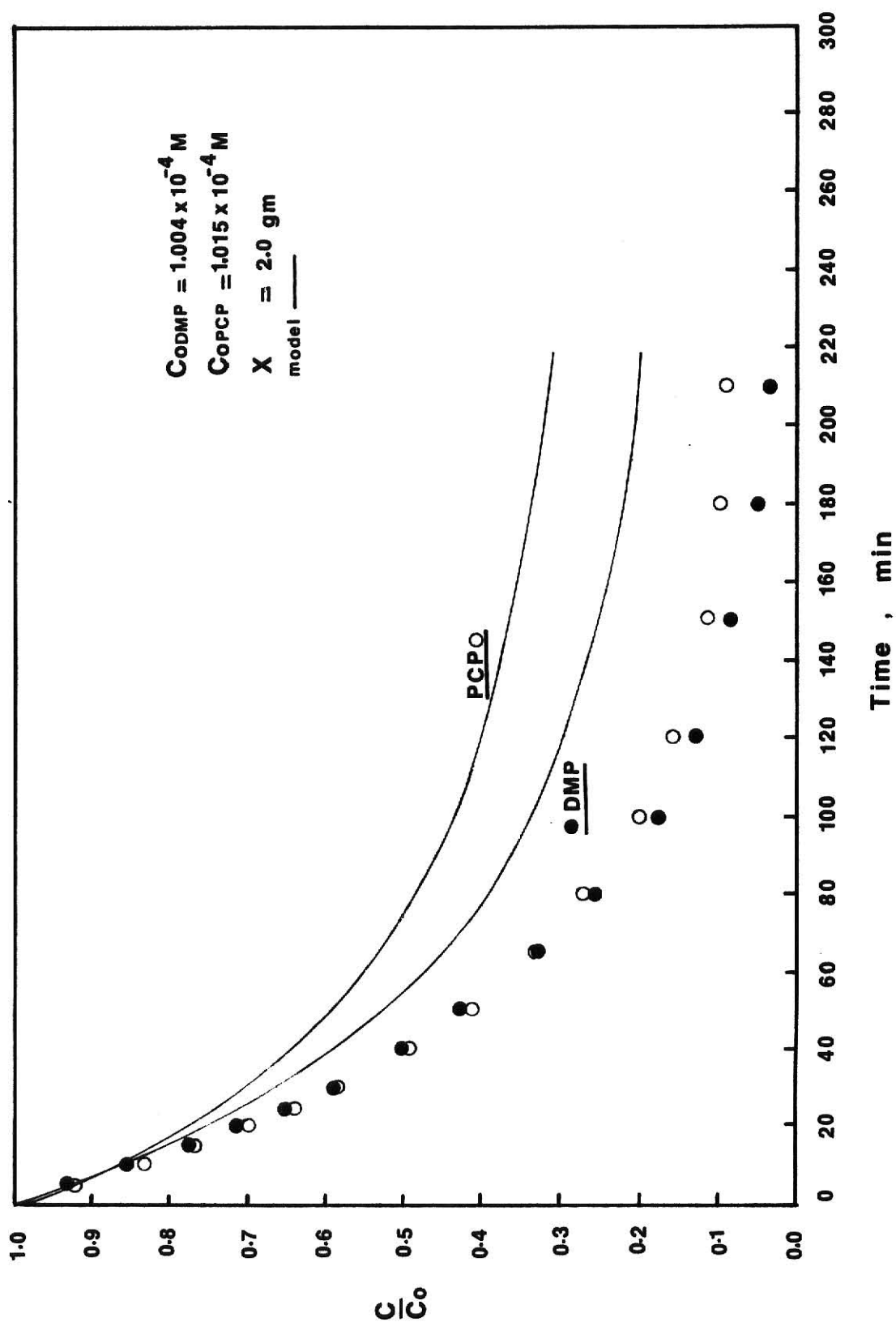


Fig. 5.21. Adsorption rate for (DMP+PCP) for carbon size #18/20 with Mathews Equilibrium model.

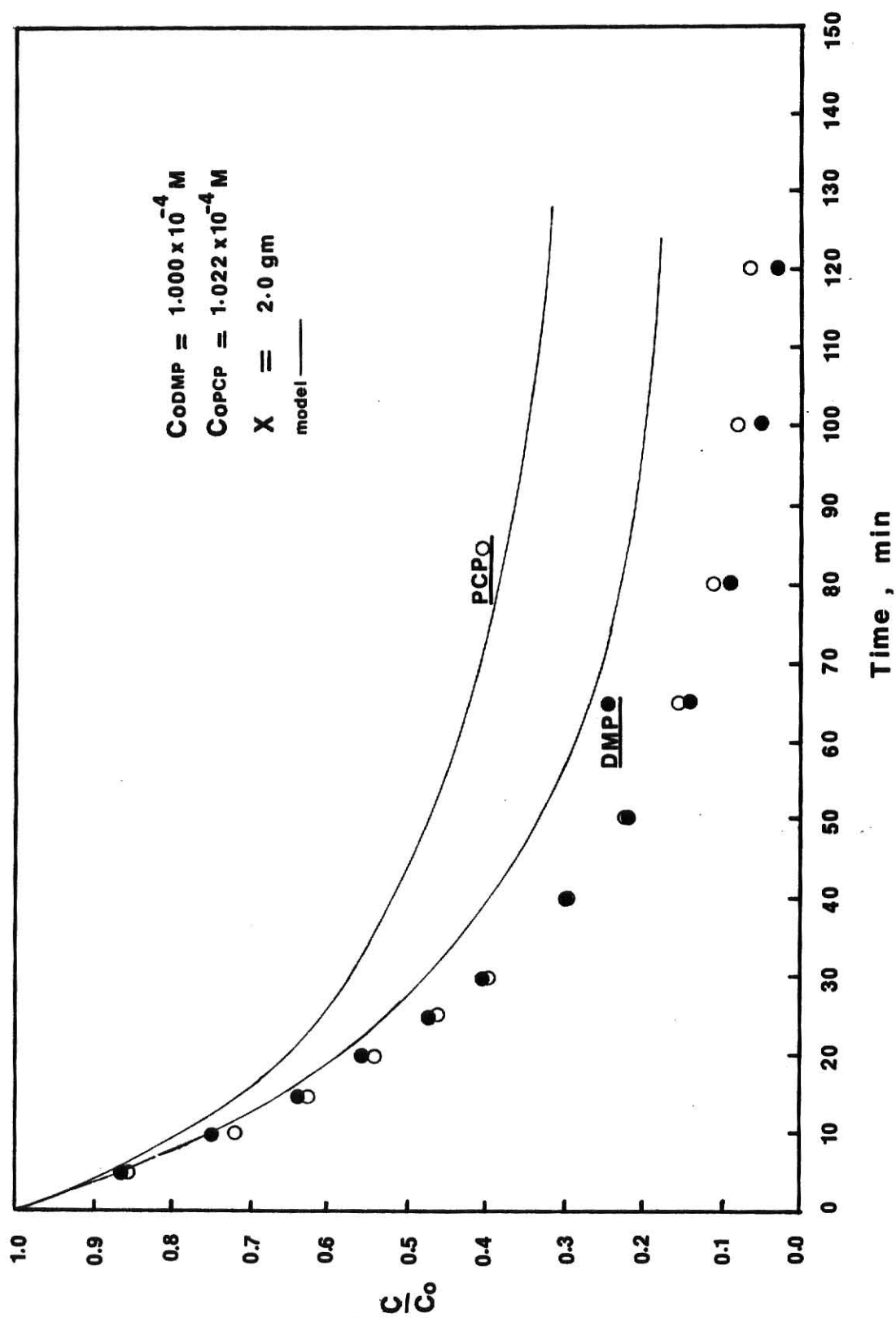


Fig. 5.22. Adsorption rate for (DMP+PCP) for carbon size #30/35 with Mathews Equilibrium model.

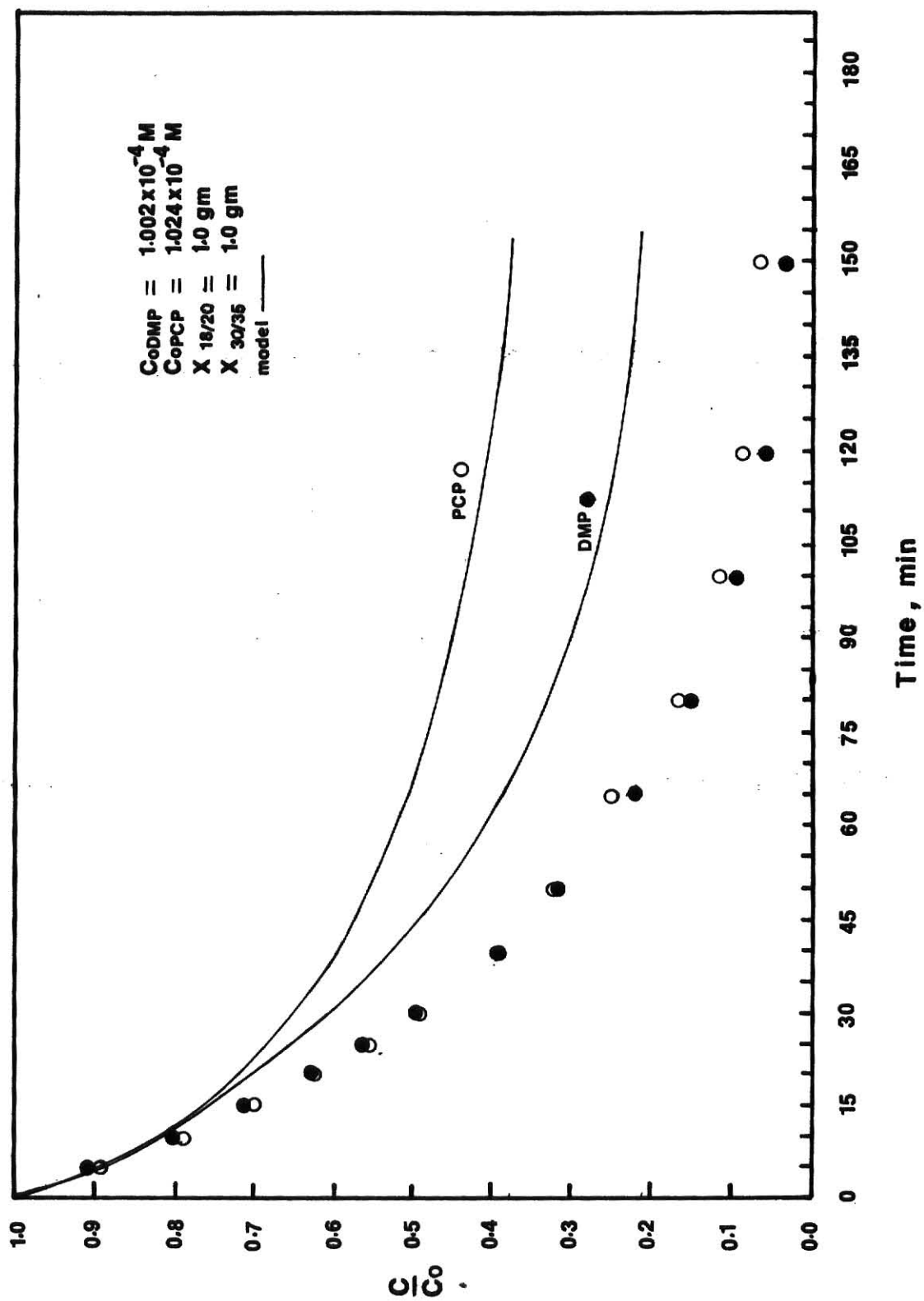


Fig- 5-23. Adsorption rate for (DMP+PCP) for carbon #18/20 + 30/35) with Mathews equilibrium model.

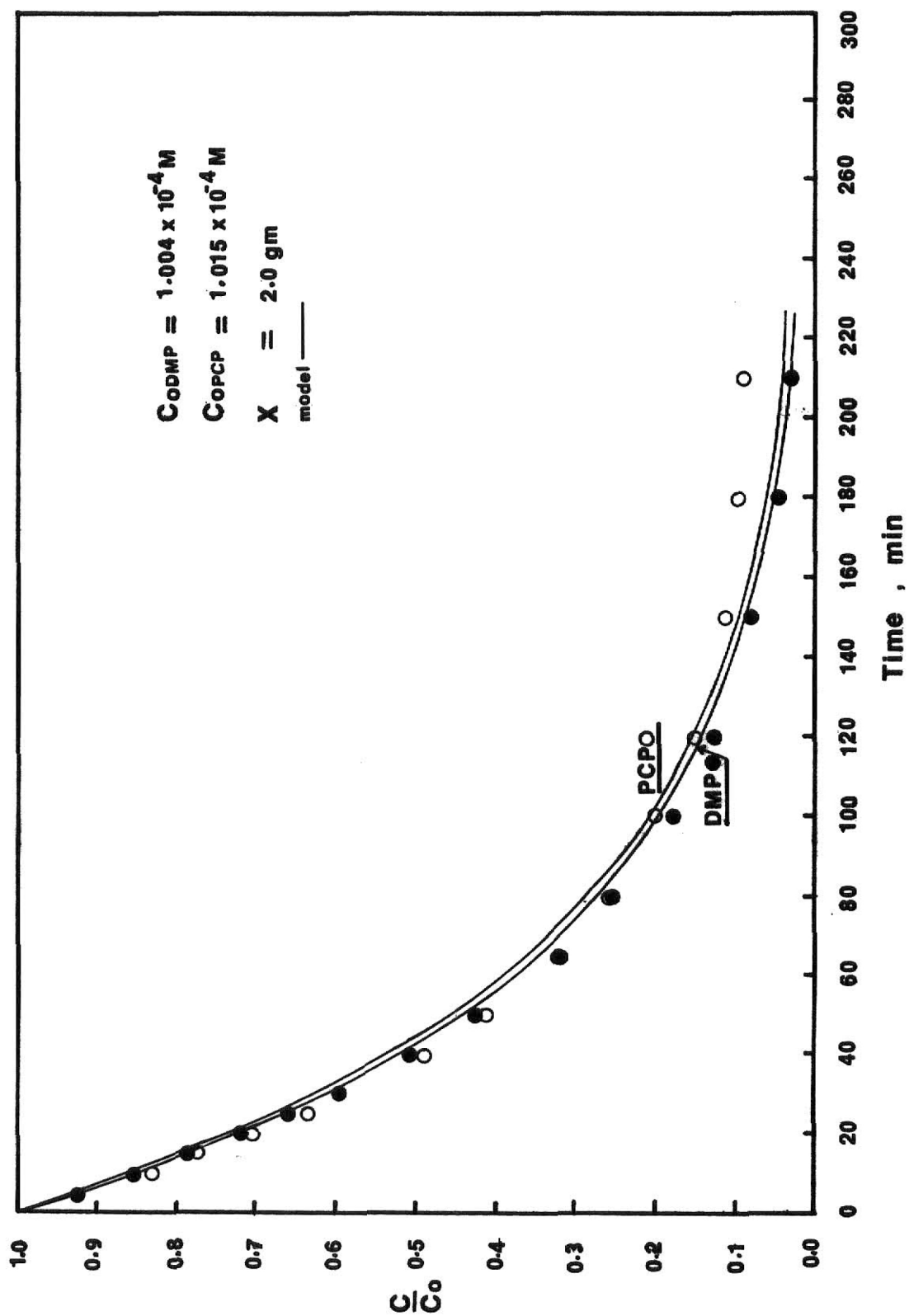


Fig. 5.24. Adsorption rate for (DMP+PCP) for carbon size #18/20 with Prausnitz Equilibrium model.

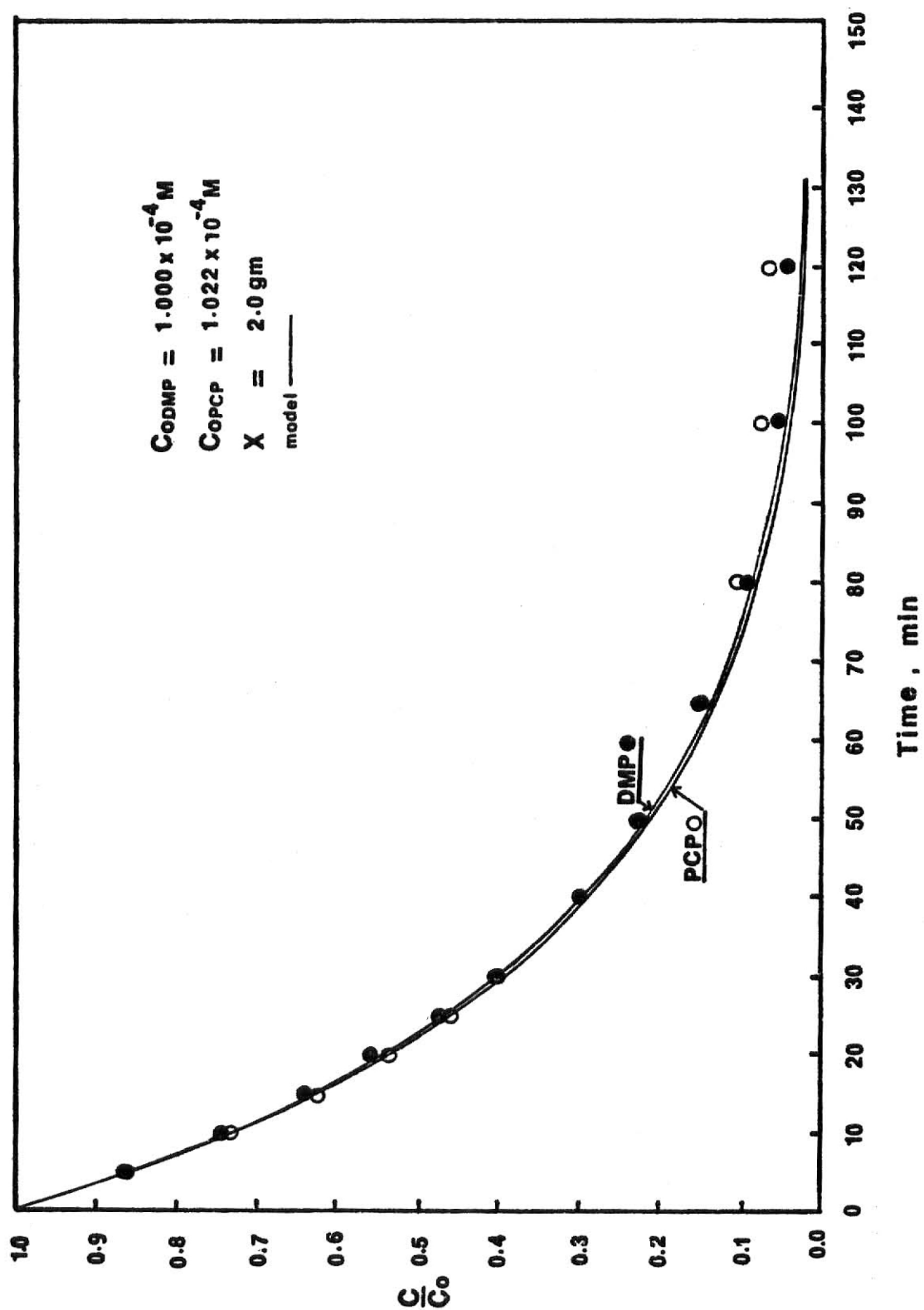


Fig. 5.25. Adsorption rate for (DMP+PCP) for carbon size #30/35 with Prausnitz Equilibrium model.

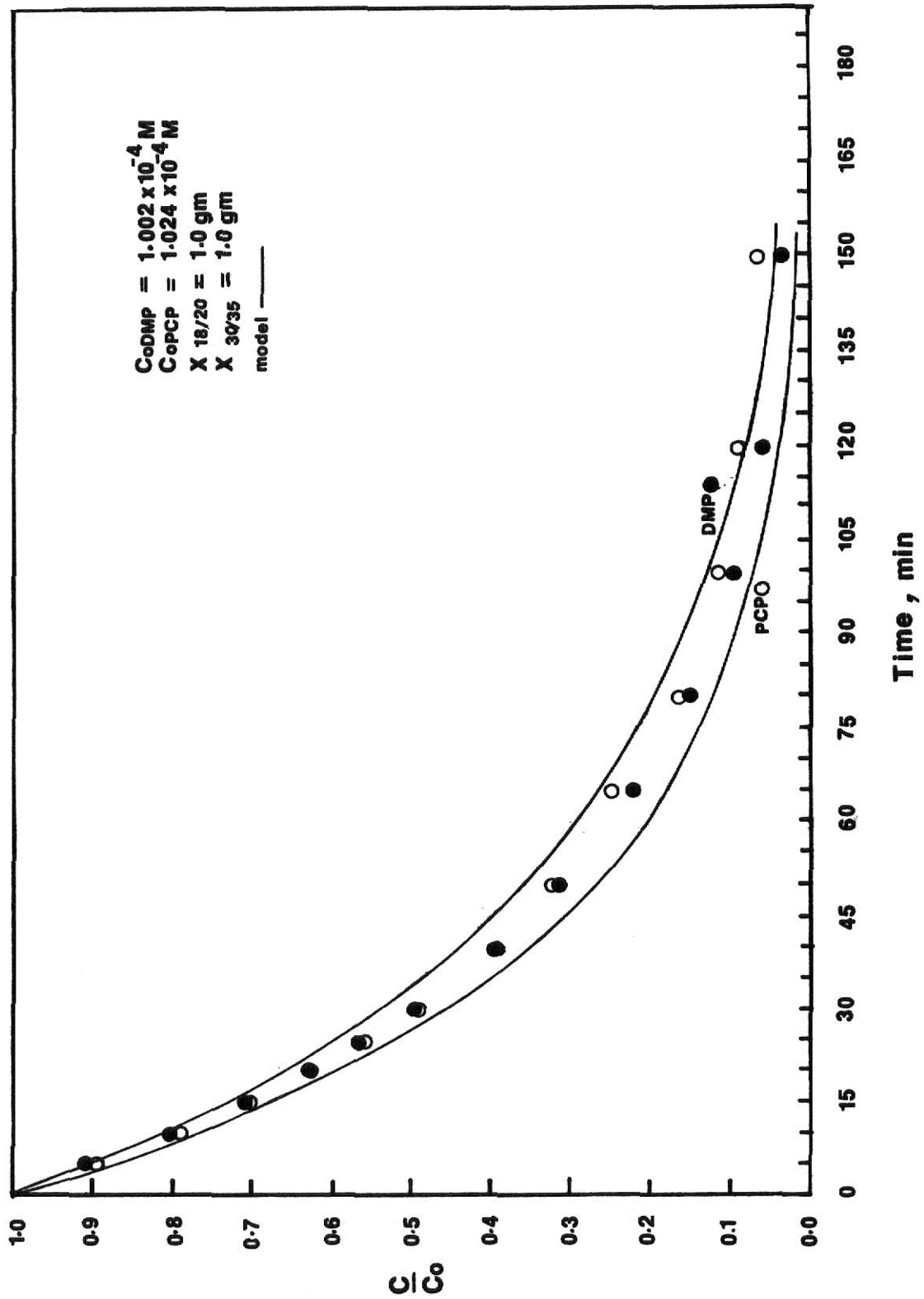


Fig. 5.26. Adsorption rate for (DMP+PCP) for carbon #18/20+30/35) with Prausnitz equilibrium model.

of good agreement between the predicted and the experimental values using Prausnitz model is rather surprising. Since the model by Mathews predicted bisolute equilibrium better than Prausnitz's model, one would expect that results using the Mathews model would be better than that by Prausnitz in this bisolute rate study. The reason for this is difficult to explain.

5.3 Fixed bed experiments

Four fixed bed experiments were carried out - two with DMP and two with PCP - to obtain experimental results to judge the efficiency of the model to take into account various size fractions in predicting the breakthrough curve.

To reduce the computer running costs, the isotherm equation used in the model is the Freundlich equation rather than the three parameter equation. For example, by using Freundlich isotherm, single-layer predictions for a 2200 minute run required computer time of about 40 to 50 seconds. But by using the three-parameter equation, the same single layer could be solved only up to 600 to 800 minutes in one minute. The Freundlich equation was used up to a point where a straight line seemed to give a good fit to the data. Since this point was sufficiently low, a linear isotherm equation was used after this point till the point of zero surface concentration. Since at very low concentrations all isotherms curve down toward the point of zero surface concentration, the Freundlich equation fitted at a higher concentration range will give higher surface concentrations at lower concentrations than true values. As indicated in the algorithm of the modification, the effluent of one layer becomes the influent to the

next layer at the same time. At the third or fourth layer, this value of influent concentration is going to be very small. It was in fact found to be of the order of 2 $\mu\text{g/l}$. Hence, a linear isotherm was incorporated. Tables 5.11 to 5.14 list all the data associated with each run. Table 5.15 gives the weights of various size fractions used in each run.

For each run, the number of layers was increased from one to three, by combining various original layers together in different ways. This was expected to improve the results as we go from one layer to original eight layers. Each total bed when divided into smaller layers was represented by averaging the properties of original layers present in that combination. Properties associated with each layer in each run are listed in Tables from 5.16 to 5.19.

Figure 5.27 shows the breakthrough curve for first run for DMP. Here, solid symbols represent experimental data and lines represent different predictions. It can be seen that the predictions will change as the grouping of original fractions is changed to form the same number of layers. Prediction of the first run with one layer, i.e., the entire bed, cuts the experimental curve. This could be expected as the actual fixed bed properties were combined into average values. For the upper layers these values are going to be larger than average value. For the lower layers, they will be smaller than average value. The layers at the top having larger values of *film transfer* coefficient are small compared to the entire height of the bed. So, the model will adsorb much more during the initial period so that the bed becomes saturated quicker than the actual case. So the predictions

TABLE 5.11
Data Associated with DMP First Run

Total Weight of Carbon	250.0 gms
Total Bed Height	25.8 cms
Influent Concentration	194.2 mg/l
Freundlich Isotherm Constant K	134.39
Freundlich Isotherm Constant n	0.1742
Linear Isotherm Constant	162.67 (at 3 mg/l)
Total Flow	500 ml/min

TABLE 5.12
Data Associated with DMP Second Run

Total Weight of Carbon	500.0 gms
Total Bed Height	55.1 cms
Influent Concentration	369.95 mg/l
Freundlich Isotherm Constant K	134.39
Freundlich Isotherm Constant n	0.1742
Linear Isotherm Constant	162.67 (at 3 mg/l)
Total Flow	800 ml/min

TABLE 5.13
Data Associated with PCP First Run

Total Weight of Carbon	250.0 gms
Total Bed Height	29.2 cms
Influent Concentration	121.53 mg/l
Freundlich Isotherm Constant K	167.38
Freundlich Isotherm Constant n	0.1019
Linear Isotherm Constant	167.38 (at 1 mg/l)
Total Flow	400.0 ml/min

TABLE 5.14
Data Associated with PCP Second Run

Total Weight of Carbon	250.0 gms
Total Bed Height	26.2 cms
Influent Concentration	59.37 mg/l
Freundlich Isotherm Constant K	167.38
Freundlich Isotherm Constant n	0.1019
Linear Isotherm Constant	167.38 (at 1 mg/l)
Total Flow	800.0 ml/min

TABLE 5.15
Weights of Carbon Size Fractions in Each Fixed Bed Run

Size fraction	DMP Run 1 PCP Run 1	DMP Run 2	PCP Run 2
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#12-#14	20.0 gms	50.0 gms	25.0 gms
#14-#16	50.0 gms	85.0 gms	40.0 gms
#16-#18	40.0 gms	90.0 gms	45.0 gms
#18-#20	50.0 gms	100.0 gms	50.0 gms
#20-#25	40.0 gms	75.0 gms	35.0 gms
#25-#30	25.0 gms	60.0 gms	30.0 gms
#30-#35	15.0 gms	30.0 gms	15.0 gms
#35-#40	10.0 gms	10.0 gms	10.0 gms

TABLE 5.16
Properties of Each Layer in DMP First Run

Layer no. From Top	Weight gm	Diameter cm	Film Transfer Coefficient
1(Log-mean)	250.0	0.1197	4.0587×10^{-3}
1(Log-mean)	90.0	0.0821	5.0464×10^{-3}
2(Log-mean)	160.0	0.1408	3.4229×10^{-3}
1(Log-mean)	25.0	0.0680	5.7816×10^{-3}
2(Log-mean)	155.0	0.1094	4.1063×10^{-3}
3(Log-mean)	70.0	0.1610	3.1078×10^{-3}
Geom. mean	250.0	0.0978	4.4499×10^{-3}
Sauter mean	250.0	0.1358	3.5138×10^{-3}

TABLE 5.17
Properties of Each Layer in DMP Second Run

Layer no. From Top	Weight gm	Diameter cm	Film Transfer Coefficient
1(Log-mean)	500.0	0.1209	3.8440×10^{-3}
1(Log-mean)	175.0	0.0833	4.8245×10^{-3}
2(Log-mean)	325.0	0.1411	3.2999×10^{-3}
1(Log-mean)	40.0	0.071	5.4108×10^{-3}
2(Log-mean)	325.0	0.1094	3.9627×10^{-3}
3(Log-mean)	135.0	0.1631	2.9727×10^{-3}
Geom. mean	250.0	0.0988	4.2647×10^{-3}
Sauter mean	250.0	0.1369	3.3719×10^{-3}

TABLE 5.18
Properties of Each Layer in PCP First Run

Layer no. From Top	Weight gm	Diameter cm	Film Transfer Coefficients
1(Log-mean)	250.0	0.1197	3.5395×10^{-3}
1(Log-mean)	90.0	0.0821	4.4057×10^{-3}
2(Log-mean)	160.0	0.1408	2.9883×10^{-3}
1(Log-mean)	25.0	0.0680	5.0475×10^{-3}
2(Log-mean)	155.0	0.1044	3.5585×10^{-3}
3(Log-mean)	70.0	0.1610	2.7132×10^{-3}
Geom.mean	250.0	0.0978	3.8849×10^{-3}
Sauter mean	250.0	0.1358	3.0676×10^{-3}

TABLE 5.19
Properties of Each Layer in PCP Second Run

Layer no. From Top	Weight gm	Diameter cm	Film Transfer Coefficients
1(Log-mean)	250.0	0.1195	5.1965×10^{-3}
1(Log-mean)	90.0	0.0815	6.8450×10^{-3}
2(Log-mean)	160.0	0.1409	4.6158×10^{-3}
1(Log-mean)	25.0	0.0680	7.7992×10^{-3}
2(Log-mean)	160.0	0.1097	5.5271×10^{-3}
3(Log-mean)	65.0	0.1635	4.1473×10^{-3}
Geom.mean	250.0	0.0977	6.0094×10^{-3}
Sauter mean	250.0	0.1355	4.7462×10^{-3}

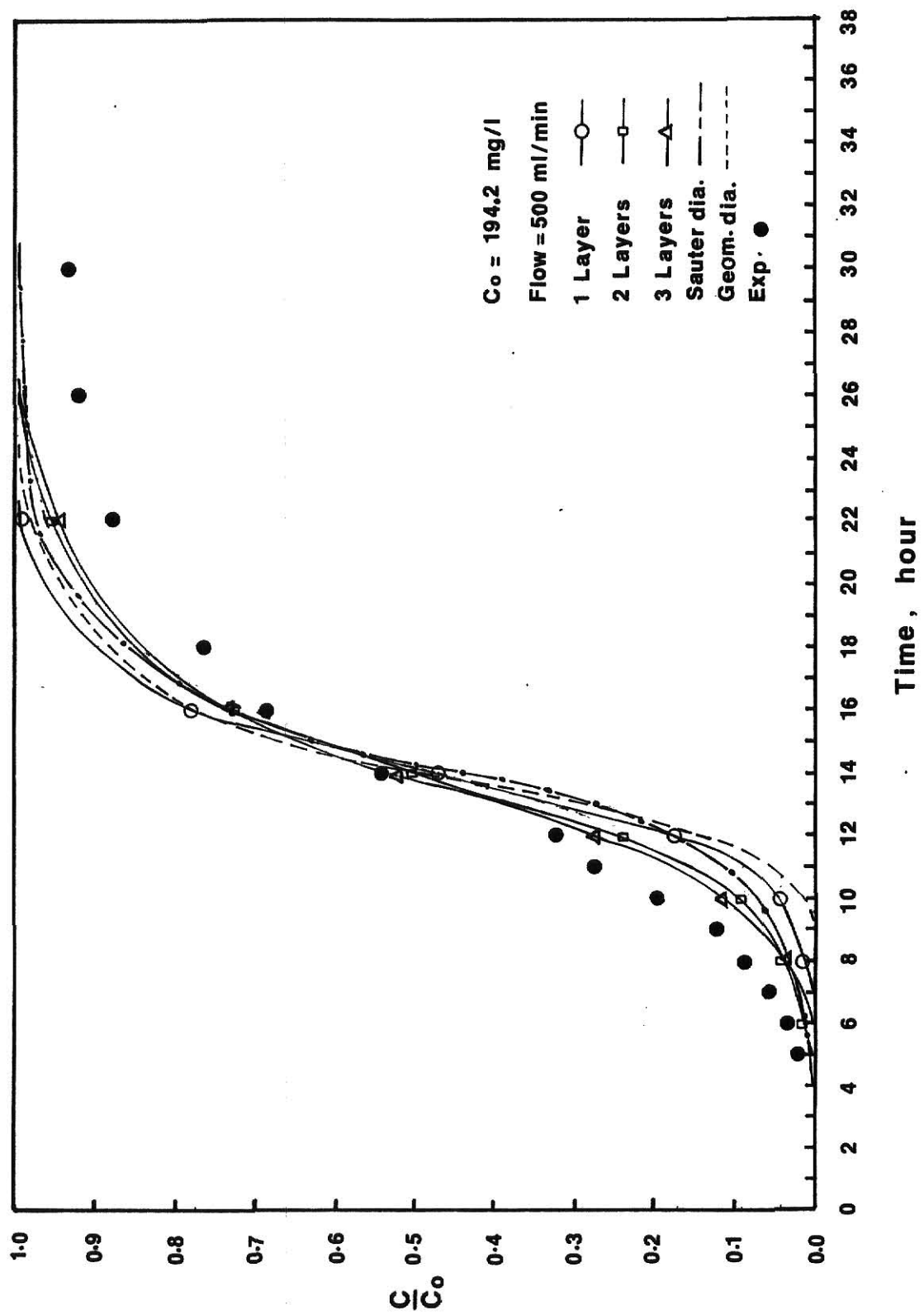


Fig.5.27. Breakthrough curve for DMP first run.

are lower initially and higher at the later period. The second curve is better than the first one, as it has moved toward the experimental points compared to the first one. These two layers were formed by combining the top and bottom four of the original fractions. Use of the three layers did improve the results, but the improvement is very small. For this layer, the top two, bottom two and middle four of the original fractions were combined. Increasing the number of layers therefore definitely seems to improve the results as we go towards the original eight layers. However, in this case all eight layers are not solved as it proved to be very costly for the computer run to try beyond three layers.

Figure 5.28 shows the breakthrough curve for DMP Run 2. This also shows that as the number of layers is increased, the prediction goes towards the experimental results. All layers combinations here are the same as previous ones. This prediction seems to be better than the first run.

Figures 5.29 and 5.30 show PCP for the first and second runs. Here also, three layers give closer agreement with experimental values than one or two layers. In Fig. 5.30, however, two layers seem to give better predictions contrary to Figs. 5.27 to 5.29. As in the DMP runs, the improvement between two and three layers is small.

The three diameters selected were tested on the basis of single layer predictions. From all four runs, the geometric mean diameter seems to give inferior predictions compared to log-mean and sauter mean diameters during the initial period of the run. The log-mean diameter and sauter mean diameter does not seem to show any difference

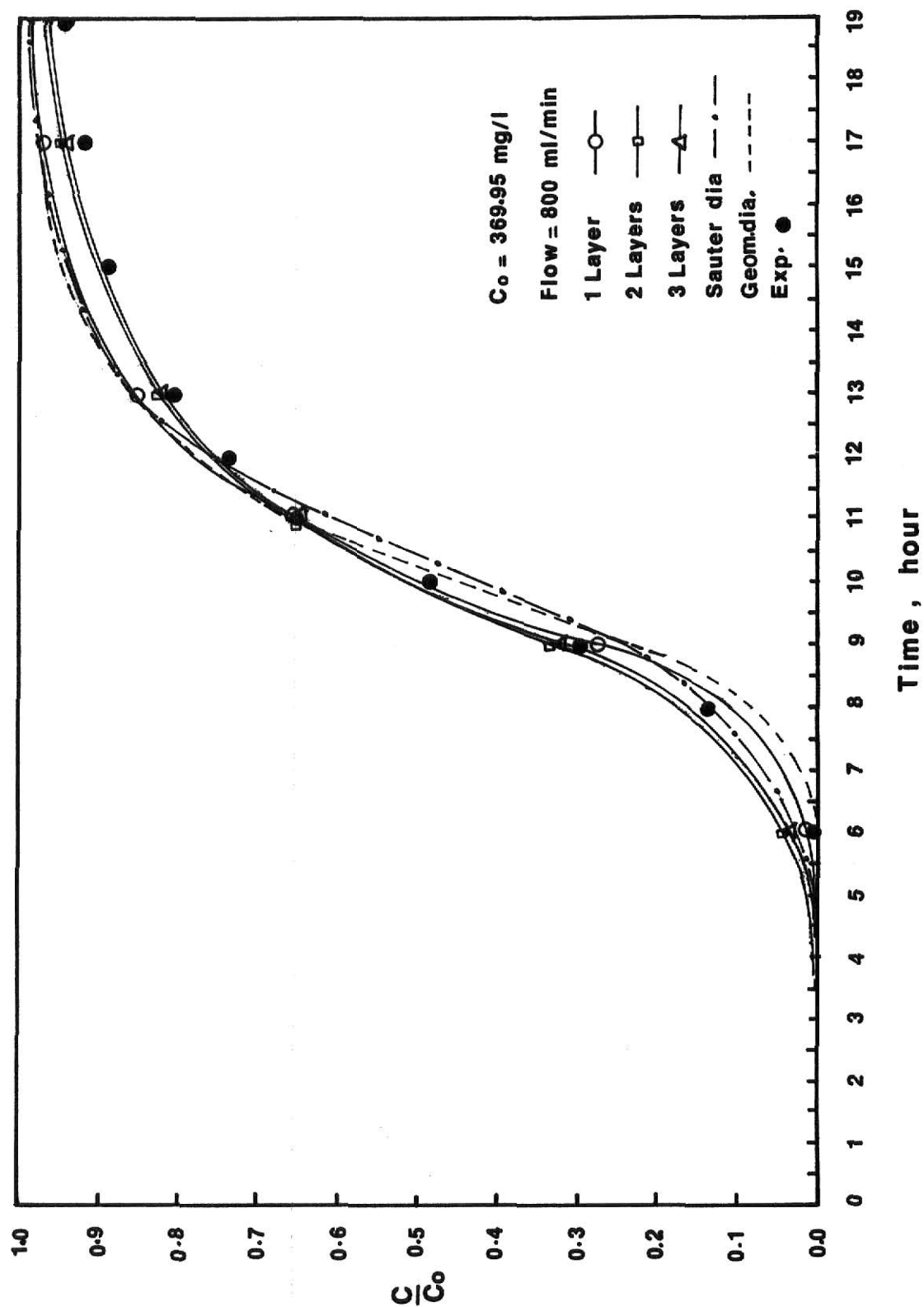


Fig.5.28. Breakthrough curve for DMP second run.

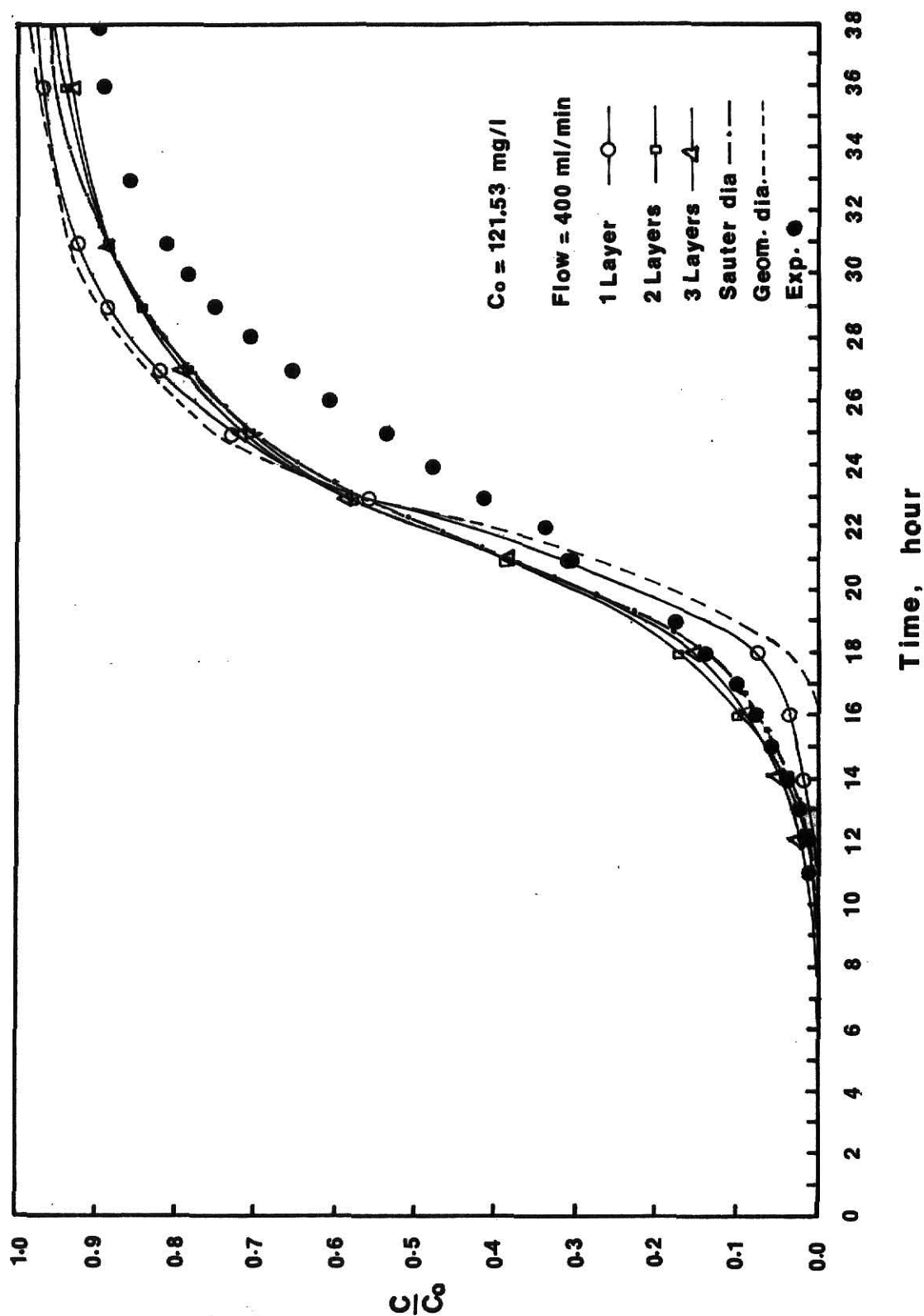


Fig. 5.29. Breakthrough curve for PCP first run.

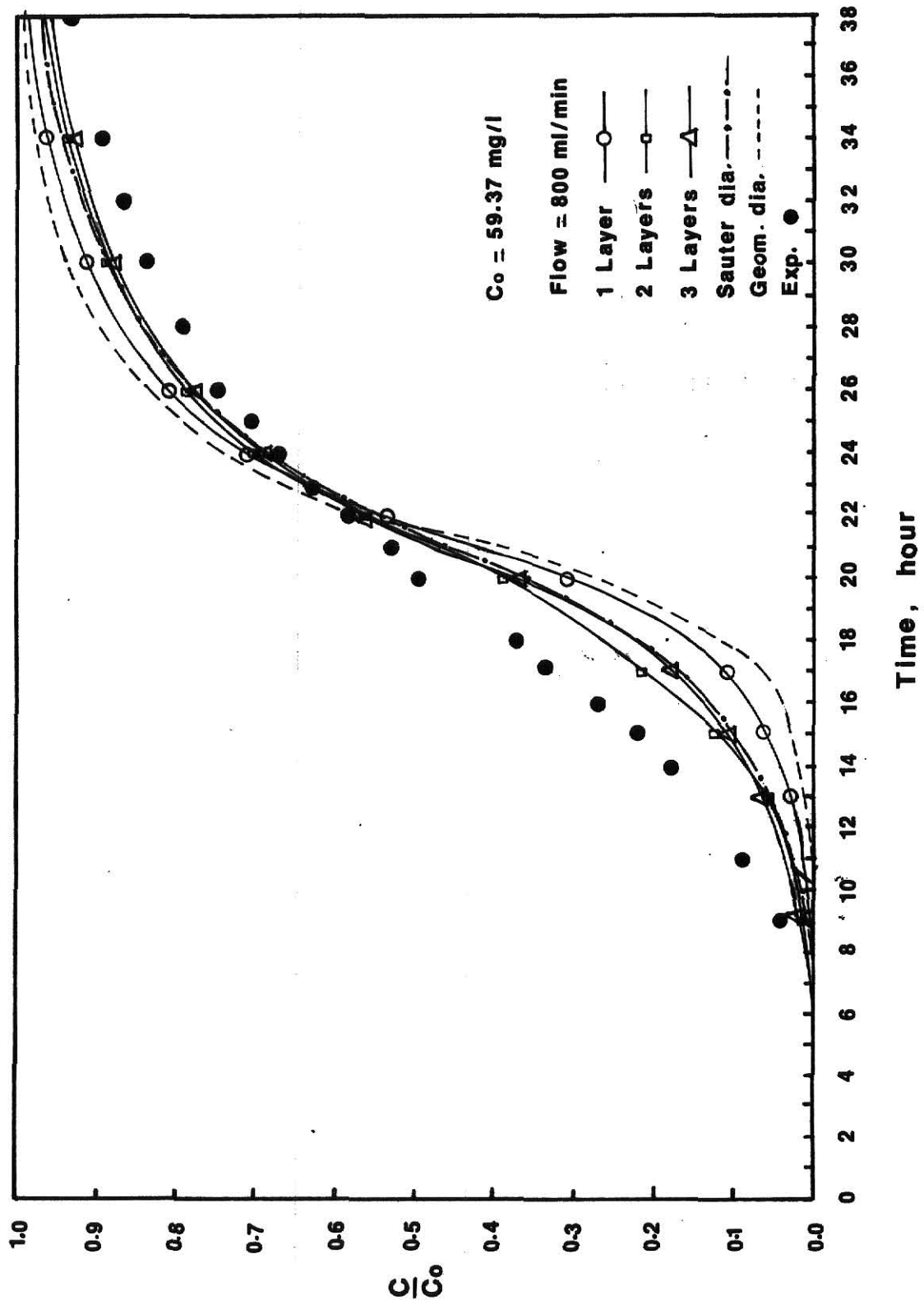


Fig.5.30. Breakthrough curve for PCP second run.

in the predictions. The predictions using the sauer mean diameter are a little better. This in part is attributed to the fact that DMP showed comparatively large differences in the surface diffusivity values for the three diameters. So, the use of better type diameter is partly offset by high surface diffusivity values. The sauter diameter is better in the sense that it is calculated by taking into account particle size distribution of carbon, whereas log-mean diameter merely represents a 50% value of diameter on log-probability paper. In the case of PCP, however, the surface diffusivity values are very small compared to DMP and difference between the three surface diffusivities is small. In fact, surface diffusivity values for log-mean and sauter mean diameters are almost the same. So the sauter mean diameter seems to give better results than the log-mean diameter. The predictions of the sauter mean diameter are comparable to the two layer prediction of the log-mean diameter.

Fixed bed experiments were also carried for DMP and PCP using constant size of carbon (#18/20). Tables 5.21 and 5.22 list the data associated with these runs. Figures 5.31 and 5.32 show the experimental and predicted values for those two runs using the three diameters. The modified model was used for the predictions. In case of DMP, all three predictions are poor. The model shows less adsorption than the experiment. One possible reason for this is that more finer particles were present in the #18/20 fraction so that more adsorption occurred. In the case of PCP, however, the geometric mean diameter continues to give inferior predictions compared to the other two diameters. The log-mean diameter gives excellent predictions with the

sauter mean diameter predictions following closely. This is contrary to the runs carried out with different size fractions. The reason for this is thought to be partly due to cancellation of positive and negative experimental as well as program errors somehow in the case of log-mean diameter.

TABLE 5.20
Data Associated with DMP Run with Carbon Size #18-20

Total Weight of Carbon	250.0 gms
Total Bed Height	27.7 cms
Influent Concentration	99.83 mg/l
Freundlich Isotherm Constant K	134.39
Freundlich Isotherm Constant n	0.1742
Linear Isotherm Constant	162.67
Total Flow	800 ml/min
Film Transfer Coefficients	
(Geometric mean)	4.4471×10^{-3}
(Log-mean)	3.6642×10^{-3}
(Sauter mean)	3.3892×10^{-3}
Diameter of Particle	
(Geometric mean)	0.0917 cm
(Log-mean)	0.1200 cm
(Sauter mean)	0.1337 cm
Surface Diffusivity	
(Geometric mean)	3.426×10^{-8}
(Log-mean)	5.077×10^{-8}
(Sauter mean)	7.456×10^{-8}

TABLE 5.21
Data Associated with PCP Run with Carbon Size #18-20

Total Weight of Carbon	250.0 gms
Total Bed Height	27.5 cms
Influent Concentration	59.77 mg/l
Freundlich Isotherm Constant K	167.38
Freundlich Isotherm Constant n	0.1019
Linear Isotherm Constant	167.38 (at 1 mg/l)
Total Flow	800.0 ml/min
Film Transfer Coefficient (Geometric mean)	5.5903×10^{-3}
(Log-mean)	4.6103×10^{-3}
(Sauter mean)	4.2604×10^{-3}
Diameter of Particle (Geometric mean)	0.0917 cms
(Log-mean)	0.1200 cms
(Sauter mean)	0.1337 cms
Diffusivity Coefficient (Geometric mean)	2.532×10^{-8}
(Log-mean)	3.690×10^{-8}
(Sauter mean)	2.361×10^{-8}

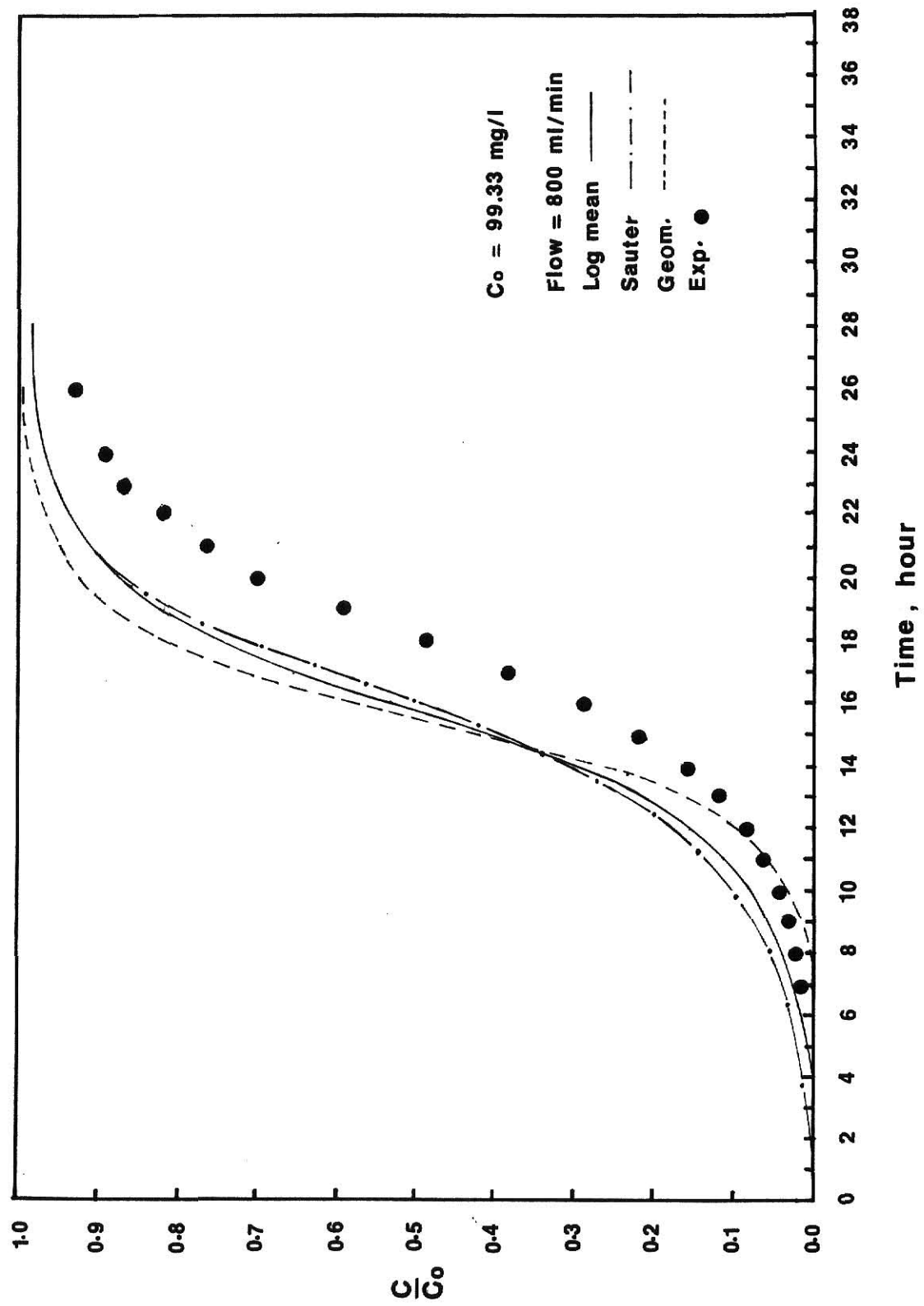


Fig.5.31. Breakthrough curve for DMP for carbon size #18/20.

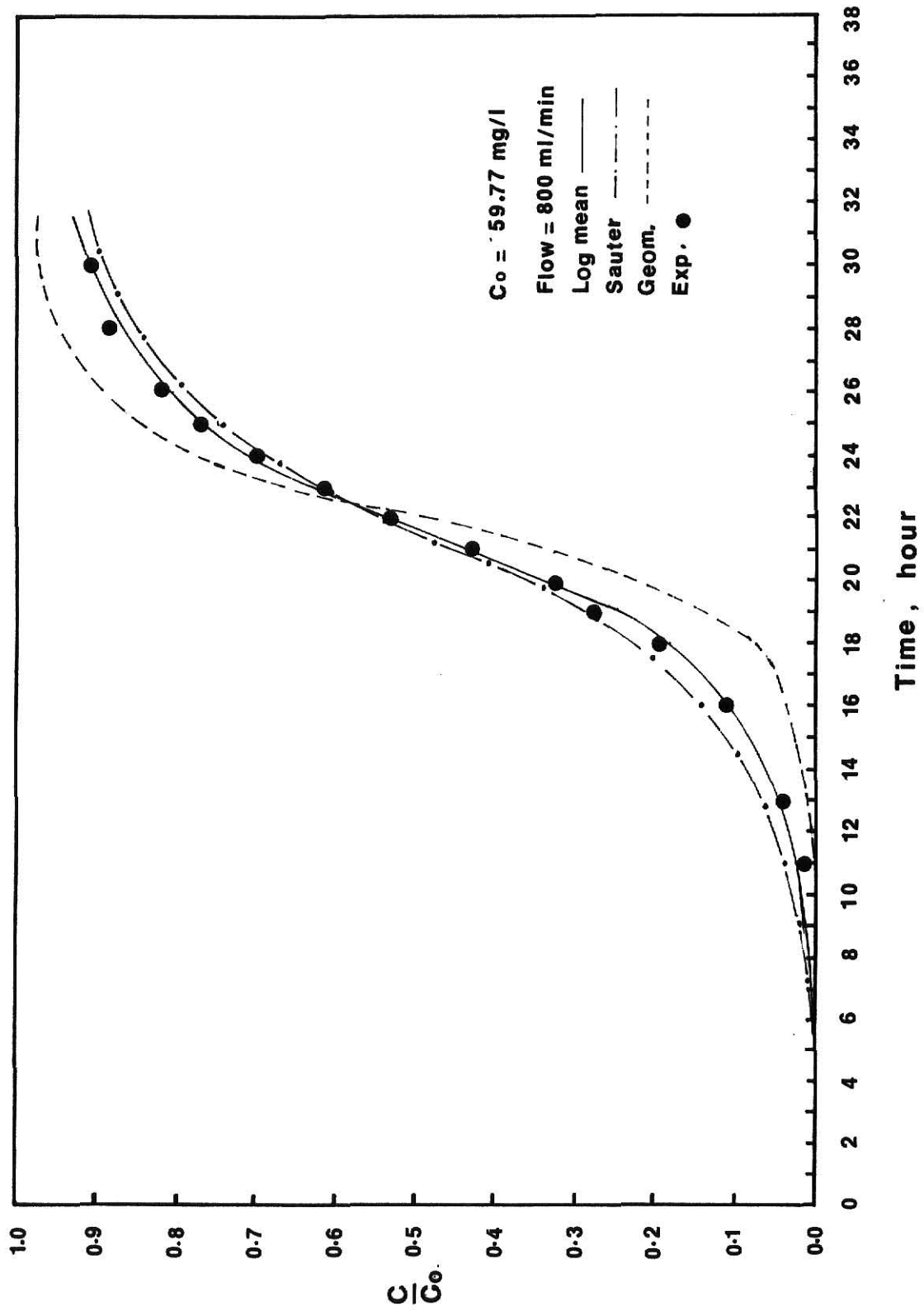


Fig. 5.32. Breakthrough curve for PCP for carbon size #18/20.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

1. The three parameter isotherm fits experimental data well.
2. The homogeneous solid phase diffusion batch kinetic model described the single solute rate data satisfactorily for dimethyl phthalate and parachlorophenol.
3. In the case of bisolute equilibrium studies, Mathews' equilibrium model gave comparatively better results than Prausnitz's model although neither of them fit the experimental data very well.
4. In bisolute rate studies, however, inclusion of the Prausnitz's equilibrium model gave better predictions than when the Mathews equilibrium model was used.
5. The concept of dividing a bed of mixed particle into a number of layers having same the size of particles seems to work well. Approximation of more layers improves the fit between the experimental data and the predictions.
6. For the three diameters used, the log-mean and sauter mean diameters give better predictions than the geometric mean diameter of a particle. The sauter mean diameter seems to describe the particle best particularly in case of solutes with small values of surface diffusivity.

6.2 Recommendations

1. The computing costs will probably be reduced with a less number of collocation points. A test has to be made with less collocation points to test efficiency of the model for loss of accuracy.
2. The model should be tested for its usefulness in pilot-plant work.
3. Effect of particle size distribution on batch kinetic studies should be evaluated to have better representation of the value of the surface diffusivity in the fixed bed model.

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APPENDIX

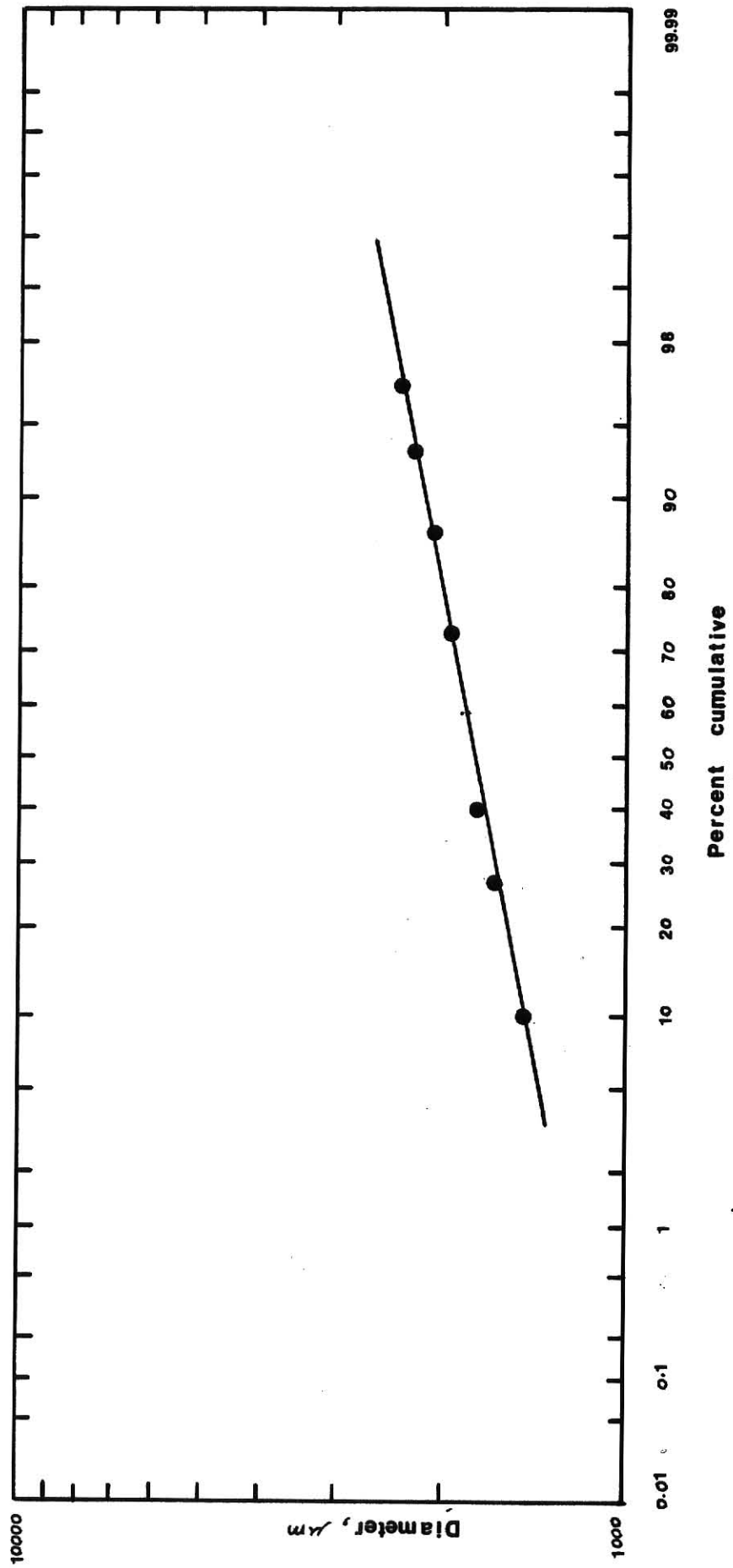


Fig.A. Particle size distribution for size #12/14.

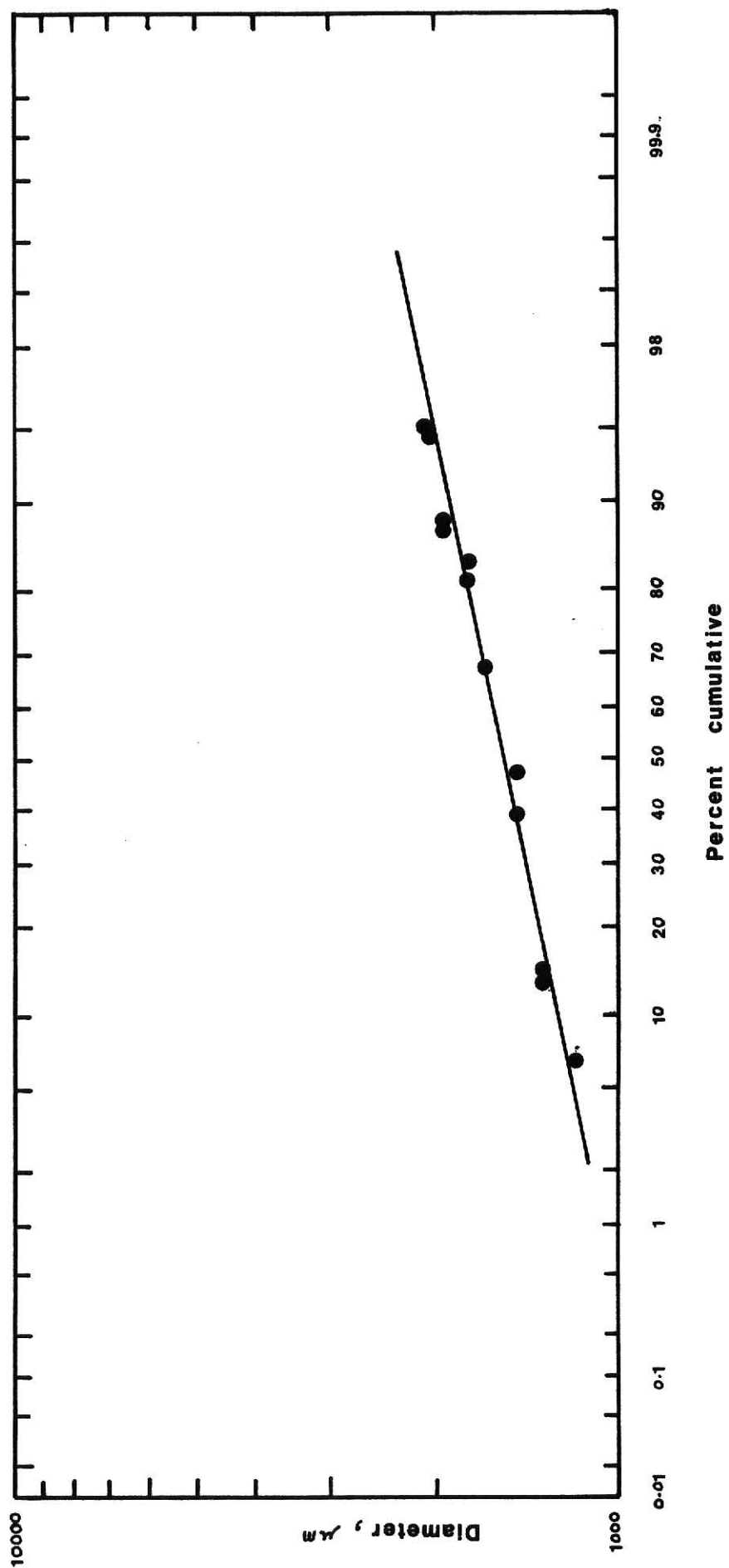


Fig.B. Particle size distribution for size #14/16.

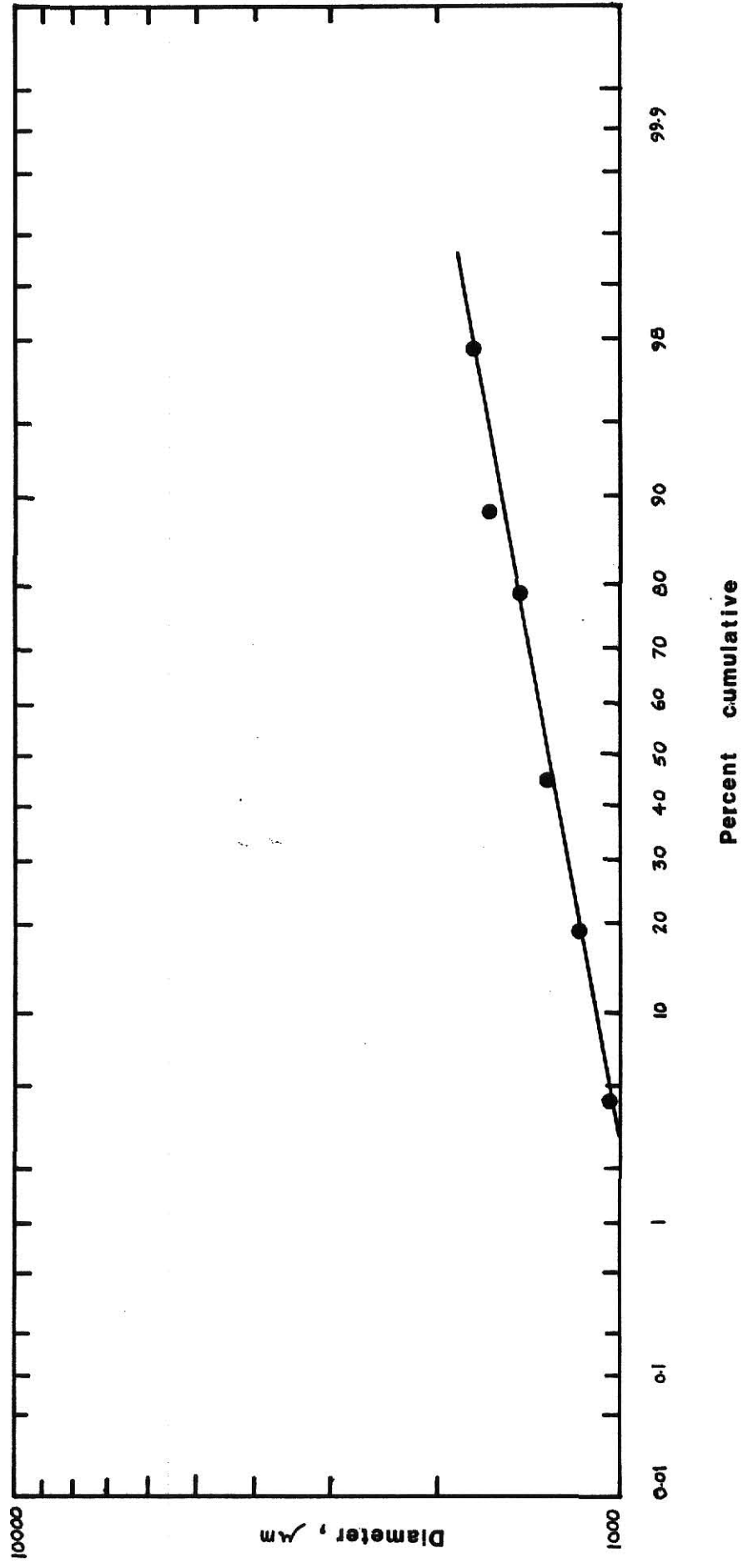


Fig. C. Particle size distribution for size #16/18.

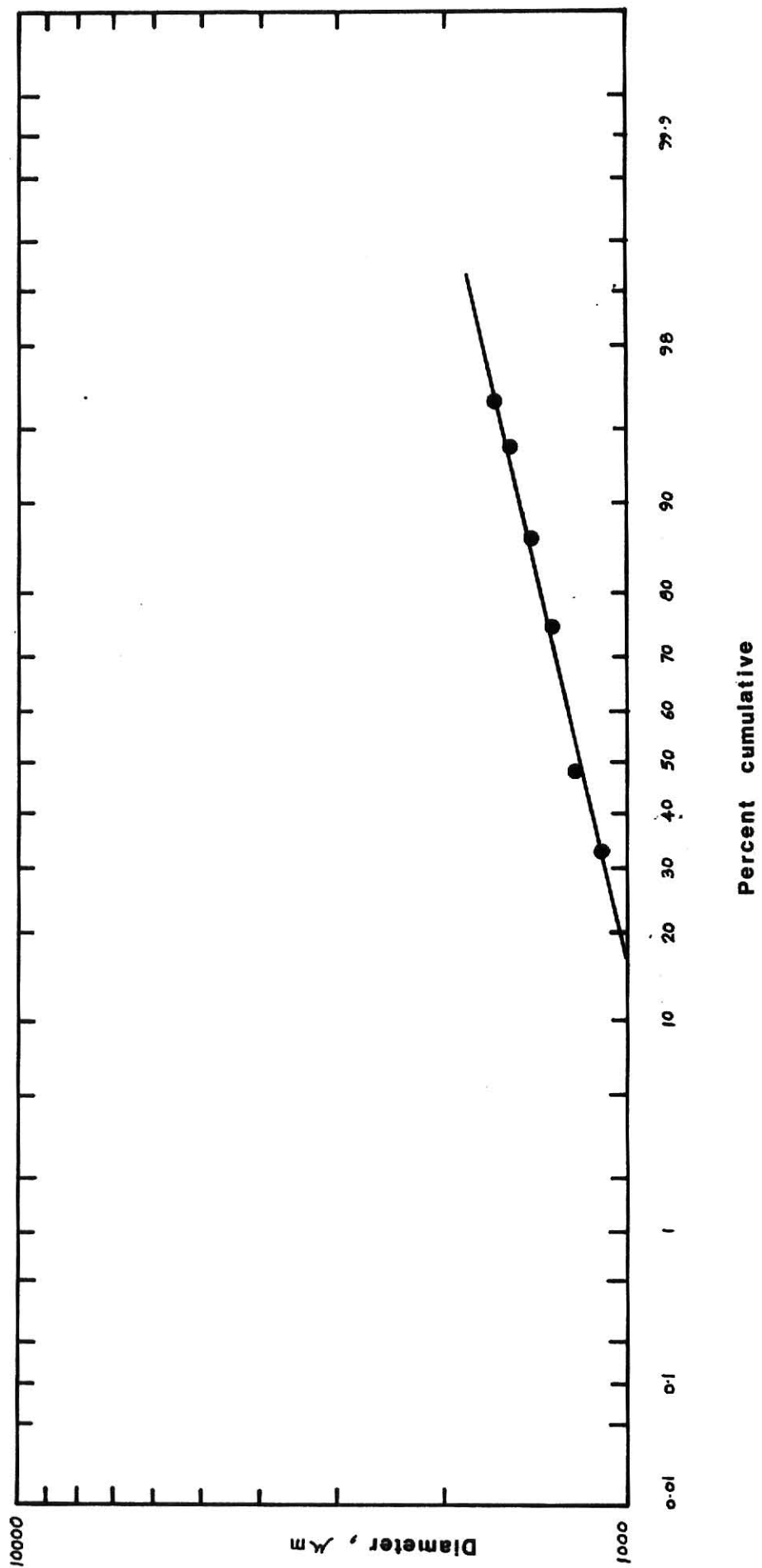


Fig. D. Particle size distribution for size #18/20.

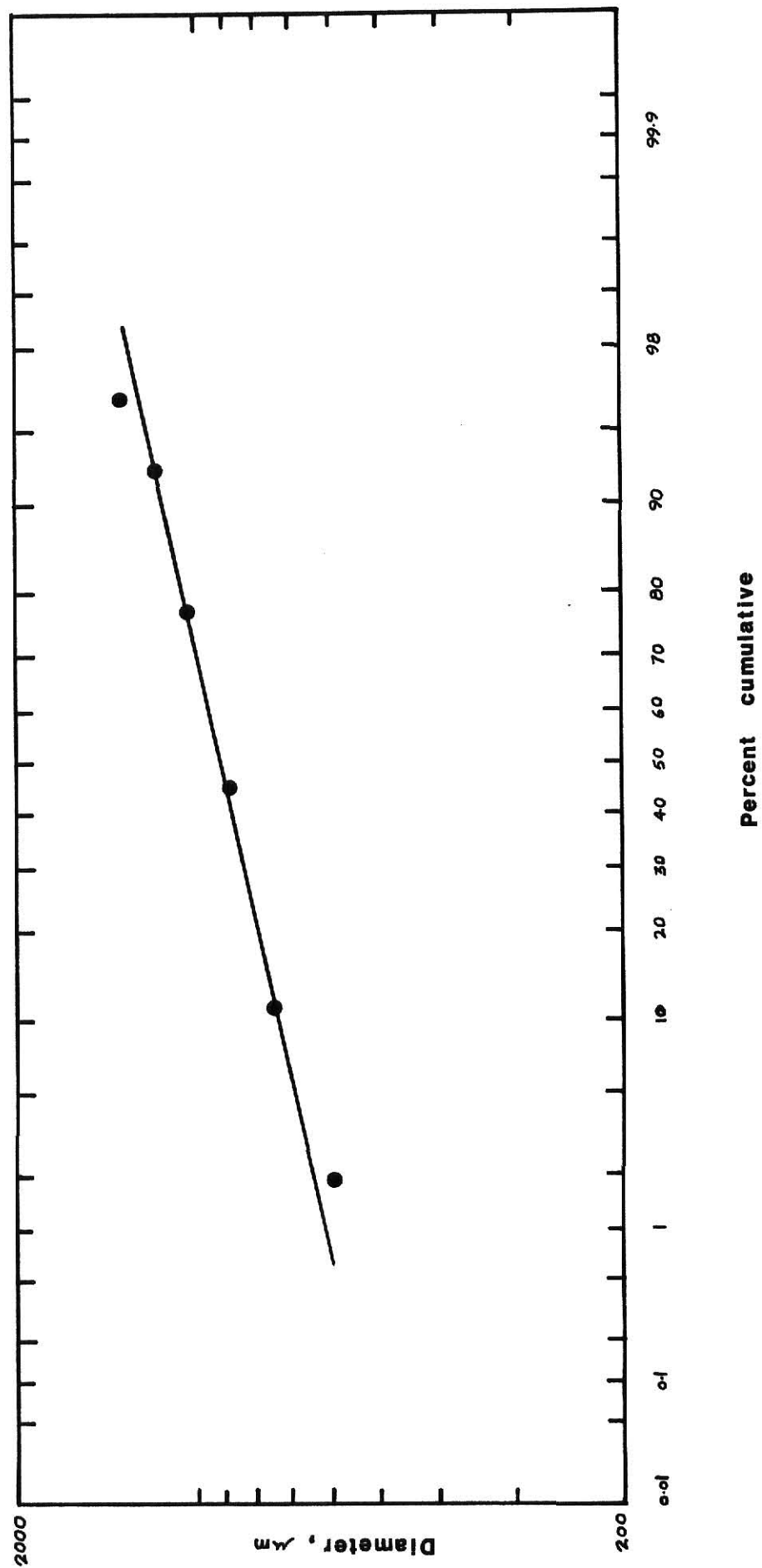


Fig. E, Particle size distribution for size #20/25.

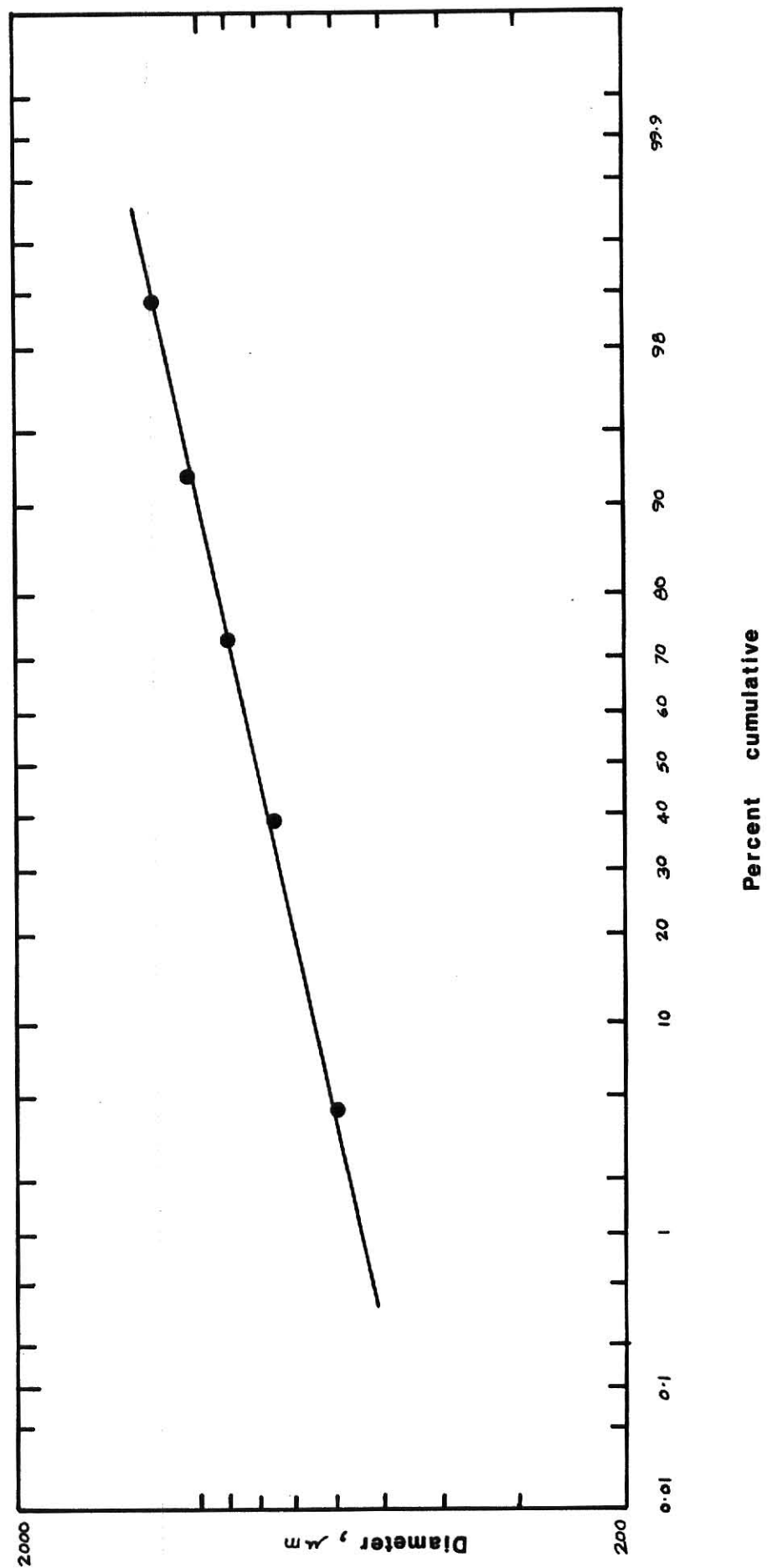


Fig. F. Particle size distribution for size #25/30.

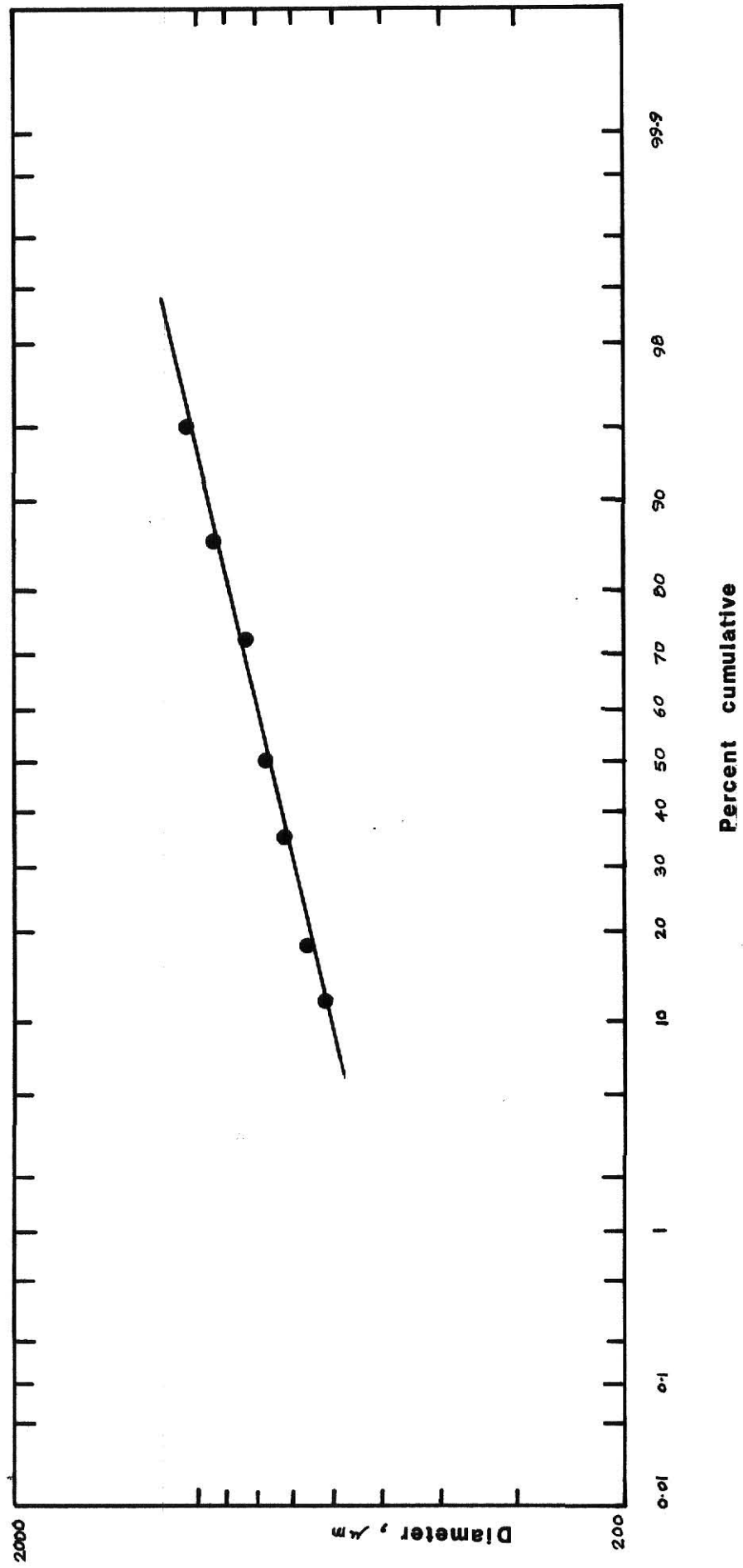


Fig.G. Particle size distribution for size #30/35.

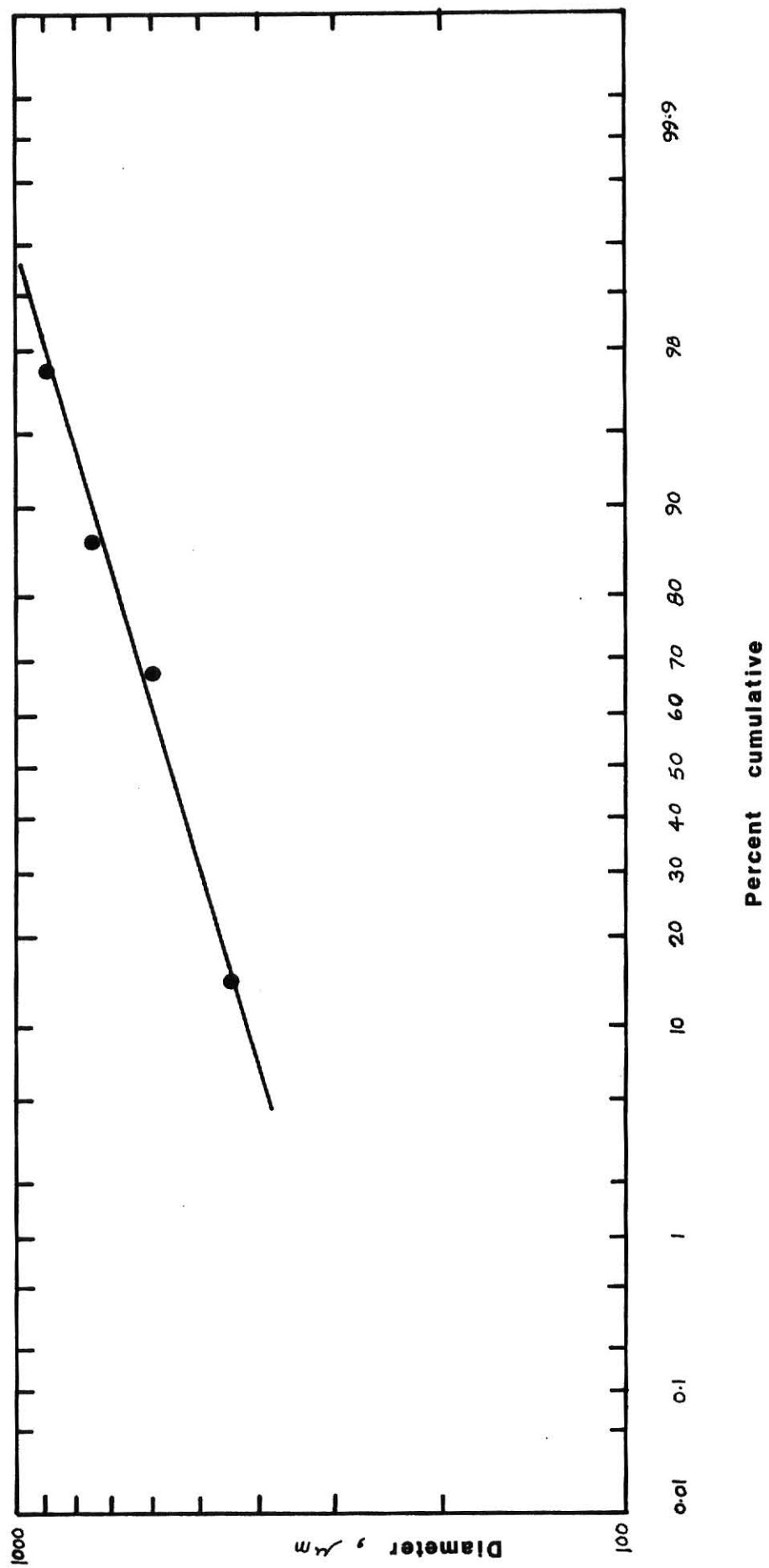


Fig. H. Particle size distribution for size #35/40.

C

CCCCC** COLUMN

C

C SINGLE SOLUTE MODEL WITH NO DISPERSION

C THIS PROGRAM IS A MODIFICATION OF THE ORIGINAL PROGRAM BY

C W. THACKER, J. CRITTENDEN AND V. SNOEYINK. THE MODIFICATION

C TAKES INTO ACCOUNT THE PARTICLE SIZE DISTRIBUTION IN THE FIXED

C BED OF CARBON. THE MODIFICATION WAS CARRIED OUT BY

C SANJAY KULKARNI ALONG WITH DR. A. P. MATHEWS AT

C KANSAS STATE UNIVERSITY.

C THIS PROGRAM SOLVES NONDIMENSIONAL FIXED BED MODEL USING

C ORTHOGONAL COLLOCATION AND AN INTEGRATION ROUTINE GEAR.

C ASSUMPTIONS ARE 1) FILM RESISTANCE AT THE PARTICLE SURFACE,

C 2) A HOMOGENEOUS PARTICLE, & 3) INTRAPARTICLE TRANSPORT IS

C BY SURFACE DIFFUSION WITH CONC. INDEPENDENT DIFFUSIVITY.

C UP TO 6 INTERNAL AXIAL COLLOCATION POINTS (8 INCLUDING

C BOUNDARY POINTS, MC=8) & 6 INTERNAL RADIAL COLL. PTS.

C (7 INCLUDING BOUND. PT., NC=7) CAN BE USED.

C RADIAL COLL. PT. 1 IS NEAR PARTICLE CENTER; PT. NC IS

C AT PARTICLE SURFACE, AXIAL COLL. PT. 1 IS AT THE BED

C ENTRANCE; PT. MC IS AT THE BED EXIT.

C N DEPENDENT VARIABLES ARE STORED IN THE VECTOR Y0 AS FOLLOWS:

C FIRST, THE INTERNAL SOLID PHASE CONCENTRATIONS, WHERE

C $Q(RADIAL, AXIAL) = Y0((AXIAL-1)*(NC-1) + RADIAL)$ FOR RADIAL =

C 1,2,...,NC-1, AND AXIAL = 1,2,...,MC (THE TOTAL NUMBER OF INTERNAL

C SOLID PHASE CONC. PTS. IS $MC*(NC-1) = NND$); SECOND, THE SOLIDC PHASE CONCENTRATION AT THE SURFACE WHERE $Q(NC, AXIAL) =$ C $Y0(NND + AXIAL)$ FOR AXIAL = 1,2,...,MC; AND THIRD, THE BULKC LIQUID CONCENTRATION, WHERE $C(AXIAL) = Y0(NND + MC + (AXIAL - 1))$

C FOR AXIAL = 2,3,...,MC (THE INFLUENT LIQ. CONC., CB11), IS NOT IN
C THE VECTOR Y0). $N = NND + MC + (MC-1) = MC*MC + (MC-1)$.
C
C UNITS AND NOTATION LIST
C MANY OF THE VARIABLES ARE EXPLAINED IN THE FORTUOI
C WRITE-UP ON GEAR
C RAD - RADIUS OF THE PARTICLE (CM)
C RHOP - APPARENT DENSITY OF THE CARBON (GM/CC CM)
C WGT - TOTAL WEIGHT OF CARBON IN THE BED (GM)
C WT - WEIGHT OF INDIVIDUAL LAYER (GM)
C CBO - INFLUENT CONC. TO THE BED (MASS/LITER)
C CN - CONC. FROM WHERE ISOTHERM IS ASSUMED LINEAR (MASS/LITER)
C QE - SOLID PHASE CONC. IN EQUIL. WITH CBO (MASS/GM)
C QN - SOLID PHASE CONC. IN EQUIL. WITH CN (MASS/LITER)
C XK,XN - FREUNDLICH ISOTHERM CONSTANTS(MAKE SURE UNITS CONSISTANT
C WITH C AND Q)
C XK1 - LINEAR ISOTHERM CONSTANT
C DS - SURFACE OR SOLID DIFFUSIVITY (SQ CM/SEC)
C KF - FILM TRANSFER COEFFICIENT (CM/SEC)
C FLRT - FLOWRATE (CC CM /MIN)
C L - TOTAL LENGTH OF BED (CM)
C DIA - COLUMN DIAMETER (CM)
C SF - SURFACE LOADING (GAL/ (SQ. FT MIN))
C VBED - INTERSTITIAL FLUID VELOCITY IN BED (CM/SEC)
C EPBED - TOTAL BED VOID FRACTION
C TAUBED - PACKED BED (NON EMPTY) CONTACT TIME (SEC)
C DGBED - SOLUTE PARTITION NUMBER FOR TOTAL BED,
C $RHOP*QE*(1. - EPBED)/(CBO*EPBED)$, (NGND)
C BEDL - LENGTH OF LAYER (CM)

C EBED - LAYER VOID FRACTION
C ED - LAYER SURFACE DIFFUSION MODULUS, $DS*DG*TAU/(RAD**2)$, (NOND)
C ST - LAYER STANTON NUMBER, $KF*(1.-EBED)*TAU/(RAD*EBED)$, (NOND)
C DG - LAYER SOLUTE PARTITION NUMBER,
C $RHOP*QE*(1.-EBED)/(CBO*EBED)$, (NOND)
C BI - LAYER BIOT NUMBER, $KF*RAD*(1.-EBED)/(EBED*DG*DS)$, (NOND)
C TAU - LAYER PACKED BED (NON EMPTY) CONTACT TIME (SEC)
C V - INTERSTITIAL FLUID VELOCITY IN LAYER, (CM/SEC)
C TDOL - TOTAL TIME OF RUN (MIN)
C TTOL - NOND. TOTAL RUN TIME OR THROUGHPUT, $TDOL*60/(TAU*DG)$
C FMIN - VALUE OF THE OBJECTIVE FUNCTION (SAMPLE DEVIATION) (NOND)
C DFMIN - DIMENSIONAL FMIN (MASS/LITER)
C ITP - NO. OF POINTS SAVED FOR PRINTING OR PLOTTING
C NDATA - NO. OF EXPERIMENTAL DATA POINTS. IF YOU JUST
C YOU HAVE NO DATA AND JUST WANT TO OBTAIN A PREDICTION
C THEN SET NDATA=0.
C TDATA - VECTOR OF EXPERIM. TIME VALUES FOR CD (MIN)
C JIN - TOTAL NUMBER OF VARYING INFLUENT CONCENTRATION VALUES.
C JIN1 - IF INFLUENT CONC. TO BED DOES NOT CHANGE, SET JIN1=0
C TTIN- VECTOR OF EXPERIMENTAL TIME VALUES AT WHICH INFLUENT
C CONCENTRATION CHANGES (MIN)
C CCIN - VECTOR OF EXPERIMENTAL INFLUENT CONCENTRATION
C IF INFLUENT CONCENTRATION IS CONSTANT, SET JIN=0? CIN AND TIN
C DO NOT NEED TO BE INCLUDED IN THE NAMELIST DATA. FOR VARYING
C INFLUENT CONCENTRATIONS.....IF CIN AT TIN = 0. IS KNOWN (I. E.
C USUALLY THE VALUE OF CBO) INCLUDE IT IN THE CIN AND TIN ARRAYS.
C IF CIN AT TIN=0. IS NOT INCLUDED IN THESE ARRAYS, CIN(1) IS USED
C FOR INFLUENT CONCENTRATION UNTIL TIN(1) IS REACHED. VARIABLE
C MUST BE IN ARRAYS IN ORDER OF INCREASING TIME.

C IF JIN IS INCORRECT, ERROR WILL RESULT BECAUSE TIN(JIN) MUST BE
C THE HIGHEST TIME VALUE OF ALL THE INFLUENT POINTS.
C VALUES (MASS/L).
C CD - VECTOR OF EXPERIM. EFFLUENT CONC. VALUES (MASS/LITER)
C NC - NO. OF RADIAL COLLOC. POINTS INCLUDING BOUNDARY
C POINT (PARTICLE SURFACE)
C MC - NO. OF AXIAL COLL. PTS. INCLUDING THE TWO BOUNDARY
C PTS. (ENTRANCE & EXIT OF BED)
C N - NUMBER OF ORD. DIF. EQNS.
C NSTEPS - MAXIMUM NO. OF CALLS TO GEAR. NSTEPS.LE.500
C OBJFUN - OBJECTIVE FUNCTION IS A SUBROUTINE DESIGNED
C TO COMPARE THE MODEL PREDICTION TO THE EXPERIMENTAL
C COLUMN RUN AND GIVE THE AVERAGE DIFFERENCE BETWEEN
C THE TWO SETS OF CONCENTRATION VALUES CORRESPONDING
C TO A GIVEN TIME VALUE.
C EPS - RELATIVE ERROR CRITERIA
C TO - INITIAL VALUE OF TIME OR THROUGHPUT T (NONDIM)
C DTO - DIMENSIONAL TO (MIN)
C TOUT - AS INPUT, VALUE OF T AT WHICH OUTPUT IS DESIRED NEXT;
C FIRST VALUE SHOULD BE LARGE ENOUGH FOR LAYERS TO
C GIVE POSITIVE VALUE OF FIRST EFFLUENT
C AS OUTPUT, CURRENT VALUE OF T (NONDIM)
C DTOUT - DIMENSIONAL TOUT (MIN)
C TSTEP - TIME INTERVAL ADDED TO TOUT FOR INPUT (NONDIM)
C DSTEP - DIMENSIONAL TSTEP (MIN)
C TINC - VECTOR OF ADDITIONAL TSTEP VALUES FOR A CHANGE
C IN THE INCREMENT OF OUTPUT (MIN)
C TIE - VECTOR OF TIMES AT WHICH TSTEP IS REASSIGNED (MIN)
C IF YOU DO NOT WANT TO SPECIFY TIE OR TINC THEN

C SET NM=0, TIE=0.0 AND TINC=0.0 IN THE DATA FILE.

C NM - SIZE OF VECTORS TINC & TIE (NM.LE.4)

C HO - INITIAL TIME STEP (NONDIM)

C DHO - DIMENSIONAL HO (MIN)

C AREA - THIS VALUE GIVES YOU THE TOTAL AREA ABOVE THE

C PREDICTED BREAKTHROUGH CURVE UP TO C/CO=1.0 . IF

C THIS VALUE IS GREATER THAN ONE WITH CONSTANT CIN THEN YOU HAVE

C VIOLATED MASS BALANCE AND THE PREDICTION IS PROBABLY

C NOT CORRECT. (CHECK YOUR UNITS)

C MF - INTEGRATION METHOD

C INDEX - SPECIFIES TYPE OF CALL TO GEAR

C COL - FILE OF RADIAL COLL. CONSTS. (SYM. GEOM.)

C UCOL - FILE OF AXIAL COLL. CONSTS. (UNSYM. GEOM.)

C NCOL - IF=1, PRINT COLL. CONSTS. IF=0, DON'T.

C AU - MATRIX OF AXIAL COLL. CONSTS.

C W & B - VECTOR & MATRIX OF RADIAL COLL. CONSTS.

C CS - VECTOR OF LIQ CONCS AT SURF (NOND)

C YO - VECTOR OF DEPENDENT VARIABLES FOR EACH LAYER (NOND)

C YYO - MATRIX OF STORAGE OF YO OF EACH LAYER

C YDOT - VECTOR OF DERIVATIVES OF DEPENDENT VARIABLES (NOND)

REAL KF, L

DIMENSION YO(63), TP(75), CP(75), TDATA(30), CD(30), CP1(30),

1TIE(2), TINC(2), CIP(75), DCP(75), DCIP(75), DTP(75), DDTP(75),

2DCD(30), DCP1(30), DTDATA(30), DATAT(30), DCIN(10), DTIN(10),

3DDTIN(10), WT(10), RAD(10), KF(10), YYO(10, 63),

4TCIN(75), TTIN(75), TIN1(10), CIN1(10), CCIN(75)

COMMON AU(8, 8), W(7), B(7, 7), CS(8)

COMMON CIN(75), TIN(75)

COMMON JIN

KSU DATA SET LISTER 3/15/83

CARD INPUT

```
COMMON NC,ND,MC,MD,ED,ST,NND,DOX,DG,CI,XK,XN,XK1,QN,CBO,QE
READ(5,965,ERR=999)NSTEPS,NC,MC,MF,NCOL,JIN,NM,NDATA,NUM,JIN1
READ(5,966,ERR=999)(KF(I),I=1,NUM)
READ(5,960,ERR=999)(RAD(I),I=1,NUM)
READ(5,960,ERR=999)(WT(I),I=1,NUM)
READ(5,960,ERR=999)IDS,CBO,EPS,XK,XN,XK1,DSTEP,L,FLRT,DHO,TOTOL,
1DTOUT1,DIA,RHOP,TIE(1),TIE(2),TINC(1),TINC(2),WGT,CN
READ(5,960)(CD(I),I=1,NDATA)
READ(5,960)(TDATA(I),I=1,NDATA)
IF(JIN.EQ.0) GOTO 5
READ(5,960,ERR=999)(CCIN(I),I=1,JIN)
READ(5,960,ERR=999)(TTIN(I),I=1,JIN)
5 AREA=3.14159*(DIA**2)/4.
SF=FLRT*2.642E-4*929./AREA
IF(NDATA.EQ.0) GO TO 15
DO 10 I=1,NDATA
10 CD(I)=CD(I)/CBO
15 ND=NC-1
MD=MC-1
NND=ND*MC
N=NND+MC+MD
DO 20 I=1,MC
READ(5,900)(AU(I,J),J=1,MC)
20 CONTINUE
READ(5,900)(W(I),I=1,NC)
DO 25 I=1,NC
READ(5,900)(B(I,J),J=1,NC)
25 CONTINUE
IF(NCOL.EQ.0) GO TO 40
```

KSU DATA SET LISTER 3/15/83

CARD INPUT

```
      DO 30 I=1,MC
      WRITE(6,900) (AU(I,J),J=1,MC)
30  CONTINUE
      WRITE(6,900) (W(I),I=1,NC)
      DO 35 I=1,NC
      WRITE(6,900) (B(I,J),J=1,NC)
35  CONTINUE
40  CONTINUE
      DO 45 I=1,NUM
      DO 45 J=1,N
      YYO(I,J)=0.0
45  CONTINUE
      CB1=CB0
      QE1=XK*(CB0**XN)
      QN=XK*(CN**XN)
      CVOL=WGT/RHCP
      BVOL=L*AREA
      EPBED=(BVOL-CVOL)/BVOL
      VBED=FLRT/(AREA*EPBED*60.)
      TAUBED=L/VBED
      DGBED=(RHCP*1000.*QE1*(1-EPBED))/(CB0*EPBED)
      EONBED=60./(TAUBED*DGBED)
      WRITE(6,905)MC,NC,XK,XN,XK1,SF,EPS,DH0,CB0,DOUT,DSTEP,TDOL,
1DS,QE1
      DO 120 ITM=1,NUM
      DO 55 J=1,N
      YO(J)=YYO(ITM,J)
55  CONTINUE
      IF(CB0.LT.CN) GOTO 56
```


KSU DATA SET LISTER 3/15/83

CARD INPUT

```
      QE=XK*(CBO**XN)
      GOTO 57
56  QE=XK1*CBO
57  BEDL=(WT(ITM)/WGT)*L
      CARVOL=WT(ITM)/RHOP
      BEDVOL=BEDL*AREA
      EBED=(BEDVOL-CARVOL)/BEDVOL
      V=FLRT/(AREA*EBED*60.)
      TAU=BEDL/V
      DG=(RHOP*1000.*QE*(1-EBED))/(CBO*EBED)
      ED=DS*DG*TAU/(RAD(ITM)**2)
      ST=KF(ITM)*(1-EBED)*TAU/(RAD(ITM)*EBED)
      BI=KF(ITM)*RAD(ITM)*(1-EBED)/(EBED*DG*DS)
      DOX=3.*DG*ST
      EON=60./(TAU*DG)
      IF(JIN.EQ.0) GOTO 70
      DO 60 I=1,JIN
          TIN(I)=TTIN(I)*EON
60  CIN(I)=CCIN(I)/CBO
      IF(ITM.NE.1)GOTO 70
      DO 65 I=1,JIN
          TIN1(I)=(TIN(I)/EON)*EONBED
65  CIN1(I)=CIN(I)
70  MA=1
      HO=DHO*ECN
      DTOUT=DTOUT1
      TO=0.0
      INDEX=1
      DO 90 ITER=1,NSTEPS
```

KSU DATA SET LISTER 3/15/83

CARD INPUT

```
TOUT=DTOUT*EON
CALL GEAR(N,TO,H0,Y0,TOUT,EPS,MF,INDEX)
CBNEW=Y0(N)*CBO
TCIN(ITER)=CBNEW
TTIN(ITER)=TOUT/EON
IF (ITM.NE.1) GOTO 71
CPI(ITER)=C I
71 IF(TCIN(ITER)) 75,75,80
75 TCIN(ITER)=CCIN(ITER-1)
80 CCIN(ITER)=TCIN(ITER)
IF(DTOUT.GE.TDTOL) GOTO 100
IF(NM.EQ.0) GOTO 85
IF(DTOUT.LT.TIE(MA)) GOTO 85
DSTEP=TINC(MA)
IF(NM.NE.MA) MA=MA+1
85 CONTINUE
DTOUT=DTOUT+DSTEP
IF(DTOUT.LT.TDTOL) GOTO 90
DTOUT=TDOL
90 CONTINUE
DO 95 J=1,N
YYO(ITM,J)=Y0(J)
95 CONTINUE
WRITE(6,950)
100 IF(ITM.EQ.NUM) GOTO 105
GO TO 115
105 DO 110 ITP=1,ITER
CP(ITP)=TCIN(ITP)/CB1
TP(ITP)=TTIN(ITP)*EONBEC
```

```
      DDTP(ITP)=TP(ITP)/EONBED
      DTP(ITP)=TP(ITP)*EPRED*DGBED
110  CONTINUE
      GO TO 120
115  JIN=ITER
      CBO=CCIN(1)
120  CONTINUE
125  IF(NDATA.EQ.0) GO TO 140
      DO 130 I=1,NDATA
130  TDATA(I)=TDATA(I)*EONBED
      CALL OBJFUN( CD, TDATA, NDATA,CP, TP, ITP, CP1, FMIN)
      DFMIN=FMIN*CB1
      WRITE(6,910)FMIN,DFMIN
      DO 135 I=1,NCATA
      DTDATA(I)=TDATA(I)*EPBED*DGBED
      DATAT(I)=TDATA(I)/EONBED
      DCP1(I)=CP1(I)*CB1
      DCD(I)=CD(I)*CB1
      WRITE(6,915)(DCD(I),CD(I),DCP1(I),CP1(I),TDATA(I),
1DTDATA(I),DATAT(I))
135  CONTINUE
140  CONTINUE
      IF(JIN1.EQ.0) GOTO 150
      WRITE(6,920)
      DO 145 I=1,JIN
      DCIN(I)=TCIN(I)*CB1
      DTIN(I)=TTIN(I)*EPBED*DGBED
      DOTIN(I)=TTIN(I)/EONBED
      WRITE(6,925)(DCIN(I),TCIN(I),TTIN(I),DTIN(I),DOTIN(I))
```

145 CONTINUE

150 WRITE(6,930)

DO 155 I=1,ITER

DCP(I)=CP(I)*CB1

DCIP(I)=CIP(I)*CB1

WRITE(6,935)(TP(I),DTP(I),CIP(I),CP(I),DDTP(I),DCIP(I),DCP(I))

155 CONTINUE

AREA=0.0

ITPM1=ITP-1

DO 160 ITP=1,ITPM1

160 AREA=(1.0-((CP(ITP)+CP(ITP+1))/2))*(TP(ITP+1)-TP(ITP))+AREA

WRITE(6,940)AREA

STOP

999 WRITE(6,945)

STOP

900 FORMAT (4F20.10)

905 FORMAT(//2X,' NO OF AXIAL COLL PTS MC, WITH TWO BOUND PTS =' ,I5/

12X,' NO OF RADIAL COLL PTS NC, WITH BOUND PT =' ,I5/

22X,' ISOTHERM CONSTANT XK =' ,E15.5/

32X,' ISOTHERM CONSTANT XN =' ,E15.5/

42X,' ISOTHERM CONSTANT XK1 =' ,E15.5/

52X,' SURFACE LOADING SF, GAL/SQ. FT MIN = ' ,E15.5/

62X,' ERROR TEST CONSTANT EPS, =' ,E15.5/

72X,' INIT. STEP SIZE DHO, MIN. =' ,E15.5/

82X,' INFLUENT CONC. CBC, MASS/LITER = ' ,E15.5/

92X,' TIME OF INIT. OUTPUT DTOUT, MIN. =' ,E15.5/

A2X,' TIME INTERVAL ADDED TO DTOUT DSTEP, MIN. =' ,E15.5/

B2X,' TOTAL TIME OF RUN TOTCL, MIN. =' ,E15.5/

C2X,' SURFACE DIFFUSION COEF. DS,SQ. CM/SEC =' ,E15.5/

KSU DATA SET LISTER 3/15/83

CARD INPUT

```
D2X, ' SURF. CONC. AT EQUIL. QE ,MASS/GRAM = ', E15.5)
910 FORMAT(2X, ' FMIN, NOND. = ', F10.7/
      12X, ' FMIN, MASS/LITER = ', F10.2////
      27X, 'EFFLUENT DATA', 12X, 'PREDICTION', 8X, ' * * * * * TIME UNITS ',
      3' * * * * */6X, 'DIM', 9X, 'NON', 9X, 'DIM', 9X, 'NON', 5X, 'THROUGHPUT',
      46X, 'BVF', 7X, 'MINUTES' /)
915 FORMAT(2X, F10.2, 2X, F10.7, 2X, F10.2, 2X, F10.7, 2X, F10.7, 2X, F10.2, 2X,
      1F10.2)
920 FORMAT(///7X, 'INFLUENT DATA', 6X, ' * * * * * TIME UNITS * * * * '
      1, ' */6X, 'DIM', 9X, 'NON', 5X, 'THROUGHPUT', 6X, 'BVF', 7X, 'MINUTES' /)
925 FORMAT(2X, F10.2, 2X, F10.5, 2X, F10.5, 2X, F15.2, 2X, F10.2)
930 FORMAT(///32X, ' * * * * * M O D E L   P R E D I C T I O N ',
      1' * * * * * */11X, ' * * * * * * * * * * NONDIMENSIONAL * * * * * '
      2, ' * * * ', 17X, ' * * * * * ',
      3'DIMENSIONAL * * * * * */5X, 'THROUGHPUT', 10X, 'BVF', 12X, 'INFLUENT'
      4, 9X, 'EFFLUENT', 9X, 'MINUTES', 10X, 'INFLUENT', 9X, 'EFFLUENT' /)
935 FORMAT(7(2X, E15.8))
940 FORMAT(5X, 'THE AREA ABOVE THE PREDICTION IS EQUAL TO ', E15.8)
945 FORMAT(' ERROR ON UNIT 4...THIS IS WHAT WAS READ IN:')
950 FORMAT(///' WARNING   MORE STEPS ATTEMPTED THAN NSTEPS; ',
      1' TDOL NOT REACHED.' /)
960 FORMAT(5E16.4)
965 FORMAT(10I4)

END
```

```
SUBROUTINE DIFFUN(N,T,YO,YDOT)
  DIMENSION YO(63),YDOT(63)
  DIMENSION BB(6,8),WH(8),AAU(8),QR(8)
  COMMON AU(8,8),W(7),B(7,7),CS(8)
  COMMON CIN(75),TIN(75)
  COMMON JIN
  COMMON NC,ND,MC,MD,ED,ST,NND,DOX,DG,CI,XK,XN,XK1,QN,CBC,QE
  DO 5 J=1,MC
    WH(J)=0.0
    AAU(J)=0.0
  DO 5 I=1,ND
    BB(I,J)=0.0
5  CONTINUE
  IF(JIN.EQ.0) GOTO 15
  CI=CINF(TIN,CIN,JIN,T)
  GO TO 20
15 CI=1.0
20 CONTINUE
  DO 40 K=1,MC
    KK=NND+K
    IF(YO(KK).LE.0.0) GOTO 35
    QR(K)=YO(KK)*QE
    IF(QR(K).LT.QN) GO TO 25
    CS(K)=((QR(K)/XK)**(1./XN))/CBC
    GO TO 40
25 CS(K)=QR(K)/(CBC*XK1)
    GO TO 40
35 CS(K)=0.0
40 CONTINUE
```

KSU DATA SET LISTER 3/15/83

CARD INPUT

```
DO 45 I=1,ND
DO 45 K=1,MC
DO 45 J=1,ND
JJ=ND*(K-1)+J
BB(I,K)=BB(I,K)+B(I,J)*YO(JJ)
45 CONTINUE
DO 50 K=1,MC
DO 50 I=1,ND
KK=ND*(K-1)+I
II=NND+K
YDOT(KK)=ED*(BB(I,K)+B(I,NC)*YO(III))
WW(K)=WW(K)+W(I)*YDOT(KK)
50 CONTINUE
III=NND+1
YDOT(III)=(ST*(CI-CS(1))-WW(1))/W(NC)
DO 55 K=2,MC
II=NND+K
JJ=II+MD
YDOT(II)=(ST*(YO(JJ)-CS(K))-WW(K))/W(NC)
DO 55 J=2,MC
KK=NND+MD+J
AAU(K)=AAU(K)+AU(K,J)*YO(KK)
55 CONTINUE
DO 60 I=1,MD
II=NND+MC+I
JJ=I+1
60 YDOT(II)=(-DG)*AAU(JJ)-DG*AU(JJ,1)*CI-DIX*(YO(II)-CS(JJ))
RETURN
END
```

KSU DATA SET LISTER 3/15/83

CARD INPUT

SUBROUTINE PEDERV(N,T,YO,PD,NO)

DIMENSION YO(63),YDOT(63)

COMMON AU(8,8),W(7),B(7,7),CS(8)

COMMON CIN(75),TIN(75)

COMMON JIN

COMMON NC,ND,MC,MD,ED,ST,NND,DOX,DG,C I,XK,XN,XK1,QN,CBO,QE

RETURN

END

KSU DATA SET LISTER 3/15/83

CARD INPUT

```
SUBROUTINE OBJFUN(CD, TD, ND, CP, TP, NP, CP1, FMIN)
  DIMENSION CD(30),TD(30),CP(75),TP(75),CP1(30)
  FMIN = 0.
  NP1 = NP - 1
  DO 1 J=1, ND
    DO 2 I =1, NP1
      IF(TD(J).LT.TP(I).OR.TD(J).GT.TP(I+1)) GO TO 2
      CAP = CP(I) + ((TD(J) - TP(I))/(TP(I+1) - TP(I)))*(CP(I+1) -
1 CP(I))
      CP1(J) = CAP
      FMIN = FMIN + (CAP - CD(J))*(CAP - CD(J))
    GO TO 1
  2 CONTINUE
  1 CONTINUE
  FMIN = SQRT(FMIN/FLOAT(ND-1))
  RETURN
  END
```

KSU DATA SET LISTER 3/15/83

CARD INPUT

```
REAL FUNCTION CINF(TIN,CIN,JIN,T)
DIMENSION CIN(75),TIN(75)
IF(T.LE.TIN(1)) GO TO 2
IF(T.GE.TIN(JIN)) GO TO 3
N1=JIN-1
DO 1 INF=1,N1
IF(T.LT.TIN(INF).OR.T.GT.TIN(INF+1)) GO TO 1
TEMP=CIN(INF)+(CIN(INF+1)-CIN(INF))*(T-TIN(INF))/
$(TIN(INF+1)-TIN(INF))
CINF=TEMP
RETURN
1 CONTINUE
RETURN
2 CINF = CIN(1)
RETURN
3 CINF = CIN(JIN)
RETURN
END
```

KSU DATA SET LISTER 3/15/83

CARD INPUT

C AXIAL COLLOCATION POINTS

-42.9999999969	47.9897606307	-6.6841453795	2.6167135801
-1.6084972187	1.3631789799	-1.6770105967	1.0000000011
-18.2772839820	14.2906542645	5.1519641532	-1.7720413716
1.0499046632	-0.8769159555	1.0724211206	-0.6387028922
5.2137639550	-10.5515250588	2.3497045595	4.1638150862
-1.9554696368	1.5123802255	-1.7959753616	1.0633062310
-2.6369381615	4.6887225881	-5.3793489019	0.5060525568
4.1907778522	-2.5263257938	2.7779891569	-1.6209292968
1.6209292944	-2.7779891521	2.5263257905	-4.1907778504
-0.5060525589	5.3793489065	-4.6887225946	2.6369381646
-1.0633062285	1.7959753570	-1.5123802223	1.9554696343
-4.1638150826	-2.3497045687	10.5515250691	-5.2137639584
0.6387028906	-1.0724211177	0.8769159535	-1.0499046618
1.7720413702	-5.1519641557	-14.2906542578	18.2772839786
-0.9999999989	1.6770105926	-1.3631789770	1.6084972168
-2.6167135784	6.6841453831	-47.9897606397	43.0000000015

KSU DATA SET LISTER 3/15/83

CARD INPUT

C RADIAL COLLOCATION POINTS

0.0098216509	0.0348850091	0.0634547451	0.0819786089
0.0795716562	0.0541203203	0.0095013229	
-62.6231645188	80.0518429494	-25.7370022958	13.1876920557
-7.9903309651	4.9756299431	-1.8646671685	
22.5789415990	-82.222282722	75.7987665505	-23.8924178637
12.2418297700	-7.1015182317	2.5966264480	
-3.9840024897	41.5998276835	-109.3190670616	90.6271578527
-27.8001695919	13.5716731252	-4.6954195182	
1.5827170544	-10.1662863557	70.2637305168	-166.9928509816
132.7230328609	-39.3857007919	11.9753576971	
-0.9863584156	5.3577700937	-22.1694945398	136.5154487421
-322.4936746925	255.9538773769	-52.1775685648	
0.9047066911	-4.5780305530	15.915842919	-59.6710697277
377.0087711456	-1024.3490142752	694.7430524273	
46.2571370165	-195.8102656097	488.5057954280	-1024.5503961815
2044.7591105876	-3127.1613810427	1767.9999998017	

NO OF AXIAL COLL PTS MC, WITH TWO BOUND PTS = 8
NO OF RADIAL COLL PTS NC, WITH BOUND PT = 7
ISOTHERM CONSTANT XK = 0.13439E 03
ISOTHERM CONSTANT XN = 0.17420E 00
ISOTHERM CONSTANT XK1 = 0.16267E 03
SURFACE LOADING SF, GAL/SQ. FT MIN = 0.10000E 02
ERROR TEST CONSTANT EPS, = 0.10000E-02
INIT. STEP SIZE DHO, MIN. = 0.15000E-03
INFLUENT CONC. CBO, MASS/LITER = 0.36995E 03
TIME OF INIT. OUTPUT DTOUT, MIN. = 0.0
TIME INTERVAL ADDED TO DTOUT DSTEP, MIN. = 0.10000E 03
TOTAL TIME OF RUN TDOL, MIN. = 0.12000E 04
SURFACE DIFFUSION COEF. DS, SQ. CM/SEC = 0.50147E-07
SURF. CONC. AT EQUIL. QE, MASS/GRAM = 0.37648E 03
QE= 376.4758300781 BEDL= 55.0999908447 ED= 0.5240919590
DG= 1525.2163085938 ST= 3.5700654984 DOX= 16335.36328
ECN= 0.0015722681H0= 0.0000002358 TOUT=

FMIN, NOND. = 0.0278844

FMIN, MASS/LITER = 10.32

TWO LAYERS

EFFLUENT DATA		PREDICTION		* * * * * TIME UNITS * * * * *		
DIM	NCN	DIM	NCN	THROUGHPUT	BVF	MINUTES
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.86	0.0023185	0.2830082	133.10	180.00
7.48	0.0202100	14.22	0.0384455	0.5660165	266.20	360.00
50.49	0.1364833	65.11	0.1759968	0.7546887	354.94	480.00
110.31	0.2981755	124.26	0.3358917	0.8490247	399.30	540.00
180.22	0.4871469	197.07	0.5326983	0.9433608	443.67	600.00
238.87	0.6456819	241.51	0.6528263	1.0376968	488.04	660.00
271.88	0.7349099	279.18	0.7546424	1.1320324	532.40	720.00
297.13	0.8031623	303.27	0.8197488	1.2263689	576.77	780.00
326.26	0.8819024	334.95	0.9054058	1.4150410	665.51	900.00
339.85	0.9186373	350.75	0.9480962	1.6037130	754.24	1020.00
347.62	0.9396402	359.44	0.9715860	1.7923851	842.97	1140.00

FMIN, NOND. = 0.0349675

FMIN, MASS/LITER = 12.94

ONE LAYER

EFFLUENT DATA		PREDICTION		* * * * * TIME UNITS * * * * *		
DIM	NCN	DIM	NON	THROUGHPUT	BVF	MINUTES
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.08	0.0002061	0.2830082	133.10	180.00
7.48	0.0202100	5.52	0.0149334	0.5660165	266.20	360.00
50.49	0.1364833	39.74	0.1074202	0.7546887	354.94	480.00
110.31	0.2981755	101.13	0.2733513	0.8490247	399.30	540.00
180.22	0.4871469	182.60	0.4935853	0.9433608	443.67	600.00
238.87	0.6456819	240.07	0.6489379	1.0376968	488.04	660.00
271.88	0.7349099	287.62	0.7774443	1.1320324	532.40	720.00
297.13	0.8031623	314.60	0.8503971	1.2263689	576.77	780.00
326.26	0.8819024	346.38	0.9362832	1.4150410	665.51	900.00
339.85	0.9186373	359.11	0.9706926	1.6037130	754.24	1020.00
347.62	0.9396402	364.98	0.9865642	1.7923851	842.97	1140.00

FMIN, NCND. = 0.0196751

FMIN, MASS/LITER = 7.28

THREE LAYERS

EFFLUENT DATA		PREDICTION		* * * * * TIME UNITS * * * * *		
DIM	NON	DIM	NON	THROUGHPUT	BVF	MINUTES
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	0.0	0.36	0.0009746	0.2830082	133.10	180.00
7.48	0.0202100	12.72	0.0343922	0.5660165	266.20	360.00
50.49	0.1364833	61.07	0.1650797	0.7546887	354.94	480.00
110.31	0.2981755	118.34	0.3198841	0.8490247	399.30	540.00
180.22	0.4871469	189.43	0.5120399	0.9433608	443.67	600.00
238.87	0.6456819	238.39	0.6443963	1.0376968	488.04	660.00
271.88	0.7349099	279.14	0.7545280	1.1320324	532.40	720.00
297.13	0.8031623	302.95	0.8188901	1.2263689	576.77	780.00
326.26	0.8819024	333.28	0.9008683	1.4150410	665.51	900.00
339.85	0.9186373	348.23	0.9412767	1.6037130	754.24	1020.00
347.62	0.9396402	356.99	0.9649646	1.7923851	842.97	1140.00

MODIFICATION OF A MATHEMATICAL MODEL TO
TAKE INTO ACCOUNT PARTICLE SIZE DISTRIBUTION
IN FIXED BED CARBON ADSORPTION SYSTEMS

by

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India, 1978

AN ABSTRACT OF A MASTER'S THESIS

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Manhattan, Kansas

1983

ABSTRACT

A mathematical model of fixed bed adsorption was modified to take into account particle size distribution of carbon particles in the fixed bed. Three different types of diameter were used. The model was used to compare the performance of a fixed bed of mixed carbon particles by lumping the original size fractions together to form a different number of layers. The model equations were generated considering film transfer and surface diffusion controlled adsorption rate. The equations were solved by the orthogonal collocation method.

Dimethyl phthalate (DMP) and parachlorophenol (PCP) were used as two solutes. Isotherms in deionized water and tap water were prepared for both single and bisolute systems. Single solute data were fitted with the three parameter isotherm, and bisolute data was fitted with both three parameter and Prausnitz isotherms. Kinetic studies were carried out on both single and bisolute systems. The results were predicted by a program written by Mathews (1975), using the three parameter model and Prausnitz's model.

Single solute equilibrium and kinetic data were described well by the models. Bisolute data, however, were not described as well. The adsorption rate was predicted better with Prausnitz's model than the three parameter model. In fixed bed runs, experimental results were tested against the modified model predictions using one, two and three layers to replace the original eight fractions. The results improved as the number of layers was increased. The predictions showed that a sauter mean diameter and log-mean diameter described the particle size better than the geometric mean diameter. The sauter diameter predicted particularly well with PCP, solute which has a low value of surface diffusivity.