

ACTIVATED CARBON ADSORPTION FOR REMOVAL OF
PRIORITY POLLUTANTS PHENOL AND NAPHTHALENE

by

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CHAPTER I

INTRODUCTION

A large number of synthetic organic chemicals are being produced by industries, and several of these are being introduced into the environment. The presence of synthetic organic compounds in the environment can have severe adverse effects. These effects include toxicity, carcinogenicity, mutagenicity, and teratogenicity in humans and animals, toxicity to aquatic life and fish, and degradation of the quality of water for human consumption. Hence, there is a need to regulate the release of toxic and hazardous chemicals to the environment and to develop control technology capable of removing hazardous organics from water to prevent further dispersion into the environment.

Over the past years, legislation has been enacted. Included are: Federal Water Pollution Control Act (Public Law 92-500), Toxic Substance Control Act (Public Law 92-500), Resource Conservation and Recovery Act (section 300, Public Law 92-580), Safe Drinking Water Act (Public Law 93-523), and Clean Water Act (section 53(a), Public Law 95-217).

A list of 129 chemical compounds (priority pollutants) was issued by Environmental Protection Agency (EPA) as a result of the 1976 Flannery Consent Decree. These priority pollutants were derived from a list of 65 pollutants in the Clean Water Act. Among the reasons for singling out these 129 pollutants are: (1) frequency of occurrence in water, (2) chemical stability and

structure, (3) amount of chemical produced, (4) availability of chemical standards and measurement.

A number of Polynuclear Aromatic Hydrocarbons and Phenolic compounds classified as priority pollutants were included in this list.

The existence of Polynuclear Aromatic Hydrocarbons (PAH) in water has recently received attention (Harrison et al., 1975; Hase and Hites, 1976; Freudenthal and Jones, 1976). PAH is most commonly found in wastewater from processing of fuels, dye manufacture, and various combustion and pyrolysis operations. Because of their multi-ring structure, they all exhibit a common trait of extremely low solubility in water.

Naphthalene and substituted naphthalenes (methylnaphthalene, dimethylnaphthalene), which are the simplest member of PAH, have been found to be more soluble in water than most other high boiling aromatic hydrocarbons, and consequently have a greater tendency to migrate from petroleum oils into the marine environment and contaminate industrial water (Rossi et al., 1976; Gruenfeld and Frank, 1977). In addition, naphthalenes are readily adsorbed by the aquatic organisms, and their toxicity to fish may exceed that of lower boiling aromatics such as benzene, toluene, and xylene (Anderson et al., 1974).

Phenolic compounds are troublesome in themselves and are considered to be one of the two most important cases of taste and odor in water supplies. As little as 0.005 mg/l of phenol will impart objectionable taste and odor to drinking water (Lanouette, 1977). Sources of phenolic compounds in natural waters include

effluent from coke ovens in steel plants, petroleum refineries, paper and pulp industries, runoff from agricultural land, sewage effluents, and decomposition of natural vegetation (Gurnham, 1955; Reid et al., 1960; Erdei, 1963). Phenols are toxic to fish at levels above 2 mg/l, and can cause a taste in fish flesh at concentrations far below the toxic level (McKee et al., 1963; EPA, 1976).

Naphthalene and phenol, which also are two organic priority pollutants in the list indicated above, can be used to represent PAH and Phenolic Compounds respectively. The prevalence of naphthalene and phenol in treated secondary industrial effluents is indicated in Tables 1 and 2.

Considerable efforts have been expended by EPA and others (Weber, 1967A) in basic research to improve conventional water and wastewater treatment techniques. Complete removal or in some cases reduction of these persistent organic compounds to an acceptable concentration has become a major concern of advanced water and wastewater treatment technology. The methods of controlling the problems associated with very low concentrations of organic compounds in water supplies have been researched (Sigworth, 1957; Spicher and Skrinde, 1963; Vaughn, 1964; Dougherty et al., 1967). The major methods of pollutant removal include: chemical clarification (coagulation, flocculation, sedimentation), filtration, activated carbon adsorption, ozone oxidation, and biodegradation. Among the unit processes for advanced treatment of water and wastewater, activated carbon adsorption has emerged as the most efficient and economical

Table 1. Prevalence of Naphthalene in Industrial Effluents

Industrial Category	Maximum Concentration Reported (ug/l)*	
	Raw Wastewater	Treated
Paint Formulating	18,000	1,830
Gum and Wood Chemicals	150	27
Leather Tanning	757	65
Ink Formulating	23	--
Textile Industry	410	255
Petroleum Refining	--	425
Pulp, Paper and Paperboard Industry	230	88
Coal Mining	410	Very Small
Timber Products, Coal Processing and Synthetic Fuels	--	Significant

*Source: EPA Development Document for Effluent Limitation Series.

Table 2. Prevalence of Phenol in Industrial Effluents

Industrial Category	Maximum Concentration Reported ($\mu\text{g/l}$)*	
	Raw Wastewater	Treated
Paint Formulating	3,800	1,240
Gum and Wood Chemicals	23,000	1,900
Leather tanning	2,500	1,400
Ink Formulating	536	18
Textile Industry	4,900	50
Petroleum Refining	--	4,200
Pulp, Papear and Paperboard Industry	640	250
Coal Mining	3	--

*Source: EPA Development Document for Effluent Limitation Series.

process of removing undersirable organic materials from dilute aqueous solutions.

The removal of refractory organics from water is a difficult task because of the different organic compounds typically present and the extremely low concentrations normally encountered. Activated carbon adsorption systems can effectively reduce the concentration of many dissolved organic compounds in waters and wastewaters. They have been applied for treatment of domestic and industrial wastewaters for removal of synthetic organic compounds which resist removal by more classical wastewater treatment methods.

The increasing public demand for more stringent control of water pollution has stimulated great intrest in the activated carbon adsorption treatment processes.

In the past years, the phenomenon of activated carbon adsorption in the phenol aqueous system, has been studied extensively (Giles et al., 1960; Morris and Weber, 1964, 1966; Snoeyink and Weber, 1967; Coughlin and Ezra, 1968; Snoeyink et al., 1969; Glusti et al., 1974; Zogorski et al., 1976; Jossens et al., 1978; Crittendan and Weber, 1978; Conway and Ross, 1980; Mathews and Weber, 1980). Only a very limited amount of the literature refers to the adsorption capacities of activated carbon for naphthalene aqueous solution (Fochtman and Eisenberg, 1979; Dobbs and Cohen 1980).

The research presented herein has three objectives:

1. To establish the adsorption isotherm for phenol and naphthalene.
2. To assess the ability of an adsorption model to predict the adsorption rates from single and multicomponent systems.
3. To compare the adsorption processes among fluidized, semifluidized, and packed carbon beds.

The scope of this research consisted of:

1. Establishing adsorption equilibria and kinetics of phenol and naphthalene.
 - (1) Adsorption equilibrium experiments for single solute and mixtures were conducted at three different temperatures to obtain isotherm parameters.
 - (2) Kinetic studies were conducted to determine adsorption rates and transport parameters. Adsorption rates of single solutes and mixtures were developed for different adsorbent particle sizes and dosages. Multicomponent adsorption rates were predicted from parameters developed from single solute studies.
2. Two phase fluidized, semifluidized, packed beds containing activated carbon were utilized to compare the effectiveness of these three types of beds for adsorption.

CHAPTER II

REVIEW OF PERTINENT LITERATURE

Adsorption Equilibrium

The adsorption isotherm is an expression of the equilibrium, at constant temperature, between the concentration of adsorbate on the adsorbent surface and the adsorbate concentration in aqueous solution. Commonly, the amount of adsorbate adsorbed per unit weight of adsorbent increases with increasing concentration, but not in direct proportion.

Representative isotherms are shown in Figure 1. In these plots, p is the vapor pressure, or condensation pressure, of the solute (Perry and Chilton, 1973). Curves that are convex upward throughout (Type I) are designated as "favorable" to uptake of solute; those that are concave upward throughout (Type III) as "unfavorable" to uptake of solute. (The terms favorable and unfavorable actually refer to the uptake step for the component to which the isotherm applies, the opposite designation holds for the discharge step; thus, elution is "unfavorable" for a component having a "favorable" isotherm.) Other isotherms (Type II, IV, V) have one or more inflection points. Adsorption isotherms can be classified as to whether they describe the adsorption of a single or competitive adsorption of two or more solutes.

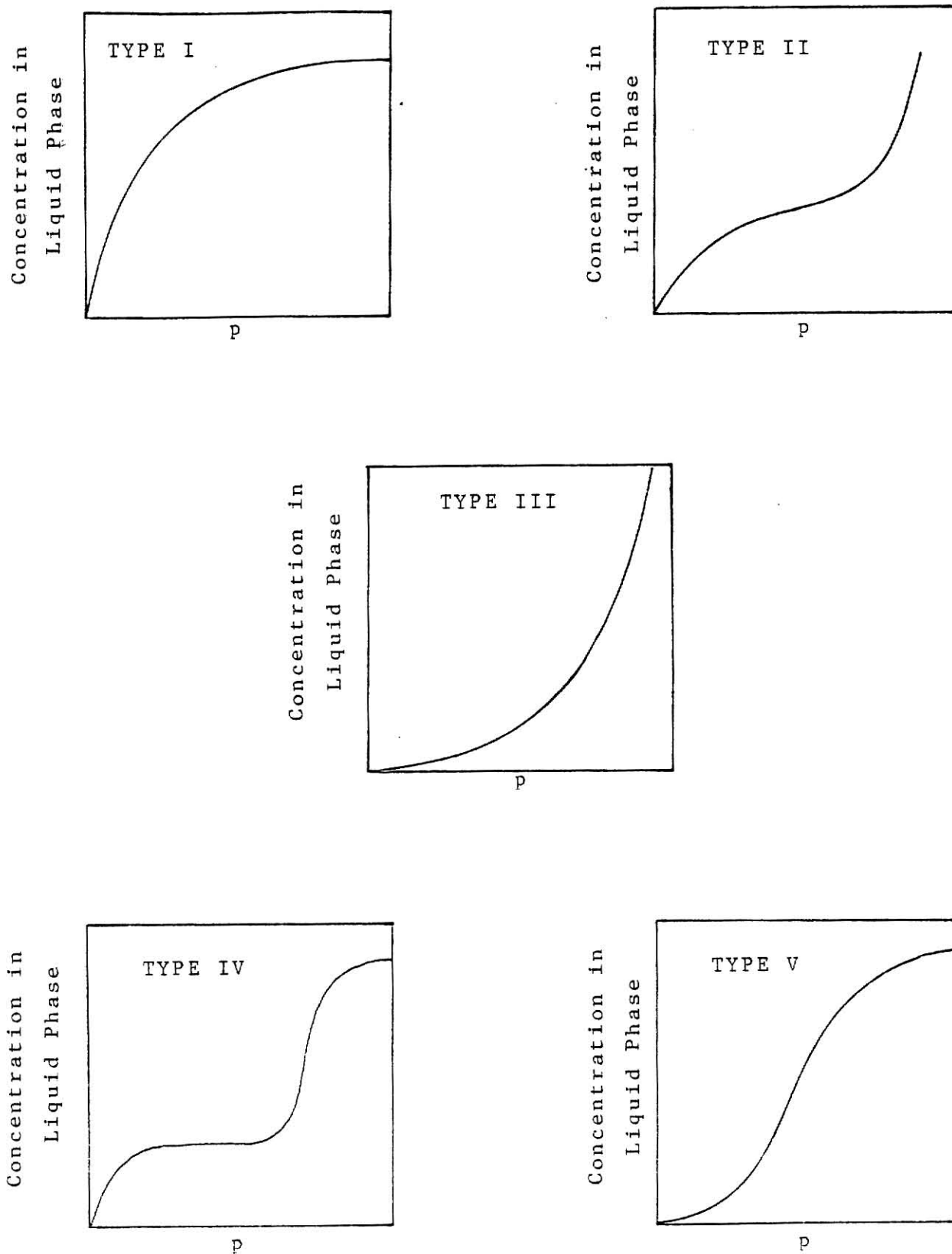


Figure 1. Representative Types of Experimental Isotherms for Physical Adsorption

Single-solute Equilibrium

Single-solute equilibrium data can generally be well described by one or more isotherm equations.

The purpose of fitting experimental data to an isotherm equation is to provide a means by which various systematic parameters exhibited in the adsorption process could be evaluated and described comprehensively.

Most researchers fit their experimental data to the Freundlich and Langmuir Isotherms. The Freundlich adsorption isotherm (Freundlich, 1926) is

$$q_e = KC_e^n, \quad n < 1$$

$$\text{or } \log q_e = \log K + n \log C_e$$

where q_e represents the number of moles of solute adsorbed per unit weight of adsorbent, C_e is the measured concentration of the adsorbate in solution at equilibrium, and K and n are parameters. Data which fit the Freundlich isotherm plot as a straight line on full logarithmic paper when the quantity adsorbed is plotted against the equilibrium concentration of adsorbate remaining in solution. The Freundlich isotherm is basically empirical but is often useful as a means for data description.

The Langmuir adsorption isotherm is theoretically developed for gas phase adsorption and adapted to adsorption from the liquid phase (Langmuir, 1918),

$$q_e = (ABC_e) / (1 + BC_e)$$

where A is the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the adsorbent surface, and B is a constant related to the energy or net enthalpy of adsorption. The basic assumption of the Langmuir isotherm are: (1) a monolayer of solute molecules is adsorbed on the adsorbent surface, (2) energy of adsorption is constant; and (3) no migration of adsorbed solute molecules on the plane of the adsorbent surface (Langmuir, 1918).

Two convenient linear forms of the Langmuir equation are,

$$C_e/q_e = 1/BA + C_e/A$$

$$\text{or } 1/q_e = 1/A + (1/BA)(1/C_e)$$

Either of these forms may be used for linearization of data that accord with the Langmuir adsorption isotherm. The Langmuir isotherm predicts a saturation surface concentration (the monolayer), A, for high solution concentrations, and it reduces to the linear isotherm at low solution concentrations. The literature on adsorption by activated carbon in aqueous systems indicates that a single set of Langmuir or Freundlich constants cannot describe adsorption over the entire concentration range of interest, for example, from 0 to 1 mmoles/liter (Snoeyink et al., 1969; Jossens et al., 1978).

Equilibrium data over a solution concentration range of several decades may not be adequately described by either Freundlich or Langmuir isotherms; therefore, an empirical equation with three parameters was proposed by Redlich and Peterson (1959), Radke and Prausnitz (1972) and Mathews and Weber (1977),

$$q_e = AC_e / (1 + BC_e^\beta), \quad \beta \leq 1$$

At low solution concentrations it becomes the linear isotherm, at high solution concentrations it becomes the Freundlich isotherm, and for the special case of $\beta = 1$ it becomes the Langmuir isotherm. The parameters A, B, and β must be estimated by the best statistical representation of the experimental data.

Another three-parameter model was recently introduced by Jossens et al. (1978),

$$\ln C_e = \ln q_e - \ln H + Kq_e^p$$

or

$$C_e = [(q_e)/H] \exp(Kq_e^p)$$

where p, H, and K are constants; q_e is the millimoles of solute adsorbed per gram of adsorbent; C_e is the concentration of solute in millimoles per liter. This equation is derived from thermodynamics under the characterization of a highly heterogeneous activated carbon surface. It expresses that the solution concentration is a function of the surface concentration.

An alternative three-parameter equation was suggested by John Newman and used by Radke and Prausnitz (1972),

$$q_e = [(1/AC_e) + \ell (1/BC_e^\ell)] / [(1/AC_e) + (1/BC_e^\ell)]^2$$

where A, B, and ℓ are parameters. But this equation does not provide an adequate fit to p-cresol and p-chlorophenol isotherms.

Multisolute Equilibrium

Until recently the most commonly employed model for describing adsorption equilibrium in multisolute systems was the Langmuir model for competitive adsorption, which was first derived by Butler and Ockrent (1930), Markham and Benton (1931). This model was based on the same assumptions as the Langmuir model for single solute systems,

$$q_i = Q_i b_i C_i / (1 + \sum_j^K b_j C_j)$$

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 of this equation are obtained from single-solute systems.

Schay et al., (1957) proposed the use of interaction terms to modify the Langmuir competitive equation to improve the description of equilibrium data. The model is

$$q_i = (Q_i b_i C_i / h_i) / [1 + \sum_j^K (b_j C_j / h_j)]$$

The h_i are interaction terms, one for each solute, and are evaluated by correlating the model to multisolute experimental data.

Jain and Snoeyink (1973) proposed a bisolute model, which is also a modification of the Langmuir model and which is based on the hypothesis that some adsorption occurs without competition when $Q_1 \neq Q_2$. Further, it was assumed that the number of sites for which there was no competition was equal to the quantity $(Q_1 - Q_2)$, where $Q_1 > Q_2$. This model is expected to be valid due to either chemical characteristics of the sites and solute or molecular exclusion,

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

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

where

q_1 and 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 and Q_2 = maximum values of q_1 and q_2 , respectively, that are obtained from single-solute systems and that correspond to monolayer coverage of the adsorbent.

Mathews (1975) has extended the three-parameter isotherm to multisolute adsorption by forwarding the following equation:

$$q_i = A_i C_i / \sum_i (1 + B_i C_i^{\beta_i})$$

The constants are evaluated from a single-solute system that is described by the three-parameter isotherm. For multisolute systems not adequately described by this equation, Mathews proposed applying the Schay et al.'s correlation procedure

$$q_i = [A_i (C_i/h_i)] / \{ \sum_i [1 + B_i (C_i/h_i)^{\beta_i}] \}$$

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

$$q_i = (B_{io} C_i^{b_{io}}) / (E_i + \sum_j B_{ij} C_j^{b_{ij}})$$

where B_{io} , B_{ij} , b_{io} , b_{ij} , E_i are parameters. For some values of the parameters, the model reduces to the Langmuir competitive model or Mathews's multisolute extension of the three-parameter isotherm. Some parameters may be obtained from multisolute data. The authors illustrated a method for determining the constants for a bisolute system in which the solutes individually conformed to the Freundlich isotherm.

Another three-parameter model was introduced by Redlich and Peterson (1959),

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

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

The ideal adsorbed solution model was developed from dilute solution thermodynamics by Radke and Prausnitz (1972A) by using the method of Myers and Prausnitz (1965) for gas mixtures. It predicts multisolute equilibrium using single-solute isotherms and is not restricted to any specific single-solute isotherm. The model is based on some assumptions: (1) the available specific surface area is identical for all adsorbates, (2) the adsorbed phase forms an ideal solution. There are some possible drawbacks to the ideal adsorbed solution model: Single-solute isotherm data is required at extremely low concentrations. The low concentration data required is generally below concentration of $5 \times 10^{-5} \text{ M}$ and varies with the solute. For strongly adsorbed solutes, predicted results are not in good agreement with experimental data. It shows systematic deviations from experimental results at high surface coverages.

Rosene and Manes (1976) have derived a multisolute model based on the Polanyi adsorption theory and thermodynamic principle. They developed a graphical technique (Correlation Curves) to predict the surface concentration according to the equilibrium solution concentration. This graphical technique was not converted to systematic equations, and it is difficult to use.

DiGiano et al. (1978) have presented a simplification of the IAS model. It is in good agreement with the IAS model in the concentration range of 0.01 mmol/l - 0.1 mmol/l, but results may

diverge at higher concentrations. When single-solute equilibrium is described by the Langmuir isotherm and all the species in the mixture have the same monolayer coverage value, then the simplified model is identical to the competitive Langmuir isotherm. For single-solute equilibrium described by the Freundlich isotherm, the simplified model gives a set of equations to determine the surface loading of every species in a mixture.

$$q_i = Qb_i C_i / (1 + \sum_{i=1}^N b_i C_i), \quad i = 1, N$$

$$q_i = K' [n' - (1/n')] [K_i C_i^{n_i}]^{1/n'} \{ \sum_{i=1}^N [(K_i/K') C_i^{n_i}]^{1/n'} \}^{n'-1}$$

where n_i , K_i are constants in the Freundlich equation describing single solute adsorption. n' and K' , the selected Freundlich constants which may be obtained by averaging the single solute values.

Transport Theory and Mathematical Development

To relate the dynamically varying solid- and liquid-phase concentrations of solute at any time and position in an adsorber, it is necessary to understand the kinetics of solute transport.

The overall rate of adsorption of solute onto granular adsorbent represents the combined effects of (Figure 2): (1) diffusion through the boundary layer of liquid surrounding the adsorbent particle (film or external diffusion); (2) diffusion

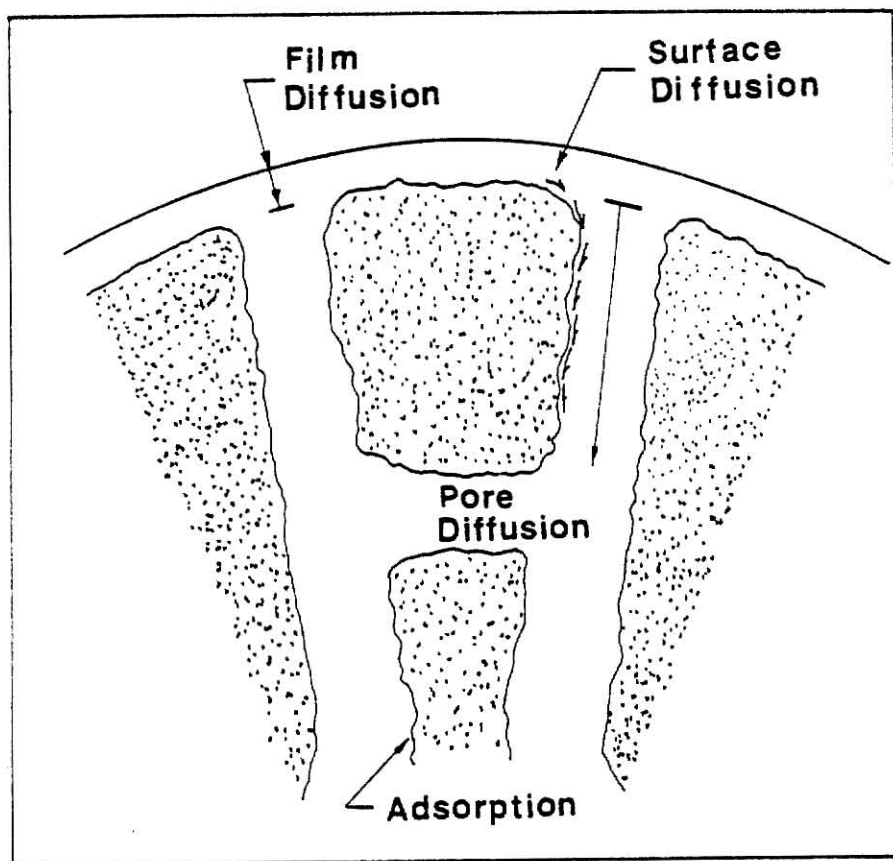


Figure 2. Adsorption on Porous Adsorbents-Rate Limiting Mechanisms.

within the pores of the particle (pore diffusion); (3) diffusion along the surface of the pores (surface diffusion); and (4) adsorption on the internal pore surfaces (adsorption). These mechanisms have been discussed in detail by Weber (1972) and Keinath (1975).

In a rapidly agitated slurry adsorber, the concentration C_k of the solute species k , and the distribution of the adsorbent particles may be assumed to be uniform throughout the reactor. The mass transfer rate of each solute across the film to the solid surface may be equated to the average uptake of the solute to give the following equation:

$$dq_k/dt = [K_{f_k} (C_k - C_{s_k})] / [V\rho(1 - \varepsilon)], \quad k = 1, N$$

C_k and q_k are the concentrations of the solute in the liquid and solid phases expressed in moles/liter and moles/g, respectively. C_{s_k} is the equilibrium concentration in the liquid phase, and K_{f_k} is the mass transfer coefficient for each solute. V , ρ and ε are the volume, density and porosity of the particle, respectively. N is the number of adsorbing species in the mixture.

The mean concentration of the entire particle of radius, R (cm), is obtained by integrating the pointwise concentration q_{i_k} over the particle as follows:

$$q_k = (3/R^3) \int_0^R q_{i_k} r^2 dr, \quad k = 1, N$$

For spherical adsorbent particle geometry and Fickian-type diffusion within the internal pores of particle, the transport of the adsorbed species into a spherical particle is represented by the transient diffusion equation as follows:

$$\partial q_{i_k} / \partial t = D_k [(\partial^2 q_{i_k} / \partial r^2) + (2/r)(\partial q_{i_k} / \partial r)] \quad k = 1, N$$

q_i is the dimensionless solid phase concentration at an internal radius r and t is reaction time. The mass balance for the batch reactor is

$$V(dC_k/dt) = -W(dq_k/dt), \quad k = 1, N$$

D_k is the surface diffusion coefficient for each solute, V is the volume of liquid in the reactor, and W the weight of adsorbent in the reactor.

The initial and boundary conditions for the liquid and solid phases are given for $k = 1, N$ by:

$$C_k(0) = C_{k_0}$$

$$q_{i_k}(r, 0) = 0$$

$$q_{i_k}(R, t) = q_{s_k}(t)$$

$$(\partial q_{i_k} / \partial t)(0, t) = 0$$

The initial concentration of solute in the liquid phase is C_{k_0} and zero in the solid phase. The surface concentration in the solid phase is an unknown function of time and the flux at the center of the particles at all time is zero.

Size of Carbon Particles

Morris and Weber (1964, 1964A) have reported results on the effect of carbon particle size on the rate of adsorption of 3-dodecylbenzenesulfonate (DBS) and alkylbenzenesulfonates (ABS). Their results indicated that the rate of adsorption was found to correlate with the inverse of the square of the diameter of the carbon particle.

An inverse relationship between rate of adsorption and carbon particle radius was observed by Dedrick and Beckmann (1967), Martin and Al-Bahrani (1978).

Based on these results and the discussions made by other researchers, it is apparent and appears significant that decreasing the carbon particle size enhances the kinetics of adsorption. Therefore, to keep the carbon particle size as small as possible is highly desirable for column type operations designed for plants, so that higher adsorption rates can be reached.

The effect of particle size on the adsorption capacity of carbon is not as clear as that for the kinetics of adsorption and appears to rely on the carbon-solute systems under research.

Weber and Morris (1964, 1964A), Cover and Pieroni (1967) found that adsorption capacity was affected by particle size; however, Dedrick and Beckmann (1967), Martin and Al-Bahrani (1978), Letterman et al. (1974) found no such effect. Since diffusion into large particles is slower, equilibrium takes a longer time to achieve for large particles. If equilibrium is not fully attained when data for the isotherm are measured, the results would show a decrease in capacity with an increase in particle size. It is also possible, however, that differences in the activation process for various size ranges of activated carbon could affect adsorption capacity (Peel, 1980).

Temperature

The dependence of adsorption capacity on the temperature of the system has been evaluated.

The effect of temperature on adsorption capacity of phenol was investigated by Snoeyink et al. (1969) and was found to be not very great. Morris and Weber (1964) studied the temperature dependence of the benzenesulfonate at 9.5°C, 30.0°C and 48.5°C. Mattson et al. (1969) studied the p-nitrophenol at 16.3°C, 25.0°C and 40.3°C. These studies indicate that the equilibrium amount adsorbed decreases with increasing temperatures. The results of this indication lead to the conclusion that the adsorption is an exothermic process. Over the narrow equilibrium concentration range 0 - 100 mg/liter of phenol on activated carbon Filtrasorb-400, the influence of temperature

can be regarded as insignificant (Peel et al., 1980). Radke and Prausnitz (1972) studied the adsorption of propionitrile and 2-propanol within the concentration range $10^{-4}\text{M} - 10^{-1}\text{M}$ under three different temperatures, and their results indicated the effect of temperature was pronounced at the lower concentrations.

Effect of pH

The influence of pH on the kinetics of adsorption, adsorptive capacity and breakthrough characteristics of commercially available activated carbon has been reported (Middleton et al., 1952; Renn and Barada, 1961; Myrick and Ryckman, 1963; Spicher and Skrinde, 1963; Ryckman et al., 1964; Robinson et al., 1967; Schwartz. Jr., 1967; Ward and Getzen, 1970; Rosene and Manes, 1976; Myers and Zolandz, 1980). The pH value have had a significant effect on the results of studies conducted in the vicinity of the pK_a . Ward and Getzen (1969, 1970) studied the adsorption of weak organic acids (benzoic acid; phenoxyacetic acid; 2, 4-Dichlorophenyl acetic acid; 2, 4-Dichlorobenzoic acid; 2, 4-dichlorophenoxy acetic acid; 3,6-Dichloro-2-methoxybenzoic acid) onto active carbon from aqueous solutions and found maximum adsorption at pH near the pK_a of the acid.

However, the phenol pK_a value of 9.89 is well above the pH range reported in most of the studies. At pH = 7 phenol exists predominantly in the neutral form, and changes in capacity appear to be due largely to the competitive effect of the increased

quantity of acid adsorbed with decreasing pH (Snoeyink, 1969). Myers and Zolandz (1980) found that in the pH range of 2 - 7 the adsorption of phenol was affected little, and they showed significant changes in capacity to be due to a change from the neutral to the anionic species at high pH.

Column Studies

The granular activated carbon column has become a widely employed treatment unit for removal of trace concentrations (usually less than 1 mg/liter) of various pollutants from surface and groundwater. Normally, this is utilized for removal of organic compounds from water via adsorption mechanisms where it is reasonably effective and efficient (Youssefi and Faust, 1980). Keinath and Weber (1968) investigated that the slope of the breakthrough portion of the concentration-time profile became steeper with increasing flow rate in fluidized beds from 6 experimental columns of which each contained the same amount of carbon. As a general rule, the longer the contacting time (i.e. decrease in flow rate), the higher the percentage of the ultimate capacity of the carbon that can be realized before appreciable breakthrough of influent organics. This was observed by Weber and Morris (1965), Martin and Al-Bahrani (1978) in their studies using fluidized beds. Removal of phenol using packed beds has been researched by Crittenden and Weber (1978), Peel and Benedeck (1980) and Modell et al. (1980).

CHAPTER III

EXPERIMENTAL MATERIALS AND METHODS

Materials

1. Adsorbents

The selected adsorbents and their properties are shown in Table 3.

The granular carbon was prepared for the studies by mechanical sieving with RO-TAP Testing Sieve Shaker (TYLER INDUSTRIAL PRODUCTS) to obtain a relatively narrow range of particles passing through U.S. Standard Mesh Sieves. From this, two sizes 18/20 (particles that pass sieve number 18 but retained on number 20) and 40/50 were chosen. Geometric mean diameters for these two groups of particles were 0.917 and 0.353 millimeter, respectively. Some granular carbon particles were ground in a household type blender to provide smaller particle sizes of 200/230 for equilibrium studies. After sieving, the carbon samples were washed several times in distilled water to remove any dusts and fines and then dried to constant weight in thin layer in an oven at 110°C. These carbon samples were stored in glass bottles until used.

Table 3. Selected Adsorbents and Their Properties *

	Filtrisorb-400	APC
Manufacturer	Calgon Co., PA.	Calgon Co., PA.
U.S. standard mesh size	12 x 40	12 x 40
Raw material	Bituminous Coal	Bituminous Coal
Physical properties:		
Surface area, m ² /g	1,000 - 1,200	1,525
Pore volume, cc/g	0.94	--
Apparent density, g/cc	--	0.34
Density wetted in water, g/cc	1.3 - 1.4	2.25
Bed density backwashed and drained, lb/ft ³	25	--
Effective size, mm	0.55 - 0.65	--
Uniform coefficient	1.9 or less	--

* Source: Calgon Activated Carbon Product Bulletin, Pittsburgh, PA.

2. Adsorbates

The solutes used in this research were obtained in the purest form available from commercial supply companies. Both reagents were obtained in crystal form, phenol as 'Baker Analyzed' reagent (Baker Chemical Co., Phillipsburg, NJ) and naphthalene as certified reagent (Fisher Science Co.). The supplier, purity, molecular weight and solubility of the chemicals are presented in Tables 4 and 5.

Diffusion coefficients in liquids are typically about four orders of magnitude smaller than in gases and are therefore more difficult to measure accurately. The recommended relation for estimation of diffusivities of non-electrolytes in liquids at low concentrations of the diffusing component is (Wilke and Chang, 1955)

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

where

D_L = diffusivity of solute at infinite dilution, cm^2/sec ;

μ = solution viscosity, centipoise;

T = absolute temperature, $^{\circ}\text{K}$;

X = association parameter;

M = solvent molecular weight;

V_o = molal volume of solute at normal boiling point.

In this study, diffusivities of phenol and naphthalene in water can be computed by using the above equation and some tables in

Table 4. Adsorbates and Their Properties

	Phenol	Naphthalene
Supplier	J.T. Baker Chemical Co.	Fisher Science Co.
Grade	Baker Analyzed Reagent	Certified Reagent
Formula	C_6H_5OH	$C_{10}H_8$
Molecular weight	94.1	128.18
pK_a	9.89	--
Melting point	43°C	80.55°C
Boiling point	181.75°C	218°C
Diffusivity in water ($10^6 \text{ cm}^2/\text{sec}$)	6.601 at 10°C	5.472 at 10°C
	8.892 at 20°C	8.215 at 24°C
	11.54 at 30°C	9.569 at 30°C

Table 5. Solubility of Solute in 100 parts of Solvent

Solute	Water	Methyl Alcohol	Reference
Naphthalene	0.003 ^{25°C}	9.5 ^{19.5°C}	**
	0.0022 ^{15°C}		(Mitchell, 1926) *
	0.004 ^{25°C}		(Mitchell, 1926) *
	0.0019 ^{0°C}		(Hilpert, 1916) *
	0.003 ^{25°C}		(Hilpert, 1916) *
		9.9 ^{25°C}	(Christiansen, 1918) *
		4.1 ^{0°C}	(Christiansen, 1918) *
		10.0 ^{25°C}	(Speyers, 1902) * (Ward, 1926) *
Phenol	8.2 ^{15°C}		**
	8.108 ^{10°C}		(Lichty, 1903) ***
	9.087 ^{20°C}		(Lichty, 1903) ***
	10.156 ^{30°C}		(Hill et al., 1926) ***

* Source: Seidell, A. (Editor), 1941

** Source: Lange, N. A. (Editor), 1979

*** Source: Stephen, H. & Stephen, T. (Editors), 1963

Perry's Chemical Engineers' Handbook, and their values are shown in Table 4.

Stock and working solutions of all adsorbates were prepared with high purity water produced by SYBRON/Barnstead Nanopure system. Distilled water was passed through the ultra pure and organic removal Hose-Nipple Cartridges and again passed through NANO Pure which consisted of 1 organic filter, 2 ultra pure filters and 1 micron filter. Stock solutions were prepared and diluted to the desired concentration with appropriate dilution water approximately 2 to 3 hours prior to the start of an experiment. All solutions were stored in a dark closet maintained at a constant temperature of 24°C. All experiments were initiated within 4 hours after preparing the appropriate solutions.

The solubility of naphthalene is very low, so the first step was to dissolve it by using methyl alcohol, and then diluting to the desired concentration but keeping the methyl alcohol concentration at 2%.

Methods

1. Kinetic Experiments

The experimental system selected for evaluating the kinetics of adsorption of phenol and naphthalene on granular activated carbon was a batch reactor. The batch technique was selected because of its simplicity and ease of evaluating the parameters

which influence the adsorption process. The basic relationship developed therein can be applied to predict the behavior of continuous adsorption systems.

A device was constructed to study the rate of adsorption and is shown in Figure 3. The reaction vessel was 4.5 liter glass jar covered with a lid. Four stainless "L" baffles of 0.5 inch width extended from the lid to 1.5 inch from the bottom of the glass jar. Agitation was provided by a stirring motor with four-bladed stainless steel impeller and the speed of the motor was controlled by a speed-control unit. The stirring rod operated at an appropriate speed so as to keep the carbon particles in suspension, yet minimize fracturing of the granular carbon during the agitation. All subsequent kinetic experiments were conducted at room temperature as 24°C, at the constant speed of 800 RPM.

For each experiment, three liters of adsorbate solution was prepared to the desired concentration and introduced into the reaction vessel. Then the stirrer was inserted and agitated the solution to reach equilibrium with the vessel. Prior to the introduction of a carefully weighed amount of carbon into the vessel, samples were withdrawn for determining the initial concentration. At time $t = 0$, the carbon was introduced into the reactor and rapidly agitated by the mixer. At selected time intervals the stirrer was stopped and the carbon particles were allowed to settle down. After the carbon particles settled, an appropriate volume of solution was pipetted out of the vessel for concentration analysis. Approximately 10 - 15 seconds were required to finish the entire sampling procedure. The volume of

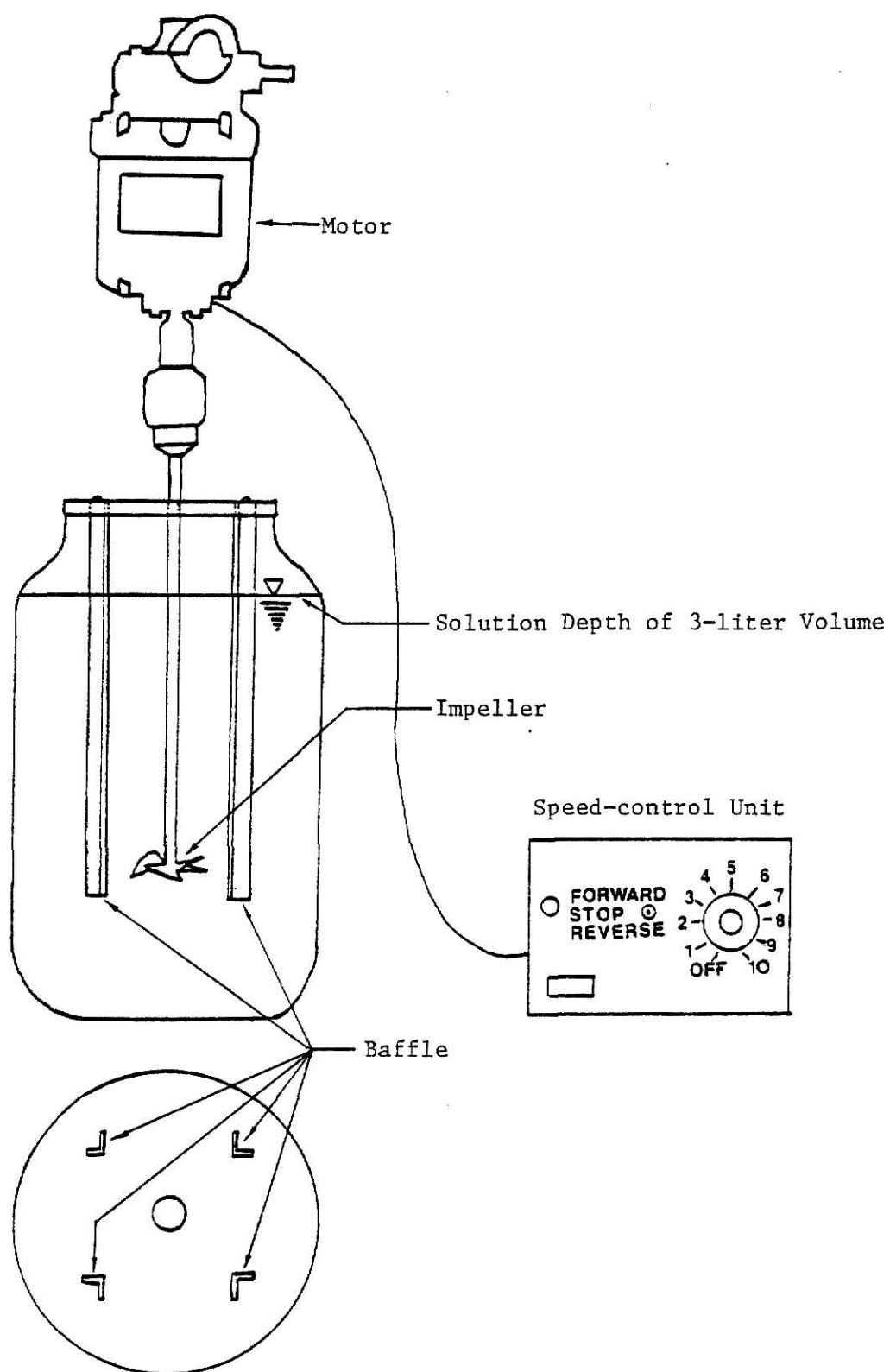


Figure 3. Schematic of the Reaction Vessel for Rate Study.

sample pipetted depended on the size of the cells used to perform the ultraviolet analysis. Since the cells should be cleaned by sample solution, 10 mm cell required a sample volume of about 6 ml while 50 mm cell required a 20 ml volume. The samples collected for analysis resulted in a small decrease in the total adsorbate available to adsorbent and a slight increase in the carbon concentration. Each 6 ml sample was only 0.2% of the total volume while each 20 ml sample represented approximately 0.7% of the total volume. Approximately 10 - 14 samples were collected when the adsorbate was analyzed in 10 mm cell but only 2 - 4 samples were needed if 50 mm cell was utilized. Correction for the decrease in adsorbate available to the adsorbent and increase in adsorbent concentration were not made because the maximum cumulative error of 3 to 6 percent was not considered significant.

2. Equilibrium Experiments

Single and bi-solute equilibrium data were obtained using the bottle-point method. Different amount of 200/230 mesh size carbon were carefully weighed into 180 ml teflon round shaped bottles. The carbon dosage was varied between 0.1 and 1.8 g/0.1 liter. Then 100 ml of solution of known phenol concentration ranging from $10^{-3}M$ to $10^{-2}M$ was added into each bottle. The bottles were tightly sealed with teflon screw caps and placed in a Controlled Environment Incubator Shaker (New Brunswick Scientific Co., Inc.) to provide agitation at the desired temperature.

For naphthalene, the carbon dosage was varied between 0.05 and 0.26 g/l and the range of initial concentration was $10^{-4}M$ to $2 \times 10^{-4}M$. As to mixture, the carbon dosage varied between 0.04 and 0.24 g/l. The ranges of initial concentration of phenol and naphthalene were $10^{-4}M$ to $10^{-3}M$ and $10^{-4}M$ to $2 \times 10^{-4}M$, respectively.

For naphthalene and mixture, the reaction vessels were 1000 ml volumetric flasks with ground glass stoppers. These flasks were washed very clean and dried in the oven at $110^{\circ}C$ before use. These flasks were also placed in the same shaker indicated above for agitation.

Several blanks containing solution without any carbon were included, and served as a check on potential biological degradation or adsorption onto teflon or glass. Several duplicate solutions with carbon were also included to determine when equilibrium is reached.

These bottles and flasks were shaken continuously for a period of 5 to 6 days to reach equilibrium of adsorption reaction. After equilibria were attained each reaction vessel was opened and samples were removed for analysis. Prior to analysis all samples were passed through a GLASS FIBER FILTER (GELMAN SCIENCE, INC.) and the residual concentration in the filtrate was analyzed. The amount of adsorption was computed from differences between the concentration in the blank samples and those in the reacting systems.

The solid or surface phase concentration, Q_e (moles/g), was then calculated from the experimental data using the following equation:

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

where C_o is the initial liquid phase concentration (moles/l), C_e , the final equilibrium liquid concentration (moles/l), and W , the activated carbon dosage (g/l).

3. Column Studies

The experimental system selected for evaluation the adsorption of phenol under continuous flow conditions is shown in Figure 4.

The column, a 2-inch diameter Plexiglas tube, 6 feet in length, was fitted at the bottom with a velocity-head dissipation chamber filled with 2-millimeter glass beads. Two pieces of 140-mesh size brass screen separated the activated carbon in the column from the glass beads in the dissipation chamber. A rigid close-fitting sieve plate was attached to a long rod which could be moved up or down to a fixed position. This was installed in the column to vary the operation from packed bed to semifluidized and fluidized beds.

A continuous flow of tapwater to the column, which had been passed through three-foot long pre-filter filled with activated carbon, was supplied from a polyethylene cylindrical tank which

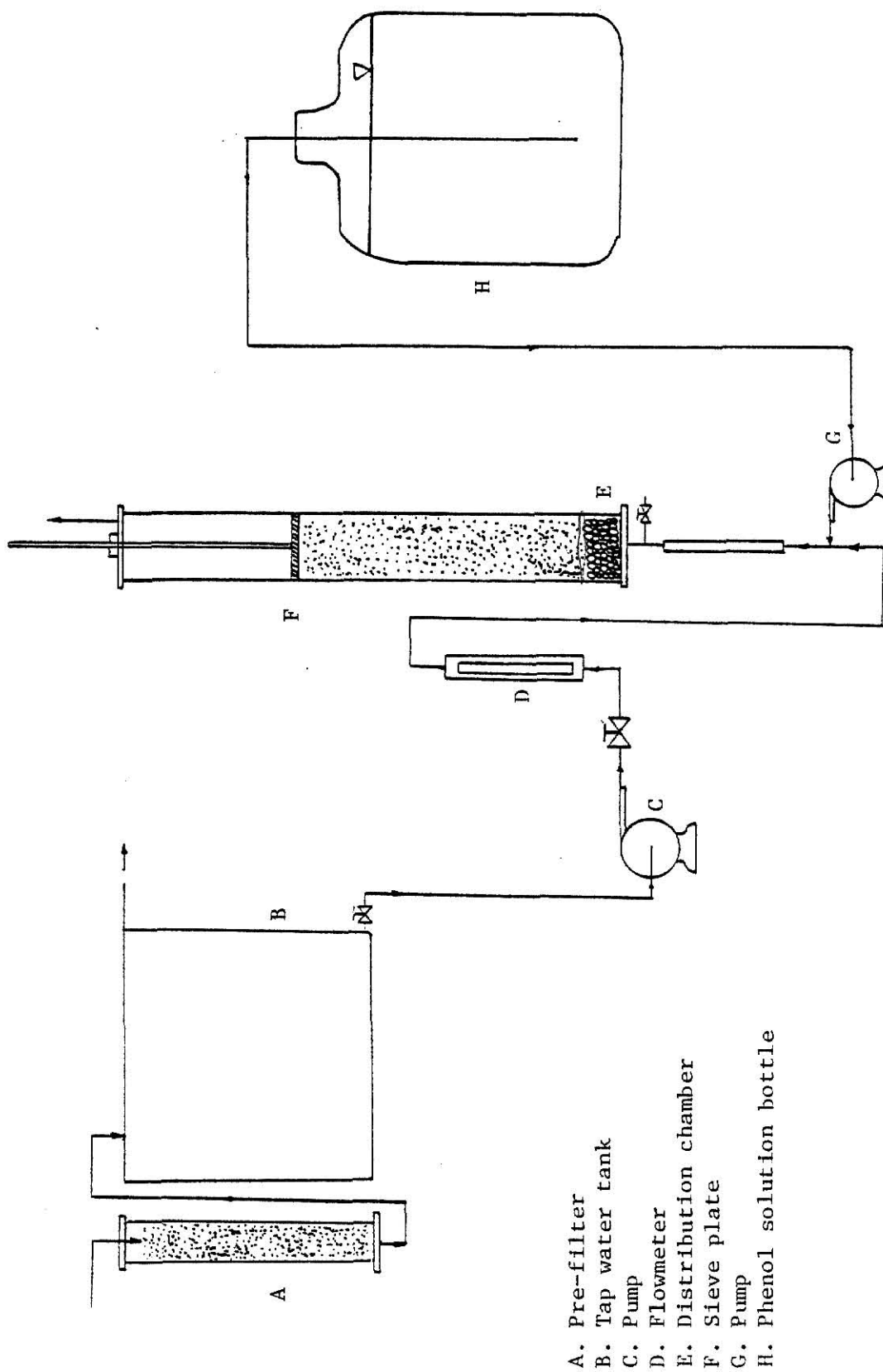


Figure 4. Schematic of Column Equipment.

had a capacity of 30 gallons (114 liters). The tank was tapped via an overflow line and continuously received tapwater, hence a constant static head was provided from this experimental setup. The tapwater was forced through the system by a centrifugal pump and initially directed through the needle valve and a flowmeter as a means of controlling and measuring the flow rate. The phenol solution was pumped from a glass jar by a metering pump and diluted to the desired influent concentration with tapwater in the mixing chamber.

The procedures in setting-up and operating the column experiments involved:

- (a) Preparation of the phenol solution at concentrations of $4.13 \times 10^{-2} \text{M}$: one 45.5 liter, two 19 liter.
- (b) Adding predetermined amounts of carbon to the column.
- (c) Allowing tapwater to flow through the column, avoiding air entrapment by lightly tapping the column.
- (d) For fluidized bed, move up the sieve plate to the top of the column and let the bed expand completely. For semi-fluidized bed, the sieve plate was moved to the location where it could partially restrict the expansion of bed. For the packed bed, the sieve plate was moved down to prevent any expansion from occurring.

Analytical Methods

Single-solute System

The concentration of adsorbate in the experimental solution was analyzed by ultraviolet light absorption spectrophotometry with a Bausch & Lomb Spectronic 710 Spectrophotometer. Preliminary investigations were conducted on each adsorbate to determine its wavelength of maximum absorbance. Once these wavelengths were established, calibration curves of standard solutions were determined for light path lengths of 10 mm and 50 mm. All of the standard calibration curves are shown in the Appendix. Molar absorptivity values for each adsorbate can be figured out from the slopes of the calibration curves and are shown in Table 6.

Bi-solute System

Several kinetic and equilibrium experiments were conducted using mixtures of two adsorbates-- phenol and naphthalene. The wavelengths of maximum absorbance for phenol and naphthalene were 270 and 286 nm, respectively. The procedure used to determine the concentration of each adsorbate in mixtures has been described by Friedel (1951).

Essentially this method consists of developing an absorbance equation at each wavelength of maximum absorbance. The assumption being that the absorbance measured in a mixed system is the sum

Table 6. Molar Absorptivities (l/mole-cm) of Solutes

Solute	Wavelength (nm)		
	286	270	221
Phenol	50	1,463	3,569
Naphthalene	3,180	4,228	50,696

of the absorbance of each compound at that wavelength. The set of simultaneous equations developed to determine the concentration of phenol and naphthalene in mixed system were:

$$A_{270} = \epsilon_{p_1} C_p + \epsilon_{n_1} C_n$$

$$A_{286} = \epsilon_{p_2} C_p + \epsilon_{n_2} C_n$$

in which C_p represents the concentration of phenol, in (moles/liter); C_n the concentration of naphthalene, in (moles/liter); and A_{270} and A_{286} the absorbances of the mixed system at wavelengths of 270 nm and 286 nm, respectively. ϵ_{p_1} and ϵ_{n_1} are the molar absorptivities of phenol and naphthalene, respectively, at wavelength 270 nm; while ϵ_{p_2} and ϵ_{n_2} are the molar absorptivities of phenol and naphthalene, respectively, at wavelength 286 nm.

CHAPTER IV

RESULTS AND DISCUSSION

Equilibrium StudiesSingle-solute Isotherms of Phenol and Naphthalene:

The three-parameter equation given below is utilized in this study to represent adsorption equilibria over a wide concentration range.

$$q_e = AC_e / (1 + BC_e^\beta), \quad \beta \leq 1$$

The isotherm parameters were estimated using a nonlinear parameter estimation computer program which was designed by Mathews (1975). The estimation program uses the principal axis method to obtain the parameters, A, B, and β that will minimize the sum of the squares of the differences between experimental and computed isotherm data.

Results from batch experiments for an equilibrium range of 10^{-6} M to 10^{-3} M of phenol are shown in Figures 5 to 8. An equilibrium concentration range of 10^{-7} M to 4.2×10^{-5} M of naphthalene are presented in Figures 9 to 11. These isotherms are plotted with respect to the equilibrium concentration of solute in the bulk solution against solute on the surface of activated carbon. The data for each solute were analyzed for adherence to

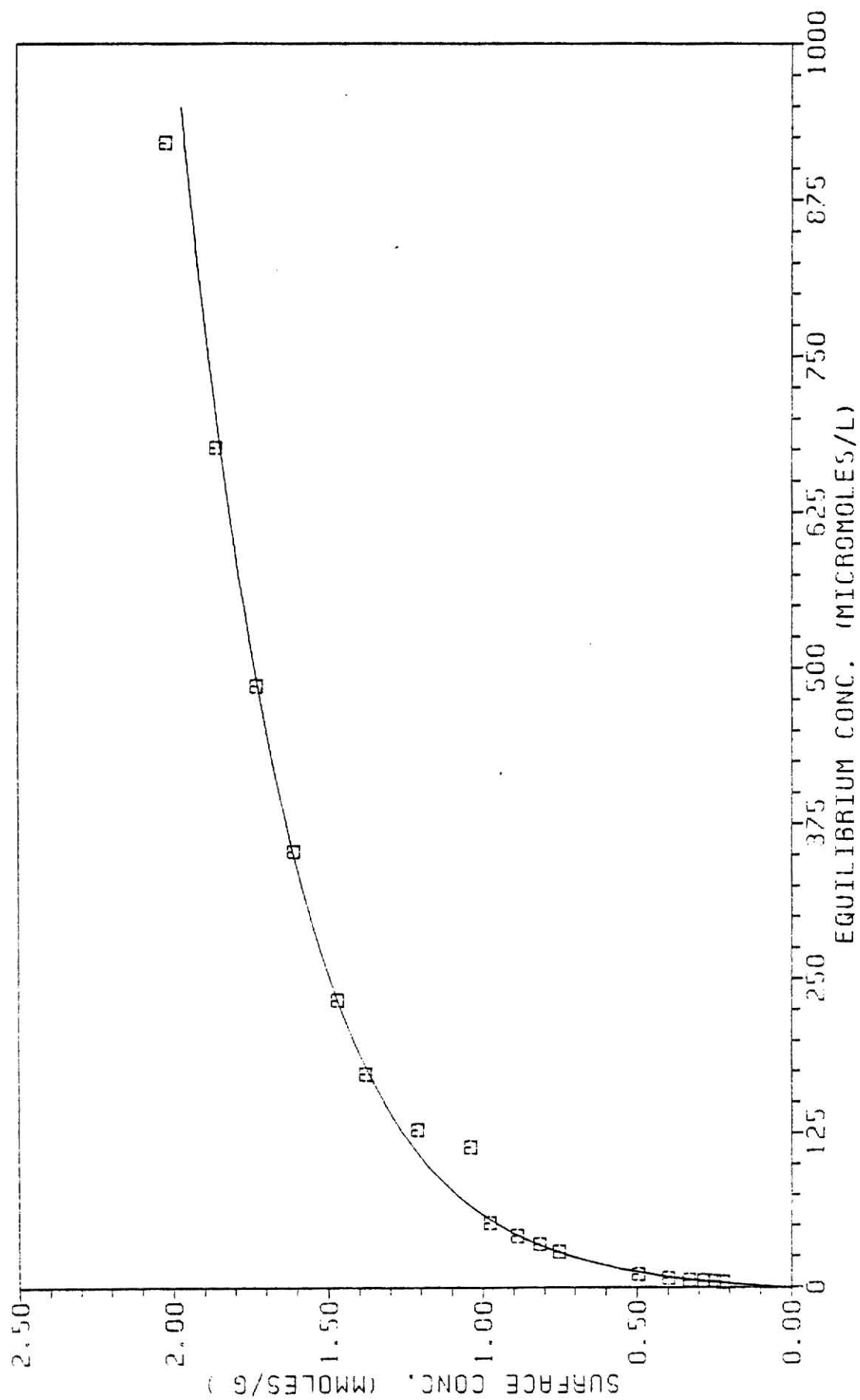


Figure 5. Adsorption Isotherm for Phenol at 10°C:
 (□) experimental data, (—) 3-parameter equation.

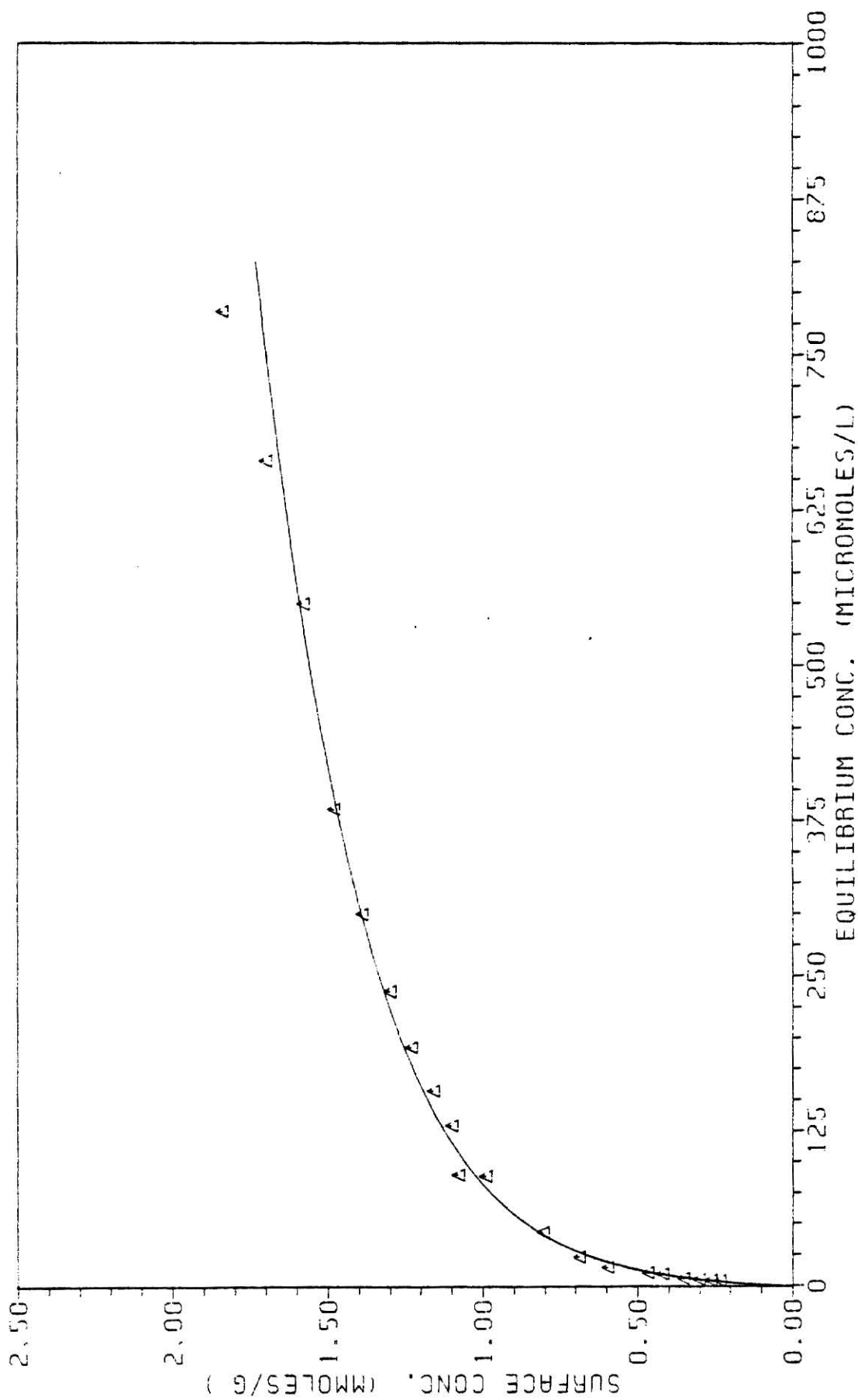


Figure 6. Adsorption Isotherm for Phenol at 20°C:
 (Δ) experimental data, (—) 3-parameter equation.

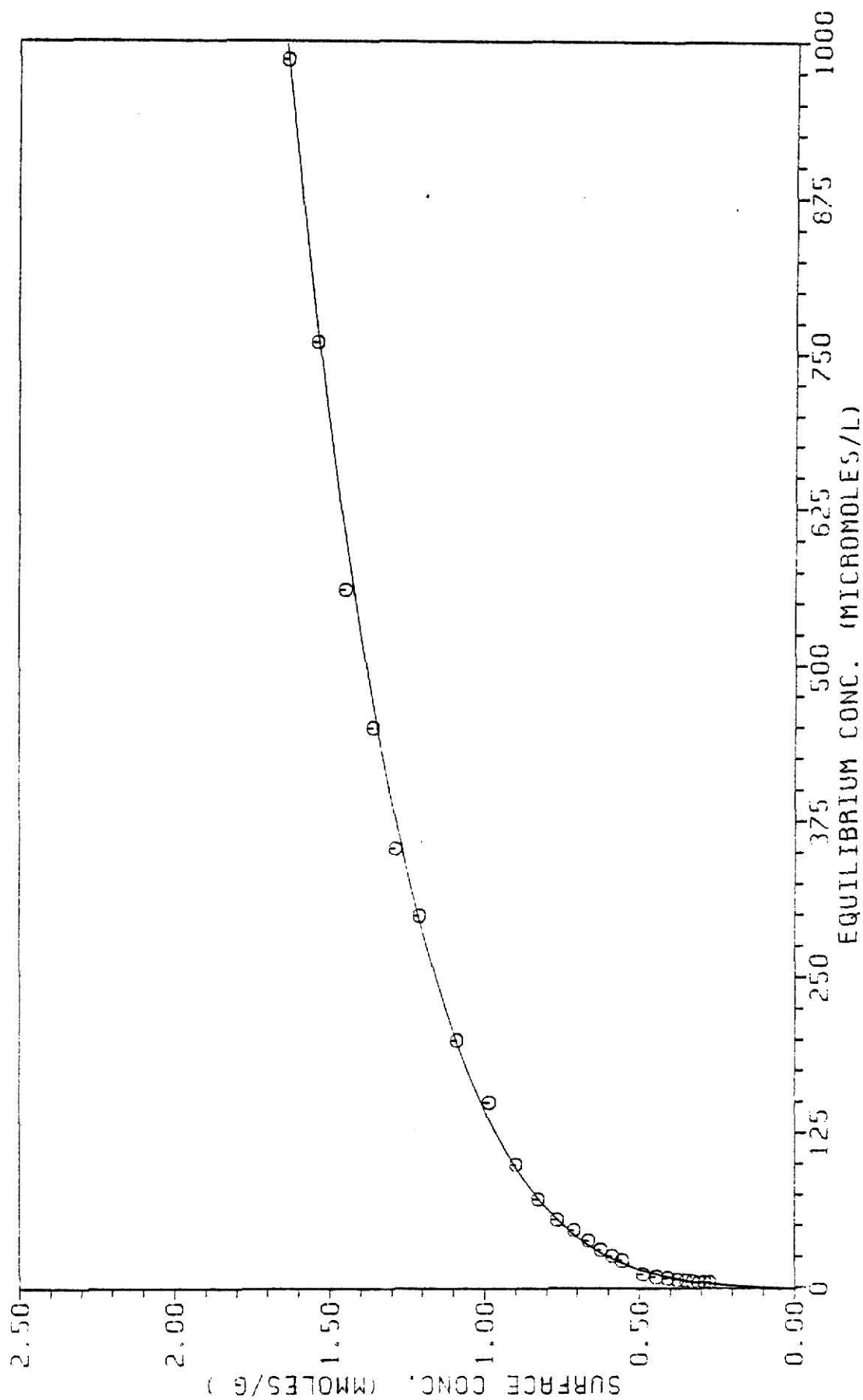


Figure 7. Adsorption Isotherm for Phenol at 30°C:
(○) experimental data, (—) 3-parameter equation.

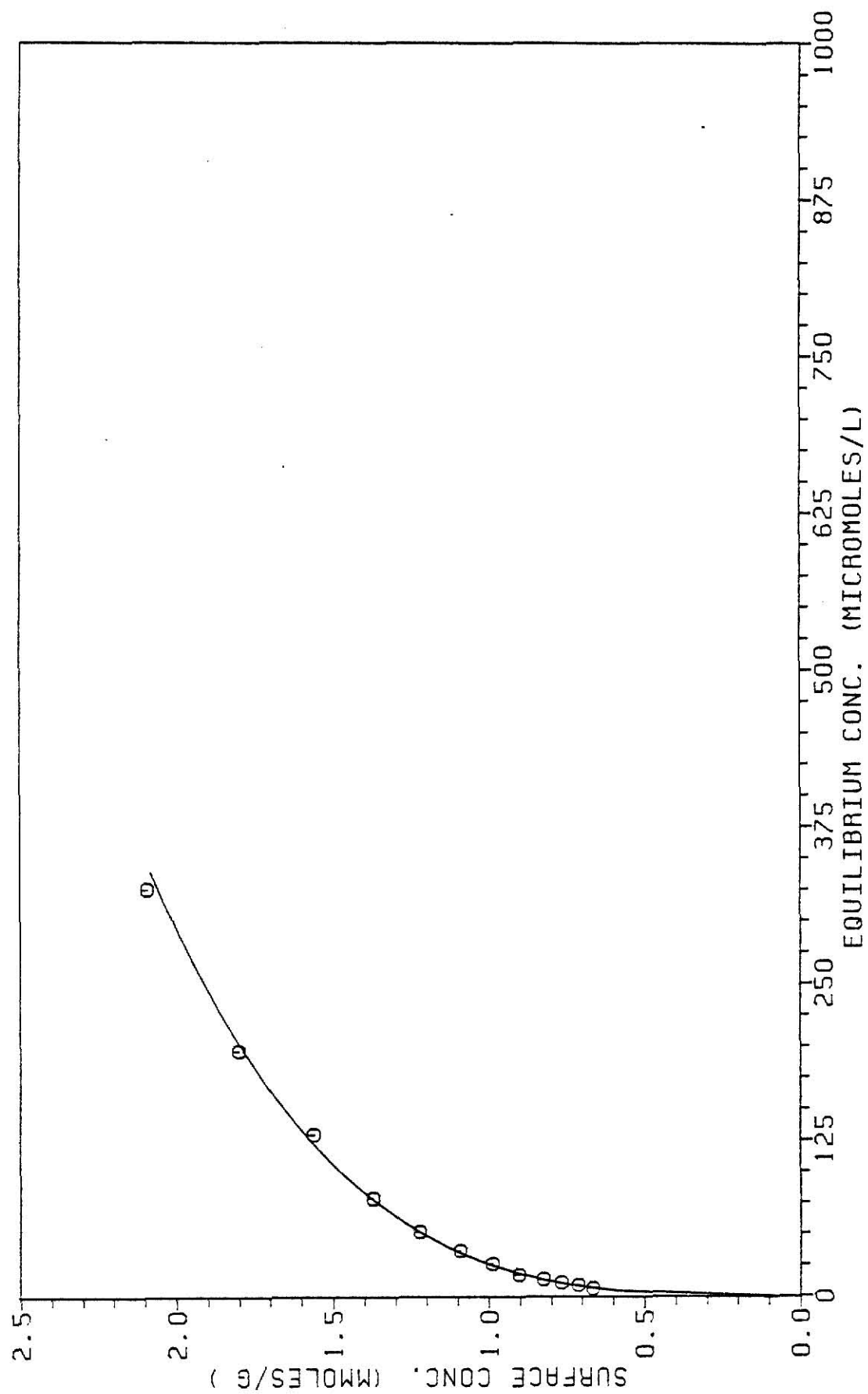


Figure 8. Adsorption Isotherm for Phenol with APC Carbon at 30°C:
(○)experimental data, (—)3-parameter equation

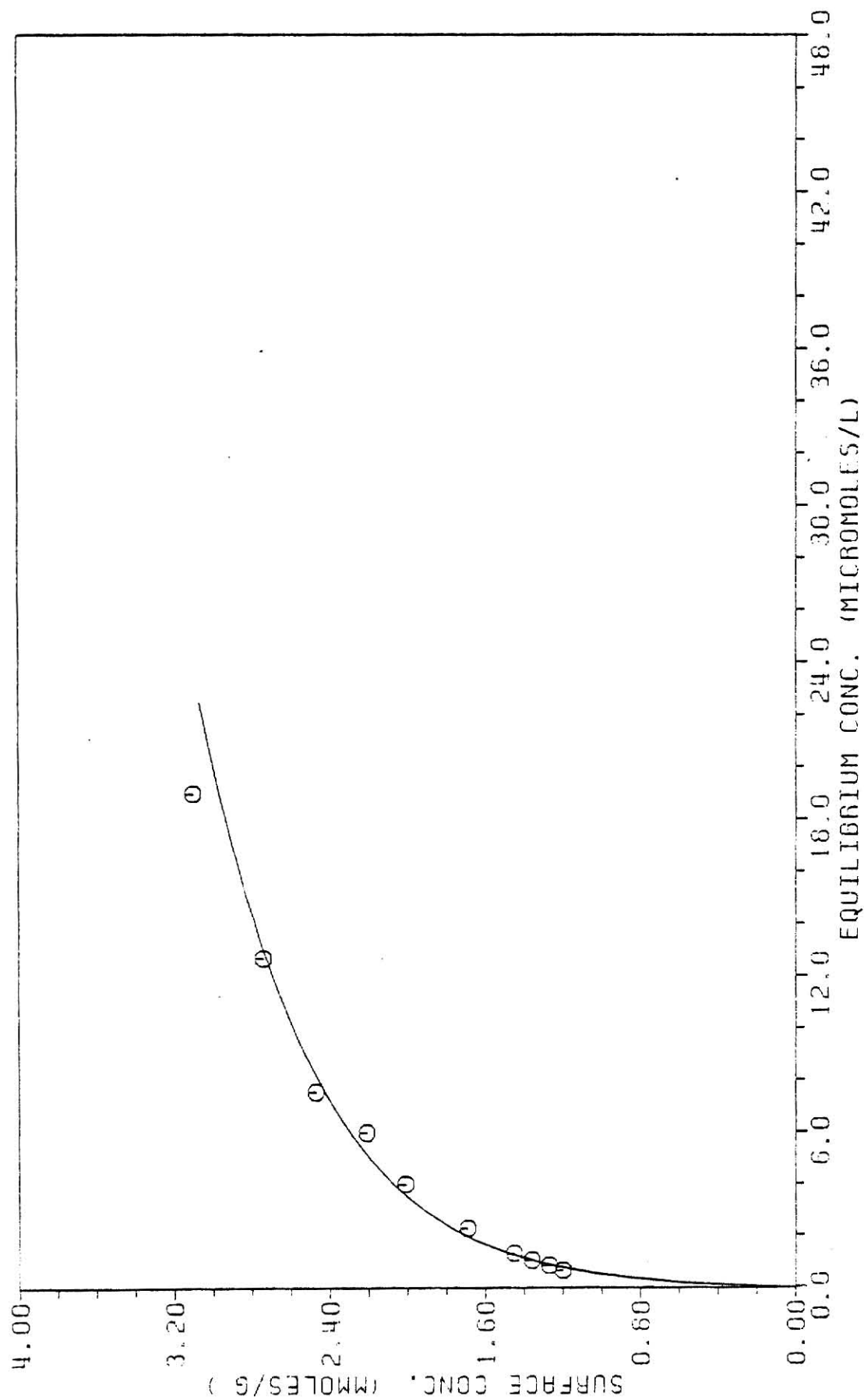


Figure 9. Adsorption Isotherm for Naphthalene at 10°C:
 (○) experimental data, (—) 3-parameter equation.

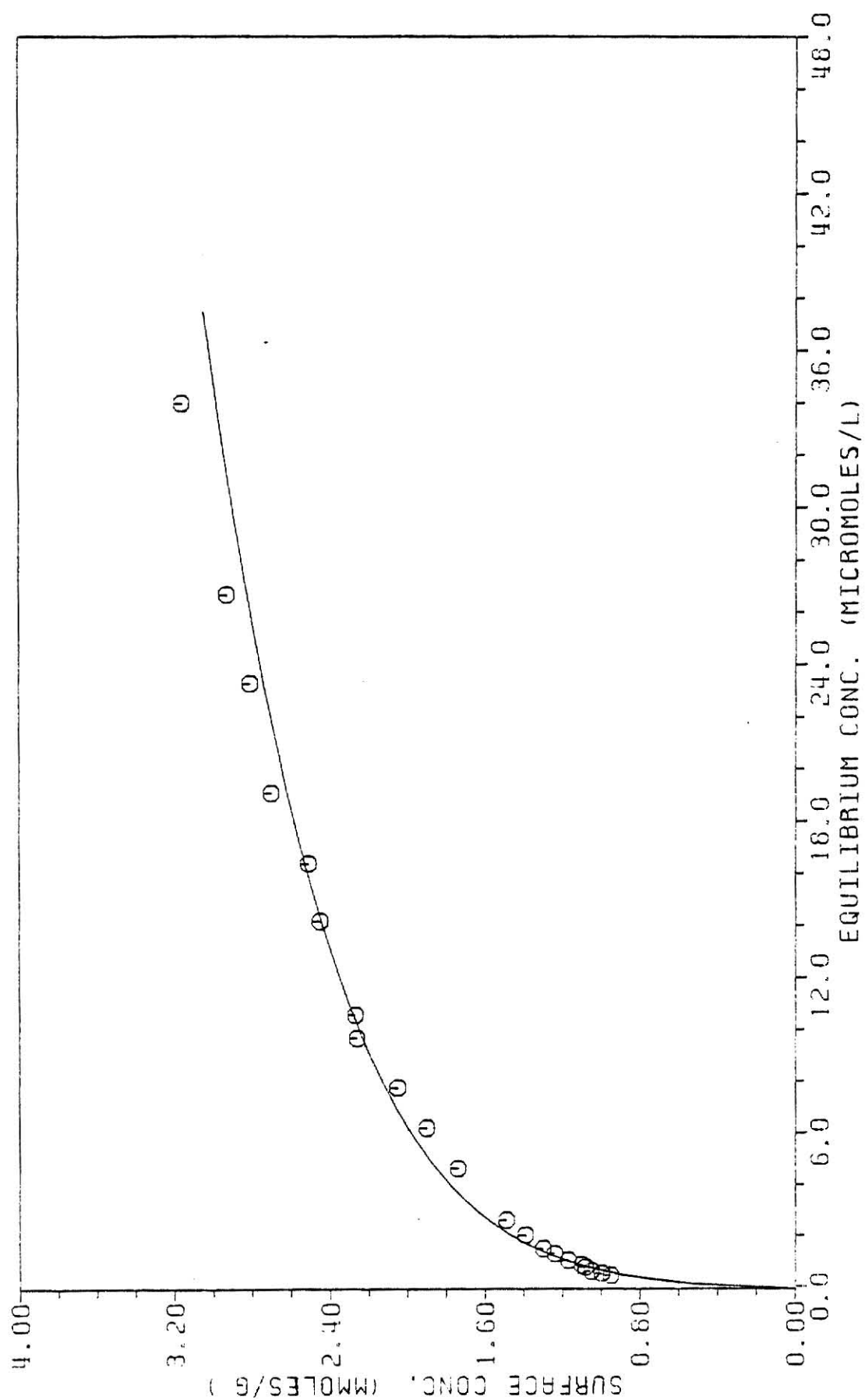


Figure 10. Adsorption Isotherm for Naphthalene at 24°C:
(O) experimental data, (—) 3-parameter equation.

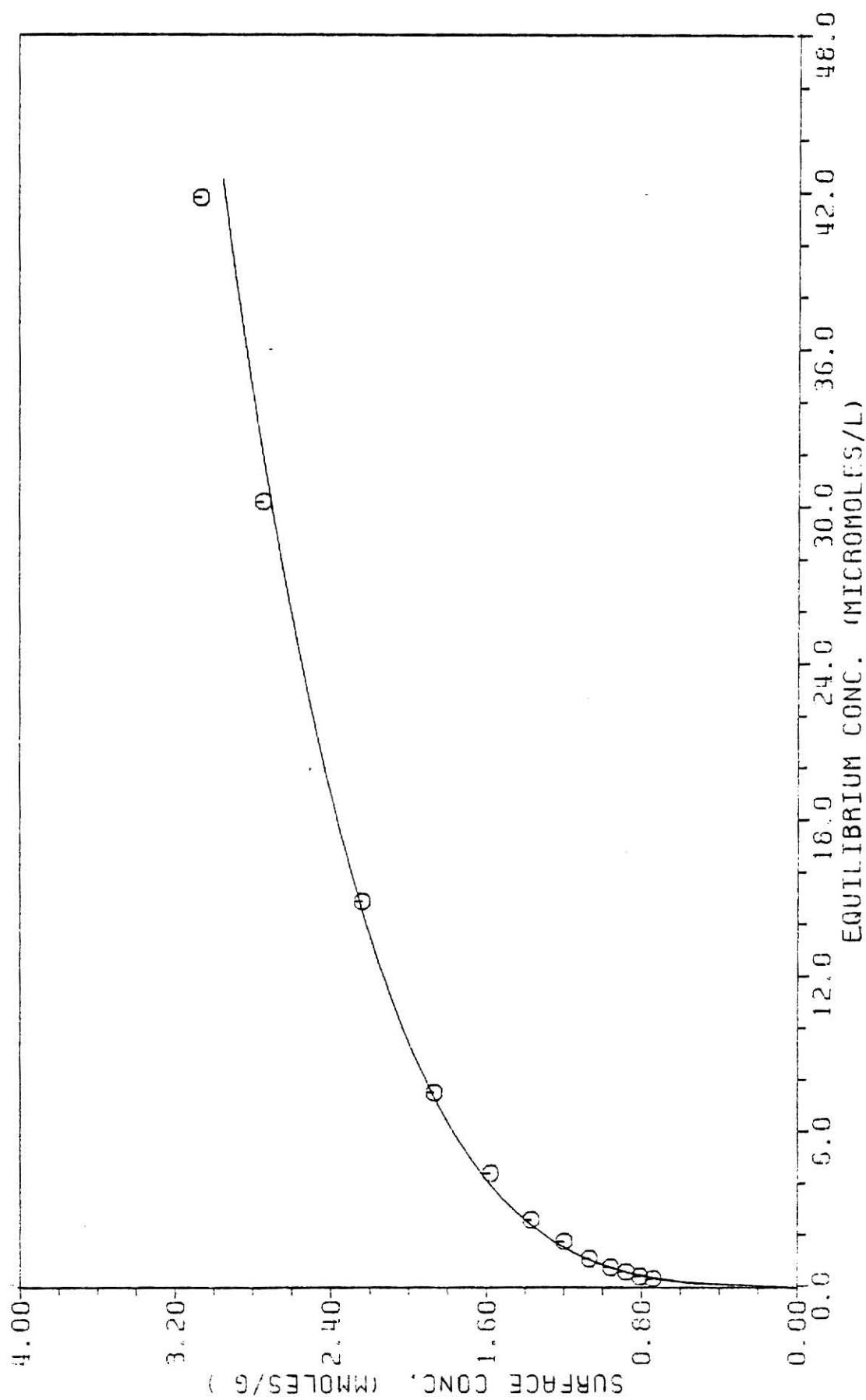


Figure 11. Adsorption Isotherm for Naphthalene at 30°C:
($\circ$) experimental data, (—) 3-parameter equation.

the three-parameter isotherm equation. Isotherm parameters are shown in Tables 7 and 8. For a given activated carbon, naphthalene adsorbs to a greater extent than does phenol. This can be seen by comparing isotherm graphs or by performing calculations with each equation. As shown in Figures 7 and 8 which illustrate the isotherms for adsorption of phenol on two different types of activated carbon (Filtrisorb-400 and APC) at a temperature of 30°C, respectively, the adsorption capacity of APC is greater in magnitude than that of Filtrasorb-400. This difference could be expected due to the larger carbon surface area possessed by APC.

Temperature Effect

Adsorption isotherms were developed for phenol at temperature 10°C, 20°C and 30°C. The results are shown in Figures 5 to 7. Another results of adsorption isotherms for naphthalene at 10°C, 24°C and 30°C are presented in Figures 9 to 11. These results illustrate that the adsorption of phenol or naphthalene is an exothermic process. The amount of adsorbed adsorbate is decreased with higher temperatures.

A method for the calculation of heat of adsorption, ΔH° , has been proposed by Bartell et al., (1951). This method consists in obtaining the equilibrium constant K from the limiting slope of the adsorption isotherms at zero concentration. After the equilibrium constant has been obtained, ΔH° can be calculated by the equation

Table 7. Isotherm Parameters of Phenol *

Temperature	A	B	β
10°C	82.3	40.3	0.8296
20°C	97.5	53.1	0.8101
30°C	183.5	110.4	0.7596
30°C (APC)	1,146.9	407.3	0.7241

* Based on Equilibrium Conc. and Surface Conc. expressed
in MMOLES/L and MMOLES/G, respectively

Table 8. Isotherm Parameters of Naphthalene *

Temperature	A	B	β
10°C	5,064	805.5	0.8184
24°C	5,232	851.2	0.7912
30°C	10,530	1,597.7	0.7485

* Based on Equilibrium Conc. and Surface Conc. expressed
in MMOLES /L and MMOLES/G, respectively

$$\Delta H^{\circ} = -RT(\ln K)$$

In this study, adsorption is

$$q = AC / (1 + BC)$$

$$\text{then } (dq/dt)_{C=0} = A$$

There are not enough data at low concentrations; therefore, heats of adsorption for phenol and naphthalene can not be computed herein.

An isosteric heat of adsorption is defined by using the expression:

$$\Delta H = \ln(C_2/C_1)RT_1T_2/(T_2 - T_1)$$

where C is the equilibrium concentration in the liquid phase with an adsorbed layer of given surface excess, and ΔH is the isosteric heat of adsorption. The isosteric heat of adsorption of phenol and naphthalene are presented in Figures 12 and 13. Both the isosteric heat of adsorption of phenol ranging from 20°C to 30°C and of naphthalene ranging from 24°C to 30°C appear temporarily a peak value during adsorption process. From the figures, the isosteric heat of adsorption is generally proportional to the surface concentration of phenol and naphthalene.

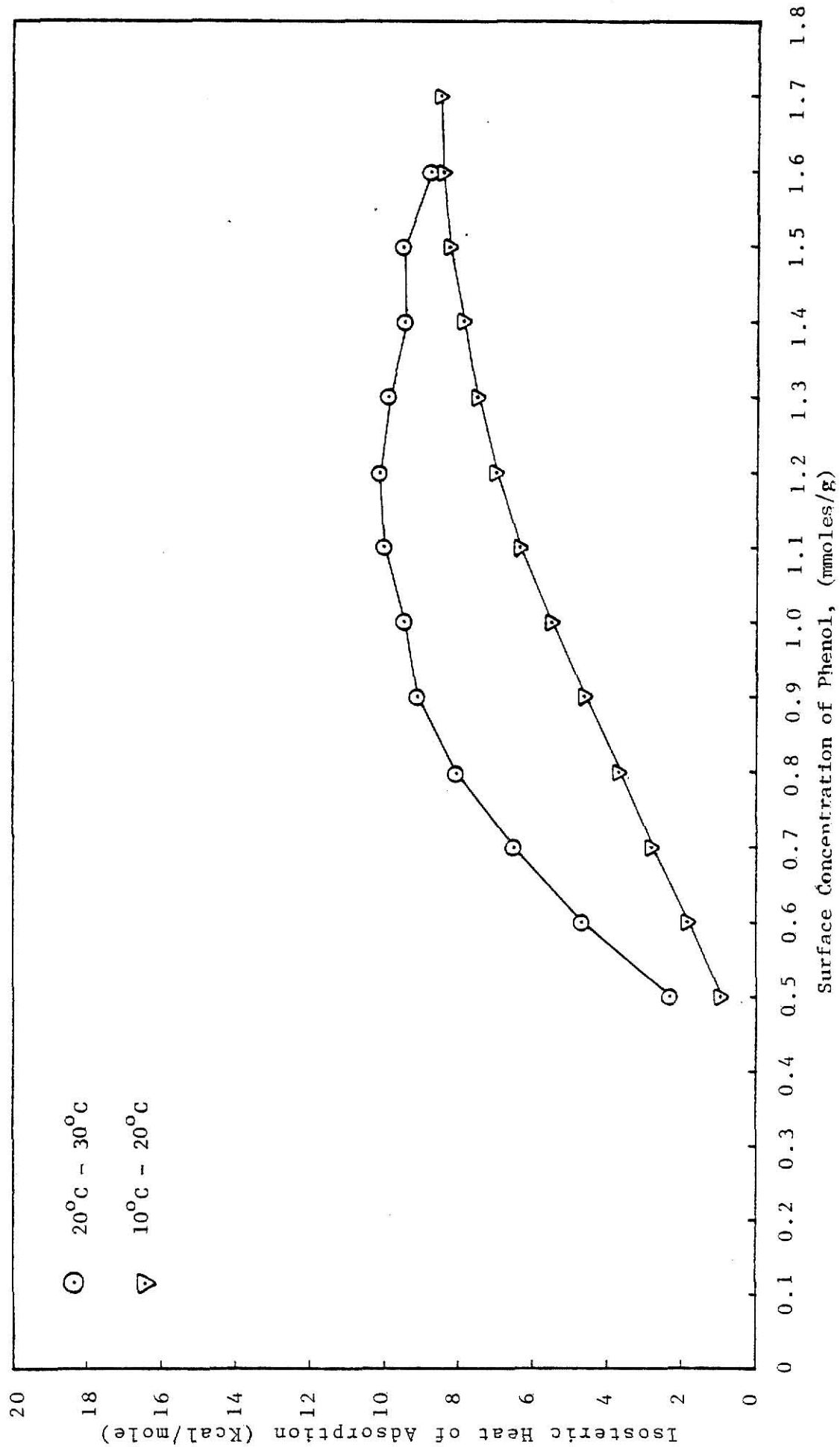


Figure 12. Isothermic Heat of Adsorption for Phenol

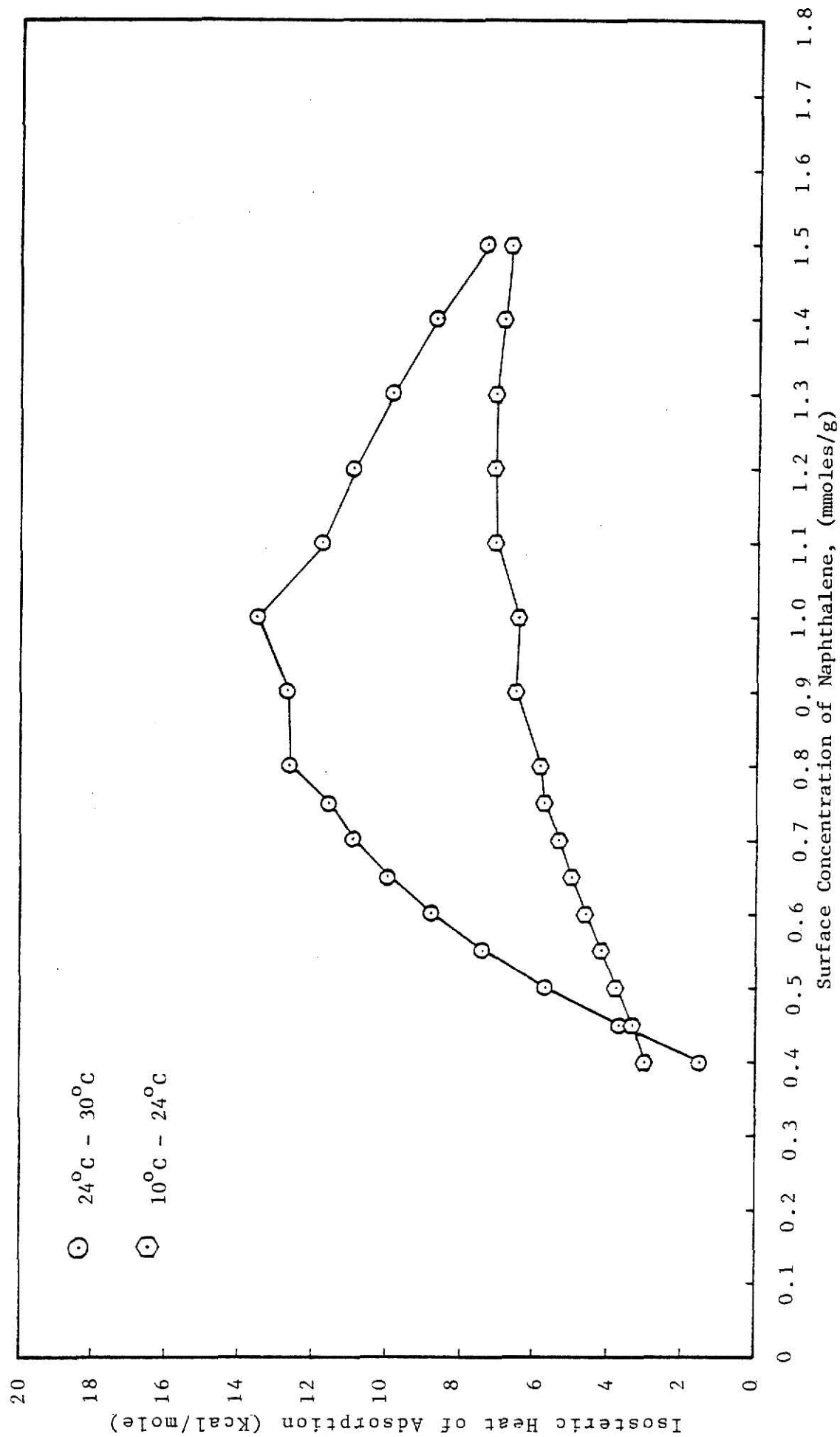


Figure 13. Isothermic Heat of Adsorption for Naphthalene

Solubility

The solubilities of phenol and naphthalene can be figured out by using Table 5 and linear interpolation method and the values are illustrated in Table 9.

The amount of adsorbed adsorbate is plotted versus the ratio of C/C_s . C/C_s is defined as the equilibrium concentration of the adsorbate in bulk solution phase divided by the compound's solubility in this phase at the temperature of the measurement. The results shown in Figures 14 through 18 indicate that the amount of adsorbed adsorbate is increased with lower solubility.

Bi-solute System

Adsorption equilibria for mixtures is represented by (Mathews, 1975):

$$q_i = A_i (C_i / h_i) / \left(\sum_j [1 + B_j (C_j / h_j)^{\beta_j}] \right)$$

The parameters A_i , B_i , and β_i for each solute are obtained from single solute equilibrium data. The h_i are interaction terms and are obtained from mixture equilibrium data using the above A_i , B_i , and β_i developed for each solute species in the parameter estimation procedure.

Adsorption equilibria for phenol-naphthalene are shown in Figures 19 to 21. In these figures, the ratio of the observed equilibrium values and computed values from the above equation

Table 9. Solubilities of Phenol and Naphthalene

Temperature (°C)	Phenol (moles/l)	Naphthalene (moles/l)
10	0.8615	1.638×10^{-4}
20	0.9656	--
24	--	2.278×10^{-4}
30	1.079	--

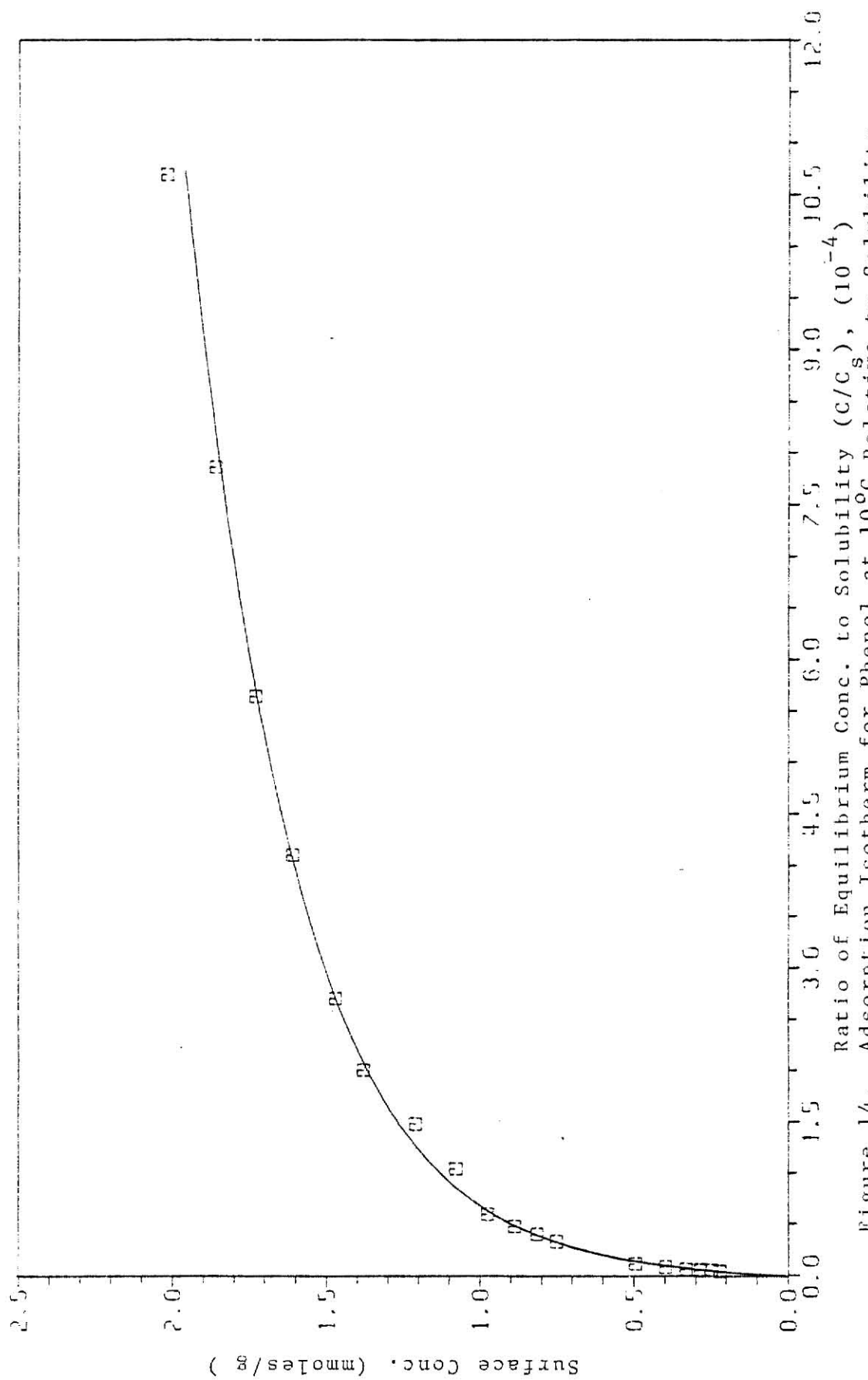


Figure 14. Adsorption Isotherm for Phenol at 10°C Relative to Solubility.

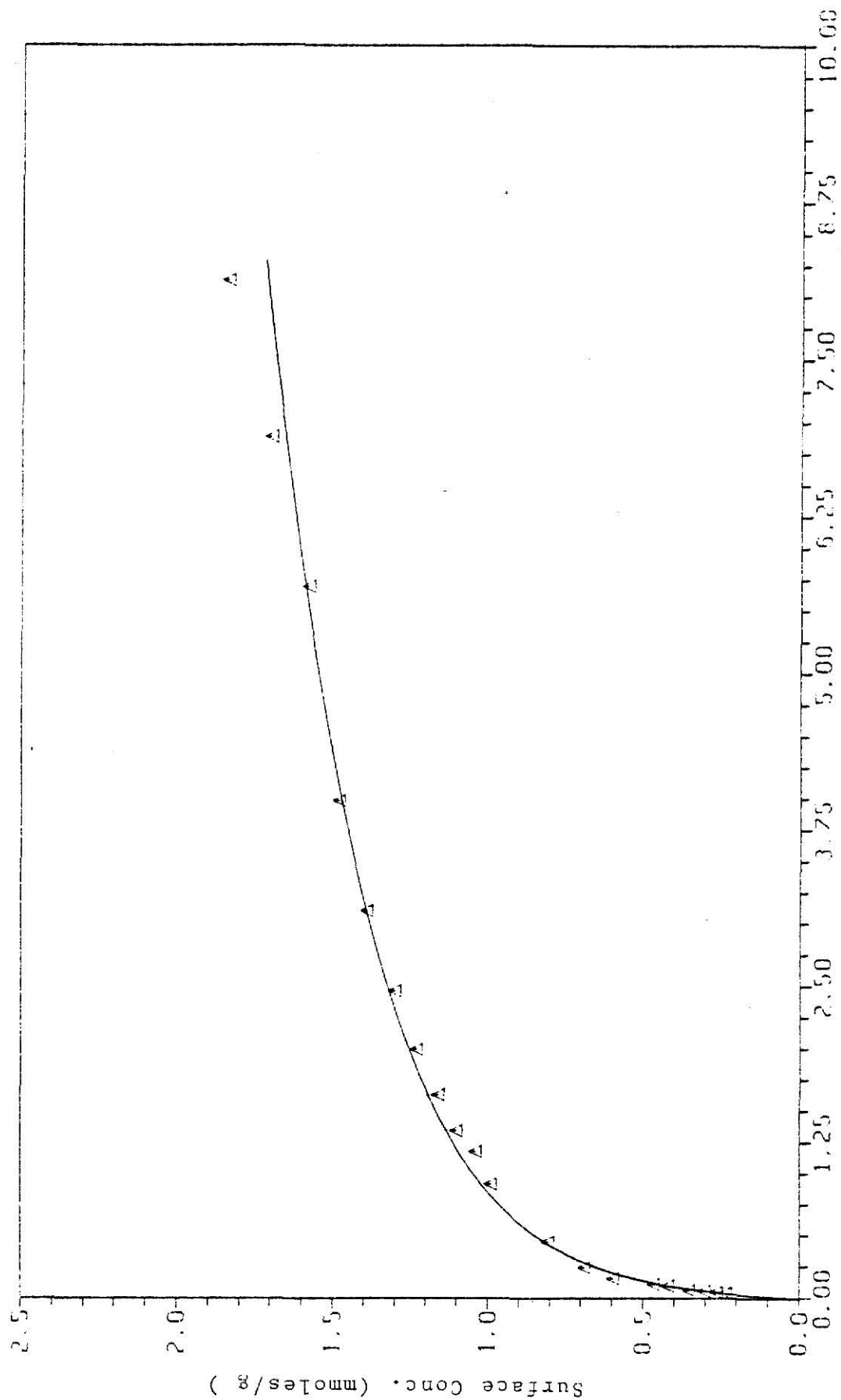


Figure 15. Adsorption Isotherm for Phenol at 20°C Relative to Solubility.

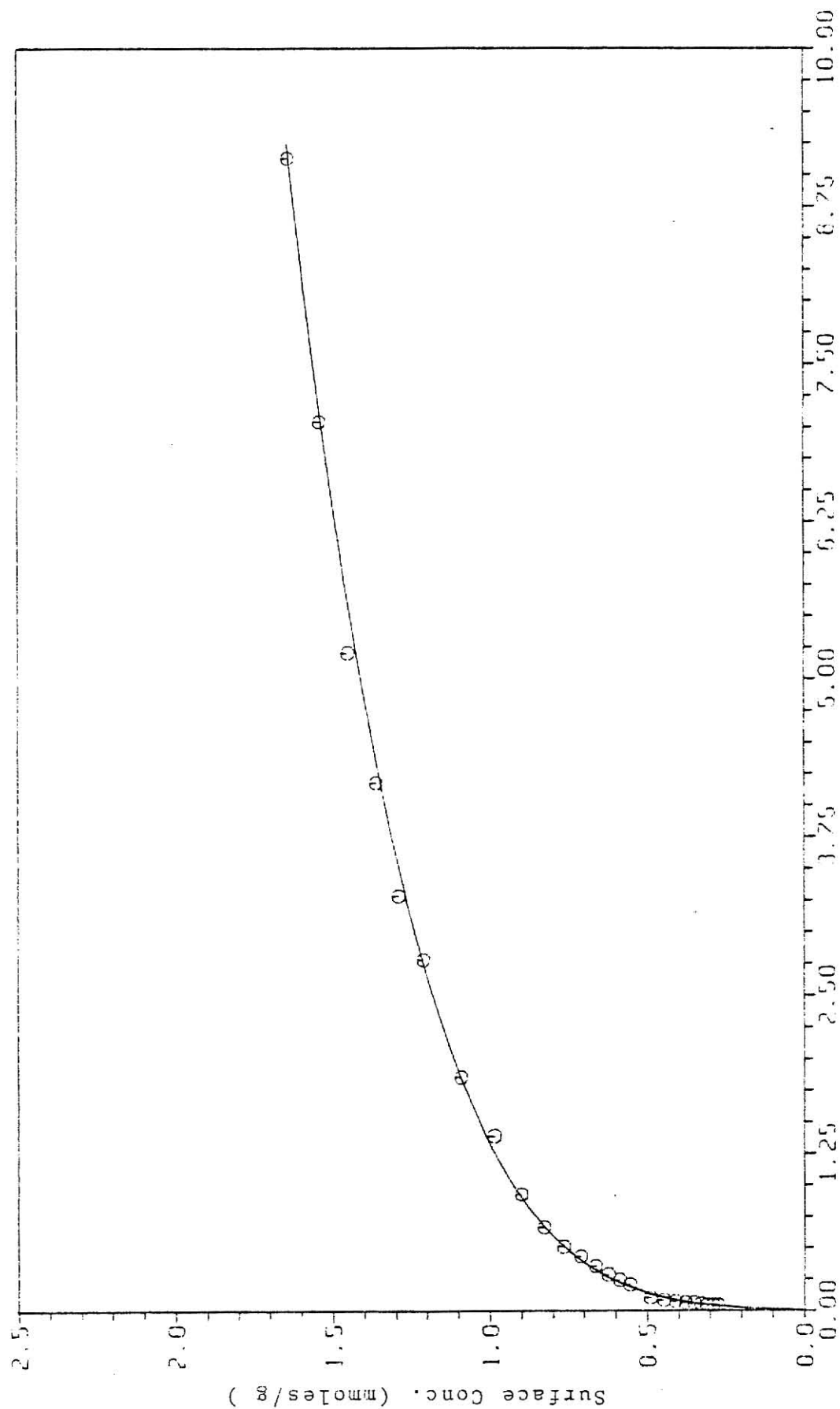


Figure 16. Adsorption Isotherm for phenol at 30°C Relative to Solubility.

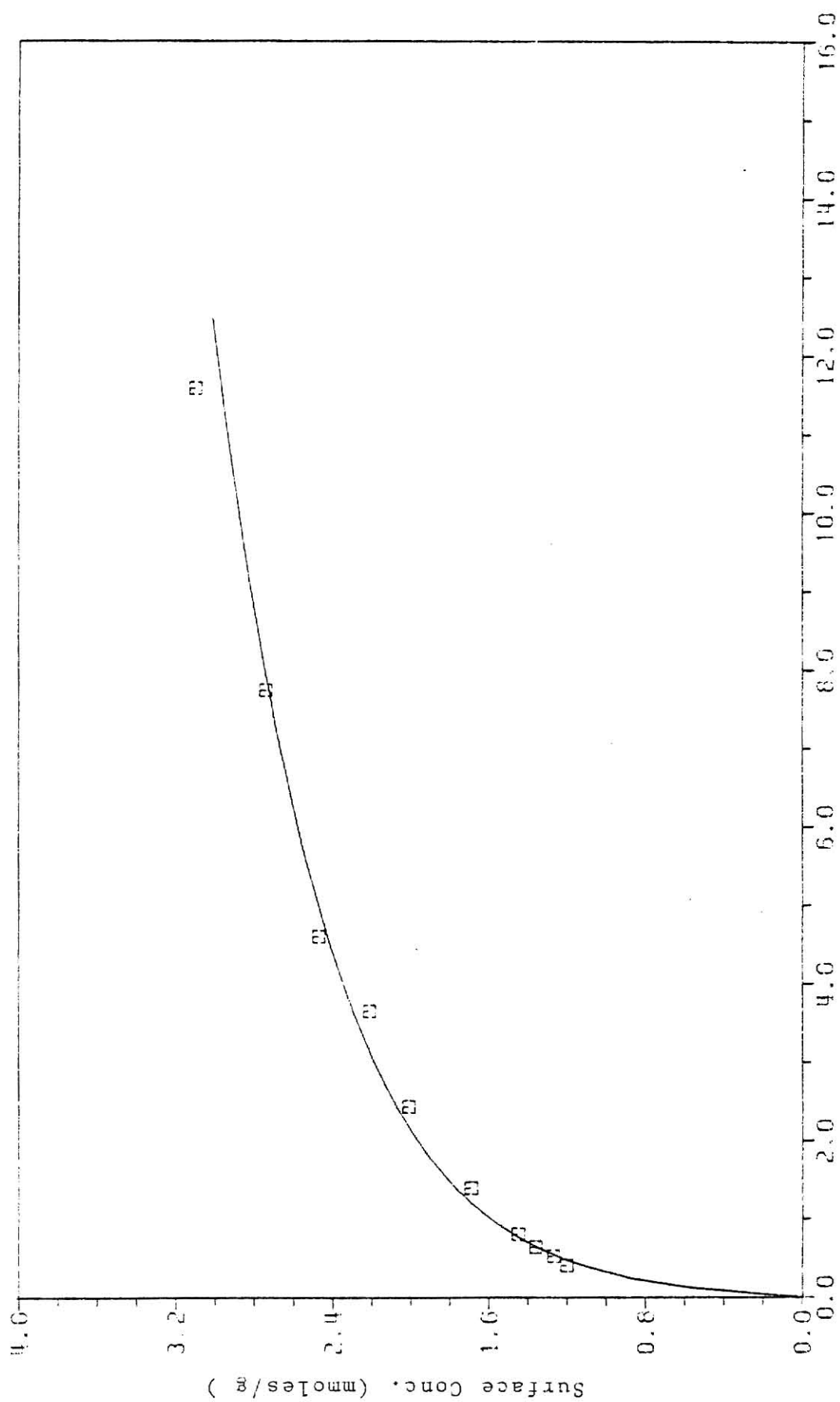


Figure 17. Adsorption Isotherm for Naphthalene at 10°C Relative to Solubility.

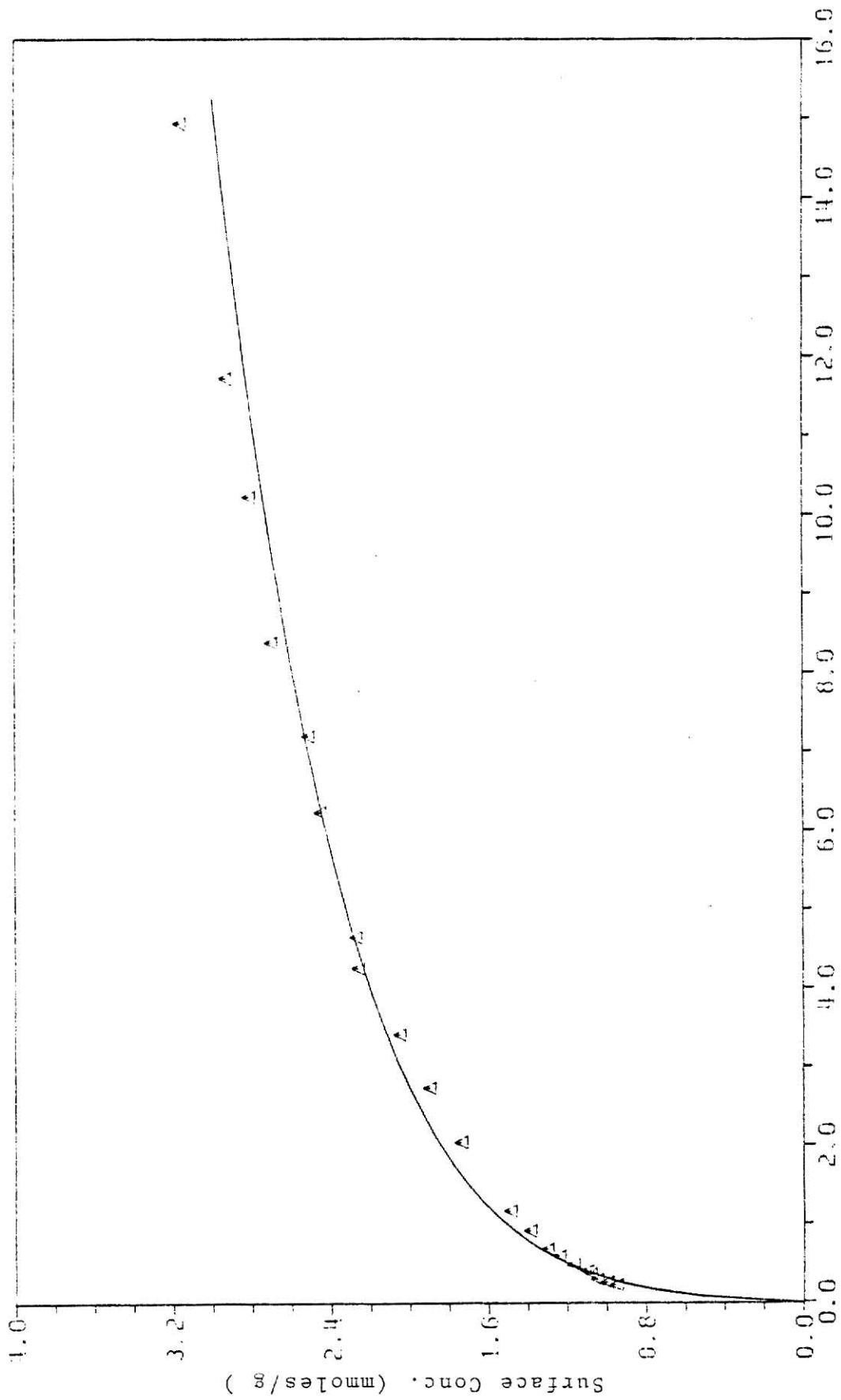


Figure 18. Adsorption Isotherm for Naphthalene at 24°C. Relative to Solubility.

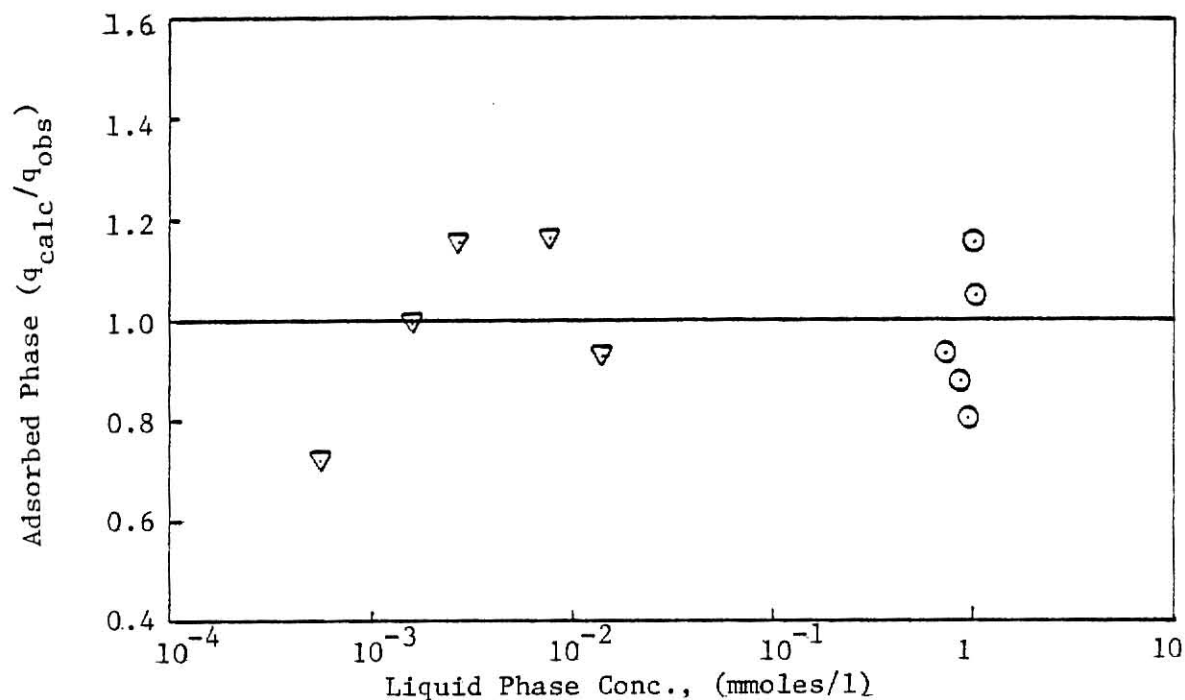


Figure 19. Adsorption Equilibria for Phenol-Naphthalene Mixture
($\odot$) Phenol, (∇) Naphthalene

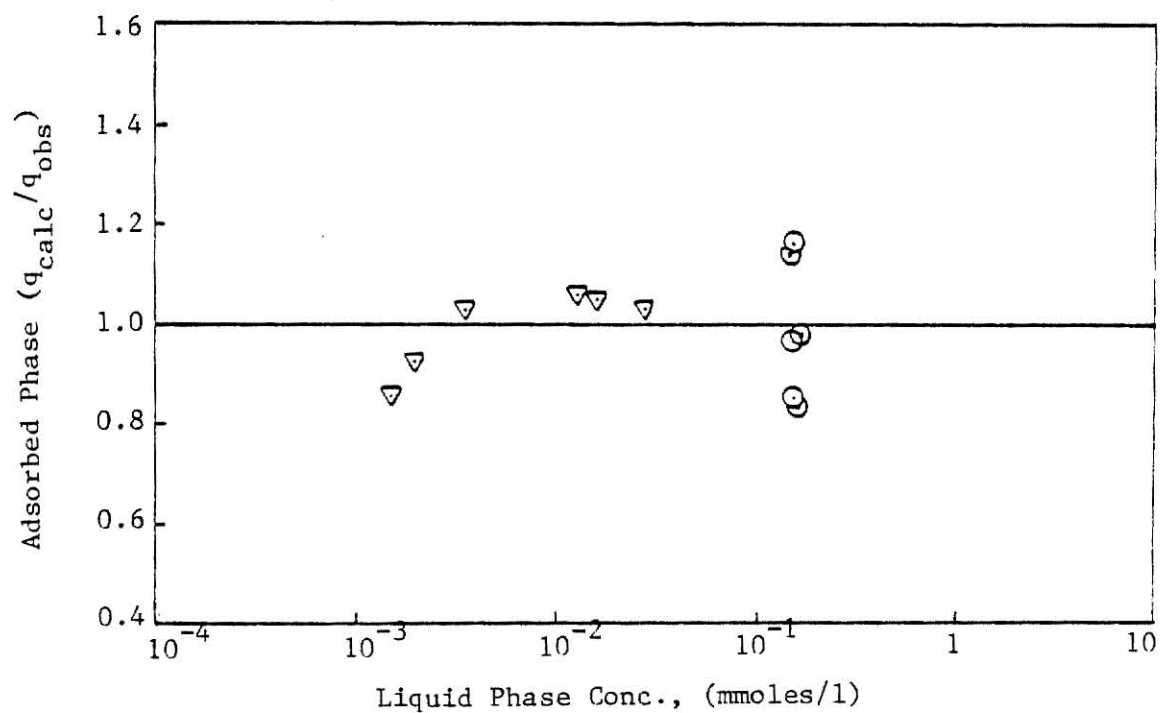


Figure 20. Adsorption Equilibria for Phenol-Naphthalene Mixture
($\odot$) Phenol, (∇) Naphthalene

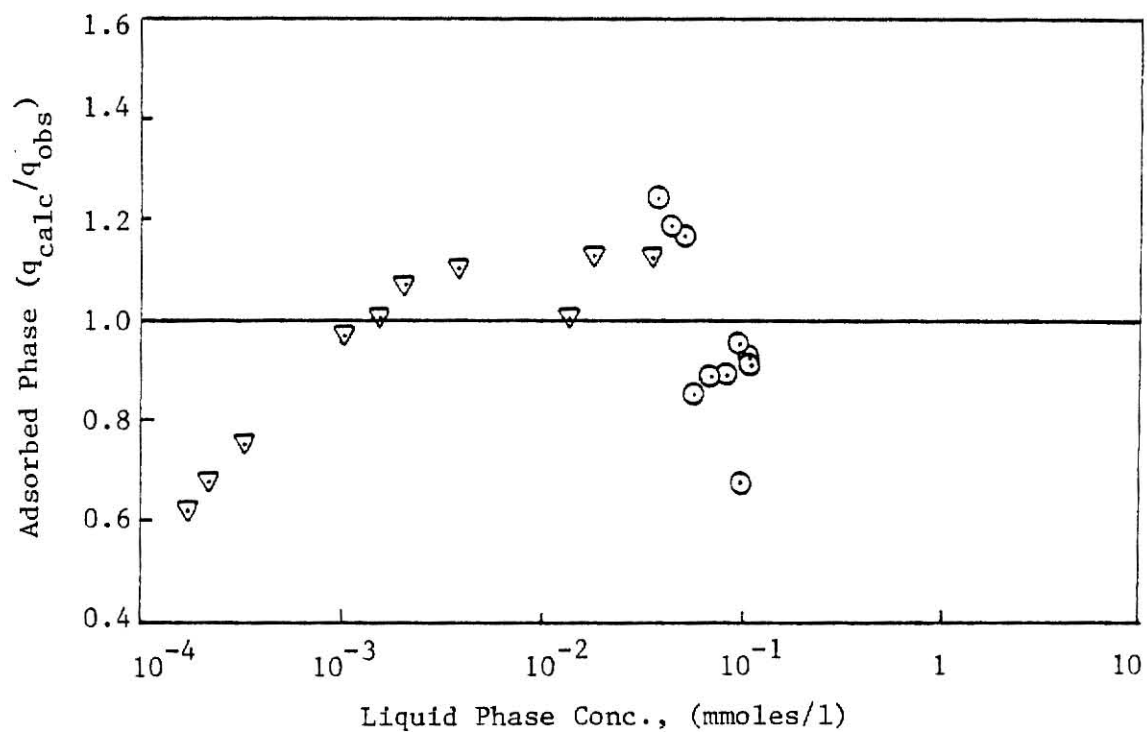


Figure 21. Adsorption Equilibria for Phenol- Naphthalene Mixture
($\odot$) Phenol, (∇) Naphthalene

are plotted against the equilibrium liquid phase concentration of the solute in the mixture. It is seen that most of the data points are well within a deviation of $\pm 20\%$. These data indicate that the above equation is suitable for correlating binary equilibrium data for use in multicomponent rate model.

Figures 22 and 23 also show the adsorption equilibria for phenol and naphthalene from mixtures. They indicate that naphthalene is much more strongly adsorbed than phenol. In order to generate isotherm points, three different initial concentration were used. As a result, the lower, definitely nonlinear isotherms of phenol appear curved in shape i.e., sharply lower loadings are indicated at higher equilibrium concentrations. The naphthalene isotherm points all appear like a linear trend shape. This same effect has been observed in different studies and seems to depend on the relative adsorption behaviour of the two components (Martin and Al-Bahrani, 1977; Frick et al., 1980); the greater the difference in adsorbability, the more curved will be the shape of the isotherm for the weaker component in the mixture when plotted on a log-log scale.

Estimation of Rate Parameters

The rate parameters of importance in the rate model are mass transfer coefficient and surface diffusion coefficients for each solute species. For this study, mass transfer and surface diffusion coefficients were estimated for each species from single solute batch reactor data by utilizing the single solute

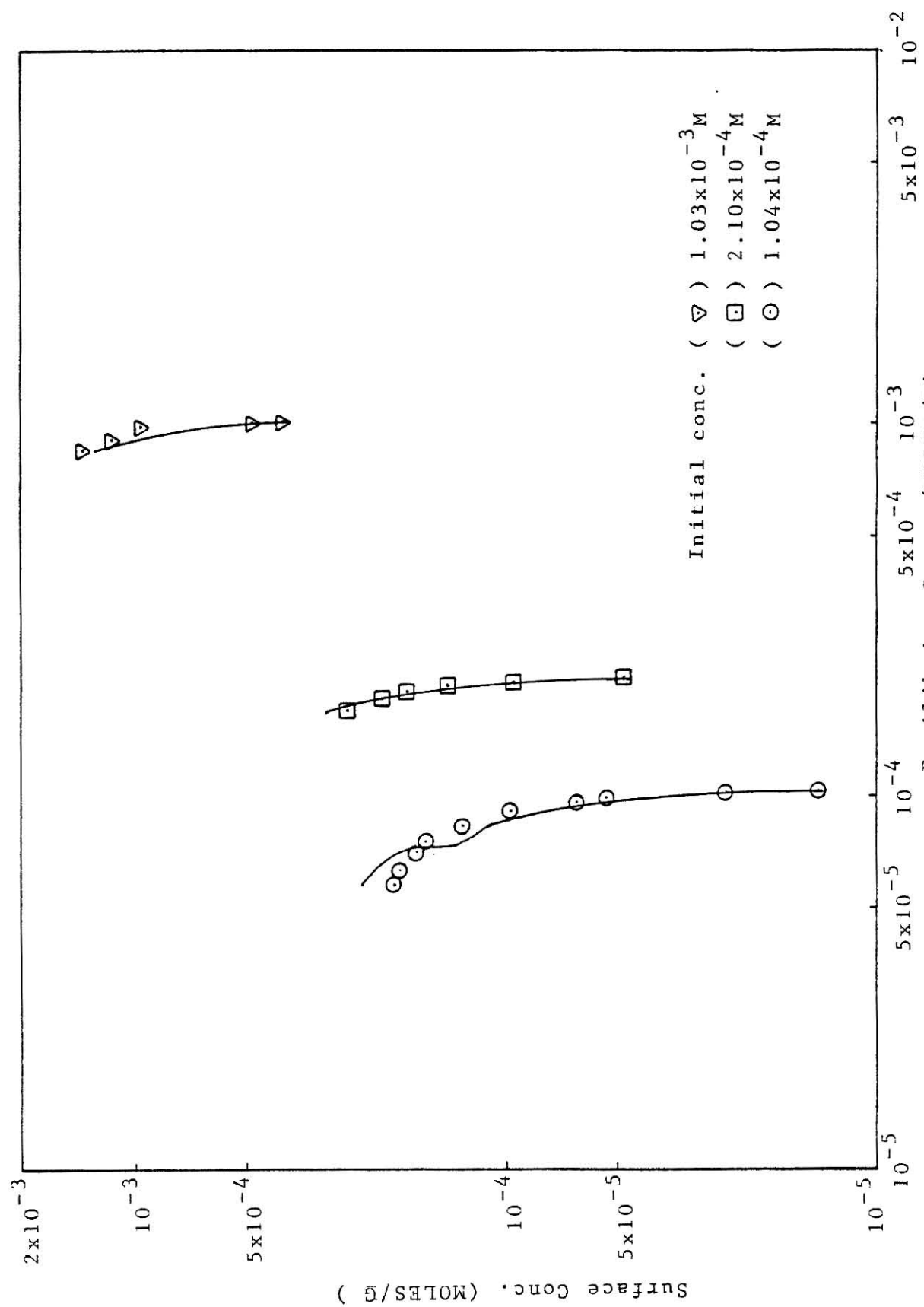


Figure 22. Adsorption Equilibria for Phenol in Mixtures.

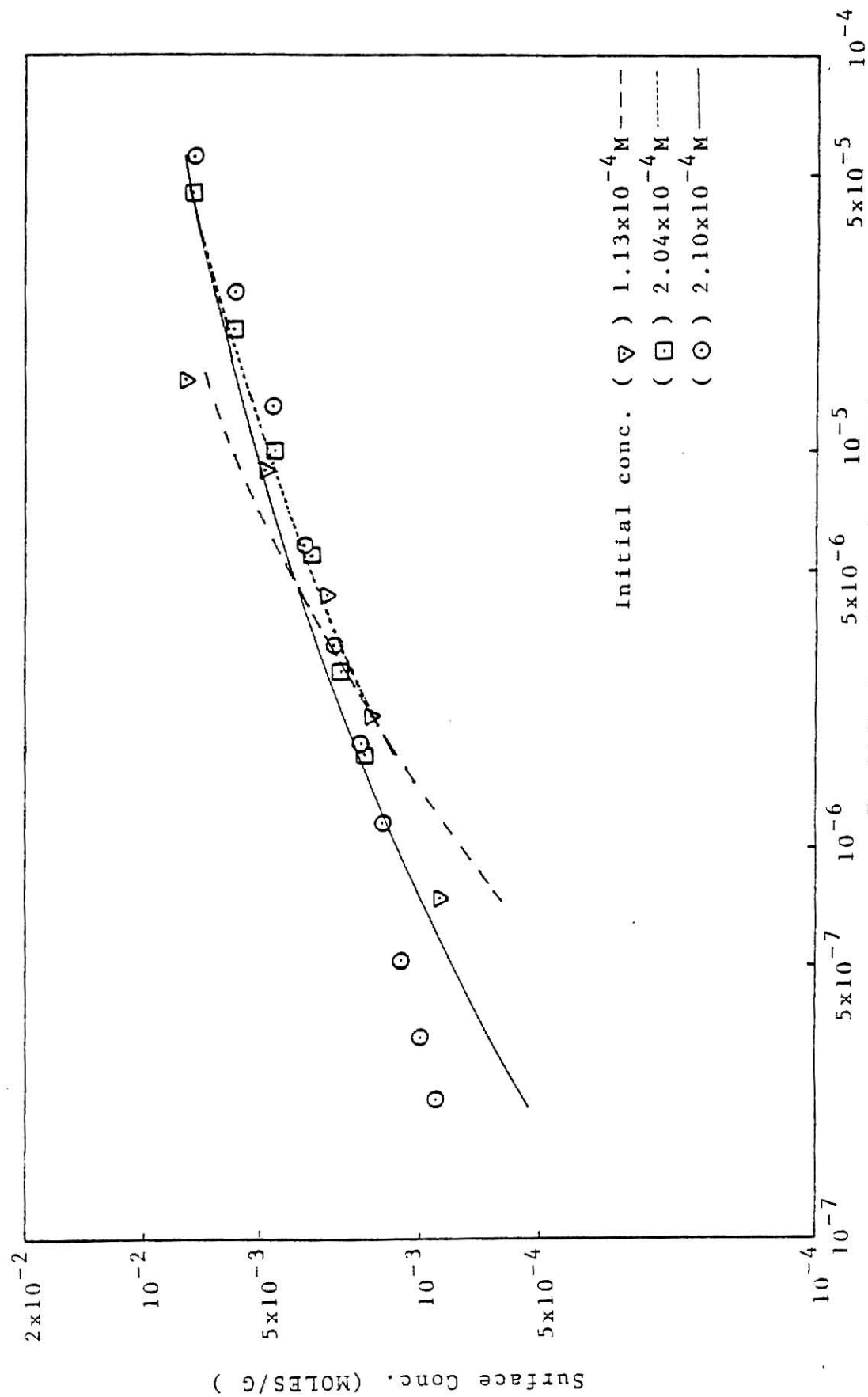


Figure 23. Adsorption Equilibria for Naphthalene in Mixtures.

adsorption rate equation for each solute. A computer program employing numerical procedure to solve the single solute rate equation, coupled with a parameter estimation procedure was used to estimate the mass transfer and surface diffusion coefficients (Mathews, 1975). The program uses the principal axis method of Brent (1971) for finding the minimum of a function, and searches for parameter values of mass transfer and surface diffusion coefficients that will minimize the sum of square of the difference between experimental and computed values of adsorption rates. The mass transfer and surface diffusion coefficients estimated for each solute are shown in Table 10. It reveals that the diffusivities for naphthalene and phenol are approximately of the same order. The naphthalene molecule appears to diffuse slightly more rapidly within the adsorbent particle.

Kinetic Studies

This section presents the results of experiments on kinetics of adsorption of phenol and naphthalene on granular activated carbon at room temperature of 24°C.

Single-solute Adsorption Kinetics

A computer program for predicting the adsorption rates for the single solute system had been developed by Mathews (1975) and was utilized to fit the experimental data. The input parameters required for the model are the single solute film transfer and

Table 10. Mass Transfer And Surface Diffusion Coefficients

Solute	K_f (cm/sec)	D_s (cm ² /sec)
Phenol	6.134×10^{-3}	3.746×10^{-8}
Naphthalene	7.000×10^{-3}	4.825×10^{-8}

surface diffusion coefficients, the single solute isotherm constants- A, B and β .

Figures 24 to 26 show the data for adsorption rates of phenol. In these three experiments 18/20 mesh size carbon was used. The experiment in Figure 24 was carried out with an initial concentration of phenol of $9.92 \times 10^{-4}M$ and the carbon dosage of 0.25 g/3 liter was used. In Figures 25 and 26, the experiments were carried out with an initial concentration of $10^{-3}M$ and carbon dosages were 0.5 and 1.0 g/3 liter, respectively. The symbols represent the experimental data and solid lines are the model predictions. The predicted profiles are in excellent agreement with the experimental data.

Figure 27 shows two sets of experimental data for adsorption rates of phenol using 40/50 mesh size carbon. Both used the same initial concentration of $10^{-3}M$, and the carbon dosage of 0.25 and 0.5 g/3 liter. The experimental rate appears to be slower than predicted after the first 20 minutes. This deviation may be attributed to the non-uniform carbon particles between mesh size 40 and 50.

The experimental data for adsorption rates of naphthalene using 18/20 mesh size carbon are shown in Figures 28 to 31. All these experiments were conducted with an initial concentration of $10^{-4}M$. The carbon dosages of 0.25, 0.5, 1.0 and 1.5 g/3 liter were used in each adsorption rate test. The predicted profiles are in good agreement with the experimental data except for the case of carbon dosage 1.5 g/3 liter of solution. This is attributed to (1) not using the filtering funnel with fritted

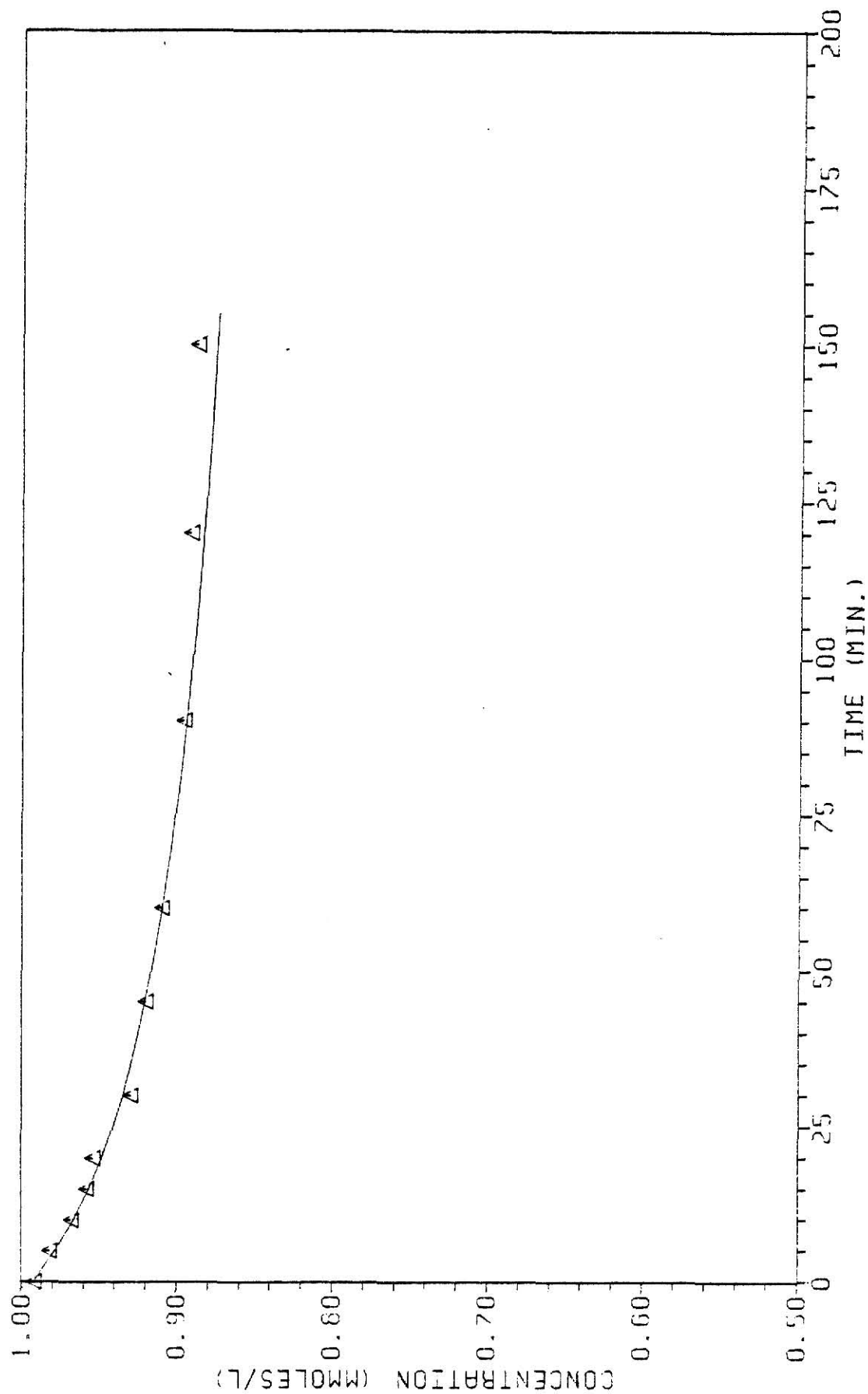


Figure 24. Adsorption Rate from Phenol: (Δ) experimental data, (—) predicted rate.

($C_0 = 9.92 \times 10^{-4} M$; carbon dosage 0.25 g/3 liter, size 18/20)

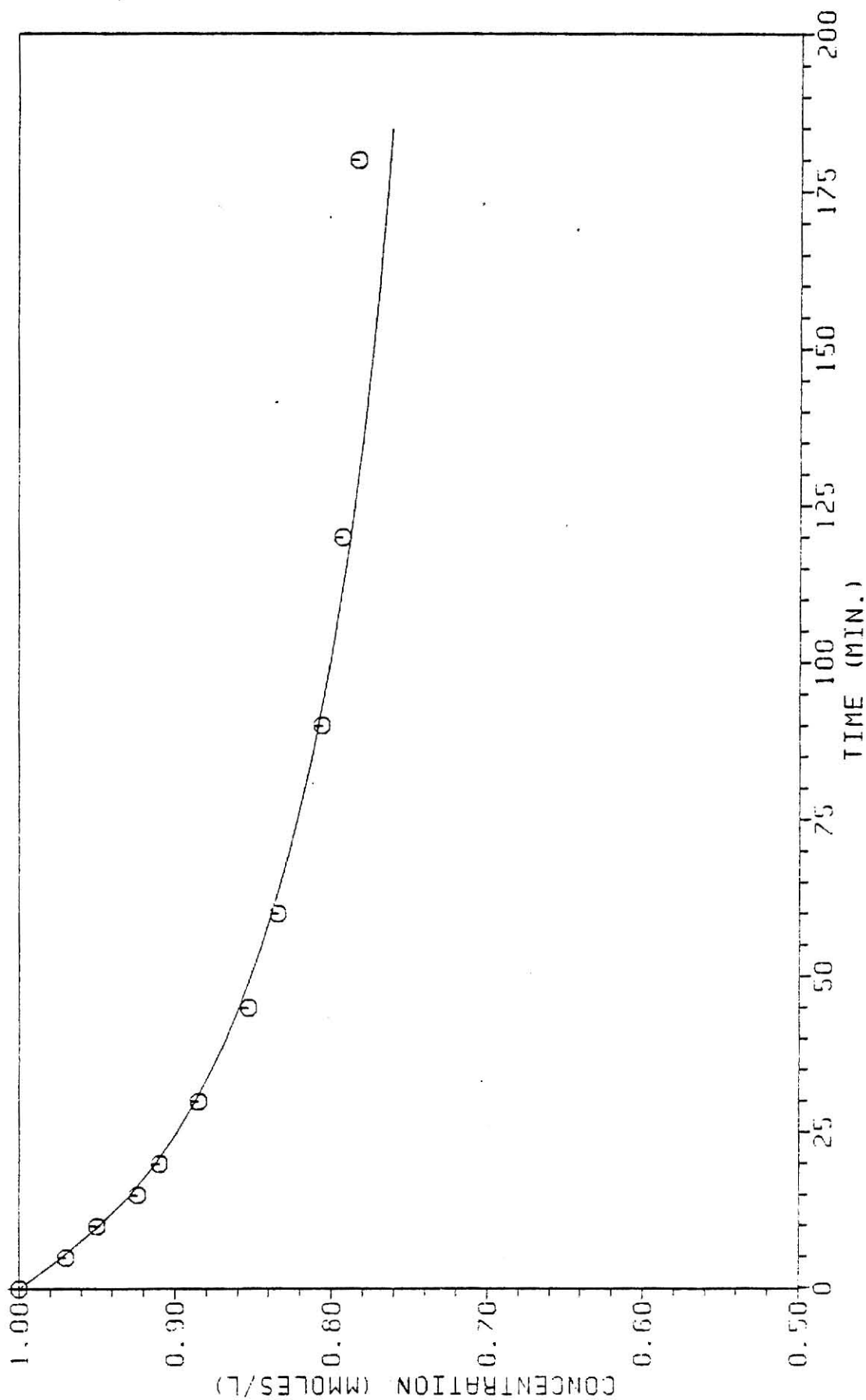


Figure 25. Adsorption Rate from Phenol: (○) experimental data, (—) predicted rate.
 ($C_o = 10^{-3}M$; carbon dosage 0.5 g/3 liter, size 18/20)

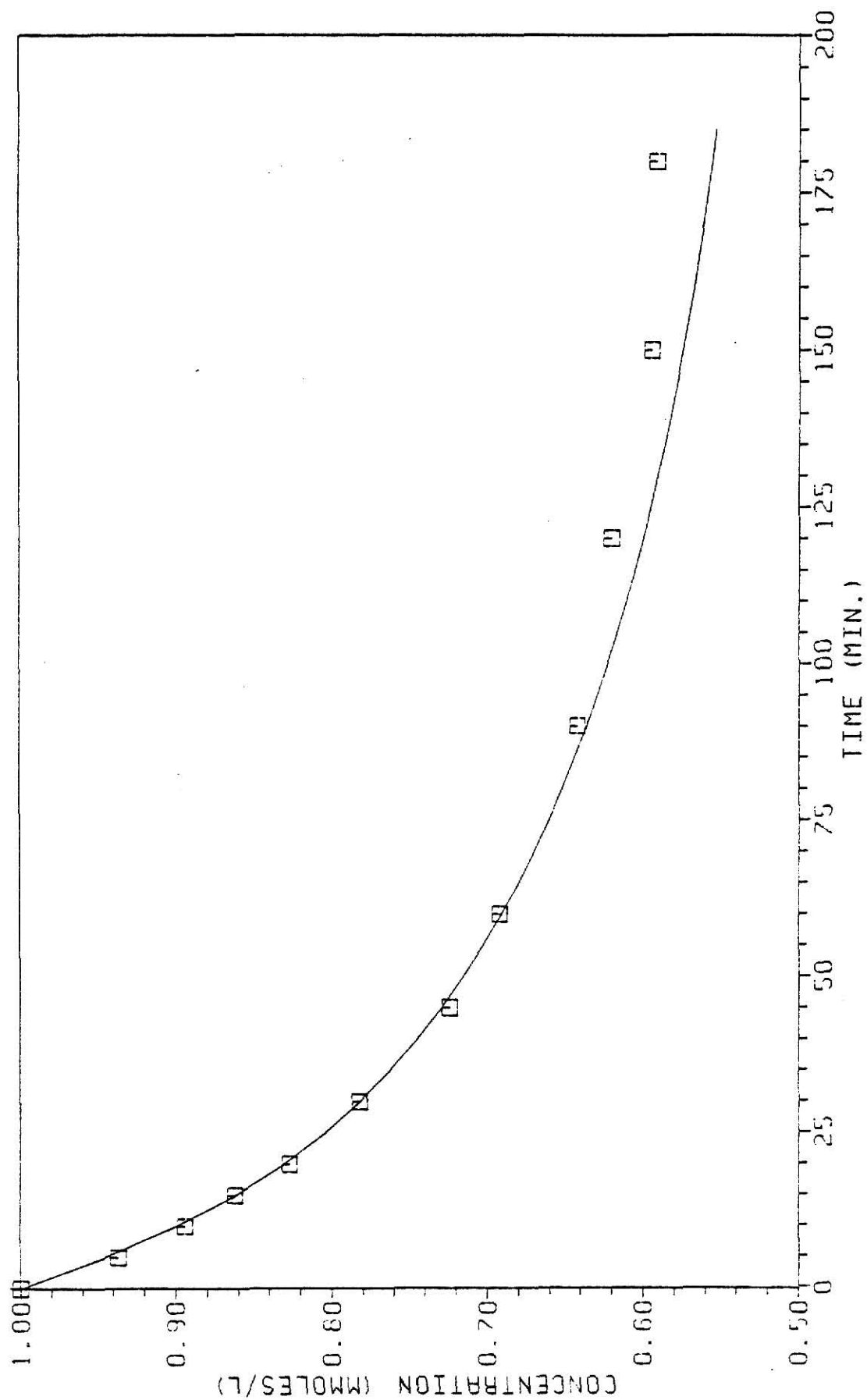


Figure 26. Adsorption Rate from Phenol: (□) experimental data, (—) predicted rate.

($C_0 = 10^{-3}M$; carbon dosage 1.0 g/ 3 liter, size 18/20)

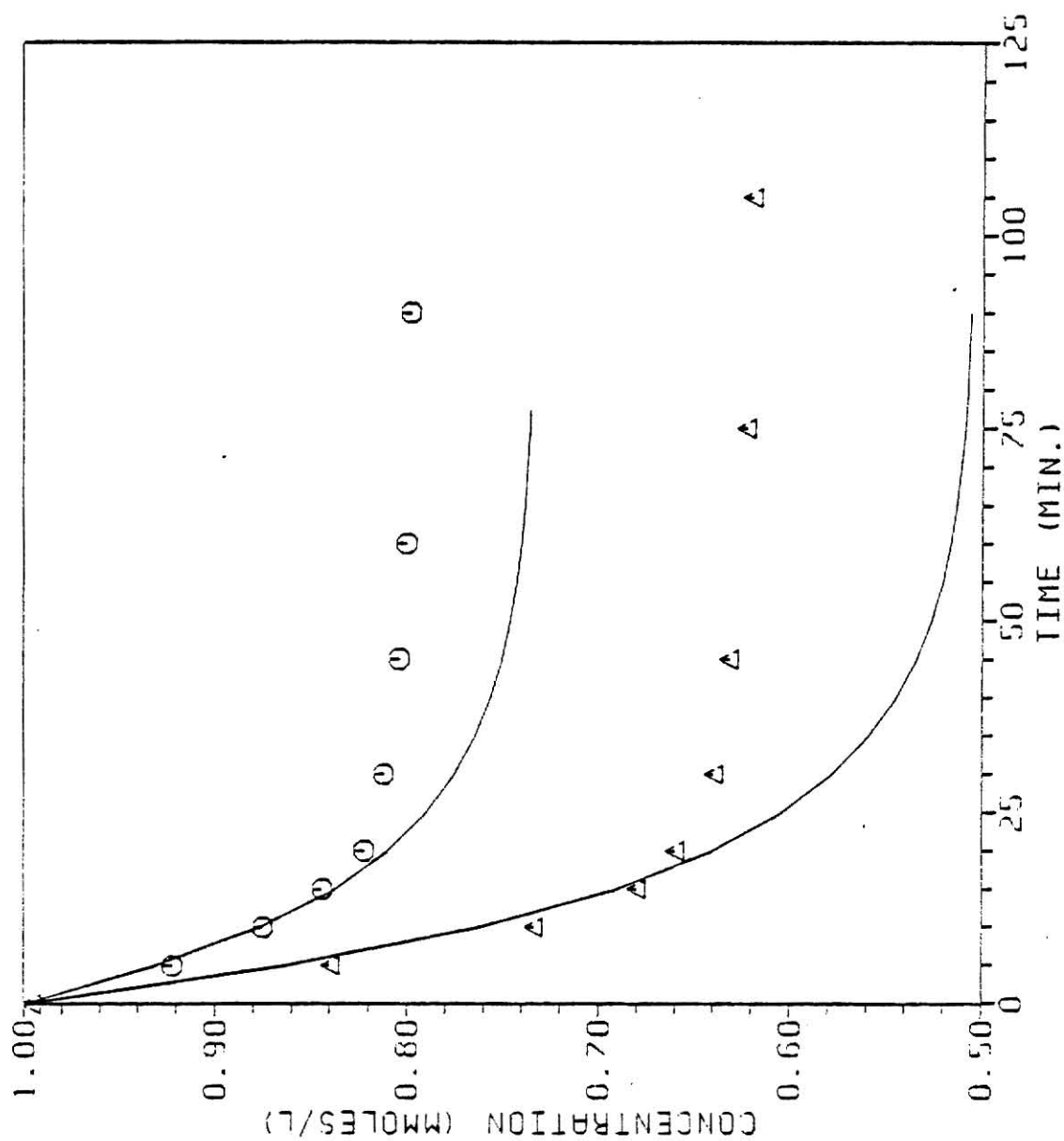


Figure 27. Adsorption Rate from Phenol: (O), (Δ) experimental data for carbon dosage 0.5 , 1.0 g/3 liter respectively; (—) predicted rate.
 $(C_o = 10^{-3} \text{M for (O)}, C_o = 9.96 \times 10^{-4} \text{M for (Δ)};$
 carbon size 40/50)

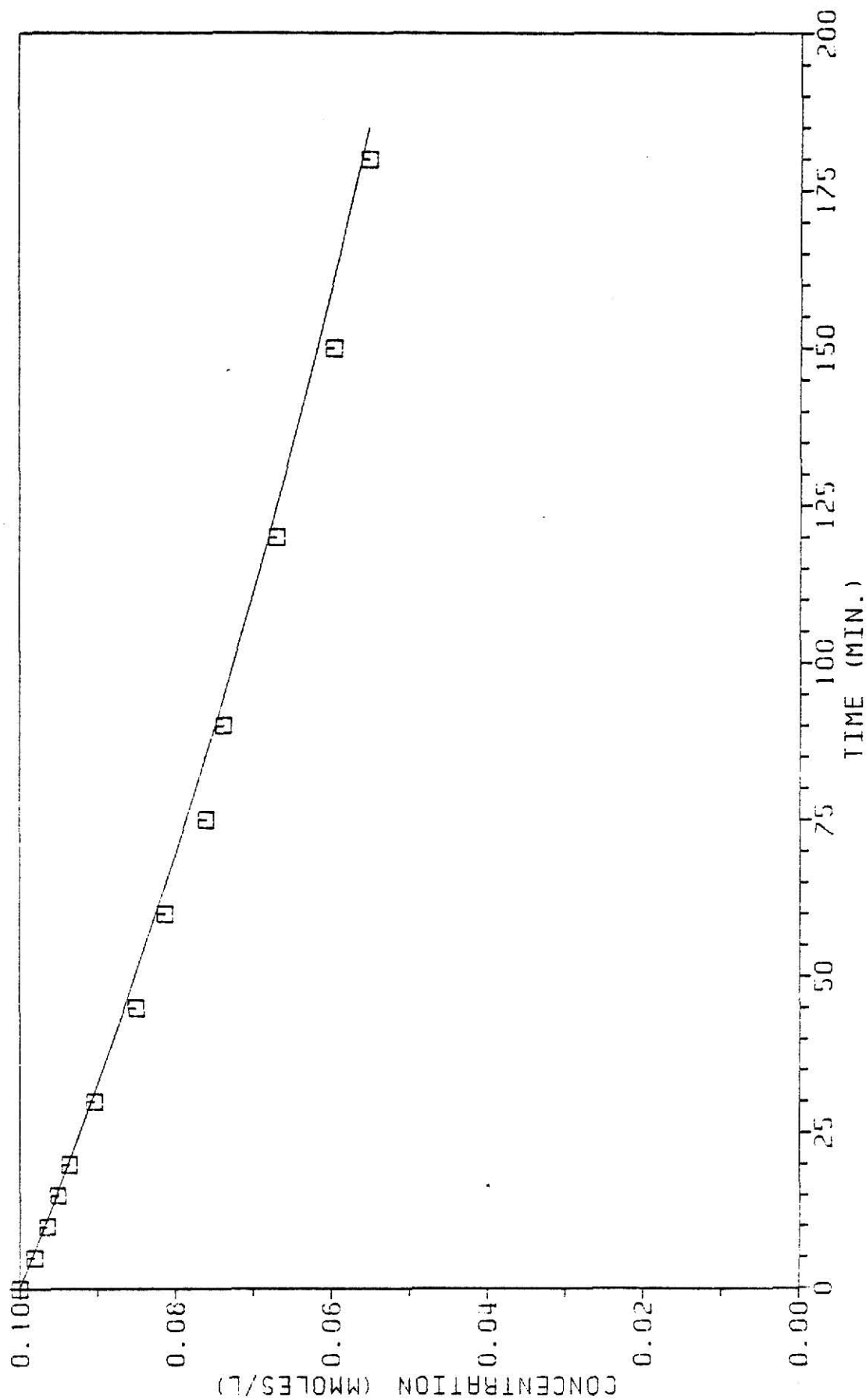


Figure 28. Adsorption Rate from Naphthalene: (□) experimental data, (—) predicted rate.
($C_0 = 10^{-4}M$; carbon dosage 0.25 g/3 liter, size 18/20)

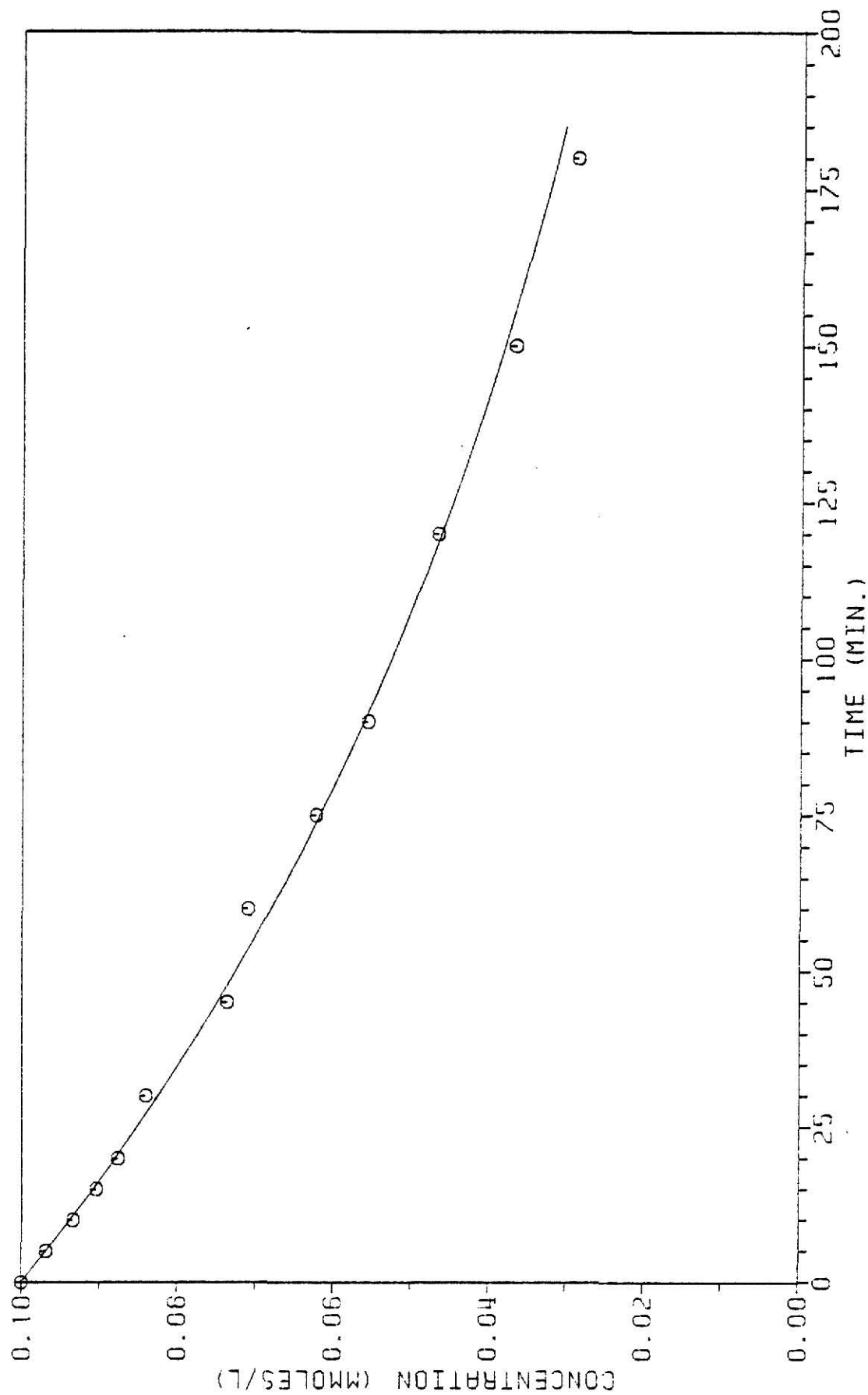


Figure 29. Adsorption Rate from Naphthalene: (○) experimental data, (—) predicted rate.
($C_0 = 10^{-4} M$; carbon dosage 0.5 g/3 liter, size 18/20)

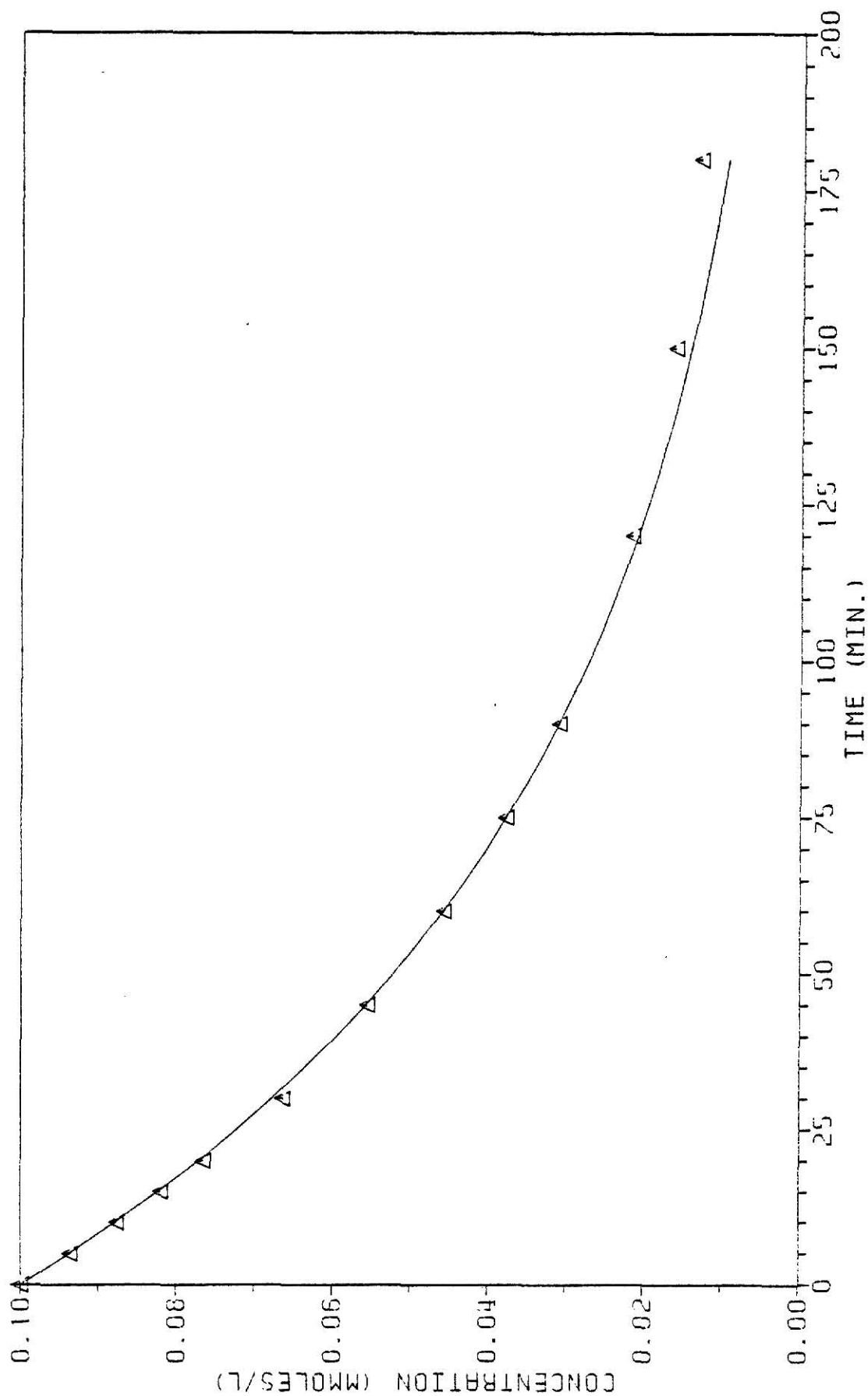


Figure 30. Adsorption Rate from Naphthalene: (Δ) experimental data, (—) predicted rate.
 ($C_0 = 10^{-4}M$; carbon dosage 1.0 g/3 liter, size 18/20)

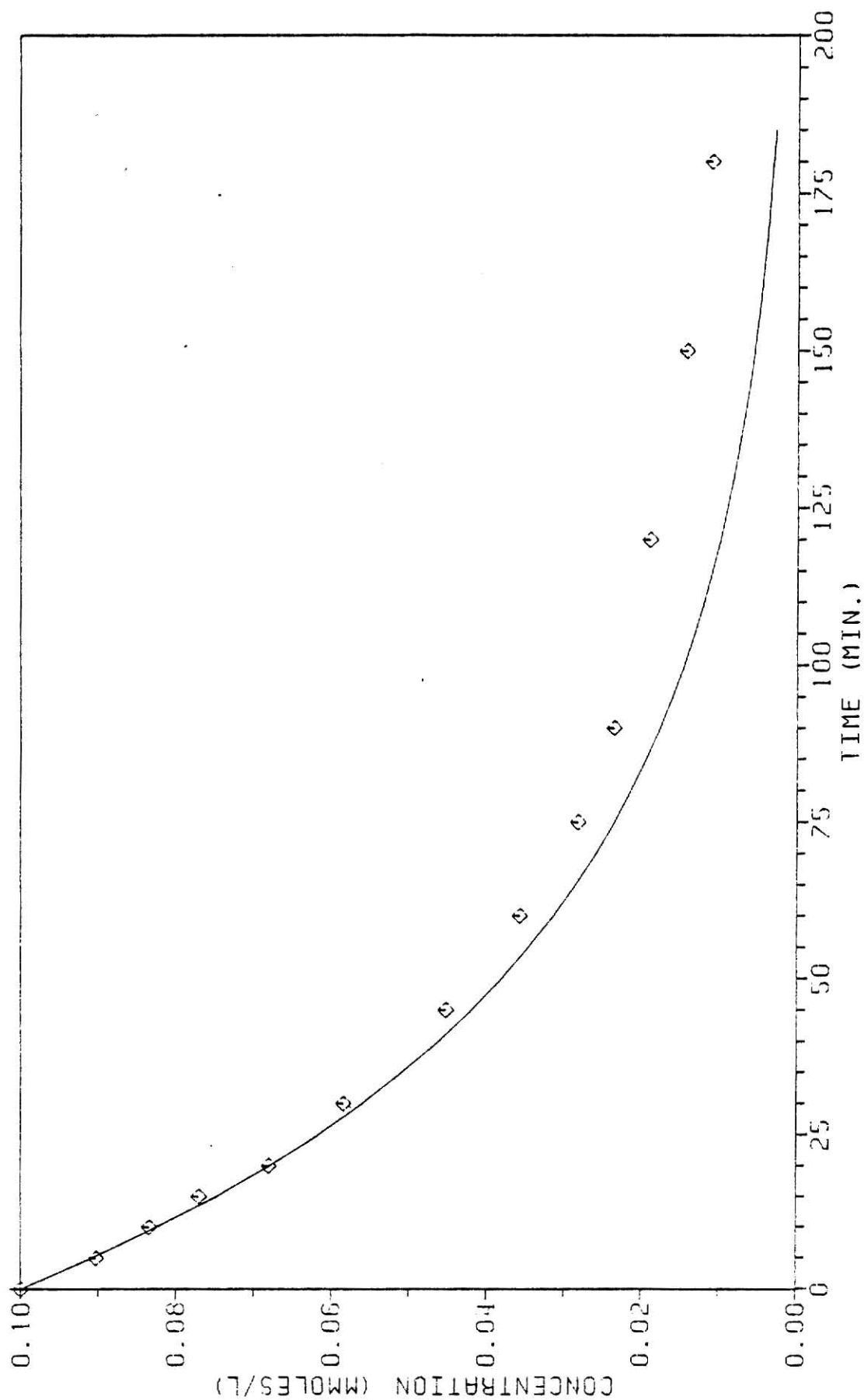


Figure 31. Adsorption Rate from Naphthalene: ($\diamond$) experimental data, (—) predicted rate.
 ($C_0 = 10^{-4}$ M; carbon dosage 1.5 g/3 liter, size 18/20)

disc (PYREX, Corning 36060), (2) which carbon fines resulting from the collision of carbon particles which made the UV readings greater because of greater absorbance of light.

Figure 32 shows two sets of experimental data for adsorption rates of naphthalene using 40/50 mesh size carbon. Both of these two tests used an initial concentration of $10^{-4}M$, and the carbon dosage of 0.25 g/3 liter and 0.5 g/3 liter, respectively. The experimental adsorption rate is a little faster than predicted value. But the model is still considered to fit very well.

Bi-solute Adsorption Kinetics

The experimental data for adsorption rates of phenol and naphthalene with differing initial concentrations, $1.23 \times 10^{-4}M$ for phenol and $9.24 \times 10^{-5}M$ for naphthalene is shown in Figure 33. The carbon dosage used in 18/20 mesh size 0.5 g/3 liter. Initial concentrations of $10^{-4}M$ for phenol and $4.34 \times 10^{-5}M$ for naphthalene were used in another rate study. The carbon dosage used in 18/20 mesh size 1.0 g/3 liter. The experimental data is presented in Figure 34.

A computer program for predicting the adsorption rate profiles for the binary system has been designed by Mathews (1975) and was used in this study. The input parameters required for the model are the single-solute film transfer and surface diffusion coefficients, the single-solute isotherm constants and the mixture equilibria coefficients.

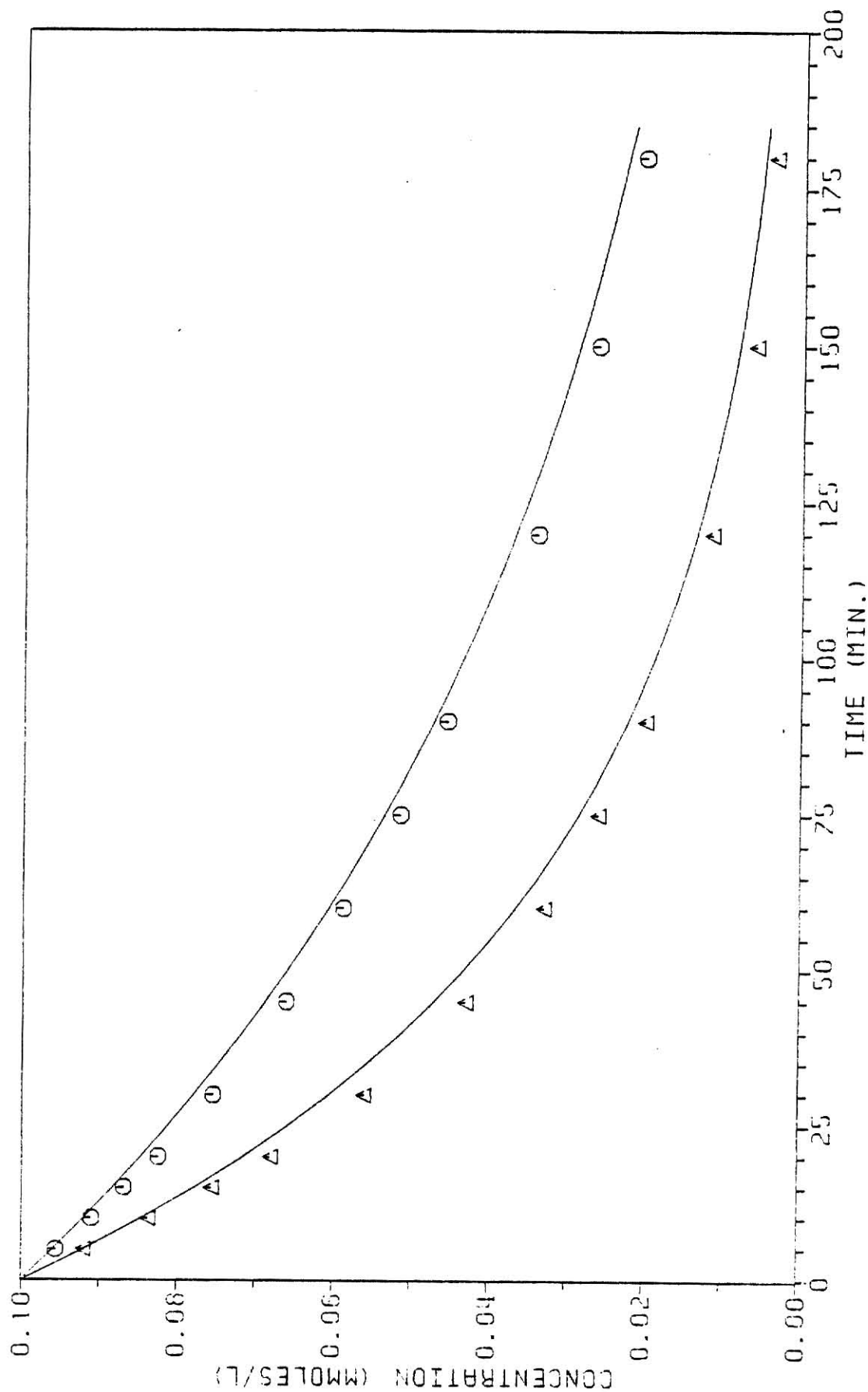


Figure 32. Adsorption Rate from Naphthalene: (○), (Δ) experimental data for carbon dosage 0.25, 0.5 g/3 liter respectively, (—) predicted rate.
 $(C_o = 10^{-4} \text{ M, carbon size 40/50})$

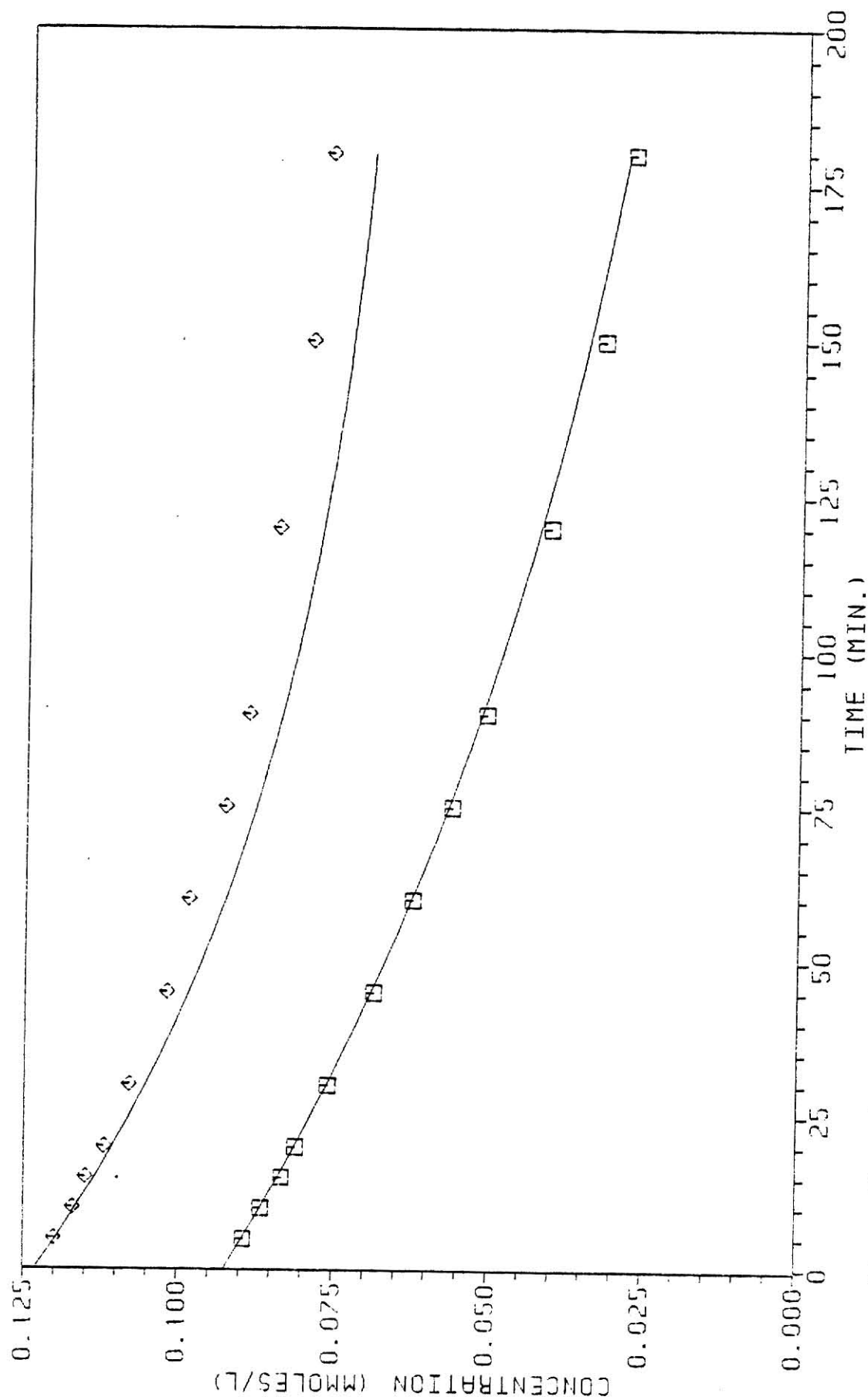


Figure 33. Adsorption Rates from Phenol-Naphthalene Mixture: ($\diamond$), ($\square$) experimental data for Phenol and Naphthalene respectively, (—) predicted rate.

(Phenol $C_0 = 1.23 \times 10^{-4} M$, Naphthalene $C_0 = 9.24 \times 10^{-5} M$; carbon dosage 0.5 g/3 liter, size 18/20)

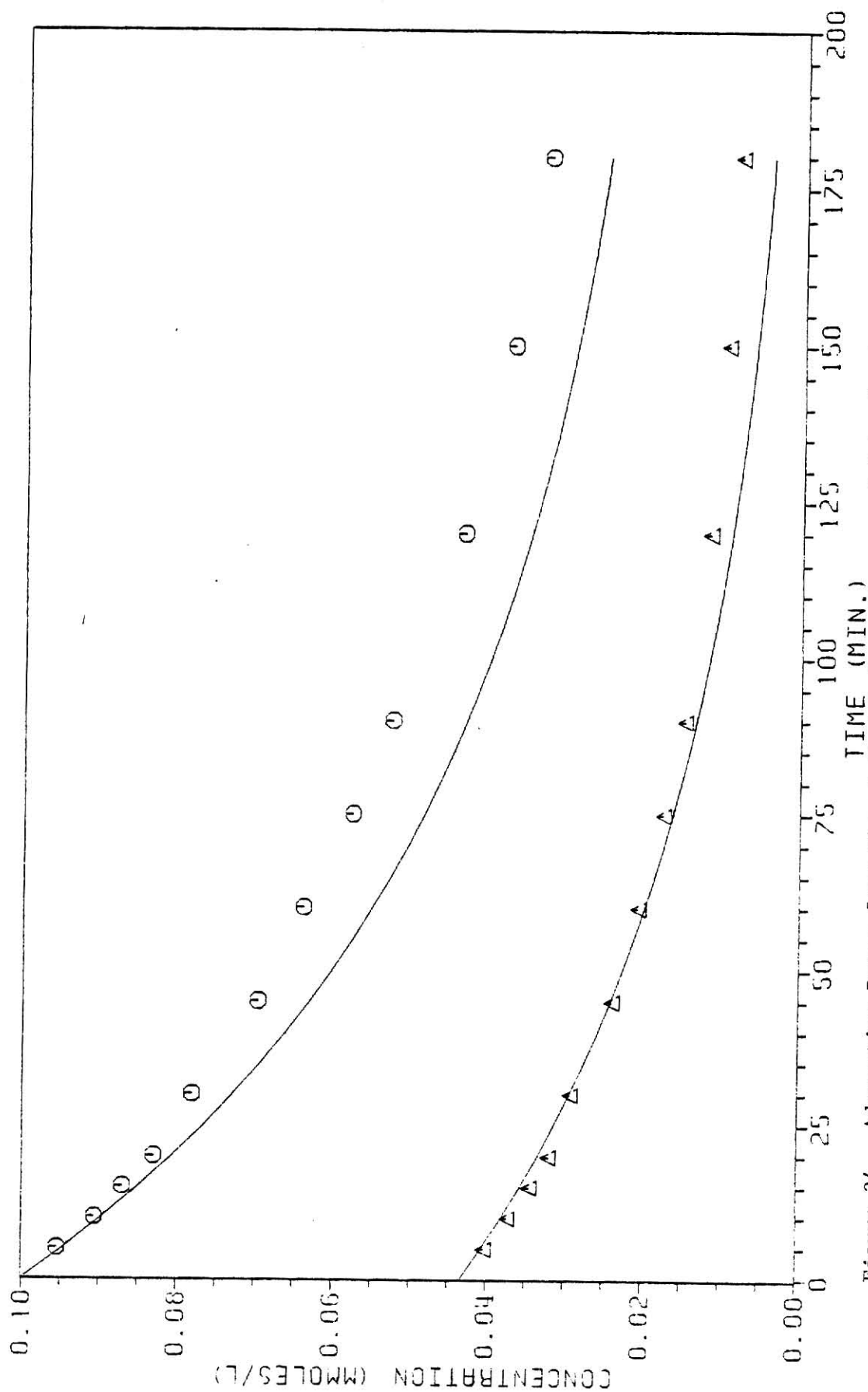


Figure 34. Adsorption Rates from Phenol-Naphthalene Mixture: (○), (Δ) experimental data for Phenol and Naphthalene respectively, (—) predicted rate.
 (Phenol $C_o = 10^{-4}M$, Naphthalene $C_o = 4.34 \times 10^{-5}M$; carbon dosage 1.0 g/3 liter, size 18/20)

The individual concentration profiles for naphthalene predicted by the model are in fairly good agreement with the measured values. However, for phenol a slight discrepancy is found between experimental data and those calculated by the model.

The model predicts a faster approach to equilibrium for phenol than was in fact observed. This can be explained by mutual interaction between the two diffusing molecules. From previous studies, both diffusivity and molecule size of naphthalene are larger than that for phenol. In addition, according an examination of the binary equilibrium data, this deviation may be attributed to the inadequate correlation of the mixture equilibrium data.

Column Studies

Three different types of column studies were conducted with activated carbon. Filtrasorb-400 carbon was used in fluidized, semifluidized, and packed beds. APC carbon was used in semifluidized and packed beds.

The salient properties of all experimental columns with Filtrasorb-400 are listed in Tables 11 to 13. The properties of columns containing APC carbon are listed in Table 14.

Breakthrough curves showing plots of C/C_0 against time show the increase in the ratio of effluent to influent concentrations as adsorption in the column proceeds. Breakthrough curves of C/C_0 versus time show the decrease in the ratio of

Table 11. Properties of Fluidized Beds
Containing F-400 Carbon

Flow Rate	5 gpm/ft ²	10 gpm/ft ²
Height of Unexpanded Bed	2.75 ft	2.75 ft
Height of Expanded Bed	3.08 ft	3.75 ft
Geometric Mean Carbon Particle Diameter	0.917 mm	0.917 mm
Weight of Carbon	647.8 g	647.8 g

Table 12. Properties of Semifluidized Beds
Containing F-400 Carbon

Flow Rate	5 gpm/ft ²	10 gpm/ft ²	20 gpm/ft ²
Height of Bed:			
Fluidized Fraction	1.83 ft	1.83 ft	2.08 ft
Fixed Fraction	1.08 ft	1.25 ft	1.50 ft
Geometric Mean Carbon Particle Diameter	0.917 mm	0.917 mm	0.917 mm
Weight of Carbon	647.8 g	647.8 g	647.8 g

Table 13. Properties of Packed Beds
Containing F-400 Carbon

Flow Rate	10 gpm/ft ²	20 gpm/ft ²
Height of Bed	2.58 ft	2.58 ft
Geometric Mean Carbon Particle Diameter	0.917 mm	0.917 mm
Weight of Carbon	647.8 g	647.8 g
Porosity of Bed	0.44	0.44

Table 14. Properties of Columns Containing APC Carbon

	Semifluidized Bed	Packed Bed
Flow Rate	14 gpm/ft ²	14 gpm/ft ²
Height of Bed:		
Fluidized Fraction	1.83 ft	0
Fixed Fraction	1.83 ft	2.67 ft
Geometric Mean Carbon Particle Diameter	0.917 mm	0.917 mm
Weight of Carbon	647.8 g	647.8 g
Porosity of Bed	--	0.29

effluent to influent concentrations as desorption occurs in the column.

For all columns studied, the general pattern of the adsorption breakthrough curve was as expected. After a trace of solute in effluent was detected, the effluent concentration rose first gradually and then sharply before approaching the value of the influent concentration. Figures 35 to 37 show these adsorption breakthrough curves which varied with the different flow rates and carbon beds.

Figures 38 to 40 show that sharper breakthrough curves resulted from increased flow rates whatever carbon bed is used. This can be partly attributed to a larger amount of solute coming into contact with the carbon per unit time which resulted in a faster approach to breakpoint and exhaustion capacity. Further, a higher flow rate means a shorter contact time between the carbon and the solute and therefore allows more chance for the solute to escape in the effluent.

For comparison purpose, $C/C_0 = 0.05$ and 0.80 were chosen for adsorption process and Table 15 shows the required time to reach these two points with different flow rates. It reveals that packed beds need the most time to reach C/C_0 of 0.05 .

Figures 41 to 43 show the desorption breakthrough curves in fluidized, semifluidized, and packed Filtrasorb-400 carbon beds at flow rate of 10 gpm/ft^2 . Table 16 presents the time required to reach C/C_0 of 0.05 for these three columns. It is contrary to adsorption, the fluidized bed needs the most time to reach C/C_0 of 0.05 . It should be noted that C_0 of initial

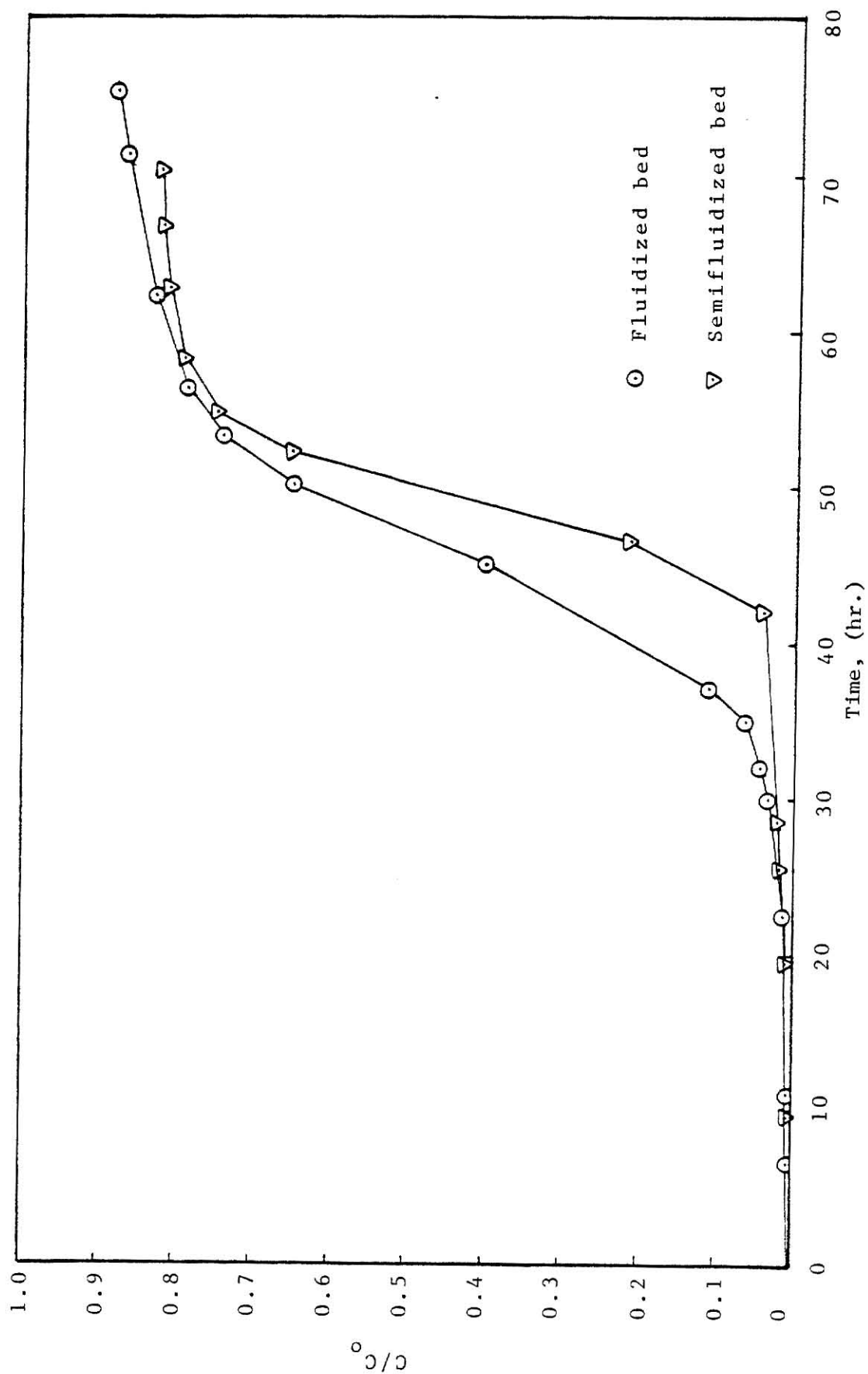


Figure 35. Adsorption Breakthrough Curves for Flow Rate 5 gpm/ft². ($C_0 = 1.0 \times 10^{-3}M$)

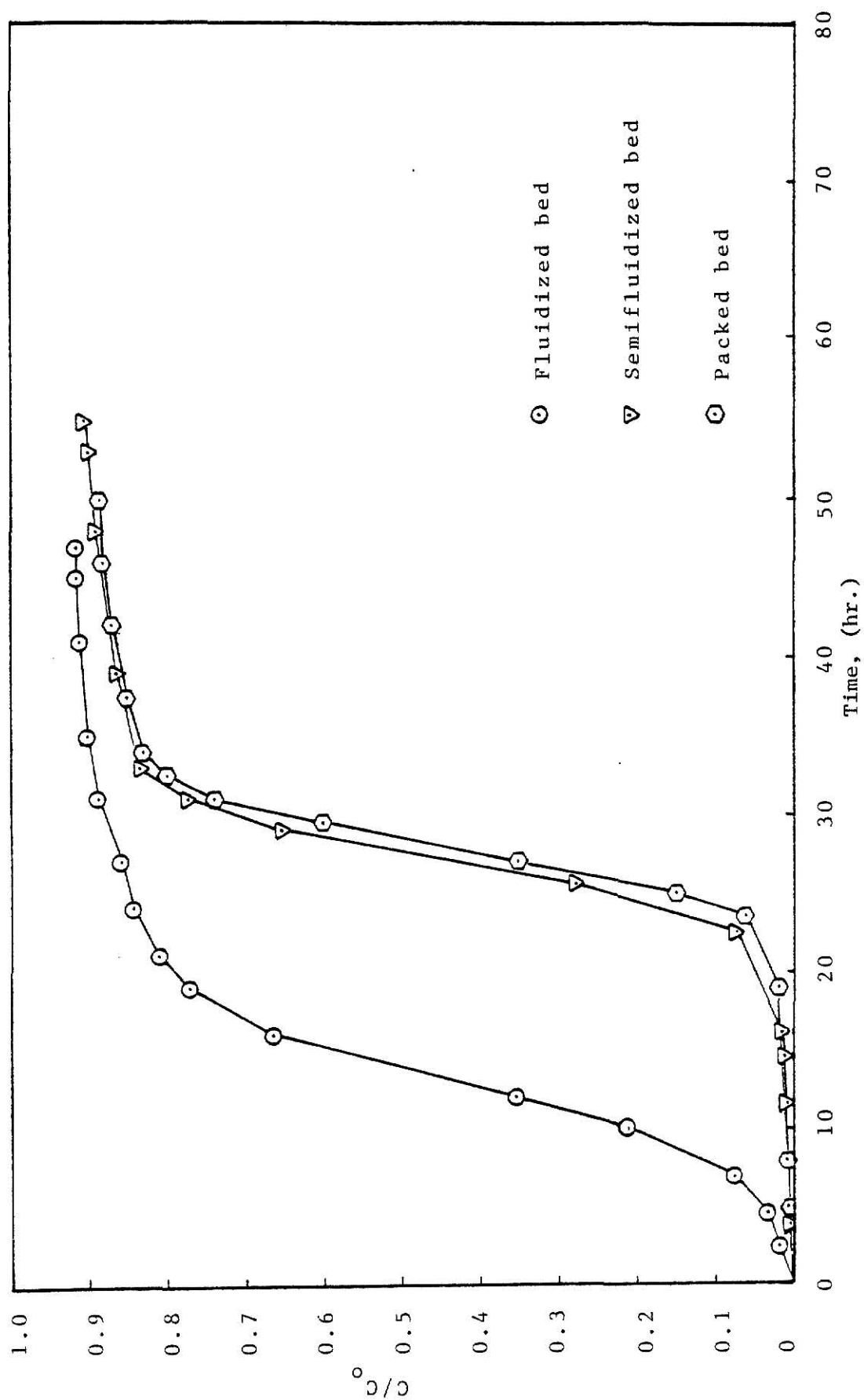


Figure 36. Adsorption Breakthrough Curves for Flow Rate 10 gpm/ft². ($C_0 = 1.0 \times 10^{-3} M$)

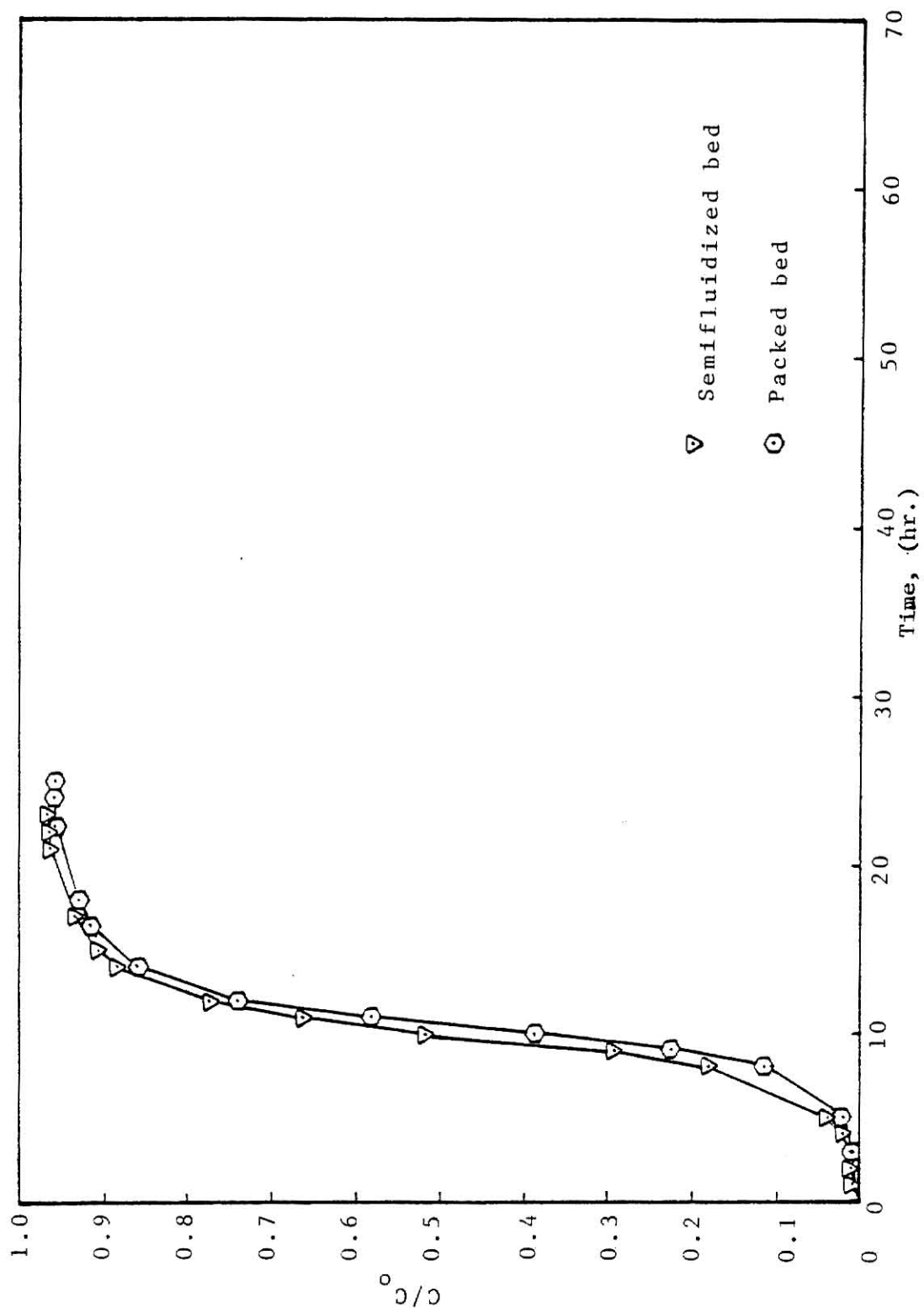


Figure 37. Adsorption Breakthrough Curves for Flow Rate 20 gpm/ft². ($C_0 = 1.0 \times 10^{-3}M$)

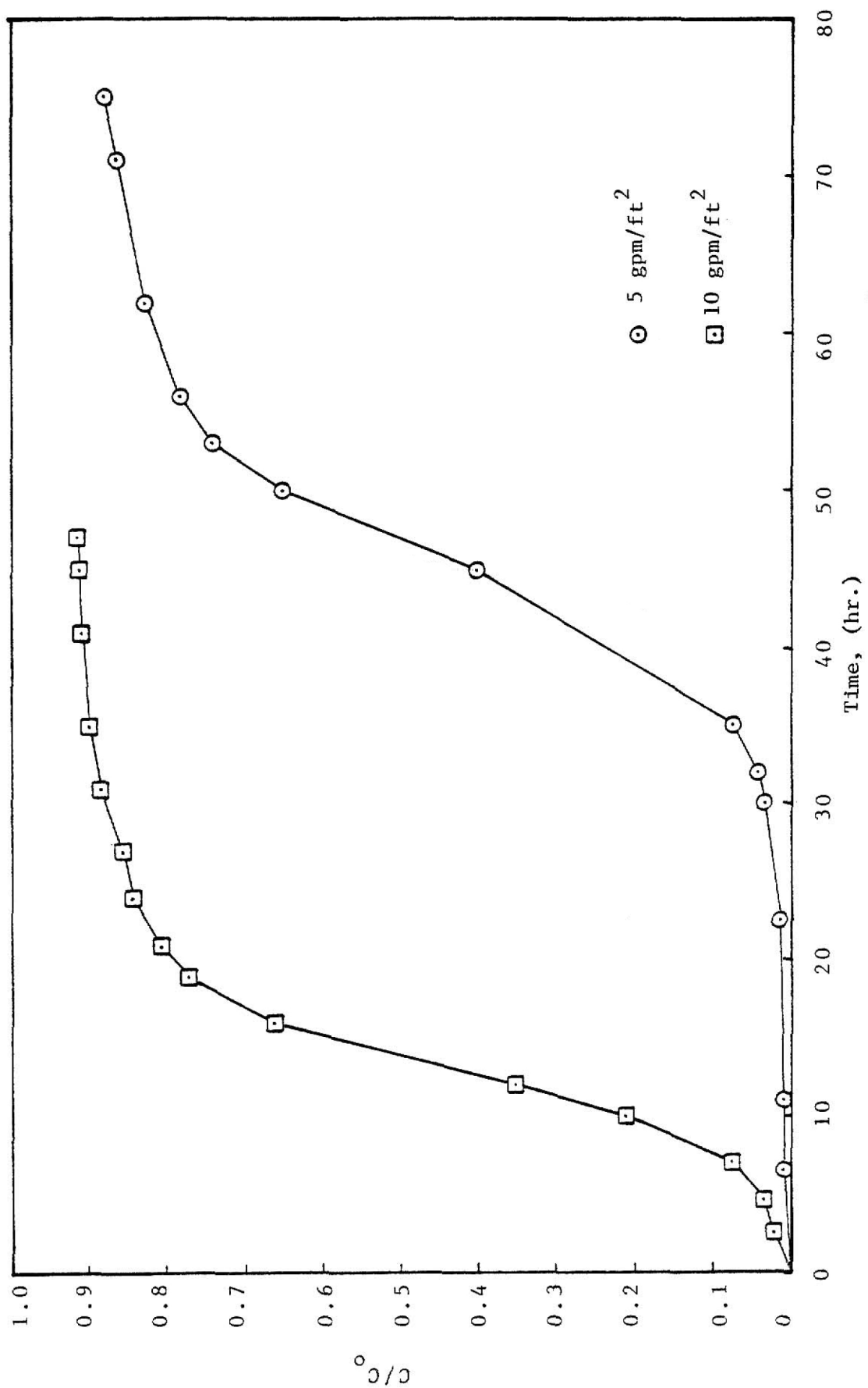


Figure 38. Adsorption Breakthrough Curves for Fluidized Bed. ($C_0 = 1.0 \times 10^{-3}M$)

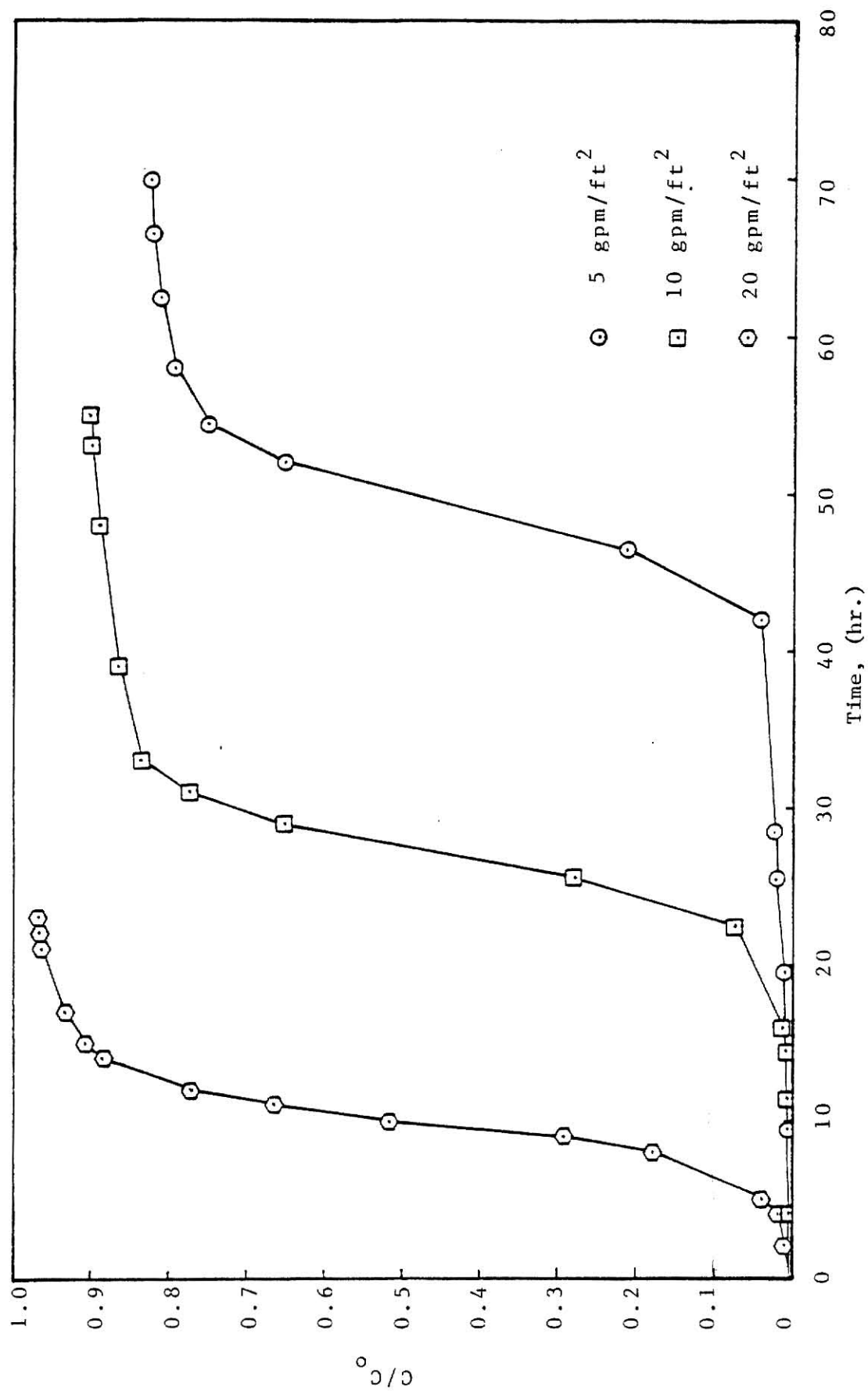


Figure 39. Adsorption Breakthrough Curves for Semifluidized Bed. ($C_0 = 1.0 \times 10^{-3}M$)

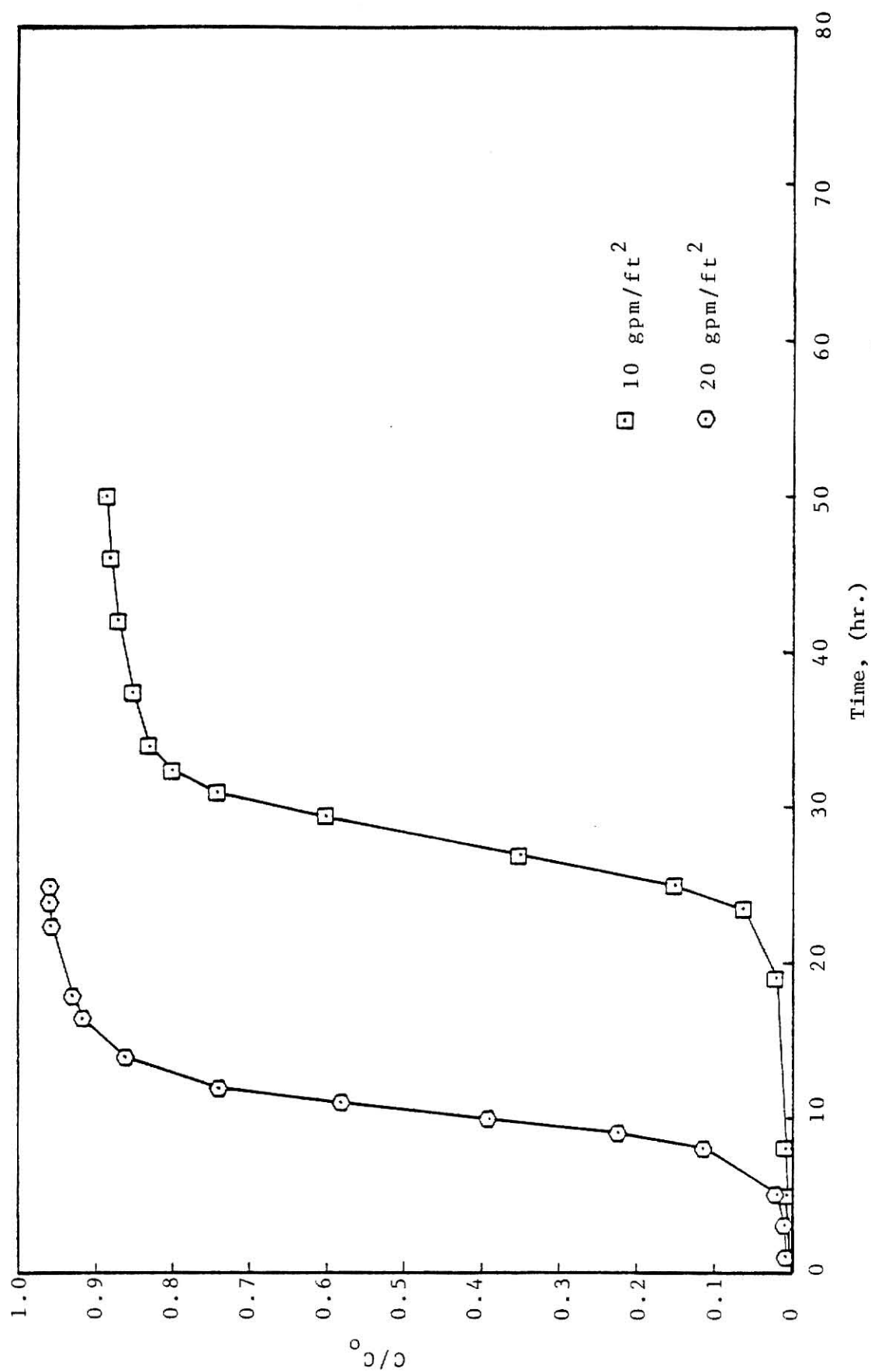


Figure 40. Adsorption Breakthrough Curves for Packed Bed. ($C_0 = 1.0 \times 10^{-3}M$)

Table 15. Time Required to Reach $C/C_0 = 0.05$ & 0.80 for
 Adsorption in F-400 Columns
 at Flow Rate 5, 10, 20 gpm/ft²

Flow Rate	Bed Category	$C/C_0 = 0.05$	$C/C_0 = 0.80$
5 gpm/ft ²	Fluidized	33.0 hr.	57.5 hr.
	Semifluidized	42.5 hr.	60.0 hr.
10 gpm/ft ²	Fluidized	5.5 hr.	20.5 hr.
	Semifluidized	20.0 hr.	32.0 hr.
	Packed	22.0 hr.	32.5 hr.
20 gpm/ft ²	Semifluidized	5.5 hr.	12.5 hr.
	Packed	6.0 hr.	13.0 hr.

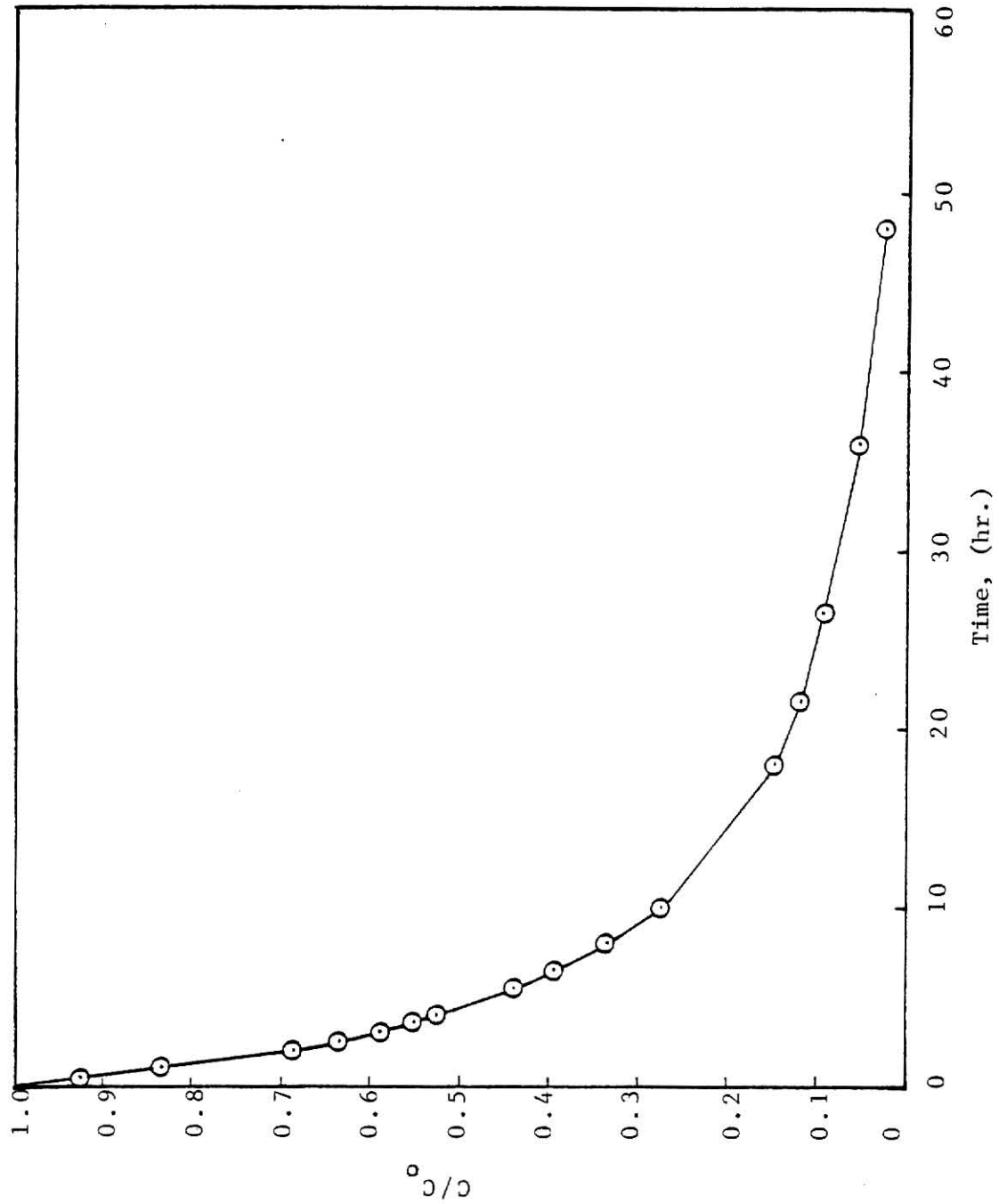


Figure 41. Desorption Breakthrough Curve for Fluidized Bed.
 ($C_o = 9.16 \times 10^{-4} M$, flow rate 10 gpm/ft²)

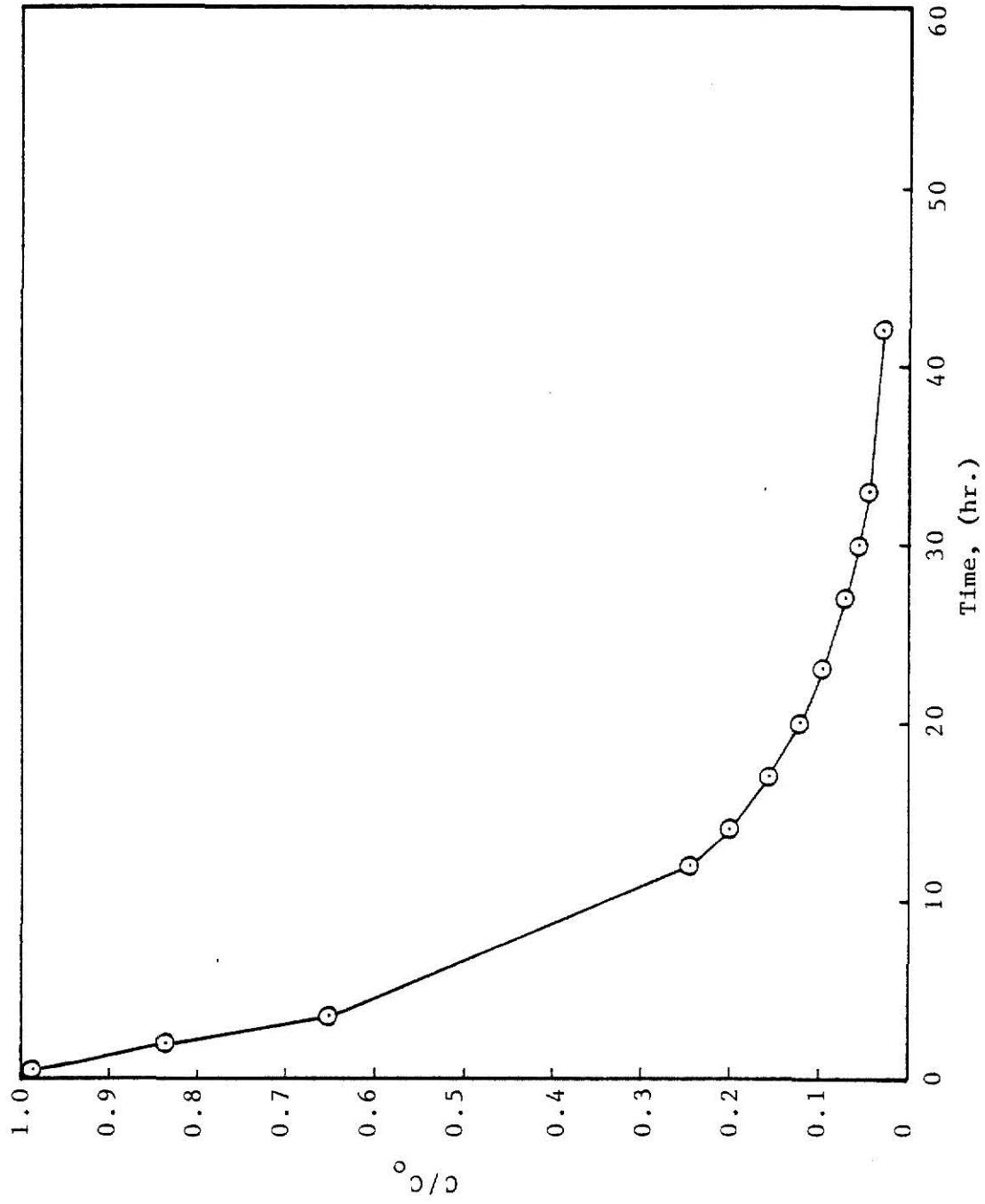


Figure 42. Desorption Breakthrough Curve for Semifluidized Bed.
($C_0 = 9.04 \times 10^{-4} \text{ M}$, flow rate 10 gpm/ft^2)

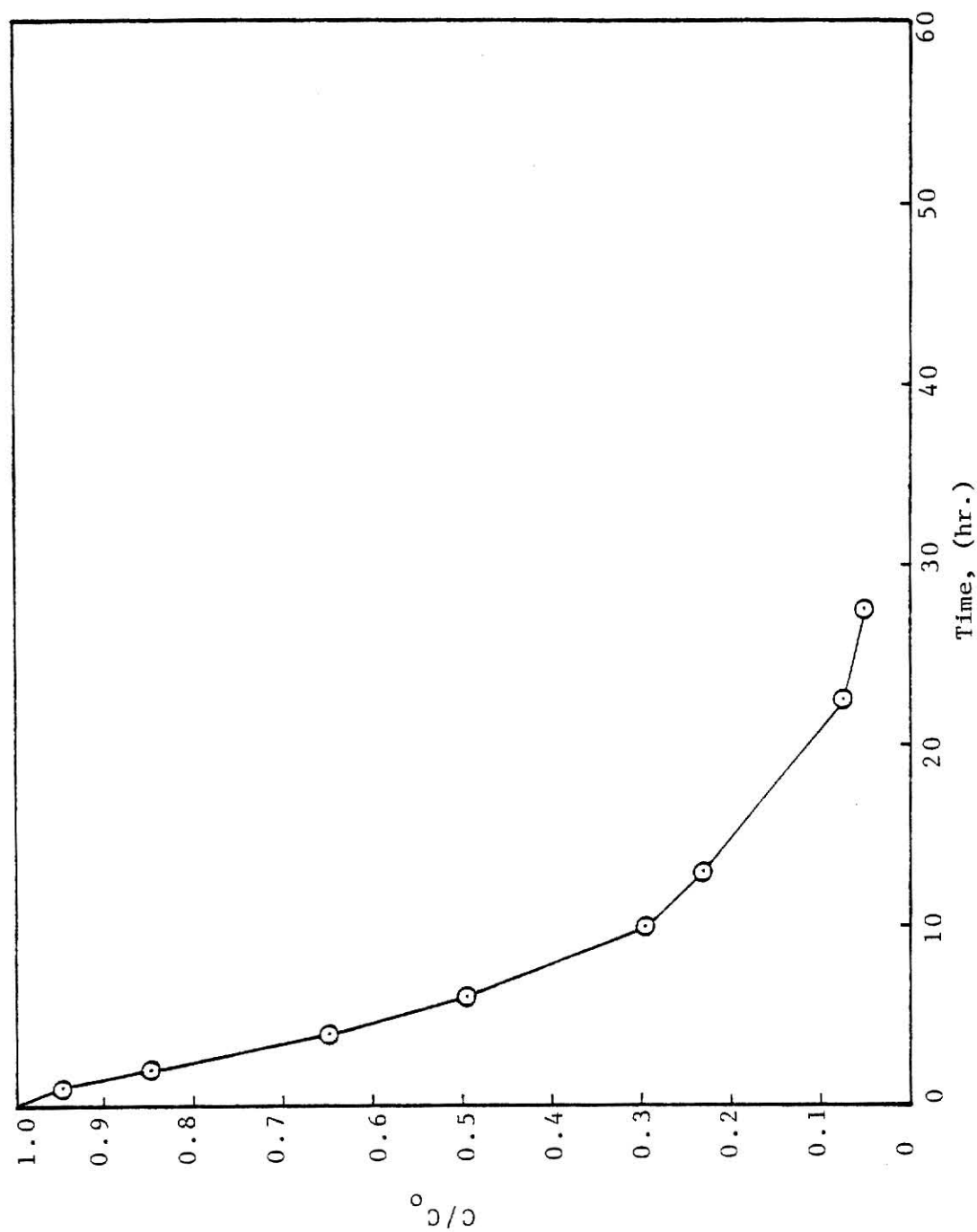


Figure 43. Desorption Breakthrough Curve for Packed Bed.
 $(C_0 = 8.85 \times 10^{-4} M, \text{ flow rate } 10 \text{ gpm/ft}^2)$

Table 16. Time Required to Reach $C/C_0 = 0.05$ for
Desorption in F-400 Columns at
Flow Rate of 10 gpm/ft²

	Fluidized	Semifluidized	Packed
Initial Conc.	$9.16 \times 10^{-4} M$	$9.04 \times 10^{-4} M$	$8.5 \times 10^{-4} M$
Time Required	37.5 hr.	30.5 hr.	27.5 hr.

concentrations are not the same for each case, therefore no conclusions can be made from these results.

Two experiments were carried out with semifluidized and packed beds filled with APC carbon at a flow rate of 14 gpm/ft². Their adsorption breakthrough curves are presented in Figure 44 and their desorption curves are shown in Figures 45 and 46. Table 17 shows the required time to reach $C/C_0 = 0.05$ and 0.90 in APC column adsorption process. Table 18 presents the time required for desorption to $C/C_0 = 0.05$.

Table 19 illustrates the computed pressure drop for fluidized, semifluidized, and packed beds containing Filtrasorb-400 and APC activated carbon under the conditions of different flow rates. The pressure drop for packed bed is calculated using Ergun's equations, and for fluidized bed using simple force balance. For semifluidized beds a linear summations is made based on the fractions of packed and fluidized sections. The pressure drop per unit amount of solute adsorbed is also shown in Table 19, and indicates that semifluidized bed is economically advantageous compared to the three types of beds.

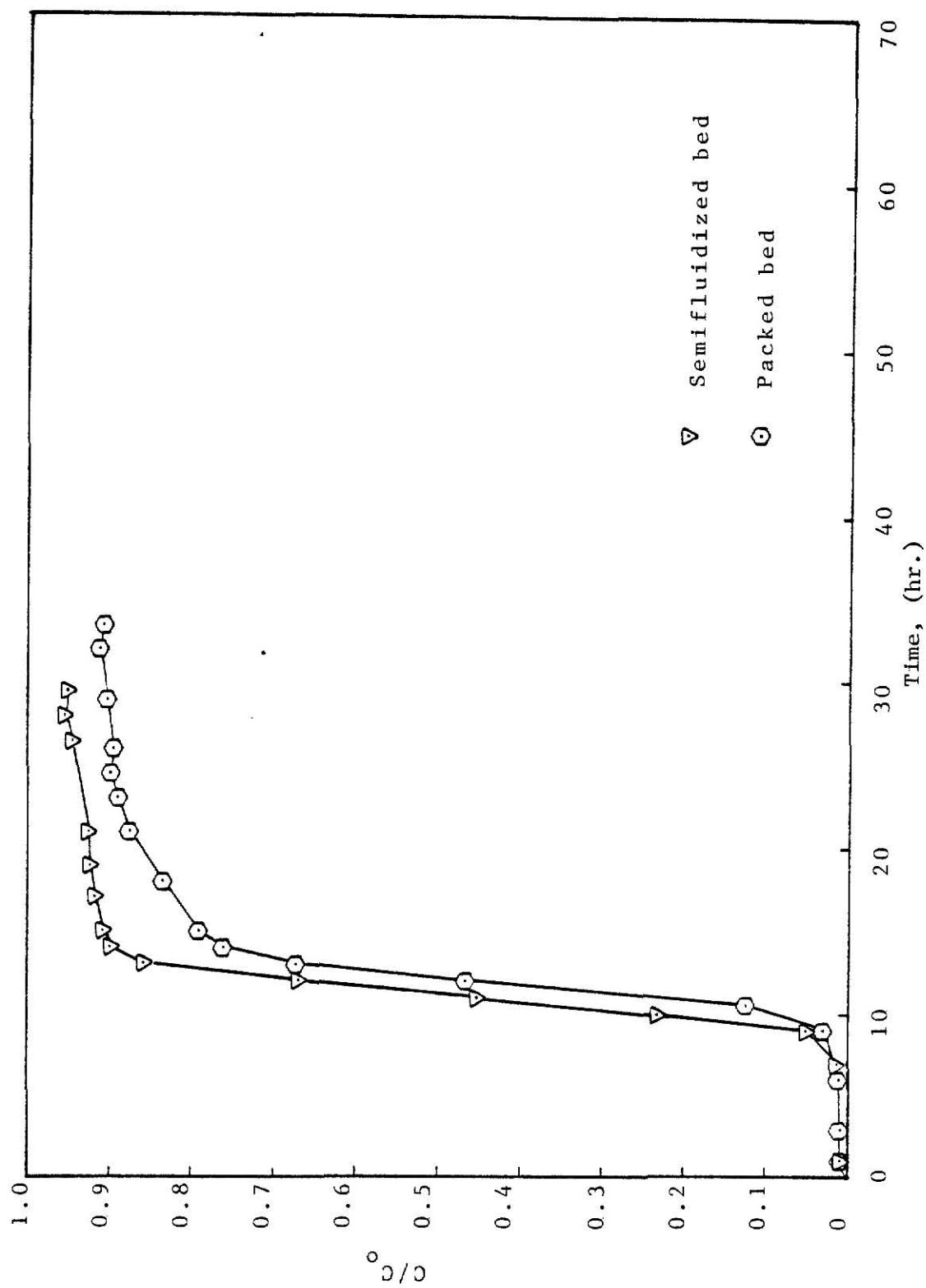


Figure 44. Adsorption Breakthrough Curves for Flow Rate 14 gpm/ft². ($C_0 = 1.0 \times 10^{-3} M$, columns containing APC carbon)

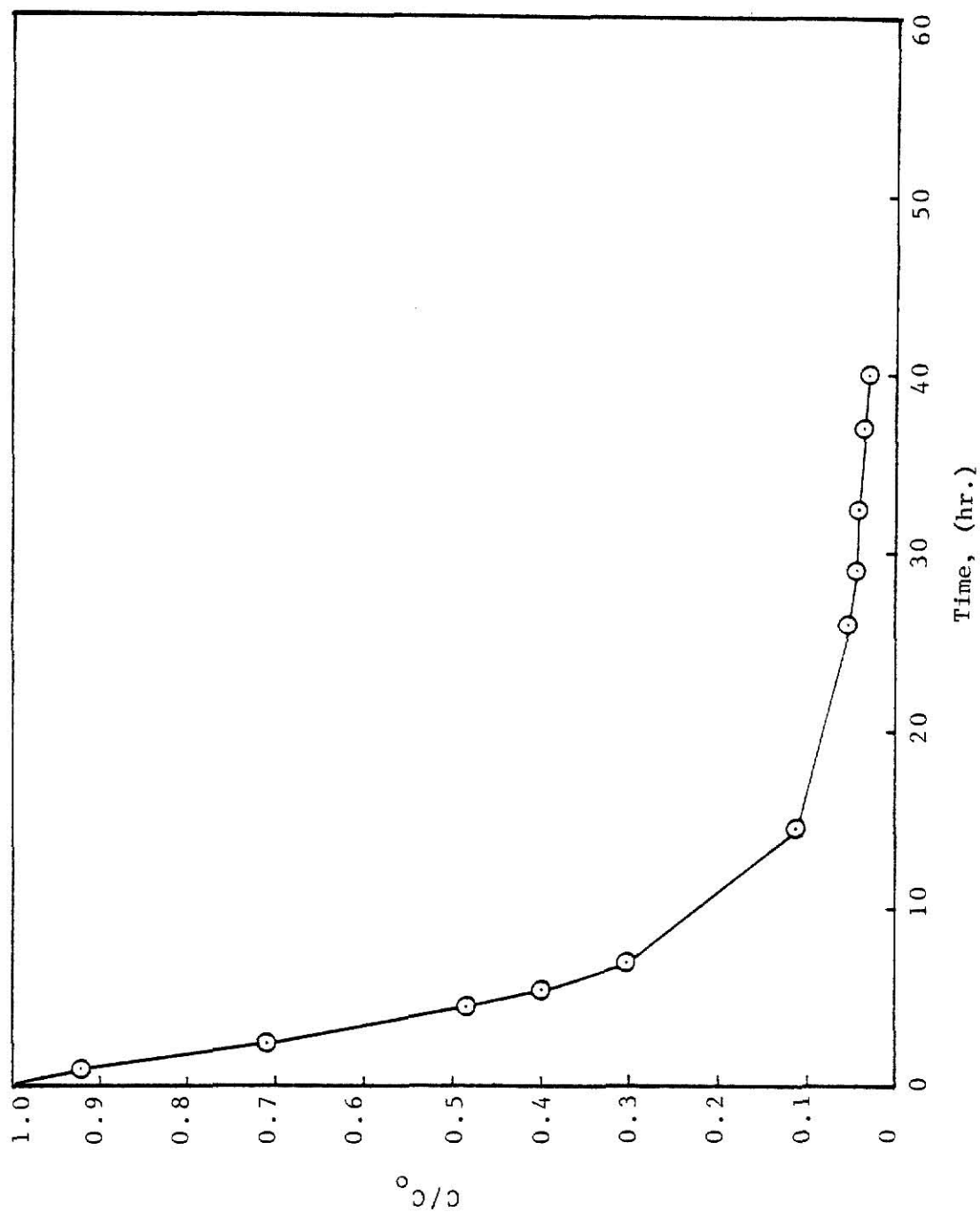


Figure 45. Desorption Breakthrough Curve for Semifluidized Bed containing APC.
 ($C_o = 9.38 \times 10^{-4} M$, flow rate 14 gpm/ft²)

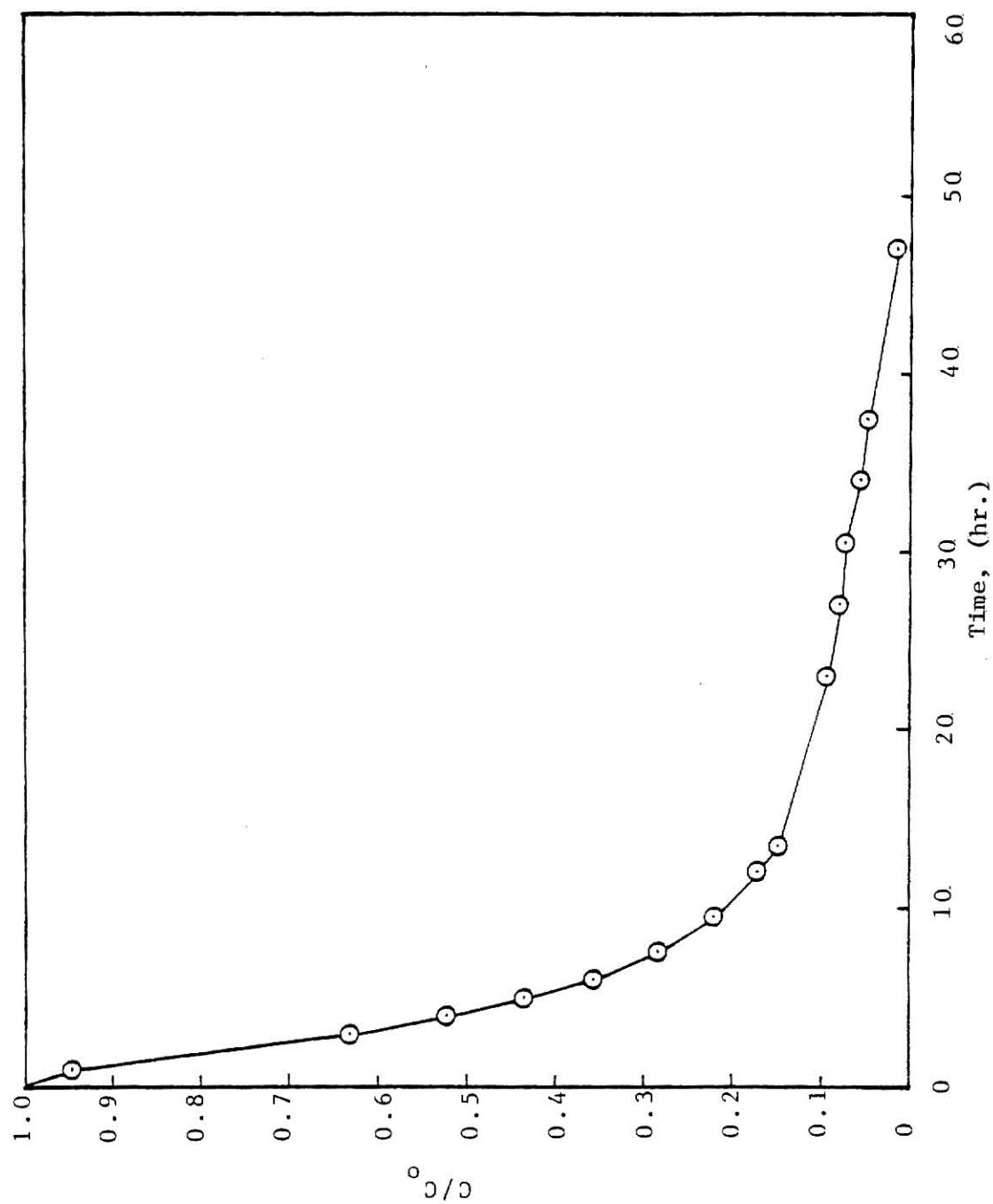


Figure 46. Desorption Breakthrough Curve for Packed Bed containing APC.
 ($C_0 = 9.08 \times 10^{-4} M$, flow rate 14 gpm/ft^2)

Table 17. Time Required to Reach $C/C_o=0.05$ & 0.90 for
Adsorption in APC Columns

Flow Rate	Bed Category	$C/C_o=0.05$	$C/C_o=0.90$
14 gpm/ft ²	Semifluidized	9 hr.	14.0 hr.
	Packed	9.5 hr.	24.5 hr.

Table 18. Time Required to Reach $C/C_o=0.05$ for
Desorption in APC Columns at
Flow Rate of 14 gpm/ft²

	Semifluidized	Packed
Initial Conc.	$9.38 \times 10^{-4} M$	$9.08 \times 10^{-4} M$
Time Required	26 hr.	35 hr.

Table 19. Pressure Drop of Fluidized, Semifluidized, and Packed Carbon Beds at Different Flow Rates

Flow Rate (gpm/ft ²)	Bed Category	ΔP (ft)	Time to Reach $C/C_0=0.05$ (hr)	Q (mole)	$\Delta P/Q$ (ft/mole)
5	Fluidized	0.363	33.0	0.820	0.443
	Semifluidized	0.588	42.5	1.056	0.557
10	Fluidized	0.297	5.5	0.273	1.088
	Semifluidized	1.050	20.0	0.994	1.056
	Packed	1.868	22.0	1.094	1.707
14	Semifluidized (APC)	11.236	9.0	0.626	17.949
	Packed (APC)	15.353	9.5	0.661	23.227
20	Semifluidized	2.474	5.5	0.547	4.523
	Packed	4.128	6.0	0.596	6.926

ΔP : Pressure Drop

Q: Amount of Adsorbed Phenol

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. Both phenol and naphthalene isotherms were well fitted by the three-parameter equation over the ranges studied.

2. Naphthalene exhibited the greater amenability to activated carbon adsorption because of its relatively low solubility in aqueous solution.

3. The results of these experiments illustrate that the adsorption of phenol or naphthalene is an exothermic process. The amount of solute adsorbed decreases with increasing temperature.

4. For two solutes belonging to phenolic and polyaromatic hydrocarbon classes with comparable diffusion coefficients, multicomponent adsorption model predicts adsorption rates satisfactorily.

5. A thorough comparison of the adsorption breakthrough curves for phenol in fluidized, semifluidized, and packed carbon beds, seems to indicate that the packed bed is the best column adsorber for adsorption because of the longest time would be needed before breakthrough occurs. As regards semifluidized bed, breakthrough time is close to that of packed bed. With APC carbon, breakthrough curves are almost identical for packed and semifluidized beds. Semifluidized beds have lower pressure drop compared to packed beds, and hence further investigation is

warranted to evaluate the economic advantage of semifluidized beds.

Recommendations

1. Extend the use of three-parameter isotherm model to other priority pollutants.
2. Use the column technique to study naphthalene and determine the competitive adsorption of phenol-naphthalene mixtures in columns.
3. Determine toxic substances removal under the process which consists of two-phase fluidized bed with carbon coupling adsorption and biodegradation resulting from attached microbial growth on the carbon particles.

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APPENDIX

STANDARD ABSORBANCE CALIBRATION CURVES
FOR PHENOL AND NAPHTHALENE

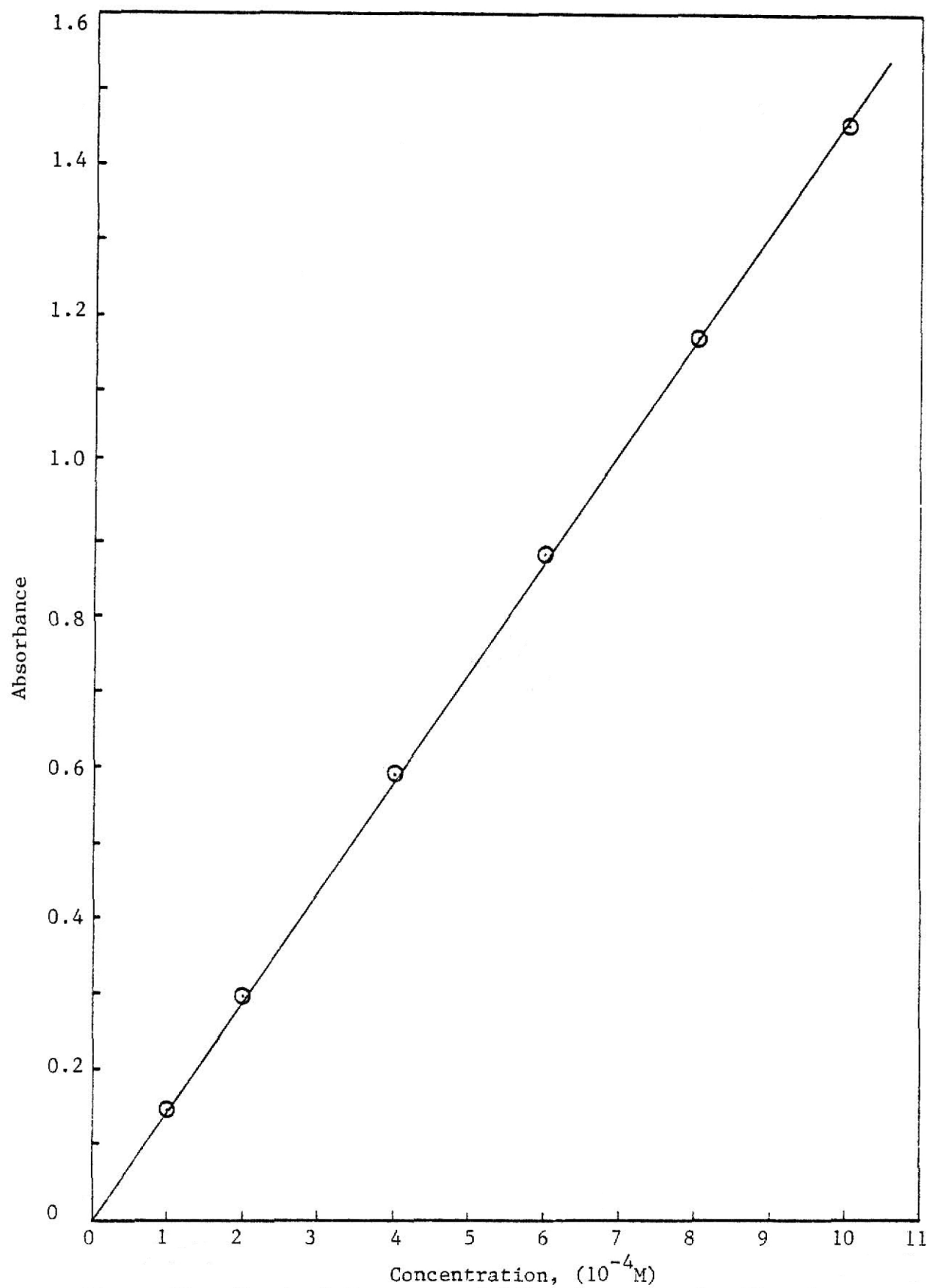


Figure 47. Standard Absorbance Calibration Curve for Phenol.
(wave length= 270 nm, cell length= 10 mm)

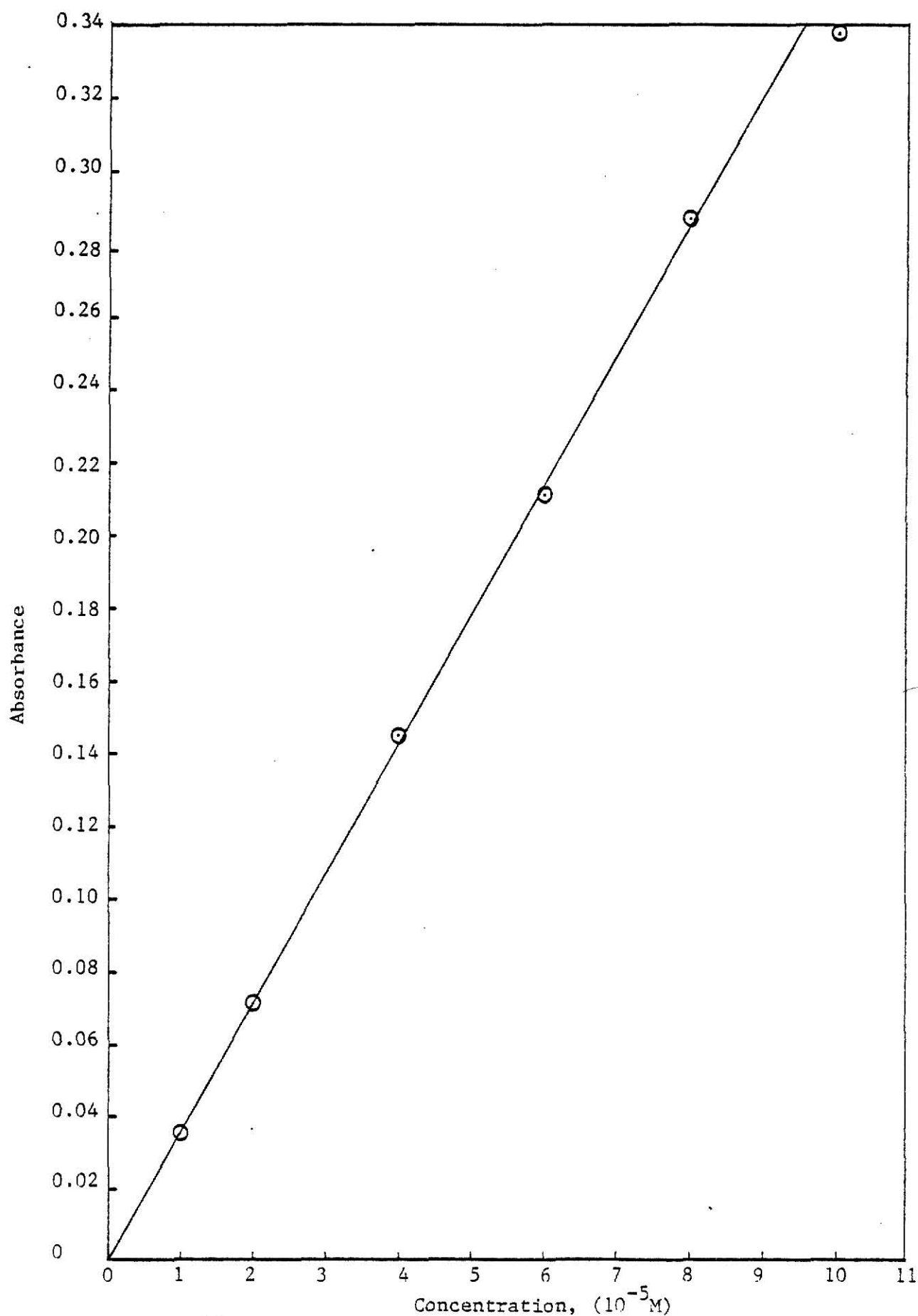


Figure 48. Standard Absorbance Calibration Curve for Phenol.
(wave length = 221 nm, cell length = 10 mm)

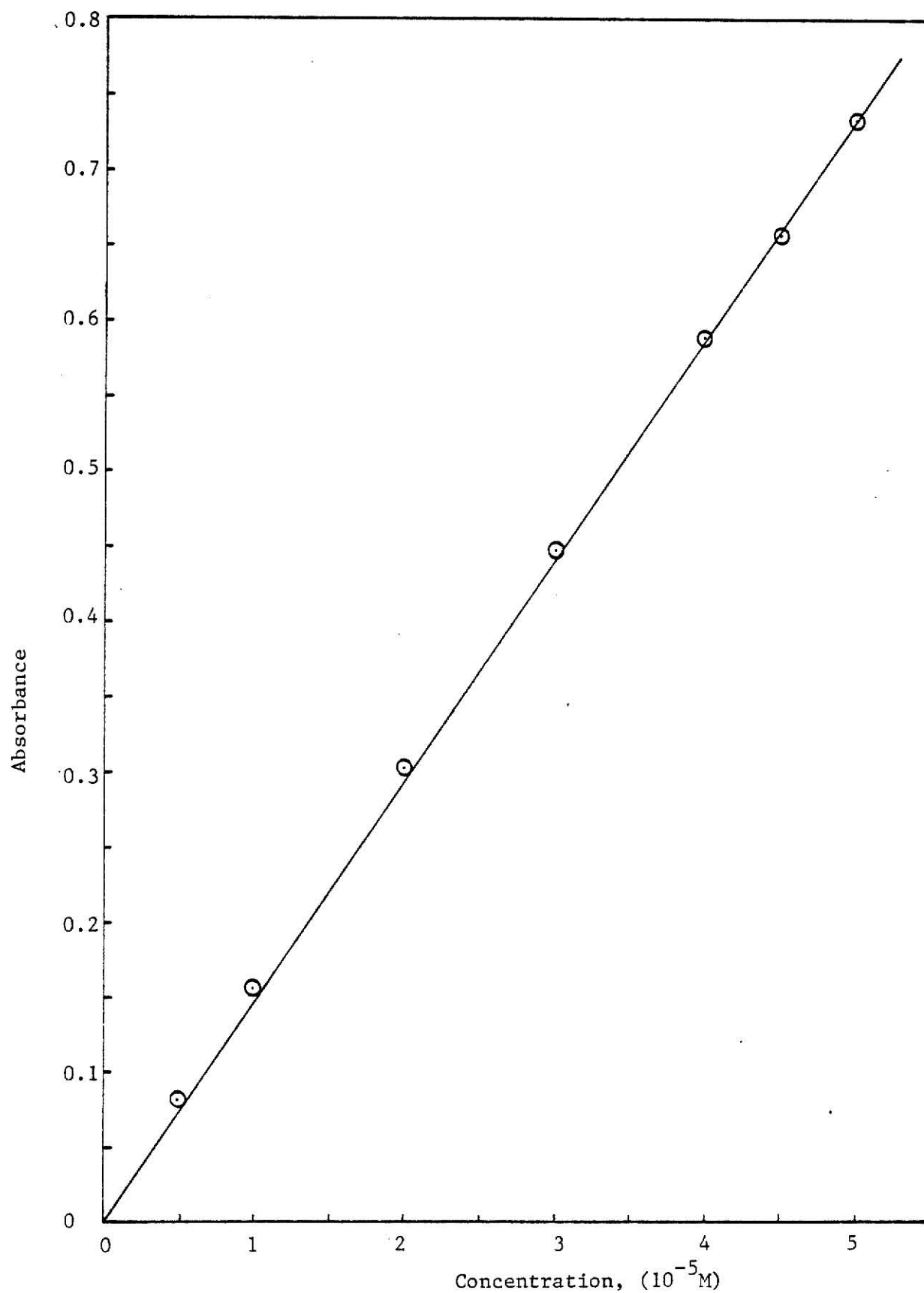


Figure 49. Standard Absorbance Calibration Curve for Phenol.

(wave length = 221 nm, cell length = 50 mm)

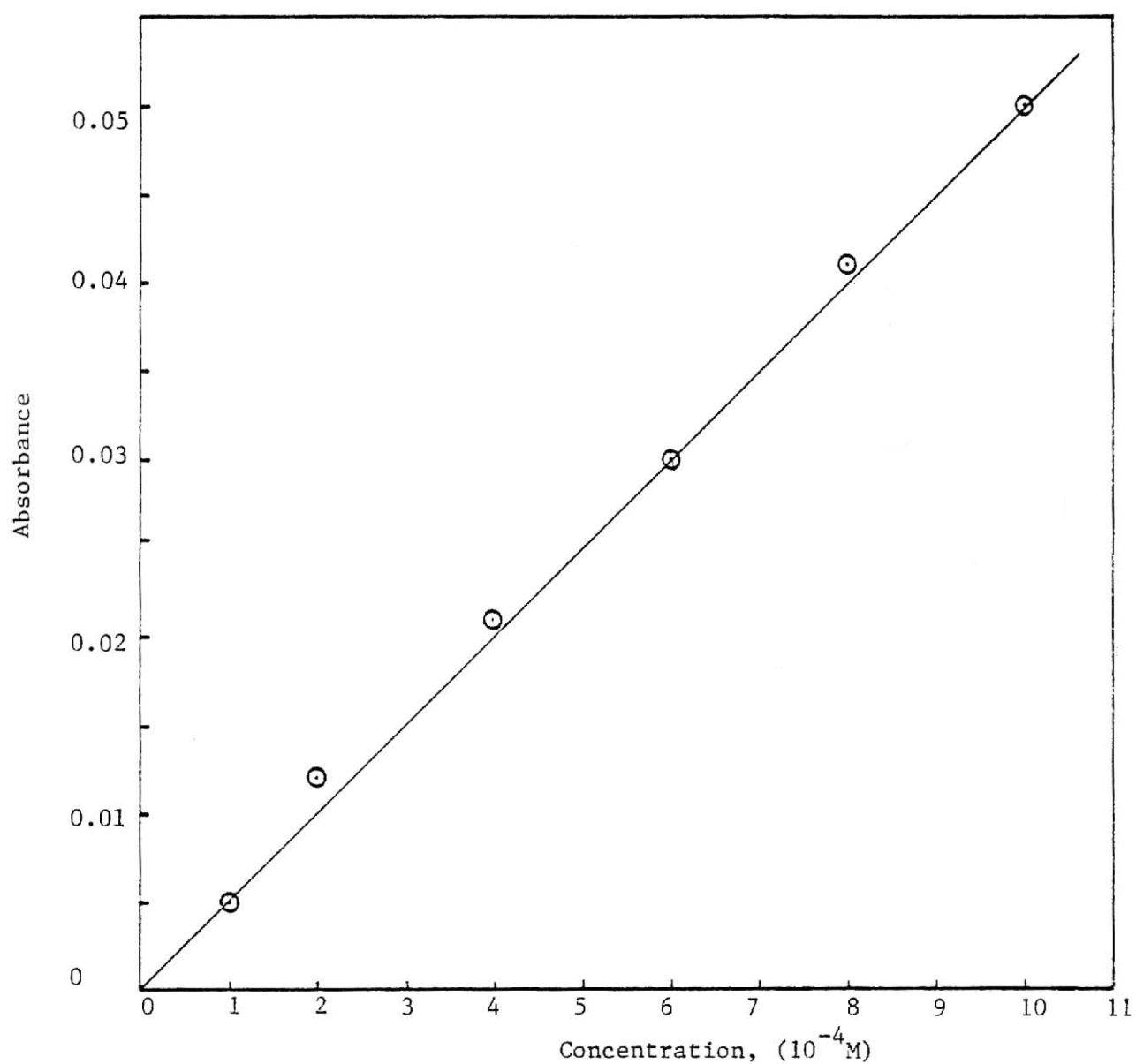


Figure 50. Standard Absorbance Calibration Curve for Phenol.
(wave length = 286 nm, cell length = 10 mm)

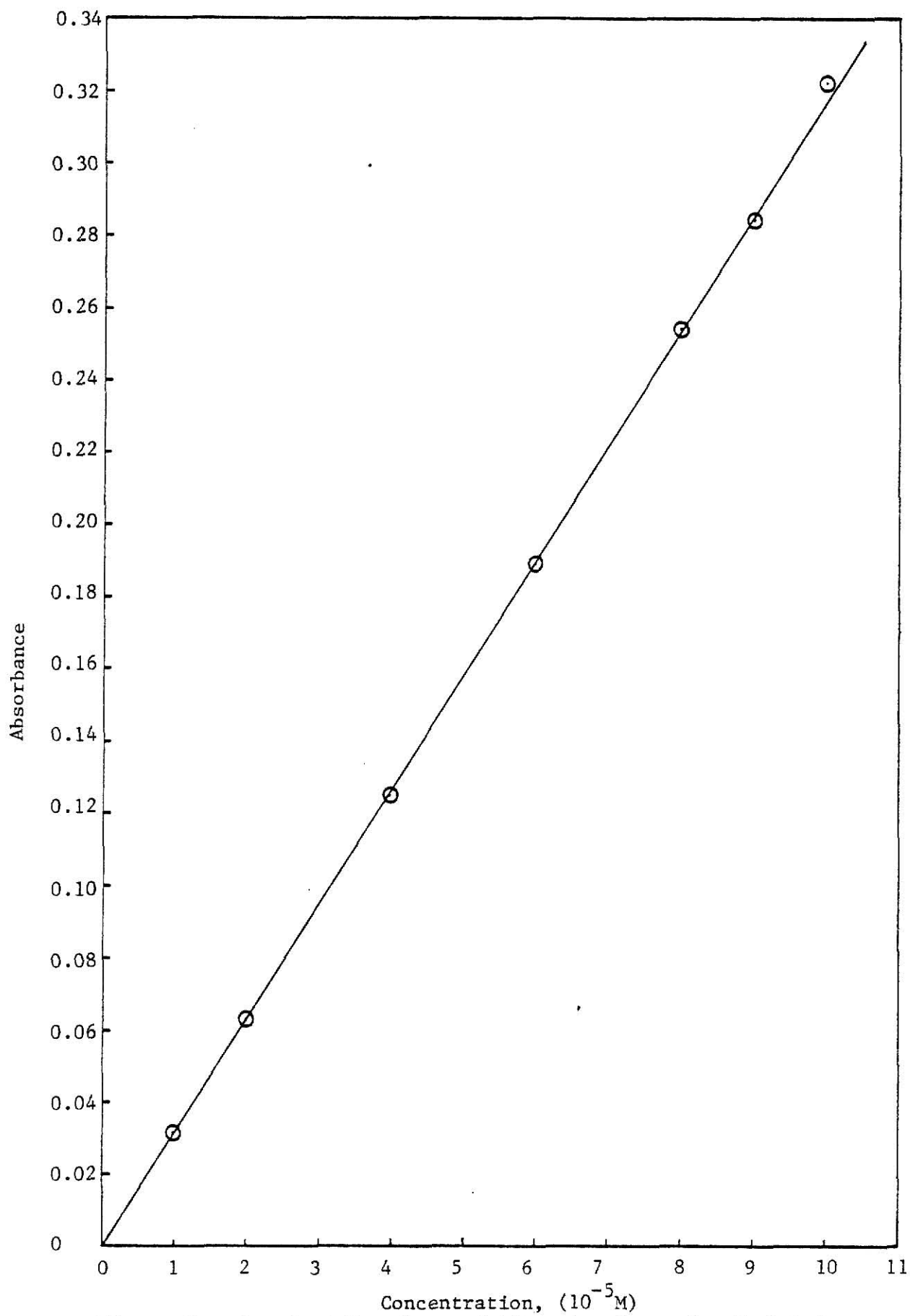


Figure 51. Standard Absorbance Calibration Curve for Naphthalene.
(wave length = 286 nm, cell length = 10 mm)

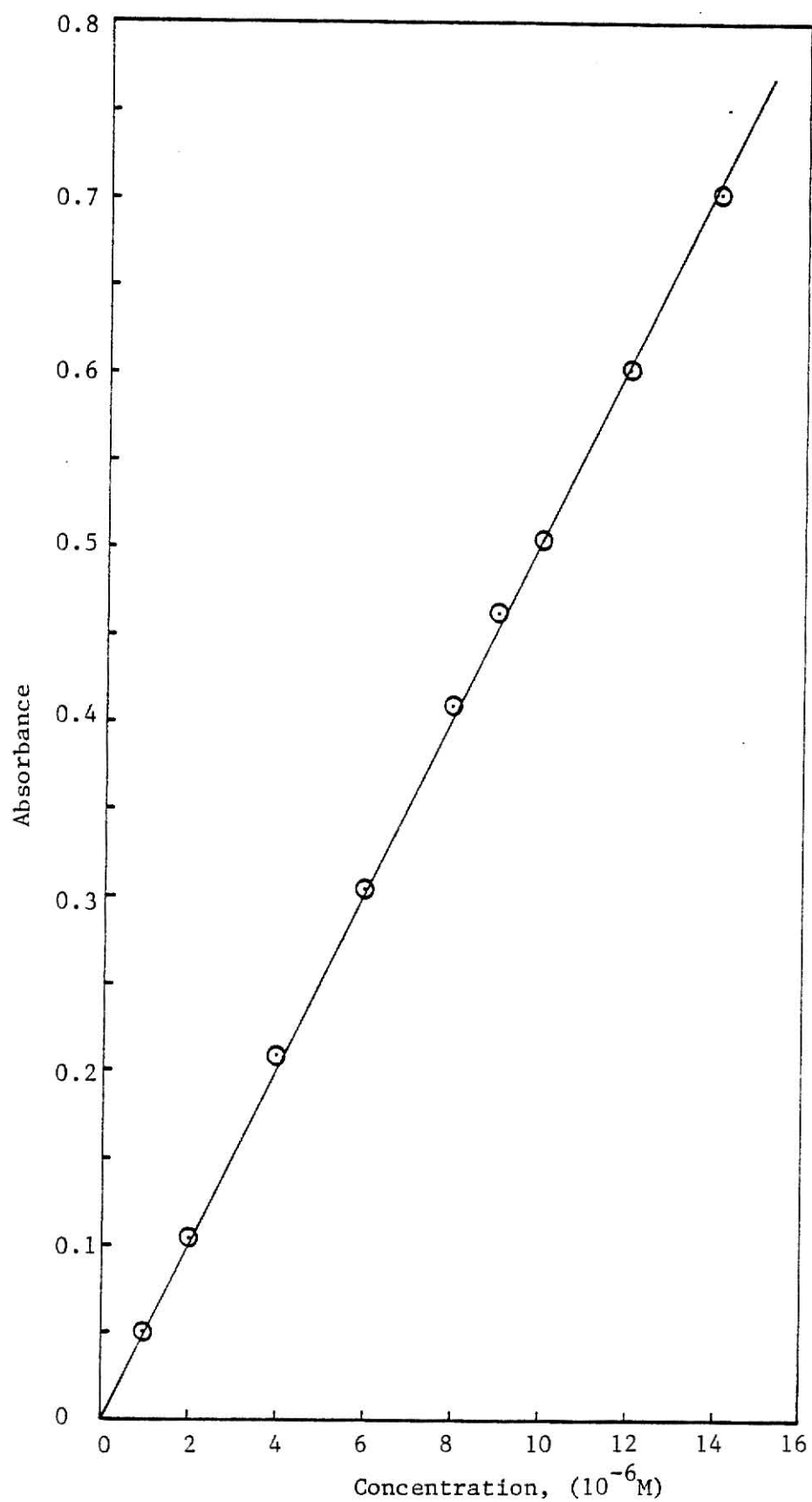


Figure 52. Standard Absorbance Calibration Curve for Naphthalene.
(wave length = 221 nm, cell length = 10 mm)

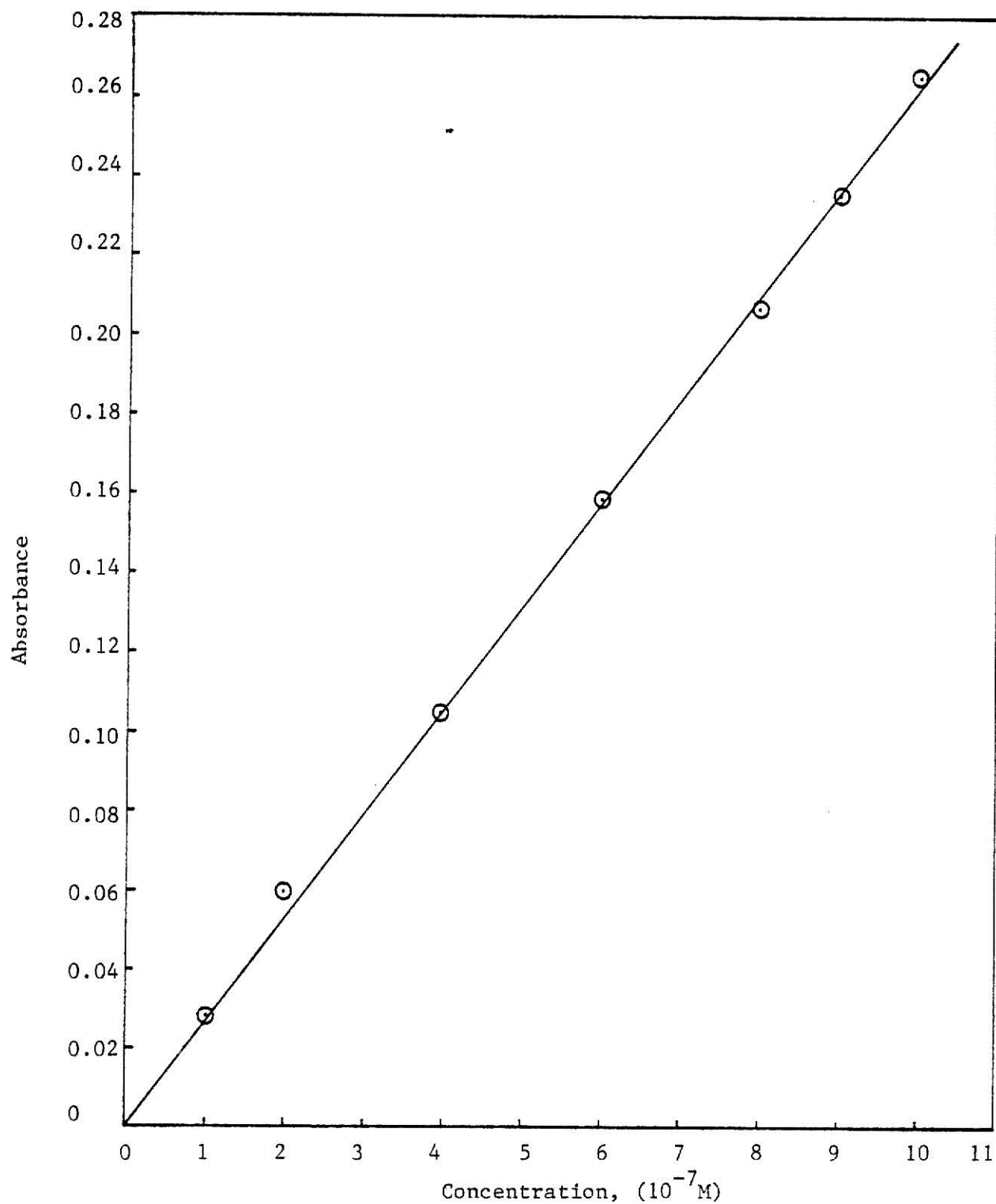


Figure 53. Standard Absorbance Calibration Curve for Naphthalene.
(wave length = 221 nm, cell length = 50 mm)

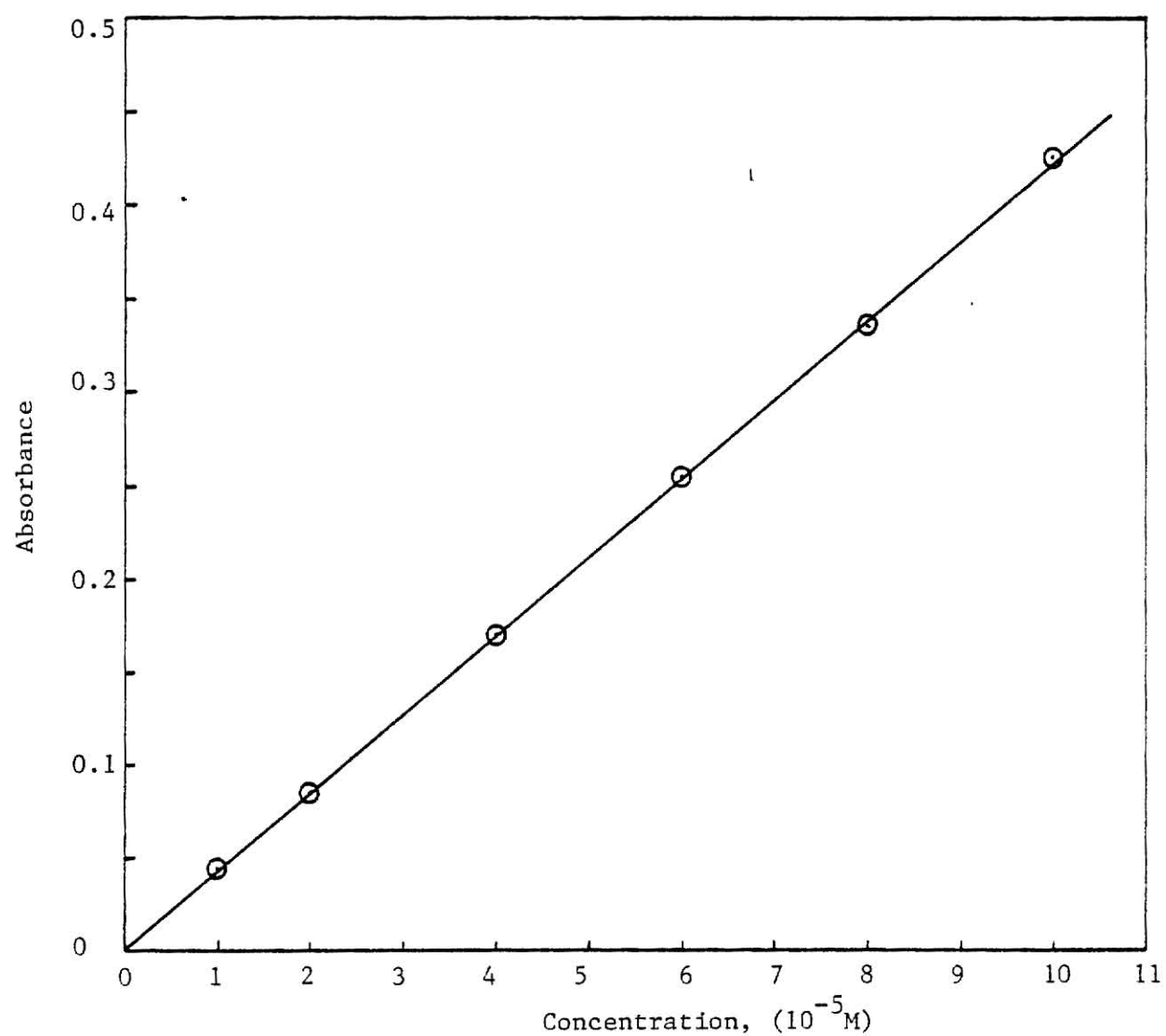


Figure 54. Standard Absorbance Calibration Curve for Naphthalene.
(wave length = 270 nm, cell length = 10 mm)

ACTIVATED CARBON ADSORPTION FOR REMOVAL OF
PRIORITY POLLUTANTS PHENOL AND NAPHTHALENE

by

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AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT

Adsorption equilibrium tests on single-solute and bi-solute system were carried out. In single-solute system, adsorption isotherms were developed for phenol at temperatures of 10, 20, and 30°C; and for naphthalene at temperatures of 10, 24, and 30°C. It was concluded that the adsorption of phenol or naphthalene is an exothermic process. Adsorption rate experiments on single-solute and bi-solute system were conducted at room temperature of 24°C.

Three-parameter adsorption models for single solute and bi-solute system were used to fit the adsorption equilibrium experimental data. Two adsorption rate models were utilized to predict the adsorption rates for single solute and bi-solute system, respectively.

The test results show that for mixtures, there is a slight discrepancy between the experimental data and for those calculated by the models. This deviation may be attributed to(1) the phenol/naphthalene interaction, and(2) the inadequate correlation of the mixture equilibrium data.

Three types of columns- fluidized, semifluidized, and packed carbon bed were used to study the adsorption of phenol. The comparison of adsorption breakthrough curves shows that packed beds and semifluidized beds have comparable breakthrough times. However, due to the lower pressure drop in semifluidized beds, this type of operation is more economically advantageous.