

SORPTIVE RECLAMATION OF PHENOLS FROM COAL CONVERSION WASTEWATER

by

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CHAPTER 1

INTRODUCTION

A principal environmental problem associated with coal gasification is the generation of wastewater containing significant quantities of phenols. Forney et al. (1974) have found that, for the Synthane process, approximately 120 gallons of water are recovered for every ton of coal gasified. Schmidt, Sharkey, and Friedel (1974) have reported a mass spectrometric analysis of gasifier condensate; the contaminants were found to include phenol, cresols, dihydric phenols, naphthols, pyridines, and indenols at total concentrations as high as 7,000 to 10,000 ppm by weight. The technology for rough treatment of this type of wastewater has existed for years; Crawford (1926) has given an interesting description of the use of benzene as a solvent in the extractive treatment of weak ammonia liquors in coke plants. The demands made upon modern treatment schemes are much more stringent, however. According to Lanouette (1977), the Environmental Protection Agency has established a permissible level for phenols of 0.02 mg/l for 1983 for the Best Available Control Technology Economically Achievable. It is apparent that treatment methods used for the control of coal conversion wastewater will have to provide decontamination factors in excess of 10^5 .

Existing methods for the treatment of phenolic wastewaters include: biological oxidation, destructive chemical oxidation,

incineration, adsorption, and solvent extraction. Gehrs (1975) states that pyridine and quinoline are not greatly affected by biological waste treatment processes, and Glasgow (1975) has found, in a preliminary economic study, that chemical oxidation of phenols is prohibitively expensive. Furthermore, given the current concern over depletion of natural resources, it is important to note that only solvent extraction and adsorption offer any opportunity for recovery of the phenolic contaminants.

Solvent extraction has been and is being used for dephenolization in coke plants: Wilson and Wells (1950) note that some German coke plants have used tri-o-cresyl phosphate ("triphos") as the solvent, Beychok (1974) states that Lurgi's Phenosolvan extraction process (developed about 40 years ago) uses isopropyl ether as the solvent, and Eddinger et al. (1965), have suggested the possible use of butyl acetate for solvent extraction in the COED process. The FMC-COED performance report indicates that the recovery of the aromatics could have a beneficial effect upon process economics. Recently, Boyer, DeGeorge and Wasserstrom (1980) have studied the optimization of water usage in the Exxon Donor Solvent Coal Liquefaction Process; liquid-liquid extraction was used to remove phenols from the wastewater and the phenols recovered could be sold as a byproduct.

Some studies of sorptive treatment processes for aqueous solutions of phenol and phenolic derivatives have been reported. Dedrick and Beckman (1967) have compared pore and homogeneous

diffusion models in a study of the adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) on activated carbon. The sorptive process was found to be adequately described by a solution to the unsteady-state diffusion equation adapted from Crank (1973). A microcore/macropore model was developed by Famularo, Mueller and Pannu (1980) and it was found that this model could quantitatively predict the performance of carbon columns for the adsorption of phenol and p-nitrophenol.

Baker, Clark, Jesernig, and Huether (1973) have reported the sorptive recovery of p-cresol from process effluent and Juntgen and Klein (1974) have described regeneration tests for activated carbon loaded with phenol. Suzuki, Misic, Koyama and Kawazoe (1978) have studied the thermal regeneration of spent activated carbon using the technique of thermogravimetry analysis (TGA). It was found that phenolic organics gave high residuals on activated carbon after heating to 800°C. The TGA technique was also used by Chihara, Smith and Suzuki (1981) to study thermal decomposition kinetics in the regeneration of powdered activated carbon.

A principal tenet of this study is that recovery of the phenolic contaminants of gasifier condensate could generate a substantial economic credit for the overall process. Therefore, if sorptive treatment with activated carbon were to be applied, it would be highly desirable to recover the sorbate molecules prior to carbon regeneration in, for example, multiple-hearth furnaces. A secondary effect of the reclamation of phenols from

coal conversion wastewater could ultimately be the reduction of the demand for synthetic (petroleum-derived) phenol by the plastics industry. Haberstroh and Collins (1974) indicate, for example, that in 1970, 210 million gallons of benzene--obtained from petroleum--were used to manufacture phenol.

This study provided the following information:

1. Kinetic and equilibrium data on the adsorption of some of the contaminants existing in high concentration in gasifier condensate that have little been considered in the literature such as o-cresol, resorcinol and catechol.
2. An examination of plausible schemes for modifying the sorbent regeneration process so that reversibly-bonded phenols could be recovered.

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CHAPTER 2

ADSORBATES AND ADSORBENT

2.1 ADSORBATES

Condensate waters from the Bureau of Mines Synthane process for coal gasification have been investigated with mass spectrometric methods to determine organic contaminants by Forney et al. (1974). It was found that phenolic-type compounds were the most abundant and present in concentrations ranging from 2,000 to 7,000 ppm. Among various phenolic compounds, phenol along with its alkyl derivatives were the most predominant. Dihydroxy benzenes were also present in high concentration, with up to 500 ppm being detected in several samples.

Throughout this study, attention was focused upon the phenolic compounds that exist in significant amounts in coal conversion wastewater, such as phenol, o-cresol, resorcinol and catechol. Hydroquinone was also studied, but consistent results were not obtained because of its tendency to form quinone in alkaline solutions. All sorbate species were obtained as the chemically pure compounds from Fisher Chemical Company. Phenol, resorcinol and catechol were obtained in crystalline form; and o-cresol in liquid form. Their properties are shown in Table 1.

2.2 ANALYTICAL DETERMINATION OF SORBATE SPECIES

Measurement of the concentration of adsorbate in the

TABLE 1
THE PROPERTIES OF ADSORBATES

Adsorbates	phenol	o-cresol	resorcinol	catechol
F.W.	94.11	108.14	110.11	110.11
M.P. (°C)	41	31	110	104
B.P. (°C)	182	191	281	246
pKa	9.89 (20°C)	10.20 (25°C)	9.81 (25°C)	9.85 (20°C)
Solubility (g/100gH ₂ O, 25°C)	9.3	2.5	123	45

experimental solutions was accomplished by the standard test method for phenolic compounds in water (ASTM D 1783-70) which involves the reaction of 4-aminoantipyrine with those compounds at a pH of 10. The antipyrine color is formed in the presence of potassium ferricyanide and is measured by photometric method; absorbance was measured against blank solutions at a wave-length of 510 nm by means of a spectrophotometer (Bausch & Lomb, Spectronic 600).

Standard solutions of the adsorbates were prepared for calibration by dissolving accurately weighed quantities of each compound in freshly boiled and cooled water. Appropriate dilutions of these solutions were made to give a series of aliquots suitable for spectrophotometric calibration.

For the range of concentrations used in this work, all solutions studied conformed to the Beer-Lambert law, showing good proportionality of absorbance to concentration at the wavelength used. However, some phenolic compounds with a substituent in the para position do not produce color with 4-aminoantipyrine and the method is not suitable in those cases.

2.3 ADSORBENT

Activated carbon has long been a substance of great importance in removal of small concentrations of dissolved organic compounds from aqueous solutions. Use of activated carbon in advanced water treatment systems has been proven to be effective and is widely applied to solve the problems of purification of industrial effluents like phenolic wastes

(Juntgen and Klein, 1974). Throughout this study, the activated carbon used as the adsorbent was from Fisher Scientific Company manufactured from coccanut charcoal (6 to 14 Mesh, Cat. No. 5-685B).

2.4 PARTICLE SIZE DISTRIBUTION OF ADSORBENT

Smith and Jordan (1964) indicated that the log-normal law serves as an excellent mathematical model for particle size distribution analysis. The vast majority of dispersed systems such as those produced by milling and grinding, tend to follow this model which is given by

$$y = \frac{1}{\ln \sigma_g 2\sqrt{\pi}} \exp \left[- \frac{(\ln x - \ln M)^2}{2 \ln^2 \sigma_g} \right] \quad (1)$$

where M is the geometric mean particle size, σ_g is the geometric standard deviation, x is the particle diameter and y is the probability density.

A common method of gathering data involves some form of observation and measurement of the number of particles falling within a given size interval or the accumulated number smaller or larger than a stated size. In this study the particle numbers were measured by image analysis of the actual carbon sample with a Bausch & Lomb Omnicon System.

The determination of M and σ_g can be made by a simple graphical method; logarithmic probability paper is utilized and the percent of all particles smaller than a stated size is plotted as a function of the logarithm of size as shown in Figure 1. By the definition of M, its value is found at the 50%

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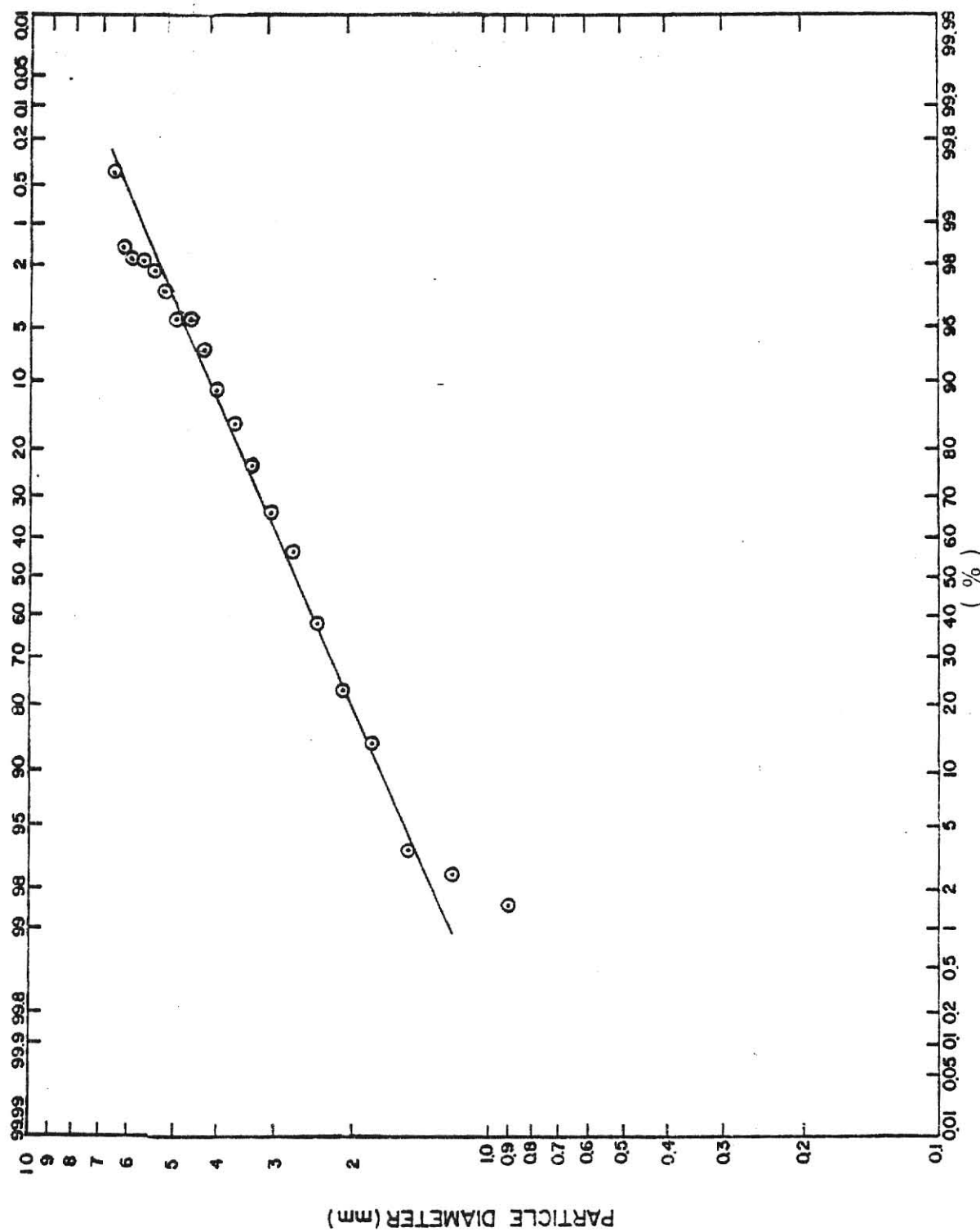


FIGURE 1 CUMULATIVE PERCENT OF PARTICLES LESS THAN STATED SIZE (%)

index; σ_g is given by

$$\sigma_g = \frac{84.13\% \text{ size}}{50\% \text{ size}} = \frac{50\% \text{ size}}{15.87\% \text{ size}}$$

The results obtained from the analysis of adsorbent showed that

$$M = 0.261 \text{ cm}$$

and

$$\sigma_g = 0.0084 \text{ cm}$$

2.5 SPECIFIC SURFACE AREA OF ADSORBENT

Computation of specific surface area is an important method for comparing potential adsorptive capacities of sorbent materials. Gas-phase measurements were performed using a Perkin-Elmer Shell Model 212D Sorptometer. In this method a stream of gas is passed over a cooled solid sample, and the surface area of the sample is determined by measuring the amount of adsorbed gas. The gas stream consists of a known mixture of a suitable adsorbate and an inert gas carrier. In general, nitrogen is used as the adsorbate and helium as the inert carrier gas.

The calculation is based on the BET equation, and a plot of this equation yields the desired data. The BET plot is a graphical representation of the BET equation:

$$\frac{P}{V_{ads} (P_o - P)} = \frac{C-1}{V_m C} \frac{P}{P_o} + \frac{1}{V_m C} \quad (2)$$

where P is the partial pressure of the adsorption gas, P_o is the saturation pressure of the adsorption gas over the solid sample at the temperature of the coolant, V_{ads} is the total volume

(STP) of adsorbed gas on the surface of adsorbent, V_m is the volume (STP) of adsorbed gas when the entire adsorbent surface is covered with a monomolecular layer, and C is a constant expressing the net adsorption energy. By plotting $P/V_{ads}(P_0-P)$ vs. P/P_0 , a straight line is obtained. The corresponding calculation data sheet for the sample of Fisher activated carbon is attached in Appendix A. The N_2 -BET specific surface area obtained for adsorbent carbon is about $1,000 \text{ m}^2/\text{gm}$.

2.6 THE POROSITY OF THE ADSORBENT

Precise measurement of the total pore volume of an activated carbon can be done by displacement of an inert gas such as helium to account for the micropore volume, and by displacement of mercury to account for the macropore volume (Weber, 1972). A good estimate can be made, however, by boiling activated carbon particles for an half hour or more in water, drying superficially on a piece of filter paper, and weighing. The method was very reproducible and would be expected to yield a realistic porosity since the carbon was used in aqueous solution. Porosity of adsorbent measured by this method was 0.42.

NOTATION

C	Dimensionless constant expressing the net adsorption energy	
M	Geometric mean particle size	cm
P	Partial pressure of the adsorption gas	mmHg
Po	Saturation pressure of the adsorption gas over the solid sample at the temperature of the coolant	mmHg
x	Particle diameter	cm
y	Probability density	
V _{ads}	Total volume (STP) of adsorbed gas on the surface of adsorbent	ml
V _m	Volume (STP) of adsorbed gas when the entire adsorbent surface is covered with a monomolecular layer	ml

GREEK LETTERS

σ_g	Geometric standard deviation	cm
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CHAPTER 3

EQUILIBRIA AND CAPACITIES FOR ADSORPTION

3.1 REVIEW OF PREVIOUS WORK

In any sorptive study involving activated carbon, knowledge of isotherms is essential, whether for system design or research purposes. The capacity of the adsorbent for uptake of adsorbate -- the position of equilibrium attained -- determines the useful life of the adsorbent. Without the knowledge of adsorption capacity, bed-life and location of the breakthrough curve cannot be predicted and kinetic performance cannot be modeled.

Snoeyink, Weber, and Mark (1969) have studied the effects of temperature and pH upon the adsorption of phenol and nitrophenol on activated carbon. They found a decrease in phenol-capacity of the carbon at lower pH and attributed it to competitive interaction between the protons and carbonyl oxygen, resulting in desorption of phenol. The adsorption capacity also decreases in higher pH ranges. This behavior is attributed to the repulsive forces between the sorbate anion and both the carbon surface and the sorbed species themselves. Wang et al. (1975) have noted that maximum sorptive capacity for organic acids often occurs at a level of acidity where $\text{pH} \approx \text{pKa}$. However, Snoeyink et. al. (1969) indicated that the effect of temperature on isotherm capacity was found to be slight.

Mattson, Mark, Weber, and Crittenden (1969) have studied the sorptive mechanisms of dephenolization with activated

carbon. They suggested that these aromatic compounds adsorb onto active carbon by a donor-acceptor complex mechanism involving carbonyl oxygens of the carbon surface acting as electron donors and the aromatic ring of the solute acting as the acceptor. Aromatic compounds with electron withdrawing substituent groups (producing lower electron density in the pi-system of the benzene ring) will form stronger donor-acceptor complexes and adsorb in larger quantities on activated carbon.

Peel and Benedek (1980) have studied the attainment of equilibrium for activated carbon isotherms. A review of published isotherms for adsorption of phenol on activated carbon indicates that there is a considerable inconsistency among the reported isotherms which was attributed to the difficulty in defining the attainment of true equilibrium. They suggested that granular carbon isotherms be evaluated over periods of at least 30 days unless rigorous studies are carried out to ensure equilibrium is obtained. The isotherms obtained by them were described well fitted by the Freundlich equation in the range of concentrations studied.

3.2 EXPERIMENT AND RESULTS

Although many studies can be found in the literature pertaining to adsorption equilibria and capacities of carbon for phenolic compounds, most of them concentrate upon the low-concentration range equilibrium. For design purposes, further information about the adsorption capacity covering high concentration ranges is necessary. For example, in the study

done by Juntgen and Klein (1974) on the purification of waste water from coking and coal gasification plants using activated carbon, the concentration of phenols treated by the pilot plant ranged from 650 to 1,400 mg/l.

The main purpose of this portion of the study was to obtain adsorption-capacity information for some phenolic contaminants that occur in high concentrations in gasifier condensate but have been rarely considered in the literature; examples are o-cresol, resorcinol and catechol. For design purposes, the maximum concentration studied was 1,100 mg/l.

Isotherm studies were performed by preparing 5-L batches of adsorbate solutions 200 ml measures of these solutions being placed in 250 ml flasks. A suitable, accurately weighed amount of adsorbent (typically, 0.04 to 1.25 g) was then added to each flask, the weights being varied so as to cover the range of equilibrium solute concentrations of interest. For each study, several flasks of solution were left without carbon for use as blanks. The flasks were tightly sealed and placed in an controlled-environment incubator to be shaken for 40 days. The temperature was kept at 25 °C. Samples from each of the solutions were analyzed at the end, the amounts sorbed were computed from the difference between the concentrations of adsorbate measured from the blanks and the depleted solutions. The pH values at equilibrium adsorption were approximately 7 for resorcinol and catechol, and about 8 for phenol and o-cresol.

The relationship between adsorption capacity and

equilibrium concentration was normally described by both the Langmuir adsorption equation and the Freundlich adsorption equation. The Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface and the assumption of a constant adsorption energy. It is expressed as follows:

$$X = \frac{Q b C}{1 + b C} \quad (3)$$

where Q is the Langmuir "monolayer" capacity constant, C is the equilibrium concentration and b is the Langmuir equilibrium constant. Although Snoeyink, Weber, and Mark (1969) have indicated that small sections of their data could be described well by this equation, it was not adequate over the entire range. Thus they also used the Freundlich equation, which has the form

$$X = K C^N \quad (4)$$

where K and N are Freundlich equation constants. This is basically an empirical isotherm but is often useful for data correlation.

Equation (3) and (4) can be expressed as two convenient linear forms, respectively:

$$\frac{C}{X} = \frac{C}{Q} + \frac{1}{Q b} \quad (5)$$

$$\text{and } \log X = \log K + N \log C \quad (6)$$

In this study, data were analyzed by computer with the SAS-79 program to find the best parameters for both linear and

nonlinear forms of each equation. The results are summarized in Table 2 and Table 3. The Langmuir equation describes data better in the linear form than in the nonlinear form. This is attributed to the over-emphasis of the small concentration range by the linear (logarithmic) form of the Freudlich equation. Since the assumption of monolayer adsorption is not adequate at high concentrations, there is not too much physical meaning for the Langmuir equation under these conditions. The Freudlich expression was selected for use throughout this study because of its better behavior at high concentrations.

Figure 2 through Figure 5 show the sorptive capacity of activated carbon for each adsorbate versus equilibrium concentration. The best nonlinear descriptions for both the Langmuir equation and Freudlich equation are compared in each Figure. The uptake capacities of four sorbate species are compared in Figure 6. Catechol shows higher uptake capacity than resorcinol and o-cresol shows higher uptake capacity than phenol; both comparisons indicate the effect of solubility -- lower solubility adsorbates tend to have higher uptake capacities.

Mattson, Mark, Malbin, Weber and Crittenden (1969) have indicated that the hydroxyl group hydrogen is very likely involved in intracomplex hydrogen bonding within the surface complex. The present experimental work shows that the uptake capacity of phenols with two hydroxyl groups is significantly higher than that for compounds with only one hydroxyl group.

TABLE 2
PARAMETER ESTIMATION OF ADSORPTION EQUILIBRIUM EQUATION
IN LINEAR FORM

Parameters	Phenol	O-cresol	Resorcinol	Catechol
<hr/>				
Langmuir Equation				
Q	263.74	252.54	292.65	331.76
b	0.01108	0.03368	0.01299	0.01015
R-Square	0.9965	0.9994	0.9960	0.9915
Freudlich Equation				
K	49.992	88.193	42.521	52.678
N	0.23319	0.15878	0.28209	0.25761
R-Square	0.9819	0.9217	0.9138	0.9424

TABLE 3
PARAMETER ESTIMATION OF ADSORPTION EQUILIBRIUM EQUATION
IN NONLINEAR FORM

Parameters	Phenol	O-cresol	Resorcinol	Catechol
Langmuir Equation				
Q	256.79	244.85	282.20	307.28
b	0.01254	0.04176	0.01558	0.01467
Residual	580.81	1462.29	1665.29	4540.66
Freudlich Equation				
K	51.494	92.245	50.352	55.009
N	0.22810	0.15021	0.25246	0.25034
Residual	344.30	1321.18	3248.96	1497.17

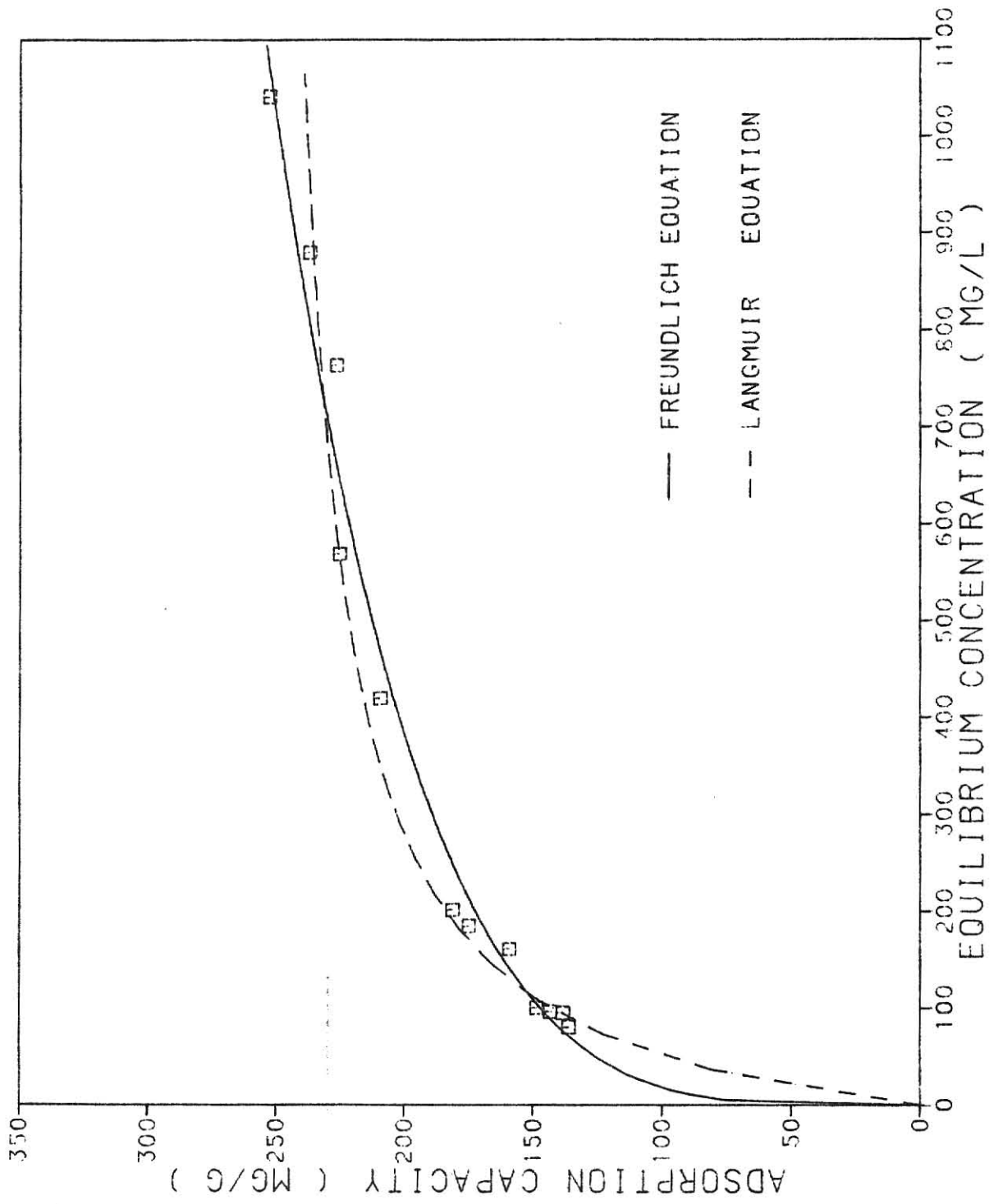


FIGURE 2 ADSORPTION ISOTHERM FOR PHENOL (25°C)

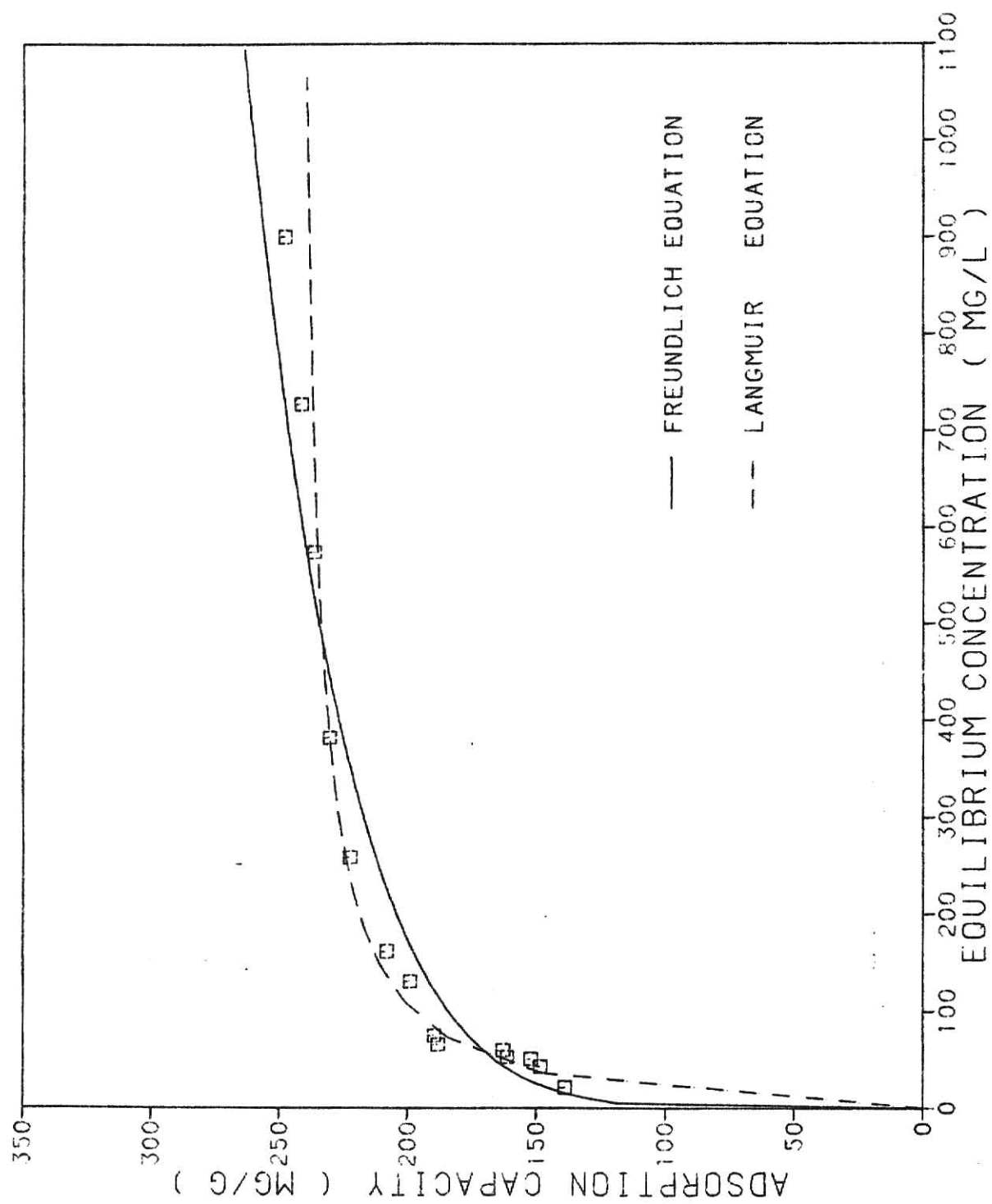


FIGURE 3 ADSORPTION ISOTHERM FOR O-CRESOL (25°C)

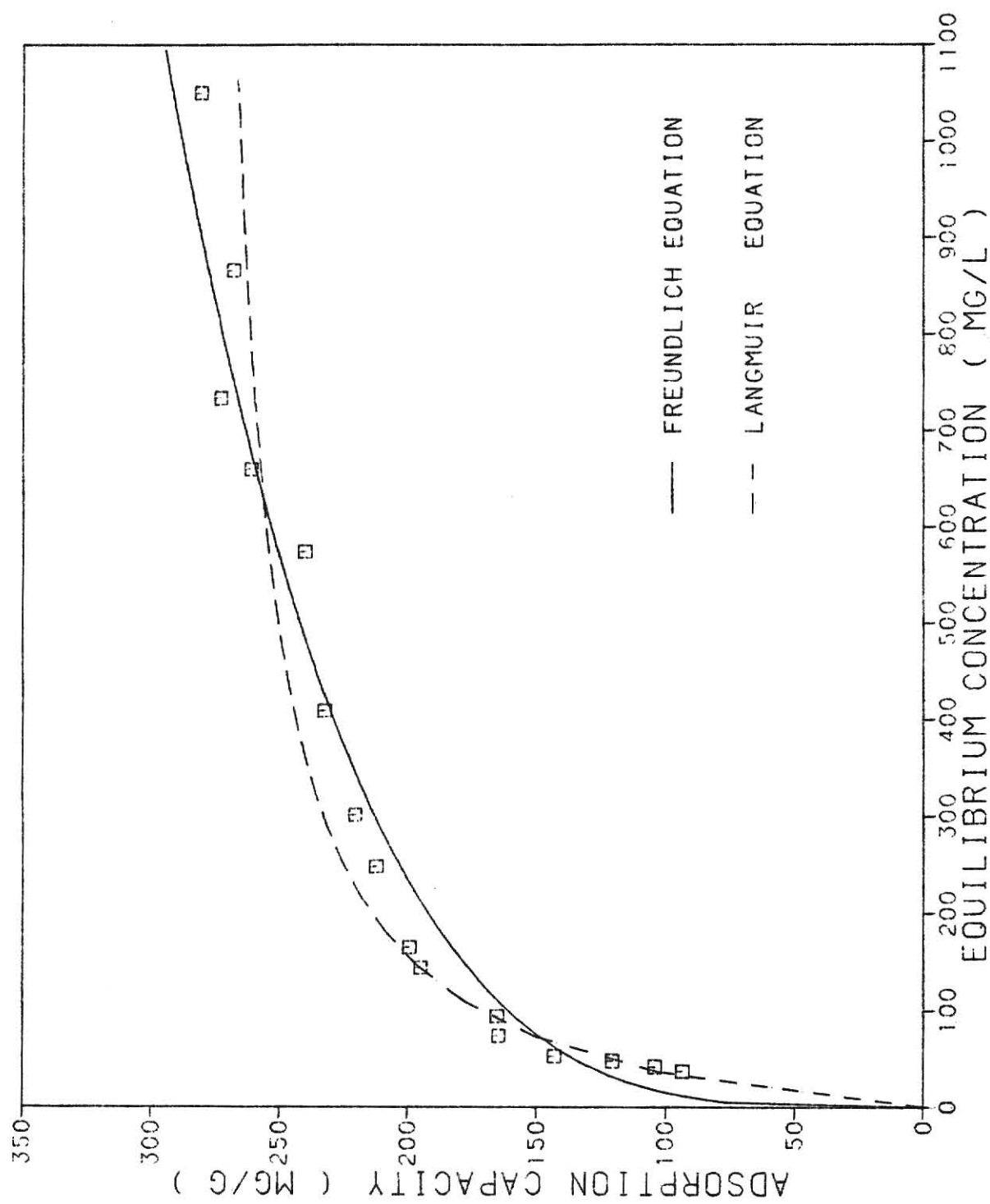


FIGURE 4 ADSORPTION ISOTHERM FOR RESORCINOL (25°C)

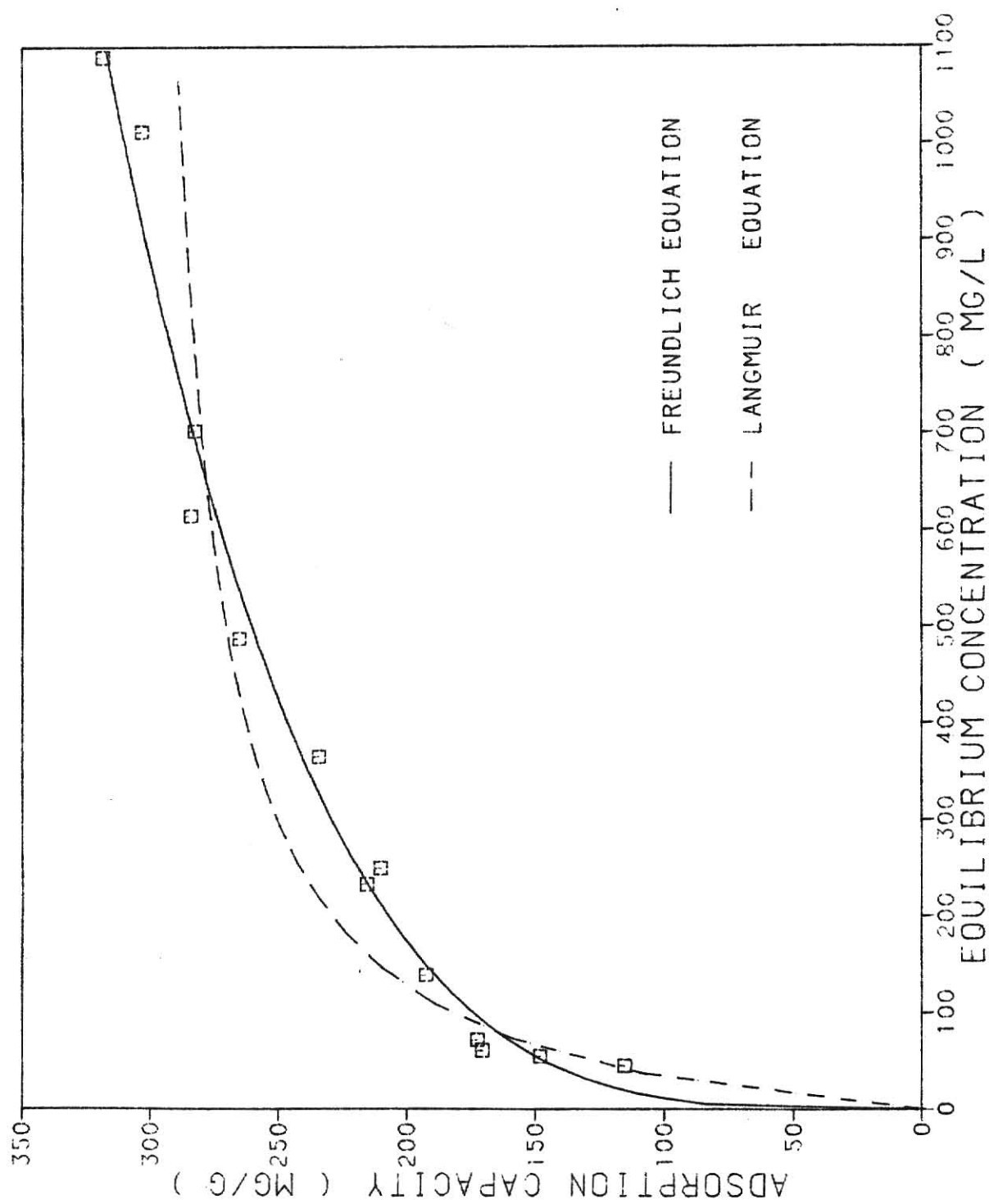


FIGURE 5 ADSORPTION ISOTHERM FOR CATECHOL (25°C)

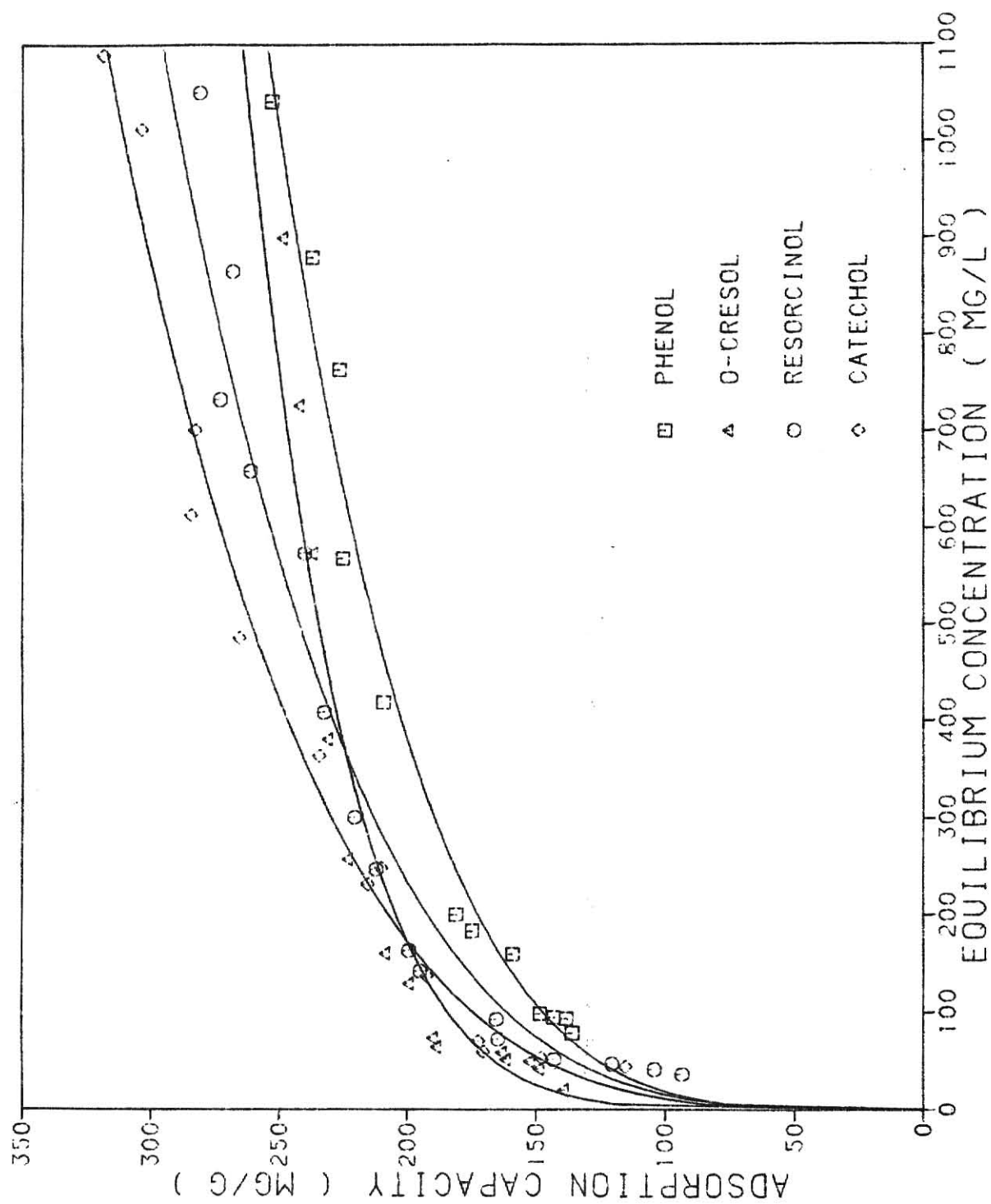


FIGURE 6 ADSORPTION ISOTHERM FOR 4 PHENOLS (25°C)

In Figure 7, adsorption capacity data were plotted versus reduced concentration (i.e., equilibrium concentration divided by solubility) to exclude the effect of solubility. In this manner, resorcinol shows higher uptake capacity than catechol; this is probably attributed to the different stereo structure of the adsorbates. O-cresol shows higher uptake capacity than phenol; this is probably caused by the existence of the methyl group as noted by Digiano and Weber (1969) in a series adsorption studies of 2-hexyl-, 2-octyl- and 2-decylbenzene sulfonate.

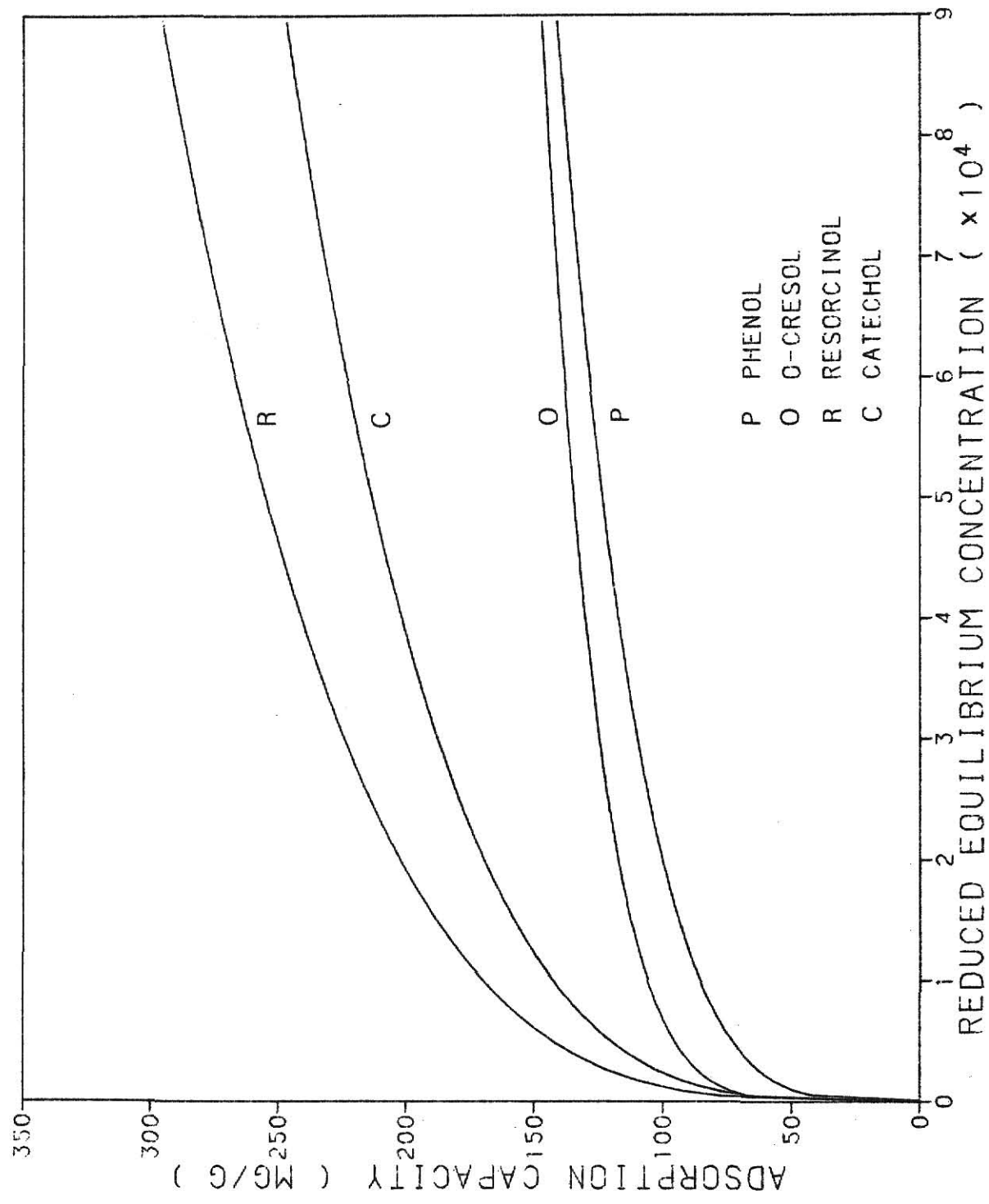


FIGURE 7 ADSORPTION ISOTHERM FOR 4 PHENOLS (25°C)

NOTATION

b	Langmuir equilibrium constant	l/mg
C	Equilibrium concentration	mg/l
K	Freudlich equation constant	
N	Freudlich equation constant	
Q	Ultimate capacity of the adsorbent Langmuir "monolayer" capacity constant	mg/g
X	Adsorption capacity	mg/g

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CHAPTER 4

ADSORPTION KINETICS

4.1 INTRODUCTION

The use of activated carbon in adsorption processes has become an effective and integral part of wastewater treatment; therefore, knowledge of adsorption kinetics is very important for the purposes of both mathematical modeling and design optimization. Although the actual process in the wastewater treatment operation is rather complex, a finite-bath system is frequently used for adsorption kinetic studies because of its advantages of expedient data collection and the fact that no complicated apparatus is required.

There are five consecutive steps in the adsorption process of the adsorbate species upon activated carbon: (1) diffusion of adsorbate through solution to the exterior of adsorbent, (2) transport of the adsorbate species across the solid-liquid interface, (3) transport of adsorbate within the pores of the adsorbent, (4) adsorption of the adsorbate onto the interior surface of the adsorbent, and (5) migration of the adsorbed species along the solid phase, i.e., surface diffusion. The resistance of each step acts both in parallel and in series with others. The combination of those resistances controls the overall rate of adsorption.

Prior to setting up the kinetic model it is necessary to determine which of the steps in the adsorption process are

significant and rate-limiting. Usually, several simplifying assumptions are required to make the problem tractable. With good mixing, it is reasonable to assume that the concentration of adsorbate in the solution is uniform, i.e., no concentration gradients exist in the bulk solution. Thus, the diffusion of the adsorbate species in the bulk solution is not significant. It is also generally agreed that the adsorption process itself is very rapid and does not represent the rate-limiting step in the uptake of adsorbate as indicated by Weber and Morris (1963). Surface diffusion is generally restricted to gases, it is usually assumed to be insignificant in aqueous systems except for some solutes of low adsorption energy as noted by Dedrick and Beckman (1967) and Brecher, et. al. (1967).

As indicated by Zogorski, Faust and Haas (1975), the overall mass transfer is generally considered to be governed by external diffusion (across the solid-liquid interface) and intraparticle diffusion. They also suggest several characteristics of the adsorbent, adsorbate, and solution phase that are of importance in determining the rate-limiting step such as particle size of the adsorbent, concentration of adsorbate, degree of mixing, etc.

Design parameters such as the diffusivity and the mass transfer coefficient can be obtained by comparing a suitable kinetic model with the experimental data. Those parameters can then be used as model input for the design of continuous flow packed bed or fluidized bed systems if the same adsorbent is to

be used.

4.2 KINETIC MODELS

Numerous adsorption models have been presented in the literature. Most of these can be categorized as follows: homogeneous solid diffusion models, pore diffusion models, and uniform state models as noted by Famularo, Mueller and Pannu (1980).

In the homogeneous solid diffusion model, adsorption occurs only on the outer surface of the particle and the solute then diffuses through the adsorbent under the influence of a radial gradient in solid-phase concentration. No attempt is made to relate the kinetics to the adsorbent particle structure in terms of surface area, pore size distribution, etc. In the pore diffusion model, the solute reaches internal surface sites by diffusion through the pore liquid. Solute concentration in the pore liquid is a continuous function of radial position and solid-phase adsorption is assumed at equilibrium with the adjacent liquid. The uniform state model is similar to the homogeneous solid diffusion model in the assumption that adsorption occurs on the outer-surface of the particle. However, a single solid-phase concentration is used to represent the average solute loading on the particle, and the mass transfer occurs as a result of the difference in solute concentration between the particle surface and interior.

Weber and Chakravorti (1974) have given a comprehensive review of those studies concerning the homogeneous solid

diffusion and pore diffusion models. They compared them by particle shape, system type, the phase in which adsorption occurred, film resistance and the method of mathematical treatment.

A microcore/macrosheIl model was developed by Famularo et. al. (1980) in which the adsorbent particle was assumed to be a sphere divided into two uniform-state regions: a macrosheIl containing macropores and a microcore containing micropores. This model quantitatively predicted the performance of carbon columns from pure-solute data for systems that follow ideal-adsorbed solution theory which assumes that the identity of neighboring molecules on an adsorbent surface has no affect on the adsorption of a specific molecule, other than a reduction of the number of sites available.

Among various models, that presented by Digiano and Weber (1969) was chosen for this study because of its simplicity and its ability to describe the batch adsorption process. This model is based on the mass balance for a given incremental radius, Δr :

RATE IN - RATE OUT + RATE OF RX = RATE OF ACCUMULATION

$$Nr4\pi r^2 \Big|_r - Nr4\pi r^2 \Big|_{r+\Delta r} = \frac{\partial}{\partial t} (\epsilon Cf + (1-\epsilon) Cs) 4\pi r^2 \Delta r \quad (7)$$

in which C_f is the fluid phase concentration, C_s is the solid phase concentration, ϵ is the porosity (fractional void space), and Nr , the superficial flux, is given by Fick's first law as

$$Nr = - D \frac{\partial Cf}{\partial r} \quad (8)$$

Dividing Equation (7) by Δr and letting Δr approach zero yields

$$D \left(\frac{\partial^2 Cf}{\partial r^2} + \frac{2}{r} \frac{\partial Cf}{\partial r} \right) = \frac{\partial}{\partial t} (\epsilon Cf + (1 - \epsilon) Cs) \quad (9)$$

The corresponding boundary equations are:

$$Cf = 0 \quad 0 \leq r < a, t = 0 \quad (10)$$

$$Cf = Cfo \quad r = a, t = 0 \quad (11)$$

$$V \frac{\partial Cf}{\partial t} = - 4 \pi a^2 D \frac{\partial Cf}{\partial r} \quad r = a, t > 0 \quad (12)$$

This is a pore diffusion model and film resistance was assumed to be negligible because of high agitation. It should be mentioned that the diffusivity here is an "effective diffusivity" which is an empirically determined quantity that should not be confused with the diffusivity of solutes in pure liquid phase.

In this study, the Freundlich isotherm was used to express Cs instead of Langmuir isotherm used by Digiano et. al. because of its better fit to the nonlinear form of adsorption capacity over a larger range of equilibrium concentrations. In many studies appearing in the literature, activated carbon

particles were sieved and only a narrow range of sizes were selected for adsorption experiments. However, in this study, carbon samples (with approximately log-normally distributed particle size) were used directly. A geometric mean radius ($M/2 = 0.1307$ cm) was used as the characteristic radius. The purpose of this approach is to simulate the conditions in industrial application.

4.3 EXPERIMENTAL METHOD AND RESULTS

The adsorption experiments were carried out in an airtight, baffled cylindrical vessel of about 3 liters capacity. A four-blade leaf-type impeller was driven by a variable speed motor. The temperature of the adsorbate solution was kept at 25°C during the experiment by immersing the reaction vessel into a water bath maintained at the desired temperature.

For each experiment, exactly 2.5 liters of adsorbate solution were prepared at the desired concentration and introduced into the reaction vessel which was then placed into the constant temperature bath. The stirrer was inserted and allowed to operate for approximately 1 hour prior to the start of each experiment to allow the temperature of the liquid in the vessel to equilibrate.

Prior to the insertion of an accurately weighed quantity of carbon into the reaction vessel, a 5 ml sample of the liquid was collected and analyzed for concentration of adsorbate to serve as the initial concentration in each experiment. The adsorbent was then introduced into the reaction vessel and rapidly

stirred. In order not to interrupt the agitation, the 5 ml sample of the liquid was collected at selected time intervals by using a syringe connected to a small teflon tube. The removal of samples for analysis resulted in a small decrease in the total adsorbate available to the adsorbent and a slight increase in the carbon concentration. The total amount of sample removed was less than 50 ml; the maximum error was less than 2% and was considered to be insignificant.

All kinetic experiments were conducted at a stirring speed of about 300 rpm (the impeller Reynolds number was about 2.0×10^5). Preliminary studies indicated that the rate of adsorption was independent of stirring at higher shaft speeds. Sufficient agitation was provided so that film resistance could be assumed to be negligible. Several adsorption experiments were conducted at different temperatures using phenol and o-cresol as adsorbates. The removal of adsorbates versus time at different temperatures is shown in Figures 8 and 9. Because of negative heat of adsorption, the equilibrium adsorption capacity should be higher at lower temperature. However, as shown in Figure 8 and Figure 9, the experimental results indicate that the adsorbate removal rate was significantly higher at higher temperature. This phenomenon is apparently the result of the functional dependence of diffusivity upon temperature. At lower temperature, adsorbate species diffuse more slowly inside the carbon particle, hence, less adsorbate can associate with the carbon surface per unit time. The adsorption reaction is

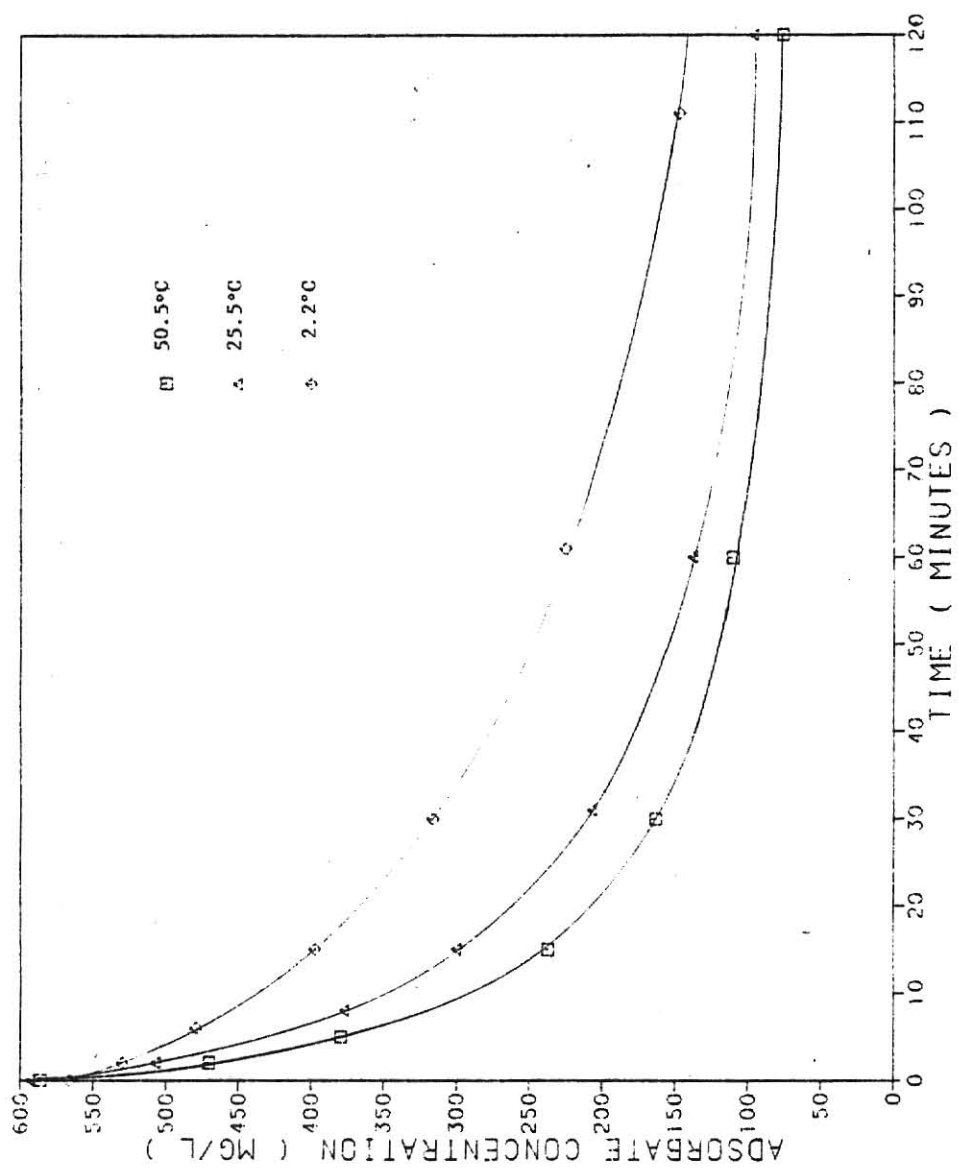


FIGURE 8 BATCH ADSORPTION AT DIFFERENT TEMPERATURES
DATA FOR PHENOL

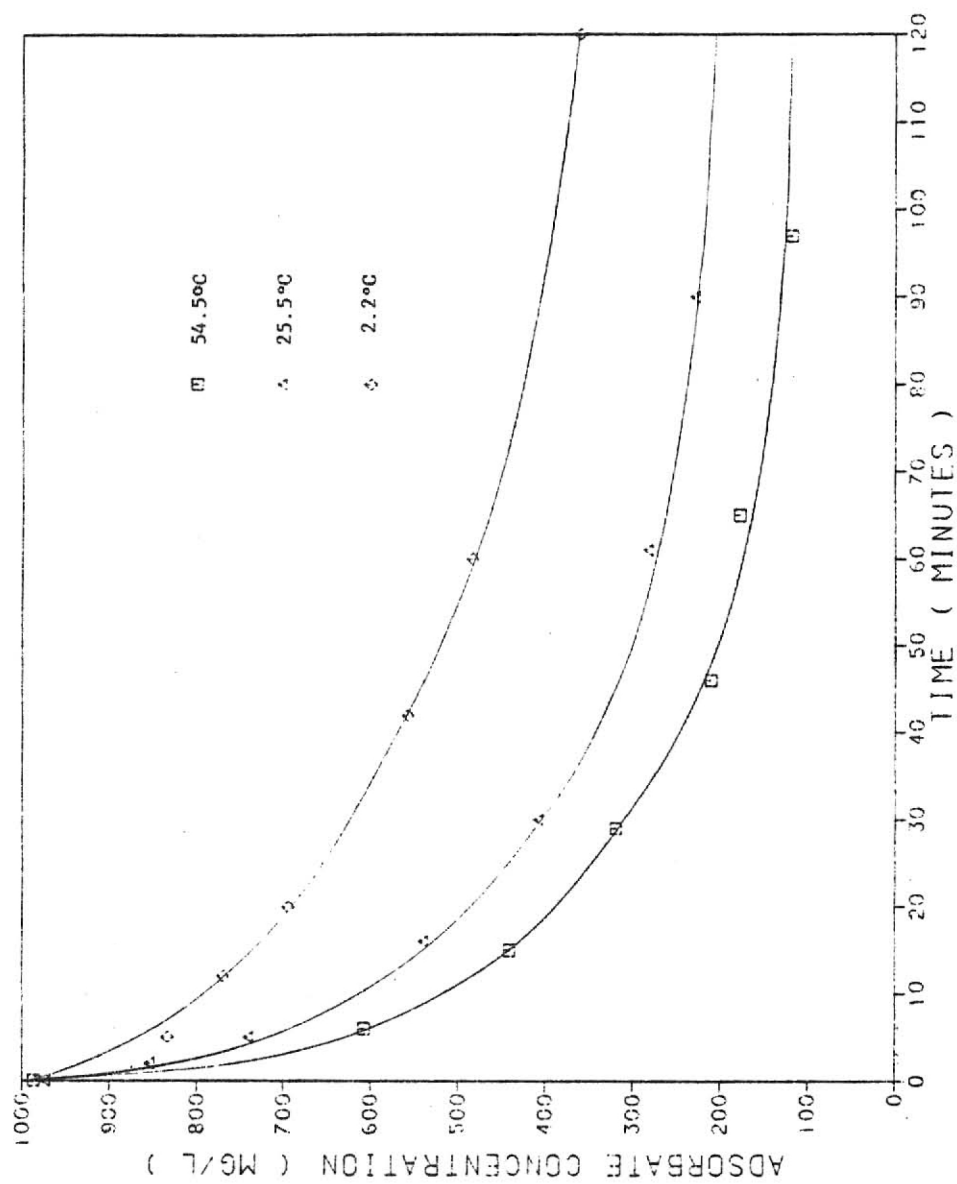


FIGURE 9 BATCH ADSORPTION AT DIFFERENT TEMPERATURES
DATA FOR O-CRESOL

generally considered as not rate-limiting, and available evidence shows that the overall rate of adsorption is governed by intraparticle diffusion.

The experimental adsorption data for phenol, o-cresol, resorcinol, and catechol are compared in Figure 10. The adsorption of phenol by the same amount of activated carbon but with two different initial concentrations is compared in Figure 11.

4.4 MATHEMATICAL TREATMENT

The implicit finite difference numerical method of Digiano et. al. was used to solve the kinetic model as stated in Equation (9), however some modifications were necessary in this study.

The first step was to put Equation (9) into dimensionless form. Solid phase concentration is expressed by $K C_f^N$ ($\rho/(1-\epsilon)$) where K and N are Freundlich equation constants and ρ is the particle density. Letting

$$\xi = r/a, \quad \theta = Dt/a^2, \quad \phi = C_f/C_{fo},$$

$$\alpha = K C_f^{N-1} \rho, \quad \text{and} \quad \sigma = \alpha \phi^N$$

The dimensionless form of Equation (9) is

$$\frac{\partial^2 \phi}{\partial \xi^2} + \frac{2}{\xi} \frac{\partial \phi}{\partial \xi} = \frac{\partial}{\partial \theta} (\epsilon \phi + \sigma) \quad (13)$$

which is then put into the finite difference equation.

Boundary equations (10), (11), and (12) can be arranged as

$$V(C_{fo} - C_f) = 4\pi \int_0^a (\epsilon C_f + (1-\epsilon)Cs) r^2 dr, \quad t \geq 0 \quad (14)$$

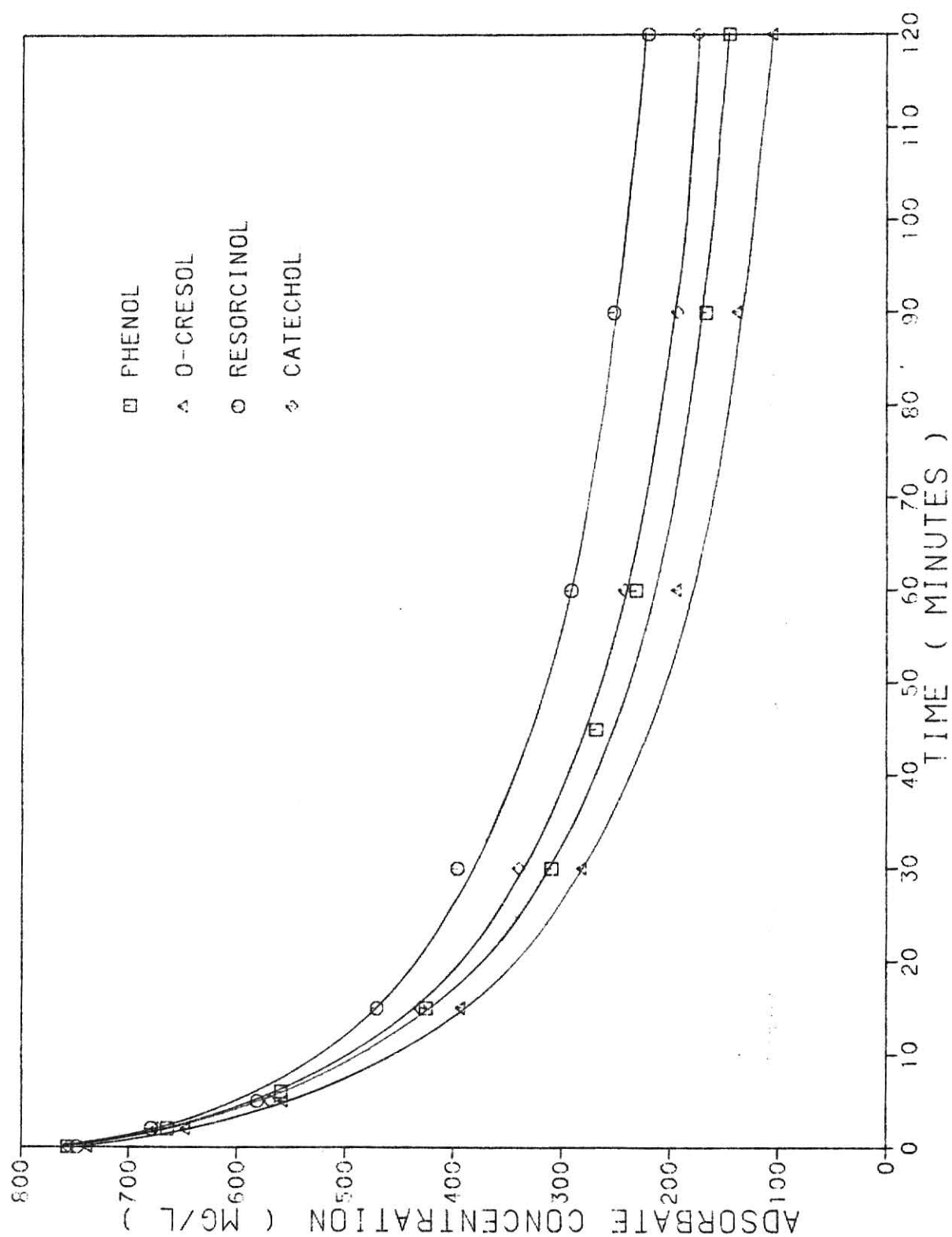


FIGURE 10 BATCH ADSORPTION FOR DIFFERENT ADSORBATES

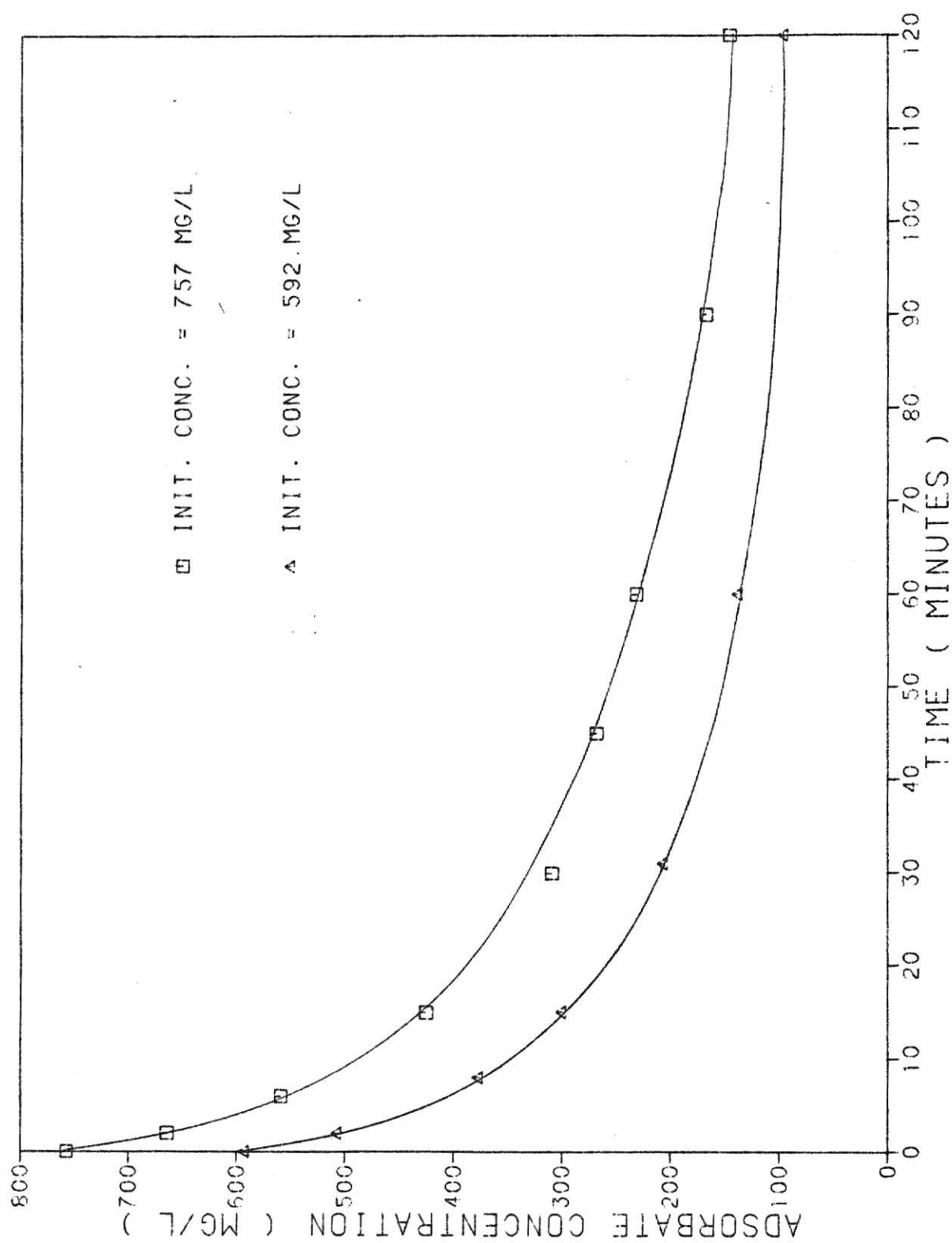


FIGURE 11 BATCH ADSORPTION AT DIFFERENT INITIAL CONCENTRATION
DATA FOR PHENOL

or in dimensionless form at $\theta \geq 0$

$$\phi = 1 - \frac{4\pi a^3}{V} \int_0^1 (\epsilon \phi + \sigma) \xi^2 d\xi \quad (15)$$

The integral in Equation (15) was calculated by Simpson's rule.

The calculation was performed with a PDP-11 minicomputer. The computer program and output results are attached in Appendix B. The radial distance was divided into 50 increments. The dimensionless concentrations for the outer 4 distance steps are listed in the computer output under the symbol C(46). It can be easily seen that they are negligibly small because the concentration gradient decreases very rapidly with distance from the exterior of the particle toward its center. So for higher efficiency, only the outermost 10 increments were actually calculated and the concentrations in the inner increments of the particle were assumed zero. This is legitimate because the time period considered is only the first few hours.

If experimental data conforms to the model, then a plot of θ versus time should yield a straight line with slope of D/a^2 . It can be noted from Figure 12 that the agreement is good. The calculated curve is compared with the experimental data in Figure 13. As observed in Figure 13, the liquid concentration decreases a little more rapidly than the calculated value after the first hour. This is due to the error caused by removal of the liquid samples and by the breakup of carbon particles, resulting in an increase in particle number and a decrease in

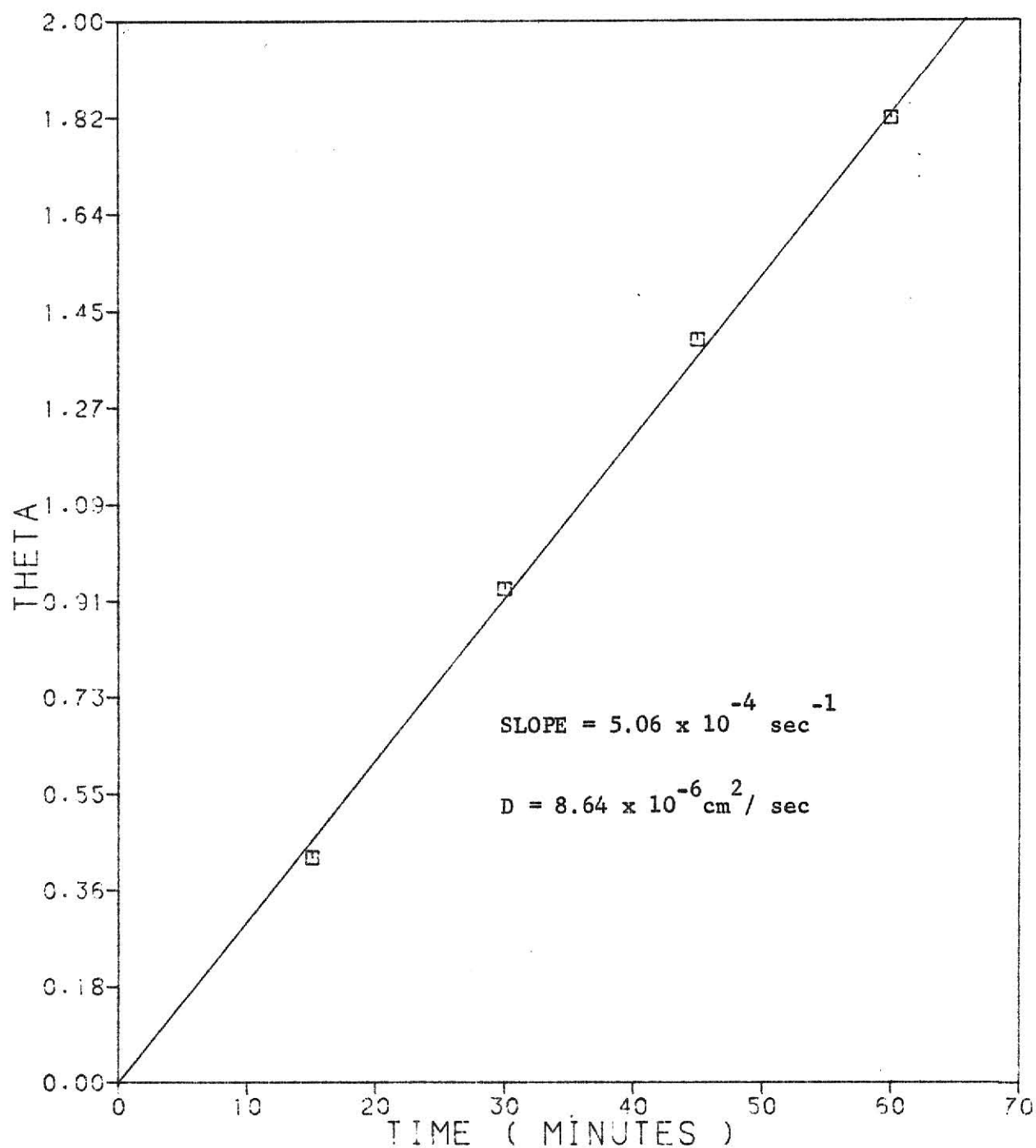


FIGURE 12 MODEL FOR PORE DIFFUSION WITH
SIMULTANEOUS NONLINEAR ADSORPTION
DATA FOR PHENOL (INIT. CONC. = 757 MG/L)

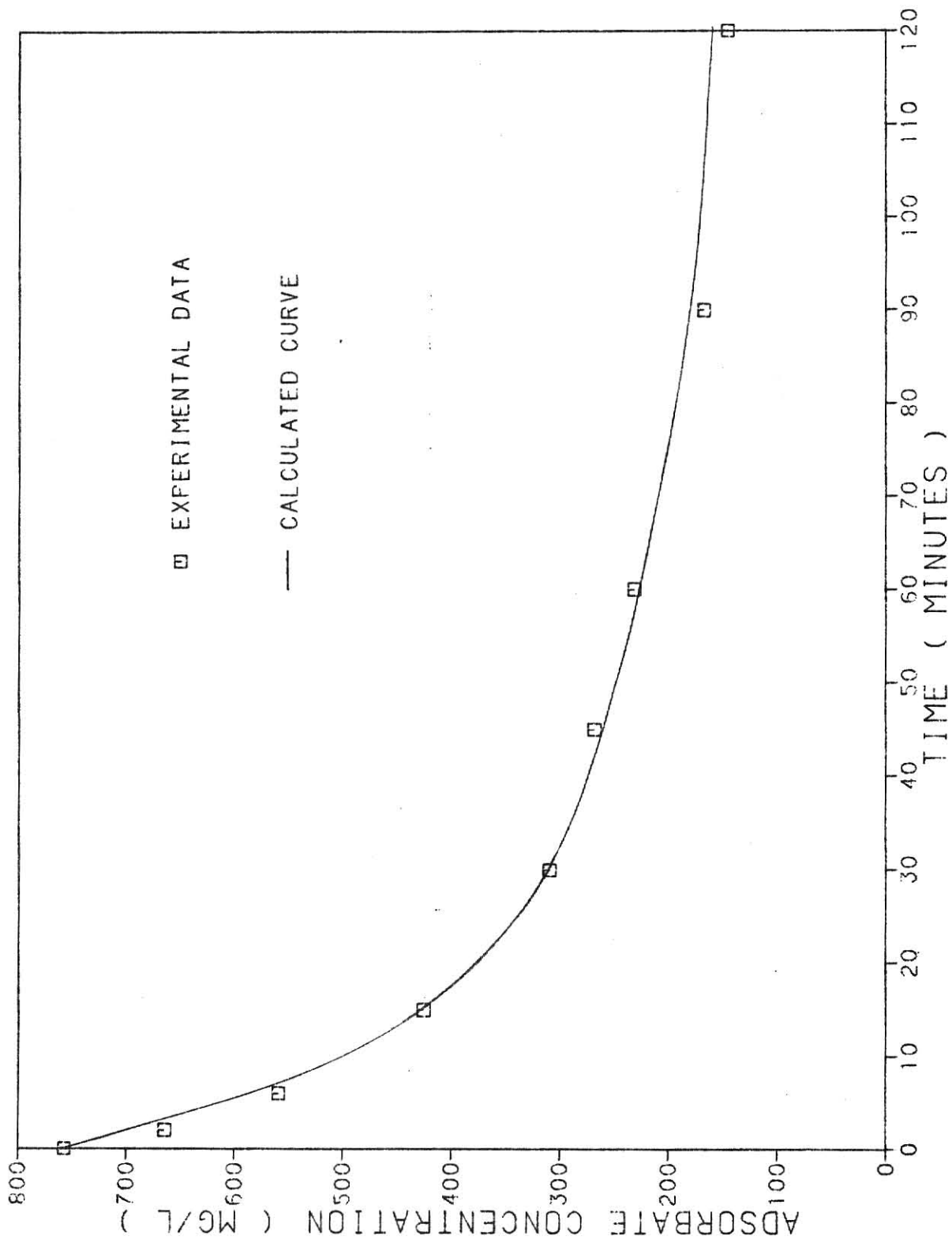


FIGURE 13 CALCULATED RATE CURVE FOR PORE DIFFUSION MODEL
DATA FOR PHENOL (INIT. CONC. 757 MG/L)

geometric mean radius.

The effective diffusivities obtained for different adsorbates and under different conditions are summarized in Table 4. It can be noted that the effective diffusivity will be influenced by initial concentration. Lower initial concentrations lead to higher diffusivities. This is probably caused by the higher binary liquid diffusion coefficient of the adsorbate at lower mole fraction since adsorbate species diffuse through the pore liquid as in a binary liquid system. Under the same conditions, the effective diffusivities of different adsorbates are in the order of phenol > o-cresol > catechol > resorcinol. This is likely caused by the difference in molecular structures. The smaller, more regularly-shaped species will tend to have higher diffusivities.

TABLE 4
EFFECTIVE DIFFUSIVITY
FOR DIFFERENT ADSORBATES AND INITIAL CONCENTRATIONS

Adsorbate	Carbon Dosage (gm)	Init. Conc. (mg/l)	Diffusivity (cm^2/sec) $\times 10^6$
Phenol	16.	592	9.74
Phenol	16.	757	8.64
O-cresol	16.	737	8.54
Resorcinol	16.	748	4.17
Catechol	16.	756	6.04

NOTATION

a	Particle radius	cm
C _f	Fluid phase concentration	mg/ml
C _{fo}	Initial fluid phase concentration	mg/ml
C _s	Solid phase concentration	mg/ml
D	Diffusivity	cm ² /sec
K	Freudlich equation constant	
N	Freudlich equation constant	
N _r	Superficial flux	mg/cm ² /sec
r	Radius parameter	cm
t	Time	sec

GREEK LETTERS

α	Dimensionless parameter ($=KCfo^{N-1}\rho$)	
ϵ	Fractional void space	
θ	Dimensionless time parameter ($=Dt/a^2$)	
ξ	Dimensionless radius distance ($=r/a$)	
ρ	Particle density	gm/ml
σ	Dimensionless solid phase concentration ($=\alpha\phi^N$)	
ϕ	Dimensionless fluid phase concentration ($=Cf/Cfo$)	

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CHAPTER 5

RECLAMATION OF PHENOLS

5.1 INTRODUCTION

The economic feasibility of the use of activated carbon in water treatment processes is highly dependent on the regeneration costs of the spent carbon. The development of successful regeneration processes has greatly aided the development and wider application of carbon adsorption treatment. Thermal regeneration has been widely used as the regeneration method. The most common industrial process for regeneration of spent carbon, according to Ramirez (1977), involves treatment in multiple hearth furnaces, in which the sorbate molecules are volatilized and destroyed.

Thermal regeneration as practiced commercially, normally consists of the process of drying at about 370°K, thermal desorption (heating to about 1073°K), and high temperature heat treatment in the presence of limited quantities of oxidizing gases such as water vapor, flue gas and oxygen. As indicated by Chihara et. al. (1981), the second step is thought to be a complicated process involving decomposition of the original adsorbates and desorption of low-molecular weight pyrolysis products, leaving adsorbed carbon.

It has been mentioned that the reclamation of phenols from coal conversion wastewater is both economically and ecologically sound. Himmelstein, Fox and Winter (1973) have done an economic

comparison of alternate regeneration schemes including thermal regeneration, solvent regeneration, and reactive regeneration (adsorbed phenols removed by caustic soda). As the adsorbate concentration of the wastewater for treatment increases, solvent and reactive regeneration systems become increasingly attractive vis-a-vis thermal regeneration, especially when valued materials are recovered. In this situation, reclamation of phenols prior to thermal regeneration may generate a significant economic credit for the overall process. In addition, the recovered compounds could relieve pressure exerted by the increasing demand for petroleum used in the synthesis of phenol and its derivatives.

Suzuki, Misic, Koyama, and Kawazoe (1978) have utilized the technique of thermogravimetric analysis (TGA) to measure the weight change when spent, granular carbon samples were heated in an inert atmosphere. The base carbon was loaded with different, single organic adsorbates, and the resultant weight change versus temperature curves were divided into three groups according to the ease of decomposition. Single desorption and cracking steps were then used to represent the numerous and complex processes that occurred. Phenol, B-naphtol, lignin, humic acid and other phenolic organics were categorized as Group (III) compounds; these exhibited a gradual change of weight with increasing temperature, and high residues on activated carbons after the temperature attained 800°C. This suggests that these organics when adsorbed on activated carbons, are not

easily recovered by thermal methods alone. However, the fraction of phenol which was decomposed and the fraction of phenol which was desorbed while retaining the phenol structure were not determined.

For the purpose of reclamation, it is important to know how much of the phenol adsorbed on activated carbon can be thermally desorbed while retaining the chemical structure, C_6H_5OH . In this investigation, a reclamation process was studied to determine the extent of thermal desorption.

5.2 EXPERIMENTAL METHOD AND RESULTS

Phenol was chosen as the adsorbate throughout this phase of the investigation. The reclamation process investigated is represented in Figure 14. Activated carbon samples loaded with phenolic compounds were put into a stainless steel heating chamber (16 cm long and 1.6 cm I.D.) as a fixed bed. I^2R heat was supplied by heating tapes and a Variac was used to adjust the power input and thereby regulate temperature.

Nitrogen was selected as the inert carrier gas which was preheated, and then passed through the heating chamber. An iron-constantan thermocouple was used to measure the outlet gas temperature. Because the gas flow rate was very small (about 2.2 liter/min. S.T.P.), the gas temperature was very close to the wall temperature. Since the temperature difference of the wall between the two ends of the chamber was very small, the outlet gas temperature was representative of the average gas temperature inside the chamber.

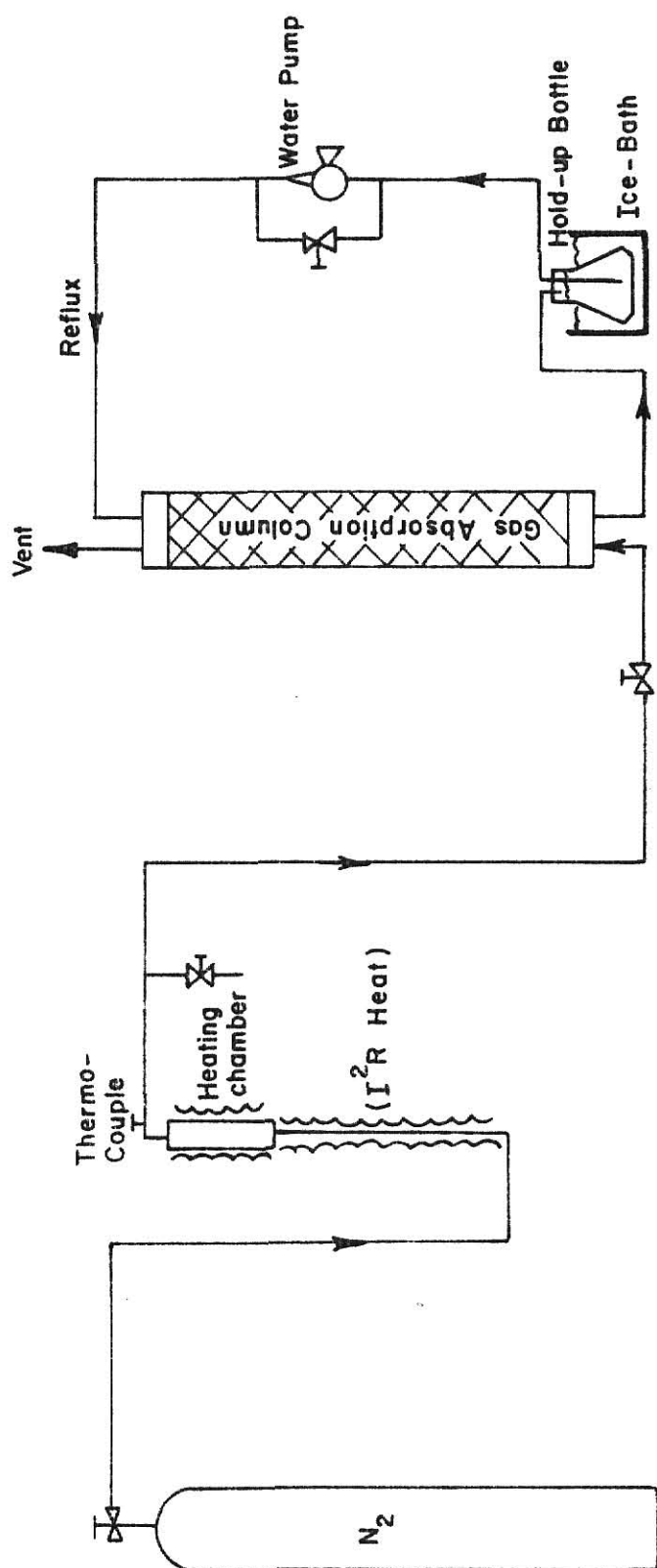


FIGURE 14 PHENOL RECLAMATION SCHEME

Desorbed phenol vapor carried by nitrogen was then introduced into the bottom of a gas absorption column (1.5 m high, 5 cm O.D.) packed with 1.6 cm O.D. plastic Pall rings and operated countercurrently. An alkaline absorbent solution was recycled by a centrifugal pump. A by-pass loop around the pump was used to regulate the liquid flow rate and an one liter hold-up bottle was installed before the pump to avoid the problem of cavitation. During the experiment, the hold-up bottle was placed in an ice bath to remove the heat due to dissipation.

The carbon samples loaded with phenol were prepared by immersing a known amount of carbon into a phenol solution which was agitated by a magnetic stirrer and allowed a sufficient time (4 hours) for adsorption. After the adsorption, the carbon particles were separated and kept in a desiccator one week at room temperature for drying. The phenol solutions were prepared by dissolving accurately weighed phenol crystals in distilled water; these solutions were used for preparing loaded carbon samples by batch adsorption. The change in concentration of the solution gave the amount of phenol loaded on the carbon. The final concentration of phenol solutions was around 600 mg/l after adsorption. The amount of phenol loaded on each carbon sample (16 gm) was about 2.5 gm, providing a typical loading of 0.15 gm/gm.

The phenol desorbed from the carbon sample was captured and accumulated in the caustic absorbent. In each experiment, 2.3

liter of 0.2 normal sodium hydroxide solution was used as absorbent which was recycled at a flow rate of about 3 liter/min. The hold-up liquid level of absorbent in the gas absorber column was about 20 cm height during operation. In such a situation, the phenol vapor carried by nitrogen was assumed to be completely captured by the absorbent because phenol is known to be easily converted to the phenoxide ion in an alkaline solution and good contact between the liquid and gas was provided.

The rate of phenol recovery can be obtained by monitoring the phenol concentration of the absorbent at selected time intervals. 5 ml absorbent sample was collected each time from the outlet of the hold-up bottle. A syringe was used to withdraw samples. Sample collection for analysis resulted in a small decrease in the total absorbent available. The total amount of sample removed was less than 50 ml; the maximum error due to the change in volume was less than 2% and was considered to be insignificant. Since the total space time for the liquid in the system was very short (about 45 seconds) and the solution inside the hold-up bottle was assumed to be perfectly mixed, the phenol concentration of the absorbent sample was assumed to represent the average concentration throughout the absorbent.

Four preliminary experiments were conducted by elevating the gas temperature to desired levels in about 30 minutes, with sufficient heating for maintenance thereafter. The fraction of

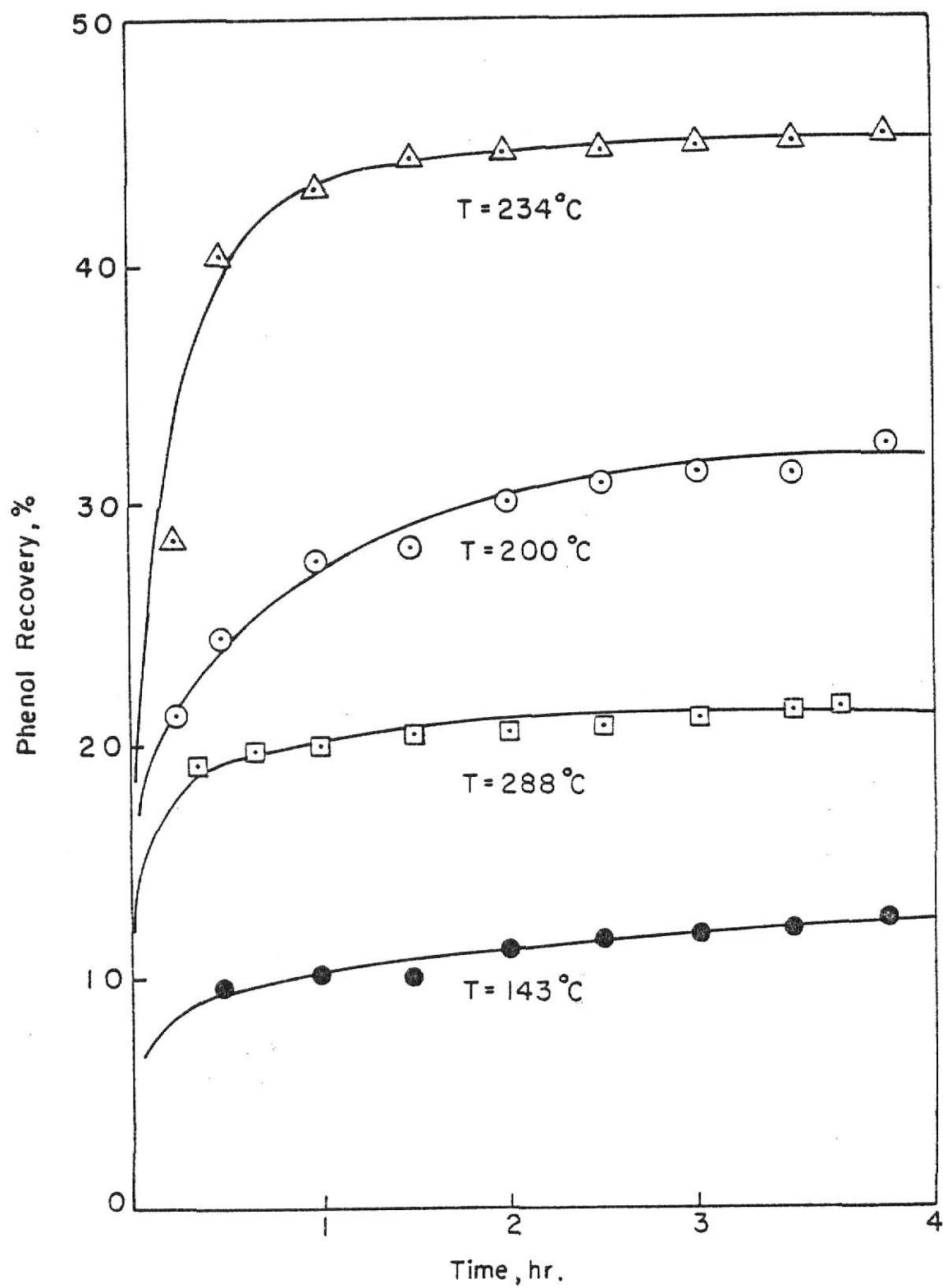


FIGURE 15 PHENOL RECOVERY AT VARIOUS TEMPERATURES

phenol recovered versus time was plotted in Figure 15. A striking feature observed is that the fraction of phenol recovered is very low at low temperature but increases rapidly at higher temperatures. The maximum recovery of phenol achieved was about 45% by weight when the gas temperature was elevated to around 230°C. However, the fractional recovery is reduced dramatically when the nitrogen temperature is further elevated. The desorption-recovery occurred mainly in the first hour and was almost insignificant after the second hour.

Another four experiments were performed under conditions where temperatures were carefully controlled, and attention was focused on the first two hours of each experiment. The first three experiments were carried out by elevating the gas temperature linearly with the same rate (6.8 °C/min.) and maintaining the gas temperature after 172°C, 243°C, and 278°C were reached respectively. The fourth experiment was carried out by elevating the gas temperature with a higher rate (11.1 °C/min.) until 280°C was reached.

The experimental results were plotted in Figure 16 which provides a clearer picture of how the desorption-recovery process is influenced by elevated gas temperature. When the gas temperature was lower than 172°C, lower temperature led to lower recovery rate. However, when the gas temperature was higher than about 243°C, slightly lower temperatures led to higher recovery rates. The same tendency can be noted in the fourth experiment; furthermore, the total recovery percentage was

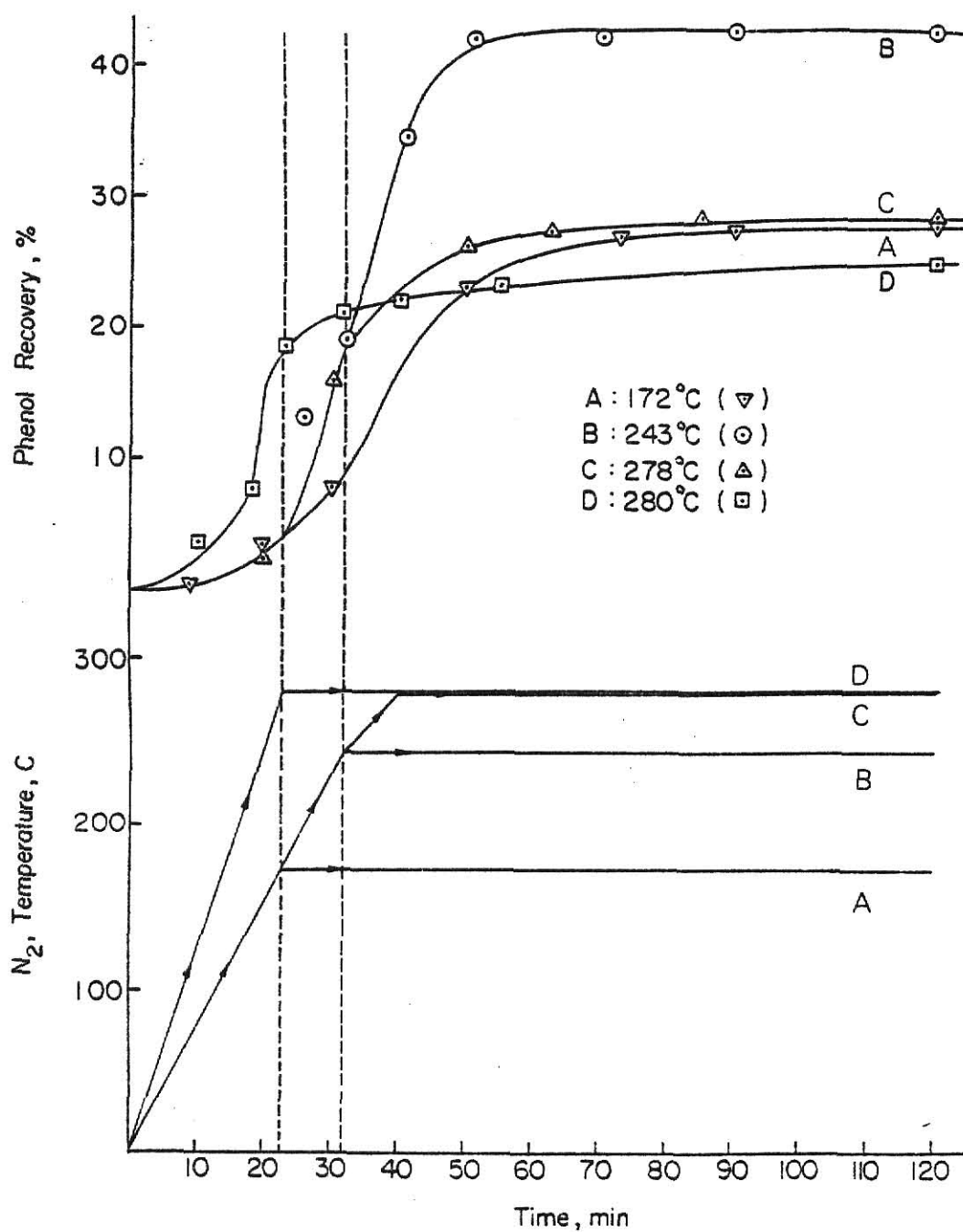


FIGURE 16 PHENOL RECOVERY AT VARIOUS CONTROLLED TEMPERATURE ELEVATIONS

rather low because the high temperature region was reached too early, leading to pyrolytic decomposition.

This kind of behavior in the desorption-recovery process can apparently be attributed to the result of the competition between thermal desorption and pyrolytic decomposition. At low temperatures, decomposition is not significant; hence higher energy input leads to higher desorption rates and a higher percentage of phenol loaded upon the carbon can be desorbed. At higher temperatures pyrolytic decomposition becomes predominant; thus if the high temperature region was reached too early phenol on the carbon surface decomposed rapidly and little could be desorbed. When the phenol on the carbon surface was mostly destroyed, of course, no further recovery could be obtained and this led to lower fractional recoveries.

5.3 KINETIC INTERPRETATION

Suzuki et. al. (1978) have set up two kinetic models to explain the TGA curves obtained in their experiments, i.e., a thermal desorption model and a thermal cracking model. Those are based on two simple physiochemical characteristics of adsorbed organics during the temperature rise period: (a) thermal desorption of volatile organics initially adsorbed on the activated carbon, and (b) decomposition of organics on the adsorbent surface where some of the volatile fragments produced are vaporized. Those two models explained reasonably well the TGA curves obtained from their Group (I) and Group (II) organic classifications, respectively. However, they did not propose

any model for the Group (III) organics (of which phenol is a member) .

Actually, in a thermal desorption process, thermal desorption and thermal cracking proceed simultaneously. It is very likely that thermal desorption is predominant for Group (I) organics and thermal cracking is predominant for Group (II) organics during the temperature rise period. However, for Group (III) organics, thermal desorption and thermal cracking occur at comparable rates; and data cannot be explained by either mechanism alone. In this study, a kinetic model including both thermal desorption and thermal cracking was developed to explain the desorption-recovery experimental results.

As a first approximation, equilibrium desorption with a Langmuirian isotherm was considered and a first order kinetic expression for the decomposition of adsorbed phenol was assumed. The model is given as follows:

$$\frac{dq}{dt} = -Kq - K' \left(q - \frac{q_{\infty}bP}{1+bP} \right) \quad (16)$$

where q represents the weight of species retaining the structure of phenol on the carbon particle surface. $-Kq$ represents the first order decomposition in which K is given by the Arrhenius equation:

$$K = K_0 \exp(- E/RT) \quad (17)$$

$q_{\infty}bP/(1+bP)$ represents the Langmuir isotherm in which q_{∞} represents the saturation adsorption capacity. The equilibrium pressure P is not defined here, but during the

temperature rise period (for the nitrogen stream) it is assumed as a first approximation to be constant in the manner of Suzuki et. al. (1978). The Langmuir equilibrium energy constant b is written in terms of heat of adsorption Q as :

$$b = b_0 \exp (Q/RT) \quad (18)$$

The difference between q and $q_{\infty}bP/(1+bP)$ represents the amount of "free" (capable of being desorbed) phenol species inside the carbon particles. K' is a constant which is proportional to mass transfer coefficient; and the entire term of $K'(q - q_{\infty}bP/(1+bP))$ represents the rate at which phenol is desorbed, carried away, and captured by gas absorbent. K' , b_0 , and q_{∞} are assumed to be temperature-independent.

Following Suzuki et. al. (1978), a rough estimate was made by assuming that $q_{\infty} = q_0$ is satisfied for the desiccated carbon samples in order to solve Equation (16). After rearrangement and substitution of Equations (17) and (18), Equation (16) becomes:

$$\frac{d(q/q_0)}{dt} = -K_0 \exp(-E/RT) (q/q_0) - K' (q/q_0 - \frac{1}{1 + \frac{1}{b_0 P} \exp(-Q/RT)}) \quad (19)$$

Let ϕ represents the fraction of phenol recovered as a function of time which can be obtained by integration:

$$\phi(t) = \int_0^t K' (q/q_0 - \frac{1}{1 + \frac{1}{b_0 P} \exp(-Q/RT)}) dt \quad (20)$$

There are five unknown parameters in Equation (19). A

Hooke and Jeeves pattern search technique were used to find those parameters. After initializing the parameter values, Equation (19) can be solved by a Runge-Kutta numerical method since the temperature can be expressed as a function of time. The fraction of recovery ϕ at different times can be obtained by integrating Equation (20) by Simpson's rule. Eight ϕ values from each of those four desorption-recovery experiments were chosen; and the objective function for parameter searching was the minimum of the sum of squares of the differences between calculated ϕ values and experimental ϕ values. Because five unknown parameters exist it is very hard to find the optimal values. Proper initial values could be chosen by referring the order of the magnitude of those parameters obtained by Suzuki et. al. (1978); nevertheless, many combinations of initial values had to be tested.

The computer program and output results are attached in Appendix C. A reasonable fit occurs when $E = 33.8$ kcal/gmole and $Q = 10.9$ kcal/gmole. The calculated ϕ values versus time were plotted in Figure 17 and compared with the experimental data.

Little previous knowledge about the actual decomposition reaction of phenol occurring on the carbon surface was available. The actual reaction may not be first order; it is also possible that several decomposition reactions occur simultaneously. On the other hand, it is questionable that phenolic species are adsorbed on the carbon surface with a

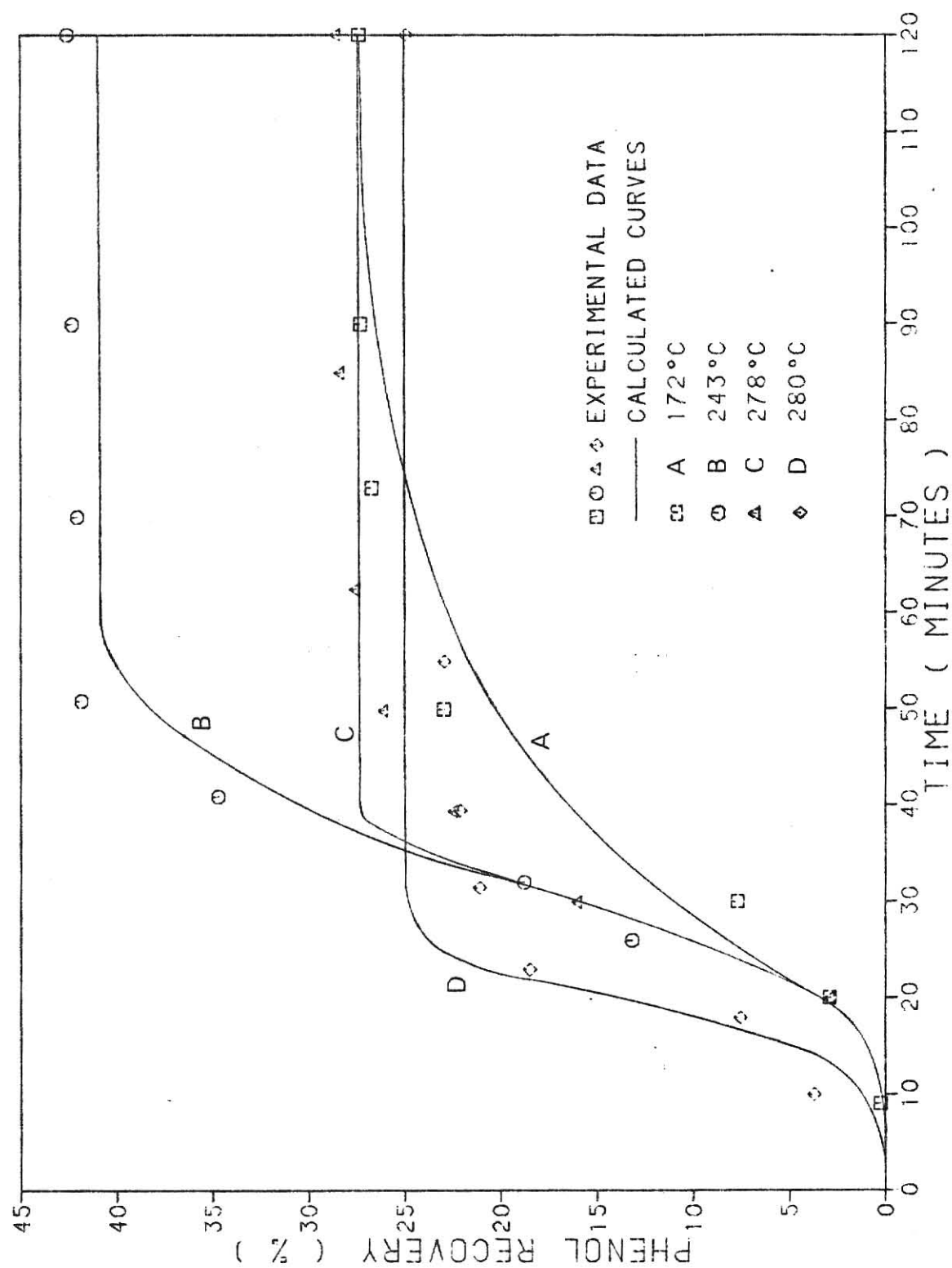


FIGURE 17 CALCULATED RATE CURVES FOR PHENOL RECOVERY MODEL

constant heat of adsorption. Probably a continuous spectrum of sorptive energies exist instead of a uniform value. Hence, the use of the Langmuir adsorption isotherm might not be justifiable.

Since only very limited information is available, the model of Equation (16) is incapable of determining E and Q values precisely although the values of E and Q obtained are reasonable in view of the magnitudes of available data. This model can only be described as a rough approximation. Nevertheless, it describes the experimental data very well. It might be useful for a rough prediction of the desorption-recovery process under other situations. Based upon this model, the optimized constant temperature operation should proceed at a temperature of about 220°C for which a recovery of about 40% of the phenol loaded on carbon could be achieved in about 40 minutes.

5.4 ECONOMIC FEASIBILITY

To bring a process to application, economic feasibility must be considered. Although a precise evaluation is not possible here, there are several things worth mentioning: The absorbent solution containing recovered phenols is suitable to the phenol plant as a raw material where phenol is recovered in the product stream, and the residual caustic is a component in the production of phenol. Thus not only is phenol recovered, but also there is no charge for the caustic soda used due to its use as a raw material as indicated by Himmelstein et. al. (1973).

Since drying has already been included in the thermal regeneration process, the desorption recovery process will not need much extra energy because the thermal load necessary for this purpose will reduce the energy requirement for the next step in regeneration.

The desorption-recovery proceeds rapidly and a 40% percent recovery is quite attractive and promising.

NOTATION

b	Langmuir equilibrium constant	1/atm
b ₀	Constant, Equation (18)	1/atm
E	Activation energy of thermal cracking	cal/gmole°K
K	First order rate constant	1/min
K ₀	Pre-exponential factor, Equation (17)	1/min
K'	Constant, Equation (16)	1/min
q	Weight of species retaining the structure of phenol on the carbon particle surface	gm
q ₀	Amount initially adsorbed	gm
q _∞	Saturation adsorption capacity	gm
Q	Heat of adsorption	cal/gmole°K
R	Gas constant	cal/gmole°K
t	Time	min
T	Temperature	°K

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CHAPTER 6

CONCLUSION

A very serious concern in the operation of coal conversion plants is the treatment of wastewater contaminated by phenol and phenol-derivatives. Earlier studies of sorptive treatment of phenolic wastewater using activated carbon have been largely limited to consideration of the behavior of phenol. In this work, the sorptive behavior of several prominent phenolic compounds in coal conversion wastewater was carefully studied; particular attention was paid to dihydric phenols in view of their affinity for water.

It was found that resorcinol and catechol both showed higher uptake capacities on activated carbon than phenol or o-cresol. This kind of behavior is probably due to the existence of two hydroxyl groups in the molecular structure involved in the adsorption process on the carbon surface. Experimental data also confirmed that lower solubility substances will have higher uptake capacity, and the existence of the methyl group had a positive influence upon the uptake capacity of the activated carbon.

The effective diffusivities obtained from batch adsorption experiments revealed a tendency for the smaller, more regularly-shaped species to have higher diffusivities. However, effective diffusivity will be a little different for different initial concentrations, with lower initial concentrations

leading to higher effective diffusivities.

Reclamation of phenols from coal conversion wastewater might generate a significant economic credit for the overall process. In addition, the recovered compounds could relieve pressure exerted by the increasing demand for petroleum used in the synthesis of phenol and its derivatives.

In the reclamation process investigated, the maximum recovery of phenol achieved was about 45% by weight when the gas temperature was elevated to around 230°C. However, the fraction of recovery was reduced dramatically when the nitrogen gas temperature was further elevated. This effect is apparently the result of pyrolytic decomposition on the activated carbon surface. At low temperature, decomposition is not significant; hence higher energy input leads to higher desorption rates and higher percentages of phenol can be recovered. At high temperature, pyrolytic decomposition becomes predominant; if the gas temperature was elevated quickly, the phenol species on the carbon surface would be decomposed rapidly rather than be desorbed. The evidence gathered in this study suggests that the fraction of phenol loaded on activated carbon that can be recovered is governed by the competition between thermal desorption and pyrolytic decomposition. Based on the constructed model, the optimized constant temperature operation is to proceed at the gas temperature around 220°C and a recovery efficiency of about 40% could be achieved in about 40 minutes.

Although the actual reclamation behavior might be different

for other sources of activated carbon or other phenolic contaminants in coal conversion wastewater, similiar behavior can be anticipated.

Since the caustic solution absorbent containing recovered phenols is suitable as a raw material to the phenol plant and since the energy used could reduce the energy required for the next step in regeneration, this reclamation process may prove to be economically feasible.

APPENDIX

- A. Calculation data sheet for the N_2 -BET specific surface area of adsorbent.
- B. Computer program and output results for pore diffusion model with simultaneous non linear adsorption.
- C. Computer program and output results for desorption-recovery model.

APPENDIX A

SAMPLE: Activated Carbon Degassing time: 2 hours Degassing temperature: 500°C				
SYMBOL	MEASUREMENT OR CALCULATION	DIMENSION		RESULT
w_2 w_1 w	Weight of Sample	tube + sample: 10.9732 grams tube: 10.9628 grams sample: 0.0104 grams		
P_T	Barometric pressure at T°K temperature	mmHg		760
T_R	Room temperature	°K	$273.16 + 25.7$ $=$	298.86
f	Correction factor for STP conditions: $f = \frac{P_T \cdot 273}{760 \cdot T_R} = 0.3595 \frac{P_T}{T_R}$		$0.3595 \frac{760}{298.86}$ $=$	0.914
	Inlet pressure of carrier gas (Helium)	in.		29.8
t_c	Soap film transit time for	sec.		38.3
v_{meter}	Volume of bubble flow meter between two calibration marks	ml.		20.0699
F_c	Flow rate of the carrier gas (helium): $F_c = \frac{60}{t_c} v_{\text{meter}}$	ml/min		31.44

SYMBOL	MEASUREMENT OR CALCULATION	DIMENSION		RESULT
p_o	Saturation pressure of N_2 at the temperature of the liquid N_2 used	mmHg	average <input type="checkbox"/> measured <input checked="" type="checkbox"/>	750.5
s_o	Area covered by one cc (STP) monolayer nitrogen	m^2/ml		4.37

SYMBOL	MEASUREMENT OR CALCULATION	DIMENSION	FIRST RUN	SECOND RUN	THIRD RUN
	Inlet pressure of the adsorption gas (N_2)	in.	10.9	25.4	39.1
t_t	Soap film transit time for total gas flow	sec.	26.6	20.0	15.7
F_t	Total ($He + N_2$) flow rate: $F_t = \frac{60}{t_t} v_{\text{meter}}$	ml/min	45.27	60.21	76.70
F_a	Adsorption gas (N_2) flow rate $F_a = F_t - F_c$	ml/min	13.83	28.77	45.26
A_{des}	Area of the desorption peak	counts	46.44	47.72	42.63
v_{cal}	Volume of the injection tube used	ml	0.3584	0.3584	0.3584
A_{cal}	Area of the calibration peak	counts	4.51	3.26	2.40

SYMBOL	MEASUREMENT OR CALCULATION	DIMENSION	FIRST RUN	SECOND RUN	THIRD RUN
v_{ads}	Volume of adsorbed gas $v_{ads} = \frac{A_{des}}{A_{cal}} v_{cal}$	ml	3.690	5.246	6.366
V_{ads}	Volume of adsorbed gas corrected to standard temperature pressure: $V_{ads} = v_{ads} f$	ml	3.373	4.795	5.819
p	Partial pressure of nitrogen $p = \frac{F_a}{F_t} P_T$	mmHg	232.18	363.15	448.46
p/p_o	Relative pressure of nitrogen		0.309	0.484	X^* 0.598
	$(p_o - p)$	mmHg	518.32	387.35	302.04
	$V_{ads} (p_o - p)$	ml·mmHg	1748.29	1857.39	1757.57
	$\frac{p}{V_{ads} (p_o - p)}$	ml^{-1}	0.1328	0.1955	Y^* 0.2552

*See one-point calculation

THREE-POINT CALCULATION			
SYMBOL	MEASUREMENT OR CALCULATION	DIMENSION	RESULT
α	The slope of the BET plot	1/ml	0.4181
β	y-intercept of the BET plot	1/ml	0.0007

SYMBOL	MEASUREMENT OR CALCULATION	DIMENSION	RESULT
V_m	Volume of adsorbed nitrogen for a monolayer: $V_m = \frac{1}{\alpha + \beta}$	ml	2.3878
S	$V_m s_o$	m^2	10.435
S_s	Specific surface area of the sample $S_s = \frac{V_m s_o}{w}$	m^2/g	1003.8

ONE-POINT CALCULATION			
SYMBOL	MEASUREMENT OR CALCULATION	DIMENSION	RESULT
α'	The slope of the BET plot $\alpha' = \frac{y}{x}$	1/ml	0.4298
V_m'	Volume of adsorbed nitrogen for a monolayer: $V_m' = \frac{1}{\alpha'}$	ml	2.327
S'	$V_m' s_o$	m^2	1016.8
S_s'	Specific surface area of the sample: $S_s' = \frac{V_m' s_o}{w}$	m^2/g	977.7

APPENDIX B

```

    DIMENSION C(51),S(51),CNEW(51),CC(51),CTEMP(51),
@STEMP(51),SNEW(51),IB(5),ST(5),SOLUTE(3)
    REAL K,N
    DATA ST/.00005,.001,.002,.005,.01/
    DATA IB/2,39,5,10,10/
    DATA R,RO,EPS,ERR/.1307,1.08,.424,.005/
    WRITE(5,*) 'ENTER DATA'
    READ(5,1) (SOLUTE(I),I=1,3)
    READ(5,*) CFI,GM,K,N
    WRITE(6,2) (SOLUTE(I),I=1,3),CFI,GM,K,N
    V=11.98/GM
    CK=K*1000.**N
    A=CK*CFI** (N-1.) *RO
    P=50.
    L=40
    ARR=12.5663706*R**3./V
    ITEST=0
    KP=P
    DELR=1./P
    IP=KP+1
    LL=L-2
    DO 50 J=1,IP
    CC(J)=0.
    C(J)=0.
    CNEW(J)=0.
    S(J)=0.
50 SNEW(J)=0.
    C(IP)=1.
    CNEW(IP)=1.
    T=0.
    DO 1003 II=1,5
    IN=IB(II)
    DELT=ST(II)
    IKK=10
    IF (II.EQ.1) IKK=100
    DO 1002 IJ=1,IN
    DO 1001 IK=1,IKK
70 INDEX=0
    M=P
60 EM=M-1
    COEF=DELT/(2.*EM*DELR**2)
    TERM=(EM-1.)*C(M-1)
    TERMS=((EM+1.)*C(M+1)-2.*EM*C(M)+TERM)*2.
    IF (SNEW(M)-CNEW(M)) 41,42,42
41 CONTINUE
    CC(M)=(EPS*C(M)+COEF*TERMS-(SNEW(M)-S(M)))/EPS
    CC(M)=ABS(CC(M))
    IF (ABS(CC(M)-CNEW(M)).GT.ERR*CNEW(M)) INDEX=1
    CNEW(M)=CC(M)
    SNEW(M)=A*CNEW(M)**N
    GO TO 43
42 CONTINUE

```

```

      SS=S(M)+COEF*TERMS-(CNEW(M)-C(M))*EPS
      SNEW(M)=ABS(SS)
      IF (SNEW(M).LE.1.E-35) GO TO 39
      CC(M)=(ABS(SS/A))**(1./N)
      GO TO 40
39  CC(M)=0.
40  IF (ABS(CC(M)-CNEW(M)).GT.ERR*CNEW(M)) INDEX=1
      CNEW(M)=CC(M)
43  M=M-1
      IF (M.GE.L) GO TO 60
      I=KP
      SUM1=0.
      SUM2=0.
31  SUM1=SUM1+(I-1)**2*(EPS*CNEW(I)+SNEW(I))
      SUM2=SUM2+(I-2)**2*(EPS*CNEW(I-1)+SNEW(I-1))
      IF (I-L) 33,33,32
32  I=I-2
      GO TO 31
33  CONTINUE
      PROD1=4.*SUM1
      PROD2=2.*SUM2
      COE=DELR**3/3.
      GRAL=COE*(P*P*(EPS*CNEW(IP)+SNEW(IP))+PROD1+PROD2)
      CC(IP)=ABS(1.-GRAL*ARR)
      IF (ABS(CC(IP)-CNEW(IP)).GT.ERR*CNEW(IP)) INDEX=1
      CNEW(IP)=CC(IP)
      SNEW(IP)=A*CNEW(IP)**N
      IF (INDEX.EQ.1) GO TO 70
      T=T+DELT
      DO 10 I=LL,IP
      CTEMP(I)=C(I)
      STEMP(I)=S(I)
      C(I)=CNEW(I)
      S(I)=SNEW(I)
      SNEW(I)=SNEW(I)+(SNEW(I)-STEMP(I))
10  CNEW(I)=CNEW(I)+(CNEW(I)-CTEMP(I))
1001 CONTINUE
      CPPM=C(IP)*CFI*1000.
      IF (T.LT.0.2) GO TO 1002
      WRITE(6,3) T,CPPM,C(IP),C(46)
1002 CONTINUE
1003 CONTINUE
1  FORMAT(3A4)
2  FORMAT(////15X,'ADSORBATE : ',3A4,
  @//15X,'INITIAL CONCENTRATION = ',F5.3,' MG/CC'/15X,'CARBON
  @ DOSAGE = ',F4.1,' GM'/15X,'K = ',F7.4,5X,'N = ',F6.4//15X,
  @'THETA = ',8X,'CONC = ',9X,'PHI = ',10X,'C(46) =' /30X,' ( MG/L ) ')
3  FORMAT(10X,4E15.4)
      STOP
      END

```

ADSORBATE : PHENOL

INITIAL CONCENTRATION = 0.592 MG/CC

CARBON DOSAGE = 16.0 GM

K = 51.4939 N = 0.2281

THETA =	CONC = (MG/L)	PHI =	C(46) =
0.2000E+00	0.3615E+03	0.6107E+00	0.0000E+00
0.2100E+00	0.3582E+03	0.6051E+00	0.0000E+00
0.2200E+00	0.3552E+03	0.5999E+00	0.0000E+00
0.2300E+00	0.3523E+03	0.5952E+00	0.0000E+00
0.2400E+00	0.3497E+03	0.5908E+00	0.0000E+00
0.2500E+00	0.3473E+03	0.5866E+00	0.0000E+00
0.2600E+00	0.3450E+03	0.5827E+00	0.0000E+00
0.2700E+00	0.3427E+03	0.5789E+00	0.0000E+00
0.2800E+00	0.3406E+03	0.5753E+00	0.0000E+00
0.2900E+00	0.3385E+03	0.5719E+00	0.0000E+00
0.3000E+00	0.3365E+03	0.5685E+00	0.0000E+00
0.3100E+00	0.3346E+03	0.5651E+00	0.0000E+00
0.3200E+00	0.3326E+03	0.5618E+00	0.0000E+00
0.3300E+00	0.3307E+03	0.5586E+00	0.0000E+00
0.3400E+00	0.3288E+03	0.5554E+00	0.0000E+00
0.3500E+00	0.3269E+03	0.5522E+00	0.0000E+00
0.3600E+00	0.3250E+03	0.5490E+00	0.0000E+00
0.3700E+00	0.3231E+03	0.5458E+00	0.0000E+00
0.3800E+00	0.3213E+03	0.5427E+00	0.0000E+00
0.3900E+00	0.3194E+03	0.5395E+00	0.0000E+00
0.4000E+00	0.3175E+03	0.5363E+00	0.0000E+00
0.4200E+00	0.3136E+03	0.5298E+00	0.0000E+00
0.4400E+00	0.3097E+03	0.5232E+00	0.0000E+00
0.4600E+00	0.3058E+03	0.5165E+00	0.0000E+00
0.4800E+00	0.3018E+03	0.5098E+00	0.0000E+00
0.5000E+00	0.2977E+03	0.5029E+00	0.0000E+00
0.5500E+00	0.2875E+03	0.4857E+00	0.0000E+00
0.6000E+00	0.2774E+03	0.4686E+00	0.0000E+00
0.6500E+00	0.2676E+03	0.4520E+00	0.0000E+00
0.7000E+00	0.2582E+03	0.4361E+00	0.0000E+00
0.7500E+00	0.2492E+03	0.4210E+00	0.0000E+00
0.8000E+00	0.2407E+03	0.4066E+00	0.0000E+00
0.8500E+00	0.2327E+03	0.3931E+00	0.0000E+00
0.9000E+00	0.2252E+03	0.3805E+00	0.0000E+00
0.9500E+00	0.2183E+03	0.3688E+00	0.0000E+00
0.1000E+01	0.2120E+03	0.3582E+00	0.3196E-37
0.1100E+01	0.2012E+03	0.3398E+00	0.3319E-30
0.1200E+01	0.1925E+03	0.3252E+00	0.9924E-25
0.1300E+01	0.1855E+03	0.3134E+00	0.1608E-20
0.1400E+01	0.1797E+03	0.3035E+00	0.3180E-17
0.1500E+01	0.1747E+03	0.2951E+00	0.1384E-14
0.1600E+01	0.1702E+03	0.2874E+00	0.1977E-12
0.1700E+01	0.1659E+03	0.2802E+00	0.1204E-10
0.1800E+01	0.1617E+03	0.2732E+00	0.3722E-09
0.1900E+01	0.1575E+03	0.2660E+00	0.6575E-08
0.2000E+01	0.1531E+03	0.2585E+00	0.7254E-07

ADSORBATE : PHENOL

INITIAL CONCENTRATION = 0.757 MG/CC

CARBON DOSAGE = 16.0 GM

K = 51.4939 N = 0.2281

THETA =	CONC = (MG/L)	PHI =	C(46) =
0.2000E+00	0.4915E+03	0.6493E+00	0.0000E+00
0.2100E+00	0.4882E+03	0.6449E+00	0.0000E+00
0.2200E+00	0.4850E+03	0.6407E+00	0.0000E+00
0.2300E+00	0.4820E+03	0.6368E+00	0.0000E+00
0.2400E+00	0.4791E+03	0.6329E+00	0.0000E+00
0.2500E+00	0.4762E+03	0.6291E+00	0.0000E+00
0.2600E+00	0.4734E+03	0.6254E+00	0.0000E+00
0.2700E+00	0.4706E+03	0.6217E+00	0.0000E+00
0.2800E+00	0.4678E+03	0.6180E+00	0.0000E+00
0.2900E+00	0.4651E+03	0.6143E+00	0.0000E+00
0.3000E+00	0.4623E+03	0.6106E+00	0.0000E+00
0.3100E+00	0.4594E+03	0.6069E+00	0.0000E+00
0.3200E+00	0.4566E+03	0.6032E+00	0.0000E+00
0.3300E+00	0.4537E+03	0.5994E+00	0.0000E+00
0.3400E+00	0.4508E+03	0.5956E+00	0.0000E+00
0.3500E+00	0.4479E+03	0.5917E+00	0.0000E+00
0.3600E+00	0.4450E+03	0.5878E+00	0.0000E+00
0.3700E+00	0.4420E+03	0.5838E+00	0.0000E+00
0.3800E+00	0.4389E+03	0.5798E+00	0.0000E+00
0.3900E+00	0.4359E+03	0.5758E+00	0.0000E+00
0.4000E+00	0.4328E+03	0.5718E+00	0.0000E+00
0.4200E+00	0.4267E+03	0.5636E+00	0.0000E+00
0.4400E+00	0.4205E+03	0.5555E+00	0.0000E+00
0.4600E+00	0.4143E+03	0.5473E+00	0.0000E+00
0.4800E+00	0.4083E+03	0.5393E+00	0.0000E+00
0.5000E+00	0.4023E+03	0.5314E+00	0.0000E+00
0.5500E+00	0.3877E+03	0.5122E+00	0.0000E+00
0.6000E+00	0.3739E+03	0.4940E+00	0.0000E+00
0.6500E+00	0.3610E+03	0.4769E+00	0.0000E+00
0.7000E+00	0.3491E+03	0.4611E+00	0.0000E+00
0.7500E+00	0.3383E+03	0.4469E+00	0.0000E+00
0.8000E+00	0.3287E+03	0.4342E+00	0.8952E-33
0.8500E+00	0.3203E+03	0.4232E+00	0.2570E-28
0.9000E+00	0.3131E+03	0.4136E+00	0.1260E-24
0.9500E+00	0.3067E+03	0.4052E+00	0.1501E-21
0.1000E+01	0.3011E+03	0.3978E+00	0.5808E-19
0.1100E+01	0.2915E+03	0.3850E+00	0.5974E-15
0.1200E+01	0.2831E+03	0.3740E+00	0.7235E-12
0.1300E+01	0.2753E+03	0.3637E+00	0.1749E-09
0.1400E+01	0.2674E+03	0.3533E+00	0.1248E-07
0.1500E+01	0.2590E+03	0.3422E+00	0.3401E-06
0.1600E+01	0.2502E+03	0.3305E+00	0.4353E-05
0.1700E+01	0.2412E+03	0.3186E+00	0.3134E-04
0.1800E+01	0.2323E+03	0.3069E+00	0.1473E-03
0.1900E+01	0.2237E+03	0.2955E+00	0.5055E-03
0.2000E+01	0.2155E+03	0.2847E+00	0.1366E-02

0.2100E+01	0.2078E+03	0.2745E+00	0.3058E-02
0.2200E+01	0.2007E+03	0.2651E+00	0.5850E-02
0.2300E+01	0.1942E+03	0.2566E+00	0.9772E-02
0.2400E+01	0.1885E+03	0.2490E+00	0.1451E-01
0.2500E+01	0.1834E+03	0.2423E+00	0.1951E-01
0.2600E+01	0.1790E+03	0.2365E+00	0.2420E-01
0.2700E+01	0.1751E+03	0.2313E+00	0.2823E-01
0.2800E+01	0.1716E+03	0.2267E+00	0.3146E-01
0.2900E+01	0.1685E+03	0.2225E+00	0.3395E-01
0.3000E+01	0.1656E+03	0.2187E+00	0.3581E-01
0.3100E+01	0.1629E+03	0.2152E+00	0.3719E-01
0.3200E+01	0.1604E+03	0.2119E+00	0.3822E-01
0.3300E+01	0.1580E+03	0.2087E+00	0.3903E-01
0.3400E+01	0.1556E+03	0.2055E+00	0.3972E-01
0.3500E+01	0.1532E+03	0.2024E+00	0.4038E-01
0.3600E+01	0.1508E+03	0.1993E+00	0.4109E-01
0.3700E+01	0.1484E+03	0.1960E+00	0.4189E-01
0.3800E+01	0.1459E+03	0.1927E+00	0.4280E-01
0.3900E+01	0.1433E+03	0.1893E+00	0.4381E-01
0.4000E+01	0.1406E+03	0.1858E+00	0.4489E-01
0.4100E+01	0.1379E+03	0.1822E+00	0.4600E-01
0.4200E+01	0.1352E+03	0.1785E+00	0.4709E-01
0.4300E+01	0.1324E+03	0.1749E+00	0.4811E-01
0.4400E+01	0.1297E+03	0.1713E+00	0.4904E-01
0.4500E+01	0.1270E+03	0.1677E+00	0.4985E-01
0.4600E+01	0.1243E+03	0.1642E+00	0.5052E-01
0.4700E+01	0.1217E+03	0.1608E+00	0.5107E-01
0.4800E+01	0.1192E+03	0.1575E+00	0.5148E-01
0.4900E+01	0.1168E+03	0.1542E+00	0.5177E-01
0.5000E+01	0.1144E+03	0.1511E+00	0.5196E-01

ADSORBATE : O-CRESOL

INITIAL CONCENTRATION = 0.737 MG/CC

CARBON DOSAGE = 16.0 GM

K = 92.2448 N = 0.1502

THETA =	CONC = (MG/L)	PHI =	C(46) =
0.2000E+00	0.4501E+03	0.6107E+00	0.0000E+00
0.2100E+00	0.4465E+03	0.6059E+00	0.0000E+00
0.2200E+00	0.4433E+03	0.6015E+00	0.0000E+00
0.2300E+00	0.4403E+03	0.5974E+00	0.0000E+00
0.2400E+00	0.4375E+03	0.5936E+00	0.0000E+00
0.2500E+00	0.4348E+03	0.5899E+00	0.0000E+00
0.2600E+00	0.4322E+03	0.5864E+00	0.0000E+00
0.2700E+00	0.4296E+03	0.5829E+00	0.0000E+00
0.2800E+00	0.4271E+03	0.5796E+00	0.0000E+00
0.2900E+00	0.4247E+03	0.5763E+00	0.0000E+00
0.3000E+00	0.4223E+03	0.5730E+00	0.0000E+00
0.3100E+00	0.4199E+03	0.5698E+00	0.0000E+00
0.3200E+00	0.4176E+03	0.5666E+00	0.0000E+00
0.3300E+00	0.4152E+03	0.5634E+00	0.0000E+00
0.3400E+00	0.4129E+03	0.5602E+00	0.0000E+00
0.3500E+00	0.4106E+03	0.5571E+00	0.0000E+00
0.3600E+00	0.4083E+03	0.5540E+00	0.0000E+00
0.3700E+00	0.4060E+03	0.5508E+00	0.0000E+00
0.3800E+00	0.4037E+03	0.5477E+00	0.0000E+00
0.3900E+00	0.4014E+03	0.5446E+00	0.0000E+00
0.4000E+00	0.3991E+03	0.5415E+00	0.0000E+00
0.4200E+00	0.3944E+03	0.5352E+00	0.0000E+00
0.4400E+00	0.3897E+03	0.5288E+00	0.0000E+00
0.4600E+00	0.3849E+03	0.5223E+00	0.0000E+00
0.4800E+00	0.3800E+03	0.5156E+00	0.0000E+00
0.5000E+00	0.3750E+03	0.5088E+00	0.0000E+00
0.5500E+00	0.3620E+03	0.4912E+00	0.0000E+00
0.6000E+00	0.3489E+03	0.4734E+00	0.0000E+00
0.6500E+00	0.3361E+03	0.4561E+00	0.0000E+00
0.7000E+00	0.3239E+03	0.4395E+00	0.0000E+00
0.7500E+00	0.3123E+03	0.4237E+00	0.0000E+00
0.8000E+00	0.3011E+03	0.4086E+00	0.0000E+00
0.8500E+00	0.2904E+03	0.3941E+00	0.0000E+00
0.9000E+00	0.2802E+03	0.3802E+00	0.0000E+00
0.9500E+00	0.2706E+03	0.3671E+00	0.0000E+00
0.1000E+01	0.2614E+03	0.3547E+00	0.0000E+00
0.1100E+01	0.2452E+03	0.3327E+00	0.0000E+00
0.1200E+01	0.2320E+03	0.3148E+00	0.0000E+00
0.1300E+01	0.2218E+03	0.3010E+00	0.0000E+00
0.1400E+01	0.2138E+03	0.2901E+00	0.0000E+00
0.1500E+01	0.2073E+03	0.2812E+00	0.0000E+00
0.1600E+01	0.2016E+03	0.2736E+00	0.5179E-33
0.1700E+01	0.1966E+03	0.2667E+00	0.3630E-28
0.1800E+01	0.1919E+03	0.2604E+00	0.3634E-24
0.1900E+01	0.1874E+03	0.2543E+00	0.8512E-21
0.2000E+01	0.1830E+03	0.2483E+00	0.6405E-18

ADSORBATE : RESORCINOL

INITIAL CONCENTRATION = 0.748 MG/CC

CARBON DOSAGE = 16.0 GM

K = 50.3522 N = 0.2525

THETA =	CONC = (MG/L)	PHI =	C(46) =
0.2000E+00	0.4675E+03	0.6250E+00	0.0000E+00
0.2100E+00	0.4636E+03	0.6198E+00	0.0000E+00
0.2200E+00	0.4600E+03	0.6150E+00	0.0000E+00
0.2300E+00	0.4566E+03	0.6105E+00	0.0000E+00
0.2400E+00	0.4535E+03	0.6062E+00	0.0000E+00
0.2500E+00	0.4505E+03	0.6022E+00	0.0000E+00
0.2600E+00	0.4476E+03	0.5984E+00	0.0000E+00
0.2700E+00	0.4448E+03	0.5946E+00	0.0000E+00
0.2800E+00	0.4421E+03	0.5910E+00	0.0000E+00
0.2900E+00	0.4394E+03	0.5875E+00	0.0000E+00
0.3000E+00	0.4368E+03	0.5840E+00	0.0000E+00
0.3100E+00	0.4342E+03	0.5805E+00	0.0000E+00
0.3200E+00	0.4316E+03	0.5771E+00	0.0000E+00
0.3300E+00	0.4291E+03	0.5736E+00	0.0000E+00
0.3400E+00	0.4265E+03	0.5702E+00	0.0000E+00
0.3500E+00	0.4239E+03	0.5668E+00	0.0000E+00
0.3600E+00	0.4214E+03	0.5633E+00	0.0000E+00
0.3700E+00	0.4188E+03	0.5599E+00	0.0000E+00
0.3800E+00	0.4162E+03	0.5564E+00	0.0000E+00
0.3900E+00	0.4135E+03	0.5529E+00	0.0000E+00
0.4000E+00	0.4109E+03	0.5493E+00	0.0000E+00
0.4200E+00	0.4056E+03	0.5422E+00	0.0000E+00
0.4400E+00	0.4001E+03	0.5350E+00	0.0000E+00
0.4600E+00	0.3947E+03	0.5277E+00	0.0000E+00
0.4800E+00	0.3892E+03	0.5203E+00	0.0000E+00
0.5000E+00	0.3837E+03	0.5130E+00	0.0000E+00
0.5500E+00	0.3702E+03	0.4949E+00	0.0000E+00
0.6000E+00	0.3571E+03	0.4774E+00	0.0000E+00
0.6500E+00	0.3445E+03	0.4606E+00	0.0000E+00
0.7000E+00	0.3327E+03	0.4448E+00	0.0000E+00
0.7500E+00	0.3216E+03	0.4300E+00	0.0000E+00
0.8000E+00	0.3113E+03	0.4162E+00	0.1481E-36
0.8500E+00	0.3019E+03	0.4036E+00	0.3771E-32
0.9000E+00	0.2934E+03	0.3923E+00	0.2111E-28
0.9500E+00	0.2858E+03	0.3821E+00	0.3327E-25
0.1000E+01	0.2791E+03	0.3731E+00	0.1814E-22
0.1100E+01	0.2677E+03	0.3579E+00	0.3524E-18
0.1200E+01	0.2585E+03	0.3456E+00	0.7542E-15
0.1300E+01	0.2507E+03	0.3352E+00	0.2966E-12
0.1400E+01	0.2438E+03	0.3260E+00	0.3412E-10
0.1500E+01	0.2373E+03	0.3172E+00	0.1560E-08
0.1600E+01	0.2307E+03	0.3085E+00	0.3458E-07
0.1700E+01	0.2240E+03	0.2995E+00	0.4275E-06
0.1800E+01	0.2171E+03	0.2902E+00	0.3290E-05
0.1900E+01	0.2100E+03	0.2807E+00	0.1730E-04
0.2000E+01	0.2028E+03	0.2712E+00	0.6723E-04

ADSORBATE : CATECHOL

INITIAL CONCENTRATION = 0.756 MG/CC

CARBON DOSAGE = 16.0 GM

K = 55.0091 N = 0.2503

THETA =	CONC = (MG/L)	PHI =	C(46) =
0.2000E+00	0.4623E+03	0.6116E+00	0.0000E+00
0.2100E+00	0.4580E+03	0.6058E+00	0.0000E+00
0.2200E+00	0.4540E+03	0.6005E+00	0.0000E+00
0.2300E+00	0.4503E+03	0.5956E+00	0.0000E+00
0.2400E+00	0.4469E+03	0.5911E+00	0.0000E+00
0.2500E+00	0.4437E+03	0.5868E+00	0.0000E+00
0.2600E+00	0.4406E+03	0.5828E+00	0.0000E+00
0.2700E+00	0.4377E+03	0.5790E+00	0.0000E+00
0.2800E+00	0.4349E+03	0.5753E+00	0.0000E+00
0.2900E+00	0.4322E+03	0.5717E+00	0.0000E+00
0.3000E+00	0.4296E+03	0.5682E+00	0.0000E+00
0.3100E+00	0.4270E+03	0.5649E+00	0.0000E+00
0.3200E+00	0.4245E+03	0.5615E+00	0.0000E+00
0.3300E+00	0.4220E+03	0.5582E+00	0.0000E+00
0.3400E+00	0.4196E+03	0.5550E+00	0.0000E+00
0.3500E+00	0.4171E+03	0.5517E+00	0.0000E+00
0.3600E+00	0.4147E+03	0.5485E+00	0.0000E+00
0.3700E+00	0.4122E+03	0.5453E+00	0.0000E+00
0.3800E+00	0.4098E+03	0.5420E+00	0.0000E+00
0.3900E+00	0.4073E+03	0.5388E+00	0.0000E+00
0.4000E+00	0.4049E+03	0.5355E+00	0.0000E+00
0.4200E+00	0.3999E+03	0.5290E+00	0.0000E+00
0.4400E+00	0.3949E+03	0.5223E+00	0.0000E+00
0.4600E+00	0.3898E+03	0.5156E+00	0.0000E+00
0.4800E+00	0.3847E+03	0.5088E+00	0.0000E+00
0.5000E+00	0.3795E+03	0.5020E+00	0.0000E+00
0.5500E+00	0.3665E+03	0.4848E+00	0.0000E+00
0.6000E+00	0.3537E+03	0.4679E+00	0.0000E+00
0.6500E+00	0.3413E+03	0.4515E+00	0.0000E+00
0.7000E+00	0.3294E+03	0.4358E+00	0.0000E+00
0.7500E+00	0.3182E+03	0.4208E+00	0.0000E+00
0.8000E+00	0.3075E+03	0.4068E+00	0.0000E+00
0.8500E+00	0.2976E+03	0.3936E+00	0.0000E+00
0.9000E+00	0.2883E+03	0.3814E+00	0.5206E-36
0.9500E+00	0.2799E+03	0.3702E+00	0.3631E-32
0.1000E+01	0.2722E+03	0.3601E+00	0.8460E-29
0.1100E+01	0.2591E+03	0.3427E+00	0.1618E-23
0.1200E+01	0.2485E+03	0.3287E+00	0.2254E-19
0.1300E+01	0.2399E+03	0.3173E+00	0.3775E-16
0.1400E+01	0.2326E+03	0.3077E+00	0.1352E-13
0.1500E+01	0.2263E+03	0.2993E+00	0.1561E-11
0.1600E+01	0.2204E+03	0.2915E+00	0.7673E-10
0.1700E+01	0.2147E+03	0.2840E+00	0.1929E-08
0.1800E+01	0.2090E+03	0.2765E+00	0.2818E-07
0.1900E+01	0.2032E+03	0.2688E+00	0.2625E-06
0.2000E+01	0.1972E+03	0.2608E+00	0.1682E-05

APPENDIX C

```

      DIMENSION P(5)
      COMMON II,NN,X(4,8),ODQ(121),Z(121)
      COMMON N,I,D(5),B(300),T(300,5),Q(300,5)
      DATA X/0.003,0.003,0.003,0.025,0.027,0.027,0.027,0.150,
@0.075,0.150,0.150,0.207,0.167,0.330,0.227,0.220,
@0.228,0.409,0.259,0.226,0.251,0.422,0.270,0.231,
@0.272,0.425,0.280,0.241,0.275,0.426,0.282,0.248/
      WRITE(5,*) 'ENTER DATA'
      READ(5,*) (T(1,L),L=1,5)
      READ(5,*) (D(L),L=1,5),H
      WRITE(6,7) (T(1,L),L=1,5)
      N=5
      NN=1
      DO 17 L=1,5
17  Q(1,L)=T(1,L)
      I=1
      B(I)=F(T(1,1),T(1,2),T(1,3),T(1,4),T(1,5))
999 CALL EXPLOR
      IF(B(I).NE.B(I-1)) GO TO 77
      DO 80 J=1,N
      IF(D(J).GE.H) GO TO 88
      80 CONTINUE
      GO TO 100
      88 DO 880 J=1,N
880  D(J)=D(J)/2.
      I=I-1
      GO TO 999
      77 DO 770 J=1,N
770  P(J)=2*T(I,J)-Q(I-1,J)
      PB=F(P(1),P(2),P(3),P(4),P(5))
      IF(PB.GT.B(I)) GO TO 9
      GO TO 999
      9 DO 90 J=1,N
      90 T(I,J)=P(J)
      B(I)=PB
      GO TO 999
100 NN=0
      WRITE(5,*) 'IT IS HERE'
      SSQ=F(T(I,1),T(I,2),T(I,3),T(I,4),T(I,5))
7  FORMAT(/////15X,'K(0)=' ,7X,'-E/R=' ,7X,'K =' ,8X,
@'1/B(0)P=' ,4X,'-Q/R=' /12X,5E12.3)
      SSQ=-SSQ
      WRITE(6,70) SSQ
70  FORMAT(/////15X,'SUM OF SQUARES =' ,F6.3)
      STOP
      END
      SUBROUTINE EXPLOR
      DIMENSION P(5)
      COMMON II,NN,X(4,8),ODQ(121),Z(121)
      COMMON N,I,D(5),B(300),T(300,5),Q(300,5)
      DO 5 J=1,N

```

```

5  T(I+1,J)=T(I,J)
   B(I+1)=B(I)
   DO 50 J=1,N
     T(I+1,J)=T(I,J)+D(J)
     BE=F(T(I+1,1),T(I+1,2),T(I+1,3),T(I+1,4),T(I+1,5))
     IF(BE.GT.B(I+1)) GO TO 55
     T(I+1,J)=T(I,J)-D(J)
     BE=F(T(I+1,1),T(I+1,2),T(I+1,3),T(I+1,4),T(I+1,5))
     IF(BE.GT.B(I+1)) GO TO 55
     T(I+1,J)=T(I,J)
     GO TO 550
55  B(I+1)=BE
550 Q(I+1,J)=T(I+1,J)
    50 CONTINUE
555 I=I+1
    RETURN
    END
    FUNCTION F(A,B,C,D,E)
    DIMENSION P(4,121)
    COMMON II,NN,X(4,8),ODQ(121),Z(121)
    F=0.
    DO 7777 II=1,4
      TX=0.
      YQ=1.
      DO 777 J=2,121
        CALL RRUNGE(1,1.,TX,YQ,II,A,B,C,D,E,DQ)
        ODQ(J)=DQ
777  CONTINUE
        ODQ(1)=0.
        CALL QSF(1.,ODQ,Z,121)
        F=F-(X(II,1)-Z(11))**2-(X(II,2)-Z(21))**2-(X(II,3)-Z(31))**2
        @-(X(II,4)-Z(41))**2-(X(II,5)-Z(51))**2-(X(II,6)-Z(61))**2
        @-(X(II,7)-Z(91))**2-(X(II,8)-Z(121))**2
        IF(NN.NE.0) GO TO 7777
        DO 77 JZ=1,121
97  P(II,JZ)=Z(JZ)*100.
7777 CONTINUE
        IF(NN.NE.0) GO TO 7778
        WRITE(6,7) ((P(II,JZ),JZ=11,61,10),(P(II,JZ),JZ=91,121,30),
          II=1,4)
7  FORMAT(///15X,'RECOVERY %'//20X,'T= 10',3X,'T= 20',3X,'T= 30'
        *,3X,
        @'T= 40',3X,'T= 50',3X,'T= 60',3X,'T= 90',3X,'T= 120'//16X,'A',
        @8F8.2//16X,'B',8F8.2//16X,'C',8F8.2//16X,'D',8F8.2)
7778 CONTINUE
    RETURN
    END
    SUBROUTINE RRUNGE(N,H,X,Y,II,AA,B,C,D,E,DQ)
    DIMENSION Y(1),F(10),Q(10)
    DO 15 M=1,5
      GO TO(1,4,5,3,7),M
1  DO 2 I=1,N

```

```

2 Q(I)=0
  A=.5
  GO TO 9
3 A=1.707107
4 X=X+.5*H
5 DO 6 I=1,N
  Y(I)=Y(I)+A*(F(I)*H-Q(I))
6 Q(I)=2.*A*H*F(I)+(1.-3.*A)*Q(I)
  A=.2928932
  GO TO 9
7 DO 8 I=1,N
  Y(I)=Y(I)+H*F(I)/6.-Q(I)/3.
  GO TO 15
9 GO TO (91,92,93,94),II
91 T=X*6.8125+298.
  IF (T.GT.445.) T=445.
  GO TO 95
92 T=X*6.8125+298.
  IF (T.GT.516.) T=516.
  GO TO 95
93 T=X*6.8125+298.
  IF (T.GT.516.) T=X*4.375+516
  IF (T.GT.551.) T=551.
  GO TO 95
94 T=X*11.078+298.
  IF (T.GT.553.) T=553.
95 DQ=(Y(1)-1./(1.+D*EXP(E/T)))*C
  IF (DQ.LT.0.) DQ=0.
  F(1)=-1.*AA*EXP(B/T)-DQ
15 CONTINUE
  RETURN
  END

```

$K(0)=$ $-E/R=$ $K =$ $1/B(0)F=$ $-Q/R=$
 0.172E+13 -0.170E+05 0.370E-01 0.900E+05 -0.549E+04

RECOVERY %

	T= 10	T= 20	T= 30	T= 40	T= 50	T= 60	T= 90	T= 120
A	0.28	3.55	11.07	16.37	20.03	22.53	26.22	27.35
B	0.28	3.55	15.83	30.45	38.11	40.78	40.86	40.86
C	0.28	3.55	15.83	27.29	27.29	27.29	27.29	27.29
D	1.02	13.60	24.90	24.90	24.90	24.90	24.90	24.90

SUM OF SQUARES = 0.012

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SORPTIVE RECLAMATION OF PHENOLS FROM COAL CONVERSION WASTEWATER

by

TAI-HSING CHA

B. S., National Taiwan University, 1978

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1982

The use of activated carbon in the sorptive-treatment of coal-conversion wastewater has been investigated. Sorptive kinetics and equilibria were determined for a number of contaminants that exist in high concentrations in gasifier condensate, but have been little considered in the literature, such as o-cresol, resorcinol, and catechol. A diffusion-controlled model with a nonlinear adsorption isotherm was used to present the kinetic results. Since the recovery of the adsorbed phenols would be desirable in terms of both process economics and the reduction in demand for petroleum currently used for synthesis, normal regeneration techniques would be preceded by a reclamation process. The first step in the recovery scheme entails thermal desorption, in which heated nitrogen is passed through a fixed bed of phenol-loaded carbon particles; the gas is then scrubbed with a caustic absorbent solution. The maximum recovery of phenol achieved was about 45% by weight when temperature was elevated to around 230 °C. However, the fractional recovery is reduced dramatically when the nitrogen temperature is further elevated. This effect is apparently the result of pyrolytic decomposition on the carbon surface.