

ADSORPTION AND THERMAL DECOMPOSITION CHARACTERISTICS
OF ORGANIC CONTAMINANTS IN COAL CONVERSION WASTEWATER

by

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CHAPTER I

INTRODUCTION

In view of the prospective trends for the supply and demand of energy, the coming shortage of crude oil is compounded by an equally serious dwindling of natural gas supplies. Because of this situation, there has been a dramatic acceleration in the development of coal gasification technology. A principal environmental problem associated with the coal gasification is the generation of wastewater containing significant quantities of toxic organic substances. The expected composition of wastewater will vary with different coal supplies and with different gasification processes and conditions. Forney et al. (1974) have shown the characteristics of wastewaters produced from the Synthane gasification of six different types of coal and compared their composition. Schmidt et al. (1974) have reported the results of a mass spectrometric analysis of a methylene chloride extract of Synthane wastewaters from various coals and illustrated that the contaminants include phenol, cresols, C₂-phenols, dihydroxy benzenes, naphthols, pyridines, and indols at total concentrations as high as 7,000 to 10,000 mg/l. Singer et al. (1978) have shown the specific organic composition of alternate coal conversion process wastewaters and demonstrated the substantial presence of phenol and simple alkylphenols in these wastewaters from a variety of coal conversion technologies.

There are several methods of treating phenolic wastewaters,

including incineration, biological treatment, chemical oxidation, solvent extraction, and adsorption. Concentrated wastes can be handled by incineration of them for complete destruction of phenols to carbon dioxide and water. According to Lanouette (1977), the heat of combustion of phenol is 13,300 Btu/lb and this heating value can be utilized in the combustion process. Therefore, the more concentrated the mixture is in phenol or other organics, the less supplemental fuel will be required.

The biological treatment most frequently used is the activated sludge system and it requires stable environmental conditions for microorganisms such as pH, temperature, sufficient dissolved oxygen, and avoidance of shock loadings of phenols. Kostenbader et al. (1969) have reported the final effluents in the range of 0.1 mg/l from raw waste loads of 1,000 mg/l. Kibbel et al. (1972) state that chemical oxidation is applied to phenol destruction in several ways: to treat highly concentrated wastewaters, as a pretreatment to biological treatment, and as a final polishing step after other treatment processes. Oxidation agents include hydrogen peroxide, ozone, chlorine dioxide, and potassium permanganate. While the phenols are destroyed, intermediate organic compounds are formed and the COD of the wastewater may remain requiring additional treatment. Glasgow (1975) has found that chemical oxidation of phenols is prohibitively expensive.

Solvent extraction has been used for dephenolization in coal conversion and coking plants. Benzene, tricresyl phosphate, and butyl acetate have been used as solvents for extraction in the

past. Beychok (1974) states that the Phenosolvan process uses isopropyl ether as the solvent for the liquid-liquid extraction of phenolic compounds produced from Lurgi coal gasification process. Scheibel (1978) proposes methyl isobutyl ketone as a candidate solvent for extractive treatment of phenolic wastewaters. Boyer et al. (1980) have studied the optimization of water usage in the Exxon Donor Coal Liquefaction Process, in which liquid-liquid extraction was used to remove phenols from the wastewater, but concluded that the activated carbon unit will be used to polish the effluent to meet effluent requirements. Greminger et al. (1982) have examined methyl isobutyl ketone and diisopropyl ether as solvents for the extraction of phenol from water and their findings lead strongly toward the use of methyl isobutyl ketone as a preferred solvent, with recovery of residual by vacuum steam stripping. In general, coal conversion wastewaters contain a large amount of dissolved ammonia and carbon dioxide, by virtue of which the pH typically lies between 8 and 9.8. At such high values of pH a significant fraction of phenols may be ionized, further discouraging extraction.

As wastewater effluent quality became more important, adsorption processes, in particular those using activated carbon, have found increased use in wastewater treatment for removal of organics. The economic feasibility of this process is highly dependent on the regeneration costs of spent carbon. There are many methods of regenerating the spent carbon, including solvent regeneration, supercritical fluid technique, biological regeneration, reactive

regeneration, and thermal regeneration.

Buelow et al. (1973) improved the conventional carbon desorption method of the early 1950s, by using chloroform and ethyl alcohol as solvents. Even during lengthy extraction of about 44 hours, the degree to which adsorbates are removed was not high. Paul et al. (1973) used ten different solvents to measure the rate of desorption of phenol from the wet spent carbon. In 2 hours of continuous extraction, most solvents including methyl alcohol, benzene, cyclohexane, and tetrahydrofuran did not desorb more than 16 % of the initial loading. Dimethyl formaldehyde was the best solvent, desorbing 28 % of the initial loading. Roller et al. (1982) have studied the regeneration of five different carbons loaded with p-chlorophenol by using methyl alcohol. The wood based carbon resulted in a superior extraction efficiency up to 46 % of the initial loading, compared to less than 28 % for other base carbons. According to Modell et al. (1980), for efficient and economic regeneration of activated carbon, the desired solvent characteristics are; high solubility for the adsorbate, favorable mass transfer properties for rapid desorption, and high volatility for subsequent separation of solutes. They have chosen a supercritical fluid (SCF CO₂) as a candidate with these characteristics. With laboratory scale experiments, they found the desorption of phenol from activated carbon is very rapid; 50 % of phenol is removed within 20 minutes and 100 % within 3 hours. Picht et al. (1981) have presented similar results which indicate

that 50 % of recovery of loaded phenol from carbon is possible with supercritical CO₂ and nearly 100 % recovery can be obtained for certain styrene-divinylbenzene polymeric adsorbents. Commercial validity of this process depends on the ability to remove solutes from the regenerant so that supercritical fluid can be recycled.

Biological regeneration of spent carbon involves the use of microbial culture for the conversion of the toxic compounds. Wallis and Bolton (1982) have studied the biological regeneration of spent carbon column loaded with phenol from water containing 1,000 mg/l. They found that the microbial uptake of phenol is the rate determining step of regeneration and that the solution concentration of phenol must be maintained at a low level so that substrate desorption from the carbon will occur. Himmelstein et al. (1973) have made an economic comparison of alternate regeneration methods including solvent regeneration, thermal regeneration, and reactive regeneration in which adsorbed phenols were removed by caustic soda.

Though Ramirez (1977) pointed out that the disadvantages of the thermal regeneration approach include the large energy requirement, adsorbent attrition of 5 to 10 % per cycle, and furnace corrosion, thermal regeneration is still commonly used for regeneration of exhausted carbon. Commercial thermal regeneration normally consists of drying at about 100°C, thermal desorption and decomposition at about 800°C, and final high-temperature treatment in the presence of oxidizing gases such as steam and oxygen in

which the pyrolytic residue is gasified. By the results from the thermogravimetric analysis (TGA), Suzuki et al. (1978) divided organic adsorbates into three groups, in which phenolic compounds were categorized as Group (III). The Group (III) compounds exhibited high residues on activated carbon after the temperature attained 800°C. The TGA technique was also used by Chihara et al. (1981) and by Umehara et al. (1983) to study thermal decomposition kinetics of loaded sucrose and sodium dodecylbenzene sulfonate, respectively, in the regeneration of powdered activated carbon.

The principal goals of this study are to obtain information on the sorptive characteristics of major constituents in coal conversion wastewater and in particular obtain:

- 1) Supplementary equilibrium data on the adsorption of little considered components such as pyridine and 2-naphthol
- 2) Characteristic thermal decomposition curves of various phenolic compounds and decomposition schemes for phenol for the temperature range of 140 to 280°C.

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CHAPTER II

MATERIALS AND METHODS

II.1 Adsorbates

Table 1 shows the results of Schmidt et al.'s (1974) mass spectrometric analysis of Synthane wastewaters, illustrating that approximately 60 to 80 % of the organic content of these waste streams is due to phenolic compounds, primarily phenol, cresols, C₂-phenols (xylenols etc.), dihydroxy benzenes, naphthols, and pyridines. Throughout this study, the experiments were carried out on single component basis using phenol, resorcinol, hydroquinone, o-cresol, m-cresol, pyridine, and 2-naphthol. o-cresol and pyridine were obtained in liquid form, while all the others in crystalline form. All adsorbates species were reagent grade and obtained from Fisher Scientific Company. Their properties are shown in Table 2.

II.2 Adsorbent

Whether used in powdered or granular form, activated carbon has been widely used in removing small concentrations of dissolved organic compounds from aqueous solution. In this study, the activated carbon used as the adsorbent was obtained in granular form from Fisher Scientific Company and was manufactured from coconut charcoal (6 to 14 mesh, Cat. No. 5 685B). The properties of this activated carbon were previously investigated by Cha (1982).

Table 1. Contaminants in Product Water from Synthane Gasification of Various Coals, after Schmidt et al. (1974). Conc. in $\mu\text{g}/\text{l}$.

Component	Illinois No. 6	Montana	N. Dakota	Wyoming	W. Kentucky	Pittsburgh
Phenol	3400	2660	3160	2790	4050	2040
Cresols	2840	2610	870	1730	2090	1910
C ₂ -Phenols	1090	780	240	450	440	620
C ₃ -Phenols	110	100	30	60	50	60
Dihydric	250	540	130	70	530	280
Benzofuranols	70	100	80	60	100	50
Indanols	150	100	140	110	110	90
Acetophenones }						
Hydroxybenzaldehyde }	60	110	—	—	60	50
Benzoic Acid }						
Naphthols	160	110	160	50	80	160
Indenols	90	90	70	10	60	30
Benzofurans	—	—	10	—	—	110
Biphenols	40	20	—	40	40	20
Benzothiophenols	110	60	—	20	20	70
Pyridines	—	60	270	120	120	130
Quinolines	—	—	20	—	—	10
Indols	—	20	70	20	20	40

Table 2. The Properties of Adsorbates.

Properties	Phenol	Resorcinol	Hydroquinone	o-Cresol	m-Cresol	2-Naphthol	Pyridine
Mol. wt.	94.11	110.11	110.11	108.13	108.13	144.16	79.1
M.P., °C	41	110	170	31	11	122	- 42
B.P., °C	182	281	285	191	202	295	115
pK _a , 25°C	10.0	9.81	9.42	10.2	9.74	8.78	5.17
Solubility, 25°C g/100 g H ₂ O	9.3	111	7.1	2.5	0.5	0.08	∞
Density, 20/4°C	1.071	1.272	1.332	1.047	1.034	1.220	0.978

Particle size distribution analyses were performed on representative samples of the carbon with Bausch & Lomb Omnicon Image Analysis System. The data were well described by the log-normal density function. Specific surface area was determined as an average N_2 -BET area of $1,000 \text{ m}^2/\text{g}$ by using Sorptometer (Perkin-Elmer Shell Model 212 D). The porosity was also reported as 0.42.

II.3 Analytical Determination of Adsorbates Species in Solution

Concentrations of phenols were measured using a colorimetric assay, ASTM D 1783-80, based on the rapid condensation of phenols with 4-aminoantipyrine followed by oxidation with potassium ferricyanide. Characteristic antipyrine colors were formed: red with phenol and o-cresol, yellow with dihydroxy benzenes, and green with 2-naphthol. For the determination of phenol, cresol, and dihydroxybenzenes, 2 % 4-aminoantipyrine solution and 8 % potassium ferricyanide solution were used, while 3 % 4-aminoantipyrine solution and 2 % potassium ferricyanide solution were used for 2-naphthol (Kolsek et al., 1961). The pH of the sample solution was adjusted to about 10 with concentrated ammonium hydroxide, and 100 ml of sample solution containing phenols was combined with 1 ml of 4-aminoantipyrine solution and 1 ml of potassium ferricyanide solution. After an appropriate time ranging from 15 to 120 minutes, the absorbance was measured against a blank solution at a wave length of 510 nm by means of a spectrophotometer (Bausch and Lomb, Spectronic 20).

Most colorimetric determinations of traces of pyridine are

based on the Koenig reaction of this compound and structurally related pyridine bases with cyanogen bromide and suitable aromatic amines. Duchemin and Casassa (1969) proposed 4,4'-diaminostilbene-2,2'-disulphonic acid (Mobay Chemical Corporation) as an excellent coupling component for the Koenig reaction. To a 50 ml of sample solution diluted with borax buffer solution (pH 7.8) 3 ml of 1 % 4,4'-diaminostilbene-2,2'-disulphonic acid solution and 3 ml of 1.5 % cyanogen bromide solution were added and mixed well. After 1 hour the absorbance was read at 490 nm against a blank solution.

Calibration curves were prepared by dissolving accurately weighed quantities of each compound in borax buffer solution for pyridine and in distilled water for phenols. Appropriate dilution of these solutions were made to give a series of aliquots suitable for spectrophotometric calibration.

Good agreements with Beer's law, a linear relationship between absorbance and concentration, were obtained for phenol, o-cresol, resorcinol, 2-naphthol, and pyridine, for the concentration range of 0.05 - 5 mg/l, 0.5 - 5 mg/l, 1 - 10 mg/l, 5 - 50 mg/l, and 0.05 - 1.0 mg/l, respectively. The resulting calibration curves are presented in the Appendix.

II.4 Thermogravimetric Analysis (TGA) Apparatus

A TGA apparatus (Perkin - Elmer Model TGS-2) was used for the determination of weight change during heating of the activated carbon samples. Details of furnace and sample-pan assembly are

shown schematically in Figure 1. The sample-pan is surrounded by an electric furnace. The furnace temperature is automatically controlled and recorded from room temperature to 700°C , with heating rates ranging from 0.3 to 160°C per minute. The activated carbon sample was placed in a platinum sample-pan (5.8 mm ID, 1.8 mm Deep) attached to the microbalance. The equipment provides for flowing a gas across a heated sample of carbon particles. During the experimental run, helium gas was introduced and the flow rate of helium was kept at $53\text{ cm}^3/\text{min}$, which is low enough that the effect of flow rate on the measurement of the weight change was negligible. Weight changes were monitored with a strip chart recorder.

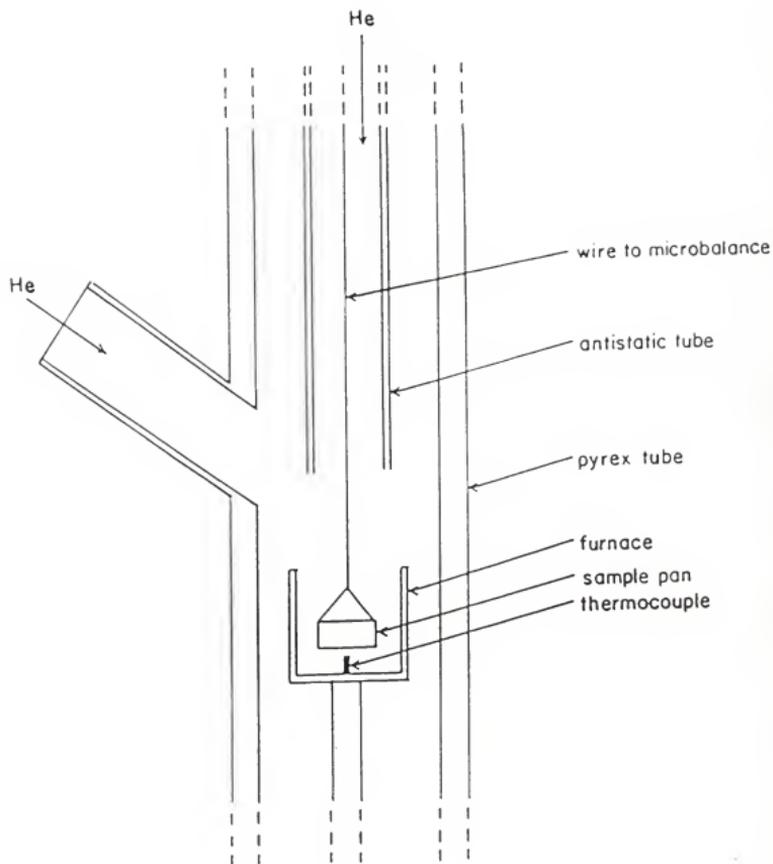


Figure I. Details of furnace and sample-pan assembly.

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CHAPTER III

ADSORPTION EQUILIBRIA

III.1 Various Models for Adsorption from Solution

At equilibrium there is a defined distribution of solute between liquid and solid phases. The adsorption isotherm is a functional expression relating the amount of solute adsorbed on the solid to the equilibrium of solute concentration at a given temperature. Experimental isotherms are useful for describing the capacity of an adsorbent to facilitate evaluation of the feasibility of adsorption for treatment, for selection of an appropriate adsorbent, and for the preliminary determination of adsorbent requirements.

The Langmuir model valid for monolayer adsorption is based on the assumptions that the energy of adsorption is constant and that there are no interactions between adsorbed molecules. The Langmuir equation has the form

$$q_e = \frac{Q^o b C}{1 + b C} \quad (1)$$

where q_e is the mass of adsorbed solute per unit mass of adsorbent at solution concentration C , Q^o is the mass of solute adsorbed per unit mass of adsorbent in complete monolayer, b is the constant which is a measure of intensity of adsorption, and C is the measured concentration in solution at equilibrium. The basic assumptions in Langmuir model are often not met in actual

systems. For example, rarely does a value of Q^0 developed for adsorption of organics from solution on activated carbon represent a true monolayer capacity (Weber, 1972). It is also unlikely in such a system that adsorption energies are uniform over all sites on the carbon surface. Such deviations limit the interpretation of values of Q^0 and b in terms of absolute surface area and adsorption energy. Nevertheless, the Langmuir equation is useful for describing equilibrium conditions for adsorption and for providing parameters (Q^0 and b) with which to qualitatively compare adsorption behavior in different adsorbate - adsorbent systems, or for varied conditions within any given system.

The Freundlich equation is a special case for heterogeneous surface energies in which the energy term, b , in Langmuir equation varies as a function of degree of adsorption.

The Freundlich equation has the general form

$$q_e = K_f C^{1/n} \quad (2)$$

where K_f and n are the constants, and n should be greater than unity. K_f and n are rough indicators of adsorption capacity and of adsorption intensity, respectively. The Freundlich equation agrees well with the experimental data over the moderate range of concentration beyond the Henry's law region. This model should not be extended beyond the valid experimental range.

The Polanyi adsorption theory for gas - solid system, based on the idea that as molecules approach a surface they are strongly attracted toward it, was extended to the liquid - solid adsorption

system by Manes and Hofer (1969). The adsorbed material is regarded as precipitated from solution as a consequence of an attractive potential. The driving force for adsorption is reduced by that of an equal volume of solvent, because the condensing solute must displace an equal volume of adsorbed solvent from the adsorption space. One may write

$$\begin{aligned} e_{s1} &= e_s - e_1 V_s / V_1 \\ &= RT \ln (C_0 / C) \end{aligned} \quad (3)$$

or

$$\begin{aligned} \frac{e_{s1}}{V_s} &= \frac{e_s}{V_s} - \frac{e_1}{V_1} \\ &= (RT/V_s) \ln (C_0 / C) \end{aligned} \quad (4)$$

where e_{s1} is the net driving force, e_s and e_1 are the adsorption potentials of solute and solvent as individual components, V_s and V_1 are the molar volume of solute and solvent, and C_0 is the saturation concentration. For a given adsorbate - adsorbent system, the theory postulates a single "correlation curve" from isotherm at any temperatures. A correlation curve is essentially a plot of the adsorbate volume adsorbed against $(RT/V_s) \ln (C_0/C)$ in Equation (4). Therefore, having determined the correlation curve for an adsorbent, one may now calculate the isotherms over a wide range of temperatures. Although this simple model is powerful and applicable even to multilayer adsorption, it has drawbacks in that it does not mention explicitly the surface area of adsorbent and it cannot explain adsorption phenomena for adsor-

bents with very fine pores.

Another approach taking comprehensive solution interactions into account has been studied by Belfort (1980). This approach, called the solvophobic interaction theory, was successfully applied to some particular adsorption systems (aliphatic homologues on activated carbon). By modifying and/or combining the Langmuir and the Freundlich equations, several semi-empirical isotherm equations have been developed for their adsorbate - adsorbent systems: Kipling (1965), Radke and Prausnitz (1972), and van Vliet et al. (1980).

III.2 Review of Previous Work

Adsorption capacity for specific single organic solutes of a homologous series is known to be a direct function of: (a) the nature of adsorbent such as surface area, pore size and distribution, and surface characteristics, (b) the adsorbate properties such as functionality, branching, hydrophobicity, polarity, molecular weight and size, and solubility, and (c) the solution conditions such as pH, temperature, and adsorbate concentration.

Mattson et al. (1969) have found major differences for the adsorption of phenol or derivatives, concluding that the major interaction with the surface of the carbon was through the pi-electron system of the ring. It is suggested that these aromatic compounds adsorb on activated carbon by a donor - acceptor complex. Carbonyl oxygen acts as the electron donor and the aromatic ring of the solute is the acceptor. The nitro group

substitution can enhance the donor - acceptor interaction by acting as an electron withdrawing group. Coughlin and Ezra (1968) have investigated the effect of surface oxides on the adsorption of phenol and nitrobenzene. The surface of the carbon was changed by oxidizing and reducing it chemically with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution and concentrated HCl with zinc amalgam, respectively. The oxidation strongly reduced the adsorption capacity for the adsorbates, while reduction of the oxidized carbon slightly increased the adsorption capacity.

There is generally an inverse relationship between the extent of adsorption of a species and its solubility in the solvent. Hansen and Craig (1954) have found that the adsorption isotherms of members of a homologous series of fatty acids or alcohols were superimposable on each other if adsorption isotherms were plotted in terms of reduced concentration C/C_0 , where C_0 is the solubility of the adsorbate in the solvent. Schwuger and Juentgen (1968) have studied the adsorption on the activated carbon of aromatic compounds including pyridine, phenol, indol, 2-naphthol, etc.. They have found that equilibrium adsorption was increased with increasing molecular weight of adsorbate up to 120 and then remained constant. Singer and Yen (1980) have found that alkyl-substituted phenols are more strongly adsorbed on activated carbon than phenol. The degree of adsorption increases as the number of the substituents increases, and as the length of the alkyl chain increases. Position of the substituent alkyl group has no effect on the extent of adsorption.

According to Kipling (1965), with rise in temperature, the adsorption isotherm usually falls to lower levels, particularly at the low concentration. This corresponds to a weakening of the attractive forces between the solute and the solid surface with increasing temperature, and corresponding increase in solubility of the solute in the solvent. Snoeyink et al. (1969) studied the effects of temperature and pH on the adsorption of phenol and nitrophenol on activated carbon. The influence of temperature was found to be small, but the adsorption capacity decreases at both lower and higher pH. This behavior at lower pH is attributed to competitive interaction between protons and carbonyl oxygen, resulting in desorption of phenol. The decrease of adsorption capacity at higher pH is explained by the repulsive forces between the sorbate anion and both the carbon surface and the sorbed species themselves.

III.3 Experimental Method

Cha (1982) has studied the adsorption isotherms of phenol, o-cresol, and dihydroxy benzenes in the concentration range up to 1,100 mg/l. Since the concentrations of phenolic contaminants in gasifier condensate are very high, knowledge of the adsorption capacity at high concentration is very useful for the design purposes. To compare the adsorption capacity of each constituents in gasifier condensate, the same procedure as that in Cha (1982) was adopted. The maximum concentration of pyridine was 1,000 mg/l and that of 2-naphthol was 600 mg/l.

Virgin activated carbon was boiled in distilled deionized water to remove fines and dried in an oven at 115°C for 48 hours and stored in a desiccator until used. The virgin carbon was from the same batch that was used by Cha (1982). 3 liters of working solution was prepared by dissolving accurately weighed adsorbate in distilled water. 180 ml portions of this solution were placed into 250 ml volumetric flasks, each containing a carefully measured quantity of activated carbon. The procedure was to fill 12 bottles in this manner, along with one bottle containing no carbon to serve as a blank. The weights of carbon added to the bottles were carefully selected to yield as wide a range of residual equilibrium solute concentration as possible for a given initial concentration. Typical amounts of carbon added were 0.02 to 1.40 gram. The volumetric flasks containing carbon and solution were tightly sealed and placed in a controlled environment incubator (Lab-Line Orbit Environ-Shaker, Lab-Line Instruments) to be shaken for attainment of equilibrium. Peel and Benedek (1980) have suggested that the adsorption isotherms on granular activated carbon be evaluated over periods of at least 30 days unless rigorous studies are carried out to ensure equilibrium is attained. The temperature was kept at 25°C . After equilibrium adsorption, the carbon particles were recovered by filtration and dried in a desiccator for one week. The amount adsorbed was determined either from the difference between the concentration of adsorbate measured in the blank solution and the depleted solution, or by weighing the carbon before adsorption and

after drying.

III.4 Results and Discussion

The pH at equilibrium adsorption for each system was measured and compared with the initial value. For pyridine initially at pH 5.5, the pH of depleted solutions ranged from 5.8 to 6.5. The pH of 2-naphthol solutions initially at 4.6 increased to 5.2 to 6.0. In view of the work by Snoeyink et al. (1969), the effect of this small change in pH during adsorption experiment was not considered to be significant.

The isotherms obtained covered a range of equilibrium solution concentrations from 120 to 920 mg/l for pyridine, and from 10 to 560 mg/l for 2-naphthol. The adsorbed amounts of adsorbate determined by concentration change were up to 260 mg/g of virgin carbon for pyridine and up to 480 mg/g of virgin carbon for 2-naphthol. The adsorbed amounts determined by weight change showed slightly lower values than those by concentration difference, and this can be attributed to the volatilization of some portions of adsorbate during drying in a desiccator. The difference between the results from two methods was 4 to 7 % for pyridine and 2 to 5 % for 2-naphthol. All the adsorption isotherm analyses were based on the data obtained from concentration change.

The relationship between adsorption capacity and equilibrium concentration was described by both the Langmuir adsorption equation and the Freundlich adsorption equation. The nonlinear Langmuir equation, Equation (1), and the Freundlich equation,

Equation (2), can be expressed in convenient forms, respectively:

$$\frac{C}{q_e} = \frac{C}{Q^0} + \frac{1}{Q^0 b} \quad (5)$$

and

$$\log q_e = \log K_f + (1/n) \log C \quad (6)$$

Data were analyzed through the SAS program to obtain the best values of parameters in both the linear and nonlinear forms of each equation. The results are summarized in Table 3 and Table 4, including the results from Cha (1982).

Figure 2 and Figure 3 show the adsorption isotherms for pyridine and 2-naphthol. The nonlinear descriptions for both the Langmuir equation and the Freundlich equation are compared in each Figure. Figures 4 and 5 are plots of the same data in accordance with the linearized forms of both adsorption equations. 2-Naphthol shows higher uptake capacity than pyridine. Composite plots of the adsorption isotherms for phenol, o-cresol, resorcinol, catechol, 2-naphthol, and pyridine are shown in Figure 6 in terms of the Freundlich expression. The adsorption data for phenol, o-cresol, resorcinol, and catechol were taken from Cha (1982). The increasing order of uptake capacity of these adsorbates on a mass basis is pyridine, phenol, o-cresol, resorcinol, catechol, and 2-naphthol.

Several factors affecting the adsorption capacity may be considered for explanation of this trend: molecular weight, solubility, and adsorptivity modulus. Table 5 shows the effect of these three factors on adsorption. Schwuger and Juentgen (1968) have

Table 3. Parameter Estimation of Adsorption Equilibrium Equation in Linear Form.

Parameters	Phenol ^a	Resorcinol ^a	Catechol ^a	o-Cresol ^a	Pyridine	2-Naphthol
Langmuir Equation						
Q^0 , mg/g	263.74	292.65	331.76	252.54	406.81	539.32
b , l/mg	0.0111	0.0130	0.0102	0.0336	0.0019	0.0117
corr.coeff.	0.9965	0.9960	0.9915	0.9994	0.9658	0.9799
Freundlich Equation						
K_f	49.992	42.521	52.678	88.193	6.131	52.905
n	4.288	3.545	3.882	6.298	1.817	2.913
corr.coeff.	0.9819	0.9138	0.9424	0.9217	0.9913	0.9891

^a These values are taken from Cha (1982).

Table 4. Parameter Estimation of Adsorption Equilibrium Equation in Nonlinear Form.

Parameters	Phenol ^a	Resorcinol ^a	Catechol ^a	o-Cresol ^a	Pyridine	2-Naphthol
Langmuir Equation						
Q^0 , mg/g	256.79	282.20	307.28	244.85	401.24	524.85
b , l/mg	0.0125	0.0156	0.0147	0.0418	0.0024	0.0132
residual	580.81	1665.3	4540.7	1462.3	3745.4	2936.7
Freundlich Equation						
K_f	51.494	50.352	52.009	92.245	6.333	54.217
n	4.384	3.961	3.995	6.657	1.964	3.044
residual	344.30	3248.9	1497.2	1321.2	388.42	692.33

^a These values are taken from Cha (1982).

Table 5. Effect of Variables on the Extent of Adsorption.

Adsorbates	Molecular Weight	Solubility, g/100g H ₂ O	Adsorptivity ^a Modulus, a _m
Pyridine	79.1	∞	1348
Phenol	94.1	9.3	4494
o-Cresol	108.1	2.5	14329
Resorcinol	110.1	111	6163
Catechol	110.1	45	6324
2-Naphthol	144.2	0.08	9185

$$^a a_m = Q^0 \cdot b \cdot d_c$$

The values of Q^0 and b are taken from Table 4.

The value of d_c is taken equal to 1.4 g/cm³, according to Frye and DiGiano (1974).

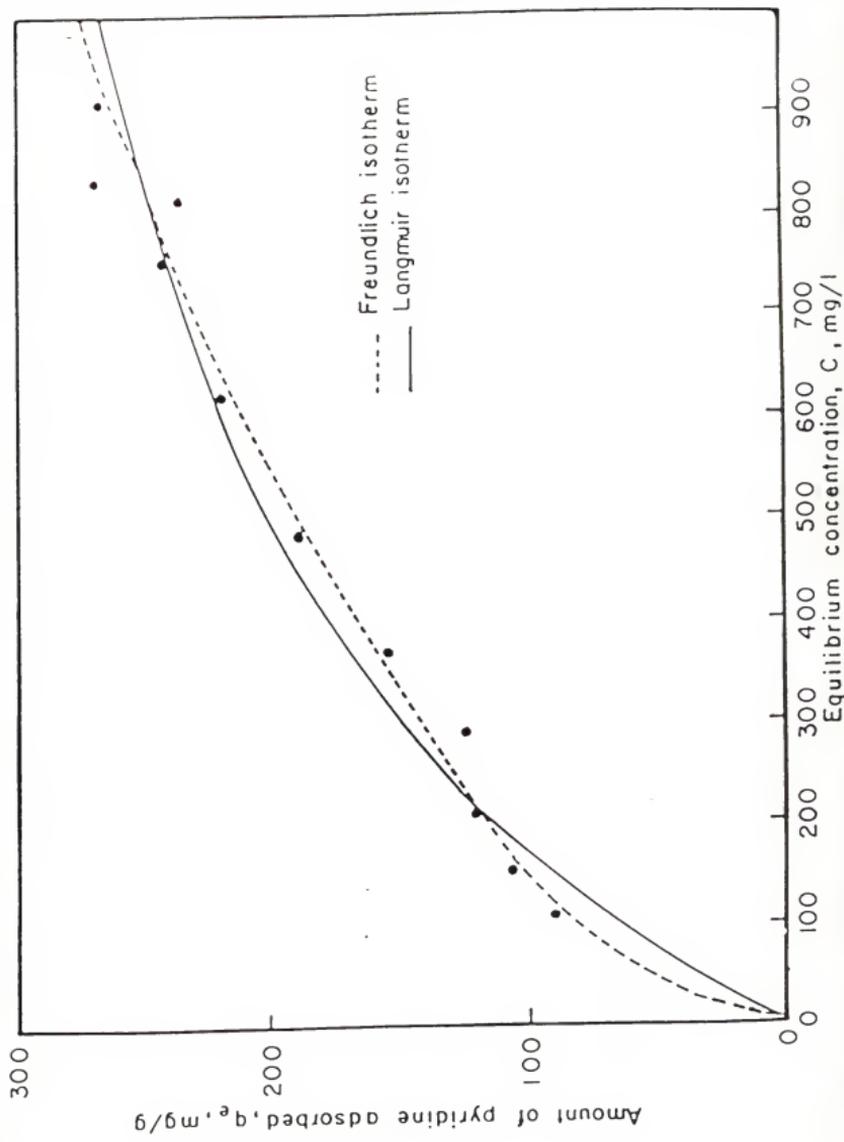


Figure 2. Adsorption isotherm for pyridine at 25° C.

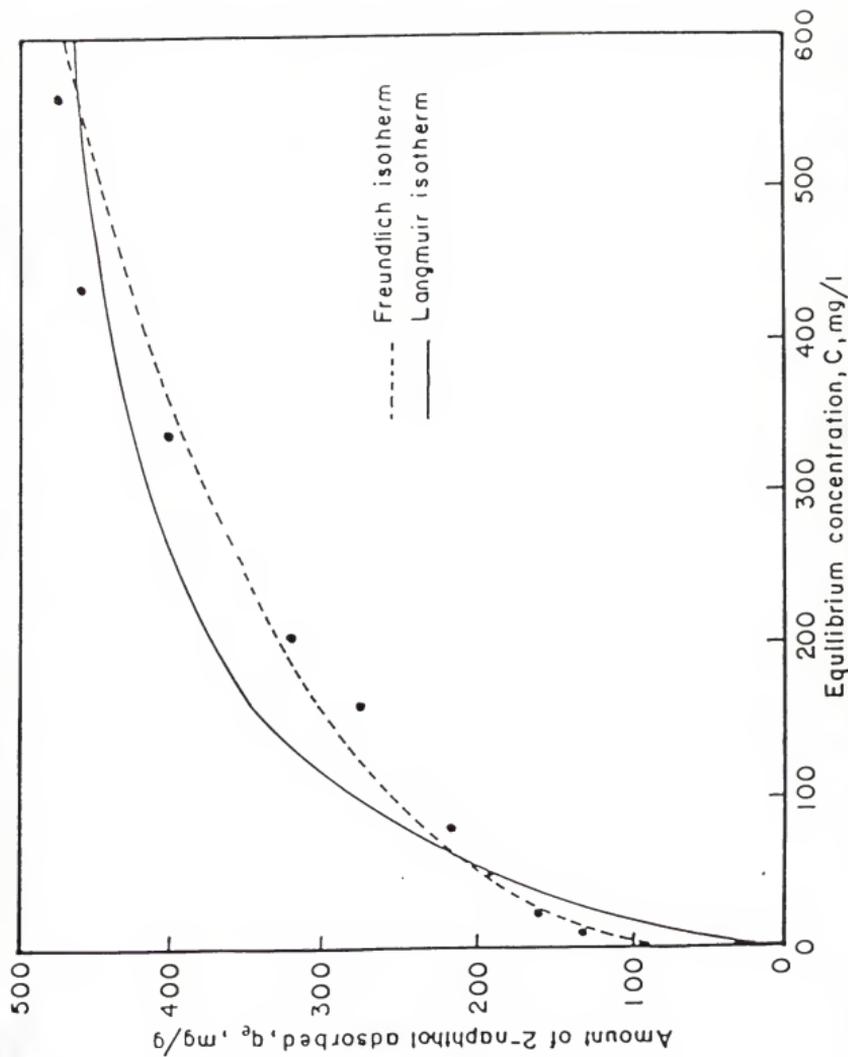


Figure 3. Adsorption isotherm for 2-naphthol at 25°C.

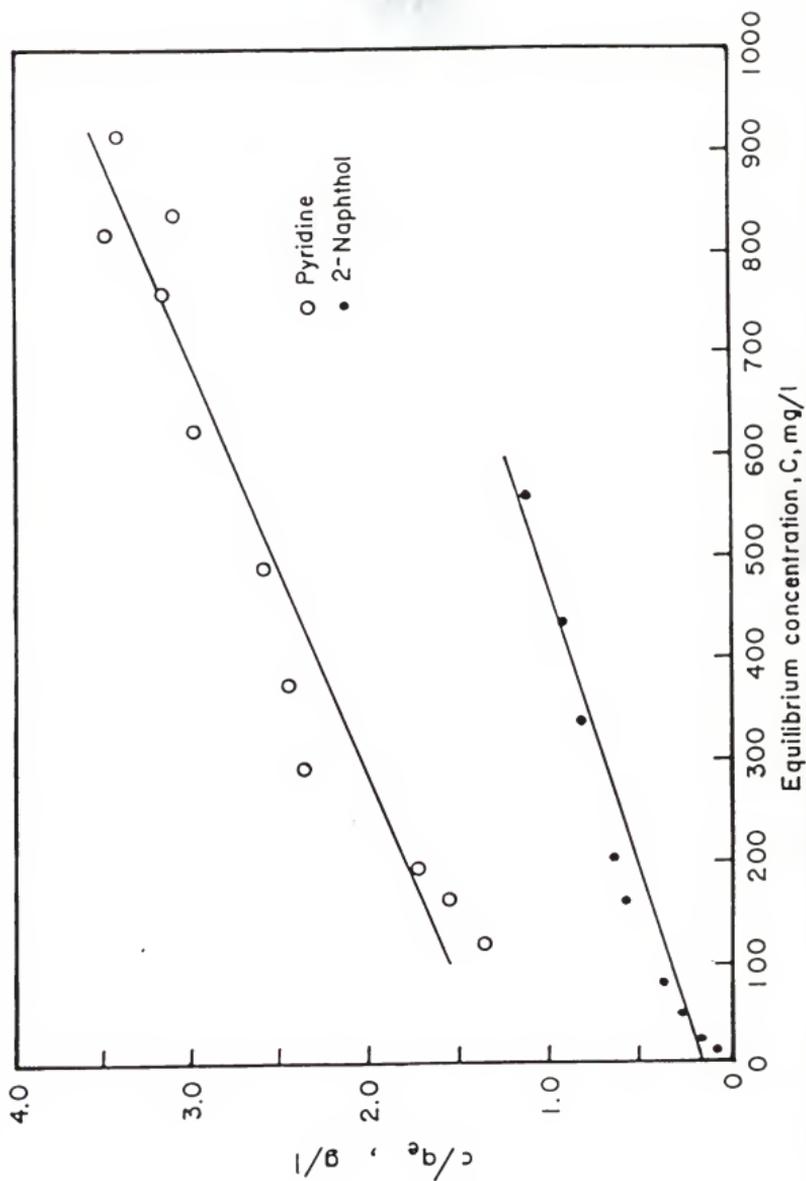


Figure 4. Linearized Langmuir relationship for pyridine and 2-naphthol.

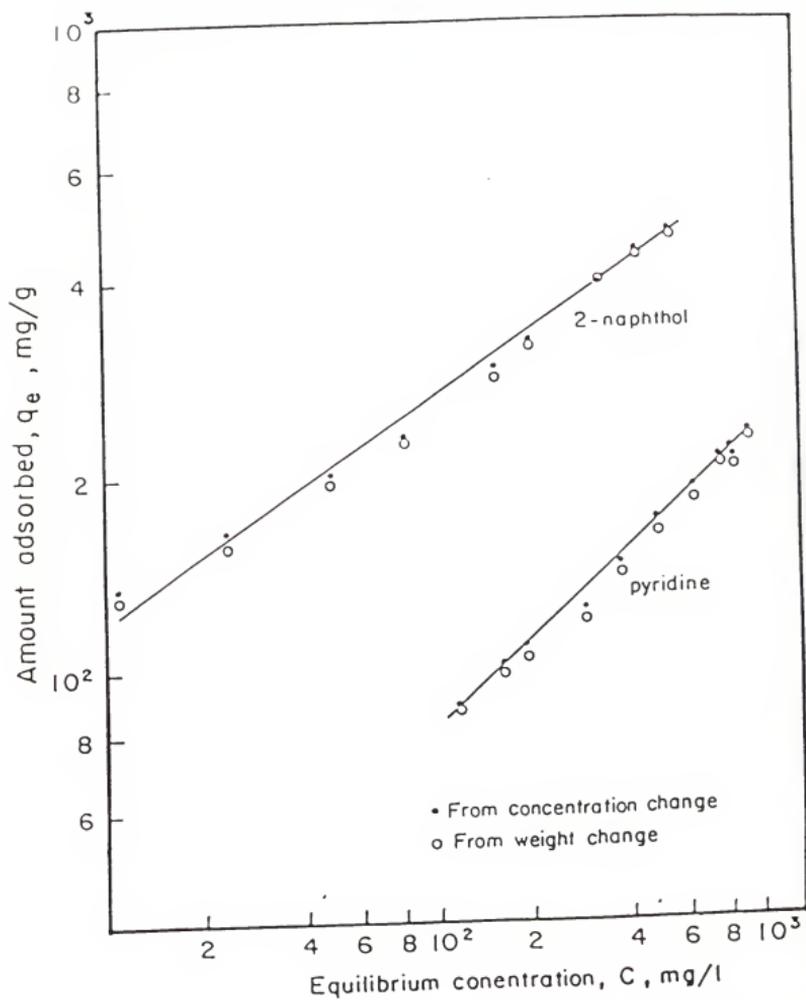


Figure 5. Freundlich isotherms for pyridine and 2-naphthol.

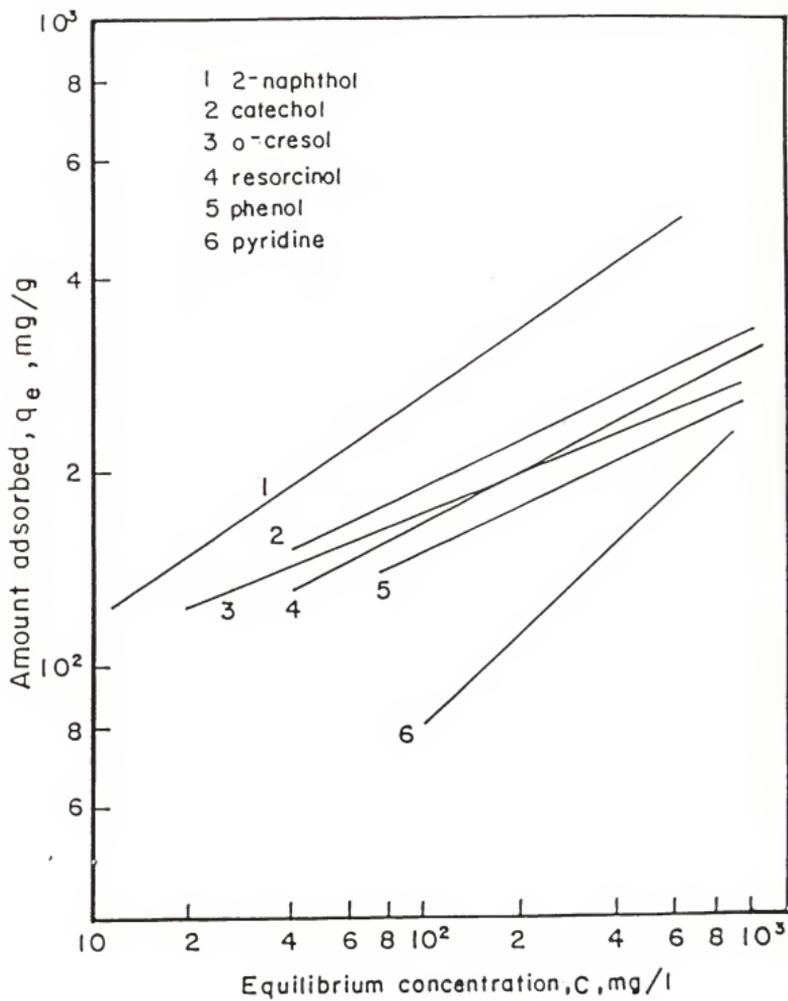


Figure 6. Freundlich isotherms for various adsorbates.

found that adsorption capacity of aromatic compounds, including pyridine and 2-naphthol, was increased with increasing molecular weight. Pyridine was found to be most weakly adsorbed on activated carbon. The experimental results are in accord with the general effect of molecular weight on adsorption: the higher molecular weight, the more strongly will it tend to be adsorbed.

An inverse relationship between the extent of adsorption of adsorbate and its solubility is shown except for the hydroxy benzenes. Mattson et al. (1969) indicated that the hydrogen in hydroxyl group is very likely involved in intracomplex hydrogen bonding within the surface complex. In that sense, it may be understood that phenols with two hydroxyl group show the higher extent of adsorption in spite of their high solubility. Catechol has higher adsorption capacity than resorcinol; this is probably attributed to the effect of solubility.

The relative adsorption capacity of various adsorbates is quantitatively described by the magnitude of the monolayer capacity term, Q^0 , in the Langmuir equation. According to Frye and DiGiano (1974), a more realistic indication of the relative adsorption capacity can be gained by combining the parameters Q^0 and b with carbon density d_c . A dimensionless parameter, a_m , termed the adsorptivity modulus can then be defined as

$$a_m = Q^0 b d_c \quad (7)$$

The parameter b is related to the ratio of adsorption and desorption and can, therefore, be considered to be dependent upon the

binding strength between the solid phase and the adsorbed molecule. The magnitude of the adsorptivity modulus gives a quantitative comparison between various adsorbate - carbon systems: higher values of a_m indicate more favorable adsorptive behavior. Table 5 shows this trend fairly well except for o-cresol. Since all the possible factors affecting adsorption must be combined together, it is hard to explain clearly the difference in adsorption capacity of various adsorbates in terms of only one factor.

Figure 7 shows the typical shape of adsorption isotherm obtained by application of Polanyi potential theory, called a "correlation curve". The Polanyi - based model was used to account for the adsorption of organic compounds from aqueous solution, more successfully for the adsorption of solid solutes than the adsorption of liquid solutes (Manes, 1980).

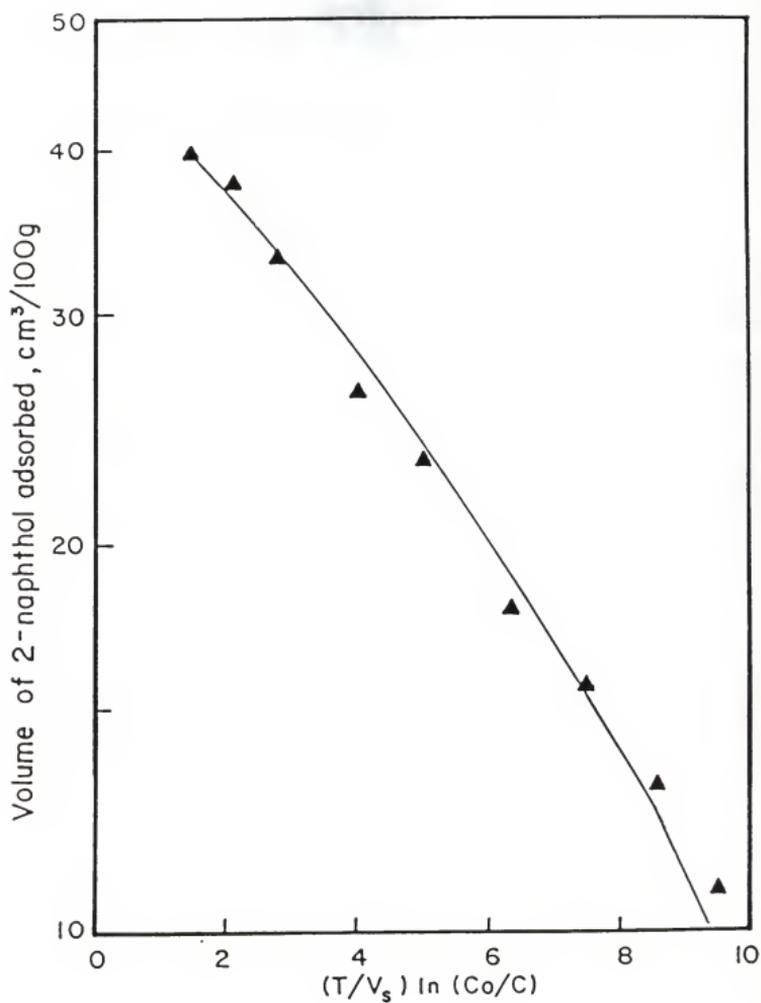


Figure 7. Adsorption isotherm for 2-naphthol at 25°C.
(by Polanyi potential theory)

NOTATION

a_m	: Adsorptive modulus	
b	: Constant in Langmuir equation,	l/mg
C	: Equilibrium concentration,	mg/l
C_0	: Solubility or saturation concentration,	mg/l
d_c	: Density of carbon,	g/cm ³
e_l	: Adsorption potential of solvent,	cm ³ ·atm/gmol
e_s	: Adsorption potential of solute,	cm ³ ·atm/gmol
e_{sl}	: Net adsorption potential of solute in solvent,	cm ³ ·atm/gmol
K_f	: Constant in Freundlich equation	
n	: Constant in Freundlich equation	
q_e	: Amount adsorbed per unit mass of adsorbent at equilibrium adsorption,	mg/g
Q^0	: Constant in Langmuir equation indicating monolayer capacity of adsorbent,	mg/g
R	: Gas constant,	cm ³ ·atm/gmol·K
T	: Absolute temperature,	K
V_l	: Molar volume of solvent,	cm ³ /gmol
V_s	: Molar volume of solute,	cm ³ /gmol

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CHAPTER IV

DECOMPOSITION OF ADSORBATES ADSORBED ON ACTIVATED CARBON

IV.1 Introduction

The use of activated carbon for purification of wastewaters is growing, and economic considerations require regeneration of spent carbon. The most often applied regeneration method consists of three steps: drying of the wet, spent carbon at about 105°C, heating to 800°C for thermal decomposition, and finally gasification of residual carbon in the presence of oxidizing gases such as water vapor and oxygen. The gasification process with an oxidizing gas is usually necessary to restore the original adsorption capacity of activated carbon. A fraction of deposited material can be removed by thermal decomposition prior to gasification. Though the reclamation of valued adsorbate species from coal conversion wastewater is feasible, not much attention has been paid to recovery of adsorbate during the thermal regeneration of activated carbon. The first stage, or drying, can sometimes be modified to facilitate desorption - recovery. Data on the characteristics of adsorbate decomposition and/or desorption are needed in order to assess the feasibility of this process.

In this study, a thermogravimetric analysis (TGA) apparatus was used to obtain the weight change curves of various adsorbates deposited on activated carbon as a function of temperature.

This type of experiment does not provide any information about the nature of the decomposition reactions since volatile products are simply purged into the atmosphere from the apparatus. However, the shape of the curves can be useful for determining the ease of decomposition of any adsorbate. Also, TGA curves can be used to obtain some kinetic data such as activation energy of decomposition reaction by postulating an appropriate kinetic model.

IV.2 Review of Previous Work

A number of investigators have reported studies of the thermal decomposition of phenolic compounds. Jones and Neuworth (1952) have studied the thermal cracking of isomeric cresols at the temperature range of 760 to 870°C. The marked thermal stability of m-cresol as compared with o-cresol or p-cresol was observed. The increased cracking rate observed in the case of o-cresol and p-cresol is attributed to a weakening of the C - H bond in the methyl group and hydroxyl group. Phenol was found to be one of the primarily cracking products of the converted cresol. Activation energies based on the first order kinetics were 75, 70, and 69 kcal/gmol for m-cresol, xylenol, and o-cresol, respectively.

Cypres and Bettens (1975) have studied the cracking of phenol and cresols at 665 to 865°C. Radioactive labelling of phenols with ^{14}C and ^3H in specific positions was used to delineate the possible reaction paths. Formation of benzene, and to some extent toluene, occurred directly from the original phenol.

Production of other aromatic compounds appeared to occur as a result of condensation of two C_5H_6 fragments.

Fillo (1979) has investigated homogeneous gas phase thermal decomposition of phenol at 740 to 980°C and of o-cresol at 610 to 830°C. Experimental data indicates that o-cresol is significantly more reactive than phenol. The activation energies for decomposition were 39.1 and 23.2 kcal/gmol for phenol and o-cresol, respectively. The mechanism of decomposition of o-cresol was found to be essentially a dealkylation to produce phenol as the only major product. Fillo also found that results from experiments on phenol decomposition in a fixed-bed of solids at 435 to 590°C indicate a substantial acceleration of the decomposition rate for lignite char solids, as opposed to the case of homogeneous gas phase decomposition of phenol. The activation energy of this heterogeneous decomposition of phenol was 31.9 kcal/gmol. By comparing the rate constants of homogeneous gas phase decomposition to that of heterogeneous decomposition, it was concluded that the presence of lignite char solids significantly increases the rate of phenol decomposition.

Suzuki et al. (1978) have utilized the TGA technique to measure the weight change when spent granular carbon samples were heated in an inert atmosphere. The virgin carbon was loaded with 32 different single organic compounds and the resultant weight change versus temperature curves were classified into three distinct groups according to the ease of decomposition and the amount of residual carbon left. Organic compounds that belong

to Group (I) are rather volatile and TGA curves can be explain by a simple desorption model. Group (II) organics are relatively easy to decompose and TGA curves were explained in terms of first order cracking kinetics. Group (III) organics, including phenol, 2-naphthol, and other phenolic compounds gave high residu-als on activated carbons after heating to 800°C.

Chihara et al. (1981) have studied the thermal regeneration of spent carbon loaded with sucrose by use of TGA apparatus. They have suggested that the intermediate phase of regeneration is a complicated process involving decomposition of the original adsorbates and desorption of low-molecular weight pyrolysis products, leaving adsorbed residual carbon. They have obtained activation energies of 35.7 kcal/gmol for the low temperature range of 134 to 155°C and 90.4 kcal/gmol for the temperature range of 155 to 500°C.

Umehara et al. (1983) have reported that thermal decomposi-tion of sodium dodecylbenzene sulfonate in the range of 20 to 700°C reduced the adsorbed material by only about 50 %. No thermal decomposition was observed below about 220°C. By inter-pretting the TGA curves they have obtained the activation energy of the decomposition reaction as 26.0 kcal/gmol.

Cha and Glasgow (1983) have studied the thermal desorption of phenol from activated carbon under a nitrogen atmosphere. The experimental study has shown that fixed-bed thermal desorption can lead to the reclamation of more than 40 % of phenol adsorbed on activated carbon by employing operating temperatures between

230 and 260°C and atmospheric pressure.

IV.3 Experimental Method

The experimental work consisted of two parts: preparation of spent carbon samples and the TGA experiments. A similar procedure to that in the adsorption equilibrium study was utilized for preparation of spent carbon samples. Virgin carbon was boiled in distilled deionized water to remove fines and dried in an oven at 115°C for 2 days and stored in a desiccator until used. The adsorption experiments were carried out on a single component basis using phenol, resorcinol, hydroquinone, o-cresol, and m-cresol, and pyridine. The spent activated carbon samples were prepared by immersing a known amount of carbon into adsorbate solutions. The volumetric flask containing carbon and adsorbate solution were placed in a controlled - environment incubator to be shaken for 5 days at room temperature. Then, the carbon particles were recovered by filtration and dried in a desiccator for one week at room temperature. From the weight change of the sample the amount of adsorbate retained in the carbon was determined. Different carbon dosages were used to obtain activated carbons containing different amounts of phenol in order to check the effect of adsorbate loading. An effort was made to minimize the effect of initial loading on TGA curves by using carbon samples with relatively constant loading (approximately 0.20 to 0.24 g/g) for each adsorbate.

The TGA apparatus shown in Figure 1 was used to determine the weight change during heating the spent activated carbon. Helium gas was introduced across a heated sample of carbon particles. The flow rate of helium gas was calibrated with a soap film flowmeter and kept at $53 \text{ cm}^3/\text{min}$ throughout the experiment. A carbon sample containing adsorbate with a weight of 10 to 20 mg was placed in the platinum sample-pan attached to the microbalance. The sample-pan was positioned inside a small ceramic furnace and the whole assembly located in the Pyrex tube. Spent carbon samples were studied in the TGA apparatus with a linear heating rate to increase the temperature from ambient to 700°C . Two constant rates of temperature increase, 10 and $20^\circ\text{C}/\text{min}$, were employed. For the purpose of kinetic interpretation of thermal decomposition at modest temperatures, the temperature was rapidly ($160^\circ\text{C}/\text{min}$) increased to one of four temperatures (140, 200, 240, and 280°C) and then held constant thereafter.

IV.4 Results and Discussion

IV.4.1 Interpretation of TGA Curves

The experimental results of thermogravimetric analysis (TGA) for each adsorbate are shown in Figures 8 through 13. These graphical data provide clear pictures of how the weight of adsorbate is influenced by temperature rise. The amount of adsorbate retained on the carbon is expressed as q , which is the ratio of the mass adsorbed per unit mass of virgin carbon. In thermal decomposition experiments it is important to maintain a very low

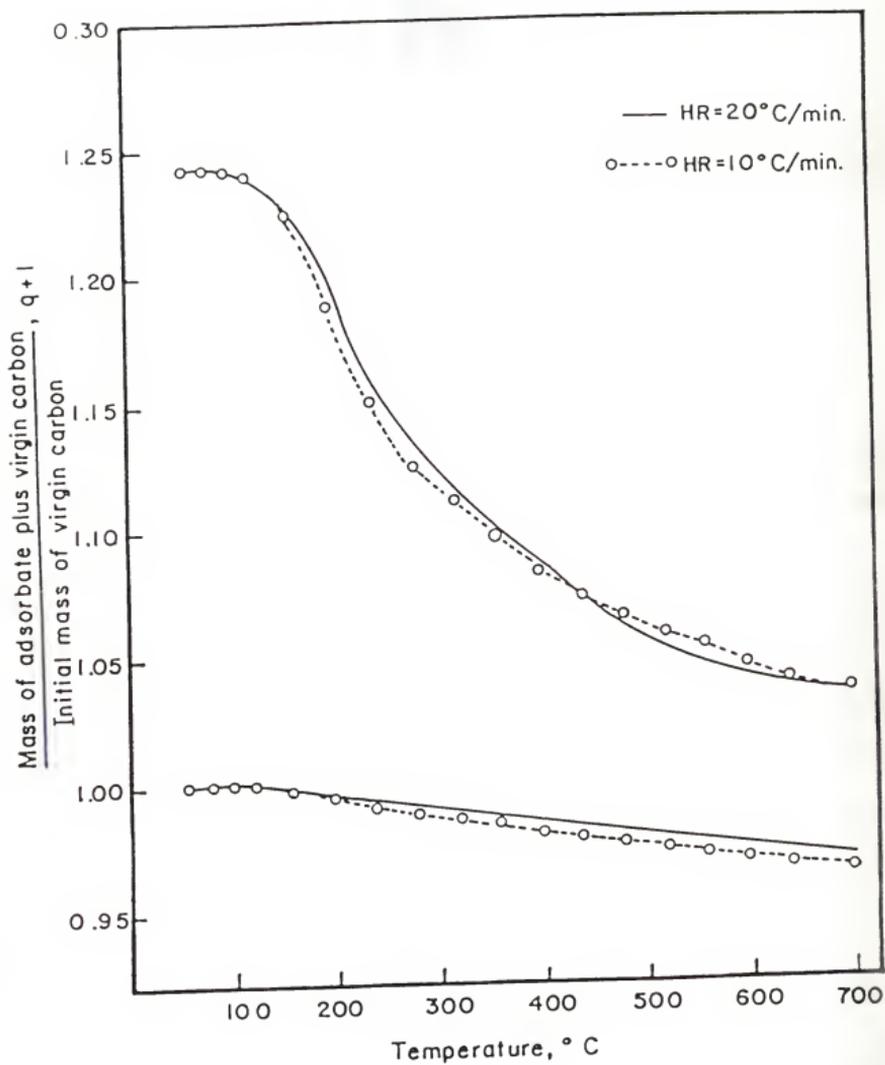


Figure 8. Temperature-weight curves for phenol and virgin carbon.

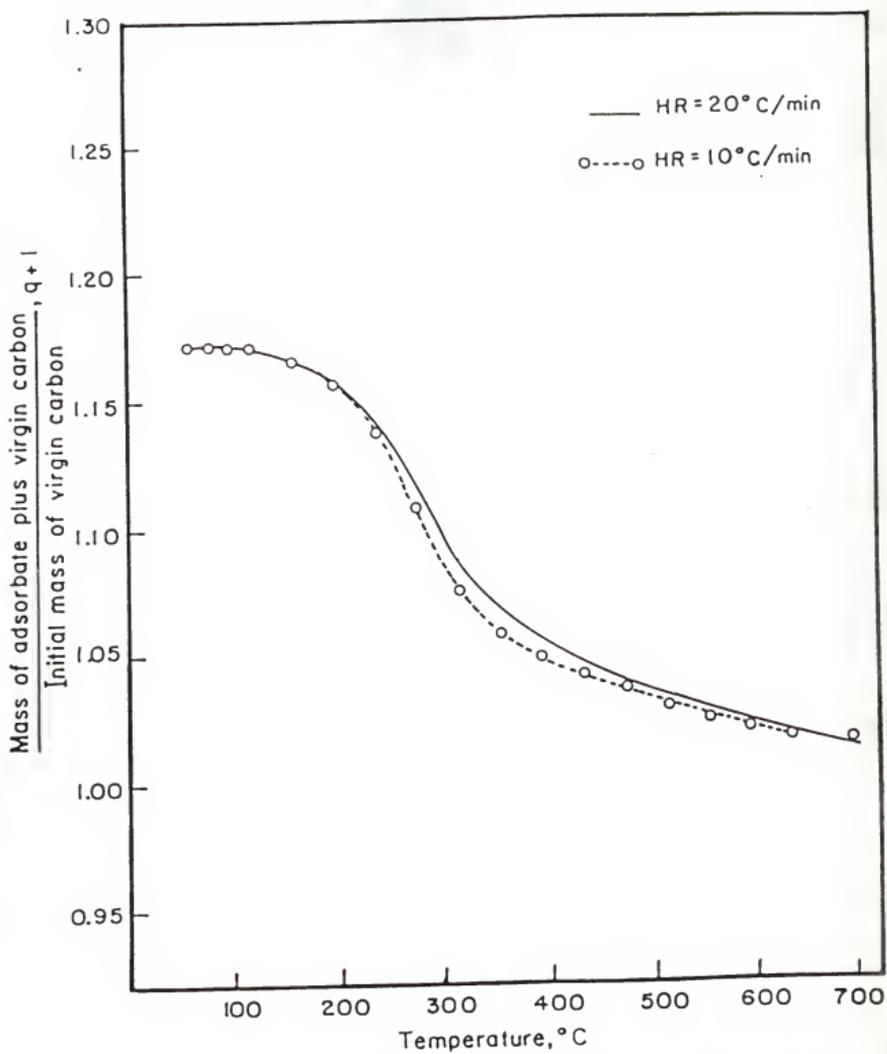


Figure 9. Temperature-weight curves for resorcinol.

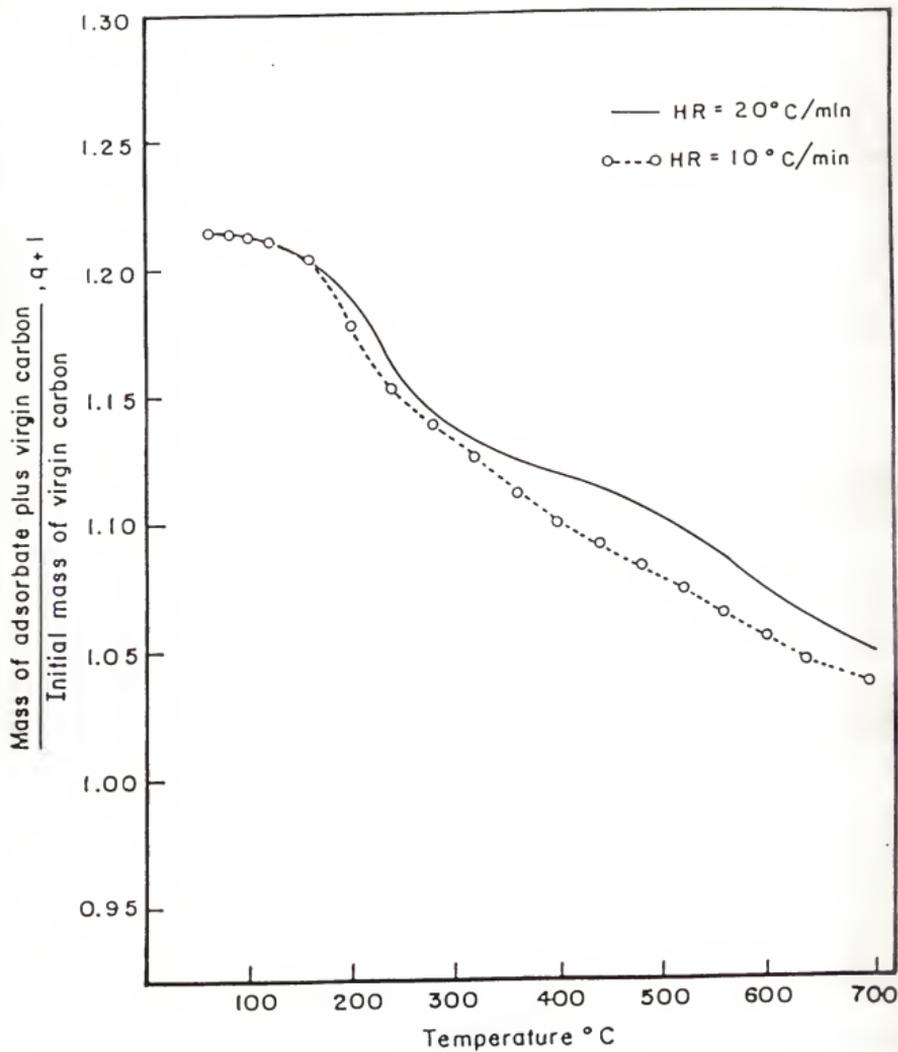


Figure 10. Temperature-weight curves for hydroquinone.

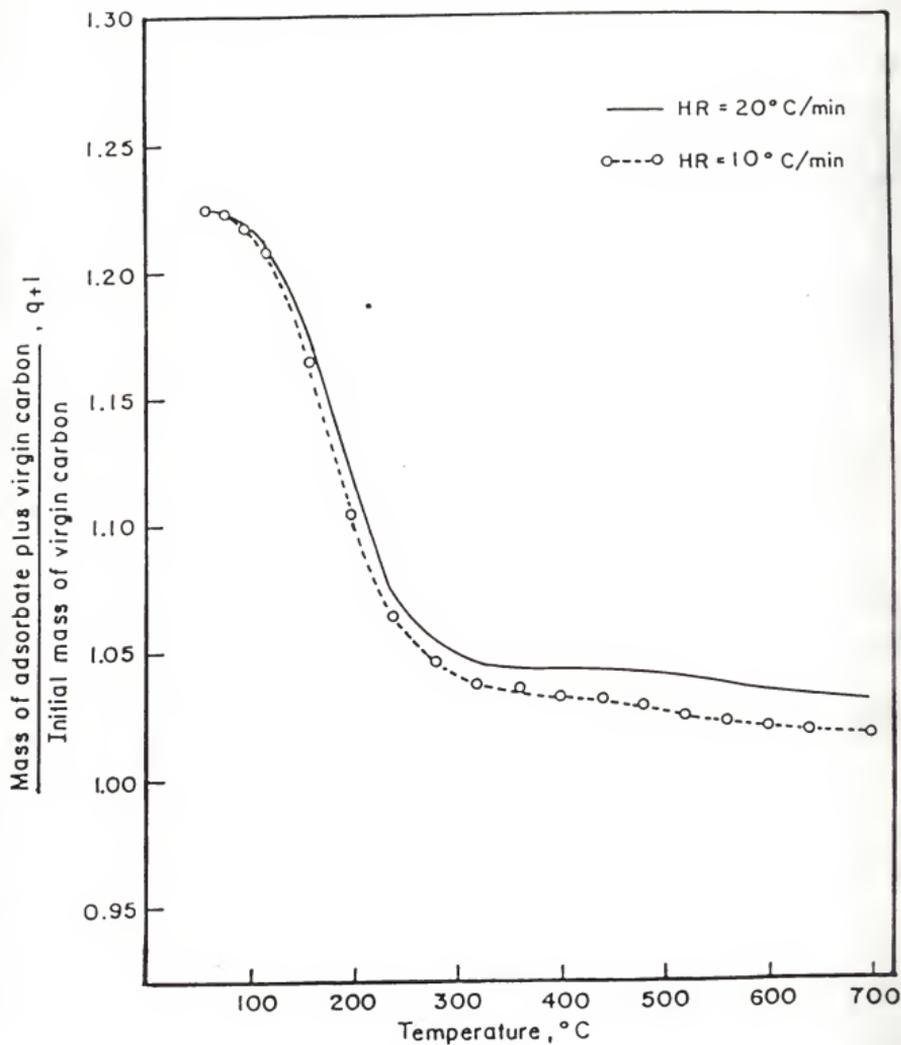


Figure 11. Temperature-weight curves for o-cresol.

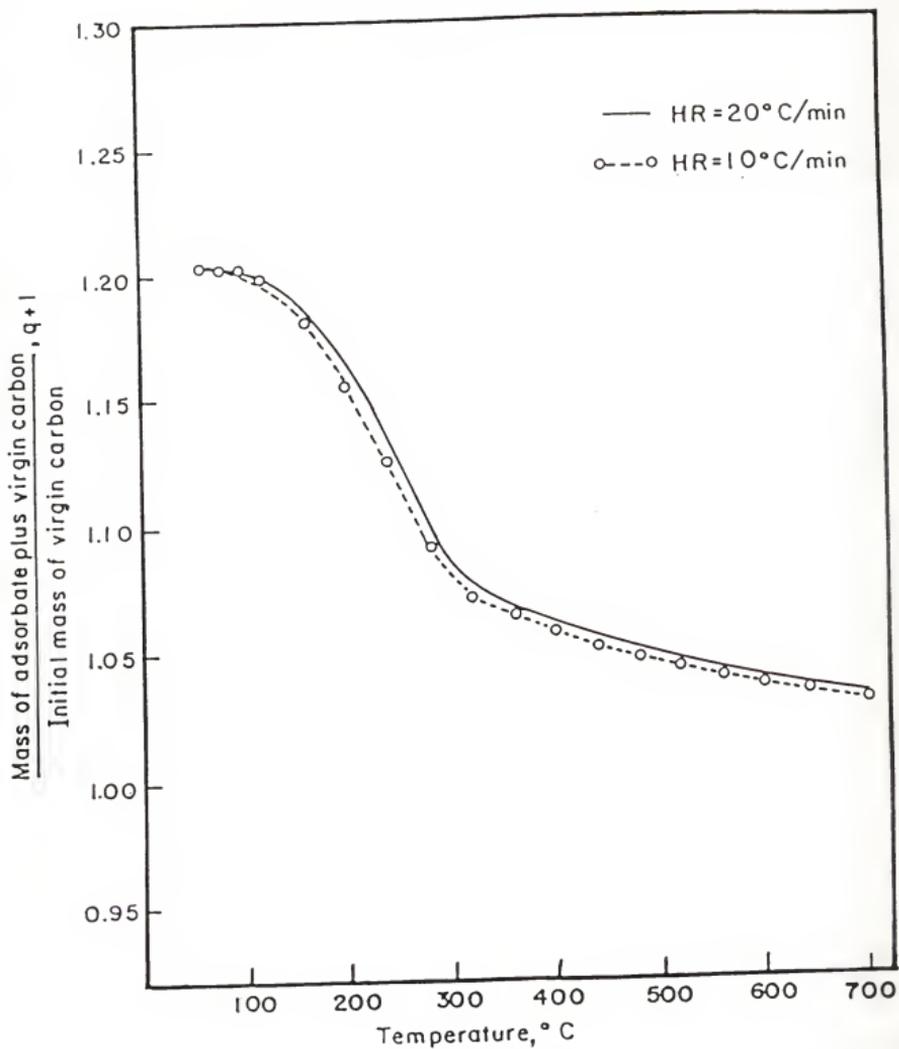


Figure 12. Temperature-weight curves for m-cresol.

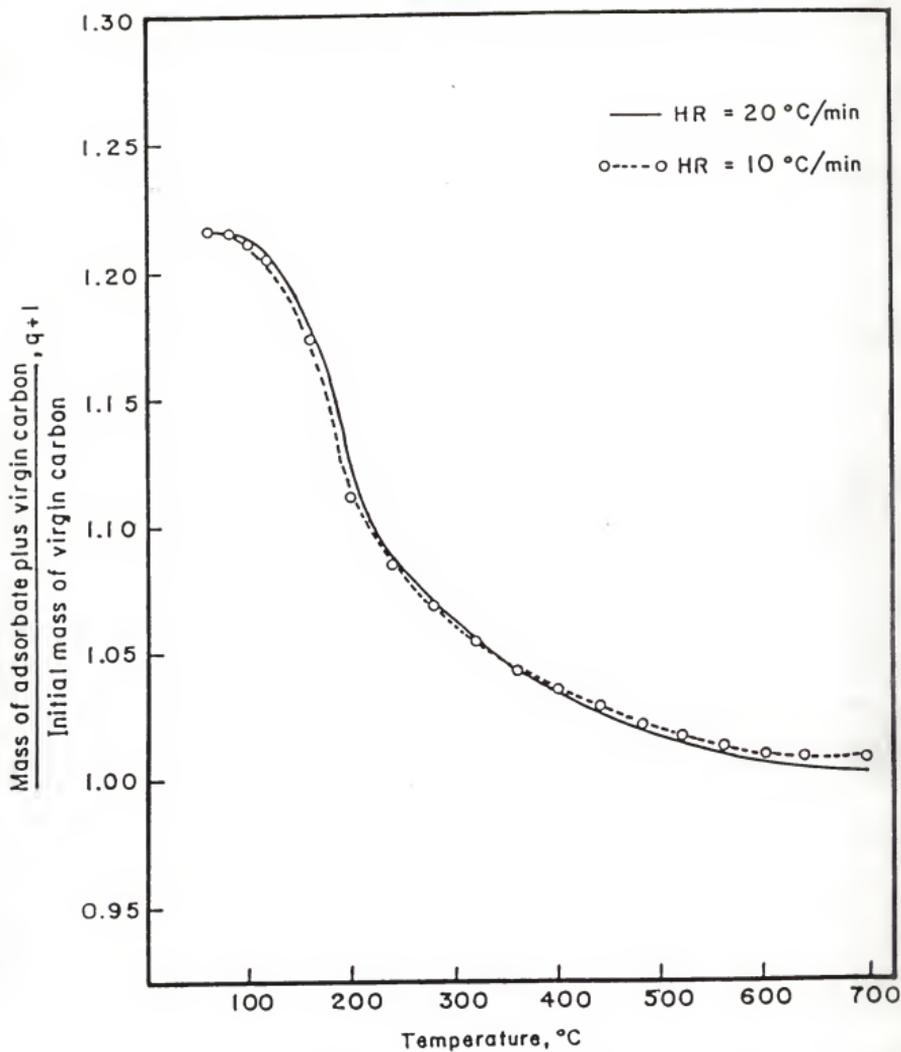


Figure 13. Temperature-weight curves for pyridine.

oxygen concentration in the carrier gas to reduce the rapid oxidation of carbon adsorbate. In Figure 8 virgin carbon without adsorbed material shows 3 to 4 % change of weight during the temperature rise. The success of oxygen concentration reduction may be evaluated from this slight weight change of the virgin carbon.

It is noted that the difference between the TGA curves for different heating rates was small over the range of 10 to 20 °C/min. In most cases, lower heating rate led to higher degree of decomposition. This behavior can be simply attributed to the longer reaction time.

The activated carbon samples loaded with different amounts of phenol were heated to 700 °C and the resultant TGA curves are presented in Figure 14, along with a TGA curve for virgin carbon. The small decrease in mass of virgin carbon at high temperature is presumably due to vaporization or desorption of residual material on the activated carbon surface. This decrease explains why the curves are almost parallel to each other at high temperature. As Chihara et al. (1981) have observed, it suggests that the ultimate decomposition product for adsorbed phenol is carbon and that this residual carbon is deposited on the surface of the adsorbent. The amounts of residual carbon at 700 °C, q_{res} , are plotted against the initial phenol loadings, q_0 , in Figure 15. It is evident that q_{res} is proportional to q_0 for the range studied.

Suzuki et al. (1978) have noted that plots of q/q_0 versus temperature were helpful to characterize TGA curves for different

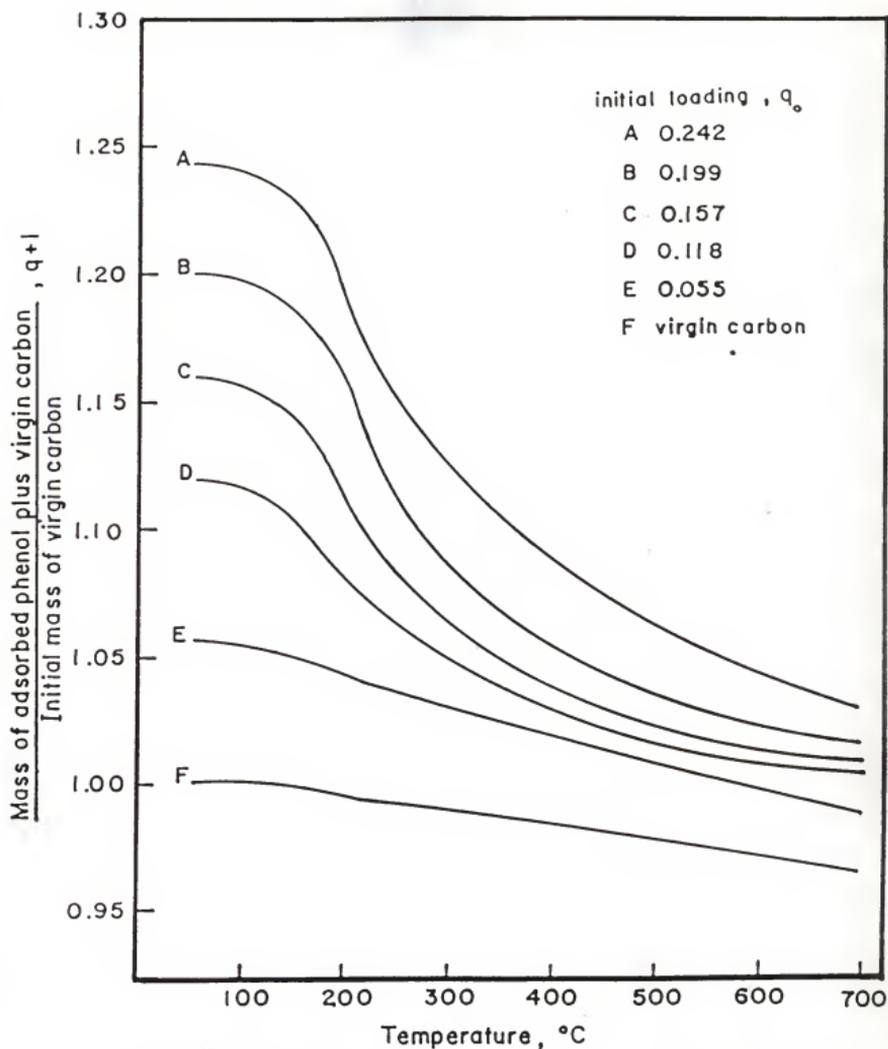


Figure 14. Temperature-weight curves for phenol adsorbed and virgin carbon. (heating rate = 20°C/min)

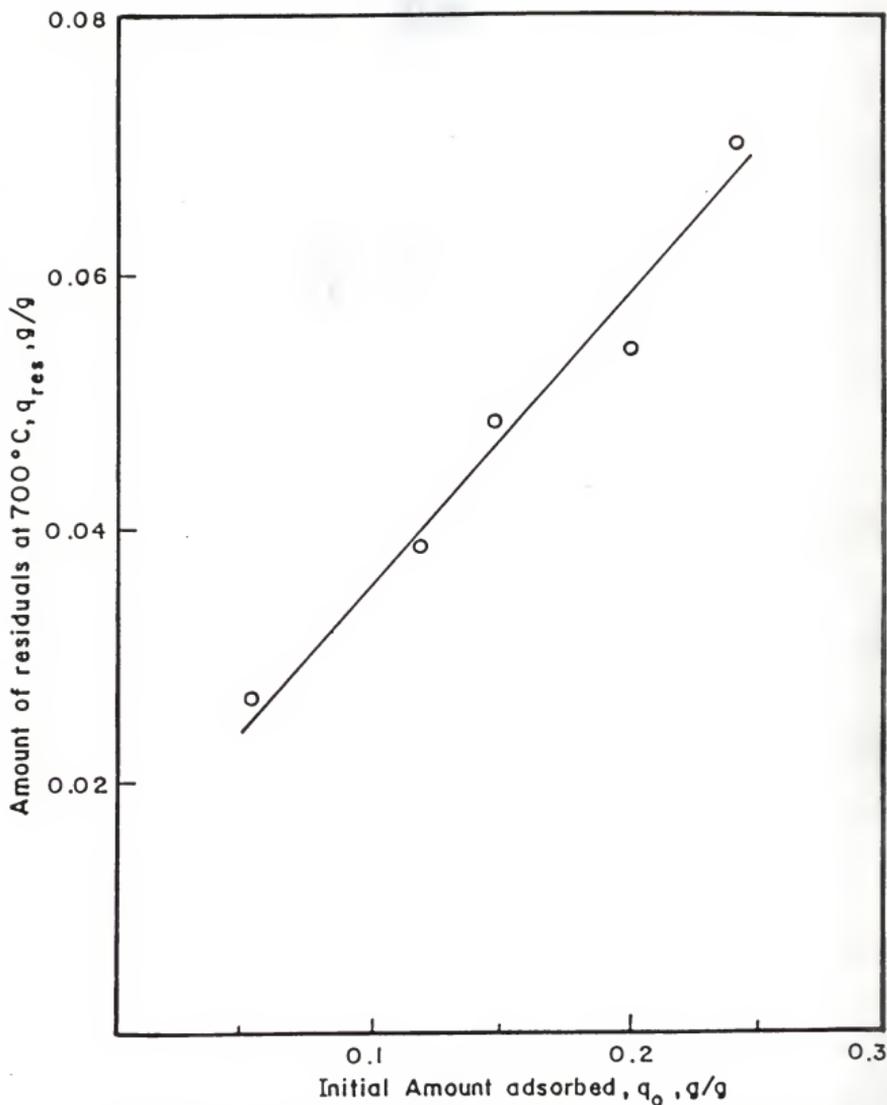


Figure 15. Effect of initial loading on the amount of residuals at 700 °C for phenol.

adsorbed species. Composite plots in which the sample weight has been corrected for the loss of virgin carbon during heating are shown in Figure 16 for various adsorbates. The data in Figure 16 indicate that o-cresol and pyridine are easier to decompose than other phenolic compounds. Suzuki et al. (1978) have stated that the temperature at $q/q_0 = 0.5$ ($T_{\frac{1}{2}}$), the boiling point, and the existence of aromatic ring in molecular structure might be significant in determining the ease of decomposition or the amount of residual carbon. Since it is very likely that thermal desorption and decomposition take place at comparable rates for moderate temperatures, it may be useful to consider the adsorption energy term as another factor affecting TGA curves. According to Adamson (1982), the constants n in the Freundlich equation and b in the Langmuir equation are related to the adsorption energy of an adsorbate onto an adsorbent surface. The values of these factors are listed in Table 6. Though these data do not give a straightforward explanation for the nature of TGA curves, qualitative guidelines can be obtained from careful investigation.

The relative ease of decomposition of o-cresol compared with phenol was observed by Fillo (1979). For a homogeneous gas' phase decomposition scheme, the activation energy of o-cresol was found to be about a half of that of phenol. Since the values of n and b are very high for o-cresol, the major reaction which takes place seems to be thermal decomposition to phenol rather than thermal desorption.

Table 6. Factors Affecting TGA Curves.

Adsorbates	B.P. (°C)	n	b	q_{res}/q_0
o-Cresol	192	6.298	0.0418	0.253
Pyridine	115	1.817	0.0024	0.172
m-Cresol	202	—	—	0.327
Phenol	182	4.288	0.0125	0.280
Resorcinol	280	3.545	0.0156	0.273
Hydroquinone	285	—	—	0.380

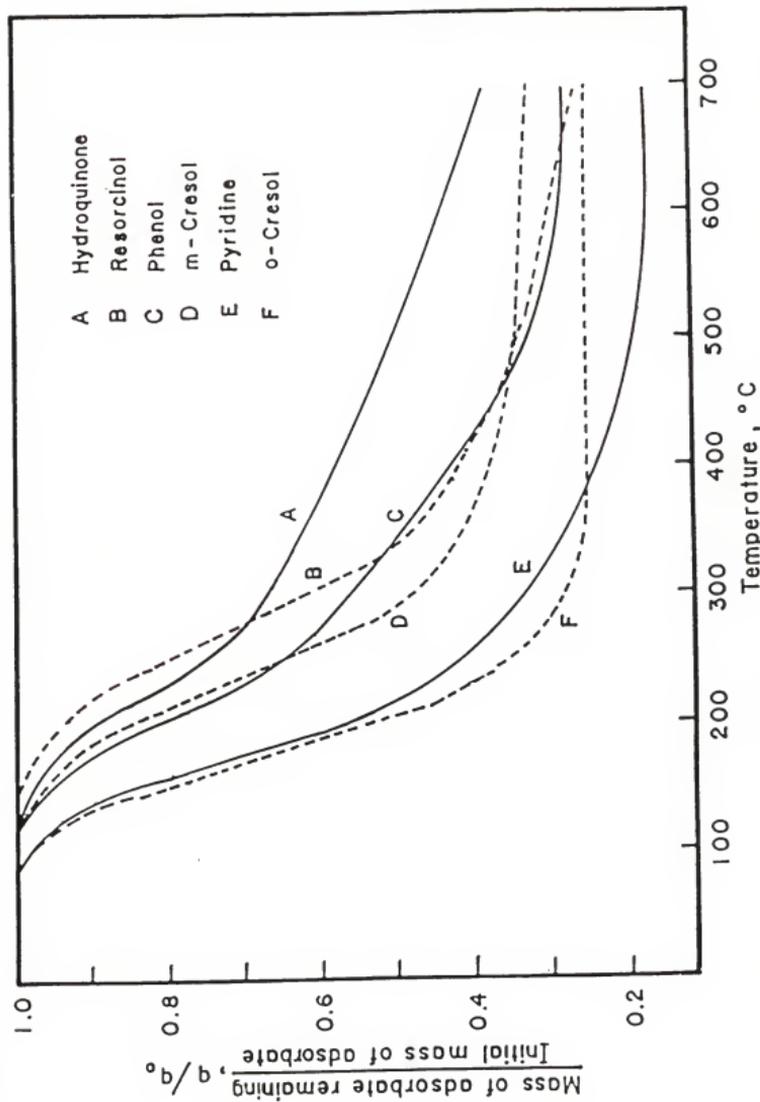


Figure 16. Temperature-weight curves corrected for the loss of virgin carbon for various adsorbates.

Another interesting point is the difference in TGA curves between o-cresol and m-cresol. Jones and Neuworth (1952) have reported the greater thermal stability of m-cresol over o-cresol. The pertinent rupture of the C - H bond in the methyl group as a result of interaction of the methyl group and hydroxyl group might not be possible in the meta position.

Pyridine is known to be a very weakly adsorbed material among aromatic organics onto activated carbon. The lowest values of n and b among the investigated adsorbates indicate that pyridine adsorbed on activated carbon will be easily desorbed rather than decomposed.

There has been little work reported in the literature on the decomposition of dihydroxy benzenes. However, the similar shape of TGA curves for phenol and resorcinol can be possibly attributed to their structural similarity in spite of large difference in their boiling points. But the bizarre shape of TGA curve for hydroquinone is not readily explainable.

IV.4.2 Kinetic Interpretation of Low Temperature Behavior

Suzuki et al. (1978) have set up two kinetic models to interpret the TGA curves obtained in their experiments, i.e., a thermal desorption model and a thermal cracking model. These two models explained reasonably well the TGA curves obtained from their Group (I) and Group (II) organic classifications, respectively. By applying the simple first order kinetics for the thermal cracking

model, activation energies of 27.7 and 25.7 kcal/gmol were obtained for sodium dodecylbenzene sulfonate and polyethylene-glycol, respectively.

Cha and Glasgow (1983) have developed a model for thermal desorption - recovery of phenol based upon the work of Suzuki et al. (1978); equilibrium desorption with a Langmuirian isotherm and the first order pyrolytic decomposition of phenol were assumed. Though the assumption of equilibrium desorption is not realistic, the proposed model described the experimental data very well. They have examined various temperature levels and found the maximum recovery yield of phenol at 240°C.

In this study another approach to kinetic interpretation of thermal desorption and/or decomposition is presented for the temperature range of interest. To obtain more suitable experimental data for kinetic study, a high heating rate of 160°C/min was employed and the desired temperature level (140, 200, 240, or 280°C) was reached within 2 minutes by use of the TGA apparatus. Figure 17 shows the results of heating the activated carbon loaded with phenol for 4 hours. Corrected experimental data for the weight loss of virgin carbon were presented in Figure 18. At low temperature the weight is gradually decreased, while the data approach some asymptotic value at higher temperature.

To analyze the experimental data, the kinetic model devised by Chihara et al. (1981) was adopted. It is assumed that the reaction scheme appears as follows : adsorbed phenol, A, first decomposes into nonvolatile adsorbed fragments, I, and volatile

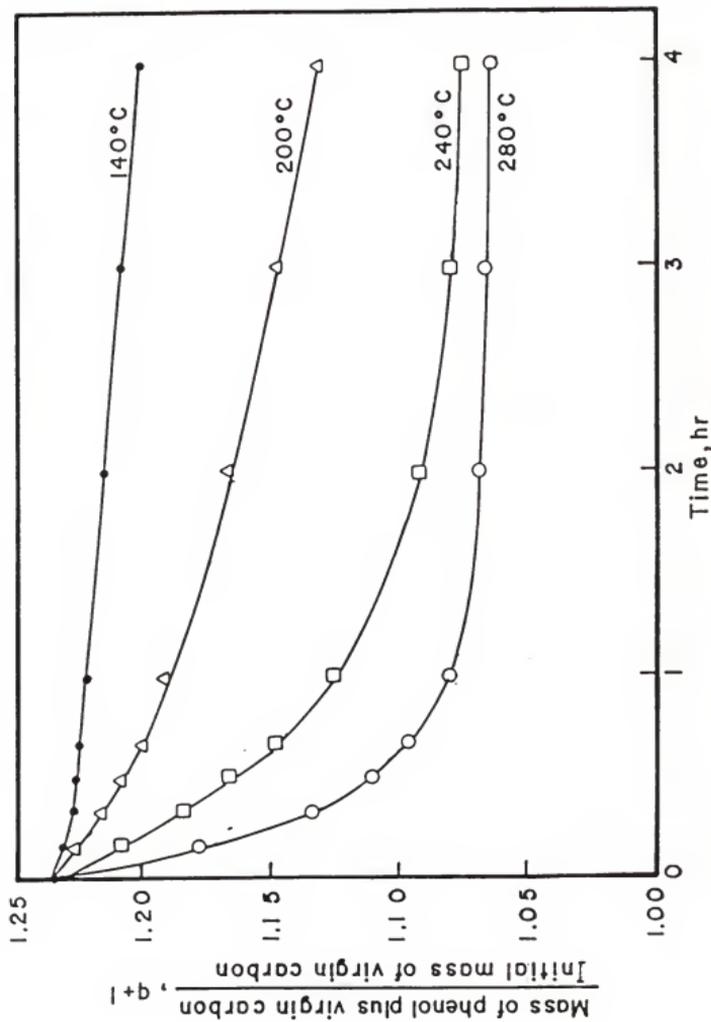


Figure 17. Time-weight curves for adsorbed phenol at constant temperature. (heating rate = 160°C/min)

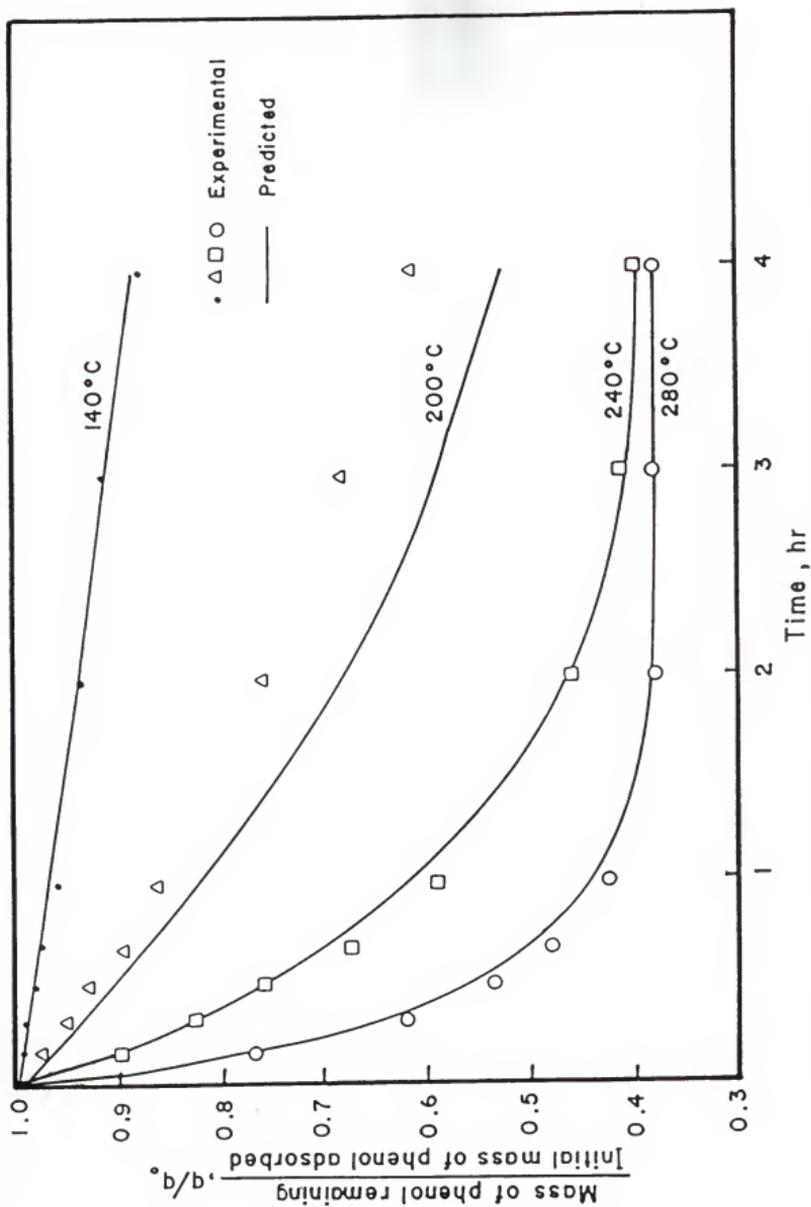
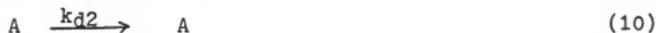


Figure 18. Experimental and predicted weight-time data at constant temperature.

fragments, G, while adsorbed phenol is also desorbed simultaneously. The process may be represented as



where k_1 , k_{d1} , and k_{d2} are rate constants for each reaction, respectively. The thermal decomposition step is commonly assumed to be first order (Shah, 1981). Then,

$$\frac{dN_A}{dt} = -k_1 N_A \quad (11)$$

$$\frac{dN_I}{dt} = i k_1 N_A \quad (12)$$

The initial condition is written

$$\text{at } t = 0, \quad N_A = N_0, \quad N_I = 0 \quad (13)$$

where N_A and N_I are moles of phenol adsorbed and moles of non-volatile adsorbed fragments. Further, the desorption processes are supposed to be rapid compared to decomposition process. Then, the amount adsorbed at any time, q , is defined

$$q = M_A N_A + M_I N_I \quad (14)$$

where M_A and M_I are average molecular weight of phenol and non-volatile fragments from decomposition. Integration of Equation (11) and Equation (12) with initial condition yields

$$N_A = N_0 \exp(-k_1 t) \quad (15)$$

$$N_I = i N_0 - i N_0 \exp(-k_1 t) \quad (16)$$

Equation (17) is obtained by substituting Equations (15) and (16) into Equation (14).

$$\frac{q/q_0 - q_\infty/q_0}{1 - q_\infty/q_0} = \exp(-k_1 t) \quad (17)$$

where

$$\begin{aligned} q_0 &= M_A N_0 \\ q_\infty &= i M_I N_0 \end{aligned} \quad (18)$$

Note that q_∞ is the mass adsorbed at $t = \infty$ in the process for the temperature range studied.

The analytical procedure used to determine values for k_1 from the data in Figure 18 is as follows. As Equation (17) indicates, straight lines are obtained on a plot of the left side versus time in Figure 19. In preparing Figure 19, q_∞/q_0 is taken equal to 0.380 in agreement with the TGA data shown in Figure 18. The k_1 values obtained from the slope of the lines in Figure 19 are displayed in an Arrhenius plot in Figure 20. The straight line through the points for these values of k_1 can be written

$$k_1 = 74.81 \exp(-16,860/RT) \quad (19)$$

The activation energy of 16.86 kcal/gmol is very low, indicating that catalyzed pyrolytic decomposition takes place on the activated carbon surface.

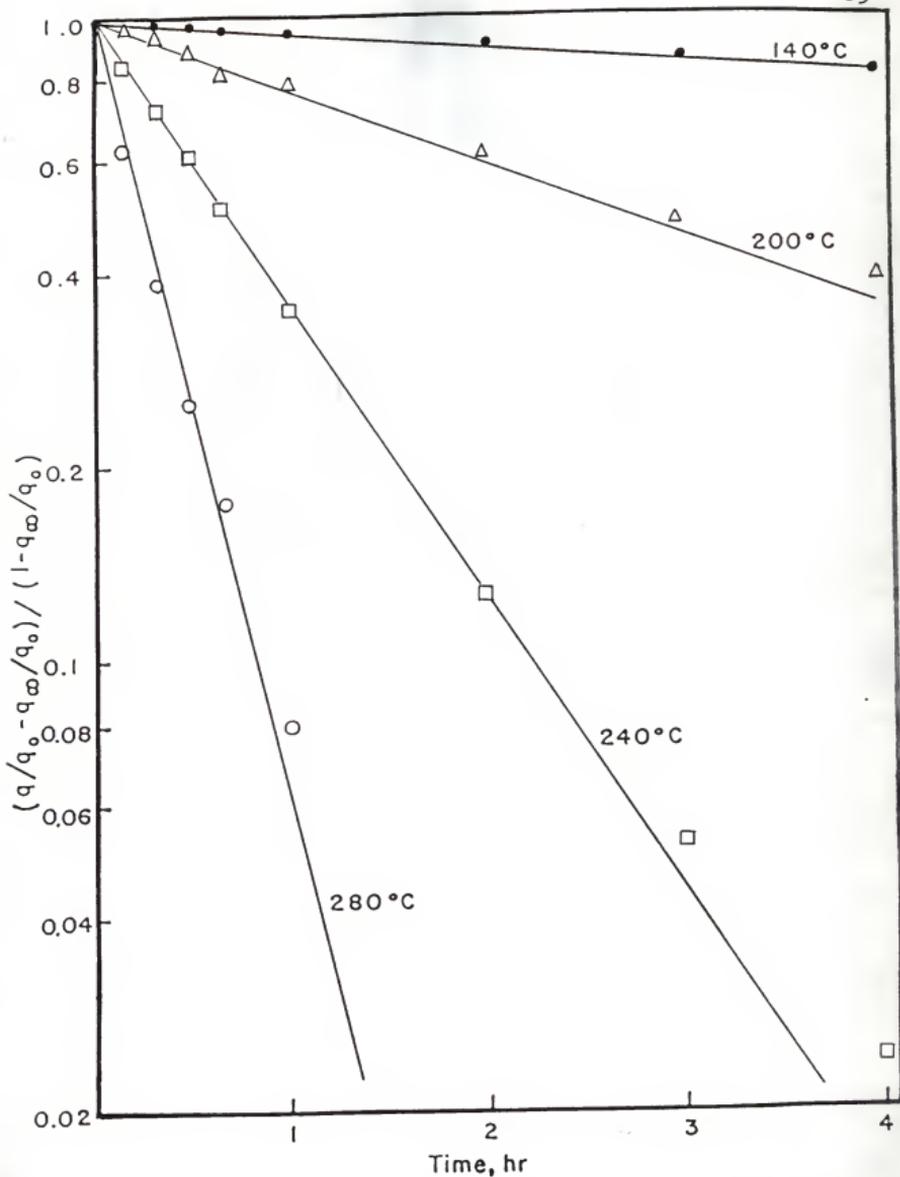


Figure 19. Low temperature decomposition kinetic data.

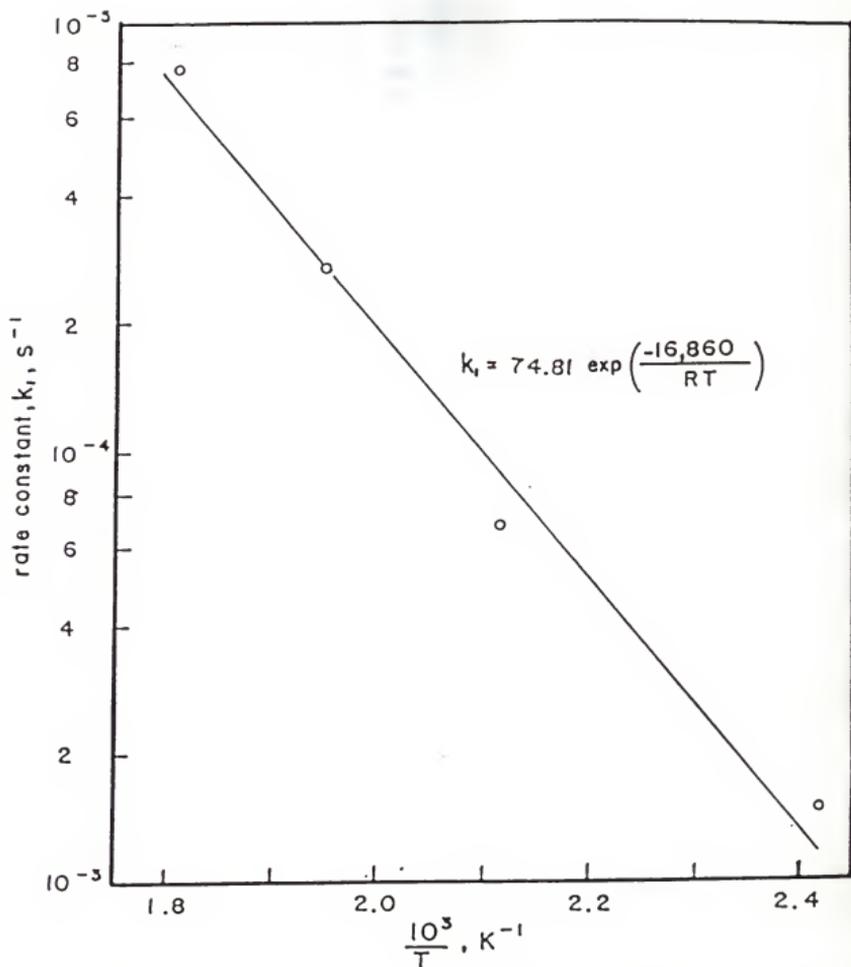


Figure 20. Arrhenius plot of rate constant for low temperature decomposition of adsorbed phenol.

The predicted weight change versus time curves at constant temperature are shown in Figure 13 by Equation (17) using Equation (19) for k_1 value. The agreement is reasonably good for the temperature range studied, although significant deviation occurs at 200°C. This is not surprising because the reaction scheme adopted may be a simplification of a much more complex process.

It is interesting to compare the results with those obtained from Cha and Glasgow (1983). In their study, the yields of phenol recovery by desorption are approximately 12, 30, 42, and 25 % at 134, 200, 240, and 278°C, respectively, for a repeated 4 hour experiment. As shown in Figure 13, the experimental data indicate that the percentages of weight loss of adsorbed phenol due to decomposition and/or desorption after 4 hours of exposure are 13, 40, 61, and 62 % at 140, 200, 240, and 280°C, respectively. Obviously, there are some inconsistencies in the experimental conditions in both cases: for example, about 30 minutes was required to reach the reaction temperature in the fixed-bed reactor using nitrogen as a carrier gas in the study of Cha and Glasgow (1983), while only 2 minutes is required for the TGA apparatus used in this investigation with helium as a carrier gas. But it is clear that desorption of phenol is more significant than thermal decomposition at temperature below 240°C and higher temperatures accelerate the pyrolytic decomposition.

NOTATION

A	: Adsorbed phenol,	
b	: Constant in Langmuir equation,	l/mg
G	: Gaseous products in decomposition reaction,	
g	: Stoichiometric coefficient for gaseous products,	
I	: Nonvolatile adsorbed products in decomposition reaction,	
i	: Stoichiometric coefficient for nonvolatile adsorbed products,	
k ₁	: First order rate constant for decomposition reaction,	l/s
k _{d1}	: Desorption rate constant for gaseous product,	l/s
k _{d2}	: Desorption rate constant for phenol,	l/s
M	: Average molecular weight,	g/gmol
N	: Moles adsorbed per unit mass of carbon,	mol/gcarbon
n	: Constant in Freundlich equation,	
q	: Mass adsorbed per unit mass of virgin carbon,	g/g
q _{res}	: Mass adsorbed at 700°C per unit mass of virgin carbon,	g/g
R	: Gas constant,	cal/gmol·K
T	: Absolute temperature,	K
T _½	: Value of T at q/q ₀ =0.5,	K
t	: Time,	s

Subscripts

A	: Phenol
I	: Nonvolatile adsorbed products
o	: Initial value
∞	: Infinite time

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CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

A principal environmental problem associated with coal gasification is the treatment of wastewater containing significant quantities of phenols and pyridine bases. Previous studies on treatment of phenolic wastewater by use of activated carbon have been concerned largely with phenol itself. In this study, adsorption and decomposition of various phenols and pyridine on activated carbon were investigated.

The results of adsorption experiments lead to the following conclusions:

- 1) Pyridine was most weakly adsorbed among the adsorbates studied, and 2-naphthol showed higher uptake capacity on activated carbon than any other adsorbate.
- 2) Experimental data confirmed that the uptake capacities of adsorbates will increase with the increasing molecular weight and with decreasing solubility.
- 3) Adsorptivity modulus, a_m , could be considered as a measure of the extent of adsorption.

The results of TGA experiments for clarifying the decomposition phenomena of adsorbates on activated carbon lead to the following conclusions:

- 1) The order of ease of decomposition or desorption was o-cresol, pyridine, m-cresol, phenol, resorcinol, and hydroquinone.

- 2) The amounts of residual carbon after heating to 700°C ranged from about 20 % for pyridine to about 40 % for hydroquinone of initial amount of adsorbate loading.
- 3) The activation energy of the assumed decomposition reaction of phenol at low temperature was found to be about 17 kcal/gmol, which indicates that the catalyzed pyrolytic decomposition takes place on the activated carbon surface.

Sorptive treatment of phenolic wastewater has been widely used for years, but little attention has been paid to the reclamation of phenolic compounds. The recovery of a portion of phenolic compounds from the carbon surface prior to thermal regeneration was found to be possible. For the purpose of recovery system design, more information about adsorption and decomposition will be required:

- 1) Since the coal conversion wastewater contains various kinds of contaminants, the actual adsorption phenomena must be competitive rather than single-component-based. Therefore, it is recommended that the multi-component competitive adsorption experiments be performed to obtain the actual uptake capacities of individual components in mixtures.
- 2) Although a number of investigators have reported studies of the thermal cracking of phenolic compounds, most of them are concerned with the cracking at very high temperatures,

at which organic compounds are likely to be completely decomposed. Thus, it is suggested that low temperature decomposition of phenolic compounds be investigated more thoroughly.

APPENDIX

Calibration curves for the determination of adsorbate concentration in aqueous solution.

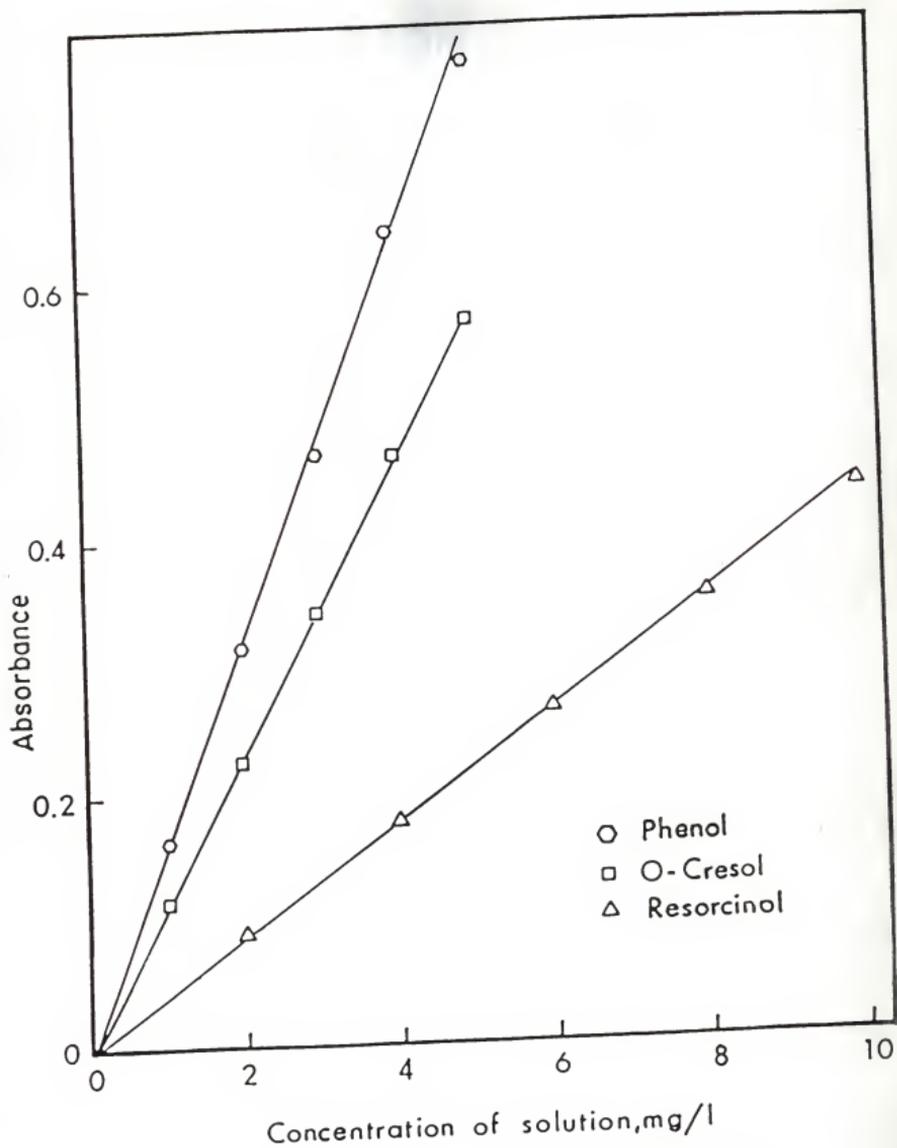


Figure.A.1. Calibration curves for various phenols
(15 minutes after adding 2% 4-aminoantipyrine).

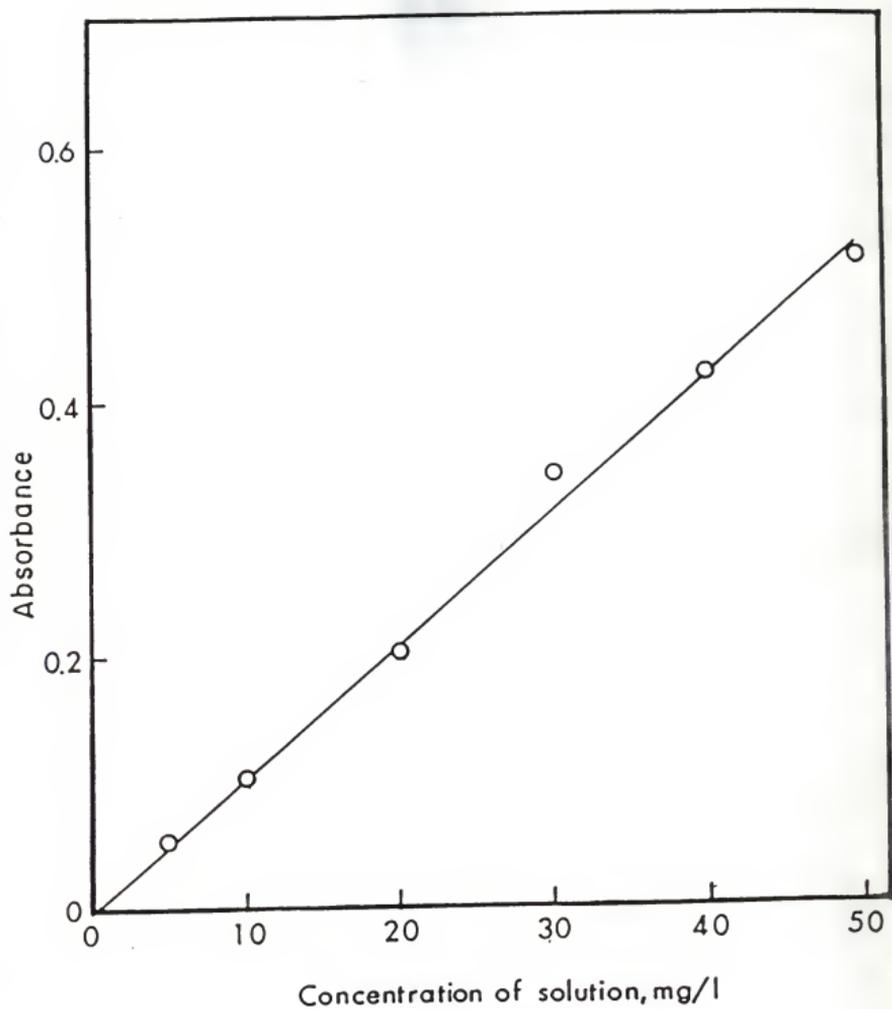


Figure A.2. Calibration curve for 2-naphthol
(2 hours after adding 3% 4-aminoantipyrine).

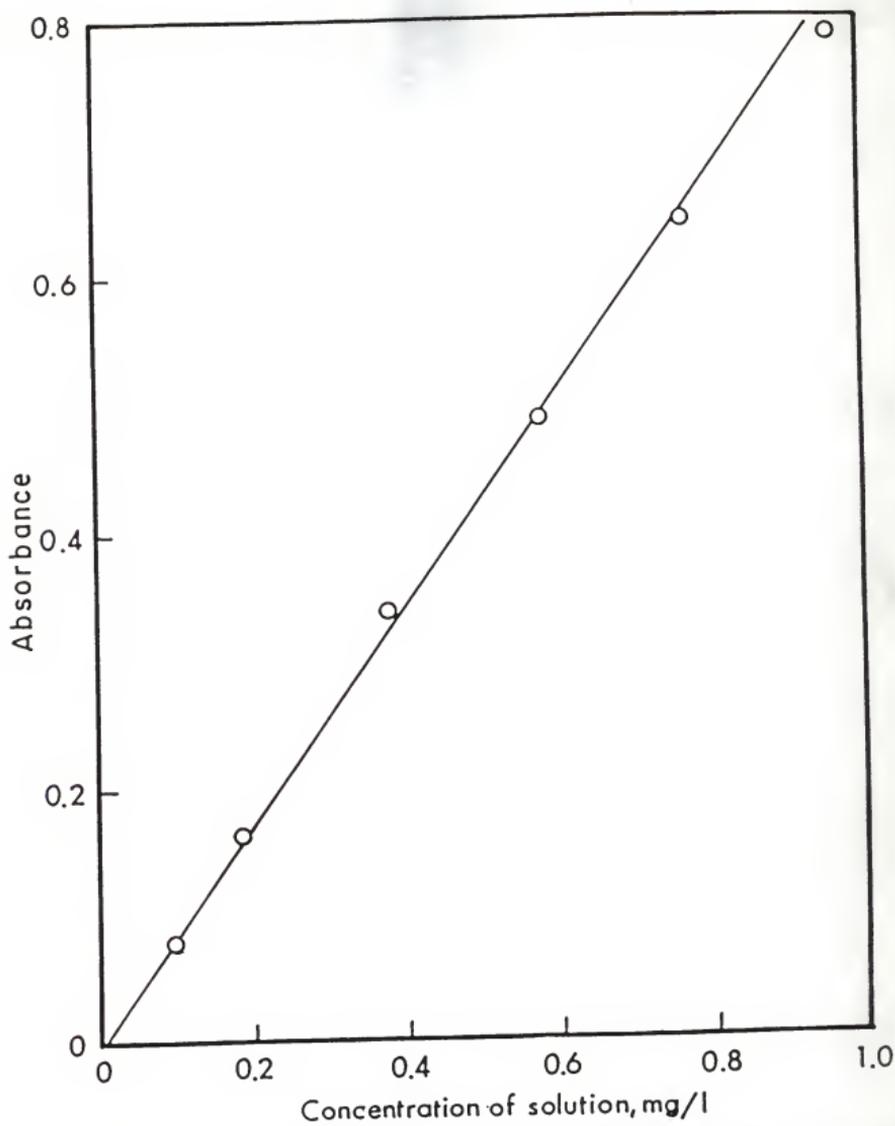


Figure A.3. Calibration curve for pyridine. (1 hour after adding 4,4'-diaminostilben-2,2'-disulfonic acid).

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ADSORPTION AND THERMAL DECOMPOSITION CHARACTERISTICS
OF ORGANIC CONTAMINANTS IN COAL CONVERSION WASTEWATER

by

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Adsorption and decomposition characteristics on activated carbon of various contaminants found in coal conversion wastewater were investigated. Adsorption equilibria were determined for major contaminants in wastewater and their uptake capacities were compared in terms of several possible factors. The uptake capacities of adsorbates increased with the increasing molecular weight and with decreasing solubility. Adsorptivity modulus could be considered as a measure of the extent of adsorption. Pyridine was found to be most weakly adsorbed, while 2-naphthol to be most strongly adsorbed on activated carbon among the adsorbates studied.

A TGA apparatus was utilized to clarify the decomposition phenomena of various phenolic compounds on activated carbon. The data were obtained by measuring mass versus time of spent carbon samples at the temperature ranging from 25 to 700°C in an inert atmosphere. Up to 40 % of initial amount of adsorbates remained on activated carbon surface as a form of residual carbon. Pyridine and o-cresol were easily desorbed and/or decomposed compared to other phenols. A kinetic study of low temperature decomposition of phenol yielded an activation energy of 17 kcal/g-mol, indicating the catalyzed decomposition takes place on the activated carbon surface.