MASTER

ADSORPTIVE BEHAVIOR
OF POLYCYCLIC AROMATIC HYDROCARBONS IN
COAL-CONVERSION WASTEWATERS

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ABSTRACT

A coupled column system was designed and assembled for use in solubility and adsorption testing. This system consists of a saturated solution generation column and an adsorption column. The generation column has been employed successfully to determine the solubility behavior of naphthalene; for nine determinations at 25 °C the aqueous solubility is 32.9 ± 1.2 milligrams per liter. However, adsorption isotherm data obtained from the coupled column system involved techniques which are limited by time constraints and accuracy. Batch adsorption shake testing using the generation column to prepare solutions offers an acceptable alternative to this system. This procedure has been employed to obtain adsorption isotherm data for naphthalene. Thirty-one data points were obtained for equilibrium concentrations from 0.00689 to 18.8 milligrams per liter. These data can be fitted to the Freundlich equation with constant values of 263 for the coefficient and 0.39 for the exponent. Adsorption and adsorption isotherm models which are more appropriate than the Freundlich equation for purposes of detailed modelling are reviewed.

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1.0 INTRODUCTION

Carnegie-Mellon University (C-MU) is under contract with the United States Department of Energy (DOE) to investigate fundamental issues regarding the adsorptive behavior of polycyclic aromatic hydrocarbons (PAH) in coal conversion wastewaters. PAH comprise a group of organic compounds produced during coal conversion processing which have been identified in liquid effluents from several coal conversion facilities. In recognition that PAH are generally toxic and that several PAH exhibit carcinogenic behavior, the United States Environmental Protection Agency (EPA) Effluent Guidelines Division has included PAH in its list of priority pollutants to be monitored in industrial effluents (Keith and Telliard, 1979). PAH in coal conversion effluents and other wastewaters have been found to be associated primarily as species adsorbed onto suspended solids rather than as dissolved species (Walters and Luthy, 1981). The association of PAH with suspended solids may play an important role in determining the environmental significance and fate of PAH. This motivates a study of the physicochemical phenomena which govern the adsorptive behavior of PAH onto suspended solids.

The major focus of this study is to investigate the manner in which specific molecular characteristics of a given compound and wastewater characteristics influence the adsorption of PAH. Efforts during the first six months of this study have been directed towards two areas:

- (1) review of equilibrium adsorption and adsorption isotherm models which have been employed by previous researchers to describe adsorption isotherm data and

- (2) development, shakedown and execution of an experimental methodology for generating adsorption isotherm data for PAH.

Progress made in each of these areas is reported below.

2.0 REVIEW OF MODELS FOR PREDICTION OF ADSORPTION BEHAVIOR AND ADSORPTION ISOTHERMS

Attempts will be made to correlate the adsorption isotherm data generated in the present study to specific molecular features of PAH. Two objectives can be identified as being fundamental to these correlation efforts:

- (1) Development of an adsorption isotherm model which provides a good fit for adsorption isotherm data and which gives a meaningful indication of adsorption capacity and
- (2) Development of a model of adsorption which provides either a molecular or thermodynamic basis upon which to predict adsorptive behavior.

These two objectives can be accomplished in some cases by a single adsorption model; however, this is not considered to be a constraint for the modeling work to be performed as part of this study.

A variety of adsorption isotherm models have been used by previous researchers to describe experimentally determined adsorption isotherm data. The Langmuir and Freundlich equations have been used extensively to represent adsorption isotherm data for adsorption of solutes from dilute solution over small concentration ranges. However, specific inherent limitations of these equations suggest that these equations alone are not well suited for the present application. The Langmuir equation was developed for gas phase adsorption onto homogeneous surfaces. Activated carbon, which is the adsorbent used in the present study, has a heterogeneous surface. For this reason, the Langmuir equation may not necessarily provide an accurate representation of the adsorption isotherm data over a wide range of surface coverages. Similarly, the Freundlich equation does not apply to the Henry's law region of the adsorption isotherm

(i.e., at infinite dilution, where adsorption capacity is proportional to solute concentration). Consequently, the Freundlich equation cannot be extrapolated beyond the experimental equilibrium concentration range to yield meaningful results. In view of these limitations, neither the Langmuir nor the Freundlich equations were considered for use as detailed predictive models in this study.

Adsorption isotherm models which have been presented in the literature which may overcome the limitations of either the Langmuir or Freundlich equations include:

- (1) the equation of Jossens et al. (1978),
- (2) the Polanyi adsorption potential theory,
- (3) the Redlich-Peterson equation,
- (4) the three parameter Newman equation,
- (5) the Toth equation and
- (6) the equation of Weber and van Vliet (1979).

In addition to these adsorption isotherm models, several models for prediction of adsorptive behavior have been presented. These include the first, second and fifth equations listed above and two other theories:

- (1) the net adsorption energy theory and
- (2) the solvophobic interaction theory.

Information regarding these models is provided below.

2.1 The Equation of Jossens et al. (1978)

Jossens et al. (1978) describe the thermodynamic development of an adsorption isotherm equation for adsorption of dilute solutes onto

heterogeneous surfaces such as activated carbon. This equation has the form:

$$C_e = \frac{q_e}{a_1} \exp(a_2 q_e^{a_3}) \quad (1)$$

where C_e is equilibrium concentration in moles per liter; q_e is the corresponding capacity in moles per gram; a_1 and a_2 are functions of temperature; and a_3 is a constant. These parameters are related to the isosteric heat of adsorption, which has the form:

$$q_{st} = q_{st}^{\circ} - C q_e^{a_3} \quad (2)$$

where q_{st}° is the isosteric heat for the solute at the limit of zero surface coverage. These relationships are:

$$C = -RT^2 \frac{da_2}{dT} \quad (3)$$

and

$$q_{st}^{\circ} = -RT^2 \frac{d \ln a_1}{dT} \quad (4)$$

where R is the ideal gas constant and T is the absolute temperature. The constants C and a_3 are related to the distribution of energy sites on the adsorbent surface.

The parameters a_1 , a_2 and a_3 in equation (1) are determined from adsorption isotherm data by curve fitting techniques. If adsorption isotherm tests are performed at enough different temperatures, then the functional dependence of a_1 and a_2 can be determined. These functionalities can be used in equations (3) and (4) to calculate C and q_{st}° , which can then be used in equation (2) to calculate the isosteric heat of adsorption q_{st} .

2.2 The Polanyi Adsorption Potential Theory

The Polanyi adsorption potential theory was originally developed for application to gas-phase adsorption, and was apparently first applied to liquid-phase adsorption of solutes by Manes and Hofer (1969). In the Polanyi theory, the driving force for physical adsorption onto the adsorbent surface is measured by the adsorption potential, which for a given adsorbent and adsorbate is a function of the distance of the adsorbate from the adsorbent surface. Physical adsorption consists of the condensation from vapor (or solution) of liquid (or solid) in those areas near the adsorbent surface in which the adsorption potential equals or exceeds the work required to concentrate the adsorbate to saturation concentration.

The adsorption potential for liquid phase adsorption is defined as:

$$\epsilon_{sl} \equiv RT \ln C_s/C_e = \epsilon_s - \epsilon_l V_s/V_l \quad (5)$$

where ϵ_{sl} is the adsorption potential associated with the adsorption of a given amount of solute accompanied by desorption of an equal volume of solvent; ϵ_s is the gas-phase adsorption potential of the solute; ϵ_l is the gas-phase adsorption potential of the solvent; and V_s and V_l are the molar volumes of the solute and solvent, respectively.

Generalized correlation curves, which are plots of volume adsorbed versus the adsorption potential per unit volume, can be obtained through manipulation of equation (5) to obtain:

$$\frac{\epsilon_{sl}}{V_s} = \frac{\epsilon_s}{V_s} - \frac{\epsilon_l}{V_l} \quad (6)$$

which can be written more compactly as:

$$\alpha_{sl} = \alpha_s - \alpha_l \quad (7)$$

where each α represents the corresponding ϵ/V . As discussed by Manes and Hofer (1969), the characteristic curves are such that the plot of volume adsorbed per gram of adsorbent versus α for a given solute and solvent take the form shown in Figure 1. These characteristic curves are independent of temperature and depend on the structure of the adsorbent. All curves in Figure 1 can be collapsed to a single curve by application of a single abscissa scale factor which represents the ratio of molar volumes of the materials of interest. The deviation from unity of the scale factor required to make two such curves coincide is a measure of the extent to which the adsorption potential deviates from proportionality to the molar volume. Manes and Hofer indicate that many researchers have found that plots of gas-phase adsorption data within a homologous series of saturated hydrocarbons onto activated carbon collapsed to a single (correlation) curve with considerable accuracy.

At this point, one limitation of the application of this model is that gas-phase adsorption data are necessary to apply the theory. However, Chiou and Manes (1973) indicate a method for obtaining characteristic curves using only liquid-phase adsorption data. This involves a plot of adsorption volume (calculated from solute density) versus $(\gamma_{sl}\epsilon_{sl})/V_s$ where V_s is the molar volume of the solute; ϵ_{sl} is calculated from equation (5); and γ_{sl} is a constant determined for each solute and is estimated as:

$$\gamma_{sl} = (P_s - P_l)/P_h \quad (8)$$

volume adsorbed
mass adsorbent

Figure 1. Typical Characteristic Curves for use in the Polanyi Adsorption Potential Theory.

where

$$P_i = [R]/V_s = (n_i^2 - 1)(n_i^2 + 2). \quad (9)$$

In these equations, n_i is the refractive index of the i th component, R is the molar refractivity, and the subscripts s , l and h refer respectively to the solid, solvent, and heptane (the last being typical of the hydrocarbon correlation curve).

Using this method, the adsorption isotherm for a given solute can in theory be estimated from the gas-phase hydrocarbon correlation curve (Manes and Hofer, 1969) or from a correlation curve determined from adsorption of selected organic adsorbates from water solution (Wohleber and Manes, 1971). This estimation requires the use of the correlation curve together with the P_i of the solute and solvent and the solubility of the solute. However, deviations have been found to occur resulting presumably from inefficient packing of the adsorbate during adsorption. A method has been proposed by Rosene et al. (1976) to overcome this problem, which involves an upward shifting of the correlation curves by adjustment of the bulk density to an assumed adsorbate density.

The applicability of this model to the adsorption of molecules as large as PAH is currently being investigated. A more detailed discussion of this theory will be provided in a later report.

2.3 The Redlich-Peterson Equation

Redlich and Peterson (1959) recognized advantages of having an adsorption isotherm equation which approaches Freundlich's equation at high concentrations and Langmuir's equation at low concentrations. Their equation has the form:

$$q_e = d_1 c_e / (1 + d_2 c_e^{d_3}) \quad (10)$$

where q_e is equilibrium capacity in milligrams per gram; c_e is equilibrium concentration in milligrams per liter; and d_1 , d_2 and d_3 are empirical coefficients and are determined by curve fitting techniques. The value of the exponential d_3 lies between 0 and 1. At high concentration, equation (10) reduces to the Freundlich equation:

$$q_e = (d_1/d_2)c_e^{1-d_3} \quad (11)$$

and at low concentrations it reduces to the low concentration limit of the Langmuir equation (or Henry's Law region):

$$q_e = A c_e \quad (12)$$

2.4 The Three Parameter Newman Equation

Radke and Prausnitz (1972) present an equation which reduces to Henry's law and to the Freundlich equation under appropriate conditions of concentration and to the Langmuir equation in special cases. This equation has the form:

$$(1/q_e) = (1/f_1 c_e) + (1/f_2 c_e^{f_3}) \quad (13)$$

where q_e is equilibrium capacity in moles per gram; c_e is equilibrium concentration in moles per liter; and f_1 , f_2 , and f_3 are empirical coefficients. The value of f_3 is constrained to be less than 1. At low concentrations, equation (13) reduces to Henry's law:

$$q_e = f_1 c_e \quad (14)$$

At higher concentrations it becomes the Freundlich equation:

$$q_e = f_2 c_e^{f_3} \quad (15)$$

In the special case where f_3 is zero, equation (13) becomes the Langmuir equation:

$$q_e = f_1 c_e / (1 + (f_1 c_e / f_2)) \quad (16)$$

The empirical coefficients f_1 , f_2 and f_3 in equation (13) are determined by best fit to the adsorption isotherm data being modeled.

2.5 The Toth Equation

The Toth Equation is presented by Toth (1971) and described by Jossens et al. (1978). The Toth equation has the form:

$$q_e = q_e^\infty c_e (g_1 + c_e^{g_2})^{-1/g_2} \quad (17)$$

where q_e is equilibrium capacity in moles per gram; c_e is equilibrium concentration in moles per liter; and g_1 and g_2 are empirical factors as is q_e^∞ , which indicates a fictitious maximum adsorption achieved at $c_e \rightarrow \infty$. Although this equation was developed for gas-phase adsorption, the theory can be extended to adsorption of solutes from dilute solution.

As described by Jossens et al. (1978), the development of equation (17) begins with the Langmuir equation:

$$q_e = q_e^\infty c_e (\alpha_1 + c_e)^{-1} \quad (18)$$

For a homogeneous surface, α_1 is independent of surface coverage and is related to the differential enthalpy of adsorption Q by:

$$\alpha_1 = \alpha_2 \exp(-Q/RT) \quad (19)$$

where α_2 is a constant; T is absolute temperature; and R is the gas constant.

For a heterogeneous surface Q depends strongly on surface coverage.

However, the Langmuir equation is still applicable provided α_1 is determined from:

$$\alpha_1 = \alpha_3 \exp(-\bar{Q}/RT) \quad (20)$$

where $\bar{Q}$ is the integral enthalpy of adsorption and is a function of q_e .

The manner in which Toth specifies this functionality is by use of a dimensionless quantity ψ defined by:

$$\psi = \frac{d \ln c_e}{d \ln q_e} - 1 \quad (21)$$

From equation (21) it is clear that isotherm data can be used to determine ψ .

Toth found that ψ for typical adsorption data on heterogeneous surfaces falls between the value of ψ obtained from substitution of the Langmuir equation into equation (21), i.e.:

$$\psi = \frac{c_e}{\alpha_2} \quad (22)$$

and the value expected from substitution of the Freundlich equation into equation (21), in which ψ is a constant. Based on this observation, Toth assigned a function of the form:

$$\psi = \alpha_4 c_e^{\alpha_5} \quad (23)$$

where α_4 and α_5 are constants. Now, with reference to empirical coefficients which appear in equation (17), if α_4 is set equal to $1/g_1$ and α_5 is set equal to g_2 , integration of equation (21) gives equation (17).

For Langmuir's equation α_5 (or g_2) is equal to one, while for Freundlich's equation these coefficients are zero. Henry's law holds for all concentrations at which α_4 (or $1/g_1$) is zero.

Two ways of applying Toth's equation can be identified. The first is to determine values for q_e , g_1 and g_2 in equation (17) by best fit methods applied to adsorption isotherm data. The second is to determine ψ from adsorption isotherm data using equation (21), and then to determine values for g_1 and g_2 from equation (23). Equation (23) can be manipulated to read:

$$\log \psi = \log \alpha_4 + \alpha_5 \log c_e \quad (24)$$

A log-log plot of ψ versus c_e should result in a straight line for which α_5 (or g_2) is the slope and $\log \alpha_4$ (or $\log 1/g_1$) is the intercept. These values can be determined by linear regression, and can be used in equation (17) for determination of q_e^∞ by a second best fit calculation.

2.6 The Equation of Weber and van Vliet (1979)

This equation has been developed to facilitate application of an adsorption isotherm model to batch rate and fixed-bed studies because equilibrium concentration is expressed explicitly as a function of capacity. The development of this isotherm equation is presented by Weber and van Vliet (1979) and is used to correlate phenol adsorption isotherm data by van Vliet et al. (1980). These latter researchers present the equation in the form:

$$c_e = h_1 q_e (h_2 q_e^{h_3} + h_4) \quad (25)$$

where c_e is the equilibrium concentration in milligrams per liter; q_e is the corresponding adsorption capacity in milligrams per gram; and h_1 , h_2 , h_3 and h_4 are empirically determined by a multiple non-linear curve-fitting technique predicated on the minimization of the sum of squares of residuals.

2.7 The Net Adsorption Energy Theory

The net adsorption energy theory is described by McGuire et al. (1978) and McGuire (1977). The net adsorption energy theory is based upon interaction energies for the solute, solvent and adsorbent; these interactions influence the adsorption of the solute. McGuire et al. suggest three interactions as being fundamental to the adsorption process: solute-adsorbent, solute-solvent, and solvent-adsorbent interactions. During adsorption, the energy associated with the solute-adsorbent interaction is counteracted by the energies associated with the other two interactions. The net adsorption energy is thus:

$$E_t = E_{1s} - E_{2s} - E_{12} \quad (26)$$

where E_t is the net adsorption energy, E_{1s} is the solute-surface interaction energy, E_{2s} is the solvent-surface interaction energy, and E_{12} is the solute-solvent interaction energy. McGuire et al. (1978) show that E_t correlates well with the adsorption capacity as calculated from adsorption isotherm data for several organic compounds fitted to the Freundlich equation. Details regarding calculation of the terms in equation (26) are provided by McGuire (1977) and will be described in a later report.

2.8 The Solvophobic Interaction Theory

The solvophobic interaction theory is described by Belfort (1979) and in a two-part article prepared from information obtained during an interview with Belfort by Miller (1980a and b). This theory has a similar starting point and objectives to the net adsorption energy concept described in Section 2.2.2, but the two theories employ different starting points.

The net adsorption energy theory relies heavily on solubility theory, while the solvophobic interaction theory incorporates all of the possible additional interactions.

According to this model, the molecular condition which exists between adsorbate molecules S_i and the adsorbent C at equilibrium is:

and is characterized by the equilibrium constant K:

$$K = [S_i C] / [S_i][C]. \quad (28)$$

According to this model

$$\ln K = -\Delta G^\circ_{ASS} / RT \quad (29)$$

where

$$\Delta G^\circ_{ASS} = \Delta G^g_{VDW, ASS} + \Delta G^\circ_{S_i C} - \Delta G^\circ_{S_i} - \Delta G^\circ_i - RT \ln(RT/P_0 V) \quad (30)$$

As described by Horváth et al. (1976), ΔG°_{ASS} is the overall standard unitary free energy change for the association in solution; $\Delta G^g_{VDW, ASS}$ is a hypothetical gas-phase interaction assumed to be driven by van der Waal forces; ΔG°_i is the total standard unitary free-energy change for species i; V is molar volume; and P_0 is atmospheric pressure.

Belfort indicates that several assumptions can be made to simplify the calculation of ΔG°_{ASS} and consequently $\ln K$, and that $\ln K$ can be related to the measurable capacity coefficient from adsorption isotherm data for different solutes. Additional information regarding the simplifying assumptions and the applications of this theory will be provided in a later report.

3.0 EXPERIMENTAL WORK

Experimental work completed to date has focused on the development of a methodology for determining adsorption isotherm data over a wide range (i.e., three to four orders of magnitude) of equilibrium concentrations. This work began with an investigation of relatively simple procedures for preparing saturated solutions for use in batch shake test experiments. Results of these and additional studies have led to a more effective method for preparing saturated solutions as well as a method for generating adsorption isotherm data.

3.1 Materials

PAH standards used in this work were obtained as crystals from Aldrich Chemical Company (Milwaukee, Wisconsin) and were used as received without correction for impurities. PAH standards were assayed by the manufacturer as having a purity of 98 percent or greater.

Water used for preparation of aqueous solutions was purified by an ion-exchange and activated carbon bed system from Continental Water Company (El Paso, Texas). All organic solvents (viz., acetonitrile, ether, methanol and methylene chloride) were certified UV grade solvents appropriate for use in HPLC analysis and were obtained from Fisher Scientific (Pittsburgh, Pennsylvania). The water and solvents were filtered through 0.45 micron filters and were deaerated under vacuum prior to use.

The activated carbon used in this study was Filtrasorb 400 and was obtained from Calgon Corporation (Pittsburgh, Pennsylvania). The activated carbon was mechanically grinded and was classified into size categories

using U.S. standard sieve trays. Granular carbon studies were performed using carbon particles that had passed through an 18 mesh (1.00 mm) screen but were retained on a 20 mesh (0.841 mm) screen. Powdered tests were performed using carbon particles that had passed through a 200 mesh (0.074 mm) screen. The carbon was washed with organic-free, deionized water, decanted, and oven dried at 105 °C overnight prior to use in adsorption studies.

3.2 Equipment

Analyses were performed by a high pressure liquid chromatographic (HPLC) system obtained from Perkin-Elmer Corporation (Norwalk, Connecticut). This system consists of a Series 3 liquid chromatograph and a model S-210 fluorescence detector. Detection was performed using excitation and emission settings of 280 and 340 for naphthalene and 305 and 430 for fluoranthene.

3.3 Glassware

All glassware used in this study was specially cleaned to minimize contamination. Glassware was washed and rinsed with organic-free, deionized water and was soaked overnight in a 1:1 HNO₃ acid bath. Glassware soaked in this manner was rinsed successively with organic-free, deionized water, methanol, and methylene chloride and dried at 105 °C.

3.4 Results and Discussion

Because PAH have low aqueous solubilities, experiments performed with aqueous solutions of these compounds are particularly vulnerable to

contamination, analyte losses and degradation effects. Mechanisms by which PAH losses may occur include photodegradation, oxidation, volatilization and adsorption onto the inner walls of the sample container. Losses by photodegradation are minimized by covering all containers used to hold PAH solutions with aluminum foil. Losses by oxidation are minimized by deaerating the water, by filling the space above solutions in containers with nitrogen, and by sealing containers tightly with foil-lined rubber stoppers or teflon-lined screw caps. Sealing sample containers in this fashion also minimizes volatile losses. To minimize adsorptive losses, contact of aqueous solutions with extraneous glassware is avoided. Where appropriate, aqueous solutions are diluted in an equal volume of methanol to help minimize all losses noted above.

Tests described below were performed at a constant temperature of 25 °C.

3.4.1 Saturated Solution Generation and Stability

Initial experimental work involved an investigation of procedures for making saturated solutions of the compound of interest and an investigation of the time stability of these solutions. Four methods were selected for generation of a saturated solution. These all involved adding a ten-fold excess (calculated from solubilities reported in the literature) of solute to approximately one liter of water in amber-glass bottles and stirring the water over extended periods of time.

The first method involved mixing crystals of the compound of interest with water. The second method involved dissolving the compound of interest in five-milliliters of methylene chloride, adding the methylene chloride solution to an empty container, and evaporating the methylene chloride into a stream of dry nitrogen. This resulted in a sample

container with inner walls precoated with the compound of interest to which water was added. The third and fourth methods involved injection of five-milliliter volumes of methylene chloride and ether solutions containing the compound of interest into water.

Results of tests performed with naphthalene (solubility of 31.7 milligrams per liter at 25 °C as reported by Mackay and Shiu (1977)) indicated that saturated solutions could be prepared in approximately one day. The first and third methods described above seemed to provide concentrations reflective of saturated solutions, while the second and fourth methods gave solutions with concentrations slightly lower (approximately ten percent) than saturated. The resulting naphthalene solutions were stable over a period of several days.

Results of test performed with fluoranthene (solubility of 0.26 milligrams per liter at 25 °C as reported by Mackay and Shiu (1977)) were not as successful as those performed with naphthalene. Difficulties were encountered in obtaining saturated solutions even after several days of stirring. Subsequent analyses of the aqueous solutions indicated that three separate compounds were present as determined by fluorescence detection.

Conclusions drawn from these tests were that it would be generally difficult to generate saturated solutions by these methods and that the resulting solutions may not be stable over long period of time. It appeared that a new technique was necessary for generation of saturated solutions. This was especially critical for high molecular weight PAH, because higher molecular weight compounds have very low aqueous solubilities.

3.4.2 Alternative Generation Systems

A literature survey was performed to review techniques employed by researchers to prepare saturated solutions in previous studies with PAH.

May et al. (1978) describes the use of a generation column in which the compound of interest is precoated onto small glass beads. The beads are then packed into a stainless steel column, and water is pumped through the column. May used this technique to determine the aqueous solubilities of several PAH. Dobbs and Cohen (1980) report the use of this system for preparation of saturated solutions for use in adsorption isotherm studies which they performed using activated carbon.

In addition to use of a column technique for generating saturated solutions, it appeared that a similar column system could be employed to obtain adsorption isotherm data. This would involve a mini-column technique employed by Rosene (1977) to study adsorption of organic compounds onto activated carbon and by Dzombak (1981) to study adsorption of PAH onto soil. This technique involves passing a solution of known adsorbate concentration at a known flow rate through a column containing a known mass of carbon and monitoring the column effluent. The effluent concentration from the carbon column results in a breakthrough curve which is displaced below a breakthrough curve obtained from a blank run where no carbon is used. Integration of the area between the carbon breakthrough curve and the blank breakthrough curve gives the mass of adsorbate adsorbed onto the carbon. Capacity can be calculated and plotted versus equilibrium concentration as a single point. Performing several such breakthrough tests at different influent (equilibrium) concentrations would provide points necessary to obtain an adsorption isotherm curve.

The coupled column technique, involving a generation column and an adsorbent column, appeared to have excellent potential in overcoming time stability problems caused by losses of the compound of interest by

mechanisms of photodegradation, oxidation, and volatilization. Enclosure of the compound within stainless steel tubing would minimize photodegradation effects. Degassing the water prior to pumping it through the system would circumvent the introduction of air into the system which would otherwise be caused by rigorous stirring of a solution. Keeping the solution in a pressurized line would also reduce the potential for volatile losses to occur.

3.4.3 Description of Coupled Column System

A coupled column system was designed and assembled for use in adsorption isotherm testing. A schematic diagram of the coupled column system is shown in Figure 2. This system has been assembled using standard stainless steel tubing and fittings. The generator column is a 0.25 inch OD (0.18 inch ID) by 20 inch column. The column is packed with 60 mesh (0.25 mm) by 80 mesh (0.177 mm) glass beads obtained from Hewlett-Packard (Pittsburgh, Pennsylvania). The beads are washed with methylene chloride and precoated with the compound of interest by adding a methylene chloride solution of the compound to the glass beads in a 250-milliliter round bottom flask and evaporating the methylene chloride solution into a stream of dry nitrogen. Glass beads prepared in this fashion typically contain one to five percent by weight of the compound of interest. The end of the column is fitted with a glass wool plug (one to two inches) and a five-micron fritted filter to act as a filter to remove microparticulates of the compound of interest and to act as a support for the packing material.

The carbon column is a 0.25 inch OD (0.18 inch ID) by 6 inch column. The column is packed with carbon doses ranging from ten-milligrams

Figure 2. Schematic Diagram of the Coupled Column System

to 100-milligrams, and also uses a glass wool plug and five-micron fritted filter to support the carbon packing. Connections between the columns and other system parts are made using 0.0625 inch OD (0.0425 inch ID) and 0.125 inch OD (0.055 inch ID) stainless steel tubing.

3.4.4 Shakedown Testing

Shakedown testing has been performed using naphthalene as the solute. Shakedown testing has involved determination of compound solubility and determination of carbon column breakthrough curves.

Naphthalene solubility was determined by passing water through the generator column and through the carbon column by-pass line to the fluorescence detector. The fluorescence detector is used to monitor the effluent concentration. Once the detector response has stabilized, a 50-milliliter sample of saturated water from the fluorescence detector waste line is collected in 50-milliliters of methanol. Several samples were collected and were analyzed by HPLC injections to determine naphthalene concentrations. Quantitation was performed using response factors from naphthalene standards prepared in 50:50 methanol:water solutions. The quantitation curve shown in Figure 3 indicates that the fluorescence response is linear up to a naphthalene concentration of about 16 milligrams per liter.

An average value of results of nine solubility tests is summarized in Table I. This result shows good agreement of the aqueous solubility of naphthalene determined by this procedure to that reported by previous researchers. This indicates that the generation column works well for preparing a saturated solution.

Figure 3. Calibration Curve for Naphthalene.

NA CALIBRATION CURVE, 280/340, 1/24/81

Table I

Comparison of Aqueous Solubility Data for
Naphthalene Reported in the Literature to the Solubility
Determined in the Present Study.

<u>Reference</u>	<u>Solubility^a</u>
Present Study (9 determinations)	32.9 ± 1.20
Versar (1979) ^b	34.4
ISHOW (1979) ^b	30
May et al. (1978)	31.69 ± 0.23
Mackay and Shiu (1977)	31.7 ± 0.2
Schwarz (1977)	30.3 ± 0.3
Eganhouse and Calder (1976) ^c	31.3
Wauchope and Getzen (1972)	31.2
Pierotti et al. (1959)	31.2
Arnold et al. (1958) ^d	34.4

^aSolubility is in units of milligrams per liter per 25 °C.

^bAs reported by Dobbs and Cohen (1980).

^cAs reported by Neff (1979).

^dAs reported by May et al. (1978).

Blank and carbon column breakthrough curves were determined using the granular carbon described in Section 3.1. Four tests were performed using granular carbon and one test was performed using powdered carbon. Results of these tests are summarized in Table II. Breakthrough curves for four of these tests are shown in Figure 4.

The first test with granular carbon (GC test 1) was performed at approximately 50 percent of saturation with 100 milligrams of carbon. The anticipated capacity at this equilibrium concentration was approximated to be 410 milligrams per gram from isotherm data for Filtrasorb 300 presented by Dobbs and Cohen (1980). The carbon breakthrough curve reached a plateau corresponding to a naphthalene concentration of 10.1 milligrams per liter (65 percent of the influent concentration). Assuming that the effluent concentration were to remain at this level until instantaneous breakthrough were to occur, the estimated time to breakthrough was 50 hours. Consequently, this run was terminated because it appeared the carbon dose was too high.

Several parameters were recognized as influencing the time required to obtain breakthrough. These included solution concentration, solution flow rate, and carbon dose. Because the flow rate of 2.5 milliliters per minute represented a desirable working flow rate, it appeared that lowering the carbon dose could reduce the duration of the test. This motivated GC test 2, performed at about the same equilibrium concentration but with one tenth of the carbon dose. The duration of the test was only twelve hours, but two limitations on system performance were noted. First, fluorescence detector response decreased during the run by approximately ten percent, requiring linear interpolation to reconstruct a blank breakthrough curve. Second, it appeared that a significant portion

Table II

Summary of Carbon Breakthrough Tests Performed with Coupled Column System
Using Granular Carbon (GC) and Powdered Carbon (PC).

	<u>GC Test 1</u>	<u>GC Test 2</u>	<u>GC Test 3</u>	<u>GC Test 4</u>	<u>PC Test 1</u>
Influent Concentration (milligrams per liter)	15.6	13.0	4.3	16.7 to 14.0	4.0
Flow Rate (milliliters per minute)	2.5	2.5	2.5	2.5	2.5
Carbon Load (grams)	0.100	0.010	0.010	0.0108	0.0096
Duration of Run (hours)	6	12	16	15	24
Calculated Capacity (milligrams per gram)	--	360	600	360	--
Comments:	Test aborted after six hours because estimated time to breakthrough was 50 hours. Carbon dose appeared to be too high.	Poor accuracy of integrating breakthrough curve. Fluorescence response was not stable and decreased with time.	Fluctuations in tail of breakthrough curve resulted in difficulty in determining breakthrough. Influent concentration and fluorescence response were stable.	Influent concentration changed with time from 16.7 to 14.0 milligrams per liter.	Test aborted because influent concentration was decreasing with time.

Figure 4. Breakthrough Curves Obtained from Coupled Column System Using Granular and Powdered Carbon.

of the area between the blank and carbon breakthrough curves was present in the tail of the curve (i.e., beyond eleven hours as shown in Figure 4). Small variations in blank and carbon breakthrough curve responses in this region can therefore result in large errors in determining area.

An interesting observation was made from the carbon breakthrough curve for this test shown in Figure 4. The curve reached a maximum of about 85 percent of influent concentration at approximately 20 minutes, then fell off to approximately 70 percent of influent concentration after about 2.5 hours. After about 4.5 hours, the curve began to rise again and followed a smooth breakthrough to influent concentration.

A similar result was observed during GC test 3. This test was performed at a equilibrium concentration of 4.3 milligrams per liter (approximately fifteen percent of saturation) which was lower than either of the two previous tests. The decrease is more dramatic for this test; as shown in Figure 4 the effluent concentration fell to nearly zero at five hours, and then began to rise in a somewhat random fashion to a relatively distinct breakthrough at approximately thirteen hours. The area represented in the tail region of this particular breakthrough curve did not appear to be as significant as was the case for GC test 2. However, large undulations in fluorescence response about the breakthrough level made it difficult to determine the point at which breakthrough occurred.

Several explanations of these observations can be provided. It is possible that complete wetting of the carbon internal surface does not occur instantaneously; rather, wetting is not complete until about one to two hours into the test. Adsorption is not effective until the carbon is thoroughly wetted. This would explain the decrease in response

observed in the curves of GC tests 2 and 3. Another explanation for this decrease relates to the desorption from the carbon of previously adsorbed materials. These materials desorb as a result of preferential adsorption of the naphthalene. This occurrence is not particularly important to the final calculation of equilibrium capacity unless the desorbing materials are sensitive to fluorescence monitoring. However, in some carbon breakthrough tests not reported here, it was observed that the initial carbon breakthrough plateau slightly exceeded the plateau from the blank breakthrough curve. Whether this resulted from desorption of materials or from other reasons is not clearly known. The undulations observed in the tail regions of GC test 3 may have resulted from the adsorption and desorption of naphthalene from low energy adsorption sites of the activated carbon. While these undulations complicate determination of breakthrough, their effect on area between the blank and carbon curves is not significant for tests of long duration.

The last granular carbon test (GC test 4) was performed in an attempt to repeat the conditions in GC tests 1 and 2. During this test, the influent concentration decreased from 16.7 to 14.0 milligrams per liter over a period of fifteen hours. This decrease in concentration was attributed to changes in the flow patterns through the generation column and generation by-pass line; the flow rate of water through the by-pass line increased with time while the flow rate through the generation column decreased. This was apparently caused by changes in pressure drop across the two lines. As the test proceeded, a slight increase in system back pressure (from about 40 psia to nearly 70 psia) was observed. This may have been due to compression of the packing material in the generation

and carbon columns. A change in pressure drop could easily result in re-distribution of the water flow rate pattern.

Despite problems encountered during testing, three adsorption isotherm points may be estimated from results obtained using the coupled column tests with granular carbon. The equilibrium concentrations and capacities from Table II for these tests are plotted in Figure 5 along with the Freundlich equation line from data of Dobbs and Cohen (1980) for adsorption of naphthalene onto Filtrasorb 300. The data for GC tests 2 and 4 compare favorably, while the result of GC test 3 indicates approximately two-and-a-half times the adsorption capacity for the indicated equilibrium concentration. Although these results are in the range observed for a similar carbon, it is believed that the procedures under which the data were obtained entailed techniques which were cumbersome, time consuming, and not sufficiently precise. However, these results suggested that, if the limitations could be overcome, the coupled column system could be used successfully to generate adsorption isotherm data.

In addition to problems with flow control, which appeared to be due to differences in construction between the generation column line and generation by-pass line, the breakthrough characteristics (i.e., curve shape and duration) imposed a limitation on the experiments. In an attempt to make these two lines more structurally similar, a dummy column having similar dimensions and packed with glass beads was installed into the generation by-pass line. In recognition that the long duration of the carbon breakthrough tests were at least partly influenced by kinetics, it was decided to perform a carbon column test using powdered carbon (PC test 1). Conditions used in this test were similar to those in GC test 3. It was thought that the use of powdered carbon in place of

Figure 5. Comparison of Isotherm Plot of Dobbs and Cohen (1980) to Isotherm Points from Coupled Column System.

granular carbon would result in more favorable kinetics and would thereby reduce the test duration and improve the breakthrough curve characteristics. However, this test was aborted because the influent concentration was again found to be decreasing with time.

At this point, it appeared that additional structural modifications of the coupled column system were required. Three structural changes appeared to be promising. The first involved introducing a separate pump to the system; flow control would be more accurate with a second pump, where one pump delivers water to the generator by-pass line and the second pump delivers water to the generation column line. The second modification involves reconstructing the two lines so that they are exactly identical in every respect. In this case, flow control would theoretically be a function of the amount of column packing (i.e., glass beads) in the dummy column. The third possibility involves installation of a sampling bomb of between 100-milliliters and 500-milliliters in volume downstream of the union of the generation column and generation by-pass lines. This sampling bomb would act as an equalization basin and would dampen the effects of increasing pressure drop on influent concentration.

A potential structural modification aimed at reducing the test duration time would be to use a smaller inner diameter carbon column. The objective of this modification would be to increase the length of the carbon packing and thereby increase contact time.

Although several structural changes could potentially overcome limitations of this system, it was anticipated that the procedures necessary to obtain sufficient data for an adsorption isotherm curve might still be cumbersome, time consuming, and not sufficiently precise.

Consequently, a decision to implement any of these structural changes in the coupled column system was tabled pending investigation of batch shake test techniques for generating adsorption isotherm data.

3.4.5 Adsorption Shake Tests

Batch adsorption isotherm shake tests were performed with naphthalene using granular and powdered carbon. Tests were performed with 125-milliliter erlenmeyer flasks. In granular carbon tests the carbon was weighed as dried granules and delivered directly to the adsorption flasks. Powdered carbon was made into a slurry by adding 1.917 grams of powdered carbon to a one-liter volumetric flask and diluting to the mark with organic-free, deionized water. Carbon doses were delivered to the adsorption flasks by shaking the slurry and pipetting one- to 25-milliliter volumes.

Saturated solutions for these tests were generated by pumping water through the generation column and collecting the effluent in an amber glass bottle. The solution was diluted prior to use in the adsorption isotherm tests. A total solution volume of 100-milliliters of solution was used in the adsorption tests. Prior to sealing the erlenmeyer flasks with aluminum foil covered rubber stoppers, the space above the solution was filled with nitrogen.

Upon completion of the shake tests, granular carbon samples were allowed to settle and powdered carbon samples were centrifuged for particle removal. Aliquots of the clear aqueous solution were withdrawn and injected directly into the HPLC for quantitation.

Results of the shake test with granular carbon are summarized in Table III. Samples were shaken for four days before equilibration was

Table III
Summary of Granular Carbon Shake Test

<u>Carbon Dose, milligrams</u>	<u>Initial Concentration, milligrams per liter</u>	<u>Equilibrium Concentration, milligrams per liter</u>	<u>Capacity^a, milligrams per liter</u>
2.3	11.1	2.67	350
4.0	↓	1.72	230
6.0		0.50	170
10.0		0.0853	110
15.2		0.0289	71
20.4		0.0134	53
30.2		0.00702	36
50.0		0.00689	21
0.0		10.4	--

^a

$$CAP = \frac{\left[\left(\frac{11.1 + 10.4}{2} \right) - C_e \right]}{C_d} \times 100$$

where CAP is capacity, C_e is equilibrium concentration, and C_d is carbon dose.

achieved. Data in Table III are plotted in Figure 6 along with a plot of the Freundlich equation line from data of Dobbs and Cohen (1980). These data show approximately a two-fold increase in adsorption capacity as determined in the present study.

One notable problem with the granular carbon test was the long time required to reach equilibrium; also, test data revealed that over four days of equilibration the blank concentration was reduced by approximately six percent. It was anticipated that powdered carbon adsorption tests would reach equilibrium faster and would thereby be less sensitive to changes in the blank concentration.

Powdered carbon adsorption tests were found to reach equilibrium over a significantly shorter period. Tests have shown that equilibration occurs within one hour. However, shake tests were performed over a period of four hours.

Results of the powdered carbon adsorption isotherm tests are summarized in Tables IV and V and are also plotted in Figure 6. The upper straight line plot in Figure 6 is the Freundlich equation line for data from all three shake test experiments, and is provided for comparative purposes. These data show similar capacities to those obtained from the granular carbon tests. In addition, no significant degradation of the blank was observed. However, the data plotted in Figure 6 show apparently low capacities for some of the low equilibrium concentrations. From Tables IV and V, one would expect the equilibrium concentrations to decrease with increasing carbon dose. However, at carbon doses of 30-milligrams or greater the equilibrium concentrations show some scatter. This presumably results from the method of delivering the carbon slurry

Figure 6. Comparison of Isotherm Data Determined in the Present Study to that of Dobbs and Cohen (1980).

Table IV

Summary of Powdered Carbon Shake Test Number One

<u>Carbon Dose, milligrams</u>	<u>Initial Concentration, milligram per liter</u>	<u>Equilibrium Concentration, milligram per gram</u>	<u>Capacity, milligram per gram</u>
1.92	22.77	7.41	800
3.83	22.54	4.02	480
5.75	22.31	1.36	360
9.59	21.85	0.193	230
13.4	21.39	0.0928	160
17.2	20.93	0.0367	120
23.0	20.24	0.0211	88
28.8	19.55	0.0159	68
32.6	19.09	0.0125	58
38.3	18.40	0.0237	48
42.2	17.94	0.0499	42
47.9	17.25	0.0147	36
0.00	23.00	23.0	--

Table V

Summary of Powdered Carbon Shake Test Number Two.

<u>Carbon Dose, milligram</u>	<u>Initial Concentration, milligram per liter</u>	<u>Equilibrium Concentration, milligram per liter</u>	<u>Capacity, milligram per gram</u>
1.92	30	18.8	580
5.75		5.28	430
9.58		0.610	310
13.4		0.288	220
17.3		0.159	170
21.1		0.225	140
24.9		0.0743	120
28.8		0.0489	100
32.6		0.0961	92
36.4		0.184	82
40.3		0.131	74
0.0		30.0	--

to the adsorption flask. For large slurry volumes (i.e., twenty milliliters or more) the time needed to fill the pipette may be significantly long to be influenced by settling of the carbon particles in the slurry. This occurrence could apparently be avoided by using only the smaller doses in shake tests and by using different feed concentrations to achieve data for different equilibrium concentrations.

4.0 FUTURE WORK

The batch shake test method will be employed to generate adsorption isotherm data for several PAH. Tests will be performed using the powdered activated carbon described in Section 3.1. Tests will be conducted in 50-milliliter centrifuge tubes fitted with teflon lined screw caps. Two- to ten-milliliter aliquots of a standard powdered activated carbon slurry will be delivered to each centrifuge by pipette. The use of centrifuge tubes as the shake test sample container allows the shake tests and particle removal (by centrifugation) to be performed in one container; this greatly minimizes potential adsorptive and other losses which may result from excessive handling of the solution. Organic-free, deionized water will be added to the carbon slurry in the centrifuge tubes as necessary to bring the slurry water volume to ten-milliliters. Forty-milliliters of an aqueous solution containing the compound of interest will be added to the centrifuge tube using a calibrated buret. A nitrogen blanket will be put over the shake test solutions, and the centrifuge tubes will be sealed and shaken for four hours at $25\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$. After shaking, the samples will be centrifuged, and aliquots withdrawn directly from the centrifuged samples will be injected into the HPLC for quantitation. Duplicate shake test samples will be used for each carbon dose to give an average single isotherm point.

Saturated solutions will be generated using the generation column described in Section 3.4.3. Aqueous solubilities for the specific PAH will also be determined.

Efforts to complete structural modifications of the coupled column system will be curtailed unless problems are encountered with this batch shake test method.

One adsorption isotherm data have been generated for several PAH, these data will be used to determine the most appropriate isotherm model of those presented in Section 2.0. Attempts will then be made to correlate adsorption capacity to molecular features.

5.0 SUMMARY

Eight adsorption and/or adsorption isotherm models have been identified as potential candidates for modelling adsorption isotherm data for adsorption of PAH onto activated carbon. A coupled column technique has been developed which generates saturated and/or diluted solutions and performs adsorption isotherm tests in one enclosed system. This system works well for generation of saturated solutions, but is currently limited in utility for generating adsorption isotherm data. Problems with flow control result in changes in the influent concentration with time, and certain other features inherent in the system may lead to poor breakthrough characteristics. While structural modifications may overcome these problems, the process of generating sufficient data for an adsorption isotherm curve by this method is cumbersome, time consuming, and not sufficiently precise. Batch adsorption isotherm shake tests using powdered carbon appear to offer an acceptable alternative to the coupled column technique and will be used to generate adsorption isotherm data for several PAH.

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