

ADSORPTION OF SUBSTITUTED AROMATIC COMPOUNDS BY ACTIVATED
CARBON: A MECHANISTIC APPROACH TO QUANTITATIVE STRUCTURE
ACTIVITY RELATIONSHIPS

By

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by

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Knowledge and understanding is a gift from God to be used for His glory.

“Whatever you do, work at it with all your heart, as working for the Lord, not for men, since you know that you will receive an inheritance from the Lord as a reward. It is the Lord Christ you are serving.” Colossians 3:23-24

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Abstract of Thesis Presented to the Graduate School
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Because of their widespread prevalence in ground and surface waters, aromatic compounds pose a significant risk to public health. Of the current biological, chemical, and physical methods for remediation of these contaminants, activated carbon has been chosen as the primary method of treatment by many water treatment facilities. Despite its widespread use, questions remain concerning the economic feasibility of activated carbon, and determining suitable carbons for specific contaminants often requires extensive experimentation, time, and cost. Previous work in developing predictors of carbon performance using quantitative structure-activity relationships (QSARs), has fallen short of providing accurate models for carbon adsorption. This study investigates the role of QSARs in predicting the adsorption of monosubstituted benzenes onto a single activated carbon and offers a general protocol for the implementation of QSARs for predictive adsorption analysis. This study has produced successful correlations among aqueous solubility, sterics, and log K. These correlations demonstrate optimistic

effectiveness for using these parameters for adsorption prediction and signify the value of the functional and effective QSAR protocol utilized in this study.

CHAPTER 1 INTRODUCTION

In 1969, Mattson et al. stated that “The mechanisms by which active carbon functions to remove phenols from aqueous solutions has never been clearly defined. A thorough understanding of the sorptive mechanisms is essential for accomplishing the most effective use of active carbon in water and wastewater treatment” (Mattson et al. 1969). Over 3 decades later, carbon scientists are still pondering the same dilemma. It is clear that activated carbon is an efficient, cost effective adsorbent for removing numerous organic materials from both gaseous and aqueous solutions. The general mechanisms of adsorption are known to be physical adsorption and chemisorption. It has also been shown that factors, such as pH and surface chemistry, play a significant role in the adsorption process (Kipling and Shooter 1966, Coughlin et al. 1968, Mattson et al. 1969, Muller et al. 1985, Vidic et al. 1993, Radovic 2001). Yet, the mechanisms that directly lead to the adsorption of an adsorbate still remain elusive. Identifying the role of functional groups in the adsorption process is an essential component to understanding these mechanisms. The carbon activation process is the fundamental step in the development of surface chemistry and functional groups. Understanding the adsorption process will enable an optimized use of activated carbon, eliminating the wasteful practice of trial and error adsorption treatment. To help circumvent this black-box method of carbon dosing, various relationships are currently being established between the adsorbate and the adsorbent. Two of these relationships are adsorption isotherms and Quantitative Structure Activity Relationships (QSARs).

CHAPTER 2 LITERATURE REVIEW

Activated Carbon

Activated carbon is an adsorbent created by treating a carbonaceous material thermally and/or chemically so that it develops internal pores that yield its characteristic high surface area. Thermal activation is commonly employed, where a carbonaceous precursor (e.g., coal, wood, nutshells) is subjected to high temperatures typically ranging from 300°C to 800°C (Mattson et al. 1969). In chemical activation, the precursor is first exposed to a chemical (e.g., NaOH, H₃PO₄), which drives pore development and is then subjected to heat treatment. Heating temperatures are typically lower for the production of chemically activated carbon. Activated carbon is commonly used in separation processes involving organic compounds, and is widely used in fields such as medicine, water and air treatment, the food and beverage industry, and industrial processes.

The Activation Process

During the activation process, an oxidizing agent breaks down the graphite structures of the carbonaceous precursor, a process known as gasification, resulting in the formation of high energy areas that serve as adsorption sites. The resulting carbon parameters (e.g., pore size distribution (PSD), functional groups) are dependent on the oxidant used. Steam (H₂O) and CO₂ are the most common agents used and will therefore be the focus of this section.

CO₂ and H₂O Activation

The literature generally agrees—with one *notable* exception (Wigmans 1989) which has been cited 134 times to date, according to the Science Citation Index—that the use of CO₂ as the oxidizing agent during carbon activation leads to an enhanced development of micropores; while the use of steam promotes the propagation of mesopores (Tomkow et al. 1977, Rodriguez-Reinoso et al. 1995, Molina-Sabio et al. 1996, Johns et al. 1999). Creation of pores resulting from the endothermic oxidation of carbon with steam or CO₂ follows Eqn 2.1 and 2.2:



With sufficient heating, CO₂ will break a carbon bond from the aromatic ring in the precursor. To satisfy the bond, the CO₂ will leave behind an oxygen molecule at the surface, thus creating CO while the remaining CO from the initial CO₂ molecule will escape as a gas (Eqn 2.1). In the case of steam (Eqn 2.2), the H₂ generated can anneal to the aromatic ring. The annealing process is slower than the formation of the CO bond, yet the former is dominant, thus resulting in a greater energetic reaction and the creation of a larger pore. If the H₂ does not anneal carbon active sites (i.e., those C atoms that are not fully saturated), the H₂ diffuses out of the carbon and can actually inhibit the forward progress of gasification (Ergun and Mentser 1965).

The impact of oxygen functional groups have been shown to effect pore development. Molina-Sabio et al. (1996) found that the evolution of oxygen functional groups as CO from the carbon surface was correlated with the CO₂ micropores and the widening of pores from steam. It should be noted that the presence of oxygen functional

groups could also affect the adsorption of target contaminants such as phenol, which will be discussed in following sections.

Adsorption Factors

Surface Area

Surface area is an important parameter to consider when creating or selecting an adsorbent. In an ideal adsorption situation—where all other conditions (such as pore size, surface chemistry, and adsorbent-adsorbate interactions) are optimal for contaminant removal—the surface area would serve as the limiting factor for the adsorption process. In this case, as the activated carbon surface area increased, so would the adsorption of the target contaminant. Manufacturers of activated carbon attempt to increase the surface area of the adsorbent with the hope of enhancing the carbon's removal efficiency. Typically, the surface area of activated carbon reaches a maximum around 1500 m²/g.

The activated carbon surface area is commonly found using a theory developed by Brunauer, Emmett, and Teller (BET) for physical adsorption. While the BET theory is inadequate as a universal equation for physical adsorption, it has been adapted to describe surface area (Dabrowski 2001). BET surface area is determined by flowing nitrogen gas at 77 K through a sample of activated carbon, allowing the N₂ to enter the pores of the carbon. From the amount of N₂ that adsorbs to the pores, the surface area is deduced. It should be noted that the BET surface area can at times be misleadingly when attempting to directly correlate it to the adsorption capacity of an activated carbon (Pope 2003). Since nitrogen gas molecules are much smaller than many target contaminants, the size of the contaminant itself should be considered with respect to the pore size distribution of the carbon.

Pore Size Distribution

Another essential parameter to consider for an absorbent is its pore size distribution (PSD). Pore size distribution is usually expressed as a graphical relationship, using pore width (\AA) as the independent variable and cumulative pore volume (cc/g) as the dependent variable. Pore widths that fall under 20 \AA are considered to be micropores, from 20 to 500 \AA are mesopores, and above 500 \AA are macropores. The variation of pore widths in an activated carbon is dependent upon the activation process. Theoretically, any precursor can have any desired PSD, yet, the degree of distribution may require more manipulation of the activation environment, and hence may be more energy (and cost) intensive.

pH

When the parameter of pH is discussed in an experiment, commonly it is used as a descriptor to express the ionic conditions of a given aqueous system. However, in the case of activated carbon adsorption, it is important to take into account the pH of the carbon surface and internal pores in addition to the aqueous medium. An internal measurement of the activated carbon is expressed through the point of zero charge (PZC). The PZC is the point at which the carbon surface has no detectable charge. In Figure 2.1, the PZC is at pH 7; therefore at a solution pH below 7, the carbon surface is positively charged and a solution pH above 7 will promote a negatively charged carbon surface. PZC is an important characteristic when predicting or describing the process of adsorption, yet is only a dominant factor when the target contaminant is close to the adsorption site. For example (assuming the contaminant is in range of the adsorption site), if the target contaminant was a cation, a solution pH greater than 7 would be desired

for the PZC illustrated in Figure 2.1. Conversely, if the target contaminant was an anion, a solution pH below 7 would be desired.

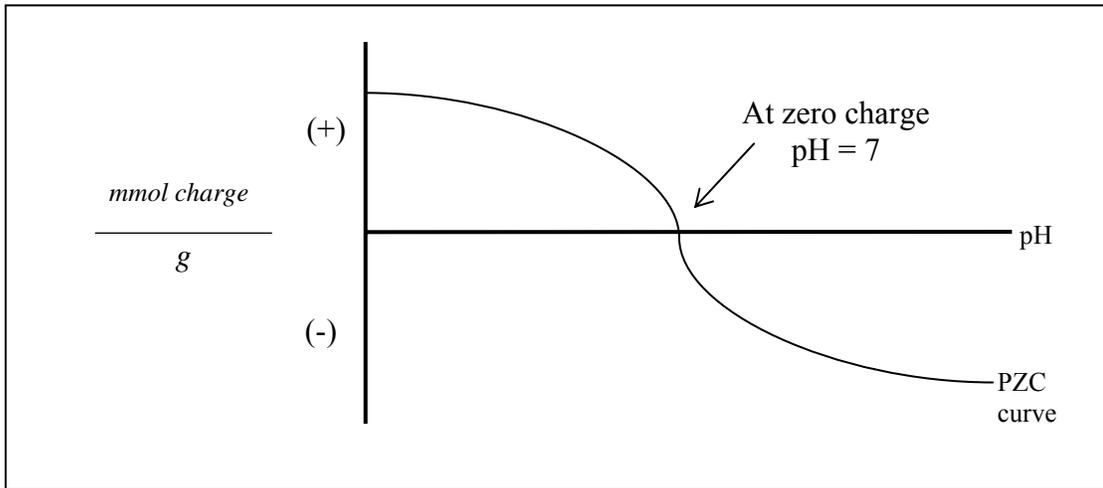


Figure 2.1. Representation of Point of Zero Charge

The zeta potential, a measurement of external charge, governs the attraction of the target contaminant to the activated carbon. Zeta potential is the measurement of electric potential at the shearing plane—the “space” between the activated carbon surface and the adjacent water molecules (Adamson 1990).

Surface Chemistry

The structure of activated carbon is graphitic in nature, consisting of molecular layers of carbon which can be viewed, according to Coughlin and Ezra, much like a polynuclear aromatic molecule (Coughlin and Ezra 1968). These layers contain carbon atoms that are bonded together with three sigma bonds and one pi bond having sp^2 hybridization. It is also possible for sp^3 hybridization (tetrahedron) to occur, which may result in cross-linking among the graphite layers (Coughlin and Ezra 1968). The carbon within this structure is microcrystalline and is held together with the graphite layers through van der Waals forces. When other atoms are bound within this system, they can be present within the layers, forming “heterocyclic” rings, or at the edges of the

microcrystalline carbon molecules, thus forming functional groups (Coughlin and Ezra 1968). Edge sites located between the graphitic layers are very reactive and are therefore prominent sites for functional groups and adsorption. It is asserted by Coughlin and Ezra (1968), that the basal face of the benzene ring can weakly adsorb through π interactions.

A discussion of activated carbon surface chemistry should also include a thorough examination of electron interactions, including electron density, electrostatics, attraction and repulsion, as well as dispersive forces and the influence of functional groups located on both the adsorbent and the adsorbate. Numerous discussions in the literature center around speculation of these interactions and many of these theories have not yet been sufficiently disproven. It is hoped that a deeper understanding of the activated carbon surface chemistry will provide the keys for unlocking the mechanisms of the adsorption process. Although questions remain, the literature gives significant insights into the surface chemistry of activated carbon; these theories will be examined in the following sections of this paper.

Predicted Adsorption Mechanisms

Despite the extensive amount of research that has advanced the field of activated carbon, the adsorption mechanisms still remain unknown. Currently, the literature has concentrated on two mechanistic theories—the theory of π - π bonding first proposed by Coughlin and Ezra (1968) and the electron donor theory proposed by Mattson et al. (1969).

π - π Bonding Theory

The π - π bonding theory takes into consideration the π bonds which occur between two p-orbitals as shown in Figure 2.2. This type of bonding occurs between the 2p

orbitals in the benzene ring presented in Figure 2.3. The electrons in the 2p orbitals travel above and below the benzene basal plane, therefore creating a delocalization of electrons about the ring. At the basal plane, weak adsorption can occur through π interactions, while at edge sites adsorption is much stronger (Coughlin and Ezra 1968).

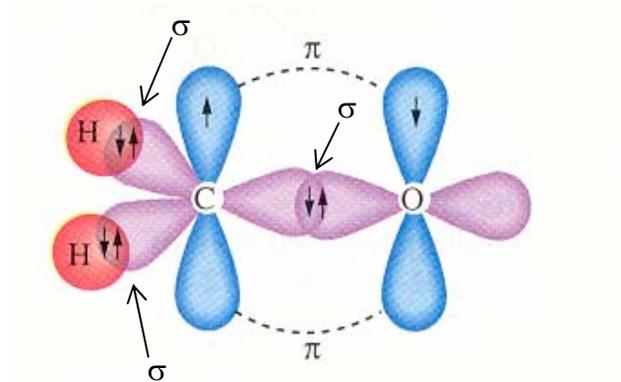


Figure 2.2. Representation of sigma and pi bonding, arrows within the atoms of formaldehyde represent electron filling in outer orbitals. Adapted from Petrucci and Harwood (1997).

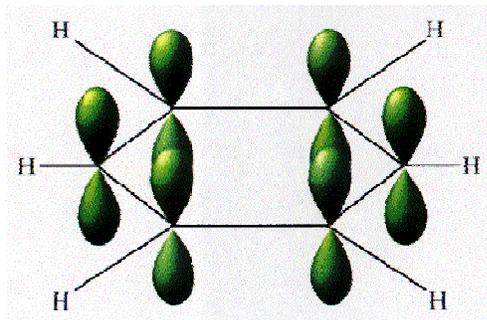


Figure 2.3. Representation of the Benzene Pi System (Source: Tedankara Library, 2003)

Species that are bonded to the graphitic edges of activated carbon can cause a disturbance in the electron density of the basal plane. For example, the presence of O₂ molecules (i.e., electron-withdrawing groups) will influence the π electron distribution by removing electrons and creating positive holes in the conduction band of the π electron system, thus decreasing the dispersive adsorption potential of the carbon surface (Coughlin and Ezra 1968, Franz et al. 2000, Radovic 2001). The opposite is also true;

removing electron-withdrawing groups from the carbon surface will increase the π electron density and therefore result in an increased adsorption potential (Radovic 2001).

Electron Donor Theory

The electron donor theory suggests that an exchange of electrons takes place during the adsorption process, whereas in π - π bonding dispersive interactions are dominant. Mattson et al. (1969) argue that Coughlin and Ezra do not explain the effects of π interactions across the distance of the basal plane as well as the mechanism of interaction of the sorbates to the basal plane. Using the nitro- group as an example, Mattson et al. (1969) suggest that as electron-withdrawing groups reduce the π electron density, the nitro-substituted aromatic would become an acceptor that would interact with a donor such as carbonyl oxygen. In a broader sense, the carbonyl oxygen would be the major donor and the aromatic ring would be the acceptor. Taking into consideration the π system interactions, Mattson et al. (1969) state that the adsorption orientations should be planar.

A notable paper by Franz et al. (2000) disagrees with the findings of Mattson et al. (1969). Mattson et al. (1969) base the electron donor theory on their observation that as surface oxygen increases so does the amount of carbonyl functional groups. As the carbonyl group serves as the major electron donor in the donor-acceptor complex, Mattson et al. credit it for the increase in phenol adsorption. Mattson et al. attribute subsequent decreases in adsorption to the formation of carboxyl functional groups. However, Franz et al. (2000) have found that an increase in oxygen functional groups leads to an increase in the formation of both carbonyl and carboxyl groups. Radovic (2001) also refutes the findings of Mattson et al., stating that “carbon oxidation does not

(necessarily) involve the conversion of carbonyl groups into carboxyl groups,” thus suggesting that the reasoning of Mattson et al. is flawed. Franz et al. (2000) suggest that the decrease in adsorption is due to the presence of water molecules that create bulky clusters on the carboxyl groups due to hydrogen bonding and block access to the adsorption sites. To support this conclusion, Franz et al. (2000) argue that if moisture is enough to block N_2 from adsorbing during BET surface analysis, that a compound much larger than N_2 should also be expected to be blocked. In agreement with the speculations of Coughlin and Ezra (1968), Franz et al. (2000) support an adsorption theory based on dispersive/repulsive interactions.

Functional Group Formation

Detection of Functional Groups

Throughout the literature, the most popular form of functional group identification is through the use of Boehm titrations (presently cited 172 times in the literature according to the Science Citation Index). Functional group identification is made through the applications of organic acid-base chemistry. These acid-base reactions examine the chemisorbed oxygen on the carbon surface, defining four acidic surface groups (Boehm 1966 and Coughlin et al. 1968):

- (I) strongly acidic carboxyl group
- (II) weakly acidic carboxyl group
- (III) phenolic hydroxyl group
- (IV) carbonyl group.

Titration is performed to identify which groups are present through a neutralization process using various bases. Group (I) can be neutralized by $NaHCO_3$, $NaCO_3$, $NaOH$, and $NaOC_2H_5$. Group (II) can be neutralized by Na_2CO_3 or stronger

bases. Group (III) functional groups are titrated with NaOH and group (IV) reacts with sodium ethoxide (NaOC_2H_5) (Boehm 1966).

In addition to Boehm titrations, other methods have been presented (e.g., X-ray detection, and Fourier Transform Infrared Spectroscopy (FTIR)), yet the success of many of these methods has not been universally accepted for the accurate description of the carbon surface—especially within the pore walls.

Types of Functional Groups Formed

From CO_2 activation

The formation of carbonyl and carboxyl groups from CO_2 activation has been reported in the literature (Mattson and Mark 1969, Johns et al. 1999, Guo and Lua 2002). Through the use of infrared internal reflectance spectroscopy, Mattson et al. (1970) have determined the presence of “significant amounts” of carboxyl and carbonyl groups which they speculate have a strong interaction at the edges of the aromatic basal planes. Although no rationale is offered, Mattson et al. (1970) have speculated that at some temperatures (300°C, 400°C, 600°C, 700°C) the use of CO_2 during activation can suppress the formation of oxide surface functional groups. In addition to carboxyl and carbonyl groups, Johns et al. (1999) have determined that CO_2 activation produces more acidic functional groups than steam activation; specifically, the presence of phenolic and lactone groups was detected. Lua and Guo (Lua and Guo 2000, Guo and Lua 2002) found that CO_2 activation of oil palm shell produced a slightly acidic surface consisting of quinones, aromatic rings, and oxygen atoms speculated to be bound at the edges of the graphitic sheets.

From H₂O activation

During the process of steam activation, in addition to oxidizing the carbon surface, steam prevents secondary char formation on the carbon by removing volatiles from the surface and can interact with both organic and inorganic matter (Petrov et al. 1994).

Through these interactions with the carbon surface, various functional groups are formed. The formation of hydroxyl (e.g., phenol and lactone), carboxyl, and carbonyl groups have been reported in the literature (Gergova et al. 1993, Petrov et al. 1994, Johns et al. 1999). While both hydroxyl and carboxyl groups were detected after steam and CO₂ activation, Johns et al. (1999) reports a decreased presence of both following steam activation.

Factors controlling which groups are formed

The functionality of a given activated carbon is highly dependant on its carbonaceous precursor and its heat treatment. Various raw materials will form varying functional groups when activated depending upon their structure and composition. For example, a precursor containing sulfur would be expected to exhibit sulfur containing functional groups, while a material void of sulfur would not form such groups unless treated with a thiochemical such as H₂S. Likewise, the intensity of heat treatment can control the degree at which surface groups are burned off, or formulated. In the previous example, if the activation temperature was intense enough to burn off the sulfur as a gas, it would be expected that a sulfur functional group would not form on the carbon surface. It therefore follows that different types of activated carbon will adsorb contaminants differently—hence, the efficiency is variable and can be tailored in the activation process. Similarly, the same activated carbon will have unique adsorption relationships with varying contaminants—i.e., the efficiency will vary according to the chemical and physical characteristics of the adsorbate.

Precursor and conditions of activation

Upon examining the significance of the activation process on the surface chemistry of an activated carbon, it is insightful to examine the functionality of the carbon both before and after the oxidation process. In the literature, two such papers were found. Gergova et al. (1993) have examined the surface of apricot stones prior to and following steam activation. The results of this study are summarized in Table 2.1. From the data, it is clear that the composition of carbon, nitrogen, and sulfur increased while hydrogen and oxygen decreased. While both nitrogen and sulfur also show an increase in percent weight, the difference is less than 1% (almost less than 0.5%) and would be difficult to argue any significant difference in comparison with the other elements. The most notable changes are between carbon and oxygen; the weight percentage of carbon increased by nearly 40% while oxygen decreased approximately 35%. It should be noted that the composition of oxygen was found by difference; hence, it was assumed that the material consisted only of carbon, hydrogen, nitrogen, sulfur, and oxygen. While the authors mention the detection of carbonyl and hydroxyl groups, they fail to draw any conclusions about the change in elemental concentration. Furthermore, the authors do not state the process by which the complete elemental analysis was performed, making it nearly impossible for the reader to derive a conclusion concerning the difference in composition.

Guo and Lua (2002) reported the change in functional groups detected on oil shell palm prior to and after CO₂ activation. The raw material oxygen functional groups consisted mainly of carbonyl groups (e.g., ketones and quinones), ethers, and phenols. After carbonization, the presence of ketones and quinones were detected, and following activation, only the presence of quinones remained. The authors attribute the loss of the ketone functional groups to the intense heating (950°C) (Lua and Gou 2000, Guo and Lua

2002). The effects of temperature on the formation of functional groups during the activation process have also been confirmed by Mattson et al. (1969). For the case of the oil shell palm, the result of the carbon surface changes resulted in a slightly acidic carbon surface (Lua and Gou 2000, Guo and Lua 2002).

Table 2.1. Elemental Analysis of Apricot Stones Before and After Steam Activation at 600°C, Adapted from Gergova et al. 1993

Elemental Analysis	Raw Material (% weight)	Activated Carbon (% weight)
C	51.45	89.67
H	6.34	2.40
N	0.20	0.58
S	0.09	0.39
O (<i>by difference</i>)	41.92	6.96

In addition to the effects of temperature, the presence of impurities in the carbonaceous precursor can lead to notable effects in the formation of surface functional groups. Mattson and Mark (1969) state that the presence of oxygen, nitrogen, sulfur, hydrogen, and ash are common impurities and that specifically the presence of oxygen and hydrogen (especially when bonded with oxygen) can have distinct effects on the adsorption process. Coughlin et al. (1968) found that the presence of chemisorbed oxygen decreased the adsorption capacity for phenol while Vidic et al. (1993) have shown the opposite effect. It should be noted that Coughlin et al. observed the adsorption of phenol in a dilute solution—it can be argued that the dilute solution accounted for the lack of adsorption and not the oxygen functional groups. In the case of a dilute solution, the driving force for adsorption is very low, thus decreasing the probability for the adsorbate and adsorbent to interact and adsorption to occur.

Optimizing the Use of Activated Carbon

Commonly, to estimate the adsorption capacity of an activated carbon, Freundlich or Langmuir isotherms are developed. However, according to Weber and DiGiano (1996) : “Despite the sound theoretical basis of the Langmuir, BET, and Gibbs models, these isotherms often fail to describe experimental solution sorption data adequately.” It is proposed that the Freundlich equation can better describe the activated carbon adsorption process than the afore mentioned models due to the heterogeneous nature of the carbon surface. It will be shown in the following sections how the Freundlich equation compares to the frequently used Langmuir model for activated carbon adsorption of benzene and monosubstituted benzenes. Developed by Herbert (Heinrich) Freundlich from empirical observations in the early 1900s, the Freundlich model offers an exponential equation, based on heterogeneous surface energy distribution, which describes the variation in adsorption heat with respect to adsorbate concentration (Weber and DiGiano 1996):

$$q_e = KC^{\frac{1}{n}} \quad \text{Eqn 2.3}$$

Where:

q_e = the mass of contaminant adsorbed per unit mass of carbon

K = “adsorption capacity”, Freundlich constant

C = concentration of the adsorbate in solution at equilibrium

$1/n$ = strength of adsorption, Freundlich constant

To validate his empirically derived equation, Freundlich utilized a special case of the Gibb’s relationship, working under the assumption that in a dilute solution Gibb’s surface excess is equivalent to the amount of contaminant adsorbed (Weber and DiGiano 1996).

The Freundlich equation can be used in designing an activated carbon system. For example, using the Freundlich constants K and $1/n$, the following equations can be used to estimate the bed life of an activated carbon (Snoeyink 1990):

$$Y = \frac{q_e}{(C_o - C_l)} \rho_{GAC} \quad \text{Eqn 2.4}$$

Where:

Y = carbon bed life

C_o = initial concentration of contaminant

C_l = final concentration of contaminant

ρ_{GAC} = apparent density of carbon

The Freundlich constants K and $1/n$ are commonly cited in the literature without a thorough discussion of what each represents. It is one intent of this paper to attempt to clarify the significance (and limitations) of these parameters. The so called “adsorbent capacity” constant K represents the influence of various adsorption energies that are associated with the heat of adsorption. However the term “adsorbent capacity” only applies when $K = q_e$, hence when $C=1$ and K is dependent solely on the change in adsorbate concentration due to adsorption (Chiou 2002). The term $1/n$ represents the sum of diverse energies associated with adsorption. The notation of $1/n$ comes from the thermodynamic derivation of the Freundlich equation, but, given that the equation is typically used empirically, the literature often uses simply “ n ” (Weber and DiGiano 1996).

Certainly “adsorbent capacity” (K) and strength of adsorption ($1/n$) should vary with varying activated carbons. Noting that no two activated carbons are identical, it should be easily deduced that the performance of varying activated carbons would also

differ. These differences could account for the discrepancies reported for the Freundlich constants in the literature. It should further be noted that the concentration range of the activated carbon used in the development of isotherms may have a significant effect on the value of K and $1/n$. It is not uncommon to find K values that differ by several orders of magnitude in the literature; for example, Table 2.2 shows three different values of K for benzene. The variation in reported values is likely due to various definitions of equilibrium conditions, the use of different carbons, and the use of varying concentration ranges for both the adsorbent and adsorbate. However, if these K values are to be used as tools in designing activated carbon systems, these differences must be accounted for and understood.

Table 2.2. Reported Values of Freundlich K for Benzene.

K	Source
0.12602	Noll 1999
1.0	Dobbs and Cohen 1980
41.7	Loll et al. 2004

An understanding of the Polanyi-Manes model (Eqn 2.5) reveals adsorption trends which are reflected in the Freundlich constants. Using the Polanyi-Manes model, the energy necessary for an adsorbate to displace a solvent (in order to be adsorbed on the adsorbent) can be calculated (Chiou 2002). For example, for similar solutions under constant conditions of temperature and pressure, more energy is required to adsorb more adsorbate due to the increased volume of solvent that must be displaced.

$$\varepsilon_{sl} = RT \ln \left(\frac{C_s}{C_e} \right) \quad \text{Eqn 2.5}$$

Where:

ε_{sl} = adsorption potential (energy required for a volume of solute (s) to displace a volume of solvent (l) in the adsorption process)

R = gas constant

T = temperature

C_s = solute concentration

C_e = equilibrium concentration of adsorbate in solution

Applying the same basic principles to the Freundlich constants, as the adsorption potential increases, the value of K should also increase, as K is a representation of the energies required for adsorption. Likewise, as the adsorbent concentration range varies, so will the concentration of adsorbate in the solution; thus leading to variation in the adsorption potential and hence a change in K. It should then follow that as the adsorbent range is varied in isotherm experiments, the resulting value of K will differ, potentially across several magnitudes.

Developed originally for air phase adsorption, the Langmuir equation (Eqn 2.6) has been widely adapted for aqueous systems by replacing the original pressure term with a term representing the solute equilibrium concentration.

$$\frac{1}{q_e} = \frac{1}{Q_a^\circ} + \frac{1}{bQ_a^\circ C_e} \quad \text{Eqn 2.6}$$

Where:

q_e = the mass of contaminant adsorbed per unit mass of carbon

Q_a° = maximum adsorption capacity

b = net enthalpy of adsorption

C_e = equilibrium concentration of adsorbate in solution

The Langmuir equation draws its theory from the condensation and evaporation of gas molecules on a solid adsorbent surface (Weber and DiGiano 1996). Condensation takes into account available adsorption sites on the adsorbent surface as well as the rates at

which the adsorbates contact the adsorbent surface. Three basic assumptions are encompassed within the Langmuir equation: (1) adsorption energy is constant throughout the activated carbon surface and is independent of surface coverage (2) there are no interactions between adsorbate molecules or migration of adsorbates to other adsorption sites (3) the carbon surface will only support a monolayer adsorption of the adsorbate (Weber and DiGiano 1996). Two constants are typically reported from the Langmuir model, Q_a° and b . Q_a° represents a condition where the activated carbon surface is covered by a monolayer—i.e. when the surface has reached its capacity according to the assumptions embedded within the Langmuir model. The constant b represents the net enthalpy of adsorption and is described by a ratio of rate constants ($k_{\text{adsorption}}/k_{\text{desorption}}$) on a mole (or mass) unit basis (Chiou 2002, Weber and DiGiano 1996).

Weber and DiGiano (1996) have shown that the Freundlich equation can be represented using the general terms of the Langmuir equation:

$$q_e = Q_{a,g}^\circ (b_g C_e)^n \quad \text{Eqn. 2.7}$$

The subscript g denotes a generalized form of the parameters where $Q_{a,g}^\circ = Q_a^\circ$, while b_g represents the Langmuir constant b and also accounts for site energy. The constant n represents the Freundlich $1/n$ and accounts for the heterogeneity of the surface site energies. With this relationship in mind, the Freundlich K becomes a function of $Q_{a,g}^\circ$ and b_g (Weber and DiGiano 1996):

$$K = Q_{a,g}^\circ b_g^n \quad \text{Eqn. 2.8}$$

The use of isotherms for estimating carbon adsorption is a typical textbook approach that is still widely used by both carbon manufacturers and its users. When used properly, isotherm constants are valuable tools for understanding the adsorption process

of a given system. Isotherm constants relate the equilibrium conditions of a carbon with an adsorbate and indicate both the capacity of the adsorbent for that adsorbate and the strength at which the adsorbate is adsorbed. When isotherm constants are known for a given carbon and target contaminant, the removal of that adsorbate can be predicted and optimized.

While empirically determined isotherm constants are useful, the development of these constants are very time consuming and their applications are limited to the conditions under which they were derived. Ultimately, to accurately represent the adsorption process for a given system, the carbon should be tested within that system. Use of a direct testing method will render a more accurate solution if conditions permit its application; such a method is carbon profiling. Carbon profiling is a valuable concept that has yet to be implemented widely in the water treatment field. By using carbon profiling, the effectiveness of an activated carbon can be observed without relying on an adsorption isotherm. Adsorption isotherms are always performed at equilibrium conditions, accounting for the effects of adsorption and desorption which are inherent in the isotherm equations. Equilibrium conditions are typically not seen on a full scale level—such as in a water treatment facility—and therefore caution should be used when estimating full-scale treatment parameters. It should be noted that the role of kinetics with respect to PAC and GAC are different. For example, in a water treatment facility, PAC would typically be added at the head of the plant (during rapid mix) so that sufficient contact time is allotted for the contaminants to interact with the carbon. Since PAC is smaller than GAC, more time is required for the contaminants to come into initial contact with the carbon. However, because of the greater internal volume of GAC, an

adsorbate may take much longer to reach equilibrium within the carbon matrix than within PAC. The following steps comprise carbon profiling:

1. Obtain a sample of the water to be treated
2. Perform dose removal studies using various amounts of the activated carbon, mimicking the plant's processes: contact times, chlorination, pretreatments, etc.
3. Generate dose removal curves
4. Determine the most effective carbon dose for removing the targeted contaminant, accounting for treatment objective and economics

While carbon profiling circumvents a limitation of adsorption isotherms, e.g., equilibrium conditions, this system still has its limitations. Much like the adsorption isotherms, carbon profiling is not performed at full-scale and is time consuming, as specific conditions must be met and optimized through a series of dose removal studies.

The traditional method of using *previously existing* isotherm constants to develop removal schemes is outdated and inefficient. Parameters rendered from the traditional methods likely do not emulate full-scale processes since isotherms are developed under equilibrium conditions and often the conditions under which the constants were derived are not addressed. Adsorption is dependent on the type of activated carbon used; yet, the isotherm parameters that are typically referenced from the literature are developed with unstated types of carbon (often using nanopure water) and therefore should not be relied upon to determine the adsorption properties of another system. The constants therefore will not reflect the interactions of natural organic matter or any other constituents that may be present in the contaminated water. It should be noted that while adsorption isotherms rely on equilibrium conditions for appropriate application of the isotherm equations, they certainly can be conducted with respect to other aspects of the intended treatment system. In this case, a similar procedure as carbon profiling can be followed

incorporating the treated water and chemicals present in the large scale process, with the condition that equilibrium exists. The decision of using carbon profiling or adsorption isotherms should be carefully considered with respect to the treatment system for which its application is intended.

The development of models that incorporate adsorption system descriptors such as kinetic rates and adsorption isotherm constants are promising tools that can incorporate the effects of unknown mechanisms into predictive adsorption analysis. By applying an empirically based model to an appropriate system, the mechanisms within the adsorption process can be described and accounted for without being fully known. Such a tool, Quantitative Structure Activity Relationships (QSAR), is becoming widely known in the medical and biological fields, but has yet to see a dominating presence in adsorption study. Blum et al. (1994) have developed a QSAR for activated carbon adsorption in water using 363 organic compounds. While this model is noteworthy, it is based on literature-derived constants—which may vary drastically with respect to experimental procedure and analysis—without a sturdy foundation, these models will not accurately portray the adsorption process. Blum et al. show an understanding of this vital point as the authors mention that “...in applying QSAR based on literature data, it is imperative to consider the relevance of the data source to one’s own investigative situation.” However, when used in conjunction with accurately descriptive parameters (i.e., case specific), QSAR can be a powerful tool for understanding activated carbon adsorption. The goal of this study was to investigate the use of adsorption isotherm constants in QSAR and to provide a protocol by which QSAR and adsorption isotherm constants can be effectively used to describe the adsorption process for a given system.

Quantitative Structure Activity Relationships

While adsorption isotherms and carbon profiling are useful in developing adsorbate-adsorbent relationships, they are time intensive and non-specific in regards to adsorbate-adsorbent structural interactions. Relying solely on isotherm relationships and profiling would require extensive laboratory analysis for each individual compound (and condition) that is to be analyzed. The adsorption of a chemical compound to activated carbon is dependent on both the chemical and physical properties of the carbon and the compound. Therefore, by knowing the chemical and physical properties, the adsorbate-adsorbent relationship can theoretically be predicted. Using known parameters to predict the activity of a compound is the focus of QSAR modeling.

Introduced into the field of biology just over four decades ago, QSARs have gained prominence in the both the biological and medical fields (Hansch and Fujita 1995). While QSARs have proven to be powerful tools for the development of numerous chemicals and medications, the adsorption field has yet to develop a robust QSAR for adsorption prediction. Within an adsorption system, a QSAR focuses on predicting the molecular interactions between the adsorbate and adsorbent (Brasquet et al. 1997). For example, in an adsorption system, the independent variable input into the QSAR would be the target adsorbate's intrinsic parameters (e.g., chemical, electronic, steric, hydrophobic properties) while adsorption parameters (e.g., isotherm constants, kinetic rates, etc.) would be the dependent variables. A modeling program based on QSAR interactions is theoretically able to predict the behavior of a given contaminant in the presence of an activated carbon—thus given the independent variable (or variables) the QSAR outputs a calculated dependent variable describing the adsorption system, for instance, an adsorption capacity.

The driving force behind a QSAR is its ability to formulate a relationship between two compounds through the use of tools such as regression analysis or pattern recognition (Lloyd 2002). Regression analysis is commonly based on a partial least squares projection, which is a multivariate statistical method; while pattern recognition is usually performed by artificial neural networks (ANNs). ANNs mathematically mimic the pattern recognition properties within the human brain, using parallel processing and weighted connections, which store the problem solving knowledge. These weighted connections are trained to specific situations through repeated exposure and comparison to truth data sets (PNNL 1997). The key advantage of the QSAR model is that a known equation or the exact pathway of reactions is not necessary. A good QSAR model can rely solely on the structural and derived experimental characteristics of the targeted compounds to predict their activity. Additionally, unknown mechanisms could ultimately be disclosed through the analysis of how substituents impact QSAR correlations.

Within the development of a QSAR, diverse parameterization is essential. Having a robust set of carefully chosen parameters increases the probability of unlocking a description of the mechanisms involved in a system. Three key components of a QSAR are: hydrophobic, electronic, and steric factors (Hansch and Fujita 1995). Table 2.3 lists various hydrophobic, electronic, steric and chemical properties that are commonly used in QSAR analysis.

While diverse parameterization is essential to a QSAR, the selection of these parameters is crucial for the healthy development of the QSAR. A primary weakness in QSAR construction is often the selection of the parameters (Hansch and Fujita 1995). Poor parameter selection can lead to collinearity problems (i.e., when two parameters are

directly affected by each other) thus creating false indications of correlation. Also, it is essential that parameters cover a wide range of space—i.e., the compound training set should be carefully selected so that multiple spectrums of the parameter scale are represented. This idea will be more fully developed in the Methods section with the introduction of Craig plots.

Table 2.3. Example of Parameters Commonly Used in QSAR Development.

Hydrophobic Properties	Π , LOG K_{OW}
Electronic Properties	σ_{Ind} , Resonance, Field Effects
Steric Properties	Molar Refractivity, Molal Refraction, E_s
Chemical/Physical Properties	Boiling Point, Melting Point, Density, Molecular Weight, Aqueous Solubility, Enthalpy, Vapor Pressure

Where σ_{Ind} represents inductive effects described by the Hammett Constant and E_s represents Taft's steric factor.

An important aspect of QSAR development that should be addressed is the selection of the training set and the specific parameters that are chosen for the correlations. There are two basic approaches to QSAR that are seen in the literature, the first approach, developed by Hansch, is an approach favored by chemists in which the components within the QSAR are intellectually analyzed with respect to their chemical activity (Hansch and Fujita 1995). The second approach, described by Wold and Dunn (1983), is based on the statistical analysis of the components for QSAR development. Certainly, while the statistical method can prove to be insightful in some instances, a strong QSAR should be constructed with a vast understanding of the components in the system in order to avoid complications such as parameter collinearity, uneven spread of parameters, and the application of implausible mechanisms. In addition, it is also

important to consider the functionality of the compounds that are within the training set; only structural changes in functional groups that can be accurately represented by available parameters should be selected (Hansch and Fujita 1995).

This present work approaches QSAR development for the adsorption process in three improved ways in comparison to past studies:

1. Dependent variables used are not from the literature, but were derived experimentally within this study
2. Degree of statistical analyses performed
3. Robust spread of parameterization

As was shown in Table 2.2, empirically derived isotherm constants selected haphazardly from the literature can be detrimental to a study. The electronic, steric, hydrophobic, and chemical parameters used within this study were not experimentally derived within the scope of this work, yet each of these parameters has been well documented within the scientific community and has strict procedures for their procurement. However, in the case of deriving the isotherm constants, many variables are present: the type of carbon used, how it was activated, the conditions under which the carbon was kept, how it was added to the system, the pH of the water in the system, the solutes used within the system, the definition of equilibrium for that system, the concentrations of carbon and solute that were used, etc. In order to normalize these variables, each of the isotherm constants used within this system was derived under uniform experimental conditions.

In order to measure the quality of the QSAR correlations, several statistical methods were used: R^2 , adjusted R^2 , standard error, F-Ratio, as well as Q^2 (a tool that measures the predictability of a correlation). This combination of statistical analyses is more diverse than other adsorption QSAR that are listed in the literature and therefore

provides a more rigorous analysis of the correlations. For example, the study of Brasquet and coworkers (1997) refers to R^2 values, but offers no other statistical validation for their resulting correlation.

As was mentioned previously, the spread of parameters is an important concept in the selection of the training set. For this study, compounds demonstrating a wide range of steric, electronic, hydrophobic, and chemical properties were selected. This variety of parameterization is essential to aid in the identification of mechanisms involved in the correlations.

CHAPTER 3 MATERIALS AND METHODS

Isotherm Methods

Adsorption isotherms were developed by adding a known concentration of contaminant, 100- $\mu\text{g/L}$, to distilled deionized (DDI) water at a pH of 5.5 ± 1.5 , the variation is due to the use of unaltered DDI water. The desired amount of powdered carbon was weighed and dried overnight at 105°C . After cooling the carbon in a desiccator, a carbon stock slurry (10,000-mg/L) was prepared by combining the carbon and DDI water by mixing on a stir plate. The slurry was stored in a desiccator at room temperature and mixed on a stir plate before each application. Isotherms were created for each target contaminant using the following concentrations of carbon: 1, 3, 5, 10, 15, 25, 50, and 75-ppm. The desired amount of carbon slurry was added to a 100-mL or 50-mL SGE gas tight Luer Lock syringe containing DDI water. The experimental data was collected for each contaminant individually using powdered Calgon F400 activated carbon with 100- $\mu\text{g/L}$ solutions of either benzene or a chosen monosubstituted benzene (shown in Table 3.1). For each run, the desired amount of contaminant was added from a stock solution to the 100-mL syringe, yielding a final volume of 100-mL. The syringe was then mixed end over end on a rotator for 2 hours to 6 hours, depending on equilibrium conditions for that target contaminant. Equilibrium conditions were determined through the development and analysis of dose removal curves over various times. The condition of equilibrium was considered achieved when the rates of adsorption and desorption appeared to be at a steady state. After mixing, the samples

were filtered into VOC vials using 25-mm Fisherbrand nylon syringe filters which were sized to allow for only the PAC to be removed (both 0.20- μm and 0.45- μm were used, depending on their availability). Samples were sealed with Teflon septa caps and stored at 4°C until analysis. All samples were analyzed with a Saturn 2100T GC/MS using a Supelco VOCOL™ Fused Silica capillary column with a Supelco SPME 75- μm CARBOXEN™ PDMS fiber, utilizing an oven temperature program that holds at 40°C for 2 minutes and then climbs to 210°C at a rate of 8°C/min. Each isotherm was replicated. Only data which produced a RSD of 20% or less were accepted.

Table 3.1. Target Contaminants Used in Isotherm and Kinetic Studies.

Target contaminants
Benzene
Isopropylbenzene
n-butylbenzene
t-butylbenzene
Isobutylbenzene
Nitrobenzene
Aniline
Benzaldehyde
Fluorobenzene
Chlorobenzene
Bromobenzene
Iodobenzene
Phenol

Development of Isotherm Data

Target Contaminants

Benzene

Benzene is a six carbon structure bonded in a cyclic formation with three resonating double bonds. The benzene ring is one of the defining characteristic of

aromatic compounds. Due to its cyclic structure, and despite its unsaturated state, benzene is a stable compound that will undergo primarily substitution reactions, such as H₂ annealing (Ouellette 1998). H₂ annealing is a critical step during steam activation which modifies the structure of the benzene rings in the graphitic carbon sheets, creating the porosity of the carbon. The electron orientation of benzene drives its unique reaction mechanisms. As was shown in Figure 2.2, the benzene ring experiences a delocalization of electrons, where the carbon atoms have three sigma bonds—two bonding with the adjacent carbon atoms and the third is bonded with a hydrogen atom. The remaining electron gives the delocalization characteristic as it orbits above and below the basal plane in a 2p orbital (Ouellette 1998). For this study, benzene has been selected as the parent compound for the QSAR training set.

Substituted benzenes

Phenol is an aromatic compound consisting of a hydroxyl functional group bonded via a sp² hybridization to a carbon atom in the benzene ring. Adding a functional group to the benzene ring can result in activating or deactivating the reactivity of the ring. Because of the addition of the hydroxyl group, phenol is a strongly activating compound—i.e, it increases the reactivity of the benzene ring. In contrast, a benzene ring substituted with a chloro- or nitro- group causes the benzene ring to be less reactive. Activating groups are more reactive and donate electrons, therefore increasing the electron density of the benzene ring. Deactivating groups are less dense (therefore less reactive) due to their tendency to attract—or withdraw electrons (Ouellette 1998). For example, in the reaction of an activating (electron donating) group with an arene (aromatic hydrocarbon), the electrons in the 2p orbital are attracted towards the arene, thus creating an increase in electron density at the benzene ring, which in turn will make

the ring more reactive (Carey 2003). In the case of phenol, which acts as a weak acid, the presence of an electron-withdrawing group on the carbon surface will cause a decrease in electron density at the benzene ring and result in a more stable, more acidic, and less negative compound. Contrastingly, in the presence of an electron-donating group, the phenol will become less acidic (Ouellette 1998). When a phenol is oxidized, it becomes a quinone—a carbon ring having two ketone (carbonyl carbon atom bonded to two other carbons) groups (Ouellette 1998). In the case of activated carbon adsorption, the functional groups present on the carbon surface will contribute to the nature of the reaction between the surface and the adsorbate.

Freundlich Isotherms

Freundlich isotherms were developed using the linearized Freundlich equation:

$$\log q_e = \log K + \frac{1}{n} \log C_f \quad \text{Eqn 5}$$

Where:

q_e = the mass of contaminant adsorbed per unit mass of carbon

K = adsorption capacity, Freundlich constant

n = strength of adsorption, Freundlich constant

C_f = final concentration of contaminant

The term q_e was determined by taking the difference in the initial and final concentrations of the target contaminant in each isotherm run and dividing it by the mass of activated carbon added to the system. All target concentration changes were attributed to adsorption to the activated carbon. The log of q_e was graphed versus log C_f to develop the Freundlich isotherm plot. A linear trendline was added to the plot using Microsoft

Excel from which the slope and y-intercept were determined. The slope represents the value for $1/n$ and the y-intercept represents the value taken as K.

Langmuir Isotherms

The Langmuir isotherm parameters were found using a linearized form of the Langmuir equation as was shown in Eqn 4. A graphic was created by plotting $\frac{1}{q_e}$ versus $\frac{1}{C_e}$. Using Microsoft Excel, a linear trendline was added from which the slope and y-intercept were taken. The slope represents the value $\frac{1}{bQ_a^\circ}$ and the y-intercept is taken as $\frac{1}{Q_a^\circ}$. The values for Q_a° and b were then determined.

Kinetic Study Methods

Kinetic runs were completed individually for each compound shown in Table 3.1 using powdered Calgon F400 activated carbon. For each run, an aliquot of F400 carbon slurry (prepared as stated above) was added to a 50-mL SGE gas tight Luer Lock syringe containing 50-mL of DDI water at a pH of 5 ± 1 , resulting in a final carbon concentration of 20-ppm. Using a Hamilton 1 to 10- μ L syringe the desired target contaminant was added from a stock solution to the 50-mL syringe, yielding a final contaminant concentration of 100-ppb. The 50-mL syringe was then rotated end over end. Kinetic studies were performed for 3, 5, 10, 15, 30, and 60 minutes. Following each kinetic run, all samples were filtered into VOC vials using 25-mm Fisherbrand 0.20 or 0.45- μ m nylon syringe filters. Samples were sealed with Teflon septa caps and stored at 4°C until analysis. All samples were analyzed with a Saturn 2100T GC/MS using a Supelco VOCOL™ Fused Silica capillary column with a Supelco SPME 75- μ m CARBOXENTM

PDMS fiber, utilizing an oven temperature program that holds at 40°C for 2 minutes and then climbs to 210°C at a rate of 8°C/min. Each kinetic run was replicated. Only data points that were sufficiently reproducible, i.e., those which produced a RSD value of 20% or lower, were accepted.

Development of Kinetic Equations

The time for each compound to reach 86% removal with F400 was incorporated into the QSAR as a kinetic parameter. The value of 86% was selected as it appeared as a removal point common to each of the compounds in the training set. The time to 86% removal was interpolated from a trendline created in Microsoft Excel from a graph of percent removal verses time.

QSAR Development

The first essential step in the development of the QSAR was the selection of a suitable training set. For the parent compound, benzene was selected, and monosubstituted functionality drove the selection of the substituents. For this study it was desired to use single substitutions within the training set to investigate the impact of a sole functional group on the adsorption system. In the selection of monosubstituted benzenes it is important to consider only the addition of functional groups that are well parameterized—i.e., that can be described by an available parameter within the QSAR. Non-descriptive groups cannot be well represented in the QSAR and therefore should be avoided in the selection of a training set. It is also important to include compounds that produce a wide spread of parameter values to ensure that the training set is representing a good range of electronic, steric, hydrophobic, and chemical properties. A diverse spread of parameter values adds robustness to the QSAR process and can be illustrated graphically using a Craig plot (Lindner et al. 2003). Figure 3.1 demonstrates the spread

of parameter values for both π and σ_{Ind} . It is important to note the spread of the data points throughout the quadrants, as the degree of spreading increases, so does the range of parameterization.

For this study, monosubstituted benzenes were selected to demonstrate a large range of steric, electronic, hydrophobic, and chemical parameterization. Table 3.2 illustrates the values of these parameters for the training set.

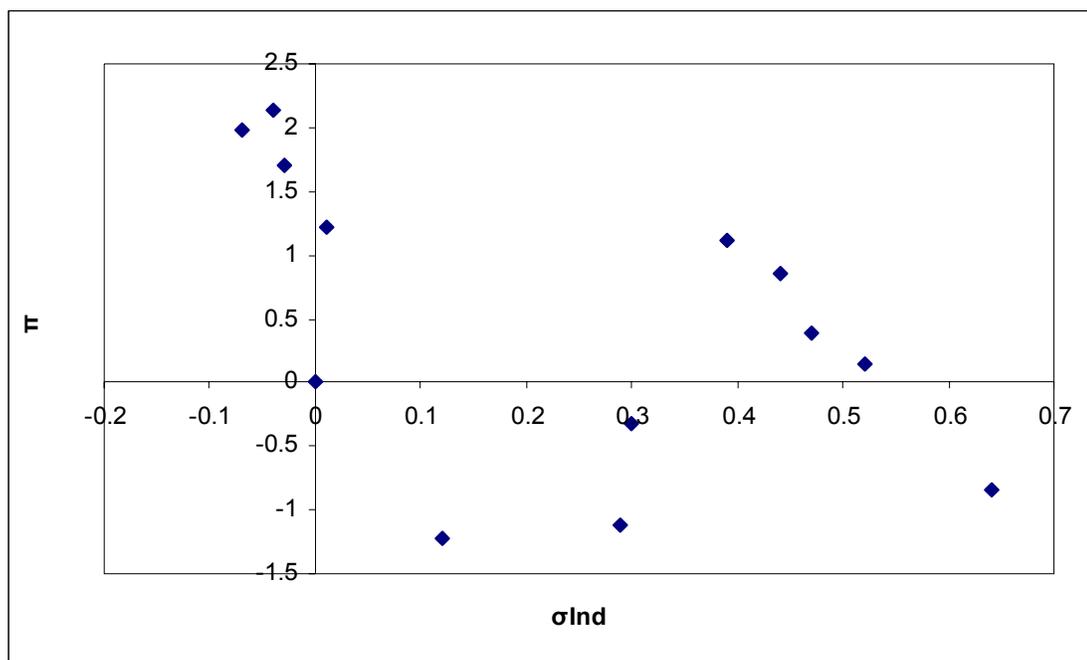
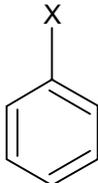


Figure 3.1. Craig Plot Illustrating the Parameter Spread of a Hydrophobicity Constant (π) and the Hammett Constant (σ_{Ind}).

After the training set was chosen, each parameter was examined for collinearity.

When plotted, any parameters that showed a linear correlation of $R^2 \geq 0.4$ were considered collinear and were not used in multilinear regression analysis.

Table 3.2. Selected Parameters Used in the QSAR Training Set (CRC Handbook of Chemistry and Physics 1999, Physical Properties of Chemical Compounds 1955, MOPAC 2004).

Monosubstituted Benzene 	Electronics Descriptors		Sterics Descriptors		Hydrophobicity Descriptors		Physical Properties		
	σ_{Ind}	ACCP	MR	Taft E_s	Log K_{ow}	π	MW (g/mole)	C_{aq} (mass %)	TOTL (Å)
Fluorobenzene (FB)	0.52	-0.115	0.09	-0.55	2.27	0.14	96.1	0.154	5.21
Chlorobenzene (ClB)	0.47	-0.103	0.6	-0.97	2.84	0.39	113	0.0387	5.55
Bromobenzene (BrB)	0.44	-0.097	0.89	-1.16	2.99	0.86	157	0.0387	5.7
Iodobenzene (IodoB)	0.39	-0.099	1.39	-1.62	3.28	1.12	204	0.0387	5.8
Nitrobenzene (NB)	0.64	0.039	0.74	-2.52	1.85	-0.85	123	0.0193	6.07
Aniline (Ani)	0.12	-0.169	0.54	-0.61	0.9	-1.23	93.1	0.21	5.84
Phenol (Ph)	0.29	-0.145	0.28	-0.55	1.48	-1.12	94.1	3.38	5.64
Benzaldehyde (Bzal)	0.3	-0.066	0.69	---	1.48	-0.32	106	8.66	7.02
Isopropylbenzene (IsoPB)	0.01	-0.106	1.5	-1.71	3.66	1.22	120	0.3	7.18
n-butylbenzene (nBB)	-0.04	-0.11	1.96	-0.16	4.26	2.13	134	0.0056	9.71
Isobutylbenzene (IsoBB)	-0.03	-0.107	1.96	-2.17	4.01	1.7	134	0.0015	8.19
t-butylbenzene (tBB)	-0.07	-0.107	1.96	-2.78	4.11	1.98	134	0.001	7.27
Benzene (Benz)	0	-0.102	0.1	0	2.13	0	78.1	0.178	4.97

Where σ_{Ind} represents the inductive effects described by the Hammett Constant, ACCP represents the charge of the para-carbon on the functional group, MR represents molar refractivity, E_s represents Taft's steric factor, $\log K_{\text{ow}}$ is the octanol-water partitioning coefficient, π represents the hydrophobicity of the compound, MW is the molecular weight, C_{aq} is the aqueous solubility in water, and TOTL is the total length of the compound, calculated by the bond lengths of the compound in the longest direction.

Parameters representing intrinsic properties of the compounds (e.g., hydrophobic, electronic, steric, chemical, physical properties) were incorporated into the QSAR as independent variables, while the parameters that were experimentally derived in this adsorption system (e.g., isotherm constants) were incorporated as dependent variables using SPSS 12.0 software (SPSS., Inc., Chicago, IL, USA). Classical QSAR procedure, as developed by Hansch, was followed for the development of correlations (Hansch and Fujita 1995). Linear, polynomial, and multilinear correlations were employed to describe the data.

Correlations that resulted from the QSAR analysis had to meet a series of stringent statistical criteria to be considered valid:

1. No collinearity of independent variables (for MLR correlations)
2. $R^2 \geq 0.7$
3. F-Ratio values must meet a 95% confidence limit
4. Standard error considered
5. Q^2 determined for goodness of predictability

Condition 1 is only applicable in regards to multi-variable analysis. Independent variables were linearly correlated; variables that produced a R^2 value of 0.4 or higher were considered collinear and were excluded from the QSAR analysis. Conditions 2 and 3 were helpful in identifying poor correlations. The F-Ratio was determined using the number of compounds in each correlation (k) and two total data sets (n), observed and calculated values. The degrees of freedom were calculated for the variance between ($v_1 = n-1$) and within ($v_2 = (n*k)-n$) the data sets and compared to an upper 5% distribution table to determine the significance of the observed and calculated data sets. As the F-Ratio values become larger than the F-distribution values, the data sets are considered to be more similar. Therefore, high F-Ratio values indicate the predicted data from the

QSAR correlation is in agreement with the observed data. The standard error (Condition 4) represents fluctuations in the sampling set and can be seen in the form of residuals in the regression lines. Clearly, low values of standard error reflect better correlations within the training set.

Condition 5 is an essential step in measuring the validation of the correlations that result from the QSAR process. When performing a Q^2 analysis, it is ideal to introduce a new compound to test the predictability of the QSAR correlation; however if the introduction of an additional compound is not feasible, an alternative method, roughly referred to as the “take one out” method, will suffice. For this alternative method, one compound from the training set is removed and the correlations are recalculated. The new correlations are then used to test the ability of the QSAR correlation to predict the value of the compound that was removed. This process is repeated for each compound within the training set and equation 3.1 is used to calculate the value of Q^2 :

$$Q^2 = 1 - \frac{\sum(y_{i,observed} - y_{i,predicted,new})^2}{\sum(y_{i,observed} - \bar{y}_i)^2} \quad \text{Eqn 3.1}$$

While no set limit has been established for Q^2 values, larger values indicate a better ability for the QSAR correlation to predict the observed values within the given system. Ideally the Q^2 should be close to the value for the adjusted R^2 , thus indicating that the new correlation did not cause a significant shift in the predicted data. For this study a difference of 0.2 between the Q^2 and adjusted R^2 was considered the maximum limit for variation. Similar, yet less stringent, statistical procedures as those outlined here have been recommended by Eriksson and coworkers (Eriksson et al. 2003).

CHAPTER 4 MANUSCRIPT

Introduction

The use and production of toxic synthetic aromatic compounds in applications such as the synthesis of rubber, paint solvents, insecticides, detergents, fragrances, fuels, and dry cleaning (USEPA 2002, USEPA 1995) continue to increase in our society, and as a result of their increased demand, the potential for introduction of these synthetic aromatic compounds into our environment is escalating. The contamination of water, air, and soils from exposures such as accidental spills, inappropriate disposal, and byproduct formation, will continue to exacerbate the condition of our surroundings without sufficient intervention and treatment. Given the increased exposure of the public to these chemicals, environmental and health impacts such as toxicity, carcinogenicity, mutagenicity, and teratogenicity in humans and animals, aquatic toxicity, and degradation of potable water quality are also anticipated to increase. To circumvent such threats, treatment methods must be established to remove synthetic aromatics from air and water. It is well known that activated carbon is capable of removing aromatic compounds from contaminated water.

Traditionally, the removal of volatile organic compounds (VOCs), a class of compounds in which many aromatics belong, from water is accomplished through the use of activated carbon and/or aeration. Activated carbon and packed tower aeration are the USEPA-recommended forms of treatment for the removal of synthetic organic contaminants, such as benzene and chlorobenzene, from drinking water (USEPA 2002,

USEPA2 2002). The most efficient method of aeration is by means of a packed tower. This system is effective, yet is rarely sufficient to achieve low maximum contaminant level (MCL) standards. It should also be noted that in cooler climates, the use of the aeration towers becomes limited—due to possible ice formation and lower kinetics (Hammer and Hammer 2001). While the efficiency of a packed tower can be optimized, this process requires an increase in tower diameter, high surface area packing materials, as well as increased tower height (Noll 1999). For some compounds these adjustments can prove costly or impossible. In order to ensure MCL regulations are met, aeration is usually coupled with activated carbon.

Activated carbon has shown to be an extremely efficient, cost effective adsorbent. As activated carbon adsorption can be reversible, captured materials can potentially be desorbed and salvaged. Activated carbon can effectively adsorb VOCs in both gaseous and aqueous media. The general mechanisms of adsorption are physical adsorption and chemisorption. Physical adsorption is driven by weak intermolecular forces, such as Van der Waals forces. It is important to note that physical adsorption does not entail the formation of a chemical bond, i.e., there is no exchange of electrons. Due to the lack of chemical bonding, physical adsorption is readily reversed (desorption). During chemisorption, a chemical bond results, thus making desorption much more difficult.

The surface of activated carbon is generally non-polar, thus facilitating the adsorption of non-polar hydrocarbons, such as benzene, n-butylbenzene, and nitrobenzene, from a polar aqueous media, such as water. The functionality of a given activated carbon is highly dependent on its carbonaceous precursor and its heat treatment. Therefore, different types of activated carbon will adsorb contaminants differently;

hence, the efficiency is variable. Likewise, the same activated carbon will have unique adsorption relationships with varying contaminants, i.e., the efficiency will vary according to the chemical and physical characteristics of the adsorbate.

Activated carbon is currently an industry standard for the removal of organic contaminants in air and water (USEPA 2002). Although industry and the USEPA are confident in the capacity of carbon to remove organics, a clear method of how this removal is accomplished is not known. Currently, there exists a disconnect between carbon scientists and carbon users (e.g., treatment plant operators, engineers). For example, in academia, it is commonly taught that activated carbon adsorption increases as solubility decreases (the Lundelius Rule). However, in the case of MIB and phenol, despite their similar size, MIB is much less soluble in water than MIB (see table 4.1), yet, as is recognized by water treatment professionals, phenol is more readily adsorbed by carbon.

Table 4.1. Size and Aqueous Solubility of MIB and Phenol (Perry and Green 1997, Whelton 2001).

Compound	Size (Å)	Aq. Solubility (mg/L)
MIB	≈6	194
Phenol	≈6	82,000

Obviously, one cannot universally state that adsorption increases as solubility decreases; another mechanism (i.e., surface chemistry) may be influencing the adsorption of these two compounds. This creates a problem. Exceptions to widely accepted adsorption trends, though generally well known among carbon scientists, rarely seem to enter into the field of actual carbon applications. The knowledge base created for future engineers and scientists in academia is carried with these professionals into the work

field, into consulting firms and municipalities. These professionals in turn continue to spread misconceptions to carbon users, such as treatment plant designers and operators. This lack of communication between the carbon scientists and users results in the improper use and constricts the utilization of activated carbon in the field. The result is a cookbook method of carbon dosing in treatment plants. To alleviate this black-box method of carbon dosing, various relationships are currently being examined between the adsorbate and the adsorbent. Two of these relationships are isotherms and Quantitative Structure Activity Relationships (QSAR). Once a carbon-contaminant relationship is established, a predictive model can be produced. This model could be a powerful tool for assisting the carbon user—helping to optimize the use of activated carbon and bridging the gap between carbon science and application. The quest for a unified adsorption theory may be surrendered for the use of such correlations, which can optimize the use of activated carbon without requiring a comprehensive understanding of the mechanisms which are involved. Ultimately, the development of such correlations may lead to an enhanced knowledge of the adsorption process. An enhanced understanding of adsorption mechanisms will lead to reduced experimentation, time, and cost of activated carbon selection.

The overall short term goal of this project is to develop a protocol for QSAR analysis of activated carbon. In order to develop such a protocol, this study will examine the predictability of QSAR for a training set of monosubstituted benzenes using Freundlich and Langmuir isotherm constants as well as kinetic rate data as dependent variables. To allow for a greater focus on the changing functionality of the training set, only one activated carbon will be used in this initial study. Other intrinsic short term

goals for this work include: examining the predictability of QSAR for this training set, determining the most descriptive isotherm equation for this training set and carbon (i.e., Freundlich or Langmuir), and an examination of the impact of kinetic rates.

Because of its widespread use in the literature, Calgon Filtrasorb 400 (F400) has been selected as the activated carbon for this study. Selected physical properties of F400 are shown in Table 4.2.

Table 4.2. Selected Physical Properties of F400 (Karanfil and Kilduff 1999).

Surface Area (m ² /g)	Ave. Pore Radius (Å)	Pore Volume (cm ³ /g)	Percent Surface Area in Pores < 20 Å	Percent Surface Area in Pores 20- 100 Å	Percent Surface Area in Pores 100- 200 Å	Percent Surface Area in Pores > 200 Å
948	12	0.566	83.7	15.0	0.90	0.40

To estimate the adsorption capability of an activated carbon, Freundlich or Langmuir isotherms are commonly developed. However, according to Weber and DiGiano (1996) : “Despite the sound theoretical basis of the Langmuir, BET, and Gibbs models, these isotherms often fail to describe experimental solution sorption data adequately.” Due to its empirical derivation, it is proposed that the Freundlich isotherm equation (Eqn 4.1) may better describe the adsorption process, since it innately accounts for the heterogeneous surface energy distribution of activated carbon.

$$q_e = KC^{\frac{1}{n}} \quad \text{Eqn 4.1}$$

Where:

q_e = the mass of contaminant adsorbed per unit mass of carbon

K = “adsorption capacity”, Freundlich constant

C = concentration of the adsorbate in solution at equilibrium

$1/n$ = strength of adsorption, Freundlich constant

Developed originally for air phase adsorption, the Langmuir equation (Eqn 4.2) has been widely adapted for aqueous systems by replacing the original pressure term with a term representing the solute equilibrium concentration.

$$\frac{1}{q_e} = \frac{1}{Q_a^\circ} + \frac{1}{bQ_a^\circ C_e} \quad \text{Eqn 4.2}$$

Where:

q_e = the mass of contaminant adsorbed per unit mass of carbon

Q_a° = maximum adsorption capacity

b = net enthalpy of adsorption

C_e = equilibrium concentration of adsorbate in solution

The Langmuir equation draws its theory from the condensation and evaporation of gas molecules on a solid adsorbent surface (Weber and DiGiano 1996). Condensation takes into account available adsorption sites on the adsorbent surface as well as the rates at which the adsorbates contact the adsorbent surface. Three basic assumptions are encompassed within the Langmuir equation: (1) adsorption energy is constant throughout the activated carbon surface and is independent of surface coverage (2) there are no interactions between adsorbate molecules or migration of adsorbates to other adsorption sites (3) the carbon surface will only support a monolayer adsorption of the adsorbate (Weber and DiGiano 1996).

While adsorption isotherms are useful in developing adsorbate-adsorbent relationships, they are time intensive and non-specific in regards to adsorbate-adsorbent structural interactions. Relying solely on isotherm relationships would require extensive laboratory analysis for each individual compound (and condition) that is to be analyzed. The adsorption of a chemical compound to activated carbon is dependent on both the chemical and physical properties of the carbon and the compound. It should then follow that by knowing the chemical and physical properties, the adsorbate-adsorbent relationship can theoretically be predicted. Using known parameters to predict the activity of a compound is the focus of QSAR modeling. By applying an empirically based model to an appropriate system, the mechanisms within the adsorption process can be described and accounted for without being fully disclosed. QSAR is becoming widely known in the medical and biological fields, but has yet to see a dominating presence in adsorption study (Hansch and Fujita 1995). Blum et al. (1994) have developed a QSAR for activated carbon adsorption in water using 363 organic compounds. While this model is noteworthy, it is based on literature-derived constants—which may vary drastically with respect to experimental procedure and analysis—without a sturdy foundation, these models will not accurately portray the adsorption process. Table 4.3 illustrates the discrepancies which can be found in the literature.

Table 4.3. Reported Values of Freundlich K for Benzene.

K	Source
0.12602	Noll 1999
1.0	Dobbs and Cohen 1980
41.7	Loll et al. 2004

Blum et al. (1994) show an understanding of this vital point as the authors mention that “...in applying QSAR based on literature data, it is imperative to consider the relevance of the data source to one’s own investigative situation.” However, when used in conjunction with accurately descriptive parameters (i.e., case specific), QSAR can be powerful tools for understanding activated carbon adsorption.

In recent years, carbon scientists have begun to examine the potential of QSAR analysis for gaining insight into the method(s) of activated carbon adsorption (Blum et al. 1994, Brasquet et al. 1997). To date, no compelling methodologies have been established for developing a protocol for QSAR-adsorption analysis. The studies examined in the literature typically utilize literature derived isotherm constants which are extracted from a variety of sources. This method of selecting parameters can become somewhat haphazard, as many sources use different experimental conditions (and different carbons) when developing these isotherm constants. To avoid this inefficient approach, this study has experimentally derived all dependent variables—under standardized testing conditions—to create uniformity between the compounds in the training set. A uniform approach to parameter development will lead to more reliable QSAR correlations. In addition to carefully developing the dependent variables, this study includes an array of electrical, steric, hydrophobic, and physical parameters as independent variables to more accurately describe and investigate the role of the adsorbate in the adsorption process. Also in contrast to most QSAR-adsorption studies present in the literature, this study implements a series of rigorous statistical tests before a correlation is accepted.

It is the hypothesis of this study that the development of a robust QSAR will enhance the understanding of the adsorption process of F400 with this given training set

of monosubstituted benzenes. Ultimately, an enhanced understanding of the adsorption process will lead to an optimized use of activated carbon.

Experimental

Adsorption Isotherms

Adsorption isotherms were developed by adding a known concentration of contaminant, 100- $\mu\text{g/L}$, and activated carbon to distilled deionized (DDI) water at a pH of 5.5 ± 1.5 , the variation is due to the use of unaltered DDI water. The experimental data was collected for each contaminant individually using powdered Calgon F400 activated carbon, which was dosed as a slurry so that accurate quantities could be developed, with 100- $\mu\text{g/L}$ solutions of each compound in the training set (see Table 4.4). The system was mixed end over end in a gastight syringe on a rotator until equilibrium was reached. After mixing, samples were filtered into VOC vials using 25-mm Fisherbrand nylon syringe filters which were sized to allow for only the PAC to be removed (both 0.20- μm and 0.45- μm were used, depending on their availability). Samples were sealed with Teflon septa caps and stored at 4°C until analysis. All samples were analyzed with a Saturn 2100T GC/MS using a Supelco VOCOL™ Fused Silica capillary column with a Supelco SPME 75- μm CARBOXEN™ PDMS fiber, utilizing an oven temperature program that holds at 40°C for 2 minutes and then climbs to 210°C at a rate of 8°C/min. Each isotherm was replicated and was only considered valid if the RSD was less than 20% and the R-square value was 0.70 or greater.

Isotherm data was formatted using the Freundlich and Langmuir isotherm equations (Eqn 4.1 and 4.2). The Freundlich and Langmuir constants were extracted from the graphical interpretation of the data for each compound in the training set. The

graphics in Figure 4.1 demonstrate (A) a dose removal curve and (B) a graphical representation of the Freundlich isotherm using n-butylbenzene as an example.

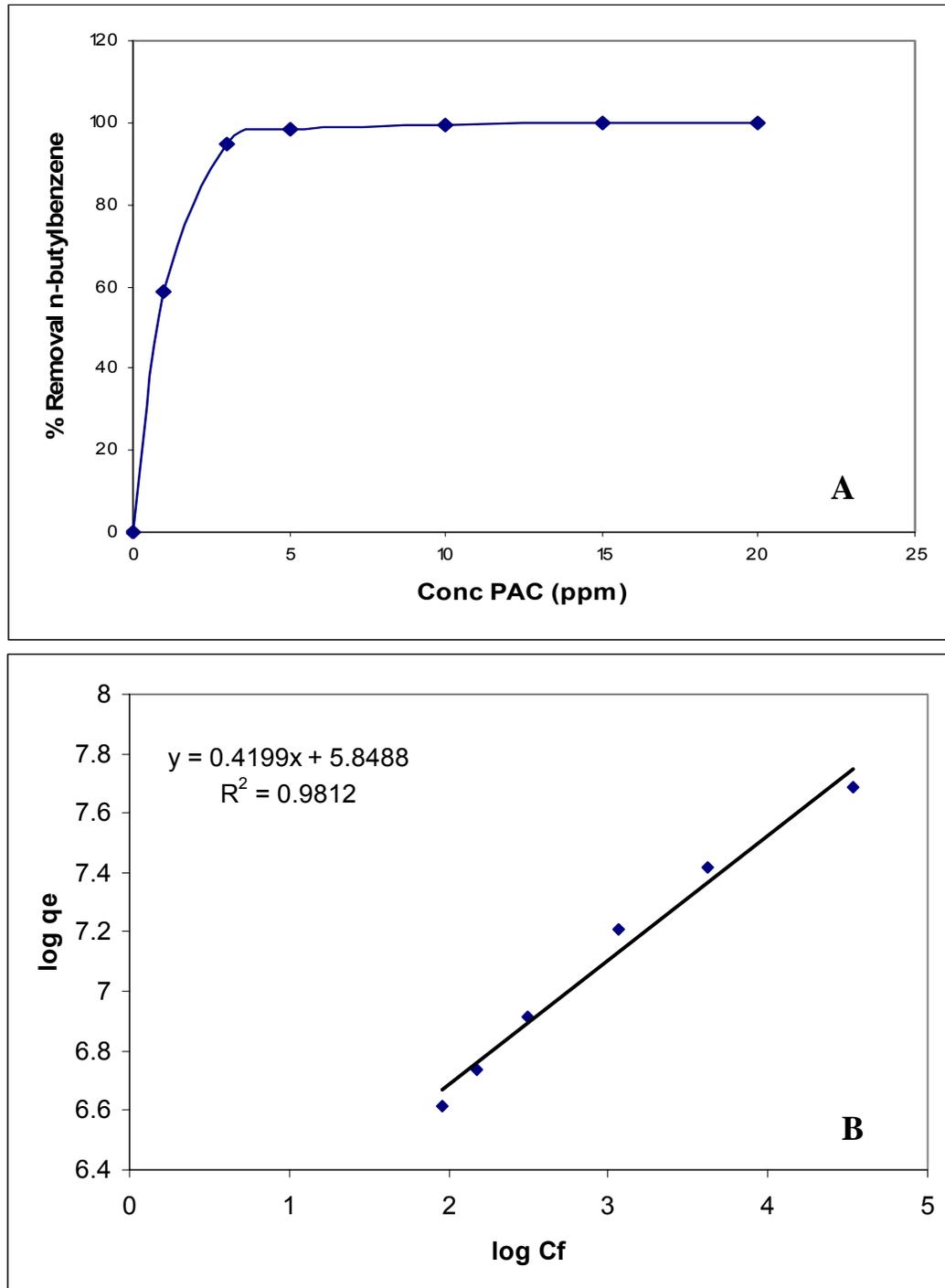


Figure 4.1. Example of Isotherm Development. (A) Dose removal curve for Isobutylbenzene and Calgon F400 Activated Carbon. (B) Freundlich Isotherm of Isobutylbenzene and Calgon F400 Activated Carbon.

Kinetic Data Collection

Kinetic studies proceeded in a similar manner, taking each contaminant individually at a concentration of 100- $\mu\text{g/L}$ with F400 at a constant concentration of 20- mg/L . Kinetic data was collected in the same manner as the isotherm data, with the exception that sample run durations were: 3, 5, 10, 15, 30, and 60 minutes. Following each kinetic run, the samples were filtered, stored, and analyzed using the same methods as described for the equilibrium samples. Kinetic data was incorporated into the QSAR by determining the time for F400 to remove 86% of the target contaminant. Experimentally derived values for this kinetic parameter ($\log t$) and selected isotherm constants are shown in Table 4.4.

Table 4.4. Experimentally Derived Values for $\log K$, $\log Q$, and $\log t$.

Compound	$\log K$	R^2	$\log Q$	R^2	$\log t$	R^2
Fluorobenzene	5.38	0.91	1.01	0.88	1.17	0.94
Chlorobenzene	5.34	0.99	1.19	0.95	1.08	0.94
Bromobenzene	5.38	0.99	1.33	0.93	1.03	0.98
Iodobenzene	5.34	0.99	1.35	0.93	1.20	0.77
Nitrobenzene	5.05	0.95	1.43	0.96	0.88	0.98
Aniline	4.38	0.97	1.26	0.99	1.78	0.93
Phenol	3.64	0.90	1.58	0.95	---	---
Benzaldehyde	4.82	0.71	---	---	0.75	0.69
Isopropylbenzene	5.38	0.92	1.53	0.87	1.06	0.85
n-butylbenzene	4.62	0.92	2.05	0.94	0.45	0.92
Isobutylbenzene	5.00	0.81	2.80	0.94	-0.01	0.96
t-butylbenzene	4.25	0.83	2.89	0.81	0.94	0.96
Benzene	4.94	0.89	0.92	0.96	1.76	0.91

Establishment of QSAR

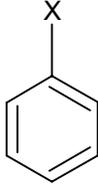
The first essential step in the development of the QSAR was the selection of a suitable training set. For the parent compound, benzene was selected, and monosubstituted functionality drove the selection of the substituents. For this study it was desired to use single substitutions within the training set to investigate the impact of a sole functional group on the adsorption system. In the selection of monosubstituted

benzenes it is important to consider only the addition of functional groups that are well parameterized—i.e., that can be described by an available parameter within the QSAR. Non-descriptive groups cannot be well represented in the QSAR and therefore should be avoided in the selection of a training set. It is also important to include compounds that produce a wide spread of parameter values to ensure that the training set is representing a good range of electronics, sterics, hydrophobic, and chemical properties.

For this study, monosubstituted benzenes were selected to demonstrate a large range of steric, electronic, hydrophobic, and chemical parameterization. Table 4.5 illustrates the values of these parameters for the training set.

After the training set was chosen, each parameter was examined for collinearity. When plotted, any parameters that showed a linear correlation of $R^2 \geq 0.4$ were considered collinear and were not used in multilinear regression analysis. Parameters representing intrinsic properties of the compounds (e.g., hydrophobic, electronic, steric, chemical, physical properties) were incorporated into the QSAR as independent variables, while the parameters that were experimentally derived in this adsorption system (e.g., isotherm constants) were incorporated as dependent variables using SPSS 12.0 software (SPSS., Inc., Chicago, IL, USA). Classical QSAR procedure, as developed by Hansch, was followed for the development of correlations (Hansch and Fujita 1995). Linear, polynomial, and multilinear correlations were employed to describe the data.

Table 4.5. Selected Descriptors of Substituent or Compound Electronics, Sterics, and Hydrophobicity (Hansch et al., 1995; Perry and Green, 1997; Schwartzenbach et al., 2003; MOPAC, 2004).

Monosubstituted Benzene 	Electronics Descriptors		Sterics Descriptors		Hydrophobicity Descriptors		Physical Properties		
	σ_{Ind}	ACCP	MR	Taft E_s	Log K_{ow}	π	MW (g/mole)	C_{aq} (mass %)	TOTL (Å)
Fluorobenzene (FB)	0.52	-0.115	0.09	-0.55	2.27	0.14	96.1	0.154	5.21
Chlorobenzene (ClB)	0.47	-0.103	0.6	-0.97	2.84	0.39	113	0.0387	5.55
Bromobenzene (BrB)	0.44	-0.097	0.89	-1.16	2.99	0.86	157	0.0387	5.7
Iodobenzene (IodoB)	0.39	-0.099	1.39	-1.62	3.28	1.12	204	0.0387	5.8
Nitrobenzene (NB)	0.64	0.039	0.74	-2.52	1.85	-0.85	123	0.0193	6.07
Aniline (Ani)	0.12	-0.169	0.54	-0.61	0.9	-1.23	93.1	0.21	5.84
Phenol (Ph)	0.29	-0.145	0.28	-0.55	1.48	-1.12	94.1	3.38	5.64
Benzaldehyde (Bzal)	0.3	-0.066	0.69	---	1.48	-0.32	106	8.66	7.02
Isopropylbenzene (IsoPB)	0.01	-0.106	1.5	-1.71	3.66	1.22	120	0.3	7.18
n-butylbenzene (nBB)	-0.04	-0.11	1.96	-0.16	4.26	2.13	134	0.0056	9.71
Isobutylbenzene (IsoBB)	-0.03	-0.107	1.96	-2.17	4.01	1.7	134	0.0015	8.19
t-butylbenzene (tBB)	-0.07	-0.107	1.96	-2.78	4.11	1.98	134	0.001	7.27
Benzene (Benz)	0	-0.102	0.1	0	2.13	0	78.1	0.178	4.97

Where σ_{Ind} represents the inductive effects described by the Hammett Constant, ACCP represents the charge of the para-carbon on the functional group, MR represents molar refractivity, E_s represents Taft's steric factor, $\log K_{\text{ow}}$ is the octanol-water partitioning coefficient, π represents the hydrophobicity of the compound, MW is the molecular weight, C_{aq} is the aqueous solubility in water, and TOTL is the total length of the compound, calculated by the bond lengths of the compound in the longest direction.

Correlations that resulted from the QSAR analysis had to meet a series of stringent statistical criteria to be considered valid:

4. No collinearity of independent variables (for MLR correlations)
5. $R^2 \geq 0.7$
6. F-Ratio values must meet a 95% confidence limit
7. Standard error considered
8. Q^2 determined for goodness of predictability

Condition 1 is only applicable in regards to multi-variable analysis. Independent variables were linearly correlated; variables that produced a R^2 value of 0.4 or higher were considered collinear and were excluded from the QSAR analysis. Conditions 2 and 3 were helpful in identifying poor correlations. The F-Ratio was determined using the number of compounds in each correlation (k) and two total data sets (n), observed and calculated values. The degrees of freedom were calculated for the variance between ($v_1 = n-1$) and within ($v_2 = (n*k)-n$) the data sets and compared to an upper 5% distribution table to determine the significance of the observed and calculated data sets. As the F-Ratio values become larger than the F-distribution values, the data sets are considered to be more similar. Therefore, high F-Ratio values indicate the predicted data from the QSAR correlation is in agreement with the observed data. The standard error (Condition 4) represents fluctuations in the sampling set and can be seen in the form of residuals in the regression lines. Clearly, low values of standard error reflect better correlations within the training set.

Condition 5 is an essential step in measuring the validation of the correlations that result from the QSAR process. When performing a Q^2 analysis, it is ideal to introduce a new compound to test the predictability of the QSAR correlation; however if the

introduction of an additional compound is not feasible, an alternative method, roughly referred to as the “take one out” method, will suffice. For this alternative method, one compound from the training set is removed and the correlations are recalculated. The new correlations are then used to test the ability of the QSAR correlation to predict the value of the compound that was removed. This process is repeated for each compound within the training set and Equation 4.3 is used to calculate the value of Q^2 :

$$Q^2 = 1 - \frac{\sum(y_{i,observed} - y_{i,predicted,new})^2}{\sum(y_{i,observed} - \bar{y}_i)^2} \quad \text{Eqn 4.3}$$

While no set limit has been established for Q^2 values, larger values indicate a better ability for the QSAR correlation to predict the observed values within the given system. Ideally the Q^2 should be close to the value for the adjusted R^2 , thus indicating that the new correlation did not cause a significant shift in the predicted data. For this study a difference of 0.2 between the Q^2 and adjusted R^2 was considered the maximum limit for variation.

Discussion of Results

From the experimentally derived isotherm parameters, only the terms representing the adsorption capacity (log K and log Q) yielded viable correlations for this training set; therefore, the isotherm data listed in Table 4.5 only shows these isotherm parameters. It is interesting to note that log K and log Q do not correlate with each other within this training set. In fact, a plot of these two parameters yields an R^2 value of 0.0804. This lack of relationship implies that while log K and log Q both represent an adsorption capacity, their actual derivation (and definition) is quite different. Webber and DiGiano (1996) present a relationship between the Freundlich and Langmuir constants shown in Eqn. 4.4:

$$K_F = Q_{a,g}^{\circ} b_g^n \quad \text{Eqn. 4.4}$$

However, the experimental results found in this study do not support this (or any) relationship between Langmuir and Freundlich constants. Scientists and carbon users should take caution when using a single parameter, such as an adsorption capacity, to describe a system.

Using the experimentally derived isotherm constants and kinetic descriptors, QSAR analyses were performed and correlations were derived. Initially, hundreds of correlations were developed and tested, yet only the six correlations shown in Table 4.6 satisfied all of the statistical validation requirements.

Correlation 1, shown in Table 4.6 and Figure 4.2, indicates that as aqueous solubility and molar refractivity increase, $\log K$, the Freundlich adsorption capacity, decreases. This decrease in adsorption is expected, as the increasing solubility of a compound will lower its tendency to come out of solution and sorb onto the carbon. This trend is commonly seen in the field of adsorption and is described by the Lundelius Rule. The increase in molar refractivity (MR), which is a frequently used indicator of molecular volume, correlates with a decrease in adsorption capacity, which is also expected for a microporous carbon such as F400. The largest compounds in this training set reach nearly 10 Å in length, when estimated through the summation of bond lengths in the longest direction of the compound. When estimating adsorption, Kasaoka and coworkers, as reported by Tennant and Mazyck (2003), have asserted that a compound will adsorb in a pore that is 1.5 to 2 times its diameter. Using this estimator, it is reasonable that the largest compounds in this training set (e.g., n-butylbenzene and isobutylbenzene) will not undergo optimized adsorption with a predominately

Table 4.6. Selected Results of QSAR Analysis with log K, log Q, and log t as the Dependent Variables.^{a,b}

Correlations	n	R ²	Adj. R ²	SE	F- Ratio	Q ²
1.) Log K = -0.196(0.0915)C _{aq} -0.258(0.326)MR+5.334	13	0.693	0.631	0.33	11.260	0.458
2.) Log K = -0.17(0.0765)C _{aq} +0.851(0.77)σ _{ind} +4.857	13	0.749	0.699	0.30	14.914	0.607
3.) Log Q = 0.558MR ² -0.457MR+1.242	12	0.781	0.733	0.33	16.07	0.582
4.) Log K = -0.187(0.083)C _{aq} -0.147(0.152)TOTL+6.024	13	0.724	0.669	0.31	13.131	0.560
5.) Log t = 0.197(0.212)C _{aq} -0.242(0.146)TOTL+2.52	12	0.715	0.651	0.29	11.266	0.603
6.) Log t = -5.836(6.68)ACCP-0.267(0.292)TOTL+2.162	12	0.703	0.637	0.30	10.644	0.694

^a C_{aq} = aqueous solubility (mass %), MR = molar refractivity, TOTL = estimated total length of compound, ACCP = measure of the para-carbon charge. Numbers in parentheses represent the 95% confidence interval (+/-) for the coefficient.

^b n = number of compounds used in correlation development, Adj. R² = adjusted R², SE = standard error. Due to inefficient data, Correlation 3 does not include benzaldehyde and Correlations 5 and 6 do not include phenol.

microporous carbon (average pore diameter less than 20 Å) such as F400. The results of this correlation appear to be sound, as only one compound showed a percent difference between observed and predicted values that was greater than 10%, t-butylbenzene.

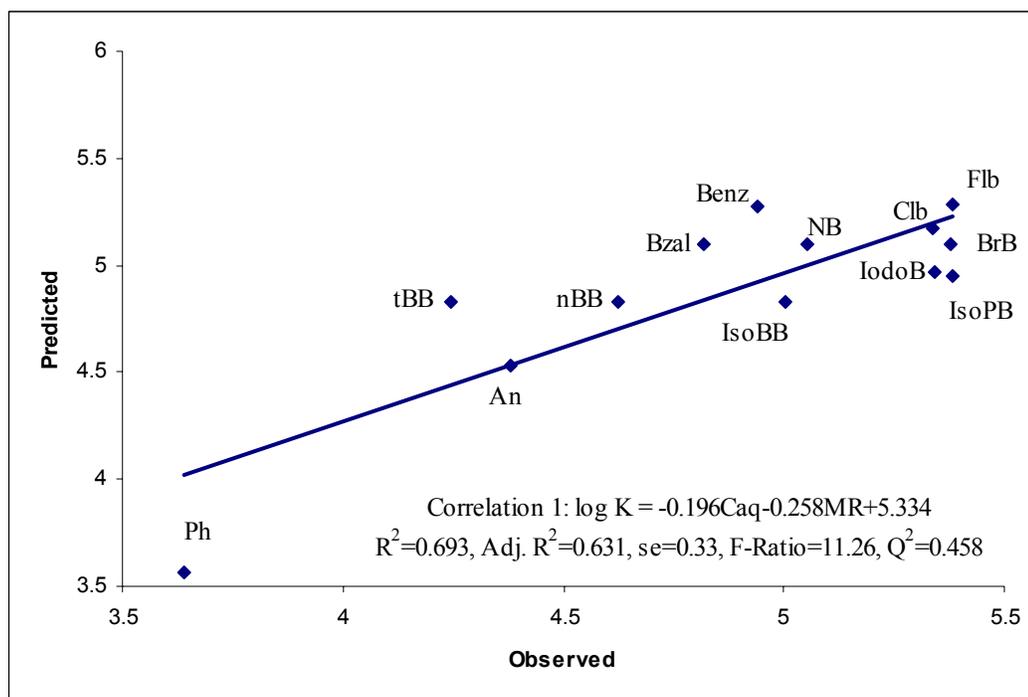


Figure 4.2. QSAR Correlation 1: Predicted versus Observed Values of log K.

The trends described by Correlation 2, shown in Table 4.6 and Figure 4.3, show a decrease in adsorption capacity (log K) with respect to an increase in aqueous solubility and a decrease in Hammett's constant, σ_{Ind} . The relationship between log K and the aqueous solubility of the training set is expected and is consistent with the results of Correlation 1. However, it is unexpected that a decrease in σ_{Ind} would lead to a reduced adsorption capacity. A decrease in σ_{Ind} indicates an increase in the electron donating potential of a compound, due to a higher electron density about the aromatic ring of the compounds in this training set. These results contrast with the π - π bonding theory developed by Coughlin and Ezra (1968) and accepted by numerous renowned carbon scientists, such as Radovic (2001). According to the π - π theory, an increase in the

electron density about the benzene ring should enhance the ability of the π electrons to interact, thus enhancing the potential for adsorption. Echoing the results seen in Correlation 1, only t-butylbenzene yielded a percent difference between predicted and observed value that was greater than 10%. Further study is necessary to confirm this trend will apply to a greater training set.

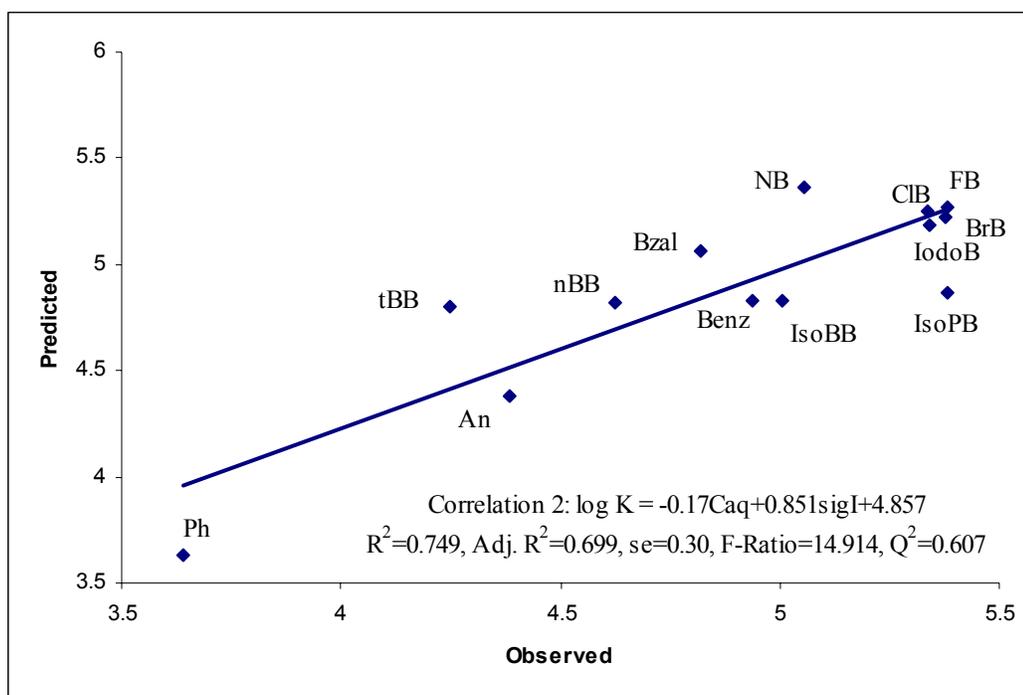


Figure 4.3. QSAR Correlation 2: Predicted versus Observed Values of log K.

Correlation 3, shown in Table 4.6 and Figure 4.4, relates the Langmuir adsorption capacity, log Q , with MR. The results found in this correlation show that the adsorption capacity increases as the MR—or molecular volume—increases, which contradicts the results found in Correlation 1. It does not seem logical that a microporous carbon, such as F400, would have an increasing adsorption capacity with increasing compound volume, as the largest compounds in this training set are approximately 10 Å in length. It should be noted that the largest compound in this training set, n-butylbenzene, showed the largest residual from the trendline in Correlation 3. The differences between

Correlation 1 and Correlation 3 confirm that the Langmuir Q and Freundlich K are describing different mechanisms for adsorption and should not be used interchangeably. Although more research comparing log K and log Q is necessary, in this particular instance, it appears that the Freundlich K is most accurately describing the adsorption of the training set with F400. Despite the R^2 value and sufficient statistical results, nine of the twelve compounds tested for this correlation showed greater than a 10% difference between predicted and observed values. In fact, of those nine compounds, six showed nearly or greater than a 20% difference. More research should be performed with an expanded training set to confirm the effectiveness of log Q for describing adsorption in relation with MR.

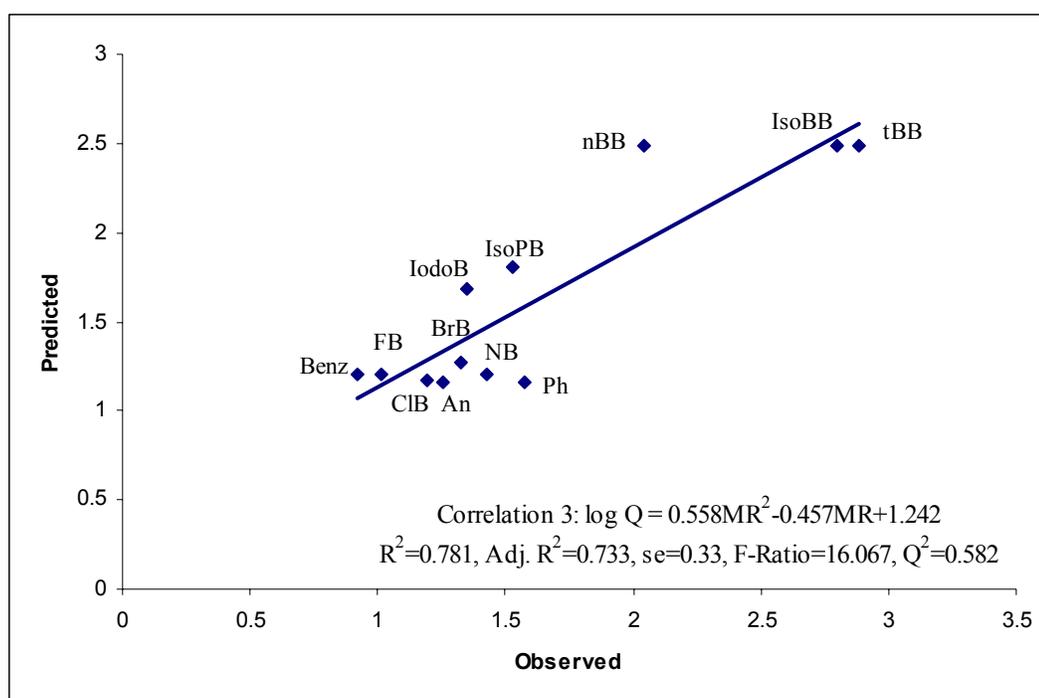


Figure 4.4. QSAR Correlation 3: Predicted versus Observed Values of log Q.

As shown in Table 4.6 and Figure 4.5, Correlation 4 states that as aqueous solubility and total length increase, log K decreases. These results were expected, and support Correlations 1 and 2 with respect to aqueous solubility. The total length

parameter is estimated from the bond lengths of the compounds in the longest dimension. An increase in total length indicates an increase in the bulkiness of the compound, and as expected for this microporous carbon, relates to a decrease in adsorption capacity. These results for total length are in agreement with the MR results for Correlation 1. As was found with Correlations 1 and 2, only one compound in Correlation 4 shows a percent difference between predicted and observed values greater than 10%, t-butylbenzene.

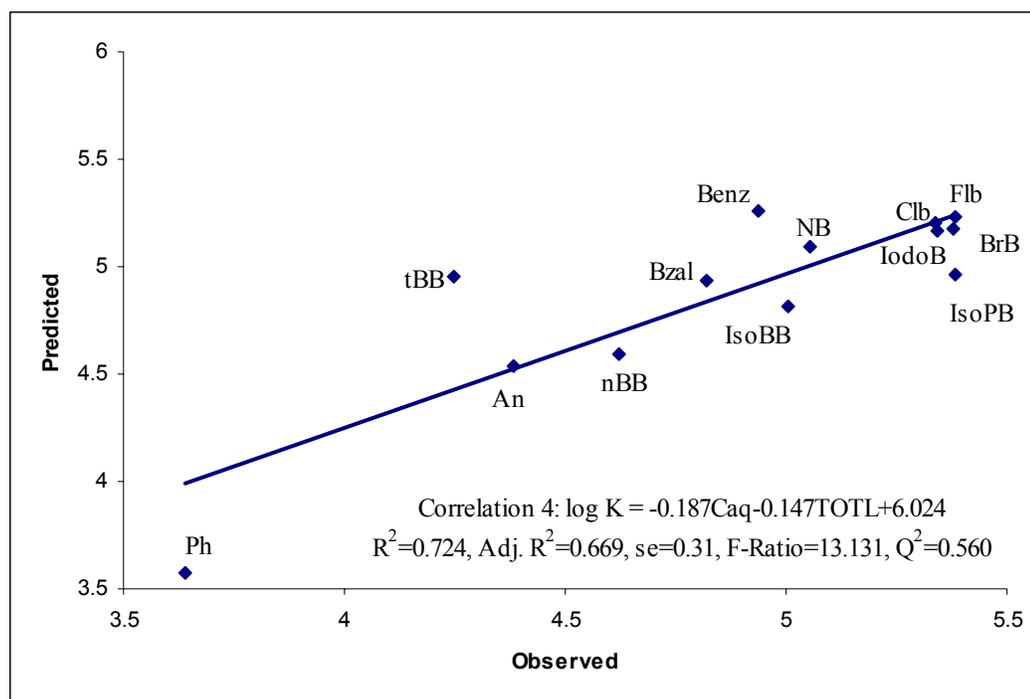


Figure 4.5. QSAR Correlation 4: Predicted versus Observed Values of log K.

Correlation 5, as shown in Table 4.6 and Figure 4.6, shows the relationship between aqueous solubility, total length, and log t. The value log t is a kinetic parameter that represents the amount of time that a 20-ppb slurry of F400 took to achieve 86% removal of a 100-ppb concentration of a target contaminant. As expected, and in support with Correlations 1, 2, and 4, a greater aqueous solubility resulted in a longer time to achieve 86% adsorption. However, in Correlation 5, a decrease in total length denoted an increase in the time to reach 86% adsorption. This finding appears to contradict with the

results of Correlations 1 and 4 which show that an increase in molecular volume and an increase in total length result in a decrease in adsorption capacity ($\log K$). This unexpected relationship between $\log K$ and total length could be an effect of steric hindrances, buttressing of the molecules against the carbon surface, pore size distribution. It should be noted that while all other correlations describe solely equilibrium conditions (which the Freundlich and Langmuir equations require by definition); $\log t$ does not represent equilibrium conditions between the carbon and contaminant. For Correlation 5, all but two compounds (aniline and iodobenzene) showed a 10% or greater difference between predicted and observed values. For these reasons, the $\log t$ results shown here cannot be accurately compared to the isotherm constant results; therefore further research should be done to confirm these findings.

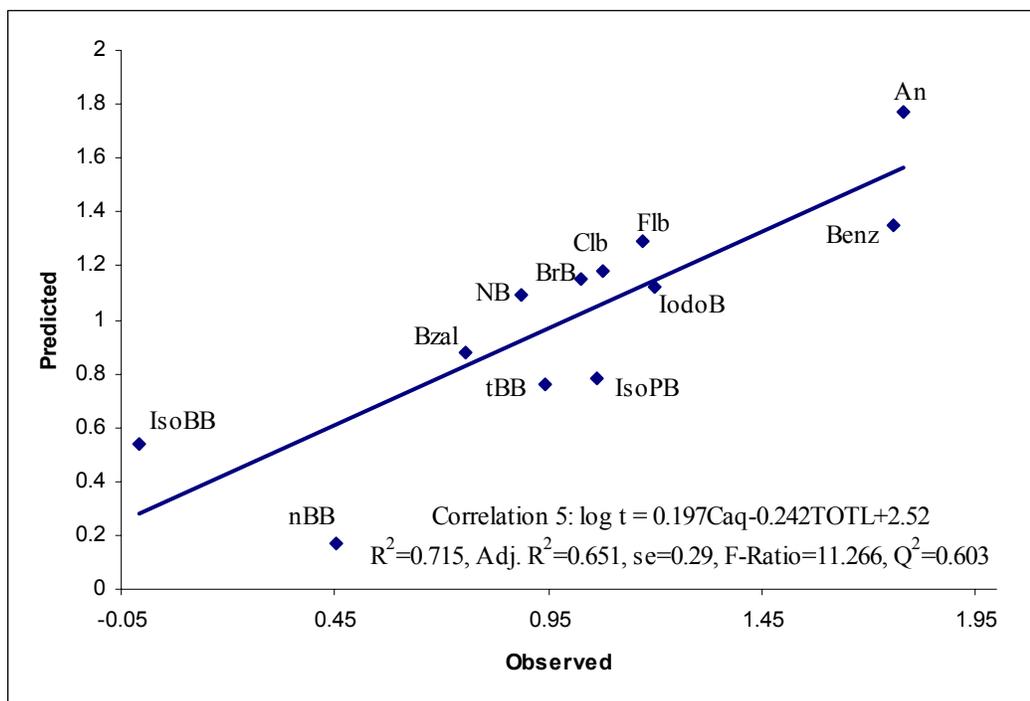


Figure 4.6. QSAR Correlation 5: Predicted versus Observed Values of $\log t$.

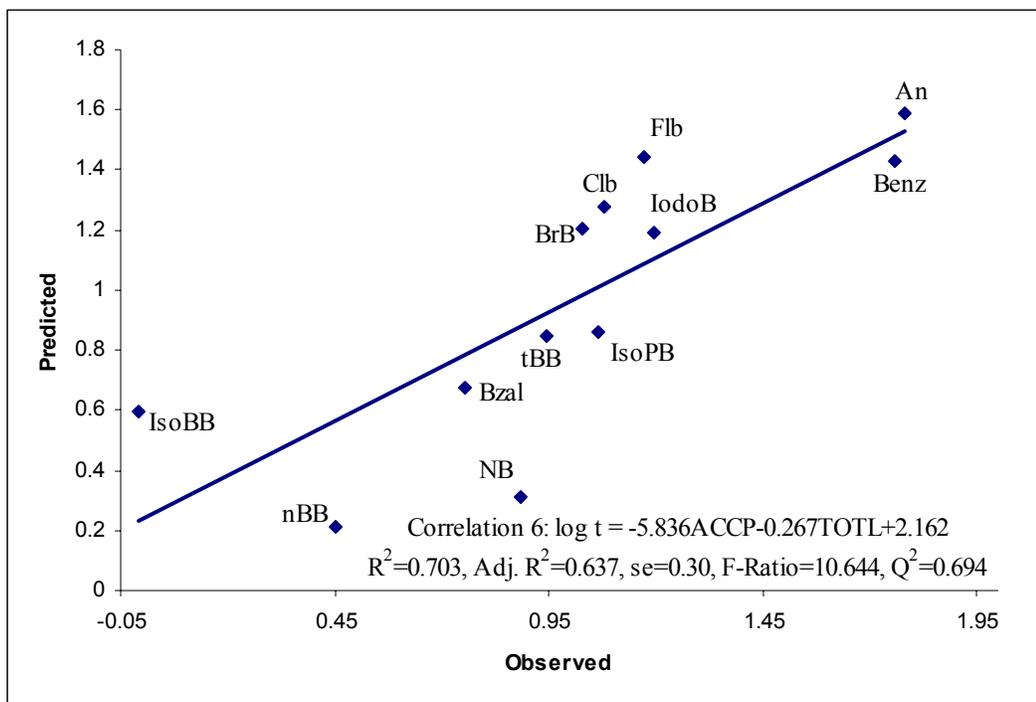


Figure 4.7. QSAR Correlation 6: Predicted versus Observed Values of log t.

The final correlation examined in this analysis is Correlation 6, shown in Table 4.6 and Figure 4.7. Correlation 6 indicates that an increase in ACCP (the charge of the carbon in the para position on the functional group of the target compound) and total length results in a decrease in the time to reach 86% adsorption of the target contaminant by F400. As ACCP increases, the functional group of the compound becomes more electron withdrawing, which indicates a reduced electron density on these carbon atoms. Correlation 6 shows that as the para carbon becomes more electron withdrawing, the time to 86% decreases—this indicates that a reduced electron density about the carbon is enhancing the uptake of the compound by F400. This finding, as seen with Correlation 2, contradicts the π - π bonding theory. Yet, as was seen in Correlation 5, the total length and log t are relating in an unexpected manner—showing a decrease in time to reach 86% as the compound length increases. Much like Correlation 5, in Correlation 6, all values except one (iodobenzene) showed percent differences between predicted and observed

values to be greater than 10%. As stated previously, the method for parameter development for log t is not ideal and further study should be performed to clarify these results.

Overall, as expected, Correlations 1, 2, and 4 support that as aqueous solubility increases, log K (adsorption capacity) decreases. As the steric factors of the compounds increase, Correlations 1 and 4 show that log K decreases. Though unexpected, Correlation 3 confirms the finding that log K and log Q do not demonstrate a distinct relationship with each other. For this reason, caution should be used when utilizing these parameters to describe an adsorption system. The correlations incorporating log t, Correlations 5 and 6, require further testing to verify the effectiveness of log t as a valid parameter for describing carbon adsorption. It has also been suggested, through Correlations 2 and 6, that π - π bonding may not be the dominant mechanism for adsorption in this training set. The successful correlations between aqueous solubility, sterics, and log K demonstrate optimistic effectiveness for using these parameters for adsorption prediction and signify the value of the functional and effective QSAR protocol utilized in this study. The critical steps of this protocol include:

- The selection of a parent compound and training set
- Standardized experimentation, at equilibrium conditions, of the training set with activated carbon(s)
- Uniform analysis of the experimental data to formulate representative dependent variables
- Careful consideration and selection of reliable and well documented independent variables
- Testing for collinear parameters
- Meticulous QSAR modeling

- Rigorous statistical validation of the QSAR correlations

The use of this protocol may be an essential step in working towards the goal of understanding the mechanisms of carbon adsorption phenomenon.

CHAPTER 5 CONCLUDING REMARKS

As stated by Mattson et al. (1969a), it is essential for the advancement of the field of activated carbon to identify and understand the mechanisms by which adsorption occurs. An understanding of the role of functional groups in the adsorption process is a key component to unveiling the mechanisms behind the process. The activation process is pivotal in the development of the surface chemistry, and indeed in the formation of functional groups present on the activated carbon. A recent workshop held by the National Science Foundation has emphasized the potential of QSARs as a tool for uncovering mechanisms in poorly understood phenomenon in the field of water treatment (NSF 2004).

Dabrowski states in his work “Adsorption—From Theory to Practice” that “. . . there is a need for close co-operation between theoretical and experimental groups, in which the experiments and models are designed to complement each other” (Dabrowski 2001). Overwhelmingly, in the literature, researchers are either developing models using past research or performing research using previously developed models. As Dabrowski implies, in order to have synergy between models and the experimental data, the researchers must integrate both into their designs. One approach that takes this into consideration is the experimental-modeling method proposed in this study. In this method, isotherm and kinetic data is collected for a training set of compounds and is included along with widely accepted physical and chemical constants to form a robust QSAR. This approach takes into consideration the effects of contaminant surface

chemistry and relies upon both experimental and modeling data to describe the mechanisms of adsorption. Ultimately, this method shall directly incorporate the effects of carbon surface chemistry as independent variables. The addition of such parameters will make for a more robust QSAR which may lead to a deeper understanding of the role of surface chemistry in the adsorption process.

If it is the intent of scientific community to advance the field of activated carbon, the mechanisms of adsorption must be identified and understood. Without the knowledge behind the process, the use of activated carbon will not be able to surpass other separation technologies. An experimental-modeling method is a doorway to understanding adsorption phenomena.

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BIOGRAPHICAL SKETCH

Born and raised in Pensacola, Florida, Jennifer graduated with an International Baccalaureate Diploma from the International Baccalaureate Program at Pensacola High School in May 1997. Continuing her education at the University of Florida, she defended for highest honors and received a Bachelor of Science degree in environmental engineering sciences in May 2002. For her master's work, Jennifer studied under Dr. David Mazyck with a focus on the adsorption of benzenes and monosubstituted benzenes onto activated carbon for water treatment applications. Jennifer currently resides in Newberry, Florida, with her husband Steve and in August 2004 she joined the water/wastewater engineering department in the consulting firm of Jones Edmunds & Associates.