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FINAL REPORT

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REMOVAL OF CHLORINATED ORGANIC COMPOUNDS BY ACTIVATED CARBON AND OTHER ADSORBENTS

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Grant No. 017-15-40087

GEORGIA INSTITUTE OF TECHNOLOGY

**SCHOOL OF CIVIL ENGINEERING
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1979



REMOVAL OF CHLORINATED ORGANIC COMPOUNDS
BY ACTIVATED CARBON AND OTHER ADSORBENTS

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ABSTRACT

This literature search has been conducted to determine the effectiveness of activated carbon and other adsorbents in removing chlorinated organic compounds from aqueous solutions. The characteristics of the adsorbent/solute/solvent systems that affect adsorption kinetics and adsorbent capacity for specific compounds are indicated. A comprehensive review of the commonly used adsorption isotherms along with pertinent adsorption isotherm data are presented. In general, it was observed that major differences exist between the procedures followed in obtaining these data and consequently care should be exercised in interpreting and using this information.

The text also includes a thorough review of adsorption kinetics and column adsorption studies and models. Finally, a listing of future recommendations is given.

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INTRODUCTION

Statement of Problem

The announcement in 1974 of the presence of potentially carcinogenic organic compounds in New Orleans' drinking water focused attention to the vast number of synthetic organic chemicals that are being introduced into the environment. An indication of the immensity of the problem is illustrated by the fact that the Registry of Chemicals of the American Chemical Society Abstract Service is growing at the average rate of about 6000 new chemicals per week (Maugh, 1978). A number of these chemicals, including the chlorinated compounds among them, may be toxic and their ultimate effect on man and the environment needs to be investigated. The presence of potentially carcinogenic compounds in natural waters is not totally due to the discharge of synthetic chemicals to the aquatic environment, however. Chlorinated organic compounds are also formed as a direct result of the chlorination process used in water and wastewater treatment plants.

Conventional water and wastewater treatment processes have been shown to be rather ineffective in the removal of some potentially carcinogenic compounds from water. The failure of such processes has prompted intensive research into the ability of more advanced technology to remove these compounds from water. Adsorption onto activated carbon and synthetic resins has been demonstrated as an effective process for the control of refractory organic matter in water and more recently it has been proclaimed by EPA as the recommended process for use in water treatment plants that exhibit problems associated with potentially carcinogenic organic matter (Symons, 1976, 1978).

Objectives of Literature Review

The objectives of the technical literature review are to evaluate the

ability of activated carbon and other adsorbents in removing organic compounds from water and wastewater with special emphasis on the chlorinated organic compounds which appear on the Environmental Protection Agency's priority pollutant list (see Table I).

Table I

Chlorinated Organic Compounds
Appearing on the Priority Pollutant List

1. Chlorobenzene
2. 1, 2, 4 - Trichlorobenzene
3. Hexachlorobenzene
4. Tetrachlorobenzene
5. Pentachlorobenzene
6. 1, 2 - Dichlorobenzene
7. 1, 3 - Dichlorobenzene
8. 1, 4 - Dichlorobenzene
9. 1, 2 - Dichloroethane
10. 1, 1, 1 - Trichloroethane
11. Hexachloroethane
12. 1, 1 - Dichloroethane
13. 1, 1, 2 - Trichloroethane
14. 1, 1, 2, 2 - Tetrachloroethane
15. Chloroethane
16. Bis (Chloromethyl) Ether
17. Bis (2-Chloroethyl) Ether
18. 2-Chloroethyl Vinyl Ether (mixed)
19. 2-Chloronaphthalene
20. 1, 1 - Dichloroethylene
21. 1, 2 - Trans-Dichloroethylene
22. Tetrachloroethylene
23. 1, 2 - Dichloropropane
24. 1, 3 - Dichloropropylene (1, 2 Dichloropropene)
25. 2, 4, 6 - Trichlorophenol
26. 2, 4 - Dichlorophenol
27. 2 - Chlorophenol
28. 3 - Chlorophenol
29. 4 - Chlorophenol
30. Trichlorophenol
31. Tetrachlorophenol
32. Pentachlorophenol
33. Dichlorophenol
34. Chloroform
35. Methylene Chloride
36. Methyl Chloride
37. Methyl Bromide
38. Bromoform
39. Dichlorobromomethane
40. Trichlorofluoromethane
41. Dichlorodifluoromethane
42. Chlorodibromomethane
43. Bromodichloromethane
44. Carbon Tetrachloride
45. Mono-Chlorocresols
46. Di-Chlorocresols
47. Tri-Chlorocresols
48. Tetra-Chlorocresols

ADSORPTION AND FACTORS AFFECTING IT

Adsorption of organic compounds onto activated carbon and synthetic resins is a complex surface phenomenon which results in the transfer of a solute from the solution phase to the adsorbent surface. This transport ultimately results in equilibrium being established between the solute in the solution phase and that adsorbed on the surface. This equilibrium state is affected by many factors, some of which are due to adsorbent characteristics, adsorbate characteristics and characteristics of the solution itself (McGuire and Suffet, 1978).

Adsorbent Characteristics

Adsorbent characteristics which affect the position of equilibrium are generally due to the overall structure of the adsorbent which is a function of the raw material from which the adsorbent is made, the method of manufacture and any treatment processes which result in different physical or chemical characteristics of the accessible adsorbing surface.

a. Activated Carbon Characteristics

Activated carbons are produced from a variety of raw materials, the most common of which are petroleum residue, coal (bituminous and Lignite), wood, peat, and coconut shells (Weber and Morris, 1964; Zogorski, 1975; McGuire and Suffet, 1978). The selection of the raw material and the activation process utilized determine the characteristics of the final product. These characteristics, which control the effectiveness of an adsorbent in removing specific organic compounds, are: surface area, pore size distribution, particle size, hardness, surface polarity, and surface functional groups.

Surface Area and Pore Structure. The surface area and pore structure of an activated carbon are two major characteristics that determine the adsorptive capacity and the size and type of adsorbate that may be removed from solution (Dubinin, 1966; Juntgen, 1976; Suidan, et al., 1978). Since adsorption is

a surface phenomenon, it follows that the capacity of the carbon for adsorption is directly related to the available surface area. This is true only up to a certain surface area per unit weight of carbon, however. As the surface area per unit weight increases, the fraction of surface associated with very small diameter pores prevails, thus rendering this fraction of the surface area inaccessible to all except very small molecules (Juntgen, 1976). An excellent discussion on the effect of the degree of activation of an activated carbon on its adsorptive properties as related to specific organic compounds may be found in an article by Juntgen (1976). In brief, he observed that for medium size molecules, like phenol, maximum adsorption capacity is attainable at a medium degree of activation (pore volume) where as for larger molecules such as the sodium salt of p-n-decylbenzene sulfonate the attainable adsorptive capacity of carbon increased steadily with the degree of activation.

Upon exhaustion, activated carbon can be regenerated via a number of processes, the most common being thermal regeneration (Hassler, 1974; Smithson, 1978). During thermal regeneration, the structural characteristics of the carbon can be markedly altered (O'Connor and Badorek, 1978). This is frequently due to the deposition of non-volatile impurities which block the access to the finer pores of the carbon, as well as an increase in the degree of pulverization upon regeneration (Juntgen, 1976a). This alteration in carbon properties during regeneration has not been taken into account in most of the available data in the literature since most available data has been obtained from studies utilizing virgin carbons. Since most thermal regeneration processes result in an attrition of only 3-8 percent of the carbon, the carbon in an adsorption bed will be composed of only 3-8 percent virgin carbon, while the remainder of the bed is composed of carbon which has been subjected to repeated regenerations.

Pore Size Distribution. Pore size and pore size distribution depend on the source of carbon, degree of activation, and number of regeneration cycles that the carbon has been exposed to (Juntgen, 1976a). Pore size distribution affects both adsorption capacity and the rate of adsorption (McGuire and Suffet, 1978). Commercially available carbons vary widely in their total pore volume and their pore size distribution. Some carbons are available which possess very narrow ranges of pore sizes while others have much larger pore size distribution ranges (Suidan, et al., 1978). The importance of the pore size distribution is due to the fact that more surface area per unit volume of pore is associated with finer diameter pores. This is a very desirable property as far as adsorptive capacity is concerned provided that these diameters are not so small as to prevent access of the adsorbate to the surface associated with these pores. This property of the carbon pore structure can be advantageous if it is desirable to selectively remove small molecules from solution such as in the case of the removal from water of trihalomethanes in the presence of humic substances (O'Connor and Badorek, 1978). Such selectivity was exhibited by a predominantly microporous carbon which gave an improvement in the removal capacity of the small sized trihalomethanes at the expense of the larger humic substances. Chow and David (1977) observed that granular activated carbon adsorption of a secondary effluent shifted the molecular size distribution towards larger molecules thus indicating a preference of lower molecular weight compounds to adsorb on the carbon. In summary, pore size distribution should be considered when selecting activated carbons for use in the removal of specific compounds.

Particle Size. Particle size does not appear to have a significant effect on the adsorption capacity of carbon for organic solutes (Crittenden and Weber, 1978). Zogorski and Faust (1978) demonstrated that the equilibrium capacity of activated carbon does not appear to be effected by the carbon particle size for organic compounds of moderate size. In their study, eight size ranges of Columbia LCK carbon ranging in mesh size from 12 x 16 to 80 x 100 U.S. Mesh were utilized to study the adsorption isotherms of seven phenolic compounds: phenol, 4-hydroxyphenol, 4-methoxyphenol, 4-chlorophenol, 4-nitrophenol, 2,4-dichlorophenol, 2,4-dinitrophenol. It is possible, however, that for larger adsorbate molecules, pore blockage to internal macropores may occur more readily when larger granules of carbon are involved. If this occurs, then the measured capacity of activated carbon for larger solutes may decrease with increasing particle size.

Zogorski et al. (1976) noted a six percent increase in the N_2 -BET surface area of Columbia LCK granular activated carbon upon crushing. This increase in surface area may be attributed to the opening of previously blocked pores. The investigators did not notice any measurable effect of this increase in the carbon surface area on capacity, however, in other instances where different solutes or activated carbons are used, this increase in surface area may have an appreciable effect on capacity.

Hardness. Hardness is a very desirable property in an activated carbon because harder carbons tend to incur less losses upon backwashing and regeneration. In addition, softer carbons release more carbon fines in the effluent from a filter thus impairing the quality of the effluent, as well as causing clogging and excessive head losses.

Surface Functional Groups and Polarity. Adsorption of organic compounds onto a porous activated carbon takes place on the walls of the micropores at

the basal graphite planes. In a virgin carbon, this surface is very non-polar and has a high affinity for organic compounds. However, when the surface is oxidized by chlorine, ozone, permanganate, or oxygen, portions of it become very polar, adsorb water strongly through a hydrogen bonding mechanism, and reduce the adsorption capacity for organic compounds by pore constriction or pore blockage mechanisms (McGuire and Suffet, 1978). Johnson and Snoeyink (1973) showed experimentally that an increase in the surface oxide concentration on activated carbon induced by the oxidation of the carbon with varying levels of chlorine resulted in a decrease in the rate of uptake of p-nitrophenol. Consequently, the presence of oxygen functional groups on carbon decreases the adsorption capacity of carbon for organic compounds as well as the rate of uptake of these compounds.

The characteristics of the oxides on carbon surfaces following reaction with oxidizing agents have been the subject of much study. A primary characteristic of at least a large fraction of these oxides is that they are acidic in nature. Boehm (1966) developed a titration procedure which permitted categorization of the oxides into four groups: (i) strongly acidic carboxyl groups which will react with bicarbonate or stronger bases, (ii) weakly acidic carboxyl groups which will react with carbonate or stronger bases but not with bicarbonate, (iii) phenolic-OH groups that will react with hydroxide or stronger bases but not with carbonate, and (iv) carbonyl groups which will react with ethoxide but not with hydroxide.

Based on the above, "a relative scale for the surface polarity of activated carbon can be constructed. Virgin activated carbon free from surface oxides is nonpolar and can adsorb organic compounds to its equilibrium capacity. As a carbon surface becomes successively more oxidized by chlorine and other oxidants, portions of the carbon surface become very polar and

adsorption capacity is reduced." (McGuire and Suffet, 1978). It has been observed that thermal regeneration of activated carbon increases the surface polarity of the carbon thus contributing to a reduction in the adsorption capacity of the carbon.

Cookson (1973) found that trace quantities of metals impregnated on carbon surfaces have a strong effect on the rate of uptake and equilibrium capacity of activated carbon for organic compounds. Copper and iron on the surface of the carbon were found to significantly influence the adsorption of butyl disulfide. The adsorption energy and the adsorption rate were found to decrease when metals are eliminated, indicating some ion-induced dipole interactions.

Parameters Used in Classifying Activated Carbons. Commercially available activated carbon are typically characterized by the following physical properties: (i) surface area, m^2/g ; (ii) apparent density, g/cm^3 ; (iii) density backwashed and drained, g/cm^3 ; (iv) real density, g/cm^3 ; (v) particle density, g/cm^3 ; (vi) effective size, mm; (vii) uniformity coefficient; (viii) pore volume, cm^3/g ; and (ix) mean particle diameter, mm. In addition, the following properties are desirable but are not always available: (i) iodine number, mg/g; (ii) molasses number, % removal of color; (iii) methylene blue number, mg/g; (iv) hardness number, g; (v) abraision number (Ro-Tap), % change in mean diameter; (vi) abraision number (NBS), % change in mean particle diameter; (vii) moisture, %; and (viii) total ash, %. Specific laboratory procedures for determining the above parameters may be found in Hassler (1974), and EPA (1973). Discussions of the meaning of some of the above parameters as far as water and wastewater applications and their limitations may be found in Hassler (1974) and Klein (1976).

b. Macroreticular Resins

Other available adsorbents which are starting to gain recognition as potential competitors to granular activated carbon are the synthetically prepared macroreticular resins. These resins are polymeric materials with varying degrees of cross-linking. A new specialized type of macroreticular resin is manufactured by the partial pyrolysis of macroreticular resins which have been substituted with a carbon-fixing moiety (Neely, 1978). In general resins have considerably smaller surface areas and larger pore structures than granular activated carbon but in some instances these resins have exhibited a higher capacity and greater specificity than granular activated carbon (Neely, 1978; McGuire and Suffet, 1978).

Another advantage associated with the use of macroreticular resins is their ease of regeneration, normally with organic solvents, without suffering appreciable losses in capacity or overall losses due to attrition (Kennedy, 1973; Zogorski et al., 1978; Neely, 1978). The principle factors limiting the wide spread use of macroreticular resins on a large scale are (i) their extremely high initial cost, and (ii) limited availability at the present time.

Adsorbate Characteristics

The position of adsorption equilibria is a function of the physical and chemical characteristics of the adsorbate, in a manner analogous to the physical and chemical characteristics of the adsorbent. The adsorbate characteristics which influence the adsorption process are: molecular size and weight, solubility and polarity, functional groups, and dissociation constants of ionizable species (Weber, 1972).

The physical and chemical characteristics of the adsorbate molecule are all interrelated and single characteristics of the adsorbate cannot

be directly utilized in determining the adsorption capacity unless all other characteristics remain constant. Therefore, it is necessary to consider the influence of each physical chemical parameter in determining the overall adsorption potential of the adsorbate. However, the following discussion will consider each individual characteristic assuming all other properties of the adsorbate molecules remain constant.

Molecular Size and Weight. Normally molecular size and weight are directly related for most solutes, that is an increase in molecular weight infers an increase in molecular size if changes in other properties are minimal. The effect of the molecular size of the solute on its removal by a porous adsorbent is directly related to the surface area of the adsorbent which is accessible to the solute. This accessible area will be a function of the total surface area of the adsorbent and its pore size distribution. As the size of the adsorbate molecule increases the accessible surface area of the adsorbent will normally decrease (Juntgen, 1976). However, in mixed solute adsorption processes larger molecules may be adsorbed preferentially, due to increased hydrophobicity, thereby blocking access to smaller pores that normally may accommodate smaller adsorbate molecules.

Solubility and Polarity. Considering aqueous systems where the solvent is very polar, the solubility of most solutes increases with an increase in polarity of the solute molecule. This increase in solubility generally decreases the tendency of the adsorbate molecule to leave the aqueous phase and adsorb on the adsorbent surface. In addition, strong interactions of highly polar solute molecules with a polar solvent increase the effective size of the solute molecule thereby reducing the accessible adsorbent surface (Adamson, 1967).

Functional Groups. Functional groups influence the polarity, solubility, size and ionization of a solute molecule depending upon the characteristics of the functional group. Therefore functional groups have a very diverse effect on the adsorption characteristics of the solute and each class of groups must be considered individually.

As stated previously, the surface of the adsorbent may contain impurities and/or reactive functional groups. These adsorbent characteristics may lead to chemical interactions between the adsorbent and adsorbate rather than the usual physical or dipolar interactions associated with adsorption. Such a phenomena may lead to preferential uptake of a particular solute and contribute to irreversible interactions between the adsorbate and adsorbent.

Ionizable Species

Solute molecules which contain ionizable functional groups exhibit in the ionized state adsorption characteristics which are widely different from those observed for the neutral species. This difference can be attributed to the fact that the ionized molecule carries a net charge and is therefore more polar, more soluble, larger in effective size and therefore less adsorbable than the neutral species. This property also affects the rate of adsorption in that the larger more soluble ionized form diffuses more slowly than the neutral species in the bulk aqueous phase as well as within the pore (DiGiano and Weber, 1973).

The following data illustrate the effect of changes in physical and chemical characteristics on adsorption capacity. Zogorski and Faust (1978) showed that the adsorption capacity of Columbia LCK carbon for seven different substituted phenols decreased with increasing water solubility, (See Table II). Similar results were obtained by Fritz (1978) using a similar series of phenols consisting of phenol, 4-chlorophenol, 4-nitrophenol and 2,4-dichlorophenol.

Table II
Solubility versus Capacity for Substituted Phenols

Adsorbate	Solubility (mmol/l)	Capacity at 0.2 mmol/l Equilibrium Concentration (mmol/g)
2,4-dinitrophenol	5.4	3.0
2,4-dichlorophenol	30	2.9
4-nitrophenol	100	2.4
4-chlorophenol	205	2.3
4-methoxyphenol	-	2.5
4-hydroxyphenol	727	1.4
phenol	903	1.4

Additional work by Fritz (1978) on a series of organic solutes consisting of benzoic acid, phenylacetic acid and dodecylbenzene sulfonate showed that at equilibrium concentrations higher than 10^{-5} moles/l, the least soluble benzoic acid was the most adsorbable followed by phenylacetic acid and then the most soluble and least adsorbable dodecylbenzene sulfonate. Similar results have been obtained by Kennedy (1973) for the adsorption of phenol, 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol on the synthetic macroreticular resin Amberlite XAD-4.

Morris and Weber (1962) in a study involving the adsorption capacity of a series of alkyl substituted benzene sulfonates onto Columbia LC activated carbon showed that the adsorption capacity increases with increasing length of the alkyl chain. The water solubility of all these compounds is quite high. The increase in adsorption capacity can be attributed to the overall decrease in the effective polarity of the sulfonate group as the hydrophobic alkyl chain increases in length (See Table III).

Table III
Molecular Weight versus Capacity for Alkyl
Substituted Benzene Sulfonates

Adsorbate	Maximum Adsorption Capacity (mmole/g)
benzene sulfonate	0.161
4-toluenesulfonate	0.222
2-hexyl benzene sulfonate	0.313
2-octyl benzene sulfonate	0.345
2-decyl benzene sulfonate	0.370
2-dodecyl benzene sulfonate	0.400
3-dodecyl benzene sulfonate	0.400
6-dodecyl benzene sulfonate	0.400
2-tetradecyl benzene sulfonate	0.435

For ionizable species in aqueous solutions, the pH of the solution plays a very important role in determining the relative distribution of that species between the neutral and ionized forms. This inturn determines the degree of adsorption in that the neutral species is much more readily adsorbed because (i) the ionic species is more polar and soluble in water, and (ii) the ionized species can also undergo electrostatic repulsion if the adsorbent surface carries a similar charge. This charge may be induced by the (i) adsorption of hydronium or hydroxide ions on the adsorbent surface, or (ii) ionization of functional groups that may be present on adsorbent surfaces.

Zogorski and Faust (1978) studied the effect of pH on the extent of adsorption of 2,4-dichlorophenol and 2,4-dinitrophenol. In both instances, they observed a maximum adsorption capacity at about one pH unit below the pK of the acid. Snoeyink et al. (1977) observed a similar behavior in the case of 2,4-dichlorophenol and 2,4,6-trichlorophenol. In all instances the adsorptive capacity of the compounds decreased slightly at pH values

below the maximum capacity pH. This may be attributed to either competitive adsorption of hydronium ions onto the carbon surface, or to the protonation of the neutral molecule that may occur at lower pH values.

Aqueous Solvent Characteristics

A third and very important component of an adsorption system consists of the nature and characteristics of the solvent surrounding the adsorbent surface and the adsorbate. The nature of the distribution of an organic compound between the solvent and the adsorbent surface is as much a function of the forces driving it out of solution as it is a function of the attraction of the adsorbent surface for that compound. In aqueous systems the solvent properties that influence adsorption are: temperature, pH, dissolved solids concentration and the presence of other adsorbates (McGuire and Suffet, 1978).

Temperature. Physical adsorption reactions are usually exothermic in nature. Because of that, adsorption capacity decreases with increasing temperature. Although the capacity of an adsorbent for a specific solute decreases with increasing temperature, the magnitude of this decrease in capacity is strongly evident only at lower surface loadings while at higher surface loadings, capacities become similar. Zogorski and Faust (1978) presented adsorption isotherm data for phenol on Columbia LCK activated carbon collected at temperatures of 8, 20 and 29°C. They observed that the amount of phenol adsorbed was influenced significantly by temperature at phenol concentrations less than 200 µmol/l. For example, when the concentration of phenol was 30 µmol/l, an increase in temperature from 6 to 29°C decreased the amount adsorbed by 42%. This dependency on temperature was negligible at phenol concentrations higher than 200 µmol/l.

pH of Solution. The hydronium ion concentration of an aqueous solution can have a significant effect on the adsorption potential of weak organic acids and bases. This effect, however, is an indirect one since the influence of the hydronium ion, in this case, is predominantly in its effect on the degree of ionization of the organic compound and as stated earlier, ionized species adsorb very differently from their neutral counterparts. Within the normal pH ranges that are encountered in water and wastewater treatment, the adsorption capacity of carbon for neutral organic compounds is not appreciably influenced by solution pH (McGuire and Suffet, 1978).

Dissolved Solids. The effect of the presence of dissolved salts on the position of adsorption has not been very well elucidated. In general, however, it has been observed that phosphate buffers had no measurable influence on the equilibria of adsorption of organic adsorbates that are in a neutral or undissociated form (Zogorski and Faust, 1978). The adsorption equilibria is, on the other hand, very much affected by the presence of inorganic salts (Coughlin and Tan, 1968). Snoeyink and coworkers (1977) stated that the phosphate buffer concentration had a marked effect on the adsorbability of humic materials with adsorption generally improving with increasing phosphate concentration. This phenomenon has often been observed for other types of phase changes, such as in liquid-liquid extraction, and is referred to as a "salting out" effect (McGuire and Suffet, 1978).

Presence of Other Organic Compounds. The presence of other adsorbable organic compounds in solution usually reduces the adsorption capacity of activated carbon for a particular organic compound (McGuire and Suffet, 1978). This phenomenon is due to the limited availability of adsorption surface area and the ensuing competition of the organic compounds for that area. This interference effect will be detailed later under the topic of competitive adsorption.

ADSORPTION ISOTHERMS AND CAPACITY REPRESENTATION

A number of data representation methods have been employed to describe the effectiveness of an adsorbent in reducing the concentration of a solute from an aqueous phase. This data presentation could be in the simple form of percent removals (Giusti et al., 1974) or it may be a description of the final state of the adsorption process in a manner that relates the extent of coverage of the adsorbent surface by the solute to the corresponding concentration of solute remaining in the aqueous phase. If the latter representation describes the relationship at a constant temperature, the resulting data constitutes what is commonly described as an adsorption equilibrium isotherm.

Percent Removal

This method of solute adsorbability representation relates the percent reduction in solute concentration when an aqueous solution of that solute is contacted with a predetermined quantity of adsorbent. The main advantage associated with this method is the ease with which data may be gathered for a number of solutes and a number of adsorbents. This method, however, provides only one data point that relates the solute surface loading of an adsorbent in equilibrium with one solution concentration of the solute. No information is given by this method on how surface loading changes with adsorbate concentration although in reality, adsorption is a dynamic process where the adsorbent is constantly exposed to varying adsorbate concentrations. Further problems with this method arise from the ease with which analytical errors can influence interpretive results when only one data point is available (McGuire, 1977). Hager (1974) published data on the treatability of 222 filtered industrial waste samples. However, only the rate of exhaustion in lb carbon/1000 gallons were reported and the removal was characterized by crude parameters.

Single Solute Adsorption Isotherm

In order to develop an understanding of the uptake potential of an adsorbent, adsorption isotherm data collected on the specific adsorbates of interest constitute a minimum requirement that is essential for estimating carbon utilization rates and treatment system performance. Extensive reviews of adsorption isotherms have been published by Sutherland (1967) and Kipling (1965) for gas/solid and liquid/solid adsorption systems, respectively. However, only the most commonly used isotherms will be discussed in this text.

Langmuir Adsorption Isotherm. The Langmuir adsorption isotherm is based on the assumptions that maximum adsorption capacity is attained at a monolayer coverage of the adsorbent surface, that the adsorption energy is constant, that the adsorbent surface is uniform, and that there is no interaction between the already adsorbed and/or the adsorbing molecules. Monolayer coverage simply means that the available active adsorption sites are occupied by only one adsorbate molecule each. A constant adsorption energy means that all of these sites are equal with respect to the energy input necessary to desorb a solute molecule from the solid phase.

The Langmuir isotherm is given by:

$$q = \frac{QbCe}{1 + bCe} \quad (1)$$

or in a linearized form as:

$$\frac{1}{q} = \frac{1}{Q} + \left(\frac{1}{bQ}\right) \frac{1}{Ce} \quad (2)$$

$$\text{or} \quad \frac{Ce}{q} = \frac{1}{bQ} + \frac{1}{Q} Ce \quad (3)$$

where q represents the mass of solute adsorbed per mass of carbon (moles/g or g/g), and Ce is the concentration of solute in the aqueous phase in

equilibrium with q (moles/l or g/l). The constant Q represents the maximum monolayer surface coverage (same units as q) and b is the adsorption energy (l/mole or l/g). The two parameters of the Langmuir isotherm can be determined from the measured adsorption equilibria by utilizing one of the two linearized forms given in Eqs. (2) and (3).

Many investigators have utilized the Langmuir adsorption isotherm model to fit their batch adsorption data successfully (Morris and Weber, 1962; Coughlin and Tan, 1968; Keinath and Weber, 1968; Getzen and Ward, 1969; DiGiano and Weber, 1972, 1973; Jain and Snoeyink, 1973; Cookson, 1973; Ishizaki and Cookson, 1974; Al-Bahrani and Martin, 1976; and Singer et al., 1978). Other authors have attempted to use the Langmuir model but rejected it when their data did not fit the linearized forms of the model given by Eqs. (2) and (3) (Paleos, 1969; Gustafson and Paleos, 1971; Snoeyink et al., 1974; Zogorski, 1975). In addition to its failure to accurately represent adsorptive data in many instances, the Langmuir adsorption isotherm model is based on a number of assumptions that are rarely met in an activated carbon/solute/water system. Of these assumptions, the statement of uniform surface properties and that adsorption energies are independent of the extent of surface coverage is most difficult to satisfy.

Freundlich Adsorption Isotherm. The Freundlich adsorption isotherm is an empirically derived equation that has been successfully employed by a number of researchers in fitting equilibrium adsorption data. This model is given by the equation:

$$q = K C_e^{1/n} \quad (4)$$

or in a linearized form

$$\ln q = \ln K + \frac{1}{n} \ln C_e \quad (5)$$

where K and n are model constants.

Several investigators have successfully applied the Freundlich model to their adsorption data (Mattson and Kennedy, 1971; Spahn and Schlunder, 1975; El-Dib and Aly, 1977; McGuire, 1977; Crittenden and Weber, 1978; Youssefi and Faust, 1978; and Dobbs et al., 1978). In some cases, the linearized plot of the data resulted in a series of segmented straight lines and in such instances, the Freundlich model constants, K and n were evaluated separately for each linear segment and are applicable only to that range of equilibrium solute concentrations, C_e , associated with that segment (Spahn and Schlunder, 1975).

Although the Freundlich adsorption isotherm model appears to fit experimental data in a rather satisfactory manner, it is handicapped by several shortcomings, the most important of which are: (i) the constants derived from the fit of the experimental data to the model are empirical and consequently, do not provide for a basis of comparison of the adsorption characteristics of different adsorbates, and (ii) to be thermodynamically acceptable, the model should satisfy a necessary thermodynamic boundary condition where at very low surface coverage, the adsorption of a solute should be proportional to the solute concentration in the aqueous phase as stated by Henry's Law (Jossens et al., 1977).

Radke and Prausnitz Isotherm. This isotherm was first used by Radke and Prausnitz (1972) in order to better fit adsorption isotherm data that did not follow a straight line on a log-log plot. This isotherm is given by the equation:

$$q = \frac{a K C_e}{K + a C_e^{1-n}} \quad (6)$$

or in a different standard form

$$\frac{1}{q} = \frac{1}{a C_e} + \frac{1}{K C_e^n} \quad (7)$$

This adsorption isotherm allows for the special flexibility of reducing to the Langmuir isotherm for values of $n = 0$, and it tends to the Freundlich isotherm at high values of C_e or when K is set to zero. This isotherm is often referred to as the three parameter isotherm. These parameters are determined through the use of a computer subroutine POWELL (McGuire and Suffet, 1978). Despite the empirical nature of this model, it seems to hold the most promise as a tool for data collection and comparison.

The Toth Isotherm. The Toth equilibrium isotherm adsorption model is based on the Langmuir equation solved for an arbitrary heterogeneous surface. This isotherm which is given by Equation (8) contains three parameters for evaluation and it provides the same flexibility offered by the Radke and Prausnitz model while providing a sounder theoretical basis. This model was used by Jossens et al. (1977) for representing single solute adsorption data for eight compounds with very satisfactory results.

$$q = q^{\infty} C_e (b + C_e^M)^{-\frac{1}{M}} \quad (8)$$

Single Solute Adsorption Equilibrium Data

The environmental engineering literature contains a large body of adsorption equilibrium data that cover a sizable number of solutes and solvents. In compliance with the objectives of this literature review, only the data that pertain to the removal of chlorinated organic compounds or to compounds listed among the priority pollutants will be reported.

Table IV contains Langmuir adsorption model for fourteen organic compounds. The data collected by Huang and Steffens () was obtained using 10 x 30 U.S. Mesh Filtrasorb 400 activated carbon. This coal base carbon has an internal surface area of $970 \text{ m}^2/\text{g}$. The equilibrium data was obtained in 250 ml Erlenmeyer flasks filled to 200 ml with solutions having

Table IV
Langmuir Parameters for Adsorption Isotherms

Reference	Compound	Q mmol/g	b l/mmol	T	Carbon	Range and Units of C_e
Huang and Steffens (19)	O-aminophenol	1.89	110.2	-	Filtrisorb 400 (10 x 30)	< 0.25 mmol/l
"	O-aminophenol	10.53	0.89	-	Filtrisorb 400 (10 x 30)	> 0.25 mmol/l
"	Pyrocatechol	1.32	89.40	-	Filtrisorb 400 (10 x 30)	< 0.25 mmol/l
"	Pyrocatechol	4.10	1.69	-	Filtrisorb 400 (10 x 30)	> 0.25 mmol/l
"	Resorcinol	1.14	67.7	-	Filtrisorb 400 (10 x 30)	< 0.25 mmol/l
"	Resorcinol	3.13	2.05	-	Filtrisorb 400 (10 x 30)	> 0.25 mmol/l
"	Phenol	1.32	38.00	-	Filtrisorb 400 (10 x 30)	< 0.25 mmol/l
"	Phenol	2.60	2.61	-	Filtrisorb 400 (10 x 30)	> 0.25 mmol/l
DiGiano and Weber (1972)	2,4-dinitro-o-cyclohexylphenol	0.85	500.0	23°C	Columbia LCK (60 x 80)	mmol/l
"	2,4-dinitro-o-sec-butylphenol	0.89	370.0	23°C	Columbia LCK (60 x 80)	mmol/l
"	2,4-dinitrophenol	0.64	300.0	23°C	Columbia LCK (60 x 80)	mmol/l
Singer et al. (1978)	phenol	g/g 0.234 mmol/g	l/mg 0.0878 l/ μ mol	23°C	PX-21 Amoco	mg/l
Morris and Weber (1962)	Silvex	1.72	0.145	25°C	Columbia LC 0.273 mm	μ mol/l
"	Parathion	1.82	1.22	25°C	Columbia LC 0.273 mm	μ mol/l
"	1-chloro-4-nitrobenzene	2.52	0.714	25°C	Columbia LC 0.273 mm	μ mol/l
"	2-(2,4,5-trichlorophenoxy) propionic acid	1.72	0.145	25°C	Columbia LC 0.273 mm	μ mol/l
"	2,4,5-trichlorophenoxy acetic acid	1.75	0.150	25°C	Columbia LC 0.273 mm	μ mol/l
"	2,4-dichlorophenoxyacetic acid	1.75	0.059	25°C	Columbia LC 0.273 mm	μ mol/l

initial adsorbate concentrations of 0.5×10^{-3} m/l. Between 0.05 to 0.5 g/l of carbon was added to the solutions of phenolic materials. Equilibrium data was collected after samples were agitated for 12 hr which may be questionable since for granular carbon a longer period is usually needed for equilibrium to be attained. For the data reported by DiGiano and Weber (1972) and Singer et al. (1978) no mention of experimental procedures was given. Morris and Weber (1962) collected batch isotherm data using 300 ml vessels that were shaken on a conventional laboratory shaker. Temperature variations during the tests were limited to 2°C. The adsorbent adsorbate systems were prepared utilizing one initial solute concentration and varying amounts of Columbia LC carbon. The reaction periods were in excess of two to three weeks, depending on results obtained from kinetic investigations.

Table V contains a listing of Freundlich adsorption isotherm constants and operating parameters for thirty eight organic compounds. The data reported by Dobbs et al. (1978) represent the adsorption capacity of these compounds on 200 x 400 U.S. Mesh Filtrasorb 300. Test solutions of these compounds were generally prepared in "mineralized" distilled water and the experiments were conducted at room temperature of 20-22°C. Tests on nonvolatile compounds were conducted in 1 liter beakers placed in a jar test machine equipped with multiple stirrers. Activated carbon was added in varying calculated volumes from a preprepared slurry. For volatile compounds, the isotherm test was conducted in eight or more one liter ground glass stoppered reagent bottles selected for uniformity of volume. The bottles, containing one liter of mineralized water were placed on a jar-test machine equipped with coordinated magnetic stirrers. While stirring, a sufficient volume of stock ethanol solution of the compound was injected with a micro-syringe below the surface of the water to minimize loss of compound. Carbon

Table V
Freundlich Parameters for Adsorption Isotherms

Reference	Compound	K mg/g	1/N	pH	T	Carbon	Range and Units of C_e
Dobbs, Middendorf and Cohen (1978)	hexachlorobutadiene	360	0.63	7	20-22°C	Filtrosorb 300 (200 x 400)	0.001 - 0.2 mg/l
"	benzidine dihydrochloride	220	0.37	7	20-22°C	Filtrosorb 300 (200 x 400)	0.03 - 8 mg/l
"	n-butylphthalate	220	0.45	7	20-22°C	"	0.4 - 3 mg/l
"	N-nitrosodiphenylamine	220	0.37	7	20-22°C	"	0.01 - 7 mg/l
"	bromoform	200	0.83	7	20-22°C	"	0.002 - 0.09 mg/l
"	pentachlorophenol	150	0.42	7	20-22°C	"	0.1 - 9 mg/l
"	dimethylphthalate	97	0.41	3-9	20-22°C	"	0.1 - 10 mg/l
"	chlorobenzene	93	0.98	7	20-22°C	"	1 - 20 mg/l
"	dibromo chloromethane	63	0.93	7	20-22°C	"	0.001 - 0.04 mg/l
"	carbon tetrachloride	40	0.84	7	20-22°C	"	0.002 - 0.2 mg/l
"	ethylenechloride	36	1.5	7	20-22°C	"	0.01 - 0.07 mg/l
"	2,4-dinitrophenol	33	0.61	7	20-22°C	"	1 - 10 mg/l
"	phenol	21	0.51	3-9	20-22°C	"	2 - 10 mg/l
"	trichloroethylene	21	0.50	7	20-22°C	"	0.0001 - 7 mg/l
"	bromodichloromethane	19	0.76	7	20-22°C	"	0.001 - 0.06 mg/l
"	bis(2-chloroethyl) ether	11	0.94	7	20-22°C	"	6 - 20 mg/l
"	chloroform	11	0.84	7	20-22°C	"	0.005 - 0.09 mg/l
"	benzene	70	2.9	7	20-22°C	"	3 - 8 mg/l
"	1-chloro - 2-nitrobenzene	130	0.46	3-9	20-22°C	"	0.08 - 8 mg/l
"	5-chlorouracil	25	0.58	7	20-22°C	"	2 - 9 mg/l
"	ethylbenzene	53	0.79	7.3	20-22°C	"	2 - 30 mg/l
"	p-xylene	85	0.16	7.3	20-22°C	"	1 - 15 mg/l
		<u>g/g</u>					
Derick and Beckman (1967)	2,4-dichlorophenoxyacetic acid	0.23	0.189	-	30.1°C	Columbia NXC (170 x 375)	1 - 40 mg/l
"	2,4-dichlorophenoxyacetic acid	0.324	0.092	-	3.1°C	Columbia NXC (170 x 375)	40 - 800 mg/l
		<u>mg/g</u>					
Foussefi and Faust (1978)	chloroform	16.5	0.60	7	22°C	Nuchar WVG (12 x 40)	µg/l
"	Chlorodibromomethane	130	0.62	7	22°C	"	µg/l
"	bromodichloromethane	150	0.51	7	22°C	"	µg/l
"	bromoform	185	0.32	7	22°C	"	µg/l
		<u>mg/mg</u>					
Al-Dib and Aly (1977)	isopropyl N-(3-chlorophenyl carbamate)	0.05	0.187	-	25°C	PAC BDH	0.2 - 10 mg/l
"	3-(4-chlorophenyl)-1,1-dimethylurea	0.066	0.333	-	25°C	PAC BDH	0.2 - 10 mg/l
"	3-(3,4-dichlorophenyl)-1,1-dimethylurea	0.095	0.109	-	25°C	PAC BDH	0.2 - 10 mg/l
"	3-(3,4-dichlorophenyl)-1-methoxy, 1-methylurea	0.08	0.157	-	25°C	PAC BDH	0.2 - 10 mg/l
"	3-(3,4-dichlorophenyl)-1-methyl, 1-n-butylurea	0.08	0.301	-	25°C	PAC BDH	0.2 - 10 mg/l
"	n-(3,4-dichlorophenyl) propionamide	0.06	0.222	-	25°C	PAC BDH	0.2 - 10 mg/l
"	n-(3,4-dichlorophenyl)-2-methylpentamide	0.10	0.238	-	25°C	PAC BDH	0.2 - 10 mg/l
		<u>mmol/g</u>					
Sahn and Schlunder (1974)	phenol	2.16	0.23	-	-	B10	0.1 - 8 mmol/l
"	phenol	3.6	9.39	-	-	B10	0.001 - 0.6 mmol/l
"	benzoic acid	3.06	0.181	-	-	B10	0.1 - 6 mmol/l

suspensions were then added in varying calculated volumes using volumetric dispensing pipettes. In all tests, however, only one hour of reaction time was allowed prior to analysis which makes it questionable whether true equilibrium was reached.

The data reported by Derick and Beckman (1967) on the adsorption capacity of Columbia NXC activated carbon for 2,4-dichlorophenoxyacetic acid was obtained utilizing 170 x 375 U.S. Mesh activated carbon at 30.1°C. No information as to the exact testing procedure or the equilibrating period was given. As for the data reported by Youssefi and Faust (1978) and Spahn and Schlunder (1975), no information on the specific test procedures is given except that the carbons used were Nuchar WVG 12 x 40 U.S. Mesh and B10, respectively. El-Dib and Aly (1977) used the powdered activated carbon BDH for their adsorption studies. This carbon was prewashed with double distilled water and oven dried at 120°C prior to use. To obtain adsorption isotherm data, varying amounts of accurately weighed powdered activated carbon (20-60 mg) were added to 1 liter portions of solutions of the pesticides studied at known initial concentration. The suspensions were stirred vigorously at $25 \pm 2^\circ\text{C}$ for fifteen minutes prior to residual concentration determinations. Once more, it is questionable if true equilibrium was reached in this limited reaction period.

The last set of single solute equilibrium adsorption isotherm data to be presented is that compiled by Fritz (1978) and fitted to the Toth Equation by Jossens et al. (1977). The adsorption data on phenol, p-nitrophenol, p-chlorophenol, and 2,4-dichloro phenol covers a range of five orders of magnitude of C_e while the data for the remaining three compounds covers four orders of magnitude of equilibrium solute concentrations. The procedure used in collecting the data was to pipette a 700 ml volume of an aqueous solution of the adsorbate of a given concentration (1-10 mmole/l) into

250 ml bottles, each containing a carefully weighed quantity of activated carbon, B10. The bottles were then shaken continuously for three to four days and then analyzed for the residual adsorbate concentration (Table VI).

Competitive Adsorption Isotherms

Competitive adsorption occurs when two or more adsorbates are competing for adsorption on the carbon surface. Weber and Morris (1964) have noted that in mixed solutions, each solute competes in some way with the others in both the rate and capacity of adsorption. Weber (1966) has further observed in a column study that a solute tends to have a more rapid breakthrough in a mixed solution than in a pure solution due to the apparent effect of competitive adsorption. A number of investigators have studied the phenomenon of competitive adsorption utilizing a number of solute systems and have attempted to mathematically model competitive adsorption with varying degrees of success. A brief description of some of these attempts is given below.

Jain and Snoeyink (1973) studied quantitatively the effect of competitive adsorption in some bisolute systems involving p-nitrophenol, p-bromophenol and sodium benzene sulfonate. They found that competitive adsorption can be predicted by a modified model of the original Langmuir equation. The Langmuir model for the competitive adsorption of n solutes as developed by Butler and Ockrent (1930) states that

$$q_i = \frac{Q_i b_i C_{ei}}{1 + \sum_{i=1}^n b_i C_{ei}} \quad (9)$$

The model given by Eq. (9) is thermodynamically consistent only in the special case of the saturation capacity at monolayer coverage, Q_i , is the same for all the competing solutes. If adsorption of a component of the solution system occurs on sites that are either inaccessible or unavailable to other components, the Langmuir model for competitive adsorption is not

Table VI
Toth Equation Parameters for Adsorption Isotherms

<u>Reference</u>	<u>Compound</u>	q^{∞} mmol/l	$b(\text{mmol/g})^M$	<u>M</u>	<u>T</u>	<u>Carbon</u>	<u>Range and Units for C_e</u>
Jossens et al. (1977)	phenol	14.15	0.3211	0.1478	20°C	B10 Lurgi	10^{-4} - 10 mmol/l
"	p-nitrophenol	11.91	0.1494	0.1072	20°C	"	10^{-4} - 10 mmol/l
"	p-chlorophenol	9.09	0.1731	0.1484	20°C	"	10^{-4} - 10 mmol/l
"	2,4-dichlorophenol	33.15	0.1466	0.0642	20°C	"	10^{-4} - 10 mmol/l
"	benzoic acid	10.87	0.2544	0.1800	20°C	"	10^{-3} - 10 mmol/l
"	phenyl acetic acid	32.48	0.2719	0.0895	20°C	"	10^{-3} - 10 mmol/l
"	o-phenyl phenol	17.20	0.1148	0.0723	20°C	"	10^{-3} - 10 mmol/l

expected to apply. Jain and Snoeyink (1973) assumed that, for a bisolute system, if $Q_1 \neq Q_2$ and $Q_1 > Q_2$, then there was competition only for Q_2 while $(Q_1 - Q_2)$ is available only to species 1. For a bisolute system, their model reduces to:

$$q_1 = \frac{(Q_1 - Q_2)b_1 C_{e1}}{1 + b_1 C_{e1}} + \frac{Q_2 b_1 C_{e1}}{1 + b_1 C_{e1} + b_2 C_{e2}} \quad (10)$$

$$q_2 = \frac{Q_2 b_2 C_{e2}}{1 + b_1 C_{e1} + b_2 C_{e2}} \quad (11)$$

However, the researchers were quick to point out the deficiencies of the model in that (i) pore blockage of the larger molecules may occur and (ii) differences between Q_1 and Q_2 may be due to surface coverage and not only to size in which the competitive Langmuir isotherm should hold.

Fritz and Schlunder (1974) employed an empirical modification of a three parameter single solute adsorption isotherm for the representation of competitive equilibrium adsorption data. This model was applied to a p-nitrophenol -phenol system utilizing B10 activated carbon from Lurgi (Frankfurt/Main). The general form of the model was

$$q_1 = \frac{a_1 C_{e1}^{(b_1 + b_{11})}}{C_{e1}^{b_{11}} + a_{12} C_{e2}^{b_{12}}} \quad (12)$$

$$q_2 = \frac{a_2 C_{e2}^{(b_2 + b_{22})}}{C_{e2}^{b_{22}} + a_{21} C_{e1}^{b_{21}}} \quad (13)$$

However, their model reduces to the Freundlich model for single solutes since their single solute data fit the Freundlich isotherm rather well.

Fritz (1978) later extended his work to include the following bisolute

systems p-nitrophenol/phenol; p-nitrophenol/p-chlorophenol; p-nitrophenol/benzoic acid; p-chlorophenol/phenyl acetic acid; and 2,4-dichlorophenol/dodecylbenzene sulfonate. Table VII contains constants for the competitive adsorption model given by Eq. (12) for each of the bisolute systems.

Jossens et al. (1977) applied the Toth single solute model as well as a new model of their own to Fritz's (1978) data and using these models and the ideal adsorbed solution theory were able to predict with reasonable accuracy the competitive adsorption data for the corresponding bisolute systems.

Another theory that is gaining recognition is the Polanyi adsorption theory which relies on thermodynamic principles and allows for the prediction of the performance of an adsorbent/solute system utilizing adsorption data for different solutes and the same adsorbent (Wohleber and Manes, 1971, 1971a; Rosene and Manes, 1977; Rosene et al., 1976).

Analytical Methods

The most commonly used methods for the analysis of specific organic compounds in water have been spectrophotometric and chromatographic techniques. Other non-specific techniques which have been used for the overall estimation of organic content of water samples include biological oxygen demand, chemical oxygen demand, total organic carbon, carbon-chloroform-extract, and non-purgeable organic carbon. These latter techniques are of little value in the characterization of real water or wastewater samples either due to their non-specificity or their lack of sensitivity.

Laboratory adsorption data can be obtained from single solute or two solute systems by utilizing simple ultraviolet or even visible spectrophotometric techniques. However, these methods do not lend themselves to the analysis of complex or unknown mixtures.

Table VII
Bisolute Adsorption Data (After Fritz (1978))

Adsorbent	Adsorbates	$\underline{a_1}$	$\underline{b_1}$	$\underline{b_{11}}$	$\underline{a_{12}}$	$\underline{b_{12}}$	$\underline{a_2}$	$\underline{b_2}$	$\underline{b_{22}}$	$\underline{a_{21}}$	$\underline{b_{21}}$	Solute Concentration Range
B10 I	PNP(1)/Ph(2)	4.18	0.215	0.58	0.096	1.04	2.83	0.37	0.71	7.43	0.56	0.01 - 0.1 mmol/l
B10 I	PNP(1)/Ph(2)	3.25	0.13	1.0	0.0185	1.2	2.16	0.23	0.77	14.0	0.70	0.1 - 10 mmol/l
LSS	PNP(1)/Ph(2)	2.40	0.13	0.53	0.0385	1.0	1.60	0.23	0.50	7.2	0.62	0.1 - 10 mmol/l
F300	PNP(1)/Ph(2)	2.05	0.13	0.50	0.022	1.1	1.45	0.21	0.70	9.3	0.78	0.1 - 10 mmol/l
B10 I	PNP(1)/PCP(2)	3.25	0.13	0.96	0.29	1.0	3.10	0.15	0.90	1.9	0.93	0.1 - 10 mmol/l
B10 I	PNP(1)/benzoic acid (2)	3.25	0.13	0.90	0.31	1.04	3.05	0.20	0.90	1.8	0.81	0.1 - 10 mmol/l
B10 I	PCP(1)/phenyl acetic acid (2)	3.10	0.15	0.65	0.25	0.67	2.20	0.21	0.49	1.65	0.64	0.1 - 10 mmol/l
B10 II P	DCP(1)/dodecyl benzene sulfonate (2)	3.86	0.12	0.39	0.48	0.25	1.41	0.05	0.57	1.16	0.37	0.1 - 10 mmol/l
B10 II K	DCP(1)/dodecyl benzene sulfonate (2)	3.86	0.12	0.39	0.23	0.60	1.08	0.06	0.24	0.70	0.41	0.1 - 10 mmol/l

Analysis of complex or unknown mixtures relies on chromatographic methods. Gas chromatographic methods are applicable to the analyses of volatile organic compounds and methods are being developed for the application of high-pressure liquid chromatography for the analysis of the semi-volatile organic compounds found in complex samples. In either instance extensive pretreatment steps are needed to prepare the samples for analysis. These steps can include solvent extraction and concentration, molecular size separation using gel-permeation chromatography and finally chromatographic analysis.

For complete and absolute identification of the compounds in an unknown complex mixture it is necessary to use gas chromatograph-mass spectrometry methods. This allows for the unambiguous identification of the organic compounds in most instances.

ADSORPTION KINETICS

The rate of uptake of organic compounds by activated carbon is dependent upon the physical and chemical properties of the activated carbon and its degree of exhaustion, the nature of the adsorbates to be removed and the mode of contacting the solution with the carbon as well as the extent of energy imparted upon mixing. Knowledge of the adsorption capacity of activated carbon for specific solutes is very important in determining the maximum or ultimate uptake by the carbon of a specific solute under the conditions of contacting (Letterman et al., 1974). However, the rate or kinetics of the uptake determine the dimensions of the contacting system as well as the efficiency of sorbent utilization.

Early kinetics investigations of the nature of adsorption of solutes onto activated carbon attempted to fit adsorption rate data to the classic zero, first and second order models with limited success (McGuire and Suffet, 1978). In 1963, Weber and Morris published a very important article where they investigated adsorption kinetics in detail. The effect on the adsorption rate of several operating parameters, such as: pH, molecular size of adsorbate, carbon particle size, and organic compound structural differences were investigated using alkylbenzene sulfonates and several other adsorbates. Perhaps the greatest contribution of the early researchers to the field of activated carbon adsorption kinetics is their ability to bring into the environmental engineering field and to expose other researchers to concepts that have been applied, refined and extensively used in chemical engineering practices. Very little innovation has been shown in these "translations", however, a well founded knowledge of the mathematical manipulations is required to enable environmental engineers to utilize these concepts.

For adsorption to occur, the solute molecules should diffuse from the bulk solution to the external surface of the adsorbent particle. If the transport rate to the external surface of the adsorbent is rate limiting, the rate of uptake may be affected by the flow conditions through the adsorber system. If the fluid velocity past the adsorbent particle is increased, the concentration boundary layer thickness should decrease causing the rate of mass transfer to poremouth or external surface to increase. Consequently, the overall rate of reaction is increased. When internal diffusion within the adsorbent pores is rate limiting, the overall rate will be unaffected by external flow conditions (Letterman et al., 1974; Keinath, 1975; Weber and Crittenden, 1975).

A very useful way of modelling diffusional transport is to treat the fluid layer next to the solid boundary as being a stagnant film of thickness δ . We say that all the external resistance to mass transfer is found within this hypothetical film, and the properties, (i.e. concentration, temperature) of the fluid at the outer edge of the film are identical to those in the bulk fluid. For the case where transport involves equimolar counter diffusion or where the solute is present in dilute concentrations, the flux is given by:

$$\text{Flux} = k_f (C_{io} - C_{is}) A_p \quad (14)$$

where k_f is a film transport coefficient, A_p is the external surface area of the particle, and C_{io} and C_{is} represent the solute concentration in the bulk solution and the particle external surface, respectively (Fogler, 1971).

When internal diffusion within the granule pores is rate limiting, the overall rate will be unaffected by external flow conditions. In this case, the parameters that affect the uptake rate are (i) the granule diameter, (iii) the solute size(s), (iii) whether the solute is neutral or

charged, (iv) the pore volume and the pore size distribution, and (v) the temperature of the solution (Suidan, 1978).

In a comprehensive study of adsorption kinetics in infinite bath experiments, DiGiano and Weber (1973) observed the dependence of the adsorbate diffusion coefficients on the form of the molecule. The anionic form of p-nitrophenol had an order of magnitude lower diffusion coefficient as compared to the neutral form of the compound. A significant ionic strength effect was also observed for the anionic form of the compounds studied.

Letterman et al. (1974) utilized the initial uptake rate of phenol and established a relationship for the transport film resistance as a function of energy input to a closed batch reactor. Crittenden and Weber (1978) utilized a relationship developed by Williamson et al. (1963) to estimate film transport resistance in a packed bed reactor. They found that the values of the film transport coefficient as obtained from this equation were superior in fitting their experimental data than those given by other correlations.

Ishizaki and Cookson (1974) utilized a second order reversible adsorption model to describe adsorption kinetics. They also observed that pore blockage due to surface oxides decreased the rate of adsorption. Spahn and Schlunder (1975) utilized experimental batch data to determine mass transfer coefficients. They observed that the mass transfer coefficients for internal transport depend on the initial concentration of the adsorbate. However, they assumed irreversible adsorption which may be a reason for the observed dependency of internal transport parameters on initial bulk concentration.

Zogorski (1975) obtained linear plots for the cumulative surface concentration, q , and the square root of time for many substituted phenols under widely varying conditions. The slope of the straight line was referred to as a removal rate and not as a relative rate constant. Zogorski (1975)

also showed the rate of uptake to be inversely proportional to the diameter of the granule, which he attributed to indicate prevailing surface film resistance. He also obtained a linear relationship between rate of removal and temperature where he obtained values of the activation energy of 1.6 for phenol and 2.2 for 2,4-dichlorophenol indicating diffusional resistances.

COLUMN ADSORPTION STUDIES

One efficient way of contacting an aqueous solution of organic adsorbates with activated carbon is through the use of a columnar or filter configuration. An adsorber column may be operated in a downflow or an upflow manner. Downflow is the preferred mode of operation when the suspended solids content of the water is low while upflow is more suitable for turbid waters. In the upflow mode of operation, the bed may be just expanded or the flow rate may be high enough to cause fluidization. In any event, for both modes of operation the constituents of the influent will eventually start emerging in the effluent and, in the absence of biological activity, will ultimately reach influent values. The time history of the emergence of these compounds is referred to as a breakthrough curve. A breakthrough curve can be thought of as a manifestation of (i) the total capacity of an adsorbent for the organic matter as they appear in the influent, (ii) the rate of adsorption which is a measure of the speed at which the total capacity is reached, and (iii) the hydraulics of the column operation. In a comprehensive study, Zogorski (1975) studied the effects of several parameters on the adsorption of substituted phenols onto a coconut shell base Columbia LCK activated carbon. The parameters investigated were pH, linear velocity and carbon particle size. McGuire and Suffet (1978) reported column adsorption study results for a mixture of nitromethane, methyl ethyl ketone, n-butanol and 1,4-dioxane. Crittenden and Weber (1978) presented breakthrough curves for single solute systems of phenol, p-bromophenol, p-toluene sulfonate, and dodecylbenzene sulfonate. In addition they collected bisolute breakthrough data on systems of phenol/dodecylbenzene sulfonate and phenol/p-toluene sulfonate. Major fluctuations in influent concentration were encountered in their studies, however, and because of that true

competitive behavior was difficult to evaluate. DiGiano (1978) presented a competitive breakthrough curve for a mixture of acetophenol/veratrole and o-cresol. He obtained the best breakthrough behavior for acetophenol which is intermediate in its adsorbability on carbon when compared to the other two compounds. The compound with the highest adsorptive capacity, o-cresol, demonstrated the fastest breakthrough. DiGiano attributed this observation to the complex dependency of breakthrough behavior on capacity as well as adsorption kinetics. Fritz et al. (1978) presented extensive data on column breakthrough from single solute and bisolute studies on p-nitrophenol and phenol utilizing B10 granular activated carbon.

A number of researchers have studied the breakthrough behavior of columns packed with macroreticular synthetic resin adsorbents. Leenheer (1970) reported on the removal of the two pesticides parathion and sevin by XAD-2 resin, while the removal of aldrin, dieldrin, DDT, DDE, and DDD from seawater by the same resin was studied by Harvey (1972). Kennedy (1973) compared the treatment potential of the effluent from manufacturers of chlorinated pesticides utilizing a macroreticular resin XAD-4 and an unidentified activated carbon. The resin outperformed the carbon in both capacity as well as regeneration efficiency when organic solvents were used.

Zogorski et al. (1978) and O'Connor and Badorek (1978) studied the removal of trihalomethanes and total organic carbon on a number of commercial activated carbons and their general conclusions were that the activated carbons that performed best in the removal of total organic carbon were the poorest in their ability to remove trihalomethanes. This observation leads to the all important question of what activated carbon is best suited for the individual or selective removal of specific constituents present

in water. McCreary and Snoeyink (1977) reported similar observations. The data reported in Tables VIII, IX and X present some pertinent experimental results from the literature. This data, however, is not complete in its description of carbon performance since it does not include the time varying effect on carbon performance.

Reference	Compound	Inf. Conc.	Eff. Conc.	% Removal	Break Through Time	Carbon Used	pH	Comments	Contact Time	S-Single Solute M-Multisolute
McCreary and Snoeyink (1977)	bis(2-chloroethyl)ether	10-100µg/l						Removal Independent of Activation	7-11 min	M
"	bis(2-chloroisopropyl)ether	10-100 µg/l						Removal Independent of Activation	7-11 min	M
"	isophorone	10-100 µg/l						Removal Independent of Activation	7-11 min	M
"	tetralin	10-100 µg/l						Removal Independent of Activation	7-11 min	M
"	dieldrin	4.3µg/l	.3µg/l					Carbon exhausted for COD and CCE removal		M
"	dieldrin	4.3µg/l	0-.05 µg/l					Fresh carbon		S
"	dichloromethane				2 days	Coal based			12 min	M
"	carbon tetrachloride				14 days	Coal based			12 min	M
"	chloroform				7 days	Coal based			12 min	M
"	bromoform				22 days	Coal based			12 min	M
EPA-600/8-77-005 (1978)	endrin	0.010		85		PAC 5mg/l				
"	endrin	0.010		92		PAC 10mg/l				
"	endrin	0.010		94		PAC 20mg/l				
"	endrin	0.010		> 99		GAC				
"	lindane	0.010		30		PAC 5mg/l				
"	lindane	0.010		55		PAC 10mg/l				
"	lindane	0.010		80		PAC 20mg/l				
"	lindane	0.010		> 99		GAC				
"	toxaphene	0.1mg/l	.07mg/l			PAC 5mg/l				
"	silvex	.01mg/l		80		PAC 5mg/l				
"	silvex	.01mg/l		80		PAC 10mg/l				
"	silvex	.01mg/l		95		PAC 20mg/l				
"	silvex	.01mg/l		> 99		GAC				
O'Connor and Badorek (1978)	trihalomethanes	5-211 µg/l		80-85		Westvaco WV6		After four months of operation		M
"	trihalomethanes	5-211 µg/l		80-85		HD 1030		After four months of operation		M
"	trihalomethanes	5-211 µg/l		80-85		NORIT ROWO.8AC		After four months of operation		M
"	trihalomethanes	5-211 µg/l		80-85		Bituminous Base		After four months of operation		M
"	trihalomethanes	5-211 µg/l		< 80		LCK		After four months of operation		M

Table IX
Column Performance and Removal Efficiency

<u>Reference</u>	<u>Compound</u>	<u>Capacity</u>	<u>Equilibrium Concentration</u>	<u>Carbon Used</u>	<u>pH</u>	<u>Comments</u>	<u>S-Single Solute</u> <u>M-Multisolute</u>
Neely (1978)	chloroform	10mg/g	1 mg/l	BPL			S
"	chloroform	8mg/g	1 mg/l	Filtrisorb 400			S
"	chloroform	6mg/g	1 mg/l	Filtrisorb 300			S
"	chloroform	4mg/g	1 mg/l	Amberlite XAD4			S
"	chloroform	28mg/g	1 mg/l	Amberlite XE340			S
Zogorski and Faust (1975)	2,4-dinitrophenol	3mmol/g	.2mmol/l	Columbia LCK	3.0	Adsorption independent of particle size	S
"	2,4-dichlorophenol	2.9mmol/g	.2mmol/l	Columbia LCK	6.3	Adsorption independent of particle size	S
"	4-nitrophenol	2.4mmol/g	.2mmol/l	Columbia LCK	6.3	Adsorption independent of particle size	S
"	4-chlorophenol	2.3mmol/g	.2mmol/l	Columbia LCK	6.3	Adsorption independent of particle size	S
"	4-methoxyphenol	2.5mmol/g	.2mmol/l	Columbia LCK	6.3	Adsorption independent of particle size	S
"	4-hydroxyphenol	1.4mmol/g	.2mmol/l	Columbia LCK	6.3	Adsorption independent of particle size	S
"	phenol	1.4mmol/g	.2mmol/l	Columbia LCK	6.3	Adsorption independent of particle size	S

Table X
Removal of Selected Metals by Activated Carbon

<u>Reference</u>	<u>Compound</u>	<u>Inf. Conc.</u>	<u>Eff. Conc.</u>	<u>% Removal</u>	<u>Carbon Used</u>	<u>Comments</u>	<u>S-Single Solute</u> <u>M-Multisolute</u>
Thiem, Badorek and O'Connor (1976)	Mercury	10 µg/l	<2 µg/l		Filtrisorb 400 PAC 40 mg/l		S
"	Mercury and Tannic acid	10 µg/l	<2 µg/l		Filtrisorb 400 PAC 40 mg/l		M
Huang and Wu (1975)	Chromium (VI)	312 mg/l		7	Coke (20 x 40 mesh)		S
"	Chromium (VI)	312 mg/l		16	Coke (100 x 200 mesh)		S
"	Chromium (VI)	5 mg/l		100	Coke (20 x 40 mesh)		S
"	Chromium (VI)	5 mg/l		100	Coke (100 x 200 mesh)		S
Huang and Ostorik (1978)	Cadmium (II)	5 x 10 ⁻⁴ M		100	Filtrisorb 400	Complete removal at pH >8.0	S
"	Cadmium (II)	5 x 10 ⁻⁴ M		100	Nuchar C-190-N	Complete removal at pH >8.0	S
"	Cadmium (II)	5 x 10 ⁻⁴ M		100	Nuchar 722	Complete removal at pH >8.0	S
Cupta and Chen (1978)	Arsenic (V)	13-35 µM		63-96	Activated Carbon (8 x 30 mesh)		M
"	Arsenic (III)	7-27 µM		80-90	Activated Carbon (8 x 30 mesh)		M

COLUMN ADSORPTION MODELS

The principal of mass conservation is central to the application of material balance relationships for the analysis of process dynamics (Weber and Crittenden, 1975). The application of a material balance to an adsorption bed results in a pair of partial differential equations for each solute entering the bed in the liquid phase and adsorbing on the solid phase. In addition, if intraparticle diffusion is considered, an additional partial differential equation is required to define the transport of each solute into and out of the particle. In this section a brief description of some models will be presented.

Mass Transfer Zone Model. The Michaels (Michaels, 1952) mass transfer zone model has a widespread application in the design of chemical engineering processes. Furthermore, the principles underlying the development of this model are common to many of the separation processes such as distillation, gas absorption and stripping, and aeration. In the development of the mass transfer zone model, it is assumed that an adsorption wave or breakthrough curve passes through the bed at a constant velocity. Another assumption made in the development of the model is that the solute concentration in the solid and aqueous phases are at steady state at any position in the adsorption wave. In addition, the rate of adsorption is assumed to be controlled by liquid film transport, and equilibrium exists between the intraparticle solute concentration and the aqueous concentration at the outer surface of the particle.

The application of the Michaels mass transfer zone model to column breakthrough data is rather simple (Weber and Crittenden, 1975). However, Michaels cautioned that this method was only applicable to those fixed-bed ion exchange systems where a sharply defined, constant width exchange zone

was formed. This situation only occurs for the carbon adsorption process where the solute has a relatively high affinity for the carbon surface (McGuire and Suffet, 1978). Zogorski (1975) observed that these conditions are satisfied during the adsorption of substituted phenols and the mass transfer zone model was very adequate in representing his experimental data. McGuire and Suffet (1978) were not successful in applying this model to characterize the adsorption of poorly adsorbed organic compounds.

Distributed Parameter Approach. The distributed parameter method represents a solution technique for the packed bed adsorption column time varying response. In this method, the packed column is analytically subdivided into a number of subreactors in series. Each subreactor is assumed to represent a completely mixed continuous flow reactor with adsorbent retention. If the number of segments is one then the response of the overall reactor will simulate that from a completely mixed reactor, while as the number of segments increases, the reactor response approaches that of a plug flow packed bed (Levenspiel, 1972). The main advantage of this solution technique is that it permits the reduction in the dimensionality of the problem by reducing the mathematical description of the model to a series of ordinary differential equations. Weber and Crittenden (1975) state that dispersion transport may be added to the individual reactor design equations, but it is the belief of the authors that this statement represents a redundancy since the choice of number of segments into which a reactor may be subdivided provides more than sufficient flexibility for the inclusion of the effect of dispersion. Keinath and Weber (1968) employed this solution technique to successfully predict column breakthrough curves from single solute systems, however, limited success was encountered when they attempted to apply this model under competitive conditions of adsorption.

Numerical Solution Techniques. A number of investigators resorted to classical finite difference numerical solution techniques to solve the intricate non-linear partial differential equations that describe the performance of packed bed adsorbers. Weber and Crittenden (1975) employed a backward and forward finite difference representation of their derivatives in predicting the performance of packed bed adsorbers for single and bisolute systems. However, a two dimensional model was employed and only film resistance was assumed. Suidan et al. (1977) and Kim et al. (1978) employed a central difference numerical technique to simulate the reduction of free and combined chlorine residuals in water. Kim et al. (1978) later employed quasilinearization and orthogonal collocation to solve the three dimensional adsorber model. Crittenden and Weber (1978) solved the three dimensional model for single as well as bisolute systems. They also allowed for a variable boundary condition on the influent solute concentration in order to better simulate fluctuating adsorber feed concentrations.

Simple Model for Data Extrapolation. Danby et al. (1946) obtained an analytical solution to a plug flow packed bed adsorber where irreversible adsorption kinetics were assumed. The uptake rate was set proportional to the solute concentration and the remaining adsorber capacity at a specific location in the bed. The solution to this model is given by

$$C = \frac{C_o}{e^{-kC_o T} (e^{kN_o L/U} - 1) + 1} \quad (15)$$

or in a linearized form

$$\ln\left(\frac{C}{C_o} - 1\right) = -k C_o T + \ln(e^{kN_o L/U} - 1) \quad (16)$$

where C_o is the influent concentration and C is the concentration in the aqueous phase after a length L of adsorber bed. U represents the linear

flow rate in the reactor and N_o is the capacity of the carbon in equilibrium with the influent concentration C_o . k is the kinetic rate constant. This model has been applied extensively by process engineers in the scale up of experimental column breakthrough data for the purpose of full scale design of a number of reactor configurations. Hutchins (1974) presents a very informative discussion on the use and application of this model for the design of activated carbon columns for the treatment of wastewater.

OTHER REMOVAL PROCESSES

The presence of chlorinated organic compounds in water and wastewater streams is most typically encountered at low concentrations. Because of their occurrence at low levels, and because of the current desire to reduce their concentration to trace levels, only processes that are efficient at such concentrations are recommended. Of these processes, adsorption onto activated carbon is highly recommended because of the favorable nature of adsorption isotherms that renders this process very efficient at low concentrations. Reverse osmosis is another candidate process, however, no information is available on its removal capability of chlorinated organic compounds present at low concentrations. Most reverse osmosis membranes have been developed for the removal of inorganic constituents from brackish waters and the efficiency of these membranes in the separation of organic compounds is suspect since these membranes have been shown to concentrate phenol in the permeate phase (EPA, 1978).

Coagulation followed by filtration have been shown to affect partial removal of some chlorinated organic compounds. Endrin, and Silvex were removed by coagulation followed by filtration to the extent of 35% and 65% respectively. However, this process was very ineffective in the removal of other pesticides such as Toxaphene and 2,4-D (EPA, 1978). Zogorski et al. (1978) investigated the effect of coagulation followed by sedimentation on the trihalomethane formation potential. They observed a 45% reduction in THM formation potential when coagulation was used whereas sedimentation alone was responsible for a reduction of only 10%.

Chemical oxidation presents another possible treatment technology for the removal of chlorinated organic compounds from the aqueous environment. The literature contains very little pertinent information on the topic,

however, the available data suggest that oxidants such as chlorine, ozone and potassium permanganate were relatively ineffective in the removal of some chlorinated pesticides when present in low concentrations (EPA, 1978).

In conclusion, adsorption onto activated carbon appears to be the most logical process to be employed in the removal of chlorinated organic compounds from water. In addition to its ability to reduce these compounds to very low levels, this process provides a treatment alternative which retains most of its adsorption capacity when the feed concentration of adsorbable contaminants is low.

SUMMARY OF FINDINGS AND RECOMMENDATIONS FOR FUTURE RESEARCH

Adsorption onto activated carbon is a complex phenomenon which is influenced as far as adsorption capacity and uptake kinetics by the physical and chemical properties of the adsorbent, the adsorbate and the aqueous medium. Among the adsorbent properties that affect adsorption, the most pertinent are surface area and pore size distribution. These two parameters establish a measure of adsorption capacity as well as uptake rate; in addition, proper selection of pore size distribution may improve the carbon selectivity towards different size adsorbate molecules in that molecules that are larger than the majority of pore sizes will be excluded. Particle size was found to influence the adsorption rate in that an increase in particle size resulted in decreased rates of uptake. Surface polarity and degree of activation of an activated carbon is greatly affected by the number of regeneration cycles an activated carbon has been subjected to. The importance of this parameter undermines the validity and usefulness of a large volume of data in that most data available in the literature have been collected on virgin carbons.

Adsorbate characteristics that were found to influence adsorption capacity and rate were molecular size and weight, solubility and polarity, functional groups, and dissociation constants for the ionizable species. In comparing the adsorption characteristics of organic compounds it is very difficult to separate the effect of the different adsorbate characteristics on the degree and rate of uptake of these compounds onto activated carbon since, in most instances, these characteristics do not vary independently of one another. For example, an increase in molecular weight of a homologous series usually results in decreased solubility and polarity which in turn favor increased adsorption capacity. This however is true provided the adsorbent surface area is still accessible to the larger solute molecules. Recent attempts

to utilize generalized parameters such as in the ideal adsorbed solution theory or the solubility parameter concept have demonstrated that more research is needed in characterizing adsorption capacity based on solute/solvent/carbon characteristics thus minimizing the need for extensive laboratory analyses in determining design parameters and in the selection of adsorbents.

The aqueous medium properties that influence adsorption kinetics and capacity the most are temperature, pH, dissolved solids concentration and most importantly the presence and nature of other competing substrates. In general, an increase in temperature has been observed to decrease adsorption capacity, however, the rate of uptake increases since diffusion, both film and pore-transport, is usually the rate controlling mechanism. Within normal ranges of pH that are encountered in water and wastewater treatment applications, the effect of the hydronium ion concentration is strictly experienced in its effect on the distribution of adsorbate molecules between neutral and ionizable forms. In general, the neutral forms are more hydrophobic and adsorb faster and to a greater extent than do the ionized species. The effect of the dissolved solids content of the aqueous medium on the adsorption capacity of various solutes is very poorly understood. References have been made to both its influence as well as to the lack of it. The effect of other adsorbable compounds on adsorption is manifested in the form of competition between the various species for the limited availability of the adsorbent surface. Compounds exhibiting stronger adsorption capacities in single solute systems tend to compete better for the adsorbent surface when exposed to that surface in the presence of other compounds that exhibit poorer adsorption capacities.

Some of the more commonly used equilibrium adsorption isotherm mathematical models were presented and discussed in detail as related to their development, range of application and limitations. The Langmuir and Freundlich adsorption isotherms represent two parameter isotherms that have been widely utilized in data representation. However, for most experimental data, these models were observed to correlate data over narrow ranges of equilibrium concentration and because of this deficiency, newer isotherm adsorption models that utilize three parameters for data representation are gaining recognition as better modeling tools.

The present effort includes an extensive literature review of available adsorption equilibrium data on the chlorinated organic compounds appearing on the priority pollutant list. In general, these data have been collected using different types and sizes of activated carbons, different reaction or contact times, different degrees of temperature and pH control and fluctuations, and different background aqueous solution contents. As a result, it is not advisable to utilize these data to establish absolute criteria on relative adsorbivity and system capacity. These data provide, at best, a measure of removal potential and capacity under the conditions used during the experimental procedure.

Adsorption equilibrium isotherm data for ten of the forty eight chlorinated organic compounds appearing in the priority pollutant list were found in the literature and are presented in the text. These compounds are: chlorobenzene, bis(2-chloroethyl) ether, 2,4-dichlorophenol, 2-chlorophenol, pentachlorophenol, chloroform, bromoform, chlorodibromomethane, bromodichloromethane, and carbon tetrachloride. Additional literature data on the adsorption capacity of activated carbon for other chlorinated organic compounds and non-chlorinated organic compounds appearing on the priority pollutant list are presented.

Included in this literature review is an overview of some of the pertinent mathematical models that have been employed in the prediction of adsorption reactor performance. Among the mathematical models presented, Danby's model and Michael's mass transfer zone model provide easy tools for data analysis and adsorber sizing and design. However, these two models are limited to systems that may be characterized by a single strength parameter in the aqueous phase such as crude parameters (TOC, BOD, COD) or in instances where one solute presents the majority of the adsorbable content of the water.

Mathematical models that rely on numerical solution techniques, on the other hand, allow for the interpretation and simulation of data involving multisolute systems. These models however are difficult to solve and formulate and, as such, their application in plant design is still very limited. A basic deficiency in the use of sophisticated modeling tools is the absence of basic data on the adsorption capacities of different organic compounds on the various commercially available carbons as well as the absence of good and widely applicable competition adsorption models that allow for accurate simulation of chromatographic effects.

Despite the availability of a sizable body of literature on the removal of organic solutes from aqueous solutions by activated carbon, the available data base is deficient in a number of areas as indicated below:

- a. Commercially available carbons should be properly characterized as far as physical and chemical properties, and these properties should be related to kinetic and capacity parameters utilizing a number of standard solutes that cover a wide range of applications. The results from such a study will shed light on methodologies for screening and selecting carbons most suited for specific applications.

- b. The methods for collecting and reporting adsorption isotherm data should be standardized.

c. Column adsorption studies, in as far as column length and diameter, flow rate and granule particle size should be standardized in order to allow for the comparison of experimental data. Where the feed solution is synthesized, a number of feed solute concentrations should be selected to cover a wide range of applications.

d. Most isotherm and column performance data have been collected on virgin activated carbons. This is inspite of the fact that the activated carbon in a packed bed adsorber has on the average undergone twenty regenerations. It is the recommendation of the authors that the effect of the number of regeneration cycles on performance parameters should be investigated.

e. Adsorption isotherm and column performance data are usually collected on a solute system where distilled water and a selected buffer system are employed. This is usually satisfactory when the solute in the feed is present at high concentrations as compared to other organic matter present in the water to be treated. For lower concentrations, however, the effect of the other organic matter present in the water may be pronounced. It is the recommendation of the authors, therefore, that the feed solution to the adsorber simulate as closely as possible the actual water or wastewater of concern.

As far as the research interest demonstrated by the Tennessee Valley Authority in the removal of chlorinated organic compounds present in the power plant waters is concerned, it is the opinion of the authors that such a research endeavour should proceed according to the following format:

a. An intensive sampling and analytical program should be established with the objective of characterizing the chlorinated organic matter present in the discharges of interest. This characterization should not be limited to the chlorinated organic compounds occurring in the waters but should

also include other compounds that may act as precursors to the formation of chlorinated compounds.

b. Once the compounds of interest have been identified, an extensive study should be conducted to determine their removal potential on several brands of activated carbon. The adsorption characteristics of these compounds should be investigated both when present in pure systems as well as when background organic matter is present. The results obtained from this phase of the experimental program will provide information on the removal capabilities onto activated carbons of several problem organic compounds present in TVA discharge waters. In addition, these results will provide the baseline data that are needed for any modeling or design effort.

c. A flexible mathematical model should be developed in order to facilitate the extrapolation of small scale experimental data to the design of full scale carbon adsorption systems.

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