

STATE-OF-THE-ART IN PREDICTING ACTIVATED CARBON PERFORMANCE

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Abstract:

Adequate theories of multicomponent gas and liquid phase adsorption have been available for 10 to 15 years. Yet the ideal of using computer simulations to determine treatment costs and to aid in design of real-world environmental systems has never fully materialized. However, current adsorption theories are accurate enough, and quite useful, for making relative comparisons of performance of different carbons and for looking at adsorption versus other technologies for new applications. The use of a gas- and liquid- phase adsorption model is evaluated for predicting performance, optimizing carbon selection, and designing systems for environmental applications.

I. MODELING ENVIRONMENTAL APPLICATIONS - DEFINITION OF THE PROBLEM

The ideal situation would be to have a computer program that instantly predicts the capital and operating cost of an optimized activated carbon system that solves a specific environmental problem in both the gas and liquid phase. In addition, the program would need to be able to account for variability in conditions and stream composition. This algorithm would allow 'what-if' type analyses to aid in design of an optimal system and account for upsets and shutdowns. Also, in the activated carbon design, the algorithm rhythm would provide instant feed back on performance leading to better activated carbon processing schemes and products. We are not there in 1996, but have made progress.

This is not a statistical error analysis or a review of existing adsorption theories. Instead it is a description of what the most practical theoretical approaches can and cannot do with environmental applications. The discussion is less mathematical and more problematical.

A. APPLICATION DEFINITION - COMPUTATIONAL PERSPECTIVE

To do a computation of performance of an adsorption system, we need to know each adsorbable component present, including water. Any background components may be important, even if nondetectable using current techniques. For each component we need concentrations and variations in concentration over the life of the system. Also the treatment objective (acceptable effluent composition) should be defined in similar terms. The required system variables are temperature of each carbon particle (Usually approximated as a simple linear or a radial temperature profile through the adsorber) and gas-phase or liquid-phase linear velocity between the particles. The stream must be a single phase, to have effective contact of the contaminants with the carbon particles and to avoid any unpredictable decay in performance. This means that for the gas phase there must be no particulate matter or freely condensed material, for the liquid phase there must be no suspended solids or precipitation within the column.

B. APPLICATION DEFINITION - REAL WORLD PERSPECTIVE

This ideal of an application description satisfying requirements for computation is rarely, if ever, obtained. Differences between the information required for computation and what is provided by the application definition are listed below.

1. Stream composition

Generally the best case scenario is a stream analysis using a gas chromatograph/mass spectrometer (GCMS) and is usually a first step for both gas and liquid phase applications. This gives a list of compounds and concentrations for a sample taken usually at one moment in time. The GCMS analysis is relatively expensive. Consequently, time averaged values and histories of stream composition are generally not available, and thus variability of composition is not well defined. The major problem with GCMS analysis is that the largest, most adsorbable molecules are also not volatile, and thus are difficult to detect with GCMS. Test methods that are less specific, such as gas or liquid chromatography (GC or LC), measure the major or critical components and give little information on background components. Nonspecific tests such as total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD), color, odor give no useful information and only hint at the composition. However, comparing the results of one of these nonspecific tests to the sum of the concentrations of the known components can be useful to find how much background material is not accounted for in the calculation. Sometimes, this background material can be approximated by substituting model compounds.

2. Carbon temperature

The temperature critical to the calculation is the temperature of the carbon where the adsorption is occurring, not the ambient or stream temperature (when gradients are present). Fortunately the carbon temperature profile in the adsorber is usually known or can be approximated.

3. Linear velocity or flow rate and its variability

Assuming no flow complication such as plugging or wall effects, the activated carbon is only concerned with the instantaneous linear velocity in the voids between it and its neighbors. This generally can be determined from the mass flow rate, void fraction, and dimensions for a given carbon system design. What generally is not included in the calculations are the fluctuations in the flow rate, or stoppage of flow due to shutdowns.

4. Variability of concentration and composition

Variability in stream compositions involves probability of upsets or spills and their magnitude, equipment operating schedules and flow rate changes, and the reliability of the sources of contamination. Few streams are consistent, but many streams that involve a leaching phenomenon, and where the equipment follows a regular routine schedule can become predictable with experience. Unfortunately this experience is generally not available during the design or evaluation stages of a project.

5. Other variables affecting performance

Other factors that can affect performance for gas-phase systems are: relative humidity, presence of condensables (including water), dusts or particulate matter (particulate size and amount). Other factors affecting performance of liquid-phase systems are: pH, conductivity, suspended solids (particulate size and amount). For humidity and pH, the effects can be estimated over a range of conditions and the performance detriment determined. Then an economic decision can be made for humidity or pH control or adjustment. The inlet end of a carbon adsorber will act as a particulate filter for dust and suspended matter, with the ability to filter material with diameters greater than one tenth of the smallest carbon particle diameter. However, operation of a carbon adsorber as a particulate filter is awkward and can be more expensive. The decision on whether to use prefilters for particulates is economical and depends on the severity of the problem. Unfortunately the adsorptive performance decay resulting from the lack of a prefilter for particulates can only be approximated crudely.

6. Defining treatment objectives

Performance is usually defined by the point at which the treatment objective is exceeded. Although objectives are usually defined, the exact point at which a treatment objective is exceeded sometimes adds uncertainty. For example, predicting the point at which a treatment objective is exceeded can be complicated when the objective is a nonspecific test result such as total hydrocarbon, TOC, BOD, COD, color, or odor, and a wide variety of components are present in the effluent of the carbon system. When the objective is cumulative mass over a time period (for example, kilograms of hydrocarbon per month), determining the calculated point at which the carbon system is exhausted and should be replaced is difficult. Percentage removal objectives for individual components can be difficult due to the potential variability of the influent stream and the time lag of a change in the influent to a change in the effluent. From a computational point of view, the simplest treatment objectives are concentration limits for individual components.

7. Regeneration (thermal or extraction)

Incorporation of a regeneration scheme, whether thermal (Steam or hot air), vacuum, or extraction (using a solvent or a pH shift) adds many more variables and uncertainty to the calculations. For example, a correlation of isotherm data as a function of temperature is required for thermal regeneration. Generally the approach is to measure several regeneration cycles and look for the system to reach a steady state. This approach is generally adequate, but does not predict the eventual exhaustion of the carbon with nonregenerable components or other operating inefficiencies that occur later in the life of the carbon bed (such as degradation of the particle to a smaller particle size or slow oxidation of the carbon structure).

II. THEORETICAL APPROACH TO ADSORPTION

A few computational approaches can be used to approximate adsorptive performance, even within the limitations of the real world descriptions of environmental applications mentioned above. In order to select an adsorption theory for predicting performance in environmental applications, the following criteria must apply. The theory must be applicable: for systems with an unlimited number of components, for use with any of the wide variety of commercial activated carbons, and for the range of system variables present such as temperature, pressure, and pH or humidity. These are not trivial requirements because they imply that a multicomponent isotherm capacity can be determined for any component for any activated carbon over a range of concentrations and temperatures, pressures, pH, or humidity. With all these variables, measuring enough points to define the multicomponent isotherm surfaces is not practical. Therefore, the theoretical approach must predict multicomponent isotherms from single component isotherm data. Also isotherm data on one

activated carbon must generalize to all other commercialized carbons (Libraries of empirical isotherms will not be available for all commercial carbons). At least two approaches can satisfy these computational requirements and the practical limitations on the amount of empirical data required. The Ideal Adsorbed Solution Theory¹ (IAS) incorporating a generalized characteristic curve², and the Polanyi Adsorption Potential Theory³ incorporating the Hansen-Fackler Modification⁴ (Polanyi). The remainder of the discussion on performance prediction will be limited to the use of these two approaches.

A. THEORETICAL APPROXIMATIONS AND ASSUMPTIONS

1. Physical adsorption predominates

The adsorbates exhibit no specific interactions with the surface or each other, including chemical reactions on other nonideal behavior. This is a good assumption for most adsorbates on activated carbons. Specific interactions do occur, for example dipole-dipole and dipole-surface oxide interactions, but they are generally less significant than the nonspecific physical attractions. If this is not the case, then a polar adsorbent like Silica gel or alumina should be used instead of a nonpolar activated carbon. If the specific interaction between adsorbates is strong, such as with dimerization, then treat the dimer as the adsorbate.

2. Bulk behavior is observed in the pores

What happens outside the particle happens inside the pores of the activated carbon. In other words, the adsorbates exhibit lateral interactions, bulk solubility limits, and melting points. The carbon structure does not alter the physical properties of the adsorbate. This is a good approximation on nonimpregnated activated carbons.

3. No molecular sieving

All adsorbates have equal access to all portions of the carbon pore structure. Generally this is a good assumption. Molecular sieving or exclusion of large or bulky molecules does occur in activated carbons in specific instances, but it is the exception and not the rule. Also, on commercial activated carbons, the pore structure is purposefully open to provide easy access. Adsorbates excluded are generally so large that they are adsorbed in another part of the structure. When exclusion does occur, accounting for it with mathematical corrections to the single component isotherm is a possibility.

4. Volume-based competition

Application is based on pore filling, and adsorbates compete on a volume basis. An adsorbate with twice the molar volume will compete with two of the smaller molecules. This is a good assumption and is why molar volume is one of the most important properties in determining adsorbability of a molecule.

B. STEPS IN THE COMPUTATION

1. Generate single component isotherms

The first step is to generate a set of single component isotherms on a carbon of interest over the range of temperatures and stream conditions. An empirical approach would require a handbook of adsorption isotherms to be determined for each contaminant, on every carbon, over the range of temperatures and pH. The solution is to generate the single component isotherms using a generalized characteristic curve for the carbon and set of specific characteristics for each adsorbate determined on a standard carbon. The IAS theory can also incorporate a generalized characteristic curve⁵ to generate the single component isotherms that are very similar to this classic Polanyi approach.⁶

First assume a pair of adsorbate properties, independent of the carbon, which can be used to scale adsorption isotherms to a single characteristic curve. One property is related to relative strength of the adsorptive interaction (Polanyi polarizability), and the other is related to the efficiency of filling the pore structure (molar volume in the pore determined from the maximum adsorption capacity at near saturated conditions). Next assume that the characteristic curve is a function of the carbon pore structure and therefore is a property of the adsorbent and independent of the adsorbate. The characteristic curve is generally presented as a distribution of pore volume over different adsorptive forces, corresponding to different pore sizes. The assumption is that the carbon pore structure is constant and fills on a volume basis and interacts with molecules in the same manner. Differences are in the number of molecules that fit into a pore and the relative strength of the interaction with the carbon structure.

With these assumptions, only one isotherm for a standard adsorbate (for example propane) is required on each carbon to determine the characteristic curve. Several simple techniques are available to generate these data easily.⁷ Then one isotherm for each contaminant is required on a standard and well-defined activated carbon to determine the adsorbate molar volume and relative

adsorption strength in the pores. The database of published isotherms on well-defined standard carbons is growing, but is still inadequately small.

2. Calculate the multicomponent isotherms

The thermodynamics of adsorption of multicomponent systems on activated carbons, both from the gas-phase and liquid-phase, has been defined by several models,⁸ but the most popular have been the Polanyi and IAS theories. Both approaches are thermodynamically consistent⁹, and calculation algorithms are available which can handle a large number of carbons and adsorbates efficiently.¹⁰ The computation determines the partial occupation of the different regions of the pore space (adsorption sites) by the different contaminants. By summing the occupation of all sites by all contaminants, under the stream conditions, a multicomponent loading on the carbon particle is determined.

3. Incorporate a kinetic model for mass-transfer resistance

Once the multicomponent thermodynamics has defined the equilibrium state, a kinetic model can be incorporated to account for the diffusion of the adsorbate into the carbon pore structure. The adsorption kinetics has been most often modeled using an approach that incorporates three or four diffusion steps: the interparticle mass transfer (bulk diffusion), intraparticle mass-transfer (pore diffusion), and finally adsorption/reorganization (surface diffusion).¹¹

The interparticle step is dependent on flow rates and column packing efficiencies. It is independent of carbon structure except its particle size and shape, and has been adequately modeled using columns of glass beads. Some modelers also add a boundary layer or film diffusion step as a second step in the interparticle (or bulk) diffusion process. The interparticle diffusion process is readily handled mathematically with few empirical parameters.

Intraparticle diffusion is independent of the flow rate or column dimensions but is highly dependent on carbon transport pore structure, often called the macropores and mesopores. Because this transport structure is specific to the carbon pore size distribution and how the pores are connected, the intraparticle diffusion coefficient can only be determined empirically. Unfortunately for nearly all 'well-designed' systems this is the slowest and thus the rate-controlling step in the adsorption process. The surface diffusion or rearrangement steps are independent of the transport pore structure but are dependent on the carbon and processes that are occurring. It also is only modeled empirically.

One goal in commercial adsorption systems design is to ensure the mass transfer zone is less than 20% of the column length to use the capacity of the activated carbon efficiently. For gas-phase adsorption systems it is generally much less than 20%. Therefore, the accuracy of the kinetic model is less critical when dealing with well-designed adsorption systems, especially in the gas-phase. Consequently, crude approximations for the interparticle, intraparticle, and surface diffusion coefficients are often used and are adequate.

4. Representation of the adsorbent column

Once the kinetics and thermodynamics are described, then a model is needed to represent the adsorption system. The column dynamics can be represented several different ways,¹² from theoretical plate (or stage-wise equilibrium) approximations, that resemble distillation column models, to calculation of widths of adsorption bands which resemble chromatography approaches. More rigorous approaches using coupled partial differential equations for heat and mass balance can also be used, but are generally not justified unless the system is complex, for example involving a complicated regeneration scheme.

Errors are also introduced when simplifying assumptions are made, like treating nonisothermal column profiles as isothermal or ignoring heat losses and treating the column as adiabatic. The other complications that can be over simplified are competitive displacement resulting in a rollover of displaced component, and concentrations within the column that are higher than the influent. Rollover increases column efficiency, but this increase is often ignored by models.¹¹ Finally, complications are added by the regeneration process, which is almost always a partial regeneration, and usually runs counter current to the adsorption flow. This results in complicated temperature and loading profiles in the carbon column and broader mass transfer zones. Simplifying approximations for regenerable systems are the same as the ones mentioned above, but are more significant and thus result in larger errors.

C. RESULTS OF THE COMPUTATION

The results of the computation describe the column performance as order of elution, adsorption band widths, rollover or displacement, mass transfer zone size, and carbon exhaustion rate to a percentage breakthrough or to an effluent concentration limit. The order of elution shows which compounds elute first and will be key in exceeding the treatment objective. The adsorption band widths define

the segregation or chromatographic separation of components on the carbon column that can be important in some purification and separation processes. Rollover or displacement behavior can be important when dealing with separation using desorption processes or adsorbate recovery processes. A mass-transfer zone is predicted for each component present, but only the early eluting components are of interest. The mass transfer zone size of these components dictates the adsorber size and is the key to the system balance between the capital cost of the adsorption system and operating cost for the replacement activated carbon. (Utility costs, for energy and water, are an additional consideration for regenerable systems.)

Finally the predicted exhaustion rates are usually in units of bed volumes treated to an effluent treatment objective, which can be a percentage of the influent concentration or it can be an absolute concentration level. This exhaustion rate determines the absolute operating cost of the system and the change-out or replacement frequency of the activated carbon in the column. The operating cost derived from the exhaustion rate, can be compared directly to costs of alternate technologies.

III. SOURCES OF ERROR

Accuracy of these methods is highly dependent on complexity and consistency of the stream, the ideality of the components, and the definition of the treatment objectives. The following discussion is not a statistical error analysis, but the relative assessment of the greatest sources of error based on experience running performance prediction calculations for general gas-phase and liquid-phase environmental applications. Table 1 lists a description of the various sources of uncertainty, and the relative importance of the contribution to the overall error of the performance predictions.

A. SINGLE COMPONENT ISOTHERM MEASUREMENT AND PREDICTION

The multicomponent adsorption models must also predict the original single component isotherms. Any errors due to oversimplification, when approximating single component behavior are incorporated in the single component prediction and carried over to the multicomponent case. Several examples of the levels of errors for single component predictions are listed in Table 2 for the Polanyi approach.

Major sources of error for the single component predictions are as follows.

1. Inaccuracies in the isotherm test or measurement - equilibrium was not attained, the carbon temperature was not controlled or measured, or the analytical errors were magnified by calculating the adsorption as a small difference between two large measurements.
2. Carbon samples were not representative - samples were contaminated (solvent vapors from the lab), out-of-date and no longer representative of the commercial activated carbon, or highly oxidized which can modify the pore structure.
3. A known isotherm was substituted for an unknown component - using an isotherm for an isomer of the adsorbate, for an adsorbate with similar molecular structures, or for an adsorbate with similar molecular formula and weight.
4. Selection of a single component adsorption theory - Polanyi and IAS can both assume a characteristic curve shape, necessary to be practical, but significantly decreases the accuracy of the predictions.

B. MULTICOMPONENT ISOTHERM PREDICTION THEORY

Most of the errors are due to the inherent assumptions of the theories.¹³ Typical errors for common components are smaller than the single component values in Table 3, but exceptional errors can magnify theoretical shortcomings and become quite large. Thus, the multicomponent errors primarily reduce the reliability of the performance prediction.

Major sources of error for the multicomponent predictions are as follows.

1. Choice of the multicomponent theory - in some simple cases the Polanyi and IAS theories are mathematically identical, but for the general case the simple Polanyi approach is less accurate than the IAS, which is less accurate than the Polanyi with the Hansen-Fackler modification.¹⁴
2. Breakdowns of the basic assumptions (sometimes the effects can be corrected for by adjusting the single component isotherm¹⁵), for example:
 - Volume-based competition - in rare instances molecular shape can affect the volume competition.
 - Molecular sieving - becomes significant specifically with large molecules and can affect competition in the smaller pores.
 - Chemisorption - nonideal systems involving highly polar or reactive species can have additional specific interactions, such as hydrogen bonding, polar interactions, dimer formation, etc.
 - Bulk behavior in the pores - unique characteristics observed only when the molecule is an adsorbate, usually due to a configuration or interaction due to the carbon structure.

C. PROBLEM DEFINITION

The two biggest concerns for accurate performance prediction are a precise identification of the background components and definition of the treatment objective. Vaguely defined background components (TOC, BOD, COD) and unknown or nondetectable compounds would add uncertainty to the prediction even if the calculation method was perfect. Empirical means of classifying the competitive effects of background components exist, even when the components are not well defined or detectable.¹⁶ However, these methods can be difficult to carry out and are only approximations.

The definition of the treatment objective also can contribute to uncertainty in the performance prediction when defined vaguely using terms like TOC, BOD, COD, non detectable, color, or odor. To compute adsorptive performance, all treatment objectives must be translated to absolute concentration levels for specific individual components for computation. Occasionally, the computation is run once just to learn the order of elution of the contaminants, which is used to decide which eluting component exceeds the treatment objective. The objective is redefined as an absolute concentration of that critical component and the computation is repeated. Table 2 lists treatment objective definitions and how to convert them to a usable form, and their effect on the accuracy of the results.

D. MODELING THE ADSORPTION SYSTEM

Other inaccuracies in the predictions are modeling of the adsorption kinetics and choice of models for the column dynamics (adsorbent bands, theoretical plates, etc.). These errors are not as critical for well designed commercial adsorption systems, where the carbon utilization is greater than 80% (the mass transfer zone of the early eluting components is less than 20% of the column). Consequently, the error contribution due to the kinetic model or the column dynamics is generally less than that of the single component isotherm approximations. The exception is for poorly designed systems with shallow beds and high linear velocities, or systems that involve a complex regeneration scheme.

IV. STATE-OF-THE-ART OF ADSORPTIVE PERFORMANCE PREDICTION

We should neither be satisfied nor be despondent over the previous discussion of current performance prediction methods. The methods are useful evaluation tools, although they fall short of our goals for environmental applications, and the situation can only improve to the future.

A. WHAT CURRENTLY CAN BE DONE ACCURATELY

The existing techniques have inherent errors due to simplifying assumptions that are necessary to make them easier to use. However, these techniques are adequate for making gross comparisons of technologies or relative performance comparisons for activated carbon product selection.

1. Relative comparison of different carbons

Many major errors in predicting adsorption isotherms cancel when making relative performance comparisons under identical conditions and stream compositions. This is often the case when trying to identify the optimal activated carbon for a specific application. Performance of several different carbon structures can be compared to select the activated carbon product with the optimum performance or price-performance ratio. The absolute performance may not be accurate, but if the same errors were reproduced for each carbon, then selecting the best performing carbon is still possible.

2. Comparison of carbon adsorption to alternative technologies

When comparing activated carbon adsorption to alternative technologies for environmental cleanups, generally differences in performance are large, or gross assumptions had to be made to equate the dissimilar systems. Consequently, the size of these errors is insignificant compared to the differences in performance or the errors introduced by the gross assumptions. When the performance (or price-performance ratio) of carbon adsorption and another technology are similar, the prediction errors can become significant. In this situation, however, the proper conclusion should be that both technologies are equal and no real performance differentiation exists. In these cases, the selection of the best technology will usually be dictated by capital-operating cost ratios, system size, available utilities, or engineering preferences.

3. Describing general behavior of activated carbon columns

The existing models are also useful in "what if" scenarios. Because the Polanyi and IAS approaches have a basis in thermodynamics, many fundamental principals are incorporated in the computations. Consequently, the methods will extrapolate to extreme conditions and predicted behavior of the system under upset conditions.

For example, they can approximate the effects of spikes in the influent concentration during upsets, or spills and dips in concentration during shutdowns (loss of the contaminant source). The bed volumes a carbon system can treat during a spike are always greater than the bed volumes that would

have been treated if the same amount of contaminant had been introduced at the average influent concentration. In terms of mass of contaminant removed per mass of carbon, the spike improved performance. However, the benefit of the spike, a band within the column with more heavily loaded carbon, decreases with additional bed volumes treated after the spike occurs due to dilution and spreading of this band. Thus the benefit of a spike is least for a fresh column and greatest for a column that was nearing exhaustion.

The situation is different for dips in concentration (disappearance of contaminants). The bed volumes a carbon system can treat during a dip are greater than the bed volumes that would have been treated if the dip had not occurred. As for bed volumes treated, the dip improves performance and the life of the carbon. Desorption of the contaminant-loaded carbon does occur, but this is less important than the decrease in influent concentration. With a dip in concentration, contaminants were removed or not added upstream, which reduces the requirements on the carbon system more than the negative effects of extraction or desorption. However, the benefit of the dip is not realized unless the influent returns to its previous concentrations and the carbon system has the opportunity to treat additional bed volumes of contaminated influent. Thus the benefit is greatest for a fresh column and is least for columns nearing exhaustion.

B. WHAT CURRENTLY CANNOT BE DONE

For most all real-world environmental applications, today's performance prediction techniques are inadequate for making cost guarantees or for determining minor improvements due that would result from evolutionary changes in equipment design.

1. Cost guarantees

The average error levels are small enough, and their effect could be incorporated into cost guarantees by conservatively adjusting the specified performance by several standard deviations. Problems arise due to the uncertainty of when the basic assumptions of the theories breakdown. The effects of these breakdowns can be large errors and represent an incalculable risk to business. Rough cost estimates can be made for comparison purposes, which are generally useful for making a decision to investigate carbon adsorption further.

2. Engineering design

For engineering design, the computations are useful only for relative sizing or selecting equipment from a catalog list. The computational errors are simply too large to measure improvements in performance due to refinements in designs, for example improved adsorbers flow patterns, optimal height to diameter (H/D) ratios, or inlet/outlet nozzle patterns. In these situations the design changes will only slightly affect performance and the effect is often less than the error in the calculations. Also effects of particulate and suspended matter cannot be considered, which often dictate design.

3. Replacing pilot-scale column simulations

Computations with theoretical models are not yet substitutes for on-site, pilot-scale, column simulation tests. This is especially true when the stream and the treatment objectives, or even the background components, are defined vaguely (using color, odor, TOC, BOD, COD, or nondetectable).

C. WHAT CAN BE DONE TO IMPROVED THE PREDICTION OF ADSORPTIVE PERFORMANCE?

The simplest way to improve the accuracy of any computational method is to incorporate more empiricism or empirically derived variables. However, the approach must also be practical as for data required. Some errors are inherent in the simplifying assumptions required to reduce the amount of empirical data required for performance prediction. For example, the presumption of a characteristic curve greatly reduces the amount of single component isotherm data required, but also is a major contributor to error. The following are several things that could be done now to improve the accuracy of the predictions in a practical manner.

1. Standardized activated carbon samples

Isotherms/adsorption data needs to be generated on standard carbons - even commercial carbons of one name change over the years. Carbons should have published carbon characterization curves or an isotherm with a single known component with data ranging more than five orders of magnitude in concentration or in partial pressure.

2. A handbook on adsorption characteristics

Accurate single component isotherm data on a wider variety of contaminants over a broader range of temperatures is needed on standard activated carbon samples with known characteristic curves. With this data the empirical adsorbate characteristics can be determined and then assembled in a handbook.

3. Additional real-world experience

Comparing more results from real world adsorption systems versus the best theoretical predictions increases the confidence in the reliability of the basic assumptions of the adsorption theories.

Eventually we may learn how to approximate backgrounds empirically and predict the breakdown of theories. We may reassess the relative importance of sources of error of existing models and direct the theoretical and empirical work being done on adsorption on activated carbon to improve the current situation.

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Table 1 Relative Importance of the Different Sources of Errors

Source of Error in Adsorption Calculations	Typical Error Contribution	Potential for Large Error in Special Cases
Single component isotherm prediction/measurement		
Analytical Errors in measurement	<10%	No
Carbon sample not representative	<20%	Yes
Substitution of an known Isotherm for an unknown component	10 to 100%	Yes
Selection of theory/technique	0 to 100%	Slight
Multicomponent isotherm prediction theory		
Choice of theory IAS vs. Polanyi	0 to 100%	Yes
Volumes-based competition	<10%	Slight
Interactions and accessibility	0 to 100%	Yes
Bulk behavior in the pores	<10%	Slight
Modeling adsorption system		
Selection of the Kinetic approaches	<20%*	No
Choice of Models for Column dynamics	<20%*	No
Problem Definition		
Stream Composition - critical and background components and concentration	10 to 100%	Yes
Background components and nondetectable compounds	50 to 500%	Yes
Treatment Objectives defined vaguely (nondetectable)	<20%	Slight
Nonspecific Test Objective (TOC, BOD, COD, etc.)	10 to 100%	Slight
Temperature - (within each carbon particle - through-out the bed)	<20%	No
Flow rate - Linear velocity/mass flow and its variability	<10%*	No
Variability of concentration and composition,	10 to 100%	No
Complex Schemas-Regeneration processes	20 to 200%	Yes

* For well-designed adsorption systems with MTZ<20% of column

Table 2 Errors in Single Component Predictions

	Average Deviation %	Range of Errors*		Concentration		Loading Range		No. of Points	Probable Cause of Error
		High % Error	Low % Error	High ppm	Low ppm	High cc/100g.carbon	Low		
Gas-phase Adsorption Isotherms (ref.15)									
Methanol @ 22C,60C	275.6%	1082%	-11.1%	3481	387	7.4	0.146	6	Chemisorption at low loadings
Toluene @ 121C	6.7%	34.7%	-6.4%	45	0.066	5.24	0.494	5	Fitting characteristic curve
Trimethyl pentane @ 117C	-61.5%	5.2%	-94.2%	50	0.068	9.36	0.153	16	Molecular sieving
Liquid-phase Adsorption Isotherms (ref.14)									
Pentanol @ 25C	4.9%	21.6%	-19.2%	13800	11	46.8	8.44	14	Fitting characteristic curve
Benzamide @ 25C	1.0%	12.0%	-10.1%	9970	160	34.5	18.1	6	Analytical (random)
o-Phthalic acid @ 25C	-0.5%	8.2%	-14.0%	1990	3.9	19.6	7.22	6	Hydration effects at high loadings

* negative error means the actual measurement was less than the predicted value

Table 3 Contributions to Errors in Computing Breakthrough Limits

Breakthrough Criterion	Example of Criteria	Sources of Additional Computation Error
Specific Objectives - Effluent Level is an Identified Key Component		
1 Absolute concentration	5ppm CHCl3	Analytical accuracy/reproducibility
2 % Breakthrough/removal	99% removal of CHCl3	#1 + Inaccuracy of Influent level Determination
3 Non Detectable	Nondetectable CHCl3	#1+Analytical Sensitivity/background interferences
Grouped Objectives - Effluent Level is a Sum of Several Key Components		
4 Class of Compounds	5ppm Chlorinated Hydrocarbons	#1,2, or 3 + know order of elution and sum breakthrough conc.
5 lb. emissions per month	10 lb. hydrocarbons per month limit	#4+integrate breakthrough curves and sum over several events
Nonspecific Objectives - Effluent Level is a Response of a Detector or Test		
6 TOC	100 ppm TOC	#4 + relative weighting factors for sensitivity to test(TOC)
7 Total Combustibles (by FID)	1 ppm Hydrocarbon as propane	#4 + relative weighting factors for FID sensitivity
8 Nonmethane hydrocarbon	1 ppm nonmethane hydrocarbon	#7 + inaccuracy of methane determination
9 COD	100 ppm COD	#6 + COD interferences (Ex. inorganic reductants)
10 BOD		#6 + BOD interferences (Ex. Low BOD due to toxics present)
11 Color		#6 + Complex formation, color shifts, turbidity corrections
12 Taste or Odor		#6 + T/O panels problems (Ex. Odor interactions, desensitizers)