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Project Summary

Evaluation of the MIDDAS System for Designing GAC Adsorbers

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The micro-diameter-depth-adsorption system (MIDDAS) was evaluated for its usefulness in determining equilibrium parameters for adsorption in granular activated carbon (GAC) systems. The system employs a column configuration for determining such parameters, rather than the traditional completely mixed batch reactor (CMBR) configuration. The equilibrium results were employed in the homogeneous surface diffusion model (HSDM) in conjunction with the short bed adsorber (SBA) technique to determine rate parameters for trichloroethylene (TCE) adsorption on GAC in both single-solute and more complex systems. The results of these studies indicated that the equilibrium capacity for TCE adsorption from distilled water was lower to a statistically significantly extent when determined by the MIDDAS technique than when determined by the CMBR technique. The rate parameter associated with transport within the adsorption particle (D_s, the surface diffusion coefficient in the HSDM) was significantly dependent on the selected isotherm capacity parameter, whereas the rate parameter associated with external mass transfer (k_f, the film transfer coefficient) was not significantly affected by changes in the isotherm. These calibrated rate parameters were used in subsequent verification studies with deep adsorption beds; the results indicated that rate parameters determined using the MIDDAS technique tended to provide better predictions of deep bed behavior than did those determined with the CMBR methodology.

The MIDDAS methodology was also employed in determining parameters for both a bi-solute system involving TCE and p-dichlorobenzene (DCB) and for a system involving TCE in a background of naturally occurring organic matter. In the bi-solute case, the equilibrium interactions between the two adsorbates were evaluated using the ideal adsorbed solution theory (IAST), which generally described the data well. Model predictions resulting from the parameters obtained with the use of these techniques were, however, not as good, with the predictions for DCB generally being superior to those for TCE. In the study involving the presence of background organic matter, TCE was added to Huron River water before use in the MIDDAS system. The predictions resulting from the parameters obtained in this case were poor, indicating the possibility of a dependence of adsorption capacity on adsorbent particle size or on other factors not accounted for in the MIDDAS approach.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction and Background

GAC treatment technology has been designated as the best available technology for removal of synthetic organic chemicals (SOCs) from contaminated water. While GAC treatment has indeed proven

to be an excellent option for removal of a broad range of SOCs commonly found in raw water sources, difficulties still remain with regard to design of technically and economically feasible systems.

Fixed-bed (or column) adsorbers represent the most practical category of reactor configuration for GAC treatment systems. The objective of GAC system design in such instances is to optimize empty bed contact time, hydraulic surface loading, and system configuration (i.e., series or parallel column operation) to yield maximum utilization GAC adsorption capacity while meeting specific treatment objectives. Various approaches have been developed to aid in the design process; computer-based mathematical models offer the dual advantage of furnishing the design engineer with important system information, as well as providing an avenue for indepth investigation of factors affecting the adsorption process.

The HSDM is a predictive model that has been validated over an extensive range of conditions. It incorporates mathematical descriptions of the major physicochemical mechanisms recognized to occur in fixed-bed systems: namely, axial flow with dispersion, local equilibria at the surface of the particle, mass transfer resistance across a hydrodynamic boundary layer surrounding the particle, and intraparticle diffusion along pore surfaces within the particle. Input parameters to the HSDM consist of phenomenological rate and equilibrium coefficients. A variety of multi-parameter isotherm models generally describe GAC equilibria well. To calibrate equilibrium models, two or more characteristic constants must be determined; in the case of the widely used semi-empirical Freundlich model, the parameters are an equilibrium capacity parameter, K_F, and a parameter, n, which relates to the magnitude of the driving force for adsorption. Rate processes in the HSDM, modeled as two resistances in series, are characterized by an external mass transfer coefficient, k_f, and an intraparticle surface diffusion constant, D_s.

Accurate estimation of model parameters is critical to reliably predict performance. Isotherm parameters such as K_F and n are traditionally obtained from CMBR equilibrium data. Values for k_f are typically determined from mass transfer correlations derived from experimental data for other systems (so-called "literature" correlations), and values for D_s are commonly obtained by fitting CMBR rate data with the use of an appropriate mathematical model. A number of difficulties and potential errors are associated with these parameter estimation techniques. Mass transfer correlations are usually developed for systems substantially different from the system to which they are applied. Furthermore, the hydrodynamic and contaminant removal characteristics of CMBR rate systems differ dramatically from those of the fixed-bed reactors used in practical GAC system designs. It is impossible to predict which solutes or classes of solutes may be most influenced by reactor configuration from first principles. If capacity measurements are in fact strongly dependent on reactor configuration for a particular GAC application, then use of CMBR-derived parameters to attempt simulation of column configurations may lead to an inaccurate description of adsorptive behavior of solution components.

The above discussion delineates one of the major difficulties associated with the use of mathematical models for GAC system design: namely, accurate parameter determination. The development of methodologies to practically and economically determine accurate input parameters has been a major focus of research over the past decade. This research has led to development of a number of bench-scale methodologies for determination of both equilibrium and rate model coefficients. The MIDDAS technique employs a combination of the SBA technique and a modified version of a high-pressure minicolumn method. It was developed as a means to provide greater accuracy in determining model equilibrium parameters in a system with the same hydrodynamic attributes as the full-scale adsorber, while doing so in a manageable time frame. The SBA technique was developed to provide greater accuracy in estimating rate parameters. The MIDDAS methodology allows simultaneous determination of external film transfer and intraparticle surface diffusion coefficients from the same set of experimental data; this obviates the need for literature correlations and CMBR-based rate studies and eliminates potential error-compounding by mutual compensation of individual errors in these coefficients during parameter search/regression analysis. The application of this methodology to estimate mass transport parameters has been demonstrated previously, and the approach offers substantial promise as a means for developing bench-scale information that can be used to facilitate and enhance full-scale system design procedures.

The overall goal of this study was to extend previous investigations of the applicability of the MIDDAS methodology to a range of practical multiple-solute/background water supply conditions for selected SOCs. A number of specific objectives relating to this aim were investigated in the studies described here, including: 1) comparison of MIDDAS and CMBR methodologies for determination of equilibrium parameters; 2) evaluation of the SBA methodology for estimation of mass transport parameters; and 3) evaluation of ideal adsorbed solution theory (IAST) in conjunction with the MIDDAS isotherm technique as an approach to modeling multisolute systems.

Materials and Methods

Materials

The adsorbent used in all experiments was Filtrasorb 400* activated carbon (Calgon Corp., Pittsburgh, PA). GAC particle size fractions were obtained by crushing and sieving carbon samples obtained from one lot of carbon. The resulting fractions were washed in distilled, deionized water to remove fines, dried overnight at 105°C, and transferred to airtight containers for storage. Carbon for immediate use was dried again to remove any moisture adsorbed in storage and stored in a desiccator.

TCE was the primary target SOC employed in this work; DCB was employed as a second target solute in bi-solute investigations. TCE and DCB were selected because they have been designated as U.S. Environmental Protection Agency priority pollutants by the EPA, have been identified in contaminated surface and groundwaters, are relatively straightforward to analyze, and represent a broad class of compounds commonly found in the environment.

Feed solutions of the target solutes were prepared through direct injection of a high-concentration stock solution of the target solute dissolved in methanol into the background water. Experiments were conducted at a temperature of 25°±2°C. All samples were extracted immediately into hexane and analyzed for TCE or DCB by packed or capillary column gas chromatography with electron capture detection.

To obtain high purity water, distilled-deionized water was processed through a Milli-Q water system (Millipore). Huron River water (HRW), collected from Argo Park in Ann Arbor, was stored and refrigerated in 55-gal stainless-steel drums until used. Approximately 100 mg/L sodium azide was added to retard bacterial growth

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

and degradation of organic matter. Batch reactor isotherm studies have shown that sodium azide does not significantly affect the adsorption equilibria of target compounds. Before use, the HRW was filtered through a 1.0 μ filter (Gelman Sciences) to remove particulate matter. No attempt was made to control pH.

Methods

Isotherm Parameters from CMBR Data

Individual 250-mL borosilicate bottles containing preweighed masses of 80/100 mesh activated carbon were filled with a solution of the designated background water spiked with either TCE or DCB. Initial solution concentrations of the target compound and carbon masses were estimated to achieve equilibrium results that spanned the concentration range of interest. Filled bottles were sealed headspace-free with the use of Teflon-lined septa and allowed to equilibrate on a rotary tumbler for 7 days. Rate studies with TCE and DCB showed that an equilibration time of 7 days was sufficient to achieve equilibrium for the carbon size used in this study. Filled, sealed bottles without carbon were also tumbled simultaneously with the sample bottles to assess volatility losses. After equilibration, samples were taken from the bottles containing carbon using a gastight syringe (Hamilton), filtered through a prewashed glass fiber filter (Gelman Sciences) in a stainless-steel filter holder (Fischer Scientific) to remove any fines in the sample, and analyzed for TCE or DCB. Other studies indicated that TCE and DCB losses onto the filters and filter holder were negligible. The mass of solute on the carbon at equilibrium, q_e, was obtained by a mass balance on the closed system:

$$q_e = \frac{(C_o - C_e)}{M/V} \qquad (1)$$

where C_o is the initial concentration of the solution, C_e is the final (equilibrium) solution concentration, M is the mass of carbon used, and V is the volume of the reactor.

Isotherm Parameters in the MIDDAS System

The MIDDAS system used to conduct column isotherm studies consisted of a packed 0.386-cm (ID) stainless-steel column operated at a superficial loading of 2.62 gpm/ft^2 (10.7 cm/min) at ambient pressure. The column was packed with successive layers of 80/100 (U.S. standard sieve) size glass beads, a measured amount of 80/100 carbon, and more 80/100 glass beads. The original MIDDAS system was modified slightly to permit experimentation with volatile compounds. The modified system, shown in Figure 1, used a declining volume, headspace-free reservoir for influent storage and a Luer-lok fitting attached to the effluent line to permit sample collection with a glass syringe. The columns were operated until the effluent concentrations were the same as their respective influent concentrations, at which point "practical equilibrium" was assumed. Effective adsorption capacities were then calculated by integrating the area above the breakthrough curve.

For single-solute systems, the semi-empirical Freundlich isotherm was used to describe experimental data. The Freundlich isotherm was chosen because it generally fits experimental data well, accounts for the surface heterogeneity of GAC, and is easily integrated into dynamic models such as the HSDM. The form of the equation is:

$$q_e = K_F C_e^{\,n} \qquad (2)$$

where q_e is the solid-phase concentration of solute in equilibrium with the final (equilibrium) solution concentration, C_e, and K_F and n are fitted phenomenologic coefficients. The parameters K_F and n were determined by a geometric mean functional regression of log-transformed experimental data.

Bi-solute equilibrium data were described by the IAST. The IAST, documented in the full report, is a theoretical method by which bi-solute adsorption effects are modeled based on single-solute isotherms.

Rate Parameter Determinations

The SBA technique was used to calibrate data to obtain values for mass transport parameters, k_f, the film transfer coefficient, and D_s, the intraparticle surface diffusivity required for model predictions of adsorber performance. The SBA technique involves determination of k_f from incipient breakthrough data, in which the carbon bed length is sufficiently short to promote immediate partial breakthrough of the target compound. Over this initial breakthrough region, the effect of D_s on the model prediction is insignificant, thus enabling explicit determination of k_f by calibrating the model to experimental data. D_s is subsequently calibrated by holding the previously determined value of k_f constant, and searching for that value of D_s that provides the best fit for the remaining portion of the curve.

Results

TCE Isotherm Study

The geometric mean functional regression method was used to determine the Freundlich parameters for TCE in Milli-Q water. Table 1 presents the isotherm parameter values with 95% confidence intervals for both MIDDAS and CMBR experimental methodologies. The regression lines and associated 95% confidence limits obtained for TCE with the use of both techniques are also presented in Figure 2. As can be seen in Figure 2, the CMBR isotherm regression line lies outside of the confidence limits of the MIDDAS isotherm regression, indicating that the two isotherms are different at the 95% confidence level.

The values of the individual regression parameters K_F and n also exhibit differences for the two isotherm methods. Examination of the data in Table 1 shows that the overall adsorption capacity of the carbon in the MIDDAS system, as measured by K_F, is reduced by approximately 43% from the CMBR case. Difference in the driving force for adsorption, as measured by n, are, however, only nominally different at the 95% confidence level. The slope of the MIDDAS-determined isotherm is slightly greater than that determined in the CMBR system, indicating perhaps an increasing equivalence of capacities given by the two techniques as the solute concentration increases. This would occur because increased concentrations provide a larger driving force for adsorption and hence may obviate factors that contribute to capacity differences in the lower concentration range.

TCE Short Bed Adsorber Rate Studies

SBA data for TCE in Milli-Q water were obtained at concentrations of 104.6, 398, and 1052 μg/L. A potential dependency of the rate parameters on concentration for TCE was observed based on the results from these three studies. Although the concentration dependency for D_s is statistically significant for two of the three cases, the dependence of k_f on concentration is marginal. Statistical significance was determined based on finding points along the 95% confidence region in the k_f-D_s parameter plane. Values for these parameters are given in Table 2. These studies confirm the findings of other researchers that more accurate rate data are obtained when parameter determination studies are conducted as near to the

Table 1. Isotherm Parameters for TCE in Milli-Q Water with the Use of MIDDAS and CMBR Techniques

Technique	K_F*	n
MIDDAS	1.10	0.564
95% Conf. Limits	(0.846, 1.43)	(0.511, 0.616)
CMBR	1.94	0.527
95% Conf. Limits	(1.72, 2.20)	(0.498, 0.555)

* Based on q_e in µg/mg and C_e in µg/L.

Table 2. Effect of TCE Concentration on Rate Parameters

Ce(µg/L)	D_s(x 10^{10} cm^2/sec) 95% Conf. Limits	k_f (x 10^3 cm/sec) 95% Conf. Limits
104.6	0.70 (0.26,2.8)	21 (6.7,30)
398	1.6 (0.7,3.4)	18 (10,23)
1052	6.6 (2.2,250)	11 (8.3,14)

anticipated influent concentration as possible.

Large Column Verification Studies

A set of large column adsorber data for TCE in Milli-Q water on 30/40 particle size GAC was obtained. The average influent concentration was approximately 1000 µg/L. Rate parameters obtained using both the CMBR-based and the MIDDAS-based isotherm and the SBA technique are reported in Table 3. Both parameter sets were used in the homogeneous surface diffusion model to predict the breakthrough profile for these systems. The predications along with experimental breakthrough data are presented in Figure 3. Although early time predictions fit the data reasonable well, in the latter portions of the breakthrough, the MIDDAS-derived parameters clearly demonstrate a better fit to the data than do those based on the CMBR isotherm. The CMBR-based predication shows a breakthrough delayed from the actual data, which is indicative of the larger capacity given by the batch reactor isotherm.

Bi-solute Predictions

SBA data were obtained for the bi-solute system consisting of DCB and TCE in Milli-Q water. To calibrate the bi-solute version of the HSDM model, the SBA data obtained from this experiment were used in conjunction with the IAST model and with both the single-solute MIDDAS and CMBR isotherm parameters for TCE and DCB. The calibrated bi-solute parameters were used to predict deep bed performance for a bisolute MIDDAS experiment. Figure 4 presents one set of data with the accompanying predictions. The data represent the experimental breakthrough profiles for influent concentrations of TCE and DCB of 754 and 2,332 µg/L, respectively. As can be seen in Figure 4, the prediction for the DCB breakthrough by the MIDDAS-based parameters is very good, whereas that for the CMBR-based parameters overpredicts adsorption of DCB. The model also nicely captures the shape of the TCE breakthrough and overshoot for both sets of parameters, although both predicted curves are displaced slightly from the experimental data.

Table 3. Rate Parameters for Large Column Data

GAC size	Isotherm	k_f(cm/sec x 10^3) (95% Conf. Limits)	D_s(cm^2/sec x 10^{10}) (95% Conf. Limits
30/40	MIDDAS	3.9 (3.8,4.2)	8.7 (7.3,11.0)
30/40	CMBR	4.0 (3.7,4.2)	3.2 (3.0, 4.1)

TCE in Huron River Water

The geometric mean regression method was used to determine the Freundlich parameters for TCE in HRW. Both the MIDDAS and CMBR experimental methodologies were employed, with trends in K_F and n similar to those observed for the Milli-Q water. SBA data were obtained for TCE in HRW for the 30/40 particle sizes. The data were used with the HSDM model to determine rate parameters for both the MIDDAS and CMBR isotherms. The results of the model calibrations are given in Table 4.

Predictions were made of TCE large column data with the use of both MIDDAS and CMBR isotherm and rate data (Figure 5). As can be seen, neither parameter set predicts the data well, with both predictions greatly overpredicting removal of TCE. Because even the MIDDAS method cannot yield a good prediction, additional factors not accounted for by the MIDDAS approach are active in this system. A rough approximation of the capacity of the carbon bed used in the large column verification study indicates a value 25% lower than would be predicted by the MIDDAS isotherm conducted in HRW. Although rate parameter determinations do indicate some reduction in D_s in the HRW from the Milli-Q case, which can cause some reduction in apparent capacity because of a slowing of the kinetics of adsorption, it is unlikely that as large of a capacity reduction as was estimated could be precipitated by only a moderate reduction in D_s.

The major difference between the MIDDAS and large column systems is particle size. The MIDDAS methodology, which uses the smaller 80/100 particle size to expedite determinations of equilibrium data, is predicated on different particle sizes having the same equilibrium capacity. Although this assumption appears to hold for the studies conducted in the Milli-Q water, additional factors that violate this requirement are clearly manifest in the HRW study. Further study is necessary to determine if modification can be made to the MIDDAS technique to enable accurate description of large column breakthrough data when background organic matter is present.

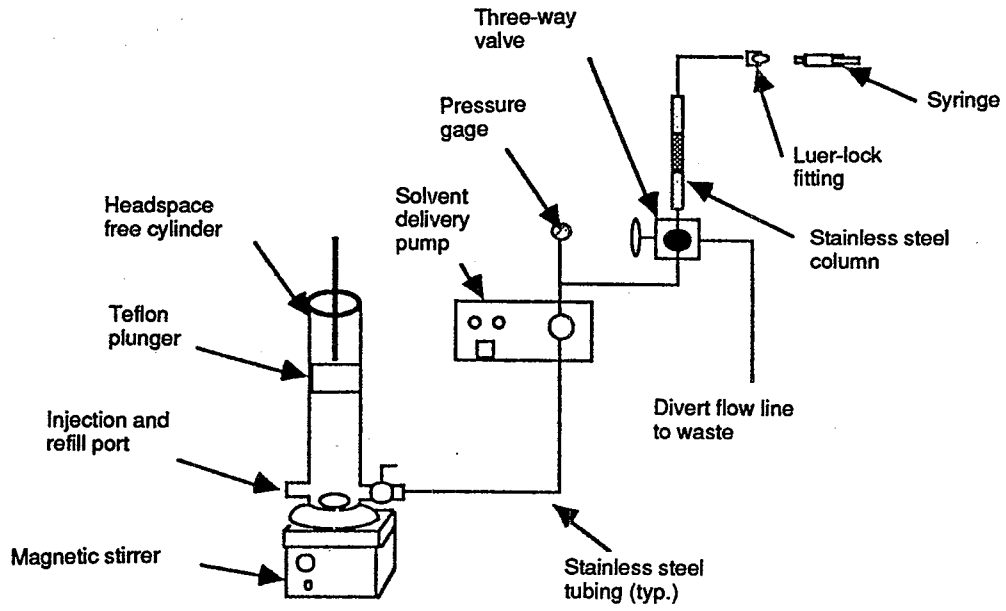

Figure 1. *Schematic of the MIDDAS system.*

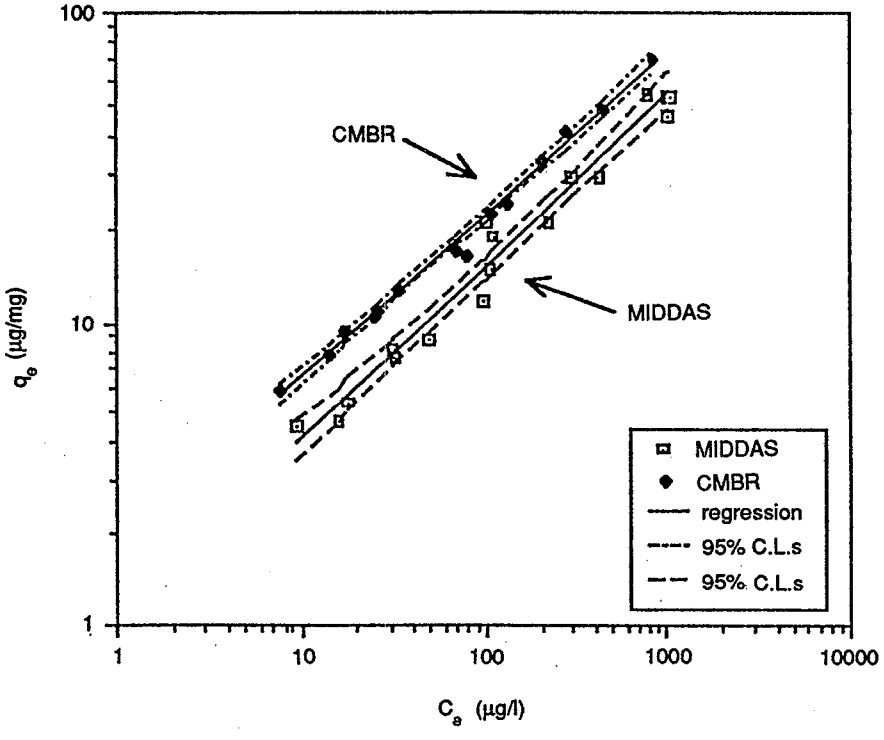

Figure 2. *Isotherms for TCE in Milli-Q water for the MIDDAS and CMBR methods.*

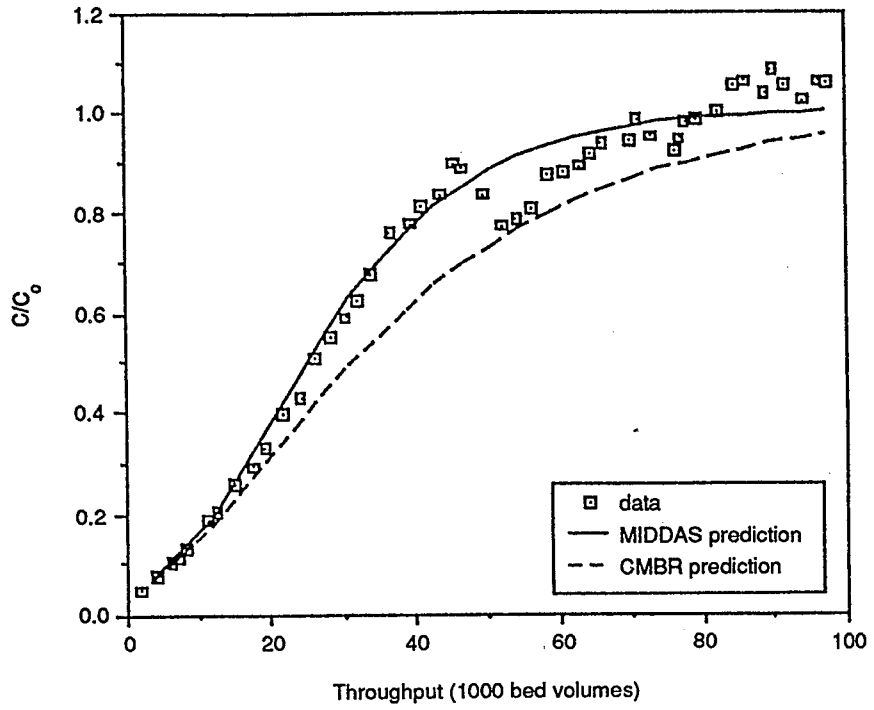

Figure 3. Prediction of large column breakthrough data for TCE in Milli-Q water using MIDDAS- and CMBR-derived isotherm and rate parameters for 30/40 particle size.

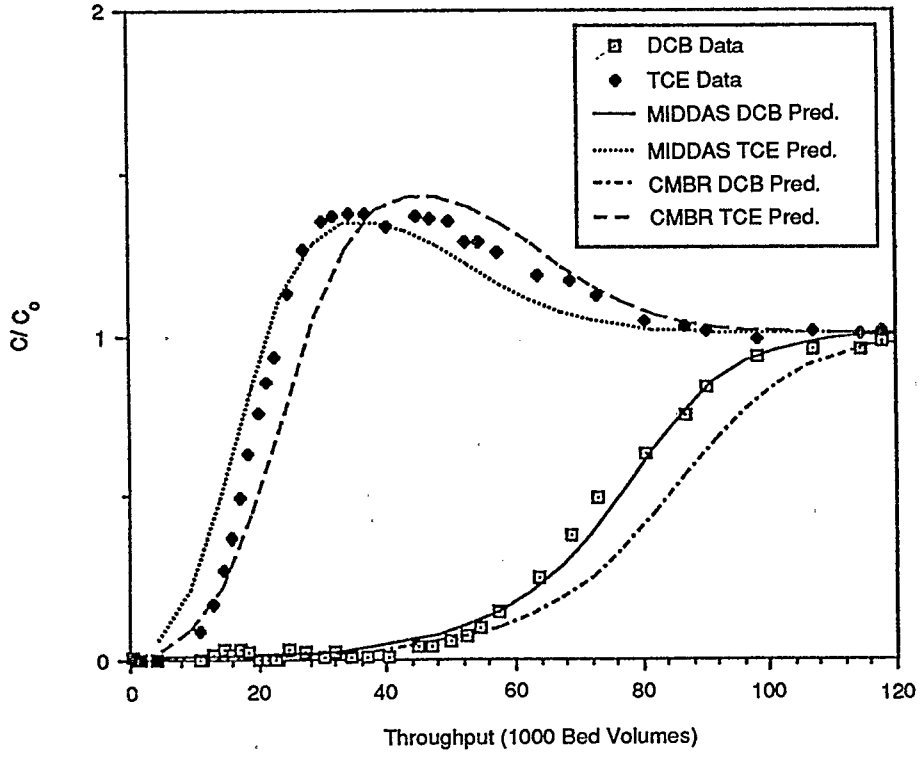

Figure 4. Sample prediction of bi-solute data.

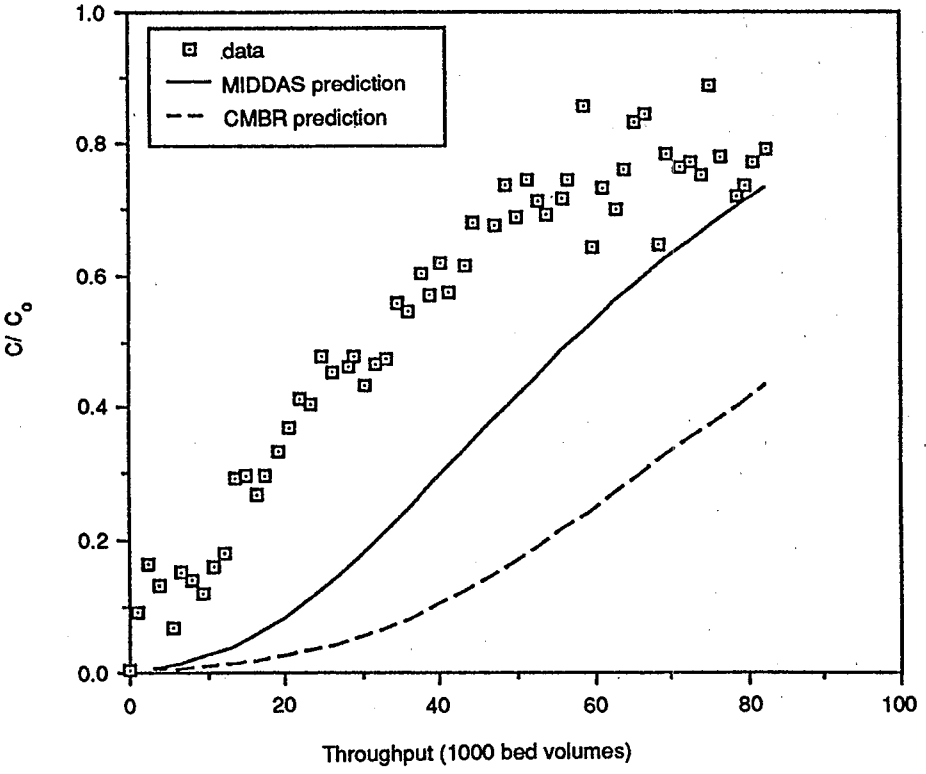

Figure 5. *Prediction of large column breakthrough data for TCE in HRW using MIDDAS and CMBR-derived parameters*

Table 4. *Rate Parameters for TCE in Huron River Water*

GAC size	k_f (cm/sec x 10^3) isotherm	D_s (cm^2/sec x 10^{10}) (95% Conf. Limits)	(95% Conf. Limits)
30/40	MIDDAS	4.0 (3.7,4.3)	1.6 (1.3, 2.1)
30/40	CMBR	4.0 (3.2,4.4)	0.80 (0.74,0.98)

Conclusions

The equilibrium capacity for TCE in Milli-Q water determined in the MIDDAS system was statistically lower than that obtained using the CMBR method, whereas the n value for the MIDDAS tended to be higher than that of the CMBR. The importance of these differences were confirmed in large column verification studies for the 30/40 and 16/20 particle sizes; the predictions made with the use of parameters based on the MIDDAS isotherm yielded predictions superior to those from CMBR-derived parameters.

As with the adsorption from Milli-Q water, the capacity for TCE in HRW in the MIDDAS system was significantly depressed from that in the CMBR determinations. Unlike the Milli-Q water results, however, neither MIDDAS- nor CMBR-based parameters provided adequate predictions of a large column verification study, with overpredictions of removal in both cases. Although isotherm determinations indicated a reduction in capacity because of competitive substances in the HRW as well as compounding reductions because of the column configuration of the MIDDAS protocol, an approximate estimate of the capacity of the carbon bed used in the large column verification study indicates a value lower still than was predicted by the MIDDAS isotherm in HRW. Rate parameter determinations do indicate a reduction in D_s in the HRW from the Milli-Q case; these determinations can cause some reduction in apparent capacity because of a slowing of the kinetics of adsorption. It is unlikely, however, that as large a capacity reduction as was estimated could be precipitated by only a moderate reduction in D_s. One obvious difference between the two systems is GAC particle size. The smaller 80/100 particle size employed in the MIDDAS system is to provide rapid attainment of equilibrium parameters while still maintaining the hydrodynamic attributes of a column system. A major assumption in the development of the MIDDAS protocol was that equilibrium capacity is not particle size dependent. Although no dependency of equilibrium capacity on particle size was manifest in the Milli-Q water studies, particle size apparently does affect the equilibrium capacity of TCE in HRW. Thus, although estimates in the MIDDAS system do improve predictions somewhat over the CMBR case, it is clear that achieving similar hydrodynamics is not necessarily enough to ensure estimate of accurate isotherm parameters and that other factors, such as particle size and the presence of background organic matter, must be addressed in further refinement of the MIDDAS methodology.

In the bi-solute studies, reductions of TCE adsorption capacity in the presence of DCB were captured qualitatively by IAST. Predictions for DCB breakthrough were quite acceptable; the MIDDAS-derived parameters achieved better predictions of the data than did the CMBR counterparts. Predictions of deep bed adsorber data for TCE were, however, only moderately satisfactory as best, comparable results were achieved by using both MIDDAS- and CMBR-based parameters.

The research presented here has sought to bring parameter estimation methods one step closer to the reactors commonly used in practice. The results have proved inconclusive, however. In some cases, the capacity estimations of the MIDDAS method were better than those of the CMBR technique; the MIDDAS method did not universally improve predictions of both single- and bi-solute data over those from CMBR-derived parameters. Moreover, although the SBA methodology itself remains a viable and facile method of rate parameter determination, the demonstrated dependency of the SBA-D_s values on capacity measurements makes such determinations susceptible to propagation of isotherm inaccuracies and hence brings the problem full-circle. The nature of these findings indicates that there are still many research areas deserving of pursuit with regard to applying the MIDDAS approach to simulation and to design of fixed-bed GAC reactors.

It is clear from this and others' works that an a priori assessment of which compounds will be most significantly affected by reactor configuration is not possible at

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this juncture. Further work is required to elucidate the exact mechanisms that bring about the reductions seen in column based systems. Factors that may play an important role in determining the sensitivity of a compound's capacity to reactor configuration include the presence of other adsorbing species, molecular size, hydrophobicity, polarity, functional groups, and carbon type.

Because the capacity of GAC for TCE is dependent on particle size for adsorption from HRW, the MIDDAS methodology may have to be modified. Further studies are necessary to determine the mechanistic causes of the observed effect.

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***Thomas F. Speth** is the EPA Project Officer (see below).*
The complete report, entitled "Evaluation of the MIDDAS System for Designing GAC Adsorbers," (Order No. PB91-234 617/AS; Cost: $19.00, subject to change) will be available only from:
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