

Sorption of TCE by Humic-Preloaded Activated Carbon: Incorporating Size-Exclusion and Pore Blockage Phenomena in a Competitive Adsorption Model

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Naturally occurring, macromolecular dissolved organic matter (NOM) is known to foul activated carbon adsorbents, reducing the ability of fixed-bed adsorbents to efficiently remove targeted synthetic organic contaminants (SOCs). An accurate description of the effects of NOM competition on SOC adsorption equilibria is required to develop dynamic models, which have application to process design and analysis. A model was developed, using an approach based on the Ideal Adsorbed Solution Theory (IAST), to predict trichloroethylene (TCE) adsorption by activated carbon preloaded with humic acid. The IAST model was formulated for a bisolute system in which TCE and humic acid single-solute uptakes were described by the Langmuir–Freundlich and Freundlich isotherms, respectively. The humic mixture was modeled as a single component based on previous studies that identified the low-molecular-weight hydrophobic fraction as the most reactive with regard to preloading effects. Isotherms for this fraction, isolated from whole humic acid using ultrafiltration, were measured, and molar concentrations were computed based on an average molecular weight determined using size-exclusion chromatography. The IAST model was modified to reflect the hypothesis that TCE molecules can access adsorption sites which humic molecules cannot and that no competition can occur on these sites. The model was calibrated with data for TCE uptake by carbon preloaded with the low-molecular-weight humic acid fraction and was verified by predicting TCE uptake by carbon preloaded with whole humic acid. Further improvement to the model was possible by accounting for pore blockage as a mechanism which can reduce the effective surface area available to TCE.

Introduction

Granular activated carbon (GAC) adsorption has been identified by the Safe Drinking Water Act Amendments of 1986 as the best available technology for removing synthetic organic contaminants (SOCs) from potable water supplies (1). GAC is particularly suited for water treatment applications because of its ability to remove a wide range of organic

compounds effectively. The presence of naturally occurring, macromolecular dissolved organic matter (NOM) can significantly reduce the efficiency of activated carbon adsorbents targeted to remove SOC. NOM components can move rapidly through fixed-bed adsorbents used in treatment applications, fouling the carbon ahead of the pollutant. Preloaded NOM is not displaced by most SOC and can thus change the properties of the adsorbent material in ways that are difficult to predict *a priori*, making design difficult.

It has been shown in many cases that the fouling or “preloading” phenomena can significantly reduce both the equilibrium capacity of GAC for SOC (2–10) and the rate of SOC adsorption (5, 10–12). An accurate description of the effects of NOM competition on SOC adsorption equilibria is required to develop dynamic models, which have application to process design and analysis. Such models, based on a mechanistic understanding of competitive interactions, will allow engineers to more accurately extrapolate process performance to a greater range of conditions and may reduce the required scope of pilot-scale studies. However, little progress has been made in understanding the competition between SOC and organic macromolecules. This is due, in part, to the complexity of natural organic matter.

From a modeling point of view, it is necessary to represent NOM properties mathematically. Because the exact composition of NOM is not known, and its composition varies among waters, it is not possible to represent properties of individual components. However, even if the composition were known, the inherent complexity of NOM would preclude formulating a mathematically tractable problem. Therefore, it is necessary to simplify how NOM properties are represented. One approach is to lump individual components into classes that have similar characteristics or reactivities. These classes may be real, based on physicochemical properties operationally defined by fractionation schemes, or may be empirical. A common approach has been to treat the NOM as one or more uncharacterized background components (8, 13, 14), whose adsorption properties are calculated by comparing single-solute SOC adsorption with adsorption from a solution containing natural organic matter. A single solute isotherm model (often the Freundlich model, Table 1) is chosen for one or more NOM components, and model parameters are estimated through a statistical optimization using a competitive adsorption model. In many cases, such models have accurately described SOC adsorption from solutions containing NOM. However, a large number of fitting parameters, which may lack physical significance, must be calculated (10). Furthermore, the fitted parameters are not unique (8) and offer little insight into the fundamental properties of NOM which govern its competitive impact on SOC adsorption.

An alternative approach, based on the Simplified Competitive Adsorption Model (SCAM) (15), has been developed (5, 10). NOM was modeled as a single component, for which Freundlich isotherm parameters were measured. The model, using three fitting parameters (including the NOM molecular weight) accurately described competitive adsorption equilibria. However, the fitted NOM molecular weights were significantly lower than those commonly reported for natural waters (16–21).

Most equilibrium, competitive adsorption modeling approaches developed to date have focused primarily on the adsorption of low molecular weight organics in the presence of natural organic macromolecules under simultaneous adsorption conditions—the NOM was not preloaded (5, 8, 10, 22). Equilibrium models that incorporate the effects of

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TABLE 1. Isotherm Models and IAST Model Formulation^a

eq	mathematical form	description
Single Solute Systems		
1	$q_2 = \frac{Q^o(bC_2)^{n_2}}{1 + (bC_2)^{n_2}}$	Langmuir–Freundlich single solute isotherm (TCE)
2	$q_1 = K_F C_1^{n_1}$	Freundlich single solute isotherm (humic acid)
Bisolute System		
3	$\pi_1 = \frac{RT}{A} \int_0^{C_1^o} K_F C_1^{n_1} \frac{dC_1^o}{C_1^o} = \frac{RT}{An_1} K_F C_1^{o n_1}$	spreading pressure for component 1. A = specific adsorbent surface area
4	$\pi_2 = \frac{RT}{A} \int_0^{C_2^o} \frac{Q^o(bC_2^o)^{n_2}}{1 + (bC_2^o)^{n_2}} \frac{dC_2^o}{C_2^o} = \frac{RTQ^o}{An_2} \ln[1 + (bC_2^o)^{n_2}]$	spreading pressure for component 2
5	$\frac{1}{n_1} K_F C_1^{o n_1} = \frac{Q^o}{n_2} \ln[1 + (bC_2^o)^{n_2}]$	equivalence of spreading pressures in the mixture
6	$C_1 = C_1^o \left(\frac{q_1}{q_1 + q_2} \right)$	Rauolt's Law expression for the liquid-phase concentration of component 1 in the mixture
7	$C_2 = C_2^o \left(\frac{q_2}{q_1 + q_2} \right)$	Rauolt's Law expression for the liquid-phase concentration of component 2 in the mixture
8	$\frac{q_1}{q_1^o} + \frac{q_2}{q_2^o} = 1$	equivalence of adsorbed molecular area per mole in single and bisolute systems
9	$C_{o,1} = q_1 D_o + C_1$	mass balance, component 1
10	$C_{o,2} = q_2 D_o + C_2$	mass balance, component 2

^a Note: C_1^o , C_2^o , q_1^o , and q_2^o are liquid and solid-phase equilibrium concentrations in hypothetical single-solute systems at a spreading pressure identical to that of mixture.

TABLE 2. Isotherm Parameters for TCE Uptake by Humic Preloaded GAC

humic material	preloading conditions			Langmuir–Freundlich isotherm		
	C_o , mg DOC/L	C_e/D_o , mg DOC/mg	q_e , mg HA/g	param	param estimate	95% C.I.
<3K HA	4.0	77	48.6	$Q^o \times 10^{-2}$	1.37	0.50, 2.23
				$b \times 10^4$	2.85	0.00, 6.68
				n	0.64	0.59, 0.68
				$Q^o \times 10^{-2}$	0.88	0.69, 1.08
<3K HA	4.0	65	75.4	$b \times 10^4$	6.48	3.38, 9.59
				n	0.71	0.69, 0.74
				$Q^o \times 10^{-2}$	1.10	0.94, 1.26
				$b \times 10^4$	4.09	2.64, 5.53
whole HA	53.5	81	45.6	n	0.66	0.64, 0.68
				$Q^o \times 10^{-2}$	1.06	0.91, 1.21
				$b \times 10^4$	4.86	3.24, 6.47
				n	0.64	0.63, 0.66
whole HA	53.5	78	51.8	$Q^o \times 10^{-2}$	0.79	0.66, 0.91
				$b \times 10^4$	6.68	4.36, 9.00
				n	0.73	0.70, 0.75
				$Q^o \times 10^{-2}$	0.79	0.66, 0.91

^a Note: Isotherm parameters correspond to uptake, q_e , in units of $\mu\text{g}/\text{mg}$, and concentration in units of $\mu\text{g}/\text{L}$: $Q^o [\mu\text{g mg}^{-1}]$; $b [\text{L } \mu\text{g}^{-1}]$; $K_F [\mu\text{g}^{1-n} \text{L}^n \text{mg}^{-1}]$; n is dimensionless. 95% C.I. is the 95% confidence interval.

preloading must account for changes in the competitive effects of NOM with loading, time, or both. The possibility that NOM loading affects competitive interactions is suggested by reports of NOM concentration-dependent competitive adsorption model parameters (10) and the effect of preloading time on isotherm parameters (1, 9). While our understanding of preloading phenomena has improved, only recently have the mechanisms of NOM preloading been identified (9, 23). Kilduff et al. (24, 25) developed a theoretical basis for these mechanisms and provided additional experimental verification. They found that direct site competition was a dominant mechanism, with pore blockage making a significant contribution to observed reductions in TCE uptake at high organic matter loadings and at high TCE concentrations. This paper advances a modeling framework based on these proposed mechanisms.

Methods and Materials

Humic Materials. Humic and fulvic acids were extracted from a Laurentian soil and were received as a dry powder. Methods used to prepare humic solutions have been described previously (26, 27). An ultrafiltration system (Amicon CH2PRS, Bedford, MA) was used to isolate the low molecular weight fraction of NOM, operationally defined as components which passed a cellulosic-type spiral-wound membrane having *nominal* molecular-weight cutoff of 3000 g/mol (<3 KHA). Additional details are described elsewhere (28). A molecular weight of 1400 g/mol was determined for this fraction using size exclusion chromatography calibrated with polystyrene sulfonate (PSS) standards, as described in detail elsewhere (27). Molar concentrations of humic substances (as humic acid) were computed based on an organic carbon content of 52% (29).

Preloading. Preloading with humic acid was done either (1) in 1-L amber-colored glass bottles, from which the carbon was recovered by vacuum filtration on a 0.2-micron filter (Gelman, Ann Arbor, MI) after equilibrating for 30 days and subsequently vacuum-dried at room temperature or (2) in the 250-mL bottles used for the TCE isotherm for periods ranging from 14 to 30 days (after which TCE was spiked into the reactor). Speth (6) measured identical preloading isotherms for dichloroethene, regardless of whether the carbon was used in a wet state or vacuum-dried. The humic acid concentrations ranged from 4 to 60 mg DOC/L, and GAC doses ranged from 0.04 to 4 g/L. The pH of all preloading reactors was kept constant at pH 7 with 10^{-3} M phosphate buffer. Humic acid concentrations were quantified by total organic carbon (TOC) analysis (TOC 500 Shimadzu Corporation, Japan).

Isotherm Experiments. Adsorption isotherm experiments were conducted using the completely mixed batch reactor (CMBR) method. Reactors were prepared by either (1) adding preloaded carbon to buffer solution and then spiking with reagent grade (pesticide free) TCE stock solution made up in methanol, as described previously (30) or (2) directly spiking the preloading reactors after the 30-day equilibration period. In neither case was the preloaded carbon exposed to fresh humic acid solution, thus ensuring that all competition was from preadsorbed organic matter. Preliminary desorption studies confirmed that preloaded humic acid did not desorb under these conditions to any measurable extent, a finding consistent with others (31). Calgon F400 carbon with a mean particle diameter of 165 microns was used for both preloading and constant-dose TCE isotherm experiments. Carbon (10–15 mg) was equilibrated with TCE solutions (initial concentrations ranged from 0.030 to 8 mg/L) in 250-mL amber-colored glass bottles sealed with screw caps and Teflon-lined silicone septa. While not directly evaluated in this work, Carter et al. (9) have confirmed that the measured isotherm does not depend on the initial TCE concentration under these conditions. Reactors were filled completely and sealed with no headspace. The reactors were kept well mixed for a period of two weeks; preliminary rate studies confirmed that this time was sufficient to reach equilibrium based on constant liquid-phase TCE concentrations. TCE was quantified by gas chromatography as described previously (30).

Adsorbent Surface Area. Preloaded carbons were dried to constant weight at room temperature in a vacuum desiccator prior to surface area analysis. Surface area and pore size distribution were measured with a Gas Adsorption Analyzer (Quantachrome Autosorb 1, Syosset, NY). Aliquots of carbon were outgassed for 48 h at room temperature to avoid causing changes in adsorbed NOM structure. The weight of the sample cell containing GAC did not change after outgassing, confirming negligible loss of material during this step. Nitrogen isotherms were measured at 77 K, and surface area was determined by fitting the Brunauer, Emmett, and Teller (BET) adsorption isotherm equation (32) to at least five low-pressure isotherm points ($p/p_0 < 0.2$) using a nonlinear regression algorithm. Precision of replicate samples averaged 5%.

Isotherm Modeling. TCE isotherm data, shown in Figure 1, were collected over a wide range of concentration. Because the data displayed some curvature on log–log coordinates, the three-parameter Langmuir–Freundlich (LF) model (33) was chosen (Table 1, eq 1) to model it. The sum of squared log-residuals was 0.119 for the Langmuir–Freundlich model as compared to 0.171 for the Freundlich model ($N = 82$). In the Langmuir–Freundlich model, the amount adsorbed at equilibrium (normalized to adsorbent mass), q_e , is a function of C_e , the equilibrium solution phase concentration, and three empirically determined parameters: Q^0 , b , and n . Q^0

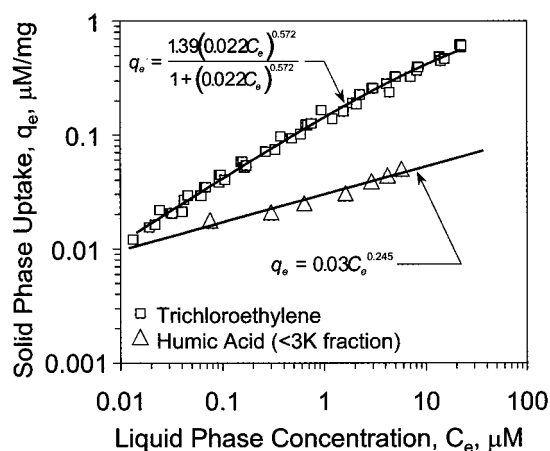


FIGURE 1. TCE single-solute isotherm (squares) and best fit Langmuir–Freundlich isotherm equation (line); <3KHA single-solute isotherm (triangles) and best fit Freundlich isotherm equation (line).

represents the adsorption capacity, b represents an average site energy, and n represents the heterogeneity of site energies (34).

Similar analysis for isotherms obtained with the <3K fraction of the humic acid showed that the classical Freundlich isotherm equation (Table 1, eq 2) accurately described the adsorption data over the concentration range of interest. The Freundlich model has two empirical parameters: K_F is a unit-capacity parameter, equal to the amount adsorbed at a value of C_e equal to unity (in whatever concentration units chosen), and n is a dimensionless parameter related to the heterogeneity of the site energy distribution.

Model Development. Ideal Adsorbed Solution Theory provides for the prediction of adsorption from mixtures based on the single solute isotherms of each mixture component. In the proposed model, the competitive effects of NOM are modeled by a single reactive component. Previous work has shown that hydrophobic, low-molecular-weight components of NOM are particularly reactive, and the competitive adsorption characteristics of this group of components are sufficiently similar to warrant their treatment as a single component (26). The IAST model requires isotherm parameters on a molar basis, and uncertainty may be introduced when the organic matter molecular weight is used as a fitting parameter. We have addressed this issue by independently measuring the average molecular weight of the reactive fraction. The polydispersity (the ratio of weight-to-number-averaged molecular weight, M_w/M_n) of the <3K ultrafiltration fraction was 1.52, significantly lower than the value of 2.94 determined for the whole humic solution, providing justification for modeling this fraction as a “single component”. Furthermore, this fraction is adsorbed preferentially from whole humic mixtures by microporous activated carbon, which excludes larger components in the mixture on the basis of molecular size. Accordingly, the effects of preloading by NOM were modeled as a bisolute system, an approach consistent with previous work (5, 8, 10).

An advantage of the IAST approach is its flexibility in allowing alternative isotherm forms, which allows for the best possible description of single solute uptake for each component. Smith (35) found that descriptions of bisolute equilibria (in the TCE/lindane system) exhibited lower errors when single solute isotherms were fitted by three-parameter isotherms, as compared to the two-parameter Freundlich isotherm. In this work, IAST equations were developed for the TCE/humic acid bisolute system using the Freundlich isotherm for humic acid and the Langmuir–Freundlich for TCE; the model formulation is summarized in Table 1. This approach yields eight independent equations (Table 1, eqs

1, 2, 5–10) in which (1) the single solute isotherm parameters (K_F and n_1 for the <3KHA, and Q^o , b , and n_2 for the TCE) and (2) the initial concentrations ($C_{o,1}$ for the <3KHA, and $C_{o,2}$ for the TCE) are known. These equations were solved simultaneously to determine the loading and equilibrium concentrations q_1 , C_1 , q_2 , and C_2 for the mixture.

The IAST was developed to account for the effects of adsorptive site competition assuming that all sites are available to both components in the mixture. However, it is possible that some adsorption sites are not involved in competition. This may occur when some adsorption sites are specific to only one component in a mixture, or when molecules have sufficiently different sizes, and the access of larger molecules to surfaces located in small pores is restricted (36). This latter scenario seems particularly likely in the TCE/humic acid system based on the large difference in their molecular weights. Furthermore, available evidence suggests that the dimensions of humic molecules are on the order of large micropores or small mesopores (16, 17, 20). Because a large fraction of activated carbon surface area is located in micropores, it is likely that humic molecules are restricted from accessing these surfaces. Consistent with these considerations, it was hypothesized that the effects of preloading would be more accurately modeled by a modified IAST procedure in which it was assumed that TCE could access sites which the humic molecules cannot. This hypothesis is represented mathematically by the parameter, θ , the fraction of the surface area on which there are no competitive effects.

The total solid-phase uptake, q_e , and capacity, Q^o , are the sum of uptake and capacity by competitive and noncompetitive surfaces:

$$q_{e,\text{total}} = q_{e,\text{comp}} + q_{e,\text{noncomp}} \quad (1)$$

$$Q_{\text{total}}^o = Q_{\text{comp}}^o + Q_{\text{noncomp}}^o \quad (2)$$

Defining a fraction of the surface area on which TCE adsorbs without competition is equivalent to defining a fraction of the capacity, θQ^o , that can be occupied with no competition. Therefore, $Q_{\text{comp}}^o = (1 - \theta) Q^o$ and $Q_{\text{noncomp}}^o = \theta Q^o$:

$$Q_{\text{total}}^o = (1 - \theta) Q^o + \theta Q^o \quad (3)$$

This is conceptually equivalent to the approach used by Jain and Snoeyink (36) in their modification to the competitive Langmuir model for a bisolute system. Therefore, in the <3KHA/TCE bisolute system, the uptake of TCE by surfaces without competition, $q_{2,\text{noncomp}}$ is

$$q_{2,\text{noncomp}} = \frac{\theta Q^o (bC_2)^{n_2}}{1 + (bC_2)^{n_2}} \quad (4)$$

Only the surface area available to both TCE and humic substances is included in the IAST calculations; therefore, the TCE single solute isotherm used in these calculations is

$$q_{2,\text{IAST}} = \frac{(1 - \theta) Q^o (bC_2)^{n_2}}{1 + (bC_2)^{n_2}} \quad (5)$$

Similarly, the mass of TCE adsorbed by surfaces without competition is not included in the initial concentration of TCE used in the IAST calculation

$$C_{o,2,\text{IAST}} = C_{o,2,\text{total}} - (D_o q_{2,\text{noncomp}}) \quad (6)$$

where D_o is the adsorbent dose, and other terms have been defined previously. All model calculations were performed using an optimization scheme based on a generalized reduced

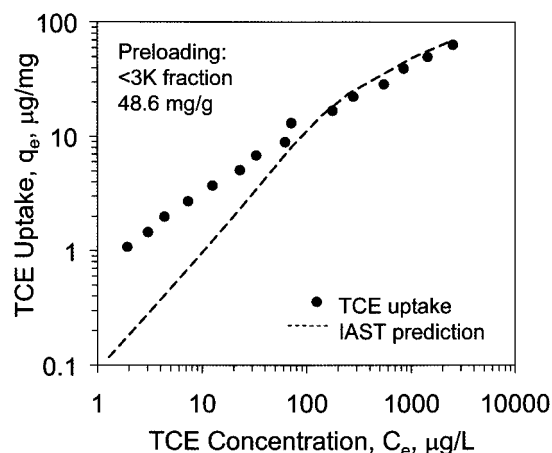


FIGURE 2. The conventional IAST prediction (dashed line) shown for carbon preloaded with the <3 K fraction, 48.6 mg/g.

gradient (GRG) nonlinear programming algorithm (37), implemented in a commercial software package (Microsoft Excel).

Results and Discussion

Predictive IAST Modeling. In a first attempt to apply the IAST model in a predictive fashion, the TCE and <3KHA single-solute isotherm parameters (Figure 1) were used as model inputs to predict the TCE uptake on carbon preloaded with <3KHA. Molar units were chosen for the single solute isotherms shown in Figure 1 to illustrate how the adsorbability of TCE and humic acid compare on the basis that they are input to the competitive model. The result, equivalent to setting $\theta = 0$ in the proposed model (i.e., competition occurs on the entire surface), is depicted in Figure 2 (similar results were obtained for a <3 K fraction loading of 75.4 mg/g, data not shown). A significant underprediction of TCE uptake (overprediction of competitive effects of <3KHA) in the low concentration (part-per billion) region of the TCE isotherm and an overprediction of TCE uptake (underprediction of competitive effects) at high TCE concentrations is evident. Difficulty in fitting isotherms for VOCs in the presence of natural organic matter have been reported previously (10). The IAST prediction shown in Figure 2 using such an approach qualitatively predicts the effects of preloading on the TCE isotherm but is not sufficiently accurate for engineering design.

The differences between the measured TCE isotherms and the IAST predictions could be attributed to the effects of nonideal competition. Such effects have been observed by other investigators, who have proposed various modifications to the IAST to account for them (35, 38). However, most proposed modifications apply additional fitting parameters which provide little additional insight into the physical/chemical phenomena involved. It was hypothesized that the IAST model overpredicts competitive effects at low TCE concentrations because the model, as originally formulated, cannot take into account sites on which no competition occurs. Accounting for sites which can be accessed by TCE but not humic molecules would have the effect of increasing the number of high-energy sites available to TCE and thus increasing the uptake in the low concentration region (30). This approach will be addressed in detail in the next section.

Model Calibration: Carbon Preloaded with <3KHA. The fraction of sites on which TCE adsorbs without competition, θ , was calibrated using isotherm data obtained from TCE adsorption on the <3KHA preloaded carbon. Several representative points spanning a wide range of TCE concentrations were used. For each point, the model-calculated TCE

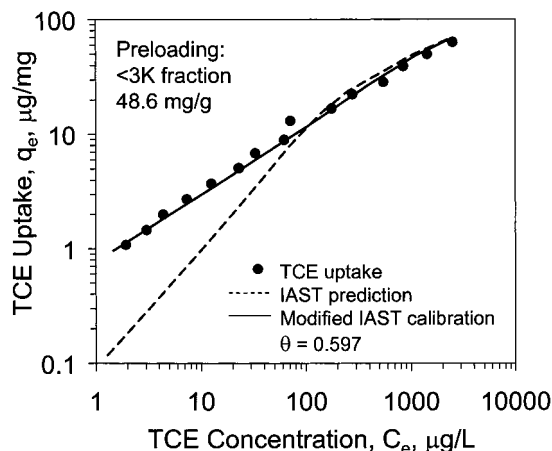


FIGURE 3. Modified IAST model calibration (solid lines) for carbon preloaded with the <3 K fraction, 48.6 mg/g. TCE uptake by carbon preloaded with <3KHA (circles) was used to calibrate the noncompetitive fraction of the surface, θ . The conventional IAST prediction (dashed line) is shown for comparison.

q_{total} was compared to the observed isotherm at the same value of C_e . Optimization was achieved by varying θ to minimize the sum of the squared residuals (SSR) for the chosen points.

Figure 3 illustrates a representative modified IAST model fit to TCE uptake by activated carbon preloaded with 48.6 mg <3KHA/g. Accounting for noncompetitive surface area increases the accuracy of the data description significantly. While this approach introduces only one fitting parameter, it was found that calibrated values of θ decreased with increased loading over the range of loading studied. Under the hypothesis that θ represents the fraction of the total surface area that TCE can access but humic molecules cannot, a decrease in θ with humic loading implies that humic molecules access smaller pores as their loading increases. This could be explained, in part, by the polydispersity of the humic solutions and competition among humic fractions. If the fractions contain a range of sizes (albeit a much narrower range than the whole humic solution), then at lower loadings a greater fraction of larger components would be present on the surface and in the pores (29). The filling of mesopores by the larger components could prevent smaller components from reaching micropore surfaces that they would otherwise be able to access. In contrast, at higher loadings, a greater fraction of smaller components would be present on the surface and in the pores and could penetrate more deeply into the pore structure. A second explanation is related to the effect of concentration on humic structure. It has been proposed that humic substance configuration becomes more spherocolloidal and rigid at high concentrations (39). It is possible that with increased loadings, surface and pore concentrations become high enough to cause adsorbed humic molecules to become more compact and better able to penetrate more deeply into the carbon pore structure.

Model Verification: Carbon Preloaded with Whole HA.

Using single solute isotherm parameters and θ -values calibrated as a function of <3KHA loading, predictions for TCE adsorption by carbon preloaded with whole humic acid solutions were calculated. To make such predictions, a value for the initial concentration of both adsorbates is required, and a value for the noncompetitive fraction of the surface must be selected. The initial concentration of reactive (competitive) organic matter in the whole humic solution was calculated based on previous findings that the <3KHA fraction represents the reactive components of the whole humic acid (26). It was determined, using ultrafiltration fractionation, that 17% (as DOC) of the humic acid organic

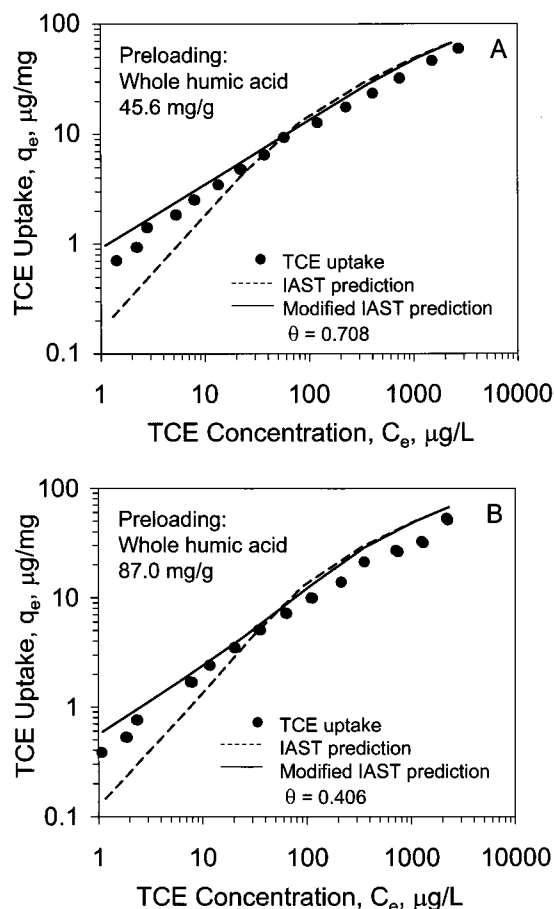


FIGURE 4. Modified IAST model predictions accounting for noncompetitive surface area (solid lines) for two preloaded amounts of whole humic acid, 45.6 (plate A) and 87.0 (plate B) mg/g. The conventional IAST prediction (dashed lines) is shown for comparison.

carbon was contributed by the <3KHA fraction. To calculate a value for the noncompetitive fraction of the surface, the correlation between θ and the <3KHA loading was used. To calculate the <3KHA loading, it was recognized that when carbon was preloaded with whole HA, only a fraction of the total HA uptake was represented by the <3KHA components. Based on previous findings that smaller, hydrophobic components are adsorbed preferentially from a whole humic solution (27), essentially all of the <3KHA components are loaded as long as the total removal of all humic acid components exceeds 17% (as DOC), as was the case in all experiments in this study.

TCE isotherms on carbon preloaded with whole HA under 10 different loading conditions were predicted. The wide range of loadings was selected to encompass the scope of conditions typically found in environmental systems. Model predictions for two representative loadings of whole HA are illustrated in Figure 4, panels A and B, where they are compared to IAST predictions made without modification to account for noncompetitive surface area. The accuracy of the model fit was markedly improved at lower equilibrium concentrations, verifying the modeling approach and supporting the noncompetitive surface area hypothesis. However, the model is less accurate at high TCE concentrations, because it is asymptotic to the single-solute isotherm and does not reproduce the competitive effects of preloading. In contrast, measured TCE isotherms are displaced downward, relative to the q_e axis, in a parallel fashion (on log-log coordinates). This suggests a reduction in TCE capacity and a corresponding reduction in the Langmuir-Freundlich value of Q^P . This type of behavior is consistent with a reduction in

the total number of available adsorption sites. These sites may be lost as a result of direct competition or as a result of a pore blockage mechanism (9, 24). The IAST model incorporates the effects of direct competition for adsorption sites but does not incorporate the effects of pore blockage. Therefore, a further modification to the IAST model to incorporate pore blockage effects was investigated.

Effects of Surface Area Reduction. It was hypothesized that pore blockage can reduce the effective surface area available to TCE and therefore the single-solute capacity parameter, Q^* . To estimate the magnitude of the pore blockage effect, BET surface area was measured before and after preloading. Significant reductions in surface area were found (25), consistent with other studies reported in the literature. For example, Newcombe et al. (40) found that the BET surface area of activated carbon from a water filtration plant was significantly decreased by adsorbed NOM, and Newcombe et al. (23) found a reduction in total surface area and micropore, secondary micropore, and mesopore volume resulting from adsorption of NOM from reservoir water.

The measured surface area reduction caused by humic preloading was correlated as a function of the whole humic loading (25). It was assumed that the reduction in the effective surface area available to TCE was in proportion to the reduction in surface area as determined by BET analysis. The reduction in surface area was incorporated into the IAST model by constraining the TCE capacity to reflect the reduced surface area available, which is equivalent to reducing the TCE Langmuir–Freundlich capacity parameter, Q^* , in proportion to the measured surface area reduction. Incorporating pore blockage effects in this way does not introduce an additional fitting parameter into the model, retaining its predictive capabilities. Representative model predictions are shown in Figure 5, panels A and B. An excellent prediction is evident over the entire TCE concentration studied; similar predictive accuracy was observed for several different humic acid loadings ranging from 12 to 87 mg/g.

Model Variations. To explore the possibility that the θ value determined from the <3K fraction preloaded carbon may be different than the θ value determined for a whole humic mixture, a correlation was developed between θ and loading using a subset of the data for TCE uptake by carbon preloaded with *whole* humic solutions. This approach maintains the assumption that smaller components represent reactive components of the whole mixture but allows the possibility that potential interactions with larger components may affect the competitiveness of this fraction, as reflected in the noncompetitive surface area. This modeling approach was satisfactory but did not improve the predictive accuracy as measured by a residual sum-of-squares statistic. This suggests that while interactions may occur between components in the whole humic mixture, they do not significantly impact how smaller, hydrophobic components adsorb and subsequently compete with TCE. This finding is consistent with the preferential adsorption of smaller natural organic matter components, including a surface water source (Huron River) (27). It is important to note, however, that molecular weight may not be a controlling characteristic in all systems, particularly if low-molecular-weight hydrophilic compounds are present. In these cases, it may be necessary to further fractionate low molecular weight components according to polarity (or hydrophobicity) to isolate a reactive fraction. It is further recognized that within a low-molecular-weight hydrophobic fraction, a range of reactivities may occur. Accounting for such heterogeneities may require increasing the complexity of the modeling approach used.

Effect of NOM Loading on Competition. As trends in the data shown in this paper suggest, and as both the traditional and modified IAST model predict, the impact of competition

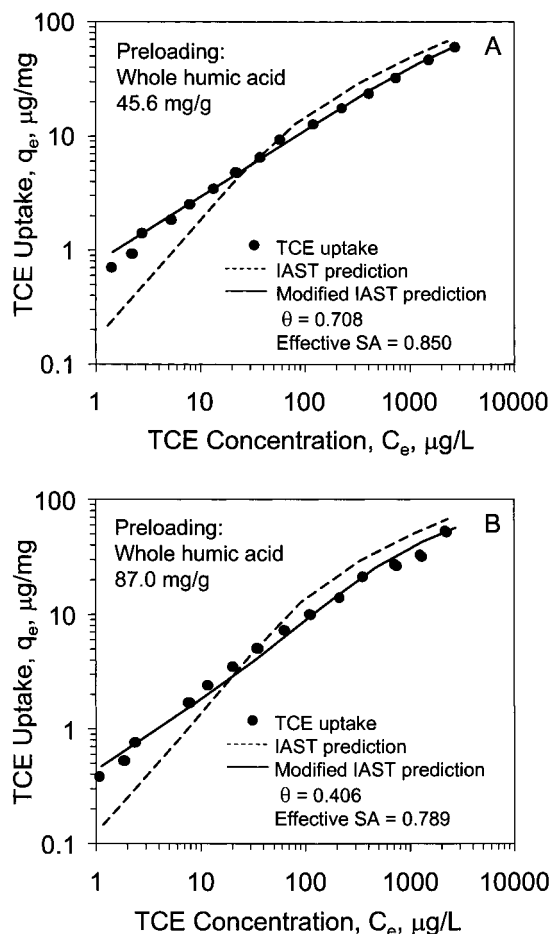


FIGURE 5. Modified IAST model predictions accounting for noncompetitive surface area and measured BET surface area reduction (solid lines) for two preloaded amounts of whole humic acid, 45.6 (plate A) and 87.0 (plate B) mg/g. The conventional IAST prediction (dashed lines) is shown for comparison.

by NOM increases with increased loading. This is shown in detail by the work of Kilduff et al., using model humic and fulvic acids (26). Cerminara et al. (41) observed earlier breakthrough of volatile organic compounds from bench-scale fixed-bed reactors when oxygen was present in the feed solution. They attributed this behavior to an increased loading of background organic matter, and subsequently increased competition, under oxic conditions. Newcombe et al. (23) found that low molecular weight NOM fractions of natural reservoir water organic matter exhibited higher uptake and exerted a greater competitive effect on the adsorption of MIB. While NOM loading has not been measured directly in many preloading studies, based on a knowledge of NOM adsorption rate, which occurs over time scales of weeks to months (depending on adsorbent particle size, among other factors), effects observed as a function of time can be interpreted in the context of loading. For example, Carter et al. (9) observed a significant increase in the competitive effects of Huron River water NOM on the adsorption of TCE over the first several weeks of preloading, and similar effects were observed by Summers et al. (3) for Rhine River water. These studies suggest that increased competition by NOM with increased loading may be a rather general trend for many different natural waters.

Role of Partitioning to Adsorbed Organic Matter. Calculations were done to evaluate the potential impact of partitioning of TCE to preloaded humic material. The estimated uptake attributed to partitioning can be expressed as a fraction of the total observed uptake, calculated as follows

$$\frac{\text{uptake attributed to partitioning}}{\text{total uptake}} = \frac{K_{oc} q_{e,HA} C_{e,TCE}}{K_F C_{e,TCE}^n} \quad (7)$$

where K_{oc} is the partition coefficient (organic carbon basis, L/mg o.c.), $q_{e,HA}$ is the humic loading (mg O.C./mg GAC), $C_{e,TCE}$ is the equilibrium TCE concentration, and K_F and n are the Freundlich isotherm parameters describing the TCE uptake by preloaded carbon. Several measured K_{oc} values for TCE on different organic materials are available in the literature, and many correlations are available. Estimates ranged from 5×10^{-5} to 1.59×10^{-4} L/mg o.c. (42, 43). The highest value was used in calculations to accentuate the potential contribution from partitioning. Furthermore, the percent uptake attributed to partitioning was largest at high humic loadings and high TCE concentrations. The Freundlich parameters for TCE uptake by GAC loaded with the highest humic loading (45.2 mg oc/g GAC = 87.0 mg HA/g GAC) were $K_F = 0.38$ and $n = 0.73$ (corresponding to q_e in units of $\mu\text{g}/\text{mg}$ and C_e in units of $\mu\text{g}/\text{L}$). Using a TCE equilibrium concentration of 2.5 mg/L (the upper end of the measured concentration range), the percentage contribution of partitioning to the observed uptake is less than 0.02%.

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Supporting Information Available

Figures of TCE concentration, C_e , $\mu\text{g}/\text{L}$, vs TCE uptake, q_e , $\mu\text{g}/\text{mg}$ (3 pages). Ordering information is given on any current masthead page.

Literature Cited

- (1) Safe Drinking Water Act Amendments of 1986 (June) PL 99–339.
- (2) Zimmer, G.; Crittenden, J. C.; Sontheimer, H.; Hand, D. W. *Proc. Am. Water Works Assoc. Annual Conference*, Orlando, FL, 1988.
- (3) Summers, R. S.; Haist, B.; Koehler, J.; Ritz, J.; Zimmer, G. *J. Am. Water Works Assoc.* **1989**, *81*, 66.
- (4) Speth, T. F.; Miltner, R. J. *J. Am. Water Works Assoc.* **1989**, *81*, 141.
- (5) Wilmanski, K.; Van Breemen, A. N. *Water Res.* **1990**, *24*, 773.
- (6) Speth, T. F. *J. Environ. Eng.* **1991**, *117*, 66.
- (7) Najm, I. N.; Snoeyink, V. L.; Suidan, M. T.; Lee, C. H.; Richard, Y. *J. Am. Water Works Assoc.* **1990**, *82* (1), 65.
- (8) Najm, I. N.; Snoeyink, V. L.; Richard, Y. *J. Am. Water Works Assoc.* **1991**, *83* (8), 57.
- (9) Carter, M. C.; Weber, W. J., Jr.; Olmstead, K. P. *J. Am. Water Works Assoc.* **1992**, *73* (8), 81.
- (10) Narbaitz, R. M.; Benedek, A. *J. Environ. Eng.* **1994**, *120* (6), 1401.
- (11) Fettig, J.; Sontheimer, H. *J. Environ. Eng.* **1987**, *113*, 780.
- (12) Carter, M. C.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1993**, *28*, 614.
- (13) Frick, B. R.; Sontheimer, H. In *Treatment of Water by Granular Activated Carbon*; McGuire, M. J., Suffet, I. H., Eds.; American Chemical Society: Washington, DC, 1983; pp 247–268.

- (14) Crittenden, J. C.; Luft, P.; Hand, D. W. *Water Res.* **1985**, *19*, 1537.
- (15) DiGiano, F. A.; Baldauf, G.; Frick, B.; Sontheimer, H. *Chem. Eng. Sci.* **1978**, *33*, 1667.
- (16) Thurman, E. M.; Wershaw, R. L.; Malcolm, R. L.; Pinckney, D. J. *Org. Geochem.* **1982**, *4*, 27–35.
- (17) Aiken, G. R.; Malcolm, R. L. *Geochim. Cosmochim. Acta* **1987**, *51*, 2177.
- (18) Beckett, R.; Jue, Z.; Giddings, C. *Environ. Sci. Technol.* **1987**, *21*, 289–295.
- (19) Reid, P. M.; Wilkinson, A. E.; Tipping, E.; Jones, M. N. *Geochim. Cosmochim. Acta* **1990**, *54*, 131–138.
- (20) Osterberg, R.; Lindqvist, I.; Mortensen, K. *Soil Sci. Soc. Am. J.* **1993**, *57*, 283.
- (21) Chin, Y. P.; Aiken, G.; O'Laughlin, E. *Environ. Sci. Technol.* **1994**, *28*, 1853–1858.
- (22) Knappe, D. R. U.; Matsui, M.; Sneoyink, V. L.; Roche, P.; Prados, M. J.; Bourbigot, M. M. *Environ. Sci. Technol.* **1998**, *32*, 1694–1698.
- (23) Newcombe, G.; Drikas, M.; Hayes, R. *Water Res.* **1997**, *31*, 1065–1073.
- (24) Kilduff, J. E.; Karanfil, T.; Weber, W. J., Jr. *J. Colloid Interface Sci.* **1998**, *205*, 271–279.
- (25) Kilduff, J. E.; Karanfil, T.; Weber, W. J., Jr. *J. Colloid Interface Sci.* **1998**, *205*, 280–289.
- (26) Kilduff, J. E.; Karanfil, T.; Weber, W. J., Jr. *J. Am. Water Works Assoc.* **1998**, *90*, 76–89.
- (27) Kilduff, J. E.; Karanfil, T.; Chin, Y. P.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1996**, *30*, 336–1343.
- (28) Kilduff, J. E.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1992**, *26*, 569.
- (29) Karanfil, T.; Kilduff, J. E.; Schlautman, M. A.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1996**, *30*, 2187–2194.
- (30) Carter, M. C.; Kilduff, J. E.; Weber, W. J., Jr. *Environ. Sci. Technol.* **1994**, *29*, 1773.
- (31) Summers, R. S.; Roberts, P. V. *J. Colloid Interface Sci.* **1988**, *122*, 367–381.
- (32) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: New York, 1982.
- (33) Derylo-Marczewska, A.; Jaroniec, M.; Gelbin, D.; Seidel, A. *Chem. Scr.* **1984**, *24*, 239.
- (34) Cerofolini, G. F. *Thin Solid Films* **1974**, *23*, 129–152.
- (35) Smith, E. H. *Water Res.* **1991**, *25*, 125.
- (36) Jain, J. S.; Snoeyink, V. L. *J. Water Pollut. Control Fed.* **1975**, *45*, 2463.
- (37) Lasdon, L.; Waren, A.; Jain, A.; Ratner, M. *ACM Trans. Math. Software* **1978**, *4*, 34–50.
- (38) Yonge, D. R.; Keinath, T. M. *J. Water Pollut. Control Fed.* **1986**, *58*, 77–81.
- (39) Ghosh, K.; Schnitzer, M. *Soil Sci.* **1979**, *129*, 266–276.
- (40) Newcombe, G.; Hayes, R.; Drikas, M. *Colloids Surf.* **1993**, *78*, 65–71.
- (41) Cerminara, P. J.; Sorial, G. A.; Papadamas, S. P.; Suidan, M. T.; Moteleb, M. A.; Speth, T. F. *Water Res.* **1995**, *29*, 409–419.
- (42) Chin, Y. P.; Weber, W. J., Jr.; Chiou, C. T. In *Organic Substances in Sediments and Water*; Baker, R. A., Ed.; Lewis Publishers: 1991; Vol. 1.
- (43) Rutherford, D. W.; Chiou, C. T. *Environ. Sci. Technol.* **1992**, *26* (6), 965–970.

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