Dynamic Modeling of Gaseous Multicomponent Trace Contaminant Adsorption

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Activated carbon is a porous material in the Trace Contaminant Control (TCC) system that physically adsorbs volatile organic compounds (VOCs) generated within spacecraft and spacesuit environments. Several isotherm models exist to predict adsorption equilibria for processes involving multicomponent systems. This paper investigates the use of Ideal Adsorbed Solution Theory (IAST) for predicting multicomponent trace contaminant adsorption behavior using single-component isotherms based on potential theory. Developing simulations for experimental breakthrough curves will gauge the validity on the sizing and design of TCC architecture. Model results on predicting bed performance and roll-up effects are compared with available multicomponent test data.

Nomenclature

A	=	Specific surface area of adsorbent (m^2/g)
A_i	=	Adsorption potential factor of component i ($K/(m^3/mol)$)
$A_{i,TDR}$	=	Modified adsorption potential factor of component i (K^2)
E_0	=	Energy of adsorption (J/mol)
n_i	=	Molar loading of component i (mol/g)
P_i	=	Partial pressure of component i (bar)
P_i^s	=	Saturation pressure of component i (bar)
P_i^0	=	Pressure of component i at T and π of mixture (bar)
R	=	Gas Constant (J/K/mol)
T	=	Adsorption temperature (K)
V_i	=	Liquid volumetric loading of component i (ml/g)
V_i^T	=	Liquid molar volume of component i at adsorption temperature T (m^3/mol)
V_{ref}^T	=	Liquid molar volume of reference component at adsorption temperature T (m^3/mol)
V_i^m	=	Liquid molar volume of component i at the normal boiling point (m^3/mol)
$V_{ref,hex}^m$	=	Liquid molar volume of reference component hexane at the normal boiling point (m^3/mol)
V_0	=	Maximum volumetric adsorption capacity of adsorbent (m^3/g)
x_i	=	Liquid mole fraction of component i in the adsorbed phase (dimensionless)
β_i	=	Affinity coefficient of component i (dimensionless)
β_i^m	=	Affinity coefficient of component i at the normal boiling point (dimensionless)
β_i^T	=	Affinity coefficient of component i at adsorption temperature T (dimensionless)

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π_i = Spreading pressure of component i (N/m)
ACHBD = Axial Charcoal Bed Efficiency
DR = Dubinin-Radushkevich
HVLA = high velocity, low aspect ratio
IAST = Ideal Adsorbed Solution Theory
ISS = International Space Station
LVHA = low velocity, high aspect ratio
PLSS = Portable Life Support Subsystem
TDR = Tangential Dubinin-Radushkevich
TCC = Trace Contaminant Control
TCCS-CP = Trace Contaminant Control Simulation computer program
VOCs = volatile organic compounds

I. Introduction

THE ultimate goal of simulating trace contaminant control (TCC) systems for spacecraft and spacesuit environments is to universalize the dynamic adsorption of a multicomponent system of volatile organic components (VOCs) while preserving reliable predictability. Activated carbon is a microporous sorbent used in TCC beds that may be chemically treated to facilitate the chemical adsorption of contaminants such as ammonia. Activated carbon, however, inherently favors the physical adsorption of VOCs, and a method of prediction solely based on carbon properties is a fundamental and thus desirable avenue of study.

TCC design is crucial in the spacecraft environments such as the Orion crew exploration vehicle. Emergency scenarios involving the production of combustion byproducts due to cabin fires depend on reliable dynamic adsorption modeling to properly size first responder respirator masks and purification systems such as the Orion Smoke-Eater filter.[1] The adsorbent, encased in the cartridge, must withstand the dynamic inlet conditions of acrolein, formaldehyde, and other toxic gases.

Applications also extend to the spacesuit air ventilation loop in the Portable Life Support Subsystem (PLSS). Circulation of gaseous components within the spacesuit volume resulting from metabolic generation and materials off-gassing require appropriate sizing to determine the life expectancy and change-out frequency of the carbon filter.[2] Desorption processes in which the sorbent undergoes regenerative operations for further use is a growing topic of interest. Methods include thermal swing and pressure swing cycling.[3]

Adsorption studies conducted by Lockheed at their Palo Alto Research Laboratory[4] were used to develop the model presented in this paper. Barnebey-Cheney untreated activated carbon, a coconut shell granular activated carbon that adsorbs VOCs more efficiently than standard charcoal, was the porous media used to generate breakthrough curves for each contaminant in an air stream. The particle size was kept constant throughout the experimental runs; however, the model can expand to consider different particle sizes and other sorbents to serve as a template for loading predictability.

A. Adsorbent Characteristics and Adsorption Equilibria

Activated carbon is a microporous material that facilitates physical adsorption, or physisorption, of contaminants. A large average pore size of 15 Ångströms and a high porosity introduces large surface area per unit volume for contaminant uptake.[5] Low surface acidity allows attracting van der Waals interactions to occur between the adsorbate and the functional groups residing on the pore surface. Induced electrical forces weakly pull adjacent molecules together while retaining the same chemical compositions. Because van der Waals forces are distance-dependent, bonding occurs directly at the gas-solid interface in which the adsorbate leaves the bulk gas and condenses onto the pore surface.[6]

Physical adsorption is an exothermic process in which mass transfer occurs from a flowing bulk fluid to the solid adsorbent surface due to differences in concentration. The rate of mass transfer is controlled by various governing resistances residing in a macroporous and microporous environment and determines the shape of the breakthrough curve for an adsorbate.[6] Curve characteristics can be quantified by an overall mass transfer coefficient, which is a function of macropore and micropore diffusion coefficients, pore size, the Reynolds number, and gas properties such as viscosity and density. The overall mass transfer coefficient can be correlated for other components as a function of key parameters.[7]

B. Adsorption Theories and Model Approaches

The Polanyi Adsorption Potential Theory is a pore-filling isotherm model that describes the adsorption of gaseous contaminants onto the pore surface occurring in the condensed phase. The theory has been used in bed design as an established bed sizing approach. The adsorption potential measures the likelihood of liquid phase adsorption in micropores as the energy required to compress a gaseous contaminant i from a partial pressure p_i to the saturation vapor pressure p_i^S at adsorption temperature T.[8] The adsorption potential factor A_i, presented in the form below as a function of contaminant liquid molar volume V_i^m at the normal boiling point, captures the degree of adsorption for a contaminant.

$$A_i = \frac{T}{V_i^m} log_{10} \frac{P_i^S}{P_i} \tag{1}$$

The potential factor varies inversely with the log of the contaminant partial pressure. Polanyi adsorption potential plots are log-log plots of volumetric liquid loadings against potential factors that result in a temperature-invariant characteristic curve for a given adsorbate-adsorbent system and for a wide range of partial pressure.

The Polanyi Adsorption Potential Theory serves as the basis for simulating adsorption processes in the Trace Contaminant Control Simulation computer program (TCCS-CP), a FORTRAN-based modeling tool initially developed by Lockheed and progressively updated by both Lockheed and NASA Marshall Space Flight Center.[9, 10] The theoretical and empirical approach predicts loading equilibrium capacities for fixed activated charcoal beds and has analyzed TCC system performance and design for Spacelab, Space Station Freedom, and eventually onboard the International Space Station (ISS). Subroutine Axial Charcoal Bed Efficiency (ACHBD) incorporates the approach in Version 8.1 of the program.[10] The routine calculates the saturation zone length as a function of bed geometry, contaminants removed, and the maximum adsorption capacity. The adsorption zone length, correlated from experimental data, depends on gas velocity.

The traditional Dubinin-Radushkevich (DR) equation, founded on the Polanyi Adsorption Potential Theory, describes adsorption in microporous solids with a pore-size-distribution-dependent adsorption potential exponent set to 2. The isotherm is expressed as

$$\frac{V_i}{V_0} = e^{-\left[\frac{RT}{\beta_i E_0} ln \frac{P_i^S}{P_i}\right]^2} \tag{2}$$

where V_i is the volumetric loading of the contaminant, V_0 is the maximum adsorbent volume available for adsorption, R is the gas constant, β_i is the affinity coefficient for contaminant i, and E_0 is the energy of adsorption for a reference compound. In the traditional DR equation, the affinity coefficient is represented by β_i^T as defined below. V_i^T is the contaminant liquid molar volume at adsorption temperature T, and V_{ref}^T is the liquid molar volume at adsorption temperature T for the reference compound:

$$\beta_i^T = \frac{V_i^T}{V_{ref}^T} \tag{3}$$

C. Multicomponent Adsorption

The single-component DR isotherm models discussed in the previous section can be applied to predict loadings for gaseous mixtures by implementing the Ideal Adsorbed Solution Theory (IAST). The IAST assumes that the adsorbent is homogenous, or maintains consistent morphology throughout the entire adsorbent surface area. Other assumptions include that the adsorbent active sites are equally accessible to all components, and the adsorbed phase

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behaves as an ideal mixture.[11] To implement IAST, the component spreading pressures, π_i, must be evaluated using the following integral:

$$\frac{\pi_i A}{RT} = \int_0^{P_i^0} \frac{n_i}{P_i} dP_i \qquad (4)$$

n_i represents the contaminant molar loading, and A is the specific surface area of the adsorbent. P_i^0, the standard contaminant pressure at the temperature and spreading pressure of the mixture, can be solved for using an expression similar to Raoult's Law for ideal solutions with x_i representing the liquid mole fraction of the adsorbed phase:

$$P_i = x_i P_i^0(T, \pi) \qquad (5)$$

Each variable must be solved for iteratively to describe the thermodynamics of the adsorbed phase in a mixture. The IAST requires that the isotherm equation implemented be thermodynamically consistent in both the Henry's Law region and at complete loading;[12] otherwise, Eq. 4 cannot be properly integrated to obtain the spreading pressure.

D. Modified DR Adsorption Isotherms

The traditional DR isotherm at complete loading appropriately results in the saturation pressure. In the limit of zero loading, however, the equation does not approach the Henry's Law limit and is therefore unreliable at extremely low pressures. For use in IAST, modified forms of the DR equation that correct thermodynamic behavior at low coverage have been studied extensively in the literature and will be discussed presently.

Previous work conducted by Ye et al.[13] correlated isotherm parameters of a proposed modified DR equation for several organic compounds on untreated activated carbon. The affinity coefficient was modified as β_i^m to depend on inherent adsorbate properties rather than on adsorption conditions. V_i^m is the contaminant liquid molar volume at the normal boiling point, and V_{ref}^m is the liquid molar volume of a reference component at the normal boiling point. The ratio includes exponential n as an empirical fitting parameter:

$$\beta_i^m = \left(\frac{V_i^m}{V_{ref}^m}\right)^n \qquad (6)$$

The affinity coefficient resulted in a stronger fit to experimental loadings of the contaminants studied with an n value of 0.69.

Work by Mahle[14] presents a modified tangential DR (TDR) form that combines the traditional DR with the proper lower limit. The form is simple to implement and does not require additional parameters. By establishing a tangential line from the origin to a point on the traditional DR curve, the modified isotherm form functions continuously for both limiting cases. A logical statement implemented in code would apply the traditional DR equation beyond this tangential point; otherwise, the tangential line would be used to predict loadings at very low concentrations.

II. Approach

A. Isotherm Development for Single Component Systems

Breakthrough data from Robell[4] were used for isotherm development. The Polanyi Potential theory was initially used to evaluate the data. Adsorption potential factors for each contaminant were calculated using Eq. 1. The Polanyi plot revealed a predominantly linear relationship between the experimental loading and the potential factor. Two linear correlations applicable to water soluble compounds and insoluble compounds for untreated type BD activated charcoal were also plotted for comparison.[15]

An alternate form of the adsorption potential factor, $A_{i,TDR}$, was explored by incorporating Eq. 6. The form is defined below. Volumetric loadings predicted by the TDR equation were plotted as a function of Eq. 7.

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$$A_{i,TDR} = \left[\frac{T}{\beta_i^m} \ln \frac{P_i^s}{P_i} \right]^2 \qquad (7)$$

Similar to Eq. 1, the alternate form is not dimensionless. The exponent n, employed in the affinity coefficient, and the adsorption energy E_0, employed in the isotherm expression, served as fitting parameters for the contaminant loadings studied. Justification for using the TDR expression was ensured before initiating model development.

B. Dynamic Adsorption Modeling

Dynamic adsorption modeling was implemented in Aspen Adsorption®, a flowsheet simulator that models and optimizes gas and liquid adsorption processes. The process flowsheet included a dynamic gas bed block from the model library, an inlet air/nitrogen stream carrying a single contaminant, and a product stream. Bed dimensions, adsorbent properties, and inlet conditions such as temperature, pressure, and component flowrates were adjusted to reflect those of each experimental run. Adsorption of oxygen and nitrogen, the carrier gases, were deemed negligible and treated as inerts in the process. The flowsheet constraints section incorporated the traditional DR and TDR isotherm equations using Eq. 6 as a user submodel.

Configuration of the bed block assumed a fluid film mass transfer model with constant overall mass transfer coefficients. The discretization method chosen mitigated the impact of numerical noise on the predicted curves. Experimental test data were fed into the estimation tool in Aspen Adsorption® to estimate an overall mass transfer coefficient for each contaminant. Dynamic runs with the estimated parameters generated predicted breakthrough curves for each run.

The viability of developing a mass transfer correlation based on component properties and bed conditions was investigated. Such a relation would create a more autonomous and complete multicomponent adsorption model that estimates mass transfer coefficients for VOCs beyond those studied by Robell,[4] which in turn would predict component breakthrough characteristics. Otherwise, requiring inputs on experimental single-component isotherms unique to run conditions limit model capability. Several parameters and formulas plotted against the mass transfer coefficient were explored in pursuit of revealing a linear relationship.

After demonstrating successful single-component model prediction, the bed block configuration was updated to include IAST in the user submodel. The flowsheet constraints section required two additional submodels to implement Eq. 4 and 5. The complementary error function, based on a rational approximation found in Numerical Recipes,[16] was also included to ensure accuracy in evaluating the spreading pressure integral.

Aspen Adsorption® offers a built-in feature combining the traditional DR with IAST. Loading predictions for the traditional DR executed in code as a user submodel with IAST was compared to those of the built-in feature to establish confidence in the customized isotherm model.

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Figure 1. Experimental and correlated volumetric loadings as a function of the Polanyi Adsorption potential factor.

Figure 2. Experimental and predicted volumetric loadings as a function of a modified adsorption potential factor.

III. Results

A. Isotherm Development for Single Component Systems

A Polanyi Plot of each contaminant along with the water soluble and insoluble correlations[15] is shown in Figure 1. At low potential factors, corresponding to relatively high contaminant concentrations, the points no longer coalesce along a characteristic curve and gradually level off to complete saturation. Consequently, the correlations are only representative for contaminants with an A value greater than 8. For values less than 8, the correlations increased dramatically in relative error. This deviation from linearity implies that an alternate form of the potential factor may better unify adsorption data.

Figure 2 plots Eq. 7 against the loadings predicted by DR and TDR isotherms. Compared to Figure 1, all of the experimental points collapse reasonably well into a single curve by fitting parameter n in Eq. 6 to the data. Minimizing the sum of relative errors between the predicted and experimental loadings resulted in an n value of 0.685, which corresponds to the value obtained by Ye et al.[13] A resemblance to previous adsorption work builds confidence in the development efforts.

The TDR isotherm was investigated to exhibit proper Henry's Law behavior for ultimate use with IAST. Loading behavior of the traditional DR, TDR, and the referenced correlation for insoluble compounds is shown in Figures 3 and 4 for ethylene. Figure 3 shows the loading behav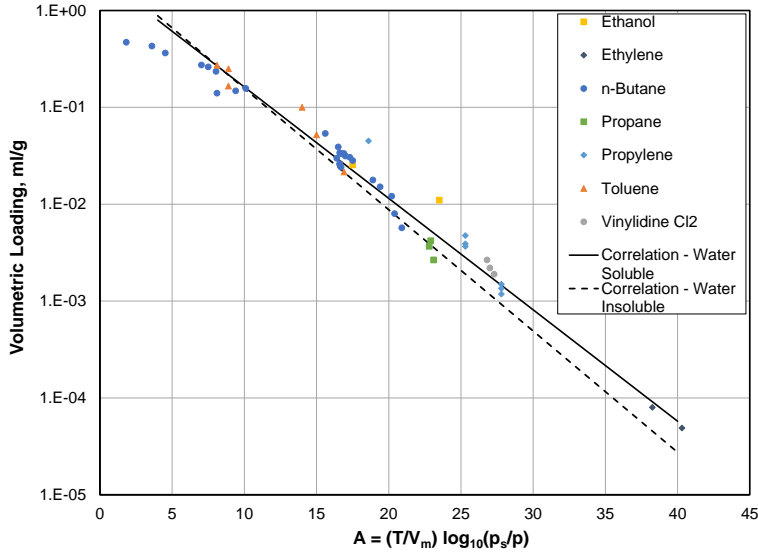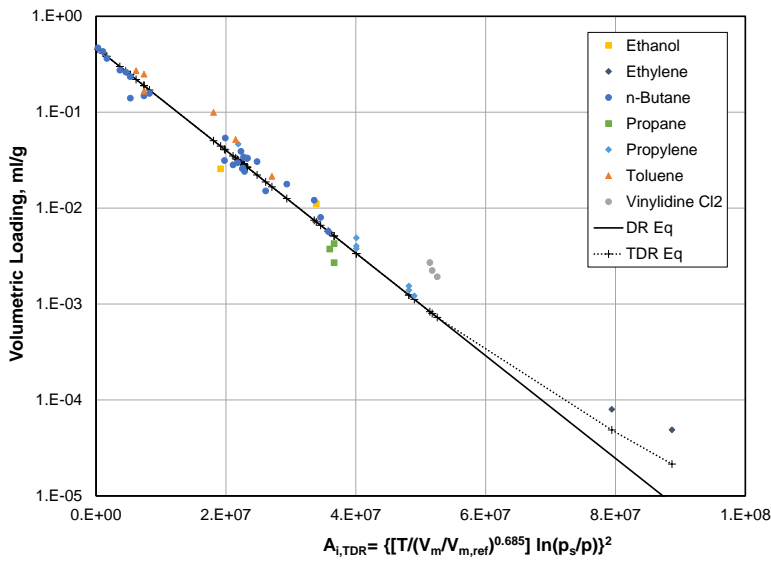ior for a wide range of partial pressure and at very low pressures, as shown in the inset. The traditional DR and TDR isotherms are identical except in the low pressure region, in which lower limit behavior is revealed in Figure 4. As pressure goes to zero, the traditional DR approaches zero loading and the water insoluble correlation approaches infinite loading. Both cases are not integrable in Eq. 4 for the spreading pressure and thus not applicable to IAST. The TDR, however, is in thermodynamic agreement and approaches the Henry's law limit.
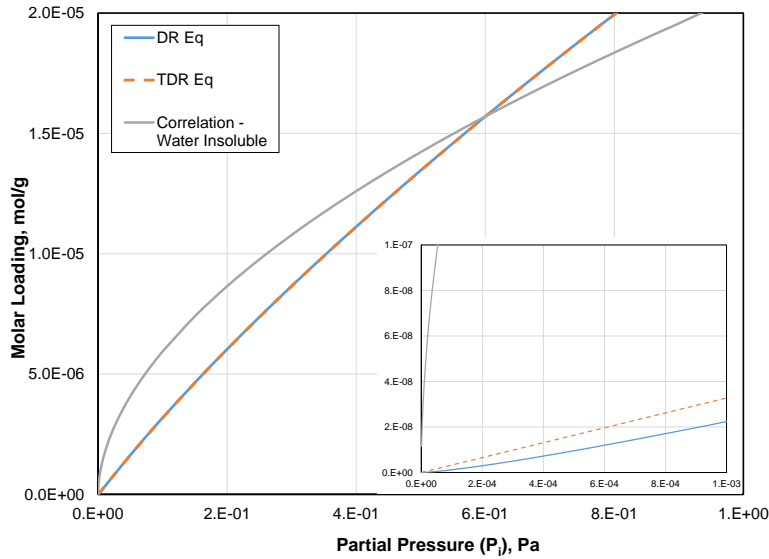
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Figure 3. Predicted loadings in the low pressure region for the DR and TDR equations and the water insoluble correlation.
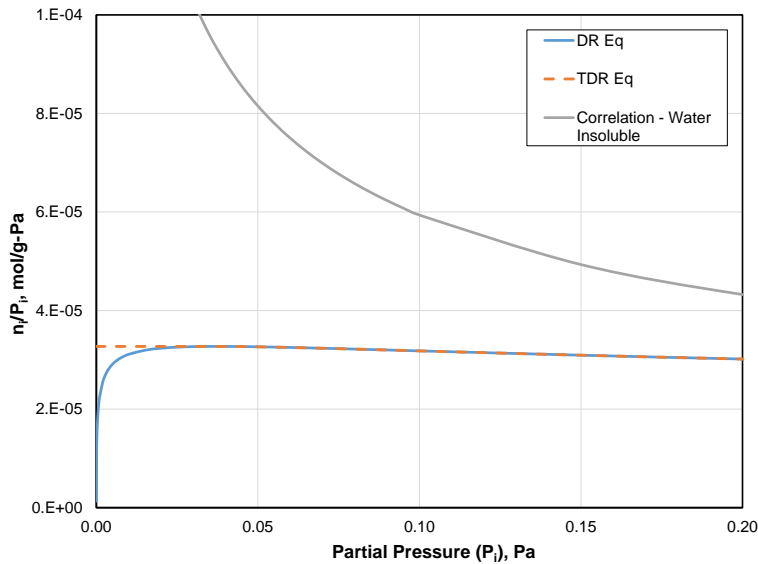

Figure 4. Henry's law comparison of the DR and TDR equations and the water insoluble correlation.

B. Dynamic Adsorption Modeling

1. Single Component Breakthrough Modeling

The overall mass transfer coefficient for each contaminant was estimated using the estimation tool in Aspen Adsorption® and used to simulate breakthrough curves. The predicted curve and experimental test points are plotted in Figures 5 and 6 for butane and propylene, respectively. Breakthrough curves for ethylene, propane, toluene, and vinylidene chloride were also generated. The results indicate successful prediction of experimental data using the TDR equation.

A generalized correlation of the mass transfer coefficient as a function of the Peclet number or a function of component properties and isotherm parameters resulted in large degrees of error and was not pursued further. Scatter in the limited data set represented indistinguishable impacts of dispersion and interparticle and intraparticle mass transfer effects. Efforts continue to arrive at a generalized correlation to ideally predict the shape of the breakthrough curve. Additional single-component adsorption data operating at a fixed flowrate and at room temperature are ultimately desired for a meaningful study.
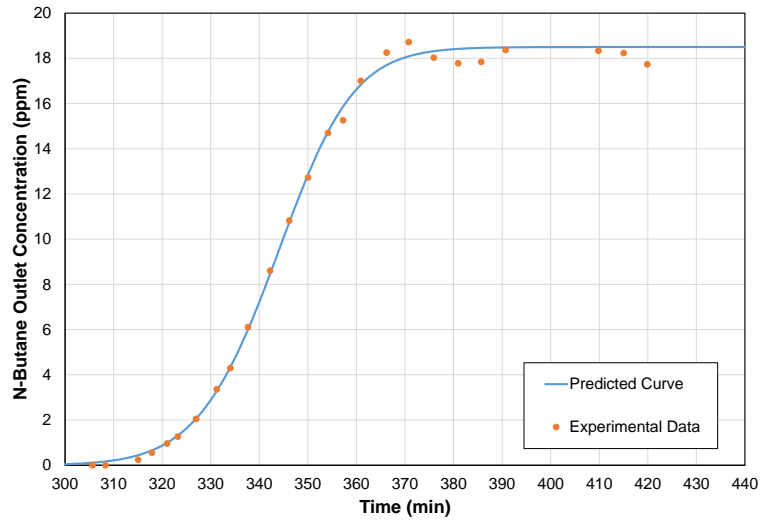
Figure 5. Comparison of Aspen Adsorption®simulated breakthrough curves and experimental data for n-butane.
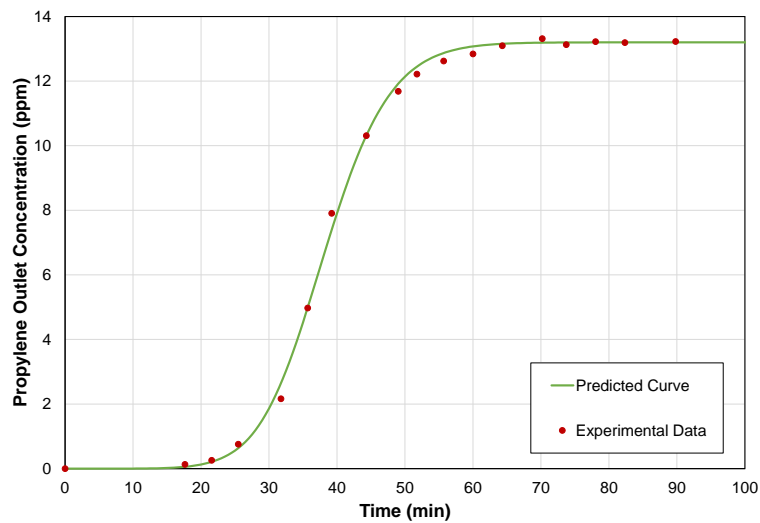

Figure 6. Comparison of Aspen Adsorption® simulated breakthrough curves and experimental data for propylene.
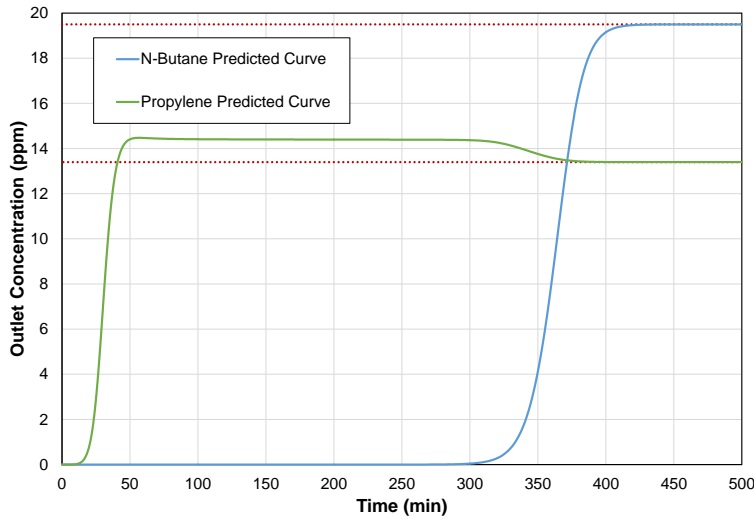
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Figure 7. Aspen Adsorption® simulated breakthrough curves and roll-up effects for a concurrent flow of n-butane and propylene.
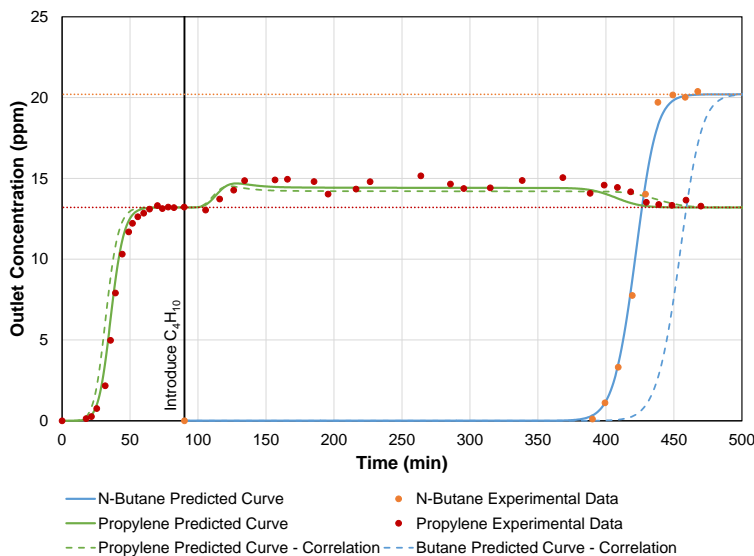

Figure 8. Aspen Adsorption® simulated breakthrough curves and roll-up effects for propylene with subsequent introduction of n-butane.

2. Multicomponent Modeling with IAST

The TDR with IAST model was challenged with a concurrent flow of n-butane and propylene in air. Simulated breakthrough curves of each adsorbate are shown in Figure 7. The red horizontal lines denote respective feed concentrations for propylene and n-butane. The figure illustrates the significance of competitive adsorption on the adsorbent surface. The more weakly adsorbed component, propylene, breaks through first. The more strongly adsorbed component, n-butane, displaces propylene from the adsorbent, resulting in a higher gas phase concentration exiting the bed than the feed concentration. As n-butane gradually breaks through after some time, propylene is no longer displaced, and the effluent returns to its original feed concentration. This phenomena, known as the roll-up effect, occurs between relatively weakly and strongly adsorbed components.

To verify model efforts, the traditional DR equation as executed in the user submodel with IAST was compared to the built-in traditional DR with IAST feature offered in Aspen Adsorption®. Eq. 6 was used as an isotherm parameter in both cases. Quantitative differences in loading predictions were insignificant, establishing confidence in the customized model.

3. Model Application

Figure 8 compares an experimental breakthrough run of n-butane and propylene in air with curves simulated by the TDR with IAST model. The red and orange horizontal lines represent feed concentrations for propylene and n-butane, respectively. Propylene initially preadsorbs and gradually exits the bed up to its feed concentration. The subsequent introduction of n-butane, designated by the vertical line, creates a roll-up effect for propylene. Roll-up persists until equilibrium is reached and the effluent resembles feed conditions.

Breakthrough simulations based on the value of E_0 obtained from the correlation are also plotted for reference. The slightly early propylene breakthrough time and delayed butane breakthrough time imply a sensitivity to the value of E_0, which plays a role in horizontally shifting the overall curve. This level of variability is inherent in both the experimental data and the universalized TDR correlation.

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IV.   Conclusions and Recommendations

A dynamic model to describe multicomponent adsorption using IAST based on single component isotherms has been developed. The isotherm was modified to calculate loadings in the Henry's Law region without compromising proper thermodynamic behavior. Experimental breakthrough data for several components on untreated activated carbon were used for model prediction. More experimental data from both stand-alone and integrated tests are needed to support efforts in validating the model, specifically with high velocity, low aspect ratio (HVLA) radial bed geometries and low velocity, high aspect ratio (LVHA) axial flow bed geometries. Experimental runs operating at room temperature and at a fixed flowrate would aid in determining a generalized mass transfer correlation, which may extend model predictions to other components. Characteristic testing of other sorbents may also be utilized to create a more sophisticated and applicable model. Ultimately, model results will be compared to predictions of the recognized FORTRAN TCCS-CP to improve bed performance design.

Acknowledgments

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