**Designing Heterogeneous Hierarchical Material Systems: A Holistic Approach to Structural and Materials Design**

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**Supplemental Material (*for online publication only*)**

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**Part I. Rationale for and Limitations of Experimental Test System**

Activated carbons (ACs) are used across industries and scales, from small devices such as battery electrodes and in-home water filtration cartridges to industrial scale processes like flue gas adsorption and wastewater treatment. These materials are often employed as adsorbents given their high surface area, porosity, and affinity for a range of adsorbates; these characteristics depend on the processing conditions and precursor carbon materials1. For example, biomass-based activated carbons made via CO2 activation tend to be slightly hydrophobic and have non-polar character, making them ideal candidates for removing organic compounds from water2–4. There are thousands of studies in the literature demonstrating the use of biomass-based ACs to remove simulated and actual water contaminants, probing both the total capacity and uptake rate through isotherms (e.g. Langmuir, Freundlich) and kinetic relationships (e.g. pseudo first-order, pseudo-second order, diffusion-limited), respectively5–12. Such relationships are used for both liquid and gas phase adsorption, and of course both capacity and rate vary with adsorbate-adsorbent pairings and processing conditions.

ACs are able to sequester a range of gas phase adsorbates such as mercury, sulfur, nitrous oxides and carbon dioxide, as well as volatile organic compounds such as toluene13–17. However, the majority of studies assessing the performance of ACs in the literature are either experimentally based or computationally driven. Experimental “cook and look” style studies, where a researcher makes one or more ACs according to a specific recipe, and runs batch adsorption experiments, are often performed with unrealistically high inlet concentrations and at such a small scale that it is not clear the results are translatable to a real application18–21. Separately, computational modeling studies, where a researcher probes the impact of operating conditions and/or material properties on AC performance, often drawing characterization and uptake rates/capacity from the literature, are routinely left experimentally unvalidated22,23. Some computational models that are “validated” are done so with physical systems that fail to capture critical aspects of the modeled system, such as using batch adsorption studies to demonstrate validity of a flowing gas model24, or done on an experimental scale that might induce boundary effects that do not exist in the model25. There are of course many studies that *are* able to develop convincing experimental validation of computational fluid dynamics (CFD) models26–28. However, few researchers use statistical methods such as Design of Experiments (DOE) approaches to sample both the experimental and computational spaces, developing both model calibrations and material optimizations. Peksen et al. demonstrated that it was possible to use these approaches in combination to optimize several parameters of a solid oxide fuel cell29. Recently, Lai et al. showed how hierarchical calibration validation of CFD models could be applied to CO2 adsorption onto ACs30. They employed a Bayesian calibration procedure with posterior model parameter distributions from one level to inform the next to describe bed pressure, temperature, capture capacity and rate of this multiphase reactive flow process. The present work was designed to use both a statistical calibration framework, as done by Lai et al., in combination with a DOE approach to computational experiments, to demonstrate how a materials system for activated carbon adsorption of toluene could be optimized.

Toluene on activated carbon was chosen as the target adsorbate-adsorbent for several reasons. First, ﻿Lillo-Ródenas and co-workers demonstrated it was possible to develop a laboratory-scale adsorption bed to study the removal of toluene on activated carbons, overcoming an oft-encountered experimental “can we do it” question31,32. Second, toluene can be monitored online via residual gas analysis, and gas tanks containing precisely known quantities of toluene in ultra-high purity nitrogen could be obtained from a commercial vendor (Airgas), such that with a flow meter, we could calibrate for toluene concentration in a gas stream knowing the partial pressures from the mass spectrometer. The activated carbons were provided by Cabot Corporation for research purposes, initially chosen to represent a range of surface areas, particle sizes and (we surmised, given available descriptions), varying affinities for toluene.

Darco G60 is an acid-washed, steam-activated carbon, used to decolorize and purify pharmaceuticals. Darco KB-G, used for both liquid and vapor applications including purification, decolorization, deodorization and catalysis, is one of Cabot’s smallest particle size chemically activated carbon available. It is made from wood residue, activated with phosphoric acid, and therefore would have a reasonably high surface oxygen content due to surface anhydrides and lactone species33. PAC200 is sourced from coal; its activation conditions are not disclosed, but it is often used for food industry applications such as decolorizing and odor removing. Its extreme heat treatment during processing likely reduces the amphoteric nature and shifts the carbon to more basic properties34. While a full chemical analysis of the activated carbons is beyond the scope of the present work, these three materials were predicted to have varying adsorption capacities and uptake rates given the physical and chemical differences. Because the surface chemical properties of the activated carbons will play a role in adsorption affinity and capacity for toluene, and they are excluded from present consideration, the ability to completely optimize the materials system based on AC selection is limited. Again, though, we highlight that the purpose of this paper is not to “pick the best material for dilute toluene adsorption,” but rather to demonstrate a coupled experimental-computational-statistical methodology to enable material system optimization.

Long-term, a goal of this computational-statistical-experimental framework is to design heterogeneous hierarchical materials where active sites dot the scaffold. Such materials are used for flue gas treatment35–38, and thus this paper establishes the groundwork to enable exploration of materials systems with both hierarchical and heterogeneous complexity. Future work will, by nature of focusing on optimizing the material and system, include a full characterization of surface functional groups, composition, acid/base properties, etc. relevant to reactive transport.

**Part II. Extended Experimental Materials and Methods**

To both calibrate and validate the CFD model we measured the adsorption of toluene, a volatile organic compound, from a high-purity nitrogen stream into packed beds of three different activated carbons (PAC 200, Darco G60, Darco KG-B). The ACs had a range of particle sizes and porosities, as described in Table S1. Before use, the activated carbons were dried overnight in a laboratory oven at 338 K.

**Table S1.** Properties of activated carbons used in present study



The ACs were loaded into “packed beds,” which consisted of a 5 mL sterile glass pipette plugged with glass wool at either end, loaded at two packing densities (low, 0.18 – 0.26 g/mL; high 0.37 to 0.61 g/mL) as shown in Figure S1. Several runs were tested using the reactor volume shown in Figure S1 (approximately 3 mL). However, after six days at low inlet concentration (20 ppm) we did not see any toluene breakthrough. Given time constraints, the volume was reduced to 0.0862 mL for all experiments. This led to breakthrough and saturation times within a 1-day timeframe.



**Figure S1.** Activated carbon packed into glass pipette to simulate fixed bed reactor

Prior to experiments, the ACs were flushed with nitrogen at 293 K for 30 minutes at a flow rate of 30 mL/min to purge oxygen and other volatile impurities. The ACs were exposed to a flowing gas containing either 20 (low) or 200 (high) ppm of toluene in high-purity nitrogen. The gas flow rate was set at either 30 mL/min (low) or 40 mL/min (high). Experiments are termed AC/x/y/z where AC is the activated carbon, x is the packing density, y is the flow rate and z is the inlet concentration. Based on the DOE matrix shown in Table 1 of the paper, each parameter (packing, flow rate, concentration) was set to a low (L) or high (H) value. A blank reactor was run using a pipette and glass wool to ensure that there was no significant adsorption to these materials. A baseline curve showed negligible uptake of toluene to these materials.

**Part III. Expanded Experimental Results**

** Figure S2.** Outlet toluene concentration as a function of time through fixed bed of ACs at high packing, high flow rate, high inlet concentration (HHH)

By monitoring the concentration of toluene in nitrogen exiting the fixed bed reactor, we can calculate the uptake rate and capacity of the activated carbon, as well as bed breakthrough and saturation times. While running replicates for every material/flow combination was too time-intensive for the scope of this work, triplicate experiments for PAC-LLH and duplicate for KBG-LLH showed reproducible uptake rates to within 1%. Figure S2 shows an example of how the different materials showed varying uptake rates (slope) and breakthrough times for the HHH conditions.

The AC capacities were (not surprisingly) a function of inlet concentration, bed packing and flow rate. Likewise, the breakthrough and saturation times varied by AC and operating conditions, as shown in Figure S3. The uptake rate was taken as the slope of the uptake curve (massadsorbed/massAC versus time) measured from when the AC was exposed to the toluene gas until the saturation point, as shown in Figure S3.

|  |  |
| --- | --- |
|  |  |
| a. Capacity of ACs | b. Breakthrough and saturation time |

**Figure S3.** Impact of operating conditions on capacity, breakthrough and saturation time

Table S2 shows a summary of experimental results for the toluene adsorption experiments. As others find in the literature33,39, surface area and porosity alone are not good predictors of adsorption capacity; KBG has the highest surface area and pore volume (and smallest particle size), but for LHL and HHH runs the lowest uptake capacity, while for LLH it has the highest uptake capacity of the three materials. This simple matrix of nine experimental runs highlights the critical role of DOE and computational modeling for the evaluation of the behavior of heterogeneous hierarchical systems. While there are clear differences between the activated carbons, there is no obvious “trend” in terms of capacity and rate behavior across experimental conditions. This further cautions of the reliance upon single experimental conditions to evaluate materials’ behavior.

**Table S2.** Summary of adsorption studies for model calibration and validation



**Part IV. Computational Fluid Dynamics Model Development**

The hierarchical nature of the AC requires a multi-scale model of the packed bed system. The computational model explicitly resolves the macroscale reactive transport of the packed bed and uses an ad hoc model to resolve the microscale reactive transport, which occurs within the AC particles. To fully resolve the macro- and micro-scale in one model would be computationally prohibitive based on the high resolution necessary for the micropores within the AC particles. The governing equations for the multi-scale model are discussed in detail in the following sub-sections. The computational domain, consists of two non-overlapping subdomains. They are incorporating the solid subdomain (the gray objects), and the gas subdomain which is fully occupied by the gas (the white space) as shown in Figure S4.

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**Figure S4:** Schematic for simulation domains

1. **Macroscale: Advection-Diffusion in a porous bed**

To develop the macroscale level governing equations, we begin by letting be the interface of the solid-gas.

Steady-state flow of an incompressible fluid in the gas subdomain, is modeled using the continuity equation:

and the momentum conservation equation:

where denote the pressure, viscosity, velocity, and density of the nitrogen gas inside , respectively, and *g* is gravity. A no-flow, no-slip boundary condition is applied at the surface of the solid particles:

The transport of toluene in packed bed at the macroscale is described by the advection-diffusion equation:

where is the material derivative using a Lagrangian frame of reference and is time, is the binary diffusion coefficient of toluene in nitrogen, and is the concentration of toluene in . The adsorption of toluene at the solid particles’ surfaces is described by the boundary condition:

where is the normal unit vector to the surface pointing outward, and is the reaction term characterizing the adsorption of toluene occurring at on. For numerical implementation this boundary conditions (Eq.7) is rewritten as a homogeneous boundary condition and a source term, which is added to the advection-diffusion equation (Eq.6)40. In this model, a Langmuir adsorption model is used:

where is the adsorption rate coefficient and is the normalized surface concentration of toluene on the surface . Let be the concentration of absorbed toluene on the surface, such that the normalized surface concentration is defined as:

where is the maximum surface concentration (adsorptivity) of toluene on . The value of determines the saturation point of the activated carbon. For mass conservation, the rate of toluene removed from the flowing nitrogen gas must be balanced by the gain of adsorbed toluene on the solid particles, i.e.:

1. **Microscale: Accounting for particle porosity**

To account for the hierarchical porosity of the AC particles, a Darcy scale model is used to simulation the reactive transport within the solid subdomain . More specifically, the diffusive system with Langmuir adsorption from equations (6)-(10) is replaced with a system of averaged coupled reaction-diffusion equations:

where and are the equivalent volumetric terms for and , respectively. Equation (11)-(14) can be derived by using standard upscaling methodologies, such as multiple-scale expansions or volumetric averaging41. Here, and are the effective diffusion coefficients and the effective rate coefficients, respectively. They are related to their counterparts on the macroscale, and through an ad hoc constitutive relationship:

where is defined as the microporosity, i.e. the fraction of void volume against total volume of . Further information including the verification of this ad hoc model is available in the literature42,43. The two components of the hybrid model are coupled by imposing the continuity of normal fluxes of the aqueous concentration along the gas-solid interface :

where the subscripts and indicates the site of the hybrid interface on which the relevant quantities are evaluated, and is the unit vector normal to pointing outside of the solid particles.

1. **Smoothed Particle Hydrodynamics to Solve the Macroscale Model**

As a mesh-free method, Smooth Particle Hydrodynamics (SPH) interpolation is built on a set of disordered points in a continuum without a grid or mesh. These points are commonly referred to as particles*.* Interpolation is based on the following concept applied on a scalar field:

where is a smoothing kernel with a support length and indicates a d-dimensional domain. The kernel is a smooth bell-shaped function with a compact support, i.e. such that and where is the Dirac delta function. Within SPH, any continuous scalar function is discretized by:

where is the position of particleandis the scalar value at that position, i.e. . Each particle is associated with a volume and the summation considers contributions from neighboring particles, i.e. those within the support length.

Implementation of the adsorption boundary condition from equations (7)-(9) for the advection-diffusion equation (6) can be challenging in domains with complex geometries. Instead, (7)-(9) is replaced with a homogenous Neumann boundary condition and a volumetric source term. Further derivation can be found in previous work42, the result is provided here only:

where the variables and defined on the surface have now been replaced with volumetric terms and inside . Within the SPH scheme, their relationships can be shown as:

Likewise, is the volumetric equivalent for the reaction rate constant . The homogeneous boundary condition (Eq.21) shows that only a small gas region and the solid region along the boundary will be affected by the adsorbing source term. Since the ‘smeared’ regions and still incorporate the general shape of the boundaries, the redefined system Eqs.(20)-(23) provides a good approximation to the original Eqs.(6)-(10). For further information on discretizing Eqs.(20)-(23) and the hybrid multiscale method (Eqs.3-5, Eqs.11-14), readers can refer to the literature 42–44.

**Part V. Calibration using Bayesian Optimization**

To calibrate the computational model, we look for values of the computational parameters *k* and *smax* (adsorption rate and capacity) that best match the output of the computational and physical experiments. Note that *k* and *smax* are material dependent. Therefore, there are three calibration problems to solve, one for each AC material.

For each material, there are three input variables: packing density, flow rate, and inlet concentration of toluene. For each of these variables, two experimental settings of Low(L) and High(H) are selected. The experimental results correspond to the output variable capacity for the following experiments: LHL, LLH, and HHH.

The quantity of interest to optimize for calibration is defined by a function , where is a function of the two parameters from the computational model . It is designed to represent the disparity between the experimental and computational outputs over the above three experiments, and is defined by

Therefore, calibration, corresponds to solving the following minimization problem:

Where set C is**:**

*

We applied the method of Bayesian Optimization to solve the above calibration problem. Bayesian Optimization is a sequential search algorithm in which, at iteration n, it provides us with the next sample point . It utilizes the history of the optimization process to make the search more systematic. It is well known that Bayesian Optimization is an effective method in cases where it is expensive to evaluate which is the case in the above calibration problem.

Bayesian optimization consists of two main components that are deployed in a sequential scheme. First, a probabilistic surrogate model is built to approximate the objective function. The surrogate provides a stochastic assessment of the value of the objective function at each design point. Then, using the surrogate, an acquisition function is defined in order to determine where to sample next. This is one iteration of the Bayesian Optimization algorithm. These steps will be repeated until the budget is finished or the optimum point does not change after some iterations. In particular, in Bayesian optimization we formulate a prior belief over the objective function, and then sequentially modify the model with the observed data via Bayesian posterior updating. To find more information about Bayesian Optimization see references45,46.

Gaussian process regression was used to develop the surrogate model. We considered two of the most common kernel functions to define the covariance matrix of the Gaussian Process (GP), Radial Basis Function (RBF) kernel, and Matern kernel.

The RBF kernel is defined as:

Parameter controls how much overall variability is in the function . is the variance of under the prior. Therefore, when is large, it means that based on the prior distribution, is likely to take a larger range of values. Parameter controls the smoothness of the GP model. When is large, the correlation between points does not last long, causing the model function to be wiggly. On the other hand, when is smaller the function will be smoother46.

For our problem we used Matern Kernel as another covariance function. This kernel is a generalization of the RBF kernel. It has an additional parameter for controlling the smoothness of the function. The Matern kernel is defined47:

where Γ is the gamma function, Kν  is the modified Bessel function  , and and are positive parameters of the covariance function.

Using the Matern kernel produced a better fit for the objective function of the calibration problem. Therefore, the values reported are based on the Matern kernel.

The Python function GaussianProcessRegressor in the sklearn48 package was used for fitting the Gaussian Process model. The function uses the default ***“fmin\_l\_bfgs\_b”*** optimizer for optimizing the kernel’s parameters.

The acquisition function shows us where to sample next using the surrogate model. We used the Expected Improvement (EI) acquisition function for our algorithm46. EI algorithm, as it was first proposed, considers only the noise free measurement cases. Since our simulations are noise free it is an appropriate choice for our problem. The expected improvement at the step n of the optimization process, is defined as:

Where

The EI has a closed form equation and can be computed in terms of normal cumulative distribution function (cdf) , and the normal probability density function (pdf) .46

Where and are mean and standard deviation of the predicted normal probability distribution in by the Gaussian process regression model.

We considered a mesh grid in out parameter space, found the value of EI at each point and picked the point that has the maximum value of EI as our next sample. Also, we double checked the maximum with L-BFGS-B method using Python48.

Based on the budget we had, we ran six iterations of the Bayesian optimization for each material and we report the minimum value observed as the optimum point. The results of six runs are shown in Table S3, Table S4 and Table S5. Note, the column in green is the optimum point observed (minimum error) and the column in red is the worst case for each material.

**Table S3.** Calibration results for PAC 200

|  |
| --- |
| PAC 200 |
| Run number | **1** | 2 | 3 | **4\*** | 5 | 6 |
|  | **﻿﻿5.00e-04** | 7.00e-04 | ﻿6.10e-04 | **﻿3.50e-04** | ﻿4.70e-04 | ﻿4.70e-04 |
|  | **﻿1.00 e+02** | ﻿8.00e+01 | ﻿1.20e+02 | **﻿1.20e+02** | ﻿8.00e+01 | ﻿1.20e+02 |
|  | **﻿2.46e-08** | ﻿2.08e-08 | ﻿9.54e-09 | **﻿3.62e-09** | ﻿4.70e-09 | ﻿6.00e-09 |
| Min With Bayesian optimization  | **2.46e-08** | 2.08e-08 | 9.54e-09 | **3.62e-09** | ﻿3.62e-09 | ﻿3.62e-09 |

**Table S4.** Calibration results for Darco G60

|  |
| --- |
| Darco G60 |
| Run number | **1** | 2 | **3\*** | 4 | 5 | 6 |
|  | **﻿﻿3.00e-04** | 5.00e-04 | **﻿﻿7.00e-04** | ﻿5.23e-04 | ﻿6.65e-04 | ﻿3.98e-04 |
|  | **﻿1.20e+02** | ﻿1.00e+02 | **﻿8.00e+01** | ﻿9.40e+01 | ﻿8.00e+01 | ﻿8.80e+01 |
|  | **﻿﻿1.16e-07** | ﻿﻿1.06e-07 | **﻿﻿﻿2.34e-08** | ﻿﻿1.00e-07 | ﻿9.17e-08 | ﻿﻿1.10e-07 |
| Min With Bayesian optimization | **﻿﻿1.16e-07** | 1.06e-07 | **2.34e-08** | 2.34e-08 | ﻿2.34e-08 | ﻿2.34e-08 |

**Table S5.** Calibration results for Darco KBG

|  |
| --- |
| Darco KBG |
| Run number | **1** | 2 | 3 | 4 | 5 | **6\*** |
|  | **﻿﻿3.00e-04** | ﻿﻿6.87e-04 | 7.00E-04 | ﻿3.75e-04 | ﻿6.48e-04 | **﻿6.48e-04** |
|  | **﻿1.20e+02** | ﻿1.02e+02 | 8.00e+01 | ﻿8.00e+01 | ﻿1.20e+02 | **﻿1.09e+02** |
|  | **﻿4.64e-08** | ﻿﻿﻿﻿4.07e-08 | 3.82E-08 | ﻿﻿﻿4.36e-08 | ﻿4.09e-08 | **﻿﻿﻿3.17e-08** |
| Min With Bayesian optimization | **﻿﻿4.64e-08** | ﻿﻿﻿﻿4.07e-08 | 3.82E-08 | 3.82e-08 | ﻿3.82e-08 | **﻿3.17e-08** |

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