

Multiscale Simulation Starting at the Molecular Level for Adsorption Process Development*

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Abstract This article presents a multiscale simulation approach starting at the molecular level for the adsorption process development. A grand canonical Monte Carlo method is used for the prediction of adsorption isotherms of methanol on an activated carbon at the molecular level. The adsorption isotherms obtained in the linear region (or adsorption constant) are exploited as a model parameter required for the adsorption process simulation. The adsorption process model described by a set of partial differential equations (PDEs) is solved by using the conservation element and solution element method, which produces a fast and an accurate numerical solution to PDEs. The simulation results obtained from the adsorption constant estimated at the molecular level are in good agreement with the experimental results of the pulse response. The systematical multiscale simulation approach addressed in this study may be useful to accelerate the adsorption process development by reducing the number of experiments.

Keywords activated carbon, methanol, adsorption isotherms, molecular simulation, grand canonical Monte Carlo (GCMC) method, process simulation and development

1 INTRODUCTION

Chromatographic separations including ion-exchange, affinity, size exclusion, and hydrophobic interaction are of fundamental importance in the adsorption process because the chromatographic processes have been widely used not only for the conventional compounds (e.g., petrochemicals and sugar) but also for pharmaceuticals (e.g., chiral compounds) and biomolecules (e.g., amino acids, peptides, and proteins). Traditionally, the adsorption process development has been based on heuristic knowledge and expertise [1], which is expensive and time-consuming.

The chemical and pharmaceutical industries face several significant challenges in the current state of the increase in globalization. Increased pressure to lengthen the protection accorded by patents has resulted in the need for rapid and effective process development. Model-based simulation and optimization of the process reduce costs and lead to processes with higher economic efficiency [2].

In this article, a multiscale simulation starting at the molecular level is addressed for methanol adsorption process development on an activated carbon, and its results are compared with the experimental results. The slit-shaped molecular structure of the activated carbon is constructed to fit physical properties measured (e.g., atom ratio, porosity, specific surface area, and density) and optimized, using the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field [3].

Grand canonical Monte Carlo (GCMC) simulation is a powerful method for studying the physical interaction of a molecule with a solid surface [4]. In GCMC simulation, the temperature, volume, and chemical potential, which could be directly related to pressure and temperature using the bulk gas equation of state, are specified, whereas the number of particles

and associated configurational energy are allowed to fluctuate. Hence, GCMC sampling is capable of yielding directly the amount adsorbed in arbitrary confined spaces as a function of pressure and temperature [5]. Using adsorption isotherms obtained from GCMC simulation, the performance of a methanol adsorption process is obtained from solving the process model described by partial differential equations for mass conservation.

2 EXPERIMENTAL

The experiments were carried out using gas chromatography with a 6.35 mm (1/4-inch) column packed by activated carbon particles (thermally treated at 900°C for 10 h) possessing the physical properties shown in Table 1. Here, the molecular simulation results are compared with the experimental results. About 7% error is observed in the specific surface areas between the predicted and experimental values.

Table 1 Physical properties measured by experiments and predicted by molecular simulation

Item	Porosity (ϵ_p)	Specific surface area (A)/m ² ·g ⁻¹	Density (ρ)/g·L ⁻¹
experimental value	0.39	1120	1280
simulation value	0.41	1040	1264.6
error/%	5.13	7.14	1.20

① The surface area obtained from Material Studio (Accelrys software Inc., USA, 2007) is 2.31×10^{-17} m², and the mass used in the simulation is 2.22×10^{-20} g.

Figure 1 shows the experimental apparatus (model name: Agilent-6850GC). The column temperature is kept constant in a range of 70–130°C, and initially, the helium gas flows at a rate of 30–90 ml·min⁻¹. At a

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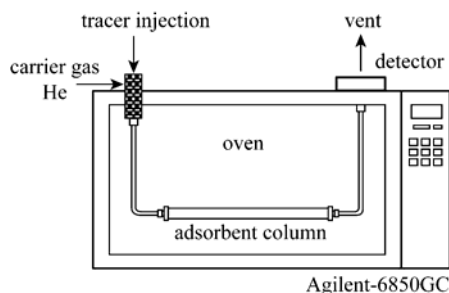


Figure 1 Experimental apparatus for methanol adsorption on activated carbon (Agilent-6850GC)

given temperature and flow rate, 1 μL methanol is injected for 0.24 s [6].

The elution concentration with time at the column exit (or chromatogram) is recorded in the UV absorbance for this pulse response. The chromatogram is used to obtain the values of the first and second moments, which are the performance indexes of the adsorption process, where the first moment is the mean residence time of methanol and the second moment is the dispersion of the peak of the chromatogram.

3 SIMULATIONS

The adsorption isotherms of methanol are calculated from GCMC simulation on the activated carbon structure optimized by the COMPASS force field. All molecular simulation is performed in Material Studio v4.1 (Accelrys software Inc., USA, 2007). The first and second moments of the elution curve are obtained from the process simulation using the adsorption isotherms estimated by GCMC simulation. The process simulation is performed in FAST-Chrom/SMB [7].

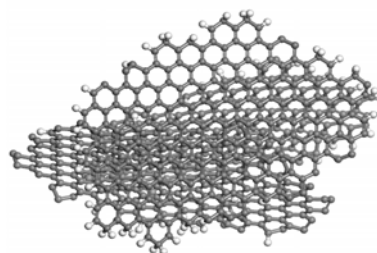
3.1 Force field (potential energy) model

The ability to represent accurately the potential energy of an ensemble of atoms is central to simulation of real materials [8]. Thus, the form of potentials (or force fields) most appropriate for a given material is carefully selected. The COMPASS force field that includes bonding (stretching, bending, torsional, and out-of-plane angle coordinate potentials) and non-bonding (electrostatic and van der Waals) interactions has been parameterized using a combined *ab initio* and empirical fitting procedure [9].

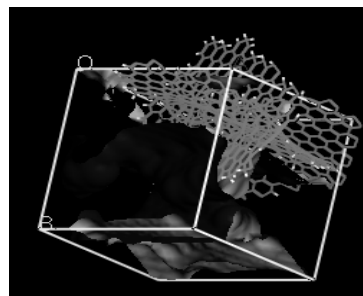
The force fields for bonding interaction use quadratic polynomials for bond stretching and angle bending. For torsions, a three-term Fourier expansion is used. The Coulombic term is used for electrostatic interactions. The Lennard-Jones potential for van der Waals interactions is represented by using an inverse 9th-power term for repulsive behavior instead of the more customary 12th-power term. The two nonbonding terms are used for interactions between pairs of atoms separated by three or more intervening atoms or those that belong to different molecules [3]. These force fields are derived at their core from *ab initio* quantum mechanical calculations (or density functional theory calculations), usually obtained at Hartree-Fock

level with large basis sets.

Using the COMPASS force field, the structure of the activated carbon used in this study is optimized, and the physical properties (see Table 1) are adjusted changing the structure. Fig. 2 shows the structure of a unit of the optimized activated carbon (molecular formula = $\text{C}_{662}\text{H}_{77}\text{O}_2$, which was confirmed by experiments). The whole system is constructed with periodic boundaries by surrounding the initial small system as shown in Fig. 2 (b).



(a) Atomic structure of the activated carbon



(b) Free volume and surface area

Figure 2 Visualization of the activated carbon structure using Material Studio Forsite (Accelrys, USA)

3.2 GCMC simulation

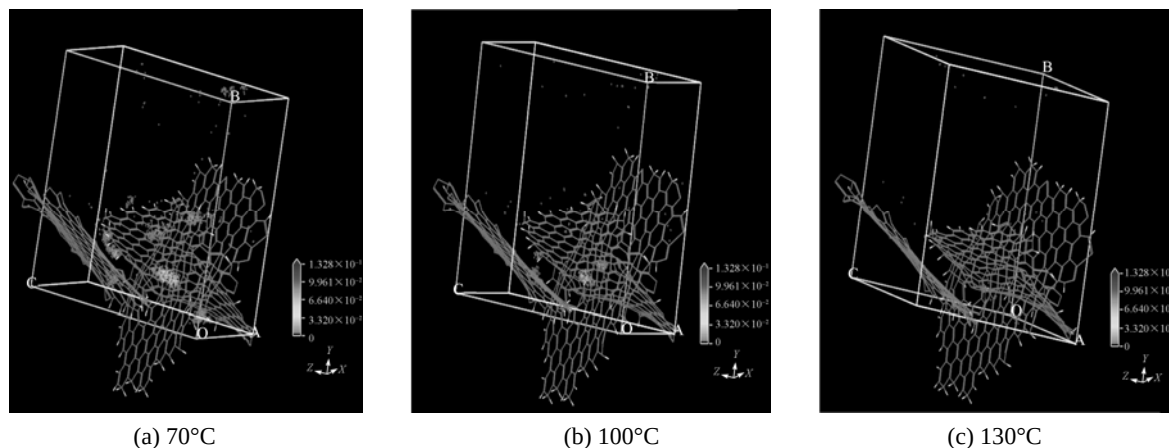
The Metropolis GCMC method is used to study the adsorption of methanol molecules on the activated carbon. In this method, only the position and orientations of the sorbate (methanol) molecules are sampled. Each conformation is treated as a rigid body. This is a method of choice for sorbate molecules, which are small in comparison with the size of the pore, and do not have a high degree of torsional flexibility. The method samples an ensemble by generating a chain of configurations with the ensemble density. Transforming a configuration is a two-stage process. First, a trial configuration is generated with probability α_{mn} . Then, either the proposed configuration, n , is accepted with a probability P_{mn} or the original configuration, m , is retained with a probability $(1 - P_{mn})$. In the traditional Metropolis method [10], trial configurations are generated without bias, $\alpha_{mn} = \alpha_{nm}$. The probability of a move being accepted is

$$P_{mn} = \min \left[1, e^{-\Delta E(r)/kT} \right] \quad (1)$$

where $\Delta E(r) = E(r_n) - E(r_m)$ is the change in configuration energy resulting from the move from the original position (r_m) to the transformed position (r_n). k is the Boltzmann constant. Five types of operation

Table 2 Input data for simulation of methanol adsorption chromatographic process

Column length (L_c)/cm	Inner diameter (ID)/cm	Bed voidage (ε_b)	Pore diameter (d_p)/cm	Flow rate (Q) /ml·min ⁻¹	Temperature (T) /°C	Pressure (p) /kPa
7	0.386	0.438	3.4×10^{-2}	50	100	101.325
$V_{\text{superficial}}$ /cm·min ⁻¹	$V_{\text{interstitial}}$ /cm·min ⁻¹	Feeding volume (V_{feed})/ml	Feeding time (t_{feed})/min	Inlet concentration (c_{in}) /mmol·ml ⁻¹	MeOH density /g·ml ⁻¹	Axial diffusivity (D_{ax})/cm ² ·min ⁻¹
417.3	846.4	1.0×10^{-3}	0.004	1.74×10^{-4}	1.04×10^{-3}	198.9

**Figure 3** Adsorption behavior of methanol on the activated carbon with respect to temperature

for generating grand canonical ensembles (conformation, rotation, translation, creation, and deletion) are used in Material Studio Sorption (Accelrys, USA). A step type is selected at random. The creation and deletion steps are attempted without bias to ensure their equal number.

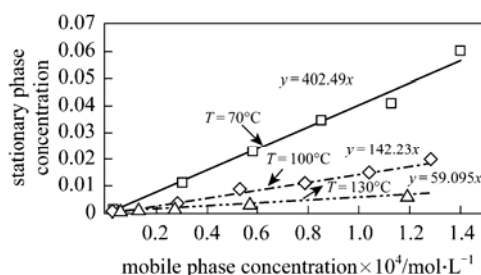
3.3 Process simulation

A packed-bed chromatographic adsorption model is described by convection-dominated parabolic partial differential equations (PDEs) for mass conservation in the mobile phase, ordinary differential equations for the sorbate adsorption in the stationary phase, and eventually algebraic equations for the adsorption isotherms between the two phases [7]. The PDEs are numerically solved by the CE/SE method within FAST-Chrom/SMB [7]. Table 2 shows input data for the process model simulation.

4 RESULTS AND DISCUSSION

The results of GCMC simulation are visualized at $T = 70, 100$, and 130°C in Fig. 3. It is observed that adsorption of methanol on the activated carbon decreases with temperature, whereas the dispersion of methanol in pores increases with temperature. As shown in Fig. 4, adsorption isotherms obtained from GCMC simulation are linear because the experiments are performed in a low range of the methanol concentration. In Fig. 4, the adsorption constants for each temperature are obtained from the mean slope of simulation points.

In Table 3, the adsorption constants (K : dimensionless) between experiment and simulation are

**Figure 4** Adsorption isotherms constant prediction by using GCMC simulation

compared at three different temperatures. As indicated in Table 3, the error between the two values is not negligible, and a further adjustment is needed in the activated carbon structure.

Table 3 Comparison of the adsorption isotherms constant between experiment and simulation

Temperature /°C	Experimental value ($K_{\text{exp}}^{\text{①}}$)	GCMC simulation value (K_{GCMC})	Error /%
70	526.74	402.49	25.6
100	163.04	142.23	12.8
130	63.71	59.10	7.2

① The original experimental value ($K_{\text{exp}}^{\text{original}}$) has the following equivalence to K_{GCMC} : $K_{\text{exp}}^{\text{original}} = (1 - \varepsilon_b) \rho_b K_{\text{GCMC}} / \varepsilon_b$. Therefore, K_{exp} shown in Table 3 is $K_{\text{exp}} = K_{\text{exp}}^{\text{original}} \varepsilon_b / [(1 - \varepsilon_b) \rho_b]$.

Using the input data in Table 2 and the adsorption constant from molecular simulation, the elution curve corresponding to the chromatogram of the experiments

is shown in Fig. 5. Its first and second moments are compared with those of the experimental results at $T = 100^\circ\text{C}$ and $Q = 50\text{ ml}\cdot\text{min}^{-1}$ as shown in Table 4.

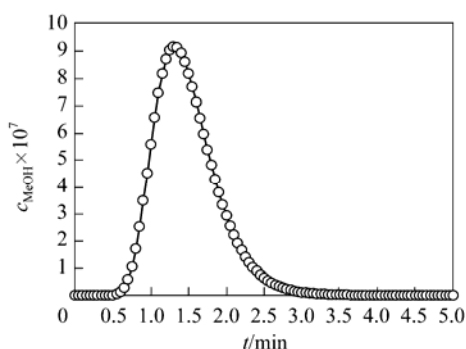


Figure 5 Elution curve at $T = 100^\circ\text{C}$ and $Q = 50\text{ ml}\cdot\text{min}^{-1}$ obtained from process simulation

Table 4 1st and 2nd moments of the elution curve at $T = 100^\circ\text{C}$ and $Q = 50\text{ ml}\cdot\text{min}^{-1}$

	Experiment/min	Simulation/min	Error/%
1st moment (mean residence time)	1.35	1.48	9.25
2nd moment (dispersion)	0.23	0.17	27.3

The difference of about 9% is shown in the first moments of the elution curve between experiment and simulation, alternatively about 13% error is shown at $T = 100^\circ\text{C}$ in Table 3 for the adsorption constants. It is observed that the discrepancy in the first moments results from both that of the adsorption constants and

Table 5 Comparison of 1st moments between experiment and simulation from methanol elution curves

Temperature/ $^\circ\text{C}$	Flow rate $\text{ml}\cdot\text{min}^{-1}$	1st moment of experiments	1st moment of simulations	Error/%
70	50	4.58	3.87	15.8
	90	2.44	2.15	12.0
100	50	1.35	1.48	9.3
	90	0.82	0.88	7.7
130	50	0.48	0.54	13.4
	90	0.28	0.30	9.1

fluid flow effects. Because the adsorption constant is predicted in the GCMC simulation without the fluid flow, it is logical that the first moment (*i.e.*, mean residence time) measured during the flow shows a different magnitude in those errors. In Table 5, the first moments between experiment and simulation are compared at $T = 70, 100$, and 130°C , and $Q = 50$ and $90\text{ ml}\cdot\text{min}^{-1}$. As seen in Table 5, the error is within 16%, indicating the potential of the multiscale simulation approach starting at the molecular level addressed in this study.

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