Screening of Carbonaceous Nanoporous Materials for Capture of Nerve Agents

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Supporting Information

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IS. Pore Size Distribution

To calculate pore size distributions of the carbons from the experimental nitrogen isotherms, we implemented the NLDFT method^{1,2}. Assuming silt-shaped pore model, the integral equation of isothermal adsorption for the case of pore size distribution can be written as the convolution¹⁻⁴,

$$Q(p) = \grave{0} dHq(p,H)f(H)$$
(1S)

where Q(p) is the total quantity of adsorbate per gram of adsorbent at the pressure p, q(p,H) is the kernel function, describing adsorption isotherm for and ideally homogenous material characterized by pore width H as quantity of adsorbate per square meter of pore surface, and f(H) is the desired pore surface area distribution function with respect to H. Eq. 1S has been extensively used for the calculation of the pore size distribution function from the experimental N₂ adsorption isotherm measured at 77 K¹⁻⁴. However, Eq. 1S should be complemented with an additional constrain,

$$f(H)^{3}0, \quad "H \tag{2S}$$

It is clear that negative values of f(H) are unphysical. One can use the regularization method with high value of regularization parameter to ensure the non-negativity of f(H). This treatment however overestimates the regularization parameter that implies the over-smoothing of f(H).

We rewrite Eqs. 1S-2S as follows,

$$Q(\mathbf{p}) = \mathop{a}_{i} q(\mathbf{p}, H_{i}) f(H_{i}) \text{ subject to } f(H_{i})^{3} 0$$
(3S)

where $Q(\mathbf{p})$ is an experimental adsorption isotherm interpolated onto a vector \mathbf{p} of pressure points, $q(\mathbf{p}, H_i)$ is a matrix of values for quantity adsorbed per square meter, each row calculated for a value of H at pressures \mathbf{p} , and $f(H_i)$ is the solution vector whose terms represent the area of surface in the sample characterized by each pore with H_i . Therefore the total surface area of studied carbonaceous material is simply given by,

$$S = \mathop{a}\limits_{i} f\left(H_{i}\right) \tag{4S}$$

In order to solve the ill-posed problem given by Eq. 3S we implemented the non-negative version of second-order Tikhonov regularization functional⁵⁻⁷, similarly to non-negative least square method of Ref. [1]. Following to Tikhonov the regularized solution of Eq. 3S corresponds to the weighted combination of the residual norm and the side constraint⁵⁻⁷,

$$\min_{\mathbf{f}} \left\{ \left\| \mathbf{q}\mathbf{f} - \mathbf{Q} \right\|_{2}^{2} + \partial^{2} \left\| \mathbf{L}\mathbf{f} \right\|_{2}^{2} \right\} \quad \text{subject to} \quad \mathbf{f}^{3} \mathbf{0}$$
(5S)

where $\|\mathbf{z}\|_2 = \sqrt{x_1^2 + x_2^2 + ... + x_n^2}$ denotes the Euclidean length of vector \mathbf{z} , \mathbf{q} is a matrix whose elements are theoretical local adsorption isotherms, \mathbf{Q} is a vector whose elements are global adsorption isotherm measured experimentally, ∂ denotes regularization parameter that controls the weight given to minimization of the side constraint relative to minimization of the residual norm, and **Lf** is a finite-difference approximation that is proportional to the second derivative of \mathbf{f} . We implemented Eq. 5S in Matlab. The regularization parameter was computed form L-curve method implemented by Hansen (see regularization tools)⁷. A regularization parameter is a parameter that is used to suppress undesired solutions (i.e. solutions of Eq. 5S that oscillate too much), by penalizing those with very high spectral frequencies that account for rich small-scale structure.

IIS. N₂ local adsorption-desorption isotherms

The N₂ adsorption-desorption isotherms in model slit-shaped carbon pores were calculated with the nonlocal density functional theory (NLDFT) method^{1,2} that is based on the mean field Tarazona's approximation^{8,9}. We treated N₂ molecules as spherical particles interacting via (12,6) Lennard-Jones potential (LJ). The local fluid density $\Gamma(\mathbf{r})$ of the adsorbate confined in a crystalline graphitic-like slit-shaped carbon pore at given chemical potential m_b and temperature T is determined by the minimization of the grand potential functional^{1,2,8,9},

$$\mathbb{W}\left[\Gamma\left(\mathbf{r}\right)\right] = F\left[\Gamma\left(\mathbf{r}\right)\right] + \int d\mathbf{r}\Gamma\left(\mathbf{r}\right)\left[V_{ext}\left(\mathbf{r}\right) - \mathcal{M}_{b}\right]$$
(6S)

where F is the intrinsic Helmholtz free energy functional, and V_{ext} is the external potential (see Eq. 4 in the main text). The Helmholtz free energy is expanded perturbatively about a reference system of hard spheres with diameter $d^{1,2,8,9}$,

$$F_{\check{e}}^{\acute{e}} \Gamma(\mathbf{r})_{\check{u}}^{\check{u}} = \check{0} d\mathbf{r} \Gamma(\mathbf{r})_{\hat{e}}^{\acute{e}} kT \left(\ln\left(\lfloor^{3} \Gamma(\mathbf{r})\right) - 1 \right) + f_{ex} \overset{\acute{e}}{\underline{e}} \overline{\Gamma}(\mathbf{r}); d_{\check{u}}^{\check{u}} \overset{\acute{u}}{\underline{u}} + \dots$$

$$\dots + \frac{1}{2} \check{0} \check{0} d\mathbf{r} d\mathbf{r}' \Gamma(\mathbf{r}) \Gamma(\mathbf{r}') \vdash_{att} \left(|\mathbf{r} - \mathbf{r}'| \right)$$

$$(7S)$$

where \mathbb{F}_{att} is the attractive part of the fluid-fluid potential, \bot is the de Broglie thermal wavelength for the adsorptive molecule, and the hard sphere excess free energy, f_{ex} , is calculated from the Carnahan-Starling equation of state¹⁰ using the smoothed density, $\overline{r}(\mathbf{r})$, proposed by Tarazona *et* al.^{8,9} The attractive part of the fluid-fluid potential is modeled by the Weeks-Chandler-Anderson formulation of the LJ potential¹¹. The bulk fluid of uniform density, r_b , is described by the following equation of state^{1,2,8,9},

$$\mathcal{M}_{b} = kT \ln\left(\mathbb{L}^{3} \mathcal{\Gamma}_{b}\right) + f_{ex}\left(\mathcal{\Gamma}_{b}\right) + \mathcal{\Gamma}_{b}f_{ex}^{'}\left(\mathcal{\Gamma}_{b}\right) + \dots$$

$$\dots + \mathcal{\Gamma}_{b} \grave{0} d\mathbf{r} \mathsf{F}_{att}\left(\left|\mathbf{r}\right|\right)$$
(8S)

$$P = P_h + \frac{1}{2} \Gamma_b^2 \, \hat{\mathbf{0}} \, d\mathbf{r} \mathsf{F}_{att} \left(\left| \mathbf{r} \right| \right) \tag{9S}$$

where P_h is the pressure of the hard sphere fluid. We used iterative numeric method developed by El-Merraoui and Tanaka¹² to solve the minimization condition for the grand potential functional. The choice of fluid-fluid and fluid-solid parameters is the most essential for the predictive capability of any molecular model. Neimark and coworkers¹³ showed that set of these parameters depends on the theoretical approach. Therefore, for both fluid-fluid and fluid-solid interactions we employed the effective parameters developed for NLDFT calculations¹³. Figure 1S depicts the N₂ filling pressure variation with the pore width computed from Eq. 6S. For comparison, we displayed the Lastoskie et al. results². Our calculations are in very good agreement with the previous study. Moreover, we were able to compute the N₂ filling pressure for smaller slit-shaped carbon pores. This seems to be very important for the analysis of the pore structure of carbonaceous materials containing significant fraction of ultramicropores, (i.e., pore width lower than 0.5 nm). Figure 2S presents the comparison between N2 adsorption isotherms at 77 K computed from NLDFT method and GCMC method. The set of fluid-fluid and solid-fluid parameters used in GCMC simulations were taken from Neimark et al.¹³ As in previous study¹³, NLDFT method reproduced the simulation results reasonably well.

IIIS. Metropolis-Ulam Monte Carlo integration

Before systematic study of nerve agent adsorption at infinite dilution and 298 K, we validated our Metropolis-Ulam Monte Carlo integration algorithm against known experimental data. Similarly to Lane and Spurling¹⁴, we studied the adsorption of Kr on graphite surface at infinite dilution. The solid-fluid potential parameters, i.e. $S_{sf} = 0.356$ nm, and $e_{sf} / k_B = 67.5$ K were taken from previous work¹⁴. Figure 7S

compares the experimental and theoretical values of Henry constants for Kr-graphite adsorption system. Both trapezoidal and Metropolis-Ulam Monte Carlo numerical integration method reproduced the experimental data very well, indicating negligible statistical noise in our Monte Carlo integration algorithm. Note that theoretical calculations can be easily extended to other temperatures that are difficult to access experimentally (see Figure 7S). For instance, the adsorption of Kr on graphite at higher temperatures is very small. Therefore it is very difficult to measure the adsorbed amount with a high precision. At low temperatures, the time to achieve equilibrium may be very long because the slow adsorption kinetics. Thus we concluded that computational extrapolation of adsorption results to different operating conditions complements the experimental measurements.

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Figure 1S. NLDFT dependence of N_2 filling pressure at 77 K on slit-shaped carbon pore width (open circles: current results, black circles: Lastoskie *et* al.²).



Figure 2S. The comparison between NLDFT and GCMC N_2 adsorption isotherms at 77 K computed for selected slit-shaped carbon pore widths: 4.46, 5.86, 8.34, and 10.9 nm.



Figure 3S. The L-curve plots used for selecting of optimal values of the regularization parameter for two studied carbonaceous films. Note that optimal value of the regularization parameter is an order of magnitude higher for C_{ox} than for C_{875} sample.



Figure 4S. Variation of the total surface area with the value of the regularization parameter computed for C_{ox} and C_{875} carbonaceous films. Total surfaces areas corresponding to the optimal values of regularization parameter are given by open squares. Note that either under-smoothing or over-smoothing of pore size distributions does not change the values of the total surface area significantly.



Figure 5S. The L-curve plots used for selecting of optimal values of the regularization parameter for two studied commercialized activated carbons. Note that optimal value of the regularization parameter is an order of magnitude higher for Norit than for D55/2 sample.



Figure 6S. Variation of the total surface area with the value of the regularization parameter computed for D55/2 and Norit commercialized activated carbons. Total surfaces areas corresponding to the optimal values of regularization parameter are given by open squares. Note that either under-smoothing or over-smoothing of pore size distributions does not change the values of the total surface area significantly.



Figure 7S. Theoretical reproduction of experimental Henry constants (open squares) measured for krypton adsorbed on graphite crystal. Trapezoidal (solid line) and Metropolis-Ulam Monte Carlo method (open circles) was used for solution of Eq. 3 (see main text).