

Supplementary Information:

Critical role of pore size on perfluorooctanoic acid adsorption behaviors in carbonaceous sorbents

Mark Robertson,¹ Bradley Lamb,¹ Anthony Griffin,¹ Lilin He,^{2,} Boran Ma,^{1,*} Zhe Qiang^{1,*}*

1. School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States
2. Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Corresponding Author

- * Lilin He – Email: hel3@ornl.gov
- * Boran Ma – Email: boran.ma@usm.edu
- * Zhe Qiang – Email: zhe.qiang@usm.edu

Small angle neutron scattering (SANS)

SANS is an experimental technique employed to assess characteristics of materials at length scales ranging from angstroms to micrometers. The intensity of scattered neutrons, along with their scattering angles, that result from interactions between a neutron beam and the atoms within a

sample enable the evaluation of the size, shape, and correlations between features within the material. The probability of the atoms within the sample to scatter incident radiation is known as the scattering length. The scattering length is determined by the interactions between a given atom and incident neutrons, and scattering length density (SLD) is the average of the scattering lengths of all the atoms within a given unit volume of a material. The intensity of coherently scattered neutrons is dependent on the SLD contrast between distinct regions of the sample. The material system investigated in this work can be illustrated as a material with populations of 3 distinct regions, each having a different SLD: carbon (SLD = $6.33 \times 10^{-6} \text{ \AA}^{-2}$), perfluorooctanoic acid (PFOA; SLD = $3.80 \times 10^{-6} \text{ \AA}^{-2}$), and the voids within the carbonaceous sorbent which is assumed to be filled with air (SLD ≈ 0). The relatively small amount of PFOA within the material system, and the much greater contrast between the voids of the sorbent and the carbon matrix would result in any scattering contributions from the PFOA molecules to be obscured by the much more intense contributions of scattering between the matrix and the voids. However, this can be prevented through a technique known as contrast matching. In contrast matching-SANS (CM-SANS), the voids are filled with a solvent that has a similar SLD to the matrix, such as deuterated water (D_2O ; SLD = $6.37 \times 10^{-6} \text{ \AA}^{-2}$). This effectively masks any SLD contrast between the matrix and the pores, making the contrast between any adsorbed PFOA and its surrounding environment the primary contributor to coherent scattering, and enabling the investigation of adsorbed PFOA aggregates.

The contrast-matched samples were exposed to incident neutrons at 3 different sample to detector distances to cover a q-range of $0.015 \text{ nm}^{-1} - 8.1 \text{ nm}^{-1}$. After exposure and the collection of 2-dimensional scattering patterns, a Python code developed in-house at Oak Ridge National Laboratory was employed to reduce the 2-dimensional scattering patterns into 1-dimensional patterns by azimuthally averaging the intensity for a given q-range, then combining the 1-

dimensional results for each sample to detector distance to provide a single master curve for each sample. The master curves were fit to the theoretical models described in the main text using SASview, an open source software developed for analyzing small angle scattering data. The SLD contrast ($\Delta\rho$ in eq 2) was derived from theoretical SLD values for PFOA and carbon and was held constant during the fitting procedure to minimize the number of varied parameters. The other parameters were varied within reasonable boundaries to attain a minimum in the fitting error. The appropriate fitting parameters for the AC sorbents and OMC sorbents are found in Table S1 and Table S2, respectively.

Table S1. Fitting parameters employed during model fitting of SANS results for AC sorbents.

	1 mg/L	12 mg/L	30 mg/L	100 mg/L
A	24.81	5.7063	7.03	9.99
$\Delta\rho$ (10^{-6} \AA^{-2})	2.4	2.4	2.4	2.4
R (nm)	0.15	0.26	0.32	0.42
L (nm)	1.90	1.25	2.07	2.46
B	1e-05	5e-05	1e-05	5e-05
n	3.79	3.5	3.02	3.67
C	5.5	6.8	9.7	11.8

Table S2. Fitting parameters employed during model fitting of SANS results for OMC sorbents.

	1 mg/L	12 mg/L	30 mg/L	100 mg/L

A	24.81	5.7063	7.03	9.99
$\Delta\rho$ (10^{-6} \AA^{-2})	2.4	2.4	2.4	2.4
R (nm)	0.49	1.03	1.99	2.86
L (nm)	29.1	44.0	41.2	46.0
G1 scale	0	0.007	0.005	0.006
G1 position	0	0.033	0.037	0.033
G1 breadth	0	0.009	0.009	0.010
G2 scale	0.37	0.01	0.02	3.8
G2 position	0.071	0.62	0.61	0.61
G2 breadth	0.008	0.010	0.008	0.045
G3 scale	0	1e-09	0.007	0.96
G3 position	0	0.106	0.087	0.076
G3 breadth	0	0.011	0.012	0.008
C	0.12	0.20	0.35	5.14

Biased approach to simulate adsorption dynamics through atomistic MD simulations

The initial water configuration was an energetically unfavorable, highly ordered lattice structure generated using Moltemplate and placed in an expanded simulation cell.¹ To randomize the structure and reduce system energy, purely repulsive Lennard-Jones parameters were applied at 350 K for 2.5 ns. After this randomization step, the cell was resized to its final dimensions, achieving a solution density of 1 g/cm³, and the system was further equilibrated for 2.5 ns. Next, the graphene sheet was inserted beneath the water layer, followed by an additional 2.5 ns of

equilibration. The temperature was gradually reduced from 350 K to 300 K over 5 ns. Once the system stabilized at 300 K, the Lennard-Jones interaction cutoff was extended to 9 Å to include attractive forces, and electrostatic interactions were introduced. After another 2.5 ns of equilibration with these updated interaction parameters, PFOA molecules were added one by one at 1 ns intervals.

The out-of-plane velocity of each PFOA molecule was constrained to move in the negative direction until it was positioned 23.5 Å above the graphene surface, simulating PFOA's approach to the surface and improving computational efficiency. Upon reaching 10 vol%, the velocity constraint in the z-direction was gradually moved in the positive z-direction until reaching a height of 43.5 Å above the graphene, to avoid any artificial compression of the adsorbed layer. After 114 ns, once all PFOA had been added, the velocity constraints were removed, and the system was equilibrated for an additional 10 ns.

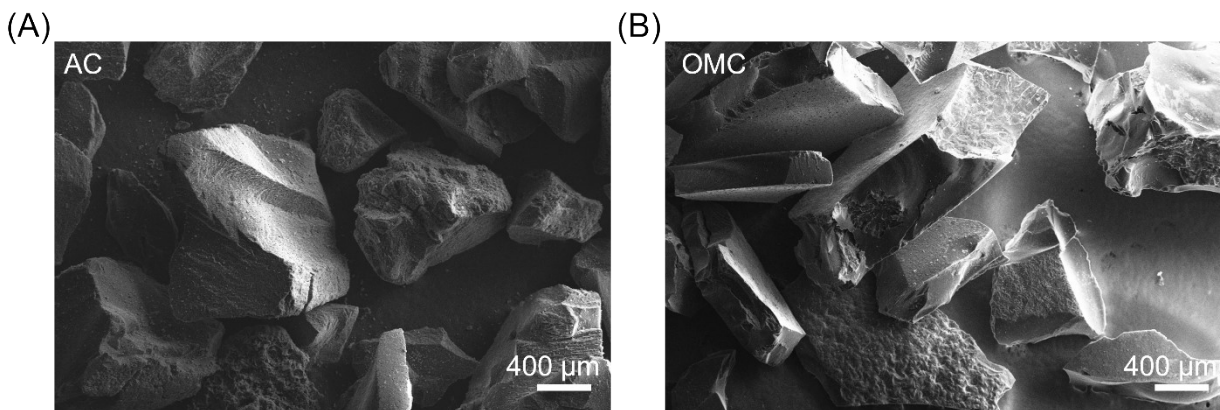


Figure S1. SEM images of (A) AC and (B) OMC sorbent particles

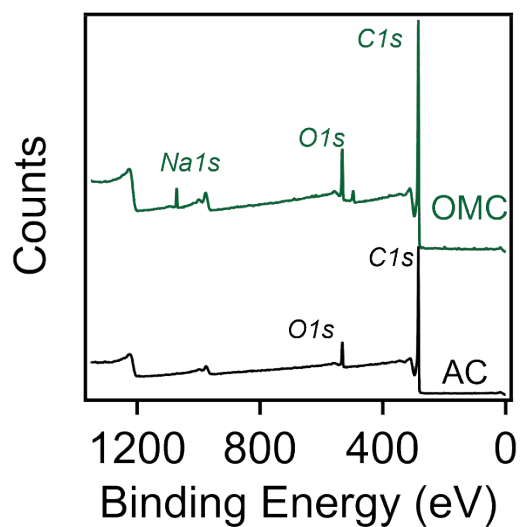


Figure S2. X-ray photoelectron spectroscopy (XPS) survey scans of the AC and OMC sorbents prior to loading with PFOA molecules.

Table S3. Atomic composition of AC and OMC determined through XPS survey scans.

	AC	OMC
<i>C1s</i>	90.6 at%	89.7 at%
<i>O1s</i>	8.0 at%	7.8 at%
<i>Na1s</i>	0.0 at%	1.0 at%
Trace Impurities	1.4 at%	1.5 at%

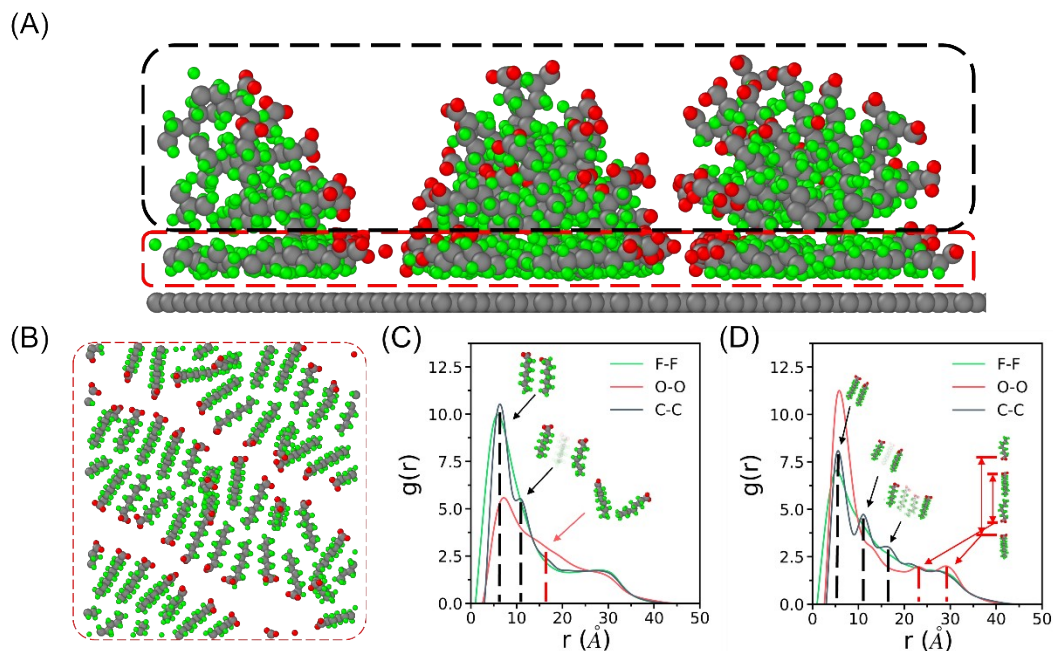


Figure S3. (A) Snapshot of adsorbed aggregates at 20 vol% after equilibration. (B) Image of the PFOA molecules adsorbed directly to the carbon surface which are highlighted by the red dashed box in Figure S3(A). (C) Pair correlation function for the molecules adsorbed to the upper portion of the PFOA aggregate which are highlighted by the black dashed box in Figure S3(A). (D) Pair correlation function for the molecules adsorbed directly to the carbon surface which are illustrated by the image in Figure S3(B).

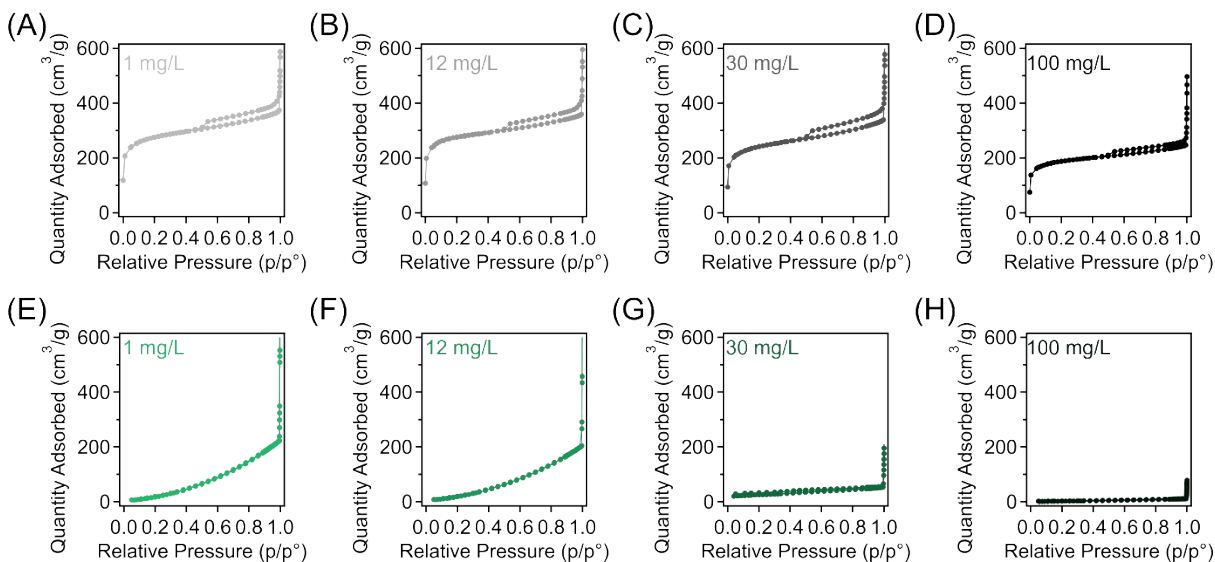


Figure S4. Nitrogen physisorption isotherms for AC sorbents after adsorption from PFOA solutions with concentrations of (A) 1 mg/L, (B) 12 mg/L, (C) 30 mg/L, and (D) 100 mg/L. Nitrogen physisorption isotherms for OMC sorbents after adsorption from PFOA solutions with concentrations of (E) 1 mg/L, (F) 12 mg/L, (G) 30 mg/L, and (H) 100 mg/L.

References

- (1) Jewett, A. I.; Stelter, D.; Lambert, J.; Saladi, S. M.; Roscioni, O. M.; Ricci, M.; Autin, L.; Maritan, M.; Bashusqeh, S. M.; Keyes, T.; Dame, R. T.; Shea, J. E.; Jensen, G. J.; Goodsell, D. S. Moltemplate: A Tool for Coarse-Grained Modeling of Complex Biological Matter and Soft Condensed Matter Physics. *J Mol Biol* 2021, 433, 166841. <https://doi.org/10.1016/J.JMB.2021.166841>.