Hands-On

Adsorption Using AiiDAlab

Carbon dioxide (CO_2), considered the main greenhouse gas, has a major impact on climate change. Its atmospheric concentration is already above 400 ppm and is predicted to hit alarming levels in 2050 if the current situation is not addressed properly. The power generation sector contributes most to the problem due the fact that power plants running on fossil fuel and coal are by far the major source of CO_2 [1]. With this aggravated situation, the world is moving towards renewable and clean energy. Biogas is a promising alternative to fossil fuel and coal [2]. Biodegradable organic matter is fermented anaerobically in the presence of bacteria to produce methane (~ 60%), CO_2 (~ 40%) and traces of impurities. Separating the CO_2 from the mixture produces biomethane (~ 98% purity), one of the cleanest and most efficient energy sources. One of the challenges is to find a suitable process, that is not energy-intensive, to separate CO_2 from CH_4. Another challenge is to store methane to be used later.

To address the aforementioned challenges, physical adsorption using Metal-Organic Frameworks (MOFs) will be investigated. IRMOF-1 was one of the first MOFs to be studied for CO_2/CH_4 separation and CH_4 storage [3]. It would be interesting to compute the adsorption properties of this material by performing molecular simulations using the AiiDAlab platform (https://www.materialscloud.org/work/aiidalab) and also compare the results with the ones reported in the article. The aim of this exercise is to familiarize yourselves with the different types of calculations needed for adsorption studies. With that being said, please proceed with the following:

1. Describe the type of calculations AiiDAlab offers for adsorption studies (4 each)
2. Compute the density ($g.cm^{-3}$), accessible surface area - ASA (A^2), accessible probe-occupiable volume - POAV (A^3) and porosity of the material (probe radius = 1.525 Å) (3 each)
3. Compute the henry coefficients for CO_2 and CH_4 at 300 K (4 each). What can you deduce ? (4)
4. Compute CO_2 and CH_4 pure isotherms at 300 K and plot the results (10 each)

In reality, CO_2 and CH_4 are adsorbed simultaneously in the mixture. One of the popular methods to predict mixture isotherms is the use of Ideal Adsorption Solution Theory (IAST) [4]. For more details refer to the original paper (https://doi.org/10.1002/aic.690110125).

5. Use pyIAST (https://pyiast.readthedocs.io/en/latest/) to obtain the binary-mixture isotherms by the linear interpolation method for a pressure range from 0.1 to 4.0. Use increments of 0.2 and plot the results (6 each)
6. Calculate the selectivity of CO_2 over CH_4 at 0.1, 1, 2 and 3 bars and 300 K (2 each). What can you deduce ? (2)
7. Prove that if y_{CO2} drops to 0.2, the selectivity doesn't change (8). What should we do to test if the selectivity is a function of temperature ? (4)
8. Explain if IRMOF-1 is a good or bad candidate for CH_4 storage (10)

Hints

1. AiiDAlab offers three different types of calculations for adsorption studies.

2. In order to obtain the full list of physical properties, use the pore analysis feature.

3. Use the following simulation parameters:
   - Zeo++ volpo samples: 10,000
   - Number of samples for block calculation: 100
   - Number of Widom cycles: 50,000
   - Number of GCMC initialization cycles: 500
   - Number of GCMC production cycles: 5,000
   - Maximum distance between pressure points: 0.6
   - Pressure range: 0.2 to 10.2 bars

4. In order to use the pyIAST package, please read the full documentation carefully, especially the section "InterpolatorIsotherm"

5. Selectivity is given by the following formula:

$$S_{CO_2/CH_4} = \frac{q_{CO_2}}{q_{CH_4}} \frac{y_{CH_4}}{y_{CO_2}}$$

   Where q is the binary loading, obtained from IAST calculations, at the adsorption conditions in mmol.g^{-1}, and y is the molar fraction of the component in the flue gas.

Use the provided data while waiting for the isotherms to finish. Make sure to replace the data with the one you get before submitting the report!

References

[1] P. Mathieu, *The IPCC special report on carbon dioxide capture and storage*. 2006.

[2] S. C. Bhatia and S. C. Bhatia, "Biogas," *Adv. Renew. Energy Syst.*, pp. 426–472, Jan. 2014.

[3] R. Babarao, Z. Hu, J. Jiang, S. Chempath, and S. I. Sandler, "Storage and separation of CO2 and CH4 in silicalite, C168 schwarzite, and IRMOF-1: A comparative study from Monte Carlo simulation," *Langmuir*, vol. 23, no. 2, pp. 659–666, 2007.

[4] J. C. Crittenden, S. W. Loper, M. Ari, P. Luft, D. W. Hand, and J. L. Oravltz, "Prediction of Multicomponent Adsorption Equilibria Using Ideal Adsorbed Solution Theory," *Environ. Sci. Technol.*, vol. 19, no. 11, pp. 1037–1043, 1985.