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How Experimental Reproducibility Affects Our Effort to Combat Climate Change

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ABSTRACT

I present the comparison of CO_2 adsorption data on ZIF-8 to show the differences in the data measured by different researchers. I used an isotherm model to fit the collected adsorption data using a simple Least Squares method using Microsoft Excel solver function. The model describes the adsorption data very well and the collected data show quite a large spread with outliers. The heat of adsorption calculated from the adsorption data also shows a very large spread. This level of spread in experimental data can lead to incorrect calculations when these data are used in large scale applications, such as gas separations or gas capture where adsorption is widely studied for uses. Through this work, I highlight the importance of producing reproducible experimental measurements that compare well with the data measured by other researchers.

Introduction

Dried seaweed is one of my favorite things to nibble on. For those who are not familiar with what dried seaweed is, it comes cut in crispy layers, often seasoned or salted, enjoyed as a snack or a side dish in Korea. They are usually packed in rectangular plastic containers with a small packet inside that asks not to consume. I have wondered what these small packets contained inside, and it turns out that they contain small transparent beads called silica gel that keep the packaging environment dry by removing moisture through a phenomenon called adsorption.

Adsorption is a physical phenomenon in which gas or liquid molecules, called adsorbates, stick to the surface of a solid, called an adsorbent (Thommes et al., 2014). Not surprisingly, the amount adsorbed will be large if an adsorbent has a large surface area. Surface areas are increased when materials have holes, or pores, in them; therefore, porous materials are known to adsorb a lot of adsorbate molecules. For example, the silica gel beads in the seaweed packages are a form of silicon dioxide with nanoscale pores, which can be described as a glass sponge with many tiny pores. These pores allow just a gram of silica gel to have roughly the same surface area as three tennis courts (Britannica, 2013). What is interesting is that different adsorbates have different affinities towards an adsorbent surface. This is the reason I find silica gel packets in the seaweed packages because water molecules like to stick, or adsorb, on a silica gel surface, keeping the seaweed snacks crispy by drying the environment.

As one can imagine, adsorption can have uses in many other applications. One exciting application is reducing the amount of carbon dioxide, CO_2, in the atmosphere to combat climate change. Carbon-based fuels account for 79 % of energy generated in the United States in 2020 (U.S. Energy Information Administration, 2021). However, the CO_2 emitted from using these carbon-based sources is a leading cause of climate change (Geiger, 2015). One industrial process that consumes about half of industrial energy in the United States is separation (Sholl & Lively, 2016), which produces things we use daily such as plastics separated from crude oil. Making these separation processes more energy efficient with a lower carbon footprint would greatly contribute to the global effort to curb climate change. One potential method of doing so is through adsorption as it can be used to separate and purify industrial gas mixtures or remove pollutants from industrial waste (Sholl & Lively, 2016) the same way that the silica gel beads separated water. Compared to conventional separation processes that typically use fossil fuel, adsorption-based separation significantly

reduces energy costs and carbon footprint. In addition, porous materials are being studied to directly capture CO_2 from power plants (Stauffer, 2020).

When researchers study how porous materials adsorb a certain adsorbate, they look at experimentally measured adsorption data. These adsorption data are usually reported in millimoles of adsorbate per a gram of adsorbent. This amount increases with pressure. Therefore, adsorption is usually reported graphically with pressure as the independent variable (x-axis) and adsorbed amount as the dependent variable (y-axis). These graphs are called adsorption isotherms (Thommes et al., 2014). Recently, researchers have pointed out that isotherms measured on the same porous material by different people often do not agree with each other (Nguyen et al., 2018). This poses an issue because reliable experimental data are required to understand the adsorption characteristics as discussed earlier.

In this paper, I collected adsorption data of CO_2 on a porous material named ZIF-8 from previously published experimental data. I show the spread of the adsorption isotherms and how this spread carries over to adsorption properties that can be calculated from adsorption isotherms. In this case, I chose the heat of adsorption. The adsorption isotherms were also described using a model to make comparison between different adsorption isotherms easier.

Methodology

Collection of Experimental Data

One does not have to compile adsorption data by going through papers that published them anymore. Today, adsorption data of numerous adsorbent-adsorbate systems are available on the Database of Novel and Emerging Adsorbent Materials compiled by the National Institute of Standards and Technology (NIST). The database can be navigated using search keywords for adsorbent, adsorbate, data properties, etc. I used the keywords “Experiment”, “ZIF-8”, and “CO2”. The database also contains simulated adsorption data, but I narrowed the search to only experimental data. However, adsorption data reported in simulation units, such as molecules per cage, still appeared during the search; therefore, these datasets were excluded to only include experimental data. ZIF-8 is a porous material with well-known steps of synthesis. It is widely studied for gas separations and CO_2 capture applications (Banerjee et al., 2008). Therefore, multiple CO_2 datasets were available on the NIST database, which is the reason for choosing ZIF-8 and CO_2 as the adsorbent-adsorbate system in this study. The pressure range was also restricted to a range from vacuum to 1.5 bar to make apt comparisons between datasets. Using this search procedure, I identified six publications that reported seven adsorption data of CO_2 on ZIF-8 between 295-300 K. The units of adsorption were mmol/g, mg/g, and cm^3 STP/g. The units were unified into mmol/g by dividing mg by the molar mass of CO_2 and cm^3 STP by 22.4 L following Avogadro's Law.

Comparison of Experimental Data

Comparison of adsorbed data reported by different researchers is difficult because the adsorption data are not taken at the exact same pressure values. Therefore, I used an isotherm model that fits the experimental adsorption isotherms described in the following (Nguyen et al., 2018):

$$n = \frac{d}{(1 + \exp\left[(-\ln(P) + a)/b\right])^c}$$

where n is the adsorbed amount, P is the pressure, and a, b, c, and d are the fitting parameters of the model. Using this model, adsorbed amounts at specified pressure values can be calculated to make comparison between adsorption datasets. I used the Least Squares method to fit the minimize the difference between the experimental data and the

data calculated by the isotherm model by changing the fitting parameters. The difference between the experimental data and the model data was calculated from the following:

$$d = \left(n_{exp} - n_{mod}\right)^2$$

$$S = \sum_{i=1}^{k} d_i$$

where d is the squared difference and S is the sum of the differences for k number of data points in a single dataset. The value of S was minimized using *solver* function in Microsoft Excel.

Heat of Adsorption

The heat of adsorption is a measure of the amount of energy released in adsorption processes (Thommes et al., 2014). Adsorption is an exothermic process, which means that energy is released when molecules are adsorbed onto a solid surface. Therefore, the same amount of energy is required to remove the adsorbed molecules during an industrial process such as gas separation. In this regard, estimating the heat of adsorption is an important practice in characterizing adsorption systems. The virial equation can be used to estimate the heat of adsorption (Czepirski & Jagiello, 1989):

$$P = n \cdot \exp\left(\frac{1}{T}\sum_{i=0}^{n1} a_i n^i + \sum_{i=0}^{n2} b_i n^i\right)$$

where a_i and b_i are virial coefficients that are used as fitting parameters and $n1$ and $n2$ are the number of these parameters. For this study, I chose $n1 = 2$ and $n2 = 1$ to obtain a good fit between the experimental data and the model. In this model, because pressure is isolated into one side, the difference between the experimental values of pressure and the values of pressure calculated by the virial equation was minimized. I used the same Least Squares method described earlier to minimize the difference. The heat of adsorption can be calculated from the following equation (Czepirski & Jagiello, 1989):

$$q = -R \cdot a_0$$

where q is the heat of adsorption, R is the gas constant, and a_0 is one of the virial coefficients. The value of R used in this study is 8.314 J/mol·K.

Results

Figure 1a shows the collected datasets used in this study. As can be seen, the collected datasets show a wide range and do not form a uniform line of datasets. Especially, the dataset published by Venna et al. (2010) and Sun et al. (2014) shown by squares and left triangles in Figure 1a, respectively, differ from the other datasets. To quantify the differences, I fitted each experimental dataset with the isotherm model described in the section titled Comparison of Experimental Data. The fitted isotherms agreed very well with the experimental isotherms as shown in Figure 1b. The goodness-of-fit is also shown by the normalized sum differences, S/k, summarized in Table 1.

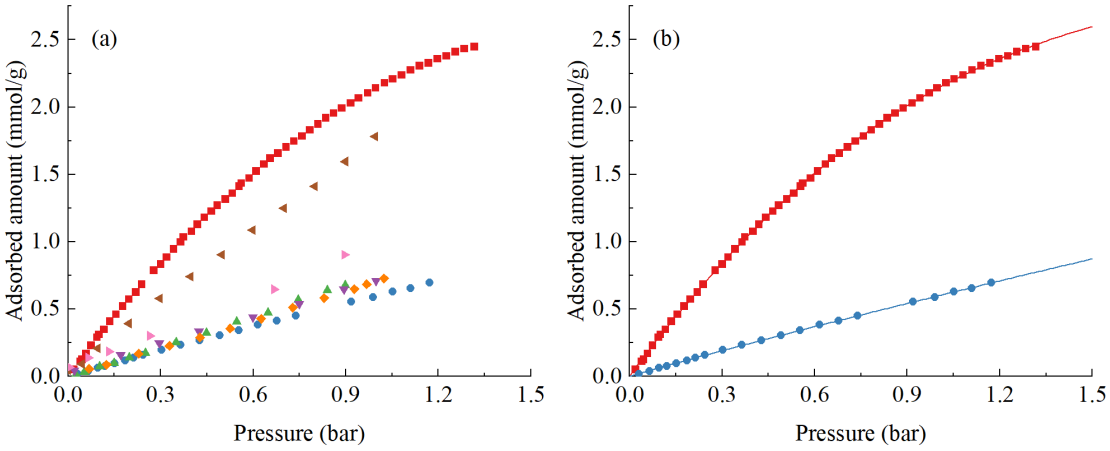

Figure 1. (a) Collection of CO_2 adsorption datasets on ZIF-8 from the following references: squares – Venna et al. (2010), left triangles – Sun et al. (2014), right triangles – Sun et al. (2014), up triangles – Huang et al. (2011), down triangles – Chen et al. (2011), diamonds – Ito et al. (2013), circles – Xu et al. (2011). (b) Examples of fitting experimental adsorption isotherms using the isotherm model, which show good agreement between the experimental data and isotherm model.

Table 1. Normalized sum differences between the experimental data and isotherm model for all datasets

Dataset	Publication	S/k
1	Venna et al. (2010)	4.33×10^{-5}
2	Xu et al. (2011)	1.07×10^{-5}
3	Huang et al. (2011)	2.52×10^{-5}
4	Chen et al. (2011)	9.19×10^{-5}
5	Ito et al. (2013)	4.46×10^{-5}
6	Sun et al. (2014)	1.39×10^{-4}
7	Sun et al. (2014)	1.27×10^{-3}

The difference in the adsorption amounts at 1 bar is approximately 1.5 mmol/g, which is larger than the adsorption amounts at 1 bar for most of the datasets collected here. Such difference can result in a large overestimation or underestimation of the amount of adsorbent needed. For example, if 2,000 million metric tons of CO_2 had to be captured using ZIF-8 by adsorption alone, which is the approximate yearly amount of CO_2 emitted by power plants in the United States (U.S. Environmental Protection Agency, 2019), the amount of ZIF-8 needed would differ 49 trillion kilograms. This difference can lead one to incorrectly estimate many things, such as the required storage space, cost, etc. Figure 2 shows the spread of the collected datasets. The graphs in Figure 2 are like the box-and-whisker plot, but I applied it to the entire pressure range. The minimum, lower bound of the interquartile range, median lines are close in range, showing that most datasets are populated on the lower range. This might suggest that the datasets that report large amounts of adsorption are outliers. However, even after I remove the two datasets (squares and left triangles), the difference at 1 bar is approximately 0.4 mmol/g, which is still quite large.

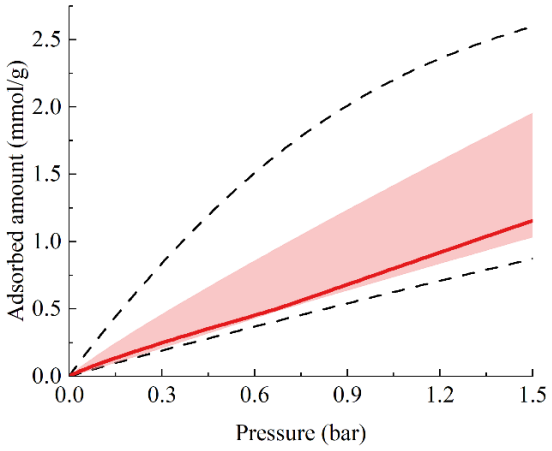

Figure 2. Distribution of the collected datasets obtained from the fitted isotherm model. The dotted lines show maximum and minimum datasets, and the red line shows the median data. The red shade shows the interquartile range.

Because the heat of adsorption is a property of adsorption systems that is estimated directly from the adsorption isotherms, they would also differ greatly in this case. As mentioned earlier, the experimental datasets were fitted using the virial equation, and again the normalized sum differences are presented in Table 2. I show examples of fitting graphically in Figure 3, which generally shows good fits. I calculated the heat of adsorption from a_0 virial coefficients, which are summarized in Table 2. The heat of adsorption of CO_2 on ZIF-8 calculated from the dataset I collected ranged from 0.87 kJ/mol to 4.25 kJ/mol. This reflects the difference in the adsorption data I showed earlier. Figure 3 shows the spread of the heats of adsorption in a scattered format and a box-and-whisker format. These graphs also show the same trend as Figure 2, heats of adsorption are populated in the lower range with two outliers. Because the heat of adsorption here is directly related to the amount of energy needed to remove CO_2 after adsorption (for example, after capturing CO_2), choosing an experimental data that reports large adsorption would lead to overestimation of energy needed. More energy means more money.

Table 2. Normalized sum differences between experimental data and virial equation for all datasets

Dataset	Publication	S/k
1	Venna et al. (2010)	5.22×10^{-5}
2	Xu et al. (2011)	2.20×10^{-5}
3	Huang et al. (2011)	5.09×10^{-5}
4	Chen et al. (2011)	3.29×10^{-4}
5	Ito et al. (2013)	7.42×10^{-5}
6	Sun et al. (2014)	4.59×10^{-5}
7	Sun et al. (2014)	3.88×10^{-4}

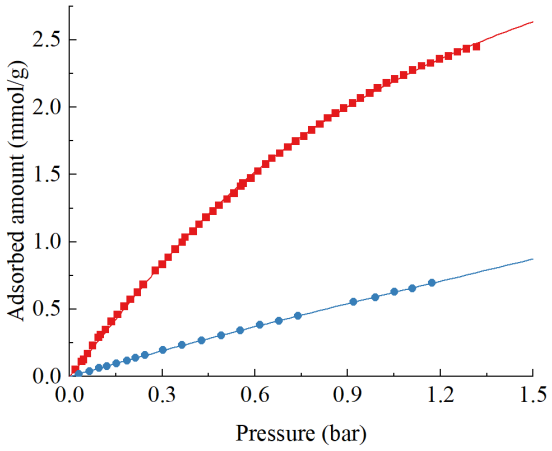

Figure 3. Examples of virial equation describing the experimental data. The symbols show experimental data shown in Figure 1 and the lines show model fits.

Table 3. Summary of a_0 virial coefficients for all datasets

Dataset	Publication	a_0
1	Venna et al. (2010)	-511.31
2	Xu et al. (2011)	-104.58
3	Huang et al. (2011)	-118.24
4	Chen et al. (2011)	-115.56
5	Ito et al. (2013)	-108.18
6	Sun et al. (2014)	-191.26
7	Sun et al. (2014)	-127.09

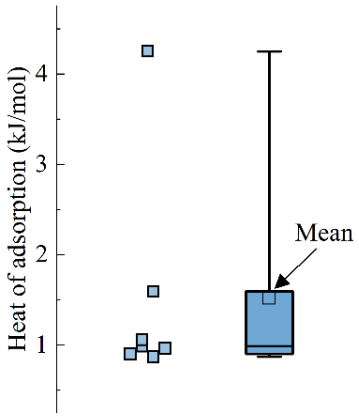

Figure 4. Scattered data points of heat of adsorption (left) and the same dataset shown in box-and-whisker plot that shows the median, mean, minimum, maximum, and interquartile range (right).

Conclusions

I collected seven adsorption data measured by six different researchers from the database created by the NIST. Then I used an isotherm model to fit the experimental data for easy comparison. I used the model fits to show the spread of these adsorption data graphically by showing the minimum, maximum, median, and interquartile range. In this comparison, the difference between the adsorption amounts at 1 bar is as large as 1.5 mmol/g. This large difference can result in a great overestimation or underestimation of the material needed for adsorption. I also calculated the amount of energy released when adsorption happens, known as the heat of adsorption, which also showed a large spread in data because it is calculated from the adsorption data directly.

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