Water Adsorption on Various Metal Organic Framework

H W B Teo\(^1\) and A Chakraborty\(^1\)

\(^1\)School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

**Abstract.** In this paper, Metal Organic Framework (MOF) undergoes \(N_2\) and water adsorption experiment to observe how the material properties affects the water sorption performance. The achieved \(N_2\) isotherms is used to estimate the BET surface area, pore volume and, most importantly, the pore size distribution of the adsorbent material. It is noted that Aluminium Fumarate and CAU-10 has pore distribution of about 6Å while MIL-101(Cr) has 16 Å. The water adsorption isotherms at 25°C shows MIL-101(Cr) has a long hydrophobic length from relative pressure of \(0 < P/P_s < 0.4\) with a maximum water uptake of 1kg/kg sorbent. Alkali metal ions doped MIL-101(Cr) reduced the hydrophobic length and maximum water uptake of original MIL-101(Cr). Aluminium Fumarate and CAU-10 has lower water uptake, but the hydrophobic length of both materials is within relative pressure of \(P/P_s < 0.2\). The kinetic behaviour of doped MIL-101(Cr), Aluminium Fumarate and CAU-10 are faster than MIL-101(Cr).

1. **Introduction**

The specialty of adsorption cooling system has caught many attentions in recent years. To provide necessary cooling, solar heat or waste heat is required to supply to the system. This cooling application can reduce the harmful effects relating to global warming and ozone depletion. To operate, the system requires an adsorbate and an adsorbent for the adsorption-desorption process. Water is usually preferred to be the adsorbate as it is non-toxic, easily available and has a high evaporation of enthalpy \([1]\). The adsorbent material is usually a high porosity and high heterogeneous material. In present, the existing adsorbents that are used for adsorption system are silica gels and zeolites \([2-5]\). These adsorbent materials assisted in thermal compression in the adsorption bed of the cooling application, thus, replacing the compressor unit of the conventional vapour compression system. However, to adopt the existing adsorbents for cooling application, large amount of space is required to install such system for cooling application purpose. The reason for the bulky size is mainly due to low uptake difference of the current adsorbent materials between adsorption and desorption process \([5]\). Thus, low working capacity is available over the cooling cycle from a small part of the total adsorption capacity of the adsorbent. Hence, large amount of adsorbent is required to be installed in the bed for sorption purposes.

Currently, a new class of microporous material namely Metal Organic Frameworks (MOFs) has been drawing many attentions due to their designable and high micro-porosity. These materials are made by the self-assembly of organic ligands and metal-containing nodes. Many researches have been ongoing for MOF + water system \([6-9]\) with high potential of replacing the conventional material due to higher water uptake – offtake difference based on its ‘S’-shaped isotherm. These material properties are able to reduce the size of the adsorption chiller, it may improve the performance of the cooling application. Thus, these materials show great potential in replacing the existing adsorbents for adsorption cooling system.
To understand the behaviour of MOF + water system, this paper targets potential MOFs to undergo surface characterisation and water adsorption experiment. The purpose of these experiments is to understand how material properties like pore size distribution and BET surface area affects the water adsorption behaviour of each individual material.

2. Experiments
The adsorbent for this paper includes MIL-101(Cr), alkali metal (Li⁺, Na⁺) doped MIL-101(Cr), Aluminium Fumarate and CAU-10. These materials will be synthesized and characterized using N₂ isotherm fitted with computed BET isotherm model to achieve the surface area, pore volume and pore size distribution. Then, a gravimetric water adsorption experiment is conducted to achieve the isotherm and kinetic results for all materials.

2.1. Synthesis
MIL-101 was performed by hydrothermal reaction method. 4g of chromium (III) nitrate nonahydrate and 1.66g of terephthalic acid were added into the reactor with 1ml of concentrated hydrochloric acid and 50 ml of deionized water before heating at 200 °C for 10 hours. The mixture was separated using a centrifugal spinning machine. After separation, the synthesized material was mixed with N₂, N-dimethylformamide (DMF) and heated at 80°C for purification. The mixture was then separated by the centrifugal spinning machine. Last, the synthesized material was dried at 80°C. Doped MIL-101 was a modification of MIL-101 structure. The synthesized MIL-101 were activated via vacuum oven at 150°C for 3 hours. The samples were mixed with hexane and stirred for 30 mins. Upon stirring, alkali metal solution (5% wt LiCl or NaCl with 1ml of deionized water) was added slowly into the suspension. The mixture was separated and the modified samples were dried at 80°C. Aluminium Fumarate was synthesized slightly different from BASF patent [10]. 2.45g of aluminium chloride hexahydrate and 1.4g of fumaric acid were added into the suspension of DMF (100ml) in a beaker. The suspension was stirred at 130°C for 4 days. The mixture was separated by a centrifugal spinning machine. The white, synthesized material was rinsed with acetone and methanol twice. Last, the synthesized material was dried at 80°C. CAU-10 was prepared by hydrothermal reaction method. 1g of isophthalic acid (1,3-H₂BDC) were dissolved in 5ml of DMF and 4g of aluminium sulphate hydrate were dissolved in 20ml of water. The solutions were mixed into an autoclave reactor and it was heated at 135°C for 12 hours. The mixture was separated by using a centrifugal spinning machine. The synthesized material was rinsed with water via sonication for three times. Then, the material was dried at 80°C.

2.2. N₂ Adsorption
The specific surface area, pore volume and pore size of the samples can be achieved by N₂ sorption isotherms at 77K, measured by Autosorb iQ (Quantachrome). The samples are degassed at 120°C to 160°C for 3 hours before N₂ adsorption. The measured isotherms data were computed with BET (Brunauer-Emmet-Teller) equation to calculate BET surface area. The isotherms data also estimate the pore size and the pore volume of the material.

2.3. Water Adsorption
The water adsorption isotherm and kinetics results of the samples are measured by Aquadyn DVS (Quantachrome) at 298K to 333K. The samples are heated at about 120°C to 160°C for 1.5 hours to remove any moisture adsorbed from the atmosphere. The samples are held by a microbalance in the chamber feel with mixture of dry N₂ and water vapour. The relative pressure in the chamber is controlled by the ratio of N₂ and water vapour measured. The mass of the samples increased as water molecules are adsorbed. Thus, the water adsorption isotherm is measured based on the weight differences from the sample’s dry weight at different relative pressure. Figure 1 shows the schematic of this analyser.
3. Results and Discussion

Figure 2 shows the N\textsubscript{2} isotherms of the samples. Based on the results shown, MIL-101 has the highest uptake among the samples. As the structure is modified, the N\textsubscript{2} uptake decreases. This may be due to the formation of micro pores after the modification, as MIL-101 are mainly meso pores. Aluminium Fumarate has a low N\textsubscript{2} uptake as compared to MIL-101. However, the uptake increases tremendously at the saturated pressure region. This is due to the large existence of macro pores in Aluminium Fumarate. Higher N\textsubscript{2} uptakes have the tendency of higher surface area and pore volumes. Table 1 shows the values of the BET surface area, pore volume and pore sizes of the samples. It is noted that MIL-101 has higher BET surface area and pore volume than the other samples. Although the BET surface area and pore volume decreases, the pore sizes of the modified MIL-101 are similar. On the other hand, Aluminium Fumarate has large pore volume with a small BET surface area due to the large existence of macro pores. CAU-10 has the smallest values for all three categories since the N\textsubscript{2} uptake is the lowest.

![Figure 2. N\textsubscript{2} Adsorption Isotherms.](image)

| Table 1. Properties of samples |
|--------------------------------|
| | BET Surface Area (m\textsuperscript{2}/g) | Pore Volume (cm\textsuperscript{3}/g) | Pore Size (Å) |
| MIL-101 | 3402.69 | 1.59 | 18.469, 23.129 |
| Li-MIL-101 | 2054.03 | 0.94 | 18.469, 23.129 |
| Na-MIL-101 | 2000.66 | 0.91 | 18.469, 23.129 |
| Aluminium Fumarate | 792.26 | 0.926 | 5.996, 7.509, 11.258 |
| CAU-10 | 553.32 | 0.25 | 5.996, 11.258 |
Figure 3 shows the water adsorption uptake at 25°C. It is shown that MIL-101 has the highest water uptake at saturated pressure region. This is common since MIL-101 has higher surface area and larger pores. The hydrophobic length and water uptake are reduced after the modification of MIL-101. It is also noted that both CAU-10 and Aluminium Fumarate have much shorter hydrophobic length and lower water uptake than MIL-101. By comparing the results with Table 1, the size of micro pores for the adsorbent is rather ideal for short hydrophobic length. Further observation shows that CAU-10 has shortest hydrophobic length since CAU-10 has the smallest pores distribution. Another interesting cross reference between Figure 3 and Table 1 is all MOFs have at least 2 major pore sizes in the structure. It is observed that the higher water uptake is related to the size of larger pores. Hence, this shows that the location of the second peak of the pore size distribution is closely related to the maximum water uptake.

Figure 3. Water Adsorption Isotherm at 25°C

Figure 4 shows the adsorption kinetics of the MOFs at a temperature of 25°C. The original MIL-101 and CAU-10 have a slow kinetics to reach its equilibrium state. Based on the Figure, both MIL-101 and CAU-10 might require a longer time to reach its steady state region. Aluminium Fumarate also displays a slow kinetic behaviour. However, the trend indicates Aluminium Fumarate has a faster kinetic than MIL-101 and CAU-10. The curve also suggests the time taken for Aluminium Fumarate to reach its steady state region. On the other hand, modified MIL-101 samples show a much faster kinetic trend from its original sample, reaching steady state around 10000s to 12000s. This shows the modification via doping of alkali metal ions increase the interaction of water molecules for the adsorbent material. Hence, the time taken for the adsorption process of water molecules is shorten.

Figure 4. Water Adsorption Kinetics at 25°C

4. Conclusions
MOF adsorbents were experimented through N\textsubscript{2} adsorption and water adsorption test. The N\textsubscript{2} isotherms showed the large number of macro pores can be found in Aluminium Fumarate surface. It is also estimated that MIL-101 samples have better surface properties than CAU-10 and Aluminium Fumarate. A pore size distribution graph showed that the MOF materials have at least two distinct distribution peaks. Further comparison with water adsorption isotherms showed that smaller distribution of pores can be a factor to reduce the hydrophobic length of the adsorbent. On the other hand, the location of the second distribution peak can determine the maximum water uptake of the adsorbent. Hence, the combination of these two factors may be the key to achieve a water adsorbent with an isotherm with a high uptake difference. The kinetics data has shown that modified MIL-101 has better capability in reaching steady state at a shorter time. Thus, in terms of higher uptake difference and faster kinetic performance, these comparisons of the MOF material would provide a good direction on new MOF adsorbent for water adsorption applications.

Acknowledgements
The authors acknowledge the financing support from Ministry of Education, Singapore (grant no. MOE 2014-T2-2-061)
5. References

[1] Jeremias, F., Fröhlich, D., Janiak, C., and Henninger, S. K., Water and methanol adsorption on MOFs for cycling heat transformation processes, *New Journal of Chemistry*, vol. 38, p. 1846, 2014.

[2] Anyanwu, E. E. and Ogueke, N. V., Thermodynamic design procedure for solid adsorption solar refrigerator, *Renewable Energy*, vol. 30, pp. 81-96, 2005.

[3] Saha, B. B., Akisawa, A., and Kashiwagi, T., Silica gel water advanced adsorption refrigeration cycle, *Energy*, vol. 22, pp. 437-447, 1997.

[4] Thu, K., Chakraborty, A., Saha, B. B., and Ng, K. C., Thermo-physical properties of silica gel for adsorption desalination cycle, *Applied Thermal Engineering*, vol. 50, pp. 1596-1602, 2013.

[5] Myat, A., Kim Choon, N., Thu, K., and Kim, Y.-D., Experimental investigation on the optimal performance of Zeolite–water adsorption chiller, *Applied Energy*, vol. 102, pp. 582-590, 2013.

[6] Canivet, J., Fateeva, A., Guo, Y., Coasne, B., and Farrusseng, D., Water adsorption in MOFs: fundamentals and applications, *Chem Soc Rev*, vol. 43, pp. 5594-617, Aug 21 2014.

[7] Ehrenmann, J., Henninger, S. K., and Janiak, C., Water Adsorption Characteristics of MIL-101 for Heat-Transformation Applications of MOFs, *European Journal of Inorganic Chemistry*, vol. 2011, pp. 471-474, 2011.

[8] Frohlich, D., Henninger, S., and Janiak, C., Multicycle water vapour stability of microporous breathing MOF aluminium isophthalate CAU-10-H, *DALTON TRANSACTIONS*, vol. 43, pp. 15300-15304, // 2014.

[9] Henninger, S. K., Schmidt, F. P., and Henning, H. M., Water adsorption characteristics of novel materials for heat transformation applications, *Applied Thermal Engineering*, vol. 30, pp. 1692-1702, 2010.

[10] Kiener, C., Muller, U., and Schubert, M., Organometallic Aluminum Fumarate Backbone Material, USA Patent US20090092818A1, 2009.