Modulation and green synthesis of metal organic frameworks for higher water uptakes and kinetics : adsorption cooling application

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**MODULATION AND GREEN SYNTHESIS OF METAL
ORGANIC FRAMEWORKS FOR HIGHER WATER
UPTAKES AND KINETICS: ADSORPTION COOLING
APPLICATION**

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

A thesis submitted to Nanyang Technological University
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from six (6) papers published in the following peer-reviewed journals where I was the first and/or corresponding author.

Chapters 4 and 5 were published in the following articles:

1. H.W.B. Teo, A. Chakraborty, S. Kayal, Post synthetic modification of MIL-101(Cr) for S-shaped isotherms and fast kinetics with water adsorption. *Applied Thermal Engineering* **120**, 453-462 (2017). DOI: 10.1016/j.applthermaleng.2017.04.018.

The contributions of the co-authors are as follows:

- A/P Chakraborty provided the initial project direction and edited the manuscript drafts.
 - I prepared the manuscript drafts. The manuscript was revised by A/P Chakraborty.
 - I synthesised and modified the MIL-101(Cr) samples in Fuel Cell Lab and these were prepared based on Dr Kayal protocols.
 - All the adsorption experiments were conducted by me in the Energy System Lab.
 - Dr Kayal assisted in the characterisations of the material, such as SEM, XRD and TGA.
 - The theoretical analysis on the isotherms and kinetics data, and the isosteric heat of adsorption were performed by me.
2. H.W.B. Teo, A. Chakraborty, Y. Kitagawa, S. Kayal, Experimental study of isotherms and kinetics for adsorption of water on Aluminium Fumarate. *International Journal of Heat and Mass Transfer* **114**, 621-627 (2017). DOI: 10.1016/j.ijheatmasstransfer.2017.06.086.

The contributions of the co-authors are as follows:

- The initial direction was proposed by me.
- A/P Chakraborty provided his advice on the direction of this work

- I prepared the manuscripts and A/P Chakraborty edited the drafts.
 - I synthesised and purified the Al Fum samples in Fuel Cell Lab with Mr Kitagawa assistance.
 - All the adsorption experiments were conducted by me in the Energy System Lab.
 - Mr Kitagawa performed the SEM analysis of the samples.
 - Dr Kayal performed the XRD and TGA characterisation of the samples.
 - The theoretical analysis on the isotherms and kinetics data, and the isosteric heat of adsorption were performed by me.
3. H.W.B. Teo, A. Chakraborty, S. Kayal, Formic acid modulation (fam) aluminium fumarate MOF for improved isotherms and kinetics with water adsorption: Cooling/heat pump applications. *Microporous and Mesoporous Materials* **272**, 109-116 (2018). DOI: 10.1016/j.micromeso.2018.06.016

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- The initial direction was proposed by me.
 - A/P Chakraborty provided his advice on the direction of this work
 - I prepared the manuscripts and A/P Chakraborty edited the drafts.
 - I synthesised, modulated and purified the Al Fum samples in Fuel Cell Lab.
 - All the adsorption experiments were conducted by me in the Energy System Lab.
 - Dr Kayal performed the TEM, XRD and TGA characterisation of the samples.
 - The isosteric heat of adsorption of the Al Fum samples was plotted by me.
4. S. Kayal, A. Chakraborty, H.W.B. Teo, Green synthesis and characterization aluminium fumarate metal-organic framework for heat transformation applications. *Materials Letter* **221**, 165-167 (2018). DOI: 10.1016/j.matlet.2018.03.099

The contributions of the co-authors are as follows:

- The initial direction was proposed by Dr Kayal.
- A/P Chakraborty provided his advice on the direction of this work

- Dr Kayal prepared the manuscripts and A/P Chakraborty edited the drafts.
- Dr Kayal synthesised and purified the Al Fum samples in Fuel Cell Lab.
- All the adsorption experiments were conducted by me in the Energy Systems Lab.
- Dr Kayal performed the SEM and XRD characterisation of the samples.

Appendix A are published in the following articles:

1. H.W.B. Teo, A. Chakraborty, W. Fan, Improved adsorption characteristics data for AQSOA types zeolites and water systems under static and dynamic conditions. *Microporous and Mesoporous Materials* **242**, 109-117 (2017). DOI: 10.1016/j.micromeso.2017.01.015.

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 - I prepared the manuscript drafts. The manuscript was revised by A/P Chakraborty.
 - Dr Fan assisted in theoretical studies of the isosteric heat at zero surface coverage
 - All the adsorption experiments were conducted by me in the Energy System Lab.
 - The theoretical analysis on the isotherms and kinetics data, and the isosteric heat of adsorption were performed by me.
2. H.W.B. Teo, A. Chakraborty, B. Han, Water adsorption on CHA and AFI types zeolites: Modelling and investigation of adsorption chiller under static and dynamic conditions. *Applied Thermal Engineering* **127**, 35-45 (2017). DOI: 10.1016/j.applthermaleng.2017.08.014.

The contributions of the co-authors are as follows:

- A/P Chakraborty provided the initial project direction and edited the manuscript drafts.

- I prepared the manuscript drafts. The manuscript was revised by A/P Chakraborty.
- Mr Han assisted in the modelling the water adsorption in AFI and CHA adsorbent structure.
- I performed the theoretical adsorption analysis of the materials based on collected experimental data.
- I wrote the simulation code based on the Thermodynamic Framework for an adsorption cooling system in MATLAB.
- I inputted the theoretical data into the simulation code and analysed the collected results.

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SUMMARY

A central challenge of cooling science today is the development of clean energy assisted adsorption chillers, and also the reduction of carbon dioxide emissions, on the urgent agenda. The efficiency of an adsorption chiller is first and foremost governed by the micro porosity, hydrophilicity and hydrothermal stability of the adsorption materials. Traditionally, inorganic porous substances such as silica gel, aluminophosphates, or zeolites have been investigated for cooling purposes. The key problem with these adsorbents is that most of the water adsorption occurs at too high relative pressures, and the loading difference over the cycle is only a small part of the total adsorption capacity. So, novel adsorbents need to be designed and synthesised.

This thesis focuses on metal organic frameworks (MOFs) for water adsorption purposes and tune the pore structures and chemical functionalities of these MOFs by alkali ions, modulation and green synthesis methods. Prior to the modification of the synthesised MOFs, a Grand Canonical Monte Carlo (GCMC) simulation is conducted to calculate water uptakes on MIL-101(Cr) and Al Fum MOFs from Henry's region to the saturated pressure with the snap-shots of molecular structure. From GCMC simulation results, the effects of alkali ions on Al Fum structure + water show that the S-shaped isotherms with shorter hydrophobic lengths at 30°C are suitable for adsorption chiller design.

At first, the alkali metal ions (Li^+ , Na^+ , K^+) were doped into the MIL-101(Cr) structure at different weight percentages varying from 5% to 40%. Hence, the MOFs characterisations were conducted by SEM, XRD, TGA and N_2 adsorption methods, and water isotherms and kinetics were measured by a thermo-gravimetric analyser. It is better to modify MIL-

101(Cr) with doping of alkali metal ions less than 40%wt to prevent disintegration of material structure. However, 5% wt of alkali metal ions with MIL-101(Cr) MOF shows better water adsorption uptakes due to high retention of water molecules at the outer cage of the MOF structure.

Secondly, Al Fum MOFs were modified with formic acid modulation, which shortens the duration of the synthesis procedure. The characterisation results show that the formic acid elongates the particles morphology of the parent Al Fum with higher thermal stability and wide micro pore distributions. The addition of 10 ml of formic acid shows the best results in terms of wide pore size distribution and higher water uptake – offtake difference, which is 12.5% higher as compared with the parent Al Fum MOF.

As a novel contribution, Al Fum MOF was synthesised by a robust environment-friendly water-based method, which is very quick as compared to the use of hazardous DMF solvent. This method provides a blueprint for industrial-scale production of Al Fum MOF. The water sorption behaviour of Al Fum MOF shows a ‘S’ – shaped curve with steep increase of uptake in a narrow pressure range ($P/P_s = 0.2 - 0.3$), which indicates its potential use in adsorption chillers and heat pump applications.

Employing experimentally obtained isotherms and kinetics data, the thermodynamic modelling of two-bed adsorption chiller is presented. The chiller efficiencies are shown in terms of the SCP (specific cooling power) and the COP (coefficient of performance). The aluminium-based adsorbents such as Al Fum and CAU-10 MOFs show relatively higher SCP and COP due to faster kinetics rate. The modulated Al Fum + water-based adsorption chiller shows 1.2 times higher SCP as compared with parent Al Fum MOF, which is due

to higher uptake – offtake difference per cooling cycle and faster kinetics. The cooling cycle is operated with heat input at 60°C. Therefore, by adopting modification with green synthesis of MOFs, a new-generation adsorption chiller is achievable in the near future.

LIST OF PUBLICATIONS INCLUDED IN THE THESIS

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JOURNAL ARTICLES

1. **Teo, H. W. B.**, Chakraborty, A., Kayal, S., Formic acid modulated (FAM) Aluminium Fumarate MOF for improved isotherms and kinetics with water adsorption: Cooling/heat Pump Applications, *Microporous and Mesoporous Materials*, 2018, 272, pp 109-116.
2. Kayal, S., Chakraborty, A., **Teo, H. W. B.**, Green synthesis and characterization of Aluminium Fumarate Metal-Organic Framework for heat transformation applications, *Materials Letters*, 2018, 221, pp 165-167.
3. **Teo, H. W. B.**, Chakraborty, A., Kitagawa, Y., Kayal, S., Experimental study of isotherms and kinetics for adsorption of water on Aluminium Fumarate, *International Journal of Heat and Mass Transfer*, 2017, 114, pp 621-627.
4. **Teo, H. W. B.**, Chakraborty, A., Han, B., Water adsorption on CHA and AFI types zeolites: Modelling and investigation of adsorption chiller under static and dynamic conditions, *Applied Thermal Engineering*, 2017, 127, pp 35-45.
5. **Teo, H. W. B.**, Chakraborty, A., Kayal, S., Post synthetic modification of MIL-101(Cr) for S-shaped isotherms and fast kinetics with water adsorption, *Applied Thermal Engineering*, 2017, 120, pp 453-462.
6. **Teo, H. W. B.**, Chakraborty, A., Fan, W., Improved adsorption characteristics data for AQSOA types zeolites and water systems under static and dynamic conditions, *Microporous and Mesoporous Materials*, 2017, 242, pp. 109-117.

7. Kayal, S., **Teo, H. W. B.**, Chakraborty, A., Prediction of phase transitions by investigating CO₂ adsorption on 1% lithium doped MIL-101(Cr) MOF with anomalous type isosteric heat of adsorption, *Microporous and Mesoporous Materials*, 2016, 236, pp 21-27.
8. **Teo, H. W. B.**, Chakraborty, A., Kayal, S., Evaluation of CH₄ and CO₂ adsorption on HKUST-1 and MIL-101(Cr) MOFs employing Monte Carlo simulation and comparison with experimental data, *Applied Thermal Engineering*, 2017, 110, pp 891-900.
9. **Teo, H. W. B.**, Chakraborty, A., Methane adsorption characteristics of HKUST-1 and MIL-101(Cr) using GCMC (Grand Canonical Monte Carlo) simulation, *Evergreen*, 2015, 2, pp 44-49.

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1. **Teo, H. W. B.**, Chakraborty, A., Aluminium based zeolites and MOFs for adsorption cooling, Transactions of the Japan Society of Refrigeration and Air Conditioning Engineers, 2018.
2. **Teo, H. W. B.**, Chakraborty, A., Water adsorption on various Metal Organic Framework, IOP Conference Series: Materials Science and Engineering, 2017, 272, pp 12-19.
3. **Teo, H. W. B.**, Chakraborty, A., Ooi, K. T., Adsorption characteristics of modified MIL-101(Cr) for gas (Mainly CH₄) storage application, ASME, ASME International Mechanical Engineering Congress and Exposition, 2015, Volume 6B: Energy.
4. Chakraborty, A., Ali, S. M., **Teo, H. W. B.**, Study of waste heat-driven adsorption cooling system employing doped MIL-101(Cr) and water as adsorbent adsorbate pair, ASME, ASME International Mechanical Engineering Congress and Exposition, 2015, Volume 6B: Energy.

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Nomenclature

Abbreviations

Acronyms	Meaning
BET	-Brunauer-Emmett-Teller Theory
C-C	-Clausius-Clapeyron relation
COP	-Coefficient of Performance
GCMC	-Grand Canonical Monte Carlo
IUPAC	-International Union of Applied Chemistry
MD	-Molecular Dynamics
MOF	-Metal Organic Framework
SCP	-Specific Cooling Power
SEM	-Scanning Electron Microscopy
TGA	-Thermo-gravimetric Analyzer
XRD	-X-ray Diffraction

Greek Letters

Symbol	Meaning	Unit
α	-pre-exponential coefficient	[-]
α_L	-Factor related to z	[-]
β_o	-sticking coefficient	[-]
β_L	-load factor	[-]
δ	-separation between adsorbent planes	Å
ϵ	-Lennard-Jones force constant	kJ/mol
γ	-time constant	s
λ	-absolute activity	[-]e
μ	-chemical potential	kJ/mol

μ_{gas}	-chemical potential of bulk phase	kJ/mol
ϕ	-adsorption potential energy	kJ
ϕ_D	-dispersion energy	kJ
ϕ_R	-repulsion energy	kJ
ρ	-density of gas	kg/m ³
ρ_l	-liquid density of adsorbate	kg/m ³
ρ_s	-density of solid adsorbent	kg/m ³
σ	-collision diameter	Å
τ	-cycle time	s
θ	-surface coverage	[-]
θ_t	-real time surface coverage	[-]
θ_{ini}	-initial adsorption fraction	[-]
ε	-solid-fluid well depth potential	kJ

Latin Symbols

Symbol	Meaning	Unit
d	-pore size of adsorbent	Å
A_s	-BET surface area	m ² /g
C	-number of components	[-]
c	-mass concentration	mol/m ³
c_p	-specific heat	kJ/(kg K)
D	-diffusivity	m ² /s
E_a	-activated energy	kJ
e	-local charge density	C
F	-degree of freedom	[-]
h	-enthalpy	kJ/kg
H_c	-pore width of solid adsorbents	nm
H^θ	-reference enthalpy	kJ
h_{fg}	-latent heat of evaporation	kJ/mol
I	-number of restricted phases	[-]

k	-Boltzmann constant	$(\text{m}^2\text{kg})/(\text{s}^2 \text{K})$
k_{ads}	-adsorption rate coefficient	s^{-1}
k_{des}	-desorption rate coefficient	s^{-1}
K_h	-Henry's coefficient	$\text{kPa} \cdot \text{kg/kg}$
M	-Molar mass	kg/kmol
m	-structural heterogeneity factor	$[-]$
m_a	-mass of adsorbate	kg
m_{chw}	-mass flow rate of chilled water	kg/s
m_{cw}	-mass flow rate of cooling water	kg/s
m_{hw}	-mass flow rate of hot water	kg/s
M_s	-mass of dried sample	kg
MC_p	-effective heat capacity	kJ/K
N_A	-Avogadro's Number	mol^{-1}
N_{bed}	-number of tubes in bed	$[-]$
N_{evp}	-number of tubes in evaporator	$[-]$
N_{cond}	-number of tubes in condenser	$[-]$
n	-surface-energy heterogeneity factor	$[-]$
$\bar{n}$	-amount of uptake	kg/kg
$\bar{n}_{max}$	-maximum amount of uptake	kg/kg
P	-pressure	kPa
P_a	-ambient pressure	kPa
P^θ	-reference pressure	kPa
P_j	-adsorption pressure at state point	kPa
P_k	-condensation pressure	kPa
P_n	-number of phase	$[-]$
P_s	-saturated pressure	kPa
P_t	-equilibrium pressure of adsorbed phase	kPa
P_{ini}	-initial pressure	kPa
Q_{evap}	-heat of evaporation	kJ
Q_{cond}	-condensation heat	kJ
Q_{ads}	-heat of adsorption	kJ

Q_{des}	-heat of desorption	kJ
q	-gravimetric water uptake	kg/kg
q_t	-dynamic gravimetric water uptake	kg/kg
Q_{st}	-isosteric heat of adsorption	kJ/kg
Q_{st}^*	-isosteric heat of adsorption at zero surface coverage	kJ/kg
r	-distance between molecules	nm
r_p	-average pore radius	nm
R	-ideal gas constant	kJ/(K mol)
s	-specific entropy	kJ/(kg K)
s_f	-specific entropy of liquid phase adsorbate	kJ/(kg K)
T	-temperature	K
t	-time	s
u	-internal energy	kJ/kg
UA_{ads}	-heat transfer coefficient for adsorption	kW/K
UA_{des}	-heat transfer coefficient for desorption	kW/K
UA_{evp}	-heat transfer coefficient for evaporator	kW/K
UA_{cond}	-heat transfer coefficient for condenser	kW/K
v_p	-micropore volume of the adsorbent	m ³
v_a	-specific adsorbed phase volume	m ³ /kg
v_g	-specific gas phase volume	m ³ /kg
V_{ads}	-volumetric uptake	m ³ /m ³
V_m	-molar volume	m ³ /mol
V_{liq}	-saturated volume	m ³
V_{bed}	-volume of bed	m ³
V_{evp}	-volume of evaporator	m ³
V_{cond}	-volume of condenser	m ³
x_a	-amount of adsorbate uptake	kg/kg
z	-coordination number	[-]

Chapter 1: Introduction

1.1 Background and Motivation

The increasing concerns over ozone depletion and global warming, augmented energy demand and CO₂ emissions have raised the interest in energy-efficient systems. Heat transformation technologies utilising environmentally friendly refrigerants have attracted much attention due to the increasing demands for air-conditioning caused by increased thermal loads, higher living standards as well as the architectural trends of buildings.

With the worldwide energy consumption increasing over time, many concerns such as future energy supplies, resources and environmental impact are raised [2]. Generally, air-conditioning systems consume 20% ~ 50% of the total daily energy consumption of a building [3-5]. Chua et al. [5] reviewed that 31% of total energy consumption in Singapore was consumed by buildings, of which 60% was used to generate cooling. For a sustainable and secure energy supply in the future, an alternative source of energy is required to provide air conditioning systems with higher energy efficiency.

With regard to the large amount of available but unused low-temperature heat, either by solar thermal collectors or waste heat from industrial processes, thermally driven adsorption chillers and dehumidifiers provide a promising approach for the solution of the cooling demands of buildings [6]. The adsorption device utilised for the adsorption-desorption process is a fin-tube heat exchanger in which the adsorbent materials are housed. The adsorption system are commercially used in countries like Japan, Germany, France, United States and China [7]. Water is generally preferred as the adsorbate for the

adsorption chiller because it is non-toxic, easily available and has a high evaporation enthalpy [8]. The major drawback of the adsorption cooling device lies in the bulky size of adsorption bed, which allows large floor area with massive footprint [9]. Therefore, it is necessary to develop novel porous adsorbents.

It is well known that the performance of adsorption cooling can be improved by modifying the pore structures of porous adsorbent, a result which opens new synthesis prospects. Secondly, there is also no cooling performance for pore widths ranging from 0.1 to 0.3 nm. The best performance is obtained at the pore width of 0.8 nm with higher pore volume for silica gel and water system. Despite the impressive progress on the materials, the development of new micro or meso-porous materials for use in adsorption cooling processes is still a fundamental research. In addition to inorganic materials such as silica gel, zeolites and aluminophosphates, a new class of microporous materials well known as porous coordination polymers or metal-organic frameworks (MOFs) has emerged.

Compared to traditional adsorbents such as silica gel, zeolites or aluminophosphates used in adsorption cooling devices, MOFs show the geometric flexibility and exhibit a much richer variety in terms of composition, pore structure and topology. The fundamental cluster/linker design of MOFs allows the tuning of pore structures and chemical functionalities over a wide range. The advantage is the mechanism of synthesis by solvothermal or hydrothermal process. Furthermore, the pore dimensions can be systematically tuned from ultra micro- to micro- to meso-porous range and even the pore surface can be functionalised through the immobilisation of functional sites like $-NH_2$, $-NO_2$, $-OH$ groups [10], thus making porous MOFs as an interesting and superior candidates over traditional porous materials. Another unique feature of the MOF + water system is the

development of ‘S’ – shaped isotherm curves. This unique isotherm curves are suitable for adsorption cooling design due to the fact that the cycled mass of water vapour for the MOF + water system is higher than that of the silica gel/zeolite + water system. By employing an ‘S’ – shaped isotherm based adsorbent + water system, the size of adsorption/desorption reactor can be minimised for the same cooling capacity and COP (coefficient of performance) of the conventional adsorption cooling device [11, 12], which indicates a significant breakthrough in cooling science and technology. The adsorption – desorption cycles for silica gel (A'B'CD) and the proposed MOF (ABCD) are shown in the insight of Figure 1.1.

Figure 1.1: Illustration of possible water loading lifts for different adsorbent material classes within a typical heat transmission cycle. Here, adsorption-desorption cycle of silica gel – water (A'B'CD) and proposed MOF – water, where the evaporator pressure (P_{evap}) is 1 kPa and the condenser pressure (P_{cond}) is 5 kPa. The SEM pictures of silica gel and MOF are shown. A comparison of adsorption chiller sizes for silica gel and MOF adsorbents are also predicted here.

The basic adsorption cooling system comprises an evaporator, a condenser and two or multi adsorption beds. To improve the effectiveness and the efficiency of adsorption cooling system, a few important aspects are required for the adsorbent material to be adopted into the adsorption device. Firstly, the designed adsorbent material must have the higher water uptake-offtake differences per batch process of adsorption cooling cycle, which allows the design of adsorption bed with less adsorbent material [11, 12]. Secondly, the designed adsorbent materials should possess relatively lower regeneration temperature ($< 65^{\circ}\text{C}$), which reduce the sensible heat loss from the adsorption beds and enhances the efficiency of the adsorption cooling device. The lower regeneration temperature ($50 \sim 65^{\circ}\text{C}$) also prevents any unnecessary phase change of water flowing in the heat exchanger while transferring heat energy to adsorbents. Thirdly, the designed adsorbent material possesses higher water uptake rates, i.e, faster kinetics for continuous cooling in short cycle time [13], which decrease the peak chilled water temperature at the end of adsorption – desorption batch process and improves the COP.

Therefore, it is concluded that the COP, power density, cost, operating lifetime and size of the adsorption chiller are governed by the adsorbent porous material and its figure of merit, i.e, porosity, water sorption capacity, hydrophilic and hydrothermal stability. So, the theme of this thesis is the development of adsorbent porous structures, such as Metal Organic Frameworks, for cooling applications.

Water adsorption research on Metal Organic Frameworks (MOF) have drawn much attention due to its promising results achieved in previous research activities [14-21]. MIL-101(Cr) is one of the highly noted material in water adsorption research due to its higher uptake of 1.01 g/g sorbent. Hence, the quantity of adsorbent needed for adsorption assisted

applications can be comparatively less than silica gel. However, MIL-101(Cr) requires higher working pressure during the adsorption process as the hydrophilic characteristics occurs at $0.4 < P/P_s < 0.5$ under room temperature conditions [14, 15], where P/P_s indicates the relative pressure.

New developed MOF materials, such as CAU-10 [19, 21], Aluminium Fumarate (Al-Fum) [16, 22, 23] and MOF-801 [20, 24, 25] are reported to be more suitable for adsorption assisted cooling applications as the hydrophobic characteristics ($P/P_s < 0.4$) of these new MOFs are lower as compared to those of MIL-101(Cr). The hydrophobic characteristic length of MOF-801, on the other hand, is observed at a relative pressure of 0.05. Therefore, higher desorption temperature is required if MOF-801 is adopted for designing adsorption chiller.

The modification of MOFs is necessary to achieve better adsorption – desorption characteristics towards adsorption related applications such as cooling, gas storage, purification, dehumidification, etc. Experiments such as Post-Synthesis Modification (PSM) were carried out to change the porous structure of the adsorbents to improve the adsorption characteristics. The modification, however, may result in achieving either lower uptake, higher hydrophobic characteristics length or unable to sustain after numerous sorption cycles [10, 26-29]. One of the PSM method is doping of alkali metal ions, which has proven to improve the uptake of H_2 adsorption [30-32]. Hence, in the hope of achieving better water adsorption characteristics, doping of alkali metal ions to MIL-101(Cr) was carried out for better performance in terms of uptake – offtake difference per adsorption cycle.

The modulation of MOFs is another method that has proven to improve the porous structure of MOF by synthesising the MOF crystals through either reducing agglomeration or generating aggregation to the MOF structure. The former enhances the synthesis process by producing higher distribution of micropores structure and faster crystal formation [24, 25]. This modification method requires long synthesis duration. For example, Al-Fum MOF requires four days to synthesise the crystal structure.

The next generation adsorption cooling device has to be small-scale and should provide cooling air efficiently to replace the currently used vapour compression system. Hence, the knowledge of MOF – water interactions as a function of pressure and temperature are essential to understand the shape of adsorption isotherms and kinetics, which is necessary for the development of next-generation functional adsorbents.

As mentioned in the previous section, the currently available adsorbent – adsorbate pairs for adsorption cooling device are mainly silica-gel – water, activated carbon – ethanol/methanol and zeolite – water pairs [33]. The most notable functional zeolites namely AQSOA-Z01 [11, 34] and AQSOA-Z05 [35, 36] achieve the water uptake – offtake difference of 0.2 g/g for the relative pressure (P/P_s) ranging from 0.1 to 0.3. This is due to its hydrophobic behaviour at low pressure region, and this behaviour helps to achieve low regeneration temperature for the desorption process. Thus, AQSOA zeolites show valuable insights on the correlation between ‘S’ – shaped isotherm adsorbent materials and performance of adsorption cooling device. However, the current adsorbents, which include all silica gels and zeolites, have low uptake – offtake differences [37] and are responsible for the large size of the thermal compressor for the adsorption device. High water stability of the material structure is a necessity to prevent the structural collapse of adsorbents after

numerous sorption cycles. Henninger et al. [17] has reviewed that certain MOFs, such as MIL-101(Cr) and CAU-10 possess this unique ‘S’ – shaped featured isotherm with high water uptake – offtake differences with good water stability. Therefore, achieving the next generation of adsorption cooling device is possible with the adoption of the MOF adsorbents.

Theoretically, the adsorption isotherm and kinetics studies provide better understanding of the adsorbent – adsorbate interactions. Isotherm models, such as Langmuir [38, 39], Tóth [40], Dubinin-Radushkevich and Dubinin-Astkhov [41-45] and the recently proposed Sun-Chakraborty model [46], deliver thermodynamic information in uptake and pressure co-ordinate system from the Henry’s region ($P \rightarrow 0$) to the saturated pressure ($P \rightarrow P_s$). Adsorption kinetics studies, on the other hand, show the basic understanding of the duration of adsorption process from the transient to the steady states and are presented in uptake – time co-ordinate system as a function of pressure and temperature. The kinetics model developed from Langmuirian analogy shows the precise kinetics parameters for the adsorbent – adsorbate interactions with respect to the working pressures and temperatures [47, 48]. These theoretical models, together with the thermodynamic framework of adsorption cooling device, are used to simulate the cooling performances and the COP.

1.2 Research Objectives

The overall aim is to enhance the adsorption properties of MOF adsorbents with controlled architecture for adsorption cooling system with better overall performance. The objectives of the thesis are:

- Gained fundamental knowledge for the characteristics of MOFs.

- Achieved an understanding for MOF – water adsorption interactions.
- Attained adsorbent materials with desired adsorption properties.
- Gained practical and theoretical understanding of synthesised MOFs + water system under static and dynamic conditions.
- Acquired the performance of the next-generation adsorption cooling employing MOF + water systems.

1.3 Scope

To achieve the objectives, the scope is summarised as follows:

- Understanding water adsorption on MOF structures employing Grand Canonical Monte Carlo (GCMC) simulation.
- Synthesis of Metal Organic Frameworks (MOFs) by green synthesis techniques with the addition of dopants or formic acid modulation for surface modification.
- Surface characterisation of MOF functional adsorbents by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), thermo-gravimetric analysis (TGA) and N₂ adsorption analysis.
- Measurement of water uptakes and kinetics on various MOFs for various pressures and temperatures employing the gravimetric methods.
- Calculation of the specific cooling power (SCP) and the coefficient of performance (COP) of adsorption cooling cycle employing experimentally confirmed isotherms and kinetics data of MOFs + water for the first time.

1.4 Layout of Report

This thesis starts off with an introduction in Chapter 1, which introduces the background of this research project and it also describes the motivation behind this research project. The objectives and scopes are also presented in this chapter.

In Chapter 2, the adsorption isotherms and kinetics are reviewed and presented. Different types of MOFs and other researchers' works with the MOFs have been reviewed in this chapter. The concepts of adsorption assisted cooling and hydrophobic characteristic length are also discussed.

Chapter 3 introduces the water adsorption isotherms curves for various MOFs + water system and the GCMC simulation, from which one can understand the interaction potentials between MOF structure and water molecules.

Chapter 4 describes the experimental details on how the MOF is synthesised and what are the procedures to perform various modifications on MOFs. Methods for characterising MOFs such as scanning electron microscope (SEM), X-ray diffraction (XRD), Thermo gravimetric analysis (TGA) and N₂ sorption isotherms are elaborated in this chapter.

Chapter 5 presents and discusses the experimental results and analyses of the isotherms and kinetics of various MOFs + water systems. This chapter also provides necessary information for optimising the modification procedure of MOFs with the desired characteristics for adsorption-based applications.

Chapter 6 illustrates the performances of the adsorption cooling cycle adopting MOFs + water systems by the theoretical modelling and simulation. The performance parameters such as COP and SCP are the main factors that categorise the potential of the MOF adsorbents towards the cooling application. Material properties as mentioned in Chapter 4 and 5 are also used to explain the reasons towards the simulated results.

Chapter 7 summarises the major findings and contributions up to now along with further recommendations for future work.

Chapter 2: Literature Review

2.1 Adsorption Process

It is well known that the adsorption of adsorbate into porous adsorbents is the result of van der Waals forces (dispersion-repulsion) and electrostatic interactions, which provide information about (a) the accumulation of large amount of adsorbate molecule into porous surface, (b) the diffusion of adsorbate into the micro, meso and macro pores of the adsorbent, and (c) the adhering of adsorbate molecule over the adsorbent pore volume. This phenomenon is known as **adsorption**. Generally, when the solid adsorbent is exposed to the adsorbate composition, the adsorption process is occurred, and the amount of uptake (or the number of adsorbate molecules) are measured under static (the adsorption isotherms) and dynamic (adsorption kinetics) conditions [49-52], which are illustrated in Figure 2.1.

Figure 2.1: Adsorbates behaviour in adsorption process [53]

Generally, both the adsorption and the desorption are considered as reversible processes for understanding these complex phenomena in a simple way. However, adsorption and

desorption are non-reversible as the process contains entropy generation [50, 53]. The driving force for physical adsorption is the interaction fields between the adsorbent and adsorbate pair. The driving force is represented by dispersion-repulsion energy as $\phi = \phi_D + \phi_R$ [54, 55] and is calculated by the Lennard-Jones potential function [56]:

$$\phi = \phi_D + \phi_R = 4\epsilon \left[\left(\frac{\delta}{r} \right)^{12} - \left(\frac{\delta}{r} \right)^6 \right] \quad (2.1)$$

where the constants ϵ and δ are characteristics of the particular molecular species, and r is the distance between centres of the interacting molecules, as illustrated in Figure 2.2 [57].

Figure 2.2: Dispersion-Repulsion Potential

In fact, the heterogeneous adsorbent surface is identified by adsorption sites with different energies distribution over the whole solid surface [58, 59]. The factors for high adsorption uptakes and rates depend on the nature of adsorbent surface area, size and pore volume with the affinity of adsorbate molecules. Under equilibrium condition, the change in adsorbate molecules with respect to the change in pressure from the Henry's region to the

saturated pressure for a given temperature represent the adsorption isotherms. However, the change in number of adsorbate molecules generating from transient up to the steady state result the adsorption kinetics, and is calculated as a function of pressure, temperature and time. The knowledge of adsorption isotherms and kinetics are essential to design the adsorption bed and understand the adsorption process [55, 60, 61]. The thermodynamic property surfaces of adsorbent – adsorbate are also needed to develop an adsorption process with the analysis of entropy generation [50].

The mathematical formulations that explain the thermodynamic property surfaces [50, 53], such as energy, enthalpy, entropy and specific heat and other thermodynamic properties such as the specific volume of adsorbed phase and isosteric heat of adsorption are furnished in Table 2.1. Once can use these equations to design an adsorption-desorption bed for cooling, dehumidification, separation, purification and desalination applications.

Table 2.1: Equations for the thermodynamic properties of adsorbent + adsorbate system

Property	Equation[50, 53]
Entropy (s)	$ds = (c_{p,s}/T + c_{p,a}/T)dT - (\partial v_s/\partial T)_P dP - (\partial v_a/\partial T)_{P,x} dP + [s_g - (v_g - v_a) dP/dT]dx$
Enthalpy (h)	$dh = (c_{p,s} + c_{p,a})dT + [v_a - T(\partial v_s/\partial T)_P]dP + [v_a - T(\partial v_a/\partial T)_{P,x}]dP + [h_g - Q_{st}]dx$
Internal Energy (u)	$du = (c_{p,s} + c_{p,a})dT + [v_s - T(\partial v_s/\partial T)_P]dP + [v_a - T(\partial v_a/\partial T)_{P,x}]dP + [h_g - Q_{st}]dx - (Pdv_s + v_s dP + Pdv_a + v_a dP)$
Specific Volume (v_a)	$v_a = v_g - [Q_{st}^{expt} - T v_g (\partial P/\partial T)_g]/T(\partial P/\partial T)_x$
Specific Heat ($c_{p,a}$)	$c_{p,a} = c_{p,g} + Q_{st}[1/T - 1/v_g (\partial v_g/\partial T)_P - \partial Q_{st}/\partial T]_P$
Isosteric heat of Adsorption	$Q_{st} = T v_g (\partial P/\partial m_g)_T (\partial m_g/\partial T)_P + T v_g (\partial P/\partial m_g)_T (\partial m_g/\partial P)_T (dP/dT)_{gas} + Q_{st} _{c-c}$

2.2 Adsorption Isotherms

An adsorption isotherm is a measure of the adsorbate uptake at a constant temperature as a function of equilibrium pressure. Applying *Gibbs'* phase rule, the degree of freedom, F , of the thermodynamic system for adsorption framework in equilibrium is written as [54]:

$$F = C - P_n + I + 2 \quad (2.2)$$

where C represents the number of components, P_n signifies the number of phases in thermodynamic equilibrium and I is the number of the bi-dimensional or restricted phase [54]. The adsorption process consists of one MOF adsorbent and water. Thus, the number of components $C = 2$. The number of phases, $P_n = 3$, for the solid phase of the MOF adsorbent, the gas phase of water vapour and the adsorbed phase of the water vapour. Since the gas phase and the adsorbed phase are meant for water, the restricted phase $I = 1$. Thus, the degree of freedom $F = 2 - 3 + 1 + 2 = 2$ and this states that the adsorption process changes according to the equilibrium pressure and temperature of the bulk phase. In the case where adsorption process is performed based on 50%/50% wt mixture of two MOFs, number of components for the process, $C = 3$, with other terms remain the same. Thus, $F = 3 - 3 + 1 + 2 = 3$, with the third function is the mass fraction of MOF mixture.

The quantity of adsorbed molecules, also known as the uptake of the adsorbates, x_a , is expressed as a function of the equilibrium pressure of bulk phase adsorbate, P , and the temperature, T . Given that adsorption isotherms are measured at constant temperature condition, the function x_a is written as

$$x_a = f(P)_T \quad (2.3)$$

Various isotherm trends can be observed during adsorption on adsorbent materials. Brunauer et al. [62] came up with the IUPAC classification in which the adsorption of gases is categorised the isotherms of five different types, as illustrated in Figure 2.3.

Figure 2.3: Five types of adsorption isotherms

Type I isotherm, also known as the Langmuir isotherm [62], shows a steep adsorption uptake towards saturated region, and this isotherm signifies adsorption on a micro porous adsorbent. Type II isotherm shows adsorption on macro porous adsorbent with a strong adsorbent-adsorbate interaction while Type III represents a weaker interaction [63]. The adsorption trend of Type IV and V are relatively alike with Type II and III, which the former achieves saturated uptake at pressure lower than the saturated pressure. Examples of the adsorbent – adsorbate pairs for these five types of isotherms are shown in Table 2.2.

Table 2.2: Types of isotherms for Adsorbent-Adsorbate pair [62]

Type of Isotherm	Adsorbent-Adsorbate system
Type I	Charcoal + Oxygen at 90.15K
Type II	Iron catalyst + Nitrogen at 78.15K
Type III	Silica Gel + Bromine at 352.15K
Type IV	Ferric oxide gel + Benzene at 323.15K
Type V	Charcoal + Water vapour at 373.15K

The adsorption isotherm equation presents the adsorption phenomena under equilibrium conditions, where the amount of adsorbate uptake is presented in terms of pressure and temperature with the parameters related to adsorption heat, adsorbate-adsorbent affinity and the surface structural heterogeneity factors. Table 2.3 shows the commonly applied adsorption isotherm models.

Table 2.3: Monolayer Surface Isotherm Equations

Isotherms	Equation	Limitations
Henry's Isotherm ^[60]	$\theta = K_h P$	Valid within extremely low pressure or concentration range
Langmuir Equation ^[60]	$\theta = \frac{b_{\infty} \exp(Q_{st}/R_g T) P}{1 + b_{\infty} \exp(Q_{st}/R_g T) P}$	Behaviour between adsorbing molecules is not considered. Accuracy of the theoretical fitting is not valid at high pressure range
Fowler-Guggenheim Equation ^[60, 63]	$bP = \frac{\theta}{1 - \theta} \exp\left(-\frac{z\phi s\theta}{R_g T}\right)$	Motion of adsorbing molecules is not considered
Hill-de Boer Isotherm ^[60, 63]	$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right) \exp\left(-\frac{z\phi s\theta}{R_g T}\right)$	Derivations at critical point region are not available

It is required to assume either a homogenous solid surface or a localised adsorbate on surface to adopt the isotherm models (in Table 2.3). The pore and surface structure for adsorbents, however, are complex in reality, which are rarely correlated with such assumptions [59]. In order to minimise this limitation, empirical or semi-empirical isotherms were derived, which is shown in Table 2.4 [64]. The empirical parameters and experimental data are found to complement each other. Thus, by changing the isotherm parameters, the theoretical model is fitted accurately with the experimental data. The

empirical isotherms, however, do not have any physical factors that are related to adsorption process. Hence, they show no physical meaning even though the isotherm fitting is adequate [61].

Table 2.4: Empirical Monolayer Surface Isotherm Equations

Isotherms	Equation	Limitations
Freundlich Equation	$\theta = K_h P^{1/n}$	Henry law limit at low pressure and saturation limit at high pressure is not available. Motion of adsorbing molecules is not considered.
Sips (LF) Equation	$\theta = \frac{(bP)^{1/n}}{1 + (bP)^{1/n}}$	Henry law limit at low pressure is not available. Molecule interaction is not considered.
Tóth Equation	$\theta = \frac{bP}{[1 + (bP)^t]^{1/t}}$	Parameter t has no theoretical relation with temperature dependence.
Dubinin-Radushkevich Equation	$\theta = \exp \left[-\frac{1}{(\beta E_0)^2} \left(R_g T \ln \frac{P}{P_0} \right)^2 \right]$	Henry law limit at low pressure is not available
Dubinin-Astakhov Equation	$\theta = \exp \left[-\frac{1}{(\beta E_0)^2} \left(R_g T \ln \frac{P}{P_0} \right)^n \right]$	Henry law limit at low pressure is not available

Sun – Chakraborty Isotherm Model

To compensate the limitations of the isotherm model and achieve a good experimental fit for all five types of isotherms, Sun and Chakraborty [46] derived a new adsorption isotherm model. The derivation includes the assumptions that s numbers of adsorbate molecules are adsorbed onto the adsorbent site during interaction [65]. Since the physical adsorption involves van der Waals force is a short-range, partition function of each isothermal site is

$q(s) = q^s(1)$ and absolute activity $\lambda = \exp(\mu/kT)$, where $\mu = \mu_{gas} + V_{ext}$. Adopting the grand partition function for each adsorptive site, the average molecules on each adsorptive site is

$$\bar{s} = \frac{\sum_{s=0}^m s \{q(1)\lambda\}^s}{\sum_{s=0}^m \{q(1)\lambda\}^s}. \quad (2.4)$$

Employing Grand potential of one particle [66] and bulk chemical potential (μ_{gas}) equation, $q(1)\lambda$ can be rewritten as $q(1)\lambda = \exp\{(RT - V_{ext} - h_{fg})/RT\}(P/P_s)$. The isosteric heat of adsorption at zero surface coverage is expressed as $Q_{st}^* = RT - V_{ext}$. Equation (2.4) can be expressed as

$$\theta = \frac{1}{\bar{s}_{max}} \frac{\sum_{s=0}^m s \exp\{s(Q_{st}^* - h_{fg})/RT\}(P/P_s)^s}{\sum_{s=0}^m \exp\{s(Q_{st}^* - h_{fg})/RT\}(P/P_s)^s}. \quad (2.5)$$

By simplifying Equation (2.5), the proposed isotherm model is expressed as [1, 46]:

$$\theta = \frac{K(P/P_s)^m}{1 + (K-1)(P/P_s)^m} \quad (2.6)$$

where the empirical factor, m , describes the heterogeneous level of the adsorbent structure and the Langmuir constant, K , is expressed by [46] $K = \alpha \exp[m(Q_{st}^* - h_{fg})/RT]$, where Q_{st}^* is the isosteric heat of adsorption at zero surface coverage, h_{fg} represents the enthalpy of evaporation and α is the pre-exponential coefficient. This isotherm model has proven to overcome the limitations of Langmuir and Tóth model [46]. The isotherm model is shown to have a good fit with experimental data of water adsorption with AQSOA-Z02 zeolite, silica gel (type RD) and MIL-100 (Cu) [1]. In this thesis, most of the experimental data based on adsorbate uptake as a function of pressure and temperature under equilibrium conditions are represented by Sun – Chakraborty isotherm model [46].

2.3 Adsorption Kinetics

The adsorption kinetics, generally, represents the dynamic behaviour of adsorbate uptakes on solid adsorbent [60]. The kinetics of the adsorption process will estimate the dynamic uptake at a designated period, i.e., how much water vapour is adsorbed during adsorption period of a cycle. The information is essential for thermal compressor design and development.

Thermal energy assisted the adsorbate molecules to take up available surface via random migration, and the chemical potential are equalized within the surface [67]. The basic formulation for diffusion phenomenon was developed with respect to Fick's first and second equations as given by

$$J = -D(c) \frac{\partial c}{\partial x} \quad (2.7)$$

and

$$\frac{\partial c(x,t)}{\partial t} = D(c) \frac{d^2 c(x)}{dx^2} \quad (2.8)$$

The term $D(c)$ is dependent on the various diffusion methods of the pore structure. Hence, the various diffusion methods are illustrated in Figure 2.4 [49]:

Figure 2.4: Various diffusion methods

Table 2.5 describes the unique features of these diffusion methods of bulk gas phase [55]. It is required to adopt more than one diffusion method to attain effectiveness. The diffusion methods are well elaborated. However, the details of adsorbate – adsorbate and adsorbent – adsorbate interactions inside the pore structure are required to predict the effective diffusivity. For understanding surface diffusivity, the linear driving force (LDF) model is applied to calculate the adsorbate uptake as a function of time. The LDF model is based on the temperature dependent reaction rates of Arrhenius equation.

Langmuir [38, 39], on the other hand, proposed another approach (based on kinetics rate of adsorption and desorption) in understanding the kinetics behaviour, which is shown as:

$$\frac{d\theta_t}{dt} = k_{ads}P_t(1 - \theta_t) - k_{des}\theta_t \quad (2.9)$$

where θ_t is the fraction uptake in terms of time, $\theta_t = \frac{\bar{n}}{\bar{n}_{max}} \cdot \bar{n}_{max}$ is the maximum amount of uptake. k_{ads} and k_{des} are the adsorption and desorption rate coefficients. P_t is the equilibrium pressure of the adsorbed phase at the point of time.

At equilibrium, $\frac{d\theta_t}{dt} = 0$, and $\theta_t = \theta$, Equation (2.21) is then expressed as:

$$\theta = \frac{K_h P}{1 + K_h P} \quad (2.10)$$

which is the Langmuir's isotherm. By expressing the Langmuir's constant as $K_h = k_{ads}/k_{des}$ and equilibrium pressure P is equal to initial pressure P_{ini} , $P = P_{ini}$, Equation (2.10) can be written as the pseudo-first-order model [68]:

$$\frac{d\theta_t}{dt} = \frac{1}{\gamma} (\theta - \theta_t) \quad (2.11)$$

where $\frac{1}{\gamma} = k_{ads}P + k_{des}$. Thus, Equations (2.9) and (2.11) will have the same adsorption kinetics expression as:

$$\theta_t = \theta \left[1 - \exp\left(-\frac{t}{\gamma}\right) \right] + \exp\left(-\frac{t}{\gamma}\right)\theta_{ini} \quad (2.12)$$

with boundary conditions $\theta_t = \theta_{ini}$ at $t = 0$ and $\theta_t = \theta_{ini}$ at $t \rightarrow \infty$.

In order to adopt the isotherm model and correlate with the kinetics behaviour, Chakraborty and Sun modified this analogy [48]. Using the isotherm model shown in Equation (2.6), the kinetics model written by Langmuir is modified to:

$$\frac{d\theta_t}{dt} = k_{ads}(1 - \theta_t) \left(\frac{P}{P_s}\right)^m - k_{des}\theta_t \left[1 - \left(\frac{P}{P_s}\right)^m \right]. \quad (2.13)$$

The kinetics behaviour is taking the consideration of the surrounding condition the adsorption process occurs. The heterogeneity factor, m , includes the heterogenous factor of the adsorbent adopted. Rearranging Equation (2.13), the first order equation becomes

$$\begin{aligned} \frac{d\theta_t}{dt} &= k_{ads} \left(\frac{P}{P_s}\right)^m - \theta_t \left\{ k_{ads} \left(\frac{P}{P_s}\right)^m + k_{des}\theta_t \left[1 - \left(\frac{P}{P_s}\right)^m \right] \right\} \\ &= k_{ads} \left(\frac{P}{P_s}\right)^m - \theta_t \frac{1}{\gamma} \end{aligned} \quad (2.14)$$

where $1/\gamma = k_{ads}(P/P_s)^m + k_{des}\theta_t[1 - (P/P_s)^m]$ is the time constant [48]. After solving the first order equation with initial condition ($\theta = \theta_{ini}$ at $t = 0$), the kinetics model is written as

$$\frac{\Delta\theta_t}{\Delta\theta} = \frac{\theta_t - \theta_{ini}}{\theta - \theta_{ini}} = 1 - e^{\frac{-t}{\gamma}} \quad (2.15)$$

Table 2.5: Diffusivity of Different Diffusion Mechanisms

Mechanism	Diffusivity	Valid Conditions
Molecular Diffusion	$D_m = \frac{0.000158T^{3/2}(1/M_1 + 1/M_2)^{1/2}}{P\sigma_{12}^2\Omega(\epsilon/kT)} (cm^2/s)$	Pressure is higher than critical value, mean free path of gas molecule is smaller than pore width, thus, collisions between molecules are primary factor
Knudsen Diffusion	$D_k = \frac{2}{3} \sqrt{\frac{8RT}{\pi M}} R_p = 9700 R_p (T/M)^{1/2} (cm^2/s)$	
Intermediate Region	$1/D = 1/D_m + 1/D_k$	Pressure is approximately of critical value, mean free path of gas molecule and pore width are almost similar. Molecular and Knudsen diffusion coexist
Poiseuille Flow	$D = PR_p^2/8\mu_p$	Pressure across a particle change, due to an event of adsorption in a vacuum system occurs
Hopping Model Surface Diffusion	$D_s = D_{s0} \frac{\theta_c}{\theta}$ $\cdot \frac{\exp\left(-\frac{E_{s0}}{RT}\right) - \exp\left(-\frac{Q_{st}}{RT}\right)}{\left[1 - \exp\left(-\frac{Q_{st}}{RT}\right)\right] \left[1 - \theta_c \left(1 - \frac{\tau_1}{\tau_0}\right)\right]}$ $\frac{\tau_1}{\tau_0} = \frac{[\exp\left(-\frac{E_{s0}}{RT}\right) - \exp\left(-\frac{Q_{st}}{RT}\right)]}{[\exp\left(-\frac{E_{s0}}{RT}\right) - \exp\left(-\frac{\lambda_{vap}}{RT}\right)]}$ $\cdot \frac{1 - \exp\left(-\frac{h_{fg}}{RT}\right)}{1 - \exp\left(-\frac{Q_{st}}{RT}\right)}$	Heat of adsorption, Q_{st} , is higher than energy barrier, E_s , at adsorption site
Surface Flow Diffusion	$D_s = \left(\frac{qRT}{SC_r}\right) \frac{d \ln p}{d \ln q}$	A surface pressure gradient is required
Micropore Diffusion	$D = D_{c0} \exp(-E_a/RT)$	Size of diffusion molecules is equivalent to the pores

2.4 Isosteric Heat of Adsorption

Adsorption is an exothermic process. Hence, the Isosteric Heat of Adsorption, Q_{st} , is defined as the differential change in heat that occurs when an infinitesimal number of molecules are adsorbed at constant P , temperature T and pore surfaces or mass of adsorbent M_s . The isosteric heat of adsorption provides necessary information about the design of adsorption bed/heat exchanger for cooling, separation, purification and dehumidification applications. Mathematically, Q_{st} is expressed by the following equation [50, 69]

$$\begin{aligned} Q_{st} &\cong T v_g \left(\frac{\partial P}{\partial x_a} \right)_T \frac{\partial x_a}{\partial T} + R T^2 \left(\frac{\partial \ln P}{\partial T} \right)_{x_a} \\ &= T v_g \left(\frac{\partial P}{\partial x_a} \right)_T \frac{\partial x_a}{\partial T} + Q_{st|C-C} \end{aligned} \quad (2.16)$$

where the first term on the right-hand side represents the isosteric heat of adsorption of the adsorbed phase as a function of pressure gradient with respect to temperature. $Q_{st|C-C}$ is the isosteric heat of adsorption simplified from the classical van't Hoff equation, which is written as [70]:

$$\frac{\partial \ln K_{eq}}{\partial T} = \frac{\Delta H^\theta}{R T^2}. \quad (2.17)$$

Employing the Langmuir isotherm, the adsorbate is assumed to be an ideal gas with negligible volume effect during the adsorbed phase, $Q_{st|C-C}$ is written as [60]:

$$\frac{Q_{st|C-C}}{R T^2} = \frac{\partial \ln P}{\partial T}, \quad (2.18)$$

The trends of isosteric heats as a function of adsorbate uptakes are classified according to the three distinctive behaviours. The first one deals with the homogenous adsorbent in which a constant Q_{st} with increasing adsorbate loading is obtained. Secondly, Q_{st} decreases

with higher uptake due to the heterogeneity factors, and thirdly, Q_{st} may increase with adsorbate loading due to the stronger lateral interactions between adsorbate molecules at higher pressure. Generally, the isosteric heat is measured by a calorimetric method or adsorption isotherms data.

2.5 GCMC Simulation

The researches of adsorption process on MOFs employing GCMC are well established [71-75], especially on gas molecules [76, 77]. However, few articles related to water adsorption on various MOF structures for cooling applications are published. Water adsorption on MOF structure is a relatively complex process as water is a polar molecule. Therefore, both Coulombic and van der Waals interactions are considered [78].

To understand the interactions between the MOF structure and water molecules, the molecular dynamics (MD) study for MOF + water system is necessary as the results based on MD methods are quite accurate and time efficient. Water adsorption isotherms can be plotted by the GCMC simulation technique. Hence, the simulation is conducted on Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), distributed by Sandia National Laboratories [79]. As mentioned, water adsorption involves the complication of van de Waals and Coulombic forces. So, precisions of the interaction properties of the molecules for MOF + water systems are necessary.

2.6 Metal Organic Frameworks

Metal organic frameworks, a new class of micro porous materials, have drawn much attention for their good surface properties and micro pores structures [19]. These materials are created by the self-assembly of organic ligands with metal-containing nodes [80].

Applications such as gas storage, separation process or sorption based heat transformation have significant improvement with this new materials [19].

The focus of water adsorption behaviour on MOFs is mainly to achieve a unique performance of adsorption cooling and desalination applications. One advantage of the MOF + water system is its excellent water uptake – offtake difference between the operating pressure for adsorption chiller (1 kPa and 5 kPa for adsorption and desorption respectively). Relatively lower hydrophobicity of MOFs + water system shows the advantages of achieving higher water uptake – offtake difference per adsorption cycle with fast kinetics as compared with the conventional adsorbents such as silica gels and zeolites. The stability characteristics of MOFs with water allows the (MOF-water) system to attain high performance level after numerous adsorption – desorption cycles. Table 2.6 shows the various of MOF + water systems that have been conducted.

From the properties shown in Table 2.6, materials such as MIL-100(Fe) and MIL-101(Cr) provide the large surface area with higher pore structure, which also allows more water vapour to be adsorbed as pressure approaches to saturation. The MOFs with smaller surface area, on the other hand, have lower uptake. However, the stability of the adsorbents with smaller surface area is better than that of adsorbent materials with larger surface area.

Table 2.6: Adsorbents on water adsorption test

Adsorbent	Thermodynamics Properties	Uptake (kg/kg)	Properties after cycle test
MIL-100 (Fe)[18]	Surface Area: 1917 m ² /g pore volume: 1.00 cm ³ /g pore width: 25 Å and 29 Å micropore volume: 0.87 cm ³ /g	0.71	Uptake: -2.97% after 20 cycles, -6.37% after 40 cycles
MIL-100 (Al)[18]	Surface Area: 1814 m ² /g Pore volume: 1.14 cm ³ /g Pore width: 25 Å and 29 Å micropore volume: 0.65 cm ³ /g	0.45	Uptake: -4.51% after 20 cycles, -6.56% after 40 cycles
MIL-101 (Cr)[14]	Surface Area: 2059 m ² /g Pore volume: 1.103 cm ³ /g Pore width: 29 Å and 34 Å micropore volume: 0.99 cm ³ /g	0.936	Mass Loss: 1.9% after 20 cycles, 3.2% after 40 cycles
CAU-10[20]	Surface Area: 600 m ² /g Pore volume: 0.26 cm ³ /g Pore width: 5.6 Å	0.365	Slight decrement in uptake after 5 cycles
MOF-801-P[20]	Surface Area: 990 m ² /g Pore volume: 0.45 cm ³ /g Pore width: 7.4Å, 5.6Å, 4.8Å	0.45	Approximate 0.1 kg/kg of adsorbent decrement in uptake
HKUST-1[20, 81]	Surface Area: 1270 m ² /g Pore volume: 0.62 cm ³ /g Pore width: 0.6 nm, 0.9 nm	0.51	Significant decrease after 5 cycles
Aluminium Fumarate[16, 23, 82, 83]	Surface Area: 792 m ² /g Pore volume: 0.93 cm ³ /g Pore width: 6 Å, 11 Å	0.41	

2.6.1 Post Synthetic Modification

In a review by Wang and Cohen [84], in order to bypass the limitations of a certain MOF, chemical modification of the material is required after the synthesis. This method is known as Post Synthetic Method (PSM). The PSM consists of several methods, and these are non-covalent interactions, coordinative interactions, covalent bonds, tandem PSM, protonation and doping with metals. Table 2.7 illustrates the type of modification for MOFs

improvements. Most of the studies as mentioned in Table 2.7 have showed potential in improving the water adsorption properties by PSM. The modifications, however, have yet to achieve the desired water adsorption properties for adsorption cooling applications.

Table 2.7: PSM of MOF with sorption test performed

Adsorbent	PSM Method	Sorption Performed	Results
H ₂ N-MIL-125 [81]	Coordinative interactions	Water Sorption	Hydrophilic characteristics improve
ED-MIL-100(Cr) [85]	Coordinative interactions	Water Sorption	Lower water uptake, slight hydrophilic characteristics
EG-MIL-100(Cr) [85]	Coordinative interactions	Water Sorption	Better water uptake, slight hydrophilic characteristics
NH ₂ -MIL-101(Cr) [26]	Coordinative interactions	Water Sorption	Better water uptake with hydrophobic characteristics
NO ₂ -MIL-101(Cr) [26]	Coordinative interactions	Water Sorption	Reduce water uptake
DETA-MIL-101(Cr) [27]	Coordinative interactions	Water Sorption; CO ₂ Sorption	Improve hydrophilic characteristics; Better CO ₂ sorption at lower pressure
Li-MIL-101(Cr) [32]	Doping	Hydrogen Sorption	Increase H ₂ uptake, increase doping amount decrease uptake
Li-Zn based MOF [31]			
Na-Zn based MOF [31]			
K-Zn based MOF[31]			
MIL-101(Al)-NH ₂ [86]	Coordinative interactions	Water Sorption	Low water uptake with hydrophilic characteristics
MIL-101-GO [29]	Coordinative interactions	Water Sorption	Increase water uptake, optimum at 6% wt
UiO-66-SO ₃ -Li UiO-66-SO ₃ -Na UiO-66-SO ₃ -K UiO-66-SO ₃ -Rb [87]	Tandem Modification: Protonation and Doping	CO ₂ Sorption	Henry selectivity for CO ₂ is good for Li and Na doped at 0.15 molar ratio
MIL-100(Fe)@xerogel MIL-100(Cr)@xerogel MIL-101(Cr)@xerogel [28]	Covalent Bonds	Water Sorption	Reduces water uptake, hydrophilic characteristics at high relative pressure decreases, optimum with higher wt %

2.6.2 Modulation

Certain MOFs, such as MOF-801 (Zr Fumarate) and UiO-66 (Zr-BDC), have their particles attracted together after synthesis. This is known as agglomeration. This strong interaction between solid particles shows limitations towards water and oxygen adsorption [25]. This will also limit the amount surface area and pore structures for adsorption purposes.

The addition of carboxylic acid, such as formic acid and acetic acid, to the synthesis of MOF reduces agglomeration or performs aggregation to the material. This method is known as modulation, where the carboxylic acid acts as a modulator for the synthesised material. It is noted that modulation is able to enhance the synthesis process and forms individual crystal structure of the adsorbent material. Studies have shown that a decent amount of modulator added improves adsorption capabilities of the adsorbent material. Table 2.8 shows the types of modulator added to MOFs and describes the improvement made to the MOFs.

Table 2.8: Modulation of MOFs

Adsorbent	Modulator	Particles size	Results
MOF-801 [20, 25]	Formic Acid	150 nm	Reduces agglomeration to create single crystal structure. Hydrophobicity is reduced with higher uptake achieved at limited dosage
Cu ₂ (ndc) ₂ (dabco) [88]	Acetic Acid	400 nm (nanorod)	Promotes aggregation with improved N ₂ and CO ₂ adsorption
UiO-66 [24]	Benzoic Acid	200 nm	Forms single crystal structure by aggregation. Improves thermal stability and reduce surface area
UiO-67 [24]	Benzoic Acid	2 µm	Forms single crystal structure by aggregation. Thermal stability and surface area are improved

2.6.3 Hydrophobic Characteristic Length

Kim et al. [89] had studied the water uptake – offtake differences of AQSOA-Z01 with adsorption and desorption temperature of 30°C and 70°C respectively. The uptake difference is twice as compared to many silica gel materials. It was then suggested that adsorbents with low hydrophobic characteristic, shown in Figure 2.5, has an advantage of generating more cooling energy employing lower heat input to the system. This phenomenon is known as “**hydrophobic characteristic length**”.

Figure 2.5: Water adsorption of AQSOA Z01 and silica gel. The red line indicates the hydrophobic characteristics length of AQSOA-Z01 [89]

A detailed simulation study of adsorption cooling application adopting AQSOA zeolites were performed and shown in Appendix A [12]. The specific cooling power (SCP) of AQSOA-Z01 is optimal at the hot water and the cooling water inlet temperature of 70°C and 30°C, respectively. This would suggest that adsorbent material with low hydrophobic characteristic length between $0.1 \leq P/P_s \leq 0.2$ is ideal for design a low temperature driven adsorption cooling device.

2.6.4 Other Notable Works

Further research towards the synthesis of MOFs were performed to achieve strong crystallinity structure and adsorption properties. It is believed that organic ligands are the main factors that influence the adsorption properties and stability of MOFs. Hence, synthesis of new MOFs involves mixing or developing organic ligands were ongoing and results were positive in terms of adsorption capabilities and structure stability or both. Table 2.9 shows a list of MOFs that were synthesized based on new organic ligands and their porous properties.

Table 2.9: MOFs synthesis with new ligands

Metal	Organic Ligands	Results	Reference
Nickel Cobalt Copper Zinc	TMBDC-DABCO	Water sorption occurs at $0.2 \leq P/P_s \leq 0.4$ with a limiting uptake of 20 mmol/g. Stable structure is observed as water uptake remains unchanged after 20 cycles	[90]
	BTTB DMBPY	Hydrophobic properties as water sorption occurs at $P/P_s \geq 0.6$. Stable structure is observed as water uptake remains unchanged after 20 cycles	
Zirconium	Pyrene-based tetraopic	High surface area with good gas adsorption uptake. High thermal and water stability	[91]

2.7 Adsorption Cooling

Cooling applications adopting the adsorption method are widely studied. As mentioned before, the current adsorbent materials adopted for this application are various types of silica gels and zeolites. Studies have mentioned that these materials require high hot water temperature to generate constant cooling process. This is because the materials are mainly hydrophilic, and hence, it requires high amount of heat energy for desorption purpose. A

large quantity of the adsorbent material is required due to its low water uptake – offtake difference per cooling cycle. Figure 2.6 shows the performance of each adsorbent material adopted in cooling applications at cooling water inlet temperature and chilled water inlet temperature of 30°C and 14.8°C, respectively with half cycle time at 400s.

Figure 2.6: Conventional material for two bed adsorption cooling application [12]

It is clearly shown that certain materials such as silica gel (RD), CaCl₂-in-silica gel and zeolite 13X/CaCl₂ have good cooling capacity. However, the effective regeneration temperature for these materials is 80°C and above. Thus, a high amount of heat energy is required to achieve such regeneration temperature. It is shown that AQSOA-Z01 requires a relatively lower regeneration temperature (65°C) to perform cooling. Hence, the COP and SCP for AQSOA-Z01 adsorption cooling application are 0.45 and 0.33 respectively. It is noted AQSOA-Z01 produces a ‘S’ – shaped, or Type V, isotherm with a limiting uptake of 0.2 kg/kg. This signifies that AQSOA-Z01 has low hydrophobic property. An advantage of this material is to achieve a high water uptake – offtake difference with low regeneration temperature (65 to 70°C). This property helps achieving good adsorption cooling performance by adopting lower heat energy and smaller cooling system.

Other than the conventional two-bed system, studies have shown various methods to enhance the cooling capacity of an adsorption system, which are illustrated in Table 2.10.

Table 2.10: Various Adsorption Cooling system

System	COP	Cooling Capacity (kW)	Description
Two Stage System [92]	0.36	3.2	Reduce the hot water inlet temperature from 70°C to 55°C with cooling water and chilled water inlet temperature of 30°C and 14°C, respectively.
Three Bed System [33]	0.38	1.9	Improved COP when regeneration temperature at 80°C with cooling water and chilled water inlet temperature of 30°C and 14°C, respectively.
Two Stage System adopting different mass ratio [93]	0.26	4.2	Highest SCP with hot water inlet temperature between 55°C to 80°C with cooling water and chilled water inlet temperature of 30.2°C and 13.5°C, respectively with an adsorbent mass ratio of 2:1 (bottom:upper)
Mass Recovery [94]	0.25	4.5	Higher SCP with longer mass recovery time with cooling water and chilled water inlet temperature of 30°C and 14°C, respectively and hot water inlet temperature range from 55°C to 80°C
Multi Bed System [95]	0.45	4.5	Great increase in SCP with cooling water and chilled water inlet temperature of 30°C and 12°C, respectively and hot water inlet temperature range from 60°C to 80°C
Three Stage System [95]	0.2	2	Highest COP when regeneration temperature at 50°C with cooling water and chilled water inlet temperature of 30°C and 14°C, respectively
Three Bed Mass Recovery [96]	0.4	6.3	Increase COP by 35% when regeneration temperature at 60°C with cooling water and chilled water inlet temperature of 30°C and 14°C, respectively

Summary

The literature has shown solutions as provided by many investigators on the improvement of adsorption application systems. However, there are no experimental data for the newly developed MOFs and water-based adsorption chiller. It is believed that the development of the porous material can be further improved to achieve higher water uptake – offtake difference and faster adsorption kinetics. It is shown from Figure 2.6 that the improved adsorption properties of the zeolitic adsorbents have achieved better cooling performance than the current conventional adsorbents. Hence, a different methodology of synthesising the adsorbent, such as modulation, improves the adsorption properties by creating more distribution of micro pores. Another alternative is to modify the synthesised material by adding new reagent into the structure and increase interaction between the adsorbent and the adsorbate.

The next chapter begins with simulation studies for understanding water interactions in MOFs and modified MOFs to calculate water uptakes, from which one can design a new MOF or modify the currently available MOFs by dopants, modulation or green synthesis methods.

Chapter 3: Water Adsorption on MOFs: Theoretical Analysis

This chapter presents molecular simulations for understanding water adsorption on various MOFs namely MIL-101(Cr), Al Fum, alkali ions doped Al Fum and CAU-10. Hence, the grand canonical Monte Carlo (GCMC) simulations have been adopted to predict the amount of water uptakes from Henry's region to the saturated pressure. The algorithms GCMC simulations are well documented, and the standard methodology is applied to predict the adsorption isotherms for water and various MOFs systems. Water molecules in this process are assumed to be real gas. Hence, coulombic interaction force and the concept of fugacity are required for the simulation.

3.1 Simulation method

For example, the structure of Al Fum MOF is plotted schematically in Figure 3.1, where both the unit and supercell ($10 \times 10 \times 2$) are shown. By linking corner-sharing aluminium octahedras with fumarate, the monoclinic lozenge-shaped cell is formed. The distance between two Al Fum layers is $6.84 \text{ \AA}$ and the inclination angle is 122.55° . Secondly, to make the simulation model more reasonable, 36 (5%) ions pairs of LiCl has been inserted randomly to build the theoretical doped Al Fum model.

Figure 3.1: Both unit and supercell ($10 \times 10 \times 2$) structure for Al-Fum. Hydrogen atoms are omitted in supercell for clarity, where $a = 9.33 \text{ \AA}$, $b = 14.21 \text{ \AA}$, $c = 12.09 \text{ \AA}$.

Numerous water models such as SPC, SPC/E [97] or TIP4P [98] have been used extensively to predict water molecule behaviours for different systems, and each model can reflect some certain characteristics of water. It should be noted here that TIP3P model [97] is selected to represent bulk water. It specifies a 3-site rigid water molecule, where the Lennard-Jones parameters and charges are assigned to one oxygen atom and two hydrogen atoms. As the simulation process going, the H-O-H angle and the two O-H bonds are held rigid. Secondly, for simplicity, the SPC/E water model (angle between the hydrogen atoms at 104.5° with respective static equilibrium charge (q) [99]) is selected.

The water adsorption simulation is performed on three different MOFs: MIL-101(Cr), Al Fum and CAU-10. For the atoms of the MOF, the LJ potential will be based on UFF force field [100]. In GCMC, the temperature (T), volume of pores (V) and chemical potential (μ) are kept constant while the number of adsorbate molecules varies. The energetic interactions between adsorbate-adsorbent and adsorbate-adsorbate are calculated by the 12-6 Lennard Jones potential and Coulombic pairwise potential as shown in Equation (3.1).

$$\phi_{ij} = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{a_i} \sum_{b_j} \frac{c q_a q_b}{\varepsilon r_{ab}} \quad (r < r_c) \quad (3.1)$$

The first term on the right-hand side of Equation (3.1) represents the short-range Lennard-Jones interaction between two different sites molecules i and j . The second term is the long-range electrostatic interaction of all point charges in both adsorbent and adsorbate molecules (summation of charges a in molecule i and charges b in molecule j). The pairwise potential well depth (ε) and collision diameter (σ) are calculated by the Lorentz-Berthelot combining rules [101] ($\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ and $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$). For the Coulombic potential

part, C indicates the energy-conversion constant, r_c is the cutoff with a value of $13\text{\AA}$ and ϵ represents dielectric constant. The pairwise force field parameters are listed in Table 3.1 [72, 100].

As the water molecule is a polar molecule, the Coulombic interaction force should be taken into consideration for adsorption process. For simplicity, the Ewald summation is used to simulate the Coulombic interaction for water adsorption process with the MOFs [72, 78]. The Coulombic interaction can be known by satisfying this equation [102]:

$$E_{Coul}(\mathbf{r}^N) = \sum_j \sum_{l>j} \frac{e_j e_l}{4\pi\epsilon_0} \frac{\text{erfc}(\alpha|\mathbf{r}_{jl}|)}{|\mathbf{r}_{jl}|} \Theta(r_{cut} - |\mathbf{r}_{jl}|) + \frac{1}{2\pi V} \sum_{k \neq 0} \frac{1}{k^2} \exp\left[-\left(\frac{\pi k}{\alpha}\right)^2\right] \frac{1}{4\pi\epsilon_0} \cdot$$

$$\left| \sum_{j=1}^N e_j \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_j) \right|^2 - \frac{\alpha}{\sqrt{\pi}} \sum_j \frac{e_j^2}{4\pi\epsilon_0} - \sum_{j=1}^M \sum_{\kappa} \sum_{\lambda>\kappa} \frac{e_{j\kappa} e_{j\lambda}}{4\pi\epsilon_0} \frac{\text{erf}(\alpha|\mathbf{r}_{j\kappa j\lambda}|)}{|\mathbf{r}_{j\kappa j\lambda}|} \quad (3.2)$$

where Equation (3.2) is a summation of four terms: (1) real-space term, (2) Fourier-space term, (3) self-correction term and (4) intramolecular term.

Table 3.1: Lennard Jones Potential of atoms for MOFs and water molecules to perform GCMC simulation

Atoms	σ ($\text{\AA}$)	ϵ/k_B (K)
H_SPCE [72]	-	-
O_SPCE [72]	3.16	78.212
Carbon [100]	3.431	52.838
Oxygen [100]	3.118	30.193
Chromium [100]	2.693	7.548
Hydrogen [100]	2.571	22.142
Aluminium [100]	4.01	254.13

Periodic boundary conditions are applied in both x and y directions while the z direction is bounded (Figure 3.1). The type of moves for water molecules within the boundary includes random translation, rotation, insertion and deletion. The fugacity is assumed to be equal to the gas-phase pressure as water vapour is considered as an ideal gas under low pressure simulation conditions. Data acquisition begins after at least 20 million GCMC running steps for equilibrium consideration.

3.2 Results and Discussion

The molecular modelling of MOF + water systems at different pressure regions are illustrated in Figure 3.2. Water molecules (blue) interactions with different MOFs structure are shown at different pressure region which adsorption simulation occurs. It is observed that MIL-101(Cr) has relatively large crystal structure as compared to Al based MOFs. At Henry's region, the amount of water molecules interacting with MOFs are very minimal, especially for MIL-101(Cr) as water molecules tend to react minimally to the large cages of the structure. The increase of pressure improves the intramolecular interaction of MOF + water system, which enhances Coulombic interaction between adsorbent – adsorbate system. Given the large crystal structure, MIL-101(Cr) is able to adsorb more water molecules because of the large distribution of atoms. Thus, water adsorption onto MOF surface increases where water molecules start to surround the C atoms of the structure as C has better LJ potentials among the non-metal atoms. As the pressure approaches to saturation, water molecules start attracting with each other to increase the water uptake on the surface of the MOF. Hence, large molecular structure, such as MIL-101(Cr), tends to have higher water uptake due to its ability to adsorb more water molecules. At low pressure region, more water molecules are moved very slowly in the MOF frameworks. As the

pressure increases, some small cluster of 2-3 water molecules are formed. The cluster size depends on the water affinity to the framework, for example, bigger clusters (4-5 molecules) could be formed for silicalite with hydrophilic defect inside.

Al Fum (Fig 3.2 b) and CAU-10 (Figure 3.2 c), on the other hand, have smaller crystal structure. Al Fum has five identical diamond-like cages while CAU-10 has a square-like cage with other smaller cages surrounding it. From Figure 3.2 (b), water molecules interact within the five cages of Al Fum at different stages of adsorption, where C atoms are distributed at the sides of the cages. Al atoms, on the other hand, located at the edges of the cages adsorb water molecules at longer range and concentrated the water molecules interaction within all five cages. Water adsorption of CAU-10 shows attraction of water molecules at small cages located at all sides of CAU-10 structure. The adsorption improves as water molecules is attracted into the large square cage and interacts with C and Al atoms located at the inner sides of the square cage. Nonetheless, both MOFs achieves limited uptake as adsorbed water molecules attracts other molecules due to higher electrostatic interaction as pressure approaches saturation.

The simulated water adsorption isotherms on the selected MOFs are shown in Figure 3.3. The isotherms are generated between the pressures from Henry's region to saturated pressure. It is found that all three MOFs have shown a unique 'S' – shaped isotherm curve when interacting with water molecules. Thus, this shows that MOFs are hydrophobic at low pressure or humidity places. However, if placed at high pressure or humidity areas, high interaction between water molecules and MOFs increase the adsorption process and produce high water uptake.

Figure 3.2: MOF + water systems molecular structure at Henry's region (left), P/P_s at 0.5 (center) and P/P_s at 0.9 (right) for (a) MIL-101(Cr), (b) Al Fum and (c) CAU-10 MOFs

Based on the simulated isotherms shown in Figure 3.3, MIL-101(Cr) has good water adsorption uptake of 1.3 g/g of sorbent, while Al Fum and CAU-10 has decent water uptake of 0.43 g/g and 0.33 g/g respectively, which is also mentioned in Chapter 2. It is also noted that MIL-101(Cr) adsorbs water molecules at much higher relative pressure as compared to Al Fum and CAU-10. It is noted that the Al based MOFs (Al Fum and CAU-10) are simulated with short hydrophobic lengths. Thus, this suggest that Al based MOFs are

preferred as the next generation adsorbent material for adsorption cooling device given that (1) the hydrophobic characteristic lengths are simulated between $0.1 \leq P/P_s \leq 0.2$, (2) water uptake – offtake differences are simulated to be higher than that of AQSOA-Z01.

Looking at the isotherms curves, MIL-101(Cr) has relatively long hydrophobic characteristic length despite the high water limiting uptake. It is shown at Table 3.1 that the LJ potentials of Cr atoms are much lower than that of Al atoms. Thus, this may be the reason for Al based adsorbents to achieve low hydrophobicity.

Figure 3.3: Water adsorption isotherms on (a) MIL-101(Cr), (b) Al Fum and (c) CAU-10 based on GCMC simulation at 25°C

Employing GCMC simulation, the effects of alkali ions dopants and modulation on the parent MOFs can be observed. The simulated adsorption isotherms between Li ions doped and the parent Al Fum for the temperature of 303.15K are shown at Figure 3.4. It is found

that the doped Al Fum improves water adsorption uptake at low pressure region, i.e., the Li ions dopants decrease the hydrophobic characteristic length. Secondly AFI/CHA and Al Fum MOF composite adsorbents also decrease the hydrophobic length as compared with original MOF structure. All these results are presented in Figure 3.4.

Figure 3.4: Effects of dopants and zeolite composites on parent Al Fum MOF for water uptakes at low pressure region (relative pressure ranges from 0.1 to 0.25). The experimentally measured uptake for Al Fum + water at 30°C is also shown here for comparison purposes.

3.3 Summary

GCMC simulations show that post-synthesised works employing dopants or modulation of composite structure change the surface characteristics of MOF structure and enhance the water uptake rates at low pressure regions or at the operating conditions of an adsorption chiller. Based on simulation results, the surface structure of the original MOFs can be changed for various applications. The next chapter deals with the synthesis and surface modification of MOFs adsorbents.

Chapter 4: Experimental Investigation: Methodology

This chapter describes the synthesis procedures of various MOFs and their modifications employing doping, modulation and green synthesis. This chapter also discusses the SEM (Scanning Electron Microscopy), XRD (X-Ray Diffraction), TGA (Thermogravimetric Analysis), surface characteristics and isotherms/kinetics measurement techniques and procedures.

4.1 Synthesis Procedures

4.1.1 MIL-101(Cr)

The reagents for the synthesis were purchased from Sigma-Aldrich. MIL-101(Cr) was synthesised using hydrothermal reaction method, which is shown in Figure 4.1. First, 4 g of chromium (III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%) and 1.66 g of terephthalic acid ($\text{HO}_2\text{C}-(\text{C}_6\text{H}_4)-\text{CO}_2\text{H}$, 99%) were added into an autoclave reactor. 1 ml of concentrated hydrochloric acid (HCl) was added to the mixture after continuous stirring for 5 minutes, resulting into a dark green, viscous substance. Next, 50 ml of deionised water was then added into the reactor before heating the solution at 200°C for 10 hours. The solution was then separated by using a centrifugal spinning machine. After the separation, the synthesised material was mixed with N, N-dimethylformamide (DMF, 99.8%) and heated at 80°C to remove any unreacted terephthalic acid from the synthesised material. After heating and stirring for 5 minutes, the solution was then separated using the centrifugal spinning machine. The green synthesised material was obtained after drying the sample in an oven at 80°C.

Figure 4.1: Schematic for Synthesis of MIL-101(Cr) MOF

4.1.2 Al Fum MOF

Al Fum was synthesised through ambient pressure reaction method, which is illustrated in Figure 4.2. First, 2.45 g of aluminium chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 98%) and 1.4 g of fumaric acid ($\text{C}_4\text{H}_4\text{O}_4$, 99%) were added into a beaker. Next, 50 ml of DMF was added into the beaker to dissolve the solid reagents, and colourless solution was achieved. The solution was heated at 130°C with continuous stirring for four days. After four days of stirring, the formation of white precipitates was observed. Then, the solution was separated by using a centrifugal spinning machine. After that, the white, synthesised material was rinsed with acetone and methanol twice. Last, the synthesised material was dried in an oven at 80°C .

Figure 4.2: Schematic of Synthesis of Al Fum MOF

4.1.3 CAU-10 MOF

CAU-10 was synthesised through hydrothermal reaction method as shown in Figure 4.3. First, 4 g of aluminium sulphate hydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, 98%) was dissolved in 20 ml of deionised water. At the same time, 1 g of isophthalic acid ($\text{C}_6\text{H}_4(\text{COOH})_2$, 99%) was dissolved in 5 ml of DMF. Next, both solutions were added into an autoclave reactor and heated at 135°C for 12 hours in an oven. Then, the solution was separated using centrifugal spinning machine to retrieve the white synthesised material. Finally, the white synthesised material was purified in deionised water via sonication, and was dried in an oven at 80°C .

Figure 4.3: Schematic of Synthesis of CAU-10 MOF

4.2 Modifications of Parent MOF

4.2.1 Post – Synthesis Modification

Doping of alkali metal salt (LiCl, NaCl, KCl) was performed to the activated MIL-101(Cr) samples. The doping concentration was set at 5 wt%, 20 wt% and 40 wt% [103]. Before the modification, activation of MIL-101(Cr) MOF was performed to further remove any water vapour, DMF, unreacted terephthalic acid and other impurities from the material. In this process, MIL-101(Cr) MOF was placed in the vacuum oven for 3 hours at 150°C and was carried out under vacuum condition.

For doping of MIL-101(Cr) MOF, at first, 5 g of activated MIL-101(Cr) sample was placed into 100 ml of hexane suspension with continuous stirring. While stirring, alkali metal salt solution was added into the suspension. The alkali metal salt solution consists of alkali metal salt (LiCl, NaCl or KCl) at different weight concentration (5%, 20%, 40%) with 1ml deionized water. After thirty minutes of continuous stirring, the hexane suspension was removed and the doped MIL-101(Cr) MOFs were dried in an oven at 80°C.

4.2.2 Modulation with Formic Acid

Modulation of Al Fum MOF with formic acid was performed as this method had been proven to achieve MOF structure with less agglomeration [25]. This method was also reported to reduce the duration of the synthesis process of MOFs. In Chapter 2, this method suggested that formic acid is a by-product from the decomposition of DMF and water. Hence, adding formic acid as the modulator of the synthesis provides the availability of water molecules for the formation of Al Fum crystals. Nonetheless, formic acid modulation of Al Fum MOF has been performed here for the first time to improve the kinetics of water molecules [104].

Modulated Al Fum MOF was synthesised through ambient pressure reaction method. First, 2.45 g of aluminium chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 98%), 1.4 g of fumaric acid ($\text{C}_4\text{H}_4\text{O}_4$, 99%) and 50ml of DMF were added into a beaker. Next, formic acid at different volume (5 ml, 10 ml, 15 ml) was added into the solution. Then, the solution was heated at 130°C with continuous stirring for two days. After that, the solution was separated via a centrifugal spinning machine. At last, the white, synthesised material was rinsed with acetone and methanol twice and was dried in an oven at 80°C.

4.2.3 Green Synthesis of Al Fum

The synthesis process of Al Fum MOFs involves hazardous solvent such as DMF. This would cause harmful environmental effects if Al Fum MOF is synthesised at an industrial-scale. “Green” synthesis method adopting less a harmful solvent, such as water, is essential for the large-scale production of these materials to prevent the harmful substances release to the environment. Hence, a “green” synthesis method has been carried out for Al Fum MOF. This synthesis has been conducted here for the first time.

The synthesis adopted the ambient pressure reaction method. 6.66 g of aluminium sulphate hydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, 98%) was dissolved in 25 ml of deionized water. Subsequently, 2.32 g of fumaric acid ($\text{C}_4\text{O}_4\text{H}_4$, 99%) and 2 ml (50% wt) of NaOH solution were mixed in 25 ml of water and stirred in a beaker. The fumaric acid solution was added to aluminium sulphate solution dropwise, creating a clear solution. The mixture was stirred continuously at 90°C on a hotplate for 60 min. White precipitate was observed, indicating the formation of Al Fum crystals from the reaction. The reaction was separated through a centrifugal spinning machine. Then, white, synthesised material was rinsed three time with deionised water. The synthesized material was dried in an oven at 80°C.

The addition of NaOH solution forms the deprotonation of fumaric acid and assists the latter to dissolve in water body. Hence, the hazardous solvent such as DMF is not required to dissolve the fumaric acid at high temperature for the formation of Al Fum crystals.

4.3 Characterisation Procedures

The synthesised materials were characterised to evaluate the shape, size, structure integrity, thermal stability, and surface and porous properties of synthesised MOFs.

X-Ray Diffraction:

Powder X-Ray Diffraction (XRD) provides information about the phase identification and crystal structure. The measurements were conducted using Shimadzu XRD-6000 diffractometer with a step size of 0.02° using monochromatic CuK_α radiation (wavelength = 0.154 nm) operating at 40 kV and 40 mA. During the experiment, the incident beam of X-Rays is projected into the crystal structure of the MOFs. The beam is then diffracted after getting contact with the atoms of the MOFs and projected on receiving slit. The intensity of the beam evaluates the crystallinity of the MOF structure.

Scanning Electron Microscopy:

The Scanning Electron Microscopy (SEM) shows the morphology and size of the adsorbent specimen. Energy Dispersive Spectrometry (EDS) is used for the elemental analysis of the specimen. During experimentation, the images of MOF structures were captured by JEOL JSM-5600LV Field Emission Scanning Electron Microscopy (FESEM) operating at 5 kV. Since the adsorbents were non-conductive, a layer of conducting material was coated on the material.

Transmission Electron Microscopy:

Transmission Electron Microscopy (TEM) provides nano-scale images and observation of any distinct feature on the MOFs. The experiment was performed by JEOL-2100Plus TEM equipment with an operating voltage of 200 kV. Before the commencement of the experiment, the powder MOFs were dispersed in isopropanol and placed in a carbon coated TEM sample grid.

Thermogravimetric Analysis:

The thermal stability of the samples is characterised by a thermographic analyzer (TGA) under a constant flow of air. Generally, the porous samples are stable if mass loss is not observed. Experiments were performed using TGA Q500 instrument. The powder sample was heated up to 550°C at a ramp rate of 10°C per min under oxygen flow. Weight loss of the material was measured as a function of temperature.

Surface and Porous Characteristics:

The surface and porous characteristics of MOFs were measured by N₂ adsorption/desorption isotherms at 77K using Autosorb iQ instrument (Quantachrome Instruments). Prior to the experimentations, the MOFs were dried at 120°C for 3 hours in vacuum condition to remove any foreign gases or vapours adsorbed on the surface of the samples. The MOFs were then submerged in liquid N₂, via a bulb cell, to perform the N₂ adsorption, a schematic diagram of the experiment is shown in Figure 4.4. The isotherm data were equipped with BET (Brunner-Emmet-Teller) isotherm model to determine the BET surface area of the samples. Under saturation, the isotherm curve determines the total pore volume of the MOFs. If a sharp increment of N₂ uptake is observed at $P/P_s = 1$, macro pores are present in the structure. Otherwise, the isotherm curve is nearly horizontal as P/P_s approaches to one. Since N₂ is saturated at $P/P_s = 1$, the total pore volume of MOFs is equivalent to the liquid N₂ that are occupying the pores of the samples. Hence, the total pore volume of MOFs can be estimated by calculating the volume of saturated N₂ (V_{liq}) adsorbed by the samples using the following equation

$$V_{liq} = \frac{P_a V_{ads} V_m}{RT}, \quad (4.1)$$

where V_{ads} is the volumetric uptake of N_2 , V_m represents the molar volume of liquid N_2 ($3.47 \times 10^{-5} \text{ m}^3/\text{mol}$), P_a and T are ambient pressure and temperature, respectively. Adopting the estimated total pore volume and BET surface area, the average pore size (r_p) can be determined by

$$r_p = \frac{2V_{liq}}{A_s} \quad (4.2)$$

Figure 4.4: Schematic diagram of the N_2 adsorption experiment

Isotherm and Kinetics measurements:

The isotherms and kinetics measurements for water adsorption on MOFs were carried out by a gravimetric analyser at various temperatures and pressures, and the schematic is shown in Figure 4.5. Hence, MOFs were dried in an oven at 120°C until there is no change in mass was observed before the commencement of the measurement. The sample cell, together with the dried MOF, was held freely inside the adsorption chamber by a microbalance, known as the Balance Head. The isothermal environment of the MOF

adsorbent was maintained by the direct radiant heating where heaters were placed outside the hermetic reaction chamber and homogenised by a waft of cooling air through the non-hermetic gap between the chamber and radiant heater. The dry MOF mass was confined in the chamber by direct heating of 65°C with continuous supply of dry N₂(99.999% purity). The Balance Head temperature was set at 15°C higher than experimental condition to prevent any chances of condensation of water vapour in the chamber. Dry nitrogen was supplied into the chamber to ensure the buoyancy effect of balance was kept.

The pressure and temperature sensors were calibrated before the experimentation for precise measurement. Water vapour generated from the humidifier was transferred to the adsorption chamber for adsorption experiment. The mass change of the MOFs was recorded as a function of time in terms of the initial pressure and set point temperature under equilibrium conditions. The pressure was increased stepwise and the water vapour uptake was measured for each pressure step till the saturated condition. Therefore, a set of water isotherm data measured from Henry's region to saturated region under equilibrium condition was recorded. Prior to the next isotherms and kinetics measurements, the MOF adsorbent in the sample cell was regenerated and purged with the supply of dry N₂. Water vapour entered the adsorption chamber (from the humidifier) for adsorption experiment. The next equilibrium uptake was measured by having the built-in-controller to increase the pressure stepwise, until a set of isotherm data of another temperature is recorded. The measurements were conducted at least three times to minimise the uncertainties of the experimental data.

The water equilibrium uptake was recorded based on the measured mass of the balance at given temperature and pressure. The balance shows the initial dry mass of the adsorbent,

$M_s(P_{ini}, T)$ where P_{ini} is the initial pressure. During the adsorption process, the mass of the MOFs increased as the water molecules were adsorbed, which depends on pressure and time. The mass of the MOFs, under equilibrium condition, becomes $M_s(P_j, T)$, where subscript j represents each pressure point. The amount of water vapour adsorbed, m_a , is determined by

$$m_{a,j} = M_s(P_j, T) - M_s(P_{ini}, T). \quad (4.3)$$

Thus, the gravimetric water uptake is calculated by

$$q_j = m_{a,j} / M_s(P_{ini}, T). \quad (4.4)$$

For dynamic measurements, the change in water uptake was recorded with respect to time, at given temperature and pressure, until the water adsorption process reaches steady state.

Hence, the dynamic water uptake is expressed by

$$\frac{\Delta \theta_t}{\Delta \theta} = \frac{M_s(P_j, T, t) - M_s(P_{ini}, T)}{M_s(P_j, T) - M_s(P_{ini}, T)}. \quad (4.5)$$

Figure 4.5: Schematic for Gravimetric Water Adsorption Analyzer for isotherms and kinetics measurement

This chapter has shown the synthesis and modification procedures of MOFs and the methodologies for characterisation on these adsorbents. The next chapter focuses on the results about the surface characterisation, isotherms and kinetics of MOFs + Water systems, which have been obtained by applying the methodologies as presented in the chapter.

Chapter 5: Experiments: Results and Discussion

The MOFs that were originally synthesised (as discussed in Chapter 4) were characterised by N₂ and H₂O adsorption methods. Hence, the surface characteristics of the synthesised MOFs were evaluated at first by SEM, XRD, TGA and N₂ adsorption/desorption methods. Later, H₂O uptakes on MOFs were measured for temperatures ranging from 25°C to 60°C and pressures up to saturated conditions. In this chapter, MIL-101(Cr), alkali dopants with MIL-101(Cr), Al Fum, modulated Al Fum and CAU-10 MOFs are considered as these adsorbents are suitable for the design and development of adsorption assisted cooling and dehumidification applications.

5.1 Characteristics of MIL-101(Cr), Al Fum and CAU-10 MOFs

5.1.1 Porous Characteristics

Figure 5.1 shows the SEM images of the parent MOF samples, from which it is observed that the size of MIL-101(Cr) MOF crystal is approximately 1 μm . Due to various compositions, the shapes of MOF structure rely on how the metal nodes are connected with the organic ligands. The size of the Al Fum sample is about 1 μm with quadrahedral shape. The shape synchronizes with the molecular structure of Al Fum. Hence, this proves that Al Fum was synthesised correctly. It is noted the particles in Al Fum MOF have a strong agglomeration, which is similar to MOF-801 structure [24, 25]. The SEM images of MIL-101(Cr) and CAU-10, on the other hand, show the individual crystals for elaborating the physical geometry of the particles. The cube-like structure is observed for CAU-10 sample with the crystal length of about 1 μm .

Figure 5.1: SEM images of MIL-101(Cr) (left), Al Fum (middle) and CAU-10 (right)

Figure 5.2 shows the powder XRD plots for these parent MOFs. At first, the synthesised MIL-101(Cr) MOF was analysed by XRD to verify its identity. The diffraction peaks corresponding to reflection planes are indexed, which are consistent with the peak positions as reported for standard MIL-101(Cr) structure, indicating that the synthesised material has the MIL-101(Cr) phase having good crystallinity. The intensity peaks appearing at small angles (2θ) in the XRD pattern indicate that this porous material possesses abundant pore in the structure. In fact, MIL-101(Cr) possesses two types of inner cages with inner diameters of 29 and 34 Å, respectively (Figure 5.2a). The intensity of the MIL-101(Cr) is found at lower angle as compared to that of Al Fum and CAU-10. This is due to that fact that MIL-101(Cr) consisting mainly of Cr metal nodes, provides strong crystallinity structure between smaller spacing. The Al based MOFs, on the other hand, have the highest peak at the angle 2θ of 8° (Figure 5.2b), suggesting the spacing of atoms are relatively small. The peaks also correlate the intensity of Al^{3+} in the adsorbent structure. The sharp peaks indicate larger crystallite size, which is also true for CAU-10 (Figure 5.2c).

Figure 5.2: XRD plots for (a) MIL-101(Cr), (b) Al Fum and (c) CAU-10

Figure 5.3 shows the TGA graphs for understanding the thermal stabilities of MIL-101(Cr), Al Fum and CAU-10 MOFs. It should be noted that each sample begins at different starting temperatures during TGA experimentation. All three samples as presented in Figure 5.1 experience similar stages as temperature increases. The first decrement of mass is occurred due to the desorption of water vapour from the outer cages of the materials. From the TGA results, it is observed that both MIL-101 and CAU-10 MOFs trap more water vapour in the outer cages of the structure as compared to Al Fum MOF. For MIL-101(Cr), the second step weight loss at the temperature of 300°C corresponds to the loss of water molecules from middle-seized cages ($\sim 29\text{\AA}$). The third stage weight loss ($\sim 25\%$) is occurred at 350°C relates to the decomposition of benzene dicarboxylate (BDC) linker of MIL-101(Cr) MOF

structure and results Cr_2O_3 as residue. It is observed that MIL-101(Cr) desorbs water vapour faster than the Al based MOFs because of larger pore size. The mass decrement at the final stage for both Al Fum and CAU-10 MOF implies the decomposition of MOF linker. Hence, Al Fum and CAU-10 MOFs are collapsed at temperatures of 460°C and 590°C respectively. These results also suggest that CAU-10 has the highest thermal stability among three adsorbents.

Figure 5.3: TGA (Thermo-gravimetric analyser) curves showing the stability analysis of parent MIL-101(Cr), Al Fum and CAU-10 MOFs

Figure 5.4 shows N_2 adsorption isotherms for the synthesised MOFs at 77 K, from which one can observe that MIL-101(Cr) possesses the highest volumetric N_2 uptake as compared with the Al based MOFs. The specific surface area of MIL-101(Cr) is calculated as $3402 \text{ m}^2/\text{g}$ (BET method) and $4688 \text{ m}^2/\text{g}$ (Langmuir method), respectively. The total pore volume (V_p) of MIL-101(Cr) is $1.59 \text{ cm}^3/\text{g}$ at the relative pressure (P/P_s) of 0.98. Secondly, the volumetric N_2 uptake on Al Fum at saturated pressure region are greatly increased from $422 \text{ cm}^3/\text{cm}^3$ to $1414 \text{ cm}^3/\text{cm}^3$, which indicates the large existence of macro pores inside

Al Fum MOF structure. Thirdly, CAU-10 has the smallest BET surface area and pore volume.

Figure 5.4: N₂ isotherms on various MOFs ranging from Henry's region to saturated pressure at 77 K.

Figure 5.5 illustrates the pore size distribution (PSD) of MIL-101(Cr), Al Fum and CAU-10 MOFs. It is found that Al Fum has the highest micro porous distribution of 5 Å among these three adsorbents as shown in Figure 5.5). In the case of Al Fum MOF, the smallest pores are estimated to have a width of 6 Å. Subsequently, the next two peaks are estimated with a width of 7 Å and 11 Å. This means that Al Fum MOF consists of a majority of micropores throughout its surface. On the other hand, the pore distribution of CAU-10 is relatively low despite having distribution peaks in the micro pore regions.

Further comparison is prepared with the surface and porous properties as shown in Table 5.1. It is obvious that MIL-101(Cr) has the highest surface and porous measurements given its high volumetric N₂ uptake and high meso porous distribution. Thus, the surface and

porous properties of MOFs are proportional to the N₂ isotherm and pore size distribution of the MOF structure.

Figure 5.5: Pore Size Distribution of three assorted MOFs ranging from micro to mesopores

Table 5.1: Surface and porous characteristics for MOFs

Adsorbent	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Radius (Å)
Al-Fum	792.26	0.926	10.91
CAU-10	553.32	0.22	10.82
MIL-101	3402.69	1.597	11.3905

5.1.2 Isotherms and kinetics for Water Adsorptions

Figure 5.6 shows the water adsorption isotherms of MOFs (MIL-101(Cr), Al Fum and CAU-10) for the temperatures from 25°C to 60°C and pressures up to 6 kPa. Hence, MIL-101(Cr) has the highest water uptake as compared to that of Al Fum and CAU-10 MOFs. Due to the high surface area and the larger meso-pore distribution, MIL-101(Cr) has the potential to achieve higher water vapour uptake at relatively higher pressures. At low pressure regions (P/P_s from 0.1 to 0.3), the water uptake is very small for MIL-101(Cr)

MOF + water system, which is not recommended for cooling applications. On the other hand, Al Fum and CAU-10 have lower hydrophobic characteristic lengths, which are observed at 0.6 kPa and 0.5 kPa under adsorption condition at 25°C. Therefore, it is believed that the high dominance of micro pores distribution has slight effect towards the hydrophobic characteristics of the adsorbents. High distribution of micro pores suggests that water molecules are fully adsorbed and occupied the micro pore volume at lower relative pressure. Thus, larger pore distribution, such as MIL-101(Cr), requires higher relative pressure for the meso pore volume to be fully adsorbed with water molecules, which explains the higher hydrophobic characteristic length. As mentioned before, the working pressure of adsorption bed for cooling application is preferred at 1 kPa and 5 kPa for adsorption and desorption process, respectively. Thus, looking at the uptake difference shown in Figure 5.6, MIL-101(Cr) has the least difference of 0.003 g/g, suggesting poor performance for cooling application despite having the highest water uptake. For the adsorption chiller operating ranges, the amount of water transfer per adsorption – desorption cycle is found higher for Al Fum and CAU-10 MOFs (Figure 5.6). The experimentally measured isotherms data are fitted with Sun-Chakraborty isotherm model equation [1] within acceptable error ranges ($\pm 5\%$ error), and the thermodynamic parameters are provided in Table 5.2. The isosteric heat of adsorption at zero surface coverage (Q_{st}^*) for MIL-101(Cr) is the lowest with high heterogeneity factor (m) among the MOFs. It is noted that shorter hydrophobic characteristic length shows higher isosteric heat of adsorption (Q_{st}^*) and lower heterogeneity factor (m) values.

Figure 5.6: Water Adsorption isotherms for (a) MIL-101(Cr), (b) Al Fum and (c) CAU-10 MOFs. The red dotted lines represent the isotherm equation fitted with experimental data.

Table 5.2: Thermodynamic parameters of adsorption isotherm equation for the three assorted MOFs + water

MOF	$Q_{st}^*(\text{kJ/kg})$	m	α	$q_m (\text{g/g})$
MIL-101	2670	9.55	6.75×10^{-4}	1
Al-Fum	2780	6.5	6.78×10^{-4}	0.407
CAU-10	3030	5	9.7×10^{-7}	0.298

Figure 5.7 shows the water adsorption kinetics of MOFs measured at the operating pressure and temperature condition for low heat adsorption cooling system ($P = 1 \text{ kPa}$, $T = 25^\circ \text{C}$ for adsorption and $P = 5 \text{ kPa}$, $T = 60^\circ \text{C}$ for desorption) as a function of time up to 3000 s. At 25°C , it is observed that Al Fum captures the faster kinetics among the MOF samples under the working condition of same temperature and pressure. This may be due to the higher distribution of micro pores, which allows more water vapour to be adsorbed at low pressure, filling up the micro pore volume. This also agrees with the slower water

adsorption kinetics of MIL-101(Cr) and CAU-10 due to the lower distribution of micro pores. At 60°C, the rate of change of water vapour for MIL-101(Cr) is faster. The experimental data is fitted with the kinetic model based on Langmuirian analogy (Equation 2.15) for understanding the interactions of water on MOF structures. Table 5.3 shows the estimated parameters related to the adsorption kinetics of MOFs + water systems. The Langmuir constant, K , is determined on the basis of the thermodynamics parameters as furnished in Table 5.2 while the coefficient of k_{ads} is associated with the BET surface area of the MOFs. The activation energy for each MIL-101 + water pair shows large energy involved during the interaction between MIL-101(Cr) with water molecules. This would suggest the generation of higher activation energy with respect to pressure and temperature. The activation energy ranges between 33 kJ/mol and 37 kJ/mol.

Figure 5.7: Water adsorption kinetics for (a) MIL-101(Cr), (b) Al Fum and (c) CAU-10. Hence, the experimental data are fitted with kinetics model based on Langmuirian analogy.

Table 5.3: Parameters for kinetics modelling based on Langmuirian analogy for MOF + water pair

System	K	k_{ads} (1/s)	β_o	E_a (J/mol)
MIL-101 + Water	5004 @ 298K 949 @ 333K	$63160.73 \left(\frac{\beta_o \cdot P}{\sqrt{T}} \right) \exp \left(\frac{-E_a}{RT} \right)$	1	43,220
Al-Fum + Water	5796 @ 298K 1082 @ 333K	$14705.93 \left(\frac{\beta_o \cdot P}{\sqrt{T}} \right) \exp \left(\frac{-E_a}{RT} \right)$	1	34,690
CAU-10 + Water	1832 @ 298K 194 @ 333K	$10270.73 \left(\frac{\beta_o \cdot P}{\sqrt{T}} \right) \exp \left(\frac{-E_a}{RT} \right)$	1	36,700
<p>$K = k_{ads}/k_{des}$. Hence the pressure P is in Pa and the temperature T is in K.</p> <p>The isotherm coefficient K is obtained from Sun-Chakraborty isotherm model [1]</p>				

5.2 Doped MIL-101(Cr)

Figure 5.8 shows the SEM images of parent MIL-101(Cr) and doped MIL-101(Cr) MOFs with 5% wt, 20% wt and 40% wt of alkali salt (Li^+ , Na^+ , K^+) impregnated into the structure. These images show the morphologies of all doped samples, which are observed to be similar to the parent MIL-101(Cr) adsorbent. The octahedral shaped particle size is within $1 \mu m$ and the images show no disorientation of MIL-101(Cr) from doping of alkaline metal ions.

Figure 5.9 shows the XRD graph of the doped MIL-101 samples with comparison of the parent material. These graphs are categorised at different weight percentages doped into the structure. At low 2θ angles, the peaks of all MOF adsorbents are relatively similar to the structure. At low 2θ angles, the peaks of all MOF adsorbents are relatively similar to the parent MIL-101(Cr). It is observed that 20% wt of (Li^+ , Na^+ , K^+) salt samples have no significant differences in the peaks. This suggests that the 20% wt doped MIL-101(Cr) MOF provides the similar characteristics as compared with the parent MIL-101(Cr) MOF adsorbent. At 40% wt doped alkali ions (for Na and K doped MIL-101Cr) samples), small peaks are observed at higher angles.

Figure 5.8: SEM of (A) Original MIL-101(Cr), (B) 5% Li-MIL-101(Cr), (C) 5% Na-MIL-101(Cr), (D) K-MIL-101(Cr), (E) 20% Li-MIL-101(Cr), (F) 20% Na-MIL-101(Cr), (G) 20% K-MIL-101(Cr), (H) 40% Li-MIL-101(Cr), (I) 40% Na-MIL-101(Cr), (J) 40% K-MIL-101(Cr)

This shows that the spaces in between atoms are disrupted, and the material structure integrity is disintegrated by doping 40% wt of alkali metal ions, which includes Li doping as Li ions are probably too small to be detected. Hence, the concentrations for doping are suggested to be 20% or less for optimum performance. However, the XRD plot for 5% wt doped alkali ions show the additional peaks at higher angle. The only difference, as compared to 40% wt doped, is the trend of the peak for 5% wt doped occurs at similar 2θ angles, suggesting that unreacted terephthalic acid is not purified from the parent MIL-

101(Cr) that were used for 5% wt doping. Nonetheless, 5% wt doping should not disintegrate the molecular structure of the adsorbent material.

Figure 5.9: XRD plots for 5% wt (top), 20% wt (middle) and 40% wt (bottom) alkali ions (Li^+ , Na^+ , K^+) doped MIL-101(Cr)

Figure 5.10 shows the TGA results for 5% wt and 20% wt doped MIL-101(Cr) MOFs.

Hence the alkali doped samples experienced a huge decrement in weight for the

temperatures ranging from 35°C to 130°C. This is due to the fact that the loss of water molecules from the outer cage of the MOF structure. Later, gradual steady decrease of weight is occurred at 130°C, indicating the loss of water molecules in the inner cage of the MOF structure. Finally, a steep drop in mass is due to the loss of water vapour from the inner cage and the decomposition of the MOF molecular structure itself. Based on the results as shown Figure 5.10, 20% wt doped samples provide better thermal stability as compared with the original MIL-101(Cr) as the molecular structure is decomposed at higher temperature while 5% wt doped samples are experienced decomposition at slightly lower temperature. However, it is observed that 5% wt Li and Na doped samples retained more water vapour at the outer cage of the structure. At higher temperature (> 335°C), the weight loss is occurred, and the structure of doped samples is collapsed at the temperature higher than 400°C. Hence, thermal stability of the parent MIL-101(Cr) is improved by the doping process.

Figure 5.10: Thermo-gravimetric analysis (TGA) for (a) 5% wt and (b) 20% wt doped MIL-101(Cr). The alkali ions doped MIL-101(Cr) MOFs are compared with the parent MIL-101(Cr)

Figure 5.11 shows the N₂ isotherms of 5% wt doped MIL-101(Cr) MOFs. Based on the graph, the N₂ uptakes for doped MIL-101(Cr) MOFs are lower as compared to the parent

MIL-101(Cr) MOF. K-MIL-101 has the lowest uptake among the doped samples due to K^+ ions are relatively larger than Li^+ and Na^+ ions. Thus, these large K^+ ions may have obstructed the N_2 atoms from entering the pores of the adsorbent. The N_2 isotherms data are used to determine the surface and porous characteristics of doped MIL-101(Cr) MOFs, which is illustrated in Table 5.4, from which the surface and porous characteristics for MIL-101(Cr) decreases after doping of alkali metal ions. This is due to the constriction of pore structure by the alkali metal ions.

Figure 5.11: N_2 isotherms of 5% wt doped MIL-101(Cr) at 77.4 K

Table 5.4: Surface and porous properties of parent and 5% wt doped MIL-101(Cr) MOFs

Samples	Surface area(m^2/g)	Pore Volume (cm^3/g)	Average Pore Size ($\text{\AA}$)
MIL-101(Cr)	3402	1.59	11.39
Li-MIL-101(Cr) (5% wt)	2054	0.94	11.39
Na-MIL-101(Cr) (5% wt)	2000	0.91	11.43
K-MIL-101(Cr) (5% wt)	1547	0.72	11.37

Figure 5.12 shows the pore size distribution of the doped MIL-101(Cr) MOFs. From there, it is observed that the distribution for doped MIL-101(Cr) MOFs is lower as compared to

parent MIL-101(Cr) MOF. It is believed that higher micro pore distribution ($< 5\text{\AA}$) for doped MIL-101(Cr) MOFs is possible due to the decrement of meso pores distribution and the addition of alkali metal ions. Therefore, doping of alkali metal ions would be a recommended modification method to achieve a decent ‘S’ – shape water adsorption isotherm [105].

Figure 5.12: Pore size distribution of 5% wt alkali metal doped MIL-101(Cr) MOFs with parent MIL-101(Cr) MOF

Figure 5.13 shows the water adsorption isotherm of the 5% wt doped MIL-101 MOFs with the parent MIL-101(Cr) for pressures ranging from Henry’s region to saturated pressure at temperature of 25°C . It is observed that the limiting water uptake of doped MIL-101(Cr) MOFs is lower, especially for K-MIL-101, as compared to that of the parent MIL-101(Cr). However, the hydrophobic characteristic lengths of doped MIL-101(Cr) MOFs are relatively shorter as compared to the parent MIL-101(Cr) MOF. With the addition of 5% wt Li, Na and K dopants, the hydrophobic length in the low relative pressure region is reduced and the water uptake at high relative pressure is lowered. From here, it is believed

that higher concentration of Li^+ ion will increase the water uptake at low pressure region due to the hydrophilic behaviours of Li dopants. Thus, it is believed that the pore distribution highly correlated to the decrement of water uptake for MIL-101(Cr) MOF. It should be noted that Li and Na doped MIL-101(Cr) MOFs have better water isotherms data than those of K-doped MIL-101(Cr) MOF.

Figure 5.13: Water adsorption isotherms of 5% wt doped MIL-101 MOFs with parent MIL-101(Cr) MOF at 25°C

Figure 5.14 shows the water adsorption isotherms of MIL-101, Li-MIL-101 (5% wt) and Na-MIL-101(5% wt) at the temperatures ranging from 25°C to 60°C with pressures up to saturated condition. From here, it is observed the water uptake – offtake difference for Li-MIL-101(Cr) MOF (5% wt) between 1 kPa and 5 kPa is observed at 0.2 g/g of sorbent, which has significant increase as compared to parent MIL-101(Cr), shown in Figure 5.6(a). It should be noted that all the isotherms data are fitted with Sun-Chakraborty isotherm model (Equation 2.6) to further understand the ‘S’ – shaped isotherm curves. The proposed model matches with experimental data within 5% to 10% error ranges, and the isotherm parameters are shown in Table 5.5. It is shown that the dopants affect the heterogeneity

factor while Q_{st}^* are nearly the same. Hence, this would suggest the heterogeneity factor is directly related to the hydrophobic length of MIL-101(Cr) MOFs + water systems.

Figure 5.14: Water adsorption isotherm of (a) MIL-101, (b) Li-MIL-101 (5% wt) and (c) Na-MIL-101 (5% wt) fitted with isotherm model [1] at temperatures 25°C (◆), 35°C (■), 45°C (▲) and 60°C (●).

Table 5.5: Thermodynamic parameters of Sun-Chakraborty isotherm model for MIL-101(Cr) MOFs + water pairs

MOF	Q_{st}^* (kJ/kg)	m	α	q_m (g/g)
MIL-101	2670	9.55	6.75×10^{-4}	1
Li-MIL-101 (5% wt)	2780	5.4	6.78×10^{-4}	0.95
Na-MIL-101 (5% wt)	2700	8.3	9.78×10^{-4}	0.89

Figure 5.15 shows the adsorption kinetics for MIL-101(Cr), Li-MIL-101(Cr) (5% wt) and Na-MIL-101(Cr) (5% wt) MOFs + water systems for the temperatures of 25°C and 60°C. The relative pressures are considered with respect to the adsorption bed operating conditions for adsorption cooling. It is noted that at 25°C, the 5% wt doped MIL-101(Cr) MOFs require less time to achieve equilibrium uptake as compared to MIL-101(Cr) MOF.

This proves that the 5% wt doped MIL-101(Cr) MOFs have better water interaction behaviour than the parent MIL-101 MOF, due to more micro-pore distributions. The experimental kinetics data as shown in Figure 5.15 are fitted with the kinetics model based on Langmurian analogy (red line) and the kinetic-parameters are evaluated. The kinetics coefficient k_{ads} , and parameters are furnished in Table 5.6. It is shown that the activation energy for doped MIL-101(Cr) MOFs is lower as compared to the parent MIL-101(Cr). Thus, this would suggest that lower activation energy shows the faster kinetics.

Figure 5.15: Water adsorption kinetics of MIL-101, Li-MIL-101 (5% wt) and Na-MIL-101 (5% wt) fitted with Langmurian analogy kinetic model at (a) 25°C and (b) 60°C

Table 5.6: Parameters of kinetics model based on Langmuirian analogy for MIL-101 MOFs + water pair

System	K	$k_{ads} (1/s)$	β_o	$E_a (J/mol)$
MIL-101 + Water	5004 @ 298K 949 @ 333K	$63160.73 \left(\frac{\beta_o \cdot P}{\sqrt{T}} \right) \exp \left(\frac{-E_a}{RT} \right)$	1	43,220
Li-MIL-101 + Water (5% wt)	390 @ 298K 96.5 @ 333K	$38126.35 \left(\frac{\beta_o \cdot P}{\sqrt{T}} \right) \exp \left(\frac{-E_a}{RT} \right)$	1	42,860
Na-MIL-101 + Water (5% wt)	5582 @ 298K 1088 @ 333K	$37124 \left(\frac{\beta_o \cdot P}{\sqrt{T}} \right) \exp \left(\frac{-E_a}{RT} \right)$	1	37,100

Figure 5.16 shows the isosteric heat of adsorption (Q_{st}) of the parent MIL-101(Cr) and 5% wt doped MIL-101(Cr) MOFs + water systems on the basis of van't Hoff relation in pressure-temperature-uptake co-ordinate systems as given by $Q_{st} = -R \frac{d \ln P}{d(1/T)}$. The slope of $\ln P$ versus $1/T$ gives the value of Q_{st}/R , where R is the universal gas constant ($R = 8.3145 \text{ J/(mol K)}$). At low pressure region, MIL-101(Cr) MOF has the highest Q_{st} . A sharp decrease of Q_{st} is followed as water uptake increases. Since MIL-101(Cr) MOF is hydrophobic material, the decrease in Q_{st} suggests weak interaction between the MOF and water molecules at low pressure region. On the other hand, Li-MIL-101 MOF (5% wt) has a sharp increase in Q_{st} in the Henry's region, followed by a gentle decrease of energy as uptake increases. The addition of Li^+ ions enhances the adsorption of water molecules onto high energy sites. Formation of micro-pores may be present due to the addition of Li^+ ions and this provides strong interaction between the water molecules and Li-MIL-101(Cr) MOF (5% wt). Na-MIL-101 MOF (5% wt) also shows an increase in Q_{st} at Henry's region, and a slight drop is observed at higher uptake ranges. This shows that Na^+ has formed certain micro-pores structure to enhance interactions between the adsorbent and water molecules. From here, it is obvious that the affinity between water molecules and Li^+ ions are stronger.

Figure 5.16: Q_{st} of MIL-101(Cr) and 5% wt alkali doped MIL-101(Cr) MOFs adopting van't Hoff relation

5.3 Modulation of Al Fum MOF

The TEM (Transmission electron microscopy) images for the parent and formic acid modulated Al Fum MOFs are shown in Figure 5.17(a – d). Hence, the morphology of parent Al Fum looks similar to quadra-hedron shape. The precursors of Al Fum are Al chloride and fumaric acid. It is well known that Al chloride provides platelets and fumaric acid is responsible for smooth surface. The particle morphology of the parent MOF is shown in Figure 5.17 (a). At 5 ml of formic acid (Figure 5.17b), the particles start to elongate. With the addition of 10 ml of formic acid, the crystal becomes more elongated (Figure 5.17c). The effect is stronger with higher dosage of formic acid added (15 ml, Figure 5.17c). The average elongated shape length is approximately observed to be 0.5 μm .

The PXRD (Powder X-Ray Diffraction) graphs of the parent and formic acid modulate Al Fum MOFs are shown in Figure 5.18. These results show that the formic acid modulated Al Fum MOFs provides the same XRD trends as compared with the original sample, where

the distinct reflection is observed at 10° . However, the small peaks are observed at higher angles. The peaks correlate here the intensity of Al ions. Hence, the addition of formic acid into Al Fum MOF does not disrupt its structure integrity.

Figure 5.17: TEM diagrams of (a) the original Al Fum and Al Fum with various formic acid concentration such as (b) 5 ml, (c) 10 ml and (d) 15 ml. Hence the modulated adsorbents show less agglomeration of particle due to the addition of formic acid.

Figure 5.18: PXRD (powdered X ray diffraction) curves for the parent and formic acid modulated (5 ml, 10 ml and 15 ml) Al Fum MOFs

The composition of the parent and formic acid modulated Al Fum MOFs were investigated by a thermogravimetric analyser (TGA). The weight losses as a function of temperature are measured for thermal stability analysis and the results are presented in Figure 5.19. Similar trends are observed for all adsorbents as presented herein. It is interesting to note that the addition of formic acid (5 ml) in Al Fum adsorbents, the steps are observed in TGA curves and a weight loss occurs nearly at 150°C during the initial stage of heating up and water molecules are removed from the pores. Due to the addition of excessive formic acid (15 ml) the structure collapses easily at higher temperature. However, the addition of 10 ml of formic acid into Al Fum adsorbent, slightly hydrophobic behaviour is observed and the TGA curve moves towards right of the parent Al Fum MOF. Therefore, the weight loss is occurred at relatively higher temperature. The complete degradation is found at above 465°C. The mass losses are linked to the removal of water and organic materials, which

includes evaporation of water molecules from the Al Fum pores with the combustion of the linker. Therefore, it can be said that these MOF samples are suitable for low temperature adsorption cooling applications.

Figure 5.19: TGA (Thermo-gravimetric analyzer) curves showing the stability analysis of Al Fum and Modulated Al Fum samples

Figure 5.20 shows the N₂ adsorption isotherm of all synthesised parent and fam Al Fum MOFs at temperature of 77.4 K. The volumetric uptakes of parent AL Fum MOF are higher as compared with other fam Al Fum adsorbents. It is also found that the fam Al Fum MOFs comprising 5 ml and 10 ml of formic acid have relatively higher N₂ uptake whilst the sample with 15 ml formic acid shows the lowest N₂ uptake. The pore width, micro pore volume and surface area are determined based on BET analysis and N₂ adsorption data. These data are shown in Table 5.7. With the addition of 5 ml/10 ml of formic acid, the BET surface area and the micro pore volume are not changed significantly as compared with parent Al Fum MOF. The formic acid increases the number of water molecules during synthesis of fam Al Fum. With the higher content of formic acid (15 ml), the amount

of water is increased in the form of yellow solution with pungent smell and hence, it may affect the structural integrity of parent Al Fum [25].

Figure 5.20: N₂ adsorption isotherms of the parent Al Fum and fam Al Fum MOFs for calculating porous properties. Hence the black solid lines indicated ‘adsorption’ and the red dotted lines define ‘desorption’.

Table 5.7: Porous properties (Brunauer – Emmett – Teller or BET surface area, pore volume and average pore size) of Al Fum and formic acid modulated Al Fum MOFs

Samples	BET Surface Area (m ² /g)	Micro pore Volume (cm ³ /g)	Average Pore Radius (Å)
Original Al Fum	792	0.43	10.9
fam (5ml) Al Fum	807	0.43	10.7
fam (10ml) Al Fum	836	0.44	10.7
fam (15ml) Al Fum	558	0.30	10.8

Figure 5.21 shows the pore size distribution, where it is observed that the modulated Al Fum adsorbents consisting of 5 ml and 10 ml of formic acid show higher concentration of micro pores ($\sim 6\text{\AA}$) as compared with those of the parent Al Fum MOF. On the other hand, the Al Fum sample with 15 ml of formic acid has lower concentration of micro pores. It is clearly stated that Al Fum should be modulated with formic acid ranging from 5 ml to 10 ml for the formation of micro pores in Al Fum structure, which also reduces the required time for the formation of Al Fum crystal structure. The addition of formic acid leads to

lesser number of nuclei during crystallisation process, which also allows the formation of larger crystal [25]. It is noted that the amalgamation of formic acid and DMF produce more water during synthesis process, which may allow Al ions to form the basic structure with fumaric acid. Hence, Al Fum nano crystal structures are formed at a short period of time. However, it is observed that higher or excessive dosage of formic acid (15 ml) degrades the structural properties of Al Fum, which is due to the fact that the amount of water content is higher with the addition of formic acid during the synthesis process.

Figure 5.21: The PSD (pore size distribution) curves of parent and fam (5 ml, 10 ml and 15 ml) Al Fum MOFs ranging from micro to meso pores.

With reference to Figures 5.20 and 5.21, the addition of 5 ml of formic acid provides crystalline structure of Al Fum with the reduction of macro pores and converts them into micro and meso pores. Therefore, the number of micro-pore increases. By the addition of formic acid up to 10ml, the Al Fum structure become more crystalline with higher micro pores distributions. On the other hand, with the addition of excessive formic acid (~15 ml),

light yellowish liquid is observed, and a pungent smell is released during synthesis. It is found that 15 ml of formic acid added to Al Fum synthesis degrades the formation of crystal, even though nano crystal Al Fum is observed (Figure 5.17).

Figure 5.22 shows the adsorption – desorption phenomena of water vapour on the parent and fam Al Fum MOFs expanding from Henry's region to $P/P_s \rightarrow 1$ at the temperature of 25° , where P_s is the saturated pressure. Hence both the adsorption and desorption isotherms provide the similar trends. The water uptakes are measured at first in the direction of higher pressure up to $P/P_s \rightarrow 1$ and later the uptakes are calculated in the direction of desorption i.e. lower pressure up to $P/P_s \rightarrow 0$. The adsorption – desorption processes of fam Al Fum + water are repeated at least two times for the reliability of the experimental data. The hysteresis behaviours are found at $P/P_s \geq 0.2$, which are occurred due to incomplete desorption process with residual water trapped in the porous adsorbents. The water desorption from Al Fum MOF provides almost the same trend as compared with its adsorption behaviour. Al Fum mainly comprises Al, C and O atoms. Hence, Figure 5.22(a) shows the comparison between the parent and fam (5 ml formic acid) Al Fum MOFs. Both isotherms at the adsorption (solid line) and desorption (dotted line) phases are relatively similar, except at the relative pressure of 0.8 where the parent Al Fum has a rise in uptake (due to more meso pores). The addition of formic acid increases the micro pore distribution in the MOF structure, which eliminates the sharp uptake at very high pressures. Figure 5.22(b) and Figure 5.22(c) show the adsorption – desorption isotherms of Al Fum with 10ml and 15ml of formic acid modulation.

Figure 5.22: The adsorption-desorption behaviours of the parent and fam Al Fum MOFs at 25°C showing the hysteresis of the MOF samples with water.

The experimentally measured water uptake data for the parent and fam Al Fum MOFs are presented in Figure 5.23 (a – d). The uptakes data are provided from 25°C to 60°C and pressures up to 6 kPa. Hence the adsorption-desorption process is added in the isotherm curves. The performances of adsorption cooling are based on the equilibrium water uptakes under adsorption and desorption working pressures and are calculated in terms of water uptake – offtake difference (Δq) per thermal compression cycle. In Figure 5.23 (a – d), the Δq for the parent Al Fum + water system is shown under adsorption chiller operating conditions, where the working pressure lies between 1 kPa and 5 kPa with the adsorption and desorption temperatures of 25°C and 60°C, respectively. From the experimental data, the Δq for 10ml formic acid assisted Al Fum (Figure 5.23c) is 12.5% higher than that of the parent Al Fum MOF (Figure 5.23a). However, the Δq for 15 ml fam Al Fum (Figure 5.23d) is found to be 18% lower as compared to the original Al Fum MOF. On the other hand, the Δq for 5 ml formic acid does not affect the overall performances. With the modulation of 10 ml formic acid, the micro-pore distribution in Al Fum adsorbent increased which also improves the rate of water adsorption. Therefore, the amount of water vapour transfers per adsorption-desorption cycle decreases.

Figure 5.23: Adsorption isotherms at various temperatures (25°C, 35°C, 45°C and 60°C) and pressures up to 6 kPa (under adsorption device operating conditions) for water uptakes on (a) parent Al Fum (b) fam (5 ml formic acid) Al Fum, (c) fam (10 ml formic acid) Al Fum and (d) fam (15 ml formic acid) Al Fum.

The study of adsorption kinetics provides information on the time required for the adsorption of water molecules on the solid porous adsorbents and determines the cycle time of a thermal compressor for adsorption cooling. The adsorption cooling cycle corresponds to the working pressure of adsorption-triggered-evaporation (1 kPa with 25°C, i.e. P/P_s (25°C) $\rightarrow$ 0.31) and desorption-activated-condensation processes (5 kPa with 60°C, i.e. P/P_s (60°C) $\rightarrow$ 0.25), where P_s is the saturated pressure. Figure 5.24 (a – d) shows the water uptake rates on original and fam Al Fum MOFs for the temperature of 25°C and 60°C, respectively. At first the kinetics data are measured at the combination of 1 kPa and 25°C. Secondly, the kinetics are measured for desorption conditions (5 kPa and 60°C).

Figure 5.24: Adsorption kinetics under adsorption and desorption conditions at (a) 25°C with relative pressure (P/P_s) of 0.31 (for adsorption cases) and at 60°C with relative pressure (P/P_s) of 0.25 (desorption cases) for water on parent Al Fum and fam Al Fum

The results are presented here up to 3000 s with respect to adsorption chiller operating conditions. It is found that the performances of adsorption kinetics are improved with the addition of formic acid and 10 ml fam provides the maximum water uptake rates at 25°C as compared with the parent and other fam Al Fum MOFs due to uniform micro-pore distribution (Figure 5.24c). The uptake rates are found be minimal for the original Al Fum MOF. The reason is that the formic acid modulation generates a large number of micro-pores in MOF structure thereby providing more interatomic and electrostatic interaction potentials for fam Al Fum MOF and water system. It should be also noted here that at 60°C

(desorption) and 25°C (adsorption), (i) the parent Al Fum reaches equilibrium at the nearly 3000s (Figure 5.24a) and (ii) the fam adsorbents achieve equilibrium at the faster time of 2500s (for 5 ml formic acid, Figure 5.24b), 1600s (for 10 ml formic acid, Figure 5.24c) and 1400 s (for 15 ml, Figure 5.24d), respectively. From Figure 5.24, it is also observed that the rate of desorption is faster than that of adsorption due to the fact that at higher temperatures and pressures, the adsorbate molecules move in the pores at faster rates. Therefore, the adsorption periods are longer than the desorption periods for and adsorption cooling operation condition [106].

The isosteric heat (Q_{st}) due to any adsorbate adsorption is calculated on the basis of Clausius-Clapeyron equation [69] as given by $Q_{st} = -R \frac{d \ln P}{d(1/T)}$, where R is the gas constant.

The gradient $\ln P/(1/T)$ at constant uptake q is calculated from the experimentally measured isotherms data at various temperatures. Figure 5.25 shows the isosteric heats for parent and fam Al Fum MOFs + water systems for the temperature varying from 25°C to 60°C. The Al Fum comprises mainly of micropores with various widths (5 – 20Å). For both parent and fam AL Fum MOFs, the Q_{st} increases rapidly at the low pressure region as water molecules first penetrate into the adsorbent sites with higher energy. Secondly, the water molecules then adsorb onto adsorbent sites with decreasing energy and a slightly lower Q_{st} is found. After completely filling the smaller pores (final stage), the adsorption affinity becomes weaker and a rapid decrease in Q_{st} is observed. After formic acid modulation, the parent Al Fum particles morphology starts elongating with the increase in micro-pore distributions.

Figure 5.25: Isosteric heats in terms of water uptakes for water adsorption on parent and fam (5 ml, 10 ml and 15 ml) Al Fum MOFs at temperatures ranging from 25°C to 60°C.

Based on the results shown, fam Al Fum with 10 ml formic acid has the best results in terms of surface characteristics, isotherms and kinetics measurements. Hence, the isotherms and kinetics data of fam Al Fum MOF (10 ml formic acid) are fitted with the proposed isotherm and kinetics model [1, 48]. The parameters are presented in Table 5.8.

Table 5.8: Isotherms and kinetics parameters for fam Al Fum MOF with 10 ml of formic acid. The parameters are determined based on the fitting with proposed isotherm and kinetics model [1, 48] on experimental data

MOF	Isotherms Parameters			
fam Al Fum (10ml formic acid)	Q_{st}^* (kJ/kg)	m	α	q_m (g/g)
	2820	5.7	2.29×10^{-4}	0.45
	Kinetics Parameters			
	K	k_{ads} (1/s)	β_o	E_a (J/mol)
	1436 @ 298 K 277 @ 333 K	$14979.53 \left(\frac{\beta_o \cdot P}{\sqrt{T}} \right) \exp \left(\frac{-E_a}{RT} \right)$	1	37,500

5.4 Green Synthesis of Al Fum

The surface and porous characteristics of green synthesised Al Fum MOF are calculated by analysing the N₂ adsorption/desorption isotherms at 77 K and results are furnished in Table 5.9. The pore size distribution curve of green synthesised Al Fum MOF, which is determined using the Non-Local Density Functional Theory (NLDFT) model, is shown in Figure 5.26. The result shows two domains of pore size of 11Å and 16Å. Thus, green synthesised Al Fum MOF contains majority of micro-pores in its structure.

Figure 5.26: Pore size distribution curve of green synthesis Al Fum MOF with domain of pore sizes of 11Å and 16Å

Table 5.9: Surface and porous characteristics of Al Fum MOF adsorbent and deliverable energy capacity (Δq)

Sample	Pore volume (cm ³ /g)	BET surface area (m ² /g)	Δq for cooling (g/g)	Δq for heat pump (g/g)
Al Fum MOF (Green Synthesis)	0.44	821	0.1	0.31
Al Fum MOF (DMF based)	0.48	792	0.06	0.31

The X-ray diffraction (XRD) pattern of synthesised green synthesised Al Fum MOF is presented in Figure 5.27(a). The five distinct diffraction peaks are observed at $2\theta = 10.2^\circ$, 15.6° , 21.7° , 31.8° and 42.7° , which are in good agreement with the standard peaks of original Al Fum MOF [22, 23]. No additional peaks corresponding to any secondary phases are observed, hence confirming the of green synthesis Al Fum MOF. The morphology and particle size of green synthesised Al Fum MOF are analysed through FESEM image which is shown in Figure 5.27(b). These Al Fum particles have quadrilateral shape with a size distribution in the range of 60-100 nm. It is also observed that particles are highly agglomerated.

Figure 5.27: (a) X-Ray diffraction peaks and (b) SEM micrographs of green synthesised Al Fum MOF

In choosing the ideal adsorbent for water adsorption, it is reported that metal carboxylates [10, 15] are extremely stable to water. So, it is anticipated that Al Fum MOF would be a logical choice for water adsorption purposes. Water vapour adsorption/desorption isotherms measured at 298 K are presented in Figure 5.28, which shows type V isotherm featuring a steep increase of water uptake in a narrow relative pressure (P/P_s) range

between 0.2 and 0.3. Later, the water uptake further increases in a gentle slope for the P/P_s above 0.3 leading to a maximum water uptake of 0.48 g/g. The narrow hysteresis observed between the adsorption and desorption processes designates the continuous reversible pore filling with water rather than irreversible capillary condensation [107]. It is noted that the water adsorption/desorption isotherm for green synthesised (water based) Al Fum MOF (Figure 5.28) shows the same trend and is well comparable with parent (DMF based) Al Fum MOF [23, 83]. For both cases, the uptake – offtake difference between the adsorption and desorption process termed as the deliverable energy capacity (Δq), is nearly the same ($\Delta q = 0.31$ g of water/g of Al Fum MOF) for heat pump application (P/P_s for desorption is 0.1 and P/P_s for adsorption is 0.3 in Figure 5.28).

Figure 5.28: Water adsorption isotherm of parent and green synthesised Al Fum MOFs. Water adsorption isotherm of AlFum MOF measured at 298 K, with solid line for adsorption and dotted line for desorption (the deliverable energy capacity Δq_1 is for cooling and Δq_2 is for heat pump applications).

However, for cooling application (P/P_s for desorption is 0.1 and P/P_s for adsorption is 0.22 in Figure 5.28), the proposed green synthesised Al Fum MOF shows better result in terms of deliverable energy capacity ($\Delta q = 0.1$ g/g for water-based Al Fum and $\Delta q = 0.06$ g/g for DMF based Al Fum MOF).

5.5 Summary

From the results obtained, MOF is suitable for the design of adsorption chiller as it provides high uptake – offtake difference and fast kinetics behaviour. Therefore, the next chapter presents simulation studies for understanding the performances of an adsorption chiller employing Al based MOF and water as adsorbent – adsorbate pair. The fitted isotherms and kinetics data, based on proposed isotherms and kinetics model [1, 48], of the Al based MOFs + water systems are also shown in this chapter.

Chapter 6: New Generation Cooling Employing Al based MOFs-Water

Based on experimentally measured isotherms and kinetics data (as discussed in the previous chapters) together with mass and energy balances for each component of the system, this chapter presents a thermodynamic framework to simulate the thermodynamic performance of an adsorption chiller. Hence, three types of aluminium based MOFs are considered, and these are aluminium fumarate (Al Fum), formic acid modulated (fam) Al Fum and CAU-10. The key parameters such as specific cooling capacity (SCP) and the coefficient of performance (COP) are evaluated for various cycle times, chilled water inlet and the driving heat source temperatures.

6.1 Thermodynamic Modelling

Figure 6.1 shows the schematic diagram of a two-bed adsorption cooling system. To ensure a continuous cooling cycle, the refrigerant (mainly water) is evaporated from the evaporator at a pressure of 1 kPa by the flow of chilled water (cooling load) in the heat exchanger (HX) as placed inside the evaporator. The evaporated refrigerant then enters the adsorption bed (in the adsorption bed, the porous adsorbents are packed on the outside of the finned-tube heat exchanger) through a valve, and the refrigerant is then adsorbed by the adsorbent material. The isosteric heat of adsorption is generated during adsorption periods, and the generated adsorption heat is transferred into the cooling water and finally the heat is released to the heat sink. At the same time, the other bed undergoes the desorption process. During desorption, the hot water is supplied through the copper tubes of the bed. Therefore, the water vapour trapped in the adsorbent pore is desorbed. The desorbed refrigerant is transferred to the condenser, where heat energy is removed from the

refrigerant via the heat exchanger and the refrigerant is condensed into liquid phase. The liquid condensate flows back to the evaporator through a capillary valve. During continuous cooling operation, both adsorption beds switch their roles at certain time for ongoing adsorption – desorption process. This means that both adsorption beds work under adsorption/desorption mode with a switching period, i.e., batch operation. One batch operation comprises adsorption/desorption and switching periods. Generally, both adsorption and desorption are occurring at the same time and the periods for adsorption and desorption processes are the same. However, the desorption periods may be shorter for multi-bed adsorption cooling.

Figure 6.1: Water (has the highest evaporation enthalpy of all known fluids and is non-hazardous) is vaporised at a low pressure, taking up the heat of evaporation (Q_{evap}). The water molecules are then incorporated into MOFs, generating the heat of adsorption (Q_{ads}). When the adsorbent material (here MOF) is completely loaded with water molecules, it is regenerated by applying driving heat (Q_{des}) for desorption. The water desorbs, condenses at a room temperature level releasing the condensation heat (Q_{cond}), and is consequently available for the next cycle.

The amount of water uptakes on various MOFs under static and dynamic conditions are calculated by the isotherm and kinetics models. It should be noted here that the isotherms and kinetics equations and the parameters on the basis of aluminium – MOFs + water systems are presented in the previous chapters. The thermodynamic model for the evaporator, condenser and beds with finned-tube heat exchangers [12, 108, 109] are illustrated in Table 6.1. Equation (6.1) shows the energy balance equation and represents

the rate of change of evaporator temperature with respect to the transfer of (i) latent heat from the evaporator to the adsorption bed and (ii) the condensate from the condenser to the evaporator with cooling load generated from the chilled water. Secondly, Equation (6.2) defines the energy balance of the chilled water that contains sensible heat transfer from the chilled water to the evaporator. Equation (6.3) illustrates the rate of change of bed temperature (both for adsorption and desorption) in which the first term of the left hand side represents the energy involved due to the isosteric heat of adsorption as a function of bed pressure and temperature and the second term define the sensible heat transfer from the bed to the cooling water (for adsorption case) or from hot water to the bed (for desorption case). The thermodynamics framework of the cooling/hot water during adsorption/desorption is shown in Equation (6.4), where the rate of change of heat transfer fluid temperature is expressed in terms of energy transfers between adsorption bed and heating/cooling fluids. Finally, the change in condenser temperature as a function of time is evaluated by considering the latent heat due to phase change in the condenser and the sensible heat transfer from the condenser to the cooling water [Equation (6.5)]. Equation (6.6) expresses the energy balances for the cooling water. Equation (6.7) expresses the mass transfer of water vapour with respect to time. The derivative of the water uptakes with respect to time, $\frac{dq}{dt}$, can be modified from Equation (2.14) and is shown in Equation (6.8).

Table 6.1: Thermodynamics Modelling for Adsorption cooling system

Part	Equation	
Evaporator	$(Mc_p)_{eff}^{evp} \frac{dT^{evp}}{dt} = -h_{fg} M^{ads} \frac{dq_{ads}^{bed}}{dt} - h_f M^{ads} \frac{dq_{des}^{bed}}{dt} + \frac{(UA)_{evp}}{N_{evp}} \sum_{i=1}^{N_{evp}} (T_{evp} - T_i) ,$	(6.1)
	$(\rho c_p)_{chw} \frac{V_{tube}^{evp} dT^i}{N_{evp} dt} = (\dot{m} c_p)_{chw} (T_{i-1} - T_i) + \frac{(UA)_{evp}}{N_{evp}} (T_{evp} - T_i)$	(6.2)
Bed	$(Mc_p)_{eff}^{bed} \frac{dT_k^{bed}}{dt} = M^{ads} \frac{dq_k^{bed}}{dt} \Delta H - \frac{(UA)_k^{bed}}{N_{bed}} \sum_{j=1}^{N_{bed}} (T_k^{bed} - T_j) ,$	(6.3)
	$(\rho c_p)_{fluid} \frac{V_{bed} dT^j}{N_{bed} dt} = (\dot{m} c_p)_{fluid} (T_{j-1} - T_j) + \frac{(UA)_k^{bed}}{N_{bed}} (T_{bed} - T_j)$	(6.4)
Condenser	$(Mc_p)_{eff}^{cond} \frac{dT^{cond}}{dt} = -h_{fg} M^{ads} \frac{dq_{des}^{bed}}{dt} - h_f M^{ads} \frac{dq_{ads}^{bed}}{dt} + \frac{(UA)_{cond}}{N_{cond}} \sum_{l=1}^{N_{cond}} (T_l - T_{cond}) ,$	(6.5)
	$(\rho c_p)_{cw} \frac{V_{tube}^{cond} dT^l}{N_{cond} dt} = (\dot{m} c_p)_{cw} (T_{l-1} - T_l) + \frac{(UA)_{cond}}{N_{cond}} (T_{cond} - T_l)$	(6.6)
Mass Balance	$\frac{dm_{ref}}{dt} = -M^{ads} \left(\frac{dq_{ads}^{bed}}{dt} + \frac{dq_{des}^{bed}}{dt} \right)$	(6.7)
	$\frac{dq}{dt} = k_{ads} \left(\frac{P}{P_s} \right)^m - q_t \frac{1}{\gamma}$	(6.8)

The performance of the system is calculated by adopting certain conditions derived from the energy balance equation. The cooling capacity of the evaporator, Q_{evap} , can be calculated by

$$Q_{evap} = \int_{q_{des}}^{q_{ads}} h_{fg} dq - (q_{ads} - q_{des}) \int_{T_{evap}}^{T_{cond}} c_{p,l} dT \quad (6.8)$$

where latent heat from evaporator to adsorption bed and sensible heat from the condenser into the evaporator are considered. The specific cooling power (SCP) signifies the cooling load of the system per mass of adsorbent with consideration of the operation and switching time of each cycle. Hence, SCP is derived as

$$SCP = \frac{1}{M_s} \left(\frac{dm_{chw}}{dt} \right) c_{p,l} \int_0^\tau (T_{chw}^{in} - T_{chw}^{out}) \frac{dt}{\tau} \quad (6.9)$$

The Coefficient of Performance (COP) studies the efficiency of the cooling system between the amount of cooling load produce and the amount of heat energy required. Hence, COP is derived as

$$COP = \frac{Q_{evap}}{\left(\frac{dm_{hw}}{dt}\right) c_{p,l} \int_0^\tau (T_{hw}^{in} - T_{hw}^{out}) \frac{dt}{\tau}} \quad (6.10)$$

Table 6.2 shows the parameters required for a typical two-bed conventional adsorption cooling device.

In this chapter, a numerical simulation of the adsorption assisted cooling device is performed on Al Fum, modulated Al Fum and CAU-10 MOFs, and the performances of the device are analysed based on COP and SCP.

Table 6.2: Parameters for simulating the adsorption cooling device

Parameters	Values (based on chiller design conditions)
Chilled water inlet temperature (°C)	10-22
Cooling water inlet temperature (°C)	20-35
Hot water inlet temperature (°C)	50-70
Half cycle time (s)	100-1000
Switching time (s)	30
Mass of adsorbent (kg)	18
Mass flow rate of hot water (kg/s) [110]	1.28
Mass flow rate of cooling water (kg/s) [110]	1.52
Mass flow rate of chilled water (kg/s) [110]	0.71
Mass flow rate of cooling water in condenser [110]	1.37
c_p of adsorbent (kJ/kg.K)	0.805
UA_{ads} (kW/K) [110]	3.942
UA_{des} (kW/K) [110]	4.241
UA_{cond} (kW/K) [110]	15.35
UA_{evp} (kW/K) [110]	4.88
$(Mc_p)_{eff}^{evp}$ (kJ/K)	8.47
$(Mc_p)_{eff}^{cond}$ (kJ/K)	11.35
$(Mc_p)_{eff}^{bed}$ (kJ/K)	100
V^{bed} (m ³)	5×10^{-2}
V^{evp} (m ³)	1.5×10^{-3}
V^{cond} (m ³)	2.2×10^{-3}
N_{bed}	30
N_{evp}	20
N_{cond}	20

6.2 Performance analysis

The performances of the adsorption chiller adopting MOFs + water systems are simulated employing (i) the mass energy balances for each component (e.g. evaporator, adsorption bed and condenser) of chiller (Table 6.2), and (ii) the static and dynamic water uptake modelling equations (as discussed in the previous chapters). Using the design parameters as shown in Table 6.2 with other parameters of adsorption isotherms and kinetics for MOFs

+ water systems (discussed in the previous chapters), the thermal behaviours and performances of the batch operated adsorption chiller are evaluated from transient to cyclic steady state conditions. In the simulation domain, both the mass and energy conservation equations are solved by the finite difference formulations along a control volume, and the updated values of the key system's variables (temperature, uptakes and offtakes, SCP and heating energy) are obtained by numerical integration in time. The calculation procedure commenced with the initialisation of variables, the system geometries and the adsorption characteristics of adsorbent-adsorbate systems. The simulation is written in MATLAB and an illustration of the written code can be found in Appendix B. The main routine of the simulation is to determine the change of pressures, temperatures and uptakes of adsorption in terms of time. The parameters of the components (evaporator, condenser, adsorber, desorber) are divided into a series of subroutines to calculate the adsorption isotherms and kinetics. The code is written such that simulation is performed within the total number of adsorption/desorption cycles are set. The simulation is validated with the experimental performances of the cooling system adopting the AQSOA zeolites [12], which is also shown in Appendix A.

The key parameters analysed in the simulation code are (a) the temperature profiles of the bed (under adsorption and desorption conditions), condenser and evaporator, and (b) the net Coefficient of Performance and the Specific Cooling Capacity.

Figure 6.2 shows the prediction of temporal histories for adsorption beds, the condenser and the evaporator. The water inlet and outlet temperatures can be found in this figure. The results are presented for the driving heat source temperature (hot water inlet temperature) of 60°C, cooling water inlet temperature of 30°C and chilled water inlet temperature at

14.8°C. Hence, the sorption reactor (Bed A) undergoes the temperature profile during desorption process while another bed (Bed B) undergoes the adsorption process. It is clearly shown that the temperatures of the beds differ from the water temperature for the adsorption/desorption process. This is because during adsorption process, the isosteric heat is released to either the water flowing through the heat exchanger or to the environment, thus, increasing the bed temperature. On the other hand, heat is transferred to the adsorbent material during desorption process. A switching time of 30 seconds is computed in this profile to simulate the change in sorption process between two beds. During switching, adsorption and desorption process are ceased. Hence, water vapour is not transferred from the evaporator to the bed, and desorbed adsorbate molecules did not enter the condenser. From here, the evaporator temperature increases slightly while condenser temperature drops to cooling water temperature during switching time.

Figure 6.2: Temperature profile of adsorption chiller adopting Al Fum + water system

Figure 6.3 (a – b) show the SCP and the COP of aluminium based MOF and water adsorption chiller as a function of hot water inlet temperature. Hence, the chilled water

inlet and the cooling temperatures are maintained at 14.8°C and 30°C, respectively with half cycle time of 500 s. The simulated and experimental cooling performance for silica gel type RD [110] and AQSOA-Z01 [11] are shown for comparison purpose. It is found that the simulated results for silica gel and AQSOA-Z01 are closely related with the experimental performances found in the literatures. Thus, the simulated results shown provide predictive insights on the performance of adsorption cooling system when adopting different adsorbent materials. From here, it is observed that the SCP trends for both CAU-10 and fam Al Fum MOFs are the same (Figure 6.3 a), with CAU-10 having a slight dominance at higher hot water inlet temperature ($> 65^{\circ}\text{C}$). This suggests that the water uptake – offtake difference for CAU-10 MOF is relatively higher at higher regeneration temperature. Despite that silica gel has higher cooling performance at higher regeneration temperature, the slight hydrophobic properties of MOFs (and AQSOA-Z01) provides decent cooling load at lower hot water temperature. On the other hand, Figure 6.3(b) shows that the COP is an increasing function up to $\sim 60^{\circ}\text{C}$, after that a decreasing trend is found, which is due to the longer hydrophobic length and the maximum water transfer per adsorption-desorption cycle. However, at relatively higher temperature ($> 60^{\circ}\text{C}$), the amount of water vapour transfer, i.e., uptake – offtake difference is not increased and more sensible heat energy is utilised per batch process. Therefore, a monotonic decrease in COP is achieved.

Figure 6.3: (a) The SCP and (b) the COP of various Al based MOFs + water based adsorption cooling system at different hot water inlet temperatures under optimum operating time (500 s) conditions. The performances for silica gel [110] and AQSOA Z01 zeolite [11] are found in these figures for comparison purpose.

Figure 6.4 shows the COP and SCP of parent Al um, fam Al Fum and CAU-10 MOFs – water based adsorption chiller for various cycle time with fixed switching time of 30 s, the driving heat source and heat sink water inlet temperatures of 60°C and 30°C, respectively. Hence, Figure 6.4(a) shows the SCP as a function of cycle time, and the SCP is found to be low at shorter cycle time due to the least water vapour transfer (~uptake-offtake difference) per adsorption cooling cycle. The maximum SCP for MOFs is found at half cycle time ranging from 600 s and 700 s due to the transfer of water vapour from bed to condenser and from evaporator to bed. At higher cycle time, the SCP drops which is due

to the fact that long cycle time causes adsorbed water vapour to be saturated onto the adsorbent [108]. This is because the water vapour molecules are moving at random motion during the desorption process, and water molecules may be adsorbed back to the adsorbent. Thus, this decreases the overall uptake – offtake differences of the adsorbents and reduces the cooling effect with the increase of cycle time.

From the simulation results, it is observed that CAU-10 shows better cooling performance with the SCP of 0.155 kW/kg at 700 s. On the other hand, fam Al Fum achieves optimum SCP of 0.146 kW/kg within the range of 700 s and 800 s. The SCP generated by these MOFs are comparable to that of AQSOA-Z01 system as the isotherms of these materials are similar shape (Type V). The SCP for parent Al Fum, however, is found to be lower than that of silica gel system due to slower kinetic rates with water molecules. Figure 6.4(b) shows the COPs of adsorption chiller utilising the MOFs – water as adsorbent adsorbate pair and the COP is observed here as an interesting function of half cycle time. At short cycle time, the COP is achieved to be low due to incomplete vapor uptake onto the MOF adsorbents with the consumption of large amount of sensible heat. The COP for fam Al Fum and water based adsorption chiller is found 0.432 at the cycle time of 500 s with the driving hot water temperature of 60°C, which is very promising as compared with the commercially available silica gel – water (COP = 0.336 at 500 s) and zeolite – water (COP = 0.426 at 500 s) assisted adsorption chillers. The COP of CAU-10 + water system is found slightly lower at 0.43 at similar cycle time. Looking at COPs and SCPs of the proposed MOFs-water adsorption chiller at similar cycle time, it is obvious that the dynamic behaviours between adsorbent + adsorbate interaction or kinetics affects the chiller efficiency.

Figure 6.4: Performance analysis of Al based MOFs + water assisted adsorption cooling system with comparison of simulated performances of silica gel and AQSOA-Z01 at different cycle times with the hot water inlet temperature of 60°C, cooling water inlet temperature of 30°C and chilled water inlet temperature of 14.8. Hence (a) shows the specific cooling capacity (SCP) and (b) shows the coefficient of performance (COP).

Figure 6.5 (a – b) show that both the COP and the SCP are increasing functions of higher chilled water inlet temperature. For hot and cooling water of 60°C and 30°C with fixed half cycle time (switching time 30 s and adsorption/desorption operation time 500 s), the SCP and COP of CAU-10 are found to be (i) 0.152 kW/kg and 0.43 at chilled water inlet temperature of 14.8°C, and (ii) 0.219 kW/kg and 0.505 at chilled water inlet temperature of 18°C. The performance for fam Al Fum system are found better than CAU-10 system when chilled water inlet temperature is 18°C or higher. This is due to the fact that the

increment of the chilled water inlet temperature increases the operating pressure of the adsorption process. Hence, the kinetics of the MOF – water interaction is faster for the evaporation temperature at 15°C as compared to have at 10°C, enhancing the SCP as the chilled water inlet temperature is higher. The SCP against the chilled water inlet temperature is shown in Figure 6.5(a). It is also observed that the SCP of CAU-10 system shifts towards fam Al Fum system when chilled water inlet temperature is lower than 18°C, then deviated slightly away when the temperature is higher than 18°C. This is because CAU-10 MOF experience lower water transfer at higher evaporator pressure. As mentioned, the operating pressure of the adsorption process increases as the chilled water inlet temperature is higher. This allows the parent and fam Al Fum MOF adsorbents to achieve higher equilibrium water uptake with increased pressure, achieving higher water uptake – offtake difference per cooling cycle. In Figure 6.5 (b), the COP of CAU-10 MOF is observed to have similar behaviour with its SCP in Figure 6.4 (a). This would suggest that CAU-10 system transfers less water vapour per cooling cycle with the use of more sensible heat as compared with Al Fum-water based adsorption cooling system. Nonetheless, the MOF systems have better performance than the current conventional adsorbent materials at standardised evaporator pressure (chilled water inlet temperature = 14.8°C) or higher.

Figure 6.5: (a) The SCP and (b) the COP against the chilled water inlet temperature for various Al based MOFs + water based adsorption cooling system with comparison of simulated performances of silica gel and AQSOA-Z01.

Figure 6.6 (a – b) show the SCP and the COP of aluminium based MOF and water adsorption chiller as a function of cooling water inlet temperature. Hence, the chilled water inlet and the hot temperatures are maintained at 14.8°C and 60°C, respectively with half cycle time of 500 s. In Figure 6.6 (a), the SCP is observed as a decreasing trend with the increase in cooling water inlet temperature. This is due to the increase of cooling water inlet temperature increases the saturated pressure in the adsorption bed. Thus, this reduces the water uptake – offtake difference for the adsorbents at higher cooling water temperature. On the other hand, Figure 6.6(b) shows the COPs for all the adsorbents decrease gradually as cooling water temperature increases up to ~30°C. Thereafter, the COP decreases rapidly

when cooling water temperature further increases. The decrement of COP is due to the fact that higher cooling water inlet temperature increases the working pressure for desorption process. This decreases the overall water uptake – offtake differences per adsorption-desorption cycle. At higher temperature ($> 30^{\circ}\text{C}$), the water uptake – offtake difference decreases significantly with higher desorption pressure and, thus, increases the amount of sensible heat energy required for the process. Therefore, a sharp decrease in COP is observed as cooling water inlet temperature is higher than 30°C .

Figure 6.6: (a) The SCP and (b) the COP of various Al based MOFs + water based adsorption cooling system with comparison of simulated performances of silica gel and AQSOA-Z01 at different cooling water inlet temperatures under optimum operating time (500 s) conditions.

6.3 Summary

These isotherm and kinetic parameters of various aluminium based MOFs – water systems, together with the theoretical models of an adsorption chiller are compiled to calculate the overall performances of the adsorption chiller in terms of SCP and COP. It is shown here that with the hot water inlet temperature of 60°C and a cooling water inlet temperature of 30°C, the MOFs, such as fam (formic acid modulated) Al Fum and CAU-10, are able to achieve higher COP and SCP when it is employed into the adsorption cooling system. It is also observed that the MOF + water systems are constantly performing better than the conventional adsorbent materials at different working parameters. Therefore, from the present simulation results, it can be concluded that the Al-based MOFs has the great potential to replace the commercially available adsorbents such as silica gel and zeolites for low temperature ($< 60^{\circ}\text{C}$) driven adsorption chiller.

Chapter 7: Conclusions and Future Work

7.1 Conclusions

This thesis focuses mainly on metal organic frameworks (MOFs) and their interactions with water for understanding S-shaped adsorption isotherms especially for the design of water-based adsorption chiller. Hence, the green synthesis (environmentally friendly) technique is applied to fabricate the MOFs. The proposed MOF increases the transfer of water vapour per adsorption-desorption cycle with faster kinetics, which reduces the size of adsorption bed and increases the cooling capacity and the COP. For the development of next generation adsorption chillers, this thesis also shows the modification of Cr and Al based MOFs employing alkali metal ions dopants and formic acid modulation. The proposed method also increases the kinetics rates.

The contributions from this thesis are

1. GCMC simulations show that the hydrophilicity of the MOFs is related to the interaction between the individual atoms of the MOFs and water molecules, while the limiting water uptake of the MOFs depends on the formation of the cage structure by the metal nodes and organic ligands, which is illustrated in Figure 3.2.
2. Modification of Al Fum MOF employing Li^+ ion was performed in GCMC simulations shows an improved water uptake – offtake difference under adsorption chiller operating ranges due to the increased water uptake at $P/P_s = 0.25$ from 0.28 g/g to 0.38 g/g. This is due to the high interactions between Li and water molecules.
3. Modification of MIL-101(Cr) MOF with alkali metal ions (Li^+ , Na^+ , K^+) dopants is experimentally performed and characterisation results show that the dosage of

alkali metal ions needs to be kept below 40% wt to prevent the disintegration of the MOF structure.

4. The pore size distribution of 5% wt doped MIL-101(Cr) is lower than that of the MIL-101(Cr) MOF as alkali metal ions occupy the meso pores of the structure. However, it is believed that micro pore distribution ($< 5\text{\AA}$) is improved.
5. The addition of alkali metal ions, especially for Li^+ and Na^+ ions, reduces the hydrophobic length of MIL-101(Cr) MOF from $P/P_s = 0.4$ to $P/P_s = 0.25$. The addition of Li^+ ion improves water uptake – offtake difference of MIL-101(Cr) MOF from $\Delta q = 0.003\text{g/g}$ to $\Delta q = 0.2\text{g/g}$.
6. The addition of alkali metal ions (Li^+ , Na^+) dopants improves the water adsorption kinetics of MIL-101(Cr) MOF. At 6000s, the dynamic water uptake of MIL-101(Cr) increases from 0.5 to 0.8 (Li-doped) and 0.7 (Na-doped).
7. Modulation of Al Fum MOF with various concentrations of formic acid (5 ml, 10 ml, 15 ml) reduces the synthesis duration from four days to two days. The particles are observed to be elongated at approximately $0.5\text{ }\mu\text{m}$ with structural integrity and higher thermal stability.
8. The formic acid modulated (fam) Al Fum MOF (10ml) has better surface (BET surface area = $836\text{ m}^2/\text{g}$) and porous (distribution at $5\text{\AA} = 0.37$) characteristics than that of parent Al Fum MOF (BET surface area = $792\text{ m}^2/\text{g}$ and pore distribution of $5\text{\AA} = 0.3$). This is due to higher water content for the Al Fum MOF synthesis caused by the reaction between DMF and formic acid.
9. The water uptake – offtake difference of fam Al Fum MOF (10 ml) is 12.5% higher than that of parent Al Fum MOF. The fam Al Fum MOF has faster water adsorption

- kinetics (dynamic water uptake for 25°C at 3000s = 0.42) than that of parent Al Fum MOF (dynamic water uptake for 25°C at 3000s = 0.3).
10. Synthesis of Al Fum MOF employing a robust environment friendly water-based method reduces the synthesis duration to one hour. The water uptake – offtake difference for water-based Al Fum MOF (0.1 g/g) is higher than that of the original Al Fum MOF (0.06 g/g).
11. Based on a numerical simulation for adsorption chiller employing Al based MOFs + water system, fam Al Fum MOF achieves an optimum SCP of 0.14 kW/kg with COP of 0.43 at operating cycle time of 500 s while CAU-10 has an SCP of 0.15 kW/kg and COP of 0.43. The hot water inlet temperature is set at 60°C with the cooling water and chilled water inlet temperature is kept at 30°C and 14.8°C, respectively.

Based on the contributions, the modification of MOFs improves the affinity with water molecules and enhance the water adsorption properties. The numerical simulation results show that the adsorption cooling system employing fam Al Fum MOF has great performance with low heat generation. Therefore, from the contributions, MOFs have great potential to replace the commercially available adsorbents such as silica gel and zeolites for low temperature (< 60°C) driven adsorption chiller.

7.2 Recommendations for Future Work

Further Characterisation of MOF

Based on the results presented in this thesis, how the material structures and compositions influence the water adsorption capabilities and hence, affect the performances of the adsorption chiller and heat pump applications. It is, therefore, necessary to further

characterise the MOFs based on its thermal conductivity and density. The higher thermal conductivity of the MOF adsorbent has proven its effectiveness towards the performances of adsorption cooling system when attached to the improved heat exchanger [111, 112]. A higher bulk density and true density of the adsorbent affects the overall volumetric uptake [113], which may lead to more water vapour attracted to the surface of the adsorbent during adsorption-desorption batch process. Thus, the modification or new synthesis method provides more degrees of freedom for considering the new MOFs as potential adsorbents for cooling applications.

Methods of binding MOFs to heat exchanger

Currently, adsorption assisted cooling, dehumidification and heat pump system adopts physical binding of silica gel onto the surface of the heat exchanger [92]. This method, however, affects the interaction between the adsorbent and water molecules. It is also unsuitable for MOFs as it is usually synthesised as powder form. Recently, Saha et al. [114] have bound activated carbon based composite adsorbent using ionic liquid. This method has shown improvement in thermal conductivity over its parent material and increases its ethanol uptake – offtake difference between the working condition of an adsorption cooling system. Hence, by binding the powder adsorbent into solid blocks, the conventional method of packing the adsorbent to the heat exchanger can be adopted.

Jeremias et al. [23] performed the coating synthesis of Al Fum onto an aluminium sheet heat exchanger surface. It is proven that the MOF adheres well to the metal surface after the synthesis process. After coating, the water limiting uptake has decreased to 0.37 g/g sorbent. On the other hand, coating synthesis improves the hydrothermal stability and

thermal conductivity of Al Fum, which is a suggested method for the MOF to be attached onto the surface of heat exchanger.

Couck et al. [115] uses 3D printing method (Direct ink writing) on SAPO-34 (AQSOA-Z02) zeolites to form a monolith structure with Methyl cellulose, a polymeric binder, for CO₂ adsorption. The monolith shows a decrease in surface area and porous structure due to the powder material are bound together. However, its CO₂ uptake slightly decreases after the monolith is produced. Hence, the printed adsorbent on heat exchanger surface is likely to be an alternative for MOFs.

Experimental Analysis

The molecular dynamics show that the MOFs + water system provides great potentials as the next adsorbent materials for adsorption assisted cooling or heat pump applications. However, as far as the results are generated from theoretical modelling, experimental data is necessary to validate this information.

Currently, Youssef et al. [116] had compared his numerical data of adsorption cooling system adopting CPO-27, a nickel based MOF, with an experimental setup. Unlike the results shown in this thesis, Youssef et al. performed the numerical simulation using Dubinin-Astakhov isotherm model and linear driving force model for isotherm and kinetics theoretical studies, respectively. Nonetheless, the comparison between the numerical and experimental results shows positive feedback for MOF + water system.

Materials Development

Currently, wide varieties of MOFs have been synthesised and experimented for water adsorption with positive feedback [8, 20, 86, 90, 117]. Still, achieving the ideal MOF as

the next generation adsorbent material for adsorption assisted applications is a long way ahead. Research of adsorption on membrane [118] and Covalent Organic Framework [119, 120] have received many positive feedback. Kayal and Chakraborty [121] performed an experimental investigation on composite material of Maxsorb III and MIL-101(Cr) for gas adsorption and it proved to achieve higher uptake than either of the material. Hence, more materials are available for adsorption cooling research in upcoming future.

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Appendix A: Studies of AQSOA Zeolites

Characterisation

Currently, the AQSOA typed zeolites are the conventional adsorbent materials for adsorption cooling application that adopts the ‘S’ shaped isotherm curves during water adsorption. Hence, it is necessary to understand the properties of AQSOA typed zeolites, its behaviour during water adsorption and how it affects the performance of adsorption cooling application with isotherm, kinetics and thermodynamic modelling.

AQSOA typed zeolites have two types of structure: AFI structure (AQSOA-Z01 and Z05) and CHA structure (AQSOA-Z02). The chemical composition of these materials can be found in Table A1. It is clearly shown that these materials consist of Al, P and O atoms. Except for AQSOA-Z05, both Z01 and Z02 has Fe and Si atoms, respectively, in the composition. Hence, the major framework for AQSOA typed zeolites are AlO_4 and PO_4 , but Z01 has an additional FeO_4 while Z02 has SiO_4 within its structure [34].

Table A1: AQSOA typed zeolites

AQSOA Zeolites	Chemical Composition	Structure	Mesh Size ($\text{\AA}$)
Z01	Fe, Al, P, O	AFI	7.3
Z02	Si, Al, P, O	CHA	3.8
Z05	Al, P, O	AFI	7.3

Surface properties of the zeolites are characterised to examine the relation with water adsorption behaviour. The experiments for characterisation are elaborated in Chapter 4. Figure A1 shows the SEM images of the zeolite materials. It is observed that both AQSOA-Z01 and Z05 have hexagonal cross section while AQSOA-Z02 has a cuboid structure. A closer look at the SEM images shows AQSOA-Z01 has rougher surface as compare to

AQSOA-Z05 despite having similar AFI structure. This may cause by the addition of Fe atoms to the AQSOA-Z01 structure.

Figure A1: SEM of AQSOA Z01 (top left), Z02 (top right) and Z05 (bottom)

Figure A2 illustrates the XRD graph of the zeolite material. The high intensity of AQSOA-Z01 and Z02 at low angle defines good crystallinity structure from the FeO_4 and the SiO_4 structure, respectively. Hence, the addition atoms to the zeolite structure high crystallinity structure for the zeolite materials.

TGA test was performed to AFI and CHA structure, shown in Figure A3. It shows that CHA structure has more mass reduction as compared to AFI structure when temperature reaches 100°C . This shows that CHA structure desorbs more water vapour as compared to the AFI structure. As the temperature increases, the CHA structure further release water vapour

from its smaller pores while AFI structure remains unchanged. Nonetheless, both materials remain stable at high temperature range.

Figure A2: XRD of AQSOA-Z01 (top), Z02 (middle) and Z05 (bottom)

Figure A3: TGA of (a) AFI and (b) CHA structure

A N₂ adsorption experiment is conducted on the AQSOA zeolites to further observe the surface properties. In Figure A4, the N₂ isotherms of the adsorbent materials are illustrated. It is clearly observed that the CHA structure has higher N₂ uptake than the AFI structure. The high N₂ interaction signifies higher surface properties of the CHA zeolite structure. With the BET isotherm model equipped, the BET surface area, total pore volume and average pore size for the zeolite material is shown in Table A2. It is clearly shown that AQSOA-Z02 has the highest BET surface area and pore volume than the AFI zeolitic structure due to its dominant N₂ volumetric uptake. Table A2 also shows that AQSOA-Z05 has the smallest average pore size while AQSOA-Z01 has the largest. This may suggest that the addition Fe and Si atoms for AQSOA-Z01 and Z02 greatly affects the surface properties of the zeolite materials since the chemical composition are almost similar. A pore size distribution curves of the AQSOA zeolites are shown in Figure A5. The curves are determined based the equipped DFT model onto the N₂ isotherms. It is shown that AQSOA-Z02 has large distribution of micro pore with size about 6Å while the AFI zeolites have its distribution around 8Å. It is mentioned in Table A1 that CHA structure has a mesh size of 3.8Å, which suggest the existence smaller pores in the CHA structure is not computed. The addition of Fe atom reduces the distribution of pores of the AFI structure. However, Table A2 shows AQSOA-Z01 has higher pore volume than Z05. Thus, the FeO₄ structure in AQSOA-Z01 may increase the distribution of larger pores, which leads to higher pore volume of AFI structure.

Table A2: Surface Characteristics of AQSOA typed zeolites

Adsorbent	BET surface area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Size (Å)
Z01	152.95	0.21	10.76
Z02	763.62	0.35	10.66
Z05	242.47	0.18	10.63

Figure A4: N₂ isotherms of AQSOA zeolites

Figure A5: Pore Size Distribution of AQSOA zeolites

Water Adsorption Isotherms and Kinetics

The experimental data of water adsorption is carried out using a gravimetric analyser, which is elaborated in Chapter 4. Figure A6 shows the water adsorption isotherms of the AQSOA zeolites at temperature range 25°C to 60°C. The isotherm points are equipped with $\pm 5\%$ error range, which indicates the repeatability of the experiment for at least three times. The isotherms are fitted with Modified Langmuir, Dubinin-Astakhov and Chakraborty-Sun isotherm models [36]. It is shown that Chakraborty-Sun isotherm model fits the “S” shaped isotherm within the acceptable error range of 5%. A close observation shows that Modified

Langmuir model has calculated a higher water uptake at saturated pressure region while Dubinin-Astakhov model does not agree with the uptake a Henry's region [1]. Nonetheless, the fitted models estimated the theoretical parameters between the zeolite material and water molecules, which is shown in Table A3.

Figure A6: Water Adsorption Isotherm on AQSOA zeolites with theoretical fittings

Comparing the parameters with the respective characterization results, the CHA material has more water content removed which is shown in Figure A3. Thus, AQSOA-Z02 has higher water uptake than the other zeolites. The rest of the parameters, taking Chakraborty-Sun model as an example, determine the shape of the isotherms for each adsorbent material. For instance, higher Q_{st}^* with lower m tends to be hydrophilic material. These shows that AQSOA-Z02 releases high amount of heat during adsorption and the surface is relatively low in heterogeneity. However, to adopt the adsorbent material for low heat cooling

application, high water uptake – offtake difference is necessary. Thus, low hydrophobic property, such as AQSOA-Z01, is ideal as the adsorbent material for cooling application. The decent hydrophobic property, due to the existence of FeO_4 , achieve slight hydrophilic behavior from its AFI counterpart. From the isotherm results, water vapor is desorbed at low temperature of 60°C for cooling application purpose.

Table A3: Isotherm theoretical parameters of AQSOA zeolites + water pair

Chakraborty- Sun							
System	q^o (kg/kg)	Q_{st}^* (kJ/kg)	m	α			
Z01 + water	0.215	3030	4.9	9.0×10^{-7}			
Z02 + water	0.29	4560	1.01	7.0×10^{-6}			
Z05 + water	0.22	2800	6.55	6.77×10^{-5}			
Dubinin-Astakhov							
System	q^o (kg/kg)	E (J/mol)		n			
Z01 + water	0.21	4000		5			
Z02 + water	0.285	7600		2.9			
Z05 + water	0.22	2700		6			
Modified Langmuir							
System	q^o (kg/kg)	z	B_L	α_L	t_1	n_1	φ_m (J/mol)
Z01 + water	0.21	3	0.6	0.002479	2	-1.5	520
Z02 + water	0.29	2.6	0.5	0.005517	2	0.5	250
Z05 + water	0.22	3	1	0.011109	1.5	-3.5	250

Figure A7 shows the adsorption kinetics of water molecules to the AQSOA zeolite materials. The kinetic study shows the time taken for AQSOA zeolites to reach equilibrium point at given temperature and pressure. The experimental data is fitted with Equation 2.15 to estimate the activation energy, E_a , for AQSOA + water system. Table A4 shows the parameters for the kinetic behavior of AQSOA zeolites with water. The activation energy for AQSOA-Z02 is estimated to be the highest among the other zeolites. From the isotherm data it is clearly shown that AQSOA- Z02 is considered hydrophilic. It is, therefore, appropriate to have such high activation energy for AQSOA-Z02 + water system given the good interaction of the system. One reason for such good interaction for AQSOA-Z02 +

water system is mainly because of the existence of Si atoms in the structure. It is known that Si has good interaction with water molecules since silica gels (SiO_2) are hydrophilic material. Hence, with AQSOA-Z02 consists of SiO_4 structure, the water interaction for zeolite is improved.

Figure A7: Water Adsorption Kinetics on AQSOA zeolites with theoretical fitting

Table A4: Kinetics theoretical parameters for AQSOA zeolites + water pair

System	$k_{\text{ads}} \text{ (1/s)}$	β_o	$E_a \text{ (J/mol)}$
AQSOA-Z01 + Water	$3526.81 \left(\frac{\beta_o \cdot P}{\sqrt{T}} \right) \exp \left(\frac{-E_a}{RT} \right)$	1	33480
AQSOA-Z02 + Water	$12993.5 \left(\frac{\beta_o \cdot P}{\sqrt{T}} \right) \exp \left(\frac{-E_a}{RT} \right)$	1	52250
AQSOA-Z05 + Water	$3471.12 \left(\frac{\beta_o \cdot P}{\sqrt{T}} \right) \exp \left(\frac{-E_a}{RT} \right)$	1	38700

The isosteric heat of adsorption studies the amount of heat released during the adsorption process. Using the van't Hoff equation (Equations 2.16 and 2.17), the Q_{st} of the AQSOA zeolites + water systems are plotted on a graph against the water uptake of the respective adsorbent materials, which is illustrated in Figure A8. It is observed that the AFI structure materials have slight similarity in terms of the trend of the curves. A small decrement can be seen near the Henry's region, which indicates the heterogeneity characteristics of the material, agreeing the m factor from Chakraborty-Sun isotherm model. As the uptake increases, Q_{st} increases slightly for both materials, with AQSOA-Z01 has better increment since FeO_4 has good water interaction. This shows a decent interaction between the adsorbent-adsorbate pairs during the adsorption process. As the uptake reaches its maximum, Q_{st} for both materials increase sharply. Thus, this shows interaction between the AFI structured adsorbent and water molecules improves due to adsorbate-adsorbate Coulombic interaction. It is also noted FeO_4 structure releases more heat during the adsorption process, which further proves its good interaction water molecules.

Figure A8: Isosteric Heat of Adsorption against water uptake for AQSOA zeolites

On the other hand, AQSOA-Z02 shows sharp increment of Q_{st} from Henry's region and the increment gets consistent as uptake increases further. With SiO_4 structure in AQSOA-Z02, water molecules adsorbed at the high energy site the start of the adsorption process, where pores are narrower with strong water interaction due to the presence of Si. Hence, even at low uptake, large amount of heat energy is released during the initial phase of adsorption process. Subsequent increment of Q_{st} suggests adsorption occurs at lower energy site with adsorbate-adsorbate Coulombic interaction present. Hence, the addition of Si not only creates micro pore distribution, it also creates more energy site to improve water adsorption properties.

Adsorption Cooling Performance: Numerical Simulation

Adopting the isotherms and kinetics models mentioned earlier, the water adsorption properties AQSOA zeolites are simulated to the adsorption cooling system to evaluate the performance via simulation. Figure A9 shows the cooling capacity (SCE) of the zeolite materials plotting against the temperature lift between evaporator and condenser, ΔT for different desorption temperature. The heat sink temperature (condenser) is set at 30°C. As such, the evaporator temperature is varied because of temperature lift. Hence, optimisation of the adsorption bed is executed based on the performance of the various low heat adsorption assisted applications. It is shown that AQSOA-Z01 has good results while adopting low regeneration temperature. This is possible due to the low hydrophobic characteristics created by the FeO_4 AFI structure. AQSOA-Z02 requires higher regeneration temperature to achieve better performance for adsorption assisted applications as the material is relatively hydrophilic. It is clearly shown that AQSOA-Z05 is not suitable for cooling application purpose due to its poor performance since the material has no structure

consist of FeO_4 and SiO_4 . However, it is still suitable for low heat desalination application given the performance data compared to that of AQSOA-Z02.

Figure A9: Specific cooling energy for adsorption cooling system adopting (a) AQSOA-Z01 + water system, (b) AQSOA-Z02 + water system and (c) AQSOA-Z05 + water system

Figure A10 shows the Dühring diagrams (pressure-temperature-uptake) of the AQSOA zeolites + water-based adsorption cooling system under cyclic steady state conditions. AQSOA-Z01 achieves a water uptake of 0.15 kg/kg of sorbent during adsorption. Similarly, the water uptake for AQSOA-Z05 is about 0.15 kg/kg. AQSOA-Z02, on the other hand, has the highest uptake at 0.22 kg/kg during adsorption phase. It is noted that the temperature taken is at 42°C despite the cooling water temperature is set at 30°C. This is due to the high

isosteric heat of adsorption for AQSOA-Z02 + water system during adsorption phase. Hence, the heat releases from the adsorbent increases the bed temperature.

During the switching period from cooling water to hot water, water vapour is desorbed from the material in certain area of the HX. Thus, the initial drop of pressure and uptake shows a slight drop of adsorption heat during this period. As time goes, the hot water temperature increases the temperature of the bed while maintaining the water uptake. Once the switching phase is completed, desorption operation begins where water uptake decreases. An observation of a slight decrease in pressure suggest that it is due to the water vapour leaving the bed as the valve connects to the condenser is open after switching phase. To achieve a low water uptake, AQSOA-Z02 requires a desorption temperature of 90°C while the AFI zeolites are functioning at 70°C. Similar phenomenon occurs during the switching from desorption to adsorption, with an increase in pressure after the switching phase suggest that water vapour entering the bed from evaporator.

Figure A10: Dühring diagram of Adsorption cooling system adopting AQSOA zeolites

Figure A11 shows the performance parameters of the Adsorption Cooling system adopting the AQSOA zeolites at different hot water temperature. The chilled water inlet temperature is fixed at 14.8°C. Both simulated results of AQSOA-Z01 and Z02 shows similar trends in terms of experimental results. It is observed that AQSOA-Z01 achieves good cooling load, in terms of SCP, with desorption temperature (T_{des}) of 70°C. SCP remains constant as hot water inlet temperature increases, which suggest maximum Δq is adopted during the cooling cycle. AQSOA-Z02 achieves an SCP of 0.26 kW/kg when T_{des} is at 80°C and above. This is because of its hydrophilic properties, maximum Δq can only be achieve at high desorption temperature.

Figure A11: SCP and COP of Adsorption Cooling system adopting AQSOA zeolites at various hot water inlet temperature

Figure A12 shows the performance parameters of the adsorption cooling system adopting AQSOA zeolites with different cycle time. The parameters are similar with those for Figure A11, with hot water inlet temperature kept at 80°C. It is shown that the optimal SCP for both AQSOA-Z01 and Z02 occurs at cycle time about 400s. The performance decreases as cycle time increases. It is due to more heat is involved in the adsorption beds where with long desorption cycles. The strong interaction between the zeolite – water pair may perform the adsorption process during desorption phase. Hence, these events cause Δq to decrease every cycle, which affects the cooling capacity. AQSOA-Z05, on the other hand, has the lowest Δq among the zeolite materials. Thus, longer cycle time provides better Δq , allowing better cooling capacity.

Figure A12: SCP and COP of Adsorption Cooling system adopting AQSOA zeolites at different cycle times

It is also observed the COP increases with longer cycle time. By doing so, it allows better heat exchange within the adsorption beds and provide ample time for water vapour to desorb fully. Using the results from Figure A12, utilising the amount of time needed to achieve the highest SCP as the time constant is ideal for the respective adsorbent material.

Appendix B: MATLAB code for adsorption cooling

The following content is the written simulation code for adsorption cooling adopting Al Fum + water system

```
function main = ADAFW12kw80()

clc; clear all; close all; clf;

global Flag1
global Tcw_in Thw_in T_chw_in T_chw_out T_w_bedA_out T_w_bedD_out
T_w_cond_out
global P_bedA P_bedD w_bedA w_bedD
global Mads Qst Rw A wm n D_so Rp Ea R Cpads hfg_C
global m_dot_cw_bed m_dot_cw_cond m_dot_hw_bed m_dot_chw
global Mhx_bedCphx_bed Mhx_condCphx_cond Mhx_evpcphx_evpc M_ref_L_cond
M_ref_L_evpc;
global UA_bedA UA_bedD U_cond A_cond U_evpc A_evpc

t_normal = 500; %Time for normal operation
t_sw = 30; %Time for switching

t_cycle = (t_normal+t_sw); %Total cycle time0
step = 5; %Evaluate every 5 seconds
N_cyc = 25; %No. of cycles evaluated

Tcw_in = 35+273; %Kelvin
Thw_in = 60+273; %Kelvin
T_chw_in = 14.8+273;

Rw = 0.4619; %kJ/kg-k
A = 6.78E-4; % (1/Pa)
wm = 0.407;
n = 6.5;
Qst = 2.78E3; %kJ/kg
hfg_C = 2442;

D_so = 2.54E-4; % m2/s
Rp = 1E-4; %m
Ea = 36.66; %kJ/mol
R = 8.3144621E-3; %kJ/mol.K
Cpads = 0.805; %Cp of Z01 (kJ/kg.K)

Mads = 18; %kg

%=====
%Heat Exchanger Parameters
%=====

%bed
Mhx_bedCphx_bed = 100; % Kg*Kj/Kg-k
```

```

UA_bedA = 3.942; % kW/m2.K
UA_bedD = 4.241; % m2
m_dot_cw_bed = 1.52; %cooling water mass flow rate (kg/s)
m_dot_hw_bed = 1.28; %Hot water mass flow rate (kg/s)

%condenser
Mhx_condCphx_cond = 24*0.386; % Kg*Kj/Kg-k
U_cond = 4.115;
A_cond = 3.73;
M_ref_L_cond = 5;
m_dot_cw_cond = 1.37; %cooling water

%evaporator
Mhx_evpcphx_evap = 8.9*0.386; % Kg*Kj/Kg-k
U_evap = 2.557;
A_evap = 1.91;
M_ref_L_evap = 12;
m_dot_chw = 0.71; %chilled water

%=====
===
%Initial Values
Time_i = 0;

T_evap_i = 30+273;
T_cond_i = 30+273;

T_bedA_i = 30+273; %Kelvin

Ps_bedA_i = 10^3*(-5.007261711E-15*T_bedA_i^6 + 1.249032418E-
11*T_bedA_i^5 - 1.135454979E-08*T_bedA_i^4 + 5.164337223E-06*T_bedA_i^3
- 1.275119405E-03*T_bedA_i^2 + 1.643475641E-01*T_bedA_i -
8.706432224E+00);
P_bedA_i = 10^3*(-5.007261711E-15*T_evap_i^6 + 1.249032418E-11*T_evap_i^5
- 1.135454979E-08*T_evap_i^4 + 5.164337223E-06*T_evap_i^3 - 1.275119405E-
03*T_evap_i^2 + 1.643475641E-01*T_evap_i - 8.706432224E+00); %kPa

hfg_bedA_i = (10^3*(6.40224E-12*T_evap_i^5 - 3.93212E-08*T_evap_i^4 +
3.63907E-05*T_evap_i^3 - 1.39601E-02*T_evap_i^2 + 4.34707E+00*T_evap_i +
1.82254E+03) - 10^3*(1.95664E-10*T_evap_i^5 - 3.36772E-07*T_evap_i^4 +
2.34408E-04*T_evap_i^3 - 8.21171E-02*T_evap_i^2 + 1.86089E+01*T_evap_i -
2.15617E+03))*1E-3;

if(Ps_bedA_i <= P_bedA_i)

    w_bedA_i = wm;

else
    w_bedA_i = wm*((A*exp(n*(Qst-
hfg_bedA_i)/(Rw*T_bedA_i)))*(P_bedA_i/Ps_bedA_i)^n)/(1+(A*exp(n*(Qst-
hfg_bedA_i)/(Rw*T_bedA_i))-1)*(P_bedA_i/Ps_bedA_i)^n));
end

```

```

T_bedD_i = 30+273;

Ps_bedD_i = 10^3*(-5.007261711E-15*T_bedD_i^6 + 1.249032418E-
11*T_bedD_i^5 - 1.135454979E-08*T_bedD_i^4 + 5.164337223E-06*T_bedD_i^3
- 1.275119405E-03*T_bedD_i^2 + 1.643475641E-01*T_bedD_i -
8.706432224E+00);
P_bedD_i = 10^3*(-5.007261711E-15*T_cond_i^6 + 1.249032418E-
11*T_cond_i^5 - 1.135454979E-08*T_cond_i^4 + 5.164337223E-06*T_cond_i^3
- 1.275119405E-03*T_cond_i^2 + 1.643475641E-01*T_cond_i -
8.706432224E+00); %kPa

hfg_bedD_i = (10^3*(6.40224E-12*T_cond_i^5 - 3.93212E-08*T_cond_i^4 +
3.63907E-05*T_cond_i^3 - 1.39601E-02*T_cond_i^2 + 4.34707E+00*T_cond_i +
1.82254E+03)- 10^3*(1.95664E-10*T_cond_i^5 - 3.36772E-07*T_cond_i^4 +
2.34408E-04*T_cond_i^3 - 8.21171E-02*T_cond_i^2 + 1.86089E+01*T_cond_i -
2.15617E+03))*1E-3;

if(Ps_bedD_i <= P_bedD_i)

    w_bedD_i = wm;

else
    w_bedD_i = wm*((A*exp(n*(Qst-
hfg_bedD_i)/(Rw*T_bedD_i)))*(P_bedD_i/Ps_bedD_i)^n)/(1+(A*exp(n*(Qst-
hfg_bedD_i)/(Rw*T_bedD_i))-1)*(P_bedD_i/Ps_bedD_i)^n));

end

%=====
===
t = Time_i;
s = 0;
cycle = 0;

g = 0;
h = 0;

for M =1:N_cyc %Main loop for evaluating cycles

    t_round = 0;
    Q_D = 0;
    Q_E = 0;
    Q_C = 0;
    Q_A = 0;

    for L = 1:step:t_cycle

        s = s+1; %s is a counter. add counter

        t = t+step; %count elapsed time

```



```

        Time(s) = t; %Time is an array containing t where
the process is evaluated at

        t_round = t_round + step; %count elapsed time in one for-next
loop

        if(t_round <= t_normal) %check whether the elapsed time has
passed the normal operation time
            Flag1 = 1 ; %adsorption/desorption
        elseif((t_round > t_normal)&&(t_round <= t_cycle))
            Flag1 = 0 ; %switching mode
        end;

        Timerangel = [Time_i t]; %set time range to be used to
solve differential eqns.
        Initialvalues = [w_bedA_i T_bedA_i w_bedD_i T_bedD_i T_cond_i
T_evap_i]; %Initial values being used to solve diff. eqns. Being
stored first to Y before it is being used.

        option1 = odeset('RelTol', 1E-4, 'AbsTol', 1E-4); %setting
error tolerance

        Y = ode45(@ddydwtdt, Timerangel, Initialvalues, option1);
%solving all the diff eqns. in ddydwtdt.m file --> the step is being
decided by matlab

        Y_t = deval(Y,t); %Y_t's values are only Y's value at t;
not all the values of Y evaluated

        %Storing the newly calculated value into array of variables

        w_bedA(s) = Y_t(1);
        T_bedA(s) = Y_t(2);
        w_bedD(s) = Y_t(3);
        T_bedD(s) = Y_t(4);
        T_cond(s) = Y_t(5);
        T_evap(s) = Y_t(6);

        if(Flag1 == 1)

            Tcw_bed_in = Tcw_in;
            Tcw_bed_out = T_w_bedA_out;
            Thw_bed_in = Thw_in;
            Thw_bed_out = T_w_bedD_out;

        elseif(Flag1 == 0)

            Tcw_bed_in = Tcw_in;
            Tcw_bed_out = T_w_bedD_out;
            Thw_bed_in = Thw_in;
            Thw_bed_out = T_w_bedA_out;

```

```

end

T_cw_cond_in = Tcw_in;
T_cw_cond_out = T_w_cond_out;

%=====
%Adsorption/Desorption Switching
%=====

if ( (mod(M,2)==1) || (M == 1) )

    T_bed2(s) = T_bedD(s);
    W_bed2(s) = w_bedD(s);
    T_bed1(s) = T_bedA(s);
    W_bed1(s) = w_bedA(s);
    P_bed1(s) = P_bedA;
    P_bed2(s) = P_bedD;

else

    T_bed1(s) = T_bedD(s);
    W_bed1(s) = w_bedD(s);
    T_bed2(s) = T_bedA(s);
    W_bed2(s) = w_bedA(s);
    P_bed2(s) = P_bedA;
    P_bed1(s) = P_bedD;

end;

Tcond_in(s) = T_cw_cond_in;
Tcond_out(s) = T_cw_cond_out;
Thw_in(s) = Thw_bed_in;
Thw_out(s) = Thw_bed_out;
T_chill_in(s) = T_chw_in;
T_chill_out(s) = T_chw_out;

Hcw_bed_out = 1E-3*10^3*(1.95664E-10*Tcw_bed_out^5 - 3.36772E-
07*Tcw_bed_out^4 + 2.34408E-04*Tcw_bed_out^3 - 8.21171E-02*Tcw_bed_out^2
+ 1.86089E+01*Tcw_bed_out - 2.15617E+03);
Hcw_bed_in = 1E-3*10^3*(1.95664E-10*Tcw_bed_in^5 - 3.36772E-
07*Tcw_bed_in^4 + 2.34408E-04*Tcw_bed_in^3 - 8.21171E-02*Tcw_bed_in^2 +
1.86089E+01*Tcw_bed_in - 2.15617E+03);

Hhw_bed_in = 1E-3*10^3*(1.95664E-10*Thw_bed_in^5 - 3.36772E-
07*Thw_bed_in^4 + 2.34408E-04*Thw_bed_in^3 - 8.21171E-02*Thw_bed_in^2 +
1.86089E+01*Thw_bed_in - 2.15617E+03);
Hhw_bed_out = 1E-3*10^3*(1.95664E-10*Thw_bed_out^5 - 3.36772E-
07*Thw_bed_out^4 + 2.34408E-04*Thw_bed_out^3 - 8.21171E-02*Thw_bed_out^2
+ 1.86089E+01*Thw_bed_out - 2.15617E+03);

```

```

H_cw_cond_out = 1E-3*10^3*(1.95664E-10*T_cw_cond_out^5 -
3.36772E-07*T_cw_cond_out^4 + 2.34408E-04*T_cw_cond_out^3 - 8.21171E-
02*T_cw_cond_out^2 + 1.86089E+01*T_cw_cond_out - 2.15617E+03);
H_cw_cond_in = 1E-3*10^3*(1.95664E-10*T_cw_cond_in^5 - 3.36772E-
07*T_cw_cond_in^4 + 2.34408E-04*T_cw_cond_in^3 - 8.21171E-
02*T_cw_cond_in^2 + 1.86089E+01*T_cw_cond_in - 2.15617E+03);

Hfg_cond =(10^3*(6.40224E-12*Y_t(5)^5 - 3.93212E-08*Y_t(5)^4 +
3.63907E-05*Y_t(5)^3 - 1.39601E-02*Y_t(5)^2 + 4.34707E+00*Y_t(5) +
1.82254E+03)- 10^3*(1.95664E-10*Y_t(5)^5 - 3.36772E-07*Y_t(5)^4 +
2.34408E-04*Y_t(5)^3 - 8.21171E-02*Y_t(5)^2 + 1.86089E+01*Y_t(5) -
2.15617E+03))*1E-3;

H_chw_in = 1E-3*10^3*(1.95664E-10*T_chw_in^5 - 3.36772E-
07*T_chw_in^4 + 2.34408E-04*T_chw_in^3 - 8.21171E-02*T_chw_in^2 +
1.86089E+01*T_chw_in - 2.15617E+03);
H_chw_out = 1E-3*10^3*(1.95664E-10*T_chw_out^5 - 3.36772E-
07*T_chw_out^4 + 2.34408E-04*T_chw_out^3 - 8.21171E-02*T_chw_out^2 +
1.86089E+01*T_chw_out - 2.15617E+03);

dq_D = (m_dot_hw_bed*step)*(Hhw_bed_in - Hhw_bed_out)/t_cycle;
Q_D = Q_D + dq_D;

dq_A = (m_dot_cw_bed*step)*(Hcw_bed_out - Hcw_bed_in)/t_cycle;
Q_A = Q_A + dq_A;

dq_E = (m_dot_chw*step)*(H_chw_in - H_chw_out)/t_cycle;

Q_E = Q_E + dq_E;

dq_C = (m_dot_cw_cond*step)*(H_cw_cond_out -
H_cw_cond_in)/t_cycle;

Q_C = Q_C + dq_C;

%Storing the newly calculated value as the initial values for
the next round of calculation
Time_i = t;
w_bedA_i = Y_t(1);
T_bedA_i = Y_t(2);
w_bedD_i = Y_t(3);
T_bedD_i = Y_t(4);
T_cond_i = Y_t(5);
T_evap_i = Y_t(6);

T_chw_in = T_chw_in;

if ((t >= (N_cyc*t_cycle - 2*t_cycle))&&(t <= (N_cyc*t_cycle -
t_sw)))

    g = g+step;

    h = h+1;

```

```

Time_plot(h) = g;

T_bed1_plot(h) = T_bed1(s) -273;
T_bed2_plot(h) = T_bed2(s) - 273;
T_cond_plot(h) = T_cond(s)-273;
T_evap_plot(h) = T_evap(s)-273;

W_bed1_plot(h) = W_bed1(s);
W_bed2_plot(h) = W_bed2(s);

P_bed1_plot(h) = P_bed1(s);
P_bed2_plot(h) = P_bed2(s);

else

a = 0 ;

end

end

Q_evap(M) = Q_E
Q_des(M) = Q_D
Q_ads(M) = Q_A;
Q_cond(M)= Q_C;

Q_add(M) = (Q_evap(M) + Q_des(M));
Q_rej(M) = (Q_ads(M) + Q_cond(M));

Error(M) = ((Q_evap(M) + Q_des(M)) - (Q_ads(M) +
Q_cond(M))) *100/(Q_ads(M) + Q_cond(M))

COP(M) = Q_evap(M)/Q_des(M);
SCP(M) = Q_evap(M)/(2*Mads);
cycle(M) = M;

w_bedA_i = Y_t(3);
T_bedA_i = Y_t(4);
w_bedD_i = Y_t(1);
T_bedD_i = Y_t(2);

end

figure (1)
plot(Time, (T_bed1-273), Time, (T_bed2-273), Time, (T_cond-273), Time,
(T_evap-273));
hold all;

figure (2)
plot(Time, (P_bed1/1000), Time, (P_bed2/1000));

```

```

hold all;

figure(3)
plot(Time, W_bed1, Time, W_bed2);
hold all;

figure(4)
plot(cycle, Q_add, cycle,Q_rej);
hold all;

figure(5)
plot(cycle,COP);

hold all;

figure(6)
plot(cycle,SCP);

hold all;

figure(7)
plot(Time_plot,T_bed1_plot,Time_plot,T_bed2_plot,Time_plot,
T_cond_plot,Time_plot, T_evap_plot );
hold all;

figure(8)
plot(Time_plot,W_bed1_plot, Time_plot, W_bed2_plot);
hold all;

figure(9)
plot(Time_plot,P_bed1_plot, Time_plot,P_bed2_plot);
hold all;

figure (10)
plot(cycle, Q_evap);
hold all;

figure(11)
plot(cycle, Q_des);
hold all;

end

function dy = ddydwdt(t, Y)

global Flag1;
global Tcw_in Thw_in T_chw_in T_chw_out T_w_bedA_out T_w_bedD_out
T_w_cond_out
global P_bedA P_bedD w_bedA w_bedD
global m_dot_cw_bed m_dot_hw_bed m_dot_cw_cond m_dot_chw

```

```

global Mads Qst Rw A wm n D_so Rp Ea R C pads hfg_C
global Mhx_bedCphx_bed Mhx_condCphx_cond Mhx_evpcphx_evpc M_ref_L_cond
M_ref_L_evpc

dy = zeros(6,1);          %dy is a 5x1 matrix; syntax = zeros(row, column)

%Storing initial values from Main function to local variables

w_bedA = Y(1); T_bedA = Y(2);

T_evpc = Y(6);

w_bedD = Y(3); T_bedD = Y(4);

T_cond = Y(5);

%=====Bed
1=====
%checking the current mode; normal mode or switching mode

if(Flag1 == 1)                                %Bed1 is under adsorption mode
    T_w_bedA_in = Tcw_in;
    m_dot_w_bedA = m_dot_cw_bed;
elseif(Flag1 == 0)                            %Bed1 is under switching mode
    T_w_bedA_in = Thw_in;                    %Pre-heating for the adsorption
process
    m_dot_w_bedA = m_dot_hw_bed;
end

if(Flag1 == 1)

    P_bedA = 10^3*(-5.007261711E-15*T_evpc^6 + 1.249032418E-11*T_evpc^5 -
1.135454979E-08*T_evpc^4 + 5.164337223E-06*T_evpc^3 - 1.275119405E-
03*T_evpc^2 + 1.643475641E-01*T_evpc - 8.706432224E+00);
    Ps_bedA = 10^3*(-5.007261711E-15*T_bedA^6 + 1.249032418E-11*T_bedA^5 -
1.135454979E-08*T_bedA^4 + 5.164337223E-06*T_bedA^3 - 1.275119405E-
03*T_bedA^2 + 1.643475641E-01*T_bedA - 8.706432224E+00);
    hfg_bedA = (10^3*(6.40224E-12*T_bedA^5 - 3.93212E-08*T_bedA^4 +
3.63907E-05*T_bedA^3 - 1.39601E-02*T_bedA^2 + 4.34707E+00*T_bedA +
1.82254E+03) - 10^3*(1.95664E-10*T_bedA^5 - 3.36772E-07*T_bedA^4 +
2.34408E-04*T_bedA^3 - 8.21171E-02*T_bedA^2 + 1.86089E+01*T_bedA -
2.15617E+03))*1E-3;
    if(Ps_bedA <= P_bedA)

        w_star_bedA = wm;

    else
        w_star_bedA = wm*((A*exp(n*(Qst-
hfg_C)/(Rw*T_bedA)))*(P_bedA/Ps_bedA)^n)/(1+(A*exp(n*(Qst-
hfg_C)/(Rw*T_bedA))-1)*(P_bedA/Ps_bedA)^n));

    end;

```

```

elseif(Flag1 == 0)

    w_star_bedA = w_bedA;
    theta_bedA = w_star_bedA/wm;
    hfg_bedA = (10^3*(6.40224E-12*T_bedA^5 - 3.93212E-08*T_bedA^4 +
3.63907E-05*T_bedA^3 - 1.39601E-02*T_bedA^2 + 4.34707E+00*T_bedA +
1.82254E+03)- 10^3*(1.95664E-10*T_bedA^5 - 3.36772E-07*T_bedA^4 +
2.34408E-04*T_bedA^3 - 8.21171E-02*T_bedA^2 + 1.86089E+01*T_bedA -
2.15617E+03))*1E-3;
    K_bedA = A*exp(n*(Qst-hfg_C)/(Rw*T_bedA));
    Ps_bedA = 10^3*(-5.007261711E-15*T_bedA^6 + 1.249032418E-11*T_bedA^5
- 1.135454979E-08*T_bedA^4 + 5.164337223E-06*T_bedA^3 - 1.275119405E-
03*T_bedA^2 + 1.643475641E-01*T_bedA - 8.706432224E+00);
    P_bedA = Ps_bedA*(theta_bedA/(K_bedA-theta_bedA*(K_bedA-1)))^(1/n);
end

T_w_bedA_out = BedHex(T_bedA, T_w_bedA_in, m_dot_w_bedA);

h_w_bedA_in = 1E-3*10^3*(1.95664E-10*T_w_bedA_in^5 - 3.36772E-
07*T_w_bedA_in^4 + 2.34408E-04*T_w_bedA_in^3 - 8.21171E-02*T_w_bedA_in^2
+ 1.86089E+01*T_w_bedA_in - 2.15617E+03);
h_w_bedA_out = 1E-3*10^3*(1.95664E-10*T_w_bedA_out^5 - 3.36772E-
07*T_w_bedA_out^4 + 2.34408E-04*T_w_bedA_out^3 - 8.21171E-
02*T_w_bedA_out^2 + 1.86089E+01*T_w_bedA_out - 2.15617E+03);
CpabeA = 10^3*(-1.35090E-11*T_bedA^5 + 2.40993E-08*T_bedA^4 - 1.71323E-
05*T_bedA^3 + 6.07609E-03*T_bedA^2 - 1.07591*T_bedA + 8.02982E01)*1E-3;

%=====Bed
2=====
%checking the current mode; normal mode or switching mode

if(Flag1 == 1) %Bed2 is under desorption mode
    T_w_bedD_in = Thw_in;
    m_dot_w_bedD = m_dot_hw_bed;

elseif(Flag1 == 0) %Bed2 is under switching mode
    T_w_bedD_in = Tcw_in; %Pre-cooling for the desorption
process
    m_dot_w_bedD = m_dot_cw_bed;

end

if(Flag1 == 1)

    P_bedD = 10^3*(-5.007261711E-15*T_cond^6 + 1.249032418E-11*T_cond^5
- 1.135454979E-08*T_cond^4 + 5.164337223E-06*T_cond^3 - 1.275119405E-
03*T_cond^2 + 1.643475641E-01*T_cond - 8.706432224E+00);
    Ps_bedD = 10^3*(-5.007261711E-15*T_bedD^6 + 1.249032418E-11*T_bedD^5
- 1.135454979E-08*T_bedD^4 + 5.164337223E-06*T_bedD^3 - 1.275119405E-
03*T_bedD^2 + 1.643475641E-01*T_bedD - 8.706432224E+00);

```

```

    hfg_bedD = (10^3*(6.40224E-12*T_bedD^5 - 3.93212E-08*T_bedD^4 +
3.63907E-05*T_bedD^3 - 1.39601E-02*T_bedD^2 + 4.34707E+00*T_bedD +
1.82254E+03) - 10^3*(1.95664E-10*T_bedD^5 - 3.36772E-07*T_bedD^4 +
2.34408E-04*T_bedD^3 - 8.21171E-02*T_bedD^2 + 1.86089E+01*T_bedD -
2.15617E+03))*1E-3;

    if(Ps_bedD <= P_bedD)

        w_star_bedD = wm;

    else
        w_star_bedD = wm*((A*exp(n*(Qst-
hfg_C)/(Rw*T_bedD)))*(P_bedD/Ps_bedD)^n)/(1+(A*exp(n*(Qst-
hfg_C)/(Rw*T_bedD))-1)*(P_bedD/Ps_bedD)^n));

    end;

elseif(Flag1 == 0)

    w_star_bedD = w_bedD;
    theta_bedD = w_star_bedD/wm;
    hfg_bedD = (10^3*(6.40224E-12*T_bedD^5 - 3.93212E-08*T_bedD^4 +
3.63907E-05*T_bedD^3 - 1.39601E-02*T_bedD^2 + 4.34707E+00*T_bedD +
1.82254E+03) - 10^3*(1.95664E-10*T_bedD^5 - 3.36772E-07*T_bedD^4 +
2.34408E-04*T_bedD^3 - 8.21171E-02*T_bedD^2 + 1.86089E+01*T_bedD -
2.15617E+03))*1E-3;
    K_bedD = A*exp(n*(Qst-hfg_C)/(Rw*T_bedD));
    Ps_bedD = 10^3*(-5.007261711E-15*T_bedD^6 + 1.249032418E-11*T_bedD^5
- 1.135454979E-08*T_bedD^4 + 5.164337223E-06*T_bedD^3 - 1.275119405E-
03*T_bedD^2 + 1.643475641E-01*T_bedD - 8.706432224E+00);
    P_bedD = Ps_bedD*(theta_bedD/(K_bedD-theta_bedD*(K_bedD-1)))^(1/n);

end

T_w_bedD_out = BedHex(T_bedD, T_w_bedD_in, m_dot_w_bedD);

h_w_bedD_in = 1E-3*10^3*(1.95664E-10*T_w_bedD_in^5 - 3.36772E-
07*T_w_bedD_in^4 + 2.34408E-04*T_w_bedD_in^3 - 8.21171E-02*T_w_bedD_in^2
+ 1.86089E+01*T_w_bedD_in - 2.15617E+03);
h_w_bedD_out = 1E-3*10^3*(1.95664E-10*T_w_bedD_out^5 - 3.36772E-
07*T_w_bedD_out^4 + 2.34408E-04*T_w_bedD_out^3 - 8.21171E-
02*T_w_bedD_out^2 + 1.86089E+01*T_w_bedD_out - 2.15617E+03);
CpabeD = 10^3*(-1.35090E-11*T_bedD^5 + 2.40993E-08*T_bedD^4 - 1.71323E-
05*T_bedD^3 + 6.07609E-03*T_bedD^2 - 1.07591*T_bedD + 8.02982E01)*1E-3;

%=====Condenser=====
===
T_w_cond_in = Tcw_in;
m_dot_w_cond = m_dot_cw_cond;

T_w_cond_out = CondHex(T_cond, T_w_cond_in, m_dot_w_cond);

```



```

h_fg_cond =(10^3*(6.40224E-12*T_cond^5 - 3.93212E-08*T_cond^4 +
3.63907E-05*T_cond^3 - 1.39601E-02*T_cond^2 + 4.34707E+00*T_cond +
1.82254E+03)- 10^3*(1.95664E-10*T_cond^5 - 3.36772E-07*T_cond^4 +
2.34408E-04*T_cond^3 - 8.21171E-02*T_cond^2 + 1.86089E+01*T_cond -
2.15617E+03))*1E-3;

h_f_cond = 1E-3*10^3*(1.95664E-10*T_cond^5 - 3.36772E-07*T_cond^4 +
2.34408E-04*T_cond^3 - 8.21171E-02*T_cond^2 + 1.86089E+01*T_cond -
2.15617E+03);
h_f_w_cond_in = 1E-3*10^3*(1.95664E-10*T_w_cond_in^5 - 3.36772E-
07*T_w_cond_in^4 + 2.34408E-04*T_w_cond_in^3 - 8.21171E-02*T_w_cond_in^2
+ 1.86089E+01*T_w_cond_in- 2.15617E+03);
h_f_w_cond_out = 1E-3*10^3*(1.95664E-10*T_w_cond_out^5 - 3.36772E-
07*T_w_cond_out^4 + 2.34408E-04*T_w_cond_out^3 - 8.21171E-
02*T_w_cond_out^2 + 1.86089E+01*T_w_cond_out- 2.15617E+03);

Cp_ref_L_cond = 10^3*(-1.35090E-11*T_cond^5 + 2.40993E-08*T_cond^4 -
1.71323E-05*T_cond^3 + 6.07609E-03*T_cond^2 - 1.07591*T_cond +
8.02982E01)*1E-3;

%=====Evaporator=====
===

T_chw_out = EvpHex(T_evap, T_chw_in, m_dot_chw);

h_fg_evap =(10^3*(6.40224E-12*T_evap^5 - 3.93212E-08*T_evap^4 + 3.63907E-
05*T_evap^3 - 1.39601E-02*T_evap^2 + 4.34707E+00*T_evap + 1.82254E+03)-
10^3*(1.95664E-10*T_evap^5 - 3.36772E-07*T_evap^4 + 2.34408E-04*T_evap^3 -
8.21171E-02*T_evap^2 + 1.86089E+01*T_evap - 2.15617E+03))*1E-3;

h_f_chw_in = 1E-3*10^3*(1.95664E-10*T_chw_in^5 - 3.36772E-07*T_chw_in^4
+ 2.34408E-04*T_chw_in^3 - 8.21171E-02*T_chw_in^2 + 1.86089E+01*T_chw_in
- 2.15617E+03);
h_f_chw_out = 1E-3*10^3*(1.95664E-10*T_chw_out^5 - 3.36772E-
07*T_chw_out^4 + 2.34408E-04*T_chw_out^3 - 8.21171E-02*T_chw_out^2 +
1.86089E+01*T_chw_out- 2.15617E+03);

Cp_ref_L_evap = 10^3*(-1.35090E-11*T_evap^5 + 2.40993E-08*T_evap^4 -
1.71323E-05*T_evap^3 + 6.07609E-03*T_evap^2 - 1.07591*T_evap +
8.02982E01)*1E-3;

%=====
===

%Adsorption kinetics
if (Flag1 == 1)
    P_A = 10^3*(-5.007261711E-15*Y(6)^6 + 1.249032418E-11*Y(6)^5 -
1.135454979E-08*Y(6)^4 + 5.164337223E-06*Y(6)^3 - 1.275119405E-03*Y(6)^2
+ 1.643475641E-01*Y(6) - 8.706432224E+00);
    Ps_A = 10^3*(-5.007261711E-15*Y(2)^6 + 1.249032418E-11*Y(2)^5 -
1.135454979E-08*Y(2)^4 + 5.164337223E-06*Y(2)^3 - 1.275119405E-03*Y(2)^2
+ 1.643475641E-01*Y(2) - 8.706432224E+00);
    hfg_A =(10^3*(6.40224E-12*Y(2)^5 - 3.93212E-08*Y(2)^4 + 3.63907E-
05*Y(2)^3 - 1.39601E-02*Y(2)^2 + 4.34707E+00*Y(2) + 1.82254E+03)-

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10^3*(1.95664E-10*Y(2)^5 - 3.36772E-07*Y(2)^4 + 2.34408E-04*Y(2)^3 -
8.21171E-02*Y(2)^2 + 1.86089E+01*Y(2) - 2.15617E+03))*1E-3;
kads_A = 18*(P_A*10^3)/(2*pi*18*R*Y(2))^0.5 * exp(-(Ea/(R*Y(2))))*912;
K_bedA = A*exp(n*(Qst-hfg_C)/(Rw*Y(2)));
w_bedA_const = kads_A*(P_A/Ps_A)^n + (kads_A/K_bedA)*(1-(P_A/Ps_A)^n);
dy(1) = (kads_A*(P_A/Ps_A)^n - w_bedA_const*Y(1)/wm)*wm;
elseif (Flag1 == 0)
dy(1) = 0;
end

%dT/dt from Energy Balance equation for BedA
dy(2) = ((Qst*Mads * dy(1))-(m_dot_w_bedA*(h_w_bedA_out-
h_w_bedA_in)))/(Mads*Cpads + Mhx_bedCphx_bed + Mads*Y(1)*CpabeA);

%Desorption kinetics
if (Flag1 == 1)
P_D = 10^3*(-5.007261711E-15*Y(5)^6 + 1.249032418E-11*Y(5)^5 -
1.135454979E-08*Y(5)^4 + 5.164337223E-06*Y(5)^3 - 1.275119405E-03*Y(5)^2
+ 1.643475641E-01*Y(5) - 8.706432224E+00);
Ps_D = 10^3*(-5.007261711E-15*Y(4)^6 + 1.249032418E-11*Y(4)^5 -
1.135454979E-08*Y(4)^4 + 5.164337223E-06*Y(4)^3 - 1.275119405E-03*Y(4)^2
+ 1.643475641E-01*Y(4) - 8.706432224E+00);
hfg_D = (10^3*(6.40224E-12*Y(4)^5 - 3.93212E-08*Y(4)^4 + 3.63907E-
05*Y(4)^3 - 1.39601E-02*Y(4)^2 + 4.34707E+00*Y(4) + 1.82254E+03)-
10^3*(1.95664E-10*Y(4)^5 - 3.36772E-07*Y(4)^4 + 2.34408E-04*Y(4)^3 -
8.21171E-02*Y(4)^2 + 1.86089E+01*Y(4) - 2.15617E+03))*1E-3;
kads_D = 18*(P_D*10^3)/(2*pi*18*R*Y(4))^0.5 * exp(-(Ea/(R*Y(4))))*912;
K_bedD = A*exp(n*(Qst-hfg_C)/(Rw*Y(4)));
w_bedD_const = kads_D*(P_D/Ps_D)^n + (kads_D/K_bedD)*(1-(P_D/Ps_D)^n);
dy(3) = (kads_D*(P_D/Ps_D)^n - w_bedD_const*Y(3)/wm)*wm;
elseif (Flag1 == 0)
dy(3) = 0;
end

%dT/dt from Energy Balance equation for Bed1
dy(4) = (((m_dot_w_bedD*(h_w_bedD_in - h_w_bedD_out) + Qst*Mads *
dy(3)))/ (Mads*Cpads + Mhx_bedCphx_bed + Mads*Y(3)*CpabeD);

%Energy balance for condenser
dy(5) = (-Mads*dy(3)*h_fg_cond - m_dot_w_cond*(h_f_w_cond_out -
h_f_w_cond_in) + Mads*dy(3)*h_f_cond)/(Mhx_condCphx_cond +
M_ref_L_cond*Cp_ref_L_cond);

%Energy balance for evaporator
dy(6) = (m_dot_chw*(h_f_chw_in - h_f_chw_out) - h_f_cond*Mads*dy(3) -
h_fg_evap*Mads*dy(1))/(Mhx_evapCphx_evap + M_ref_L_evap*Cp_ref_L_evap);

end

function [T_w_bed_out] = BedHex(T_bed, T_w_bed_in, m_dot_w_bed)

global UA_bedA UA_bedD Thw_in Tcw_in

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if (T_w_bed_in == Tcw_in)
    Cp_w_bed = 10^3*(-1.35090E-11*T_bed^5 + 2.40993E-08*T_bed^4 -
1.71323E-05*T_bed^3 + 6.07609E-03*T_bed^2 - 1.07591*T_bed +
8.02982E01)*1E-3;
    T_w_bed_out = T_bed + (T_w_bed_in - T_bed)*exp((-
UA_bedA)/(m_dot_w_bed*Cp_w_bed));
elseif (T_w_bed_in == Thw_in)
    Cp_w_bed = 10^3*(-1.35090E-11*T_bed^5 + 2.40993E-08*T_bed^4 -
1.71323E-05*T_bed^3 + 6.07609E-03*T_bed^2 - 1.07591*T_bed +
8.02982E01)*1E-3;
    T_w_bed_out = T_bed + (T_w_bed_in - T_bed)*exp((-
UA_bedD)/(m_dot_w_bed*Cp_w_bed));
end
end

function T_w_cond_out = CondHex(T_cond, T_w_cond_in, m_dot_w_cond)

global U_cond A_cond

Cp_w_cond = 10^3*(-1.35090E-11*T_cond^5 + 2.40993E-08*T_cond^4 -
1.71323E-05*T_cond^3 + 6.07609E-03*T_cond^2 - 1.07591*T_cond +
8.02982E01)*1E-3;

T_w_cond_out = T_cond + (T_w_cond_in - T_cond)*exp((-
U_cond*A_cond)/(m_dot_w_cond*Cp_w_cond));

end

function T_chw_out = EvpHex(T_evp, T_chw_in, m_dot_chw)

global U_evp A_evp

Cp_w_evp = 10^3*(-1.35090E-11*T_evp^5 + 2.40993E-08*T_evp^4 - 1.71323E-
05*T_evp^3 + 6.07609E-03*T_evp^2 - 1.07591*T_evp + 8.02982E01)*1E-3;

T_chw_out = T_evp + (T_chw_in - T_evp)*exp((-
U_evp*A_evp)/(m_dot_chw*Cp_w_evp));

end

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