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## A NEW GENERATION COOLING DEVICE EMPLOYING MOF

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**ABSTRACT:** This article presents the thermodynamic framework of a single effect two-bed adsorption chiller employing “HKUST-1 type metal organic frameworks (MOFs)” as adsorbent and water as adsorbate, which is based on the experimentally validated adsorption isotherms and kinetics data. The experimentally measured MOFs + water based isotherms and kinetics data are fitted with Toth and Langmuir adsorption isotherm models and LDF kinetics equations. Compared with the experimentally measured isotherms and kinetics based numerical performance data of conventional adsorption chiller (RD silica gel + water pair), we found that the new working pair provides better cooling capacity and performances. From numerical simulation, it is found that the cooling capacity can be increased up to 27% of the parent silica gel + water adsorption chiller and the coefficient of performance (COP) can be improved up to 5% at optimum conditions.

### 1. INTRODUCTION

The development of a new generation cooling device substituting the conventional vapor compression refrigeration system is motivated by two main factors. Firstly, there is a global thrust towards the minimal usage of primary energy source from fossil fuels. Due to the rapid population growth and massive industrial development over the last few decades world's primary energy demand has been increased by more than 100% from 1971 to 2010 [1]. Non-renewable energy resources are limited and will run out soon if alternative sources of energy are not used. The second factor is the ecological problem. The global warming potential (GWP) of conventional refrigerants contributes to the growth of greenhouse gas in the atmosphere which can potentially cause dangerous climate change by global warming [2-4].

Adsorption cooling system (ADC) uses waste heat or renewable energy instead of electrical energy to compress the refrigerant from evaporator pressure to condenser pressure. In addition to this unlike conventional cooling systems it uses water as refrigerant which is not responsible for the global warming. In spite of having all these benefits, ADC has a main drawback of having low Coefficient of Performance (COP) and Specific Cooling Power (SCP). COP of ADC ranges from 0.3 to 0.4. SCP of ADC has been reported 0.4 to 0.5 in different researches [5-31]. Due to the low SCP, the AD system requires more adsorbent to obtain the same amount of cooling capacity at the evaporator. In order to accommodate the adsorbent ADC requires bulky adsorption reactors. Commercial applications of ADC have been inhibited due to the giant system footprint, bulky reactors and massive adsorbent

requirements.

Numerous researches have been carried out to increase the SCP and COP of AD cycle. Saha et al., developed a dual mode multi stage silica gel-water adsorption chiller system where the first operating mode is to work at high COP along with high temperature driving heat source and the second mode is to work with low temperature driving heat source and at low COP as well. The optimum COP value obtained was only 0.3 [8]. El-Sharkawy et al., studied the effects of adsorption and desorption time on COP. The optimum COP was found to be 0.42 when adsorption and desorption duration was 300 and 350 second respectively [10].

Adsorbent of an AD cycle is a critical variable and the system performance depends on how the solid adsorbents perform both in equilibrium and kinetics [11]. Plenty of adsorbent-adsorbate pairs have been investigated both theoretically and experimentally. Chan et al., reported the COP and SCP of AD cooling system using Zeolite was 0.42 and 13.7 (W/Kg), in contrast using Zeolite/CaCl<sub>2</sub> composite adsorbent the COP and SCP was 0.76 and 18.6 (W/kg) [12]. Wang, X., and Chua, H.T. studied the performance of a two bed AD cycle using Silica gel-water and found that the optimum COP was 0.4. [13]. Saha et al., conducted another study to compare the performance of AD cooling cycle using Silica gel - water and SWS-1L - Water pair. 25% improvement in COP and 20% in SCP have been noticed after using SWS-1L - Water instead of Silica gel - water [14].

In case of most adsorbent maximum water adsorption

## Nomenclature

$A$	Area ( $m^2$ )	$h$	Enthalpy (Kj/Kg)
$C_p$	Specific heat (Kj/KgK)	$t$	Time (s)
$D_{so}$	Kinetic Constant ( $m^2/s$ )	$U$	Overall heat transfer coefficient (KW/ $m^2K$ )
$E_a$	Activation Energy (Kj/Kg)	$COP$	Coefficient of Performance
$q^*$	Equilibrium uptake (Kg/Kg of Adsorbent)	$SCP$	Specific Cooling Power
$q_m$	Limiting Uptake (Kg/Kg of Adsorbent)	Subscript	
$q$	Instantaneous Uptake (Kg/Kg of Adsorbent)	<i>ads</i>	Adsorption
$K_0$	Pre-exponential constant	<i>des</i>	Desorption
$Q$	Heat	<i>cw</i>	Cooling Water
$R$	Gas Constant (Kj/Kg-mol)	<i>hw</i>	Hot Water
$T$	Temperature ( $^{\circ}C$ )	<i>HX</i>	Heat Exchanger
$P$	Pressure (KPa)	<i>chw</i>	Chilled Water
$R_p$	Particle Radius (mm)	<i>cond</i>	Condenser
$M$	Mass (Kg)	<i>evp</i>	Evaporator
$\dot{m}$	Mass flow rate (Kg/s)	<i>ref</i>	Refrigerant

occurs at high partial pressure. But in adsorption cooling cycle adsorption occurs at very low partial pressure. As a result only a small portion of adsorbent capacity is utilized which causes the low COP and SCP. In order to enhance the adsorption at low partial pressure a new micro-porous material with uniform structure and large surface area ( $5500 m^2/gm$ ) has been introduced which is named as Metal Organic Framework (MOF). SEM images of silica gel and MOF are presented in Fig. 1 to compare their structures.

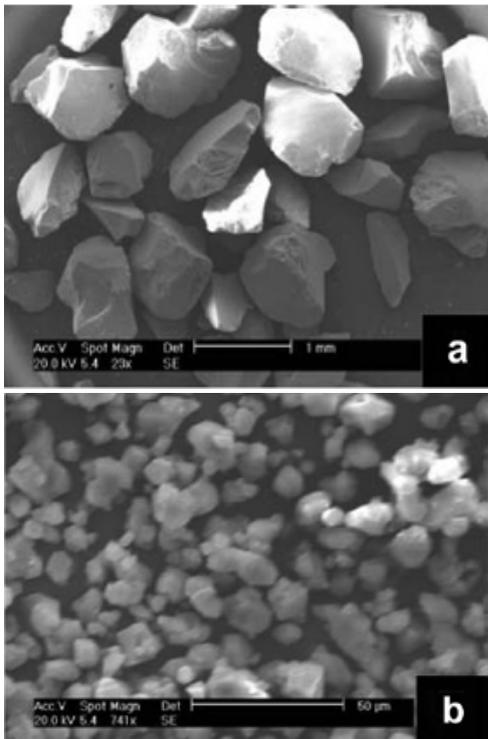


Fig. 1 SEM image of (a) Silica gel and (b) MOF

MOF structure consists of two main components: the organic linkers and the inorganic metal centres. These components are connected to each other by coordination bonds to form a network [10]. In this study Copper

based MOF HKUST-1 ( $C_{18}H_6Cu_3O_{12}$ ) is investigated for adsorption cooling application. This study aims at investigating and comparing the optimum COP and SCP of a two bed AD cycle using Silica gel – water and MOF - water pair.

## 2. SYSTEM DESCRIPTION

The two bed AD cycle comprises four heat exchangers namely a condenser, an evaporator, and two sorption (adsorber/desorber) reactors which is shown in Fig. 2.

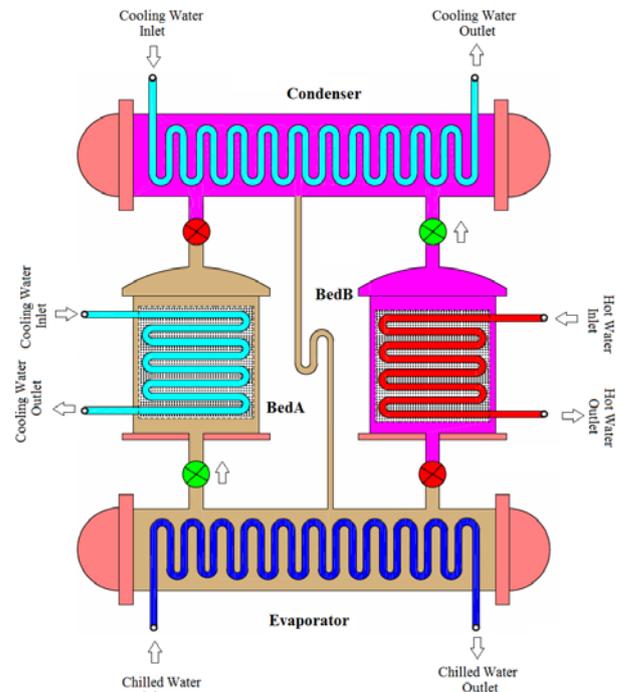


Fig. 2 Schematic Diagram of ADC

In the adsorption system two refrigerant valves are placed between the evaporator and the adsorber/desorber reactors while the other pair of valves

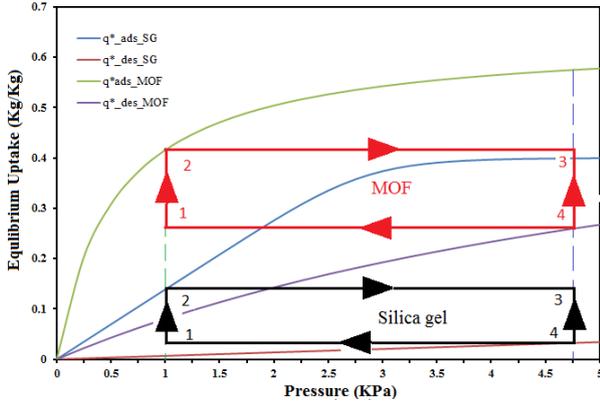


Fig. 3 Thermodynamic Cycle of ADC

is installed between the condenser and the adsorption reactors to control the flow of refrigerant throughout the system. The evaporator and the condenser are connected together through a bended tube to maintain a pressure difference between them. The system is operated in four modes A, B, C and D, are presented in Table 1. In mode A, receiving latent heat from the chilled water, refrigerant water evaporates in the evaporator at evaporator pressure and flows to the Bed A (adsorber) through the valve V1 while the valve V2 remains closed. Refrigerant vapor is then adsorbed at Bed A while the cooling water flows through the Bed and removes the generated heat of adsorption. During this process valve V3 remains closed. At the same time hot water flowing through bed B heats up the sorption bed so that the vapor which was adsorbed into the bed in the previous cycle is desorbed and desorbed vapor goes to the condenser through the valve V4. Cooling water flows through the condenser to cool the desorbed vapor below the saturation temperature of condenser. As a result the vapor changed its phase to liquid. Finally the condensed liquid water fluxes back to the evaporator through the bended tube. In this mode, adsorption and desorption process are taken place at Beds A and B respectively. At this junction of time the system is switched to the switching mode. All the valves are closed, hot water and cooling water flows through the Bed A and B respectively. Bed A is under preheating and Bed B is under precooling operation. Mode C and D are reverse of Mode A and B.

Table 1 Chiller Operation Modes

Mode	Bed A	Bed B	V1	V2	V3	V4
A	Ads.	Des.	ON	OFF	OFF	ON
B	Pre Heat	Pre Cool	OFF	OFF	OFF	OFF
C	Des.	Ads.	OFF	ON	ON	OFF
D	Pre Cool	Pre Heat	OFF	OFF	OFF	OFF

A basic adsorption cooling cycle consists of four thermodynamic processes namely, adsorption, preheating, desorption and pre-cooling are shown in Fig.

3. In the adsorption cooling cycle adsorption process is the first occurred when the heat of adsorption is generated within the bed while water vapor is adsorbed in silica gel or MOF porous structure at adsorption pressure. Next process is preheating when the hot water flows through the bed as a result the bed temperature increases and the pressure reaches to the desorption pressure. Process followed by preheating is desorption process when hot water continues to flow through the bed. During this process bed receives heat from hot water and regenerates the water vapor from silica gel which is already adsorbed during adsorption process.

### 3. MATHEMATICAL MODELING

#### 3.1 Adsorption Isotherms and Kinetics

Adsorption isotherm model is the equation used to calculate the amount of adsorbate vapor uptake by adsorbent at different temperatures and pressures. Several isotherm models have been employed for simulation of AD chiller. In this study Toth's isotherm model is used for silica gel and Langmuir model is used for MOF. These models are given by equation (1) and (2) respectively.

$$q^* = \frac{q_m K_0 \exp\left(\frac{Q_{st}}{RT}\right) P}{[1 + \{K_0 \exp\left(\frac{Q_{st}}{RT}\right) P\}^t]^{1/t}} \quad (1)$$

Where  $q^*$  is the amount of adsorbate at equilibrium conditions,  $q_m$  denotes the monolayer uptake capacity,  $Q_{st}$  is the isosteric heat of adsorption,  $K_0$  is the pre-exponential constant and  $t$  is dimensionless Toth's constant.

$$q^* = \frac{q_m [b \cdot (\frac{P}{P_s})]}{[1 + b \cdot (\frac{P}{P_s})]} \quad (2)$$

The Values of these constants are shown in Table 2.

Table 2 Isotherm properties of Silica gel and MOF [8,10]

Type	$q_m$ (Kg/Kg)	$K_0$ (Pa <sup>-1</sup> )	$Q_{st}$ (Kj/Kg)	t
Silica gel	0.4	7.3e-13	2800	8
	$q_m$ (Kg/Kg)		b	
MOF	0.64		8.33	

The transient uptakes of adsorbent at specific temperature and pressure are given by the adsorption kinetics which is calculated from the conventional linear driving force (LDF) model as shown in equation 3.

$$\frac{dq}{dt} = \frac{F \cdot D_{so} \exp\left(\frac{-E_a}{RT}\right)}{R_p^2} (q^* - q) \quad (3)$$

where  $D_{so}$  is the kinetic constant,  $E_a$  is the activation energy,  $R_p$  is the particle radius,  $q^*$  is the equilibrium uptake, and  $q$  denotes the instantaneous uptake. LDF equation parameters are listed in Table 3.

Table 3 LDF equation parameters of Silica gel and MOF [10]

Type	$F \cdot D_{so}$ (m <sup>2</sup> /S)	$E_a$ (KJ/mol)	$R_p$ (m)
Silica gel	15x2.54e-4	42	0.17e-3
MOF	4.08e-3	49.9	8e-6

### 3.2 Energy balance

The lumped parameter model is used to describe the energy balance of adsorber/desorber where both adsorbents and heat exchanger metals are assumed to have the same temperature. The energy balance of adsorber/desorber is given by,

$$(M_{ads}C_{p,ads} + M_{HX,bed}C_{p,HX} + M_{abe}C_{p,abe}) \frac{dT_{ads/des}}{dt} = \pm Q_{st}M_{ads} \frac{dq_{ads/des}}{dt} \pm \dot{m}_{cw/hw}C_{p,cw/hw}(T_{ads/des})(T_{cw/hw,in} - T_{cw/hw,out}) \quad (4)$$

where the left hand side of equation (3) provides the amount of sensible heat required to cool down or heat up the adsorbent, adsorbate and heat exchanger tube. The first term on the right hand side represents the heat input during desorption process or the heat released during adsorption process. The second term indicates the total amount of heat added to the system during desorption or heat released during adsorption process. The outlet temperature of the water from both adsorber/desorber heat exchanger which is estimated using log mean temperature difference method and is calculated by equations (5) and (6)

$$T_{cw,out} = T_{bed} + (T_{cw,in} - T_{bed}) \exp\left\{\frac{-UA}{\dot{m}_{cw}C_{p,cw}(T_{bed})}\right\} \quad (5)$$

$$T_{hw,out} = T_{bed} + (T_{hw,in} - T_{bed}) \exp\left\{\frac{-UA}{\dot{m}_{hw}C_{p,hw}(T_{bed})}\right\} \quad (6)$$

The energy balance of the condenser is expressed by,

$$(M_{cond}^{ref}C_p(T_{cond}) + M_{HX,cond}C_{p,HX}) \frac{dT_{cond}}{dt} = h_f(T_{cond})M_{ads} \frac{dq_{des}}{dt} - \dot{m}_{cw}C_{p,cw}(T_{cond})(T_{cond,out} - T_{cond,in}) - h_{fg}(T_{cond})M_{ads} \frac{dq_{des}}{dt} \quad (7)$$

The outlet temperature of water from condenser heat exchanger is given by,

$$T_{cond,out} = T_{cond} + (T_{cond,in} - T_{cond}) \exp\left\{\frac{-UA}{\dot{m}_{Cp,hw}(T_{cond})}\right\} \quad (8)$$

The energy balance of the evaporator is written as,

$$(M_{evp}^{ref}C_p(T_{evp}) + M_{HX,evp}C_{p,HX}) \frac{dT_{evp}}{dt} = \dot{m}_{chw}C_{p,chw}(T_{evp})(T_{chw,in} - T_{chw,out}) - h_{fg}(T_{evp})M_{ads} \frac{dq_{ads}}{dt} - h_f(T_{cond})M_{ads} \frac{dq_{des}}{dt} \quad (9)$$

The outlet temperature of water from evaporator heat exchanger is given in equation (10)

$$T_{evp,out} = T_{evp} + (T_{evp,in} - T_{evp}) \exp\left\{\frac{-UA}{\dot{m}_{Cp,chw}(T_{evp})}\right\} \quad (10)$$

### 3.3 Mass balance

Neglecting the mass of gaseous phase of refrigerant the mass balance of AD cooling system is expressed as,

$$\frac{dM_{ref}}{dt} = -M_{ads} \left( \frac{dq_{ads}}{dt} + \frac{dq_{des}}{dt} \right) \quad (11)$$

where  $M_{ads}$  is the amount of total adsorbent used in two beds,  $q_{ads}$  and  $q_{des}$  is the amount of water vapor adsorbed and desorbed during adsorption and desorption processes.

### 3.4 System Performances

Energy required to regenerate water vapor from the adsorbent is expressed by

$$Q_{des} = \dot{m}_{hw}C_p(T_{des})(T_{hw,in} - T_{hw,out}) \quad (12)$$

Concurrently the energy rejected to adsorb water vapor into the adsorbent material is calculated by

$$Q_{ads} = \dot{m}_{cw}C_p(T_{ads})(T_{cw,out} - T_{cw,in}) \quad (13)$$

Heat removed from the regenerated water vapor to change its phase to liquid is estimated by

$$Q_{cond} = \dot{m}_{cw}C_{p,cw}(T_{cond})(T_{cond,out} - T_{cond,in}) \quad (13)$$

Energy received from the chilled water to evaporate the refrigerant water is given by

$$Q_{evp} = \dot{m}_{chw}C_{p,chw}(T_{evp})(T_{chw,in} - T_{chw,out}) \quad (14)$$

The energy balance of the whole AD cooling system can be written as

$$Q_{des} + Q_{evp} = Q_{des} + Q_{cond} \quad (15)$$

Cycle average heat removed from the load to the chilled water is given by

$$Q_{Load} = \frac{\int_0^{t_{cycle}} \dot{m}_{chw}C_{p,chw}(T_{chw,in} - T_{chw,out})dt}{t_{cycle}} \quad (16)$$

Here  $t_{cycle}$  is the total duration of adsorption or desorption processes and switching process which is expressed by

$$t_{cycle} = t_{ads/des} + t_{switching} \quad (17)$$

Cycle average heat added to regenerate the vapor is

$$Q_{add} = \frac{\int_0^{t_{cycle}} \dot{m}_{hw} C_{p,hw} (T_{hw,out} - T_{hw,in}) dt}{t_{cycle}} \quad (17)$$

Finally the performance of the AD cycle is calculated in terms of COP and SCP and are given by

$$COP = \frac{Q_{Load}}{Q_{add}} \quad (18)$$

$$SCP = \frac{Q_{Load}}{M_{ads}} \quad (19)$$

#### 4. RESULTS AND DISCUSSION

The principal performance parameters of the AD cooling system are COP and SCP. These parameters are calculated by simulating the mathematical models for

Table 4 Parameter values used in simulation

$M_{ads}$	20 kg
$C_{p,ads}$	0.921 KJ/kg
$M_{HX,bed} C_{p,HX}$	180 Kg*(KJ/kg-K)
$U_{bed}$	0.250 KW/m <sup>2</sup> -K
$A_{bed}$	41.7 m <sup>2</sup>
$\dot{m}_{cw-bed}$	1.9 kg/s
$\dot{m}_{hw-bed}$	1.9 kg/s
$M_{HX,cond} C_{p,HX}$	12.62 Kg*(KJ/kg-K)
$\dot{m}_{cw-cond}$	1 kg/S
$U_{cond}$	4.115 KW/m <sup>2</sup> -K
$A_{cond}$	3.71 m <sup>2</sup>
$M_{HX,evp} C_{p,HX}$	3.434 kg*(KJ/kg-K)
$\dot{m}_{chw-evp}$	1.2 kg/s for Silica gel and 1.5 Kg/Sec for MOF
$U_{evp}$	1.250 KW/m <sup>2</sup> -K
$A_{evp}$	3.5 m <sup>2</sup>
$M_{cond}^{ref}$	70 kg
$M_{evp}^{ref}$	100 kg
$T_{chw,in}$	15 <sup>0</sup> C
$T_{cw-bed-in}$	30 <sup>0</sup> C
$T_{cw-cond-in}$	30 <sup>0</sup> C
$T_{hw-bed-in}$	85 <sup>0</sup> C
$t_{cycle}$	420 Sec
$t_{sw}$	30 Sec

various cycle time, switching time, heat source temperature and mass flow rate of cooling water and hot water. The optimized values of the ADC model parameters for silica gel and MOF are presented in Table 5. Fig. 4 shows the transient temperature profiles of the major components such as Bed A, Bed B, condenser and evaporator of the ADC containing 36 kg of silica gel and MOF. It should be noted that the same evaporator temperature 7<sup>0</sup> C can be obtained by flowing 1.5 Kg/s chilled water for MOF and 1.2 Kg/s for silica gel beds. Fig. 5 demonstrates the influences of cycle time on cycle average COP and SCP of ADC using silica gel and MOF as adsorbent materials. It can be seen that the COP increases with the cycle time. Increase in COP is attributed to the reduction in sensible heat exchange due to the smaller ratio of switching time to adsorption or desorption time. Maximum COP of ADC is 0.46 and 0.52 at cycle time 450 Sec and 850 Sec for silica gel and MOF, respectively.

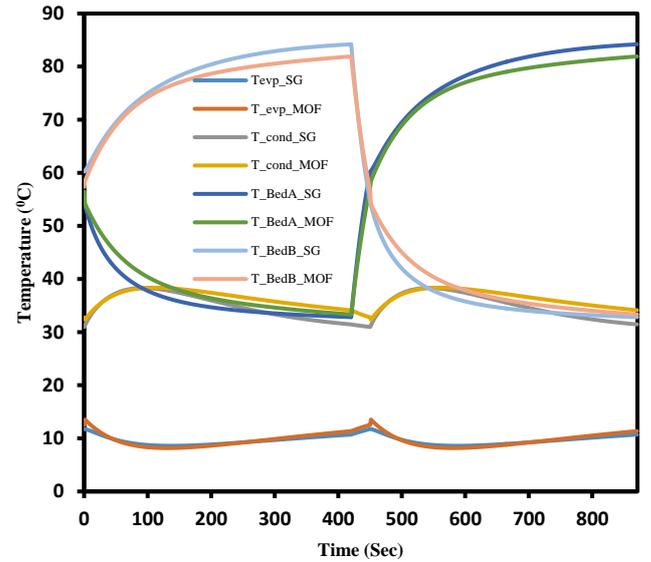


Fig. 4 Transient Temperature Profiles of the major components of AD Cooling System

The SCP of AD cooling system decreases at shorter cycle time due to the insufficient adsorption and desorption. The SCP using silica gel and MOF reaches its maximum value at 250 s and 300 s respectively. Further increase in cycle time causes reduction in SCP. It is obvious that the maximum values of COP and SCP is not obtained at the same cycle time. Optimum values of cycle time noticed at 400 s and 550 s for silica gel and MOF.

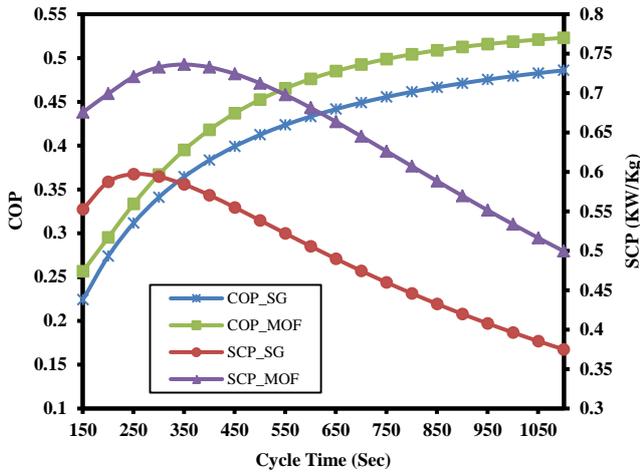


Fig. 5 Effect of cycle time on COP and SCP

Adsorption and desorption process takes place in adsorption reactors until the amount of uptake reaches the saturation. Then the beds are switched to precooling and preheating mode.

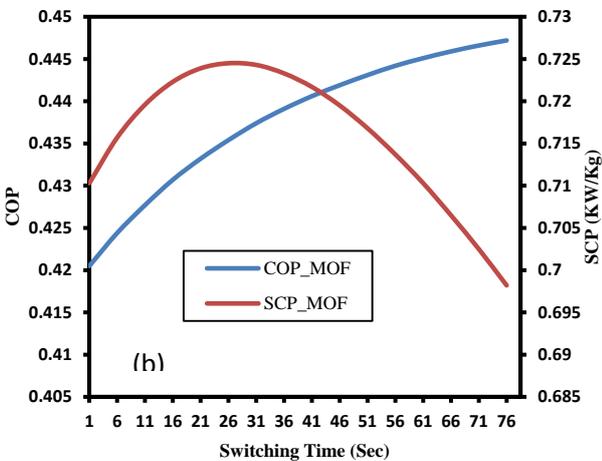
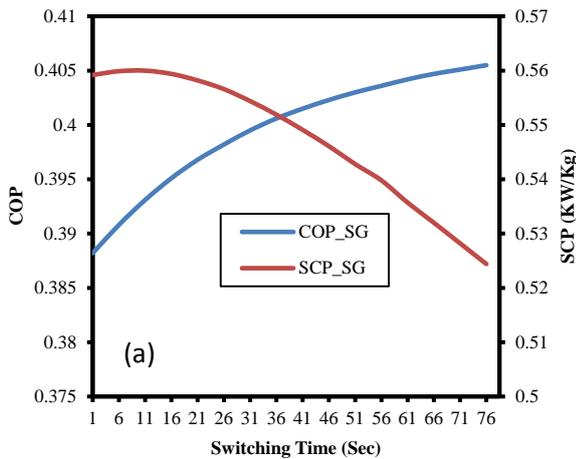


Fig 6 Effect of switching time on ADC Performance for (a) Silica gel and (b) MOF

Figs. 6 (a) and (b) show the effect of switching times on ADC performance. The COP of ADC using both Silica gel and MOF increases with the switching time and the SCP decreases with the switching time for both silica gel and MOF. But SCP for MOF increases initially up to a peak value of 0.72 (KW/kg) when switching time is 26 Sec and finally decreases. Considering COP and SCP, optimum values of switching time is 30 sec for silica gel and 35 sec for MOF.

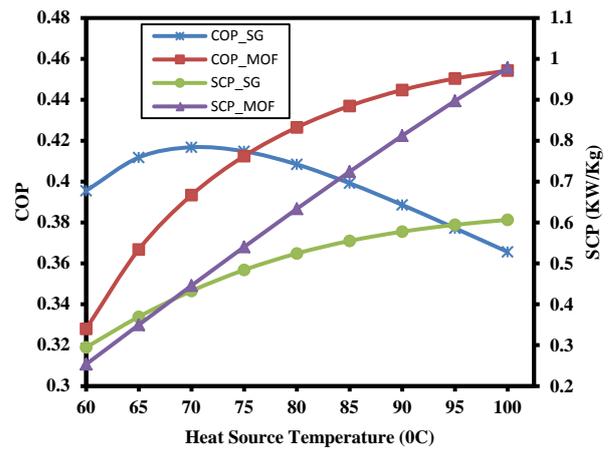


Fig 7 Effect of driving heat source temperature on COP and Cycle Average Chilled Water Temperature

System performance at different driving heat source temperature is presented in Fig. 7. For MOF, the COP increases with the heat source temperature. The highest COP 0.42 is obtained at 70<sup>0</sup> C for silica gel and decreases at higher temperature. The reason is that when heat source temperature is higher than 70<sup>0</sup>C, desorption energy is no more effective. In case of MOF, SCP increases consistently with the increase in heat source temperature. On the other hand for silica gel, SCP remains fixed at 0.6 (KW/kg) when heat source temperature is higher than 95<sup>0</sup>C. Optimum heat source temperature for silica gel and MOF are 80<sup>0</sup>C and 90<sup>0</sup>C.

Hot water flow rate is another important parameter that affects the performance of ADC. Figs. 8 (a) and (b) show the influence of hot water flow rates on ADC performance. It can be observed that for both silica gel and MOF, SCP shows an initial increasing trend up to a maximum value then remains constant at higher flow rate.

In contrast although COP for MOF shows the same trend as SCP, silica gel initially decreases to it's lowest value and remains fixed at higher flow rate. The optimum values of hot water flow rate for silica gel and MOF can be realized at 1.2 kg/s and 2.2 kg/s, respectively.

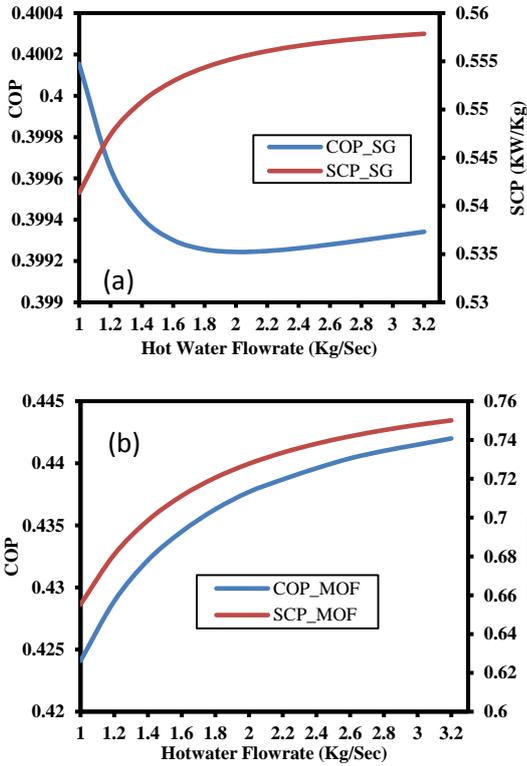


Fig 8 Effect of hot water flow rate for (a) Silica gel and (b) MOF

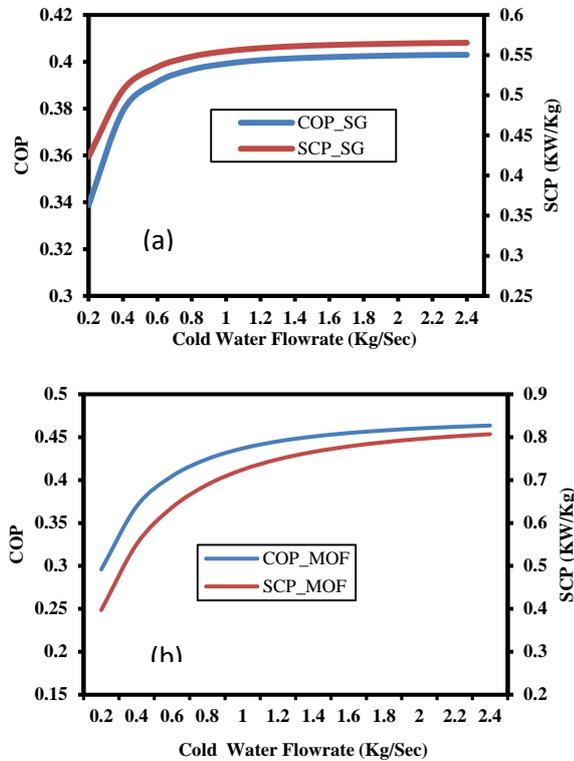


Fig 9 Effect of cold water flowrate for (a) Silica gel and (b) MOF

Increase in cold water flow rate through the condenser enhances the condensation and regeneration of refrigerant water from desorption bed which in turn increases the COP and SCP of ADC. Fig. 9 (a) and (b) demonstrates the consequences of change of cold water flow rate through the condenser for silica gel and MOF. Both COP and SCP increases with the increase in cold water flow rate. The optimum values of cold water flow rate for silica gel and MOF are found 1 kg/s and 2 kg/s.

Table 5 List of Optimized Parameters

Parameters	Value		Optimized Performance			
	Silica gel	MOF	Silica gel		MOF	
			SCP	COP	SCP	COP
Cycle Time (Sec)	400	550	0.57	0.38	0.68	0.48
Switching Time (Sec)	30	35	0.55	0.39	0.72	0.44
Heat Source Temp. ( $^{\circ}$ C)	80	85	0.52	0.40	0.81	0.45
Hot Water Flowrate (Kg/Sec)	1.2	2.6	0.55	0.40	0.74	0.44
Cold Water Flowrate (Kg/Sec)	0.8	2.2	0.54	0.39	0.80	0.46

The optimized parameters of both silica gel and MOF based ADC for 36 kg of both adsorbents are presented in Table 5.

## 5. CONCLUSIONS

An effective lumped mathematical model is used to predict the performance of MOF+water and silica gel+water based ADC. The COP and the SCP are the two most important performance parameters of ADC. The values of COP and SCP stemmed from the simulation different cycle times, switching times, heat source temperatures, hot water flow rates and cold water flow rates for silica gel and MOF are compared. Observations from the comparison of performance using silica gel and MOF as adsorbents are noted as follows:

- COP using MOF is slightly higher than that of silica gel. It can be noted that for the optimized parameters COPs found to be 0.40 and 0.45 respectively.
- In case of MOF, SCP improves significantly. This study found that optimum SCP of ADC for MOF is 0.75 (KW/kg) which is about 27% higher than that of silica gel.

Since the SCP is higher for MOF the size of bed required for the same amount of cooling load from an ADC using silica gel is 27% lower, which can offer a significant reduction in initial investment.

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