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An Introductory Study on Adsorption Isotherms for Atmosphere Water Harvesting

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Abstract: *Water scarcity is a global concern that affects a large portion of the world's population. In order to provide fresh drinkable water, adsorption based atmospheric water harvesting (AWH) has become extremely important in recent years. The adsorption isotherm is significant to understand the water vapor uptake behavior of the adsorbents. A proper understanding and interpretation of adsorption isotherms are critical for overall improvement of pathways of the adsorption mechanism as well as efficient design of adsorption system. In this regard, adsorption isotherm modeling was utilized for the potential adsorbents including MOF-801, AQSOA Z01-zeolites, aluminum phosphate with LTA topology ($AlPO_4$-LTA), and alum fumarate MOF. Langmuir, Freundlich, and Dubinin Radushkevich (D-R) isotherm models have been employed for best fit of experimental plots of adsorption isotherms for studied adsorbents. The results shows that the D-R model fit the experimental plots of adsorption isotherms of studied adsorbents as compared to Langmuir, Freundlich model.*

Keywords: Adsorption isotherms; adsorbents; atmosphere water harvesting; modeling

1. INTRODUCTION

Water scarcity is a global issue that affects a large portion of the world's population, with half of the world's population living in water-stressed (arid) areas by 2025. The population facing water scarcity is expected to exceed 5 billion by 2040, as climate change causes drought to exacerbate in arid areas and worldwide water use continues to rise [1]. Fig.1 represents water stress regions around the world by 2040. Membrane and thermal desalination technologies provide water in many parts of the world [2,3]. Due to their high initial cost, drop in specific cost with greater capacity, and extensive infrastructure and primary energy requirements, these technologies are often more suitable for large-scale centralised production [4,5]. Atmospheric water harvesting (AWH) could be a viable option for decentralised drinking water production, particularly in locations where liquid water is rare. It can also provide a point-of-use solution, where infrastructure and drinking water are physically separated from contaminated water supplies.

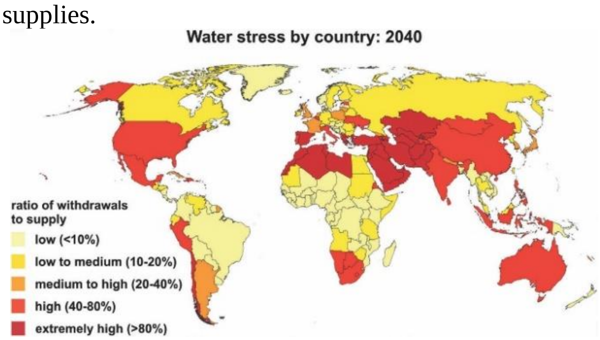

Fig. 1. Water stress regions around the world by 2040, reproduced from [6].

The AWH can be done with three different ways (1) dew collector (2) condensation by cooling up to dew point temperature, and (3) by utilizing adsorbents (sorbents) [7,8]. Dew collectors accumulate water vaporizers rather than water vapors, hence they can only work when relative humidity is greater or equal to 100% [9–12]. Many commercial plug-in systems (such as WaterGen and AquaBoy) work by condensing water vapors onto refrigerant coils, however they can only work when relative humidity is greater than or equal to 30% [13]. The adsorbent based approaches utilize adsorbent materials to capture water vapors from air, and then heated to desorb water vapors in an enclosed area to condense these vapors. A good adsorbent material is one which capture high moisture content at low relative humidity and can be easily regenerated at low energy to desorb the water vapors [14–16].

1.1. Potential Adsorbents for Atmosphere Water Harvesting (AWH)

Adsorption based AWH is getting huge interest in arid and semi-arid regions because it employs adsorbents. Numerous adsorbents are being used for the AWH including solid adsorbents such as metal organic frameworks (MOFs), silica-gel, zeolites, and hygroscopic salts such as lithium chloride (LiCl), lithium bromide (LiBr), calcium chloride ($CaCl_2$) [17–21]. The potential adsorbents are being used for the AWH, which captures water vapors at low relative humidity are MOF-801 [20], AQSOA Z01-zeolites [22,23], aluminum phosphate with LTA topology ($AlPO_4$-LTA) [24], alum fumarate MOF [25,26]. The MOF-801 has several potentials including capture water vapors at relative humidity of 10%, good adsorption behavior, good performance, recycling and exceptional stability [20]. Fig. 2(a) shows scanning electron microscope (SEM) images of the MOF-801 and its crystal structure. The AQSOA Z01-zeolites exhibit S-shape isotherm with hydrophobic behavior at low relative pressure. Fig. 2(b) shows SEM images and crystal structure of AQSOA Z01-zeolites. The $AlPO_4$-LTA exhibit significant water vapors uptake at very narrow relative pressure and have incredible cycling constancy [24]. Fig. 2(c) represents SEM image and crystal structure of $AlPO_4$-LTA. The alum fumarate MOF also exhibits S-shape isotherm (type-5) and adsorb water vapors at low relative pressure. The SEM image and crystal structure of alum fumarate MOF are represented in Fig. 2(d).

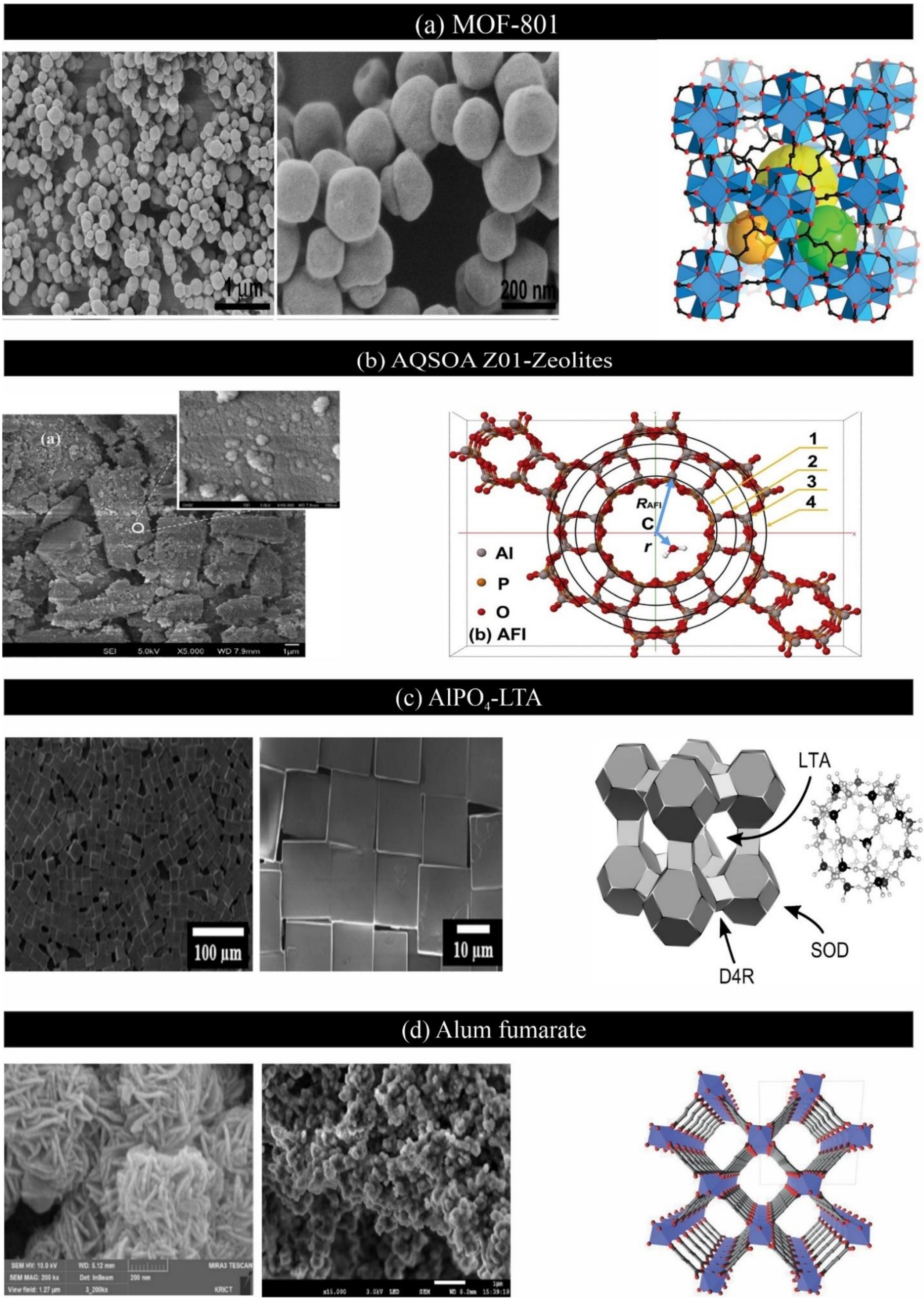

Fig. 2. SEM images and crystal structure of (**a**) MOF-801 [20,27], (**b**) AQSOA Z01-zeolites [22,23], (**c**) $AlPO_4$-LTA [24,28], and (**d**) alum fumarate MOF [25,26].

2. ADSORPTION ISOTHERM MODELING

Information of adsorption isotherms is significant to understand the moisture uptake behavior of the adsorbents. Adsorption isotherms have distinct patterns due to the characteristics of pore structure, adsorption process, and adsorbent/adsorbate interactions [29]. A proper understanding and interpretation of adsorption isotherms are crucial to get improvement of pathways of the adsorption mechanism as well as efficient adsorption system design. Recently, linear regression analysis has been one of the most extensively used approach for determining the best fit adsorption models. However, fundamental distortion produced by linearization, numerous error functions have been employed to address this shortcoming. In this regard, nonlinear isotherms modeling is extensively used to define the best fit adsorption models. Langmuir [30], Freundlich [31], and Dubinin Radushkevich (D-R) [32] are most commonly used models. The detail of these models is represented in Table 1.

Table 1.Adsorption isotherm models used in this study.

Model	Equation	No.
L-M	$q_e = q_{max} K_L \dfrac{P/P_o}{1 + K_L\, P/P_o}$	Eq. (1)
F-M	$q_e = q_{max}\,(P/P_o)^{1/n}$	Eq. (2)
D-R	$q_e = q_{sat}\, exp\left[-\left(\dfrac{k_o}{b} RT_{ads}\, ln \dfrac{P_o}{P}\right)^n\right]$	Eq. (3)

In equation (1), q_e is adsorption uptake [g/g], q_{max} is maximum adsorption uptake [g/g], K_L is constant for energy or net enthalpy of adsorption [-], P/P_o is relative pressure [-]. In equation (2), n is constant which measures the adsorption intensity [-]. In equation (3), q_{sat} is maximum adsorption capacity [g/g], k_o is constant related to energy adsorption [-], b is activation energy of adsorbent [kJ/kg], R is constant [kJ/g k], T_{ads} is adsorption temperature [°C].

3. RESULTS AND DISCUSSION

Above mentioned adsorption isotherm models have been applied for best fit of MOF-81, AQSOA Z01-zeolites, AlPO4-LTA, and alum fumarate MOF. Fig. 3 represents comparison of adsorption isotherm models for best fit of MOF-801 experimental observations measured at 25°C adsorption temperature. Dubinin Radushkevich (D-R) model is most suitable for modeling of MOF-801 as compared to Langmuir and Freundlich. Fig. 4 represents a comparison of adsorption isotherm models for best fit of AQSOA Z01-zeolites experimental observations measured at 25°C adsorption temperature. It has been observed that Langmuir and Freundlich model fit linearly. In contrast, D-R model represents best fit of experimental plots of AQSOA Z01-zeolites. Fig. 5 shows comparison of adsorption isotherm models for best fit of AlPO4-LTA experimental observations measured at 25°C adsorption temperature. The D-R model represents better fit for experimental plots of AlPO4-LTA as compared to Langmuir and Freundlich model. Fig. 6 represents comparison of adsorption isotherm models for best fit of alum fumarate MOF experimental observations measured at 25°C adsorption temperature. The D-R adsorption isotherm model represents best fit for experimental plots of the alum fumarate MOF as compared to Langmuir and Freundlich model.

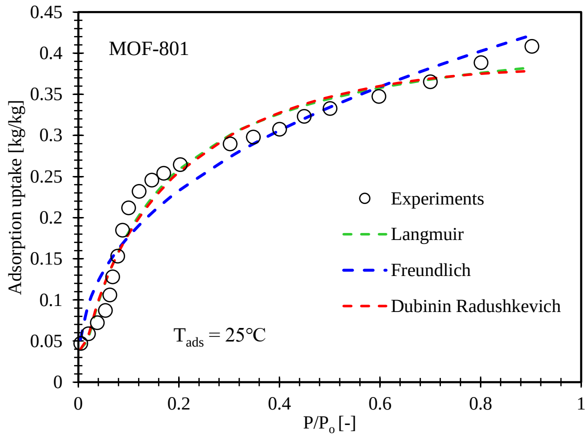

Fig. 3. Comparison of adsorption isotherm models for best fit of MOF-801 experimental observations measured at 25°C adsorption temperature.

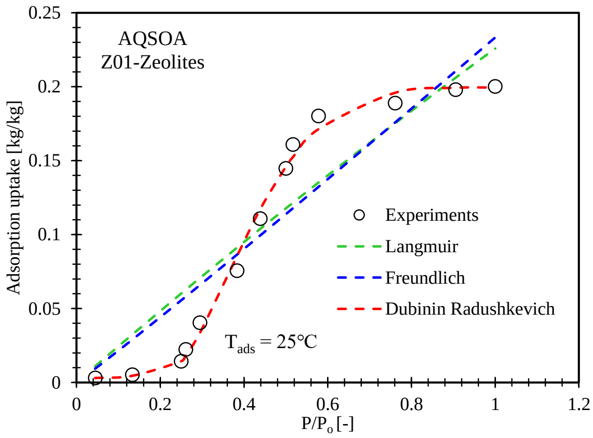

Fig. 4. Comparison of adsorption isotherm models for best fit of AQSOA Z01-zeolites experimental observations measured at 25°C adsorption temperature.

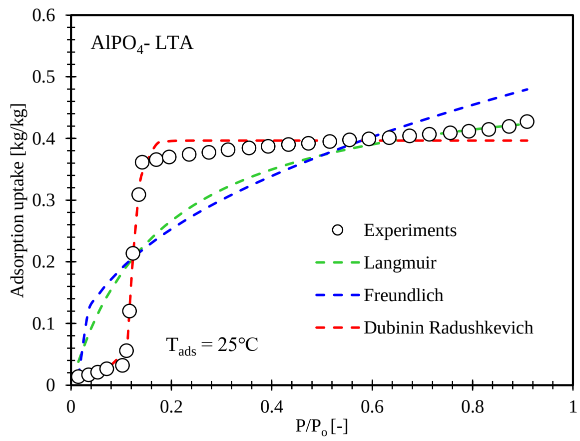

Fig. 5. Comparison of adsorption isotherm models for best fit of AlPO4-LTA experimental observations measured at 25°C adsorption temperature.

Table 2 represents fitting constants or hyperparameters of adsorption isotherm models for the studied adsorbents. The D-R model offers better results for adsorption isotherm fitting of selected adsorbents.

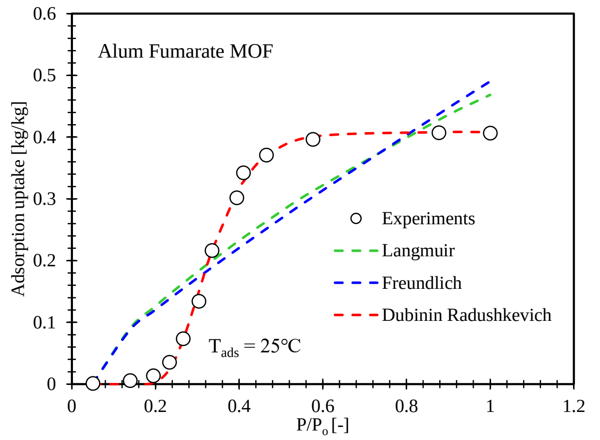

Fig. 6. Comparison of adsorption isotherm models for best fit of alum fumarate MOF experimental observations measured at 25°C adsorption temperature.

Table 2. Fitting constants of adsorption isotherm models for the studied adsorbents.

Model	Hyperparameters	R^2
MOF-801		
Langmuir	$K_L = 6.9628 \pm 0.72472$ $q_{max} = 0.4435 \pm 0.01565$	0.96695
Freundlich	$q_{max} = 0.43949 \pm 0.01601$ $n = 2.52906 \pm 0.17957$	0.93459
D-R	$q_{sat} = 0.37972 \pm 0.01585$ $k_o = 0.0014 \pm 0.02529$ $b = 0.04394 \pm 0.79583$ $n = 1.75692 \pm 0.4992$ $R = 0.46191 \pm 0$ $T_{ads} = 25 \pm 0$	0.9576
AQSOA Z01-zeolites		
Langmuir	$K_L = 0.08867 \pm 0.3238$ $q_{max} = 2.77235 \pm 0.50942$	0.84182
Freundlich	$q_{max} = 0.23368 \pm 0.02209$ $n = 0.96591 \pm 0.16746$	0.84092
D-R	$q_{sat} = 0.19941 \pm 0.00444$ $k_o = 0.04131 \pm 0.17547$ $b = 0.48273 \pm 2.04314$ $n = 3.07424 \pm 0.65324$ $R = 0.46191 \pm 0$ $T_{ads} = 25 \pm 0$	0.99207
ALPO4-LTA		
Langmuir	$K_L = 5.15279 \pm 1.47638$ $q_{max} = 0.54364 \pm 0.05171$	0.78013
Freundlich	$q_{max} = 0.49926 \pm 0.0352$ $n = 2.36827 \pm 0.39839$	0.68349
D-R	$q_{sat} = 0.39649 \pm 0.00386$ $k_o = 5.804E-5 \pm 5.8E-6$ $b = 0.00143 \pm 1.404E-4$ $n = 22.1093 \pm 4.92743$ $R = 0.46191 \pm 0$ $T_{ads} = 25 \pm 0$	0.98754
Alum fumarate MOF		
Langmuir	$K_L = 0.47531 \pm 0.559$ $q_{max} = 1.45412 \pm 1.318$	0.73861
Freundlich	$q_{max} = 0.49044 \pm 0.0672$ $n = 1.14609 \pm 0.2593$	0.71441
D-R	$q_{sat} = 0.4081 \pm 0.006$ $k_o = 0.19596 \pm 0.17659$ $b = 2.69159 \pm 2.41519$ $n = 5.229 \pm 0.65766$ $R = 0.46191 \pm 0$ $T_{ads} = 25 \pm 0$	0.99669

4. CONCLUSIONS

Adsorption based atmosphere water harvesting (AWH) has become an emerging technology to provide potable water to overcome water scarcity problem. The adsorption isotherm is significant to understand the water vapors uptake behavior of adsorbents. Understanding and interpreting adsorption isotherms is crucial for overall improvement of adsorption mechanism pathways as well as efficient adsorption system design. Adsorption isotherm modelling describes the behavior of water vapor uptake by adsorbents. Therefore, in this study, the adsorption isotherm modeling has been employed for potential adsorbents including MOF-801, AQSOA Z01-zeolites, aluminum phosphate with LTA topology (AlPO4-LTA), and alum fumarate MOF. Langmuir, Freundlich, and Dubinin Radushkevich (D-R) models have been utilized for best fit of experimental plots of adsorption isotherms for studied adsorbents. Results show that the D-R model fit the experimental plots of adsorption isotherms of considered adsorbent materials as compared to Langmuir, and Freundlich model.

Conflict of interest

The authors declare no conflict of interest.

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