Mass transfer in atmospheric water harvesting systems

Thomas Lassitter\textsuperscript{a}, Nikita Hanikel\textsuperscript{b}, Dennis J. Coyle\textsuperscript{c}, Mohammad I. Hossain\textsuperscript{a}, Bryce Lipinski\textsuperscript{c}, Michael O’Brien\textsuperscript{c}, David B. Hall\textsuperscript{c}, Jon Hastings\textsuperscript{b}, Juan Borja\textsuperscript{c}, Travis O’Neil\textsuperscript{c}, S. Ephraim Neumann\textsuperscript{b}, David R. Moore\textsuperscript{c}, Omar M. Yaghi\textsuperscript{b}, T. Grant Glover\textsuperscript{a,c,}\textsuperscript{*}

\textsuperscript{a} Department of Chemical & Biomolecular Engineering, University of South Alabama, Mobile, AL 36688, United States
\textsuperscript{b} Department of Chemistry and Kavli Energy Nanoscience Institute, University of California, Berkeley, CA 94720, United States
\textsuperscript{c} GE Global Research, 1 Research Circle, Niskayuna, NY 12309, United States

\textsuperscript{*} Corresponding author.
E-mail address: glover@southalabama.edu (T. Grant Glover).

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1. Introduction

A variety of technologies exists to purify water including desalination, distillation, filtration, and reverse osmosis. However, these techniques each depend on access to a liquid water source, which may not always be available. To address this issue, atmospheric water harvesting (AWH) technology has been developed, which provides an alternative to locating, cleaning, and moving liquid water to its end application location. (Tu et al., 2018; Yang et al., 2021; Alsaeedi, 2018; Bagheri, 2018; Fatkieh et al., 2018; Kalmutzki et al., 2018; Macedonio et al., 2012; Zhou et al., 2020; Kim et al., 2017; Kim et al., 2018; Hanikel et al., 2019).

Several methods exist to collect water from the atmosphere including dehumidifying devices based on refrigerants as well as dew and fog collection systems. However, refrigerant-based systems are limited to dew points near 0–5 °C, and dew/fog collection systems are limited to geographic regions where dew and fog are present. Adsorbent-based materials do not suffer from these limitations and provide a means of collecting water in exceptionally dry environments. (Klemm et al., 2012; Gido et al., 2016; Peeters et al., 2020).

While a wide variety of adsorbent materials exists that can capture water, careful selection of a material to provide a practical and energetically efficient system requires an understanding of the water working capacity of the material, the energy required to release the adsorbed water, and the ease with which the material can be implemented into a practical system. (Yang et al., 2021; Zhou et al., 2020) For example, traditional porous adsorbent materials, such as zeolites 13X and 5A, have a steep adsorption isotherm at low RH resulting in a high water loading, but the water is adsorbed very strongly, which increases the energy requirements for regeneration and makes these adsorbents less practical for water harvesting. (Kalmutzki et al., 2018; Zhou et al., 2020; LaPotin et al., 2020) Likewise, silica gels (Sleiti et al., 2021) adsorb water less strongly than zeolites but have an almost linear adsorption isotherm with some hysteresis, which may diminish the working capacity of the material. (Kalmutzki et al., 2018; Zhou et al., 2020; Rajniak and Yang, 1993) Activated carbon on the other hand adsorbs a significant amount of water and has an “S-shaped” adsorption isotherm, which is important when considering the working capacity during adsorption cycling, but the majority of the water loading occurs at 40 % relative humidity (RH) or higher over the temperature range of 25–125 °C, limiting its relevance as a water-harvesting material. Also, similar to silica gel, the water adsorption isotherm of activated carbon contains
some hysteresis. (Rudisill et al., 1992).

Salts are also commonly examined as candidate materials because of their low cost and wide availability. However, the performance of salts can be limited due to deliquescent, which hinders kinetics, leads to system corrosion, and may result in challenges with the recovery of the solid sorbent. (Yang et al., 2021; Zhou et al., 2020; Li et al., 2018) To solve this problem, salts are often incorporated into porous materials, (Xu et al., 2020; Ji et al., 2007; Kallenberger and Froba, 2018) hollow structures, (Li et al., 2020; Yang et al., 2020) or polymer networks. (Li et al., 2018; Yang et al., 2021) However, because the mechanism of water capture is still driven by the salt in the pore, these composite materials must still contend with deliquescence in the pores, poor adsorption kinetics, and challenging regeneration requirements. (Zhou et al., 2020)

Additionally, salts contained in porous materials may change over time and age with repeated adsorption and desorption cycles. (Rossin et al., 1991) Likewise, liquid sorbents, such as concentrated salt solutions, (Wang et al., 2019) also have high uptake capacity, but suffer from kinetic limitations and high energy requirements for desorption relative to other adsorbents. (Yang et al., 2021; Zhou et al., 2020)

With these design constraints in mind, MOFs are appealing for water harvesting because these materials can provide single-atom scale control of the water adsorption isotherm. (Glover and Mu, 2018; Yaghi et al., 2019) In this way, MOFs can be designed for water adsorption in a specific RH range via an S-shaped isotherm and the hysteresis commonly seen in other adsorbents is not as prevalent. The control of the S-shaped adsorption portion of the isotherms, coupled with limited hysteresis, results in a large working capacity, which facilitates system design by enabling the almost stepwise release of water during desorption. (Kalmutzki et al., 2018; Roque-Malherbe, 2007) These key features position MOFs as the optimal adsorbents for water sorption applications in any climate. (Kalmutzki et al., 2018; Hanikel et al., 2019; Xu and Yaghi, 2020; Rieth et al., 2019; Towsif Abbab et al., 2018; Logan et al., 2020)

While numerous materials have been examined for water harvesting from a thermodynamic capacity perspective, less effort has been devoted to understanding the kinetics of gas adsorption. But the kinetics of the adsorption process are equally important, especially when the adsorbent is actively cycled between adsorption and desorption to increase water yield. In general, there is a lack of available data detailing the transport diffusion of water vapor in MOFs, which limits the design of water-harvesting systems and more broadly the understanding of mass transfer in porous materials. (Hossain and Glover, 2019; Laurenz et al., 2021; Canivet et al., 2014; Canivet et al., 2014; Burch et al., 2014; Nemilaw and Kumar, 2020; Furukawa et al., 2014)

Diffusion in adsorbents is complex and requires an explanation to describe the different diffusion parameters that are reported in the literature. (Skoulidas and Sholl, 2005) Skoulidas et al., provide an explanation of diffusion detailing that Eq. (1) describes the transport diffusion where \( D_s \) is the transport diffusivity that is the proportionality constant relating macroscopic flux to a spatial concentration gradient in Fick’s law. The transport diffusion is also commonly referred to as either the Fickian diffusivity, the chemical diffusivity, or the collective diffusivity. However, it is often convenient to define the transport diffusivity in terms of the corrected diffusivity \( D_s \) as shown in Eq. (2). The partial derivative involving concentration and fugacity is the thermodynamic correction factor and is defined by the single-component adsorption isotherm. The corrected diffusivity is equal to the Maxwell-Stefan diffusivity in single-component systems.

It is important to distinguish the transport diffusivity from the self-diffusivity, \( D_s \), as the self-diffusivity describes the motion of individual particles at an equilibrium condition versus the movement of molecules under a concentration gradient. In an isotropic, three-dimensional material, the self-diffusivity is related to the mean-squared displacement of tagged particles after time \( t \) by the Einstein relation as shown in Eq. (3), where \( \vec{r}(t) \) is the position vector of a tagged particle at time \( t \) and the angular brackets indicate an ensemble average. (Skoulidas and Sholl, 2005) In dilute concentrations, the diffusivities are equal. In applications where it is necessary to describe net mass transfer under non-equilibrium conditions, such as modeling membranes or pressure-swing adsorption systems, it is the transport diffusivity that is of particular interest. (Skoulidas and Sholl, 2005)

\[
\begin{align*}
J &= -D_s \nabla c \\
D_s &= -D_0 \left( \frac{\partial \ln f}{\partial c} \right)_T \\
D_s &= \lim_{t \to \infty} \frac{1}{6t} \langle (\vec{r}(t) - \vec{r}(0))^2 \rangle \\
J &= -D_s \nabla c
\end{align*}
\]

There are several techniques available to measure the diffusion of gases in MOFs which can be broadly divided into macroscopic methods, including gravimetric and volumetric uptake methods, zero-length column (ZLC) chromatography, (Brandani et al., 1996; Brandani et al., 1995; Eic and Ruthven, 1989; Gunadi and Brandani, 2006; Silva and C., Rodrigues, A. E., 1996) and frequency response (FR), which measure transport diffusivity; and microscopic methods, which includes quasi-elastic neutron scattering (QENS), pulsed field gradient (PFG) nuclear magnetic resonance (NMR), and infrared (IR) spectroscopy, which measure self-diffusivity. (Glover and Mu, 2018; Sharp et al., 2021) While some microscopic methods can measure transport diffusivities, such as coherent QENS and IR spectroscopy, (Sharp et al., 2021) they typically measure self-diffusivities.

Of these methods, FR techniques can identify and quantify the rate-limiting mass transfer mechanism. (Glover and Mu, 2018; Wang, 2021; Wang and LeVan, 2011) In particular, frequency response is a technique whereby one variable of a system in equilibrium is perturbed periodically and the response of another variable is monitored. Because the technique is periodic, there is less dependence on the initial conditions of the system and random error tends to average out over many oscillatory periods, which is another advantage of this method. Further, to generate one data set, the experiment is repeated over a broad range of perturbation frequencies reducing error that might be associated with calculating the diffusion rate based on one experimental data set.

Although numerous models could be examined with FR, the models shown in Eqs. (4)–(6) are helpful when considering diffusion in solid-phase adsorbents.

**External Fluid Resistance**

\[ \rho_s \frac{dn}{dt} = k_e (c - c^*) \]  

**Micropore Diffusion**

\[
\frac{dn}{dt} = \frac{D_s}{r^2} \left( \frac{\partial n}{\partial r} \right) 
\]

**Linear Driving Force**

\[ \frac{dn}{dt} = 0 \text{ at } r = 0 \\
\frac{dn}{dt} = k_l (n^* - n) \text{ at } r = R 
\]

In particular, Eq. (4) describes the transport of molecules to the surface of the adsorbent driven by the difference in concentration in the fluid phase, where \( c \) is the fluid phase concentration, \( c^* \) is the concentration in the fluid at the adsorbent particle, \( \rho_s \) is the density, \( a \) is the area, \( t \) is time, and \( k_e \) is the transport coefficient. Molecules on the surface of the adsorbent then diffuse into the particle and the diffusion can be described by different models (Eqs. (5)–(7)) depending on the governing mechanism.

Eq. (5) provides a model where surface diffusion is governing based on a description of the microparticle as spherical in the nanoporous domain where \( n \) is the adsorbate concentration in the nanopore, \( n^* \) is the equilibrium adsorbate concentration in the equilibrium state, \( t \) is the
radial coordinate for the microparticle (i.e., nanoporous domain), \( R \) is the radius of the microparticle, and \( D_p \) is the diffusivity.

However, a linear driving force can also be used to describe the diffusion into the adsorbent, as shown in Eq. (6) where \( k_d \) is the linear driving force coefficient. (Glueckauf, 1955; Hossain et al., 2016; Do and Mayfield, 1987) The linear driving force model can provide an accurate approximation of diffusion; however, it is also useful for describing systems in which the rate-limiting mass transfer step is a surface barrier where a constrictioin at the pore mouth is the dominant resistance, as discussed by Wang and Levan. (Wang and LeVan, 2011).

For some adsorbents, resistance in the macropore must also be accounted for and can be described as

\[
\frac{\rho_p n}{\partial t} + \frac{\partial \rho_p}{\partial t} = \frac{\rho_p D_p}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_p}{\partial r} \right) \tag{7}
\]

\[
c_p = c \text{ at } r = R_p
\]

\[
\frac{\partial c_p}{\partial r} = 0 \text{ at } r = 0
\]

where \( \rho_p \) is the particle density, \( \epsilon_p \) is the macroporosity, \( c_p \) is the gas-phase concentration in the macropores, \( r \) is the radial coordinate, and \( R_p \) is the radius of the macropore domain. For a linearized system, the adsorbed phase concentration is in equilibrium with the gas phase concentration in the macropores such that

\[
n' = K_c p \tag{8}
\]

where \( K \) is the isotherm slope. With the linearized isotherm, Eq. (7) can be simplified as,

\[
\frac{\partial c_p}{\partial t} = \frac{1}{\left(1 + \frac{\alpha_k p}{\gamma} \right)} \frac{D_p}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_p}{\partial r} \right) \tag{9}
\]

where Eq. (9) has the same mathematical form as Eq. (5) (Ruthven, 1984) even though the type of concentration being described, and the type of diffusivity are different. Thus, the analytical solution of macro- and micropore diffusion model will be the same, and any data set that can be fit by the micropore diffusion model will be fit equally well by the macropore diffusion model. The fitting parameter for these models can be defined as \( \eta \) where this term corresponds to macropore or micropore depending on the governing phenomena as (Tovar et al., 2016; Tovar, 2016)

\[
D_p \text{ macropore} \eta = \frac{D_p}{r^2} \left( 1 + \frac{\alpha_k p}{\gamma} \right) \tag{10}
\]

Thus, fitting data to these models alone cannot identify micropore versus macropore mass transfer control. However, the characteristic length for macropore diffusion is the effective radius of the particle, whereas for micropore it is a smaller micropore radius. Thus, if the mass transfer is controlled by the macropore diffusion the mass transfer parameter will be a function of the particle size of the adsorbent, whereas if micropore diffusion is the controlling mechanism, the mass transfer parameter will not be strongly dependent on particle size. This approach allows for the differentiation of the mechanism, which is important as the macropore model has been found to be the governing resistance in some adsorbents (Giesy and LeVan, 2013; Hossain et al., 2019; Tovar, 2016).

Lastly, transport diffusivities depend on the adsorbed phase loading, and in systems with sharp changes in adsorption loading as a function of pressure, such as those in water-harvesting MOFs, it is helpful to separate the influence of a steep adsorption isotherm on the measured kinetic rate. This can be accomplished following the approach outlined by Ruthven (Ruthven, 1984) where Eq (1) is written in terms of the gradient in chemical potential to produce the Maxwell-Stefan form of the flux equation,

\[
J_i = -Bc_i \frac{\partial \mu}{\partial x} \tag{11}
\]

\[
\mu = \mu_0 + RT \ln p \tag{12}
\]

\[
\frac{\partial \mu}{\partial x} = R T \frac{\partial n}{\partial c} \frac{\partial c}{\partial x} \tag{13}
\]

\[
J = -BRT \frac{\partial n}{\partial c} \frac{\partial c}{\partial x} \tag{14}
\]

\[
D_i = BRT \frac{\partial n}{\partial c} \frac{\partial c}{\partial x} = D_0 \Gamma \tag{15}
\]

where \( B \) is the molecular mobility, \( c \) is the total concentration in the pore, and \( \frac{\partial c}{\partial x} \) is the gradient in chemical potential, and substitution leads to an expression where \( BRT \) is referred to as \( D_0 \), the corrected diffusivity. (Ruthven, 2004; Ruthven et al., 2008) This term accounts for the molecular mobility effects. The \( BRT \) term is referred to as the thermodynamic correction factor, and accounts for the equilibrium effects on the measured diffusivity and can also be written as \( \Gamma \). Therefore, for a system of interest with an experimentally measured isotherm, it is possible to calculate the thermodynamic correction factor and the value of corrected diffusivity, \( D_0 \), can be determined using an experimental value of the diffusivity obtained at a particular pressure.

Procedurally, the ratio of the amplitude of the response to the amplitude of the perturbation is plotted against the perturbation frequency, and a transfer function comprised of the models discussed is used to model the response. Because the shape of the response curve is dictated by the assumed mechanism, only appropriate models will accurately fit the data. The sensitivity of the technique to different models can prevent erroneously assuming a governing mass transfer resistance. Also, the technique helps prevent unknowingly fitting numerous adsorption phenomena, such as heat effects, pressure drop, and dispersion, into a mass transfer term. (Knox et al., 2016; Wang et al., 2021).

FR experiments have utilized perturbations in the volume of a batch system, (Yasuda, 1976; Yasuda, 1982; Yasuda and Matsumoto, 1989; Yasuda, 1993; Hossain et al., 2019; Valyon et al., 2000; Song and Rees, 1997; Song and Rees, 2000; Song and Rees, 2008; Onyestyátki et al., 1995; Onyestyátki et al., 1996; Onyestyátki and Rees, 1999; Hossain et al., 2019; Hossain, 2014) as well as perturbations in the flow rate, (Park et al., 1998; Park et al., 1998) pressure, (Sward and LeVan, 2003; Wang et al., 2003; Wang and LeVan, 2005; Wang and LeVan, 2005; Giesy and LeVan, 2013; Wang and LeVan, 2008) and concentration (Osier and Wilhelm, 1953; Glover et al., 2008; Hossain and Glover, 2019; Kramers and Alberda, 1953; Li et al., 1989; Liu et al., 2010; Tovar et al., 2016; Wang et al., 2013; Wang and LeVan, 2007; Tovar et al., 2016) of the inlet of a flow system. Of these methods, flow-through FR methods are advantageous because the flow-through design reduces heat effects thereby allowing the system to be treated isothermally. Additionally, concentration swing frequency response (CSFR) is preferred when only a small amount of adsorbent is available as it can be used to examine single adsorbent particles and crystals. (Glover et al., 2008; Wang and LeVan, 2007) This is especially useful in the characterization of newly designed materials, of which only a small amount may be available.

In this work, CSFR was used to examine the diffusion of water in MOF-303. To illustrate the atomic-scale control that reticular chemistry provides over macroscopic mass transfer properties, MOF-333, which is isosstructural to MOF-303 and contains furan-2,4-dicarboxylate in place of 1H-pyrazole-3,5-dicarboxylate, was also examined. With these data measured, a diffusion rate between these values was targeted through the synthesis of an MTW variant of MOF-303 and MOF-333, 4/4-MTV-MOF, where the linkers are in a 50/50 ratio. The diffusion rates of
each MOF as a function of concentration and crystal size were determined. Lastly, the mass transfer data were used to model the breakthrough behavior of MOF-303 on both a coated tube and a packed-bed and the relationship between convective flow and solid phase diffusion is considered in the context of atmospheric water harvesting.

2. Experimental

2.1. CSFR system and mathematical models

A CSFR system, similar to the one used by Glover et al., was used to complete the CSFR measurements. (Glover et al., 2008) Helium was passed through a water saturator cell that was located in a temperature-controlled water bath, allowing for gas phase water concentrations to be controlled by setting the water bath temperature. The pressure was controlled at 50 torr above atmospheric pressure using a pressure controller (MKS Baratron type 640B) upstream of the saturator. A second helium stream was mixed with the adsorbate feed stream prior to the adsorbent bed. Both streams were controlled using MKS mass flow controllers and the adsorbate gas concentration fed to the adsorbent bed was determined. Lastly, the mass transfer data were used to model the breakthrough behavior of MOF-303 on both a coated tube and a packed-bed.

The effluent gas from the adsorbent bed was sampled by an Agilent 5973 mass spectrometer. Dry weights for the CSFR experiment are required and the amount of sample used for each CSFR experiment is listed in the Supplemental Information (SI). For MOF-303, several grams of material were available and a dry weight was determined by first outgassing 100–200 mg of powder at 120 °C under vacuum using a Micromeritics Smart Vac Prep unit for 12 hrs. The CSFR bed was then loaded with a smaller portion of the dried material. Then the Micromeritics sample cell containing the residual not loaded in the CSFR bed was outgassed and the dry weight of the residual MOF-303 was determined. The weight in the CSFR bed was determined by the difference in the dry weights of the sample contained in the Micrometrics sample cell.

Smaller quantities of MOF-333 and 4/4-MTV-MOF were available compared to MOF-303, and it was not possible to load a sample cell for outgassing without losing the majority of the sample. Therefore, the vial containing the sample was used to determine the weight in a similar approach as was done for MOF-303. In this case, the vial containing the sample and its plastic cap were weighed, the cap was removed, and the sample was baked in an oven at 90 °C for 12 hrs. At the end of 12 hrs, the vial was capped and weighed. The CSFR bed was then loaded, and the vial was baked again without the cap at 90 °C for 12 hrs, at the end of which the vial was capped and the dry weight of the residual was measured. The weight in the CSFR bed was determined by the difference in the dry weight of the sample vial.

Additional material was available when examining larger-crystal versions of MOF-303, 333, and MTV. Therefore, the larger crystal samples (MOF-303, MOF-333, 4/4-MTV-MOF) were regerminated using a TA Q500 Thermogravimetric Analyzer under a dry flow of nitrogen at 15 mL/min and heated to 120 °C with a ramp rate of 2 °C/min and held isothermally at 120 °C for 15 hrs. The CSFR bed was weighed, the sample was loaded after TGA regeneration, and after loading the sample in the CSFR bed, helium was pushed across the bed for 12 hrs. After 12 hrs, the bed was weighed again to determine the dry weight.

After regeneration, the adsorbent was placed in the adsorbent bed at room temperature (25 °C), and a constant, unperturbed feed of water in helium at the selected humidity was passed through the bed overnight to equilibrate the bed at the selected water loading. The flow rates of the two helium streams were perturbed sinusoidally at a selected frequency and each stream was 180 degrees out of phase relative to the other. The resulting feed stream to the adsorbent bed had a constant total flow rate with a sinusoidal adsorbate concentration oscillating around the equilibrium state. To maintain the linearity of the system, the amplitude of the perturbations for both streams was kept small. Specifically, the swing used in this work was ± 0.4 sccm on each stream. In this work, CSFR experiments were conducted over a frequency range of 0.00005 to 0.05 Hz. Unless noted otherwise, all measurements were performed at 25 ± 1 °C.

The mathematical model described by Wang and LeVan (Wang and LeVan, 2007), as well as the kinetic rate equations given by Wang et al. and Wang and LeVan, were used to model the system. (Wang and LeVan, 2011; Sward and LeVan, 2003; Giesy and LeVan, 2013) For a non-isothermal condition, the particle was assumed to be at a uniform temperature, and the heat transfer resistance was assumed to be between the bed and the bed wall. The energy balance was written as,

\[ m_b C_b \frac{dT}{dt} + m_s \Delta H_s \frac{dn}{dt} = F_w \Delta h_n - F_{in} \Delta h_n - hA(T - T_{wall}) \]  

\[ (16) \]

where \( m_b \) is the mass of adsorbent, \( C_b \) is solid heat capacity, \( T \) is the temperature, \( \Delta H_s \) is isosteric heat of adsorption, \( \Delta h \) is the heat transfer coefficient between the bed and the wall, and \( A \) is the area of the bed for heat transfer. Since the amplitude of the perturbation in concentration in CSFR experiments was small, the isotherm was linearized as

\[ n' = n_{ref} + K(P - P_{ref}) \]  

\[ (17) \]

where \( K \) is the local slope of the isotherm, \( \frac{dn}{dT} \) evaluated at \( P_{ref} \). In the case of non-isothermal conditions, the linearized isotherm can be expressed as,

\[ n' = n_{ref} + K(P - P_{ref}) - K_T(T - T_{ref}) \]  

\[ (18) \]

where \( K_T \) is the negative of the slope of the isobar evaluated at \( T_{ref} \).

2.2. Synthesis of MOFs and production of MOF-coated tube

MOF-303 was synthesized using the procedure outlined in the SI of previous work. (Hanikel et al., 2019) Briefly, 1H-pyrazole-3,5-dicarboxylic acid, monohydrate (7.50 g, 43.1 mmol) was dissolved in deionized H₂O (725 mL) and LiOH solution (2.57 M, 25 mL). The resulting solution was heated for 30 min in a preheated oven at 120 °C. Afterward, AlCl₃·6H₂O (10.4 g, 43.1 mmol) was added to the solution. Any precipitate was dissolved under sonication and vigorous shaking. Once a clear solution was obtained, the hot reaction mixture was put in a preheated oven at 100 °C, where it was kept for 15 hrs. Then, the precipitate was filtrated out and washed with water. The white solid was subsequently washed with methanol for 24 hrs in a Soxhlet apparatus and air-dried for 3 days. The product was further dried under vacuum (<10⁻³ mbar) for 24 hrs. Full activation of the MOF was conducted under vacuum (~10⁻³ mbar) and at 150 °C for 6 hrs, yielding a pure, desolvated product (3.6 g). MOF-333 and 4/4-MTV were synthesized using the procedure outlined in the SI of previous work, (Hanikel et al., 2021) where MOF-333 was composed from the single linker furan-2,4-pyrazole-3,5-dicarboxylic acid, and the 4/4-MTV-MOF exhibited a 1:1 ratio between 1H-pyrazole-3,5-dicarboxylate and furan-2,4-dicarboxylate.

For the packed-bed experiments and the experiments involving MOF coated on tube walls, MOF-303 was purchased from NovoMOF and used as received. The MOF-coated tubes containing different thicknesses of MOF coating were produced by placing MOF-303 from NovoMOF into a GE polymer-binder system comprised of a mixture of poly(vinyl alcohol) and poly(acrylic acid) (OBrien et al., 2022) and flowing the polymer MOF solution over the interior tube surface and subsequently curing the solution. The tubes used for these experiments were 3D-printed from Inconel. The binder did not impact the crystallinity or porosity of the MOF-303 (as shown via powder X-ray diffraction analysis and adsorption isotherms shown in the SI) and only reduced the water loading by the equivalent mass of binder added.
3. Results and discussion

3.1. Adsorption rates collected with CSFR

During a diffusion experiment, the MOF sample was first equilibrated with a known amount of water, after which the concentration was oscillated sinusoidally, and the effluent was monitored to observe the corresponding oscillations in effluent amplitude. The effluent amplitude is diminished relative to the inlet amplitude due to adsorption occurring. The ratio of the inlet and effluent amplitudes can be calculated and a single data point can be placed on a plot of amplitude versus frequency. The process is repeated for numerous frequencies and several data points are produced. The shape of the data points as plots of amplitude versus frequency are sensitive to the mechanism of the adsorption that is occurring and with accurate models for these mechanisms, the diffusion rates can be determined.

Shown in Fig. 1 are the ratios of the effluent to feed amplitude for several MOF samples and several different humidities, all at room temperature. The diffusion rate data for MOF-303 and MOF-333 are shown in Fig. 1a and 1b, respectively, where these materials differ only in their linker composition with MOF-303 comprised of a pyrazole (1H-pyrazole-3,5-dicarboxylate) and MOF-333 comprised of a furan (furan-2,4-dicarboxylate). Shown in Fig. 1c is the diffusion data for a multivariate (MTV) MOF where the linkers are in a 50/50 ratio, which is designated 4/4-MTV-MOF, as reported previously.

Along with these data points are lines fit to the data corresponding to the micropore diffusion model, Eq. (5), and the linear driving force model, Eq. (6). Each model fit at every humidity produces an adsorption kinetic rate parameter, and thus the extracted parameters are based on several oscillating adsorption experiments repeated at several different frequencies.

As shown in Fig. 1, there are some differences between the quality of the micropore and LDF model fits. For example, for MOF-333 shown in Fig. 1b, the LDF fits the data reasonably well until the humidity approaches 20 %, at which point deviations between the LDF model and the data are observed at high frequencies. To examine this in more detail, Fig. 2a shows the high-frequency region of Fig. 1b, and it can be seen that the 20 and 22 % data sets illustrate significant differences between the LDF and micropore models with the LDF model showing a distinctly different shape compared to the data. When the LDF model is not required to fit data at higher frequencies this shape becomes more pronounced as shown by the 60 and 80 % RH data in Fig. 1b. The deviations between the LDF and the micropore models are also found near 15 % RH for 4/4-MTV-MOF and 12 % for MOF-303 coinciding with the steep portion of the isotherms of these materials. In general, the data show that the LDF model can approximate the micropore model and that

![Image of frequency response curves for MOF-303, MOF-333, and 4/4-MTV-MOF.](image-url)

*Fig. 1. Frequency response curves for (a) MOF-303 (b) MOF-333, (c) 4/4-MTV-MOF. The dashed lines are the LDF model and solid lines are the micropore diffusion model (d) Isotherms from Hanikel et al. where circles indicate where diffusion measurements were completed (Hanikel et al., 2019; Hanikel et al., 2021).*
the error associated with the LDF assumption is most prevalent where the isotherm is the steepest.

When measuring adsorption kinetics, it can be challenging to isolate the impacts of thermal effects and these effects must be considered carefully for both flow-through and batch adsorption kinetic experiments. The milligram sample size and flow-through design of CSFR minimize these impacts and the assumption of isothermal conditions can, in many cases, be made. (Hossain and Glover, 2019; Yasuda, 1976; Wang et al., 2003; Wang and LeVan, 2008; Brandani et al., 1998; Ruthven et al., 1980; Ruthven and Lee, 1981; Giesy et al., 2012) To confirm this assumption, a comparison was made between the micropore diffusion model, and the non-isothermal micropore diffusion model as shown in Fig. 3. Both the non-isothermal and isothermal models fit the data equally well and result in nearly identical mass transfer rates. The isothermal assumption is likely valid because the adsorbed component is present only in trace amounts and therefore the rate of heat generation is dwarfed by the convection of heat away from the sorbent.

The extracted diffusion rates for each MOF as a function of relative humidity are plotted in Fig. 4. The results in Fig. 4 are significant because they show that reticular chemistry can tailor the diffusion rate of a material allowing for engineering optimization between uptake and rate that has not been readily possible with other materials. In this case, the substitution of a pyrazole for a furan in the linker is a change of only

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**Fig. 2.** Data from Fig. 1b for MOF-333 showing the deviation in the LDF and micropore models for a selection of frequencies. To ensure clarity, not all data in Fig. 1b is shown.

**Fig. 3.** A comparison of the non-isothermal diffusion model (dashed) to the isothermal diffusion model (solid) for (a) MOF-303, (b) MOF-333, and (c) 4/4-MTV-MOF. The data shows that the isothermal model fits equally well as the non-isothermal model.
a few atoms that provides macroscopic changes on the adsorption kinetics of water in the MOF. While previous adsorbents, such as zeolites and carbon molecular sieves, have been designed to sieve out particular molecules for a separation, these results show that MOFs provide a means of not simply excluding molecules but rather tailoring the speed of their travel through a porous solid. For example, the minimum water diffusion rate in MOF-333 is approximately a decade slower than MOF-303.

Fig. 4 also shows that a minimum in the diffusion rates occurs that corresponds to the steepest portions of each MOF isotherm with MOF-303 having significant uptake near 10% RH, MOF-333 having a step uptake closer to 20% RH, and the 4/4-MTV-MOF with its uptake between these two materials. Although the change in the MOF linker is small, it has a large impact on the isotherm, and appropriately, a large impact on the diffusion rate. Likewise, the impact of the isotherm slope on the observed diffusion rate needs to be considered when explaining the observed minimum in the diffusion and is captured by calculating the corrected diffusivity in Eq. (2).

This equation shows that the observed transport diffusivity is a function of molecular mobility, termed the corrected diffusivity, and the slope of the adsorption isotherm. To examine this in more detail, the slope of the isotherm at each loading where the diffusion data was collected was calculated by linear interpolation of the isotherm data and used to determine the corrected diffusivity. Fig. 5 compares the transport and the corrected diffusivities as well as the adsorption isotherm and shows that the transport diffusivity minimum shown in Fig. 4 corresponds to the steep portion of the adsorption isotherm. However, the

Fig. 4. Diffusion time constant as a function of concentration. The minimum in the diffusion rate is seen to correlate with the steep uptake step in the isotherm. Lines are guides for the eye. For the MTV material, a replicate data set was collected as shown with open green circles where the same sample was characterized a second time to illustrate the reproducibility of the CSFR data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Corrected and transport diffusivities for water in (a) MOF-303, (b) MOF-333, and (c) 4/4-MTV-MOF, overlayed with adsorption isotherms to illustrate the impact of equilibrium effects on transport diffusion measurements. Isotherms as from Figure 1 (Hanikel et al., 2019; Hanikel et al., 2021).
corrected diffusivity shows significantly less variability as a function of humidity compared to the transport diffusivity.

The corrected diffusivity for MOF-303 and 4/4-MTV-MOF are fairly constant, with only slight decreases in molecular mobility at very low loadings. The data for MOF-333 are slightly more scattered with the largest variation occurring at the steepest point in the adsorption isotherm. This result is consistent with the very steep slope in this region impacting the corrected diffusivity calculations.

A key portion of this comparison shows that the observed minimum in transport mobility is occurring not because of a large change in molecular mobility, but rather because of a significant change in the adsorption isotherm loading that is occurring at the given RH. This distinction is important because it helps ensure that when discussing the performance of these MOFs that the observed rate behavior is attributed to both thermodynamics and kinetics. Additionally, while this distinction is helpful to understanding the materials, the transport diffusivity that reflects the combined thermodynamic and mobility effects remains the rate that will govern diffusion processes in these materials.

This observation, that nonlinearity in the adsorption isotherm strongly influences trends in the diffusion coefficient, is consistent with observations in the literature, particularly in the adsorption of condensable vapors. (Brandani et al., 1995; Jobic et al., 2004; Kärger, 2015)

For example, minimums in diffusivity in both activated carbon and UiO-66 MOF have been reported. (Hossain and Glover, 2019; Glover et al., 2008) For UiO-66, it has been shown that a constant corrected diffusivity can be assumed and the isotherm slope can be used to predict the concentration dependence of the diffusion data with reasonable accuracy. (Hossain and Glover, 2019)

The results in Fig. 5 are consistent with the results shown for UiO-66 as the data in Fig. 5 shows a nearly constant corrected diffusivity and the isotherm slope driving the observed minimum in the diffusion data.

Regarding the diffusive length scale, the rates measured by CSFR are captured as $\frac{D_s}{r^2}$ and information about $r^2$ is not provided in these experiments. It is possible that the diffusional path length is the entire MOF crystal or a small collection of MOF crystals, but in this case, MOFs provide a unique opportunity to examine the impact of adsorbate size on diffusion because crystals of the same chemical composition and crystalline phase can be produced in various sizes.

Therefore, to better understand the controlling diffusion length scale and the trends between materials, MOF-303, MOF-333, and 4/4-MTV-MOF were synthesized again but with larger crystal sizes as shown in Fig. 6. For comparison, the MOF-303 material examined initially is shown in Fig. 6a and shows agglomerations of smaller MOF crystals into larger clusters as compared to Fig. 6d that shows MOF crystals that are closer to 20 µm individually. The raw frequency response data is shown in Fig. 7a and the diffusion rates extracted from each of these experiments are shown in Fig. 7b, where the data from the original samples from Fig. 4 are replotted for comparison. The diffusion data on the larger crystals are effectively the same as the original materials. Given that the MOFs have the same composition and crystalline structure, it can be assumed that the diffusion rate, $D_s$, was the same in these materials, and with $\frac{D_s}{r^2}$ appearing to have nearly identical values, that the diffusive length $r^2$ was similar for both sets of materials. It is possible that the smaller crystals are forming aggregates with similar diffusive lengths as either the larger crystals, or both samples produced aggregates of similar sizes regardless of crystal size.

Beyond noticing that for the crystal sizes studied the diffusion rates are effectively the same, broader conclusions are somewhat difficult because there are only 6 samples compared and only 3 similar data points. It is interesting to note, however, that the crystal sizes in the SEM...
follow the general trend of MOF-333 > 4/4-MTV-MOF > MOF-303, which is consistent with the observed transport diffusion rates with MOF-303 having the fastest rates and MOF-333 the slowest. However, these results only highlight that more work is required to fully understand the impact of MOF crystal size on gas diffusion rates.

In addition to measuring diffusion data at ambient temperature, we also measured the diffusion rates of water at 40 °C on MOF-303 as shown in Fig. 8. As expected, the minimum in the diffusion data shifts slightly to a higher RH, consistent with the water isotherm at 40 °C, shown in the SI. The rate of diffusion at 40 °C are faster than those of 25 °C, as expected, and provides insight into the change of adsorption rates that will take place during heated desorption steps in water-harvesting systems. Tabulated mass transfer data for each MOF is reported in the SI.

To provide perspective on the diffusion rates of water into these materials, they were compared to the water diffusion rates for activated carbon, which we have also measured using CSFR. (Glover et al., 2008) The results are shown in Fig. 9a and show that even though a minimum in the diffusion occurs, the adsorption rate of water in MOF-303 is fast throughout the adsorption process compared to activated carbon. The diffusion data have also been plotted versus loading as shown in Fig. 9b, which shows that the minimum diffusion rate extends over a wide range of loadings illustrating that in many cases the water transport diffusion rate is nearly constant.

3.2. Application of adsorption rate data

During the evaluation of new materials, it is common to complete breakthrough measurements to determine adsorbate loading and separation performance. (Glover and Mu, 2018; Britt et al., 2009; Grant Glover et al., 2011) Concentration-dependent mass transfer data and equilibrium isotherms form the foundation for understanding and modeling this type of behavior. As a broadly applicable example of evaluating a MOF for water harvesting, MOF-303 was pressed into pellets, without a binder, and ambient air was pulled through the MOF-303 adsorption bed. The inlet and effluents of the breakthrough system were monitored to produce the breakthrough curve shown in Fig. 10. This breakthrough test was conducted on 3.11 g of MOF-303 in a tube that was 1.5 in. in diameter with additional details in the SI.

It is important to note that the unique shape of the breakthrough curve shown in Fig. 10 occurs not because of mass transfer effects, but rather because of the shape of the adsorption isotherm. It has been shown by others that this type of behavior is consistent for adsorbents with Type IV and V isotherms and occurs because of inflection points in those isotherms. Specifically, isotherms of this type have transitions from favorable to unfavorable adsorption that results in changes in the breakthrough curve from a more shock-like curve to a more dispersed curve. (LeVan and Carta, 2008) Others have also documented this behavior on water adsorption on aluminum fumarate breakthrough curves. (Bozbiyik et al., 2017) Therefore, because the unique shape is a result of the isotherm, and the isotherm shape can be controlled by

Fig. 7. (a) CSFR data and (b) diffusion rates in larger crystal MOF samples (triangles), compared with powders (circles).

Fig. 8. Water diffusion rate vs RH for MOF-303 at 40 °C (a) CSFR data and (b) diffusion rates for MOF-303.
Atomic-scale changes to the MOF link, reticular chemistry provides a way to tune this behavior that has traditionally not been possible.

A COMSOL Multiphysics model of the breakthrough curve in Fig. 10 was developed using a 2D axisymmetric porous domain to represent the packed bed (details provided in the SI). As shown in Fig. 10, the model captures the breakthrough behavior and includes the atypical breakthrough behavior resulting from the isotherm.

Beyond a packed-bed design, it is also possible to envision water-harvesting devices that utilize coatings of MOFs on surfaces. Therefore, to gain a better understanding of the role of diffusion resistance and water capture in these systems, MOF-303 was contained in a polymer and coated on a tube wall (Fig. 11).

3.3. Macropore diffusion rates collected with CSFR

Because the MOF in Fig. 11 is deployed in a polymer matrix, it was uncertain if micropore diffusion or macropore diffusion would be the controlling mass transfer mechanism. Therefore, CSFR was used to quantify a piece of the MOF-303 polymer coating. As discussed above, the micropore and macropore diffusive models have the same mathematical form, therefore, measurements were performed on three separate pieces of the composite of varying diameters. As seen in Fig. 12, the response curves show a dependency on particle size, which confirms a macropore limitation (Giesy and LeVan, 2013; Hossain et al., 2019; Tovar, 2016).

Measurements of the macropore diffusion rate were completed at 10, 40, and 60 % RH on the largest piece of composite and the results are shown in Fig. 13. The data show that the response curves depend on RH, but the macropore diffusivity of the polymer composite is less dependent on gas concentration than the micropore diffusion rates for MOF-303.
MOF-333, or 4/4-MTV-MOF. This is because the response reflects the effective diffusivity, which for systems with nonlinear isotherms is generally a function of concentration. In particular, the effective diffusivity is defined as (Ruthven, 1984)

$$D_e = \frac{D_p}{\frac{2K}{\varepsilon_p} + 1}$$ (19)

and it can be seen that if the macropore diffusivity is constant, the effective diffusivity depends on concentration because the isotherm slope is a function of concentration. When this is accounted for, a value for the macropore diffusivity that is independent of concentration is obtained and is only a function of the macropore structure of the material in which diffusion is occurring. Because this value of $D_p$ is intrinsic to the material and geometry independent, it was calculated using the density (183.2 kg/m$^3$) and porosity (0.584) of the piece of composite. The porosity was determined using

$$\varepsilon_p = 1 - \frac{\rho_s}{\rho}$$ (20)

where $\rho_s$ is the skeletal density, 440 kg/m$^3$. The isotherm slope in the calculation of $D_p$ was obtained from the CSFR fitting process.

With the diffusion quantified, a breakthrough test was completed using the coated tube, and the results were modeled using COMSOL, which are shown in Fig. 14. In the tube case, an additional diffusional resistance from the surface of the coating to the tube wall was included in addition to a micropore diffusion parameter. In this way, the tube model accounts for the mass transfer of water through the tube (convective flow), from the coating surface to the micropores (macropore diffusion), and from the micropores to the adsorption site (micropore diffusion). For computational simplicity, the micropore diffusion was described using the MOF-303 LDF coefficients from CSFR measurements completed on the pure powder of smaller crystals.

The modeling results accurately predict the breakthrough behavior and show that CSFR can provide values suitable for modeling not only packed-bed behaviors, but also coated tubes and other film-based contactors.

Isotherms were collected for both the pure powder MOF-303, the polymer film made using MOF-303, and pieces of MOF-303 contained in a binder but not in a film, and these isotherms are reported in the SI. The average of the experimental isotherms for the film and pieces was used to model the capacity of the coating in the tube. The model is in good agreement with the breakthrough data. Breakthrough data and model predictions for 3 additional tubes are reported in Figure S12 and all show good agreement between the models and the experiments.

3.4. Diffusion versus convection numerical modeling

To understand the different adsorption regimes of the simple tube-based water harvester, the COMSOL model was used to explore the impact of coating thickness on the water capture rate, and two limiting regimes were identified as shown in Fig. 15. While this problem has been examined in previous work, (Sartory, 1978; Tereck et al., 1987) this work extends the treatment to finite mass transfer rates in sorbent layers where thickness cannot be neglected. In Fig. 15, red is used to represent high water content close to the feed concentration, and blue is used to represent dry conditions. In the first case, the coating thickness was 0.5 mm and the flow rate was 0.177 m/s whereas in the second case, the coating thickness was increased to 1 mm with a flow rate of 5 m/s. As shown in Fig. 15a, the flow rate of water vapor through the tube in this configuration is slow enough such that all the water that enters the tube is adsorbed and no water exits the effluent of the tube. This type of operational regime is important when the breakthrough of the adsorbate cannot be allowed, such as toxic gas filtration, flue gas filtration, or chemical separations, and depending on the type of water-harvesting system design, could be important for some water-harvesting systems.

Fig. 13. (a) CSFR response curves and (b) extracted macropore diffusivities as a function of RH for a 3.39x2.09 mm piece of MOF-303/polymer composite at 25°C.

Fig. 14. MOF-303 coated-tube, water adsorption, breakthrough experimental data (points) and model (lines).
3.5. Diffusion and convection time scale and limiting cases

With these results in mind, it would be helpful to examine the process more generically and determine when convection or macropore diffusion is governing the adsorption of water in the system by examining the relative timescales of each process. For this analysis, the flow through a tube whose inner walls are coated with a layer of sorbent is considered. To formulate a model, the convective flux down the channel, the tube whose inner walls are coated with a layer of sorbent is considered.

The dimensionless loading at \( C_0 \) and \( Carta, 2008 \) where \( r \) is sorbent density, \( n^* \) is the equilibrium partition ratio that often appears in packed bed analysis, (LeVan and Carta, 2008) where \( r \) is sorbent density, \( n^* \) is the equilibrium loading.

Likewise, for the MOF domain

\[
\frac{dC}{dt}_{\text{MOFside}} = \frac{dC}{dt}_{\text{MOFside}}
\]

Using the above equations and defining the following dimensionless parameter gives

\[
Bi = \frac{v\delta}{D_m}
\]

which, upon rescaling the \( \psi \) derivatives to \( \eta \) ones by multiplying the \( \psi \) containing term by \( \frac{\delta}{\eta} \), collecting like terms, and simplifying, gives

\[
0 = \left( \frac{1}{Bi\lambda} - \frac{1}{Pe_\gamma} \right) \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( \eta \frac{\partial \psi}{\partial \eta} \right) + \frac{\lambda}{Bi} \frac{\partial^2 \psi}{\partial \xi^2} - \frac{D\psi}{Bi\lambda} (1 - \phi) + \frac{\partial \psi}{\partial t}
\]

Eq. (26) that can be used to understand when diffusion or convection is dominating adsorption. In the following, the contributions of axial and radial dispersion are neglected since the term \( \frac{\delta}{\eta} \) can be assumed to be very small. Thus, Eq. (26) can be simplified as

\[
0 = \left( \frac{1}{Bi\lambda} - \frac{1}{Pe_\gamma} \right) \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( \eta \frac{\partial \psi}{\partial \eta} \right) + \frac{\lambda}{Bi} \frac{\partial^2 \psi}{\partial \xi^2} - \frac{D\psi}{Bi\lambda} (1 - \phi) + \frac{\partial \psi}{\partial t}
\]

for the purposes of the following treatment. Indeed, it is also possible to neglect the term \( \frac{\delta}{\eta} \) entirely, and the governing terms in the above are the groups \( \frac{1}{Bi\lambda} \) and \( \frac{D\psi}{Bi\lambda} \), as will be made apparent in the following.

3.6. Limiting behaviors

There are 3 limiting cases in this analysis. The process can be limited by the rate of convection down the tube, the rate of diffusion into the layer, or the rate of adsorption (which is typically a micropore diffusion limit).

The term \( \frac{\delta}{\eta} \) expands to \( \frac{\delta}{\eta} \) and can be seen to be the ratio of the macropore diffusion rate into the layer, \( \frac{\delta}{\eta} \), vs the convection rate down the tube axially, \( \frac{\delta}{\eta} \). Thus, a large value implies that diffusion into the layer is faster than convection and the limiting factor is the convection time down the tube. In this case, the bed is starved of feed and the uptake is limited by how quickly moisture is fed into the tube via convection. In contrast, small values imply that convection overwhelms diffusion, the bed is flooded with feed, moist air is blown out of the
The diffusion rates were applied to model the behavior of a simple water-harvesting contactor to understand the balance between convective and diffusion time scales. A mass balance analysis was completed to identify the limiting behaviors of a water-harvesting system and to show when diffusion would provide a rate-limiting system behavior.

The results show the examination of mass transfer kinetics from the water molecule to a simple representative water-harvesting system. The data highlight the importance of understanding not only the adsorption capacity in water harvesters but also diffusion rates in MOFs materials. The results apply to a variety of different water-harvesting designs as well as other adsorption devices and shed light on the connection between atom-precision synthesis, diffusion, and process design.

Declaration of Competing Interest

The authors declare the following competing financial interest(s): O. M.Y. is co-founder of Water Harvesting Inc. and ATOCO Inc., aiming at commercializing related technologies. T.G.G. is a co-founder of ATOCO Inc. The remaining authors declare no competing interests.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ces.2023.119430.

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