CO-ADSORPTION AND PURE-COMPONENT ISOTHERM MEASUREMENTS ON DIRECT AIR CAPTURE ADSORBENTS USING THE DVS VACUUM

John P Young[1*], Vladimir Martis[2], Susana Garcia[1], Mijndert van der Spek[1]

[1]Research Centre for Carbon Solutions, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

[2] Surface Measurement Systems, Unit 5, Wharfside, Rosemont Road, London, HA0 4PE, United Kingdom

* Corresponding author e-mail: jpy1@hw.ac.uk

Abstract

Temperature vacuum swing adsorption processes that employ amine-functionalised adsorbents are a promising technology to enable carbon dioxide removal directly from the atmosphere. These adsorbents capture carbon dioxide selectively over nitrogen from the air. They also capture significant amounts of water. The co-adsorption of carbon dioxide and water is still poorly understood due to the difficulty of measuring this effect. To date, water adsorption and co-adsorption measurements were time-consuming as breakthrough or equilibrium adsorption experiments were required for each point on an isotherm. Additionally, data required for the accurate modelling of the process includes pure-component water and carbon dioxide isotherms at a range of temperatures and co-adsorption isotherms at a range of temperatures and relative humidities. Attempting to model direct air capture (DAC) processes without this complete set of data might lead to a limited understanding of the process. As a result, process design may be sub-optimal, and the chosen operating conditions might be inefficient. Here we demonstrate how co-adsorption isotherms and pure-component isotherms can be measured swiftly on an amine-functionalised adsorbent using the Dynamic Vapour Sorption (DVS) Vacuum instrument. We also show how the obtained data can be used to perform first-order kinetic analysis. In this study, Lewatit VP OC 1065® is chosen as an example of an amine-functionalised adsorbent, as it is believed to be similar to the sorbents used by some commercial DAC companies.

Keywords: Direct air capture, adsorption, DVS Vacuum

1. Introduction

Climate change is the most pressing issue of our time. Humanity is currently in a race to restrict the warming of earth to 1.5 °C to avoid catastrophic effects on both the natural world and the human population. In the likely scenario that this target is missed, net negative emissions will be required to bring the temperature back down to the desired range. [1] Carbon dioxide removal (CDR) on a vast scale will be required to implement net negative emissions. One technology that can be utilised to this end is direct air capture (DAC) coupled with long term carbon dioxide storage. Realmonte et al. showed, using bottom-up energy systems modelling, that a carbon tax of just $50 per tonne of CO_2 will be needed by 2030 in order to meet the 1.5°C scenario when DAC is available as a technology. [2] Without DAC, this figure goes up to $2119 per tonne of CO_2 by 2030, and the scenario is completely infeasible without any CDR. The study also does the same analysis using a different model, with a top-down macroeconomic emphasis, and come to a required carbon tax of $151 per tonne of CO_2 with DAC and $446 per tonne of CO_2 without DAC by 2030 to meet the 1.5°C scenario.

Currently, the most mature technology for DAC is temperature vacuum swing adsorption (TVSA) using amine-functionalised adsorbents. Examples of companies currently implementing this are Climeworks, Global Thermostat, and Oy Hydrocell. [3]–[5] Despite the significant advancements made by industry, the academic community still has some significant contributions to make to DAC. The co-adsorption of water and carbon dioxide onto amine-functionalised adsorbents is still poorly understood. It is understood that there is some enhancement of carbon dioxide adsorption under wet conditions. [6]–[10] However, mechanistic mathematical adsorption isotherm descriptions are required to accurately model and optimise the TVSA processes employing these materials. Gathering equilibrium co-adsorption data has been time-consuming to date. Some effort was made by Veneman et al. to gather co-adsorption data using breakthrough experiments on a commercially available amine-functionalised adsorbent, Lewatit VP OC 1065®. [7] Nevertheless, only 12 data points were collected at different relative humidities and temperatures, whilst CO_2 partial pressure was kept constant. Presumably, this was due to the time-intensive nature of breakthrough experiments. An extensive range of temperatures, CO_2 partial pressures, and relative humidities are required to build and fit an accurate co-adsorption isotherm model. Furthermore, there are questions about the accuracy of measured breakthrough data. There are a few different operating variables to control in breakthrough experiments, and the reactor outlet concentration must be measured precisely. These factors all add to the potential for experimental error. Veneman et al. also use breakthroughs to measure water adsorption isotherms, but the less time-consuming thermogravimetric analysis (TGA) is used for CO_2 isotherms. A volumetric method

combined with gas chromatography was used by Didas et al. for measuring co-adsorption isotherms on an amine-functionalised silica. [11] Aside from amine-functionalised adsorbents, Wilkins and Rajendran also used breakthrough experiments to measure the competitive adsorption of CO_2 and N_2 on zeolite 13X. [12] Meanwhile, Hefti et al. combined gravimetric experiments with gas chromatography to measure the same competitive adsorption on zeolites 13X and ZSM-5. [13]

A piece of equipment that may be quicker and more effective at measuring pure CO_2 adsorption, pure H_2O adsorption, and co-adsorption is the DVS Vacuum. [14] This has previously been used by Su et al. to measure CO_2 and H_2O isotherms on an amine-functionalised Mg-MOF-74. [15] The DVS Vacuum uses a microbalance to measure the weight change of a sample subjected to various conditions. The temperature, pressure, and composition in the sorption chamber can be controlled very accurately.

This study sets out to show how co-adsorption isotherms and water adsorption isotherms on a commercially available amine-functionalised adsorbent, in the form of Lewatit VP OC 1065®, can be measured using the DVS Vacuum. Beyond this study, this methodology can be extended to other adsorbents, given that certain assumptions hold. These will be discussed in the Experimental method and analysis section. In future work, the data collected here will be used to develop a mechanistic mathematical water-CO_2 co-adsorption isotherm model that can be extended to any amine-functionalised adsorbent. It is hoped that this will lead to more accurate modelling of DAC processes, and therefore improved optimisation and enhanced efficiency.

2. Experimental method and analysis

The material investigated, Lewatit® VP OC 1065, was obtained from Sigma-Aldrich. It is a divinylbenzene (DVB) crosslinked polymer functionalised with primary amine groups with an average pore diameter of 25 nm, a bead size of 0.315 – 1.25 mm, pore volume of 0.27 cm³ g^{-1}, surface area of 50 m² g^{-1}, and bulk density of 630 – 710 g l^{-1}. [14] Meanwhile, the heat capacity is reported as 1.58 kJ kg^{-1} K^{-1}. [23]

Figure 1 shows a schematic of the DVS Vacuum. In the experiments presented in this work, the gas and vapour used are CO_2 and water. A turbomolecular pump enables the pressure in the chamber to reach as low as 10^{-6} mbar. This ensures very thorough outgassing of the sample prior to adsorption. The vacuum pump, coupled with various control valves, allows very accurate control of the sorption chamber pressure during adsorption and desorption measurements. The temperature in the sorption chamber can range from room temperature up to 400°C whilst the whole system, apart from the gas storage and vacuum pumps, is inside an incubator (temperature-controlled enclosure) operating in the temperature range from 20 up to 70°C. The incubator temperature sets the maximum limit of the solvent's partial pressure in the sorption chamber as the saturation pressure at this temperature. The set partial pressure of
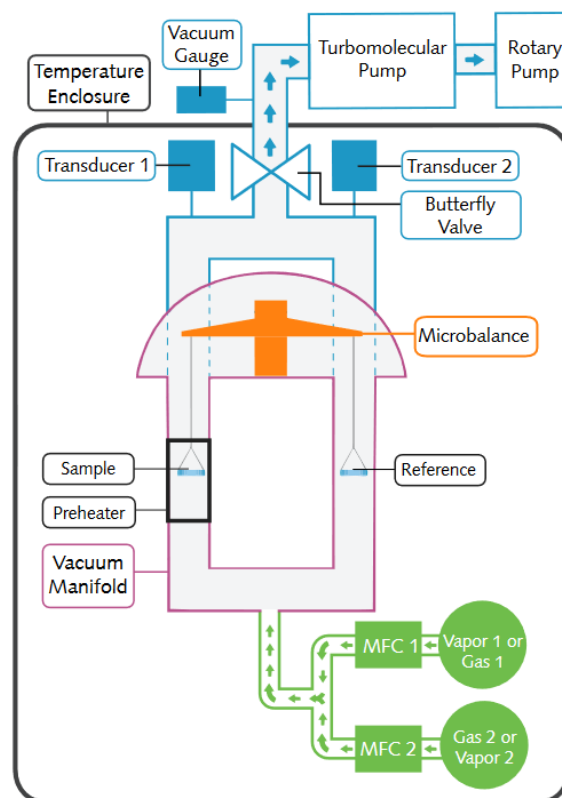

Figure 1: A simple schematic of the DVS Vacuum.

water is introduced under vacuum without the interference of a carrier gas at the set experimental temperature. Such measurements will provide true water adsorption isotherms eliminating the impact of water adsorption on the structure. The sample's weight is measured directly and continuously using Surface Measurement Systems' UltraBalance with a resolution of 0.1 µg. The whole system is controlled via the control software, allowing the user to create and modify experimental methods easily. The method can be set to measure a whole isotherm, including a desorption branch in one experiment. It also allows the collection of multiple adsorption/desorption isotherms with in-situ outgassing between cycles in a single experiment. The sorption measurements can be done in a fixed time mode or mass equilibrium mode where the mass equilibrium criterion is set as the change in mass per minute (dm/dt). The control software automatically calculates and checks the dm/dt criterion against the set dm/dt value. When the sample's mass has reached equilibrium at a certain partial pressure of the gas or vapour, the control software automatically moves on to the next partial pressure step in the method. Due to this highly automated system, the labour time required to measure an isotherm is very low, whilst the actual time the equipment takes to measure an isotherm is dependent on the sample itself, the adsorbate, and the experimental conditions defined in the method.

The DVS Vacuum can be operated in a "dynamic", "semi-static", or "static" mode. In dynamic mode, the downstream and upstream sorbate flow is controlled, while changes in sample mass are continuously monitored. In a typical experiment, vapour or gas flows at a constant rate over a sample while the total system

pressure is kept constant. Meanwhile, in static mode, the upstream and downstream control valves are closed upon the injection of a sorbate in the chamber (similar to manometric systems). At the same time, changes in sample mass are continuously monitored using the UltraBalance. There are two options for static mode: semi-static and true static. The difference between these two options is that in semi-static mode, more sorbate molecules are added to the chamber when the pressure inside the vacuum chamber decreases below the set pressure due to sorption of molecules by the sample. On the other hand, in true static mode, when the partial pressure drops below the set pressure, more molecules are not injected into the chamber and the sample is simply left to equilibrate.
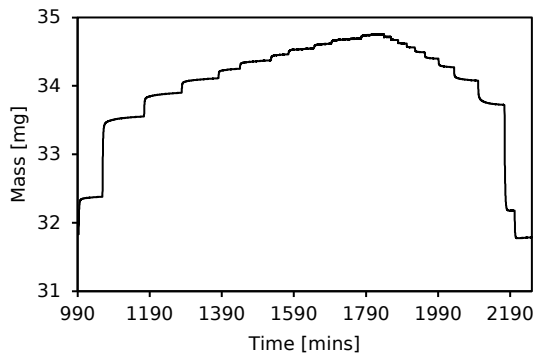

Figure 2: Mass vs time graph obtained from a CO_2 isotherm experiment at 75°C that measures both the adsorption and desorption branches.

In a typical experiment with Lewatit VP OC 1065®, around 50 mg of the sample mass is loaded into the metal pan that hangs from the microbalance. The first step in the method used here involves heating the sample to 100 °C under the highest achievable vacuum for 12 hours. This ensures thorough degassing of the sample with the removal of any H_2O, CO_2, or N_2. Then a cooling step is implemented to bring the sample back down to the temperature of interest while maintaining the same level of vacuum. Next, the sorbate pressure in the sorption chamber is increased stepwise as per the method, and the sample mass in the chamber is allowed to equilibrate at each step. The desorption branch is performed in a similar manner, that is, the pressure is decreased stepwise with the sample mass equilibrating at each step. Figure 2 depicts typical sorption raw data showing changes in the sample mass during adsorption and desorption as a function of time. Pure H_2O sorption experiments were done in dynamic mode whilst pure CO_2 experiments were done in semi-static mode, with pressures ranging up to 1 bar. Dynamic mode was chosen for water sorption experiments to maintain the purity of water vapour in the sorption chamber. Any gases dissolved in the liquid water flask or desorbed molecules would quickly be flushed away from the sample. It also allows better control of pressure at extremely low values. Semi-static mode is used for CO_2 experiments, as the gas source is expected to be high purity, and it will eliminate any effect flow may have on the measurements. It also protects the vacuum pumps from corrosion and uses much less gas.

Veneman et al. showed that the presence of CO_2 does not affect H_2O adsorption on Lewatit VP OC 1065®. [7] Other literature also shows that this assumption holds for other types of amine-functionalised adsorbents, such as silica and cellulose. [6], [11] If this was not previously known, other experiments such as breakthroughs would be required to confirm this, as it is a hard constraint on this method. Thompson and Zones have previously used this assumption to measure competitive adsorption on a zeolite with the DVS Vacuum. [16] Using this assumption, that CO_2 does not affect H_2O adsorption, we can measure CO_2 co-adsorption isotherms under wet conditions. This is done in semi-static mode, so the amount of CO_2 and H_2O in the chamber is known. The first pressure increase in the co-adsorption isotherm measurement is a pure water step. The pressure is equilibrated at the relative humidity of interest. Here we need to carefully ensure the mass of the sample has fully equilibrated. We have made the assumption that this amount of water adsorbed is now constant for the rest of the experiment, as is the chamber's relative humidity. Each subsequent pressure addition of pure CO_2 allows an isotherm to be built.

For pure-component isotherms, the saturation loading, q_i^* [mol kg^{-1}], at the end of step n is calculated according to Equation 1.

$$q_i^* = \frac{m_n - m_0}{m_0 M_{w,i}} \qquad 1.$$

Where m_n [kg] is the mass of the sample at the end of step n, m_0 [kg] is the mass of the sample at the end of the degassing step, and $M_{w,i}$ [kg mol^{-1}] is the molecular weight of adsorbate i.

For co-adsorption CO_2 isotherms, the loading of H_2O is calculated from Equation 2.

$$q_{H_2O}^* = \frac{m_1 - m_0}{m_0 M_{w,H_2O}} \qquad 2.$$

Where m_1 [kg] is the mass of the sample at the end of the water adsorption step. The CO_2 loading at the end of step n in the co-adsorption experiments is calculated according to Equation 3.

$$q_{CO_2}^* = \frac{m_n - m_1}{m_0 M_{w,CO_2}} \qquad 3.$$

The same raw data from the DVS, shown in Figure 2, can also be used to do some kinetic analysis. Equation 4, shows a common kinetic model called the linear driving force (LDF) model. [17] This is the most popular choice for process modelling due to its simplicity and effectiveness at predicting breakthrough.

$$\frac{dq_i}{dt} = k_{LDF}(q_i^* - q_i) \qquad 4.$$

Here k_{LDF} [s^{-1}] is the LDF constant, t [s] is time, and q_i [mol kg^{-1}] is the loading at any given time in the step. The model can be fit to each pressure step in order to obtain the LDF constant for that pressure and temperature.

The Toth model is also used to fit pure-component CO_2 isotherm data and this presented in equations is presented in Equations 5-8 below: [18]

$$q^*_{CO_2} = \frac{n_\infty(T)b(T)p_{CO_2}}{\left(1 + \left(b(T)p_{CO_2}\right)^{t(T)}\right)^{\frac{1}{t(T)}}} \qquad 5.$$

Where, n_∞ [mol kg^{-1}] is the loading of CO_2 that is approached at an infinite pressure, b [Pa^{-1}] is the affinity of CO_2 to the adsorbent, p_{CO_2} [Pa] is the partial pressure of CO_2, and t [−] is an exponential factor.

$$n_\infty(T) = n_{\infty,0} \exp\left(\chi\left(1 - \frac{T}{T_0}\right)\right) \qquad 6.$$

Where $n_{\infty,0}$ [mol kg^{-1}] is n_∞ at the reference temperature T_0 [K], T [K] is the temperature, and χ [−] is a factor used to describe the temperature dependency.

$$b(T) = b_0 \exp\left(\frac{-\Delta H_0}{RT_0}\left(\frac{T_0}{T} - 1\right)\right) \qquad 7.$$

Where b_0 [Pa] is b at the reference temperature, ΔH_0 [J mol^{-1}] is the isosteric heat of adsorption, and R [J mol^{-1} K^{-1}] is the universal gas constant.

$$t(T) = t_0 + \alpha\left(1 - \frac{T_0}{T}\right) \qquad 8.$$

Where t_0 [−] is t at the reference temperature, and α [−] is a factor used to describe the temperature dependency.

3. Results and discussion

3.1 Water adsorption

Water isotherms were measured at three different temperatures, including both adsorption and desorption branches.
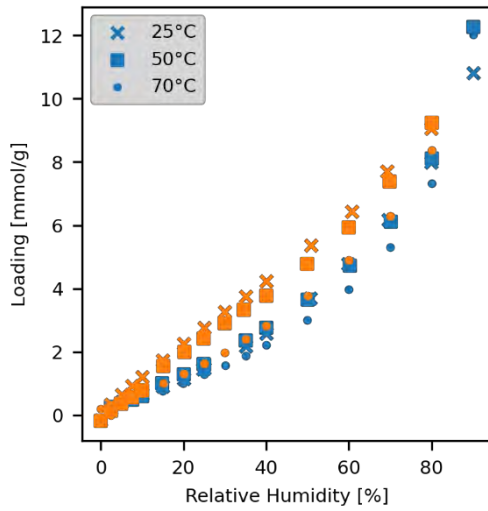

Figure 3: Lewatit VP OC 1065® H₂O isotherms showing both adsorption (blue) and desorption (orange) branches for three different temperatures.

Figure 3 shows H₂O isotherms, which are type III, indicating multilayer adsorption clustering around favourable sites. This is consistent with the expectation that water would form hydrogen bonds with the amine groups on the adsorbent, and then subsequently more water would form hydrogen bonds onto this first layer. The hysteresis exhibited is type H3, which describes macropore adsorbents with pores partially filled by

condensate. [19] This again is consistent with what we would expect from this adsorbent.

In Figure 3 there are 45 adsorption points, which would require 45 individual breakthrough experiments if we were to measure these isotherms in a breakthrough set up. Meanwhile, it would not be possible to measure the desorption branch completely. On the other hand, in the DVS Vacuum, these measurements take just three experiments, each lasting between half a week and a week, meaning a full set of water isotherms was measured in the space of three weeks at most.

3.2 Carbon dioxide pure component adsorption and co-adsorption

Pure-component carbon dioxide isotherms were measured at two temperatures and then fit to the Toth model in order to present them as solid lines, so the co-adsorption isotherms can be compared point-for-point. [18] The parameters shown from this fitting process are found in Table 1. The R^2 value for this was 0.99.

Table 1: Parameters found for the pure-component CO_2 isotherm fit to the Toth equation.

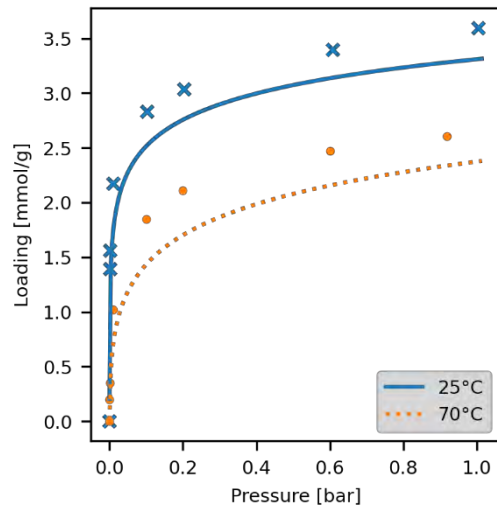| Parameter	Value	Unit
T_0	298.15	K
$n_{\infty,0}$	6.80	mol kg^{-1}
χ	0.424	-
b_0	21.2	Pa^{-1}
$-\Delta H_0$	134000	kJ mol^{-1}
t_0	0.149	-
α	0.401	-

Figure 4: Lewatit VP OC 1065® Pure CO₂ isotherms calculated from the Toth model are shown as lines, whilst the markers are experimental CO₂ isotherms subjected to a relative humidity of 30%. The blue crosses refer to the co-adsorption isotherm at 25°C, whilst the orange dots refer to the co-adsorption isotherm at 70°C.

Figure 4 shows pure CO₂ isotherms compared to CO₂ co-adsorption isotherms at 30% relative humidity for two different temperatures, 25°C and 70°C. The isotherms are type I as expected by a chemisorbent material. It is seen

that the presence of 30% humidity enhances the amount of CO_2 adsorbed as literature has previously suggested for amine-functionalised adsorbents. [6]–[10] Gebald et al. previously presented 4 points of a CO_2 co-adsorption isotherm at two different temperatures under a constant partial pressure of water, resulting in relative humidities of 21% and 92%, for amine-functionalised cellulose. [6] Meanwhile, Didas et al. presented 3-4 points of a co-adsorption isotherm at one temperature for three different amine-functionalised silicas with varying amine coverage. [11] To the authors' knowledge, this is the closest any previous literature has come to presenting a full co-adsorption isotherm, like in this study, on an amine-functionalised adsorbent. One drawback is that the assumption that CO_2 does not affect water adsorption must hold for this method to give valid results. This is something that may not be true for other types of adsorbents. Indeed, preliminary breakthrough experiments may be needed to verify the assumption or establish a different method to use in the DVS Vacuum.

3.3 Kinetic analysis of water adsorption

LDF constants, which are mathematically similar to first-order rate constants in the area of chemical kinetics, were fitted to raw data for water adsorption isotherm measurements.
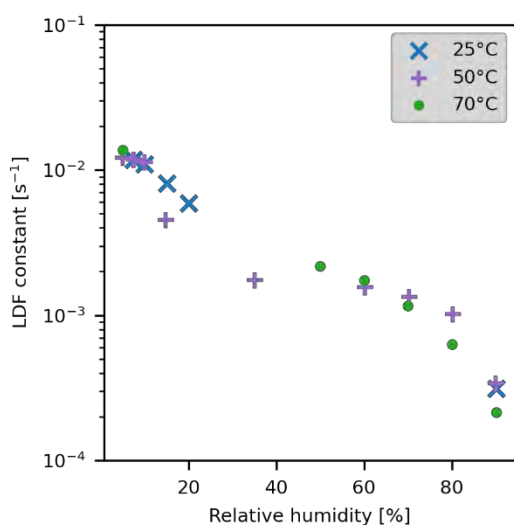

Figure 5: LDF constants for water adsorption fitted to raw data used for building the isotherms. Sometimes, it is hard to find a suitable model fit, and in these cases, the points have been removed from this graph. The tolerance for this removal is an R^2 value of less than 0.9.

Figure 5 shows LDF constants of water adsorption, plotted against relative humidity for three different temperatures. No clear trend with temperature is observed when plotted against relative humidity. The authors propose that this is because converting pressure to relative humidity already takes temperature into account. However, there is a clear decreasing trend between the LDF constants and relative humidity: the kinetic rate deteriorates with approximately two orders of magnitude when moving from 0 to 90% RH. This is important for modelling purposes and cycle design, as the prospective plant's environmental circumstances may

have a considerable influence on the rate-based adsorption of water, and therefore on energy performance. Some individual points in Figure 5 deviate from the trend, potentially due to some experimental error, and fitting errors caused by imperfections in the mass change over time graph like the one presented in Figure 2.

More work does need to be done to assess whether these LDF constants also hold when scaling up from a gravimetric to a breakthrough set-up. This is key since real processes involve fixed-bed columns like those used in a breakthrough set-up. There may be additional or fewer mass transfer barriers in a fixed-bed column, for example, film resistance. At the same time, it has previously been shown by Casas et al. that the values of the LDF constants do not have an enormous effect on breakthrough modelling results, so the values from a gravimetric set-up may be a sufficient approximation if a breakthrough experiment is unavailable. [20]

4. Conclusion and future work

Water and co-adsorption isotherms have been measured on Lewatit VP OC 1065®. The DVS Vacuum enables the efficient measurement of co-adsorption isotherms under the condition that one of the component's adsorption is unaffected by the other. It is also very effective for measuring water adsorption isotherms in comparison to using a breakthrough set-up. The enhancing effect of water on CO_2 adsorption for amine-functionalised adsorbents has been confirmed, and the most complete CO_2 co-adsorption isotherms on these adsorbents yet have been measured. The same raw data that was used to measure the isotherms was also used to perform kinetic analysis, and LDF constants were calculated for water adsorption. A decreasing trend with relative humidity was observed for these values. Further assessment is required to check how these values predict mass transfer in breakthrough columns.

In future work, we will complete a full assessment of equilibrium adsorption on Lewatit VP OC 1065® to model the pure component isotherms and co-adsorption isotherms using mechanistic descriptions. Next, breakthrough experiments will be used to study the dynamics of pure-component and co-adsorption. We hope this will lead to the establishment of Lewatit VP OC 1065® as a benchmark DAC sorbent since it is one of the few commercially available, amine-functionalised adsorbents.

Acknowledgements

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