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Evaluating solid sorbents for CO₂ capture: linking material properties and process efficiency via adsorption performance

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Expanding populations and growing economies result in higher energy needs. Meeting this increasing demand, while lowering carbon emissions, calls for a broad energy mix and commercial deployment of solutions like carbon capture and carbon removal technologies. The scale-up of these solutions is partially hindered by the lack of materials-related information, particularly in the case of solid adsorption-based carbon capture technologies. Furthermore, experimental measurement parameters used and how data is presented lack uniformity, which makes material comparisons extremely difficult. This review examines the current state of solid sorbent characterization for carbon capture, exploring physical and chemical properties, performance parameters, and process indicators. Adsorbent performance parameters demonstrate to be the crucial link between intrinsic material properties and the overall adsorption process effectiveness and therefore are the focus of this work. This paper outlines the relevant techniques used to measure Key Performance Indicators (KPIs) related to adsorption performance such as CO₂ adsorption capacity, selectivity, kinetics, ease of regeneration, stability, adsorbent cost, and environmental impact. Additionally, this study highlights the relevant experimental conditions for diluted versus concentrated CO₂ streams. Lastly, efforts in harmonizing experimental data sets are considered, and an outlook on solid sorbent characterization for carbon capture processes is presented. Overall, the aim of this work is to provide the reader a critical understanding of KPIs from atomic to process scale, highlighting the importance of experimental data throughout.

KEYWORDS

adsorption, adsorbent, carbon capture, DAC, post-combustion capture, characterization, MOFs

1 Introduction

The continuously increasing concentration of CO₂ in the atmosphere due to anthropogenic emissions has caused an estimated 0.8°C–1.2°C rise in average global temperature (Siegelman et al., 2021). These warming levels can have severe effects on our planet and its inhabitants, including extreme weather events, sea-level rise, species extinction and risks to human health (IPCC, 2018). To avoid these catastrophic events, carbon capture, utilization, and storage (CCUS) has been proposed as one of the potential solutions for

decarbonizing sectors like energy, chemicals, construction, and other industries as well as for pulling CO₂ out of the atmosphere (i.e., carbon dioxide removal). Despite its important role in mitigating climate change, CCUS commercial deployment has been slow and its impact on global CO₂ emissions is currently limited. As of 2021, global CO₂ capture capacity from power and industrial facilities reached 40 Mt, representing only 0.12% of the annual global energy-related CO₂ emissions (IEA, 2020). According to the International Energy Agency (IEA), CCUS capacity needs to increase to 7,600 MtCO₂/year to achieve net zero by 2050 (IEA, 2021).

CCUS involves the capture of CO₂ from industrial processes and its subsequent transport via road, rail, or sea. CO₂ can be used to produce valuable products such as chemicals, fuels, and building materials, or directly stored in carbon sinks. Although economically attractive, the environmental impact of CO₂ utilization must be evaluated carefully to avoid potential net CO₂ emission increase. Carbon capture systems can be classified into post-combustion, pre-combustion, and oxy-combustion; with post-combustion capture (PCC) systems being the most mature and adopted worldwide due to their retrofit ability (Bui et al., 2018) (See Figure 1). Each of these systems can employ different technologies for gas separation such as chemical absorption, solid adsorption, or membrane separation (Bui et al., 2018). More recently, other CO₂ removal systems such as direct air capture (DAC) and bioenergy with carbon capture and storage (BECCS) have been proposed to help compensate

for emissions from hard to decarbonize sectors such as aviation (Bui et al., 2018; Becattini et al., 2021).

While there is a clear need to ramp up the commercial implementation of CCUS, there are various associated challenges, such as high costs, lack of governmental policies and uncertain public acceptance (Jones et al., 2017). Currently, liquid absorption is considered the most mature and economic technology for PCC (Bui et al., 2018). However, a promising alternative is gas phase adsorption with solid sorbents, which has showed some advantages over liquid absorption. These include energy savings, no use of water make-up streams, and the flexibility to capture CO₂ using different regeneration modes and process configurations (Bui et al., 2018; Kiani et al., 2020; Wang and Song, 2020; Liu et al., 2021).

Evaluating solid sorbents poses a significant challenge due to the vast array of materials and potential process configurations involved. The pursuit of the ideal solid sorbent for various carbon capture applications has been a primary focus of research. However, transitioning a material from the laboratory to pilot scale requires a thorough grasp of its adsorbent properties, adsorption performance, and process efficiency. This progression demands a combination of experimental and computational efforts, which can be both costly and time-consuming, resulting in incomplete or incomparable data sets across different materials. In this study, we aim to shed light on this pipeline highlighting the relevant Key Performance Indicators (KPIs) at each stage, to achieve a comprehensive material

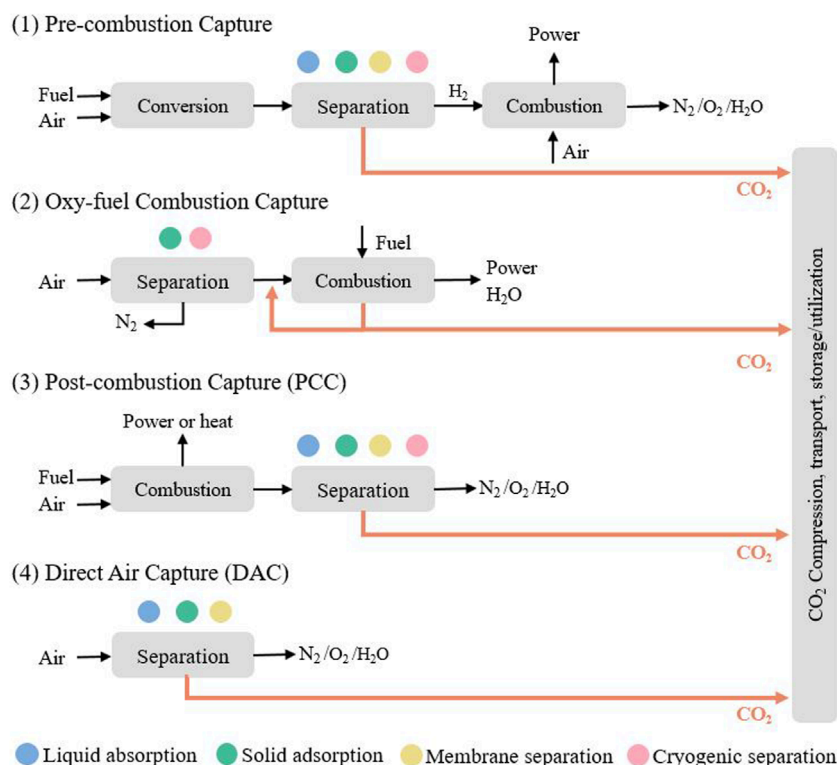


FIGURE 1 Carbon capture systems including pre-combustion, oxy-fuel combustion, post-combustion, and direct air capture with possible separation technologies.

characterization, underscoring the significance of precise and reproducible experimental data.

1.1 Adsorption technology in carbon capture

At present, adsorption technology for CO₂ capture is at pre-commercial demonstration with pilot projects including CO₂ capture from power generation, iron, steel, chemical and cement industries, as well as DAC (Bui et al., 2018; IEA, 2020; Lin et al., 2021). In adsorption-based carbon capture processes, CO₂ concentrates on a solid surface (e.g., activated carbon, alumina, metallic oxides, or zeolites). Adsorption can occur through two different mechanisms, physisorption or chemisorption. Physisorption involves non-bonding interactions between adsorbent and adsorbate, while chemisorption involves the formation of weak chemical bonds. After adsorption, molecules are released or desorbed by a change in temperature (temperature swing adsorption [TSA]), pressure (pressure swing adsorption [PSA], vacuum swing adsorption [VSA]) composition (moisture, pH swing adsorption) or combinations thereof. The recovery of CO₂ is related to the binding strength of adsorption, defined by the adsorption enthalpy (ΔH_{ads}). It is commonly claimed that a boundary between physisorption and chemisorption exists for the CO₂ adsorption enthalpy (e.g., 45–50 kJ/mol) (Patel et al., 2017). However, physisorption systems that display values above 50 kJ/mol can also occur (Denayer et al., 1998; Kim et al., 2016).

Adsorbents for CO₂ capture can be classified into four main groups: (1) organic, (2) inorganic, (3) Metal Organic Frameworks (MOFs)/Porous Coordination Polymers (PCPs) and (4) hybrid adsorbents (Sreenivasulu et al., 2015; Liu et al., 2021). For specific material performance data, we draw the attention of the reader to several studies on the recent advances in solid sorbents for PCC and DAC systems (Samanta et al., 2012; Lee and Park, 2015; Sreenivasulu et al., 2015; Ünveren et al., 2017; Nie et al., 2018; Webley and Danaci, 2019; Liu et al., 2021; Siegelman et al., 2021), (Shi et al., 2020; Shi et al., 2022; Wu et al., 2022; Low et al., 2023; Panda et al., 2023). Alongside adsorbent development, their practical implementation has been assessed from an engineering and techno-economic perspective (Bui et al., 2018; Hu et al., 2019; Yang et al., 2019; Danaci et al., 2020; Liu et al., 2021; Raganati et al., 2021), (Azarabadi and Lackner, 2019; Sinha and Realff, 2019; Danaci et al., 2021).

These studies highlight the increasing variety of solid sorbents for carbon capture, and the prevalent use of amine-functionalized adsorbents that deliver superior CO₂ absorption and selectivity. Additionally, a shift in lab-scale material synthesis has been observed, moving away from powders towards monoliths, pellets, and structured adsorbents which are better suited for large-scale processes. While analyzing performance data of specific materials is beyond the scope of this work, there is unanimous agreement among the cited studies about the importance of comprehensive material characterization. However, discourse on its execution and measurement remain scarce, and it is precisely this gap the current work aims to fill.

1.2 Point source capture

Refers to the capture of CO₂ from flue gas or other concentrated industrial waste gas. Table 1 shows the composition of CO₂-containing mixtures in different industries, together with their respective temperature and pressure conditions; the composition of air is included for reference.

1.3 Direct air capture (DAC)

Direct air capture (DAC) is the capture of CO₂ from ambient air, a process that has gained attention as a negative emissions technology for net CO₂ removal. Nevertheless, DAC faces technical and economic limitations due to the exceptionally low concentration of CO₂ in ambient air (see Table 1) which is ~200 times more dilute than the flue gas of a gas-fired power plant, and thus requires high gas flows and highly specific adsorbents. Cost estimates for DAC are about an order of magnitude greater than point source capture. (Sinha and Realff, 2019; Erans et al., 2022; Herzog, 2022). Despite its high cost, DAC could be used to mitigate CO₂ emissions of processes where the addition of a capture unit is not feasible due physical/space constraints or where mobile emissions are involved (Sendi et al., 2022).

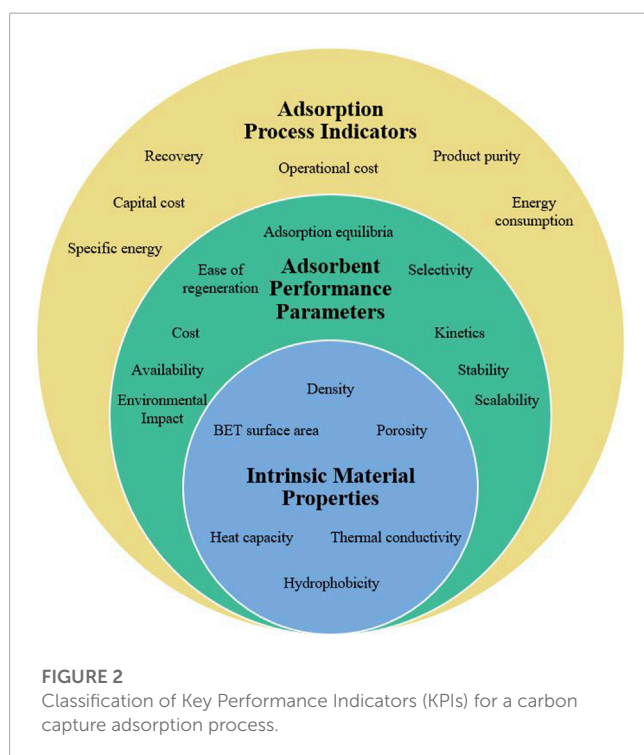
1.4 Key performance indicators (KPIs)

To effectively design, evaluate and compare CO₂ adsorbents for point source capture or DAC, it is important to understand the Key Performance Indicators (KPIs) relevant to each carbon capture process. For simplicity, throughout this work, KPIs are classified into three main groups (1) intrinsic material properties, (2) adsorbent performance parameters and (3) process performance indicators (see Figure 2). Intrinsic material properties refer to the basic characterization parameters that are typically measured to understand an adsorbents physical and chemical composition, such as density, BET area, porosity, etc. On the other hand, adsorbent performance parameters are the metrics used to measure adsorbent efficiency under certain process conditions, they typically include adsorption capacity, selectivity, and kinetics. Lastly, process performance indicators include metrics like recovery, product purity and energy consumption. These can be optimized to achieve a more efficient and cost-effective carbon capture process.

The intrinsic material properties and related characterization techniques are well established. For some commercial materials like activated carbon (AC) its physical and chemical characterization has been standardized by the American Society for Testing and Materials (ASTM) (Bläker et al., 2019). Similarly, process performance indicators such as purity and recovery are typically set targets for a separation process and have been mathematically described for TSA/PSA processes (Rajagopalan et al., 2016). On the other hand, some adsorbent performance parameters are not yet standardized, and can be measured with a wide range of experimental techniques at varying conditions. Therefore, adsorption performance data for solid sorbents is often not consistent and difficult to compare. This issue has been raised both by the carbon capture and adsorption communities. For instance, Espinal et al., underline insufficient materials-related

TABLE 1 Flue gas composition and conditions for different industries, air composition is included for reference.

Industrial process	CO ₂ concentration in feed (vol%)	Main impurities (vol%)	Typical conditions
Power generation	5%–15%	70%–75% N ₂ , 6%–18% H ₂ O, 6%–14% O ₂ , trace SO _x , H ₂ S, NO _x	1 bar, 40°C–90°C
Cement industry	14%–33%	50%–75% N ₂ , 6%–12% H ₂ O, 2%–5% O ₂	1 bar, 40°C–75°C
Steel industry	20%–22%	5%–46% N ₂ , 4%–54% CO, 3%–6% H ₂ , 4% H ₂ O, 1% CH ₄	1 bar, 30°C
Air	0.04%	78% N ₂ , 20% O ₂ , 1% Ar	1 bar, location dependent



measurements, standards and data on solid sorbents which is critical for understanding and evaluating the overall performance of an adsorption-based carbon capture process (Espinal et al., 2013). Additionally, the National Institute of Standards and Technology (NIST) and the Council for Chemical Research (CCR) have highlighted the need to enhance experimental capability to better understand adsorption rate, diffusional mechanisms, and competitive adsorption capacity, all of which are key parameters regarding adsorbent performance (NIST, 2015; Walton, 2019).

This work comprehensively reviews advanced experimental measures of adsorbent performance parameters like adsorption capacity, selectivity, kinetics, and stability. It evaluates each technique's advantages and limitations, and considers the suitable conditions for point source capture versus DAC. Furthermore, it provides a critical discussion on the interrelationship among the different KPIs, emphasizing on data reproducibility and standardization. Lastly, it concludes with a forward-looking commentary on the experimental characterization of solid sorbents for carbon capture. While a detailed examination of computational methods is not included, readers are directed to the work by Farmahini et al., for an in-depth review of computational approaches (Farmahini et al., 2021).

To present the information in an orderly manner, this paper guides the reader through the usual experimental pathway followed to assess a newly prepared CO₂ capture material from laboratory to pilot scale (see Figure 3). It is important to point out that each material is different, and its analysis may vary depending on its specific characteristics. Experimental characterization is not a one-size-fits-all procedure and is subject to instrumentation and time availability.

2 Intrinsic material properties

The intrinsic material properties of an adsorbent describe the nature of the material outside the context of an adsorption process (i.e., physico-chemical properties). Typically, the first stage in material characterization is identification (i.e., to determine whether the desired material has been produced), also providing insight into the structure of the adsorbent. For crystalline or well-ordered materials this can be accomplished using diffractive ion (Galarneau et al., 2003; Papageorgiou et al., 2013; Zhou et al., 2018; Middelkoop et al., 2019) or scattering techniques (Kruk and Cao, 2007; Gu et al., 2022). Materials may also be investigated to probe chemical species or bonds present using elemental analysis (Geng et al., 2016; Wang and Okubayashi, 2019; Lee et al., 2022), X-ray fluorescence (Somerset et al., 2004; Bao et al., 2022), or spectroscopy (Meador et al., 2015; Wang and Okubayashi, 2019; Hadjiivanov et al., 2021).

2.1 Textural properties

Once the material's composition has been confirmed, the determination of its surface area and pore morphology is typically a priority. A suite of techniques exist to measure BET surface area and pore morphology (Schlumberger and Thommes, 2021), the most common being physisorption of gases such as N₂, Ar, or CO₂. A report published by the International Union of Pure and Applied Chemistry (IUPAC) details the methodology and best practices for characterizing porous solids via gas physisorption, from sample preparation to data interpretation (Thommes et al., 2015). A range of resources are available on this topic, and the reader is directed to them for additional details (Rouquerol et al., 2007; Ambroz et al., 2018; Bardestani et al., 2019).

The textural and geometric properties of porous materials can also be evaluated computationally (Nguyen et al., 2008; Coudert and Fuchs, 2016). Quantitative differences between simulations and experimental data do exist in literature (Garberoglio et al., 2005; Chowdhury et al., 2009), due to factors such as the measurement

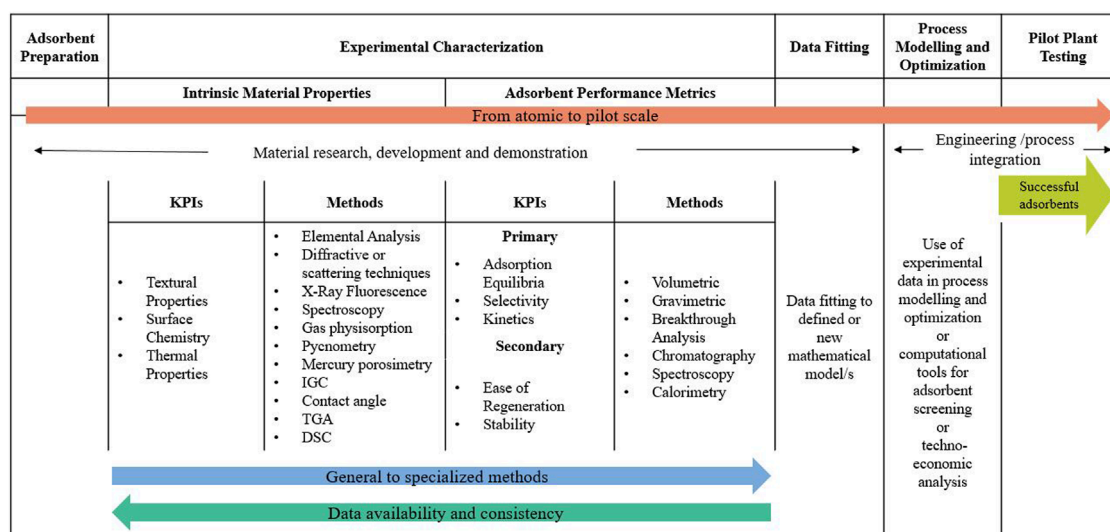


FIGURE 3

Experimental pathway to assess newly prepared CO₂ capture materials from atomic to pilot scale.

technique(s) used and the associated sample activation procedure (Thommes et al., 2015; Couderc and Fuchs, 2016). Textural properties such as crystal size and shape (Zhang et al., 2014; Hobday et al., 2021), and the presence of defects (Liang et al., 2018) within the material can be difficult to account for in computational predictions. Nevertheless, a combination of both is required to obtain accurate data. For example, obtaining information about the pore structure in materials that exhibit an interconnected pore network of different pore sizes including micro-, meso- and macropores (e.g., hierarchically ordered zeolites) can be experimentally challenging. Here, statistical mechanical models such as NLDFT and molecular simulation-based methods can be coupled with gas physisorption to obtain a comprehensive pore size analysis (Schlumberger and Thommes, 2021). Recently, dual-gas analysis techniques have also been proposed to enhance the resolution and accuracy of pore-size distribution analyses (Jagiello et al., 2019; Blankenship et al., 2022; Jagiello and Kenvin, 2022).

For applications in which the adsorbent bed's structure is a concern, when using monoliths or pellets, quantifying the total porosity and/or packing density of the material during operation is important. Studies on monolithic MOF's have used bulk density to highlight high volume-relative properties compared to their powder equivalents (Tian et al., 2015; Tian et al., 2018; Hunter-Sellars et al., 2020a; Madden et al., 2022). Bulk and packing densities, and subsequent void fractions, may be determined through experimental means, such as envelopment (pycnometry) (Benyahia and O'Neill, 2005; Hunter-Sellars et al., 2020a) or mercury porosimetry (Liu et al., 2018). Furthermore, the mechanical stability of adsorbents can be measured by compression (Lawson et al., 2020), or by tensile strength (Bazer-Bachi et al., 2014). Lastly, determination of the geometry and form factor of the adsorbent, which can strongly influence the subsequent bed's mass and heat transfer, may be determined using a variety of techniques including

light scattering (Kim et al., 2012) and microscopy (Lu et al., 2022).

2.2 Surface chemistry and chemical functionality

Alongside surface area and pore morphology, surface chemistry can strongly influence CO₂ adsorption capacity, interaction strength, and selectivity. Examples of rational tuning of surfaces include enhancing hydrophobicity (Piscopo and Loebbecke, 2020; Sáenz Cavazos et al., 2021) and amine-functionalization (Vilarrasa-García et al., 2015; Ünveren et al., 2017; Zhang and Du, 2022). The dispersive and specific chemical contributions to surface energy, and by extension a metric of hydrophobicity, can be determined by conducting liquid contact angle (Kozbial et al., 2014) or inverse gas chromatography measurements (Hamieh et al., 2020) using several fluid probes with different chemistries.

For amine functionalized materials, distinguishing between primary, secondary, and tertiary amines, each of which forms different byproducts during reactions with CO₂, may be done using NMR spectroscopy (Moschetta et al., 2015; Shimon et al., 2018). Finally, the total loading of amine within a composite material, such as a mesoporous alumina or silica, can be determined using thermogravimetric burn-out procedures (Suja et al., 2019), provided the thermal stability of the amine-containing compound is significantly lower than the support.

2.3 Thermal properties

Adsorbent stability, including thermal stability is key to determining adsorbent drying and regeneration conditions. Adsorbent stability is a wider topic and is further explored later in this report (see Section 3.5). Thermogravimetric analysis (TGA)

is typically used to analyze mass loss events as a function of temperature and/or gas environment to help determine the thermal stability of a material. Regarding some amine-functionalized adsorbents, it is important to highlight that the thermal stability of physically attached amines (e.g., via wet impregnation) will strongly depend on their volatility. This volatility is related to their chemistry (Zhang et al., 2012; Liu et al., 2013), molecular weight (Heydari-Gorji and Sayari, 2012; Liu et al., 2013), and their dispersion within the pores or external surface of a support (Son et al., 2008).

Differential scanning calorimetry (DSC), with or without TGA can provide information about the specific heat capacity of the adsorbent material (Mu and Walton, 2011; Querejeta et al., 2019). A material's heat transfer properties can be measured in a multitude of ways, typically involving monitoring the temperature profile of a fixed volume of sample during exposure to a heating element (Menard et al., 2007; Wu et al., 2021). For samples with low thermal conductivity, laser flash analysis is also considered a useful technique (Wang et al., 2018).

3 Adsorption performance parameters

Following initial material characterization and insight into inherent material properties, adsorbents typically undergo a series of tests to evaluate key adsorption performance metrics such as CO₂ uptake, selectivity, and kinetics, labeled as primary adsorption performance parameters (see Figure 3). If a material demonstrates potential through these primary KPIs, secondary performance parameters like ease of regeneration, stability, cost and environmental impact are then assessed. This classification does not diminish the importance of secondary KPIs; they are simply evaluated after the primary ones due to the latter's 'quicker' measurement process.

3.1 CO₂ adsorption capacity

Refers to the amount of CO₂ retained by an adsorbent at a single relevant concentration and temperature, at thermodynamic equilibrium (Raganati et al., 2021). It is sometimes referred to as total capacity (q). The CO₂ capacity can be reported per mass (gravimetric capacity), volume (volumetric capacity) or sometimes as molar basis of adsorbent material. It is important to note that the volumetric capacity (and to a lesser extent, the gravimetric one) is influenced by the density and structure of the material (e.g. in the case of monoliths) (Chanut et al., 2016; Bingre et al., 2018; Iacomi et al., 2019).

Working adsorption capacity (WC) is a more process-relevant metric derived from q (Mason et al., 2011; Elfving et al., 2017; Raganati et al., 2020). WC refers to the amount of CO₂ captured in an adsorption/desorption cycle, defined as the difference between two capacities corresponding to the adsorption and desorption conditions.

$$WC = q_{ads} - q_{des} \quad (1)$$

Equilibrium adsorption capacity is reported more frequently than WC, though the latter is better suited for adsorbent comparison

(Wu et al., 2022; Low et al., 2023). Ideally, comprehensive screening in a large pressure and temperature range should be performed. This is a challenging prospect, as often, researchers lack the time, instrumentation, or sufficient material quantity to report extensive datasets. Advances in instrument automation and parallelization, alongside modeling approaches, could help ease this burden. Several simple computational tools have been proposed to minimize the burden of acquiring large sets of experimental data, expediting the screening of adsorbents for CO₂ capture (Maring and Webley, 2013; Subramanian Balashankar et al., 2019; Danaci et al., 2020; Pai et al., 2020).

Single-component isotherms are one of the most ubiquitous methods of probing an adsorbent's CO₂ uptake by measuring equilibrium capacity as a function of adsorbate concentration at a fixed temperature. The CO₂ concentration range will dictate the applicability for a particular process (see Table 1). For materials proposed for point source capture, concentrations can range between 5%–33% CO₂ by volume, depending on the industrial process, while materials for DAC must be assessed at concentrations near 400 ppm to match ambient CO₂ levels. Alongside adsorption, the desorption and subsequent hysteresis can provide information regarding the reversibility of the process or the presence of mass transfer limitations (Ravikovitch and Neimark, 2005; Sircar et al., 2011), both of which will impact material regeneration. Hysteresis can also be used to probe phenomena such as structural changes during the sorption process (Culp et al., 2008; Wu et al., 2016; Rahman et al., 2020), and to obtain information about the materials pore morphology (Sing and Williams, 2004).

There are several experimental techniques that can be used to measure single-component gas adsorption, here we discuss the most used in carbon capture studies, including volumetric and gravimetric techniques, breakthrough analysis and desorption methods. Table 2 includes the advantages, disadvantages, and limitations of the gas sorption techniques included in this work. It should be noted that simple metrics such as total CO₂ capacity, and pure component WC, are not sufficient to guarantee success in an adsorption process (Maring and Webley, 2013; Rajagopalan et al., 2016; Danaci et al., 2020). These metrics should be used as decision criteria to undertake further detailed experimental work.

3.1.1 Volumetric methods

Volumetry relies on an indirect measurement of amount adsorbed, through knowledge of state variables in the system such as pressure, temperature, and volume before and after adsorption occurs. Practically, this is achieved through expansion of gas from a calibrated reference volume to a second volume containing the sample. Pressure is monitored throughout the experiment, and appropriate equations of state are used to calculate the changes in the gas phase quantities, which correspond to the net or excess amount adsorbed if the cell volume or total accessible volume are known, respectively, (Mohammad et al., 2009). The amount of material commonly used for volumetric experiments will depend on its CO₂ uptake, but also on the size of the reference and cell volumes, and accuracy of the pressure transducers. For most commercial instruments, amounts between 50 mg and 1 g are common (Mason et al., 2015). Volumetry is the most common method for probing the applicability of an adsorbent to carbon capture. In a recent review investigating sorbents for DAC, 47 out

TABLE 2 Gas sorption techniques comparison table including advantages, disadvantages, and limitations.

Gas sorption technique	Advantages	Disadvantages	Limitations	Typical amount of sample required
Volumetric	Most common used method, well understood, wide range of temperatures and pressures, amenable to parallelization to enable high throughput.	Pressure gradients between sample and reference can be significant at low partial pressures, possible incremental errors.	Requires additional gas analyzing method for measuring multicomponent adsorption.	50 mg–1 g
Gravimetric	Dynamic mode available that can enhance kinetics, low amount of sample required.	Change in analysis gas density may require additional experimental corrections particularly at higher partial pressures.	Requires additional gas analyzing method for measuring multicomponent adsorption.	1–50 mg
Breakthrough (Fix-bed)	Can provide both equilibria and kinetic information, preferred technique for multicomponent adsorption.	Not suitable for collection of large data sets	Not suitable for fine powders.	1–10 g
Desorption (ZLC)	Can provide both equilibria and kinetic information, low amount of sample required, relatively fast experimental measurements.	More susceptible to experimental errors.	Diffusivity measurements limited to Henry's constant region.	<15 mg

of 53 CO₂ isotherms on different reported materials were recorded using volumetric instrumentation (Low et al., 2023). Notably, for higher pressures volumetry was nearly as common as gravimetry (7 out of 13 isotherms) in an inter-laboratory study (Nguyen et al., 2018).

As pressure is the measured variable, the accuracy of pressure transmitters is paramount in volumetry, particularly for the low concentration region of 400 ppm CO₂, corresponding to a pressure of 40.5 Pa or 0.3 Torr. In this regime kinetics may be slow, and care should be taken for each point to fully reach equilibrium. Leak checks are particularly important in these conditions when studying under vacuum. Moreover, pressure gradients between the sample and reference volume may start to become significant at lower pressures when there is a large difference in temperature between the two volumes (e.g., during isotherm measurement at 77 K), requiring the use of thermal transpiration corrections (Takaishi and Sensui, 1963). A second notable aspect of volumetry is that it is an incremental measurement (each measured point is a delta from the previous). Regardless of the CO₂ concentration, significant compounding of errors can occur if many isotherm points are recorded sequentially (Mohammad et al., 2009). In typical volumetry, a single variable is monitored, which precludes the measurement of multicomponent adsorption. Coupling with an analytical method capable of sampling the gas phase such as gas chromatography (GC) or mass spectroscopy (MS) is required to complete the mass balance and determine the composition of each adsorbed species and measure multi-component adsorption (see Section 3.2.1).

Volumetric techniques are highly amenable to parallelization by using a common dosing volume. A parallel system with six individual sample cells was used by Wiersum et al., to record CO₂ and N₂ isotherms on several standard materials to develop a KPI suited to post-combustion conditions (Wiersum et al., 2013). Bae et al. used a more complex parallelization setup to investigate up to 28 samples of zeolites for post-combustion CO₂ capture, by recording single component CO₂ and N₂ isotherms at 3 temperatures, totaling 35 isotherms in 3 days. Most commercial

instrumentation can be purchased with up to three sample ports (Bae et al., 2013).

3.1.2 Gravimetric methods

Together with volumetric techniques, gravimetric methods are among the most used to measure pure component adsorption isotherms (Low et al., 2023). Gravimetric instruments measure the net force resulting from changes in sample weight (Wang et al., 2021). A well-known benefit of gravimetric methods is that they typically require a low amount of sample: as little as 1 mg can be used to obtain reliable results for single component measurements. Furthermore, they can be used in a *dynamic* mode (Thompson and Zones, 2020) and can operate at either atmospheric pressure or under vacuum. Their dynamic operation mode entails a continuous flow of gas over the adsorbent, which significantly enhances the kinetics of adsorption, by (i) maintaining a constant concentration of CO₂ around the sample and (ii) overcoming some diffusion barriers through forced convection. It also is not subject to cumulative errors that can occur for volumetric approaches.

When using gravimetric instruments to measure gas adsorption, regardless of the application, it is important to account for secondary contribution to the force balance from buoyancy and drag (Wang et al., 2021). Nevertheless, for carbon capture, when studying high-capacity physi- or chemisorbents utilized in DAC, sample weight changes will likely dominate. Whereas for high pressure applications (i.e., point source capture), the change in analysis gas density may require additional experimental corrections. Given the different microbalance configurations such as single arm (often magnetically suspended), or dual arms either symmetrical or asymmetrical. Correct accounting of force contributions for each configuration is important (Wang et al., 2021). Like vacuum volumetry, in vacuum gravimetric instruments, it is key to ensure there are no leaks when performing each experiment and that the temperature is accurately controlled. Furthermore, at high bulk fluid densities the accurate determination of the sample volume becomes critical (Pini, 2014; Brandani et al., 2016; Nguyen et al., 2019).

Gravimetric measurements can also be performed with adapted TGA systems and results have been reported in several CO₂ screening studies (Plaza et al., 2008; Choi et al., 2012; Ojwang et al., 2018). While these can be straightforward to record single-point uptakes in a carrier gas, measuring complete, pure component isotherms generally requires the use of dedicated instruments. Commercial gravimetric instruments are available from different suppliers and like volumetric instruments, they require an additional gas detector to measure *true* multi-component adsorption (see Section 3.2.1). Gravimetric systems are less amenable to parallelization compared to volumetric systems, as often the bulk and the cost of the system is dictated by the microbalance. However, systems which can accommodate multiple samples at the same time are commercially available. Gravimetry also has the potential of automation, by using an autoloader to increase throughput (Chanut et al., 2017). For reference, simplified schematics of typical volumetric and gravimetric experimental setups are depicted in Figure 4.

3.1.3 Breakthrough analysis

Breakthrough methods are based on the fixed-bed principle, in which, the response to a step change in adsorbate concentration is monitored at the end of a packed column of adsorbent. The shape of the resulting breakthrough curve or curves provides equilibrium, bed transport and kinetic information (Dantas et al., 2011; Patel, 2019). A typical breakthrough instrument consists of three main sections: generation, adsorption and detection (see Figure 5A). Generation is where the desired adsorbate or mix of gases is prepared at a constant flowrate, for carbon capture experiments typically a mixture of CO₂ and N₂ is used. The mixture of gases then enters the adsorption section into the adsorbent packed column. The column can typically be regenerated *in-situ* via heating using a water bath, oven, or heating tape, or via vacuum through a vacuum pump. As the gas is being adsorbed, the column starts to saturate until each gas reaches the “breakthrough point” (see Figure 5B). Finally, the concentration profile of each gas is monitored at the exit of the column using a gas detector, typically a mass spectrometer, a thermal conductivity detector (TCD), or a non-dispersive infrared (NDIR) gas analyzer.

Following the completion of the experiment, either after a designated cycle time or upon sample saturation, the concentration profile can be integrated to calculate the amount of CO₂ adsorbed and by extension the adsorption capacity (*q*). Providing the detector can independently measure multiple species’ concentrations without interference, the “breakthrough” and “equilibrium” adsorption capacity for each species can be calculated according to:

$$q = \frac{(F_{in} \cdot t) - V_{dead} - \int_0^t F_{out} dt}{m} \quad (2)$$

where F_{in} is the inlet flowrate of the specific gas, t is the adsorption time, V_{dead} is the dead volume of the system, F_{out} is the outlet concentration of the specific gas and m is the dry mass of the adsorbent (Oschatz and Antonietti, 2018). Important to consider when carrying out breakthrough experiments is to correctly account for the dead volume of the system (V_{dead}), this integral should be calculated between the signals of the sample column and a

“blank” response with an equivalent volume but no adsorbent present (Rajendran et al., 2008). It should be noted that in the case of highly competitive systems, e.g., CO₂/H₂O, CO₂/N₂, CO₂/H₂ etc. It may be necessary to also perform a desorption experiment, as the integration of very small areas can yield inaccurate results (Wilkins et al., 2021).

The amount of sample required in breakthrough experiments will depend on the CO₂ uptake of the material and the size of the column. Breakthrough systems usually require a higher amount of sample than volumetric or gravimetric systems. However, best practices have been recently proposed to address this issue (Wilkins et al., 2022). Due to the fixed-bed configuration, samples in fine powder form may result in high pressure drops, therefore breakthrough systems are better suited to work with monoliths or pellets.

In general, breakthrough is the preferred method to measure multi-component adsorption (Shade et al., 2022) (see Section 3.2.1). Despite some commercial instruments available in the market, the use of home-built breakthrough experimental systems is still prevalent (Shade et al., 2022). A comprehensive understanding of the critical features of an experimental rig and systematic experimental procedures in an in-house build system have been described by Wilkins et al. (2021). It should be noted that good breakthrough performance alone does not indicate good process performance, e.g., small plant size or low cost. However, breakthrough experiments are an important step in gathering experimental data to evaluate adsorbents and undertake rigorous process modelling.

3.1.4 Desorption methods

Desorption methods may include gravimetric and volumetric desorption, the Zero-Length Column (ZLC) and the differential column technique (DCT) (Shade et al., 2022). Here we focus on the ZLC method which is widely used in gas sorption studies for carbon capture (Mangano et al., 2013; Hu et al., 2015; 2018; Krishnamurthy et al., 2020).

The Zero-Length Column (ZLC) system, a short packed-bed typically <1 cm in length, acts as a breakthrough method under low flowrates using either the uptake or desorption curve. The manipulation of flow rates/pressures, feed concentrations, humidity, and temperatures, limited when using traditional chromatographic equipment, allow the simulation of industrially relevant conditions. CO₂ concentration is typically measured using a similar suite of sensors as breakthrough (Teng et al., 2017).

At low purge flow rates, the integration of the desorption curve allows a measurement of total amount adsorbed or desorbed (Brandani et al., 2003). Since the mass balance in the ZLC column is well defined, adsorbed concentrations can be calculated with ease, often without the need for blank measurements (the empty system must be characterized at least once). The advantages of the ZLC technique arise from the nature of the small, packed bed, with sample mass used usually <15 mg (Mangano et al., 2013). A smaller bed is required to maintain the zero-length assumption, and minimize heat effects, but it also equates to short experimental times (typically <1 h) making the technique useful for high throughput measurements (Mangano et al., 2013). Naturally, a smaller sample mass means that the associated observed uptake is more susceptible to experimental or measurement errors, which arise from signal

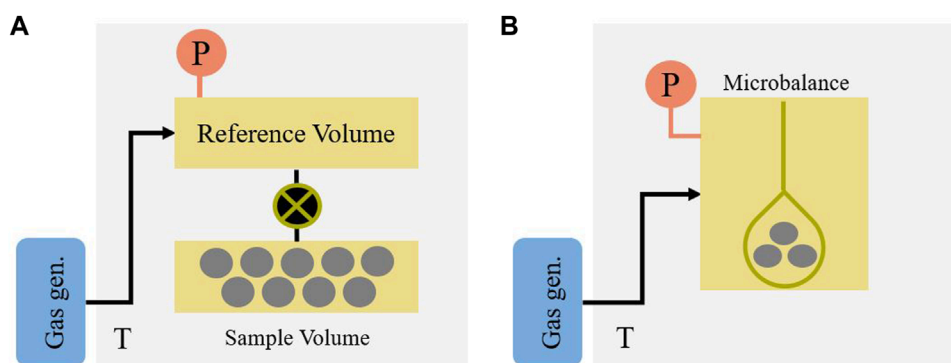


FIGURE 4
Simplified schematic of typical (A) volumetric experimental setup and (B) gravimetric experimental setup.

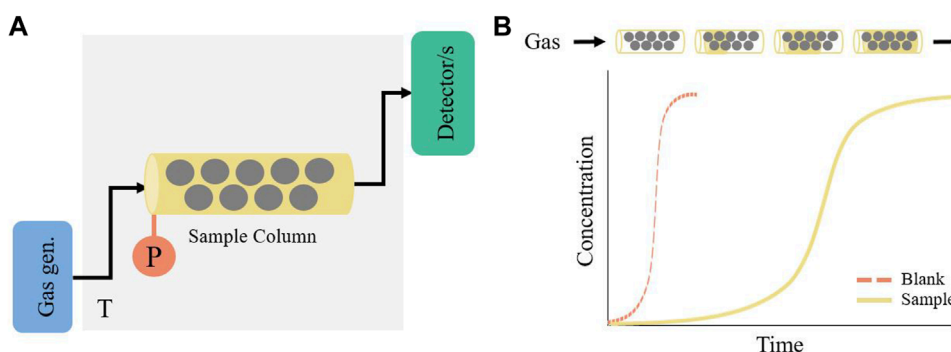


FIGURE 5
(A) Simplified schematic of a breakthrough experimental setup and (B) graphical representation of a breakthrough curve as gas travels through the packed column.

noise, the incorrect use of flowrate, or an incorrect measurement of the blank response. An insight into the correct analytical procedures has been provided by Brandani et al., for all ZLC measurements (Brandani and Mangano, 2021). Further to measuring CO₂ uptake, the ZLC method has also been used to obtain full isotherms by running multiple adsorption-desorption steps. Finally a recently proposed method also allows the simultaneous determination of isotherms and kinetics (Azzan et al., 2022).

3.2 Selectivity

Selectivity is the preferential adsorption one component over others in a mixture at process conditions. In any real-world CO₂ adsorption process, the presence of competing gases will inevitably affect both the rate and adsorption capacity of CO₂. This effect can range from reduced performance to irreversible saturation of the material. As such, it is generally desirable to increase any adsorbents' selectivity towards CO₂ over other competing adsorbates. It should be noted that in certain cases, the presence of other components can be beneficial for the capture process (Wang et al., 2011; Zárate et al., 2016). Underlying effects for selective adsorption in solid sorbents

may be provided by equilibrium separations (i.e., the selective uptake of CO₂ based on physical interactions) or kinetic separations (i.e., the selective uptake of CO₂ due to faster diffusivity than other components).

There are several related parameters which are often defined as selectivity. For an equilibrium process, selectivity (S) at a specific pressure and temperature is defined as the ratio of the concentration of the target component in the adsorbed phase and the concentration in the gas phase. Calculation of this metric necessarily implies knowledge of the composition of the two phases. However, true multicomponent adsorption data is difficult to obtain. Instead, single component isotherms measured with volumetric or gravimetric methods are often used to assess a material's adsorption affinity towards each species (Hunter-Sellars et al., 2020b; Principe and Fletcher, 2020; Xie et al., 2020). This approach is typically done using the ideal adsorbed solution theory (IAST), which is a thermodynamic approach analogous to Raoult's law for the gas phase (Myers and Prausnitz, 1965; Walton and Sholl, 2015).

An alternative method used to approximate selectivity from single component isotherm data, is the Henry's law (Knaebel, 1995). This method is useful when the full isotherm data is not available

since selectivity is calculated based on the Henry's coefficients (K_H) of the gases following the Eq. 3.

$$S_{\frac{CO_2}{N_2}} = \frac{K_H(CO_2)}{K_H(N_2)} \quad (3)$$

The use of thermodynamic approaches to predict multicomponent data is widespread, though simplified approaches like IAST and Henry's law have their own limitations. For example, IAST approximation is not valid when the assumption of an ideal adsorbed phase is not met (Chen and Sholl, 2007; Fraux et al., 2018). This is particularly relevant to cooperative interactions between guest molecules, chemisorption or flexible hosts (Chen and Sholl, 2007; Fraux et al., 2018). Furthermore, Henry's selectivity assumes the preference of one guest over the other at infinite dilution, without considering real adsorption behavior like site coverage, heterogeneity or pore filling (Xu et al., 2020). Finally, the ratio of Henry's constants will reflect real mixture selectivity only at low pressures and loadings (Oschatz and Antonietti, 2018).

3.2.1 The importance of multicomponent adsorption measurements

To obtain a better prediction of process performance, optimize efficiency, and increase the chances of success, it is necessary to characterize all interactions with other gases present (N_2 , O_2 , H_2O , etc.) (NIST, 2015; Bui et al., 2018; Low et al., 2023). Researchers should aim to perform measurements under conditions that are as close as possible to the actual process being investigated. Multicomponent gas adsorption measurements remain complicated and time-consuming despite the wide range of available techniques (Shade et al., 2022). Here, we discuss some of the issues that gas sorption methods present when measuring multicomponent adsorption, highlighting those arising from CO_2 and H_2O mixtures.

The presence of water vapor is relevant for both point source capture and DAC (Marx et al., 2013). In the case of point source, it has been observed that in physisorptive solids like zeolites, H_2O can compete with CO_2 for binding sites leading to losses in adsorption capacity (Brandani and Ruthven, 2004; Mfoumou et al., 2018). Whereas in the case of some chemisorptive solids, such as amine-impregnated porous media, H_2O can promote carbamate formation and thus cooperative binding of CO_2 molecules which often lead to increased CO_2 capacity (Choi et al., 2011; Zhang et al., 2017; Pokhrel et al., 2018; Gaikwad et al., 2021).

Breakthrough methods together with volumetric methods, appear to be the most popular to report multi-component adsorption data in general (Shade et al., 2022). Breakthrough data reporting has increased since 2010 due to the method's ability to evaluate specific separation processes with a small number of data points (Shade et al., 2022). However, when water vapor is present, breakthrough experiments can face several challenges such as water condensation within the system (Wilkins et al., 2020) or sample breakage during direct reactivation (like in the case of zeolites) (Breck, 1973). Process conditions and reactivation temperatures should be carefully considered to avoid this scenario. Typically, water vapor is generated through a bubbler, and reaching a constant mole fraction of H_2O in the mixture can take several minutes (Wilkins et al., 2020). When generating a mixture of CO_2/H_2O it is important to make sure

that the desired concentration is reached before feeding it through the packed column (Wilkins et al., 2020).

Hyphenated volumetric methods are the second most common for multi-component adsorption measurements. Commercial instruments require a GC or another analytical method to determine the composition of the gas phase. For multi-component carbon capture experiments, specifically in the case of CO_2/H_2O mixtures, volumetric instruments are limited to low relative humidity due to the nature of their set-up.

Gravimetric methods can be useful in the measurement of multi-component adsorption both qualitatively and quantitatively. Gravimetric methods have been used to screen the effect of water vapor on the CO_2 adsorption performance of different materials. In these studies, water is typically pre-adsorbed on the sample followed by CO_2 . The CO_2 uptake is determined by the difference between the mass after CO_2 adsorption and the mass before CO_2 adsorption (Chanut et al., 2017; Sáenz Cavazos et al., 2021). When employing this method, the assumption that H_2O is not displaced by CO_2 should be made. However, as observed by Chanut et al., this depends on the adsorbent's affinity to water, and this assumption may be valid only for hydrophobic materials where water can move freely and does not have a strong interaction with the adsorbent (Chanut et al., 2017). These experiments are useful to obtain qualitative information about multicomponent adsorption. However, to determine the individual amount of each adsorbed species, the concentration of the gas phase or the distributions in the adsorbed phase should be known (Broom et al., 2020).

In all the above methods, it is important to make sure the gas detection method used does not interfere with the species present in the mixture. For instance, it is well known that mass spectrometers can have issues when dealing with high relative humidity. Or as highlighted by Wilkins et al., CO_2 can interfere with capacitance-based relative humidity sensors (Wilkins et al., 2020). Correct calibration measurements can help mitigate this problem but should be performed for each experiment, which can be a time-consuming task.

3.2.2 Capacity versus selectivity, what is more important?

An ideal CO_2 adsorbent should exhibit both a high capacity and selectivity towards CO_2 (Patel et al., 2017). However, often reported improvements in one property, come at the expense of the other (Oschatz and Antonietti, 2018). There have been some material breakthroughs like the case of SIFSIX, which contains optimal pore size and chemical functionality that enables a "sweet spot" for high capacity and selectivity (Nugent et al., 2013). SIFSIX materials have proven to be useful both for point source capture (Nugent et al., 2013) and DAC (Shekhah et al., 2014).

If a view is taken that a specific separation performance (product purity and recovery) must be achieved, then a minimum selectivity and CO_2 working capacity are required. It is generally not possible to predict the working capacity required *a priori*, and some amount of process modelling is required. It should also be noted that the improved selectivity must be achieved by reducing N_2 (or light-component) adsorption, and not by increasing CO_2 adsorption (Maring and Webley, 2013; Rajagopalan et al., 2016; Rajagopalan and Rajendran, 2018; Danaci et al., 2020; Subraveti et al., 2022).

In the adsorption process context, total CO₂ capacity is not proportional to process performance. The working capacity is the key metric in that case. For example, Mg-MOF-74 displays excellent total CO₂ capacity, however, under VSA conditions it is not possible to remove the CO₂ effectively and this significantly hampers performance (Maring and Webley, 2013; Danaci et al., 2020). On the other hand, adsorbents such as UTSA-16 and CALF-20 display “low” CO₂ capacity, however, their CO₂ isotherm shape and low N₂ adsorption result in good process performance under VSA conditions (Khurana and Farooq, 2016; Danaci et al., 2020; Nguyen et al., 2022). Therefore, it is necessary to optimize CO₂ working capacity, and selectivity (minimum N₂ adsorption), in tandem to increase the chances of good process performance.

3.3 Kinetics

Kinetic information is critical to the simulation of adsorption/separation processes, process scale-up and design (Taddei and Petit, 2021; Low et al., 2023). Despite its importance, kinetic parameters are less reported than gas adsorption and selectivity in adsorptive-based CCS studies (Low et al., 2023). The small critical diameter of CO₂ results in intra-particle mass transfer processes that can be limited by either micropore diffusion and or surface diffusion. Often with porous materials there is a hierarchy of pore sizes, through which adsorbates must diffuse. These pores may resist the overall mass transfer in the form of:

- Micropore intraparticle resistance.
- Transport resistance observed on the particle surface.
- Meso- and macropore interparticle diffusion.

Diffusion in porous materials can be classified into molecular and effective diffusion. Generally, molecular diffusion follows the movement of molecules from a gas or liquid phase solution into or out of a single pore, whereas effective diffusion is the sum movement of molecules through the entire pore network, tortuosity (Levy et al., 2015). Further distinctions can be made between self-diffusion and counter-diffusion, with the former an assessment of diffusion between same molecules, and the latter an assessment of diffusion in the presence of competing molecules (Brandani et al., 2000). In particles, diffusion can occur at several length scales interparticle diffusion typically comprises of macropore (macroscopic) diffusion within a packed bed, whereas intra-particle/inter-crystalline diffusion is made up of both macropore and micropore, and intra-crystalline comprises of micropore (microscopic) diffusion (see Figure 6) (Bhatia, 1997). The most common methods to measure the different types of diffusion are presented below. Each technique follows the rate of diffusive migration of molecules from saturated porous materials, however, they differ in the measurement mode and in the significance of the data produced (see Table 3).

3.3.1 Gravimetric and volumetric methods

Many of the modern gravimetric and volumetric systems continuously monitor changes in adsorbate loading as a function of time during simulated process conditions, this allows the dynamics of the sorption process to be quantified (Hong et al.,

2016; Ojwang et al., 2018). Due to the system's numerous transport resistances, it is common to fit experimental data to different diffusion models (e.g., film or intraparticle) to provide information on the rate-controlling process during adsorption. It is important, however, not to simply use just goodness-of-fit to identify the most suitable diffusion model (Loganathan et al., 2014). Alongside careful consideration of model assumptions and their relevance in different adsorbate-adsorbent systems, a recent review by Wang et al., concluded that kinetic parameters derived from gravimetric and volumetric data can be strongly influenced by the nature and conditions of the experimental method. This can include but is not limited to the dynamics of the experimental system reaching equilibrium in a similar timeframe to the adsorption; external mass transfer resistances in aggregated particles; isotherm nonlinearity (i.e., differences in adsorption and desorption kinetics in a similar pressure region) and non-isothermal conditions (Wang et al., 2021). The authors recommend several experimental guidelines and checks that should be carried out such as: testing multiple particle sizes, sample masses and configurations; reducing the magnitude of pressure or concentrations changes in the system; and accounting for experimental effects related to buoyancy, flowrate, drift, and heat transfer (Wang et al., 2021).

3.3.2 Zero-length column

The operating conditions in ZLC may be manipulated to assert kinetic or equilibrium control, allowing the determination of parameters such as diffusion constants, mass transfer coefficients (Brandani and Mangano, 2022) and equilibrium adsorption coefficients (Brandani et al., 2003). For ZLC kinetic experiments, packed beds (<15 mg) made up of small particles of a known radius are used (Gibson et al., 2016). The system may be run at high purge flow rates resulting in kinetically controlled desorption, or at low purge flow rates resulting in equilibrium-controlled desorption. By measuring the concentration loss from a packed bed at high purge flow rates, a measurement of the gradient allows the limiting diffusion kinetics to be determined. Further, ZLC diffusion experiments can aid in decoupling kinetic and mass transfer limitations in functionalized materials with amine impregnation, or hydrophobic modification (Teng et al., 2017; Gelles and Rezaei, 2020). In cases of competitive adsorption, binary mixtures of CO₂ and other components may be run to assess the impact of the competing molecule on uptake kinetics (Brandani and Ruthven, 2004). Finally, diffusion experiments have been used to probe structural changes in flexible adsorbents upon adsorption of CO₂, by running diffusivity measurements pre- and post-material saturation with CO₂ (Lozinska et al., 2012). It is important to note that ZLC measurements of diffusivity are typically restricted to the Henry's constant region (Eic and Ruthven, 1988).

3.3.3 Pulsed-field gradient (PFG) NMR

Pulsed-Field Gradient (PFG) NMR allows the determination of microscopic CO₂ diffusion in porous materials by recording relaxation of polarized nuclei. This technique measures the average molecular diffusion of adsorbates through intraparticle and interparticle pores. Under longer diffusion analysis times, the PFG-NMR technique can also provide information on the much more hindered diffusion occurring where adsorbates interact with pore walls, providing effective diffusion constants (Díaz et al., 2010).

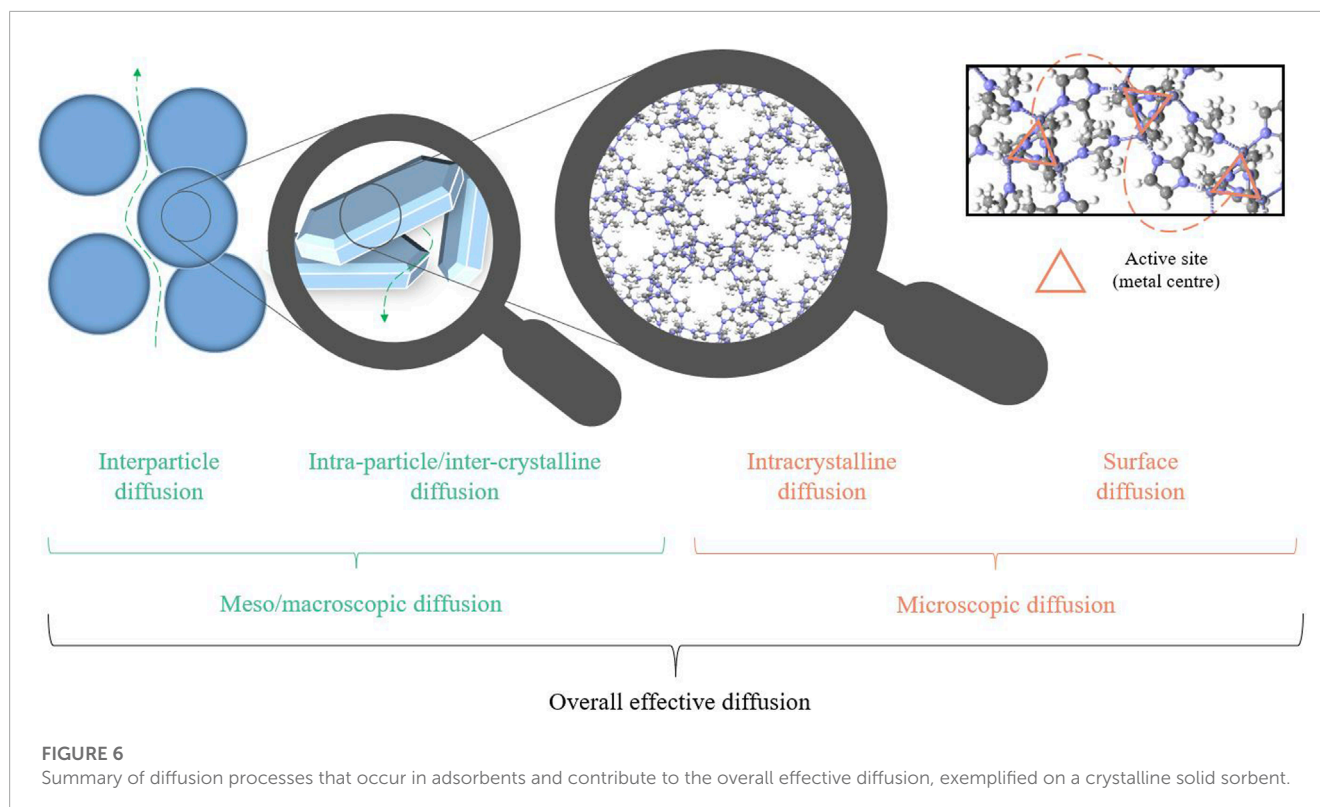


TABLE 3 Types of diffusion that can be measured with different methods including the typical orders of magnitude of results obtained.

Method	Scale	Type of sample	Sample phase	Diffusion constant	D, magnitude/ $\text{cm}^2 \text{s}^{-1}$	Comments
Pulsed-Field Gradient NMR	Microscale	Particles/extrudates	Vapor/Liquid/Gas	Pore diffusion	10^{-5} – 10^{-7}	Can be used to calculate effective diffusion if the measurement time is long enough
Zero-Length Column	Macroscale	Particles/extrudates	Vapor/Liquid/Gas	Effective counter-diffusion	10^{-6} – 10^{-9}	—
Sorption	Macroscale	Particles	Vapor/Gas	Effective diffusion	$\sim 10^{-10}$	Can be used to analyze extrudates, however measurement space renders particles ideal
Quasi-Elastic Neutron Scattering	Microscale	Particles	Vapor/Gas	Molecular/Pore diffusion	10^{-4} – 10^{-8}	Can be used to track the diffusion of individual or multiple molecules

Instead of measuring limiting diffusion, PFG-NMR can measure the varying contributions of different diffusional pathways (such as intrapore or interpore) dependent on the diffusion analysis time (Mueller et al., 2012; Pugh and Forse, 2023). Furthermore, since the technique can also make direct measurements of the adsorbate bulk diffusion, a comparison of bulk diffusion/transport diffusion provides more meaningful comparisons across different adsorbates compared to the effective diffusion constants achieved by ZLC. PFG-NMR requires a larger sample compared other methods, around ~ 100 mg (Grenier et al., 1994). Multicomponent diffusion may be measured easily with PFG-NMR when adsorbates possess different NMR active nuclei (Rittig et al., 2003), for example CO_2 and NO_x diffusion may be decoupled by measurement of the ^{13}C and ^{15}N nuclei respectively. The reader is also directed to some recent

works summarizing the PFG NMR technique (Baniani et al., 2021; Kärger et al., 2021).

3.3.4 Quasi-elastic neutron scattering (QENS)

Quasi-Elastic Neutron Scattering (QENS) is a microscale technique that provides molecular scale self-diffusion constants, and transport-diffusion constants at larger length scales. These diffusion constants are calculated from scattering functions which depend on the space-time positions of atoms (Kruteva, 2021). QENS experiments can provide information around the transport diffusivity of adsorbed CO_2 and N_2 in adsorbent materials (Papadopoulos et al., 2004). QENS diffusion constants are often comparable to those found from molecular dynamics due to the similar time (10^{-13} – 10^{-7} s) and length scales (Embs et al., 2010).

Since neutron scattering requires a source of neutrons of known momentum, specialist facilities are required.

3.4 Ease of regeneration

Following the capture of CO₂, the adsorbent must be regenerated to release CO₂ for conversion or storage, and for its re-use in subsequent adsorption cycles. As mentioned before, regeneration can be accomplished through the application of elevated temperatures, sweeping gas or vapor, reduced pressure, or combinations thereof.

In pressure swing adsorption processes (PSA/VSA), the ease of regeneration is reflected by the pressure of the blowdown and desorption steps. As compressors and vacuum pumps can represent a large percentage of the operating costs, it is recommended to have an adsorbent that takes up all its CO₂ capacity in a narrow limit of pressure and preferentially close to process conditions (Ho et al., 2008; Subraveti et al., 2019). Here, isotherm-based analysis, WC and process modeling are used to understand the overall process performance.

Regarding temperature swing adsorption processes (TSA), the regeneration step requires heat input sufficient to desorb CO₂ to a desired working capacity, based on optimal process conditions. The regeneration heat requirement accounts for (Zhang et al., 2016):

1. The sensible heat necessary to increase the adsorbent bed from the adsorption temperature to the desorption temperature.
2. The heat of desorption, or the energy required to overcome the physical or chemical interaction between CO₂ and the adsorbent.

The first term is dominated by the heat capacity of the material (see Section 2.1.3) and the adsorbed phase, while the second is quantified by the enthalpy of adsorption (ΔH_{ads}). As mentioned before, ΔH_{ads} is a measure of the interaction strength between an adsorbent and bound CO₂.

ΔH_{ads} in carbon capture studies is often calculated through the application of the Clausius-Clapeyron equation and is less frequently measured using calorimetry. For a practical guide on how to calculate ΔH_{ads} via adsorption isotherms through the Clausius-Clapeyron approach we direct the reader to the work of Nuhn and Janiak (Nuhn and Janiak, 2020), open-source tools are also available to assist with these calculations (Iacomi and Llewellyn, 2019).

Enthalpy of adsorption can also be measured directly through determination of evolved heat throughout adsorption, by using a calorimetric setup. In its most common embodiment, isotherms and adsorption enthalpies are measured simultaneously by placing the sample in one side of a Tian-Calvet differential calorimeter and performing a volumetric measurement while recording and integrating the calorimeter signal (Llewellyn and Maurin, 2005). The experiment is more challenging, as it involves non-trivial instrumentation and larger sample amounts, however, it provides an unequivocal, direct measurement of ΔH_{ads} .

3.5 Stability

Promising CO₂ adsorbents should remain stable over thousands of adsorption and regeneration cycles (Bui et al., 2018). Beyond

assessing the mechanical, chemical, and thermal stability of an adsorbent, it is crucial to gauge its cycling stability under pertinent operational conditions. This comprehensive evaluation is essential to grasp a holistic picture of the adsorbent's stability. Cycling experiments are usually performed using breakthrough or modified TGA apparatus (Low et al., 2023). However, often only a few cycles are performed (~10) due to time constraints (Low et al., 2023). Furthermore, other impurities such as H₂O, O₂ and other acidic gases can induce sorbent degradation or deactivation, this is often measured indirectly via mass loss events (Sayari et al., 2012a; Si et al., 2019) or reductions in adsorption performance (Thouchprasitchai et al., 2018; Elfving et al., 2021). A recent study by van Paasen et al., investigated the impact of these types of degradation on an amine-functionalized adsorbent used for post-combustion CO₂ capture (van Paasen et al., 2021). However, these indirect methods usually offer a limited understanding of the mechanisms by which adsorbents degrade. Below, different degradation pathways that can occur and how they can be identified are discussed.

3.5.1 CO₂-induced degradation

Adsorption based on chemical reaction of amine groups with CO₂ can, alongside formation of carbamate and bicarbonate, form urea linkages, significantly inhibiting the ability of the adsorbent to capture CO₂ (Sayari et al., 2012b). This degradation is exacerbated at elevated temperatures and CO₂ concentrations, such as those observed in point source capture or processes using high-purity CO₂ as a desorption sweep gas (Choi et al., 2016). The exact conditions necessary for urea formation depend on a range of factors including the nature of the amine (Sayari et al., 2012a), and the presence of water vapor within the gas stream. The presence of urea linkages can be confirmed using either *ex-situ* (Sayari et al., 2012b) or *in-situ* (Said et al., 2020) spectroscopic analysis.

3.5.2 Oxidative stability

Compared to many sorbents such as zeolites and carbons, the volatile and organic nature of amine-based chemisorbents makes reactions with oxygen a concern. Oxidation of grafted amines was confirmed by Calleja et al., who, through pre- and post-exposure DRIFT spectra, detected additional bands attributed to C=N stretching vibrations (Calleja et al., 2011). These changes were used to explain significant losses in CO₂ capacity, which could not be fully attributed to losses in nitrogen content, measured via elemental analysis (Calleja et al., 2011). Furthermore, MOFs with open metal sites can bind O₂ irreversibly above a certain temperature depending on the material (Bloch et al., 2011).

Since early studies, the dependence of amine oxidation on material- and process-specific factors has been investigated. This includes, but is not limited to: the temperature during oxidation (Nezam et al., 2021); oxygen concentration (Min et al., 2018); the presence of water vapor (Sayari and Belmabkhout, 2010) or CO₂ (Min et al., 2018) in the environment; the size and chemistry of the amine(s) (Calleja et al., 2011; Heydari-Gorji et al., 2011); and the presence of chemical additives within the composite (Min et al., 2018). Analysis of the chemical composition of the sample, or the species emitted during oxidation may be accomplished using spectroscopic methods (Meng et al., 2019), e.g. mass, infrared,

NMR. These techniques are then combined with metrics of CO₂ capture, typically measured using gravimetric, volumetric, or fixed-bed methods to understand the role of oxidation on performance. While analysis of chemical changes *in-situ* presents additional complexity in terms of experimental design, the value of detecting chemical changes during realistic process conditions is a key driving force to the different experimental approaches being developed (Du et al., 2010; Köck et al., 2013; Moore et al., 2018; Roztocki et al., 2021).

3.5.3 Hydrolytic stability

Water is ubiquitous in CO₂ capture applications, typically existing as either vapor, pressurized steam, or condensed liquid. As mentioned previously, a material's affinity for water vapor may be assessed via its surface chemistry (Ding and Jiang, 2020), or by isotherm analysis (Fröhlich et al., 2014). Compared to water vapor, steam can have much more significant impacts on material stability due to its high temperature and pressure. Porous silicas, commonly used as amine-functionalized supports, can undergo structural collapse during steam exposure. This effect, typically detected via porosimetry or electron microscopy, has been observed in several silica-based materials (Fayaz and Sayari, 2017; Min et al., 2018). The presence and extent of collapse appears to depend on both process conditions, such as temperature and duration of steaming, and material properties, such as the pore size and wall thickness (Zhang et al., 2005; Jahandar Lashaki et al., 2019). The nature of steam exposure makes *in-situ* analysis difficult, compared to the relatively mild pressures and temperatures of ambient levels of humidity.

3.5.4 Stability to acidic gases and other impurities

Compared to levels of CO₂, N₂, O₂ and H₂O, acidic gases such as SO₂, NO₂, and H₂S are found at significantly lower concentrations. However, even at part-per-million concentration levels, amine-functionalized adsorbents can undergo irreversible reactions with SO₂ and NO₂, measured via Raman spectroscopy, leading to significant reductions in CO₂ capacity (Rezaei and Jones, 2013). This irreversibility has also been confirmed in multi-component fixed-bed measurements, finding that while CO₂ and NO_x can both be adsorbed simultaneously, the latter compound was not removed during regeneration (Xu et al., 2005). The impact of these acidic gases on supported amines appears to be dependent on the nature of the supported amine (Rezaei and Jones, 2014), the temperature of the system (Liu et al., 2014), and the gases' concentration (Liu et al., 2011). For example, Liu et al. found that while NO had no significant influence on CO₂ capacity up to 400ppm, SO₂-induced losses increased from 2%–3% at 300ppm to 24%–25% at 400ppm, hypothesized to be due to the formation of heat-stable salts (Liu et al., 2011). Alongside reactions with amines in functionalized adsorbents, SO₂ has been found, via diffraction measurements, to induce structural degradation in Mg₂(dobdc) (Yeon et al., 2015) and Mg₂(dobpdc) (Jo et al., 2017). In the case of CO₂ removal, ambient air, where concentrations of these compounds are not expected to exceed the part-per-billion concentration range, performance losses due to these species are typically neglected (Stedman et al., 1997; Sanz-Pérez et al., 2016; Zhang et al., 2021).

3.6 Adsorbent cost and environmental impact

Determining the adsorbent cost for a carbon capture process at scale can be difficult, particularly for novel materials being synthesized and tested only at laboratory scale. Using the price of raw materials and energy required during the synthesis process is often used to estimate the adsorbent cost (Sinha et al., 2017). Researchers have also proposed the use of factors and rules of thumb, highlighting that their use may not apply when the raw materials are expensive and cannot benefit from economies of scale (Sinha et al., 2017; Danaci et al., 2021). Recently, Azarabadi et al., proposed a model that can estimate how much the adsorbent should cost in order to have an economically feasible process, rather than how much its actual bulk price or production cost is (Azarabadi and Lackner, 2019). The model was built for DAC, but the principle can also be applied to point source capture, and it demonstrates useful to set a limit or benchmark on the adsorbent cost (Azarabadi and Lackner, 2019). Nevertheless, the model predictions can be greatly influenced by particular CO₂ markets and the adsorbent lifetime. The problem with the latter is the scarcity of accurate data available in literature (Azarabadi and Lackner, 2019). It should be noted that there are many factors that dictate the economic feasibility of an adsorption process, and even if the adsorbent is 'free', other costs may still dominate the cost of CO₂ capture (Subraveti et al., 2022).

The environmental impact of adsorbents for CO₂ capture is rarely reported in the literature. There are very few studies that include experimental characterization together with the environmental impact of newly proposed adsorbents (Fayemiwo et al., 2019; Leonzio et al., 2022a; Leonzio et al., 2022b). Usually, Life Cycle Assessment (LCA) is used to evaluate the environmental performance of a process or product. Studies like the one by Grande et al., have assessed the environmental footprint of adsorbents themselves (Grande et al., 2017), while others have analyzed both the adsorbents together with the carbon capture process (Deutz and Bardow, 2021; Leonzio et al., 2022b; Heidari et al., 2022). When looking at the adsorbent production as a system boundary, it is important to highlight that between 60%–91% of their total carbon footprint comes from their production and the rest from their end of life (Deutz and Bardow, 2021). Furthermore, amine synthesis and the utilization of organic solvents can have a significant impact on climate change. Albeit efforts towards *green* synthesis procedures, many of the novel proposed materials are functionalized using amines. Ultimately, both the adsorbent production/disposal and use in a specific capture process are required to have a comprehensive environmental impact assessment. Studies like the one from Heidari et al., which investigates the most suitable adsorbent option from an environmental, economic, and technical perspective can be very valuable (Heidari et al., 2022).

4 Process performance indicators

Full experimental characterization of promising adsorbents for CO₂ capture should be coupled with process modelling and techno-economic analysis to better understand and optimize an actual

process. Usually, key process performance indicators include purity, recovery, productivity, energy consumption, specific energy, and cost (Farmahini et al., 2021; Taddei and Petit, 2021; Low et al., 2023).

Experimental data obtained from the intrinsic material properties and adsorbent performance parameters is often required to build and validate process models. One of the main challenges here is finding a full and comparable set of data at relevant process conditions for different adsorbents. It is important to note that isotherms of at least three temperatures are required for all species considered in the modelling. Furthermore, experimental data for adsorption isotherms is formed by discrete points and require an analytical expression describing adsorption equilibria to serve as input in process models. The most common approach to obtain this is the dual-site Langmuir (DSL) adsorption model (Farmahini et al., 2018). However, it is important to consider the actual mechanism of adsorption in the different materials used (physi- and/or chemisorbents), as they may require different mathematical models to accurately describe them. Indeed, for the new proposed materials, it can be difficult to find a suitable analytical expression (Farmahini et al., 2021). One way to overcome this limitation is to perform a set of single-component breakthrough experiments at different fluid phase concentrations and describe the relationship as a set of discrete points (Rajendran et al., 2020). Recently, Farmahini et al., compiled an exhaustive list of the input parameters required for a PSA/VSA process simulation and while some depend on design specifications or can be obtained from literature, more than half require some sort of experimental method (Farmahini et al., 2021).

When evaluating process performance indicators, it is important to understand the differences between point source capture and DAC processes. For instance, in point source capture, purity and recovery are usually set values and optimization tends towards cost minimization. Whereas in DAC processes there is no current specification on recovery and optimization focuses on minimizing specific energy (Low et al., 2023). It should be noted that for DAC processes, although cost and energy are important considerations, the key requirement is for the process to have net CO₂ removal from the atmosphere. This will indirectly impose some requirements on CO₂ recovery, and the end-use of CO₂ will impose some requirements on the purity of the CO₂. Nevertheless, the ultimate goal will always be to reduce the overall cost of CO₂ capture, and therefore linking process modelling with techno-economic analysis plays a key role. The main drawback observed here is the lack of adsorbent cost and lifetime data availability (Danaci et al., 2021; Farmahini et al., 2021).

5 Interconnection between KPIs

In previous sections there have been brief mentions of the interconnections between the different KPIs. Undoubtedly, understanding these links can help devise more effective and tailored solutions for adsorption-based carbon capture processes. In a recent study, Taddei and Petit discussed the different existing links between process and sorbent parameters focusing specifically on MOFs (Taddei and Petit, 2021). It is important to note that not all materials will behave the same and interconnections between KPIs can vary depending on the specific material structure. However, it is possible

to establish some 'common' relationships between material intrinsic properties, adsorption performance and process effectiveness.

Starting with CO₂ adsorption capacity, the adsorbent surface area and pore morphology parameters typically affect material suitability in CO₂ capture applications. For free-standing physi- and chemi-sorbents, these properties can directly influence CO₂ uptake by increasing the number of available sites for CO₂ to interact with (Alazmi et al., 2018; Akpasi and Isa, 2022); while for amine-functionalized chemisorbents, the degree of amine grafting or impregnation, and the subsequent accessibility of these amines strongly depends on the support's morphology (Franchi et al., 2005; Vilarrasa-García et al., 2015; Zhang and Du, 2022). Aside from CO₂ adsorption capacity, the rate at which the CO₂ molecules diffuse through solid sorbents and adsorb on active sites is important to determine process parameters like cycle time and overall process productivity (Wu et al., 2022). Regarding the ease of regeneration, strong binding of CO₂ to the adsorbent can result in greater energy consumption in the desorption step, hamper CO₂ recovery, and increase capture costs (Patel et al., 2017). Moreover, adsorbent stability and lifetime can have an impact on the operating expenses of a capture facility, adsorbents that degrade rapidly or lose their capture efficiency over time necessitate frequent replacements, contributing to increased operating costs.

Indeed, this work underscores the necessity of a thorough characterization of solid sorbents for CO₂ capture, extending beyond the conventional parameters of capture capacity or selectivity. It directs particular attention on how to measure the often overlooked but vital aspects such as kinetics and material operational stability. By offering a holistic understanding of the materials' performance under realistic working conditions, informed decisions can be made on their practical utility. The insights gathered from comprehensive assessments could catalyze the development of more robust, efficient, and economically viable carbon capture technologies.

6 Data reproducibility and homogenization efforts

The critical evaluation of literature pertaining to solid sorbents for CO₂ is often hampered by data availability and reproducibility. Calculation of KPIs detailed above can be highly variable, not only due to material variability and experimental conditions, but also due to user choices (Park et al., 2017). We highlight a recent interlaboratory study that emphasizes the lack of reproducibility in the determination of BET areas from the same raw data (Osterrieth et al., 2022). Many measurements are only reported graphically, making interpretation of exact numbers difficult. Further knowledge of secondary metadata, such as activation temperature, assumed dead volume, flowrates, is invaluable for understanding the full picture.

Special mention should be given to several efforts which attempt to introduce standardization and shareability to all KPI-relevant data, adsorption in particular. One of the first attempts towards this end is the NIST ISODB, a collection of more than 32 k isotherms digitized from published data (Siderius et al., 2015). The authors also introduce a standard sharable format based on JSON, which can encode isotherm data and metadata, both for

single and multi-component adsorption. More recently, a large-scale collection of more than 900 multicomponent isotherms were assembled (Cai et al., 2021). This study, which analyzed more than 11 k publications, could only unearth about ~50 CO₂/N₂ isotherms, underlining a lack of complete multicomponent adsorption data in existing literature.

Progress has been made towards developing a data format that is both human- and computer-readable, an adsorption information file, or AIF, analogous to a crystallographic CIF (Evans et al., 2021). The AIF aims to become the *de facto* standard for sharing isotherm data and is currently the focus of an IUPAC project (IUPAC, 2021). A similar IUPAC standardization effort is underway with the aim of providing best practices and guidelines for diffusion measurements (IUPAC, 2015). These initiatives can hopefully gain traction within the adsorption community, and help establish a common language that would aid the efforts of screening solid sorbents for CCUS (Pini et al., 2022).

7 Conclusion and outlook

Achieving technical maturity and wide scale implementation of CO₂ capture from relevant sources (flue gas or air) requires an integrative approach, from understanding the intrinsic material properties at an atomic scale all the way through pilot-scale testing and demonstration plants. Experimental adsorbent characterization techniques play a key role in helping researchers understand an adsorbent's physical and chemical characteristics as well as adsorption performance and can be coupled with process modeling and techno-economic analysis to optimize cost and process performance.

Thorough adsorbent characterization is complex and time-consuming task. Performing the full gamut of experiments requires access to expensive laboratory instrumentation and often, specialized equipment and people for adsorption measurements. It is acknowledged that all the characterization proposed here is unreasonable for a single research group to carry out. Therefore, cooperation and collaboration between multidisciplinary laboratories is required to enhance, fast-track, and share best practices regarding sorbent characterization and evaluation.

In terms of measurement and characterization, new adsorbents are normally prepared in milligram scale batches. Although a difficult endeavor, adsorption equipment manufacturers should aim to develop instruments and techniques that are compatible with such low sample amounts. It would also be desirable to undertake these measurements in a somewhat standardized manner including both equilibrium and kinetics data sets, to facilitate comparison between adsorbents and publications.

From a materials design perspective, the “adsorbent–process marriage” remains ever relevant (Sircar, 2001). The required adsorbent properties are a function of the process conditions, co-adsorbing components, any impurities present, and the cycle-design. Therefore, fundamental materials characterization is the first step that feeds into adsorption process modelling and design. Generating these links between materials properties and process behavior is imperative to better understand them.

In terms of adsorption scale-up and commercialization, there are several factors that need to be addressed. Adsorbent cost should be as low as possible, and reagents used in their preparation should be bulk or commodity chemicals. Although not front-of-mind in the past, the environmental impacts should also be evaluated through a ‘cradle-to-grave’ life-cycle analysis, especially if overall process decarbonization is desired. The behavior of novel adsorbents is also unknown from a disposal perspective and needs to be investigated further. Adsorbent recycling or raw material recovery could also be considered.

Adsorption-based carbon capture processes will play a role in industrial decarbonization, and carbon dioxide removal from the atmosphere. There has been significant focus on adsorbent development for carbon capture applications over the last two decades. However, a divide remains between “materials” and “process”. If it is desired to expedite technology development and deployment, the divide needs to be bridged. We hope that this work highlights the entwined nature of adsorption processes, initiates discussions between parties, and encourages more coordinated research efforts towards deeper understanding of adsorption performance.

Author contributions

The authors confirm contribution to the paper as follows: PS: initial study conception, design, writing—original draft preparation. PS, EH-S, PI, and SM: conceptualization, writing—original draft preparation, review, and editing. DD: writing, review, and editing. DW: review and editing. All authors contributed to the article and approved the submitted version.

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Conflict of interest

Author PI is employed by Surface Measurement Systems.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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