



This is a repository copy of *Experimental studies, molecular simulation and process modelling\simulation of adsorption-based post-combustion carbon capture for power plants: a state-of-the-art review.*

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/197562/>

Version: Published Version

---

**Article:**

Akinola, T.E., Bonilla Prado, P.L. and Wang, M. [orcid.org/0000-0001-9752-270X](https://orcid.org/0000-0001-9752-270X) (2022) Experimental studies, molecular simulation and process modelling\simulation of adsorption-based post-combustion carbon capture for power plants: a state-of-the-art review. *Applied Energy*, 317. 119156. ISSN 0306-2619

<https://doi.org/10.1016/j.apenergy.2022.119156>

---

**Reuse**

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here:

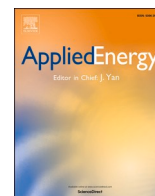
<https://creativecommons.org/licenses/>

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.



[eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk)  
<https://eprints.whiterose.ac.uk/>



# Experimental studies, molecular simulation and process modelling simulation of adsorption-based post-combustion carbon capture for power plants: A state-of-the-art review

Toluleke E. Akinola, Phebe L. Bonilla Prado, Meihong Wang\*

Department of Chemical and Biological Engineering, University of Sheffield, Sheffield S1 3JD, United Kingdom

## HIGHLIGHTS

- Lab synthesis of various adsorbents for adsorption-based PCC.
- Bench and pilot-scale experimental studies of adsorption-based PCC.
- Molecular simulation of adsorbents for post-combustion carbon capture.
- Process modelling simulation and techno-economic analysis of adsorption-based PCC.
- Achievements, challenges and future prospect in adsorption-based PCC.

## ARTICLE INFO

### Keywords:

Post-combustion carbon capture  
Adsorption  
Lab synthesis  
Experimental studies  
Molecular simulation  
Process modelling and simulation

## ABSTRACT

Adsorption-based post-combustion carbon capture is a promising emerging technology for capturing CO<sub>2</sub> emissions from fossil-fueled power plants due to the ease of adsorbent regeneration in comparison with solvent-based technologies. To increase its competitiveness, research efforts have focused on the development of new adsorbent materials and processes. This paper presents a state-of-the-art review of such efforts, focusing on lab synthesis and characterization of adsorbent materials, (carbon capture) experimental studies, molecular simulation, process modelling simulation and techno-economic analysis. Most experimental studies on adsorption-based post-combustion capture are at bench scale. Just a few experimental studies are at pilot scale. There are currently no commercial deployment of adsorption-based post-combustion capture technology. This review paper points out challenges encountered in these experimental investigations utilizing different adsorbent materials, limiting its commercial deployment. These gaps in experimental investigations need further research especially in the chemical modification of the adsorbent materials to increase the adsorption capacity. Molecular simulation of adsorbents and process modelling simulation of carbon capture processes are cost-effective and time efficient approaches for the assessment of adsorbents' CO<sub>2</sub> capture performance. The review also highlighted the need for more research in the model development of adsorbent materials at molecular scale and the model development of adsorption-based post-combustion process adopting new reactor configurations to further reduce the cost of CO<sub>2</sub> capture.

## 1. Introduction

### 1.1. Background

Fossil fuel combustion for power generation, industrial processes and transportation is the biggest source of anthropogenic CO<sub>2</sub> emissions, which contributes majorly to global warming [1,2]. Atmospheric CO<sub>2</sub>

levels could reach catastrophic level in the future if CO<sub>2</sub> emission continues unabated. Reducing CO<sub>2</sub> emissions could prevent its undesired effects such as extreme weather conditions [1], ocean acidification [2] and sea-level increase [3].

Carbon capture, CO<sub>2</sub> utilization and storage (CCUS) are considered the most strategic technologies for sustainably and economically meeting carbon emission reduction targets (CERTs) [4–6]. Among

\* Corresponding author.

E-mail address: [Meihong.Wang@sheffield.ac.uk](mailto:Meihong.Wang@sheffield.ac.uk) (M. Wang).

<https://doi.org/10.1016/j.apenergy.2022.119156>

Received 20 October 2021; Received in revised form 6 April 2022; Accepted 15 April 2022

Available online 25 April 2022

0306-2619/© 2022 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

various CCUS technologies, post-combustion carbon capture (PCC) technology is the most investigated due to its suitability for retrofitting in existing power plants to treat flue gas with low CO<sub>2</sub> partial pressure [7]. Currently, solvent-based PCC technology using mono-ethanolamine (MEA) as solvent is the most mature approach for capturing CO<sub>2</sub> from power plants and it is commercially deployed. Despite its maturity, key issues such as 1) the large size of equipment resulting in high capital cost, 2) the high energy requirement for solvent regeneration, and 3) the corrosive and degradable nature of MEA solvent, are major concerns contributing to a significant drop in power-plant efficiency and cost increase of CO<sub>2</sub> capture [8,9].

## 1.2. Motivation

In the quest to reduce the CO<sub>2</sub> capture cost and increase the power-plant efficiency, alternative CO<sub>2</sub> separation technologies in PCC are being explored. Adsorption-based PCC has been identified as a promising emerging technology on the IPCC special report on carbon capture and storage [10]. The adsorption-based technology do not pose corrosion issues and has the potential to reduce the energy penalty of the CO<sub>2</sub> capture process, making it an appealing option to the solvent-based PCC technology [6,9,10,12]. However, challenges associated with the development of new adsorbent materials and the capture process have limited its advancement to commercial deployment [8]. In order to take full advantage of its benefits, it is imperative to review the status of the technology, address the challenges and point out future prospects.

## 1.3. Aim and novel contributions

This paper aims to give a state-of-the-art assessment on the advancements in the lab synthesis and characterization of adsorbent materials, carbon capture (using adsorbents) experimental studies, as well as molecular simulation of adsorbents, process modelling and simulation of carbon capture (using adsorbents). Several review papers on adsorption-based PCC are available in the literature [8,13,22,14–21].

- Samanta et al. [13] reviewed the characterization and mechanism of various solid sorbents at PCC conditions. Similarly, Sreenivasulu et al. [16] discussed the adsorption mechanism, material characteristics, and synthesis methods of micro and mesoporous adsorbents for carbon capture. Zhao et al. [18] also assessed the application of carbon-based adsorbents in PCC, where the synthesis methods and structure-performance relationships were discussed.
- Hussin et al. [22] reported on the recently published patents for various adsorbents from 2014 to 2018 for CO<sub>2</sub> capture.
- Lin et al. [17] and Younas et al. [21] reviewed progress and challenges in the development of MOFs for CO<sub>2</sub> capture from post-combustion flue gas while Mukherjee et al. [20] reviewed ongoing research on the synthesis of activated carbon from various sources for adsorption-based PCC
- Ben-Mansour et al. [8] carried out a review on three physical adsorbents (e.g. zeolites, MOFs, and carbon-based adsorbents) adopted for adsorption-based PCC, as well as experimental work carried out to study the adsorption-based PCC process and mathematical models developed to simulate the process (mainly using fixed-bed reactors). Shafeeyan et al. [15] also discussed various studies on the mathematical modelling of fixed-bed columns for CO<sub>2</sub> capture using adsorbents.
- Hedin et al. [14] reviewed adsorbents for PCC and related swing adsorption (VSA and TSA), materials and system integration. Siegelman et al. [19] also reviewed the challenges and opportunities associated with adsorption-based PCC and discussed several promising candidate adsorbent materials (e.g. MOFs, Zeolites, Amine-functionalized silicas and porous organic networks)

Some of the review papers mentioned above focused on the

development and utilization of one or a few adsorbents and adsorption process types for PCC through experimental studies [10–12,14–19], while some other review papers focused on the mathematical model development of adsorption-based PCC process (specifically fixed-bed column) [6,13]. This review paper is different from most of the previous review papers in the following ways (1) it reviews lab synthesis (approaches) and characterization of different adsorbents for adsorption-based PCC; (2) it provides a review of the various adsorption-based carbon capture experimental studies at bench and pilot-scale; (3) it critically reviews the current activities in molecular simulation and analyses how the molecular simulation studies complement lab synthesis of adsorbent materials. (4) it also critically reviews the current activities in process modelling, simulation and techno-economic analysis (TEA) of adsorption-based PCC; (5) it tries to identify challenges ahead and predict potential breakthroughs of adsorption-based PCC.

## 1.4. Paper outline

Section 2 will briefly introduce various adsorbent materials and processes suitable for adsorption-based PCC technology. In section 3, a review of lab synthesis and characterization of different adsorbents for PCC. In section 4, carbon capture experimental studies at bench and pilot scales are presented. A review of recent studies on molecular simulation will be detailed in section 5. Section 6 reviews process modelling, simulation and techno-economic analysis of the adsorption-based PCC. Section 7 will address the knowledge gap and future directions to accelerate the technology for commercial deployment. Concluding remarks will be drawn in section 8.

## 2. Adsorption-based post-combustion carbon capture

Adsorption-based PCC process involves the transfer of CO<sub>2</sub> molecules in the flue gas, in bulk phase at atmospheric pressure and high temperature, to a solid surface [1,7]. The attached CO<sub>2</sub> molecules called the adsorbate, form a film on the surface of the solid material, denominated adsorbent [1,7]. This occurs due to physical forces (physisorption) and/or chemical bonds (chemisorption). Finally, the adsorbent is regenerated through desorption and the CO<sub>2</sub> molecules are released from its surface [1,7]. A unique feature of the adsorption-based PCC is the great flexibility in design [12,23]. Several adsorption-based PCC processes have been proposed based on the adsorbent materials used and process types (regeneration mode and contactor configuration) [12,19,23]. This review paper focuses on a few adsorbent materials and process types suitable for capturing CO<sub>2</sub> from power plant flue gas stream.

### 2.1. Adsorbent materials for adsorption-based PCC

#### 2.1.1. Ideal characteristics for adsorbent materials

The selection of the adsorbent material depends on the characteristics it exhibits and the operation conditions it will be used for. Several desirable traits for the adsorbent materials used in PCC are reported in the literature, mainly a high capture capacity and a high CO<sub>2</sub>-selectivity at low partial pressures (<0.2 bar) [24–26]. These traits are interrelated with additional characteristics that affect the process performance (e.g. high porosity, high thermal stability and low level of technical complexity) [27].

From the process design perspective, tolerance towards impurities [25] plays a major role in extending the life of the adsorbent for several cycles. Flue gases from power plants commonly contain 3–15 vol% of CO<sub>2</sub> [28], combining with other gases which can reduce the adsorbent capacity such as water vapour, O<sub>2</sub>, NO<sub>x</sub> and even SO<sub>x</sub> [29–31]. Temperature stability is also important, especially when regeneration is through temperature swing. Flue gases are generated at low pressure (e.g. 1 bar) at a wide temperature range. Post-combustion applications are usually between 40 and 200 °C [29–31] although some industrial streams can reach higher temperatures (from 150 to 400 °C). This is

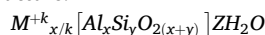
challenging for adsorbents with low optimal adsorption temperature such as carbonaceous materials (CMs) (50 °C, 1 bar), zeolites (0–100 °C, with a wide range of pressures) or MOFs (room temperature and 35 bar) [32,33].

Other desired traits for enhancing the cyclic use of adsorbents are: attrition resistance (mechanical stability), low production cost, high recycling ability, and a low-temperature gap between the adsorption and regeneration temperatures [30,34,35]. The regenerability of the materials [36] and the reversibility of the adsorption [37] are key for selecting the adsorbent and the regeneration process. Table 1 presents a summary of the characteristics of the adsorbent materials that influence the adsorption capacity and their relation with the adsorption cyclic process.

### 2.1.2. Common adsorbents for PCC

It is important to mention that adsorbent materials do not necessarily exhibit all the desired ideal characteristics. Popular adsorbents that have shown promising results for PCC applications and displayed many of the desired traits include zeolites, CMs, metal-organic frameworks (MOFs) and hydrotalcites (HTs). Table 2 summarizes the advantages and challenges of each adsorbents discussed.

**2.1.2.1. Zeolites.** Zeolites are highly ordered microporous crystalline aluminosilicates [25] which usually present a honeycomb structure [38] although they can exhibit diverse topologies, pore sizes and openings [39]. They can be found in nature or synthesized [39]. The latter is preferred as it enables controlling their porosity and crystallinity [40]. In zeolites, the Al (III) and Si (IV) atoms form a negatively charged structure that is balanced with interleaved exchangeable cations ( $M^{+k}$ ), e.g. Li, Na, K, Mg, Ca, Ba [39]. Their general chemical formula is the following, where Z is the number of water molecules present in the structure:



A typical example of commercial zeolite is Zeolite 13X [41]. As adsorbents, zeolites show high adsorption capacity [8,42], fast kinetics and the ability to maintain their initial adsorption capacities after several cycles [33]. However, their poor thermal stability creates a challenge for their application in power plants [27]. Their performance also decreases in the presence of polar gases (e.g. water [8,25,38] or SO<sub>2</sub> [37]). Additionally, when used at high pressures (>2 bar), zeolites require high regeneration temperatures [8].

**2.1.2.2. Carbonaceous materials (CMs).** The term CMs refers to

**Table 1**  
Adsorbent characteristics influencing adsorption capacity [25,27,30,35].

Category	Adsorbent characteristics	Relation to the cyclic process
Structure	<ul style="list-style-type: none"> <li>High porosity</li> <li>High surface area</li> </ul>	An increase in porosity can increase the surface area. Higher surface areas usually lead to higher adsorbent capacities.
Stability	<ul style="list-style-type: none"> <li>Thermal (minimal degradation of the material)</li> <li>Mechanical (resistance to attrition)</li> <li>Chemical (tolerance towards impurities)</li> </ul>	The stability of the material to sustain the adsorption capacity and characteristics throughout several cycles extends the life of the material and reduces cost.
Behaviour	<ul style="list-style-type: none"> <li>Selectivity for CO<sub>2</sub> over other gases</li> <li>Affinity to CO<sub>2</sub></li> </ul>	These will determine kinetics and CO <sub>2</sub> diffusion rate, which in turn affect will affect regenerability
Production	<ul style="list-style-type: none"> <li>Low cost</li> <li>Availability</li> <li>Recyclability</li> </ul>	Synthesis of the adsorbent and residues handling must be cost-effective to scale up adsorption-based PCC systems

**Table 2**  
Advantages and challenges of different adsorbents for PCC [8,25,30,53].

Adsorbents	Advantages	Challenges
Zeolites	<ul style="list-style-type: none"> <li>High CO<sub>2</sub> adsorption capacity at mild operating conditions (0–100 °C)</li> <li>Fast CO<sub>2</sub> adsorption kinetics</li> <li>Good cyclic stability and Mechanical stability</li> </ul>	<ul style="list-style-type: none"> <li>Poor Thermal Stability</li> <li>Requires high regeneration temperature</li> <li>Performance drop in the presence of polar gases</li> </ul>
CMs	<ul style="list-style-type: none"> <li>Low production cost</li> <li>Insensitivity to moisture</li> <li>Reduced energy requirement</li> </ul>	<ul style="list-style-type: none"> <li>Low CO<sub>2</sub> adsorption capacity and selectivity</li> <li>Low thermal stability</li> <li>High attrition rates in cyclic process</li> </ul>
MOFs	<ul style="list-style-type: none"> <li>High CO<sub>2</sub> adsorption capacity</li> <li>Flexible design- ability in terms of structure and function</li> <li>Tunable pore size</li> </ul>	<ul style="list-style-type: none"> <li>Low performance at partial pressure of CO<sub>2</sub></li> <li>Low economic efficiency</li> <li>Tedious and complication synthesis</li> <li>Sensitive to moisture</li> <li>Difficult to use at high temperatures due to destroying the MOFs structure</li> </ul>
HTs	<ul style="list-style-type: none"> <li>Low regeneration energy requirement</li> <li>Low heat of adsorption</li> </ul>	<ul style="list-style-type: none"> <li>Relative low CO<sub>2</sub> adsorption</li> <li>Low mechanical stability</li> </ul>

activated carbons (AC), graphene, mesoporous carbon, carbon nanotubes (CNT) [25,38], charcoal and coal [8], graphite, graphene oxide (GOx), carbon aerogels, polymer-based carbon [43].

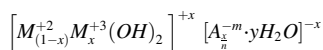
CMs can be obtained from naturally existing sources or spent materials, reducing their cost and increasing their commercial availability. For example, AC can be produced by pyrolysis of carbon-containing resins, fly ash or biomass [8]. The CM's source plays an important role in the final adsorption capacity since different precursors exhibit various pore sizes and surface areas [25,38].

CMs usually show a low CO<sub>2</sub> adsorption capacity and selectivity [28]. Degasification is the preferred regeneration process for these materials since the CO<sub>2</sub> attachment to the adsorbent is weak [25,38]. AC is a popular CM choice since it has a high surface area and large pore volume [37]. A large surface area makes it efficient for high-pressure adsorption [8], especially at high CO<sub>2</sub> concentration. Moreover, AC shows reproducible and consistent adsorption behaviour [29]. Another advantage is that, in contrast with zeolites, AC has a higher water tolerance, reduced energy requirement for regeneration and lower cost [44]. On the downside, some authors argued that their micro-pore structure presents low thermal stability [37] and high attrition rates in cyclic processes [25]. A detailed review of AC for carbon capture can be found in Rashidi and Yusup [45].

**2.1.2.3. Metal-organic frameworks (MOFs).** MOFs are a relatively new material introduced in 1995 [46]. They are hybrid nano-porous materials made of organic linkers spreading inorganic clusters apart. Usually, the organic linkers are found on the "edges" of a cubical structure, with the inorganic clusters forming the vertexes [38].

The advantages of MOFs as adsorbents are their well-defined porous volume, tunable pore sizes and extremely large surface areas [38]. Currently, over 81,000 different MOFs have been registered in the Cambridge Structural Database [40]. Promising variants are M-MOF-74 (M being a metal as Mg or Co) and HKUST-1 [40]. The main drawbacks of MOFs as adsorbents are their low thermal stability in comparison with other adsorbents such as zeolites and CMs [41] and the fact that their large-scale production is still challenging and expensive [25].

**2.1.2.4. Hydrotalcites (HTs).** HTs are natural anionic basic clays [47]. They are the most common layered-double hydroxide (LDH) studied for CO<sub>2</sub> capture. HTs are composed of cationic and anionic layers. The cationic layers resemble the mineral brucite [48], with the difference that the divalent cations (generally Mg<sup>+2</sup>, although Cu, Ni, Mn, Zn have been used [36,49]) are partially substituted by trivalent cations (such as Al, Fe, Cr, V [49]). The cations are surrounded by six OH<sup>-</sup> ions coordinated in an octahedron, and share edges to form infinite sheets that are stacked one upon another. As a result, a layered network held by hydrogen bonds is formed [50]. As the HTs layers are positively charged, balancing anions and water molecules are typically located in the interlayer region. The general formula for HTs is [51]:



HTs are attractive adsorbents for CO<sub>2</sub> capture because they have a lower regeneration energy requirement and can work in a wide range of temperatures, from 200 to 500 °C [25,52]. They present relatively low heat of adsorption [49] and fast kinetics, which interestingly improve in the presence of water [51]. Furthermore, HTs show high selectivity for CO<sub>2</sub> and easy regeneration through temperature and pressure swing [36,51]. They are widely available and are cheaper than alkaline ceramics although more expensive than alkali-meta based oxides [25]. The disadvantages of HTs are their relatively low CO<sub>2</sub> adsorption capacity [30] and low mechanical stability [53].

There are other types of adsorbent materials that make more use of the chemisorption process than physisorption, and other composite materials tailored to improve their performance. For example alkalinized alumina Al<sub>2</sub>O<sub>3</sub> [54], K<sub>2</sub>CO<sub>3</sub> on a support material [55], poly-amine (PEI) on support silica [56] and metallic oxides on zeolites [57].

## 2.2. Adsorption process types

The adsorption-based CO<sub>2</sub> capture technology from post-combustion flue gas is generally classified based on the mode of adsorbent

regeneration chosen [58]. Common regeneration methods adopted are reducing the pressure (pressure/vacuum swing adsorption, PSA/VSA), increasing the temperature (Temperature swing adsorption, TSA), or a combination of both [8,58].

### 2.2.1. Pressure/vacuum swing adsorption (PSA/VSA)

PSA is a well-established gas separation technique employed in air separation, gas drying and hydrogen purification separation [59]. In PSA processes, adsorption occurs at elevated pressure while desorption is carried out at reduced pressure [8,58,59]. The application of PSA technology for pre-combustion carbon capture has shown promise due to its low energy consumption. Since the feed stream is already at high pressure, rapid cycling time in fixed-bed columns is achieved [59]. However, the PCC process flue gas condition does not favour PSA [58,60,61]. This is because increasing the flue gas pressure, usually around atmospheric pressure, results in a rise in energy consumption and invariably increases the cost of the PCC process. An alternative to the PSA is the VSA [58,60,61].

VSA is a form of PSA in which adsorption is performed at atmospheric pressure or slightly higher pressure while the adsorbent is regenerated under vacuum conditions [58,60–62]. The fixed-bed configuration is mostly adopted for VSA with physical adsorbents [23,63]. The basic VSA steps include pressurization, adsorption, forward blowdown and reverse evacuation [23,64,65]. As depicted in Fig. 1, the flue gas is pressurized to atmospheric pressure at the pressurization step [64,65]. In the adsorption step, CO<sub>2</sub> is adsorbed at atmospheric pressure [64,65]. For the forward blowdown step, the column pressure is reduced to an intermediate pressure with the aim to remove as much N<sub>2</sub> as possible while retaining CO<sub>2</sub> in the column [64,65]. Thus, increasing CO<sub>2</sub> purity. The enriched CO<sub>2</sub> is recovered in the reversed evacuation step by decreasing the column pressure to vacuum [64,65]. The cycle begins with the pressurization step. Despite the simplicity of operating this basic VSA step, studies have shown that this step can lead to either low CO<sub>2</sub> purity or recovery [23,64].

Many alternative combinations of steps and configurations have

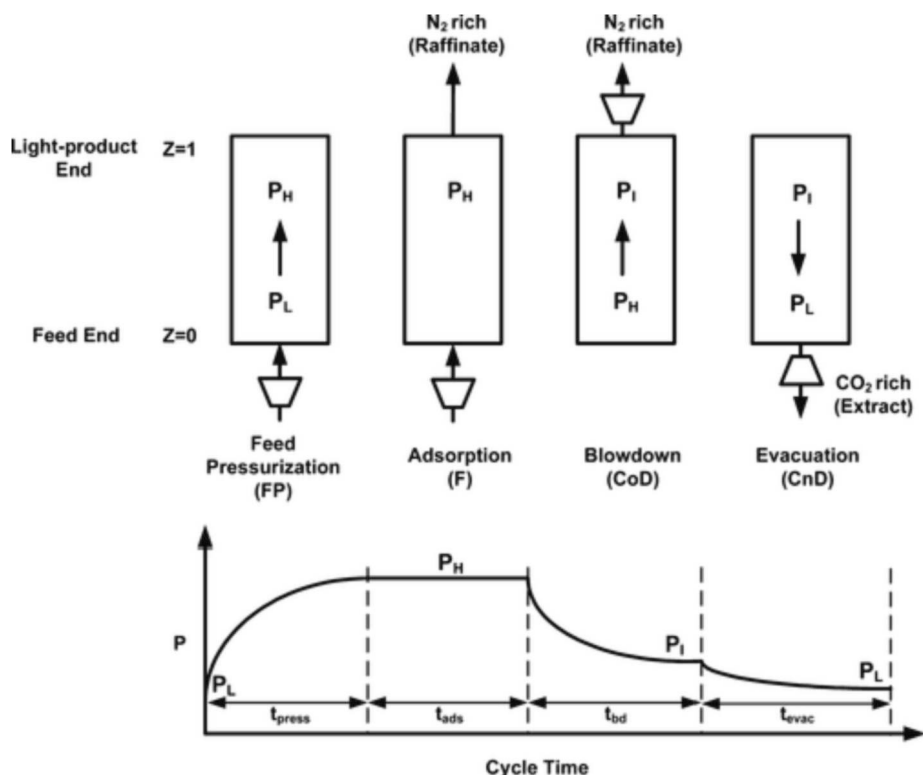


Fig. 1. Basic VSA 4-step cycle [65].

been explored to improve the separation performance in terms of CO<sub>2</sub> recovery and purity [23,60,62,66,67]. For example, 2-stage VSA has shown promising results as an efficient approach in terms of energy consumption, while still meeting the target of 90% CO<sub>2</sub> recovery and 95% purity [60,63]. Studies have shown that a single-stage system can achieve similar performance with competitive energy consumption, however, it requires vacuum conditions which are difficult to implement on large systems [60].

An advantage of the strategic integration of VSA processes in power plants is that they only involve flue gas pre-processing. VSA regeneration processes do not require steam extraction from the power plant [60,68]. On the other hand, the main drawback is the power consumption required to drive the vacuum pumps and fans [60,68] (see Table 3). Additionally, the scalability of VSA units has limited their application in large power plants as studies suggest they would create an excessively large footprint [58]. The need for process intensification of VSA unit is critical for its large-scale implementation.

### 2.2.2. Temperature swing adsorption (TSA)

TSA systems regenerate the adsorbent through a temperature increase via hot gas or steam [8,69]. They have been of interest for retrofitting in power plants due to their ability to utilize low-grade thermal energy for regeneration [8,58,61]. TSA can be applied for both physical and chemical adsorbents, being more suitable for the latter [58,61].

Fig. 2 shows a schematic of the basic 4-step TSA cycle in a fixed bed configuration [70]. This includes adsorption, preheating, desorption and precooling [70]. A major drawback of TSA in fixed-bed columns is the long duration of the heating and cooling steps, in the order of hours (see Table 3). This has restricted its use to small-scale applications [58,61]. If TSA is to compete with solvent-based PCC regarding costs, an intensification of the process is required to attain rapid cycle time.

Alternative column configurations with better transfer performance such as fluidized-bed column and moving-bed column have been explored to overcome this challenge [23,58,61]. The strong mixing in these configurations favours a quick heat transfer. However, if mixing is set in a co-current gas-solid flow it can result in lower average CO<sub>2</sub> loadings since the adsorbent is in equilibrium with the effluent [71]. On the other hand, it is still challenging to use moving-bed columns for large-scale because the gas velocity must be kept low. This leads to large diameters and mechanical difficulties when handling solids in large-scale operations [71].

The electrical swing adsorption (ESA), a derivative of TSA that employs low voltage electric current to heat the adsorbent by the Joule effect, is considered as another potential to reduce the energy penalty of adsorption-based CO<sub>2</sub> capture [71,72]. It has been identified to be an appealing option for fast heating of the adsorbent and CO<sub>2</sub> desorption

**Table 3**  
VSA and TSA Challenges [57,59].

Process types	Challenges
VSA	<ul style="list-style-type: none"> <li>- Impurities and water present in flue gas pose a challenge to VSA process</li> <li>- Large footprint</li> <li>- High capital cost</li> </ul>
TSA	<ul style="list-style-type: none"> <li>- Fixed bed               <ul style="list-style-type: none"> <li>o Low heat transfer rates</li> <li>o Large heat exchange area</li> <li>o Large energy consumption</li> <li>o High pressure drop</li> </ul> </li> <li>- Fluidized bed               <ul style="list-style-type: none"> <li>o More difficult handling of heat fluxes</li> <li>o Larger temperature difference between desorption and adsorption</li> <li>o Product purity level are limited compared to the best fixed-bed</li> <li>o Increased complexity</li> </ul> </li> </ul>

rate enhancement [23,72]. However, the cost of electrical energy adopted for ESA is more expensive than the low-grade heat adopted for TSA [23]. ESA is most likely better suited for small-scale operations [71].

### 2.2.3. Novel swing adsorption methods

The development of the adsorption-based PCC technology to achieve high CO<sub>2</sub> purity and recovery, at a reduced energy consumption requirement, is key for the commercial deployment of the technology at an industrial scale. The common regeneration approaches (VSA and TSA) are encountered with several challenges as discussed above. Some attempts have been made to overcome these challenges by adopting hybrid regeneration approaches such as the combined vacuum and temperature swing adsorption (VTSA). The VTSA shows high purity and productivity for solid adsorbents with less energy intensity [73]. However, the VTSA requires a long cycle time for an adsorption-desorption operation due to the heat transfer between the heat exchanger and the solid is not fast [73]. Fujiki et al. [73] proposed a steam-aided VSA (SA-VSA) process using an amine-based adsorbent. Studies from the experiments showed that the SA-VSA is effective for recovering CO<sub>2</sub> with high purity (98%) and recovery rate (93%). Cloete et al. [74] investigated the novel swing adsorption reactor cluster (SARC) for PCC from a cement plant. The SARC employs a combination of temperature swing (using heat pumps) and pressure swing (using vacuum pumps) to capture CO<sub>2</sub> with solid adsorbents using electrical power [74]. The process was able to achieve competitive energy efficiency with a specific energy consumption per CO<sub>2</sub> avoided of 2.04 MJ<sub>LHV</sub>/kg<sub>CO2</sub>.

Other studies on hybrid regeneration methods have been carried out. Sun et al. [75] employed a moisture swing adsorption (MSA) for CO<sub>2</sub> removal from natural gas using sorbent of ion exchange membranes loaded with CO<sub>3</sub><sup>2-</sup> ions. The reversible transformation between CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> at room temperature and normal pressure governs the CO<sub>2</sub> adsorption/desorption cycles. Studies showed that the energy consumption of the MSA process is less than the MDEA-based CO<sub>2</sub> removal process (187.38 kJ/Sm<sup>3</sup> for MSA and 954–1304 kJ/Sm<sup>3</sup>).

Cuesta and Song [76] explored the pH swing adsorption (pHSA) process for ambient CO<sub>2</sub> capture using activated carbon black adsorbents and immobilized carbonic anhydrase biocatalysts. The pHSA exhibits strong operational energy and CO<sub>2</sub> capture efficiency by incorporating advantages from both TSA and MSA. The pHSA system has the potential to reduce energy use and operating costs associated with CO<sub>2</sub> capture.

## 2.3. Summary

Researchers and scientists have encountered several challenges for the commercialization of adsorption-based PCC processes, mainly associated with the development of adsorbent materials and cyclic processes [8]. To compete with solvent-based PCC processes, adsorbents must exhibit 1) high CO<sub>2</sub> capture capacity and selectivity, 2) fast adsorption kinetics, 3) mechanical, thermal and chemical stability, 4) ease of regeneration, 5) low cost, 6) energy-efficient cyclic process [71,77]. Zeolites and CMs are popular for adsorption-based PCC, HTs show promising results and MOFs have been studied for larger-scale applications.

Widely used cyclic processes for adsorbent regeneration include VSA, TSA and a combination of both, aiming at the reduction of the energy requirement. Efforts to improve both the adsorbent materials and the cyclic processes through lab synthesis, experimental tests and modelling at molecular and process scale will be discussed in the following sections.

## 3. Lab synthesis and characterization of adsorbents for PCC

In this section, we present the findings of the synthesis and characterization of various adsorbents for PCC at lab scale. Characterization is

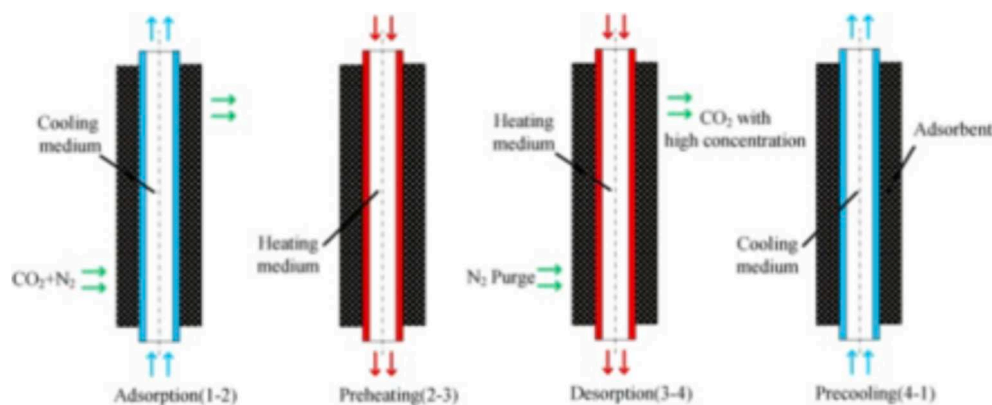


Fig. 2. Basic TSA 4-step cycle [70].

usually carried out using X-ray powder diffraction (XRD) or Fourier-transform infrared (FTIR) spectroscopy to determine the crystal structure whereas thermogravimetric (TGA) analysis is used to monitor the evolution of the structure during calcination [36]. Scanning electron microscopy (SEM) is typically used to observe the morphology and obtain high quality images, sometimes coupled with energy dispersive spectroscopy (EDX) to determine the chemical composition. The Brauer-Ernzhof-Teller (BET) methodology is used to measure the surface area, similarly the Horvath-Kawazoe model for obtaining the pore size distribution and the t-plot method for calculating the micro-pore volume [78].

### 3.1. Zeolites

#### 3.1.1. Lab synthesis

Zeolites synthesis is generally carried out with a mixture of aluminate and silicate solutions subjected to elevated temperatures in a closed reaction systems for various periods to produce a supersaturated solution that undergoes spontaneous nucleation and crystallization processes [79]. The choices of raw material and synthesis method are key to achieving cost-effective zeolites [80]. Different raw materials (natural or man-made) have been adopted for the synthesis of zeolites which include coal fly ash, biomass fly ash, kaolin [79,80]. Key factors that affect the choice of raw materials include raw-material cost, cost of production, high production yield and amount of foreign substances. Various approaches have been adopted to produce synthetic zeolites, including hydrothermal methods, ionothermal methods, solvo-thermal methods, alkali-fusion method, sol-gel method, alkali-leaching method, microwave method and ultrasound energy method [80]. Each approach has its pros and cons as detailed in Table 4.

Amongst the methods listed in Table 4, hydrothermal method is conventionally adopted for zeolite synthesis. The performance of the hydrothermal method is affected by several parameters including pressure, temperature, batch composition, Si/Al ratio, reactant materials, overall alkalinity, aging time, template condition and seeding [80,81]. Several attempts on zeolites synthesis via hydrothermal methods have been reported [82–86]. The hydrothermal method is traditionally adopted due to several advantages, which include low energy consumption, ease of maintenance, low air pollution. However, Meng and Xiao [87] highlighted the limitations of the conventional hydrothermal method which includes low efficiency of the process due to long time periods and relatively high temperature, expensive autoclave needed for the process and corrosive slurries produced that are detrimental to the zeolite structure. Thus, hydrothermal synthesis is far from an optimum environmentally friendly zeolite synthesis technology. To overcome these limitations, researchers have developed several alternative approaches, including microwave-assisted hydrothermal approach, alkali-fused hydrothermal approach, ultrasound-assisted hydrothermal

Table 4  
Zeolite synthesis methods advantages and limitations .

s/n	Synthesis method	Advantages	Limitations
1	Hydrothermal	High reactivity, Low pollution and energy consumption; Good crystal quality	Expensive autoclave Corrosive slurries
2	Iono-thermal	Production of large crystal and easy to control crystal composition	High operating time High toxic chemicals production
3	Solvo-thermal	Easy control over the size, Shape distribution, Crystalline product	Expensive autoclave Organic solvent needed
4	Alkali-fusion	Uses low-grade raw materials; High quality anhydrous zeolites production	High energy consumption and cost
5	Alkali-leaching	Enables the use of impure raw materials and offers efficient products t.	Expensive and time consuming
6	Sol-gel	Less energy consumption; Expensive equipment not needed	Cost of precursors; Residual porosity and OH groups difficult to avoid;
7	Microwave	Faster reaction; Selective heating, Higher temperature	Water evaporation; Heat force control difficulty
8	Ultrasound energy	Simple, rapid reaction, high crystal growth rate, uniform particle size distribution and morphology; nucleation process control	

adapted from [80]

approach [80]. For instance, Yit Siew Ng et al. [88], adopted the ultrasound-assisted hydrothermal approach for zeolite RHO, highlighted that the synthesis duration of zeolite RHO was significantly reduced from 7 days to 2 days compared to the conventional hydrothermal method.

The solvo-thermal and ionothermal methods are similar to the hydrothermal synthesis method with the exception of the type of solvent used. The solvo-thermal method uses organic solvent while the ionothermal method uses ionic liquid as solvent for zeolite synthesis. Similar to the hydrothermal method, the same factors affect the performance of the solvo-thermal and ionothermal methods. A key advantage of the solvo-thermal method is that the method offers easy and precise control of the size and shape distribution of the zeolite product. The ionothermal method produces large size of crystals. It is also easy to control the growing crystal composition. Several studies have been reported on zeolites synthesis via solvo-thermal [89–92] and ionothermal method [93–97]. A major limitation of the solvo-thermal method is the use of alcohol as organic solvent, which greatly affects

the nucleation rate and crystal growth[80]. The ionothermal method, however, produces toxic chemicals and operates for a longer period[80]. Despite these limitations, the use of these methods is gaining popularity for zeolite synthesis in the research community[80].

Ayele et al.[98] compared the alkali-fusion method with the conventional hydrothermal method for the synthesis of type A zeolite. The study highlighted the advantages of alkali-fusion method over the conventional hydrothermal method. The alkali-fusion method allows the use of low-grade materials without purification. However, high energy consumption remains an issue. The alkali-leaching sol-gel, microwave and ultrasound methods for zeolites have also been reported by researchers. These studies highlighted the advantages and limitations. Amongst these methods, the ultrasound energy method is gaining much attention due to its great influence on zeolite synthesis, which includes its rapid reaction rate, suitable particle size distribution and morphology [80].

### 3.1.2. Characterization

Several experimental studies on the characterization of diverse zeolites, to assess their potential for CO<sub>2</sub> capture from power plant flue gas, have been reported[99–101]. In some of these studies, CO<sub>2</sub> adsorption capacity of zeolites were recorded with the TGA analysis at a wide temperature range (25 °C–877 °C) and atmospheric pressure. Morales-Ospino et al. [99] also assessed the CO<sub>2</sub> adsorption capacity of type X and A zeolites synthesized from fly ash in comparison with commercial zeolite 13X materials. It was noted in the study that the synthesized zeolite exhibited slightly lower CO<sub>2</sub> adsorption capacities than the commercial zeolites. All samples show good selectivity for CO<sub>2</sub> capture. Wu et al. [101] assessed the CO<sub>2</sub> adsorption performance of zeolite L samples with different crystal morphologies (cylindrical, disk-shaped and nanosized). Among these samples, the nanosized zeolite L showed the highest CO<sub>2</sub> adsorption capacity of 70 cm<sup>3</sup>/g with BET specific surface area of 427.2 m<sup>2</sup>/g and a total pore volume of 0.382 cm<sup>3</sup>/g. The study recorded an IAST selectivity for CO<sub>2</sub>/N<sub>2</sub> of 198 at 25 °C and 1 bar. The nanosized zeolite L demonstrated a higher mass-transfer rate [101]. Key factors that affect the CO<sub>2</sub> adsorption on zeolites include basicity (influenced by Si/Al ratio), pore size and electric field strength as a result of the exchangeable cation present in their cavities. The optimization of these factors along with temperature and pressure are key to enhancing the CO<sub>2</sub> adsorption capacity [102].

Chong et al. [103] investigated thermal stability as well as the cycling stability of the zeolite 5A and 13X under humid conditions. The study reported that the zeolites exhibited high thermal stability as the TGA shows negligible weight-loss after being heated to 800 °C. However, the CO<sub>2</sub> capacity of zeolites decreases with an increasing number of cycles in humid conditions. The study suggested that the formation of a stable hydrogen bonding network between H<sub>2</sub>O and the exposed metal cation leads to the gradual decrease of CO<sub>2</sub> adsorption capacity.

## 3.2. CMs

### 3.2.1. Lab synthesis

A variety of CMs adsorbents considered for CO<sub>2</sub> capture have been developed from diverse sources which include sawdust [104], coal, peat, skins of coffee beans [105], olive stones [106], coconut shells, almond shells [45] and even waste Coca-Cola® [107]. The use of biomass sources are gaining much attention in the bid to develop low-cost CMs for CO<sub>2</sub> capture. These CMs includes ACs, carbon aerogels, carbon nanotubes, graphene and biochar [43]. This review focuses on ACs.

Various synthesis methods such as pyrolysis, hydrothermal carbonization, molten salt carbonization and ionothermal carbonization have been adopted for the preparation of CMs. Table 5 details the advantages and limitations of each synthesis strategy. Amongst these strategies, pyrolysis is most common. Pyrolysis usually occurs at temperatures below 800 °C in order to devolatilize the material, whereas oxidation is typically carried out between 800 and 1000 °C [45]. The volatilization

**Table 5**  
CMs synthesis methods advantages and limitations .

s/n	Synthesis method	advantages	Limitations
1	Pyrolysis	<ul style="list-style-type: none"> <li>• Most conventional method for char synthesis</li> <li>• High porosity</li> <li>• High product yield</li> </ul>	<ul style="list-style-type: none"> <li>• Requires biomass with low moisture</li> </ul>
2	Hydrothermal Carbonization	<ul style="list-style-type: none"> <li>• Suitable for wet agriculture residues</li> <li>• Lower energy consumption</li> </ul>	<ul style="list-style-type: none"> <li>• Slow process</li> <li>• Low surface area and porosity</li> <li>• Needs activation (chemical or physical)</li> </ul>
3	Molten Salt Carbonization	<ul style="list-style-type: none"> <li>• Low cost</li> <li>• Versatile for a variety of agriculture waste</li> </ul>	<ul style="list-style-type: none"> <li>• Detailed generation and mechanism for CMs synthesis still needs more investigation</li> </ul>
4	Ionothermal carbonization	<ul style="list-style-type: none"> <li>• Ionic liquids can be adopted as solvent, template and catalyst</li> <li>• Enables porous carbon production in a one-step process</li> </ul>	<ul style="list-style-type: none"> <li>• Intensive energy consumption of ionic liquid recycling</li> </ul>

adapted from [109]

of substances promotes the widening of existing pores and the formation of new ones. In consequence, there is also an increase in the internal surface area [108]. However, a major limitation is the energy-intensive nature of the process due to the drying of the biomass [109]. Hydrothermal carbonization is an alternative approach that allows the use of wet biomass. The hydrothermal carbonization is operated at a relatively mild temperature (150 °C–350 °C), which reduces energy consumption. However, the process is quite slow due to the long residence time (ranging from hours to days). The pyrolysis and hydrothermal carbonization processes are typically followed by a subsequent physical activation in the presence of oxidants such as air, CO<sub>2</sub> or steam [45]. Depending on the precursor, chemical activation can also be used to improve the pore volume of the AC. In this method, the precursor is impregnated with a dehydrating agent prior to carbonization such as KOH, NaOH, ZnCl<sub>2</sub> or H<sub>3</sub>PO<sub>4</sub> (acidic, alkaline or salt mediums). In this case, the activation temperature is between 600 and 800 °C which could reduce the energy required for the production [45]. However, if chemical activation is applied, the adsorbent requires intensive washing to remove residual chemicals and impurities [45].

Ionothermal carbonization approach enables a one-step synthesis of CMs using ionic liquids without the need for activation as the ionic liquid does not only act as a solvent but also as a template for pore structuring[109]. Despite the ability to develop highly porous CMs, in one step, within a short period (residence time ranges from one to several hours), the energy consumption intensity of ionic liquid recycling is a key limitation. To deal with this limitation, molten salts are adopted for carbonization due to the ease to recover the molten salt [110]. Wang et al.[110] prepared a porous N-AC using low price chitosan with LiCl-ZnCl<sub>2</sub> molten salt, which demonstrated high CO<sub>2</sub> capacity, good selectivity and excellent recyclability[110].

### 3.2.2. Characterization

In general, CMs have a weak affinity to CO<sub>2</sub>, dominated by physisorption with the heat of adsorption less than 25 kJ/mol. In consequence, CMs usually show a low CO<sub>2</sub> adsorption capacity and selectivity (CO<sub>2</sub>/N<sub>2</sub> 5 and CO<sub>2</sub>/CH<sub>4</sub> < 3) [28]. This is explained by CMs relatively uniform electric potential on their surface and low enthalpy adsorption [8], as is the case of AC, unless the material is chemically modified [38].



ACs show reproducible and consistent adsorption behaviour [29]. ACs have higher water tolerance, require less energy for regeneration and are cheaper [44]. Their highest adsorption capacity is reached at temperatures under 50 °C and pressure over 4 bar [25]. They lose their adsorptive properties after 250 °C [37] unless chemically modified. One of the main factors that affect the adsorption capacity of AC is the pore size. At atmospheric conditions, narrow micropores (<1 nm) assist in CO<sub>2</sub> retention into the pore wall and block N<sub>2</sub> passage. The fraction of micropore volume is a primary contributor to the CO<sub>2</sub> adsorption, even more influential than the surface area [45]. For example, AC from sawdust can achieve an adsorption capacity of 8 mmol/g even with a low surface area of 1,643 m<sup>2</sup>/g if the micropore volume is near 73%, whereas samples with a surface area of 2,435 m<sup>2</sup>/g only captured 4.73 mmol/g when the micropore volume was 29% [111]. Nonetheless, ACs with high surface area can be advantageous for high-pressure applications [8].

Balsamo et al [112] investigated the effect of inlet CO<sub>2</sub> concentration and temperature on the adsorption performance of a synthetic nanoporous AC obtained from a mixture of coal tar pitch and furfural. From the study, the CO<sub>2</sub> intake increases with temperature (30 °C, 50 °C and 80 °C) [112]. The researchers attributed this to the increase in mass transfer rate due to the higher process driving force. On the other hand, for a fixed inlet CO<sub>2</sub> concentration, the breakthrough curve showed a shift towards a lower break-point time as the temperature increases, indicating a reduction in the adsorption capacity [112].

Regeneration experimental study on the effect of the regeneration operating condition on AC, carried out by Cen et al. [113], showed that a lower vacuum pressure, about 4 kPa as the desired limit, results in a higher regeneration efficiency (>90%) and the working capacity becomes larger [113]. Investigation of the re-utilization of AC F50 revealed that a constant CO<sub>2</sub> adsorption capacity is maintained after 15 consecutive cycles [112].

It is important to highlight that the operation conditions of ACs tend to the lower temperature range. For example, after 10 regeneration cycles at 25 °C, carbons co-doped with N and O presented high regenerability [114]. Although Di Biase and Sarkisov [29] argued that AC is stable at high temperatures as well [29], Leon et al. [37] commented that their micropore structure presents low thermal stability. Also, the soft nature of AC results in high attrition rates in cyclic processes [25]. This could be a challenge when scaling up the adsorption process.

### 3.3. MOFs

#### 3.3.1. Lab synthesis

MOFs are usually produced through a modular synthesis in which the metal ions and organic ligands are combined to yield the crystalline and porous framework [115]. Synthesis methods are usually regarded as conventional or modern. [116]. Each synthesis method was detailed in Table 6 with their respective advantages and limitations to industrial implementation. Amongst the several methods, solvo/hydro-thermal is the most common. This involves heating the reagents dissolved in a solvent in a close autoclave reactor. It has been observed that higher pressures and longer time render bigger crystals [116]. When using water as the solvent in an effort to avoid the hazardous nature of the solvents, it is called hydrothermal. The most promising modification to this synthesis process is to assist it with microwave heating, especially for large-scale synthesis of MOFs. For a more detailed description of each method, the reader can refer to [116,117].

The properties of MOFs, such as pore sizes and pore functionalities, can be fine-tuned by modifying the length and functionality of the ligands [115]. However, these inorganic ligands are usually expensive, which makes their large-scale production difficult [25] and hinders their utilization in commercial applications. This is why scaling up the continuous production of MOFs is a great achievement. MOF Technologies™, a partner in the GRAMOFON project was able to develop a continuous MOF production process at pilot-scale (production rate of

**Table 6**  
MOFs synthesis methods advantages and limitations adapted from [116,117].

s/n	Synthesis method	Advantages	Limitations
1	Solvo/hydrothermal method	<ul style="list-style-type: none"> <li>Wide operating temperature regime</li> <li>Ease of heating and cooling temperature ramps to help crystal growth</li> <li>Easy industrial transposition</li> </ul>	<ul style="list-style-type: none"> <li>High cost of sealed enclave</li> <li>High energy consumption</li> <li>Long reaction time</li> </ul>
2	Microwave heating method	<ul style="list-style-type: none"> <li>Simple and energy-efficient approach</li> <li>High yield and reduced crystallization time</li> <li>Easy control of the reaction parameters</li> <li>Control of morphology, phase selectivity and particle distribution</li> </ul>	<ul style="list-style-type: none"> <li>Difficult to isolate large single crystals</li> <li>No easy and quick industrial implementation</li> </ul>
3	Ultrasonic synthesis method	<ul style="list-style-type: none"> <li>Efficient isolation of phase-pure materials</li> <li>Homogeneous particle size and morphology in short periods</li> <li>Suitable for nano-sized MOFs</li> </ul>	<ul style="list-style-type: none"> <li>Ultrasound waves can break crystallites, which hinders the formation of large single-crystals for X-ray diffraction studies</li> </ul>
4	Electrochemical synthesis	<ul style="list-style-type: none"> <li>Rapid synthesis</li> <li>Good porosity</li> <li>Controllable particle morphology</li> <li>Continuous synthesis</li> <li>Reduced solvent required</li> <li>Mild reaction conditions</li> </ul>	<ul style="list-style-type: none"> <li>Low yield</li> <li>More by-products produced</li> </ul>
5	Continuous flow chemistry	<ul style="list-style-type: none"> <li>Rapid synthesis</li> <li>Precise control on reaction parameters</li> <li>Lower energy consumption</li> <li>Easy integration</li> </ul>	<ul style="list-style-type: none"> <li>High temperature and pressure</li> </ul>
6	Milling	<ul style="list-style-type: none"> <li>No pressure and temperature required</li> <li>Good yield and reproducibility</li> </ul>	<ul style="list-style-type: none"> <li>Low output</li> <li>Difficult to separate for X-ray single-crystal diffraction</li> <li>Long equipment downtime</li> </ul>
7	Twin-screw extrusion	<ul style="list-style-type: none"> <li>Easy integration</li> <li>Used in continuous manufacturing process</li> </ul>	<ul style="list-style-type: none"> <li>Material loss</li> <li>Slow process speed</li> <li>Non-uniform crystal structure</li> <li>Special instrumentation is needed</li> </ul>

1–10 kg/hr) [118,119]. The process minimizes the use of solvent, reduces costs and enables the manufacture of customized geometries for different applications.

Studies reveal that the performance of powdered MOFs can decrease up to 10% when they are scaled and shaped [120]. An innovative MOF shaping process is the use of hydrocolloids to prepare spheres of MOFs as in molecular gastronomy methods [121]. With this method, the MOFs

**Table 7**  
HTs synthesis methods advantages and limitations adapted from [127].

s/n	Synthesis method	Advantages	Limitations
1	Co-precipitation method	<ul style="list-style-type: none"> <li>Allows control of charge density</li> </ul>	<ul style="list-style-type: none"> <li>Low yield of well-crystallized HT-like phase</li> </ul>
2	Urea Hydrolysis	<ul style="list-style-type: none"> <li>Large particle size is obtained</li> <li>Allows preparation of HT compounds with a high charge density</li> </ul>	<ul style="list-style-type: none"> <li>Operated at high temperature</li> </ul>
3	Solvo/hydrothermal	<ul style="list-style-type: none"> <li>Enables improved crystallized structures</li> <li>Results in particle size increase</li> </ul>	<ul style="list-style-type: none"> <li>Long reaction time</li> </ul>
4	Combustion synthesis	<ul style="list-style-type: none"> <li>Short crystallization time</li> <li>No solvents required</li> </ul>	–
5	Sol-gel method	<ul style="list-style-type: none"> <li>Cost effective</li> <li>Simplicity</li> <li>Enables control of homogeneity and structural properties of HTs</li> </ul>	–
6	Microwave Irradiation	<ul style="list-style-type: none"> <li>Fast heating can be achieved</li> <li>Reduced period of aging and tedious washing</li> </ul>	–
7	Steam Activation	<ul style="list-style-type: none"> <li>Improves crystalline structures</li> </ul>	<ul style="list-style-type: none"> <li>May deteriorate the quality of HT</li> </ul>

do not show degradation; and when using chitosan as the particle-forming agent, the created spheres show a higher crushing strength than Zeolite 13X [121]. The use of hydrocolloids has been successfully used to produce Ni-MOF beads in kilogram quantities [122].

Chemical modifications to increase the CO<sub>2</sub> capture capacity of MOFs, such as the addition of amines and polarising functional groups after their synthesis is common [115]. Loading the MOF framework with poly-ethyleneimine is popular for improving the adsorption capacity (~2 mmol/g for a BET surface area of 480 m<sup>2</sup>/g) [116].

### 3.3.2. Characterization

MOF's high adsorption capacity is usually explained by their extra high porosity and the interaction of the CO<sub>2</sub> with the framework, resulting in capacities higher than zeolites and AC, especially at room temperature and high pressure (~35 bar) under equilibrium conditions [25]. Examples of MOFs with high adsorption capacity are HKUST-1 (3.3 mmol/g, with BET surface area of 850 m<sup>2</sup>/g), UIO-66 (2.323 mmol/g, with BET surface area >1,400 m<sup>2</sup>/g) and Cu<sub>3</sub>(BTC)<sub>2</sub> (4.4 mmol/g, with BET surface area >1,400 m<sup>2</sup>/g) [116]. Additionally, due to the interaction of the framework with the quadrupole of CO<sub>2</sub>, MOFs exhibit high CO<sub>2</sub>-selectivity [38]. However, their high adsorption capacity is limited to a low-temperature range, from 0 °C to 30 °C [116], a challenge for post-combustion applications. For example, Cu-BTC can achieve an adsorption capacity of 9.59 mmol/g at 0 °C at atmospheric conditions, but it decreases to 5.33 at 25 °C [123]. Additionally, for gas mixtures under dynamic conditions, the CO<sub>2</sub> adsorption capacity of MOFs decreases abruptly [8], especially in the presence of moisture. When water is present, the MOF's surface area reduces, possibly due to a partial collapse of the pores [38] as the water molecules displace the ligands, destroying the crystal lattice [25].

MOFs tend to have low thermal stability [41], thus recent studies focus on this issue. Studies comparing different MOFs (with Mn, Fe, Mg, Co, Zn) have shown that MOF-Mn and MOF-Mg are promising candidates for TSA cycles, approximating their behaviour with the weighted-dual site Langmuir (w-DSL) isotherm [124]. It is observed that higher productivity is achieved when the heating temperature of the TSA cycle is maximal and the cooling temperature is minimal, ~227 °C and ~20 °C respectively, attributed to the sharp decrease in the adsorption capacity associated with the temperature increase [124]. Preliminary experiments with the MOF UiO-66, synthesized by the sol-gel method

**Table 8**  
Characteristics of the approaches to calculate the PES.

	Quantum Mechanics	Molecular Mechanics
<b>Accuracy level</b>	<ul style="list-style-type: none"> <li>Differentiates atoms nuclei and electrons</li> <li>Can describe electrons interactions</li> </ul>	<ul style="list-style-type: none"> <li>The atom is described as a sole entity [152]</li> </ul>
<b>Input required</b>	<ul style="list-style-type: none"> <li>The atomic number of the elements in the system</li> <li>Initial configuration of the atoms in the system [155]</li> </ul>	<ul style="list-style-type: none"> <li>Force Field (FF) containing the parameters for the functions representing the interaction of the particles, usually derived from experimental data or QM calculations [155]</li> <li>Examples of FF used for studying adsorption processes: CLAYFF [158], AMBER [159], TraPPE [160–163], UFF [162,164,165], DREIDING [166] and ReaxFF [157,167]</li> </ul>
<b>Advantages</b>	<ul style="list-style-type: none"> <li>Capable of modelling the creation or breaking of bonds (chemical reactions) and dynamic processes [168]</li> </ul>	<ul style="list-style-type: none"> <li>Lower computational power requirement [169]</li> <li>Larger systems can be simulated (up to millions of atoms) thanks to the use of simple-interatomic potentials [155]</li> </ul>
<b>Disadvantages</b>	<ul style="list-style-type: none"> <li>High computational cost</li> <li>Better suited for smaller systems (hundreds of atoms) [155]</li> </ul>	<ul style="list-style-type: none"> <li>It is difficult to create an adequate Force Field adapted to the structure and conditions of the simulation. [155]</li> </ul>
<b>Basis Theory</b>	<ul style="list-style-type: none"> <li>Ab initio: Molecular Orbital Theory</li> <li>Semi-empirical: Hückel, Valence Bond theory, Density Functional Theory (DFT) [168,170]</li> </ul>	<ul style="list-style-type: none"> <li>Newtonian laws</li> </ul>
<b>Common applications</b>	<ul style="list-style-type: none"> <li>Geometry optimization of the system</li> <li>Calculation of interaction forces between small pieces of the structure and few gas molecules</li> </ul>	<ul style="list-style-type: none"> <li>Molecular dynamics simulations</li> <li>Monte carlo simulations</li> </ul>

has shown promising results with PSA regeneration.

MOF and GOx composites (MOF/GOx) have been proposed for improving the thermal and electric conductivity of MOFs and subsequently, their efficiency for TSA, electrical swing adsorption (ESA) and microwave swing adsorption (MSA) regeneration [125]. MOF/GOx with 5 wt% GOx has shown suitability for MSA process. In other experiments, MOF/GOx showed a CO<sub>2</sub> adsorption working capacity of 7.5 wt% after 9 cycles and a significant reduction of the time and energy requirement by 50% [118].

## 3.4. HTs

### 3.4.1. Lab synthesis

Co-precipitation is the most usual synthesis process for HTs. Metallic salts containing the desired cations, e.g. Mg(NO<sub>3</sub>)<sub>2</sub> • 6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub> • 9H<sub>2</sub>O, are dissolved in deionized water. Then, a precipitation agent is added, such as NaOH, as well as a solution of the desired anion, for example Na<sub>2</sub>CO<sub>3</sub>. The precipitation agent also controls the pH of the reaction, which influences the cationic ratio [52] and crystallinity of the

final product [25]. The precipitate is then separated, washed and dried [126]. Other common methods for HTs synthesis are urea hydrolysis, solvo/hydrothermal process, microwave irradiation and sol-gel [50]. Table 7 details HT synthesis methods advantages and limitations. Othman et al [127] gave a comprehensive review of the different methods of HTs synthesis [127].

The properties of the final synthesized HTs depend on many factors. The lateral size of the layers and the degree of stacking. For example, vary depending on the conditions for their synthesis [128]. The usual thickness of one layer is 4.8 Å [129], with the interlayer distances varying from 0.3 to 3 nm [127]. The composition of HTs (i.e. the combination of cations, anions, and the ratio of the cations  $M^{+2}/M^{+3}$ ) can greatly influence the interaction between the CO<sub>2</sub> molecules and the HTs, as well as the regenerability, cyclic stability and kinetics of the adsorbent [25]. For example, experiments varying the interlayer anions have shown that the morphology, and thus the BET surface area, can also be affected. HT containing CO<sub>3</sub> presented a spheroidal “sand rose” morphology, with approximately 400 to 450 nm of diameter, and “petals” of 24–25 nm, each containing between 30 and 32 brucite-like sheets. In comparison, HTs synthesized with other anions such as NO<sub>2</sub>, SO<sub>4</sub>, Cl and HCO<sub>3</sub> exhibited a “stone” morphology, with non-porous particles from several to several-tenth μm [52], with larger anions producing a greater interlayer space [25].

The surface and structural properties of HTs in crystalline phase are not suitable for reversible CO<sub>2</sub> sorption. This is because the CO<sub>2</sub> sorption in the crystalline HT is driven by the acid-base reaction of Mg-OH and CO<sub>2</sub> to form Mg(HCO<sub>3</sub>)<sub>2</sub>, which is irreversible [36]. In order to increase the adsorption capability and surface area of the HTs, a thermal treatment called calcination is used. This treatment produces mixed metal oxides that show high thermal stability, good dispersion of the metals, and high surface area [130]. The mixed metal oxides present Lewis basicity, whereas the CO<sub>2</sub> is a weak Lewis acid [24], and thus calcination increases the CO<sub>2</sub> adsorption capacity of the material. It is important to control the calcination temperature. This is because the number of active basic sites of Mg-O for adsorption decreases when the calcination temperature is too high. This phenomenon is attributed to the formation of crystal MgO [36] and Al<sub>2</sub>O<sub>3</sub> [25]. The optimal calcination temperature for Mg-Al-CO<sub>3</sub> HT has been reported as 400 °C [34].

### 3.4.2. Characterization

The adsorption capacity of HTs is usually regarded as low in contrast with other adsorbents. For example, Mg-Al-CO<sub>3</sub> HTs adsorption capacity (depending on the synthesis and calcination methods) ranges from 0.1 to 0.92 mmol/g with a BET surface area in the range of 55 to 258 m<sup>2</sup>/g. However, they have the advantage of being able to operate in a much higher temperature range, from 100 °C to 400 °C [24,36,48,52,129,131].

There are different studies investigating how to increase the adsorption capacity of HTs. They can be divided on synthesis method variations, composition variations, impregnation with alkali metals and the use of supporting materials. Many studies prefer the co-precipitation synthesis method, possibly due to the easiness of the process and the capacity to tune the characteristics of the final material. Regarding the composition variation, experiments using CO<sub>3</sub><sup>2-</sup> as the anion have reported the highest adsorption capacity. For example, the adsorption capacity at 300 °C and 1 bar is 0.5 mmol/g whereas for HT using OH<sup>-</sup> as anions is 0.2 mmol/g [33]. The cations also influence the properties of the material. Trivalent cations determine the structure evolution of the material after calcination [52] while changing the divalent cation with other elements such as Be<sup>+2</sup> or Cd<sup>+2</sup>, results in materials different to HTs [127]. Interestingly, a specific and strong affinity for CO<sub>2</sub> is more relevant than the available surface area or the pore volume. HTs impregnated increased their adsorption capacity in more than 50% compared with non-impregnated samples [132].

To the best knowledge of the authors there are no published experimental studies focusing on the regeneration of HTs in PCC conditions.

Most of the studies are aimed at increasing the adsorption capacity and current projects such as DISPLACE are still in the development stage [133]. However, modelling the desorption isotherms is possible based on the equilibrium theory of adsorption in fixed beds [132].

Researchers expect that an easier regeneration of K-promoted HT, modified with Ga using PSA beds [132]. On the other hand, experiments in pre-combustion carbon capture conditions and TSA have shown that the CO<sub>2</sub> adsorption capacity of K-promoted HTs reduced to 7% after ten cycles, which is attributed to the partial conversion of the K<sub>2</sub>O promoter into K<sub>2</sub>CO<sub>3</sub> [134].

## 4. Experimental studies and commercial deployment on adsorption-based carbon capture

This section details the current status of various adsorbent-based carbon capture experimental studies at different scales. These scales are generally categorized into bench, pilot and commercial scale.

### 4.1. Bench-scale experimental studies for carbon capture

#### 4.1.1. Research triangle Institute (RTI) bench-scale test

The RTI's bench-scale system was commissioned by RTI International at the RTI's Energy Technology Development Facility (ETDF) located in North Carolina, USA. The RTI's bench-scale contactor evaluation unit (CEU) is a multi-stage fluidized moving-bed reactor (FMGR), which uses an adsorbent comprised of poly-ethylene mine (PEI) on silica as a support material, carrying out adsorption at 50–90 °C and TSA regeneration above 110 °C [56].

Experimental studies using this test facility included verification of key parameters that affect the efficiency of the solid sorbent-based CO<sub>2</sub> capture process when implemented on coal-fired power plants, natural gas combined cycle (NGCC) power plants and cement plants. The bench-scale test unit can capture 0.15 tCO<sub>2</sub>/day. Test campaigns were carried out to assess the performance of the adsorbent-based PCC bench-scale system using simulated flue gas (flowrate varied from 300 to 900 SLPM) from coal-fired power plant with 15 vol% CO<sub>2</sub> concentration. The BsCEU was able to maintain 90% CO<sub>2</sub> capture over a long period by adjusting the solid circulation rate). During the test campaign, it was observed that as the adsorption temperature increased, the regenerator heat duty decreased.

The BsCU was implemented to treat flue gas from a cement plant at Norcem in Brevik, Norway. However, researchers found that the CO<sub>2</sub> loading capacity of the adsorbent drops 30% after 100 adsorption/regeneration cycles in the presence of 100 ppm of SO<sub>2</sub> in the flue gas, indicating the need for deep scrubbing before the capture unit [56].

#### 4.1.2. Precision combustion Inc (PCI) bench-scale test

A bench-scale PCC system was installed at the national carbon capture center (NCCC) test bay in the United States by PCI and a test campaign was carried out to assess the operability of the system [135]. The bench-scale system is a compact, low-temperature swing PCC system that utilizes high internal volume nano-sorbents (MOFs) supported on a tailorable microlith substrate for cost-effective carbon capture [136]. The sorbent bed geometry is 0.43 inner diameter (ID) × 0.44 outer diameter (OD) × 0.41 height (H) [136].

The test campaign was conducted, for 2 cycles, using a simulated flue gas flowrate of 60 L/min with a composition of 8 vol% CO<sub>2</sub>, 8.1 vol% O<sub>2</sub>, 83.9 vol% N<sub>2</sub>. Sorbent showed a stable performance throughout the test campaign with a cycle time of 27 min and capturing CO<sub>2</sub> of 0.0066 t/day [137].

#### 4.1.3. InnoSeptra, LLC bench-scale test

InnoSeptra LLC carried out a bench-scale development and test of a novel adsorption process for PCC with a capacity of 1 tCO<sub>2</sub>/day at Indian River coal-fired power plant in USA [138]. This was aimed at demonstrating the effectiveness of an innovative fixed-bed adsorption-based

CO<sub>2</sub> capture technology utilizing a combination of novel physical sorbents with low heats of sorption and novel TSA cycles [138].

The bench-scale test utilized dry flue gas (flowrates of 80 and 100 SCFM) with 10–12 mol% of CO<sub>2</sub> and about 50 ppm SO<sub>2</sub> [138]. The test campaign includes variation of adsorption temperature (25–33 °C), adsorption time and flue gas flowrate. Key findings from the test indicate that the performance of the CO<sub>2</sub> capture unit can be enhanced by accelerated bed cooling [138].

#### 4.1.4. TDA 4-bed VSA bench scale system

TDA in USA carried out experimental tests on CO<sub>2</sub> adsorption and desorption using adsorbent material consisting carbon material modified with surface functional groups in a 4-bed VSA bench scale system [139]. The bench scale system shown in Fig. 3 was used to treat flue gas (flowrate of 28 SLPM) from coal-fired power plant with a CO<sub>2</sub> concentration of 13.2 vol% [139]. The bench scale system is housed on a skid dimensioned 1.83 m length (L) × 0.61 m width (W) × 1.83 m height (H). The 4-bed VSA bench system was able to achieve 95% CO<sub>2</sub> capture and above 90 vol% CO<sub>2</sub> product purity [139]. The sorbent material maintained stable performance in the presence of 370 ppmv NO<sub>x</sub> and 50 ppmv SO<sub>x</sub> [139]. Further experimental test assessing the performance of amine functionalized resins adsorbent structure in the 4-bed VSA bench scale system will be carried out. This is under the second phase of the TDA project on a new sorbent process for transformational carbon capture process [139].

#### 4.1.5. 1-bed rapid PSA bench-scale system

The university of south Carolina (USC) designed, developed and demonstrated a bench-scale process for efficient and cost-effective separation of CO<sub>2</sub> from flue gas using PSA [140]. The bench-scale system, located at NCCC USA, utilized the 1-bed PSA column (see Fig. 4) with 0.038 m ID and 0.4572 m H to assess the performance of Zeolite 13X adsorbent to capture CO<sub>2</sub> from flue gas with a flowrate of 12 SLPM and 15 vol% CO<sub>2</sub> [140]. The experiment on the bench-scale system revealed that zeolite 13X achieved a performance of 90% CO<sub>2</sub> capture (recovery) and 95 vol% CO<sub>2</sub> purity [140] (see Fig. 5).

#### 4.1.6. VeloxoTherm™ bench-scale testing station (VTS)

The VeloxoTherm™ bench-scale testing station developed by Svante was used to assess the performance of CALF-20 MOF sorbent using flue gas from the cement plant at Larfarge's Richmond cement plant, Canada [141]. The VeloxoTherm™ process uses the rotating bed reactor,

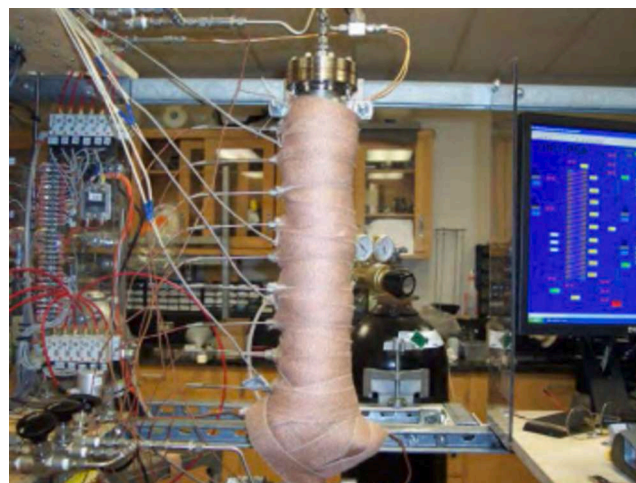


Fig. 4. Pictorial view of the 1-bed rapid PSA bench-scale system at NCCC [140].

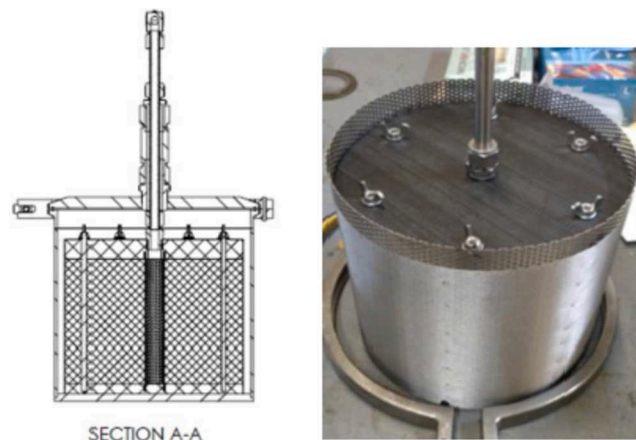


Fig. 5. Radial flow bench scale unit [151].

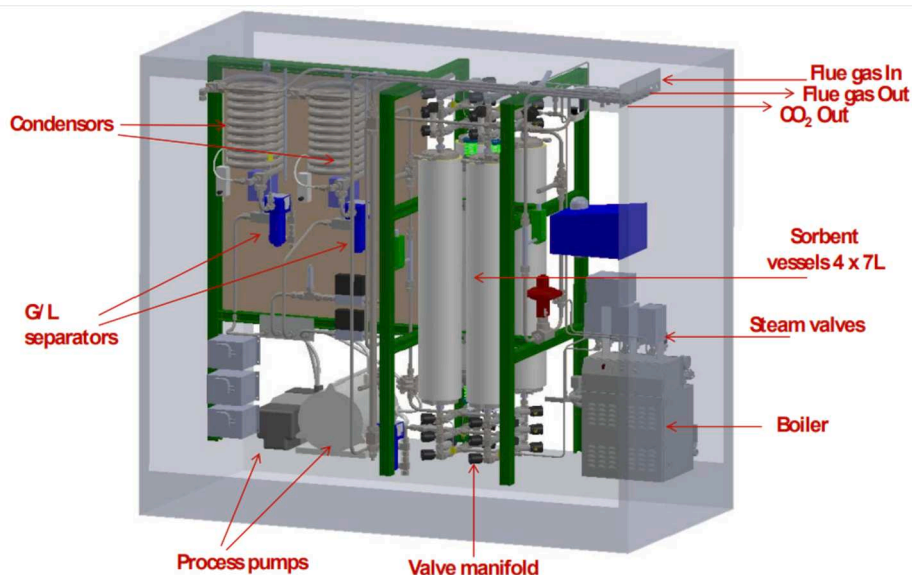


Fig. 3. Pictorial view of the 4-bed VSA bench-scale system [139].

specially created for reducing cycle time (<60 s) and energy consumption of the VTSA process [142]. Adsorption is carried out at 50 °C, although due to the exothermic reaction the bed temperature increases to 80 °C [143], and desorption occurs at 110 °C [144]. The long-term test of the VeloxoTherm™ process at the scale of 0.1 tCO<sub>2</sub>/day using CALF-20 MOF Structured Adsorbent Beds (SABs) to treat cement flue gas with a composition of 17 vol% CO<sub>2</sub>, 10 vol% O<sub>2</sub>, 5 vol% H<sub>2</sub>O, 68 vol% N<sub>2</sub> showed a very good performance [141]. The VTS contains 8 sorbent beds with the overall dimension of 0.025 m (L) × 0.025 m (W) × 1 m (H) [141].

#### 4.2. Pilot-scale experimental studies for carbon capture

##### 4.2.1. Handong dry-sorbent CO<sub>2</sub> pilot plant

The pilot Hadong dry-sorbent CO<sub>2</sub> capture system led by the Korea Electric Power Research Institute (KEPRI) is the largest adsorption project registered, with a capture capacity of 200 tCO<sub>2</sub>/day, equivalent to a 10 MW coal-fired SCPC power plant [145–147]. This pilot unit is located at the Hadong power plant in South Korea and operated from April 2014 to 2017 using a specially developed adsorbent: KEPCO2P2. The material consisted of 35 wt% K<sub>2</sub>CO<sub>3</sub>, which reacts with CO<sub>2</sub>, and 65 wt% of a support material [145] for solids management. The dry-sorbent pilot facility was able to handle 35,000 Nm<sup>3</sup>/h of flue gas with CO<sub>2</sub> concentration from 14 to 15 vol%, which consists of using a fluidized-bed type carbonator for, a fluidized-bed type regenerator, sorbent cooler and several cyclones [55]. The pilot-scale plant is housed in 34 m (L) × 15 m (W) × 59 m (H) building. The adsorption was carried out at 80 °C and regeneration of the sorbent at 200 °C [18,147].

Over 1000-hr continuous operation of the pilot plant has been performed and the results showed that the dry-sorbent gave a stable performance of 80% CO<sub>2</sub> capture rate and 95% CO<sub>2</sub> purity in the regenerator throughout the test campaign.

##### 4.2.2. TDA Pilot-scale unit at NCCC

TDA Research Inc carried out pilot-scale test on the solid-sorbent-based PCC slipstream pilot unit installed at National Carbon Capture Center (NCCC), Wheat Ridge, Colorado, USA [148]. The pilot-scale is housed on a skid with 12.2 m (L) × 9.8 m (W) × 3.5 m (H) dimension. The pilot-scale unit consists of a multiple (10 sorbent bed) fixed bed contactor with a capture capacity of 10 tCO<sub>2</sub>/day (0.5MWe). The test aim was to demonstrate the performance of alkalinized alumina (Al<sub>2</sub>O<sub>3</sub>) as adsorbent and PSA regeneration at realistic conditions [148]. Adsorption takes place at 140–150 °C and 1 bar with a flue gas flowrate of 0.6 kg/s and 12 mol% CO<sub>2</sub> (equivalent to 0.5MWe), whereas regeneration occurs at the same temperature range, with an increase of pressure to 1.11 bar using steam [54]. The test campaign showed that the pilot unit successfully maintained high purity CO<sub>2</sub> of above 90 mol% [54,149]. Future plans include the upscaling of the process to 25 MWe [54].

#### 4.3. Bench and pilot facilities for carbon capture under development

##### 4.3.1. TDA fixed-bed radial flow bench-scale unit at TCM

TDA is developing a fixed-bed radial flow bench-scale unit to test the CO<sub>2</sub> capture capacity performance of MOF adsorbents at TCM site [150]. The bench-scale unit is designed to capture CO<sub>2</sub> with a capacity of 0.04 tCO<sub>2</sub>/day using flue gas from coal-fired power plant [151]. The novel radial flow contactor shown in Fig. 5 increases the feasibility of using sorbents in fixed-beds for post-combustion capture by reducing the pressure drop through the beds and allowing for rapid sorbent regeneration [150,151]. The radial flow configuration allows for multiple use of modular beds for ease of scale-up to large scale [150,151].

#### 4.4. Summary

Although extensive research and development on adsorption-based PCC technology have been carried out, all investigations have been

mainly limited to bench and pilot scale. The largest pilot plant is the Hadong dry-sorbent CO<sub>2</sub> pilot plant in South Korea with a capture capacity of 200 tCO<sub>2</sub>/day. No commercial deployment (at or over 1 million tons CO<sub>2</sub> captured per year) has been attained for the technology. Thus, adsorption-based PCC has not been fully demonstrated.

## 5. Studies through molecular simulation

Molecular simulations are time and cost-effective computational methods that are complementary to the synthesis and experimental methods of adsorbent materials [40]. They comprise a diverse range of methods and techniques in continuous evolution. Molecular simulations can guide the experimental studies by providing insights into CO<sub>2</sub> adsorption and desorption mechanisms of the adsorbent materials [152]. When aided by data science, molecular simulation facilitates the large-scale screening of porous materials for discovering useful adsorbents [40,153]. This will aid in narrowing down the choices of promising adsorbent materials [154]. This is very key as there is a large number of available adsorbent materials and it is practically impossible to these adsorbents purely using experimental methods. Since molecular simulation provides insights into adsorbents synthesis and the CO<sub>2</sub> adsorption mechanisms, we consider it must be included in relevant reviews on the topic. This section introduces key concepts of the area of molecular simulation and presents a summary of the findings and insights given by molecular simulation studies that complement the experimental investigation of the materials mentioned in previous sections.

### 5.1. Key concepts

#### 5.1.1. Potential energy surface (PES)

The PES describes the energy of a system as a function of the position of the particles or elements. Knowing the PES enables the calculation of macro-properties of the system such as the temperature or pressure [155,156]. There are two main approaches to describing the atomic interactions and calculating the PES: (a) quantum mechanics (QM); (b) classical mechanics (also known as molecular mechanics MM), each with different levels of accuracy [155]. QM methods are capable of differentiating the atom's nuclei and electrons, whereas classical mechanics take the whole atom as a sole entity. The characteristics of these approaches are summarized in Table 8. In addition to these approaches, some semi-empirical methods that are halfway the two levels of accuracy also exist [155], e.g. ReaxFF [157]. Upon calculating PES, Common means in which it can be traversed and searched include geometry optimization (GO), molecular dynamics (MD) and Monte-Carlo (MC) simulation.

#### 5.1.2. Geometry optimization (GO)

GO, also known as energy minimization (EM), involves minimizing the energy of the atom configuration with respect to its geometry [155]. This is done by varying the bond parameters systematically to follow the potential energy curvature until a minimum is reached [155]. GO is essential to determine the proper molecular arrangement in space. After GO, An optimized structure is obtained which can be used to carry out further molecular simulations such as MD and GCMC.

#### 5.1.3. Molecular dynamics (MD) simulations

MD simulations are used to study the evolution of a system with time, usually carried out with MM. In MD simulation, the PES is explored by solving Newton's laws of motion for the system. The evolution of the system through time is usually investigated in femtoseconds (10<sup>-15</sup> secs) scale [40]. This enables the examination of kinetic processes [171]. Non-equilibrium conditions analysed with MD enables the evaluation of the rate of adsorption and diffusion properties of adsorbents [40]. Insight from MD enables the proposal of CO<sub>2</sub> diffusion mechanism through the adsorbent materials [40]. An important disadvantage of the MD

approach is timescale. It is challenging to simulate a system for more than 1–10 ns, so it is hard to contrast with experimental data [155]. Due to computational power limitations, it is not practical to simulate a real adsorption process, which takes at least several minutes [172].

#### 5.1.4. Monte Carlo (MC) simulations

MC simulations search for local minimums in the PES by sampling different system configurations. These configurations are generated based on random changes in the particle position according to pre-defined rules [155]. Grand Canonical Monte Carlo (GCMC) molecular simulation is one of the most common methods for investigating adsorption and separation in crystalline porous materials [40]. GCMC can provide information regarding the gas uptake and selectivity of the material at different temperatures and pressures, which can be used to obtain the gas adsorption isotherms in various adsorbents [40,153,173,174]. The isotherms obtained can be adopted for the mathematical model development of adsorption based PCC process.

#### 5.2. Molecular simulation studies of CO<sub>2</sub> capture on zeolites

Experimental calorimetric and volumetric adsorption techniques that provide information regarding the composition and general structure of the zeolites cannot differentiate between different types of cation sites. Other techniques such as X-ray crystallography and neutron diffraction, used to characterize the zeolite structure, fail to provide information of the adsorption energy [175]. Computational studies tackle these shortages by providing information of the interaction energy and its components based on the structure of the adsorbent and the adsorbate [176].

##### 5.2.1. GO

GO calculations correspond to studies of the structure. GO using DFT calculations of the QM approach is very popular to study the topology and charges of zeolites framework. However, DFT alone is not capable of representing weak molecular interactions, such as the dispersion. It was the development of the DFT- Coupled-Cluster DFT/CC method that enabled the description of the interactions of CO<sub>2</sub> molecules with various alkali-metal exchanged zeolites [175,177].

For example, in the work of Zukal et al [205], DFT/CC calculations revealed that there are three main factors influencing the CO<sub>2</sub> adsorption enthalpy: 1) The coordination of the cation in the framework, 2) the existence of a “dual cation site” and 3) the effect of the dispersion interaction between the adsorbent and the adsorbate (~20 kJ/mol). The highest interaction energies of the adsorption corresponded to “dual cation sites”, where a CO<sub>2</sub> molecule is bridged between two alkali metal cations [177]. Other studies found that dispersion interactions play a key role in adsorption, accounting for about 50% of the interaction energy [204,205].

##### 5.2.2. MD simulation

MD simulations has been used for screening different zeolite structures, based on the diffusivity of the gas on the adsorbent. Studies showed that NaX (Si/Al ratio 1.18) and NaY (Si/Al ratio 2.56) zeolites are the best CO<sub>2</sub> adsorbent options [154]. the good performance was attributed to the electrostatic interactions of the CO<sub>2</sub> and to the high permeability derived from the large open pore structure and their high degree of correlation [154]. The predicted permeation selectivity of NaY membranes for CO<sub>2</sub>/N<sub>2</sub> agreed with previous experimental results [178]

##### 5.2.3. GCMC simulation

Insights obtained from GCMC simulations show that NaY zeolites exhibit a higher maximum adsorption capacity than NaX zeolites, attributed to the volume effect of Na cations in the zeolite framework. Researchers also observed that the available volume for packing the gas molecules becomes more important at higher pressures [173]. Studies using zeolite 13X showed that the presence of moisture can hinder CO<sub>2</sub>

capture performance due to the reduced accessible pore volume and the shift from heterogeneous adsorption across 3 sites to competitive adsorption at up to a relative humidity of 15% [172].

In general, molecular simulation studies of CO<sub>2</sub> adsorption in zeolites has corroborated the importance of the cationic charge distribution. It is the position of the cations which induces heterogeneity of the framework, and creates electric field gradients. Quadrupole molecules, such as CO<sub>2</sub>, are strongly adsorbed in these gradients, which can be reflected as a high selectivity [172]. Interestingly few simulations of zeolites report chemisorption of CO<sub>2</sub>, possibly due to the temperature and pressure considered in the simulations, as well as the assumption of a rigid framework.

#### 5.3. Molecular simulation studies of CO<sub>2</sub> capture on CMs

Unlike MOFs and zeolites, CMs do not possess a crystalline structure. Their pore size distribution and morphology depends on the synthesis procedure and precursor material, as mentioned in section 4.2. Due to their complex structure, experimental measurements from X-ray and neutron diffraction are not able to provide their structure [179]. From a computational chemistry perspective, it is then imperative to first create a realistic structural model of the CM before studying its adsorption capacity.

In general, CMs can be modelled in computational studies as independent, non-interconnecting slit-shaped pores [174], sometimes with smooth and homogeneous walls [180]. The simplest structure representation is the idealized carbon slit-shaped pore, which is in agreement with experimental measurements that suggest the predominance of slit-shaped pores in the region of 0.4 to 1.5 nm [105]. It must be noted however, that this model is oversimplified and does not account for the pore connectivity nor the highly disordered pore structure of many CMs [179].

The “dumbbell” shape model was proposed to improve pore representation [179]. In this modification of the idealized slit pore model, a constriction is added to the pore channel, which then resemble a “dumbbell” shape. It enhances pure CO<sub>2</sub> adsorption results, explained by the stronger adsorbate-adsorbent interaction energy caused by the restriction. Widening the pore size increases the number of CO<sub>2</sub> molecules the structure can accommodate. At high pressures, the pore accessible volume governs the CO<sub>2</sub> loading, explaining the CMs observed experimentally [179].

##### 5.3.1. GO

Another approach to studying the behaviour of CO<sub>2</sub> on the surface of CMs is the use of DFT calculations. However, in this case, the GO of the structure is not the main aim. Instead, the energy of adsorption can be calculated for a fragment of the CMs structure when CO<sub>2</sub> is positioned at different locations near fragment. This approach gives insights into the role of functionalised groups in the CMs surface. For example, N<sub>2</sub> and O<sub>2</sub> co-doped porous coal-derived carbons (NOCKs) have a higher adsorption capacity than adsorbents with only O-modifications.

Wang et al [130] reported an adsorption capacity of 4.46 mmol/g at 25 °C and 1 bar in contrast with 3.85 mmol/g capacity of non-modified coal precursor [114]. Another insight from this study was that despite the doping, the pore structure (~1 nm in diameter) has a greater influence in the adsorption capacity than the N and O content [114].

##### 5.3.2. MD simulations

Moliner et al. [181] carried out a MD simulation study to assess the effect of temperature, pressure and pore width on the adsorption of an equi-molar CO<sub>2</sub>/N<sub>2</sub> mixture on a natural-based microporous CM using LAMMPS MD package via classical mechanics approach. The study revealed that the CO<sub>2</sub> adsorption capacity increased at a higher pressure and low temperature. However, the CO<sub>2</sub> adsorption capacity is slightly lowered as pore size is increased, the position of adsorption peaks are not affected by these factors.

MD studies of the separation of a  $\text{CO}_2/\text{CH}_4$  mixture with graphite at high pressure (40 bar), best fit for pre-combustion capture, showed that charged defects on the surface of the adsorbent could be used to enhance the separation [182].

### 5.3.3. GCMC simulations

GCMC simulation studies of CMs (e.g. ACs) reveal that  $\text{CO}_2$  adsorption capacity increases when adsorbent surface has a higher concentration of oxygen atoms. Disordered surfaces also show enhanced adsorption in contrast with homogeneous graphitic surfaces [180].

GCMC simulation studies show that the gas-solid interactions are extremely strong in micropores, e.g.  $< 1$  nm, because of the overlapping potentials of opposing walls and the single energy minimum located at the centre of the pore [108]. Furthermore, for even smaller pores, the repulsive interaction of the opposite walls starts to interfere, leading to a reduced attraction of the gases [174]. On the other hand, for wide enough pores, the wall attraction is almost negligible and the fluid density is closer to the bulk one.

### 5.4. Molecular simulation studies of $\text{CO}_2$ capture on MOFs

Searching for adequate MOFs for  $\text{CO}_2$  capture can be very challenging due to a large number of possible combinations of the organic “linker” molecules and inorganic “secondary building units. For a thorough description of different types of MOFs, the reader can refer to [183]. Molecular simulations can provide insights of the adsorption process and explore scenarios that cannot be investigated experimentally [184]. Moreover, new and hypothetical MOFs can be easily screened using molecular simulation even before they are synthesized [185].

#### 5.4.1. GO

DFT studies have been used to study the interaction between the quadrupole moment of the  $\text{CO}_2$  and the open metal sites in the MOFs [183]. However, DFT calculations are usually applied to obtain the partial charges of the MOF framework and for optimizing the geometry of the structure in order to optimize force field parameters [162,165]. Nevertheless, DFT has deficiencies when used to model dispersion interactions of the system. Other methods can model weakly bonded systems, as the Møller-Plesset (MP2), but at a much higher computational cost [183]. The charge equilibration method has also been used to calculate the MOF framework partial charges, with an increase in speed of ~50% [185].

#### 5.4.2. MD simulations

MD simulations have been used to compute the self-diffusivity and the corrected diffusivity of  $\text{CO}_2$ . MD studies on the MIL-47(V) MOF showed that at low loading, the  $\text{CO}_2$  adsorption close to the pore wall is mainly due to its interaction with the carboxylate group and the adsorbate molecules sit preferentially in the centre of the pore at higher pressure as a consequence of their strong self-interaction [186]. On the other hand, simulations on MIL-53(Cr) showed that the  $\text{CO}_2$  molecules align themselves along the direction of the tunnel, parallel to each other. This led to a double interaction with the hydroxyl groups present at the pore wall [187].

#### 5.4.3. GCMC simulations

GCMC studies have shown that the electrostatic interactions between the  $\text{CO}_2$  molecules are essential for predicting the inflection and steps in the adsorption isotherms in MOFs [188]. Yazaydin et al [185] proposed a combined experimental and modelling methodology to screen for promising MOFs [185]. They combined experimental data with GCMC simulations using the electrostatic interactions model Lennard-Jones (LJ) and different FFs parameters. The partial charges of the MOFs structures were derived from DFT calculations [185]. MOF structures and the  $\text{CO}_2$  molecules are considered to be rigid. This approach for

MOFs screening showed a good agreement with the experimental  $\text{CO}_2$  uptake. They observed that the MOFs M/DOBDC, HKUST-1, UMCM-150 and UMCM-150(N)<sub>2</sub> have a particularly good  $\text{CO}_2$  uptake. They attributed it to the open metal sites density, measured either per unit of surface area or per unit of free volume material [185].

A GCMC systematic computational study comparing Mg-MOF-74, CUBTC and zeolite 13X showed that Mg-MOF-74 is a promising material for VTSA processes, with better tolerance to impurities than zeolite 13X [189]. The combination of GCMC simulations with macroscopic PSA adsorption has recently been developed as a general evaluation metric for rapid screening of adsorbents [190]. A similar approach including molecular simulation process optimization and machine learning models also showed MOFs were promising materials in VSA settings [191].

### 5.5. Molecular simulation studies of $\text{CO}_2$ capture on HTs

The characterization of HTs, which are anionic clay minerals, is often problematic due to their polymorphic nature and the variability of their composition [171,192]. Experimental data from techniques such as X-ray diffraction have a limited resolution due to the structural disorder and small particle size [193]. Molecular simulations can provide some insights out of reach of experimental techniques.

#### 5.5.1. GO

The complexity and size of HT structures usually rule out the use of quantum mechanics approach except to understand the interactions between small compounds and reactive groups on the clay sheets and to analyse small clusters with DFT [199,223]. For example, DFT calculations of the fresh structure [194] and metallic oxides were used to elucidate the calcination process and the top-tactic transformation of Mg-Al LDH [195]. The results showed that at 330 °C, the decomposition of the  $\text{CO}_3^{2-}$  into  $\text{CO}_2$  and residual  $\text{O}_2$  occurs via a monodentate intermediate, thermodynamically favoured over a bidentate. This means that only one of the oxygen atoms of the  $\text{CO}_3^{2-}$  attaches to the cationic layer. In consequence, a hydroxyl  $\text{OH}^-$  of the layer detaches and forms a water molecule. It was only after the water evaporated that the  $\text{CO}_2$  molecule also detached from the structure. When heated at 450 °C, the structure of the HT framework is maintained in the cationic layer direction, however, there is a significant migration of the cations in the c-axis, perpendicular to the layers. Al atoms displayed a much lower mobility than the Mg atoms, attributed to the stronger electrostatic interaction between the  $\text{Al}^{3+}$  and the  $\text{O}^{2-}$  and  $\text{OH}^-$ .

#### 5.5.2. MD simulations

Initial attempts to create FFs capable of modelling clay minerals showed that hydrated clays are very sensitive to the model used to represent the water molecules, since they must reproduce properties for both bulk water and the interacting energies of the interlayer spacing and hydration energies [196]. A key work for achieving the computational representation of clays was the development of a general FF for clay materials by Cygan, Liang and Kalinichev referred to as CLAYFF [158]. MD simulations with CLAYFF to elucidate the thermal decomposition of the structure of an Mg-Al-Cl structure showed that at 926.85 °C the HT had turned into periclase, returning to an amorphous oxide structure at 1,426.85 °C [197]. Other MD studies using CLAYFF and Mg-Al-Cl HT suggest that water molecules create an extensive H bond network, which changes the orientation of the interlayer  $\text{CO}_3^{2-}$  and increases the diffusivity of  $\text{CO}_2$  in the adsorbent [198]. Studies of Ni-Al LDH showed that hydrated structures had a larger inter layer spacing, which resulted in a decrease of the electrostatic interaction between the adjacent sheets. In general, results suggest that larger atomic charges and smaller inter atomic distances result in larger binding energies [199].

### 5.5.3. GCMC simulations

GCMC simulations for static adsorption analysis with CLAYFF in Mg-Al-Cl structure showed there is no significant difference in the adsorption capacity of structures with altered Mg/Al ratio. The adsorption process showed a type II isotherm, which indicates multilayer adsorption [197]. Other studies using the consistent-valence force field (CVFF) studied the structural transition in a thermal gradient. They showed a discrepancy between the experimental and computed diffusivities. Researchers attributed this to two main factors. 1) during synthesis, aggregates create a polycrystalline material, whereas atomic computational models only consider a single crystal. As a result, diffusion takes place in the inter-particle regions, rather than in the interlayer space as expected in a single crystal.

Second, the computational method used for calculating the diffusivities is an unsteady state method, whereas experimental techniques are steady-state and equilibrium techniques [200].

## 6. Process modelling/simulation and techno-economic analysis of adsorption-based carbon capture

Model development involves the use of coupled partial differential equations to represent the flow field, mass and energy balances within columns to predict the behaviour of the adsorption system [15,201,202]. After model development, the model is validated with experimental data before it can be used for further process analysis. This section focuses on research carried out on modelling and simulation of adsorption-based PCC process using a fixed-bed or a fluidized bed column.

### 6.1. Process modelling and simulation for the fixed-bed adsorption column

#### 6.1.1. Current status of modelling of a fixed-bed adsorption column

Utilization of the fixed-bed column for the adsorption-based PCC process is very popular due to its advantages of simplicity of implementation for either PSA/VSA or TSA and low utility and maintenance cost especially for PSA process type [201]. In the fixed-bed column, steady-state condition never exists during adsorption [203]. Hence, mathematical models of the fixed-bed adsorption column are generally expressed in dynamic state.

For the fixed-bed column, the dynamic behaviour is generally classified based on 1) the nature of the relationship between the gas species and the solid adsorbent at equilibrium and 2) the complexity of the mathematical model necessary to describe the adsorption mass transfer mechanism [8,15]. The nature of the gas-solid equilibrium can be represented with equilibrium isotherms such as Langmuir, Freundlich and Toth. Different models exist to describe the mass transfer mechanism and are generally classified into the local equilibrium model and mass transfer resistance model [201]. The local equilibrium model is based on the assumption of negligible effect of the mass transfer resistances. In contrast, the mass transfer resistance models take into account the several resistances that hinder the transfer of molecules from the bulk gas phase to an adsorption site on the internal surface of the adsorbent particle. The potential resistances include external film resistance and intra-particle diffusional resistances, macropore diffusional resistances and micropore diffusional resistance [15]. The dominance of any one of these potential resistances is dependent on the specific system conditions. It should be noted that more than one of the resistances to mass transfer could be dominant. Rigorous mathematical models can be used to express the dominant resistances to mass transfer, which will accurately predict the behaviour of the fixed-bed adsorption column. However, the complexity associated with the rigorous mathematical model reduces their practical applicability. Hence, simpler models such as linear driving force (LDF) approximations are desirable. In these approximations, the model practical applicability is increased without reducing its accuracy. This is sufficient for representing physical adsorption (physisorption). However, for the chemical adsorption, the

model also has to take into account the surface reaction mechanism. The gas-solid reaction kinetic model are generally categorized into model-fitting kinetic reaction models, model-free kinetic reaction models and generalised kinetic models. With model-fitting kinetic models being the simplest models and generalised kinetic models being more complicated to implement. Details of the gas-solid reaction kinetic model can be found in [204]. Other assumptions generally made for fixed-bed column models includes plug flow pattern or axially dispersed plug flow pattern, negligible radial variation in temperature and concentration, ideal gas behaviour, negligible heat transfer between gas and solid adsorbent and negligible pressure drop across the bed [8,15].

#### 6.1.2. Studies of fixed-bed adsorption-through modelling and simulation

Various studies on the model development and simulation of the solid-sorbent-based PCC process have been carried out as shown in Table 9. Most of these studies are focused on TSA and PSA/VSA cycles. An extensive literature review on the modelling and simulation of the fixed-bed column has been carried out by Shafeeyan et al. [15] and Ben-Mansour et al. [8]. The majority of these studies adopted a simpler model (LDF approximation method) to represent the mass transfer mechanism within the adsorbent particles.

Regarding model validation, most of the studies have validated their models using experimental data from lab-scale tests. Few models have been validated using experimental data from pilot-scale demonstrations [64,67,205]. For example, Wang et al. [205] carried out a model validation of VSA, TSA and VTSA by comparing the predicted CO<sub>2</sub> recovery, CO<sub>2</sub> purity and productivity with their respective experimental data. The model predictions showed good agreement with their respective experimental data, with an approximate error percentage of less than 10%, showing that the model is accurate and reliable. However, further pilot-scale validation is required to verify the diffusion mechanism, especially for newly developed novel adsorbent materials.

Recent studies based on modelling and simulation of the fixed-bed adsorption analysed several aspects of the adsorption process. They include assessments/screening of various adsorbents and process optimization based on several key performance indicators (CO<sub>2</sub> purity, CO<sub>2</sub> recovery, energy performance and productivity) [206–212], economic analysis [208,213], comparison of several PSA/VSA/TSA cycle configurations [62,208,211,214] and assessment of novel fixed-bed column configurations [106,215]. The models in these studies were developed using commercially available software such as Matlab®, Fortran®, gPROMS® and Aspen Adsorption®. Key findings from revealed adoption of novel cycle and column configurations has significant impact on reducing its energy consumption and invariably the CO<sub>2</sub> capture cost.

Simulation analysis carried out by Riboldi et al. [216] on the integration of an advanced supercritical (ASC) pulverized coal-fired power plant with fixed-bed VSA adsorption process with zeolite adsorbent material showed that the power plant efficiency is lower (28%) compared to when ASC power plant is attached to solvent-based PCC process (33.4%). The simulation study also showed that a large footprint is required for the fixed-bed VSA adsorption process to handle the entire flue gas flowrate from the power plant, which makes it on uncompetitive compared to the solvent-based PCC process. Thus, modelling and simulation of a novel VSA cycle configuration integrated with power plant is essential to understand its technical and economic impact on the power plant.

### 6.2. Process modelling and simulation for Fluidized-bed adsorption column

#### 6.2.1. Current status on modelling of a fluidized-bed adsorption column

The unique qualities of the fluidized bed adsorption column, such as faster heat transfer and high compactness compared to fixed-bed column, have made them the most attractive for TSA-based PCC, especially when using chemical adsorbents [222]. Hence, understanding the mechanism of the fluidized bed column, through modelling and



Table 9

Summary of the Fixed-bed adsorption column modelling studies for CO<sub>2</sub> capture.

s/n	Authors	Application	Regeneration	Gas –solid equilibrium relationship	Mass transfer	Steady-state/ Dynamic	Validation data	Software
1	Zhao et al. [210]	A comprehensive performance evaluation of TSA for PCC	TSA	1. Activated carbon: Toth Isotherm 2. Zeolite 13X: Extended Sips 3. Zeolite NaUSY: Dual-site Langmuir 4. Mg-MOF-74: Dual-site Langmuir	N/A	Dynamic	N/A	Matlab® (ode15s)
2	Plaza et al. [12]	Evaluation of a novel multibed heat-integrated VTSA PCC process	VTSA	Ideal adsorption Solution	LDF	Dynamic	Experimental data obtained from Plaza et al. [217–219]	Aspen Adsorption® V8.0
3	Wilkins and Rajendran [220]	Measurement of competitive CO <sub>2</sub> and N <sub>2</sub> adsorption on Zeolite 13X for PCC	VSA	Dual-site Langmuir	LDF	Dynamic	Experimental data	Matlab® (ode15s)
4	Ben-Mansour et al. [209]	Evaluation of Mg-MOF-74 for PCC through PSA	PSA	Extended Langmuir	LDF	Dynamic	Complete experimental data set for CO <sub>2</sub> capture using zeolite M 13X	Matlab®
5	Joss et al. [207]	Rational design of temperature swing TSA PCC	TSA	Binary Sips	LDF	Dynamic	Experimental data from Marx et al. [221]	Fortran®

simulation, for proper process design and optimization is paramount.

The mechanism of the fluidized-bed adsorption column is classified based on the complexity of the mathematical model required to describe (a) gas-solid interaction and (b) the hydrodynamics. The gas-solid interaction models are generally classified into the equilibrium model and the kinetic model. Details of the model classification have been addressed in section 7.1.1.

Model representation of the hydrodynamic phenomena with the fluidized bed adsorption column is quite complicated as the hydrodynamics vary significantly between the fluidization regimes [223]. Computational fluid dynamics (CFD) simulators are capable of modelling the full hydrodynamics within the fluidized bed column [223,224]. However, the extreme computational complications and time demand to reach solution have limited its use for process design and optimization [223]. Few hydrodynamic models have been developed, which capture the important hydrodynamic characteristics of the system, while remaining computationally simple [223]. These models include Kunii and Levenspiel model [17,20], Kato and Wen [223,225] and de Souza-Santos [223,226,227].

### 6.2.2. Studies of fluidized-bed adsorption through modelling and simulation

Modelling and simulation studies on the fluidized bed adsorption column are gaining much attention. These studies include the modelling (steady state [223] and dynamic [228]) of bubbling fluidized bed (BFB) adsorption column for CO<sub>2</sub> capture. Kunii and Levenspiel model represent the hydrodynamics for BFB, while a model-fitting reaction kinetic model represents the gas-solid reaction mechanism. Another modelling study on the BFB adsorption column assessed the novel configuration (multi-stage) and heat exchange between the columns [229]. However, these models were not validated. Thus, the fidelity of the models is yet to be verified.

Modelling and simulation studies on the circulating fluidized bed (CFB) adsorption column include the assessment of the different configurations [230], performance evaluation of the adsorbent material based on key process performance indicators [5] and assessment of heat recovery [224]. These models are limited to steady-state. Only the CFB adsorption column model carried out by Park et al. [224] was validated by experimental data obtained in the Korea Research Institute of Chemical Technology (KRICT) pilot plant. It should be mentioned that only dataset from the adsorber operation was obtained. Thus, only the model for adsorber was validated.

### 6.3. Techno-economic analysis (TEA) of adsorption-based PCC process

The growing interest in climate change mitigation pathways calls for a reliable techno-economic analysis (TEA) of adsorption-based PCC process. TEA assesses the economic viability of the adsorption-based PCC technology based on the efficient use of the adsorbent material in a contactor type. Samanta et al. [13] carried out a review of previous studies on TEA of adsorption-based PCC systems using various contactor types. It highlighted the challenge of limited process design and economic analysis due to the lack of adequate data on adsorbent materials in various contactor configurations. Recently, a few studies on TEA of adsorption-based PCC have been carried out.

Khurana and Farooq [231] carried out a performance assessment of 4-step and 6-step VSA using zeolite 13X and UTSA-16 based on levelized cost of electricity (LCOE). Results showed that UTSA-16 has a lower LCOE than zeolite 13X for both 4-step and 6-step cycles [231]. The study also revealed that the lowest achievable LCOE for 4-step and 6-step cycle are 2.6% and 11.8% lower than the minimum LCOE using UTSA16 for 4-step and 6-step cycles respectively [231]. Sensitivity analysis revealed that the LCOE is most sensitive to vacuum pump efficiency and annualization factor [231].

Danaci et al. [213] assessed the performance of 25 adsorbents using a 3-step VSA for different CO<sub>2</sub> capture scenarios (NGCC, pulverized coal power plant, cement plant and steel mill) based on CO<sub>2</sub> purity, CO<sub>2</sub> recovery and annualized capture cost. The study utilized a simplified VSA model that does not consider the column dynamics to carry out the analysis [213]. Results from the analysis showed that UTSA-16 gave the best performance. However, the performance were below the 90% targets in term of purity and recovery (69 mol% CO<sub>2</sub> purity and 81 mol% CO<sub>2</sub> recovery) [213]. The study revealed that a large footprint (at least 18000 m<sup>2</sup>) is required for NGCC scenario, which imposes a limitation on retrofitting possibilities [213]. Also, the capture cost is generally high compared to the use of amine-based solvents [213]. The study also highlighted that optimizing the adsorbent properties in terms of CO<sub>2</sub>/N<sub>2</sub> selectivity and heat of adsorption has a great impact on increasing CO<sub>2</sub> purity and recovery, and reducing CO<sub>2</sub> capture cost gives the best performance [213].

Subraveti et al. [232] carried out a techno-economic assessment of a 4-step VSA process for PCC from steam-methane reformer dried flue gas containing 20 mol% CO<sub>2</sub>. A comprehensive techno-economic optimization model was developed, which takes into account VSA process model, vacuum pump performance, scale-up, process scheduling and a

thorough cost model [232]. In the study, 3 adsorbents (2 MOFs: UTSA-16, IISERP MOF2 and 1 zeolite 13X) were optimized to minimize the CO<sub>2</sub> capture cost [232]. Results showed that the 4-step VSA process with IISERP MOF2 outperforms the other 2 adsorbents with the lowest CO<sub>2</sub> capture cost of €33.6/tonne CO<sub>2</sub> and an associated CO<sub>2</sub> avoided cost of €73/tonne CO<sub>2</sub> [232]. However, the CO<sub>2</sub> avoided cost obtained for VSA is higher than that of the baseline MEA-based absorption process by 9.6% [232].

Subraveti et al. [233] carried out an integrated techno-economic optimization of a 2 single-stage PVSA cycle for PCC to determine the lowest possible cost of CO<sub>2</sub> avoided for different industrial flue gas CO<sub>2</sub> compositions and flowrates by optimizing the adsorbent properties and process design variables simultaneously. Key findings of the study revealed that the CO<sub>2</sub> composition in flue gas significantly impacts the cost limits of PVSA. The 4-step PVSA cycle and 6-step PVSA cycle has 8% and 35% lower cost compared to MEA-based CO<sub>2</sub> capture respectively for CO<sub>2</sub> compositions  $\geq 7.5\%$  over a range of flue gas flowrates.

Jung et al. [234] presented a techno-economic assessment method to evaluate 4 adsorption-based PCC process, which includes fluidized-bed, moving-bed, fixed-bed and rapid TSA configuration based on rigorous simulation and experimental isotherm/kinetics of amine-functionalized solid adsorbents [234]. The performance of each adsorption process was evaluated based on the cost of electricity, CO<sub>2</sub> capture and CO<sub>2</sub> avoidance [234]. TEA results revealed that the fixed-bed adsorption process gave the lowest CO<sub>2</sub> capture cost of \$48.1/tonne CO<sub>2</sub>. Amongst the configurations evaluated, only the CO<sub>2</sub> capture cost of fluidized-bed adsorption process (\$75.2/tonne CO<sub>2</sub>) is higher than the MEA-based CO<sub>2</sub> capture process with 30 wt% (\$62.8/tonne CO<sub>2</sub>) [234].

## 7. Knowledge gaps and future directions

### 7.1. Achievements so far

#### 7.1.1. Lab synthesis and characterization of adsorbent materials for PCC

Several approaches on the synthesis of different adsorbents for PCC have been extensively explored in the Lab scale. The adsorbent material properties are greatly influenced by the raw materials composition and synthesis approaches. In most cases, the composition of the material can be modified by selecting different reactants, as in the case of zeolites, MOFs and HTs [111,131,140]. On the other hand, the adsorptive characteristics of the CMs depend more on the precursor, which in most cases cannot be fine-tuned unless chemically modified [45]. The adoption of cost-efficient synthesis approaches is key to the development of a low cost, environmentally friendly adsorbent with large surface area. Promising cost-efficient synthesis approaches have been identified in terms of cost, environmental impact, energy consumption, process speed. For example, Microwave heating and Ultrasonic methods have been identified as a promising synthesis approach for zeolites, MOFs and HTs in terms of the above parameters. For the synthesis of CMs, the molten salt carbonization has shown a lot of promises.

For each promising synthesis approach, the adsorbents have demonstrated high CO<sub>2</sub> capacity, with good CO<sub>2</sub>/N<sub>2</sub> selectivity and fairly good cyclic stability under humid conditions, which reflects the PCC conditions. For HT, The calcination process is of great importance to increase its surface area and adsorption capacity [130].

Adsorption studies have shed light on the behaviour of the CO<sub>2</sub> molecules in contact with the solid material. First, the size of the pores must be enough to allow the entrance of the molecules. Second, modifying the components of the adsorbent structure can further increase the adsorption capacity, depending on the interaction of their electric field and the quadrupole moment of the CO<sub>2</sub>. Weaker electric fields lead to a weaker affinity to CO<sub>2</sub> and lower selectivity, and ease the regeneration process, as seen with CMs [8]. On the other hand, a strong electric field can be a disadvantage in the presence of polar gases, especially water [8]. This can hinder the adsorption capacity of the adsorbent as in the case of zeolites and MOFs. From the materials discussed, MOFs and HTs

are among the most promising.

#### 7.1.2. Experimental studies on adsorption-based PCC process

Major progress has been made for adsorption-based PCC process through bench and pilot scale experimental studies. These studies explored various contactor configuration types (fixed bed and fluidized bed) as well as several regeneration types (PSA, TSA, VSA, VTSA) for adsorption-based PCC process. Currently, the largest pilot-scale plant in the world is located at Hadong power plant, South Korea with a capture capacity of 200tCO<sub>2</sub>/day. The adsorption-based PCC process experimental studies using several solid adsorbents showed promising results. This has given the basis for further experimental work at the pilot-scale to advance its TRL.

#### 7.1.3. Molecular simulations

Molecular simulations has contributed a lot to understanding the relationship between the structure and property for each adsorbents. The molecular simulation technique have been able to give clarifications on the underlying adsorption mechanisms involved at the microscopic scale through MD and GCMC, which complements the experimental studies. Significant advances has been made in the application of molecular simulation techniques for screening novel adsorbents for post-combustion CO<sub>2</sub> capture process.

#### 7.1.4. Process modelling and simulation

The advancement in the computational capacity of available modelling and simulation tools has enabled the detailed model development and simulation studies of adsorption-based PCC process (especially fixed-bed) by various research groups [235–240]. Simple approximations were adopted to represent the mass transfer mechanism for fixed-bed and hydrodynamics for fluidized-bed, which reduces the complexity of the models without reducing the accuracy of the model when validated against experimental data [64,67,205]. Significant progress in screening of various novel adsorbents based on the key performance indicators of the adsorption-based PCC process through process analysis and optimization has been attained using model developed [206–212]. Also, several novel cycles and column design have been explored through process modelling and simulation to achieve cost-efficient adsorption-based PCC process [66,233].

## 7.2. Challenges ahead

### 7.2.1. Lab synthesis and characterization of adsorbent materials for PCC

Despite the advanced investigations of promising adsorbent synthesis approaches, these investigations have been carried out at lab scale. The large-scale deployment of these promising synthesis approaches has been difficult to attain due to the issue with a scalability from lab scale to large scale at a reduced cost and environmental issues (especially for MOFs).

For the other adsorbents such as zeolites, CMs, another challenge lies in the variability of raw materials, resulting in inconsistent adsorption characteristics. On the other hand, HTs requires further study since it greatly influences the structure of the adsorbent. Chemical modification of the adsorbents by adding functional groups or supporting materials increases adsorption capacity, but it also increases the complexity and cost of synthesis. This is why the computational approach to investigate relevant combinations of functional groups and adsorbents is complementary to experimental studies.

### 7.2.2. Experimental studies on adsorption-based PCC process

Despite progress in the experimental studies of the adsorption-based PCC process at bench and pilot scale, there is no commercial deployment of the adsorption-based PCC technology. Major challenges encountered during the bench and pilot-scale test that have limited its commercial deployment includes;

- 1) The continuous large-scale production of the adsorbent.

Specialized adsorbents for PCC can be difficult and expensive to produce. 2) Heat management and temperature control. Due to the exothermic nature of adsorption, it is imperative to control the temperature of the adsorption column to prevent the loss of adsorption capacity. 3) Achieving solids handling and circulation control. The manipulation of the adsorbents in powder form is challenging and can affect the pressure drop in the column. Residues management of the spent material requires attention as well. 4) the possible decrease of the process efficiency due to the presence of other pollutants. Some adsorbents are less tolerant towards common pollutants in flue gases, especially water. Due to its polar nature, the pollutants highly interact with the electric field of the adsorbents framework, reducing the number of active sites for CO<sub>2</sub> adsorption.

### 7.2.3. Molecular simulation

Most of the molecular simulation studies lack the representation of chemical reactions, this means that CO<sub>2</sub> chemisorption, which is relevant at higher temperatures or in cases where a reactive functional group is added (e.g. PEI) is not represented.

Additionally, simulations tend to use pure crystalline structures and assume they are rigid in order to accommodate periodic boundary conditions. However, it is extremely difficult to synthesize defect-free crystal structures without interfaces between grain boundaries. Under reactive environments, the structure may change. Care must be taken when extrapolating the simulations results, taking into account the time restrictions of the simulations. For example, tested temperatures between 0 °C and 25 °C are not representative of realistic PCC conditions, thus results from studies at this temperature range are mainly useful for MOFs comparison. Challenges for QM simulations remain related to the computational power and the size of the simulated system.

### 7.2.4. Process modelling and simulation

Despite the extensive process modeling and simulation studies of the adsorption-based PCC, One major challenge is the utilization of the model developed for process control and real-time optimization. For appropriate and efficient process control design and implementation, the optimal operation of the adsorption-based PCC process in the face of disturbances and set-point changes is very critical especially when coupled with a power plant. The direct use of first principles adsorption-based PCC models for process control and real-time optimization are impractical due to high computational demand because of large partial differential and algebraic equations, despite the use of simpler models to represent the adsorption mechanism. Thus, it is imperative to obtain a reduced model that captures the essential dynamics of process.

## 7.3. Perspectives or potential breakthrough

### 7.3.1. Lab synthesis and characterization of adsorbent materials for PCC

The development of adsorbents with higher adsorption capacity, which are more tolerant towards pollutants is under development. Next important steps are scaling up the production and reduction of the costs. Research which looks into the working capacity of the adsorbents will be crucial to develop complete PCC units. Most of the research carried out uses in adsorption columns with 0.5–1 g of adsorbent, without regeneration. Thus, investigating heat management and solids handling becomes very difficult. Future research must take this into account.

### 7.3.2. Experimental studies on adsorption-based PCC process

A potential bypass to challenge 1 in section 8.2.2 is the use of commercially available materials, even though if their performance is not as good as tailored adsorbents. It was interesting to observe the use of K<sub>2</sub>CO<sub>3</sub> for the largest pilot plant in Hadong. The carbonation reaction rate for the K<sub>2</sub>CO<sub>3</sub> was considered too slow to be practical at large scale until recently [34]. Reactor and process design can address the challenges 2 and 3. The use of fluidized beds and waste heat are a possible solution for this the implementation of a heat integration strategy. A

possible solution to the low pressure drop and dust formation is to vary the size of the pellets or to change the design of the reactor. The MOF-Microlith project exemplifies this. Mixed matrix membranes of MOF and polymers have shown high energy-efficiencies and a smaller footprint, a direction now pursued by MOF Technologies™ [118].

### 7.3.3. Molecular simulation

Potential breakthrough on molecular simulation studies is closely related with the advancement in computational methods. The creation of new theories that allow the reduction of computational demand could make simulations more efficient, as in the case of DFT calculations.

The development of adequate FFs for each adsorbent could improve the accuracy of the models. They should account for reactive environments at pressure and temperature conditions relevant for PCC adsorption settings. On the other hand, the advent of new technologies that enhance computational power could facilitate the simulation of larger systems.

Additionally, the development of fast screening tools (such as adopting machine learning technique for molecular simulation) can enable researchers to focus efforts on relevant adsorbents. Such screening tools are mostly developed for MOFs. Similar screening tools for other materials could promote the development of adsorption-based PCC.

### 7.3.4. Process modelling and simulation

Further research on the technical performance of newly developed novel process/cycle configuration using tailored-made adsorbent materials should be investigated through process modelling and simulation. This is to discover what configuration is competitive with the solvent-based PCC process.

Another potential breakthrough is the adoption of data-driven modelling approach to obtain a reduced model that captures the essential adsorption-based PCC process dynamics. With the computational advancement in data science and artificial intelligence, various data-driven technique are available to obtain a reduced model from experimental data. Further research should explore the implementation of data-driven modelling approach to obtain reduced models for process control and real-time optimization.

## 8. Conclusion

A growing interest on research of the adsorption-based PCC has been directed towards development of new adsorbent materials and new processes. A state-of-the-art assessment of research work was carried out so far in adsorption-based PCC. This includes lab synthesis and characterization of adsorbent materials, experimental studies of the adsorption-based PCC process in bench and pilot scale, molecular simulation-based studies of adsorbents and process modelling/simulation of carbon capture processes. Currently, there is no commercial deployment of the adsorption-based PCC technology. Based on the recent developments, challenges ahead and potential breakthroughs were highlighted. More efforts in the future should be focused on the following: (1) cost-efficient large scale synthesis of adsorbents for large scale PCC application; (2) development of fast screening tools for adsorbents through molecular simulation and machine learning techniques; (3) More large-scale demonstrations of the adsorption-based PCC process using novel adsorbents with novel process configurations to reduce energy consumption as well as the cost of CO<sub>2</sub> capture. Thus, further research efforts are required to advance the adsorption-based PCC technology to large-scale commercial deployment.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

This research was financed by the National Council for Science and Technology of Mexico (CONACYT), the Grantham Centre for Sustainable Futures at the University of Sheffield and EPSRC under Grant No. EP/N024540/1 Novel Adsorbent to Integrated Energy-efficient Industrial CO<sub>2</sub> capture.

## References

- [1] IPCC. IPCC special report on the impacts of global warming of 1.5 °C - Summary for policy makers. Incheon; 2018.
- [2] Moreira D, Pires JCM. Atmospheric CO<sub>2</sub> capture by algae: Negative carbon dioxide emission path. *Bioresour Technol* 2016;215:371–9.
- [3] EPA. Climate Change Indicators: Sea level. *Clim Chang Indic*; 2016.
- [4] Akinola TE, Oko E, Wu X, Ma K, Wang M. Nonlinear model predictive control (NMPC) of the solvent-based post-combustion CO<sub>2</sub> capture process. *Energy* 2020; 213:118840.
- [5] Zhang Z, Wang T, Blunt MJ, Anthony EJ, Park A-HA, Hughes RW, et al. Advances in carbon capture, utilization and storage. *Applied Energy* 2020;278:115627.
- [6] Lou F, Zhang A, Zhang G, Ren L, Guo X, Song C. Enhanced kinetics for CO<sub>2</sub> sorption in amine-functionalized mesoporous silica nanosphere with inverted cone-shaped pore structure. *Appl Energy* 2020;264:114637.
- [7] Lawal A, Wang M, Stephenson P, Koumpouras G, Yeung H. Dynamic modelling and analysis of post-combustion CO<sub>2</sub> chemical absorption process for coal-fired power plants. *Fuel* 2010;89:2791–801.
- [8] Ben-Mansour R, Habib MA, Bamidele OE, Basha M, Qasem NAA, Peedikakka A, et al. Carbon capture by physical adsorption: Materials, experimental investigations and numerical modeling and simulations - A review. *Appl Energy* 2016;161:225–55.
- [9] Bui M, Gunawan I, Verheyen V, Artanto Y, Meuleman E, Feron P. Dynamic modeling and validation of post-combustion CO<sub>2</sub> capture plants in Australian coal-fired power stations. *Energy Procedia* 2013;37:2694–702.
- [10] IPCC. Capture of CO<sub>2</sub>. In: Metz B, Davidson O, Coninck H de, Loos A, Meyer L, editors. *IPCC Spec. Rep. Carbon Dioxide Capture Storage*, Cambridge: Intergovernmental Panel on Climate Change; 2005, p. 431.
- [11] Jiang L, Gonzalez-Diaz A, Ling-Chin J, Roskilly AP, Smallbone AJ. Post-combustion CO<sub>2</sub> capture from a natural gas combined cycle power plant using activated carbon adsorption. *Appl Energy* 2019;245:1–15.
- [12] González Plaza M, Rubiera González F. Evaluation of a novel multibed heat-integrated vacuum and temperature swing adsorption post-combustion CO<sub>2</sub> capture process 2019.
- [13] Samanta A, Zhao A, Shimizu GKH, Sarkar P, Gupta R. Post-Combustion CO<sub>2</sub> Capture Using Solid Sorbents: A Review. *Ind Eng Chem Res* 2012;51:1438–63.
- [14] Hedin N, Andersson L, Bergström L, Yan J. Adsorbents for the post-combustion capture of CO<sub>2</sub> using rapid temperature swing or vacuum swing adsorption. *Appl Energy* 2013;104:418–33.
- [15] Shafeeyan MS, Wan Daud WMA, Shamiri A. A review of mathematical modeling of fixed-bed columns for carbon dioxide adsorption. *Chem Eng Res Des* 2014;92: 961–88.
- [16] Sreenivasulu B, Sreedhar I, Suresh P, Raghavan KV. Development Trends in Porous Adsorbents for Carbon Capture. *Environ Sci Technol* 2015;49:12641–61.
- [17] Lin Y, Kong C, Zhang Q, Chen L. Metal-Organic Frameworks for Carbon Dioxide Capture and Methane Storage. *Adv Energy Mater* 2017;7.
- [18] Zhao H, Luo X, Zhang H, Sun N, Wei W, Sun Y. Carbon-based adsorbents for post-combustion capture: a review. *Greenh Gases Sci Technol* 2018;8:11–36.
- [19] Siegelman RL, Milner PJ, Kim EJ, Weston SC, Long JR. Challenges and opportunities for adsorption-based CO<sub>2</sub> capture from natural gas combined cycle emissions. *Energy Environ Sci* 2019;12:2161–73.
- [20] Mukherjee A, Okolie JA, Abdelrasoul A, Niu C, Dalai AK. Review of post-combustion carbon dioxide capture technologies using activated carbon. *J Environ Sci (China)* 2019;83:46–63.
- [21] Younas M, Rezakazemi M, Daud M, Wazir MB, Ahmad S, Ullah N, et al. Recent progress and remaining challenges in post-combustion CO<sub>2</sub> capture using metal-organic frameworks (MOFs). *Prog Energy Combust Sci* 2020;80.
- [22] Hussin F, Aroua MK. Recent trends in the development of adsorption technologies for carbon dioxide capture: A brief literature and patent reviews (2014–2018). *J Clean Prod* 2020;253:119707.
- [23] Dhoke C, Zaabout A, Cloete S, Amini S. Review on Reactor Configurations for Adsorption-Based CO<sub>2</sub> Capture. *Ind Eng Chem Res* 2021;60:3779–98.
- [24] Bhatta LKG, Subramanyam S, Chengala MD, Bhatta UM, Venkatesh K. Enhancement in CO<sub>2</sub> adsorption on hydrotalcite-based material by novel carbon support combined with K<sub>2</sub>CO<sub>3</sub> impregnation. *Ind Eng Chem Res* 2015;54: 10876–84.
- [25] Bhatta L, Subramanyam S, Chengala MD, Olivera S, Venkatesh K. Progress in hydrotalcite like compounds and metal-based oxides for CO<sub>2</sub> capture: A review. *J Clean Prod* 2015;103:171–96.
- [26] Lu X, Jin D, Wei S, Zhang M, Zhu Q, Shi X, et al. Competitive adsorption of a binary CO<sub>2</sub> – CH<sub>4</sub> mixture in nanoporous carbons: effects of edge-functionalization. *Nanoscale* 2015;7:1002–12.
- [27] Pramod CV, Uppendur K, Mohan V, Sarma DS, Dhar GM, Prasad PSS, et al. Hydrotalcite-SBA-15 composite material for efficient carbondioxide capture. *J CO<sub>2</sub> Util* 2015;12:109–15.
- [28] Zhao Y, Liu X, Han Y. Microporous carbonaceous adsorbents for CO<sub>2</sub> separation via selective adsorption. *RSC Adv* 2015;5:30310–30.
- [29] Di Biase E, Sarkisov L. Systematic development of predictive molecular models of high surface area activated carbons for adsorption applications. *Carbon N Y* 2013; 64:262–80.
- [30] Salaudeen SA, Acharya B, Dutta A. CaO-based CO<sub>2</sub> sorbents: A review on screening, enhancement, cyclic stability, regeneration and kinetics modelling. *J CO<sub>2</sub> Util* 2018;23:179–99.
- [31] Hallenbeck AP, Kitchin JR. Effects of O<sub>2</sub> and SO<sub>2</sub> on the capture capacity of a primary-amine based polymeric CO<sub>2</sub> sorbent. *Ind Eng Chem Res* 2013;52: 10788–94.
- [32] Garcés-Polo SI, Villarreal-Rocha J, Sapag K, Korili SA, Gil A. Adsorption of CO<sub>2</sub> on mixed oxides derived from hydrotalcites at several temperatures and high pressures. *Chem Eng J* 2017;332:24–32.
- [33] Choi S, Drese JH, Jones CW. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* 2009;2:796–854.
- [34] Wang Q, Luo J, Zhong Z, Borgna A. CO<sub>2</sub> capture by solid adsorbents and their applications: current status and new trends. *Energy Environ Sci* 2011;4:42–55.
- [35] Fakhroleslam M, Fatemi S. Comparative simulation study of PSA, VSA, and TSA processes for purification of methane from CO<sub>2</sub> via SAPO-34 core-shell adsorbent. *Sep Sci Technol* 2016;51:2326–38.
- [36] Ram Reddy MK, Xu ZP, Lu GQ (Max), Diniz da Costa JC. Layered Double Hydroxides for CO<sub>2</sub> Capture: Structure Evolution and Regeneration. *Ind Eng Chem Res* 2006;45:7504–9.
- [37] León M, Díaz E, Bennici S, Vega A, Ordóñez S, Auroux A. Adsorption of CO<sub>2</sub> on hydrotalcite-derived mixed oxides: sorption mechanisms and consequences for adsorption irreversibility. *Ind Eng Chem Res* 2010;49:3663–71.
- [38] Younas M, Sohail M, Leong LK, Bashir MJK, Sumathi S. Feasibility of CO<sub>2</sub> adsorption by solid adsorbents: a review on low-temperature systems. *Int J Environ Sci Technol* 2016;13:1839–60.
- [39] Cheung O, Hedin N. Zeolites and related sorbents with narrow pores for CO<sub>2</sub> separation from flue gas. *Rsc Adv* 2014;4:14480–94.
- [40] Pardakhti M, Jafari T, Tobin Z, Dutta B, Moharrer E, Shemshaki NS, et al. Trends in Solid Adsorbent Materials Development for CO<sub>2</sub> Capture. *ACS Appl Mater Interfaces* 2019;11:34533–59.
- [41] Garcés SI, Villarreal-Rocha J, Sapag K, Korili SA, Gil A. Comparative Study of the Adsorption Equilibrium of CO<sub>2</sub> on Microporous Commercial Materials at Low Pressures. *Ind Eng Chem Res* 2013;52:6785–93.
- [42] Dantas TLP, Luna FMT, Silva Jr IJ, Torres AEB, de Azevedo DCS, Rodrigues AE, et al. Modeling of the fixed-bed adsorption of carbon dioxide and a carbon dioxide - nitrogen mixture on zeolite 13X. *Brazilian J Chem Eng* 2011;28:533–44.
- [43] Kamran U, Park SJ. Chemically modified carbonaceous adsorbents for enhanced CO<sub>2</sub> capture: A review. *J Clean Prod* 2021;290:125776.
- [44] Lian Y, Deng S, Li S, Guo Z, Zhao L, Yuan X. Numerical analysis on CO<sub>2</sub> capture process of temperature swing adsorption (TSA): Optimization of reactor geometry. *Int J Greenh Gas Control* 2019;85:187–98.
- [45] Rashidi NA, Yusup S. An overview of activated carbons utilization for the post-combustion carbon dioxide capture. *J CO<sub>2</sub> Util* 2016;13:1–16.
- [46] Yaghi OM, Li G, Li H. Selective binding and removal of guests in a microporous metal-organic framework. *Nature* 1995;378:703–6.
- [47] Ding Y, Alpay E. Equilibria and kinetics of CO<sub>2</sub> adsorption on hydrotalcite adsorbent. *Chem Eng Sci* 2000;55:3461–74.
- [48] Oliveira ELG, Grande CA, Rodrigues AE. CO<sub>2</sub> sorption on hydrotalcite and alkali-modified (K and Cs) hydrotalcites at high temperatures. *Sep Purif Technol* 2008; 62:137–47.
- [49] Halabi MH, De Croon MHJM, Van Der Schaaf J, Cobden PD, Schouten JC. High capacity potassium-promoted hydrotalcite for CO<sub>2</sub> capture in H<sub>2</sub> production. *Int J Hydrogen Energy* 2012;37:4516–25.
- [50] Baskaran T, Christopher J, Sakthivel A. Progress on layered hydrotalcite (HT) materials as potential support and catalytic materials. *RSC Adv* 2015;5:98853–75.
- [51] Miguel CV, Trujillano R, Rives V, Vicente MA, Ferreira AFP, Rodrigues AE, et al. High temperature CO<sub>2</sub> sorption with gallium-substituted and promoted hydrotalcites. *Sep Purif Technol* 2014;127:202–11.
- [52] Wang Q, Wu Z, Tay HH, Chen L, Liu Y, Chang J, et al. High temperature adsorption of CO<sub>2</sub> on Mg-Al hydrotalcite: Effect of the charge compensating anions and the synthesis pH. *Catal Today* 2011;164:198–203.
- [53] Garcia-Gallastegui A, Iruretagoyena D, Gouvea V, Mokhtar M, Asiri AM, Basahel SN, et al. Graphene oxide as support for layered double hydroxides: Enhancing the CO<sub>2</sub> adsorption capacity. *Chem Mater* 2012;24:4531–9.
- [54] Elliot J, Yi F. Pilot Unit Testing at NCCC of Sorbent based CO<sub>2</sub> Capture Project # DE-FE0012870 2020.
- [55] Park YC, Jo SH, Kyung DH, Kim JY, Yi CK, Ryu CK, et al. Test operation results of the 10 MWe-scale dry-sorbent CO<sub>2</sub> capture process integrated with a real coal-fired power plant in Korea. *Energy Procedia* 2014;63:2261–5.
- [56] Nelson TO, Kataria A, Mobley P, Soukri M, Tanthana J. RTI's Solid Sorbent-Based CO<sub>2</sub> Capture Process: Technical and Economic Lessons Learned for Application in Coal-fired, NGCC, and Cement Plants. *Energy Procedia* 2017;114:2506–24.
- [57] Gollakota S, Yu M. Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO<sub>2</sub> Capture Project Information. *Technol Sheet* 2020:1–2.
- [58] Webley PA. Adsorption technology for CO<sub>2</sub> separation and capture: a perspective. *Adsorption* 2014;20:225–31.
- [59] Grande CA. Advances in Pressure Swing Adsorption for Gas Separation. *ISRN Chem Eng* 2012;2012:982934.

- [60] Riboldi L, Bolland O. Overview on Pressure Swing Adsorption (PSA) as CO<sub>2</sub> Capture Technology: State-of-the-Art. Limits and Potentials. *Energy Procedia* 2017;114:2390–400.
- [61] Abanades JC, Arias B, Lyngfelt A, Mattisson T, Wiley DE, Li H, et al. Emerging CO<sub>2</sub> capture systems. *Int J Greenh Gas Control* 2015;40:126–66.
- [62] Liu Z, Grande CA, Li P, Yu J, Rodrigues AE. Multi-bed Vacuum Pressure Swing Adsorption for carbon dioxide capture from flue gas. *Sep Purif Technol* 2011;81:307–17.
- [63] Wang L, Liu Z, Li P, Wang J, Yu J. CO<sub>2</sub> capture from flue gas by two successive VPSA units using 13XAPG. *Adsorption* 2012;18:445–59.
- [64] Krishnamurthy S, Rao VR, Guntuka S, Sharratt P, Haghpanah R, Rajendran A, et al. CO<sub>2</sub> capture from dry flue gas by vacuum swing adsorption: A pilot plant study. *AIChE J* 2014;60:1830–42.
- [65] Haghpanah R, Majumder A, Nilam R, Rajendran A, Farooq S, Karimi IA, et al. Multiobjective Optimization of a Four-Step Adsorption Process for Postcombustion CO<sub>2</sub> Capture Via Finite Volume Simulation. *Ind Eng Chem Res* 2013;52:4249–65.
- [66] Shen C, Liu Z, Li P, Yu J. Two-Stage VPSA Process for CO<sub>2</sub> Capture from Flue Gas Using Activated Carbon Beads. *Ind Eng Chem Res* 2012;51:5011–21.
- [67] Wang L, Yang Y, Shen W, Kong X, Li P, Yu J, et al. CO<sub>2</sub> Capture from Flue Gas in an Existing Coal-Fired Power Plant by Two Successive Pilot-Scale VPSA Units. *Ind Eng Chem Res* 2013;52:7947–55.
- [68] Riboldi L, Bolland O. Evaluating Pressure Swing Adsorption as a CO<sub>2</sub> separation technique in coal-fired power plants. *Int J Greenh Gas Control* 2015;39:1–16.
- [69] Ntiemoah A, Ling J, Xiao P, Webley PA, Zhai Y. CO<sub>2</sub> Capture by Temperature Swing Adsorption: Use of Hot CO<sub>2</sub>-Rich Gas for Regeneration. *Ind Eng Chem Res* 2016;55:703–13.
- [70] Jiang L, Roskilly AP, Wang RZ. Performance exploration of temperature swing adsorption technology for carbon dioxide capture. *Energy Convers Manag* 2018;165:396–404.
- [71] Bui M, Adjiman CS, Bardow A, Anthony EJ, Boston A, Brown S, et al. Carbon capture and storage (CCS): The way forward. *Energy Environ Sci* 2018;11:1062–176.
- [72] Grande CA, Rodrigues AE. Electric swing adsorption for CO<sub>2</sub> removal from flue gases. *Int J Greenh Gas Control* 2008;2:194–202.
- [73] Fujiki J, Chowdhury FA, Yamada H, Yogo K. Highly efficient post-combustion CO<sub>2</sub> capture by low-temperature steam-aided vacuum swing adsorption using a novel polyamine-based solid sorbent. *Chem Eng J* 2017;307:273–82.
- [74] Cloete S, Giuffrida A, Romano MC, Zaabout A. The swing adsorption reactor cluster for post-combustion CO<sub>2</sub> capture from cement plants. *J Clean Prod* 2019;223:692–703.
- [75] Sun X, Zhu L, Wang P, Zhao W, Chen X. CO<sub>2</sub> removal from natural gas by moisture swing adsorption. *Chem Eng Res Des* 2021;176:162–8.
- [76] Cuesta AR, Song C. pH swing adsorption process for ambient carbon dioxide capture using activated carbon black adsorbents and immobilized carbonic anhydrase biocatalysts. *Appl Energy* 2020;280:116003.
- [77] Liu RS, Shi XD, Wang CT, Gao YZ, Xu S, Hao GP, et al. Advances in Post-Combustion CO<sub>2</sub> Capture by Physical Adsorption: From Materials Innovation to Separation Practice. *ChemSusChem* 2021;14:1428–71.
- [78] Sun M, Gu Q, Hanif A, Wang T, Shang J. Transition metal cation-exchanged SSZ-13 zeolites for CO<sub>2</sub> capture and separation from N<sub>2</sub>. *Chem Eng J* 2019;370:1450–8.
- [79] Belviso C. State-of-the-art applications of fly ash from coal and biomass: A focus on zeolite synthesis processes and issues. *Prog Energy Combust Sci* 2018;65:109–35.
- [80] Khaleque A, Alam MM, Hoque M, Mondal S, Haider J Bin, Xu B, et al. Zeolite synthesis from low-cost materials and environmental applications: A review. *Environ Adv* 2020;2:100019.
- [81] Johnson EBG, Arshad SE. Hydrothermally synthesized zeolites based on kaolinite: A review. *Appl Clay Sci* 2014;97–98:215–21.
- [82] Ma Y, Yan C, Alshameri A, Qiu X, Zhou C, Li D. Synthesis and characterization of 13X zeolite from low-grade natural kaolin. *Adv Powder Technol* 2014;25:495–9.
- [83] Younesi H, Ghasemi Z. Preparation and characterization of nanozeolite NaA from rice husk at room temperature without organic additives. *J Nanomater* 2011;2011.
- [84] Ghasemi Z, Younesi H. Preparation of free-template nanometer-sized Na-A and -X zeolites from rice husk ash. *Waste Biomass Valorization* 2012;3:61–74.
- [85] Park SH, Yang J-K, Kim J-H, Chung C-B, Seo G. Eco-friendly synthesis of zeolite A from synthesis cakes prepared by removing the liquid phase of aged synthesis mixtures. *Green Chem* 2015;17:3571–8.
- [86] Feng K, Zhang F, Li SF, Sun CY. The synthesis of ZSM-5 using natural clay of Qinghai Salt Lake and its Pb(II) adsorption. *IOP Conf. Ser. Earth Environ. Sci.*, vol. 81, 2017.
- [87] Meng X, Xiao F-S. Green Routes for Synthesis of Zeolites. *Chem Rev* 2014;114:1521–43.
- [88] Yit Siew Ng T, Leng Chew T, Fong YY. Synthesis of small pore zeolite via ultrasonic-assisted hydrothermal synthesis. *Mater Today Proc* 2019;16:1935–41.
- [89] Sethaya N, Chindaprasit P, Pimraksa K. Preparation of zeolite nanocrystals via hydrothermal and solvothermal synthesis using of rice husk ash and metakaolin. *Mater Sci Forum* 2016;872:242–7.
- [90] Marthala VRR, Hunger M, Kettner F, Krautscheid H, Chmelik C, Kärger J, et al. Solvothermal synthesis and characterization of large-crystal all-silica, aluminum-, and boron-containing ferrierite zeolites. *Chem Mater* 2011;23:2521–8.
- [91] Jamil AK, Muraza O, Al-Amer AM. Microwave-assisted solvothermal synthesis of ZSM-22 zeolite with controllable crystal lengths. *Particology* 2016;24:138–41.
- [92] Takako N, Takuji I, Chie A, Yasuhisa H, Yoshimichi K, Takaaki H. Solvothermal synthesis of -Lit-type zeolite. *Cryst Growth Des* 2012;12:1752–61.
- [93] Wang L, Wei Y, Wang B-C, Xu Y-P, Ma H-J, Tian Z-J, et al. Structure directing role of amines in the microwave-enhanced ionothermal synthesis of zeolite. *Shiyou Xuebao, Shiyou Jigong/Acta Pet Sin (Petroleum Process Sect* 2006;22:42–4.
- [94] Wang XJ, Yan CL. Synthesis of nano-sized NaY zeolite composite from metakaolin by ionothermal method with microwave assisted. *Inorg Mater* 2010;46:517–21.
- [95] Yan Y, Cai R, Liu Y, Gu S. Ambient pressure dry-gel conversion method for zeolite MFI synthesis using ionic liquid and microwave heating. *J Am Chem Soc* 2010;132:12776–7.
- [96] Wu Q, Hong X, Zhu L, Meng X, Han S, Zhang J, et al. Generalized ionothermal synthesis of silica-based zeolites. *Microporous Mesoporous Mater* 2019;286:163–8.
- [97] Cai R, Sun M, Chen Z, Munoz R, O'Neill C, Beving DE, et al. Ionothermal synthesis of oriented zeolite AEL films and their application as corrosion-resistant coatings. *Angew Chemie - Int Ed* 2008;47:525–8.
- [98] Ayele L, Pérez-Pariente J, Chebude Y, Díaz I. Conventional versus alkali fusion synthesis of zeolite A from low grade kaolin. *Appl Clay Sci* 2016;132–133:485–90.
- [99] Morales-Ospino R, Goltzman Y, Torres AEB, Vilarraza-García E, Bastos-Neto M, Cavalcante CL, et al. Assessment of the potential use of zeolites synthesized from power plant fly ash to capture CO<sub>2</sub> under post-combustion scenario. *Adsorption* 2020;26:1153–64.
- [100] Petrovic B, Gorbounov M, Lahiri A, Soltani SM. Biomass Combustion Fly Ash-Derived Nanoporous Zeolites for Post-Combustion Carbon Capture. *Proc. IEEE Conf. Nanotechnol.*, vol. 2021–July, 2021, p. 233–6.
- [101] Wu L, Liu J, Shang H, Li S, Yang J, Li L, et al. Capture CO<sub>2</sub> from N<sub>2</sub> and CH<sub>4</sub> by zeolite L with different crystal morphology. *Microporous Mesoporous Mater* 2021;316:110956.
- [102] Bonenfant D, Kharoune M, Niquette P, Mimeault M, Hausler R. Advances in principal factors influencing carbon dioxide adsorption on zeolites. *Sci Technol Adv Mater* 2008;9.
- [103] Chuah CY, Li W, Yang Y, Bae T-H. Evaluation of porous adsorbents for CO<sub>2</sub> capture under humid conditions: The importance of recyclability. *Chem Eng J Adv* 2020;3:100021.
- [104] Hirst EA, Taylor A, Mokaya R. A simple flash carbonization route for conversion of biomass to porous carbons with high CO<sub>2</sub> storage capacity. *J Mater Chem A* 2018;6:12393–403.
- [105] Stoeckli F, Guillot A, Siasli AM, Hugi-Cleary D. The comparison of experimental and calculated pore size distributions of activated carbons. *Carbon N Y* 2002;40:383–8.
- [106] Plaza MG, Rubiera F. Evaluation of a novel multibed heat-integrated vacuum and temperature swing adsorption post-combustion CO<sub>2</sub> capture process. *Appl Energy* 2019;250:916–25.
- [107] Boyjoo Y, Cheng Y, Zhong H, Tian H, Pan J, Pareek VK, et al. From waste Coca Cola® to activated carbons with impressive capabilities for CO<sub>2</sub> adsorption and supercapacitors. *Carbon N Y* 2017;116:490–9.
- [108] Jain SK, Pikunic JP, Pellenq RJM, Gubbins KE. Effects of activation on the structure and adsorption properties of a nanoporous carbon using molecular simulation. *Adsorption* 2005;11:355–60.
- [109] Yang D-P, Li Z, Liu M, Zhang X, Chen Y, Xue H, et al. Biomass-derived carbonaceous materials: recent progress in synthetic approaches, advantages, and applications. *ACS Sustain Chem Eng* 2019;7:4564–85.
- [110] Wang P, Zhang G, Chen W, Chen Q, Jiao H, Liu L, et al. Molten Salt Template Synthesis of Hierarchical Porous Nitrogen-Containing Activated Carbon Derived from Chitosan for CO<sub>2</sub> Capture. *ACS Omega* 2020;5:23460–7.
- [111] Zhu XL, Wang PY, Peng C, Yang J, Bin YX. Activated carbon produced from paulownia sawdust for high-performance CO<sub>2</sub> sorbents. *Chinese Chem Lett* 2014;25:929–32.
- [112] Balsamo M, Budinova T, Erto A, Lancia A, Petrova B, Petrov N, et al. CO<sub>2</sub> adsorption onto synthetic activated carbon: Kinetic, thermodynamic and regeneration studies. *Sep Purif Technol* 2013;116:214–21.
- [113] Cen Q, Fang M, Wang T, Majchrzak-Kuceba I, Wawrzynczak D, Luo Z. Thermodynamics and regeneration studies of CO<sub>2</sub> adsorption on activated carbon. *Greenh Gases Sci Technol* 2016;6:787–96.
- [114] Wang Y, Hu X, Hao J, Ma R, Guo Q, Gao H, et al. Nitrogen and Oxygen Codoped Porous Carbon with Superior CO<sub>2</sub> Adsorption Performance: A Combined Experimental and DFT Calculation Study. *Ind Eng Chem Res* 2019;58:13390–400.
- [115] Sumida K, Rogow DL, Mason JA, McDonald TM, Bloch ED, Herm ZR, et al. Carbon dioxide capture in metal-organic frameworks. *Chem Rev* 2012;112:724–81.
- [116] Aniruddha R, Sreedhar I, Reddy BM. MOFs in carbon capture-past, present and future. *J CO<sub>2</sub> Util* 2020;42:101297. doi:10.1016/j.jcou.2020.101297.
- [117] He Q, Zhan F, Wang H, Xu W, Wang H, Chen L. Recent progress of industrial preparation of metal-organic frameworks: synthesis strategies and outlook. *Mater Today Sustain* 2022;17:100104.
- [118] Casaban J. Advancing the commercial application of Metal Organic Frameworks for industrial decarbonisation; 2020.
- [119] MOF Technologies - Adsorbent nanomaterials. Website 2020.
- [120] AIMPLAS. The Gramofon process: newsletter. Newsletter 2020:1–6.
- [121] Spjelkavik AI, Aarti DS, Didriksen T, Blom R. Forming MOFs into spheres by use of molecular gastronomy methods. *Chem - A Eur J* 2014;20:8973–8.
- [122] Krishnamurthy S, Blom R, Ferrari MC, Brandani S. Adsorption and diffusion of CO<sub>2</sub> in CPO-27-Ni beads. *Adsorption* 2020;26:711–21.
- [123] Szczęśniak B, Choma J. Graphene-containing microporous composites for selective CO<sub>2</sub> adsorption. *Microporous Mesoporous Mater* 2020;292.

- [124] Hefti M, Joss L, Bjelobrk Z, Mazzotti M. On the potential of phase-change adsorbents for CO<sub>2</sub> capture by temperature swing adsorption. *Faraday Discuss* 2016;192:153–79.
- [125] Muschi M, Devautour-Vinot S, Aureau D, Heymans N, Sene S, Emmerich R, et al. Metal-organic framework/graphene oxide composites for CO<sub>2</sub> capture by microwave swing adsorption. *J Mater Chem A* 2021.
- [126] Hutson ND, Attwood BC. High temperature adsorption of CO<sub>2</sub> on various hydroxalcalite-like compounds. *Adsorption* 2008;14:781–9.
- [127] Othman MR, Helwani Z, Martunus FW. Synthetic hydroxalcalites from different routes and their application as catalysts and gas adsorbents: A review. *Appl Organomet Chem* 2009;23:235–46.
- [128] Winter F, Koot V, Van Dillen AJ, Geus JW, De Jong KP. Hydroxalcalites supported on carbon nanofibers as solid base catalysts for the synthesis of MIBK. *J Catal* 2005;236:91–100.
- [129] Hutson ND, Speakman SA, Payzant EA. Structural effects on the high temperature adsorption of CO<sub>2</sub> on a synthetic hydroxalcalite. *Chem Mater* 2004;16:4135–43. <https://doi.org/10.1021/cm040060u>.
- [130] Muñoz V, Zotin FMZ, Palacio LA. Copper-aluminum hydroxalcalite type precursors for NO<sub>x</sub> abatement. *Catal Today* 2015;250:173–9.
- [131] Hanif A, Dasgupta S, Divekar S, Arya A, Garg MO, Nanoti A. A study on high temperature CO<sub>2</sub> capture by improved hydroxalcalite sorbents. *Chem Eng J* 2014; 236:91–9.
- [132] Silva JM, Trujillano R, Rives V, Soria MA, Madeira LM. High temperature CO<sub>2</sub> sorption over modified hydroxalcalites. *Chem Eng J* 2017;325:25–34.
- [133] Spallina V, Martynov S, Porter R, Mahgerefteh H. System simulation for integration of CO<sub>2</sub> capture technologies into steelworks and CCUS clusters. *Advanced Carbon Capture for Steel Industries Integrated in CCUS. Clusters* 2021.
- [134] Wu YJ, Li P, Yu JG, Cunha AF, Rodrigues AE. K-Promoted Hydroxalcalites for CO<sub>2</sub> Capture in Sorption Enhanced Reactions. *Chem Eng Technol* 2013;36:567–74.
- [135] O'Palko A, Loebick C, Baird B, Weissman J, Anderson A. High-Efficiency Post Combustion Carbon Capture System. Phase I Proj Rev Meet 2020.
- [136] Loebick C, Weissman J. High-Efficiency Post Combustion Carbon Capture System DOE SBIR Phase 1 Contract # DE-SC0017221. 2017.
- [137] Loebick C, Weissman J, Baird B, Roux S, Ryan E. High-Efficiency Post Combustion Carbon Capture System DOE SBIR Phase 2 Contract # DE-SC0017221. 2018.
- [138] Jain R. Bench Scale Development and Testing of a Novel Adsorption Process for Post-Combustion CO<sub>2</sub> Capture. 2015.
- [139] Alptekin G, Jayaraman A, Copeland R. Post-Combustion CO<sub>2</sub> Capture System for Existing Coal-fired Power Plant. 2015.
- [140] Ritter JA. Bench-Scale Development and Testing of Rapid PSA for CO<sub>2</sub> Capture. 2015.
- [141] Hovington P, Ghaffari-Nik O, Mariac L, Liu A, Henkel B, Marx S. Rapid Cycle Temperature Swing Adsorption Process Using Solid Structured Sorbent for CO<sub>2</sub> capture from Cement Flue Gas. Available SSRN 3814414 2021.
- [142] Svante. A Center For Testing and Innovation 2020.
- [143] Long JR. Amine-appended Metal-Organic Frameworks as switch-like adsorbents for energy-efficient carbon capture. *Natl Energy Technol Lab Carbon Capture 2020 - Integr Rev Webinar - Oct 5-7 2020*.
- [144] Neaton JB, Long JR, Haracznyk M. Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture 2019.
- [145] Global CCS Institute. Facilities. CO<sub>2</sub>Re Facilities Data; 2020.
- [146] Hadong power station. *Global Energy Monit Wiki*; 2021.
- [147] Dry Y-K. Solid Sorbent CO<sub>2</sub> Capture Project of 10 MWe scale. *Carbon Sequestration Leadersh Forum*; 2015.
- [148] O'Palko A, Hancu D, Elliot J. Sorbent Based Post-Combustion CO<sub>2</sub> Slipstream Testing. *Proj Land Page - Natl Energy Technol Lab*; 2019.
- [149] Yi JE and F. Pilot Unit Testing at NCC of Sorbent based CO<sub>2</sub> Capture; 2020.
- [150] TDA Research Inc. Transformational Sorbent System for Post-Combustion Carbon Capture: Project Technology Sheet n.d. <https://netl.doe.gov/project-information?p=FE0031734> (accessed June 22, 2021).
- [151] Alptekin G, Jayaraman A. Transformational Sorbent System for Post Combustion Carbon Capture (Contract No. DE-FE-0031734). Wheat Ridge, CO: 2019.
- [152] Jensen F. Introduction to Computational Chemistry. vol. 90. 2nd ed. Wiley; 2007.
- [153] Wilmer CE, Snurr RQ. Towards rapid computational screening of metal-organic frameworks for carbon dioxide capture: Calculation of framework charges via charge equilibration. *Chem Eng J* 2011;171:775–81.
- [154] Krishna R, van Baten JM. In silico screening of zeolite membranes for CO<sub>2</sub> capture. *J Memb Sci* 2010;360:323–33.
- [155] Greenwell HC, Jones W, Coveney PV, Stackhouse S. On the application of computer simulation techniques to anionic and cationic clays: A materials chemistry perspective. *J Mater Chem* 2006;708–23.
- [156] Cramer CJ. Essentials of Computational Chemistry Theories and Models. vol. 42. 2004.
- [157] Van Duin ACT, Dasgupta S, Lorant F, Goddard WA. ReaxFF: A reactive force field for hydrocarbons. *J Phys Chem A* 2001;105:9396–409.
- [158] Cygan RT, Liang J-J, Kalinichev AG. Molecular Models of Hydroxide, Oxyhydroxide, and Clay Phases and the Development of a General Force Field. *J Phys Chem B* 2004;108:1255–66.
- [159] Billemont P, Coasne B, De Weireld G. Adsorption of Carbon Dioxide, Methane, and Their Mixtures in Porous Carbons: Effect of Surface Chemistry, Water Content, and Pore Disorder. *Langmuir* 2013;29:3328–38.
- [160] Jin Z, Firoozabadi A. Fluid Phase Equilibria Methane and carbon dioxide adsorption in clay-like slit pores by Monte Carlo simulations. *Fluid Phase Equilib* 2013;360:456–65.
- [161] Teo HWB, Chakraborty A, Kayal S. Evaluation of CH<sub>4</sub> and CO<sub>2</sub> adsorption on HKUST-1 and MIL-101(Cr) MOFs employing Monte Carlo simulation and comparison with experimental data. *Appl Therm Eng* 2017;110:891–900.
- [162] Lin LC, Kim J, Kong X, Scott E, McDonald TM, Long JR, et al. Understanding CO<sub>2</sub> dynamics in metal-organic frameworks with open metal sites. *Angew Chemie - Int Ed* 2013;52:4410–3.
- [163] Potoff JJ, Siepmann JI. Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen. *AIChE J* 2001;47:1676–82.
- [164] Rappé AK, Casewit CJ, Colwell KS, Goddard WA, Skiff WM. UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations. *J Am Chem Soc* 1992;114:10024–35.
- [165] Addicoat MA, Vankova N, Akter IF, Heine T. Extension of the Universal Force Field to Metal-Organic Frameworks. *J Chem Theory Comput* 2014;10:880–91.
- [166] Mayo SL, Olafson BD, Goddard WA. DREIDING: A generic force field for molecular simulations. *J Phys Chem* 1990;94:8897–909.
- [167] Huang Y, Cannon FS, Watson JK, Reznik B, Mathews JP. Activated carbon efficient atomistic model construction that depicts experimentally-determined characteristics. *Carbon N Y* 2015;83:1–14.
- [168] Leach AR. Molecular modelling Principles and applications. 2nd ed. Dorchester: Prentice Hall; 2001.
- [169] Aktulga HM, Fogarty JC, Pandit SA, Grama AY. Parallel reactive molecular dynamics: Numerical methods and algorithmic techniques. *Parallel Comput* 2012; 38:245–59.
- [170] Yu HS, Li SL, Truhlar DG. Perspective: Kohn-Sham density functional theory descending a staircase. *J Chem Phys* 2016;145.
- [171] Suter JL, Anderson RL, Christopher Greenwell H, Coveney PV. Recent advances in large-scale atomistic and coarse-grained molecular dynamics simulation of clay minerals. *J Mater Chem* 2009;19:2482–93.
- [172] Purdue MJ, Qiao Z. Molecular simulation study of wet flue gas adsorption on zeolite 13X. *Microporous Mesoporous Mater* 2018;261:181–97.
- [173] Zhang J, Burke N, Zhang S, Liu K, Pervukhina M. Thermodynamic analysis of molecular simulations of CO<sub>2</sub> and CH<sub>4</sub> adsorption in FAU zeolites. *Chem Eng Sci* 2014;113:54–61.
- [174] Konstantakou M, Gotzias A, Kainourgiakis M, K. A. A. T. GCMC Simulations of Gas Adsorption in Carbon Pore Structures. In: Mordechai S, editor. *Appl. Monte Carlo Method Sci. Eng., IntechOpen*; 2011.
- [175] Nachtigall P, Delgado MR, Nachtigallova D, Areal CO. The nature of cationic adsorption sites in alkaline zeolites - Single, dual and multiple cation sites. *Phys Chem Chem Phys* 2012;14:1552–69.
- [176] Thang HV, Grajciar L, Nachtigall P, Bludský O, Areal CO, Frýdová E, et al. Adsorption of CO<sub>2</sub> in FAU zeolites: Effect of zeolite composition. *Catal Today* 2014;227:50–6.
- [177] Zukal A, Pulido A, Gil B, Nachtigall P, Bludský O, Rubes M, et al. Experimental and theoretical determination of adsorption heats of CO<sub>2</sub> over alkali metal exchanged ferrierites with different Si/Al ratio. *Phys Chem Chem Phys* 2010;12: 6413–22.
- [178] Hasegawa Y, Tanaka T, Watanabe K, Jeong BH, Kusakabe K, Morooka S. Separation of CO<sub>2</sub>-CH<sub>4</sub> and CO<sub>2</sub>-N<sub>2</sub> Systems Using Ion-exchanged FAU-type Zeolite Membranes with Different Si/Al Ratios. *Korean J Chem Eng* 2002;19: 309–13.
- [179] Gholampour F, Yeganegi S. Molecular simulation study on the adsorption and separation of acidic gases in a model nanoporous carbon. *Chem Eng Sci* 2014;117: 426–35.
- [180] Tenney CM, Lastoskie CM. Molecular simulation of carbon dioxide adsorption in chemically and structurally heterogeneous porous carbons. *Environ Prog* 2006; 25:343–54.
- [181] Moliner C, Antonucci B, Focacci S, Heap JM, Martel AM, Hamzah F, et al. Molecular dynamics simulation of the interactions between carbon dioxide and a natural-based carbonaceous microporous material. *Chem Eng Trans* 2021;86: 1111–6.
- [182] Trinh TT, Tran KQ, Bach QV, Trinh DQ. A molecular dynamics simulation study on separation selectivity of CO<sub>2</sub>/CH<sub>4</sub> mixture in mesoporous carbons. *Energy Procedia* 2016;86:144–9.
- [183] Li JR, Ma Y, McCarthy MC, Sculley J, Yu J, Jeong HK, et al. Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks. *Coord Chem Rev* 2011;255:1791–823.
- [184] Agrawal A, Agrawal M, Suh D, Fei S, Alizadeh A, Ma Y, et al. Augmenting the Carbon Dioxide Uptake and Selectivity of Metal-Organic Frameworks by Metal Substitution: Molecular Simulations of LMOF-202. *ACS Omega* 2020;5:17193–8.
- [185] Yazaydin AO, Snurr RQ, Park TH, Koh K, Liu J, LeVan MD, et al. Screening of metal-organic frameworks for carbon dioxide capture from flue gas using a combined experimental and modeling approach. *J Am Chem Soc* 2009;131: 18198–9.
- [186] Salles F, Jobic H, Devic T, Llewellyn PL, Serre C, Férey G, et al. Self and transport diffusivity of CO<sub>2</sub> in the metal-organic framework MIL-47(V) explored by quasi-elastic neutron scattering experiments and molecular dynamics simulations. *ACS Nano* 2010;4:143–52.
- [187] Salles F, Ghoufi A, Maurin G, Bell RG, Mellot-Draznieks C, Férey G. Molecular dynamics simulations of breathing MOFs: Structural transformations of MIL-53 (Cr) upon thermal activation and CO<sub>2</sub> adsorption. *Angew Chemie - Int Ed* 2008; 47:8487–91.
- [188] Walton KS, Millward AR, Dubbeldam D, Frost H, Low JJ, Yaghi OM, et al. Understanding inflections and steps in carbon dioxide adsorption isotherms in metal-organic frameworks. *J Am Chem Soc* 2008;130:406–7.

- [189] Bahamon D, Díaz-Márquez A, Gamallo P, Vega LF. Energetic evaluation of swing adsorption processes for CO<sub>2</sub> capture in selected MOFs and zeolites: Effect of impurities. *Chem Eng J* 2018;342:458–73.
- [190] Leperi KT, Chung YG, You F, Snurr RQ. Development of a General Evaluation Metric for Rapid Screening of Adsorbent Materials for Postcombustion CO<sub>2</sub> Capture. *ACS Sustain Chem Eng* 2019;7:11529–39.
- [191] Burns TD, Pai KN, Subraveti SG, Collins SP, Krykunov M, Rajendran A, et al. Prediction of MOF Performance in Vacuum Swing Adsorption Systems for Postcombustion CO<sub>2</sub> Capture Based on Integrated Molecular Simulations, Process Optimizations, and Machine Learning Models. *Environ Sci Technol* 2020;54:4536–44.
- [192] Zhang ST, Yan H, Wei M, Evans DG, Duan X. Valence force field for layered double hydroxide materials based on the parameterization of octahedrally coordinated metal cations. *J Phys Chem C* 2012;116:3421–31.
- [193] Wang J, Kalinichev AG, Kirkpatrick RJ, Hou X. Molecular modeling of the structure and energetics of hydrotalcite hydration. *Chem Mater* 2001;13:145–50.
- [194] Yan H, Wei M, Jing M, Li F, Evans DG, Duan X. Theoretical study on the structural properties and relative stability of M(II)-Al layered double hydroxides based on a cluster model. *J Phys Chem A* 2009;113:6133–41.
- [195] Zhang ST, Dou Y, Zhou J, Pu M, Yan H, Wei M, et al. DFT-Based Simulation and Experimental Validation of the Topotactic Transformation of MgAl Layered Double Hydroxides. *ChemPhysChem* 2016;2754–66.
- [196] Teppen BJ, Rasmussen K, Bertsch PM, Miller DM, Schäfer L. Molecular dynamics modeling of clay minerals. 1. gibbsite, kaolinite, pyrophyllite, and beidellite. *J Phys Chem B* 1997;101:1579–87.
- [197] Gao M, Khalkhali M, Beck S, Choi P, Zhang H. Study of Thermal Stability of Hydrotalcite and Carbon Dioxide Adsorption Behavior on Hydrotalcite-Derived Mixed Oxides Using Atomistic Simulations. *ACS Omega* 2018;3:12041–51.
- [198] Khorshidi ZN, Khalkhali M, Zhang H, Choi P. Molecular Dynamics Study of the Role of Water in the Carbon Dioxide Intercalation in Chloride Ions Bearing Hydrotalcite. *J Phys Chem C* 2018;acs.jpcc.8b01691.
- [199] Li H, Ma J, Evans DG, Zhou T, Li F, Duan X. Molecular Dynamics Modeling of the Structures and Binding Energies of  $\alpha$ -Nickel Hydroxides and Nickel - Aluminum Layered Double Hydroxides Containing Various Interlayer Guest Anions 2006;1:4405–14.
- [200] Kim N, Harale A, Tsotsis TT, Sahimi M. Atomistic simulation of nonporous layered double hydroxide materials and their properties. II. Adsorption and diffusion. *J Chem Phys* 2007;127.
- [201] Siahpoosh M, Fatemi S, Vatani A. Mathematical modeling of single and multi-component adsorption fixed beds to rigorously predict the mass transfer zone and breakthrough curves. *Iran J Chem Chem Eng* 2009;28:25–44.
- [202] Pai KN, Prasad V, Rajendran A. Practically Achievable Process Performance Limits for Pressure-Vacuum Swing Adsorption-Based Postcombustion CO<sub>2</sub> Capture. *ACS Sustain Chem Eng* 2021;9:3838–49.
- [203] Valenciano R, Aylón E, Izquierdo MT. A critical short review of equilibrium and kinetic adsorption models for VOCs breakthrough curves modelling. *Adsorpt Sci Technol* 2015;33:851–69.
- [204] Fedunik-Hofman L, Bayon A, Donne SW. Kinetics of solid-gas reactions and their application to carbonate looping systems. *Energies* 2019;12:2981.
- [205] Wang L, Liu Z, Li P, Yu J, Rodrigues AE. Experimental and modeling investigation on post-combustion carbon dioxide capture using zeolite 13X-APG by hybrid VTSA process. *Chem Eng J* 2012;197:151–61.
- [206] Subramanian Balashankar V, Rajendran A. Process Optimization-Based Screening of Zeolites for Post-Combustion CO<sub>2</sub> Capture by Vacuum Swing Adsorption. *ACS Sustain Chem Eng* 2019;7:17747–55.
- [207] Joss L, Gazzani M, Mazzotti M. Rational design of temperature swing adsorption cycles for post-combustion CO<sub>2</sub> capture. *Chem Eng Sci* 2017;158:381–94.
- [208] Yancy-Caballero D, Leperi KT, Bucior BJ, Richardson RK, Islamoglu T, Farha OK, et al. Process-level modelling and optimization to evaluate metal-organic frameworks for post-combustion capture of CO<sub>2</sub>. *Mol Syst Des Eng* 2020;5:1205–18.
- [209] Ben-Mansour R, Bamidele OE, Habib MA. Evaluation of Mg-MOF-74 for post-combustion carbon dioxide capture through pressure swing adsorption. *Int J Energy Res* 2015;39:1994–2007.
- [210] Zhao R, Liu L, Zhao L, Deng S, Li S, Zhang Y. A comprehensive performance evaluation of temperature swing adsorption for post-combustion carbon dioxide capture. *Renew Sustain Energy Rev* 2019;114:109285.
- [211] Maruyama RT, Pai KN, Subraveti SG, Rajendran A. Improving the performance of vacuum swing adsorption based CO<sub>2</sub> capture under reduced recovery requirements. *Int J Greenh Gas. Control* 2020;93.
- [212] Maring BJ, Webley PA. A new simplified pressure/vacuum swing adsorption model for rapid adsorbent screening for CO<sub>2</sub> capture applications. *Int J Greenh Gas Control* 2013;15:16–31.
- [213] Danaci D, Bui M, Mac Dowell N, Petit C. Exploring the limits of adsorption-based CO<sub>2</sub> capture using MOFs with PVSA – from molecular design to process economics. *Mol Syst Des Eng* 2020;5:212–31.
- [214] Luberti M, Oreggioni GD, Ahn H. Design of a rapid vacuum pressure swing adsorption (RVPSA) process for post-combustion CO<sub>2</sub> capture from a biomass-fuelled CHP plant. *J Environ Chem Eng* 2017;5:3973–82.
- [215] Plaza MG, Rubiera F, Pevida C. Evaluating the Feasibility of a TSA Process Based on Steam Stripping in Combination with Structured Carbon Adsorbents To Capture CO<sub>2</sub> from a Coal Power Plant. *Energy Fuels* 2017;31:9760–75.
- [216] Riboldi L, Bolland O, Ngoy JM, Wagner N. Full-plant Analysis of a PSA CO<sub>2</sub> Capture Unit Integrated In Coal-fired Power Plants: Post-and Pre-combustion Scenarios. *Energy Procedia* 2014;63:2289–304.
- [217] Plaza MG, Durán I, Querejeta N, Rubiera F, Pevida C. Experimental and simulation study of adsorption in postcombustion conditions using a microporous biochar. 2. H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub> adsorption. *Ind Eng Chem Res* 2016;55:6854–65.
- [218] Plaza MG, Durán I, Querejeta N, Rubiera F, Pevida C. Experimental and simulation study of adsorption in postcombustion conditions using a microporous biochar. 1. CO<sub>2</sub> and N<sub>2</sub> adsorption. *Ind Eng Chem Res* 2016;55:3097–112.
- [219] Plaza MG, Durán I, Rubiera F, Pevida C. Adsorption-based Process Modelling for Post-combustion CO<sub>2</sub> Capture. *Energy Procedia* 2017;114:2353–61.
- [220] Wilkins NS, Rajendran A. Measurement of competitive CO<sub>2</sub> and N<sub>2</sub> adsorption on Zeolite 13X for post-combustion CO<sub>2</sub> capture. *Adsorption* 2019;25:115–33.
- [221] Marx D, Joss L, Hefti M, Mazzotti M. Temperature swing adsorption for postcombustion CO<sub>2</sub> capture: single-and multicolumn experiments and simulations. *Ind Eng Chem Res* 2016;55:1401–12.
- [222] Yang C, Du Z, Jin J, Chen J, Mi J. Epoxide-functionalized tetraethylenepentamine encapsulated into porous co-polymer spheres for CO<sub>2</sub> capture with superior stability. *Appl Energy* 2020;260:114265.
- [223] Lee A, Miller DC. A one-dimensional (1-D) three-region model for a bubbling fluidized-bed adsorber. *Ind Eng Chem Res* 2013;52:469–84.
- [224] Park J, Won W, Jung W, Lee KS. One-dimensional modeling of a turbulent fluidized bed for a sorbent-based CO<sub>2</sub> capture process with solid–solid sensible heat exchange. *Energy* 2019;168:1168–80.
- [225] Park YC, Jo S-H, Lee D-H, Yi C-K, Ryu CK, Kim K-S, et al. The status of the development project for the 10 MWe-Scale dry-sorbent carbon dioxide capture system to the real coal-fired power plant in Korea. *Energy Procedia* 2013;37:122–6.
- [226] De Souza-Santos ML. A new version of CSFB, comprehensive simulator for fluidised bed equipment. *Fuel* 2007;86:1684–709.
- [227] Suh D-M, Sun X. Particle-scale CO<sub>2</sub> adsorption kinetics modeling considering three reaction mechanisms. *Int J Greenh Gas Control* 2013;17:388–96.
- [228] Modekurti S, Bhattacharyya D, Zitney SE. Dynamic modeling and control studies of a two-stage bubbling fluidized bed adsorber-reactor for solid-sorbent CO<sub>2</sub> capture. *Ind Eng Chem Res* 2013;52:10250–60.
- [229] Pröll T, Schöny G, Sprachmann G, Hofbauer H. Introduction and evaluation of a double loop staged fluidized bed system for post-combustion CO<sub>2</sub> capture using solid sorbents in a continuous temperature swing adsorption process. *Chem Eng Sci* 2016;141:166–74.
- [230] Zanco SE, Mazzotti M, Gazzani M, Romano MC, Martínez I. Modeling of circulating fluidized beds systems for post-combustion CO<sub>2</sub> capture via temperature swing adsorption. *AIChE J* 2018;64:1744–59.
- [231] Khurana M, Farooq S. Integrated Adsorbent Process Optimization for Minimum Cost of Electricity Including Carbon Capture by a VSA Process. *AIChE J* 2019;65:184–95.
- [232] Subraveti SG, Roussanaly S, Anantharaman R, Riboldi L, Rajendran A. Techno-economic assessment of optimised vacuum swing adsorption for post-combustion CO<sub>2</sub> capture from steam-methane reformer flue gas. *Sep Purif Technol* 2021;256:117832.
- [233] Subraveti SG, Roussanaly S, Anantharaman R, Riboldi L, Rajendran A. How much can novel solid sorbents reduce the cost of post-combustion CO<sub>2</sub> capture? A techno-economic investigation on the cost limits of pressure–vacuum swing adsorption. *Appl Energy* 2022;306:117955.
- [234] Jung W, Lee J. Economic evaluation for four different solid sorbent processes with heat integration for energy-efficient CO<sub>2</sub> capture based on PEI-silica sorbent. *Energy* 2022;238:121864.