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# A review on progress made in direct air capture of CO<sub>2</sub>

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## ABSTRACT

As the concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere continues to rise, and the reality of global warming challenges hits the world, global research societies are developing innovative technologies to address climate change challenges brought about by high atmospheric concentration of CO<sub>2</sub>. One of such challenges is the direct removal of CO<sub>2</sub> from the atmosphere. Among all the currently available CO<sub>2</sub> removal technologies, direct air capture (DAC) is positioned to deliver the needed CO<sub>2</sub> removal from the atmosphere because it is independent of CO<sub>2</sub> emission origin, and the capture machine can be stationed anywhere. Research efforts in the last two decades, however, have identified the system overall energy requirements as the bottleneck to the realization of DAC's commercialization. As a result, global research community continues to seek better ways to minimize the required energy per ton of CO<sub>2</sub> removed via DAC. In this work, the literature was comprehensively reviewed to assess the progress made in DAC, its associated technologies, and the advances made in the state-of-the-art. Thus, it is proposed to use traditional heating, ventilation, and air conditioning (HVAC) system (mainly the air conditioning system), as a preexisting technology, to capture CO<sub>2</sub> directly from the atmosphere, such that the energy needed to capture is provided by the HVAC system of choice.

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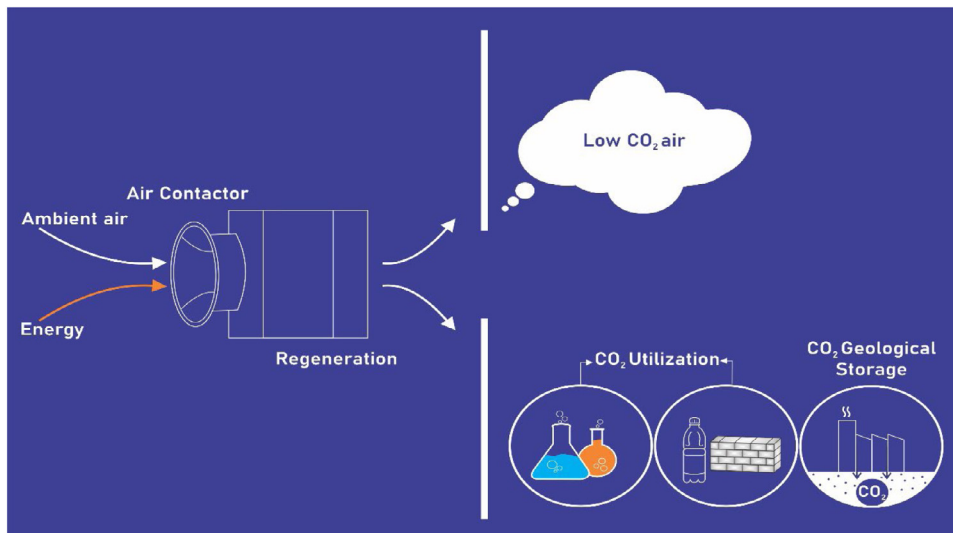
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## 1. Introduction

CO<sub>2</sub> is the most abundant greenhouse gas in the earth atmosphere today; its concentration currently stands at ~400 ppm by volume, while others (such as N<sub>2</sub>O and CH<sub>4</sub>) that have higher potency for global warming are in trace amounts (McCarthy et al., 2001; Altamash et al., 2020). Moreover, CO<sub>2</sub> is also the most radiative forcing, non-condensing, and longest-lived greenhouse gas in the atmosphere (Myhre et al., 2014). N<sub>2</sub>O and CH<sub>4</sub> can only last for about 114 years and 12 years, respectively, CO<sub>2</sub> can stay up in the atmosphere for millennia (Solomon et al., 2007). The two most anthropogenic activities, which have allowed about 100 ppm increase in the atmospheric concentration of CO<sub>2</sub> in the past 100 years are widespread deforestation (either for agricultural purposes or for urbanization expansion) and fossil fuel consumption. Within the same period, the global surface mean temperature has recorded ~1 °C increase (Hansen et al., 2011). As predicted, a 2 °C rise in the global surface mean temperature above pre-industrial era could cause irreparable damages to the Earth's ecosystem, which include, but not limited to, ocean acidification, mass extinction of biodiversity and severe weather conditions (Pachauri et al., 2014; Amhamed et al., 2022). Climate experts have warned, "If emissions of all greenhouse gases to the atmosphere were to stop today, though very unlikely, the climate impacts of the existing concentrations of N<sub>2</sub>O and CH<sub>4</sub> in the atmosphere would dissipate in few decades, whereas the existing CO<sub>2</sub> in the atmosphere would remain behind to warm the globe for centuries to come" (Hausfather, 2015). To reverse the trend, the best proactive measures should have been taken decades ago when the effects, such as sea level rise, global warming, etc. of climate change were just appearing. Whatever measures taken today is largely reactive in nature.

As reported by Keith (2000), there are about four approaches to address global warming, namely; adaptation, geoengineering, mitigation, and industrial carbon management (ICM). Adaptation is simply to live with and modify human behaviors around global warming problems; like construction of barriers to address the rise in sea level. Geoengineering involves actively addressing the problems by manipulating the environment to countervail any direct impact of climate change; for example, shielding the earth from certain amount of direct sunlight by the modification of albedo in space. Mitigation, as the name implies, is to avoid the consumption of fossil-based fuels by switching to energy sources with low carbon contents, e.g., nuclear, wind or solar energy. The last approach, ICM, deals with persistent consumption of fossil-based fuels while capturing the accompanied CO<sub>2</sub> for storage (CCS) or for utilization (CCU), is the most touted strategy to tackle the current and foreseeable future global climate change challenges. Although it has been reported (Campbell, 2019) that all the strategies are to be combined to combat climate change challenges head-on, some strategies require stringent policy frameworks for their applications and implementations. As a result, the focus of this review is on ICM whose implementation requires more of technical engagements rather than policy frameworks. This review, however, does not support unbridled consumption of fossil-based fuels as inferred in ICM definition, the current energy reality is that fossil fuels may remain the main energy driver for at least the next century (Sovacool, 2016), and the world scientific community must devise means to capture the accompanied CO<sub>2</sub>, especially to lower the current CO<sub>2</sub> concentration in the atmosphere.

There are several available options for CO<sub>2</sub> emissions reduction in the atmosphere. Most plants can only capture their emissions in the range of 50%–94% (Leeson et al., 2017), the uncaptured CO<sub>2</sub> clearly finds its way into the atmosphere. Even in an ideal industrial setup, in which 100% of CO<sub>2</sub> generated is captured onsite, it is still technically difficult to directly apply end-of-pipe capture system to the CO<sub>2</sub> emitted by transport sector (i.e., marine, aviation and land transports), which contributes about 50% to global greenhouse gas (GHG) emissions (Seipp et al., 2017a). These realities point to undeniable necessities to create ways to either return the atmospheric concentration of CO<sub>2</sub> to the pre-industrial era or find means to reduce its impacts on humans/environment in a way that is independent of CO<sub>2</sub> generation origin.



**Fig. 1.** Schematic representation of direct air capture of CO<sub>2</sub> with utilization and storage.  
Source: Redrawn from David Sandalow et al. (2018).

Returning the atmospheric concentration of CO<sub>2</sub> to the pre-industrial era is almost impossible to achieve in this century, but keeping the global warming at  $\sim 1.5$  °C more than the pre-industrial era is possible but will involve adoption of aggressive carbon dioxide removal (CDR) technologies, which must ensure the removal of between 100 and 1000 GtCO<sub>2</sub> by the year 2100 (Rogelj et al., 2018).

Among all the current CDR technologies, direct air capture (DAC) is the likely technique to deliver the needed CO<sub>2</sub> removal because it is independent of CO<sub>2</sub> emission origin, and the capture machine can be stationed anywhere, especially in a location where the price of energy is very cheap or where renewable energy is relatively abundant.

A typical direct air capture process has: (1) air contacting medium containing the sorbent and, (2) regeneration segment. The contacting medium (see Fig. 1) allows ambient air to be exposed to the sorbent and enables airflow through the system to increase adsorption (if solid sorbent is used) or absorption (if liquid sorbent is used) of CO<sub>2</sub> in the air. DAC technology is relatively new, only few players are involved in its applications (Nemet et al., 2018). Interest in DAC has recently received some boosts with companies and countries pledging their supports to cut CO<sub>2</sub> releases to “net zero”. Such interests include reducing their emissions to the bare minimum, while compensating for any residual emissions with programs such as direct air capture or tree planting. Although there are efforts to capture CO<sub>2</sub> cheaply from the atmosphere, researchers are equally seeking the perfect method to store it – mostly in abandoned oil and gas wells or other appropriate geological formations – to avoid CO<sub>2</sub> leaking back into the atmosphere.

In addition to energy efficiency, the choice of a DAC technology is influenced by the capital expenses (CAPEX), operating expenses (OPEX), process reliability, equipment availability, operation flexibility, transportability, and size of the DAC unit, as well as integration of sustainable source of energy with DAC. Therefore, researchers need to reassess the technology for possible leap improvements rather than relatively small gains that are recorded whenever a new material or a new technique is reported. This is because there is no better time to rescue the planet from atmospheric CO<sub>2</sub> associated global warming. As a result, in this work, bibliometric analysis was first performed to identify any research gap, key research areas and trends and then based on the analysis result, the most cited literatures were carefully reviewed to evaluate the progress that made in DAC technology since 2002, in terms of related technologies, and the improvements made in the state-of-the-art. It was therefore proposed that the use of traditional HVAC system (mainly the air conditioning system), as a preexisting technology, to capture CO<sub>2</sub> directly from the atmosphere, such that the energy required to capture is provided by the HVAC system: whether it is the air conditioning system (in temperate climates) or the heater (in cold climates). This might be the potential for a leap improvement in the DAC technology.

## 2. Bibliometric analysis

By utilizing the bibliometric analysis, quantitative techniques were applied to bibliometric data to gain a one-step overview of current DAC technologies and key research areas, encapsulate the DAC research gap, know the current trend in DAC research, and obtain novel ideas for investigation. In this bibliometric analysis, scientific databases of Scopus and Web of Science were used to provide inputs to VOSviewer software to construct network maps and shed lights on the emerging trends in article and journal performances and explore the intellectual structure of DAC domain in the extant literature and the cumulative scientific knowledge. This helped us meticulously review the literature to assess the progress

made in DAC, its associated technologies, and the advances made in the state-of-the-art. The results of a bibliometric analysis focusing on DAC related studies over the past two decades are shown in Fig. 2.

In the analysis, four steps procedure suggested by Donthu et al. (2021) was used as a base guideline. In the first step, the aims and scope of the study were defined, in the second step, the technique for bibliometric analysis was chosen, in the third step, data were collected for bibliometric analysis, and in the fourth step, the bibliometric analyses were compared. These steps are repeated in rigorous ways by using keyword clustering and co-occurrence network analysis to filter results and identify DAC research gaps, research hotspots and carbon capture with utilization and storage and main regeneration options in DAC. By applying the keyword co-occurrence analysis technique, the connection between different research topics can be determined by examining the internal relationship between comparable words that have emerged simultaneously in a set of literature (Emich et al., 2020; Fahimnia et al., 2015).

Bibliometric data were collected on May 10, 2022, by research on the web search engines of Scopus and Web of Science. The research was performed using a time frame from 2002 to July 2022 to consider the articles that have been published over time. At the end of the search, information on 2814 articles was exported and then duplicate documents were removed manually, then the data were imported into the VOSviewer (version 1.6.18) to create a network map of author keyword co-occurrence. In early-stage, 20055 keywords were obtained, and then keywords were considered with a minimum number of ten occurrences after compiling all search files. Search terms in the search engine box included the followings: “direct air capture”, “direct air capture” and “atmospheric CO<sub>2</sub> concentration”, “direct air capture” and “carbon capture”, “direct air capture” and “carbon dioxide removal”, “direct air capture” and “carbon capture storage technologies”, “direct air capture” and “greenhouse emission”, “direct air capture” and “MOF”, “direct air capture” and “KRAFT”, “direct air capture” and “aqueous solution”, “direct air capture” and “sorbent”, “direct air capture” and “pressure swing adsorption”, “direct air capture” and “vacuum swing adsorption”, “direct air capture” and “pressure–vacuum swing adsorption”, “direct air capture” and “temperature swing adsorption”, “direct air capture” and “temperature–vacuum swing adsorption”, “direct air capture” and “moisture swing adsorption”, “DAC” and “design air contactor”, “direct air capture” and “carbon capture utilization”, “direct air capture” and “indoor air quality”, “direct air capture” and “air conditioner”. From almost 2000 scientific published papers since 2002, the most productive countries were the United States (618 papers), China (222 papers), the United Kingdom (177 papers), Germany (131 papers), and Canada (107 papers).

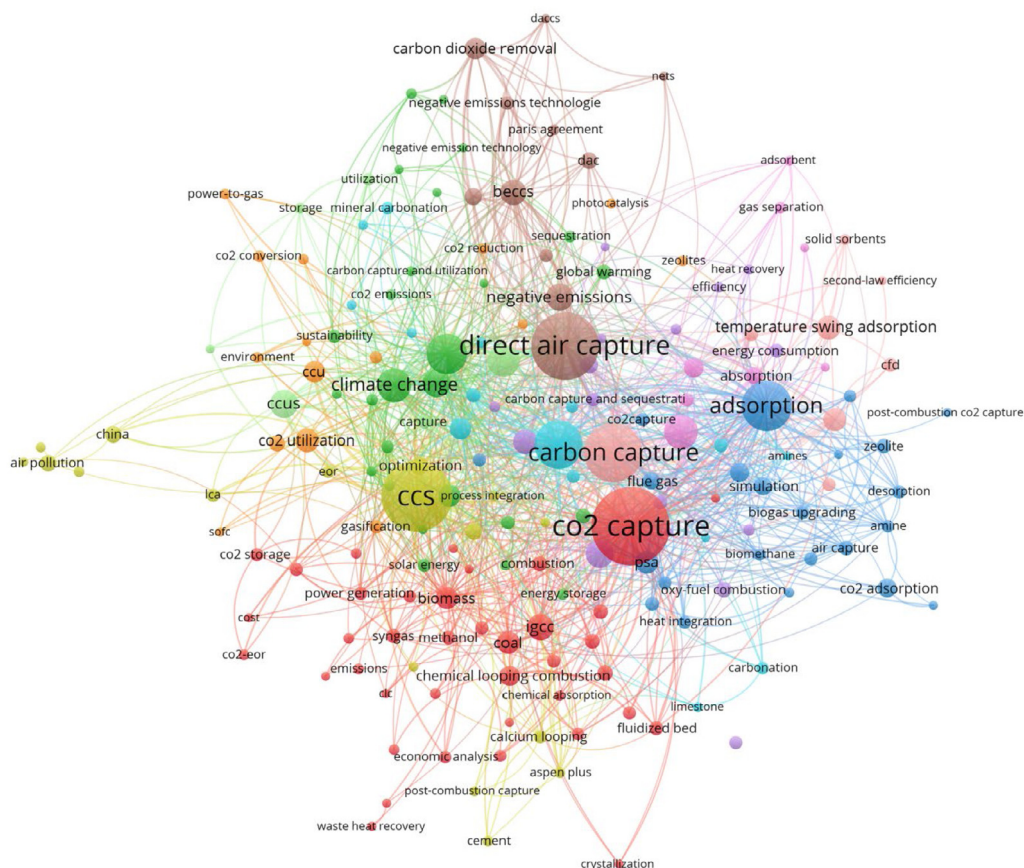
The results showed that most DAC research focused on (a) the design of air contactor with the utilization of liquid-based and solid-based, (b) regeneration options to minimize overall energy consumption, (c) assessment of future process integration with proven existing technology such as air-conditioning systems, (d) improvement in nanoscale carbon nitrides and metal–organic-frameworks (MOFs) in terms of stringent health, environmental conditions, and maximize the capture efficiency of selected sorbent materials, (e) major existing technology assessment of pressure swing adsorption (PSA), vacuum swing adsorption (VSA), pressure–vacuum swing adsorption (PVSA), temperature swing adsorption (TSA), temperature–vacuum swing adsorption (TVSA), moisture swing adsorption (MSA), and calcium-based Kraft process, (f) CO<sub>2</sub> utilization and storage applications. Gap analysis results showed that DAC technology has not yet reached its capability maturity level in contrast to existing carbon capture and storage technologies (CCS), however many potential technologies and materials are under development, and are aimed to be encapsulated in this review paper.

### 3. Sorbent system for DAC

Carbon dioxide (CO<sub>2</sub>) is an acid gas, which means in most cases the sorbents (either solid or liquid) used to extract CO<sub>2</sub> from gas streams are usually conditioned to be basic in nature for the sorption to occur. After the initial sorption, the next stage is to release (desorb) the captured CO<sub>2</sub> from the sorbent (regeneration), which returns the sorbent to its original (pre-sorption) state in readiness for the next rounds of capture. The crucial part of DAC is the sorbent, and an ideal sorbent for DAC system must fulfill some set of conditions. The first set of conditions that must be satisfied before other important parameters are: the capture must be done at ambient conditions because it is uneconomical to pressurize, cool or heat large quantity of air (which rules out membrane or cryogenic based separation technologies) and the energy for capture must be sourced from non-carbon based form of energy in order to ensure that more CO<sub>2</sub> is not released during capture (i.e., to attain negative emission). If these first set of conditions are met, then the listed sorbent properties below must be satisfied depending on the applications:

- High selectivity
- High capacity
- Fast transport and kinetic properties
- Thermal and chemical stability
- Mechanical properties (case of solid sorbent)
- Ease of loading (case of solid sorbent)
- Resistance to fouling
- Ease of regeneration
- Low cost



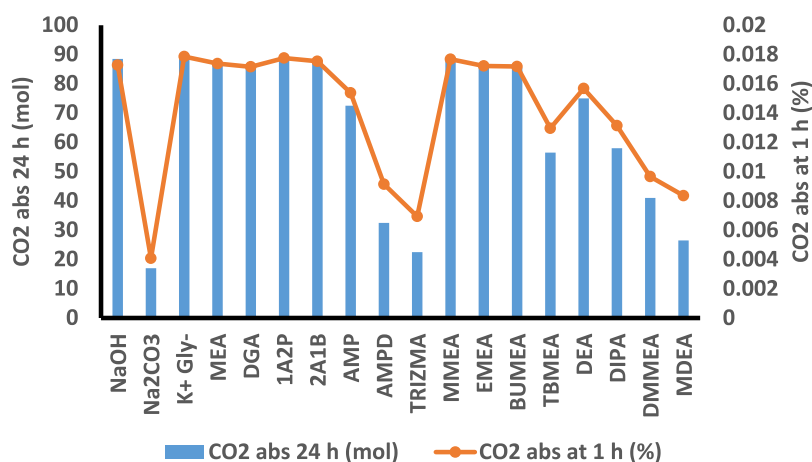


**Fig. 2.** Bibliometric analysis network map of direct air capture (DAC) keywords co-occurrence, 2002–Jun2022..

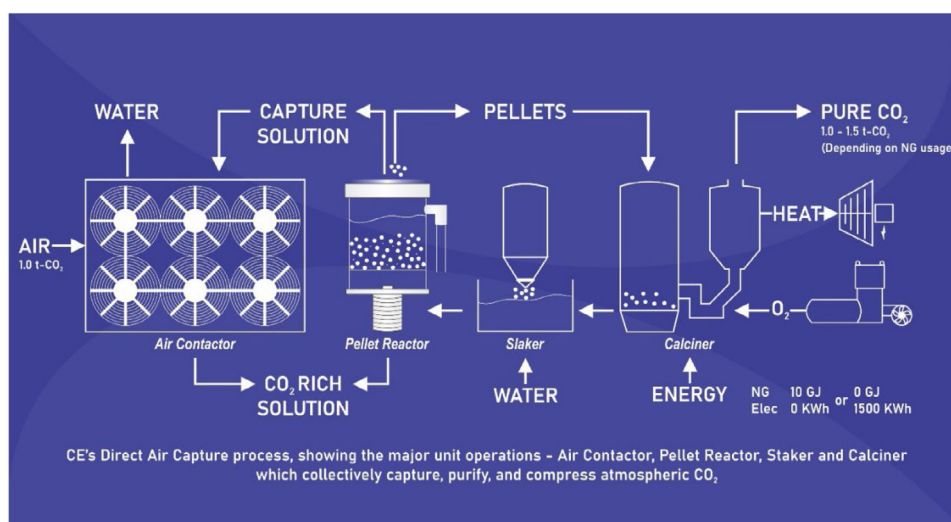
Although no material has been identified with all the above outlined characteristics satisfied, persistent research efforts have been shown, especially in the last two decades (Sanz-Pérez et al., 2016), to develop different classes of liquid as well as solid based sorbents that have potentials applicable to DAC technology, like solid-supported amines (Wang et al., 2011; Choi et al., 2011b,a), metal-organic framework (MOFs) (McDonald et al., 2012; Bhatt et al., 2016), alkali- and alkaline-earth bases (such as  $\text{Ca}(\text{OH})_2$ , KOH and NaOH) (Bacocchi et al., 2006; Zeman, 2007; Stolaroff et al., 2008; Mahmoudkhani and Keith, 2009).

### 3.1. Liquid sorbents

Aqueous monoethanolamine (MEA) is the most researched sorbent for CO<sub>2</sub> capture at point sources, and the template on which other alkanolamines are referenced. For direct air capture, MEA was reported to be inefficient in removing CO<sub>2</sub> at concentration of 400 ppm (Socolow et al., 2011). Moreover, alkanolamines were reported to have lower absorption rate compared to alkaline liquid sorbents, degrade when exposed to oxygen (Lepaumier et al., 2009), have high regeneration energy requirement due to the absorption of water and by and large, environmentally unfriendly (Veltman et al., 2010). However, a recent screening study of different alkanolamines under DAC conditions (0.044% of CO<sub>2</sub> in air) was conducted, the results are shown in Fig. 3. The results showed that some amines can reach the adsorption capacity of NaOH after 24 h. Moreover, amines can achieve similar absorption rate based on the reported absorption percentage after 1 h. The advantage of these amines over aqueous alkali hydroxides is that they have the potential to consume less low grade thermal energy in regeneration (Barzagli et al., 2020). Pyrrolizidines based sorbent was also used experimentally to absorb CO<sub>2</sub> from compressed air at 400 ppm over nine days, and the results showed higher weight of sorbents, which indicate CO<sub>2</sub> absorption and there was no oxidation of the sorbent, but the absorption temperature was not indicated (Hanusch et al., 2019). Other study investigated the use of hydrophobic phenyl group into alkylamines, and they found that OXDA, MXDA, PXDA did not absorb any water with CO<sub>2</sub> under DAC conditions (Inagaki et al., 2017). Other sorbents that have potentials for application in DAC are ionic liquids (ILs) due to their low melting point and the ability to tailor their properties by structural manipulations. Several research activities have been reported to investigate ILs as substitutes for alkanolamines as sorbents for CO<sub>2</sub> capture at point sources (Hasib-ur Rahman et al., 2010; Ramdin et al., 2012; Gurkan



**Fig. 3.** CO<sub>2</sub> absorption percentage of unhindered amines at 1 h and total absorbed CO<sub>2</sub> moles after 24 h compared to aqueous alkali hydroxide (NaOH) under the same conditions based on amine concentration of 1.5 mol. dm<sup>-3</sup> (Barzagli et al., 2020).



**Fig. 4.** Direct air capture based on high temperature liquid sorbent by Carbon Engineering.  
Source: Redrawn from C. Engineering (2022).

et al., 2010). This is mainly due to their relatively lower regeneration energy and low volatility (Ramdin et al., 2012). For DAC applications, Chen et al. (2017) created a pyrene based conjugated polymer and [P4444][p-2-O] ionic liquid to capture CO<sub>2</sub> from ambient air with a selectivity of 98.8%, and the subsequent photo-reduction to CO under visible light. One good property of ILs is that, when functionalized with amines, they allow both physical and chemical interactions with CO<sub>2</sub>, which improve absorption capacity greatly at low CO<sub>2</sub> partial pressures (Niedermaier et al., 2013; Chen et al., 2013). However, the process involved is difficult to scale up and very costly.

The latest benchmark sorbents for application in DAC system involves the use of aqueous solution of potassium hydroxide (Keith et al., 2018) or sodium hydroxide (Zeman, 2007). However, the aqueous alkali is regenerated at high temperature (> 900 °C). In fact, one of the key players in DAC (Carbon Engineering) constantly optimizes its system, one of which is the change of sorbent used from aqueous NaOH to aqueous KOH in order to increase capture efficiency (Smith et al., 2019; Holmes et al., 2013). The current plant setup of Carbon Engineering is shown in Fig. 4, in which CO<sub>2</sub> in ambient air is selectively absorbed by aqueous solution of KOH to form carbonates and the carbonates form are sent to calciner to energetically release the CO<sub>2</sub>. However, this regeneration energy is huge, and it is what makes solid sorbent application in DAC more attractive than the liquid-based sorbents; with solid sorbents, regeneration can be achieved at lower temperature (< 400 °C). Thus, solid sorbent-based DAC is economically more attractive because its regeneration energy requirement can be supplied from the waste heat from industrial processes can handle, which when integrated would eventually lead to lower operating costs.

In a bid to find solutions to the huge regeneration energy involved in this DAC benchmark, Custelcean et al. (2019) demonstrated a bench-scale absorption based direct air capture of CO<sub>2</sub> using aqueous salts of amino acid (potassium sarcosinate and potassium glycinate). To regenerate the salt of amino acid, the resulting CO<sub>2</sub>-rich component was reacted with solid meta-benzene-bis(iminoguanidine) (m-BBIG) at room temperature to crystallize out hydrated m-BBIG carbonate salt. The carbonate crystals formed, (m-BBIGH<sub>2</sub>)(CO<sub>3</sub>)(H<sub>2</sub>O)<sub>n</sub> (n = 3–4), was mildly heated to around (60–120 °C) to release the captured CO<sub>2</sub> to quantitatively regenerate solid m-BBIG. The low regeneration temperature offered by the crystallization process avoids heating up the aqueous amino acid sorbents, and as a result reduces their loss via oxidative and thermal degradation. The sarcosine/m-BBIG system offered CO<sub>2</sub> cyclic capacity (measured through three cycles) in the range of 0.12–0.20 mol/mol. Although the regeneration energy required (360 kJ/mol or GJ/ton CO<sub>2</sub>), which involves enthalpy of water and CO<sub>2</sub> released, is higher than that reported for the benchmark of DAC system (involving CaCO<sub>3</sub> at 278 kJ/mol or 6.3 GJ/ton CO<sub>2</sub>), the core advantage of using m-BBIG/amino acid system is the regeneration temperature (60–120 °C), which can be sourced from low-grade waste heat unlike the required temperature (900 °C) reported for the benchmark system to break down CaCO<sub>3</sub>.

In a recent reported account of low temperature liquid sorbent, Seipp et al. (2017b) described an aqueous system involving the use of guanidine for direct CO<sub>2</sub> capture from the atmosphere and bound the resulting guanidine–CO<sub>2</sub> amalgam as carbonates. The carbonates obtained are held together by weak guanidinium–hydrogen bonding with low aqueous solubility, enabling its separation from solution to be achieved easily by filtration (without the need for evaporation). For quantitative regeneration of guanidine sorbent, CO<sub>2</sub> can be released from the carbonate crystals at temperature range of 80–120 °C.

The huge regeneration energy budget is still a barrier for tested liquid sorbents, and it is what makes solid sorbent application in DAC more attractive than the liquid-based sorbents; with solid sorbents, regeneration can be achieved at lower temperature (< 400 °C). Thus, solid sorbent-based DAC is economically more attractive because its regeneration energy requirement can be supplied from waste heat that industrial processes can handle, which when integrated would eventually lead to lower operating costs.

### 3.2. Solid sorbents

Solid-based sorption is divided into physisorption and chemisorption, and these are subdivided into organic and inorganic types. For inorganic chemisorption, solid CaO, Ca(OH)<sub>2</sub>, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and NaOH have all been tested to capture CO<sub>2</sub> in ambient air. The associated problems; in the case of solid NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and NaOH are the low adsorption rates and high regeneration temperature (> 927 °C) (Nikulshina et al., 2008). In the case of CaO and Ca(OH)<sub>2</sub>, higher rates of adsorption were achieved but only at elevated temperature (> 400 °C) (Nikulshina et al., 2007, 2009), which is not practical for DAC system.

In a recent work, Samari et al. (2019) demonstrated and compared the performance of two lime-based sorbents for direct air capture of CO<sub>2</sub> in a fixed bed reactor. The lime-based sorbents consisted of mixed limestone (10% calcium aluminate and 90% natural limestone) and 100% natural limestone. The best performance was obtained when the sorbents were pre-humidified and the inlet air was at 55% relative humidity, which was better than the performance obtained when the inlet air alone was humidified. The worst performance was obtained with a completely dry system (having no humid inlet air nor humidified sorbents). When the performance of the sorbent systems was compared over nine cycles, the mixed limestone had a slow decay (from 80 to 71%) than the natural limestone (from 93 to 76%), which is reported to be a result of better porosity of the former. The breakthrough curves of the two systems were later fitted with shrinking-core gas–solid reaction model, which revealed that mixed limestone had better effective diffusivity due to its better porosity. With all the improved performance reported, it is important to note that the regeneration temperature was at 850 °C, which is still very high for cost implication. Other solid metal oxides and hydroxides which have been tested for CO<sub>2</sub> capture in air include Mg(OH)<sub>2</sub> and MgO (slow kinetics of adsorption) (Stolaroff et al., 2005), and Zn(OH)<sub>2</sub> (could not be regenerated) (Colombo, 1973). In submarine atmosphere, LiOH was used for CO<sub>2</sub> removal with good adsorption rates, however, the Li<sub>2</sub>CO<sub>3</sub> formed could not be regenerated (Campbell, 2019). A good metal hydroxide that showed promising adsorption rates and low regeneration energy is AgOH (Ranjan and Herzog, 2011), however, scaling up any process involving the use of silver, gold or platinum has always been difficult due to their exorbitant cost.

For physisorption of inorganic type, the interactions governed by CO<sub>2</sub> trapping in solid-state, open-structure systems, such as those found in microporous materials like MOFs and zeolites, make tuning CO<sub>2</sub> equilibrium easy, particularly in a given environment. This provides a low-energy and efficient way of storing/releasing CO<sub>2</sub> when entrapped in these materials pores. Zeolites for example, when tuned appropriately, provide efficient and selective adsorption/desorption of CO<sub>2</sub> in low concentration regime due to a number of zeolite intrinsic properties; pore architecture, nature of extra framework cations, low price, crystal size and chemical composition are just few of them (Choi et al., 2009; Siriwardane et al., 2001; Zukul et al., 2010). For example, a number of research activities, involving zeolite 13X (Kumar et al., 2015), γ-alumina (Rege et al., 2000), K-LSX, Li-LSX and Na-LSX (Stuckert and Yang, 2011) have been reported, the major problem with using these sorbents for DAC is their low CO<sub>2</sub> selectivity in humid air. For example, Kumar et al. (2015) investigated five materials (involving four physisorbents porous materials and one chemisorbent material) for their capacity to selectively adsorb CO<sub>2</sub> from either point sources or for direct air capture applications. The four physisorbent materials investigated are SIFSIX-3-Ni, (hybrid ultramicroporous material), Mg-MOF-74/Mg-dobdc and HKUST-1 (MOFs),



**Table 1**

Isosteric heat of adsorption, gas sorption, selectivity, and kinetic data for different physisorption materials at 298 °K (Mukherjee et al., 2019).

Material	CO <sub>2</sub> Qst <sup>a</sup> (kJ mol <sup>-1</sup> )	CO <sub>2</sub> uptake <sup>b</sup> (mmol g <sup>-1</sup> )	N <sub>2</sub> , 1 bar (mmol g <sup>-1</sup> )	H <sub>2</sub> O, 1 bar (mmol g <sup>-1</sup> )	SCW	SCN	t <sub>90</sub> <sup>c</sup> (mins)
Mg-MOF-74	42	0.05	0.85	33.33		238	20–40
Zeolite 13X	39	0.4	0.42	18.76		562	
ZIF-8	27	0.0006	0.1	1.44	0.08	3.1	
SIFSIX-18-Ni-β	52	0.4	0.04	1.64/0.96	16.2		1
SIFSIX-3-Ni	45	0.4	0.16	8.8		1438	1
NbOFFIVE-1-Ni	54	1.3	0.15	10.09	0.03	6528	1
TIFSIX-3-Ni	49	1.2	0.18	7.46		8090	1

<sup>a</sup>Virial fitting of CO<sub>2</sub> sorption data collected between 0 and 10 mbar.

<sup>b</sup>Under the conditions of 500 ppm of CO<sub>2</sub> and temperature of 298 K.

<sup>c</sup>The time to reach 90% of CO<sub>2</sub> uptake under conditions of 1 bar and 303 K.

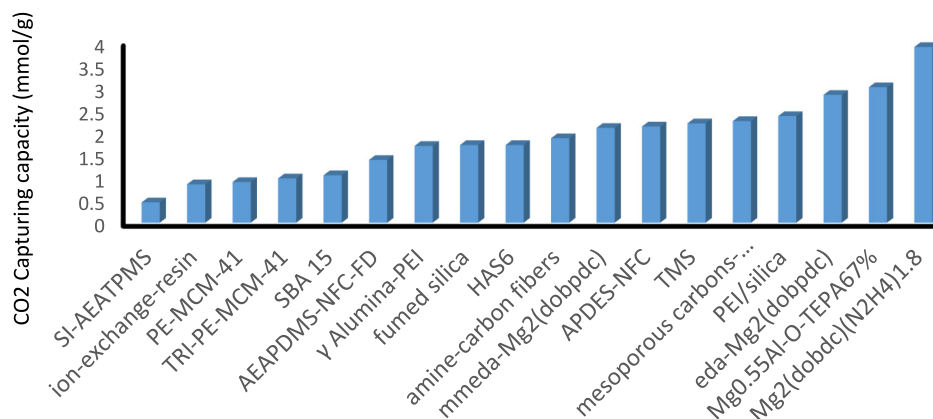
and Zeolite 13X (inorganic). The one chemisorbent material investigated is TEPA-SBA-15 (an amine-modified mesoporous silica). The results obtained showed the four physisorbents to be capable of effectively removing CO<sub>2</sub> from CO<sub>2</sub>-rich gas mixtures, however, reaction and competition with water vapor in the atmosphere considerably reduced their DAC capability. Mukherjee et al. (2019) Integrated hydrophobicity from methyl groups and inorganic anions into ultramicroporous material, resulting in creating a material (SIFSIX-18-Ni-β) with fast kinetics and high selectivity and was compared to other physisorption materials as illustrated in Table 1. SIFSIX-18-Ni-β was reported to have faster kinetics under CO<sub>2</sub> concentration of 1000 ppm compared to TEPA-SBA-15 and the tabulated isentropic heat is lower than typical chemisorption values (90 kJ/mol); however, the regeneration energy will include the desorption heat of adsorbed water and nitrogen which leads to higher energy requirements compared to chemisorption materials. Moreover, the CO<sub>2</sub> uptake of the materials in Table 1 is low in comparison with chemisorption materials. The chemisorbent material was not highly affected by the presence of water vapor. However, the energetics of the chemisorbent is not as promising for recycling as the physisorbents such as SIFSIX-3-Ni. Further research is necessary for physisorbent materials to adequately compete with chemisorbent materials for application in DAC. Faujasites (FAU) X and Y are a group of the most synthesized and used zeolites. Zeolite Y is inside the famous FCC catalysts (with some modifications of the original Y-zeolite, one can get a wide variety of FCC catalysts). X has a Si/Al ratio from 1 to about 1.5 and Y has a Si/Al ratio > 1.5, which makes it more structurally stable but with a lower ion exchange capacity than X. The synthesis procedure is very well established and documented in the literature (the Synthesis Commission of the International Zeolite Association (IZA)) (IZA, 2020). However, the synthesis of the nanoscale-FAU material developed by a group at University of Calgary in Canada is novel and has been patented recently (Nassar et al., 2019). This material is a Type-X FAU zeolite, which may be interesting for CO<sub>2</sub> capture from the intake air. Keeping in mind that commercial production recipes of FAU aluminosilicates are only “insinuated” in the patent literature and precise details are not provided.

In a recent development, Wilson and Tezel (2020) demonstrated the CO<sub>2</sub> capture ability of seven commercially available structured Faujasite zeolites (G5CO<sub>2</sub>M, APG-III, Ca-X, Na-LSX, Z10-01, Z10-02ND and Na-X HP) in dry ambient air through a packed bed in a temperature vacuum swing adsorption (TVSA) process. Three materials (APG-III, Z10-02ND and Na-LSX) with the smallest SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios also had the highest CO<sub>2</sub> selectivity among the Faujasites tested. APG-III and Z10-02ND had the highest diffusion time constant of CO<sub>2</sub>, the characteristics that make them popular for air purification purposes. To achieve 95% CO<sub>2</sub> concentration from about 400 ppm in dry air, four step TVSA was employed, which involves pressurization with feed, adsorption, blowdown, and desorption. Further analysis of the Faujasites, especially of APG-III and Z10-02ND (owing to their air purification characteristics), is needed for direct air capture application in humid environments.

Unless they are functionalized with amines (Hicks et al., 2008; Gebald et al., 2011; Lu et al., 2013) to increase their CO<sub>2</sub> selectivity, their use would only be confined to a condition where CO<sub>2</sub> is to be removed from dry air.

The literature is replete with amine-functionalized physisorption materials for DAC application. Darunte et al. (2016) functionalized MOFs, MIL-101(Cr), with two amines, branched and low molecular weight poly(ethylene imine) (PEI-800) and tris (2-amino ethyl) (TREN) to form two composites, MIL-101(Cr)-PEI-800 and MIL-101(Cr)-TREN. At high loadings of TREN, the MIL-101(Cr)-TREN composites exhibited high CO<sub>2</sub> capacities, however a substantial loss of amines was detected over multicycle operations of temperature swing adsorption, which is linked to the relative volatility of TREN. On the other hand, MIL-101(Cr)-PEI-800 composite showed a better stability over multicycle operations. At low amine loadings, MIL-101(Cr)-PEI-800 composite displayed low amine efficiencies, but when amine loadings were increased, amine efficiencies improved considerably. At the peak of amine loadings, kinetic limitations related to pore blockage led to only slight increase in uptake and significantly slowed adsorption kinetics. With these drawbacks, the authors concluded that these adsorbents are not very efficient for DAC applications.

In another recent development, Anyanwu et al. (2019) grafted commercially available silica gels of different pore sizes with a triamine (N<sup>1</sup>-(3-Trimethoxysilylpropyl)diethylenetriamine) in dry conditions to investigate the CO<sub>2</sub> capture



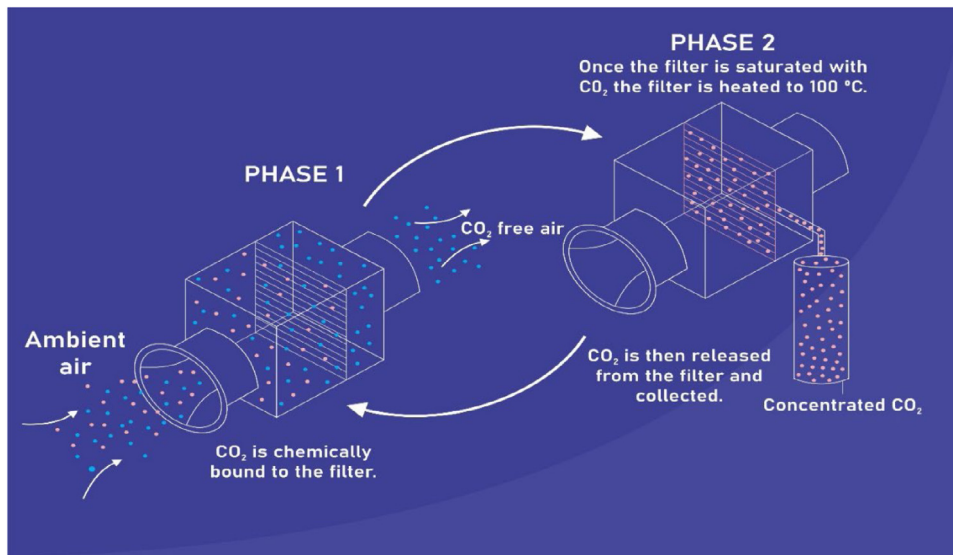
**Fig. 5.** CO<sub>2</sub> capacity of different amines modified materials under DAC conditions, the reference for eda-Mg<sub>2</sub>(dobpdc), Mg<sub>2</sub>(dobdc)(N<sub>2</sub>H<sub>4</sub>)1.8 and mmeda-Mg<sub>2</sub>(dobpdc) is (Liao et al., 2016), SBA 15, AEAPDMS-NFC-FD, fumed silica, HAS6, TMS and mesoporous carbons-PEI is (Wang et al., 2015), TRI-PE-MCM-41, ion-exchange-resin, amine-carbon fibers and PEI/silica is (Gebald et al., 2011), γ Alumina-PEI is (Sakwa-Novak and Jones, 2014), Mg<sub>0.55</sub>Al-O-TEPA67% is (Zhao et al., 2022), APDES-NFC is (Gebald et al., 2014), and SI-AEATPMS is (Wurzbacher et al., 2011).

performance. Silica gel with the largest pore size (150 Å) and lowest surface area (309 m<sup>2</sup>/g) had the best performance and was selected for wet-grafting conditions. At 75 °C and 1 bar, the wet-grafted 150 Å gels resulted in 2.3 mmol/g adsorption capacity, fast CO<sub>2</sub> uptake and good cycle stability. For direct air capture ability (carried out at 25 °C in ambient air having CO<sub>2</sub> concentration of 415 ppm), the wet-grafted 150 Å silica gels resulted in CO<sub>2</sub> capture capacity of 1.098 mmol/g as against 0.773 mmol/g recorded under dry-grafting conditions. Kwon et al. (2019) prepared Poly(ethyleneimine)-impregnated sorbents utilizing bimodal meso-/macroporous hierarchical silica support materials (PEI-H-SiO<sub>2</sub>). The authors reported unexpected performance of the sorbents when used in both direct air capture (using simulated air at 400 ppm CO<sub>2</sub> concentration) and flue gas (10% CO<sub>2</sub> concentration) conditions at a fixed temperature. The reported unexpected observations are; (i) efficiency of sorption performance is influenced by the applied impregnation method and (ii) at near room temperature and dry CO<sub>2</sub>, the sorbents displayed similar sorption capacities in both direct and flue gas conditions, showing step-like CO<sub>2</sub> adsorption isotherm. The maximum adsorption capacity reported were 4.1 and 2.6 mmol/g at optimized adsorption temperature for flue gas and direct air capture conditions, respectively. When CO<sub>2</sub> was mixed with water vapor to simulate ideal atmospheric condition (at 400 ppm), adsorption capacity of the simulated direct air capture increased to 3.4 mmol/g, indicating predictable carbon capture efficiency during high humidity season. One of the main and initial parameters which should be used to assess the sorbent performance is its CO<sub>2</sub> capacity. The capacity of sorbent differs based on CO<sub>2</sub> concentration levels and the existed species in the gas. A comparison among different chemisorption materials on their reported CO<sub>2</sub> capacity under DAC conditions is shown in Fig. 5. Other parameters like cyclic capacity and energy requirements highly affect a sorbent's CO<sub>2</sub> capture performance; however, these parameters can be illustrated if only full cycles were implemented, and this is discussed in Section 4.2.6.

As Liu et al. (2021) briefly reported, solid sorbents with narrow micropores can aid CO<sub>2</sub> adsorption enthalpy, which is good for DAC application. However, the use of amines to enhance the capture capacity of the solid sorbents may lead to pore blocking effects, which could reduce the sorption capacity, the kinetics, and lower the CO<sub>2</sub> diffusion into the pores' architecture. As a result, a pore structure with good hierarchy and connectivity is desired for effective CO<sub>2</sub> sorption.

For anion exchange resins, their CO<sub>2</sub> uptake as well as their regeneration technique is very good as reported in the literature (Lackner and Wright, 2016; Wang et al., 2013a), although sorption of CO<sub>2</sub> is achieved when the resins are dry and desorption occurs when they are wet (a condition known as moisture swing). The major impediment for their use in DAC is the need to always make the resins dry, which is unsuitable to atmospheric condition in humid climate.

The current state-of-the-art in solid sorbents are MOFs (Sinha et al., 2017) and amine-based solids (Sujan et al., 2019a). In amine-based solids, Climeworks is known to have conditioned its solid sorbents to capture CO<sub>2</sub> at ambient conditions and at regeneration temperature in the range of 80–100 °C. Climeworks was founded in 2009 in Switzerland by Climeworks (2019), till today, the company is still a key player in CO<sub>2</sub> removal from the atmosphere using solid sorbents. In 2014, the company partnered with Sunfire and Audi to launch a pilot plant that captures 80% of CO<sub>2</sub> in ambient air for further conversion of the captured CO<sub>2</sub> to synthetic diesel. In 2017, Climeworks launched a new commercial scale CO<sub>2</sub> removal plant in Switzerland that delivers CO<sub>2</sub> to a nearby greenhouse for agricultural purposes. Other works by Climeworks involve the DAC to storage that was developed in Iceland (Climeworks, 2017) to permanently sequester CO<sub>2</sub> in geologic formations. The current plant setup of Climeworks is shown in Fig. 6, in which CO<sub>2</sub> in ambient air is selectively adsorbed onto a filter by a solid sorbent, once the filter is saturated with CO<sub>2</sub>, it is heated to about 100 °C temperature for regeneration. The modular design of Climeworks is beneficial to DAC for several reasons. It reduces operating costs, promotes scalability, accommodates diversity in deployment, resolves transportation challenges, and enables automated



**Fig. 6.** Direct air capture based on low temperature solid sorbent by Climeworks.  
Source: Redrawn from Beuttler et al. (2019), licensed under CC BY.

manufacturing. Adsorption and desorption of CO<sub>2</sub> are carried out within one device, the “CO<sub>2</sub> Collector”. Designed for efficient fit within a steel frame, six collectors can be placed inside a standard 40 ft. shipping container. The fan, which draws in air for adsorption to occur, and the two lids at the entry and exit that form an airtight enclosure to hold the CO<sub>2</sub> in place during desorption, are the only moving parts in the collector. Modules are designed to operate as an integrated system, and capacity can be expanded with the addition of new modules (Gutknecht et al., 2018).

#### 4. Advances on state-of-the-art DAC technologies

The current state-of-the-art in DAC system employs both liquid and solid based systems for selective removal of CO<sub>2</sub> from ambient air. Two important parameters that have seen great advancement over the years to improve DAC efficiency are the design of air contactors and sorbent regeneration techniques.

##### 4.1. Design of air contactors

There are not too many available options in the literature on the design of air contactor for liquid-based DAC system; to the best of our knowledge, only two have been reported. The first being the state-of-the-art air contactor by Carbon Engineering (detailed design drawing and analysis can be found in Holmes and Keith, 2012). The second is a membrane based gas–liquid contactor (Favre and Svendsen, 2012), however, there are no reported studies on this for DAC application, the available information on the designer’s website indicates that the technology is being prepared for future commercial projects (co2circulair, 2022).

In contrast to the liquid based DAC system, the literature is replete with different designs of air contactor for solid based DAC system (Erans et al., 2022). For example, fixed-bed (Bajamundi et al., 2019; Yu and Brilman, 2017; Wurzbacher et al., 2012; Gebald et al., 2013), fluidized-bed (Zhang et al., 2014), moving-bed (Yu and Brilman, 2020; Schellevis et al., 2020), fiber (Sujan et al., 2019b), and monolith (Sinha et al., 2017; Sakwa-Novak et al., 2016) contactor designs have all been studied for DAC applications. It is important to note that most contactor designs have been touted as the best by those researchers that apply them, however, improvement/changes in packing surface area, reaction kinetics or sorbent particle size can be controlled in one design to claim superiority over an alternative design. What is mostly reported, however, and again adopted by Climeworks, is fixed-bed contactor design (Bajamundi et al., 2019; Yu and Brilman, 2017; Wurzbacher et al., 2012; Gebald et al., 2013). It is important to note that in some recent work, moving-bed contactor design have gained traction. The reason behind this is for pressure drop reduction, avoidance of low height/diameter ratios, and adsorption performance improvement (Yu and Brilman, 2017; Schellevis et al., 2020).

##### 4.2. Regeneration options in DAC

Although an important design variable of a practical DAC technology is to maximize the capture efficiency of selected sorbent materials. The regeneration procedure, however, dictates the system overall energy requirements, which must be

minimized for realistic DAC operations. Maximizing CO<sub>2</sub> working capacity is one of the main objectives in the regeneration process, this is critical because if the CO<sub>2</sub> working capacity is low, the acceptable adsorbent cost becomes extremely low, thereby making the entire process economically unrealistic (Azarabadi and Lackner, 2019). Here we are highlighting the regeneration options reported in the literature.

#### 4.2.1. Pressure swing, vacuum swing, and pressure–vacuum swing adsorptions

Pressure swing adsorption (PSA) as a regeneration technique has been reported not suitable for DAC due to excessive compression of inlet gas, which add additional cost to the system operation (Sumida et al., 2012).

The working principle of VSA is similar to PSA, the main difference being that in VSA adsorption occurs at atmospheric pressure, while desorption occurs at pressures below the atmospheric pressure via the use of a vacuum pump (Dineen, 2020). VSA should be a more realistic regeneration technique for DAC than PSA, because it does not involve excessive compression of inlet gas. However, it has been reported that VSA is not a realistic regeneration option for DAC application because the desorption operation happens below 0.4 mbar (Zhu et al., 2021).

Pressure–vacuum swing adsorption (PVSA) is a blend of the PSA and VSA techniques, wherein adsorption and desorption occur above and below atmospheric pressure, respectively. However, the technique is not economically favorable for DAC, especially with the compression of inlet gas.

#### 4.2.2. Temperature swing and temperature–vacuum swing adsorptions

Temperature swing adsorption (TSA) is largely the regeneration option adopted for chemisorbents-like solid amines or other amine-functionalized solids. In laboratory-scale studies of amine-based CO<sub>2</sub> adsorbents, TSA is the preferred regeneration alternative (Sanz-Pérez et al., 2016). However, the disadvantage is that the produced CO<sub>2</sub> is diluted, and the amine is subject to significant oxidative degradation at temperatures slightly above 100 °C during desorption (Ahmadalinezhad and Sayari, 2014). The use of inert gas rather than air may prevent oxidative degradation. However, this can be costly at large scales. The use of pure CO<sub>2</sub> as stripping gas is an option for TSA for producing high-purity CO<sub>2</sub>, but this approach is associated with a risk of urea formation due to adsorbent deactivation (Jahandar Lashaki et al., 2019; Buijs, 2019). Since desorption takes place in an atmosphere containing high concentrations of CO<sub>2</sub>, the working capacity is also reduced. Steam stripping is a derivative of TSA, wherein saturated steam is employed as an inert gas purge, and pure CO<sub>2</sub> can be produced by the condensation of water from the product gas (Bos et al., 2019; Li et al., 2010a). The main disadvantage of this process is deactivation of the adsorbent through leaching of the amines (Sakwa-Novak and Jones, 2014; Chaikittisilp et al., 2011). Steam can be generated with this process at temperatures lower than 100 °C if vacuum is added in order to enhance desorption rate, but steam leaching of amines remains a serious issue (Wijesiri et al., 2019).

Temperature–vacuum swing adsorption (TVSA) technique combines vacuum and temperature swing for CO<sub>2</sub> desorption, which has the capacity to concentrate CO<sub>2</sub> from air close to 100% (Wurzbacher et al., 2012; Wijesiri et al., 2019). Nevertheless, this technique decreases the achievable CO<sub>2</sub> working capacity and increases the necessary temperature swing in comparison to TSA (Wurzbacher et al., 2011; Elfving et al., 2017). The reason is because in TVSA technique, to avoid product dilution, the inlet is closed when desorption takes place, leading to the formation of CO<sub>2</sub>-concentrated atmosphere in the vacuum pump and adsorption chamber when the gas is produced (Wurzbacher et al., 2011; Bajamundi et al., 2019). Although desorption temperature may be increased to increase CO<sub>2</sub> working capacity, but this increases the energy requirements for the process and there is a risk of thermal degradation of the adsorbents. Elfving et al. (2021) reported an experimental work to compare TSA and TVSA for direct air capture in terms of regeneration specific energy, CO<sub>2</sub> working capacity, and adsorbent regeneration. The work mainly focused on the assessment of TVSA with inert gas or air purge flow and the condition without gas purge flow. The study thus concluded that, using the air purge flow below 100 °C together with the mild vacuum mode gives better CO<sub>2</sub> working capacity, specific energy requirements, and regeneration of the adsorbent than the TVSA process with no inflow.

Wilson and Tezel (2020) used a single bed system packed with 20 g of zeolite X to demonstrate the capture and concentration of CO<sub>2</sub> from a dry ambient air stream using four-step TVSA (i.e., pressurization, adsorption, blowdown, and desorption). In the study, CO<sub>2</sub> was concentrated from 400 ppm to 95%, resulting in a total capture fraction of 81%. The low selectivity ratio (1.35 of CO<sub>2</sub>) meant that a simple two-step adsorption cycle could not guarantee 95% purity level because other atmospheric gases like O<sub>2</sub>, N<sub>2</sub>, and Ar could co-adsorb, thereby diluting the product gas. As a result, a four-step adsorption cycle was selected. Just like steam-assisted TVA, a recent study by Zhu et al. (2021), on solid supported amines, reported a three-step steam-supported temperature vacuum-swing adsorption (S-TVSA) for DAC application. One of the reported advantages of the process is the adsorption of H<sub>2</sub>O during the steam purge regeneration operation, which aided the CO<sub>2</sub> recovery with the heat supplied by the steam. The study further carried out the sensitivity analysis of the parameters and showed the trade-off correlation between performance and energy consumption. The study thus recorded the optimal CO<sub>2</sub> capture capacity of 4.45 mol · kg<sup>-1</sup> day<sup>-1</sup> at 0.295 MJ · mol<sup>-1</sup> energy requirement for the steam purge working at 90 °C temperature and 0.3 bar pressure, although no information was provided on the steam leaching of amines.



#### 4.2.3. Calcium-based Kraft process

The calcium-based Kraft process is the regeneration technique used in liquid alkaline absorption processes. Utilizing sodium hydroxide, the technique has been used for the removal of cellulose from wood in the paper industry. When sodium hydroxide is exposed to  $\text{CO}_2$  in the atmospheric air, the carbonate formed is reacted with calcium hydroxide to form calcium carbonate, and to regenerate the sodium hydroxide sorbent in the process known as Causticization. The calcium carbonate formed is then treated in a process known as calcination to release pure  $\text{CO}_2$ . This process requires large amount of energy input ( $178.2 \text{ kJ} \cdot \text{mol}^{-1}$ ) or temperature that ranges between  $600^\circ\text{C}$  and  $900^\circ\text{C}$  for separating pure  $\text{CO}_2$  from  $\text{CaCO}_3$  (Sanz-Pérez et al., 2016). Although one of the key players in DAC (Carbon Engineering) has relentlessly been optimizing this process, one of which is the change of sorbent used from aqueous  $\text{NaOH}$  to aqueous  $\text{KOH}$  in order to increase process efficiency (Smith et al., 2019; Holmes et al., 2013).

Recovery of subsequent alkaline solution in the traditional Kraft process is highly energy demanding. However, energy consumption can be reduced by using alternative regeneration processes. For example, in contrast to the conventional regeneration process, Mahmoudkhani and Keith proposed a titanate regeneration cycle that required half the amount of energy (Mahmoudkhani and Keith, 2009), whereas Kim et al. recently proposed an electrochemical approach for the recovery of  $\text{LiOH}$  from spent  $\text{CO}_2$  adsorbents (Kim et al., 2021). Moreover, Shu et al. (2020) used a  $\text{H}_2$ -recycling electrochemical cell to demonstrate simultaneous solvent recovery and desorption of  $\text{CO}_2$  through experimental means. The study achieved more than 95% purity level of  $\text{CO}_2$  at  $374 \text{ kJ} \cdot \text{mol}^{-1}$   $\text{CO}_2$  desorption energy. This is equivalent to the desorption energies reported by Keith et al. (2018) in their thermodynamic cycle and Sabatino et al. (2020) in their bipolar membrane electrodialysis at  $338 \text{ kJ} \cdot \text{mol}^{-1}$  and  $236 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively.

#### 4.2.4. Moisture swing adsorption

The purity level of  $\text{CO}_2$  obtained at regeneration of a DAC system is determined by the purpose of utilization. If the purpose of utilization is for agricultural greenhouse, in which low-concentration  $\text{CO}_2$  is desired, moisture swing adsorption technique can be selected to favor the intended use. For example, to enhance agricultural greenhouse with  $\text{CO}_2$ , the gas can be captured directly from the outside atmosphere and released inside the greenhouse using  $\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  based adsorbents. Rodríguez-Mosqueda et al. (2019) examined the effect of temperature, air flow rate, and water vapor pressure on  $\text{CO}_2$  desorption. From the results obtained, in comparison with Na-based adsorbents, K-based adsorbents have lower energy consumption and higher  $\text{CO}_2$  capture capacity. The capture capacity obtained was  $0.1 \text{ mmol CO}_2/\text{g adsorbent}$ , which was regenerated at  $50^\circ\text{C}$  with  $90 \text{ mbar H}_2\text{O}$ . The authors thus concluded that although the capacity obtained was lower than what are obtained with amine-based adsorbents, it is enough to satisfy the required  $\text{CO}_2$  in greenhouses. In another study, Wang et al. (2020) were able to increase the adsorption capacity of Moisture Swing Adsorption (MSA) system in which they grafted quaternary ammonium functional group onto high surface area mesoporous polymers. The resulting adsorbent had ultra-high kinetics half time of  $2.9 \text{ min}$  and a cyclic adsorption capacity of  $0.26 \text{ mmol g}^{-1}$  under atmospheric condition.

Moisture swing absorption (MSA) uses the traditional ion hydration procedure to trap and selectively release  $\text{CO}_2$  from the atmosphere (Shi et al., 2018). The technique comprises of coating heterogeneous ion exchange resin on a solid support (usually polymeric materials). By using an amine-coated anion exchange resin, for example, it is possible to capture  $\text{CO}_2$  from dry atmospheric air, and then release it with hydration or exposure to liquid or water vapor (Wang et al., 2013b). MSA is fascinating as it substitutes the required energy input of a PSA or TSA technique, simply requiring a water source, with the latent heat of evaporation, delivering all the required energy to drive the process (Wang et al., 2011). The major disadvantage of the process, however, is that the capture must be achieved in a dry atmospheric condition, which is not suitable for humid regions.

#### 4.2.5. Other regeneration option

Crystallization is another technique that offers DAC technology a low-cost  $\text{CO}_2$  separation from sorbents with minimal chemical and energy inputs. Seipp et al. (2017b) used aqueous guanidine sorbent (PyBIG) to capture  $\text{CO}_2$  from the atmosphere, binding it as crystalline carbonate salts ( $\text{PyBIGH}_2(\text{CO}_3)(\text{H}_2\text{O})_4$ ) by guanidinium hydrogen bonding. The solid obtained from the reaction has a very low aqueous solubility ( $K_{sp} = 1.0\text{--}(4) \times 10^{-8}$ ), which makes filtration a viable option for separating the solid from solution. As the crystals are heated to  $80\text{--}120^\circ\text{C}$ , the bound  $\text{CO}_2$  is released, and the guanidine sorbent is quantitatively regenerated. In a similar work within the same group, Brethomé et al. (2018) reported the crystallization of amino acid salts (sarcosine and glycine) with PyBIG to form a carbonate crystal ( $\text{PyBIGH}_2(\text{CO}_3)(\text{H}_2\text{O})_4$ ), which regenerated the salts of amino acid with mild heating from  $80\text{--}120^\circ\text{C}$ .

#### 4.2.6. Comparing full DAC systems

The direct  $\text{CO}_2$  capture from air puts some restrictions on the sorbents and regeneration methods. These restrictions can be represented by the low concentration of  $\text{CO}_2$  in air, the existence of moisture, oxygen, and nitrogen with much higher concentrations than  $\text{CO}_2$ . Full DAC cycles should be considered to account for all DAC conditions' restrictions for a comprehensive comparison among different capturing methods. Accordingly, Tables 2 and 3 below show only the studies that simulate a full adsorption/desorption cycle under real DAC condition. Table 2 gives insight on the main parameters of different liquid-based DAC systems and clarifies the disadvantage and advantages of different systems. Among the studies using the kraft process, Keith et al. (2018) developed the most optimized cycle in which they use  $\text{KOH}\text{--}\text{Ca}(\text{OH})_2$



**Table 2**

The main parameters of liquid sorbents under full DAC conditions cycles based on different regeneration methods.

Sorbent material	Regeneration method	Capacity	Adsorption conditions	Desorption conditions	Energy <sup>a</sup> (kJ/mol.)	Ref
NaOH–Ca(OH) <sub>2</sub> -option A	Kraft Process	0.42 MtCO <sub>2</sub> /y	500 ppm, ambient	900 °C	387th and 79.2 elec	Bacocchi et al. (2006) <sup>b</sup>
NaOH–Ca(OH) <sub>2</sub> -option B	Kraft Process	0.42 MtCO <sub>2</sub> /y	500 ppm, ambient	900 °C	264th and 70.4 elec	Bacocchi et al. (2006)
NaOH–Ca(OH) <sub>2</sub>	Kraft Process		380 ppm, ambient	900 °C	319th and 123 elec	Zeman (2007)
NaOH–Ca(OH) <sub>2</sub>	Kraft Process		400 ppm, ambient	900 °C	190–390th	Stolaroff et al. (2008) <sup>c</sup>
KOH–Ca(OH) <sub>2</sub>	Kraft Process	0.98 Mt-CO <sub>2</sub> /year	400 ppm, 20C and 64% RH	900 °C	178.2th and 63.7 elec	Keith et al. (2018) <sup>d</sup>
NaOH–Na <sub>2</sub> O·3TiO <sub>2</sub>			400 ppm	860 °C	150th	Mahmoudkhani and Keith (2009) <sup>e</sup>
NaOH–H <sub>2</sub> -recycling electrochemical	Electro chemical		DAC conditions		374th	Shu et al. (2020) <sup>f</sup>
glycine amino acids-PyBIG	Crystallization	0.28 mol/mol cyclic capacity	ambient conditions	8–120 °C	223th and without water 75th	Brethomé et al. (2018) <sup>g</sup>
H <sub>2</sub> O-trichelating iminoguanidine ligand (BTIG)	Crystallization	0.99 mol/mol CO <sub>2</sub> uptake	ambient conditions	60–150 °C	169th and without water 81th	Cai et al. (2020)
liquid AAS hydrogel particles (LAHPs)		0.96 mmol/g CO <sub>2</sub> uptake	420 ppm CO <sub>2</sub>	40–90 °C		Xu et al. (2021) <sup>h</sup>

<sup>a</sup>“th” means thermal energy while “elec” means electrical energy.<sup>b</sup>Calculations based on 70% efficiency for pumps and compressors and an average 90% efficiency for heat transfer units. Paper provided detailed specification for calcination cycle and analysis.<sup>c</sup>Single drop model was implemented and validated with experimental work, the required thermal energy only was calculated, and different energy values are based on different contactors.<sup>d</sup>The carbon engineering latest system, the energy based on their Aspen plus simulation.<sup>e</sup>Energy is the summation of reaction enthalpies. Theoretically, the cycle regeneration energy is about half of energy (90 kJ/mol) required for lime cycle (178.3 kJ/mol), electrical energy requirements was not counted.<sup>f</sup>Experimental desorption energy is 374 kJ/mol while theoretical is 164 kJ/mol.<sup>g</sup>Crystallization approach advantage is that no Amine leaching, no volatilization of low molecular amines.<sup>h</sup>The behavior of different AASs such as PSA (potassium sarcosinate), PA (potassium β-alanine), PP (potassium L-proline), PL (potassium lysinate), PSE (potassium serinate) and PM (potassium 2-methylalaninate), respectively were evaluated and compared.

and reported thermal and electrical energy requirements of 178.2 and 63.7 kJ/mol., respectively. Other studies used crystallization and electrochemical regeneration methods which have their advantages, as indicated in Table 2, but the energy requirement is still higher than Carbon Engineering optimized cycle (Shu et al., 2020; Brethomé et al., 2018; Cai et al., 2020). NaOH–Na<sub>2</sub>O·3TiO<sub>2</sub> (Stolaroff et al., 2008) has the potential to achieve lower energy consumption but needs to be fully analyzed in full absorption/desorption cycle. The materials that use physisorption to capture CO<sub>2</sub> were not included because they show very low capacity compared to chemisorption under DAC conditions as shown in Table 1 and Fig. 5, they adsorb high number of water molecules which contribute to high regeneration energy (Mukherjee et al., 2019) and no full DAC cycles studies using physisorption material was found. Finally, the chemisorption materials which show a high CO<sub>2</sub> equilibrium capacity that can reach up to 3.89 under DAC conditions is Mg<sub>2</sub>(dobdc)(N<sub>2</sub>H<sub>4</sub>)1.8 as shown in Fig. 5. However, the comprehensive performance of these materials can be assessed only in full adsorption and desorption cycles. Table 3 shows studies that investigate these materials in full cycles and highlight the main parameters that should be considered such as stability and regeneration energy. In general, some cycles demonstrated high stability of the sorbents with cyclic stability reaching up to 2.31 for Mg<sub>0.55</sub>Al-O-TEPA67%. From the energy point of view, although the heat of adsorption of CO<sub>2</sub> in amines is low (about 90 kJ/mol CO<sub>2</sub>) compared to liquid sorbents, which is 178.2 kJ/mol CO<sub>2</sub> for NaOH, the regeneration energy of solid sorbents reached in a study (Gebald et al., 2014) is 390 kJ/mol CO<sub>2</sub> of thermal energy compared to 178.2 kJ/mol CO<sub>2</sub> of thermal energy for cycle developed by Keith et al. (2018). It was reported that the regeneration energy of 390 kJ/mol CO<sub>2</sub> can be reduced to 90 kJ/mol CO<sub>2</sub> if there are no water molecules adsorbed with CO<sub>2</sub>, which highlights the area of research development for a physisorption material that does not adsorb any water to be a target for future research.

## 5. DAC with utilization

Presently, carbon dioxide sequestration in geological formations is economically feasible only if it is utilized for enhanced oil recovery (EOR) (Wilcox et al., 2017; Amhamed and Abotaleb, 2019). An important point to note, however, is that only insignificant amounts of CO<sub>2</sub> (roughly 0.2 Gt/yr) are presently utilized for industrial activities when compared to the annual amounts (32 Gt/yr) generated by human activities around the world. Like point source capture technologies,

**Table 3**

The main parameters of solid sorbents under full DAC conditions cycles based on different regeneration methods.

Sorbent material	Regeneration method	Desorption capacity (mmol/g)	Adsorption conditions	Desorption conditions	Energy (kJ/mol.)	Stability	Ref.
$\gamma$ -Alumina-PEI	TCS with Steam and N <sub>2</sub> purging	1.7	400 ppm, 30 C and 50%RH	115 C		Capacity was reduced to 0.66 mmol/g after 24 h because of Amine leaching	<a href="#">Sakwa-Novak and Jones (2014)</a>
mesoporous carbons-PEI	TCS-N <sub>2</sub> purging	2.58	400 ppm, 25 C and 80% RH	110 C		3% drop in adsorption capacity after 10 cycles	<a href="#">Wang et al. (2015)</a>
fumed silica-PEI-33	TVSA	1.74	420 ppm, 25 C and 67%RH	85 C, 0.086 mbar		3.5% capacity reduction after 4 cycles. No degradation due to the oxygen	<a href="#">Goeppert et al. (2011)</a>
SI-AEATPMS	TVS	0.2–0.26	400–440 ppm, 25C, 40% RH	74–90C, 50–150 mbar	430th, 9.6 mech <sup>a</sup>	stable capacity of 0.19–0.17 mmol/g over 40 consecutive adsorption/desorption cycles	<a href="#">Wurzbacher et al. (2011)</a>
SI-AEATPMS	TCS	0.45	400–440 ppm, 25C, 40% RH	90 C	430th	no degradation due to the urea groups occur, as other TCS cycles	<a href="#">Wurzbacher et al. (2011)</a>
AEAPDMS-NFC-FD	TCS with Argon	1.39	506 ppm, 25 C, 40% RH	90 C		over 20 consecutive 2-h adsorption/1-h-desorption cycles, yielding a cyclic capacity of 0.695 mmol CO <sub>2</sub> /g	<a href="#">Gebald et al. (2011)</a>
APDES-NFC	TVS	2.13	400 ppm, 25 C and 80% RH		97.6–390.4th <sup>b</sup>	Cyclic capacity of 1 mmol/g over 100 TVS cycles	<a href="#">Gebald et al. (2014)</a>
Mg0.55Al-O-TEPA67%	TCS with N <sub>2</sub>	3	400 ppm, 25 C	100 C		they simulate cyclic stability of 2.31 mmol/g using TSA	<a href="#">Zhao et al. (2022)</a>

<sup>a</sup>The study indicates that thermal energy can reach 166 kJ/mol if the capacity goes up to 2 mmol/g.<sup>b</sup>The energy can go up to 390.4 kJ/mol because of adsorbed water molecules.

only utilization of the captured CO<sub>2</sub> can provide the needed economic incentives for DAC technology to be widely commercialized. The future perspectives of carbon capture and utilization is relatively bright because the global monetary value of products that can be produced from CO<sub>2</sub> is estimated to be around \$5 trillion ([Rosell, 0000](#)). From this estimate, DAC facilities are faced with stiff competition from other facilities that commercially capture CO<sub>2</sub> (such as point source facilities and natural sources of CO<sub>2</sub>) to be sold in price-competitive markets around the world. Moreover, DAC facilities have cost disadvantage when compared to capture from point sources or natural sources due to the maturity of the latter. However, DAC facilities are favored in terms of: (i) scalability: they can provide the exact quantity of CO<sub>2</sub> required by a consumer and (ii) location/mobility: the facilities can be built close to CO<sub>2</sub> consumers, which removes CO<sub>2</sub> transportation cost.

### 5.1. CO<sub>2</sub> utilization in agriculture

In agriculture, some research activities have reported the effects of increasing CO<sub>2</sub> concentration in agricultural greenhouse on vegetative plants' yields ([Poorter, 1993](#); [Saha et al., 2015](#); [Xu et al., 2014](#)). In 2017 ([Gutknecht et al., 2018](#)), Climeworks launched a DAC facility in Hinwil, Switzerland, to provide captured CO<sub>2</sub> to the nearby greenhouse for vegetable cultivation. Low-grade heat for regeneration was provided by the nearby waste incineration plant. Although the conventional agricultural greenhouse fertilization uses concentrated carbon dioxide obtained from flue gas or from reactions between ammonium bicarbonate and sulfuric acid (which mostly results in gas contamination), research has shown that the required CO<sub>2</sub> concentration for natural algae and plant cultivation is about 1%–3% and 0.1–0.2%, respectively ([Park et al., 2012](#)). For example, application of moisture swing sorbents/technique ([Wang et al., 2011](#); [C.-I. Hou et al., 2017](#)) in DAC can provide the right CO<sub>2</sub> concentration (1%–5%) for plants and algae cultivation. In a study to determine the ideal concentration of CO<sub>2</sub> to act as a gas fertilizer in agricultural greenhouses, [C.-I. Hou et al. \(2017\)](#) employed moisture swing adsorption technique to analyze the effect of CO<sub>2</sub> concentration on lettuce cultivation, and the result obtained showed 1000 ppm as the optimum CO<sub>2</sub> concentration to achieve the desired accelerated cultivation. In the same study, the capture cost was calculated to be approximately \$35 per ton of CO<sub>2</sub> and the minimum energy required (at 45 °C desorption temperature) to achieve 3% outlet CO<sub>2</sub> concentration was 35.67 kJ/mol. Direct air capture can utilize the low thermodynamic energy required for gas separation to provide CO<sub>2</sub> for agricultural greenhouses. [Brilman et al. \(2013\)](#)

combined DAC with utilization via algae cultivation, to optimize the energy required for the process, and the regeneration was performed at a temperature range of 70–80 °C (which provides a low CO<sub>2</sub> purity) instead of above 100 °C (which offers high CO<sub>2</sub> purity) because algae cultivation does not require pure CO<sub>2</sub>.

For future perspective, in an attempt to increase food production, conserve agricultural lands, reduce CO<sub>2</sub> concentration in the atmosphere through the application of direct air capture technique and utilize captured CO<sub>2</sub> in agricultural greenhouses, Bao et al. (2018) proposed and demonstrated the concept of urban vertical greenhouse farming in a project termed Carbon Enrichment for Plant Stimulation (CEPS). The authors thus concluded that the adoption of CEPS in urban environment has the capacity to remove about 500 million tons of CO<sub>2</sub> per year from the atmosphere and increase food supplies 15 times more than conventional field farming.

## 5.2. Other CO<sub>2</sub> utilizations

Despite the renewed interests in electrochemical conversion of CO<sub>2</sub> to platform chemicals, a search through the literature has revealed a dearth of research work that utilizes electrochemical conversion technique for chemical production that uses CO<sub>2</sub> obtained from DAC as a feedstock. One exception is the study by Smith et al. (2019) that recently analyzed the importance of electrolyzers in CO<sub>2</sub> conversion landscape taking 10,000 tons of methanol production per day as a case study. The objective of the study was to provide advanced analysis (e.g., energy requirements and the physical scales) of a system that converts CO<sub>2</sub> obtained from DAC into fuels via electrolyzers, and sources required energy from renewable energy. From the analysis, the study provided viewpoints on the feasibilities and scale comparisons of large plants versus small plants and decentralized methods versus centralized method for energy-dense fuels production via CO<sub>2</sub> electrolyzers, incorporating renewable energy sources.

Other reported studies in carbon utilization involve: DAC of CO<sub>2</sub> in Ca(OH)<sub>2</sub>–CaCO<sub>3</sub> cycle at high temperature, coupled with concentrated solar power for syngas reforming (Nikulshina et al., 2006); DAC of CO<sub>2</sub> via polyamine sorbent followed by in situ hydrogenation of CO<sub>2</sub>, using Ru-based catalyst, to produce CH<sub>3</sub>OH (Kothandaraman et al., 2016). Carbon Engineering air-to-fuel (in short called A2F) technology, which uses thermo-catalytic conversion of CO<sub>2</sub>, in the presence of hydrogen, to produce hydrocarbon fuels (Zhu, 2019). In most cases, depending on the purpose of utilization, CO<sub>2</sub> obtained from DAC meets the requirements to be a feedstock in synthetic fuels and materials production (Bhanage and Arai, 2014). For instance, some industries such as long-distance heavy transportation and aviation sectors, which are difficult to electrify, could indirectly be electrified using synthetic fuels (e.g., Fischer–Tropsch fuels or synthetic methane) obtained from CO<sub>2</sub> conversion (Verdegaal et al., 2015). In addition, polymers and many other hydrocarbon products, which formerly relied on fossil based sources, may also be synthesized from CO<sub>2</sub> obtained from DAC (Olah et al., 2009). In a comprehensive simulation and optimization study of five different configuration scenarios (which include the base case), Marchese et al. (2021) investigated Fischer–Tropsch synthesis of hydrocarbons using CO<sub>2</sub> obtained from DAC as a feedstock (at 400 ppm CO<sub>2</sub> concentration and a throughput of 250 kt/h of air). Reverse water–gas shift reaction and an alkaline electrolyzer were used to produce the needed syngas. The study compared the tradeoffs of each scenario taking into account the environmental perspective and production cost. The highest system efficiency of 36.3% was obtained in one scenario and a reported CO<sub>2</sub> maximum conversion efficiency of 68.3%. Also, in a power-to-X project in Troja, Italy, Climeworks and partners demonstrated the feasibility of using Fischer–Tropsch technique together with other CO<sub>2</sub> conversion technologies to synthesize renewable methane (Beuttler et al., 2020).

## 6. DAC with storage

One major advantage that DAC has over the conventional point source capture system is that the capture machine can be stationed anywhere, i.e., DAC system can be moved to CO<sub>2</sub> storage site where the captured CO<sub>2</sub> can be permanently stored onsite. This prevents the construction of expensive pipeline networks that may be used to transport CO<sub>2</sub> to storage location, and it equally circumvents the required regulations that come with pipeline construction. It is important to note that DAC with storage is a complementary NET option and it is not a replacement for other NETs (Realmonte et al., 2019).

The majority of current carbon capture and storage projects inject CO<sub>2</sub> as a separate buoyant phase into sedimentary basins where it is expected to be trapped beneath an impervious cap rock (Metz et al., 2005). The CarbFix project in Iceland has launched the development of an alternative method in which CO<sub>2</sub> is dissolved in water prior to or during its injection into fractured and porous basalt rocks (Gislason and Oelkers, 2014). Since the dissolved CO<sub>2</sub> is not buoyant, the fluid injected into the reservoir is in fact denser than the surrounding reservoir fluid due to the presence of CO<sub>2</sub>, so it will not rise. As a result, solubility trapping takes place rapidly and no cap rock is needed to seal the CO<sub>2</sub> in Sigfusson et al. (2015). The gas-charged water aids metals release from the basalts, like iron, magnesium and calcium, which react with the injected CO<sub>2</sub> to form carbonates, like siderite, magnesite, and calcite, respectively, which results in permanent geological storage of the CO<sub>2</sub> (Snæbjörnsdóttir et al., 2017). The CarbFix concept is what is now adopted by Climeworks, as part of European Union funded research named CarbFix2, to permanently store air captured CO<sub>2</sub> in geologic formations in a safe, scalable, and economically feasible way (Gutknecht et al., 2018).

Other research activities have also reported the integration of CO<sub>2</sub> storage with DAC. Goldberg et al. (2013) proposed a combination of DAC with location-specific carbon sequestration in oceanic formations (at Kerguelen Island in the Indian Ocean), whereby the required energy is sourced from wind energy within the Island, and the captured CO<sub>2</sub> that

is not stored can be used for syngas production. In a 2017 report (Nguyen, 2017), Climeworks launched a DAC facility in Hellisheidi, Iceland, in a geothermal plant. The geothermal plant provides the low-grade heat needed to desorb CO<sub>2</sub> from the adsorbent filters, and the captured CO<sub>2</sub> is permanently sequestered in geologic formations within the plant. In a 2018 report (Gutknecht et al., 2018), the plant injects 10,000 tonnes of CO<sub>2</sub> per year into the basaltic formations at approximately 700 m below the surface in about 250 °C bed temperature. The purity level of CO<sub>2</sub> captured through DAC is immaterial if the captured CO<sub>2</sub> is to be stored in geological formations because the impurities that can accompany the captured CO<sub>2</sub> are mainly O<sub>2</sub> and N<sub>2</sub> (Tsuji et al., 2021), which are known to be environmentally friendly. However, for point sources CO<sub>2</sub> capture intended for storage, the purity level of CO<sub>2</sub> is usually very high because point sources flue gases have impurities such as NO<sub>x</sub> and SO<sub>x</sub>, which are known to be environmentally unfriendly. As a result, Tsuji et al. (2021) recently discussed the possibility of geological storage of the mixture of CO<sub>2</sub>-N<sub>2</sub>-O<sub>2</sub> obtained through a membrane based DAC system. The study evaluated the potentials of low purity CO<sub>2</sub> in geological formation based on molecular dynamic simulations. The results obtained show that the density of CO<sub>2</sub> decreases with decrease purity level, which shows that impure CO<sub>2</sub> is less efficient than pure CO<sub>2</sub> in geological storage, especially at shallow depth of ~1000 m. The study thus concluded that more research is needed to determine the fate of impure CO<sub>2</sub> stored at deeper depths because density of CO<sub>2</sub> is higher at deeper reservoirs. Since overall energy requirement for DAC is still high for the technology to make mass market, McQueen et al. (2020) recently carried out a cost analysis of DAC with storage using low-thermal energy obtained from geothermal and nuclear power plants in the United States. The objective of their study is to find a pathway for accelerated deployment of DAC. The study suggested energy partnerships between nuclear and geothermal energy companies coupled with good policy frameworks from policymakers to build interest in DAC technology. Based on the partnership opportunities proposed, up to 19 MtCO<sub>2</sub> can be removed annually in the United States alone for as little as \$200-\$300 per tonne.

## 7. Direct air capture of CO<sub>2</sub> through the air-conditioning system

### 7.1. Impact of indoor CO<sub>2</sub> levels on the health and the role of HVAC

The air conditioning (AC) system is one of the greatest inventions of the twentieth century, and with persistent global warming challenges, the AC usage is projected to further increase in cities across the world (Dittmeyer et al., 2019a). In an urban area like Doha, the indoor air quality has consistently remained poor partly due to rise in atmospheric CO<sub>2</sub> level, which is circulated indoors by the AC system. For example, in May 2019 in Doha, Qatar Environment and Energy Research Institute (QEERI) air quality monitoring station showed an observed monthly average CO<sub>2</sub> concentration of 475 ppm, which is more than the global average. The consequences of which are the high rate of respiratory infections. For example, the rates of childhood asthma in the United States have more than doubled since 1984, a development that has largely puzzled scientists. Deteriorating atmospheric pollution, which exposes children to asthma-causing dust mite and cockroach dander is to be blamed. The main culprit however is the level of atmospheric CO<sub>2</sub>, which studies have suggested to be 60% higher in large U.S. cities than in rural areas (Zwilling, 2019). As reported in the Journal of Allergy and Clinical Immunology, ragweed, a plant that produces a common allergen, responds to higher CO<sub>2</sub> level in the atmosphere by growing faster, flowering earlier and producing significantly large amount of pollens, especially more in the cities than in rural communities (D'Amato et al., 2017; Ahmad et al., 2017). In most cities across the world, there have been several studies conducted to determine the impacts of increase in indoor CO<sub>2</sub> level on the health of the occupants, especially at schools. Increase in indoor CO<sub>2</sub> level has been linked to wheezing attacks in children with asthma history (Kim et al., 2002), especially at school where air circulation may be poor (Meter.com, 2019). In 2009, Jung et al. reported a study conducted in South Korea at 20 private schools to determine whether increase in indoor CO<sub>2</sub> level has effects on the cognitive ability of students. The study concluded that at 85% increase in CO<sub>2</sub> level more than the prescribed indoor air quality standard (800–1000 ppm), the general complaints from students were tiredness and muscular pains among others (Jung et al., 2009). Another study (Fox et al., 2003) conducted in the US correlated the increase in indoor level of CO<sub>2</sub> in heavily occupied school buildings with increase in airborne bacterial markers. In Portugal, 51 elementary schools comprising of 1019 students were sampled, and in some cases, the level of indoor CO<sub>2</sub> could reach as high as 1950 ppm. The associated sicknesses (cough, headache, rhinitis, wheezing and irritation of mucus membrane) with such CO<sub>2</sub> levels were prevalent during the fall and winter seasons (Ferreira and Cardoso, 2014). Although one may argue that sick building syndrome (SBS) is only associated with CO<sub>2</sub> level above the standard range mentioned above, there have been reported cases of sickness even at level below 1000 ppm (Seppänen et al., 1999).

Air-conditioning system plays an important role in controlling ventilation rates in most urban societies today. Any innovation in the AC system to circulate healthy air in buildings would resonate across the world (Sadiq et al., 2021; Essehli et al., 2020). The American Society of Heating, Refrigeration, and Air-conditioning Engineers (ASHRAE) recommends 10 L/s per person as the ventilation rate for office buildings (Persily, 2015). This value corresponds to 870 ppm indoor CO<sub>2</sub> concentration, which assumes outdoor CO<sub>2</sub> concentration to be 350 ppm with per person indoor CO<sub>2</sub> generation rate at 0.31 L/min Erdmann et al. (2002). Going by ASHRAE standards and reported studies from different continents outlined in the preceding paragraph, the current outdoor CO<sub>2</sub> concentration (> 400 ppm) would contribute immensely to the indoor CO<sub>2</sub> concentration which may further affect the wellbeing of building occupants. Hence, the idea of using the AC unit as a platform for CO<sub>2</sub> capture, if widely implemented, could bring about a major change in greenhouse gas controls.





**Fig. 7.** Doha Tower in West Bay (Doha, State of Qatar), formally known as Burj Doha.

The current AC system circulates outdoor air indoors; the system takes in hot air, filters out dust particles, lowers the air temperature and then releases the air to the building. Apart from dust particles separation through the embedded filter, the constituent of the original hot air remains unaltered. There have been reported research efforts to integrate DAC with the HVAC systems, especially in improving indoor air quality (Kim and Leibundgut, 2015; Gall et al., 2016; Lee et al., 2015; Han et al., 2016; Hu et al., 2017) or saving energy in buildings (Kim et al., 2015) or addressing climate change challenges (Zhao et al., 2019). Although some of the studies were carried out to actively integrate DAC with building HVAC systems' architecture (Zhao et al., 2019; Bryan and Salamah, 0000), others were simply conducted to test adsorption capacity of different adsorbents in indoor environment (Gall et al., 2016; Lee et al., 2013). Kim and Leibundgut (2015) proposed a new ventilation arrangement that integrates DAC with HVAC systems. Their work simulated air recirculation strategies in the breathing zone using the recommended occupancy diversity factors by Duarte et al. (2013) and ASHRAE Standard 90.1 2004 (ASHRAE, 2004). The authors thus recommended the use of low air recirculation ratio coupled with CO<sub>2</sub> capture device to reduce energy consumption in buildings' HVAC systems. In another work from the same group (Kim et al., 2015), 30%–60% energy savings were reported when DAC was integrated with the HVAC systems. In a study by Zhao et al. (2019), the thermodynamic analysis of CO<sub>2</sub> capture from indoor air and outdoor air in buildings was reported using amine functionalized cellulose as the chemisorbent material in a TVSA system. The study reported 20 kJ/mol. as the minimum separation work for the assumed outdoor air concentration of 400 ppm, and second-law optimal efficiencies of 31.60%, 37.55% and 44.57% for indoor air concentrations of 1000 ppm, 2000 ppm and 3000 ppm, respectively. It is, however, important for future studies to carry out life cycle assessment, economic and emissions analysis of DAC integration with the existing buildings HVAC systems. In a moisture-swing DAC capture system, Bryan and Salamah (0000) proposed the utilization of the CO<sub>2</sub>-enriched ventilation exhaust to integrate DAC with building HVAC systems. Although the idea was still in design development stage according to the authors, a preliminary order of magnitude calculations were carried out to determine the available annual CO<sub>2</sub> for capture in office buildings the United States, and the results showed 5 million tons of CO<sub>2</sub> when applied to only 50% of office buildings.

#### 7.1.1.1. Estimates of the available CO<sub>2</sub> to be captured in a specific building

In order to have an idea about the quantity of CO<sub>2</sub> available for capture in a specific building (whether the cooling to the building is supplied by the conventional AC system or district cooling technique), we can estimate the airflow using a standard air change per hour (ACH) for office buildings, which is 5–10 times per hour (Dittmeyer et al., 2019b). For illustration, taking Doha Tower (a flagship building at West Bay in Doha) as a case study. The building is cylindrical in shape (as shown in Fig. 7) with base diameter of 45 m, 46 floor levels, and ceiling height of 3 m. The floor area of the building is 1591 m<sup>2</sup>, which is approximately 1000 m<sup>2</sup> if factors, such as elevators, staircases and other non-available spaces are removed.



Using the number of floors above the ground (46) (Ponzini and Arosio, 2017), the total available office space area is 46,000 m<sup>2</sup>. With 3 m ceiling height, the available volume of air is 138,000 m<sup>3</sup>. Doha Tower air flow rate based on the air change per hour given above is between 0.69–1.38 M m<sup>3</sup> · h<sup>-1</sup>. Taking the concentration of CO<sub>2</sub> in air as 400 ppm (equivalent to 0.0004 kg of CO<sub>2</sub> per kg of air), and density of CO<sub>2</sub> in air as 1.98 kg/m<sup>3</sup>, the available CO<sub>2</sub> that can be captured within Doha Tower is between 0.55–1.1 tCO<sub>2</sub> · h<sup>-1</sup>, the average of which is 0.83 tCO<sub>2</sub> · h<sup>-1</sup>.

Although the CO<sub>2</sub> adsorption efficiency of some adsorbents/absorbents can reach up to 90% (from 400 ppm down to 40 ppm) (Keith et al., 2018; Zhao et al., 2019; Young et al., 2021; Sayari et al., 2016), if we assume a worst-case scenario of 50% adsorption efficiency, the average captured CO<sub>2</sub> within Doha Tower becomes 0.41 tCO<sub>2</sub> · h<sup>-1</sup>.

## 7.2. Potential sorbent materials for direct air capture of CO<sub>2</sub> in indoor environment via the air-conditioning system

Any sorbent material that qualifies to be used in DAC of CO<sub>2</sub> through the air conditioning systems (AC) must satisfy some stringent health and environmental conditions. The AC system has been relied on for ages to deliver outside air directly into a spatial volume through the perimeter of the building, and as a result, one objective is to enhance indoor air quality by reducing the concentration of CO<sub>2</sub> entering the building for health benefits of the occupants. The other objective deals with the reduction of atmospheric concentration of CO<sub>2</sub>. Therefore, the idea of using the AC units for CO<sub>2</sub> capture, if widely implemented, could bring about a major change in atmospheric greenhouse gas controls. To enhance indoor air quality, a number of sorbents have been reported for CO<sub>2</sub> removal from indoor environment. Gall et al. (2016) investigated the use of commercially available soda lime, Ca(OH)<sub>2</sub>, MgO, and Mg(OH)<sub>2</sub> applied to a modeled shelter-in-place accommodation, which may have high indoor CO<sub>2</sub> concentration. The results obtained showed about 80% reduction in CO<sub>2</sub> concentration (from 2500 ppm to 550–750 ppm) for an assumed 8-hr occupancy period. Another study (Hu et al., 2017) tested the feasibility of using activated carbon impregnated with MgO and CaO for CO<sub>2</sub> removal in indoor environment for air quality enhancement. Other reported studies include the use of activated carbon monoliths (Lee et al., 2015), and amine impregnated Y-type zeolites (Lee et al., 2013) for CO<sub>2</sub> capture for air quality enhancement. Although the obtained results by Lee et al. (2013) showed CO<sub>2</sub> capacity of 158 mg/g adsorbent, which is high for an ultra-low concentration CO<sub>2</sub> stream, the use of amine in indoor environment requires caution because it has been reported elsewhere that amine is subject to significant oxidative degradation at temperatures slightly above 100 °C during desorption (Ahmadalinezhad and Sayari, 2014), which may be harmful to the occupants. Other sorbents with relatively moderate CO<sub>2</sub> capacity under DAC conditions and hold potentials to be used in indoor environment are nanoscale carbon nitrides and MOFs.

### 7.2.1. Nanoscale carbon nitrides

Carbon nitride (CN) is a fascinating material that has attracted interests for applications in different fields. Since the infusion of nitrogen atoms in the carbon morphology has the ability to increase the conducting, mechanical, energy-storage and field-emission properties as well as create basic sites on the material (Thomas et al., 2008; Kawaguchi et al., 2004; Qiu and Gao, 2003; Jin et al., 2009). In comparison to the bulk CN, mesoporous nanoparticle CN has a large pore size, high surface area and large active sites ready for reaction or attraction, creating improvement in performance especially in carbon capture applications (Li et al., 2010b). For example, Deng et al. (2012) synthesized porous carbon nitride-carbon nanocomposite from mesoporous silica SBA-15, the resulting nanoparticle has pore diameter of 6.3 nm with surface area between 278–338 m<sup>2</sup>/g and high nitrogen content of 25%. When tested at 25 °C and 1 atm for carbon capture application, the capacity was 2.35 mmol/g. In another work, Lakhi et al. (2015) synthesized nanoparticles carbon nitride of pore volume (1.1 cm<sup>3</sup>/g), pore diameter (8.3 nm), surface area (802 m<sup>2</sup>/g) and CO<sub>2</sub> capture capacity at 25 °C and 1 atm was 1.14 mmol/g. For application in DAC system, CN and its composites need to undergo rigorous screening exercise with scientific community, starting with computational models to extract, enhance and tune CN CO<sub>2</sub> adsorption characteristics at ambient condition to what can be fitted into the HVAC systems. This is because CN is an environmentally friendly material (Tian et al., 2013) with no safety hazard to humans to the best of our knowledge.

### 7.2.2. Metal-organic-frameworks (MOFs)

One of the key characteristics of MOFs is their high specific surface area and pore size, which has allowed the materials to be relevant for many applications involving gas separation, storage, and catalysis (Mueller et al., 2006; Kitagawa et al., 2004; Lee et al., 2009; Zhao et al., 2004; Zavahir et al., 2022). The main consideration to maximize gas uptake within the pores of MOFs is to increase the quantity of adsorptive sites in the material. Furukawa et al. (2010) were particularly successful in synthesizing ultrahigh porous MOFs with pore diameter of 4.8 nm, pore volume of 3.6 cm<sup>3</sup>/g, BET surface area of 6240 m<sup>2</sup>/g and CO<sub>2</sub> uptake capacity of about 150 mg/g at 25 °C and 1 atm. Although moisture affects MOFs negatively, and they normally require too much CO<sub>2</sub> partial pressure to be useful in direct air capture. However, a team of scientists at EPFL (Ecole Polytechnique Federale de Lausanne, Switzerland) (Boyd et al., 2019) has designed a new material that prevents the CO<sub>2</sub>/H<sub>2</sub>O competition, meaning that it is not affected by water molecules and can selectively capture CO<sub>2</sub> out of wet flue gases more efficiently than even commercial materials. This is an indication that with persistent efforts in tuning and screening of MOFs, its DAC applications in humid climate are possible. In fact, efforts are already yielding good results. For example, a water vapor repellent MOFs for DAC application has been reported by Sadiq et al. (2020), in which specially tuned nanocomposite MOFs were demonstrated at pilot-scale. The report showed a low regeneration

energy of 1.6 kWh/kg CO<sub>2</sub> at optimum regeneration temperature of 80 °C, delivering maximum CO<sub>2</sub> purity of 80%. Additionally, Guo et al. (2021) reported a composite material involving polyacrylates and MOFs that adsorbed CO<sub>2</sub> in a simulated air with 50% relative humidity achieving a CO<sub>2</sub> uptake of 1.44 mol/kg. On whether MOFs are environmentally friendly to warrant their use indoors, although the synthesis routes (solvothermal strategies) of most MOFs have raised environmental and health concerns due to the toxic solvents used in their preparations (Thomas-Hillman et al., 2018; Zhu and Liu, 2019). However, concerted research efforts have been launched lately, as reviewed by Kumar et al. (2020), on green and environmentally friendly MOFs synthesis devoid of toxic chemicals. Their proven adsorptive uptake of CO<sub>2</sub> cannot be overlooked when selecting adsorbent candidates for applications in HVAC systems, which make green MOFs potential candidates.

## 8. Conclusion and recommendations

This work has carefully reviewed the literature to assess the progress made in direct air capture of CO<sub>2</sub> with emphasis on sorbents, regeneration options, renewable energy option, storage, utilization, and state-of-the-art.

- On sorbent system, both liquid and solid sorbents are at advanced stage of developments; while high regeneration energy is associated with state-of-the-art liquid sorbents, the contemporary solid sorbents are either faced with low CO<sub>2</sub> selectivity in humid climates or leaching of supports when functionalized with amines.
- On regeneration, TVSA seems to be the preponderantly reported regeneration technique with minimal drawbacks when pure CO<sub>2</sub> is desired, while MSA is adjudged suitable when low purity CO<sub>2</sub> is desired especially for use in agricultural greenhouses. PSA, PVSA and VSA are largely reported to be unsuitable for DAC due to additional cost requirements in pressurizing or depressurizing the inlet gas.
- On storage, CO<sub>2</sub> sequestration in geological formations is economically feasible only if it is utilized for enhanced oil recovery (EOR) otherwise, there is currently no economic incentive to capture CO<sub>2</sub> directly from the atmosphere and send to geological formations.
- On utilization, CO<sub>2</sub> conversion to platform chemicals is gaining traction, the major drawback, however, is finding inexpensive catalysts to be used in electrochemical conversion of CO<sub>2</sub> to value-added chemicals.
- On state-of-the-art, liquid (NaOH or KOH) and solid (amine based) sorbents are still being further improved and optimized by the two top startups (Carbon Engineering and Climeworks) in DAC.

In general, our findings point to undeniable fact that atmospheric concentration of CO<sub>2</sub> has continued to rise despite all the publicities surrounding global warming challenges. Research efforts on carbon capture for either storage or utilization are gaining traction, and by and large there are strong interests in direct air capture of CO<sub>2</sub>. Notwithstanding the efforts in DAC research activities, commercialization of the technology in large scale is still surrounded by bottlenecks that are associated with high cost of capture and high sorbent regeneration energy. To minimize the cost of capture, however, we have proposed the use of traditional HVAC system (mainly the air conditioning system), as a readily available technology, to capture CO<sub>2</sub> directly from the atmosphere, such that the energy needed to capture is provided by the HVAC systems: whether it is the air conditioning system (in temperate climates) or the heater (in cold climates). With these, carbon capture research community can be made aware of the opportunities inherent in HVAC systems to reduce atmospheric concentration of CO<sub>2</sub> if the proposed technology is widely adopted in cities across the world.

## CRedit authorship contribution statement

**Ahmed Sadiq:** Data collection, Methodology, Writing – original draft. **Yasser Abdullatif:** Data collection, Engineering drawing, Writing up. **Brahim Aissa:** Data collection, Writing – second draft preparation. **Arash Ostovar:** Investigation, Methodology. **Nashaat Nassar:** Reviewing and editing. **Muftah El-Naas:** Reviewing and editing. **Abdulkarem Amhamed:** Conceptualization, Investigation, reviewing and editing.

## 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.

## Data availability

Data will be made available on request.

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