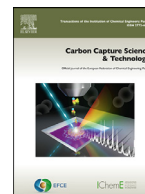




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Review

Latest advances and challenges in carbon capture using *bio-based* sorbents: A *state-of-the-art* review



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ABSTRACT

Effective decarbonisation is key to ensuring the temperature rise does not exceed the 2 °C set by the Paris accords. Adsorption is identified as a key technology for post-combustion carbon capture. This rise in prominence of such processes is owed to the fact that application of solid sorbents does not lead to the generation of secondary waste streams. In fact, sorbents can be produced from waste material (e.g. bio-based sorbents). Bio-based sorbents have become an increasingly attractive option; food waste, agricultural and municipal sources can be employed as precursors. These sorbents can be physically and chemically activated and then further modified to produce sorbents that can capture CO₂ effectively. The employment of these types of sorbents, however, often entails geological and operational challenges. Understanding how these sorbents can be deployed at scale and the geological challenges associated with bio-based sorbents are key research areas that must be further investigated. Process modelling and machine learning can provide insights into these challenges especially within optimization of adsorption processes and sorbent development. This paper aims to provide a *state-of-the-art* review of the synthesis of bio-based sorbents and their application within post-combustion carbon capture processes as well as the recent trends of utilizing machine learning for the development of these sorbents, and the design of the corresponding adsorption processes alike.

1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) has recognized carbon (CO₂) capture as an inseparable set of technologies required to meet carbon emission targets by 2050 (Naimoli, 2021). The urgency to address the threat faced by global climate change has led the UK government to set out an ambitious target to reduce 80% of the nation's carbon emissions by the end of this decade. Despite having a global warming potential of 1, CO₂ remains in the ecosystem for a very long time due to its chemical stability, and as a result of the current emission rates, it is known to be the primary greenhouse gas (GHG) contributing to climate change. In order to reduce global carbon emissions, different approaches including improvement in energy efficiency,

application of non-carbon based fuels, and carbon capture and storage (CCS) technologies have been proposed (Ochedi et al., 2020).

IPCC, highlights guidance on land management options, harvested wood products carbon accounting, and an in-depth methodology to evaluate GHGs. Improvements in harvesting, storage, transport and packaging to reduce food losses and waste can be obtained based on these reports. IPCC is sensitive towards future developments of socioeconomic aspects including population, income, and trade as they are directly linked to socioeconomic factors including population, income, and trade.

More recently, the ambitious “10-point plan” was introduced by the UK's government in 2021. This report strongly underlines the important role of CCS in our fight against climate change. Post-combustion

Abbreviations: AI, Artificial Intelligence; ANN, Artificial Neural Network; BTC, Breakthrough curve; CAPEX, Capital Expenditures; CCS, Carbon Capture and Storage; DoE, Design of Experiment; GHG, Greenhouse Gas; HTC, Hydrothermal Carbonisation; IPCC, Intergovernmental Panel on Climate Change; LCA, Life Cycle Assessment; ML, Machine Learning; OPEX, Operating Expense; PFO, Pseudo-First Order; PSA, Pressure Swing Adsorption; PSO, Pseudo-Second Order; PTSA, Pressure-Temperature Swing Adsorption; TSA, Temperature Swing Adsorption; TVSA, Temperature-Vacuum Swing Adsorption; VPSA, Vacuum-Pressure Swing Adsorption; VSA, Vacuum Swing Adsorption.

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carbon capture process can be coupled with major stationary emission sources to separate CO₂ from the emitted flue gases, hence reducing their GHG footprints (Ding et al., 2020). This involves steel, cement and iron plants, refineries, petrochemical sites, and fossil fuel-fired power plants amongst others. However, the cost and efficiency of carbon capture are still the main concerns (Goel et al., 2021). Regardless, carbon capture processes are expected to play a vital role in climate change mitigation, hence the urgency of process improvement and cost reduction. The attractive benefit of such processes is that they can be almost readily retrofitted to existing plants (Valdovinos-García et al., 2020).

Various techniques including absorption, membrane separation, microbial system, and cryogenic distillation, have been studied to advance post-combustion carbon capture within the past few years (Nakao, 2019). These techniques are typically compared based on their energy consumption, capital and operating expenditure (CAPEX and OPEX) and the associated waste/environmental considerations. Currently, amine absorption is used as the benchmark for CCS (however, adsorption-based systems have been previously recommended for thermal power plants (Zerobin and Pröll, 2020)). The main drawbacks of these liquid solvents are their toxicity and secondary pollution (e.g. fugitive emissions) as well as equipment corrosion. Further, they require large quantities of water that need to be continuously heated (and cooled) in order to provide an optimum temperature for the solvent solution (Aliyan, 2017). However, these issues are absent if deploying adsorption technologies. Further, implementation of bio-based sorbents minimizes production of chemical and biological sludge throughout the process.

Thus, adsorption has become more attractive in carbon capture as it aims to address the concerns associated with both energy consumption and waste generation – the key operational issues currently associated with solvent-based carbon capture. Adsorption technology has presented positive outlooks on environmental pollution control, as well as resource utilization, based on high-tech materials.

In adsorption processes, a chemical species is *adsorbed* (now referred to as *adsorbate*) on the solid surface of a sorbent. The amount of adsorbate adsorbed is a function of pressure (if gas) or concentration (if liquid) when the process is run at a constant temperature (Omokpariola, 2021). Temperature and pressure are two of the main determining factors for the selection of a suitable sorbent with effective regeneration used in a particular application. Industrial adsorption technologies are based on pressure swing adsorption (PSA), vacuum swing adsorption (VSA), temperature swing adsorption (TSA), or a combination of these processes (Gupta and Li, 2022). Adsorption is the 2nd generation of capture technologies and is projected to advance the next generation of carbon capture processes (Brickett et al., 2020). More recently, CO₂ separation using solid sorbents (e.g. oxide-based sorbents) has gained more momentum in the industry as this technique has presented promising results in terms of overall efficiency and costs (Papalás et al., 2020). This technique has been deployed to purify H₂ in hydrogen production processes and is being studied to reduce the cost associated with post-combustion carbon capture.

Surface area, pore volume, the porous structure and the physico-chemical properties are the main factors when selecting a sorbent for a target separation. Moreover, process parameters (such as combustion temperature/pressure in the case of carbon capture) are equally important when deciding on a particular sorbent. The combustion flue gas temperature is typically divided into three categories; low temperature (< 200 °C), intermediate temperature (200 – 400 °C), and high temperature (> 400 °C) (Gao et al., 2017). High temperature processes limit the application of certain solid sorbents as many properties and formations change at temperatures above 400 °C. However, controlled intermediate temperature allows for the application of unique solid sorbents - especially *bio-based* sorbents (Ruhaimi et al., 2021).

One of the traditional sorbents used with an adequate adsorption capacity and selectivity is zeolite NaX (commercially known as 13X). However, the regeneration energy requirement is the main drawback of

this class of sorbents. On the other hand, carbon-based sorbents (e.g. activated carbon) are associated with low cost, enhanced stability under moisture conditions, and ease of regeneration. Based on this, many studies have focused on low-cost bio-based sorbents to present a cost-effective approach for the production of low-cost sorbents for carbon capture. In particular, this has resulted in introduction of bio-based sorbents, prepared from biomass waste materials, for carbon capture (Lucaci et al., 2019).

2. Motivation and paper's roadmap

In this work, we have reviewed the current advancements in the synthesis and application of bio-based sorbents used in carbon capture. This review was agreed based on the “10-point plan” introduced by the UK's government in 2021, as well as the increasing attention on publications featuring “carbon capture”, “CO₂”, and “bio-based sorbents” (Petrovic et al., 2022). We have presented the reader with the most recent synthesis, activation, and modification methods, as well as the equilibrium, kinetic and mass transfer studies. The paper is followed by a technical presentation of current designs used to synthesise such chemical processes. Finally, due to the nature of such sorbents, geological and operational challenges in employing bio-based sorbents have been discussed in detail. The paper aims to portray a clear outlook of the pros and cons associated with the utilization and deployment of bio-based sorbents in post-combustion carbon capture. This is especially timely, given the trajectory of research in this area, and the expected scale-up of adsorption CCS within this decade. It is noteworthy that the terms *sorbent* and *adsorbent* have been used interchangeably within this manuscript.

3. Bio-based sorbents for carbon capture

There are well-known activities centered on the food and agriculture industry, resulting in continuous generation and accumulation of large amounts of biomass worldwide. Many of such emissions are regrettably discarded at the moment (causing secondary pollution), or they may be converted into animal feed, or compost. Current landfill waste management techniques are introducing valuable strategies to minimize the growing environmental concerns in this field. Such strategies include preparation of value-added products derived from biomass. For instance, spent coffee powder has been used in soil remediation, activated carbon and biodiesel production. The resulting solid waste from biodiesel production can be used as feedstock to produce activated carbons. One of the more recent developments in this field is the introduction of efficient bio-based sorbents to adsorb CO₂ which aim to reduce the overall capture cost *via* adsorption. Studies have recently introduced unique bio-based activated sorbents derived from green waste materials (Table 1). Potentially the low ash content, optimized process economics, and being more environmentally-friendly, are some of the key advantages of the application of bio-based sorbents in carbon capture (Plaza et al., 2014).

In order to transform biochar/hydrochar into a highly porous carbonaceous sorbent, activation treatment (physical or chemical) is frequently employed. The porosity, polarity, and hydrophobicity with activation treatment can be improved. Bio-derived sorbent's surface area and total pore volume significantly improved upon activation (up to 1000 m²g⁻¹ and 0.7 cm³g⁻¹, respectively) (Ogungbenro et al., 2018). Although physical activation is more eco-friendly than chemical activation (i.e. the absence of secondary pollution due to the use of chemical reagents) (M. Gorbounov et al., 2022), the latter gives a higher surface area and carbon yield overall (Li et al., 2021). Another method used to improve the biochar/hydrochar adsorption capacity is surface modification. In this method, generally, heteroatoms (i.e. nitrogen, sulphur) or metal oxides (CuO, MgO) are doped onto carbons. This can enhance the adsorption capacity of the prepared biochar/hydrochar (Yuan et al., 2020).

Table 1
Latest bio-based activated sorbents and their applications.

Biomass	Treatment type	Application
Date stone (Danish et al., 2021)	Physical	CO ₂ capture
Rambutan peel (Zubbri et al., 2021)	Chemical (KOH)	CO ₂ capture
Tea seed shell (C. Quan et al., 2020)	Chemical (KOH)	CO ₂ capture
Palm kernel shell (Rashidi et al., 2021, Nasri et al., 2014)	Physical	CO ₂ capture
Pine cone (Kaya and Uzun, 2021)	Chemical (KOH)	Methyl orange adsorption and CO ₂ capture
Taihu blue algae (H. Wang et al., 2021)	Chemical (KOH)	CO ₂ capture
Fruit waste (Serafin et al., 2021)	Chemical (KOH)	CO ₂ capture
Acai stone (de Souza et al., 2020)	Chemical (KOH)	CO ₂ capture
Mango seed shell (Correia et al., 2018)	Chemical (KOH/CO ₂)	CO ₂ capture
Pinewood sawdust (C. Quan et al., 2020)	Chemical (H ₂ SO ₄) and Physical	CO ₂ capture
Olive mill waste (González and Manyà, 2020)	Chemical (KOH/CO ₂)	CO ₂ capture
Argan fruit shells (Boujibar et al., 2018)	Chemical (KOH/NaOH)	CO ₂ capture
Bamboo (Wei et al., 2012, Ismail et al., 2022)	Chemical (KOH, and H ₃ PO ₄)	CO ₂ capture
Coconut shells (Abdeljaoued et al., 2018)	Physical	CO ₂ /CH ₄ Separation
Coconut shells (Sujiono and Zabrian, 2022)	Chemical (NaOH/H ₃ PO ₄ /ZnCl ₂)	Wastewater treatment
Areca nut seeds (Supriya et al., 2021)	-	CO ₂ capture
Nauclea diderrichii (Omrogie et al., 2021)	Chemical (KOH)	Adsorption of ibuprofen, methylene blue, and CO ₂
Waste sugarcane bagasse (Guo et al., 2020)	Physical and chemical (air, CO ₂ , H ₃ PO ₄ and NaOH)	CO ₂ capture
Soybeans (X. Zhang et al., 2022)	Chemical (K ₂ C ₂ O ₄ ·H ₂ O, and CaCO ₃)	Dye removal
Rice husks (Eisa Khoshnood, 2021)	Chemical (K ₂ CO ₃ and KOH)	-

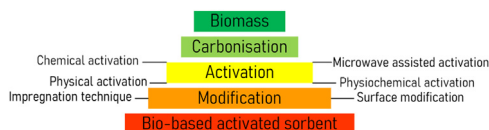


Fig. 1. Bio-based sorbent activation techniques.

3.1. Synthesis and activation

Biomass waste materials are generally carbonised at about 600 °C under an inert atmosphere, and later activated through various techniques (Fig. 1) (Panwar and Pawar, 2022). Chemical activation is carried out in an alkaline or acidic solution, while physical activation utilizes steam or other gases at ~800 °C. An alternative to the described above methods is a self-activation technique. This process employs the gases evolved off the precursor during carbonisation as the activating agents, hence, (potentially) constituting energy savings and a lesser environmental impact (Xia and Shi, 2016). This method has been recently deployed to derive bio-based adsorbents for carbon capture using celery waste as the starting biomass (Khosrowshahi et al., 2022). Here, however, we have focused on the two main production pathways, namely, chemical, and physical activation.

3.1.1. Chemical activation

Chemical solutions used in activation oxidise the surface, form oxygen-containing functional groups and can consequently affect the physicochemical properties of the sorbent, such as hydrophilic and hydrophobic characteristics, and sorption capacity (Sun et al., 2022; Chen, 2019). Chemical activation generally increases the porosity and surface area of the bio-based sorbent by extracting soluble organic compounds. Alkaline treatment is generally performed using NaOH, NaHCO₃, Ca(OH)₂ and etc., while acidic treatments are carried out using HCl, H₂SO₄, C₆H₈O₇ and HNO₃ amongst others. Alkaline solution (NaOH), was reported to affect the bio-based sorbent structure by saponification and conversion of ester groups to carboxylates and alcohols (Maheswari and Murugesan, 2011). Alternative activating agents have also been introduced to further activate bio-based sorbents, for example, NaNO₃ (Dong et al., 2022), KCl (Cao et al., 2022), La(NO₃)₃ (Shen et al., 2022) and (CH₃)₂NH (Jia et al., 2018).

The advantages of preparing bio-based sorbent at high temperatures include an increase in the removal of volatile, and decomposable species

from the bio-based sorbents, which in turn, would enhance microporosity (Khamkeaw et al., 2019). A bio-based sorbent was prepared using tea seed shell powder (10 g) at 700 °C for 2 h with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere (80 mL min⁻¹) (C. Quan et al., 2020). Activation of the biochar was initially carried out using KOH and distilled water with an impregnation ratio of 1:4 (C:KOH; weight basis). The bio-based sorbent was later activated through a pyrolysis process at 700 °C for 2 h at a heating rate of 10 °C min⁻¹.

Chemical activation appears to have gained wide acceptance in industrial applications. Chemical modification of bio-based sorbents alters the porous structure, may add to the number of surface functional groups and create new binding sites (Petrovic et al., 2022). Meanwhile, this type of modification requires precise optimization, since strong acidic or basic solutions can result in destruction and structural damage of the adsorbent's morphology. In order to reveal the presence of any interparameter interactions and to provide valuable insight into the governing forces, their prominence and impacts on response variables (such as total surface area, adsorption capacity and etc.), the application of the Design of Experiment (DoE) has been recommended in the authors' earlier work (Ketabchi et al., 2017; M. Gorbounov et al., 2022). It allows precise optimization via simultaneous evaluation of a combination of input parameters. Common experimental designs of DoE include Factorial, Central Composite, Box-Behnken, Taguchi Orthogonal Arrays (M. Gorbounov et al., 2022). For instance, the central composite design was used to study the impact of activating agents on a number of output parameters including yield, iodine number and CO₂ adsorption capacity (Khalili et al., 2015), whilst Box-Behnken design was employed to obtain optimum CO₂ adsorption capacity using a pitch-based activated carbon (Yu et al., 2020).

More recently, studies have introduced bio-based aerogels as a new class of bio-based sorbents. Bio-based aerogels are prepared using biomass-based polymers, mainly polysaccharides, and possess unique properties such as high porosity, large specific surface area, biocompatibility, durability, low toxicity, renewability and ultra-light density properties (Liu et al., 2021; Tamura et al., 2002). Biopolymers with unique features include cellulose (abundant, hydrophilic, biodegradable, highly rich in hydroxyl groups and a low-cost precursor), chitosan (highly porous, carrying highly reactive amino and hydroxyl groups, and cell adhesive properties), lignin (low density, high specific area and insoluble in inert solutions), pectin (water soluble, acts as an emulsifier and rapidly biodegradable), and tannin (highly conductive, soluble in water and alcohol and possessing high mechanical strength). As such, these sorbents are considered to be attractive for use in fluidised-bed

reactors due to better processability and ease of regeneration, hence, offering potential for industrial applications.

Bio-based aerogels have found their application in gas-phase sorption and CO₂ capture, metal ion adsorption, drug delivery, and oil-water separation. Studies have reported successful CO₂ capture at room temperature using cellulose-crosslinked polyethyleneimine (Wang and Okubayashi, 2019), chitosan grafted graphene oxide (Hsan et al., 2019), cellulose-derived hierarchical porous carbon (Hsan et al., 2019), cellulose nanofibril grafted with aminosilane (Hsan et al., 2019), montmorillonite-reinforced chitosan-polybenzoxazine nanocomposite (Wu et al., 2018), cellulose/silica composite (Y. Miao et al., 2020), cellulose aerogels (Y. Miao et al., 2020) and arginine containing chitosan-graphene oxide aerogels (Hsan et al., 2022). Synthesis of bio-based carbon aerogels is carried out through a number of steps: refinement (washing and cutting into small pieces), hydrothermal process (small pieces are placed into an autoclave), solvent exchange (water in hydrogel is replaced with acetone), freeze drying (extraction of the cryogel), and carbonisation (pyrolysis between 600 – 1000 °C) (Sam et al., 2020). Such materials have been investigated in the literature. For instance, a bio-based aerogel derived from seaweed for the purposes of CO₂ adsorption has been prepared through acid dissolution, solvent exchange, supercritical CO₂ drying, and pyrolysis under N₂ (Primo et al., 2012).

3.1.2. Physical activation

Physical properties that have a direct impact on sorption capacity include surface area and porosity. Surface area and porosity of plant-based sorbents are reported to be much more pronounced than that of biosolid and manure (Shafawi et al., 2021; An et al., 2021), which was linked to the higher carbon content of former sorbents. Generally, surface area and porosity of sorbents are evaluated *via* gas adsorption analysis where gases/vapours are employed accordingly. Physical changes of the sorbents' properties (i.e. total pore volume and size distribution, porosity and density) are evaluated by tracking changes in sample overall volume and weight uptake. Physical activation improves sorbent efficacy by removing surface impurities and functional groups as well as developing porosity. This type of activation is considered more practical and sustainable following its simplicity and efficiency.

Physical activation is based on pyrolysis (similar to the chemical activation techniques) and gaseous activation. Pyrolysis involves the carbonisation of carbonaceous precursor in an inert atmosphere (ranging from 400 to 850 °C), resulting in char production. The char is then partially gasified using oxidising agents such as ozone, steam, CO₂ and air. This method, however, is energy intensive and requires high temperature. As a result of energy consumption concerns, alternative thermal activation techniques (microwave, ultrasound irradiation, electrochemical modification and etc.) have found their way to economically activate and enhance char performance through adsorption capacity improvements (Anerao and Salwatkar, 2022). Steam activation was recommended to enhance adsorbate selectivity (Soltani et al., 2021). Activation techniques can be adopted according to the expectations in the associated adsorption process. For example, a number of studies have reported higher surface areas and micropore volume using a mixture of the phosphoric acid and potassium hydroxide (Osman et al., 2020; Wang et al., 2019).

Activating agents breach into the internal structure of sorbent, widen blocked pores and result in higher adsorption capacities. Ozone (O₃) activation involves a fast gasification followed by a slow surface functionalization (Braghiroli et al., 2020). Ultraviolet excitation of oxygen at 242 nm results in gaseous ozone. Ozone, as a strong oxidizing agent, attacks on both edge and basal plane carbon atoms of the biochar through a gentle and reversible adsorption process (Jimenez-Cordero et al., 2015; Anto et al., 2021). The advantage of ozone over other activating agents is the required activation energy; ozone activation requires ~ 45 KJ mol⁻¹ while steam and CO₂ activation require 117 and 159 – 179 KJ mol⁻¹, respectively. Controlled dosage, timing (generally 10 min), temperature (below 100 °C) and adequate cycles of ozone activation

can increase adsorption rate and capacity by developing pores, modifying chemical compositions, increasing acidic oxygen functional groups, and increasing oxidation level of the adsorbent surface. Uncontrolled activation was reported to decrease adsorption capacity by resulting in destruction of micropores, enhanced surface oxidation and an increase in polar hydrophilic groups (Jimenez-Cordero et al., 2015).

Steam activation entails diffusion, chemisorption and gas shift reactions. Water molecules are diffused and eventually chemisorbed on to the active sites of the pores forming an oxygen surface complex. Through steam activation of biochar produced from miscanthus, despite the decrease in surface area, no significant change in sorption capacity was detected (Shim et al., 2015). Wood pellet activated biochar was reported to show a relatively higher stability and CO₂ adsorption under dry treatment conditions (C. Zhang et al., 2022). Both steam and CO₂ activation techniques enhance hydrophilic behaviour of the adsorbent and therefore higher adsorption capacities are reported under dry conditions as water molecules can occupy active sites of the adsorbent. Both steam and CO₂ are also effective in reforming aromatic rings. Meanwhile, steam activation was found to be more effective at reforming both single and multiple aromatic rings as compared to CO₂ (Feng et al., 2018). It needs to be noted that adsorbents (from almond shells) activated with steam possessed a higher organic compound adsorption capacity as compared to CO₂ activated adsorbents which was attributed to the differences in surface area of the adsorbents (Toles et al., 2000). Classically, steam activation provides wide distribution of micropores and mesopores while CO₂ activation results in micropores. When comparing cost of steam generation from water to employing chemicals, steam activation was reported considerably cheaper than CO₂ activation (Yek et al., 2021). Meanwhile, application of air (oxygen) as an oxidizing agent is another economic technique to physically activate the adsorbent. Further, comparing air to CO₂ for activation of biochar derived from sugarcane bagasse, the latter was found to be more effective (Ghafar et al., 2021). Additionally, CO₂ activation results in a higher degree of carbonization (Jung and Kim, 2014). CO₂ activation follows the endothermic Boudouard reaction as CO₂ undergoes dissociative chemisorption on to the surface of the char; $C + CO_2 \leftrightarrow 2CO$ (Huang et al., 2021). At temperatures higher than 700 °C, activation with CO₂ was found to be more beneficial than N₂ as it resulted in a higher content of alkali metals (including sodium, potassium, and calcium) (Tian et al., 2017). Comparing to steam, higher concentration of micropores and larger micropore volume were reported upon CO₂ activation (Leng et al., 2021). With optimal pore size for carbon adsorption having been reported to be five times that of adsorbate molecule size (Liu, 2019), it is worth noting that impregnation may adversely lead to the blockage of micropores, decreasing the overall adsorption capacity of the sorbent. It is understood that micropores play the main role in physical adsorption of CO₂. This is linked to the overlapping force fields of the adjacent pores' walls of the ultramicropores with the CO₂ molecules, which capture and hold the adsorbate molecules inside the pores. As a result, CO₂ activation could be considered the most effective physical activation method following development of micropores and mesopores which are favourable in the context of post-combustion carbon capture.

3.2. Physical and chemical modification

Various techniques have been employed to introduce effective yet economical bio-based sorbents with unique features for CO₂ adsorption. This includes physical treatments, impregnations (for instance impregnation with ammonia (Kopac and Kirca, 2020), or deep eutectic solvents (Ariyanto et al., 2021)), and chemical modification (for instance amine grafting of acid-activated bentonite (Horri et al., 2019)). Such surface modifications are generally adopted to improve CO₂ capture performance *via* tuning surface area and pore size (Conde-Mejia et al., 2012), and through the introduction of effective surface functional groups (B. Petrovic et al., 2021). Recently, a number of comprehen-

sive technical reviews on the impact of the introduction of surface functional groups onto sorbents' surface for CO₂ capture have been published (Petrovic et al., 2022; B. Petrovic et al., 2021).

Bio-based sorbents' increased fixed carbon content has been reported to have a favorable impact on interparticle forces between CO₂ and bio-based sorbents (Serafin et al., 2021; Ayucitra et al., 2017). Higher CO₂ adsorption capacity of activated bagasse-derived bio-based sorbent (Boonpoke et al., 2012), as compared to activated rice husk-derived bio-based sorbent (Boonpoke et al., 2011), can be linked to the higher fixed carbon content of the former which was reported to be 84.5 wt%. Higher carbon content of wood wastes, and their relative global abundance are the major reasons for their attractiveness in this research field (Fapohunda et al., 2018). Additionally, bio-based sorbents typically contain unfavorable minerals that can potentially hinder the adsorption performance. Therefore, carbonization and activation temperature could play a critical role in the removal of such components. Recently nanoporous zeolite as a CO₂ sorbent was synthesized from industrial-grade biomass combustion fly ash generated in one of the largest biomass combustion power plants in the UK by the authors (B. Petrovic et al., 2021). Fusion-assisted hydrothermal method resulted in moderately zeolitic sorbents that showed to effectively (and reversibly) adsorb CO₂.

Some studies have recommended different surface modifications in order to add specific types of functional groups to enhance CO₂ uptake capacity of the sorbents. Such functional groups can be categorized based on their type of heteroatom; O-Heteroatoms (phenolic (Wang et al., 2015), carboxylic (Wu et al., 2010; Biswas et al., 2013; Torrisi et al., 2010), quinone (Wang et al., 2015), lactone (Bai et al., 2015; Lee and Kim, 2013), carbonyl (Pels et al., 1995; Nelson and Borkman, 1998), ethers (Zeng et al., 2016; Cmarik et al., 2012), esters (Molavi et al., 2018), and hydroxyls (Liu et al., 2018)), N-Heteroatoms (amine (Nie et al., 2018; Su et al., 2010), nitro (Torrisi et al., 2010; He et al., 2015), amide (Ratvijitvech et al., 2014; Safarifard et al., 2016), imine (Mastalerz et al., 2011), nitrile (Mahurin et al., 2014), pyrrole (Lim et al., 2016), pyridine (Lim et al., 2016; Wang et al., 2017), pyridone (Sevilla et al., 2011), quaternary amines, pyridine-N-oxides, and cyanides), S-Heteroatoms (Biswas et al., 2013) (sulphones, sulphoxides, and sulphonic acids), halogens (Torrisi et al., 2010), hydrocarbon surface functional groups (alkyl (Torrisi et al., 2010), alkene (Kronast et al., 2016), arene (Cmarik et al., 2012)). The advantages of the above modifications have been discussed in detail in our previous work (B. Petrovic et al., 2021). It was reported that surface modification increases binding energy and selectivity over N₂. Adequate and optimized modification has been highly recommended to avoid pore blockage affecting adsorption process.

3.3. CO₂ adsorption equilibrium, kinetics and mass transfer studies

Apart from the activation methods, adsorption parameters (such as process pressure and temperature) play a critical role and have direct influence on the CO₂ adsorption capacity. Adsorption processes at higher pressures exhibited a relatively higher CO₂ adsorption capacity (Table 2). Equilibrium and kinetic models as well as mass transfer studies are employed to further describe the behaviour of the system.

3.3.1. Equilibrium CO₂ adsorption isotherms

Equilibrium isotherms are essential as they provide insight into the relationship and interactions between the adsorbate and the adsorbent, assist characterization of the material's surface as well as the affinity towards the adsorbate. The outcome can then facilitate an experimentally informed process model to evaluate the viability of the process through the analyses of capital and operating expenditures (i.e. CAPEX and OPEX).

In order to describe the adsorption process, Langmuir (single and multisite), Freundlich, Sips, Toth and Dubinin-Radushkevich isotherms have been commonly employed. Equilibrium isotherms play a key role

in designing an efficient sorption system. Mathematical calculations of the adsorption equilibrium are performed to apply the equilibrium data to a specific sorption system. A fixed-bed reactor/column was employed to obtain adsorption isotherms for CO₂ using low-cost carbon black with magnetite fine particles (Raganati et al., 2018). Here, at a specific temperature and CO₂ partial pressure, the equilibrium CO₂ uptake by the sorbent was measured. This was done by analysing the measured breakthrough curve according to the mass balance equation applied to the process (Eq. (1)), where q_e (mmol g⁻¹) is the specific CO₂ adsorption capacity of the sorbent, m is the mass of sorbent in the bed, and $F_{CO_2,in}$ and $F_{CO_2,out}$ are the molar flowrate of CO₂ at the inlet and outlet of the bed, respectively, and t_s is the time required to reach complete sorbent saturation. In order to model the experimental adsorption isotherms, the data were fitted to Langmuir, Freundlich, Sips, Toth and Dubinin-Radushkevich equations with Freundlich and Toth being reported to provide the most accurate fit. Equilibrium studies suggested that the adsorption process of CO₂ on carbon black coated with magnetite fine particles is a multilayer adsorption process and involves heterogeneous surface binding. Additionally, the Dubinin-Radushkevich model fitting suggested that the adsorption in this system was neither purely physisorption nor purely chemisorption, and that both mechanisms were present.

$$q_e = \frac{1}{m} \int_0^{t_s} (F_{CO_2,in} - F_{CO_2,out}) dt \quad (1)$$

Equilibrium CO₂ capacities are used to compare different sorbents. For example, the equilibrium uptake of a dealkaline lignin-derived microporous carbon (activated with KOH) was reported to be 7.24 mmol g⁻¹ (Saha et al., 2018), while for lignin-derived hydrochar (also activated with KOH) the value was 4.6 mmol g⁻¹ (Sangchoom and Mokaya, 2015). Meanwhile, the CO₂ adsorption capacity of dealkaline lignin-derived carbons activated with ammonia (NH₃) was reported to be 5.48 mmol g⁻¹ (Saha et al., 2017). In another study, the CO₂ uptake at room temperature for porous carbon spheres prepared by physical activation of starch-derived char was reported to be 21.2 mmol g⁻¹ (Y. Li et al., 2016), while this value for porous carbons derived from rice husk (activated with KOH) was reported as 6.24 mmol g⁻¹ at 0 °C (Li et al., 2015). Maximum CO₂ adsorption capacity for KOH-activated porous carbons based on poplar anthers was reported to be 51.3 mmol g⁻¹ (Song et al., 2014), while the CO₂ uptake of empty palm fruit bunch-derived biochar (activated with KOH) was reported as 3.71 mmol g⁻¹ (Parshetti et al., 2015). Similarly, chemical activation of activated carbon based on African palm shell using H₃PO₄, ZnCl₂ and CaCl₂, resulted in bio-based sorbents with CO₂ adsorption capacities of 5.77, 17.44, and 7.61 mmol g⁻¹, respectively (Vargas et al., 2013). In another study, CO₂ uptake of pine wood was reported to be 1.35 mmol g⁻¹ (Tian and Zhang, 2016).

Adsorption, however, starts with the target molecule diffusing into the sorbent. As such, the applicable diffusion mechanism are *intraparticle* or *pore diffusion* (amongst others). Pore size and structure are the two main parameters at play for the pore diffusion mechanism. Macropores are considered essential for bulk fluid transport while the dominant forces for mesopores are capillary phenomena. Similarities in the sizes of the pore and the adsorbate molecule can significantly limit mass transport. Transport of mass involves multi-species mixture; in case of adsorption mass transfer occurs in the pores and channels of the sorbent. Mass transport through pores is described through a number of mechanisms including Knudsen diffusion, surface diffusion, molecular or bulk diffusion, and Poiseuille flow (Petrovic et al., 2022). Knudsen diffusion happens when the membrane pore radius (r) is smaller than the mean free path (λ) of the gas molecules (D. Yang et al., 2021). Surface diffusion mechanism takes place when the gas molecules are not able to escape from the surface potential field and are adsorbed on the pore wall and travel along the surface (Qian, 2021). Molecular diffusion mechanism (a function of both temperature and pressure) occurs when mass transport is mainly controlled by collisions between molecules and

Table 2
CO₂ adsorption capacity of bio-based sorbents at different pressures and temperatures.

Bio-based sorbent	Activation method	Isotherm models employed	Temperature (°C)	Pressure (bar)	CO ₂ adsorption capacity (mmol g ⁻¹)
Coconut shell chars (Tangsatitkulchai et al., 2016)	Thermal (250°C)	Freundlich and Sips	-0.15	2.5	1.50
	Thermal (350°C)	Freundlich and Sips	-0.15	2.5	2.15
	Thermal (450°C)	Freundlich and Sips	-0.15	2.5	3.60
Cherry stones (Álvarez-Gutiérrez et al., 2016)	Physical (CO ₂)	Sips and Toth	49.85	2.5	2.85
	Physical (Steam)	Sips and Toth	49.85	2.5	2.50
Pine cone (Khalili et al., 2015)	Chemical (H ₃ PO ₄)	Langmuir and Freundlich	34.85	2.5	2.80
Macroalgae industrial waste (Ferrera-Lorenzo et al., 2014)	Chemical	-	25	1	5.48
	(KOH)	-	-0.15	1	8.60
Palm shell (Vargas et al., 2013)	Chemical (CaCl ₂)	Dubinin–Radushkevich	-0.15	20	7.61
	Chemical (ZnCl ₂)	Dubinin–Radushkevich	-0.15	20	17.44
	Chemical (H ₃ PO ₄)	Dubinin–Radushkevich	-0.15	20	5.77
Empty palm fruit bunch (Parshetti et al., 2015)	Chemical (KOH)	Langmuir, Freundlich, and Temkin	25	1	3.71
Poplar anthers	Chemical (KOH)	Type I	25	1	51.3
Starch-derived hydrochar (Y. Li et al., 2016)	Physical (CO ₂)	Type Ib	25	20	21.20
	Physical (CO ₂)	Type Ib	25	14	17
	Physical (CO ₂)	Type Ib	25	10	13.70
	Physical (CO ₂)	Type Ib	25	5	8.50

within the bulk phase (Hayes and Kolaczowski, 1997). Poiseuille flow occurs when the main force for diffusion is applied parallel to the channel walls between gas molecules and sorbent pores (Gallen et al., 2021).

Sorbent structure plays a key role in incorporation and combination of these mechanisms as they do not occur independently. A combination of Knudsen and Poiseuille flow mechanisms was found essential to develop a 2D computational fluid dynamics model using COMSOL to simulate heat and mass transfer as well as fluid flow in vacuum membrane distillation (Yadav and Singh, 2022). Consideration of both molecular and Knudsen diffusion was reported effective for carbon capture in a fixed-bed column based on a biocatalytic membrane (Rasouli et al., 2021). Consideration of both surface diffusion and molecular diffusion mechanisms was recommended for CO₂ separation in mixed matrix membranes (Nematollahi et al., 2022; Amooghin et al., 2019). In another study, a combination of molecular and Knudsen diffusion mechanisms was considered to compare the kinetic behaviour of wood pellets with coal under various temperatures (Al-Qayim et al., 2017). The coefficients in this study revealed intrinsic reactivity independence from fuel type and tank. At 1000 °C biomass char combustion reactivity was reported to be much higher than that of coal chars. This phenomenon was linked to the highly porous structure of the biochar formed at this temperature.

In the context of CCS *via* adsorption, CO₂ molecules attach onto the surface of the sorbent. Adsorbate properties (molecular size, molecular weight and polarity) and the sorbent surface properties (polarity, pore size and spacing) define the overall efficiency of the process. Based on the interaction between the adsorbate and the adsorbent, the adsorption process is divided into chemical and physical adsorption. Weak bonding including van der Waals and electrostatic forces between the adsorbate and the sorbent is attributed to physical adsorption (also known as physisorption) (Khraisheh et al., 2020). Moreover, difference in dipole and/or quadrupole moments can significantly lower the adsorption efficiency, especially on solids with low adsorption potentials (AbdulKareem et al., 2018). Molecules with strong quadrupole moments (e.g. CO₂) interact stronger with the electrostatic field and result in a more effective adsorption within the pores (Grekov et al., 2021).

On the other hand, adsorption *via* chemical bonding (i.e. chemisorption) involves chemical interactions between the adsorbate and the sorbent's surface. Chemisorption can take place at lower concentrations and pressures and can occur at relatively high temperatures (hence, potential applications in post-combustion CCS) (Suo et al., 2021). Sorbents that were chemically activated and/or modified (e.g. nitrogen-doped) are, classically, prone to chemical adsorption due to the presence of various surface functional groups. Such materials have shown higher adsorption capacities at elevated temperatures which could be attributed to expo-

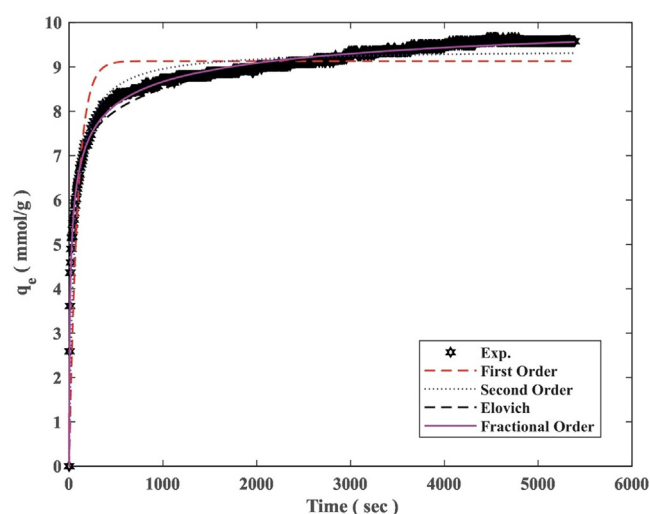


Fig. 2. An example of CO₂ adsorption capacity and corresponding desirable kinetic models for assessment of CO₂ adsorption on bio-based sorbents. Adapted with permission from (Khosrowshahi et al., 2022), through Copyright Clearance Center's RightsLink® service. Copyright (2022) Elsevier.

sure of larger surface areas (often achieved with chemical activation) and more active sites (due to the developed functional groups) (Shi and Liu, 2021; Rehman and Park, 2017).

3.3.2. Kinetics of CO₂ adsorption

Adsorption kinetic studies are performed to understand the adsorption process and to determine the adsorption rate as well as to shed light on the adsorption mechanism. Such investigations could also reveal the possible rate-controlling step of the adsorption process. Some of the key adsorption kinetic models (including pseudo first-order (PFO), pseudo second-order (PSO) and Avrami models) are presented in Fig. 2 and further described in Table 3, where “Q_t” is the amount of species adsorbed at time “t”, “Q_e” is the amount of species adsorbed at equilibrium, “K₁” is the rate constant of the first order model, “K₂” is the rate constant of the second order model, “K_{av}” is the Avrami rate constant and “n_{av}” is the Avrami model exponent of time which is related to the adsorption mechanism changes (Mahmoud and Saryel-Deen, 2017; Sivarajasekar and Baskar, 2019).

In order to accelerate CO₂ adsorption kinetics, chemical and physical treatments are employed to minimise diffusional resistance in the

Table 3
Non-linear forms of the PFO, PSO, Avrami and Elovich equations.

Model	Non-linear equation
PFO	$Q_t = Q_e(1 - e^{-K_f t})$
PSO	$Q_t = \frac{K_1 Q_e^2 t}{1 + K_2 Q_e t}$
Avrami	$Q_t = Q_e(1 - e^{-(k_{av} t)^{1/n}})$
Elovich	$\frac{q_t}{q_m} = K_E C_e e^{-\frac{q_t}{q_m}}$

Table 4
Intra-particle diffusion and Boyd's film-diffusion model kinetic equations.

Model	Kinetic equation
Intra-particle diffusion	$\frac{M_t}{M_{eq}} = K t^n$
Boyd's film-diffusion	$\frac{q_t}{q_{eq}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt)$

meso- and/or micropores. Fast adsorption is considered beneficial and is directly associated with adsorption mechanism, bed size, and unit capital costs (Loganathan et al., 2014). In addition to the mentioned kinetic models, studies have applied a fractional order kinetic model based on Avrami kinetic model of particle nucleation (Angkanawisan et al., 2022). This model has been mainly employed to evaluate the adsorption kinetics of amine-functionalised sorbents (M. Yang et al., 2021; Wang et al., 2022). The models are based on kinetic and diffusion observations and reflect the influence of surface adhesion as well as external and internal diffusions. In a study by Álvarez-Gutiérrez et al., Avrami kinetic model revealed that the adsorption of CO₂ on cherry stone-based carbons, was a function of contact time at elevated concentrations (Álvarez-Gutiérrez et al., 2017). A further kinetic model presented in Table 3 is the Elovich equation, which is based on a kinetic principle assuming multilayer adsorption (adsorption capacity increases exponentially with adsorption) (Farouq and Yousef, 2015). In this model, “q_e” is the amount of species adsorbed at equilibrium (mg g⁻¹), “q_m” is the monolayer adsorption capacity (mg g⁻¹), “K_E” is the Elovich equilibrium constant (L mg⁻¹) and “C_e” represents the equilibrium concentration of the adsorbed species (g L⁻¹).

PFO has been found to be suitable to predict physical adsorption of CO₂ as it represents a reversible interaction between the sorbent and the adsorbate (Kodasma et al., 2019). Meanwhile, a solid diffusion rate-controlled process is better described using PSO. Application of PSO is generally recommended to predict adsorption behaviour based on chemical interactions (i.e. when gas molecules chemically bind to the sorbent's surface). The models' accuracies are assessed based on their error functions and regression coefficient (R²) values.

In addition to the adsorption rate-based kinetic models, mechanistic kinetic models should be considered to understand the governing adsorption mechanisms. The latter is often applied to understand the mass transfer mechanism in bio-based sorbents. The common mechanistic kinetic models include intra-particle (Fickian) diffusion and Boyd's film-diffusion models (Table 4) (Bayu et al., 2022). In the Fickian diffusion model, “M_t” and “M_{eq}” represent the mass of species adsorbed at time “t” and the equilibrium adsorption, respectively, whereas “K” is a characteristic constant and “n” is the diffusional exponent. In the Boyd's film-diffusion model “q_t” and “q_{eq}” are the amount adsorbed at a given time “t” and at equilibrium, respectively (Álvarez-Gutiérrez et al., 2017).

“Bt” in Boyd's model is a mathematical function of $\frac{q_t}{q_{eq}}$ such that:

- For $\frac{q_t}{q_{eq}} > 0.85$, $Bt = f\left(\frac{q_t}{q_{eq}}\right) = -0.4977 - \ln\left(1 - \frac{q_t}{q_{eq}}\right)$
- For $\frac{q_t}{q_{eq}} < 0.85$, $Bt = f\left(\frac{q_t}{q_{eq}}\right) = \left(\sqrt{\pi} - \sqrt{\pi - \left(\frac{q_t}{q_{eq}}\right)^2}\right)^2$

The intra-particle diffusion model is applied to label successive mass transfer stages through an adsorption process. The stages include boundary layer diffusion, intra-particle diffusion and the final equilibrium

stage (Deng, 2022). In this model, each stage is represented by a slope with the smallest slope representing the rate-controlling step. Boyd's film-diffusion model is often employed in order to differentiate between external mass transfer resistance and the rate-limiting step. This becomes more essential when two adsorbates are present in the gas mixture, resulting in external resistance to mass transfer. In this model, the main resistance to adsorption is considered to be from the gas film surrounding the sorbent surface. Kinetic studies involving both intraparticle diffusion and Boyd's film-diffusion models revealed an impact from both of these models on adsorption of CO₂ onto the palm kernel shell activated carbon (Rashidi et al., 2021). Intraparticle diffusion was confirmed by applying Boyd's film-diffusion model in CO₂ adsorption with cocoa shell-derived hydrochar grafted with aminosilane (Vieillard et al., 2018). Following the strong physical interaction, CO₂ adsorption of cocoa shell-derived hydrochar grafted with aminosilane was best described using PFO kinetics and intra-particle diffusion mechanisms.

3.3.3. Mass transfer mechanisms

In addition to equilibrium and kinetic studies, mass transfer studies are also vital to provide information about the rate and mechanism of transport between gas and bio-based sorbent surface. Mass transfer studies are employed to model the rate of adsorption (Pashaei et al., 2022). Batch studies are mostly focused on investigating diffusion of adsorbate particles onto the surface of the bio-based sorbent and include local hydrodynamic effects of the gas-phase near the surface. Meanwhile, column studies are employed to scrutinise the breakthrough curves (BTCs) as well as to validate the performance of the bio-based sorbent from bench-top to pilot scale testing. BTCs are then used to describe the dynamic adsorption process and to further predict the performance of a fixed-bed column (Ang et al., 2020). BTCs are also deployed to design adsorption units based on experimental data (Lestinsky et al., 2015). Breakthrough characteristics assist in describing the inherently dynamic behaviour of adsorption systems. Mathematical studies of breakthrough characteristics in removing organic and inorganic contaminants are performed through Adams-Bohart, Thomas and Yoon-Nelson models. Recently, Buckingham p theorem was employed (based on film parameter, CO₂ loading, concentration ratio, partial pressure to total pressure ratio, film thickness ratio and diffusion ratio) to develop correlation equations to predict CO₂ mass transfer flux into methyldiethanolamine solution (Ghaemi et al., 2020).

Adsorption and separation efficiency are a function of column dimensions including column height and diameter. Theoretically, taller columns would result in higher adsorption efficiency (Khakharia et al., 2014), i.e. product purity and the better usage of the bed length, whereas column diameter is mainly decided by the gas flow rate and other operational considerations for the column.

4. Recent advances in process design

Finding a way to reduce the carbon footprint within carbon capture processes has been receiving growing attention. The use of biomass (as sorbent or sorbent precursor) has been suggested to be a potential route serving this purpose (Dicko et al., 2018). The processes of using biomass as an adsorbent involves three conceptual levels: biomass conversion to porous CO₂ sorbents; efficient absorber/desorber design and optimum process configuration; and intensification of the entire process for optimized energy consumption, CAPEX and OPEX, product purity and etc. This section focuses on the most recent advances in process design and modelling as well as both sorbent preparation and application.

Biochar is one of the key materials used in CO₂ adsorption within the past decades (Li et al., 2021). Biochar production process when backed by the use of renewable energy (i.e. solar energy integration) in the regeneration process can play an important role in achieving negative-emission targets. Pyrolysis and hydrothermal carbonisation (HTC) are

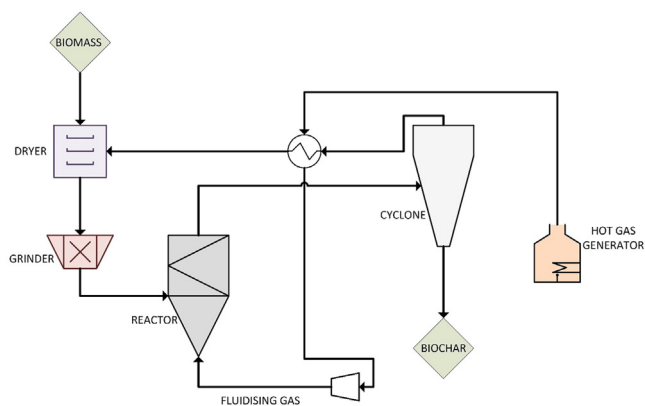


Fig. 3. Simplified process flow diagram of pyrolysis process.

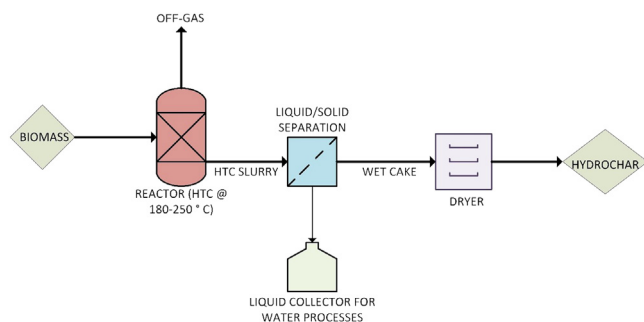


Fig. 4. Simplified process flow diagram of an HTC process.

the main processes employed in converting biomass to biochar. However, other technologies such as gasification, surface modification, and physical/chemical activation have also been studied in the literature (Yang et al., 2019; Cui et al., 2019; Shi et al., 2019).

Fig. 3 shows a schematic diagram of the pyrolysis process. This process is typically carried out at temperatures between 300 and 900 °C and in a zero (or near-zero) oxygen environment (Yang et al., 2019). To achieve high yield of biochar (i.e. >30 wt%), “slow pyrolysis” is often employed where the temperature and heating rate are lower than in conventional pyrolysis and the hold time is longer (Bamdad et al., 2018). Microwave-assisted pyrolysis is a novel alternative in which the biochar yield is higher than for conventional pyrolysis. This method is also faster, more energy efficient and cost-effective than the conventional processes (J. Li et al., 2016).

With biomass containing a significant amount of moisture, HTC processes can be employed to convert biomass to a porous CO₂ sorbent. In this process, the feedstock is mixed with water and heated at a temperature between 180 and 260 °C for up to 240 min (Yang et al., 2019; Wang et al., 2018). The wet product dries and becomes a highly carbonaceous solid called hydrochar. HTC processes have been proposed to be more applicable when dealing with biomass due to the high yield of the hydrochar (40 – 70 wt%) as well as the conditions of the feedstock (i.e. raw biomass is often wet), as well as. As such, this carbonisation approach could be more suitable and cost-effective than pyrolysis (Zhang et al., 2019; Zubrik et al., 2017). Fig. 4 depicts a schematic diagram of the HTC process.

Gasification is another thermo-chemical process in biochar production. The process produces *syngas* (i.e. a mixture of CO and H₂) with a low biochar yield (<10 wt%). Nevertheless, since a large volume of biomass is acceptable for gasification, a significant amount of biochar would be simultaneously generated. Therefore, gasification could be considered a promising route to biochar production (Li et al., 2021). However, to be viable at scale, improvement of overall process yield is essential.

Once the bio-based sorbent has been prepared with the desired specifications for CO₂ adsorption, a suitable adsorption/desorption reactor must be designed for optimal operation. The design is informed by the adsorption and regeneration processes. For this purpose, three types of reactors have been mostly studied in the literature: packed-bed, fluidised-bed and moving-bed reactors. These designs can be investigated from four perspectives: mass transfer, heat transfer, energy-saving in the gas phase, and energy-saving in the solid phase. The adsorption step is usually performed under (or close to) ambient conditions (i.e. 25 – 65 °C and atmospheric pressure). The CO₂ is then released during the regeneration step by increasing the temperature (TSA), or decreasing the pressure (PSA) in the reactor. Since TSA processes can be integrated with low-grade thermal energy (90–120 °C), a well-designed reactor is essential to achieve optimum operation (Liu et al., 2017; Zhao et al., 2018).

The design and build of packed-bed reactors are well established, making them often the first choice for adsorbers. On the flip side, maintaining a high level of heat and mass transfer in packed-beds can be challenging. As such, alternative options could be considered. Using fluidised-bed reactors would improve the heat and mass transfer performance, and moving-bed reactors normally also demonstrate excellent heat and mass transfer between the phases involved in separation (Li et al., 2021).

With adsorption and desorption being exothermic and endothermic, respectively, an optimal heat/mass transfer system is essential. A good heat and mass transfer in the adsorption/desorption process can pave the way for a more viable route towards the deployment of negative-emission technologies. There is an abundance of investigations aimed at process simulation and optimization of different types of adsorbers. Park, Won (Park et al., 2019) simulated a turbulent fluidised-bed for a CO₂ capture process using a polyethyleneimine-silica sorbent. They used the Kunii-Levenspiel core-shell model and kinetic equation of the sorbent to evaluate the profiles of the CO₂ concentrations in the gas and solid phase, as well as the bed temperature. Through simulation, it was shown that sensible heat recovery *via* heat exchange between the rich and spent sorbent streams plays a crucial role in enhancing the process energy performance.

Dietrich, Schöny (Dietrich et al., 2018) designed a continuous TSA for CO₂ capture. In this process, the authors employed multi-stage fluidised-bed columns that act as the adsorber and the desorber. They found that the dynamic CO₂ loading of the sorbent could be increased by dropping the operating temperatures in the adsorber. Their research revealed that a low heat transfer surface area (due to high CO₂ feed rates) could significantly decrease the capture efficiency. This was mainly associated with the formation of large gas bubbles at high feed-gas velocities, which hindered gas-solid contact, leading to a reduction in CO₂ loading.

Overall, the fluidised and moving-bed reactors demonstrate a better performance in terms of gas-solid contact when compared to packed-bed reactors. However, the adsorber type and design also depend on the sorbent type. Since there are several experimental research on bio-based sorbents and many simulation studies on the heat and mass transfer of adsorbers, sophisticated models could be utilized to design customised adsorbers using bio-based sorbents.

Some studies on the adsorber’s geometry have investigated the adsorbers’ size (i.e. height and diameter) and the integration of heat exchangers into the adsorbers. In a study by Kim, Son (Kim et al., 2013), a moving-bed reactor coupled with a plate heat exchanger was conceptually designed. The design, referred to as intermittently moving-bed, has been experimentally tested by Son, Won (Son et al., 2016) and simulated in a series of works by Jung, Park (Jung et al., 2017), (Jung et al., 2018).

Overall, designing a process with optimal heat transfer in the system (and between the adsorber and the desorber) plays a crucial role in bio sorbents’ performance. The key indicators for such an optimal design are the energy consumption alongside the CO₂ adsorption capacity,

productivity and purity. In a study conducted by Jung, Park (Jung et al., 2018), it was found that the heat of adsorption and the specific heat capacity play a major role in designing the process. Further, sensitivity analysis showed that when the heat of adsorption and the heat capacity are reduced by 10%, the total energy demand could drop from 255 to 244 kWh $t_{CO_2}^{-1}$. At the same time, while the other parameters are kept constant, the changes in the bed dimensions have a less noticeable impact on the energy demand and overall CAPEX/OPEX.

4.1. Cyclic adsorption/desorption processes

Generally, the adsorption-desorption cycle takes place by either changing the temperature or pressure in the process. In TSA, the desorption column is heated with a sweep gas introduced to “carry away” the desorbed CO_2 molecules. However, when the pressure is changed during the desorption process, the process is referred to as PSA. Here, the desorption cycle normally operates at atmospheric pressure, while the adsorption cycle is run under pressure for enhanced adsorption. If the adsorption is performed at atmospheric pressure, then the desorption cycle is carried out under vacuum, hence vacuum swing adsorption (VSA). PSA and TSA have been combined to develop various process configurations to improve the overall process efficiency. Temperature-vacuum swing adsorption (TVSA), vacuum pressure swing adsorption (VPSA) and pressure-temperature swing adsorption (PTSA) are the other designs that have been used in CO_2 adsorption.

TSA process configurations could, perhaps, be the most suitable option for bio-based sorbents as their adsorption mechanism is mainly physical (i.e. significantly dependant on the temperature variation due to the absence of covalent bonds between the sorbent and the adsorbate). In classical TSA designs, the process is run isobarically with the adsorber at a low temperature and the desorber at a higher temperature (Ünveren et al., 2017). While heat must be removed in the adsorption step, it must be supplied during the desorption stage. This energy could be supplied with heat integration systems or low-grade sustainable sources such as solar thermal energy (Liu et al., 2017; Zhao et al., 2018; Almasri et al., 2022).

Li, Deng (Li et al., 2019) studied TVSA thermodynamically. Based on their findings, the TVSA process, compared to classical TSA, was quicker to run, and required lower temperatures (i.e. lower energy consumption) for the regeneration step while obtaining higher CO_2 recovery. The vacuum pump used in the desorption step could elevate the CO_2 productivity of the process by evacuating the adsorption bed to the desired desorption pressure. This could be appropriate for bio-based sorbents as they are susceptible to degradation at high temperatures; hence lower temperatures for desorption would be preferable.

PTSA is associated with lower OPEX compared to TSA, which is due to the lower temperature required in the desorption column. In comparison, the energy efficiency of TVSA has been found to be generally higher than PTSA (Zhao et al., 2017). Zhao, Zhao (Zhao et al., 2017) investigated these two processes and concluded that the solid sorbents' physical properties significantly impact the adsorption isotherm in both designs. Therefore, it is necessary to investigate the link between the design and the type of bio-based sorbent used in the process.

Marx, Joss (Marx et al., 2016) employed jacketed columns to modify a PSA setup to its TSA counterpart. In this work, experimental studies were used to simulate a cyclic CO_2 adsorption TSA process. Good agreement between the simulations and the experiments was reported in this work. The generated model was capable of predicting the temperature and composition profiles as well as the adsorption performance under different conditions. Their research could be further utilized for bio-based sorbents to investigate the CO_2 adsorption performance in TSA processes.

A bio-based sorbent (derived from olive stones) was studied in a multi-bed TVSA process (Plaza and Rubiera, 2019). In this work, a dynamic simulation of the cyclic steady-state process was carried out to assess the overall performance of the CO_2 adsorption process. The sim-

ulated process was modelled to operate between 30 °C and 1.05 bar and 80 °C and 0.05 bar. Therefore, low-grade heat (e.g. solar thermal energy) is expected to be able to meet the heat demand in the process. Nevertheless, using vacuum to regenerate the sorbent led to higher electricity consumption than the benchmark technology (i.e. amine absorption).

A number of process configurations have been proposed which could potentially improve the overall efficiency of the application of bio-based sorbents. For instance, a two-column three-step TSA process using spherical pellets of zeolite 13X has been proposed by Marx, Joss (Marx et al., 2016). Zeolite 13X is the most often used adsorbent in the CO_2 separation process, thus, could be considered as a benchmark. Regardless, the process comprised three steps, namely, adsorption, heating and cooling. During the first stage the feed was passed through the column while the column temperature was regulated by cooling water passing through the column's water jacket. In this step, an N_2 -rich stream was produced. During the next stage, the column was heated, and a CO_2 -rich stream was produced. At the third step, the column was cooled down again and the feed passed through at a minimal flow rate to maintain atmospheric pressure. No product was produced in this step. The results from Marx, Joss (Marx et al., 2016) showed that longer adsorption periods led to a better overall cyclic capacity, productivity and purity of CO_2 but caused lower recovery at the desorption step. For higher recovery, the heating/cooling time at the second and third steps should be longer to create a larger temperature swing, which limits the productivity of CO_2 , thus constituting a trade-off between productivity and recovery of CO_2 . Further, their developed model was able to simulate the behaviour of a two-column three-step cyclic TSA process, demonstrating good agreement with the experimental data.

Several other TSA configurations have been studied, such as the four-step TSA (Joss et al., 2015), six-step TSA (Joss et al., 2017) and also PTSA (Cloete et al., 2019), which could be similarly adopted and developed for bio-based sorbents. It might be argued that in the cycle configuration design process, the function of an extra step (i.e. pre-heating and recycling the gas phase) should be prioritised for better performance of bio-based sorbents.

Adsorption is an exothermic reaction, while desorption is endothermic. Therefore, it is conceptually possible to integrate thermal energy from the adsorber to the desorber, hence an intensified process, ultimately resulting in optimum process OPEX. Consequently, a heat recovery unit should be an integral part of any process design. For example, a novel PSA self-heat recovery CO_2 capture process was developed by Song, Kansha (Song et al., 2015). In their process, a heat pump was used to take the heat from the exothermic adsorber and supply it to the endothermic desorber. The authors simulated the process in terms of mass and energy balance and found that around 60% of the input energy could be saved in this proposed configuration, thus constituting a significant reduction in energy consumption which could also be exploited for bio-based sorbent processes.

In another study by Mondino, Grande (Mondino et al., 2019), a heat recovery system was employed in a moving-bed TSA system working with zeolite 13X as the adsorbent. The authors found that around 35% of the total energy required is saved when considering a heat recovery system which is very promising. Further, Drechsler and Agar (Drechsler and Agar, 2019) found that the maximum heat recovery in conventional systems could be approximately 50%.

Another way to optimize energy consumption in the adsorption process is to use solar energy to recover the sorbent. The efficiency of this type of energy in recovering the sorbent has been investigated in various studies (Liu et al., 2017; Zhao et al., 2018; Zhao et al., 2015). There is no doubt that integrating sustainable solar energy as a green source of energy can even further suppress carbon emissions in the adsorption process. Zhao et al. (Liu et al., 2017; Zhao et al., 2018; Zhao et al., 2015) extensively reviewed solar-assisted carbon capture systems. In their work, energy-efficiency and process integration were investigated. The work led to understanding the feasibility of solar-

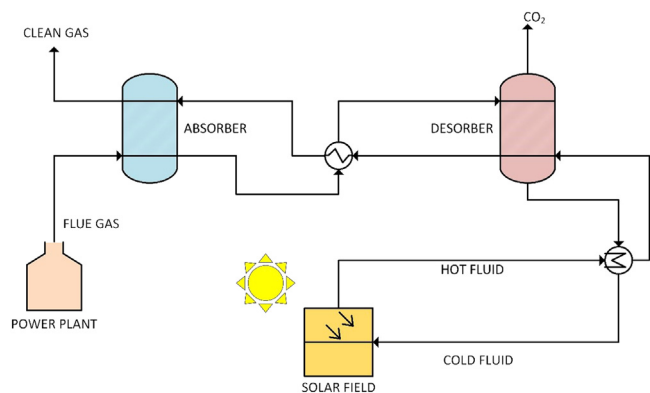


Fig. 5. Simplified process flow diagram of solar-assisted carbon capture system.

assisted CCS in post-combustion CO₂ capture processes. It was learnt that the temperature range required in the absorbent regeneration process is in the same range as the temperature provided by solar thermal collectors, which means that solar-assisted CCS could be efficiently deployed (Zhao et al., 2018). In this study, three types of sorbents (i.e. zeolites 5A and 13X as well as an alternative sorbent which was synthesised via a reaction of an aqueous suspension of nanofibrillated cellulose and 3-aminopropylmethyldiethoxysilane) were investigated in a solar-assisted PTSA process. Fig. 5 illustrates the schematics of a simplified solar-assisted CCS process.

In addition to studies focused on minimising energy consumption in the adsorption process, several studies have been done on optimizing gas purity and recovery. Mondino, Grande (Mondino et al., 2019) studied the moving-bed TSA process at high regeneration temperatures and obtained the purity and recovery of CO₂ at 95.8% and 98.2% at 270 °C, respectively. Fig. 6 compared the CO₂ adsorption performance of different process designs.

Since bio-based sorbents are mainly carbonaceous, with physisorption being the dominant mechanism, adsorption should be carried out at as low temperatures as possible for higher uptakes due to the low adsorption enthalpy of <math><40 \text{ J mol}^{-1}</math> (Sharma and Dhir, 2021). Optimum adsorption is done below 70 °C (Sharma and Dhir, 2021) and therefore, 270 °C is considered high for bio-based sorbents. As a result, the process should be optimized at lower temperatures to fulfil the bio-based sorbents' requirements (i.e. the dominance of physical adsorption). Wang, Liu (Wang et al., 2012) simulated a five-step TVSA process working with zeolite 13X-APG at a regeneration temperature of 90 °C, which is only a bit higher than the optimum adsorption temperature (70 °C). Nevertheless, such conditions could still be suitable for bio-based sorbents. Based on the authors' simulation, a 92.2% CO₂ recovery and a 93.6% CO₂ purity were successfully achieved. In another study (Marx et al., 2016), the energy consumption of a TSA process was tested and simulated at a temperature range of 100 – 150 °C. The results showed a significant gap between the actual and simulated values. The reported discrepancy shows that other energy consumption sources in the process should be carefully considered in future studies.

In general, it can be concluded that in CO₂ adsorption processes using bio-based sorbents, the extent of energy recovered and the purity of the recovered CO₂ should be the focus of the process designer. Sorbent development, adsorber design, and the adsorption process optimization should all be simultaneously considered together to understand the effectiveness of the bio-based sorbents in successfully achieving the negative-emission targets when considering such technologies.

4.2. The role of machine learning in adsorption processes

This section provides a concise description of machine learning (ML) techniques and the recent development of incorporating ML into the

Table 5
Common advantages and disadvantages of ML.

Machine Learning	
Advantages	Disadvantages
Applicable to a number of research fields	Dimensionality
Increased automation	Ethical considerations
Ease of trends and pattern identification	Algorithm selection

process modelling of adsorption-based carbon capture. Specifically, we have identified the need for further research into combining ML and quantitative structure activity relationship to discover *bio-based* adsorption for carbon capture purposes as well as utilizing ML to screen for *bio-based* pre-cursors material that can then be synthesised into adsorbents for carbon capture application. Often due to the variation in chemical composition associated with *bio-based* precursor sample it is often difficult to determine optimal synthesis routes for adsorbents for carbon capture. Incorporating ML will allow for vast amounts of data relating to the characterization of the precursor material and how it relates to its CO₂ adsorption capacity, to determine optimal characteristics of pre-cursor material to ensure efficient *bio-based* adsorbents for carbon capture application.

ML is a subset of artificial intelligence (AI) that allows computer programmes to learn through algorithms and high-level statistical tools to improve over time for robust optimization, prediction and data clustering. ML is a powerful technique which facilitates the optimization of highly non-linear systems (Yan et al., 2021). ML has a vast array of applications across several research areas: medical diagnostics (Bhavsar et al., 2021), image recognition (Wu and Chen, 2015), and natural language processing (Hirschberg and Manning, 2015) are just a few areas in which machine learning has been applied with great effect. Within the context of chemical engineering, the recent application of ML has been applied to process modelling (Khan and Lapkin, 2022; Rebello et al., 2022) and optimization (Yu et al., 2021) and molecule screening for novel catalysts and sorbents (Mehta et al., 2021; Nkulikiyinka et al., 2022).

Within process modelling, the operation of various separation units, including adsorption/desorption columns, can be approximated via ML. However, the heavy reliance of ML models on available data may bring about challenges associated with data availability and quality, as these would directly impact the prediction accuracy of the developed ML model. With regards to sorbent synthesis and process optimization, abundant data is available in the literature for a wide range of sorbents and processes (Yan et al., 2021). ML provides researchers and industry experts with a tool to build models that can interpret highly non-linear systems at speed. However, ethical considerations such as interpretability must be considered upon application (Yan et al., 2021; Horvitz and Mulligan, 2015). Table 5 lists the common advantages and disadvantages of ML.

ML can be categorized into three different training methods: supervised, unsupervised and reinforcement learning. Supervised learning uses labelled datasets to train algorithms to classify data or predict outcomes accurately, and the training set teaches models to yield desired output (Dey, 2016; Choudhary and Gianey, 2017). It's commonly used when the input-output is known in which it can learn the relationship between the input-output, so when utilized, it can predict outputs (Fumo, 2017). Supervised learning can be subdivided into classification and regression. Classification assigns data to categories, recognizes entities within a dataset and then draws a conclusion on how these entities should be characterized, whereas regression is utilized to understand the relationship between dependant and independent variables (Edwards, 2018).

Unsupervised learning is used when the dataset is unlabeled, and the algorithms attempt to discover patterns or groupings within the data without the need for human intervention (Yan et al., 2021). Unsupervised learning is usually utilized for three main tasks: clustering, as-

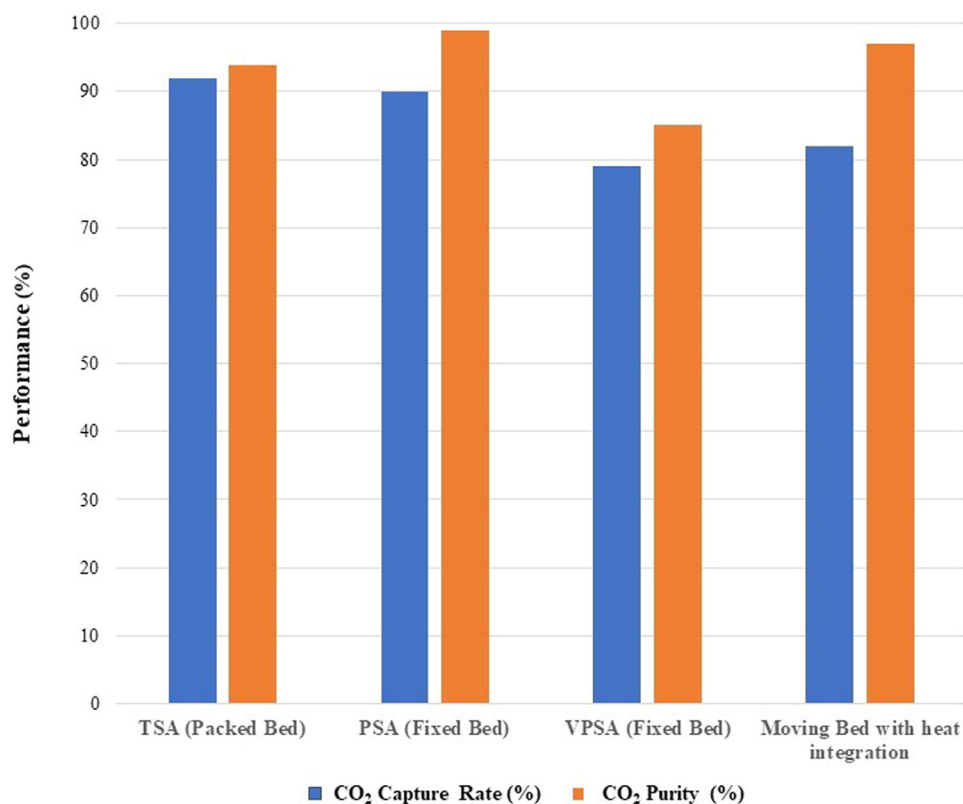


Fig. 6. CO₂ capture performance of different process designs: TSA (packed-bed) (Marx et al., 2016), PSA (fixed-bed) (Ishibashi et al., 1996), VPSA (fixed-bed) (Wang et al., 2013), moving-bed with heat integration (Kim et al., 2013).

sociation and dimensionality reduction (Dey, 2016). Clustering groups unlabeled data based on similarities or differences; the association uses a rules-based method to find relationships between variables in a given dataset (M. IBM 2020). Dimensionality reduction is used to reduce the number of features within a dataset so that is manageable and problems such as overfitting do not arise (M. IBM 2020). Recent developments within ML training have used semi-supervised learning in which it uses a smaller labelled dataset which can then guide the classification and extraction of data across a larger unlabeled dataset (Ouali et al., 2020).

Reinforcement learning is not trained *via* training data; it learns *via* trial and error, and successful outputs are reinforced the develop the best recommendation for a problem (Dey, 2016). It has been commonly used to develop games such as the AlphaGO (Silver et al., 2016). A recent phenomenon within ML has been deep learning. Improved computational power has allowed for the development of deep learning, which is a specific type of machine learning that utilizes complex neural networks (>3 layers) to process and learn from large amounts of data (M. IBM 2020).

Table 6 provides a brief description of common algorithms utilized. Fig. 7 provides a simple guide to selecting the correct type of learning method and algorithm for a particular task depending on various factors. Selecting what learning method to use is usually dependant on whether the data is labelled or unlabeled. Once the training type is selected, choosing the algorithm is selected based on various factors such as interpretability, speed and accuracy of the algorithm.

Within sorption processes, ML has been used for two main purposes, modelling of sorption processes such as PSA, TSA and sorbent screening for novel sorbents. The rise of deep learning has allowed for complex processes such as PSA to be modelled with high accuracy (Rebello et al., 2022). Within this section, we aim to discuss the latest research on the incorporation of machine learning within screening for novel bio-based sorbents and its application within the process optimization of PSA.

Porous sorbents can be chemically and/or physically tuned to suit a particular application (Stock and Biswas, 2012). This would readily allow for tailor-making sorbents to enhance their performance in remov-

ing CO₂ from a gaseous mixture such as post-combustion flue gases. On the other hand, conventional experimental procedures are expensive and time-consuming when it comes to discovering and synthesizing novel sorbents (Moghadam et al., 2019). ML's frameworks for developing, characterizing, and tuning the porous structures were created using computational approaches (Rosen et al., 2020; Wilmer et al., 2012). ML application is also beneficial in selecting a CO₂ sorbent when considering other factors such as sensitivity to moisture, synthesizability, and total life cycle costs. A study conducted by Collins et al. (Yuan et al., 2020) revealed that ML's genetic algorithm could successfully optimize the pores' functional groups, resulting in improvement of MOFs' physical features. Novel sorbent features such as hydrophobic adsorbaphore (i.e. two aromatic cores or binding sites, one for water and one for CO₂) have also been studied using ML models. In addition, since moisture may hamper adsorptive CO₂ uptake, its impact can be further investigated *via* ML for a particular sorbent once appropriate experimental datasets are available (Boyd et al., 2019).

Further work has utilized artificial neural networks (ANNs) to develop models that can predict key parameters for CO₂ capture using carbonaceous adsorbents which have been synthesized from biomass precursors (Mashhadimoslem et al., 2021). The developed ANNs have been shown to predict CO₂ adsorption capacity of activated carbons accurately (with high R² values), from inputs such as pyrolysis temperature, adsorbent porosity volume, adsorption temperature, and adsorption pressure.

Optimization of cyclic adsorption processes is mostly done using nonlinear partial differential equations. Moreover, due to their cyclic and transient nature, adsorption processes are highly dynamic processes. As a result, nonlinear partial differential equations are needed to be solved in time and space for each step in a cycle sequence, iteratively, a process that requires extensive and complex computational resources. Therefore, machine learning approaches can be employed to develop and optimize cyclic adsorption procedures for CO₂ adsorption systems to address such issues (Yan et al., 2021).

Table 6
A brief description of common ML algorithms and their task type.

Algorithm	Task Type	Description
Linear regression	Regression	Fits linear models with coefficients, correlates each data feature to output, and is able to predict future values (Choudhary and Gianey, 2017).
Logistic regression	Classification	Predicts likelihood of dependant variable belonging to a category (Choudhary and Gianey, 2017).
Decision tree	Regression and Classification	Classifies values into groups. The tree consists of nodes and branches, where nodes are the groups into which the data is classified, and the branches are values the nodes can take (Dey, 2016).
Naïve Bayes	Regression and Classification	Conditional probability creates trees based on the probability of an event happening (Dey, 2016).
Support Vector Machine (SVM)	Regression, classification and outlier detection	Working off of margin classification draws margins between classes to classify data. The decision boundary is chosen based on the nearest data point that maximises the distance of all the classes within the dataset (Dey, 2016).
Random Forest	Regression, classification and clustering	A combination of many decision trees that operates as an ensemble, each tree will produce output, and the output with the most votes is the model prediction (Yan et al., 2021).
Neural Networks	Regression, classification and clustering	Non-linear mapping structure maps input and output with layers of nodes in between, the value of nodes in output based on the activation function of nodes in hidden layer and interconnection of nodes (Yan et al., 2021).
K-means clustering	Clustering	Groups the data in K number of clusters based on existing similarities using mean as the centre point for clusters. Usually utilized for numerical data (Dey, 2016).
K-modes clustering	Clustering	Groups the data in K number of clusters using the mode. Often utilized for categorical data (Dey, 2016).
Hierarchical Clustering	Clustering	Splits clusters amongst hierarchical trees to form a classification system. It has many methods for clustering the dataset hierarchy, such as single linkage cluster, complete linkage clustering and Wards Linkage (M. IBM 2020).
Gaussian Mixture Model	Clustering	The probabilistic technique uses gaussian mixtures to cluster the data density distribution of the dataset (Dey, 2016).
Principal Component Analysis (PCA)	Dimensions reduction	Reducing the dimensions of a dataset to increase the speed. Often used with other ML algorithms to simplify the inputs required to reduce computational cost (Dey, 2016).
Single Value Decomposition (SVD)	Dimensions reduction	Decomposes a matrix into smaller matrices, exposing properties of the original matrix (Dey, 2016).
K-Nearest Neighbour	Classification	Uses proximity to classify data into groups (Dey, 2016).
Apriori Algorithm	Association	The association-based algorithm mines through datasets and determines proceeds by identifying the frequent individual items in the database and extending them to larger and larger item sets as long as those item sets appear sufficiently often in the database (M. IBM 2020).
Gradient boosting tree	Regression and Classification	It is a set of decision trees used to boost. Random forests build each tree independently, while gradient boosting builds one tree at a time (Yan et al., 2021).

For a complicated 8-step PSA process built for pre-combustion CO₂ capture, Subraveti, Li (Subraveti et al., 2019) devised a neural network-based optimization technique to identify the Pareto solutions of multi-objective maximization of CO₂ recovery and CO₂ purity. The neural network-based simulation was ten times quicker than high-fidelity simulations for the PSA optimization. Xiao, Li (Xiao et al., 2020) also employed a multi-output feed-forward neural network architecture to predict productivity, recovery, and purity in the PSA optimizations instead of building a surrogate model for each performance indicator. In another study on hydrogen and CO₂ recovery from the tail gas of a steam methane reforming plant, Vo, Oh (Vo et al., 2020) developed an integrated process model based on a mix of multiple feed-forward neural networks that describe the input-output mapping structure of the cryogenic, membrane, and PSA units.

In another study on post-combustion CO₂ capture, neural networks were utilized to build basic steps in a conventional PSA module (Leperi et al., 2019). This work tested each neural network model for predicting five state variables at ten points along the column. The studied variables were CO₂ molar loading, absolute pressure, column temperature, CO₂ gas phase mole fraction and N₂ molar loading. Furthermore, one neural network was applied at each end of the column to predict the total amount of gas at the inlet and outlet of the column. This method enabled the authors to create several PSA cycles and investigate their performance according to the neural network models at each step.

Research has shown that supervised learning algorithms can be successfully integrated into optimization techniques. With the advancements in machine learning, greater attention should be paid to the dynamic modelling of adsorption processes. Leperi's work is an example of using ANNs to predict the dynamics of several essential component phases of PSA processes. Such methodologies are beneficial, especially for constructing and assessing various CO₂ capture adsorption systems (Leperi et al., 2019).

Further work has been done by Jablonka et al. (Jablonka, 2021), in which an ANN model was developed for the purpose of forecasting of amine emissions from a carbon capture plant. Further analysis of the

model allows for insight into parameters that are key for emission mitigation as well as identifying the need for different emission mitigation strategies dependent on the solvent used. Further highlighting the potential ANNs have within industry for process control and safety. ANNs modelling can provide great insight into the dynamic nature of processes at great speed.

Increasing the generalization ability of such ML models is also vital for reliable predictions. These models can also help researchers understand how different intensive factors (such as temperature, pressure, gas composition, and solid composition) impact the process. ML may be used to deal with the high dimensionality of adsorption process optimizations. The correlation between the key performance indicators and the decision variables can be determined using ML's semi-supervised/unsupervised algorithms. These algorithms help find important decision factors for optimization and the structural connection between inputs and outputs of the process.

While the majority of machine learning studies are focused on pilot-scale processes with commercial sorbents, several of these ML techniques can also be used for lab-scale adsorption with bio-based sorbents once the required datasets are at hand. Application of machine learning within the development of bio-based sorbents was presented in Figs. 8 and 9. The figures show how machine learning has been predominantly utilized within the development of bio-based sorbents for carbon capture and how it overcomes the conventional modelling and material screening processes.

5. Geological challenges associated with the application of bio-based sorbents

Low adsorption capacity of bio-based sorbents is a well-known problem which would translate into the need for increased quantity of sorbents to achieve separation targets. Various treatment techniques have been suggested using less quantity of bio-based sorbents while still maintaining a high degree of separation. Through these thermal and chemical treatments, an advanced lightweight bio-based sorbent with larger

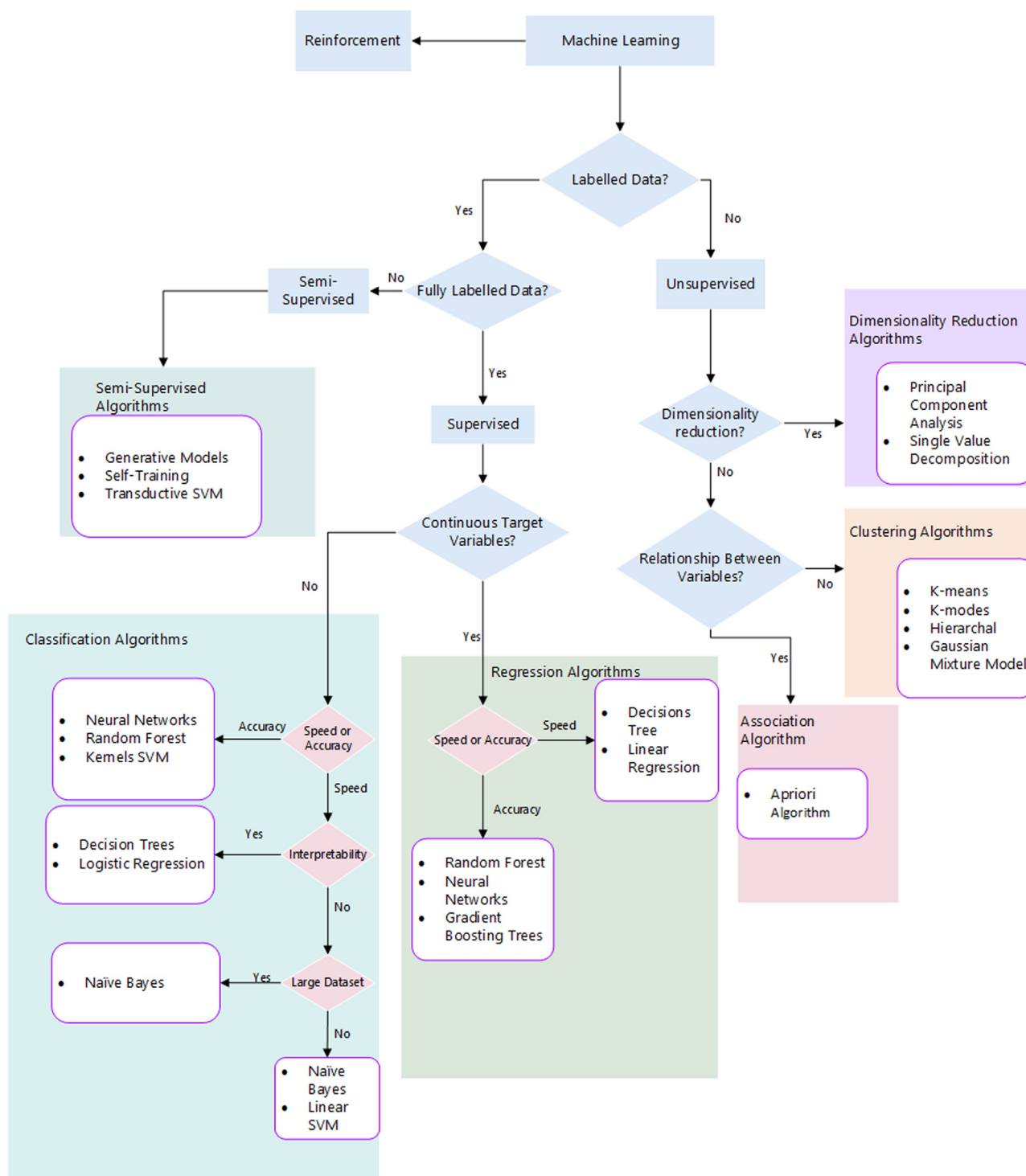


Fig. 7. Simplified diagram for the selection of ML algorithms.

surface area, higher degree of porosity, higher thermal and mechanical stability is obtained. Environmental considerations are another set of challenges that occur during the preparation and enhancement process. Odor, potential emissions, and discharge of hazardous components during chemical treatments are some of the concerns that need to be monitored and/or controlled.

Biomass composition and the associated physicochemical properties, to a great extent, suffer from geological dependency. For instance, a bio-based sorbent derived from spent Brazilian coffee has a different performance as compared to a spent Indonesian coffee. Fibre content, acid-

ity, porosity, density, surface area, and even processing condition are amongst the main factors for these differences. Through a recent study, surface area of Vietnamese rice straw bio-chars was reported to be 30% more than that of Japanese rice straw bio-chars, while the surface area of Vietnamese rice husk bio-chars was slightly more than that of Japanese rice husk bio-chars (Do et al., 2019). As a result, every region is able to produce bio-based sorbent with unique features. However, the main concerns are availability of non-edible feedstock, seasonal variability amongst others (Uwaoma et al., 2021). Moreover, the need for continual supply of bio-based sorbents should be considered. Unless the biomass

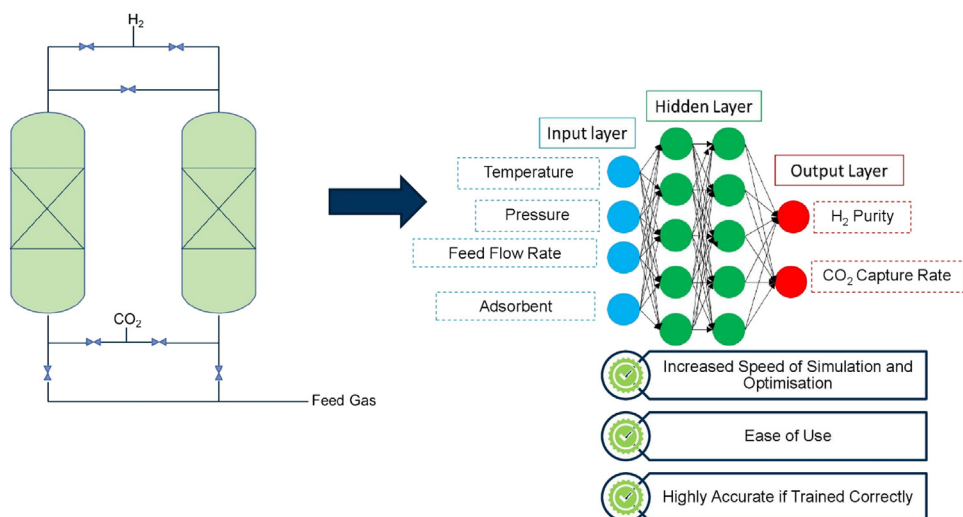


Fig. 8. Conventional approach to process modelling in comparison to machine learning approach and the advantages of incorporating machine learning into this approach.

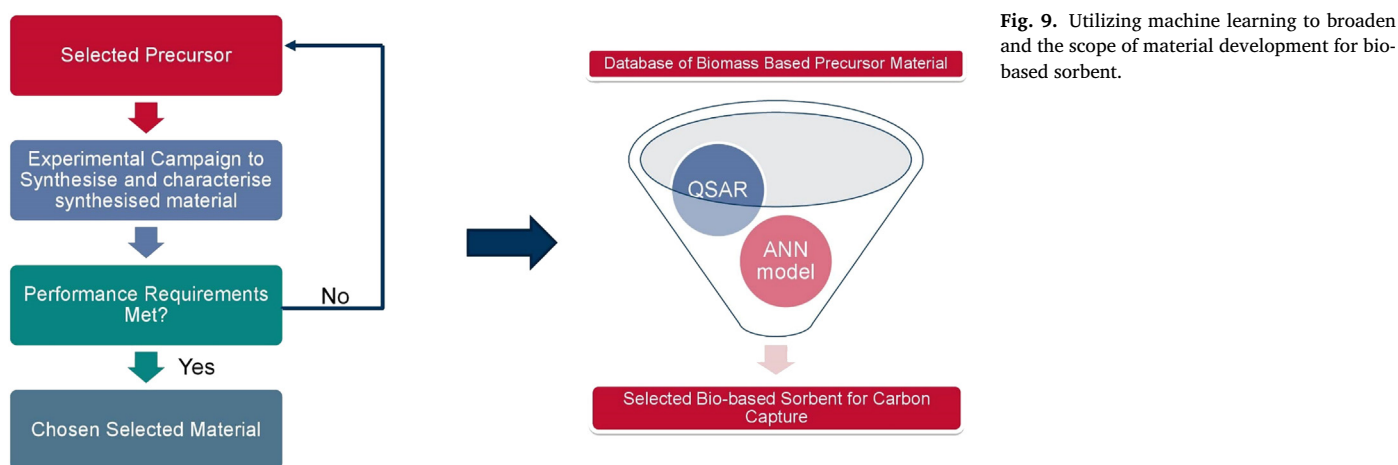


Fig. 9. Utilizing machine learning to broaden and the scope of material development for bio-based sorbent.

is sourced via a sustainable process, the technology may be deemed to be environmentally unfriendly and would have little impact on climate change mitigation overall.

Climate change has direct impact on the quality, physical structure, and chemical components of plants and trees. Similar to fruits' life cycles, the supply for certain biomass resources is seasonal and storage is the recommended solution for the supply throughout the year. For instance, Côte d'Ivoire experiences significant temperature variation between the north and the south depending on the season, ranging from 22 °C to a maximum average of 32 °C (Koua, 2022). As a result, following the increasing demand for the application of unique biomass materials, bulk storage has been found beneficial.

As mentioned previously, climate change directly influences the physical content and structure of biomass. Physical shape (irregular size), bulk density, the space it requires for storage and storage costs are some other key challenges in the deployment of the technology at scale. Chemical treatment methods in addition to wet/dry milling stages were found beneficial to change the physical structure of the material (Akhlisah et al., 2021; Wang et al., 2021). In this way, tailored particles are stored more easily and require less space as they have reached an appropriate size allowing controlled application. Such treatment benefits transportation costs as well. There are remote areas (e.g. islands) that are home to unique types of materials; however, their collection and transportation constitutes a challenge. Therefore, appropriate treatment can reduce transportation costs as well as the required storage space (Fytli and Zabaniotou, 2018).

Selection of biomass type, chemical treatment route and activation process are another set of challenges. For example, bagasse and rice husk were treated with ZnCl_2 at 500 °C for 1 h in nitrogen atmosphere (Boonpoke et al., 2012; Boonpoke et al., 2011). Despite similar surface area values (923 – 927 $\text{m}^2 \text{g}^{-1}$), bagasse-derived biochar presented higher CO_2 adsorption capacity (76.9 mg g^{-1}) than that of the rice husk-derived biochar (57.1 mg g^{-1}) at 30 °C. An alternative study produced an olive stones-derived biochar impregnated with NH_3 at 800 °C for 2 h which possessed a higher CO_2 adsorption capacity (110 mg g^{-1}) than that of the pristine olive stone-derived material (88 mg g^{-1}).

Another challenge in this field is global competition for supplying food. The demand for food is growing exponentially due to rising standards of living (Miner and Raftery, 2012). At the same time, countries generally adopt their own environmental policies and regulations. In some countries including China, India, the United States and Brazil, food supply has a high level of priority (Pengliang and Shuna, 2022; Kocak et al., 2022). This limits the access to certain biomass resources, particularly edible feedstocks. Furthermore, biomass requires natural resources (e.g. land and water) to grow. As a result, the requirements of food production have limited the land and water access to grow biomass materials. This has directed studies towards waste biomaterials for different applications rather than fresh biomaterials. Recently, a study presented spent coffee ground-derived sorbents for CO_2 capture from flue gas (Mukherjee et al., 2021).

A further concern is the cultivation cost. Unit cultivation cost of biomass is comprised of all the costs related to the cultivation of biomass

including the cost of renting, farming, harvesting one unit of land and a final sale price in the region (excluding shipping costs for delivery to biorefineries) (Cooper et al., 2019).

6. Operational challenges associated with the application of bio-based sorbents

Many challenges impede wide implementation of bio-based sorbents. For instance, degradation and/or decomposition of such adsorbents at high temperatures is an issue in this field (Sadrul Islam and Ahiduzzaman, 2012). Following the nature of bio-based sorbents, synthesising highly uniform and compositionally homogeneous materials is a key challenge. Therefore, quality control at different stages of the process is highly recommended to maintain a constant separation performance throughout the whole process of CCS. Replacement and/or reactivation of bio-based sorbents is required once a specified reduction in the efficiency is observed.

Bio-based sorbents can demonstrate a limited adsorption capacity compared to other sorbents. In addition, regeneration depends on the mechanism of adsorption and the mechanical stability of the material. The process configuration (e.g. regeneration pathway) needs to be carefully selected not only based on costs, but also with regards to possible impacts on the sorbents' stability and on the surface functional groups. Moreover, the applied chemical treatment itself may not be efficient, and through particular cases could be destructive, depending on the physicochemical properties of the initial biomass being considered.

A detailed techno-economic review of the current state-of-the-art of bio-based sorbents and adsorption technologies as a whole is out of the scope of this paper. Further, any such assessment would depend greatly on the evaluated materials, process configuration, gas flow rate, CO₂ concentration impurities and etc. Nevertheless, adsorption technologies (similar to membrane separation) have been shown to be better-suited towards low recovery rates and small scale operations, whereas current absorption-based capture methods have a wider range of applicability (Zanco et al., 2021). As such, the gap between the commercialised amine solutions and bio-based sorbents is yet to be bridged; with a key issue for the latter stemming from the required pre-drying of flue gas due to poor resistance to moisture of most adsorbents. Future sorbent development, perhaps, could be aimed at battling this issue as this lack of data has slowed down commercial and industrial scale-up. Hence, recovery, reusability and resistance to moisture (amongst others) are crucial aspects that should be addressed in order to be competitive in the open market.

Additionally, improving bio-based sorbents' cyclability is a key step forward. For instance, soybean derived adsorbent was prepared through chemical treatment (with ZnCl₂ at 600 °C for 2 h), physical activation (with CO₂ at 600 °C for 2.5 h) and washing with HCL (Thote et al., 2010). The CO₂ adsorption capacity of this sorbent was reported to be 42 mg g⁻¹ both at first and after four consecutive cycles. In another study, carpet wastes were selected to prepare bio-based sorbent via chemical activation with KOH at 600 – 900 °C for 1 h (Olivares-Marin and Maroto-Valer, 2011). This precursor (i.e. carpet waste) was reported to contain both natural and synthetic materials. The CO₂ uptake of the carpet waste-derived sorbent was reported to stay constant at a value of 138 mg g⁻¹ even after five cycles. Alternatively, rice straw was pyrolysed using a microwave at 100 – 250 W to derive bio-based sorbents (Huang et al., 2015). At 20 °C the adsorption capacity of this carbonaceous adsorbent was reported to be 77 mg g⁻¹, however, this value was reported to drop by 8 – 10% after eight cycles. In another study, to produce bio-based sorbents, coffee grounds were put through ammoxidation by melamine at 160 °C and KOH activation at 600 °C for 1 h (Huang et al., 2015). The CO₂ adsorption capacity of the coffee ground-derived sorbent was reported 117.5 mg g⁻¹ at 35 °C but decreased to 110 mg g⁻¹ after 10 cycles. Similarly, coconut shells were carbonised at 500 °C for 2 h, mixed with urea in the air at 350 °C for

2 h and activated with KOH at 650 °C for 1 h resulting in an adsorbent that could capture 220 mg g⁻¹ (at 25 °C) and 214.5 mg g⁻¹ after 5 cycles (Yang et al., 2015). Pine cone was carbonised at 600 °C for 1 h and activated using KOH at 600 °C for 1 h (Zhu et al., 2016). The sorbent demonstrated an uptake of 209 mg g⁻¹ at room temperature and maintained a stable uptake of 6 – 7 wt% CO₂ during the cyclic tests.

It can be understood from the available data that, generally, bio-based sorbents are well capable of maintaining their CO₂ adsorption capacity for at least three to four cycles. Though, some outliers as, for example, a cellulose-cross-linked polyethyleneimine bio-based aerogels (produced via a sol-gel technique with hydrolysis and a cross-linking reaction), presented an efficient CO₂ adsorption capacity after ten cycles (Wang and Okubayashi, 2019). However, the challenges associated with using biomass-based carbon aerogels are mainly related to the synthesis process (Sam et al., 2020). The synthesis process is time consuming (sol-gel polymerisation), and expensive (due to freeze-drying or supercritical CO₂ drying). Moreover, their amorphous structure of the material limits the selectivity in certain applications of such bio-based sorbents. Also, modification of the microstructure is also challenging. As a result, further studies are recommended to optimize the operational procedure, to prevent the breakdown of the micropore structure facing capillary tension, and to enhance the membrane selectivity.

A further operational challenge is associated with the displacement of finer sorbent particles/powder at high gas flow rates. In order to ensure of good performance at critical conditions, studies have suggested using immobilised particles of bio-based sorbents (in pellet, briquet, masterbatch form and etc.) to ensure greater applicability and facilitated recovery (Zhang et al., 2007; Dong et al., 2020; Karimi et al., 2021).

The life cycle of bio-based sorbents also needs to be equally considered. Life cycle assessment (LCA) is an environmental assessment tool that studies the environmental impact of a product over its entire life cycle (Razman et al., 2022). It includes energy consumption and emissions based on electricity and landfill, cultivation, storage, drying, size reduction, conveying systems, blending, briquetting/pelleting, curing/cooling, screening (to remove impurities), packaging, overseas transportation, application and disposal processes (Glushkov et al., 2021) and the latter might constitute an additional challenge. As a result, to demonstrate an economical yet effective process, studies have introduced the same biomass sorbents used for multiple applications (Almendros et al., 2015). In this way, a batch system can be suggested, reusing spent bio-based sorbent as biofuel for the same process, thus negating potential issues associated with disposal. Moreover, recycling spent bio-based sorbents and using them as catalysts was learnt to be an alternative solution to address direct disposal concerns (Agarwal et al., 2020).

Through LCA, biomass combustion emissions was reported as the main hotspot for several evaluated impact categories including transport distance, particulate matter formation, and human toxicity (González-García and Bacenetti, 2019). Studies use LCA to select an efficient bio-based sorbent with low energy consumption and impact. For instance, alginate extraction waste was selected over commercial activated carbon as it showed lower impacts in all categories through LCA analysis (Nishikawa et al., 2018). Similarly, LCA was conducted based on an experimental VPSA system to compare environmental impacts of two highly efficient sorbents, namely, zeolite 13X and a carbon molecular sieve (Gonzalez-Olmos et al., 2022). Replacement of sorbent and waste treatment showed less impact on LCA, as compared to the overall amount and type of the energy consumed. Use of renewable energy was reported to increase the carbon capture efficiency of the VPSA process up to 96% and 84% for the zeolite 13X and carbon molecular sieve, respectively. Further to LCA, whole system analysis can be suggested to validate the value of emerging technologies in this field. Whole system analysis includes dynamic demand profiles, building installations, the distribution network and heat supply sources where each subsystem is treated as an individual module (Baldvinsson and Nakata, 2016).

7. Conclusion

Environmental, economic, and efficiency concerns followed by the UK's 10-point plan on climate change targets have inspired recent studies on CO₂ capture/removal using efficient, yet cost-effective sustainable solid sorbents (e.g. biomass-based sorbents). This is especially important since adsorption-CCS has been recognized to be the 2nd generation of capture technologies with anticipated deployment at scale within this decade. Abundance of, and accessibility to suitable precursors, hydrophobic properties and low adsorption heats are some of the advantages of bio-based materials in the context of carbon capture. Moreover, the application of bio-based sorbents addresses concerns of waste management, selectivity, toxicity and equipment maintenance (when compared to their solvent-based counterparts). In order to accelerate the deployment of this technology, physical treatments as well as a plethora of chemical modifications have aimed at improving CO₂ capture performance via enhancing textural properties. In addition, equilibrium, kinetic and mass transfer studies are essential to evaluate the adsorption capacity, adsorption rate and adsorption mechanism, which would then directly inform the techno-economic analyses for the processes at scale. The extent of energy recovered/consumed, as well as the purity of the recovered CO₂, are found to be the two main focus points through process design and simulation. Incorporation and combination of machine learning and quantitative structure activity relationship techniques has also proven beneficial for both lab- and pilot-scale studies. Additionally, LCA is a powerful tool in environmental assessment of the impact of a product over its entire life cycle. This is especially important when considering bio-based sorbents, due to energy consumption and emissions based on electricity and landfill, cultivation, briquetting/pelleting, application, disposal process and etc. Further in-depth review of the operational and environmental challenges in actual application of bio-based sorbents on industrial scales are some of the key recommendations for future studies.

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.

The authors would like to confirm the absence of a conflict of interest in this work.

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