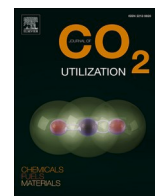




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Review Article

# Biomass/Biochar carbon materials for CO<sub>2</sub> capture and sequestration by cyclic adsorption processes: A review and prospects for future directions

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## ARTICLE INFO

## Keywords:

CO<sub>2</sub> capture  
Adsorption technology  
Waste management  
Sustainability  
Global warming

## ABSTRACT

The persistent enhancement of greenhouse gases in the atmosphere originated from anthropogenic activities, especially CO<sub>2</sub>, resulted in several serious global challenges. In this way, employing biomass, biochar, etc., as a low-cost precursor for CO<sub>2</sub> adsorbent is promising not only in the view of hydrophobic character and abundant resources, but also is an illustrious strategy for solid wastes management as a consequence of the exponential population expansion. Herein, key concepts on adsorption technology, waste management, and different activation techniques on raw carbons materials have firstly been discussed. Afterwards, almost all accomplished studies on cyclic adsorption processes e.g. PSA, TSA, VSA, etc., which employed biomass/biochar as a source of adsorbents have been extensively reviewed, that gives a precise knowledge for large scale application of these materials. Furthermore, in the last part of this work, biomass/biochar adsorbent based samples, which have already been studied for CO<sub>2</sub> capture, but till now, they have not been evaluated at the bench/pilot scale by cyclic adsorption process, are introduced for future directions. Also for the reader's of this work, key concepts of each section have been summarized in the form of simple figures and tables that will help to identify clearly the prominent accomplished works till now.

## 1. Introduction

### 1.1. Global warming and carbon capture

Escalating level of greenhouse gases (GHGs), mainly methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), chlorofluorocarbons (CFCs), and nitrous oxide (N<sub>2</sub>O), has contributed to the global climate change [1], which among all GHGs, CO<sub>2</sub> is the main responsible for global warming [2,3]. Fossil fuels combustions including coal, petroleum and natural gas industries [4–6] are responsible of more than 80 % of the existing CO<sub>2</sub> in the atmosphere [7], which is approximately 32 Gt produced per year [2,8], where a triple growth is expected by current rising level till 2050 [7]. Tangang et al. reported that anthropogenic greenhouse gas emissions contributes to minimum 3–5 °C temperature enhancement on the planet by the end of this century, which results in 95 cm sea level rising [9]. In this way, Carbon Capture and Storage (CCS) [10,11], strategy has

emerged as a combination of various technologies to reduce and capture global CO<sub>2</sub> emissions [12], which according to the BLUE Map Scenario of the International Energy Agency (IEA), this policy can conduct to 19 % reduction of CO<sub>2</sub> emissions by 2050 [13]. Currently, the regions responsible for the highest percentage of global CO<sub>2</sub> emissions from fossil fuel combustions are China (28.0 %), United States (15.0 %), European Union (9.9 %), India (6.4 %), and Russia (4.5 %) [8]. To date, the vast majority of CCS studies have focused on developing novel technologies for carbon capture from coal-fired power plants [14,15] which in terms are responsible for 27 % of the global energy and 44 % of anthropogenic energy-related CO<sub>2</sub> emissions [8,12,16]. It is worth mentioning that the typical flue gas of power plants generally contains ~15 % CO<sub>2</sub> and different percentage of N<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub> and Ar (based on natural gas-fired power plants or coal-fired boilers) [12].

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<https://doi.org/10.1016/j.jcou.2022.101890>

Received 8 December 2021; Received in revised form 4 January 2022; Accepted 7 January 2022

Available online 17 January 2022

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Nomenclature			
AC	Activated carbon	AMP	2-amino-2-methyl-1-propanol
AlCl <sub>3</sub>	Aluminium chloride	PEI	Polyethylenimine
CO <sub>2</sub>	Carbon dioxide	DETA	Diethylenetriamine
CH <sub>4</sub>	Methane	TETA	Triethylenetetramine
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid	TEPA	Tetraethylenepentamine
H <sub>3</sub> PO <sub>4</sub>	Phosphoric acid	DIPA	Diisopropylamine
HCl	Hydrochloric acid	PEHA	Pentaethylenehexamine
HTC	Hydrothermally carbonized	TEA	Triethanolamine
K <sub>2</sub> CO <sub>3</sub>	Potassium carbonate	DGA	Aminoethoxyethanol (Diglycolamine)
KOH	Potassium hydroxide	TREN	Tris (2-aminoethyl) amin
MgCl <sub>2</sub>	Magnesium chloride	BET	Brunauer-Emmett-Teller surface area
MgO	Magnesium oxide	CCS	Carbon capture and storage
N <sub>2</sub>	Nitrogen	GHGs	Greenhouse gases
NaOH	Sodium hydroxide	IEA	International energy agency
ZnCl <sub>2</sub>	Zinc chloride	MOFs	Metal organic frameworks
CPTMS	3-cholopyltrimethoxysilane	MSWs	Municipal solid wastes
MEA	Ethanolamine	PSA	Pressure swing adsorption
DEA	Diethanolamine	VSA	Vacuum swing adsorption
MDEA	Methyl Diethanolamine	TSA	Temperature swing adsorption
		OS	Olive stone

## 1.2. Adsorption technology

Absorption, adsorption and membranes are three main technologies for gas capture and sequestration [17], which a comparison between these technologies for CO<sub>2</sub> capture is presented in Table 1. Currently, chemical absorption by amine-based solvents is the most prevalent one, which is broadly employed in the petroleum and petrochemical industries [18,19]. Besides the high potential of absorption process by chemical solvents, it has several drawbacks including high corrosion rate of equipment, high-energy consumption during the regeneration process and the solvent cost as well as the GHGs emissions [17,20,21]. On the other hand, due to the limitations of traditional fossil fuel resources, efforts have been intensified to develop sustainable sources of energy such as the biogas, biofuel and solar energy [22]. It is worth noting that biogas upgrading to biomethane by adsorption processes results from a similar technology as the one used for CO<sub>2</sub> capture on the post-combustion processes, with some differences in operating conditions [23,24]. In the recent decades, adsorption technologies attracted a significant attention in the view of environmental preservation and producing clean energy [25–28]. To this end, different classes of sorbents including zeolites [29], activated carbons [30], metal organic frameworks (MOFs) [31,32], metal oxides materials [33], silica [34],

lithium zirconate [35], etc. [36], have been proposed for carbon capture and sequestration by adsorption, being crucial for large scale applications, to consider sustainability, stability, loading capacity, regeneration condition, density and hydrophobic/hydrophilic character, simultaneously [17].

Among different evaluated sorbents in the recent decades, carbon-based materials are highly attractive one for gas capture and storage for several reasons [14,17,18]. First, these materials can be considered as low-cost sorbents, prepared from a broad sustainable sources including animal wastes [37], agricultural residues [34], plant wastes [38,39], coals [40], as well as pyrolysis of fly ash [41], raw biomass [42, 43] and carbon containing resins [44]. Also, activated carbons are hydrophobic materials, which is one of the key qualities of these samples in comparison with most of zeolites and MOFs to overcome the moisture effects in the gas purification studies [38,39,45]. In addition, generally, gas adsorption onto the porous carbons has a lower heat of adsorption than other sorbents [17], which nominates this adsorbent as an excellent candidate for cyclic adsorption processes [46]. Furthermore, unlike the microporous organic polymers, there are not any complexity or concern regarding the synthesis, cost and environmental aspects of synthesis of carbon-based adsorbents [11,18,20,33].

## 1.3. Cyclic adsorption processes

Cyclic adsorption process was firstly patented in 1932, but its first application was presented thirty years later, by a patent developed by Skarstrom [48] considering the commercialization of synthetic zeolites. Generally, to develop a continuous adsorption process, a fixed bed column is operated by cycling through a specified sequence of steps including adsorption and regeneration steps [25,49]. Since, the adsorption equilibrium is obtained by specified operating conditions including temperature, pressure and compositions, hence, the regeneration process is developed by changing one of these parameters [50]. Accordingly, beside the performance of adsorbents, the design of a cyclic adsorption process with high efficiency requires some engineering factors. In this way, the driving force for the separation process in a pressure swing adsorption (PSA) process is obtained by swinging the operating pressure between the high and low pressure steps. In the 1980s, the vacuum swing adsorption (VSA) was proposed to increase the working performance of the overall process, especially in the low-pressure regeneration step [25,51], which in this cyclic adsorption

**Table 1**

A comparison on the capability of prevalent separation technologies for CO<sub>2</sub> capture and storage based on some key factors [47].

Key Factors	Adsorption	Membrane	Chemical Adsorption
Capital cost	Moderate	Low	High
Operational cost	Moderate	Moderate	High
Selectivity (for CO <sub>2</sub> )	High	High (especially with novel adsorbents)	Low to moderate
Recovery (for CO <sub>2</sub> )	High recovery (>90 %)	Low to High (based on type of membrane)	High recovery (>90 %)
Reliability	High	Moderate	Low (corrosion, solvent losses)
Maturity	Moderate	Low	High
Environment Friendliness	Very environment friendly	Depends on type of membranes (polymers, carbon based or amine synthesized)	Not environment friendly (amine emission to the atmosphere)

process, the feed gas is delivered to the adsorber at the atmospheric pressure or slightly higher than 1 bar, while the bed regeneration is typically performed at 0.01–0.1 bar [52,53]. Another cyclic adsorption process can be developed by changing the temperature, which is called temperature swing adsorption (TSA) process, that was firstly developed by Kahle [54]. In this case, the desorption is accomplished by increasing the temperature to regenerate the adsorbents (due to the exothermic nature of the adsorption processes), followed by a cooling process of the adsorption bed for the next cycle [54,55]. Recently, in this way, moving bed type of temperature swing adsorption (MBTSA) has also been developed by Knaebel [56]. In addition, Svante's carbon capture technology [57] structured adsorbent laminate (spaced sheets), proprietary process cycle design, and a rotary mechanical contactor to capture, release and regenerate the adsorbent in a single unit. However, PSA process due to the simplicity as well as lower required energy is the most preferred one [52], while it has some limitations regarding the required purity and recovery using a single step process [50]. But still, the large flexibility of PSA is the main advantage of this process, which may be because of this reason, it has a broad applications in the various areas [21,50].

Up to now, significant progress has been attained on the cyclic adsorption processes to achieve purities as high as 99.999 % for gas separation and purification in the way of biogas upgrading [58], natural gas sweetening [59], hydrogen purification [60], post-combustion studies [61], etc. [62]. To design a highly productive cyclic adsorption process, the separation performance depends on several factors such as pressure and temperature levels, cycle configuration, also the number, direction and sequence of the cycle steps [63]. In addition, the adsorbent performance is one of the key elements, which has a major effect on the efficiency of the cyclic adsorption process [25,26]. In the recent decades, different types of adsorbents have been evaluated for separation and purification technologies, whereas the activated carbon is still one of the most popular and attractive adsorbents for such propose [64–66].

#### 1.4. Solid wastes management

Bio-based carbon materials including biomass, biochar and other residual wastes are abundant, low cost and sustainable carbon resources [67,68], which recently attracted a significant attention as a source of potential adsorbents for gas capture and sequestration, as well as water treatment [68–70]. According to the United Nations Environment Program (UNEP) report, 140 billion tons of biomass are annually generated throughout the world [70,71], being the major ingredients of these materials: wooden wastes, agricultural wastes and residual wastes [70,72]. Wooden wastes as lignocellulosic biomass are residues derived from the wood processing, that show relatively a high percent of carbon [73]. In this way, because of low ash and sulfurs contents of these samples, efforts have been made to employ these materials for carbon capture and storage as interesting precursors for post combustion studies and biogas upgrading [73,74]. Wooden shells are the other type of wastes, while the capacity of these biomass is lower than residues of wood processing, but still they are a precious renewable source of carbon that nominates them as ideal raw materials for activated carbons. Some of the major sources of wooden shells are almond shells, pine cones, coconut shells, peanut shells, rice husks and palm kernel shells (PKSs) [68–70,75,76]. For instance, coconut shells as dust-free wooden shells have a high purity accompanied with a regular porous structure, which just in one case, around 577,000 tons of these waste samples are annually produced in Malaysia [76,77]. Also, almond shells as other type of wastes biomass was produced in an amount of 425 million lbs in 2001, that the management of this waste requires more practical applications [78–80]. One of the attractive agricultural byproducts, which has emerged as an interesting precursor for carbon based sorbents is corncob with a gross output in excess of 20 million tons per year in China [81]. On the other hand, wood ash (WA) arises from the combustion of biomass materials is a potential threat to the atmosphere, whereas Germany by producing

more than 12 million tons, annually, is the major provenance in the European Union [82,83]. The mentioned waste materials are as instances of the huge capacity of wood and agricultural industries in the world, which can be considered as remarkable and economical sources [84]. An overall overview on the capacity of some significant biomass/biochar samples throughout the world is provided in Table 2.

Nowadays, municipal solid wastes (MSWs) as a side effect of urbane lifestyle have contributed to the global environmental challenges [30]. MSWs is one of the main sources of the methane emission to the atmosphere also, flooding, jeopardizing public health, contamination of underground water and ecosystem destruction are some of other destructive effects of MSWs [104,105]. According to the World Bank report [106], 2.01 billion metric tons of MSWs were produced per year in 2018, while this amount is expected to reach 3.40 billion metric tons per year in 2050 [106], which United States, Canada, and the European Union by having 16 % of global population, are responsible for more than 34 % of the world's MSWs [106]. Currently, ~ 13.5 % of today's waste is recycled and 5.5 % is composted, while 40 % of worldwide generated waste is not properly managed [30]. To this end, waste treatment techniques are looking for new routes that can be more feasible and efficient by reducing the volume and toxicity of waste materials [105]. In this way, Karimi et al. [30] introduced derived compost from municipal solid wastes as a source of biochar for CO<sub>2</sub> capture.

#### 1.5. Carbon activation techniques

Generally, carbonization or activation of the carbon precursors require different pre-treatment steps. Firstly, biomass/biochar carbon samples need to be washed, afterwards dried at ~100 °C for a specified time to remove the impurities and contaminants [17,30,107,108]. The size of raw samples is also necessary to be defined and standardized in a

**Table 2**

An overall overview on the capacity of some significant biomass/biochar production throughout the world.

Type of Sample	Cyclic Adsorption Study	Country/Region	Year	Production Capacity (tons/year)	Reference
Olive	Done	Spain	2020	6,559,884	[85]
Pine sawdust	Done	Mexico	2019	280,000	[86]
Oat	Done	Russian Federation	2020	4,761,365	[87]
Wood pellet	Done	Global	2020	52,700,000	[88]
Lignin	Done	Global	2019	100,000,000	[89]
Coconut	Done	Indonesia	2019	17,130,000	[90]
Almond	Done	United States of America	2020	2,002,742	[91]
Oil tea	Done	China	2018	56,250,000	[92]
Whitewood	Done	Finland	2019	11,800,000 m <sup>3</sup> /year	[93]
Animal waste (manure)	Done	Vietnam	2017	26,361,000	[94]
Rice	Not done	China	2020	148,500,000	[95]
Peanut	Not done	China	2020	16,685,915	[96]
Palm	Not done	Indonesia	2012	25,400,000	[97]
Coconut shell	Done	Malaysia	2005	577,000	[76]
Pine cones	Done	Andalusia	2012	55,200	[98]
Wood ash	Not done	Germany	2008	12,000,000	[82]
Bagasse	Not done	Brazil	2020	758,000,000	[99]
Bagasse	Not done	India	2020	306,000,000	[100]
Corn cob	Not done	China	2015	20,000,000	[81]
Argan fruit shells	Not done	Morocco	2015	80,000	[101]
Eggs	Not done	Global	2015	5,150,000,000 eggs	[102, 103]

specific range using milling and sieving techniques [107–110]. Routinely, the prepared carbon precursors are activated by physical (thermal) and/or chemical methods [111]. The physical activation is a two-step process, which at the first step, the carbon materials are carbonized under the inert gas in the temperature range of 400–850 °C and atmospheric pressure. Then, the activation is accomplished following CO<sub>2</sub>, NH<sub>3</sub>, steam or air at around 600–900 °C to construct the porous structures [108,111–113]. It should be considered developing a highly porous carbon structure requires a wide elimination of internal amount of carbon [114]. In general, employing this technique has the advantage of avoiding impurities or additives in the synthesized samples [115].

Chemical activation as one-step technique involves impregnation or mixing of raw samples with a chemical agent(s), and subsequent carbonization at a temperature lower than 600 °C [111,112,116,117]. To this end, different chemical solutions are employed including KOH, NaOH, K<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, MgCl<sub>2</sub>, MgO, AlCl<sub>3</sub>, and ZnCl<sub>2</sub> [37, 70,112,114,118–122], which result in upgrading a cross-link formation due to the dehydration of proper ties and developing a rigid matrix [112, 114]. This structure has a higher activated carbon yields since no carbon burn-off is necessary [113,114], also because of less susceptibility to volatile loss and volume contraction during the carbonization [112, 113]. In addition, chemical activation generally contributes to the very high surface areas by having the possibility to control the microporosity, e.g., [116,123]. It should be considered, the formation of porosity depends on several factors including: the type of activation agent, the mixing process, the impregnation method, the time and temperature of pyrolysis, also the flow of inert gas during the carbonization step [68, 112,114,124,125]. As discussed, the properties of synthesized activated carbons strongly rely on the activating reagent. For example, ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> contribute to the higher yields compared to KOH, accompanied with less porosity, which the acidic factor of ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> are suitable for developing large pore structures [114]. It is worth noting, the source of the carbon is also one of the key factors that determines the required pre-treatment step and the activation technique [37,47,70, 125].

### 1.6. Objective

Up to now, abundant number of review studies related to the gas capture and storage (by focusing on CO<sub>2</sub> capture) and the biomass/

biochar, also their applications have been presented. Generally, accomplished studies have focused on the source of biomass [37,68,72], the synthetic techniques [20,112,114], activation methods of raw samples [69,72,114,125] or the process of gas capture (post-combustion, pre-combustion or oxy-fuel combustion) [21]. In the current study, based on scopes of carbon capture and storage (CCS) technology also regarding the solid waste management a comprehensive review has been presented in a holistic and comprehensive way to the scientific community. To this end, at the first section, almost all performed studies, which employed the bio-based carbon materials (e.g. biomass, biochar, wastes, etc.,.....) as a source of adsorbent for gas storage and sequestration in the bench or large scale by cyclic adsorption processes (e.g. PSA, TSA, VSA,...) have been reviewed, that gives an accurate grasp for industrial applications of these materials. Then, in the second part of this work, biomass/biochar samples, which have already been introduced as attractive carbon precursors for gas capture and storage, but till now, they have not been evaluated using cyclic adsorption processes for the large scale, are investigated as guidelines for future directions, that to the best of our knowledge, is the first review paper that evaluates the potential of biomass/biochar materials by adsorption technology in this way. The goal of this study has been schematically summarized in Fig. 1.

## 2. Cyclic adsorption processes using Biomass/Biochar

As previously mentioned, recently, several studies have considered the potential of bio-based carbon materials for gas capture and storage [126–130]. In the recent years, numerous adsorbents with different sources such as wood [126,131], corncobs and bamboo [132], coconut-shell [133,134], rice hull [135], sunflower's stem pith [136], Conocarpus stem [137], palm shell [138], and other agricultural/animal wastes [139,140] have been studied for gas adsorption processes. The evolution of an agricultural/animal waste-to-adsorbent process is schematically shown in Fig. 2 [141–145]. In this way, many researchers have considered the capacity of waste materials as a source of adsorbent in the cyclic adsorption processes to have a better grasp for application of these materials in the industrial scale. In this section, detailed description of these studies has been reviewed and analyzed for different processes including PSA, TSA, VSA, and mix of cyclic adsorption processes.

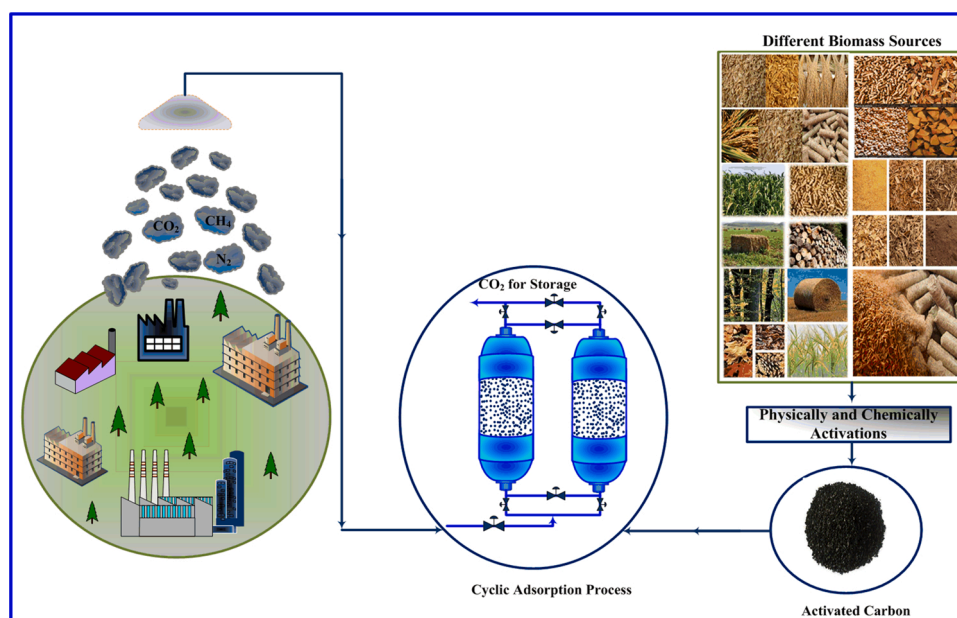


Fig. 1. Carbon capture and storage using derived activated carbons from biomass/biochar samples by cyclic adsorption processes.

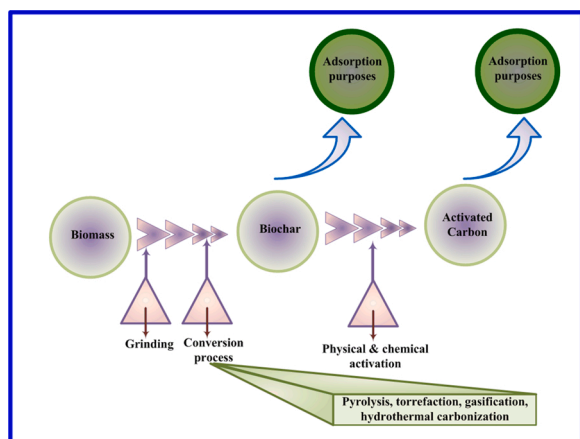


Fig. 2. The schematic diagram of biomass-to-adsorbent process.

### 2.1. Pressure swing adsorption (PSA)

According to the reports [146,147], there are different kinds of pollutions emitted from oil/gas refineries and petrochemical complex effluents [148], power plants [149], biogas processes [58], manufacturing corporations [150], etc., which require a treatment process for gas capturing and sequestration [151]. Among different separation processes including membrane technology [152,153], absorption process, distillation [154], centrifuge [155] and cryogenic [156] processes, etc. PSA technology has been introduced as an economically and environmentally friendly strategy to capture the pollutions from different industries [157,158]. For instance, a PSA process with two adsorption beds is represented in Fig. 3. Up to now, the potential of different adsorbents including commercial and synthesized samples have been investigated for cyclic adsorption processes [159], which in this section, (almost) all studies on derived activated carbon from biomass/biochar are discussed in details. It is worth noting, Langmuir [160], Sips [161], Klinkenberg [162], Anderson [163], Toth [163], dual-site Langmuir [163], Redhead and Fowler – Guggenheim [164], are among the most popular isotherm models to describe the adsorption equilibrium experimental data fundamental for developing the most convenient cyclic processes.

In 1948, one of the first studies on employing carbonaceous solid wastes on adsorption process was accomplished by Berl Walter George [165]. In this way, he investigated wood and lignite as a source of activated carbon, which the synthesized materials were activated by potassium salts in a temperature range of 800–1200 °C. A year later, in other study [166], George M Good and Bernard S Greensfelder introduced coconut shells, fruit pits, and cohune nut shells as valuable sources of activated carbons for petrochemical processes. According to our comprehensive literature survey, Ohsaki and Abe [167] were the first ones to consider the fixed beds filled with a carbonaceous adsorbent

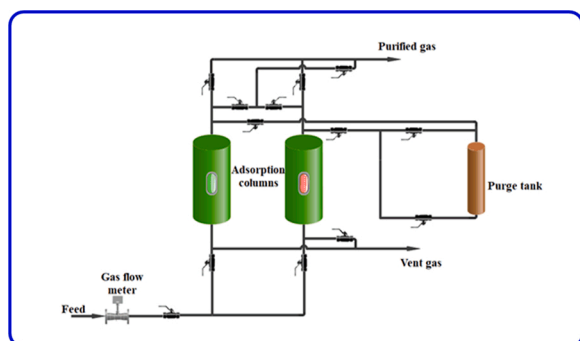


Fig. 3. A simple presentation of a PSA process with two adsorption beds.

(coconut shell charcoal) through the pressure swing adsorption technology for carbon dioxide capture at the post-combustion process. The adsorbent was prepared in the following five steps: 1) coal tar addition to coconut-shell charcoal powder, 2) carbonizing at 750–900 °C, 3) washing in the dilute mineral acid solution, 4) heating up to around 1000 °C and keeping for 1 h in this temperature, and 5) cooling by an inert gas.

The capacities of maple and maritime wood, pine and coconut shells for the separation processes in a pilot-scale applications were studied by Kacem et al. [64]. To this end, the waste carbon materials were physically activated using water vapor and CO<sub>2</sub> at the high temperature. Then, they evaluated the selectivity, adsorption capacity, and the sustainability of prepared activated carbon. On the grounds, CO<sub>2</sub> loading of synthesized samples was measured at the pressure range of 0.4–8 bar and 298 K, also the separation of CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> was performed by pressure swing adsorption at 5–30 bar. The results showed derived sorbents from the maple wood, maritime wood and pine and coconut shells (as ACs) mixed with SC (PICACTIF SUPERCAP) had the highest capacity for adsorption technology between all synthesized samples and considered zeolites (11 mol CO<sub>2</sub>. kg<sup>-1</sup> adsorbent at 8 bar and 298 K). In the next step, a PSA unit was developed for AC–SC and Z-13X samples, as two efficient sorbents for CO<sub>2</sub> adsorption. The results proved that AC–SC sample had an excellent potential for large scale applications of CO<sub>2</sub> adsorption in a broad range of pressure up to 30 bar [64]. In another study, Sudibandriyo and Oratmangun [158] developed activated carbon derived from the betung bamboo for separation of methane from H<sub>2</sub>/CH<sub>4</sub> mixture. The samples were chemically treated by employing H<sub>3</sub>PO<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub> as chemical agents to activate prepared bamboo waste materials. The textural properties of these samples illustrated a high surface area, which is favorable for gas purification studies (465.2 m<sup>2</sup>. g<sup>-1</sup>). Accordingly, they designed a pressure swing adsorption process for hydrogen purification at the pressure range of 1–6 bar and the temperature of 10–30 °C. They reported the maximum CH<sub>4</sub> adsorption in the PSA process around 0.247 mmol/g at 6 bar and 10 °C.

Olive and cherry stones are among the most popular waste materials, which have been studied for adsorption processes [168–171]. Recently, Alvarez-Gutierrez et al. [172] studied these samples for separation of carbon dioxide and methane for biogas upgrading. The samples were firstly calcinated by CO<sub>2</sub> at the high temperature, then a PSA unit in a bench-scale equipped with a fixed-bed adsorption column was developed and loaded by prepared activated carbons. In line with that, the cyclic process represented the steady state operating conditions after 6 adsorption-desorption cycles in a pressure range of 3–18 bar [173]. Alvarez-Gutierrez et al., concluded the olive and cherry stones have a great capacity for biogas upgrading in the industrial scale. Recently, some other studies have devoted for modeling and simulation of PSA for adsorption processes. On the grounds, Karimi et al. [174], evaluated the capacity of derived compost from municipal solid wastes as a source of biochar for CO<sub>2</sub> capture. In this way, samples were activated in five different ways using sulfuric acid treatment and thermal activation at 400 and 800 °C. They reported a sample which has been treated with H<sub>2</sub>SO<sub>4</sub> firstly, then activated at 800 °C has the highest uptake capacity between all prepared samples accompanied with adsorption capacity in the range of commercial carbon materials (2.6 mmol/g at 40 °C and 2.5 bar). In the next step, the process scale-up was accomplished by designing a conceptual PSA unit for best obtained sample, and they reported derived compost from municipal solid wastes has an excellent capacity as a source of adsorbent for CO<sub>2</sub> capture at the post-combustion operating conditions. They introduced their study as a green route for municipal solid waste management and carbon capture and storage [174].

Balahmar et al. [175] proposed a novel mecha-chemical method for activation of biomass samples (wood sawdust and lignin). Hence, the samples as well as activating agent (KOH with KOH/hydrochar ratio of 2) at 740 MPa were transformed to the pellets, afterwards, the thermal activation was implemented at 600–650 °C. This technique resulted in

AC with a higher porosity compared with conventional ones, with similar pore size. In addition, the surface area of derived adsorbent was around 25 % higher than the prepared samples with conventional one. The maximum volumetric uptake capacity was 3.4 and 4.1 mmol.g<sup>-1</sup> for pure CO<sub>2</sub> and flue gas study (20 % partial CO<sub>2</sub> pressure and 80 % partial N<sub>2</sub> pressure) at 25 °C and 6 bar (for pure experiments) and 1.2 bar (for flue gas tests) respectively, through the PSA process.

Costa Vilella et al. [176] studied on the capacity of bio-based carbon materials for biogas upgrading by considering the environmental aspects of this process and developing an optimized process for biogas upgrading. Fig. 4. demonstrates this process, which is equipped with a pressure swing adsorption process and employed waste materials [144, 176]. To this goal, they studied two low-cost materials including: babassu and coconut shells, which are available abundantly in the environment as agriculture by-products. Firstly, the washed samples were crushed and then, sieved in the particle range of 3–5 mm. Afterwards, a one-step activation process with CO<sub>2</sub> stream was employed to activate the samples. The measured surface areas for synthesized samples were 1452 and 809 m<sup>2</sup>/g (respectively for babassu and coconut shell), which are proper for separation of CO<sub>2</sub>/CH<sub>4</sub> mixture. Also, they reported there is not a significant difference between the CO<sub>2</sub> adsorption capacity of prepared adsorbents, but activated carbon originated from the coconut shell showed a better selectivity than other one, by the selectivity of 4.2 and the working CO<sub>2</sub> adsorption capacity of 1 mmol/g at 1 bar and 20 °C in comparison with selectivity of 0.90 at 1 bar and the loading capacity of 0.75 mmol/g at the same operating conditions for babassu sample. Thus, they concluded the AC derived from coconut shell has a better potential to be employed in the PSA technology for biogas upgrading.

The separation of carbon dioxide from a gas mixture in a cyclic adsorption process with two columns filled with derived adsorbent from the kenaf was studied by Kamarudin et al. [177]. To this end, the raw kenaf was functionalized by amine agents such as MEA, DEA, MDEA, AMP, PEI, DETA, TETA, TEPA, DIPA, PEHA, TEA, and DGA. They reported the adsorption capacity of raw kenaf around 0.624 mmol/g for CO<sub>2</sub> at 1 bar and 0 °C, also 2.086 mmol/g for kenaf treated with TEPA. On the other hand, the raw kenaf presented more interesting regeneration results in comparison with MEA-functionalized and TEPA-functionalized kenaf [177].

### 2.1.1. Developed PSA under humid operating conditions

Water vapor is one of the undesired components in the gas mixture, which has adverse effect on the loading capacity of sorbents especially MOFs, Zeolites, etc. [178–180]. To this end, recently, several ACs originated from agricultural wastes have been considered to study water vapor effects on the separation and purifications processes including natural gas sweetening, biogas upgrading, air drying, and post-combustion processes [181–183]. As already discussed, bio-based AC are interesting

alternatives for gas adsorption purposes due to their low cost, vast availability, and high-adsorption capacity as well as hydrophobic character [184,185]. The process of preparation of these sorbents and their application through the biogas upgrading process is briefly illustrated in Fig. 4. Accordingly, developed PSA units concerning the water vapor effects on the adsorption process, have been entirely reviewed in this section. A simple PSA experimental setup for gas drying is also schematically demonstrated in Fig. 5 [186].

The capacity of olive stone-biochar adsorbent for application in the post-combustion operating conditions was evaluated by Plaza et al. [187]. Accordingly, the raw samples were activated in an oxidation procedure, after that, the adsorption of CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> from the flue gas was evaluated using the developed PSA. They reported the uptake capacities of 7, 1.1, and 0.4 mmol/g for H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub>, at 1.4 bar and 25 °C, respectively. Plaza et al. [187] eventually concluded the biochar originated from the olive stone is an effective adsorbent with a simple regeneration procedure to be employed in the PSA processes for pilot plant applications [188].

Duran et al. [38] employed the PSA technology through one-bed adsorption system to evaluate the adsorption capacity of the biomass activated carbon for biogas upgrading process. The adsorbent was AC derived from pine sawdust, which was activated by CO<sub>2</sub> through the physical activation method. The adsorption-desorption ability of adsorbent was tested through 6 cycles in the pressure range of 1.2–10 bar and at 30 °C. In the dry conditions, the highest CO<sub>2</sub> uptake capacity was 2.4 mmol/g at 30 °C and 120 kpa, while the highest loading capacity was 1.64 mmol/g at the same operating conditions and presence of moisture. Duran et al. [38] concluded the pine sawdust AC is able to work effectively for biogas upgrading through the PSA process without any requirement for water vapor separation unit.

Ghanbari et al. [163] studied the adsorption equilibrium and the heat effects of water vapor adsorption on the lignocellulose samples (flax shives). In other study, Ghanbari et al. [164] evaluated the physical properties of bio- flax shives as well as investigated the water vapor adsorption capacity of these samples (about 0.9 g water/g adsorbent). To this purpose, a fixed bed column with 51 cm height and 4.9 cm of inner diameter filled with dried flax shives, afterward, the separation of water vapor from the natural gas was accomplished at the pressure range of 101.3–300 kpa at two different isotherms (24 and 35 °C). The results showed the maximum loading capacity of 0.9 g water/g adsorbent at 24 °C and 300 kpa. Also in 2019, Ghanbari and Niu [189] derived a cost-effective bio-sorbent from oat hulls to separate the water vapor from the methane through a PSA process. They evaluated the effects of key parameters of developed PSA such as pressure, temperature, feed flowrate, feed concentration, and adsorbent particle size on the adsorption performance using the full factorial method in the pressure range of 1–3 bar, and temperature domain of 24–35 °C. Ghanbari and Niu reported a higher H<sub>2</sub>O adsorption capacity of considered samples than commercial adsorbents, which the maximum loading of water vapor on oat hulls was around 630 mg/g at 3 bar and 24 °C, that proved the priority of oat hulls towards molecular sieves (about 230 mg/g), alumina (290 mg/g), and silica gel (420 mg/g). They also observed a stable performance of samples in the adsorption/desorption process through fifty cycles. Dhabhai et al. [190] investigated nonpolar gas drying using canola meal samples loaded in a PSA unit for drying the industrial feeds (natural gas). Accordingly, five key operating parameters, as Ghanbari and Niu study [189], were investigated. They concluded the temperature and water vapor concentration had the most significant impact on the adsorption process, also the maximum water vapor loading capacity reported 0.165 g/g at 130 °C and 1.4 bar [190]. Finally, they illustrated the results can be developed for other nonpolar gas systems. In another study, Ranjbar et al. [191] utilized one fixed-bed system filled with canola meal to adsorb water vapor from ethanol-water vapor mixture. The column was fabricated from stainless steel with dimension of 4.75 cm diameter and 50 cm length. All basic parameters, as Ghanbari and Niu study [189], were investigated and the maximum

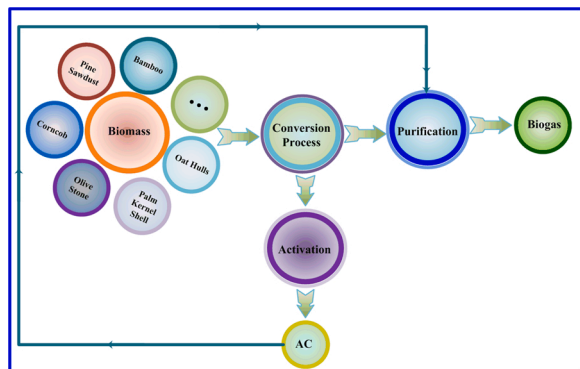


Fig. 4. Proposed optimized process for biogas production/upgrading using biomass sources.

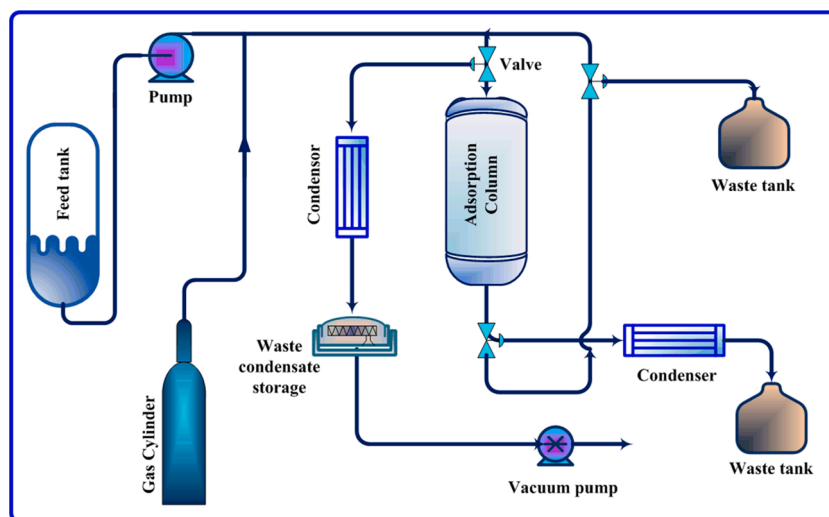


Fig. 5. A simple PSA experimental setup for gas drying.

uptake capacity of water vapor on the canola meal was 0.0202 g/g at 90 °C and 2.43 bar. In a similar study [192], the separation of butanol-water vapor mixture was studied using canola meal sample packed in a fixed bed column through a PSA unit. They reported the maximum loading capacity of water vapor around 0.48 g/g at 111 °C and 2.1 bar in 16 adsorption/desorption cycles. Pressure-swing dryer for air dehumidification was investigated by Anderson et al. [193]. On the grounds, two columns with dimension of 4.1 × 10.6 cm were employed and each one loaded with around 40 g of dried starch and cob grits (specific surface area of 0.51 m<sup>2</sup>. g<sup>-1</sup>). The synthesized adsorbent showed a stable dehumidification result after 70 h of adsorption/desorption cycles.

In Supporting Information, the distribution of different studied bio-based carbon materials in the developed PSA processes is illustrated in Fig. S1a, also the samples investigated under humid operating conditions are demonstrated in Fig. S1b. Furthermore, as shown in Fig. S2, CO<sub>2</sub> and H<sub>2</sub>O are the most favorable gases for studied PSA processes.

## 2.2. Vacuum swing adsorption (VSA)

As already extensively discussed, the second class of cyclic adsorption processes, which has been significantly studied for gas separation and purification purposes is the vacuum swing adsorption (VSA) [194]. Generally, VSA process includes side by side fixed beds, that operates in four main steps as: 1.adsorption, 2.blowdown, 3.evacuation, and 4. pressurization [194,195]. This process is schematically demonstrated in Fig. 6. From the literature, VSA using packed beds with bio-based carbon materials is a novel topic for CO<sub>2</sub> sequestration that has been completely reviewed in this section.

According to the literature, one of the first developed VSA units using bio-originated adsorbent was developed by Xu et al. [196] in 2013. In this way, the potential of coconut shell Acticarb (supplied by Activated Carbon Technologies Pty Ltd., Australia) as a source of adsorbent for gas adsorption was evaluated in a developed VSA unit, contained a fixed bed with diameter and length of 4.9 and 56.0 cm, respectively, also packed with 0.52 kg adsorbent. The prepared activated carbon had 921.7 m<sup>2</sup>. g<sup>-1</sup> BET surface and 493 kg.m<sup>-3</sup> bulk density. The adsorption equilibrium isotherms of CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> were measured in a temperature range of 25–60 °C and pressure of 0–1 bar. The bed through the VSA sequences goes under vacuum pressure: 2.2 kpa. Xu et al. reported that CO<sub>2</sub> and H<sub>2</sub>O had a little interaction on the adsorption process, also the CO<sub>2</sub> adsorption capacity on the AC was around 3.1 mmol.g<sup>-1</sup> at 20 °C and 1.20 bar [196].

In another study, derived activated carbons from crushed and sieved

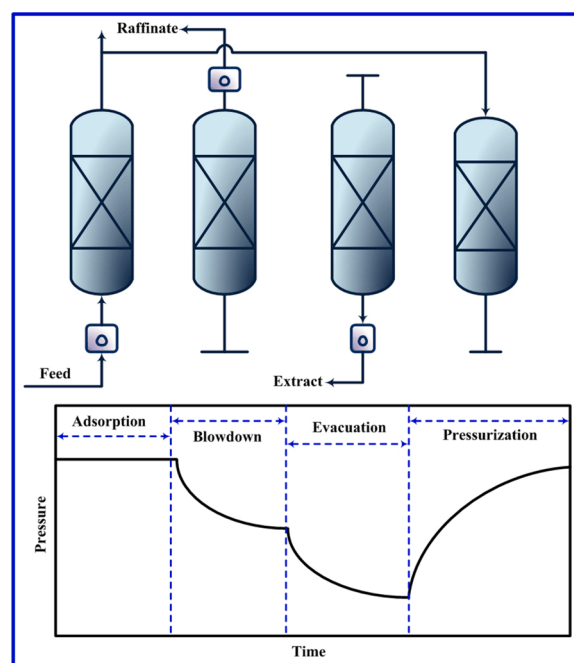


Fig. 6. A simple schematic of VSA process with four main steps.

olive stones also almond shells for CO<sub>2</sub> capture was studied by Gonzalez et al. [151]. The biomass samples in the sizes of 1–3 mm, were activated using a single step process by CO<sub>2</sub>. The adsorption column was filled with 2.8 g of olive stones with 295 kg.m<sup>-3</sup> (bed density) and 0.45 bed void, as well as, 2 g of almond shells with 2.5 kg.m<sup>-3</sup> bed density, and 0.6 bed void. Afterwards, the uptake capacity of samples were measured in 0–50 °C and 1.20 bar. The adsorption column was fabricated by stainless-steel with height and diameter of 15 cm and 9.12 mm, respectively. They reported the highest adsorption capacity of CO<sub>2</sub> around 4.65 mmol.g<sup>-1</sup> at 0.95 bar and 0 °C for olive stones, also 3.7 mmol.g<sup>-1</sup> at 1.20 bar and 0 °C for almond shell-originated adsorbent [151]. Finally, Gonzalez et al. concluded the prepared samples have an excellent potential for carbon capture and sequestration due to the lower heat of adsorption during the regeneration process accompanied with acceptable loading capacity [151].

Zhang et al. [197] employed oil tea shells (OTS) for ultra-microporous AC production. The OTS samples illustrated excellent

structural characteristics such as 2676 m<sup>2</sup>.g<sup>-1</sup> of BET surface. It is worth indicating that the OTS was activated by chemical technique through the mixing with aqueous KOH solution. The maximum CO<sub>2</sub> uptake reported 6.15 mmol.g<sup>-1</sup> at 1 bar and 273 K. The selectivity experiments were conducted and the results showed 43.5, 7.4, and 5.9 for CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and CH<sub>4</sub>/N<sub>2</sub>, respectively, at 1 bar and 298 K. In comparison with other biomass-derived adsorbents, OTS illustrated a high CO<sub>2</sub> uptake; also a promising selectivity regarding the CO<sub>2</sub>/N<sub>2</sub> was observed (43.5 at 1 bar and 298 K). Finally, Zhang et al. concluded the VSA cycles are able to effectively separate CO<sub>2</sub> from the gas mixture using prepared adsorbents [197].

The ability of VSA process to maximize the CO<sub>2</sub> separation from the flue gas was investigated by Duran et al. [65]. To this end, a 3-bed VSA also 1-bed vacuum and temperature swing adsorption process were developed, afterwards, the effect of the number of beds, cycle design, and operating conditions were studied. Due to the wide availability of pine sawdust in the region (Spain), this sample was considered as a source of AC. The prepared AC was activated physically by CO<sub>2</sub> through a single step process. 4.48 g of activated carbon was packed in a cylindrical bed with a diameter of 1.3 cm and height of 12.5 cm. The VSA experiments were implemented at 50 °C and 0.005–1 bar, which through the vacuum cycles, the bed conducted till 0.005 bar. In this way, four different beds and process configurations were investigated as: (1) VSA with 4 steps using 3 columns, (2) VSA with 5 steps using 3 columns, (3) VSA with 5 steps using 4 columns, and (4) VTSA (vacuum temperature swing adsorption) with 5 steps using 3 columns. For instance, 4-steps vacuum swing adsorption using 4 columns is illustrated in Fig. 7. It is worth mentioning that via the arrangement constituted of maximum 4 beds, CO<sub>2</sub> purity was enhanced from 8% to about 40 %; also recoveries were reported more than 95 %. In another study, microporous biochar originated from the olive stones was introduced as a source of adsorbent for gas capture and storage in the post-combustion operating conditions (at 1.2 bar and temperature range of 0–70 °C) by Plaza et al. [198]. The raw samples were activated in a single-step oxidation process that resulted in a granular AC with 415 m<sup>2</sup>.g<sup>-1</sup> of BET surface. The CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms were described by Toth adsorption model. Adsorption outcomes indicated the highest CO<sub>2</sub> and N<sub>2</sub> adsorption capacities around 3.1 and 0.55 mmol.g<sup>-1</sup> at 1.2 bar and 0 °C, respectively [198]. Finally, they illustrated that modeling results have an acceptable agreement with experimental values in a wide range of temperature and CO<sub>2</sub> composition in the feed, which proved promising outcomes for VSA process.

Hao et al. [199] investigated four different biomass-derived adsorbents including grass cutting, horse manure, beer waste, and bio-sludge from a waste water treatment plant. They employed physical and chemical activation techniques toward hydrothermally carbonized (HTC) biomass. For physical activation method, they considered 5 g of HTC biomass in a vertical reactor under a steady flow of CO<sub>2</sub>, which the

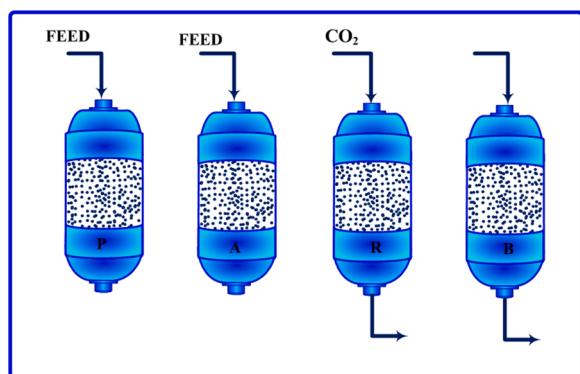


Fig. 7. A 4-step vacuum swing adsorption using 4 columns; P:Pressurization, A: Adsorption, R:Purge, and B:Blowdown.

temperature increased 10 °C/min up to 800 °C (for 2 h). On the other hand, for chemical activation of beer waste, 2 g of sample was impregnated by 8 ml of 85 % H<sub>3</sub>PO<sub>4</sub>, kept at room temperature through the overnight, then dried at 100 °C for 2 h. In the final step, the sample was activated under the flow of N<sub>2</sub> at 600 °C for 1 h. For pH equilibration of Chemically Activated Carbon (CAC), the sample was washed by hot and distilled water to pH = 7, then dried at 100 °C. The highest CO<sub>2</sub> and N<sub>2</sub> uptakes were attributed to HTC grass cutting (physically activated carbon (PAC)), which was 4 mmol.g<sup>-1</sup> and 0.51 mmol.g<sup>-1</sup> for HTC horse manure (PAC) at 1 bar and 0 °C, respectively. Then, the adsorption process developed through the VSA unit, which resulted in nine cyclic adsorption/desorption processes for CO<sub>2</sub> adsorption on the PAC originated from HTC grass cutting. It is worth indicating that the maximum CO<sub>2</sub> uptake after nine cycles was decreased only around 3%, which was an excellent cyclability. They also reported the same excellent cyclability for other HTC biomass through the pressurization/vacuum cycles in the developed VSA process [199].

Fig. 3S (Supporting Information) illustrates the distribution of different biomass/biocr samples, which have been employed in the VSA studies. As shown, olive stones is the most favorable sample in the developed VSA processes. It is worth pointing out that interesting comparisons between the capacity of studied wastes carbon materials and some of the prevalent commercial sorbents can be found in [68,69,125,195,200]. However, derived ACs from biomass have been applied in several vacuum swing adsorption studies, but still there is some necessity to improve the energy consumption especially in the VSA cycles [195].

### 2.3. Temperature swing adsorption (TSA)

As already discussed, adsorption/desorption intervals in the TSA process occurs via cyclic bed temperature variation. To this end, adsorption and desorption processes are developed in the low and high temperature, respectively [201]. In the conventional application of the TSA, adsorption beds were packed with different commercial adsorbent such as activated carbon, zeolites, metal organic frameworks (MOFs) etc. for air or natural gas drying processes [202]. For purification processes or in the cases with high curved convex isotherms, the TSA process is preferable compared to other adsorption processes [203]. After the adsorption step in the TSA sequences, the bed temperature rises to accomplish the regeneration process using a hot non-condensable gas purge or steam [102,103]. For instance, a four-step TSA process for CO<sub>2</sub> adsorption is illustrated in Fig. 8.

Carbon capture from post-combustion operating conditions has been studied by many researchers by employing different commercial sorbents or biomass samples [72,112,114]. Recently, Plaza et al. [204] investigated CO<sub>2</sub> capture from the flue gas via TSA process, which the adsorption breakthrough experiments were conducted using wood (C), peat (R), and agricultural (A) biomass as a source of ACs. The samples were activated by phosphoric acid, steam, and CO<sub>2</sub>, respectively. They reported the prepared samples can easily capture CO<sub>2</sub> in the post-combustion operating conditions accompanied with promising desorption potential by rising the temperature up to 373 K. The breakthrough tests were carried out at 1.30 bar and 303 K. The TSA cycle was constituted of a simple two-step via two columns with equal duration of adsorption and desorption sequences. Desorption step was accomplished by 2.6 cm<sup>3</sup>.min<sup>-1</sup> of N<sub>2</sub> purging. Also, the biomass samples were stable after 40 cycles and no sign of decomposition was reported [204].

In another study, Plaza et al. [188] investigated the capacity of olive stones (OS) for carbon capture from the flue gas at the presence of the water vapor. On the grounds, the raw samples were activated in a single step activation process using CO<sub>2</sub> at the high temperature, which resulted in an adsorbent with solid density and BET surface area around 1969 kg.m<sup>-3</sup> and 1113 m<sup>2</sup>.g<sup>-1</sup>, respectively. The adsorption equilibrium isotherms for the flue gas components including CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O were developed in 25–70 °C and 0–35 kpa. The results showed carbon



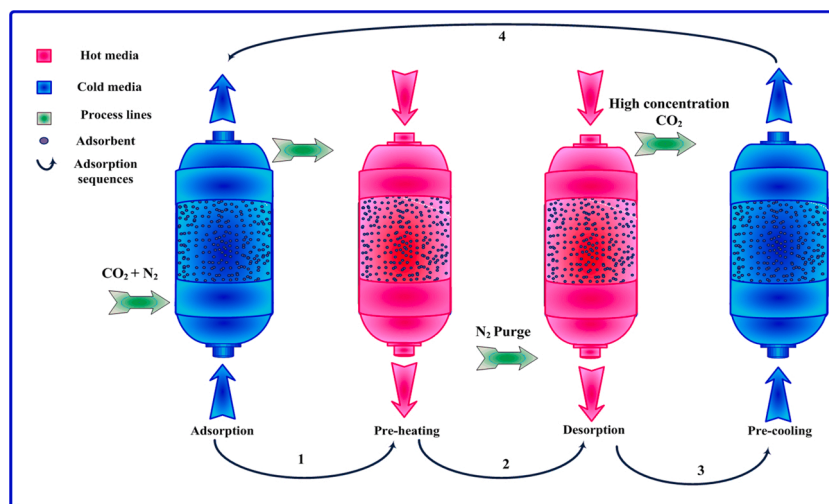


Fig. 8. A 4-step TSA process for CO<sub>2</sub> capture and sequestration.

dioxide and water vapor have more adsorption capacities on OS activated carbon than O<sub>2</sub> and N<sub>2</sub>, also, CO<sub>2</sub> is desorbed faster than H<sub>2</sub>O in the desorption step. They also reported that the water vapor is adsorbed in a similar way of carbon dioxide with no interaction between CO<sub>2</sub> and H<sub>2</sub>O adsorption through the multicomponent adsorption process. Finally, the stability of developed TSA unit obtained after four adsorption/desorption cycles with a reasonable performance [188].

Adelodun et al. [205] employed coconut shell-based activated carbon to sequester carbon dioxide from flue gas or indoor air. The commercial ACs originated from coconut shells were modified by one of these three steps including: pre-ozonation, pre-calcination with KOH (under N<sub>2</sub> atmosphere at 600 °C and through 2 h), and amination at 800 °C. The highest CO<sub>2</sub> adsorption capacity was attributed to the pre-calcinated AC samples with 2.525 mmol.g<sup>-1</sup> at the room temperature and atmospheric pressure. Then, Adelodun et al. [205] investigated the desorption ability of selected derived AC with rising bed temperature. Desorption (regeneration) was implemented by passing the hot N<sub>2</sub> over the adsorbent surface, which the duration of rising temperature up to 500 °C was 60 min. They observed that more than 86 % of adsorbed carbon dioxide was desorbed below 500 °C. The results proved that the studied samples can be efficiently employed in the TSA process.

Zubbri et al. [206] studied the rambutan peel to derive metallized biochar for CO<sub>2</sub> adsorption capacity. Rambutan peel was synthesized to biochar in a single-step pyrolysis at three different temperatures of 500, 700, and 900 °C. Firstly, the biochar was treated by hot N<sub>2</sub> flow and modified by impregnation using some magnesium salts such as magnesium nitrate > magnesium sulphate > magnesium chloride > magnesium acetate. The adsorbent produced through the 900 °C pyrolysis (specific surface area of 569.64 m<sup>2</sup>.g<sup>-1</sup>) showed the higher CO<sub>2</sub> adsorption capacity around 1.556 mmol.g<sup>-1</sup> at 30 °C, while the biochar impregnated with 5% magnesium nitrate represented the highest CO<sub>2</sub> adsorption performance (1.745 mmol.g<sup>-1</sup>) among other magnesium impregnation methods [206]. Furthermore, a TSA process was developed to evaluate the regeneration ability of the biochar through the different cycles with adsorption and desorption temperatures, 30 and 110 °C, respectively, which a stable CO<sub>2</sub> adsorption capability up to 25 cycles was proved [206].

#### 2.4. Mixed cyclic adsorption processes

Generally, choosing the type of cyclic adsorption processes depends on several factors including: type of adsorbent, the percentage of components in the gas feed, the kind of processes (e.g., post-combustion, pre-combustion and oxy-fuel combustion) etc [207,208]. As already discussed, in the conventional way, CO<sub>2</sub> is captured using amine-based

aqueous solution [208], while recently, cyclic adsorption process has been employed for CO<sub>2</sub> sequestration not only for less required energy, but also for high CO<sub>2</sub> purity and recovery as well as less destructive environmental effects [208,209]. In some cases, to elevate the adsorption performance the benefits of two or three cyclic adsorption processes are combined which results in PVSA, VTSA, etc.

CO<sub>2</sub> capture in the post-combustion condition has been frequently investigated in the cyclic adsorption process. Plaza et al. are the ones who devoted much of their efforts to develop novel sustainable adsorbents for CO<sub>2</sub> capture by different adsorption processes. In this way, Plaza et al. [188] studied a VTSA unit to investigate the impact of water vapor on CO<sub>2</sub> adsorption. To this end, the olive stones biomass samples were activated using a single step carbonization process by CO<sub>2</sub>, also equilibrium adsorption isotherms were developed in 25–70 °C. The results showed the CO<sub>2</sub> and H<sub>2</sub>O adsorbed significantly higher than N<sub>2</sub> and O<sub>2</sub>. Through this study, no reduction in CO<sub>2</sub> and H<sub>2</sub>O coadsorption was observed, in comparison with CO<sub>2</sub> adsorption in the dry feed, while higher CO<sub>2</sub> adsorption attributed to the slower adsorption kinetics of H<sub>2</sub>O. Afterwards, Plaza et al. proposed the combination of VSA and TSA to utilize the advantages of both processes [188]. The cycles of VTSA were similar with TSA and the regeneration step was accomplished by raising the temperature up to 70 °C as well as reducing the pressure until 1 kpa. Convincing results of the VTSA process were obtained after four steps, which proved the suitability of developed unit for CO<sub>2</sub> adsorption using olive stones in the wet operating condition.

In another study, Plaza and Rubiera [210] designed an adsorption process to sequester the CO<sub>2</sub> from a coal fired power plant. They employed a novel multi-bed heat-integrated VTSA process to separate 85 % of the CO<sub>2</sub> produced in a coal fired power plant. A competitive adsorption of CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O was considered through a non-isothermal/non-equilibrium dynamic fixed-bed adsorption model. The adsorbent was prepared by direct oxidation of olive stones, which strongly adsorbed CO<sub>2</sub> and had a low adsorption capability and affinity towards H<sub>2</sub>O. The adsorbent bed was vertical tube bundle with some tube placed inside the bundle. The adsorbent was packed in the tubes and an external tube with a thermal fluid (water) flowing inside, was circulating the bundle. The VTSA process temperature was varied between 30–80 °C, also the maximum and minimum pressures through the process were 2 and 0.05 bar, respectively. The VTSA process resulted satisfying energy consumption for CO<sub>2</sub> sequestration from a post-combustion power plant effluent in comparison with other post-combustion technologies such as solvent technology [210]. Plaza et al. [211] also evaluated the capacity of olive stones and almond shells for CO<sub>2</sub> uptake in the post-combustion process. To this end, the raw samples were chemically and physically activated by CO<sub>2</sub> and

amination, respectively. Firstly, the olive stones and almond shells were grounded and sieved to the particle sizes around 2 mm. Thereafter, the samples were carbonized via a N<sub>2</sub> stream at 873 K. The adsorption screening tests were accomplished in a stainless steel vertical bed with 203 mm height and 9 mm diameter, which resulted in 4.4 and 4.2 mmol.g<sup>-1</sup> loading at 115 kpa and 273 K for olive stones and almond shells samples activated physically by CO<sub>2</sub>, respectively; also a higher selectivity towards CO<sub>2</sub>/N<sub>2</sub> was observed for almond shells samples [211]. The characterization and adsorption tests approved that aminated samples showed narrower porosity, but higher volumetric capacities. In this case, aminated almond shells represented higher volumetric CO<sub>2</sub> adsorption capacity (than aminated olive stones), selectivity, and admissible adsorption kinetics. To evaluate the adsorption/desorption cycles, the samples were tested through TSA, VSA, and VTSA processes. The vacuum temperature swing adsorption was performed between 303 and 373 K and it revealed the high stability of prepared samples for CO<sub>2</sub> uptake in the large scale applications [211]. In the study conducted in 2015, Plaza et al. [212] employed the green coffee biomass as a low-cost microporous carbon precursor to synthesize CO<sub>2</sub> adsorbent. The green coffee residue was firstly dried at 100 °C for 4 h, then, pelletized to the diameter of 4 mm and height of 3 mm. The prepared pellets were activated using a single-step procedure by CO<sub>2</sub>, which at the maximum capacity, adsorbed 3.8 mmol CO<sub>2</sub>.g<sup>-1</sup> at 1.2 bar and 0 °C. Also, prepared activated carbons showed great capacity for CO<sub>2</sub>/N<sub>2</sub> separation at the post-combustion operating conditions. Furthermore, different adsorption cycles were developed to understand the large-scale adsorbent performance of prepared samples. Through the VTSA process, the recovery factor of CO<sub>2</sub> was 84 % and the productivity was 2.9 mol.kg<sup>-1</sup>.h<sup>-1</sup>. In the developed unit, adsorption occurred at 50 °C and 130 kpa as well as regeneration performed at 70 °C and 10 kpa. In another effort, Zhao et al. [213] proposed a ventilation system integrated with a TVSA adsorption technology. They developed amine-functionalized cellulose activated carbon for carbon capture and storage. It is worth mentioning that the highest CO<sub>2</sub> capacity was 2.54 mmol.g<sup>-1</sup> at 296 K and 1 bar in the dry condition [214]. In a TVSA process, Zhao et al. studied some key parameters such as CO<sub>2</sub> concentration, adsorption and desorption temperatures, also the effect of the desorption pressure. For reducing the costs and energy, they proposed employing wind or solar energy to provide the power needed for the developed process [213]. Zhao et al. concluded that the product purity and adsorption temperature had a direct impact on the net cost of the TVSA process. The minimum energy required for direct air capture process integrated with TVSA process was 20 kJ/mol for CO<sub>2</sub> level at 400 ppm at the effluent.

Wawrzynczak et al. [215] studied experimentally and numerically the oxy-combustion flue gas purification by adsorption technology for CO<sub>2</sub> sequestration. Derived activated carbons from coconut shells were employed to evaluate the adsorption equilibrium capacity of CO<sub>2</sub>, which was 7.15 mmol.g<sup>-1</sup> at 10 bar and 30 °C. The prepared coconut shell adsorbent samples had 470 kg.m<sup>-3</sup> bulk density and 1087 m<sup>2</sup>.g<sup>-1</sup> BET surface, which was loaded in four fixed-beds to develop VPSA technology. The feed gas constituted of 81.5 % CO<sub>2</sub>, 14.4 % N<sub>2</sub>, 3.9 % O<sub>2</sub>, and 0.2 % Ar, that were compressed by a diaphragm pump prior the injection to the bottom of the adsorber. Also, the lean gas (product purified from CO<sub>2</sub> at the high pressure) and CO<sub>2</sub>-rich gas (as low pressure product) were extracted from the top and the bottom of the adsorber column, respectively. Evaluation of the VPSA process showed that the single-stage VPSA unit with final product pressure of 18 bar (128 kW h/t CO<sub>2</sub>) can be comparable with CO<sub>2</sub> compression and purification unit based on the phase separation method (116 kW h/tCO<sub>2</sub>). They reported that the VPSA requires more energy when the pressure of the ultimate product increases [215].

Date seeds as a source of activated carbon via CO<sub>2</sub> capture process was studied by Bahamon et al. [216]. To this end, 0.35 g of AC was packed in an adsorption cell and equilibrium adsorption isotherms were investigated. The maximum CO<sub>2</sub> uptake on the date seed ACs was 4 mmol.g<sup>-1</sup> at 350 kpa and 25 °C. Also, binary mixtures including CO<sub>2</sub>/N<sub>2</sub>

and CO<sub>2</sub>/CH<sub>4</sub> adsorption were studied and compared with pure CO<sub>2</sub> adsorption ability of produced ACs. Bahamon et al. [216] also studied the effect of the water vapor on the adsorption process; they observed that the water vapor does not have any significant impact on adsorption results, but affects the energy needed for the cyclic adsorption processes. Finally, they proposed date seeds-ACs employment in the VPSA process for CO<sub>2</sub> sequestration due to the hydrophobicity character of ACs as well as satisfying the energy performance of developed unit in the wet operating condition.

Recently, other swing adsorption processes such as concentration and moisture swing adsorptions [217] have been developed and investigated experimentally. In 2019, Plaza and Rubiera [218] developed a vacuum, temperature and concentration swing adsorption process (VTCSA) for CO<sub>2</sub> separation from the flue gas. The cyclic process was designed to separate 85 % of the emitted CO<sub>2</sub> and obtain a product stream with 95 % of CO<sub>2</sub> in a dry stream. In this way, the flue gas considered as CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O through two different configurations of cyclic adsorption process, and employed activated carbons derived from the direct oxidation of olive stones as adsorbent. Both VTCSA cycle configurations went through five predefined steps including: 1) pressurization with feed, 2) adsorption, 3) rinse, 4) co-current depressurization, and 5) production step. The two VTCSA configurations differed in the step sequences such as: constituted a rinse step carried out by a fraction of the product and constituted a co-current depressurization step to a lower pressure level. It is worth mentioning that in the configuration with rinse step, 95 % purity and 85 % recovery with evacuation pressure of 0.2 bar were achieved in the steam/feed molar ratio > 0.16. On the contrary, the configuration with co-current depressurization was able to produce a high-purity CO<sub>2</sub> product, while was not able to meet the 85 % of CO<sub>2</sub> recovery target in the operation range. By developed VTCSA process, the requirement for the specific heat duty was decreased compared to the benchmark absorption technology. On the other hand, Plaza and Rubiera [218] declared that still more studies are necessary to optimize the adsorbent to make the process more competitive with other CO<sub>2</sub> sequestration technologies.

The distribution of different biomass/biochar carbon samples, which have been employed in the combined cyclic adsorption processes are illustrated in Fig. S4 (Supporting Information). As can be observed, the olive stones is the most favorable one between all considered samples. Also, a summary of different biomass/biochar carbon samples employed in the cyclic adsorption processes, accompanied with applied activation techniques as well as, adsorption loading capacity are demonstrated in Table 3. In addition, BET surface area and bulk density of these samples as main textural properties of prepared ACs are reported in Table 4.

### 3. Prospects samples for future cyclic adsorption processes

Recently, many studies have been conducted to evaluate the possibility of gas adsorption on the derived AC from biomass/biochar through the cyclic processes. As every upcoming technology, more studies are strictly needed to evaluate and optimize the operation and/or adsorbent quality. In this section, we classified almost all studies conducted on waste-originated adsorbents (with a special focus on bio-based carbon materials) for gas sequestration and storage, but have not yet been evaluated in the pilot/bench/large-scale using cyclic adsorption processes. In this way, these studies have been reviewed in this section, which can pave the path for future works on waste management and carbon capture studies.

#### 3.1. Wooden wastes

##### 3.1.1. Peanut shells waste

Peanut shells are one of the abundant and low-cost wastes, which can be broadly found in many countries as eco-friendly agricultural byproducts with an efficiency of 6 million tons in 2010 [219,220]. Derived carbon samples from the peanut shells upon activated with

**Table 3**

A summary of biomass/biochar carbon based-adsorbents studied for gas storage and sequestration by cyclic adsorption process.

Adsorbent	Origin of adsorbent	Adsorbate	Pressure (bar)	Temperature (°C)	Type of activation	Adsorption technique	Adsorption capacity	Selectivity	Reference
AC	Maple/maritime wood and pine/coconut shell	CO <sub>2</sub>	8	25	Physical	PSA	10.8 mmol/g adsorbent (from maple)	–	[64]
AC	Coconut shell	CO <sub>2</sub> & CH <sub>4</sub>	1	20	Physical	Gravimetric	1 mmol CO <sub>2</sub> /g	CO <sub>2</sub> /CH <sub>4</sub> 4.2 @ 1 bar	[176]
	babassu coconut	CO <sub>2</sub> & CH <sub>4</sub>	1	20	Physical	Gravimetric	0.75 mmol CO <sub>2</sub> /g		
AC	Kenaf	CO <sub>2</sub>	1.03	25	Chemical	PSA	2.086 mmol CO <sub>2</sub> /g (functionalized with TEPA)		[177]
Biochar	Olive stone	H <sub>2</sub> O, N <sub>2</sub> & CO <sub>2</sub>	1.4	23–70	Physical	Breakthrough	PSA	7 mmol CO <sub>2</sub> /g of H <sub>2</sub> O	[187]
AC	Olive and cherry stone	CO <sub>2</sub>	3–18	25	Physical	Gravimetric	PSA	2.53 mmol/g (at 3 bar & 25 °C)	CO <sub>2</sub> /CH <sub>4</sub> 2.53 @ 3 bar [172]
AC	Betung bamboo	CH <sub>4</sub>	1–6	10–30	Chemical	PSA	0.247 mmol/g (at 6 bar & 10 °C)		[158]
AC	Flax shives	Natural gas Dehydration	1.013–3	24–35	Chemical and physical	Gravimetric	PSA	0.9 g H <sub>2</sub> O /g (at 300 kpa & 24 °C)	[164]
Direct usage*	Oat hulls	Natural gas Dehydration	1.013–3	24–35	–	Gravimetric & Volumetric	PSA	0.63 g H <sub>2</sub> O /g (at 300 kpa & 24 °C)	[189]
Direct usage*	Canola meal	Nitrogen Drying	0.4–1.4	110–130	–	Breakthrough	PSA	0.165 g H <sub>2</sub> O /g (at 140 kpa & 130 °C)	[190]
Direct usage*	Canola meal	Water Removal from Ethanol Vapor	1.36–2.43	90–110	–	Breakthrough	PSA	0.020 g H <sub>2</sub> O/g (at 243 kpa & 90 °C)	H <sub>2</sub> O/Ethanol 1.93 @ 2.43 bar & 90 °C [191]
Direct usage*	Canola meal	Water Removal from Butanol Vapor	1.35–2.01	95–111	–	Breakthrough	PSA	0.48 g H <sub>2</sub> O /g (at 201 kpa & 111 °C)	H <sub>2</sub> O/Methanol 5.4 @ 2.01 bar & 111 °C [192]
Direct usage*	Corn starch and cob	Air Drying	3.2	25	Chemical	Breakthrough	PSA	–	[193]
AC	municipal solid wastes	CO <sub>2</sub>	0–3	40–100	Chemical and physical	Breakthrough	PSA	2.6 mmol/g (at 250 kpa & 40 °C)	[174]
AC	Coconut shell	CO <sub>2</sub> , H <sub>2</sub> O & N <sub>2</sub>	0–1	25–60	–	Breakthrough	VSA	3.5 mmol CO <sub>2</sub> /g (at 120 kpa & 20 °C)	CO <sub>2</sub> /N <sub>2</sub> 8.75 @ 1.2 bar & 20 °C [196]
AC	Olive stones	CO <sub>2</sub>	1.2	0–50	Physical	Breakthrough	VSA	4.65 mmol/g (at 95 kpa & 0 °C)	[151]
AC	Almond shells	CO <sub>2</sub>	1.2	0–50	Physical	Breakthrough	VSA	3.70 mmol/g (at 100 kpa & 0 °C)	CO <sub>2</sub> /N <sub>2</sub> 7.4 @ 0.1 bar & 0 °C [151]
AC	Oil tea shells	CO <sub>2</sub>	0.15–1	0–20	Chemical	Breakthrough	VSA	6.15 mmol/g (at 100 kpa & 0 °C)	[197]
AC	Pine sawdust	CO <sub>2</sub> & N <sub>2</sub>	0.005–1	50	Physical	Breakthrough	VSA	–	[65]
AC	Olive stones	CO <sub>2</sub> & N <sub>2</sub>	1.2	0–70	Physical	Breakthrough	VSA	3.1 mmol CO <sub>2</sub> /g (at 120 kpa & 0 °C)	[198]
AC	Agricultural waste	CO <sub>2</sub>	1.3	30–60	Chemical	Breakthrough	TSA	2.25 mmol/g (at 110 kpa & 30 °C)	CO <sub>2</sub> / N <sub>2</sub> 5.4 @ 1.1 bar & 30 °C [204]
AC	Olive stones	CO <sub>2</sub> & H <sub>2</sub> O	0.2–1.3	20–130	Chemical	Breakthrough	VTSA	1 mmol CO <sub>2</sub> /g (at 130 kpa & 30 °C)	CO <sub>2</sub> / N <sub>2</sub> ~20@ 50 °C [188]
AC	Coconut shell	CO <sub>2</sub>	1	20–600	Chemical	–	TSA	2.525 mmol/g (at 100 kpa & 20 °C)	[205]
AC	Horse manure	CO <sub>2</sub>	0–1.01	0–100	Physical	Breakthrough		3.8 mmol CO <sub>2</sub> /g (at 100 kpa & 0 °C)	CO <sub>2</sub> /N <sub>2</sub> 19.4 @ 0.1 bar & 0 °C
AC	Grass cutting	CO <sub>2</sub>	0–1.01	0–100	Physical	Breakthrough		3.9 mmol CO <sub>2</sub> /g (at 100 kpa & 0 °C)	CO <sub>2</sub> /N <sub>2</sub> 14.5 @ 0.1 bar & 0 °C
AC	Beer waste	CO <sub>2</sub>	0–1.01	0–100	Physical	Breakthrough		3.3 mmol CO <sub>2</sub> /g (at 100 kpa & 0 °C)	CO <sub>2</sub> /N <sub>2</sub> 16.4 @ 0.1 bar & 0 °C [199]
AC	Bio-sludge of a water treatment plant	CO <sub>2</sub>	0–1.01	0–100	Physical	Breakthrough		2.1 mmol CO <sub>2</sub> /g (at 100 kpa & 0 °C)	CO <sub>2</sub> /N <sub>2</sub> 14 @ 0.1 bar & 0 °C
AC	Beer waste	CO <sub>2</sub>	0–1.01	0–100	Chemical	Breakthrough		2.6 mmol CO <sub>2</sub> /g (at 100 kpa & 0 °C)	CO <sub>2</sub> /N <sub>2</sub> 26.7 @ 0.1 bar & 0 °C
AC	Wood sawdust and lignin	CO <sub>2</sub>	1–6	600	Mechanochemical	Volumetric		3.4 mmol CO <sub>2</sub> /g (at 600 kpa & 25 °C; Pure CO <sub>2</sub> feed)	[175]
			0.2–1.2	600	Mechanochemical	Volumetric	VSA	4.1 mmol CO <sub>2</sub> /g (at 120 kpa & 25 °C; Flue gas feed)	
Biochar	Rambutan peel	CO <sub>2</sub>		30–100	Physical	Breakthrough	TSA	1.745 mmol CO <sub>2</sub> /g (at 30 °C)	CO <sub>2</sub> /N <sub>2</sub> 20.4 @ 1 bar & 30 °C [206]
AC	Beech wood	CO <sub>2</sub> & H <sub>2</sub> O	0.0002–1.05	10–80	Physical	Volumetric	TVSA	2.54 mmol CO <sub>2</sub> /g (at 100 kpa & 23 °C)	[214]
AC	Coconut shell	CO <sub>2</sub> , N <sub>2</sub> & O <sub>2</sub>	0–10	30	Physical	Thermogravimetric	VPSA	7.15 mmol CO <sub>2</sub> /g (at 1000 kpa & 30 °C)	[215]
AC	Olive stones & Almond shells	CO <sub>2</sub> & N <sub>2</sub>	0–1.2	0–30	Physical	Breakthrough	VTSA		CO <sub>2</sub> /N <sub>2</sub> 3 @ 1.1 bar & 30 °C [211]

(continued on next page)

Table 3 (continued)

Adsorbent	Origin of adsorbent	Adsorbate	Pressure (bar)	Temperature (°C)	Type of activation	Adsorption technique	Adsorption capacity	Selectivity	Reference
AC	Green coffee	CO <sub>2</sub>	0–1.2	0–50	Physical	Thermogravimetric	4.4 mmol CO <sub>2</sub> /g olive stones(at 115 kpa & 30 °C) 3.8 mmol CO <sub>2</sub> /g (at 120 kpa & 0 °C)	CO <sub>2</sub> /N <sub>2</sub> 15–25 @ 1.3 bar & 50 °C	[212]

\* Direct usage refers to the direct application of waste as adsorbent, just after drying, grinding, and sieving.

chemical agent, generally show a high pore volume and specific surface volume, which nominate them as an excellent candidate for gas capture and sequestration [221,222]. In this way, Li et al. [221] focused on synthesis of carbon-based microporous adsorbent originated from the peanut shells. The highly microporous sample was chemically activated by KOH and thermally treated in a different temperature range: 680–780 °C, which it resulted in adsorbents with the micropore volumes between 0.73–0.79 mL.g<sup>-1</sup> and S<sub>BET</sub> varied from 1713 to 1893 m<sup>2</sup>. g<sup>-1</sup>. Accordingly, the adsorbent activated at 680 °C and 1 bar showed the highest CO<sub>2</sub> adsorption capacity with 7.25 mmol.g<sup>-1</sup> at 0 °C and 1 bar. Li et al. [221] also concluded that peanut shells-originated adsorbents have a promising capacity for carbon capture studies. In another comparative study, which sought to develop carbon-based adsorbents [222], peanut shells and sunflower seed were investigated as the precursors for high-capacity CO<sub>2</sub> adsorption. It was illustrated the sample originated from the sunflower seeds has a higher CO<sub>2</sub> uptake compared to derived adsorbent from peanut shells. Deng et al. [222], also investigated the impact of activation temperature and KOH/carbon mass ratio, which reported, the S-973–1.25 (sunflower seed activated in 973 K with KOH/carbon mass ratio of 1.25) and P-973–1.00 (peanut shell activated in 973 K with KOH/carbon mass ratio of 1.25) samples through five adsorption/desorption cycles. The CO<sub>2</sub> uptake results through five cycles proved that the samples fabricated from peanut shells and sunflower seeds can be applied in CO<sub>2</sub> adsorption process effectively. The maximum CO<sub>2</sub> uptake by sunflower seed-originated adsorbent (activated by KOH at 973 K with KOH/carbon ratio of 1.25) was 7.05 mmol.g<sup>-1</sup> at 0 °C and 1 bar.

### 3.1.2. Argan fruit shells

Recently, the agricultural activities related to the argan fruit (*Argania Spinosa*) has rapidly increased, because of worldwide growing interest in the oil of this species [223]. For instance, in Morocco, more than 4000 tons of argan oil is annually produced, which its hard shell promoted up to 80.000 tons per year [101]. Currently, this hard shell that is rich by lignocellulose is considered as an agriculture by-product without any significant economic value [224,225]. Boujibar et al. [226] evaluated the potential of argan fruit shells, gathered from the southern region of Morocco, as a N-doped adsorbent. This nanoporous CO<sub>2</sub> adsorbent was chemically activated by KOH or NaOH. Afterwards, the obtained sample was activated chemically through two different methods namely impregnation and physical mixing. The results revealed that both activating agents had significant impacts on enhancing the surface area and adsorbent porosity. The highest CO<sub>2</sub> uptake capacity observed by Boujibar et al. was about 5.65 mmol.g<sup>-1</sup> at 25 °C and 1 bar [226].

### 3.1.3. Palm kernel shells

Indonesia and Malaysia are the largest palm oil exporters in the world [227], which in one case, there are more than 5.8 million hectares of lands under palm oil cultivation in Malaysia, that produced 19.5 and 2.5 million tons of crude palm oil and palm kernel cake, respectively, in 2018 [227,228]. These palm kernel shells (PKS) have an excellent capacity to be considered as a source of energy and also, adsorbent for gas storage and sequestration [229]. Recently, low-cost porous CO<sub>2</sub>

adsorbent synthesis from palm kernel was studied by Nasri et al. [75]. PKS was carbonized at 700 °C, thereafter activated physically by CO<sub>2</sub> stream. The CO<sub>2</sub> loading capacity of the prepared PKS was around 7.32 mmol.g<sup>-1</sup> at 30 °C and 4 bar. They reported the PKS activated carbon as an interesting and sustainable adsorbent for gas adsorption purposes [75].

### 3.1.4. Paulownia

Yorgun and Yildiz [73] studied the potential of Paulownia wood as low-cost precursor of AC for carbon capture and storage. On the grounds, impregnation ratio and the final carbonization temperature as two effective parameters on the porous structure of the activated carbon were investigated. Yorgun and Yildiz reported that 400 °C is the most effective final carbonization temperature, also the impregnation ratio of 4 was achieved as optimal impregnation ratio. The highest reported BET surface area and total pore volume were 2806 m<sup>2</sup>. g<sup>-1</sup> and 1.746 cm<sup>3</sup>. g<sup>-1</sup>, respectively [73]. In another study, Zhu et al. [230] considered a simple one-step carbonization-activation of paulownia sawdust biomass to synthesize activated carbon for CO<sub>2</sub> sequestration applications. They investigated the synthetic conditions including KOH/biomass mass ratio, the activation temperature, and activation time impact on adsorbent structure and CO<sub>2</sub> adsorption capacity. The highest CO<sub>2</sub> uptake at the optimized conditions (KOH/biomass: 4, activation temperature: 700 °C, and activation time: 1 h) was 8 mmol.g<sup>-1</sup> at 0 °C and 1 bar, which is comparable with the maximum loading capacities of commercial adsorbents [141,231,232].

### 3.1.5. Poplar anthers

Poplar is a genus of deciduous flowering trees that is widespread species in Asia, Europe and North America [233]. As instance, more than 8.5 million hectares in China are cultivated with poplar [234]. While this species has a special structure, morphology and chemical compositions, but its applications have not been studied very well [233]. Truly, a high percentage of nitrogen (>4%) also the ready facilitation of the poplar anther introduce this sample as an excellent precursor nitrogen-containing carbonaceous with highly porosity for separation processes [233,234]. Song et al. [233] developed poplar anthers-based adsorbents to sequester CO<sub>2</sub> at the post-combustion operating conditions. They investigated the key parameters, (including: KOH/biomass mass ratio, the activation temperature, and activation time impact on adsorbent structure and CO<sub>2</sub> adsorption capacity [230]), and found that pre-carbonization step, activation temperature, and KOH mass ratio significantly affected on the loading of prepared adsorbents. They observed 51.3, 2.04, and 0.25 mmol.g<sup>-1</sup> CO<sub>2</sub> adsorption at 50, 1, and 0.1 bar, respectively, at 25 °C.

### 3.1.6. Populus

Populus is a major industrial tree species, which has a broad application in timber, bioenergy, pulp manufacturing, tissue development and also for biological studies in the way of long-term survival in response to the climatic changes [235–238]. Recently, Ekhlesi et al. [239] derived an activated carbon from populus wood biomass (PWB) and evaluated its CO<sub>2</sub> adsorption capacity and economical aspect of adsorption process. Firstly, the PWB samples were carbonized under

**Table 4**

A summary of some main characters of textural properties of most prevalent biomass/biochar carbon-based adsorbents in developed cyclic adsorption processes.

Adsorbent origination	BET surface (m <sup>2</sup> . g <sup>-1</sup> )	Bulk density (kg. m <sup>-3</sup> )	Reference
Maple/maritime wood and pine/coconut shell	2187	280	[64]
Coconut shell	1452	N/A*	[176]
Babassu coconut	809	N/A	[176]
Olive stone	925	442	[172]
Cherry stone	903	N/A	
Betung bamboo	465.2	N/A	[158]
municipal solid wastes	279	333	[174]
Coconut shell	921.7	493	[196]
Olive stones	1113	N/A	[151]
Almond shell	822	NA/	[151]
Olive stones	415	455	[198]
Wood	1361	196	
Peat	942	427	[204]
Agricultural wastes	588	399	
Olive stones	1113	1969	[188]
Horse manure	749	N/A	
Grass cutting	841	N/A	
Beer waste	622 (Physically activated) 1073 (Chemically activated)	N/A	[199]
Bio-sludge of a water treatment plant	489	N/A	
Wood sawdust and lignin	1313	950	[175]
Rambutan peel	504.58	N/A	[206]
Olive stones	1113	1969	[188]
Coconut shell	1087	470	[215]
Green coffee	522	421	[212]

\* Not available.

atmosphere pressure, afterwards chemically activated by KOH to prepare the sample. Accordingly, some effective parameters through AC preparation including KOH/carbon mass ratio (2–4 g/g), heating temperature (750–950 °C), and heating time (30–90 min) were investigated. The highest CO<sub>2</sub> uptake (7.2 mmol.g<sup>-1</sup> at 0 °C and 1 bar) was observed at KOH/carbon, heating temperature, and heating time of 3:1, 850 °C, and 60 min, respectively. Finally, they estimated that AC production from the populus wood biomass in the industrial scale requires about 25 \$ per kg investment.

### 3.1.7. *Eucalyptus camaldulensis*

*Eucalyptus camaldulensis* wood is generally employed as a raw sample to prepare activated carbon because of its high carbon content [234]. Effect of different chemical activating agents on derived AC from *Eucalyptus camaldulensis* wood (ECW) for CO<sub>2</sub> adsorption was studied by Heidari et al. [74]. To this end, activating agents of ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub> with different impregnation mass ratios were investigated. In addition, ECW activated by KOH as a popular chemical reagent followed by a pyrolysis process was also studied. Among various CO<sub>2</sub> adsorbents derived through mentioned processes, the activated carbons obtained through KOH activation showed the largest surface area (2594 m<sup>2</sup>. g<sup>-1</sup>) and the maximum micropore content (98 %), which this sample represented the highest CO<sub>2</sub> uptake capacity: 4.10 mmol.g<sup>-1</sup> at 30 °C and 1 bar.

### 3.1.8. Residual wooden wastes

Residual wooden wastes are types of lignocellulosic biomass containing relatively high carbon contents [73,240], which are annually produced in a huge amount throughout the world without any specific economical applications [84]. Totally, 20 % of the total input mass in the wood industry results in residual wastes in three forms including: wood sawdust, chips, and offcuts [241]. These types of biomass due to the high content of carbon also low percent of sulfur and ash, are ideal materials

to be employed as precursors of low-cost activated carbon for CO<sub>2</sub> adsorption [73,74]. Lately, the mixture of sawdust, cellulose, and starch were employed by Sevilla and Fuertes [242] to produce porous CO<sub>2</sub> adsorbent via chemical activation. The chemical activation of KOH employing two different ratios of KOH/precursor = 2 & 4 in the activation temperature range of 600–800 °C were carried out to prepare the samples. According to textural properties, the sample prepared with KOH/precursor = 4 represented the larger pore size and the surface area; however, the sample prepared with KOH/precursor = 2 showed higher CO<sub>2</sub> capacity. In this way, the sample activated at 600 °C using KOH/precursor = 2 had the maximum CO<sub>2</sub> uptake of 4.8 mmol.g<sup>-1</sup> at 25 °C and 1 atm.

## 3.2. Agricultural wastes

In recent years, the agricultural wastes (AW) have attracted a significant attention as a low cost adsorbent for wastewater treatment and gas adsorption processes [243,244]. Derived activated carbons from AW are considered as a valuable route to reduce the environmental concerns related to the accumulation of natural agro-wastes as well as to cover up the challenges possessed by commercial carbon materials [144,244,245]. In the following, recent studies on derived activated carbon from AW for CO<sub>2</sub> capture are discussed, while they have not been evaluated for potential applications in the large/pilot scales by cyclic adsorption process.

### 3.2.1. Coffee ground

Coffee as a favorite drink has one of the most notable residues in the world that is cultivated in more than 80 countries by having 7.0 million tones yield globally [246–248]. According to the reports, soluble coffee has nearly 50 % share of processed coffee in the globe, which each kilogram of this soluble coffee results in 2 kg of wet spent coffee residue [246]. Recently, coffee wastes management has been a major concern for environmental advocates [249]. Accordingly, coffee grounds (CGs) due to the high percent of carbon have been introduced as an interesting candidate for CO<sub>2</sub> capture [249]. Silva et al. [249] studied the potential of coffee ground in the Brazilian soluble coffee industry. To this end, they evaluated the capacity of coffee residue as a bio-sorbent. Hence, the coffee residue was firstly dried, afterwards activated via N<sub>2</sub> flux at 100 °C for 2 h. A combination of physical (by carbon dioxide) and chemical (by KOH) activations onto coffee grounds was investigated by Plaza et al. [118]. They illustrated activated carbons prepared by KOH have a higher adsorption capacity for carbon capture (which the maximum CO<sub>2</sub> loading capacity was 4.9 mmol.g<sup>-1</sup> at 298 K and 1 bar), while physically activated samples showed a higher selectivity. In another study, Travis et al. [250] investigated the activation temperature and KOH/CGs mass ratio on biomass-derived samples of coffee grounds for carbon capture and storage. Travis et al. observed the maximum BET surface area around 2785 m<sup>2</sup>. g<sup>-1</sup>, which led to a 23.27 mmol.g<sup>-1</sup> CO<sub>2</sub> loading at 0 °C and 10 bar.

### 3.2.2. Rice wastes

Rice waste is one of the most popular waste materials, which has extensively been considered as a source of adsorbent in the recent years [251–260]. Jang et al. [252] employed the rice husk ash as a silica source to synthesize the CO<sub>2</sub> adsorbent. They reported 1024 m<sup>2</sup>. g<sup>-1</sup> as the S<sub>BET</sub> for the prepared samples with a structure-directing template of mesoporous MCM-48 (mesoporous silica compounds). The initial activation of MCM-48 was carried out with He atmosphere at 383 K for 2 h. They observed a very fast kinetic of CO<sub>2</sub> adsorption with maximum loading of 0.069 mmol.g<sup>-1</sup> at 323 K and atmospheric pressure. In another study, Bhagiyalakshmi et al. [253] synthesized silica-based sorbents such as MCM-41, MCM-48, and SBA-15 for CO<sub>2</sub> adsorption. The Si–OH sites were functionalized by 3-chloropropyltrimethoxysilane (CPTMS), then grafted with amine compounds. Between all amine-grafted samples, MCM-48/TREN had the maximum CO<sub>2</sub> loading

capacity around 70 mg.g<sup>-1</sup> (at 25 °C and 1 atm) in which the adsorption capacity was in order of MCM-48/TREN > MCM-41/TREN > SBA-15/TREN. On the grounds, Bhagiyalakshmi et al. [254] also studied on SBA-15 originated from the rice husk ash as the silica source and grafted with tris (2-aminoethyl) amine (TREN) through the stepwise growth technique. The characterization tests showed that SBA-15 had the maximum surface area ( $S_{\text{BET}} = 790 \text{ m}^2 \cdot \text{g}^{-1}$ ) than other grafted versions. Also, the maximum CO<sub>2</sub> capacity of SBA-15/TREN/G2 was comparably high (100 wt% at a short time of adsorption) at 25 °C. Highly-efficient Li<sub>4</sub>SiO<sub>4</sub>-based adsorbent for CO<sub>2</sub> sequestration purposes at the high temperature was developed by Wang et al. [255]. Two rice husk ash samples were prepared and then calcinated in the presence of Li<sub>4</sub>SiO<sub>4</sub> at 800 °C. Their observations showed the rice husk sample with higher metal content has a better potential for CO<sub>2</sub> capture capacity due to the smaller activation energies for the chemisorption and diffusion processes than that of pure Li<sub>4</sub>SiO<sub>4</sub>. In 2012, Witton [256] employed rice husk ash as a low-cost silica precursor and chitosan (polyethyleneimine (PEI)) as a support for CO<sub>2</sub> adsorption purposes. The impact of bimodal porous silica supports accompanied with different PEI contents (10, 20, 30, 40, and 50 wt%), were investigated in different temperatures (60, 75, 85, 90, 95, and 105 °C) for carbon capture and storage. Witton reported [256] that at PET content < 20 wt%, the adsorption process was controlled thermodynamically, while in the higher PEI content (30 wt%), the CO<sub>2</sub> adsorption was controlled by the kinetic of process. Finally, Witton concluded that PEI-loaded bimodal porous silica materials are economical, eco-friendly, and high-efficient for carbon capture. In this way, Hemalatha et al. [257] investigated the impact of Ceria content (3, 5, 7, 11, and 19 wt%) in NaZSM-5 originated from the rice husk ash on CO<sub>2</sub> capture. The maximum CO<sub>2</sub> uptake on CeO<sub>2</sub>(5%)/NaZSM-5 was 130 mg.g<sup>-1</sup> at 25 °C and 1 bar. Their observations showed the adsorption capacity varied in order of CeO<sub>2</sub>(5%)/NaZSM-5 > CeO<sub>2</sub>(3%)/NaZSM-5 > CeO<sub>2</sub>(7%)/NaZSM-5 > CeO<sub>2</sub>(11 %)/NaZSM-5. Finally, Hemalatha et al. [257], proposed NaZSM-5 as an excellent candidate for CO<sub>2</sub> sequestration. Wang et al. [258] considered the cost-effective samples derived from the rice husk ash (RHA) pretreated by citric acid (CRHA). The CRHA as the precursor of silicon source was employed to prepare Li<sub>4</sub>SiO<sub>4</sub>-based adsorbent using thermally activation at 700 °C. They reported the maximum CO<sub>2</sub> uptake around 6.92 mmol.g<sup>-1</sup> at 680 °C and atmospheric pressure for CRHA--Li<sub>4</sub>SiO<sub>4</sub>. In another study, Zeng and Bai [259] developed a new technique to synthesize large-pore silica material via a temperature-controlled process without any pore expander addition. The prepared mesoporous adsorbent (MS-400(25)), which was originated from the rice husk ash, was fabricated at 400 °C, then treated with NaOH at 25 °C, that resulted in the CO<sub>2</sub> adsorption capacity around 173 mg.g<sup>-1</sup> at 75 °C and atmospheric pressure. Zhang et al. [260] also reported that pre-deashing of the raw rice husk can significantly improve the nitrogen-enriched biochar (N-Char).

### 3.2.3. Sugarcane bagasse

Sugarcane is one of the main agricultural crop which generally cultivated in the tropical and subtropical areas [261]. Brazil and India are the biggest production sources of the sugarcane in the world, that annually produced more than 758 and 306 million tons sugarcane crop, respectively [99,100]. Approximately, sugarcane cultivation supplies more than 80 % of global sugar demand of the world [262,263], that the sugarcane bagasse is the major byproduct of this industry [264]. This biomass sample includes nearly 32–45 % cellulose, 20–32 % hemicellulose, 17–32 % lignin, 1.0–9.0 % ash and some other ingredients [265, 266]. Typically, the bagasse is burnt that contributes to the environmental pollutions [261]. Thus, the management of this waste materials is important not only in the way of environmental protections, but also introduces as a sustainable products for large scale applications [267]. To this end, recently, sugarcane bagasse has been investigated for different applications including: biofuels (ethanol), electricity, enzymes and biosorbent [266,268,269]. Alhassan et al. [270] studied unmodified

(UMAC), acid (AMAC), and base modified activated carbon (BMAC) from sugarcane bagasse for CO<sub>2</sub> capture applications. The characterization tests showed that the BMAC with better pore structure and surface area (800.6 m<sup>2</sup>. g<sup>-1</sup>) has a great potential for CO<sub>2</sub> adsorption processes, which its loading capacity was 1.102 mmol.g<sup>-1</sup> at 25 °C and 1 bar.

### 3.2.4. Corn cobs

Corn is among the main agricultural crops that annually more than 520 million tons of this species is produced in the worldwide [271]. North America (42 %), Asia (26 %), Europe (12 %) and South America (9%) are the main production sources [272]. According to the reports [271], a major part of cultivated corn is utilized as animal food (around 64 % of global production), and the share of human consumption is around 19 %, while about 5% of global production is lost as waste. Recently, derived agricultural wastes from corn industry have been considered as a new source of energy (bioethanol) and/or economic precursors for activated carbon [271,273]. Tsai et al. [274] investigated the activation temperature and type of activating agents (KOH and K<sub>2</sub>CO<sub>3</sub>) of corn cobs-originated carbon materials. They demonstrated a relation between increasing temperature through activating process, the adsorbent surface area and total pore volume. Also it was reported that the sample activated chemically by KOH afterwards through a physical activation at 800 °C for 1 h had the highest  $S_{\text{BET}}$  with 1806 m<sup>2</sup>. g<sup>-1</sup> and total pore volume of 0.87 cm<sup>3</sup>. g<sup>-1</sup>, which showed a textural properties in the range of commercial carbon materials [274].

### 3.2.5. Tobacco wastes

Tobacco is a favorable cultivated crop, which up to 20 % of produced tobacco in the world maybe lost during harvesting, handling and processing steps as scrap, dust and midrib [275]. Tobacco waste has been already extensively investigated as a source of bioactive compounds [275,276]. Li et al. [277] evaluated the carbonization process of tobacco stems-based carbon activated by H<sub>3</sub>PO<sub>4</sub>. They declared that increasing pyrolysis temperature enhances the weight loss and decreases the yield of char. In a similar way of [277], H<sub>3</sub>PO<sub>4</sub> was employed as the activating agent of prepared sample that showed more effective impact on the adsorbent pore size [277]. In another study, Sha et al. [278] employed a simple pre-treatment process (by methanol) to synthesize the micro/meso-porous carbons derived from tobacco waste materials. Accordingly, 700 °C was opted as the optimal temperature of calcination, in which, AC with 1104 m<sup>2</sup>. g<sup>-1</sup> of BET surface area was developed. Also, they reported 3.6 mmol.g<sup>-1</sup> as highest CO<sub>2</sub> uptake capacity of prepared sample at 0 °C and 1 bar. They concluded that a pre-treatment process is an effective method to prepare a valuable adsorbent from abundant and economical tobacco waste.

### 3.2.6. Eggshell wastes

Egg and chicken meat are two of key ingredients in the food and pastry industries. According to the reports, up to 5150 million eggs are produced per year to supply the world requirement [102,103], that results in many tons of eggshells as wastes in the hatchery process [103]. Generally, three costly techniques including landfilling [279], composting [280] and incineration [281] are employed to manage the eggshell wastes. Accordingly, novel economic environmental-friendly routes are necessary. Witton [282] derived a calcium oxide-base CO<sub>2</sub> adsorbent from the eggshell waste and compared with commercial calcium-based adsorbents. They introduced the prepared sample as an attractive adsorbent for CO<sub>2</sub> adsorption applications. Eggshells and red mud (Rm) were investigated as precursors to produce calcium-based CO<sub>2</sub> adsorbent by He et al. [283]. The effect of some key factors including sodium leaching ratio and Rm/eggshells doping content as Ca precursor on CO<sub>2</sub> adsorption capacity were investigated. They observed that the eggshell-derived adsorbent with 10 wt% Rm doped (surface area of 5.74 m<sup>2</sup>. g<sup>-1</sup>) demonstrated an excellent CO<sub>2</sub> uptake capacity. Castilho et al. [284] employed Eggshells, shellfish, and cuttlefish bones

wastes as rich sources of calcium to develop a CaO-based CO<sub>2</sub> adsorbent.

### 3.2.7. Agaricus

Wang et al. [285] employed Agaricus for the first time to produce macroporous and uniform microporous activated carbons for CO<sub>2</sub> capture purposes. Ar flow was used at 773 K for carbonization step and followed by a KOH activation process. The highest CO<sub>2</sub> uptake was 5.5 mmol.g<sup>-1</sup> at 0 °C and 1 bar. Afterwards, they indicated some features including CO<sub>2</sub>/N<sub>2</sub> selectivity, high stability, and ease of adsorbent regeneration, which made Agaricus-based sorbents more interesting in carbon capture processes.

### 3.2.8. Mesua ferrea L. Seed cake

Kudinalli et al. [111] focused on pre-treatment effect of Mesua ferrea L. seed cake on CO<sub>2</sub> adsorption capacity. They pointed out that a calcination step at 650 °C under N<sub>2</sub> atmosphere for 4 h can significantly improve the CO<sub>2</sub> loading capacity. They reported 2.6 mmol.g<sup>-1</sup> at 25 °C and 1 bar as highest CO<sub>2</sub> uptake capacity.

### 3.2.9. Soybean oil cake

Recently, the limitations of fossil fuel resources and the fluctuation of petroleum price also political stimulants contributed to the growing

interests on sustainable source of energy [286,287]. Bioenergy is one of the main candidates that attracted a significant attention in the last decades. Compared to the other potential applicants to be considered as raw materials in this industry, soybean oil is the most common feedstock for biodiesel production [288,289]. Typically, biodiesel is derived from the soybean oil through transesterification reaction also “cake” as pressed materials is a major waste material during soybean oil processing [288]. Currently, soybean is the third agricultural products in the world (after wheat and corn), which its global production is: North America 42 %, Latina America 31 %, Asia 24 %, EU 2% and Africa 1% [288]. Also, Brazil is among the major producers and consumers of biodiesel in the world with estimated capacity of 5.8 billion liters in 2012 [288]. Lingo-cellulosic-based activated carbon from the soybean oil cake was the major object of the study conducted by Tay et al. [121]. The samples were prepared using pyrolysis process at 600 and 800 °C, then followed by a chemical activation by KOH and K<sub>2</sub>CO<sub>3</sub>. In the considered study, the impact of chemical reagents and activation temperature on the derived adsorbent from soybean oil cake were studied. Tay et al. [121] found that derived AC by K<sub>2</sub>CO<sub>3</sub> is more effective for gas adsorption than prepared sample by KOH in terms of porosity and lower ash and sulfur content.

**Table 5**

A summary of biomass/biochar carbon based-adsorbents and their performance for CO<sub>2</sub> capture and storage as prospects for future cyclic adsorption studies.

Adsorbent	Origin of adsorbent	Adsorbate	Type of activation	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Adsorption capacity	Reference
AC	Rice husk ash	CO <sub>2</sub>	Chemical	1024	0.069 mmol.g <sup>-1</sup> (at 323 K and atmospheric pressure)	[252]
AC	Rice husk ash	CO <sub>2</sub>	Chemical	1101.2	70 mg.g <sup>-1</sup> (at 298 K and 1 atm)	[253]
SBA-15/TREN/G2	Rice husk ash	CO <sub>2</sub>	Chemical	8	–	[254]
CeO <sub>2</sub> (5%)/NaZSM-5	Rice husk ash	CO <sub>2</sub>	Chemical	303.32	130 mg.g <sup>-1</sup> (at 298 K and 1 atm)	[257]
Aerosil-Li <sub>4</sub> SiO <sub>4</sub>	Rice husk ash	CO <sub>2</sub>	–	<2	6.92 mmol.g <sup>-1</sup> (at 953 K and 1 atm)	[258]
MS-400 (25)	Rice husk ash	CO <sub>2</sub>	–	484	173 mg.g <sup>-1</sup> (at 348 K and 1 atm)	[259]
Biochar	Rice husk ash	CO <sub>2</sub>	with NH <sub>3</sub>	451.02	18.1 mg.g <sup>-1</sup> (at 393 K and 1 atm)	[260]
Biochar	Peanut shells	CO <sub>2</sub>	Chemical	1713	7.25 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[221]
Biochar	Peanut shells	CO <sub>2</sub>	Chemical (KOH/C mass ratio:1; activated at 973 K)	956	5.25 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[222]
Biochar	Sunflower seed	CO <sub>2</sub>	Chemical (KOH/C mass ratio:1.25; activated at 973 K)	1790	7.05 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[222]
Activated carbon	Coffee grounds	CO <sub>2</sub>	Physical and chemical	831	4.9 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[118]
Activated carbon	Coffee grounds	CO <sub>2</sub>	Chemical	2785	23.27 mmol.g <sup>-1</sup> (at 273 K and 10 bar) 5.09 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[250]
Activated carbon	Fly ash	CO <sub>2</sub>	Chemical	27	0.175 mmol.g <sup>-1</sup> (at 298 K)	[299]
Activated carbon	Fly ash	CO <sub>2</sub>	Chemical	294–319	1.5 mmol.g <sup>-1</sup> (at 328 K)	[301]
Activated carbon	Fly ash	CO <sub>2</sub>	Physical	1075	1.579 mmol.g <sup>-1</sup> (at 303 K)	[303]
SBA from fly ash with 50 % PEI loading	Fly ash	CO <sub>2</sub>	Physical	407	110 mg.g <sup>-1</sup> (at 308 K and 1 bar)	[304]
Lithium-based sorbent	Fly ash	CO <sub>2</sub>	Chemical	–	107 mg.g <sup>-1</sup> (at 873 K and 1 bar)	[305]
Solid sorbent	Fly ash	CO <sub>2</sub>	Chemical	–	0.305 mmol.g <sup>-1</sup> (at 303 K and 1 atm)	[302]
AC	Date seeds	CO <sub>2</sub>	Chemical	422.94	78.71 mg.g <sup>-1</sup> (at 293 K and 1 bar)	[306]
AC	Corn cobs	CO <sub>2</sub>	Chemical & Physical	1806	–	[274]
AC	Sawdust, cellulose and starch	CO <sub>2</sub>	Chemical	1260	4.8 mmol.g <sup>-1</sup> (at 298 K and 1 atm)	[242]
AC	Carpet waste	CO <sub>2</sub>	Chemical	1272	138 mg.g <sup>-1</sup> (at 298 K and 1 bar)	[291]
AC	Algae	CO <sub>2</sub>	Chemical	1940	7.4 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[292]
AC	Argan fruit shells	CO <sub>2</sub>	Chemical	1889.63	5.65 mmol.g <sup>-1</sup> (at 298 K and 1 bar)	[226]
AC	Palm kernel	CO <sub>2</sub>	Physical	167.08	7.32 mmol.g <sup>-1</sup> (at 303 K and 4 bar)	[75]
AC	Sugarcane bagasse	CO <sub>2</sub>	Chemical	800.6	1.102 mmol.g <sup>-1</sup> (at 298 K and 1 bar)	[270]
AC	Soybean oil cake	–	Chemical	1352.86	–	[121]
N-dopped porous Carbon	Tobacco wastes	CO <sub>2</sub>	Chemical	1104	3.6 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[278]
AC	Paulownia sawdust	CO <sub>2</sub>	Chemical	1643	8 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[230]
Graphene	Populus wood biomass	CO <sub>2</sub>	Chemical	1317.1	7.2 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[239]
AC	Enteromorpha prolifera	CO <sub>2</sub>	Chemical	418	2.386 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[294]
AC	Agaricus	CO <sub>2</sub>	Chemical	2264	5.5 mmol.g <sup>-1</sup> (at 273 K and 1 bar)	[285]
AC	Eucalyptus camaldulensis wood	CO <sub>2</sub>	Chemical	2594	4.10 mmol.g <sup>-1</sup> (at 303 K and 1 bar)	[74]
Hydrochar	Lignin waste	H <sub>2</sub> & CO <sub>2</sub>	Chemical	1502	7.4 mmol CO <sub>2</sub> .g <sup>-1</sup> (at 273 K and 1 bar)	[293]
AC	Poplar anthers	CO <sub>2</sub>	Chemical	3322	2.04 mmol.g <sup>-1</sup> (at 298 K and 1 bar)	[233]
AC	Mesua ferra L. seed cake	CO <sub>2</sub>	Physical	184.1	2.6 mmol.g <sup>-1</sup> (at 298 K and 1 bar)	[111]

**Table 6**

A comparison between the CO<sub>2</sub> uptake capacity of some of the recent derived ACs from biomass/biochar samples and other commercial adsorbents.

No.	Adsorbent	Temperature (K)	Pressure (bar)	CO <sub>2</sub> uptake (mmol g <sup>-1</sup> )	Reference
1	β-Zeolite	313	1	1.48	[7]
2	Natural zeolite tuff	298	0.2	0.72	[307]
3	4A Binder-free zeolite	313	1	3.85	[308]
4	Zeolite 13X	298	5	3.2	[309]
5	ZIF-8	298	1	0.67	[310]
6	Merlinoite zeolite	298	0.1	3.5	[311]
7	HKUST-1	298	1	4.1	[312]
8	Fe-BTT MOF	298	1	3.1	[313]
9	NH <sub>2</sub> -MIL-125	273	1	4.0	[314]
10	NH <sub>2</sub> -MIL-53	303	5	2.3	[315]
11	ZJNU-43 MOF	296	1	4.6	[316]
12	CPM-5 MOF	273	1	3.6	[317]
	TMOF-1	298	1	1.4	[318]
	dmen-Mg <sub>2</sub> (dobpdc)	313	1	4.3	[319]
13	Commercial AC	313	0.15	0.3	[320]
14	Modified AC	313	1	2.5	[17]
<b>Derived AC from:</b>					
15	Kenaf	298	1.03	2.086	[177]
16	Olive stone	298	3	2.53	[172]
17	Compost	313	2.5	2.6	[174]
18	Coconut shell	293	1.2	3.5	[196]
19	Oil tea shells	273	1	6.15	[197]
20	Almond shells	273	1	3.70	[151]
21	Agricultural waste	303	1.1	2.25	[204]
22	Wood sawdust and lignin	298	6	3.4	[175]
23	Peanut shells	273	1	5.25	[222]
24	Coffee grounds	273	1	4.9	[118]
25	Sugarcane bagasse	298	1	1.102	[270]
26	Tobacco wastes	273	1	3.6	[278]

### 3.3. Other biomass

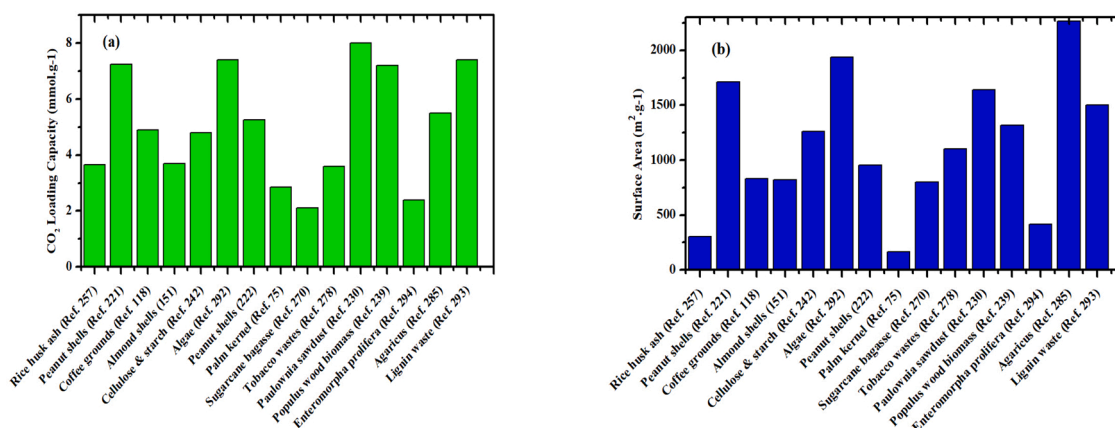
Despite its importance in the waste management not only for reducing waste dumping and burning in the environment, but it is also attractive economically roadmap to utilize an abundant source of biomass/biochar in the large-scale applications. In this way, carpet-waste adsorbents were developed for the first time by Olivares-Marin and Maroto-Valer [290]. On the grounds, different samples were employed by Olivares-Marin et al. [291] and activated chemically by KOH at the temperature range of 600–900 °C, at activating agent/char

mass ratio of 0.5–4. They concluded that all studied parameters had significant impact on the microporosity of the synthesized CO<sub>2</sub> adsorbents.

The mixture of algae and glucose was also evaluated as the precursor of AC by Sevilla et al. [292]. The highest CO<sub>2</sub> capture capacity of synthesized adsorbents reported 7.4 mmol.g<sup>-1</sup> at 0 °C and 1 bar. They observed that amines solution had a significant impact on CO<sub>2</sub> capture in the structure of microporous CO<sub>2</sub> adsorbents, unlike the pyridinic-N, pyridonic/pyrrolic-N and quaternary-N. In another study, KOH activation of hydrothermally carbonized lignin waste at KOH/carbon mass ratio of 2 was employed by Sangchoon and Mokaya [293] to adsorb CO<sub>2</sub> up to 7.4 mmol.g<sup>-1</sup> at 0 °C and 1 bar. In another study, a sustainable way to produce N-doped porous carbon was developed by Zhang et al. [294]. They employed an ocean pollutant, *Enteromorpha prolifera*, as the precursor to develop adsorbent via hydrothermal carbonization and activation by KOH. The samples were collected from the JiaoNan coastal district in Qingdao, China. The CO<sub>2</sub> adsorption experiments were implemented at the temperature range of 0–75 °C and the highest CO<sub>2</sub> uptake was 2.386 mmol.g<sup>-1</sup> at 0 °C and 1 bar.

Fly ash is generally produced from the fuel gases of power plants, while is not technically classified as a bio-based carbon sample, but is still one of the abundant solid wastes. It is reported, over 160 million tons of fly ash is annually produced in China, and more than 500 million tons in worldwide [295,296]. This carbonaceous material waste can cause significant problems for soil and water [295,296]. Recently, fly ash has attracted a notable attention as a carbon based adsorbent also in porous silica-based materials [297,298]. Gray et al. [299] considered fly ash enriched by amine for the gas adsorption purposes. Maroto-Valer et al. [300] tried to develop activated carbon from fly ash with high surface area for CO<sub>2</sub> capture. To this end, raw sample was activated by steam at 850 °C, which led to an adsorbent with higher surface area of 1075 m<sup>2</sup>.g<sup>-1</sup>. Pelletizing of amine-enriched carbon-based fly ash in the structure of poly (vinyl chloride) (PVC) was the aim of other study conducted by Wilfong et al. [301]. They developed a rigid pellet of PVC/FA/sorbet network, which the most efficient combination of the pellet components adsorbed 1.33 mmol CO<sub>2</sub>.g<sup>-1</sup> at 55 °C (20 %wt of FA; PVC with molecular weight of 62,000 g.mol<sup>-1</sup>), also it was accessible to enhance the maximum CO<sub>2</sub> loading to 1.87 mmol.g<sup>-1</sup> by PVC<sub>62</sub> replacement with PVC<sub>43</sub> at the same temperature. The effect of moisture on the adsorption capacity of derived samples from fly ash was illustrated by Siriruang et al. [302]. They found that the maximum CO<sub>2</sub> uptake was 3.75 μmol.g<sup>-1</sup> at 30 °C, 1 atm, and 10 wt% moisture contents.

A summary of biomass/biochar carbon based-adsorbents and their main specifications as prospects for future cyclic adsorption studies is represented in Table 5. Also, a comparison between the CO<sub>2</sub> uptake capacity of some of recent derived AC from biomass/biochar and other



**Fig. 9.** A comparison between (a) CO<sub>2</sub> loading capacity and (b) surface area of some of the prevalent biomass/biochar carbon materials.



developed adsorbents is illustrated in Table 6. In addition, CO<sub>2</sub> loading capacity and surface area of some of the most prevalent biomass/biochar carbon materials are depicted in Fig. 9.

#### 4. Future challenges

The rising level of GHGs derived from anthropogenic activities has emerged as main challenge of mankind in the current century. Accordingly, numerous efforts have been made for developing novel technologies and policy making to avoid an environmental calamity. One of the recent technologies, which has showed promising results, is the adsorption technology with solid materials. The obtained advances in this way can be classified in two main categories including (I) material science by the discovery of the new materials, also (II) engineering aspects to find more efficient ways for sample regeneration. To this end, in this work, a holistic review was presented on the potential of biomass/biochar carbon materials as a source of adsorbent for carbon capture and sequestration in the bench/pilot scales applications. While, in the previous sections, detailed descriptions of this study have been represented in depth, but here, some other challenges are introduced, which can be considered for the future directions.

- The number of possible “steps” in the cyclic adsorption processes is one of the key parameters to design a highly efficient adsorption process, while it does not have a broad range, accordingly, developing an algorithm for automatic generation of PSA cycles and tuning the various steps can be so helpful in this area [321].
- From the literature, employing bio-based carbon samples in the VSA process for CO<sub>2</sub> capture is a novel topic, which requires more efforts, as well as, some necessities to improve the energy consumption for VSA developing.
- Regarding the progress of different machine learning approaches in the various areas [322–324], employing machine learning in developing the adsorption process is the other challenge, which can be considered as a tremendous asset for future efforts.
- Tunable properties and tailored surface chemistry of activated carbons, also developing functionalized biohybrid samples using inorganic and organic nanostructures (e.g. metals, metal nitrides, metal oxides and/or amines) are prospects that have a great potential to open the new windows.
- The development of highly effective CO<sub>2</sub> capture in the post-combustion operating conditions (e.g. flue gases of refineries, petrochemical complexes and power plants) and pre-combustion processes (e.g. biogas upgrading) requires a detailed design of processes in the adsorption/desorption cycles to optimize the energy consumption. Furthermore, the characteristics of adsorbents, the cost of modified chemicals and treatment procedures are the other criteria, which is essential to be considered in developing a productive adsorption process. Accordingly, the assessment of mentioned factors requires to be considered, simultaneously, using novel topologies such as life cycle assessment (LCA) and response surface methodology (RSM) for a successful process design.
- In recent years, the power sector has shown a growing reliance on natural gas, which this rapid worldwide growth of natural gas consumption has contributed to enhanced CO<sub>2</sub> emissions from gas-fired power plants [12]. However, despite the extensive investigation on finding novel sorbents for carbon capture and storage, few researches have devoted to address the unique challenges of CCS from natural gas-fired power plants [12]. In this way, regarding the vast variety of biomass/biochar carbon-based adsorbents, this area can be an interesting one for next endeavors.
- As already extensively discussed in Section-3, there is a broad range of biomass/biochar samples, which have not yet been investigated by the cyclic adsorption processes, including: wooden wastes (e.g. peanut shells waste, Argan fruit shells, palm kernel shells, Paulownia, Poplar anthers, Populus, eucalyptus camaldulensis and,

residual wooden wastes) and agricultural wastes (e.g. coffee ground, rice wastes, sugarcane bagasse, corn cobs, tobacco wastes, eggshell wastes, Agaricus, Mesua ferrea L. seed cake, soybean oil cake). Accordingly, these biomass samples can be considered as promising prospects for future directions.

#### 5. Conclusion

Solid adsorption has been introduced as an economical and environmental friendly technique for gas separation and storage, which is considered as an interesting strategy for last goal of CCS to cut down the CO<sub>2</sub> emissions. To this end, different classes of adsorbents including MOFs, zeolites, silica, lithium zirconate, etc., have been investigated for CO<sub>2</sub> capture purposes, which the cost and sophisticated synthesis of these sorbents for large scale applications still remain as main challenges. Among different classes of sorbents, activated carbons (ACs) due to abundant sources, hydrophobic character, and lower heat of adsorption are considered as an excellent candidate for pilot scale utilizations. In this way, developing low-cost sorbents from plentiful sustainable sources of biomass/biochar has attracted a significant attention for gas sequestration and storage. To this end, in the recent decades, numerous researches have devoted to synthesis, characterization, activation and modification of derived activated carbons from bio-based carbon materials. Routinely, most of the reported studies in the literature evaluated the uptake capacity of prepared samples in the milligrams scale and ideal operating conditions, while for the industrial scale, data acquisition is highly imperative in the bench scale or pilot scale. Commonly, cyclic adsorption processes including PSA, VSA, TSA, VPSA etc., are the main strategy to attain this purpose. Hence, this study presented an up-to-date review of accomplished studies on developed cyclic adsorption processes employing different sources of biomass as a source of adsorbent for gas separation and storage. Also, the potential of biomass/biochar samples, which have already been proved as promising carbon precursors for gas adsorption, but have not been studied in the bench/pilot scales so far, were introduced for future studies. It was revealed, employing the sustainable sources of carbon materials can be a viable option in the way of “Net-Zero Emissions” for industrial or related applications. The represented results showed physically and chemically activations significantly increase the textural properties of biomass samples including porosity, surface active sites and BET surface area, which results in activated carbons with uptake capacity in the range of commercial adsorbents. Also, the evaluation of developed cyclic adsorption processes for CO<sub>2</sub> capture as well as the low capital investment for synthesis of these sorbents nominate the derived activated carbon from sustainable sources as an attractive candidate for large scale applications.

#### 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.

#### Acknowledgments

This work was financially supported by project: POCI-01-0145-FEDER006984-Associate Laboratory LSRE-LCM funded by European Regional Development Fund (ERDF) through COMPETE2020, Programa Operacional Competitividade e Internacionalização (POCI), and by national funds through Foundation for Science and Technology (FCT, Portugal), also ERDF under Programme PT2020 to CIMO (UID/AGR/00690/2020). Furthermore, Mohsen Karimi recognizes a PhD research grant awarded by FCT under SFRH/BD/140550/2018.

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jcou.2022.101890>.

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