



An overview of the application of agricultural waste in CO₂ adsorption for environmental protection

Samaneh Ghanbarlou¹, Davood Kahforoushan¹, Hossein Abdollahi²✉, and Soroush Ziaei¹

¹Department of Chemical Engineering, Sahand University of Technology, Tabriz, Iran

²Department of Polymer Engineering, Urmia University, Urmia, Iran

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*Corresponding author:

H. Abdollahi

✉ h.abdollahi@urmia.ac.ir

Emissions of greenhouse gases, including carbon dioxide, have an adverse effect on the environment. Therefore, many international researchers are concerned about the use of fossil fuels. So, to prevent further irreversible climate change, it is necessary to reduce the temperature and CO₂ emissions by 2050. For this purpose, agricultural wastes are very effective and economical sources as one of the methods of CO₂ capture. The main objective of this research was to investigate the role of agricultural wastes in carbon dioxide capture and the factors affecting their performance with the aim of protecting the environment. The present research is of the type of applied research and analytical-descriptive in terms of research method. The findings showed that agricultural wastes (biomass) like bamboo wastes, olive stones, peanut shells, walnut shells, sugarcane bagasse, cottonwood, rice straw, coffee grounds are effective in CO₂ capturing. they are also inexpensive and non-toxic, and show an adsorption capacity of up to 21 mmol/g and a surface area of up to 3900 m²/g. while petroleum or coal-based adsorbents have an adsorption capacity of about 160-900 mg/g and a surface area between 850-3800 m²/g.

Highlights

- Agricultural waste enables eco-friendly CO₂ capture.
- Biomass adsorbents show high capacity (21 mmol/g).
- Surface modification enhances CO₂ selectivity.
- Waste valorization reduces pollution and costs.
- Global agricultural residues support carbon capture.



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1. Introduction

The global need for energy has increased due to the rapid growth of industries. It is expected to double its current levels by 2050 (Leung et al., 2014). Hence, the use of conventional fossil fuels, including coal, petroleum, and natural gas has expanded, so that the origin is about 85% of the total energy of the universe (He et al., 2021). International researchers are concerned about the increasing use of fossil fuels due to their negative impact on the environment, resulting in the emission of greenhouse gases, including carbon dioxide (CO₂) (Oliever

et al., 1994). Cement, Iron and steel factories, oil refinery, Fossil-fuel power plants, and other industrial factories are the main sources of greenhouse gas emissions, with CO₂ being the primary greenhouse gas, with 30 Bt emitted annually (He et al., 2021). Without climate change policies, it is estimated that greenhouse gas emissions will increase by 25-90% by 2030, and atmospheric CO₂ concentrations will reach 600-1550 ppm (Nebojsa et al., 2000).

To prevent the destructive and irreversible effects of climate change, temperature increases must be reduced and CO₂

Fig. 1 graphically shows the vocabulary of keywords related to the research, which has a lot of connections and relationships. The number of articles collected for this research was more than 200 domestic and foreign articles, while only 102 of them were directly used in this research. The articles were studied and reviewed in the adsorption process and its mechanism, the characteristics of efficient adsorbents and the reason for using agricultural waste as adsorbents and its advantages, methods of agricultural-based composites, operating conditions for using each type of these wastes and their properties and performance.

3. Results and Discussion

3.1 Adsorption process and its mechanism

There are technologies for separating CO₂ from the flue gas stream, including wet scrubbers, regenerable dry adsorbents, temperature and pressure swing absorption, chemical looping, membranes, and cryogenic distillation (Leung et al., 2014).

Adsorption is one of the CO₂ removal methods that has been studied more than other methods due to its recyclability, energy saving, high stability, corrosion resistance, and industrial scale applicability (Ouyang et al., 2018).

In adsorption, unlike absorption processes that use liquid absorbents, solid adsorbents are used to bind CO₂ on their surfaces. High specific surface area, high selectivity, and high regenerability are among the main criteria for selecting the type of adsorbent. Common adsorbents include: molecular sieves, activated carbon, zeolites, graphene, carbon nanotubes, calcium oxides, lithium zirconate, and hydrotalcite-like materials (HTCs) (Leung et al., 2014) and mesoporous silica materials such as MCM-41 (Chen et al., 2023), and SBA-15 (Sanz et al., 2013), Metal-organic frameworks (MOFs) (Chand et al., 2020) and zeolitic imidazolate frameworks (ZIFs) (Abraha et al., 2023), and aminated graphite oxide (AGO) composites (Zhang, Y. et al., 2018).

Adsorption is a mass transfer process in which a substance is transferred from one phase to another (Lewis et al., 1924). According to the different attraction forces between materials, they can be divided into chemical adsorption and physical adsorption. In adsorption, some components of the fluid are transferred to the surface of a solid surface adsorbent, which is a porous solid with a lot of pores, which means that we do not only have a surface, but also porosity, and the higher the porosity, the greater the adsorption capacity. In Fig. 2, the surface adsorption process is depicted. Pollutants accumulate on the surface of the adsorbent due to physical forces such as van der Waals forces, hydrogen bonding, hydrophobic interactions, polarity, and steric forces. Dipole-dipole interactions and π - π interactions in chemistry also produce adsorption effects (Lyubchik, 2013; McCabe et al., 2018; Saleh, 2021).

Adsorption can be used for decolorization, degassing, detoxification, deodorization, concentration, purification, separation, and in many other fields (Shi et al., 2022; Crini et al., 2019). The adsorbed CO₂ gas can be stored underground and used in the food industry for carbonated beverages, injection into oil wells to compensate for pressure drops and increase oil recovery, cooling food such as meat and fruit (as

dry ice), extinguishing fires, especially fires caused by electricity and liquid flammable materials, etc. (Alie, 2004; Herzog et al., 1997).

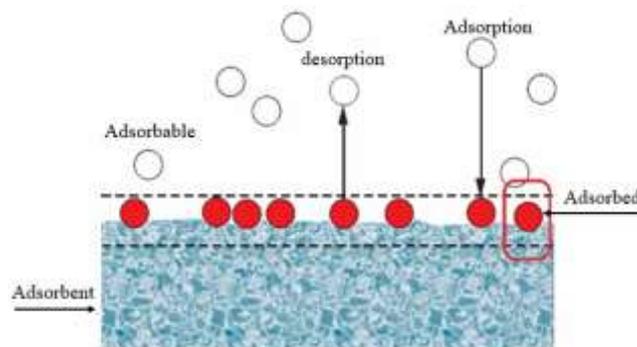


Fig. 2 A description of the surface adsorption process

The three main types of CO₂ capture processes are: Post-combustion capture process, this process removes CO₂ from the flue gas after combustion (Demessence et al., 2009; Leung et al., 2014; Wall, 2007), pre-combustion absorption process in which fuel, usually coal or natural gas, is treated before combustion (Leung et al., 2014; Metz et al., 2005; Olajire, 2010) and the adsorption process in oxy-fuel combustion, where oxygen is used instead of air (Leung et al., 2014).

There are several challenges to the application of adsorption at an industrial and real-world level. Although the advantages of adsorbents over other methods are obvious, their economic feasibility is primarily a matter of consideration, and their feasibility must be examined in terms of raw materials, recyclability, adsorption capacity, corrosion resistance, thermal and chemical stability, maintenance cost, etc

3.2 Characteristics of CO₂ adsorbents and surface properties

Since the adsorption performance is mainly determined by the adsorbate-adsorbent interactions, accurate theoretical prediction of thermodynamic and physicochemical properties is very important for the design of new adsorbent materials as well as understanding the adsorption mechanisms (Kwon et al., 2017).

The design and size of the pores play an important role in the CO₂ adsorption process, for example, to achieve efficient adsorption, the adsorbent must have a large volume and surface area of fine pores (<0.5-0.7 nm). The large volume and surface area of these smaller pores, compared to micropores (0.7-2 nm) or mesopores (42 nm), increases the adsorption potential (Kumar, S. et al., 2020).

Regarding the physicochemical requirements of an adsorbent, it can be said that an efficient adsorbent must have basic characteristics such as low cost of raw materials, low heat capacity, fast adsorption kinetics, high adsorption capacity, recyclability, low energy consumption, high CO₂ selectivity, and good thermal, chemical, and mechanical stability in the process (Choi et al., 2009; Pérez-Ramírez et al., 2008).

Surface characteristics, tunable textural properties, high adsorption affinity for CO₂, rapid adsorption, low cost, easy recovery, and the importance of waste resources have led to a wide range of studies in this field. The characteristics of some

agricultural wastes suitable for CO₂ adsorption, which make them effective for adsorption and increase their adsorption capacity, include: high porosity and micropore volume, higher surface area, higher volume, surface chemistry, etc.

In addition to the textural properties, numerous studies have confirmed the significance of surface chemistry in CO₂ adsorption capacity. Given the acidic nature of CO₂, modifying activated carbon surfaces by removing/neutralizing acidic groups or replacing them with suitable basic groups is a common approach to enhance carbon adsorption capacity. Heteroatom doping (e.g., CO₂, N, B, P, S, and O) plays a crucial role in CO₂ adsorption. Adding nitrogen-containing functional groups on the carbon surface is the most common type of functionalization due to improved electrical conductivity, reduced oxidation, and enhanced surface properties like surface polarity and basic sites (Rouzitalab et al., 2020; Xing et al., 2012).

To achieve this goal, the use of amine-based polymers is under intensive investigation. In this context, Vergase and Karanikolos examined and compared various polymers, including polyethyleneimine (PEI), polypropyleneimine (PPI), polyallylamine (PAA), polyaniline, amino dendrimers, and hyperbranched polyamines for surface modification. Most research efforts focus on PEI-based systems due to their high amine density, primary amine chain ends, availability, relatively low cost, and sufficient thermal stability up to 90 °C. Additionally, PEI is compatible with a wide range of supports, such as silica materials (SBA-15, MCM-41, fumed silica, precipitated silica, mesoporous silica foam, silica gel, and other silica materials), clays, carbon materials (graphene, CNTs, fullerenes, activated carbon, carbon spheres), aluminas, MOFs, zeolites, porous polymers, and especially biomasses (Varghese et al., 2020).

Other compounds, including metal oxides or polymeric compounds, are also used as surface modifiers for adsorbents. For instance, to alkalinize the surface of the base material, alkaline or alkaline earth metal oxides (Guo et al., 2020) silicates such as K₂CO₃ (Boonprasop et al., 2017; Hu et al., 2017), MgO, CaO (Sun, J. et al., 2019) and Li₄SiO₄ (Guo et al., 2020; Yang et al., 2018) have been used. Hidayu and Muda tested the adsorption of several metal oxides (BaO, MgO, CuO, CeO₂, TiO₂) on coconut and date palm shells, finding that CO₂ adsorption, regardless of the adsorbent, depends on surface area, surface modifier, and pore structure (Hidayu et al., 2016).

However, calcium-based adsorbents experience a reduction in adsorption capacity over various adsorption/desorption cycles due to sintering and completely heterogeneous fluidization behavior caused by the intraparticle attraction forces compared to the particle weight. Therefore, thermally stable inert materials such as Al₂O₃, ZrO₂, CeO₂, MgO, Y₂O₃, MnO₂, La₂O₃, TiO₂, CuO, Nd₂O₃, especially Al₂O₃, which has both low cost and high thermal stability, are used to reduce the sintering effect (Azimi et al., 2019).

Biomass-based materials possess specific characteristics that pose challenges for life cycle assessment (LCA), reuse, recycling, or energy/material recovery (Nishikawa et al., 2018). The comprehensive properties of these materials have recently attracted significant scientific attention; however,

most of these advanced techniques only evaluate materials before use. Consequently, many researchers have focused their efforts on improving new bio-adsorbents without understanding the potential wash-out effects and the entire lifecycle, which may adversely impact material applications.

3.3 Performance of Biomass-Based Adsorbents

Recently, inexpensive agricultural waste (biomass waste) such as bamboo waste, olive stones, peanut shells, walnut shells, sugarcane bagasse, cork, coffee grounds, and others have been used for CO₂ adsorption. Table 1 shows the adsorption performance of some of these biomass wastes (Ochedi et al., 2020).

Each of the adsorbents listed in the table can be prepared in either a single-step or two-step process. The single-step method involves the pyrolysis of a mixture of raw materials and an activator, while the two-step method employs carbonization and activation (Guo et al., 2020; He et al., 2021). The adsorption capacity depends on the type of material, pyrolysis conditions, and type of activator, which influence surface pore improvement (Ochedi et al., 2020).

One major issue with using adsorbents is their poor performance in terms of adsorption capacity and selectivity under low partial pressure conditions, which is exacerbated in the presence of moisture. Water can occupy active sites or jeopardize the stability of the adsorbent. To overcome these issues, functionalizing the adsorbent is crucial (Varghese et al., 2020).

Moreover, the nitrogen deficiency in biomass limits its use for adsorption, which must be enhanced through surface chemistry modification methods. On the other hand, the long-term stability and durability of these materials have not yet been determined. Additionally, waste materials may produce pollutants during the process, affecting adsorption. The safe disposal of used bio-adsorbents must also be considered.

3.4 Performance of Biomass-Based Adsorbents

The adsorption of CO₂ using various porous materials is rapidly advancing due to the use of inexpensive monomers, ease of preparation, and their diverse applications (Senthilkumaran et al., 2021).

Activated carbons are considered the most effective and useful adsorbents due to their large active surface area, well-developed porous structures, and good mechanical properties, which can result in high adsorption capacity (Arami-Niya et al., 2012; Sumathi et al., 2009). Additionally, activated carbon has extensive applications due to its chemical properties (such as surface groups) and physical properties (such as surface area and pore size) (Xie et al., 2014). Adsorbent materials can be made highly efficient, easy to use, and in some cases, even regenerable (Viswanathan et al., 2009). Agricultural waste such as jatropha, corn cob, coconut shell, oil palm fiber, sawdust, and date stone are of interest (Hidayu et al., 2016; Waribam et al., 2020).

Biomass-derived adsorbents show adsorption capacities of up to 21 mmol/g and surface areas of up to 3900 m²/g, whereas petroleum-based or coal-based adsorbents exhibit adsorption capacities of around 160-900 mg/g and surface areas between 850-3800 m²/g. Additionally, many methods for preparing

mesoporous materials require toxic and expensive agents. However, using biomass can alleviate these issues without reducing adsorbent performance. Particularly, considering the higher annual waste production and its prospects, waste

materials such as red mud, lime mud, tires, eggshells, slag, oil shale ash, paper waste, biomass tar, cement waste, sludge, and other industrial residues should be further considered (Ochedi et al., [2020](#)).

Table 1 CO₂ adsorption performance for adsorbents prepared from some of these biomass wastes.

Feedstock/Sorbent	Activating Agent/modification	Surface Area (m ² /g)	Pore Vol. (m ³ /g)	Temperature (°C)	Pressure (bar)	Adsorption Capacity (mmol/g)	Selectivity CO ₂ /N ₂	Ref.
Date Waste	KOH	2367	1.148	0	1	6.4	41.53	(Li, J. et al. 2019)
Garlic Peel	KOH	1262	0.7	25	1	4.22	-	(Huang, G. et al., 2019)
Waste Tea	ethylenediamine	11.80	0.4	30	1	108.97(mg/g)	-	(Rattanphan et al., 2020)
Coffee Grounds	α-Fe ₂ O ₃	375	0.2	0	1.2	1.68	-	(Kirbiyik, 2019)
Common Nettle	KOH	1581	0.761	0	1	4.22	-	(Szymańska et al., 2019)
Walnut Shell	H ₃ PO ₄	1512.6	74.65%	30	1	3.55	-	Asadi-Sangachini et al., 2019)
Lotus seed	KOH	2230	0.96	0	30	26.4	-	(Singh et al., 2019)
Chitosan mixture	N-HPC-xs	895	1.43	0	1	3.38	111.3	(Zhan et al., 2019)
Sunflower	KOH	3072	1.77	0	1	4.09	40	(Sun, H. et al., 2019)
Cypress Sawdust	H ₃ PO ₄ /HNO ₃	1134	0.95	0	1	2.8	469	(Zhang, S. et al., 2020)
Rice Husk	K ₂ CO ₃	1097	0.83	25	1	3.1	7.6	(Li, M. et al., 2019)
Food waste	CO ₂	830.3	0.49	25	1	4.36	-	(Opatokun et al., 2017)
Rice Straw	-	1	122.2	0	20	0.083	77(mg/g)	(Huang, Y. et al., 2015)
Coca Cola	KOH	1405	0.8	25	1	22.5	-	(Boyjoo et al., 2017)
Pine Cone Shell	KOH	3931	-	0	1	7.63	-	(Li, K. et al., 2016)
Sugar Cane Bagasse	TETA	-	-	25	1	5.01	-	(Luo et al., 2016)
Pomegranate Peels	KOH	585	0.28	0	1	4.52	15.1	(Serafin et al., 2017)
Bean Dreg	KOH	2792	-	25	1	4.2	5.3	(Xing et al., 2012)
Algae+Glucose	KOH	1300-2400	1.2	0	1	7.4	-	(Sevilla et al., 2012)
Chrysanthemum	ZnCl ₂	1840	1.16	25	1	3.8	-	(Du et al., 2017)
Olive Stone	CO ₂	1079	0.5	25	1	2.4	-	(Plaza et al., 2009)
Gelatin And Starch	KOH	1636	0.51	0	1	7.49	98	(Alabadi et al., 2015)
Soy Bean	ZnCl ₂ /CO ₂	811	0.33	30	0.15	0.93	-	(Thote et al., 2010)
Water Chestnut	KOH	3401	2.5	0	1	6	40.6	(Wei et al., 2018)
Palm Kernel Shell	CO ₂	367.8	0.2199	25	1	2.13	7	(Rashidi et al., 2017)
Eucalyptus	KOH	1260	0.62	25-0	1	4.8-6.6	5.4	(Sevilla et al., 2011)
Pea Nut	KOH	1383-761	0.2-0.1	0	1	5.33	16	(Idrees et al., 2018)
Peanut Shell	KOH	956	0.43	25	0.15	1.54	5.6	(Deng et al., 2015)

Cont....								
Feedstock/Sorbent	Activating Agent/modification	Surface Area (m ² /g)	Pore Vol. (m ³ /g)	Temperature (°C)	Pressure (bar)	Adsorption Capacity (mmol/g)	Selectivity CO ₂ /N ₂	Ref.
Cotton Stalk	NH ₃	627.15	0.25(ml/g)	20	1	99.42(mg/g)	-	(Zhang, X. et al., 2014)
Coconut Shell	Urea/K ₂ CO ₃	1082	0.39	0	1	5.12	56	(Yue et al., 2018)
Bamboo	KOH	2000	0.34	0	1	7	-	(Wei et al., 2012)
White Wood	KOH	1400	0.62	25	1	1.8 (mol/kg)	-	(Shahkarami et al., 2015)
African Palm Shell	KOH	1890	0.82	0	1	6.3	-	(Ello et al., 2013)
Almond Shell	CO ₂	1090	0.5	25	1	2.6	-	(Plaza et al., 2010)
Honeycomb	H ₃ PO ₄	1320	0.47	0	1	3.12	-	(Vargas et al., 2013)
Wheat Straw	-	20.20	0.041	25	1	34.4(mg/g)	-	(Xu et al., 2016)
Cotton Wood	-	367	0.39	25	1	71(mg/g)	-	(Creamer et al., 2016)

Many countries, including China, Indonesia, Nepal, Thailand, Malaysia, Japan, Nigeria, and the Philippines, use their crop residues to produce bioenergy and compost. Many researchers have worked on biomass pretreatment techniques for fuel conversion (Bhuvaneshwari et al., 2019; Kumar et al., 2009). In our country, various agricultural residues from the cultivation of grains and sugarcane, including husks, bran,

bagasse, and molasses, are also utilized. These residues are natural resources that traditionally contribute to soil sustainability and fertility through direct plowing or composting (Bhuvaneshwari et al., 2019; Hayashi et al., 2014; Monforti et al., 2013). Fig. 3 illustrates the annual production of various agricultural residues in our country and some other countries.

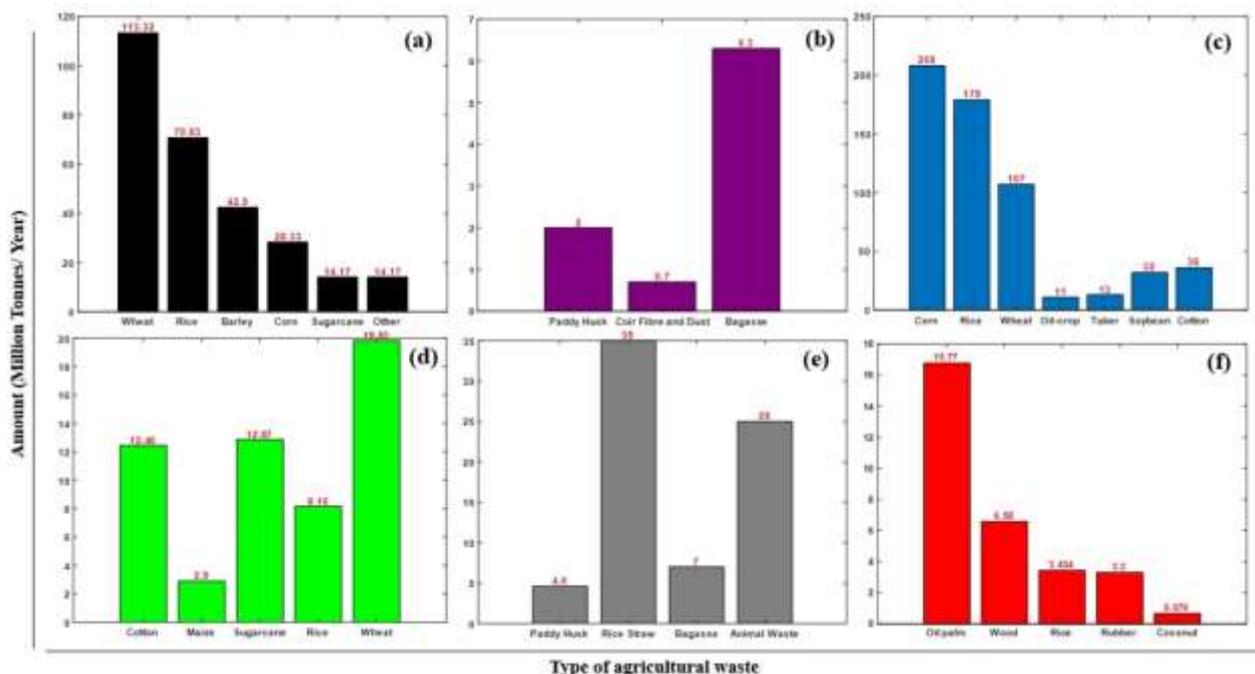


Fig. 3 Types of waste produced in the agricultural sector along with their production statistics: a) China, b) Sri Lanka, c) Iran, d) Malaysia, e) Thailand, and f) Pakistan (Hamda et al., 2023; Khouzani et al., 2022; Nagendran, 2011; Nath et al., 2023; Sahu et al., 2024).

There are several challenges for the application of bio-adsorption at the industrial and practical levels. Although the advantages of bio-adsorbents are evident, their economic feasibility is a primary concern, and currently, only a few bio-adsorbents are available on the market. The production costs

of bio-adsorbents include production, maintenance, raw materials, transportation, labor, and distribution expenses.

4. Conclusion

1. In adsorption, unlike absorption processes that use liquid adsorbents, solid adsorbents are used to bind CO₂ on their

surfaces. High specific surface area, high adsorption capacity, high selectivity, regenerability, fast kinetics, availability of raw materials, and low cost are the main criteria for selecting the type of adsorbent.

2. The development of adsorbent materials from agricultural residues not only addresses the disposal and management of agricultural waste but also plays an effective role in removing the greenhouse gas CO₂. Using waste instead of disposing of it in the environment helps reduce pollution and improve soil and water quality.

3. Bio-adsorbents show adsorption capacities of up to 21 mmol/g and surface areas up to 3900 m²/g, while petroleum-based or coal-based adsorbents exhibit adsorption capacities of around 160-900 mg/g and surface areas between 850-3800 m²/g.

4. Most methods for preparing mesoporous materials require toxic and expensive raw materials, but using biomass in the preparation of CO₂ adsorbents can address these issues without reducing adsorbent performance.

Other parameters in adsorption, such as kinetics, stability, regenerability, heat of adsorption, and selectivity, are also of great importance. The research community should expand systematic evaluation studies. Ultimately, it is important to establish a systematic database with information including (a) selection of raw materials (availability, properties, cost), (b) preparation methods and their effects, and physicochemical properties of adsorbents, (c) effects of other components of flue gas, (d) conditions for adsorbent regeneration, (e) disposal measures for used adsorbents, (f) cost analysis, and (g) environmental impacts of materials. Such a database will facilitate informed decision-making.

Suggestions for this area include: Firstly, researchers can examine different methods to optimize the process, such as studying chemical compositions. Additionally, the effects of various environmental conditions, such as temperature, humidity, and pH, on process efficiency should be investigated by researchers. Moreover, research can explore new methods such as using bacteria or plants to enhance the CO₂ adsorption capacity of agricultural residues. Using these methods can improve adsorption efficiency and reduce costs associated with adsorption processes. Finally, one of the most important aspects of future research is examining the application of agricultural residues on a larger scale.

Statements and Declarations

Data availability

This is a review study and no data were generated or analyzed.

Conflicts of interest

The author of this paper declared no conflict of interest regarding the authorship or publication of this paper.

Author contribution

S. Ghanbarloo: data collection, research, analysis of results, correction of writing errors, and revisions; D. Kahforoshan: assistance in the final version of the article; H. Abdollahi: research management, analysis of results, correction of writing errors, and methodology; and S. Ziaei: drawing figures and data analysis.

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