# Bio-based Sustainable Aerogels for $CO_2$ Capture: Opportunities and Outlook

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## Abstract

Bio-based aerogels with customizable porosities and functionalities constitute significant potential for $CO_2$ capture. Developing bio-based aerogels from different polysaccharides and proteins is a safe, economical, and environmentally sustainable approach. Polysaccharides are biodegradable, sustainable, renewable, and plentiful in nature. Because of these advantages, the use of bio-based aerogels with porosity and amine functionality has attracted considerable interest. In this review we have discussed the recent development in the synthesis of bio-based aerogels and their application in $CO_2$ capture.

**Keywords:** Bio-based aerogel, polysaccharide, synthesis, drying and $CO_2$ adsorption

## Introduction

Bio-based aerogels are typically made from sustainable materials, like proteins, starch, sugar cane and vegetable oils etc. Besides, biopolymers (like cellulose, alginate, chitosan, lignin, pectin, etc.) have also been used effectively for bio-based aerogel preparation (1). Thanks to their special properties, including biocompatibility, durability, low toxicity and renewability, bio-based aerogels can become the key component in novel functional materials and utilized for different applications (**Figure 1**)(2).

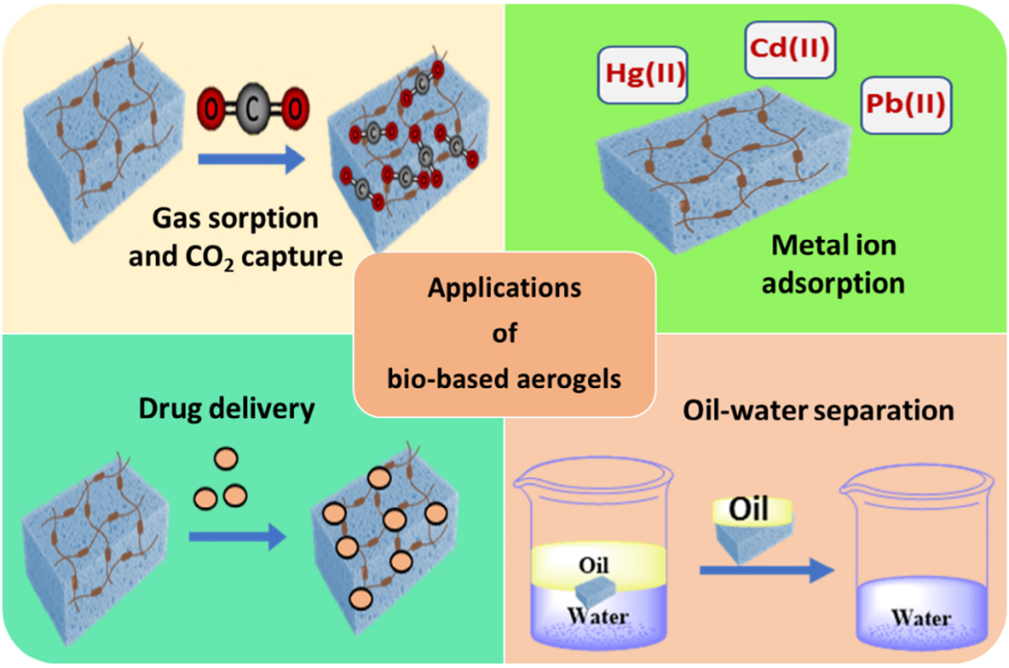



**Figure 1. Applications of aerogels in different fields.**

The functional biocompatibility, reusability, high porosity and environmentally friendly properties of bio-based aerogels can also be applied in air cleaning ($CO_2$ capture) as the carbon dioxide is one of the primary atmospheric greenhouse gas. Over the last centuries, massive burning of fossil fuels has significantly raised its pre-industrial carbon dioxide levels about 280 ppm to 413 ppm by today (Aug 2020) (3). According to an Intergovernmental Panel on Climate Change (IPCC) study, a large amount of carbon dioxide emissions is the key cause for current global temperature shifts and related issues, like ocean acidification and level rising, global warming, affecting human life or growth. Therefore, to deal with climate change, there is a desperate need to decrease the concentration of carbon dioxide and its emission (4).

While several reviews on the subject of preparation methods and different applications of aerogels have been published recently, this form of publications is advantageous considering the multitude of publications on these topics, yet there are very few papers on the applicability of bio-based aerogels for carbon dioxide capture. In this review article, we discuss recent literature and studies about the bio-based aerogel and synthesis of bio-based aerogels. Mainly, the application in the $CO_2$ capture by bio-based aerogels was discussed.

**Synthesis of bio-based aerogels**

The general procedure used for the synthesis of bio-based aerogels is represented in **Figure 2**. There are several examples where proteins and polysaccharides have been used for the preparation of bio-based aerogels (5,6). Specifically, the first step requires the dissolution of the proteins and polysaccharides in a specified solvent with continuously stirring for a particular time interval. Afterwards, utilizing either physical, enzymatic or chemical crosslinking agents, the wet gel (hydrogel) with a 3D structure can be prepared (7,8). The word "wet-gel (hydrogel)" is correlated with the 3D polymeric structure, which is capable of consuming and retaining a significant volume of solvent (9,10).

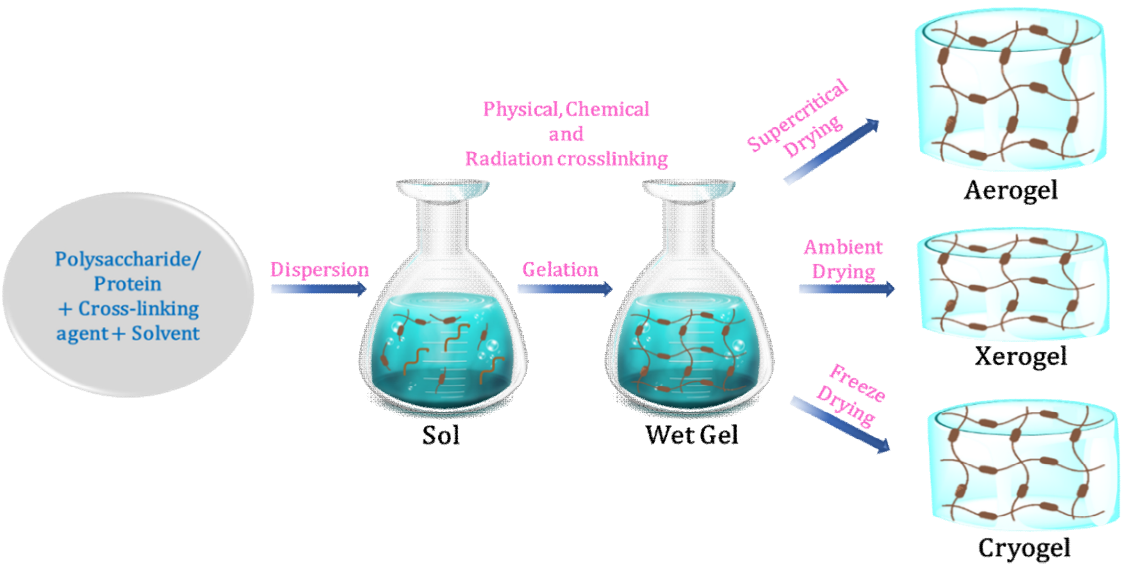



**Figure 2.** Schematic method for synthesizing the different bio-based aerogels. The distribution of pore size and surface morphology depends upon the drying process.

Going back to the procedure of bio-based aerogel formation occurs using a drying technique to transform the wet gel to aerogel. It's well established that the drying strategies primarily affects the porosity and surface area of the bio-based aerogels. In bio-based aerogel development, the final and the most important stage is the drying phase (7). Different drying techniques are used to prepare bio-based aerogels which are listed below: -

**Supercritical drying process**

In supercritical drying, fluid drying is done beyond the solvent critical point contained within the gel pores by putting the wet gel within the closed container. As there is no interface present in the vapour and liquid phase in this process, which contributes to the reduction of capillary stresses (11). Supercritical drying may preserve the structure of the gel and create products that have a higher surface region, smaller pore size and low shrinkage rate. By utilizing this process, pores and properties of the nano-meter scale are maintained. But in certain situations, leads to poor thermal conductivity than that of air.

Within the framework of using biopolymers for aerogel construction, which involves leveraging their maximum capacity, many studies have been conducted on preparation times and lower costs to promote aerogel output scale-ups (12). At the same period, many methods for simplifying the production processes have been suggested to reduce the price of aerogels. In this matter, supercritical dry was substituted by ambient pressure drying and freeze-drying as inexpensive and environment friendly techniques.

**The ambient pressure drying process**

It is a successful approach utilized for manufacturing speedup. This new technique plays the role of passivating the wet gels pore surface. During the drying of the samples, there is reduction in the probability of creation of new chemical bonds by passivation. However, the solvent filled in the pores is exchanged with the hydrocarbon and less surface tension solvent to resolve capillary stress produced on the pore walls (1,12). The approach to drying by this process is the easiest method which contributes to the preservation of the energy consumed by other techniques and contributes to preparing such aerogels. Although utilization of this method results in the creation of the solid substance (such as aerogel), which could have little porosity and significant shrinkage.

**Freeze drying process**

It is an incredibly simple, economically and environmentally sustainable drying process that can be used to create a highly spongy aerogel. In this process of drying, the liquid within the sample is solidifies and then transferred under very low pressure by a vacuum pump. Typically, this material is spongier than other aerogels collected by different drying methods. The freezing intensity plays a key role in the freeze-drying method and can change the consistency of pores(1). In the case of rapid freezing, small pore sizes aerogel will develop, while large pores are produced when freezing is slow. In this process, the solvent is chosen based on temperature (freezing) and the sublimation rate (12).

**Bio-based polymeric aerogels**

Aerogels from bio-based polymers are more versatile compared to conventional inorganic aerogels. Bio-based aerogels are primarily synthesized by sol-gel and drying methods (13). Aerogels have been made from a variety of biopolymers like cellulose, proteins, alginate, starch, chitosan etc. Out of this cellulose, aerogels exemplifies the largest class of bio-polymer aerogels because of wide density, mechanical properties, surface area and mesoporosity (**Figure 3**) (14). The majority of bio-based polymers are non-toxic and are often component of our daily diet. They are particularly appropriate for food and biomedical applications like injury treatment or the distribution of drugs (15).

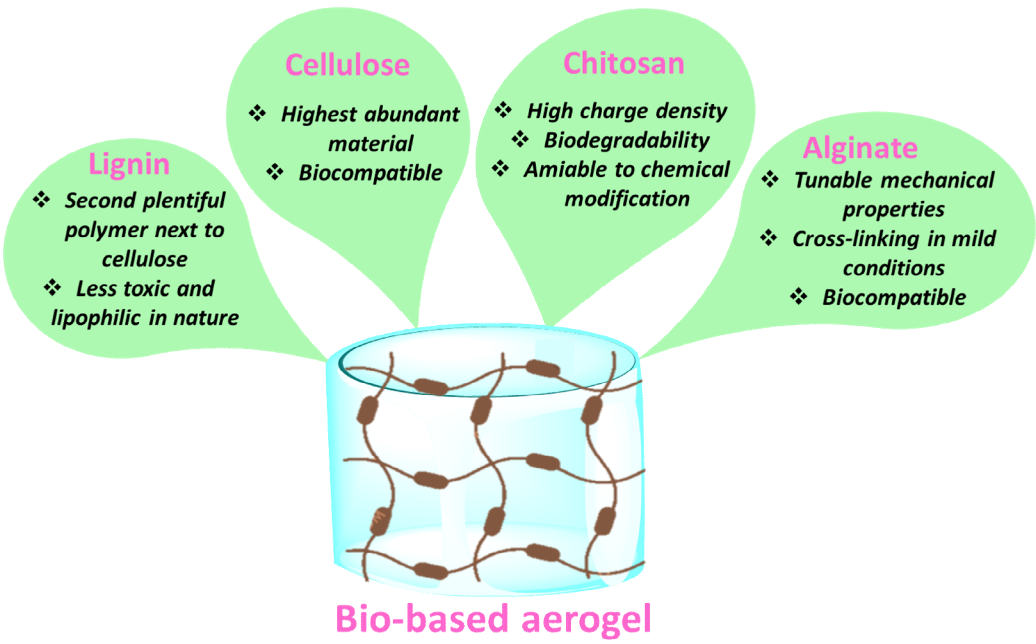



**Figure 3. Different bio-polymers are used for bio-based aerogel.**

After analysing literature, it has been found that many types of aerogels can be made by doing a little modification in the bio-polymers. All of these modifications can be adjusted by selecting suitable precursors and treating conditions (**Figure 4**). Compared to their counterpart components, suitable material combinations can demonstrate excellent characteristics and functionalities. Despite all these expanded activities, very few bio-based aerogels have been used for $CO_2$ adsorption and presented themselves with important research (16).


**Figure 4. Different types of aerogels and their properties.**

**$CO_2$ adsorption on bio-based aerogels**

A possible approach to tackle weather & environmental shifts is to reduce $CO_2$ pollution to the atmosphere as the central and primary greenhouse gas. The system for trapping $CO_2$ needs to be applied efficiently and on a very wide scale. New techniques focus at efficient removal of $CO_2$ from flue gas through isolation of membranes and scrubbing of liquid amines. Nonetheless, this flagship processing tolerates from numerous issues like processing, high plant machinery corrosion, oxidative deterioration of the aqueous amines, and a high potential for harmful by-product production during $CO_2$ capture (17).

Bio-Based aerogels are considered to be the new material for atmospheric $CO_2$ capture which is capable of minimizing the problems with the above-listed technologies. For enhancing the reactivity of bio-based aerogels against $CO_2$ capturing, one effective approach is to trap an amine moiety on the surface of biobased adsorbents (like alkanolamines). The plausible mechanism for adsorption of $CO_2$ on the amine-functionalized biobased aerogel is depicted in Figure **5**. It is understood that amine moieties have a good attraction to molecular $CO_2$. The $CO_2$ molecules combine with amine moieties in the appearance of humidity and give intermediates (carbamate). Ammonium carbamate production was found in the appearance of humidity by sorption of $CO_2$ and in case of dry $CO_2$ sorption less carbamic acids were produced. The amine-functionalized bio-based aerogel may be formed by attaching the active compounds to the surface of an adsorbent with amine moieties by forming both chemical and physical interactions(18).

$$CO_2 + RNH_2 + RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+$$

In this regard, Wang et al., developed aerogel based on cellulose-cross-linked polyethyleneimine, utilizing sol-gel technique with hydrolysis and cross-linking reaction (19). The surface area for prepared bio-based aerogel was 234.2 $m^2g^{-1}$ and the highest tendency of sorption was 2.31 mmol $g^{-1}$ (25°C) in dry $CO_2$ environment. The cellulose-cross-linked polyethyleneimine bio-based aerogel has been found to show significant carbon dioxide adsorption after ten reuse cycles. These finding had revealed that the prepared bio-based aerogel performs a significant role as dry carbon dioxide adsorption. Hsan et al. prepared the chitosan grafted graphene oxide aerogel for $CO_2$ adsorption and the BET surface area was 33.32 $m^2g^{-1}$(20). The highest adsorption was 0.257 mmol $g^{-1}$ at 24.85°C. Zhuo et al. developed cellulose-derived hierarchical porous carbon bio-based aerogel for carbon dioxide adsorption (21). The carbon aerogel triggered with $CO_2$ had a large target area of 1364 $m^2g^{-1}$. The hierarchical porous carbon aerogel derived by cellulose demonstrated a strong carbon dioxide adsorption potential of 3.42 mmol $g^{-1}$, which suggests the probability of utilizing prepared material for $CO_2$ adsorption.

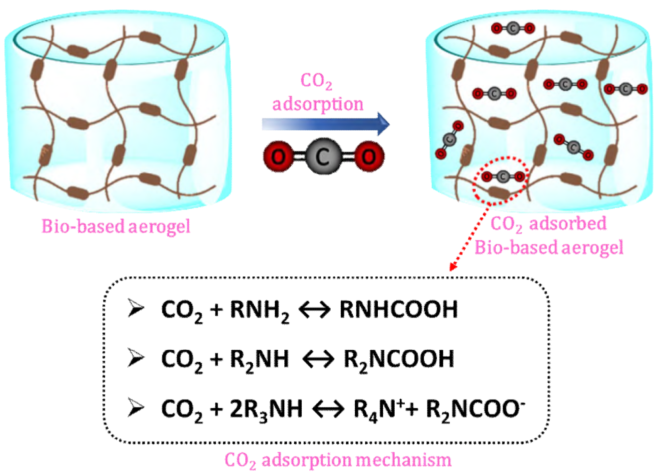



**Figure 5. Schematic depiction of $CO_2$ chemisorption on amine-modified bio-based aerogels.**

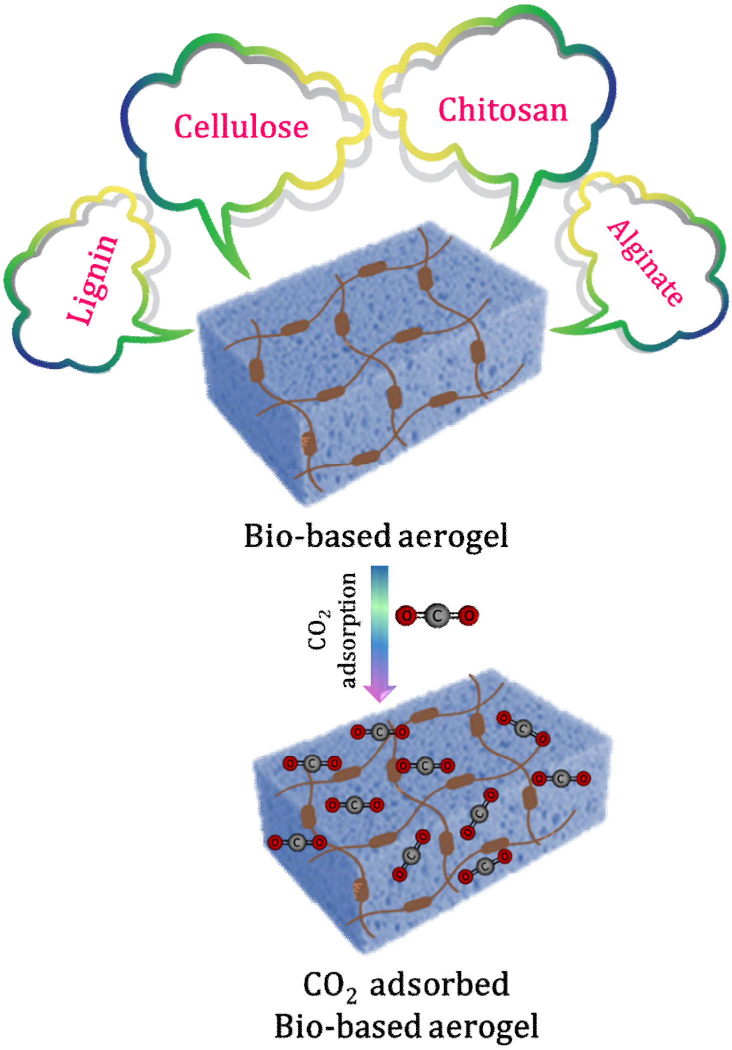
Additionally, cellulose nanofibril grafted with amino silane show good adsorption of $CO_2$ (1.91 mmol $g^{-1}$) (22). Montmorillonite-reinforced chitosan-polybenzoxazine nanocomposite biobased aerogel was synthesized by Alhwaige et al., and reported surface area 679 $m^2g^{-1}$(23). The maximum adsorption tendency for carbon dioxide was 5.72 mmol $g^{-1}$. The capture adsorbents require low water sorption as well as strong thermal regeneration capability to trap $CO_2$ at a large scale appropriate to industrial equipment.

| **Sr. No.** | **Biobased adsorbent** | **BET surface area ($m^2g^{-1}$)** | **Maximum $CO_2$ adsorption (mmol $g^{-1}$)** | **Adsorption temperature (°C)** | **References** |
|---|---|---|---|---|---|
| **1.** | Cellulose-crosslinked polyethyleneimine | 234.2 | 2.31 | 25 | (19) |
| **2.** | Chitosan grafted graphene oxide | 33.32 | 0.257 | 24.85 | (20) |
| **3.** | Cellulose-derived hierarchical porous carbon | 1364 | 3.42 | 24.85 | (21) |
| **4.** | Cellulose nanofibril grafted with aminosilane | 51.8 | 1.91 | 25 | (22) |
| **5.** | Montmorillonite-reinforced chitosan-polybenzoxazine nanocomposite | 679 | 5.72 | 25 | (23) |
| **6.** | Cellulose/silica composite | 154 | 3.68 | - | (24) |
| **7.** | Cellulose aerogels | 132.72-245.19 | 1.96-11.78 | Room temperature | (25) |

## Conclusion and future direction for research

It is essential that $CO_2$ adsorption on adsorbent materials at low temperatures can be extended to resolve energy and environmental-related challenges and have positive opportunities for economic growth and social impact. Sad to say, there is so far inadequate detail in the literature regarding these research areas. This study also addressed chemically-modified biobased adsorbents, which can be specifically utilized as adsorbents to absorb $CO_2$ at low temperature. Furthermore, bio-based (polysaccharides) aerogel provides strong opportunities for potential $CO_2$ adsorption applications. Nevertheless, the connection between the biopolymers' molecular structure and the amine moieties is still unpublished. Future work may rely on these structure-property connections to obtain influence at the molecular level over the properties of biopolymer-based amine moiety modified aerogels for the highly effective $CO_2$ adsorption.

**Graphical abstract**

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