SCIENTIFIC PAPER

ADVANCEMENTS IN PHYTOMASS-DERIVED ACTIVATED CARBON FOR APPLICATIONS IN ENERGY STORAGE SYSTEMS

Kalyani Palanichamy[1], Banuprabha Thakku Rangachari[2], Sridhar Jayavel[3,*], Aravind Dhandapani[4], and Varagunapandiyan Natarajan[5]

[1]Department of Chemistry, DDE, Madurai Kamaraj University, Madurai-625021, Tamil Nadu, India.

[2]Department of Chemistry, Mary Matha College of Arts and Science, Periyakulam, Tamil Nadu, India.

[3]Department of Biotechnology, DDE, Madurai Kamaraj University, Madurai-625021, Tamil Nadu, India.

[4]University Science Instrumentation Centre, Madurai Kamaraj University, Madurai-625021, Tamil Nadu, India

[5]Department of Chemical Engineering, King Khalid University, Abha, 61421, Saudi Arabia

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* **Corresponding author:** jsridharbiotech@mkuniversity.ac.in, Telephone:+91-452-2459185

Abstract

Phytomass i. e. plant biomass-derived active carbon is a versatile electrode material for energy devices owing to their natural and ubiquitous abundance, variety, ecocentrism and unique physical properties. This article intricately reviews the recent advancements in phytomass derived activated carbon (PAC), chiefly for the supercapacitor electrodes and notably, phytomass including different parts of the plants limited to, stem, leaf, flower, seed, fruit and root for deriving ACs bestowed with excellent electrochemical performance have been considered. Advancement in the preparation of AC from phytomass, important facts associated with synthesis, physical and electrochemical attributes have also been elaborated, which is expected to furnish a fruitful direction towards advocating supercapacitors – the green energy packs. Surface of PAC is usually decorated with organic functional moieties containing heteroatoms like O, &/or S/N (referred to as self-doped heteroatoms). The synergy of these heteroatoms in enhancing the pseudocapacitance of the PAC electrodes in supercapacitors has also been featured. Further, the review provokes insights on strategies, prominent challenges, prospects and imminent opportunities and hopeful trend in support of AC from various plant parts that may power our energy-based society, scientific industries and in establishing sustainable energy sector as well by harnessing Nature's potential.

Keywords: Activated Carbon, Phytomass, Heteroatoms, Supercapacitors, Self-doped heteroatoms, Circular bioeconomy

Highlights:

- Covers the cost effective methods for the production of activated carbon from agricultural wastes
- Highlights the market potentials of Phytomass derived Activated Carbon (PAC) in the energy sector
- Methods to enhance the performance of PAC electrodes on super capacitors are featured
- Discussed the need for sustainable bioeconomy

Introduction

The thinning of ozone layer, the rise in global temperatures and the depletion of natural resources apparently leads to significant environmental challenges to the highest degree and poses severe threat to the societal safety issues. In our current landscape, we witness a confluence of rapid wealth and energy expansion amidst the alarming rise in pollution levels, culminating in the decline of both public health and environmental well-being as well. The escalation in the utilization of fossil fuels and natural resources during industrial and post-industrial advancements might be the underlying causes for the aforementioned issues. Hence, we have been attempting hard to find substitute green avenues for generating less-polluting energy and accordingly many research institutions have come together in promoting renewable, green and clean energy technologies for replacing conventional energy resources. One alternative approach to address exponential growing demand of wealth and energy alongside increasing pollution and its detrimental effects on public and environmental health is the paradigm transition towards a “sustainable and circular bio-economy”. A circular bio-economy is sustainably designed to minimize waste, make the most of existing resources, and reduce environmental impacts. Thus, the hunt for eco-friendly and low-cost materials is becoming more evident for example, through the use of renewable resources.

In the array of alternative energy sources, biomass has evolved into an essential and integral component of ecosystems. As a result, biomass assumes a crucial role as a renewable energy source [1], holding substantial promise for the generation of biofuels used in transportation, electricity, and heating applications [2]. The significance of green energies and a closer focal point on biomass will be an instrument for the future energy security and sustainable development based on circular bio-economy. With the recent scientific discoveries and inventions exploiting this inexpensive, abundant and natural biomass, promising technologies have been developed and are proposed to be capable for generation of electricity, heat, and bio-based liquid fuels. Speaking of biomass, by definition, it refers to a blend of naturally occurring substances sourced from plants like shrubs, trees, algae, and crops, encompassing all materials with an organic matrix, excluding plastics and similar products derived from petrochemicals and fossil materials [3].The most important categories of the sources of biomass are [4];

1. Residues from agriculture and forestry

2. Residues from animals

3. Algal biomass

4. Crops grown in aquatic environments

5. Municipal solid waste (excluding metals and plastics)

6. Residues from waste streams (excluding metals and plastics)

According to reports, the global biomass reserves for land and aquatic ecosystems are estimated at approximately 1.8 trillion tons and 4 billion tons, respectively. The total biomass in the world, particularly in energy viewpoint has a prospective production capability of 33,000 EJ; corresponding to more than 80 times the annual energy utilization in the world [5]. So, the biomass has attracted many researchers to use it as an alternative energy resource.

Nevertheless, as we witness in the modern age of renewable and sustainable energy, the quest for green alternatives to conventional power sources is more pressing than ever. As the world grapples with environmental challenges and seeks to reduce its carbon footprint, innovative technologies are emerging. One such technology revolves around super capacitors, devices with the potential to revolutionize energy storage. These super capacitors, often seen as the missing link in the transition to clean energy, rely on advanced materials. One promising avenue involves harnessing the potential of phytomass derived activated carbon, a natural resource that presents a sustainable and environmentally friendly solution. Hence, the present review on phytomass plant biomass-derived activated carbon for supercapacitor applications is motivated by several unique aspects of the plants used and their potential contributions to energy storage technologies, as mentioned below.

1. Novelty of materials: The paper highlights the use of underutilized plant materials as sources for activated carbon. These materials are not traditionally recognized for their potential in energy applications, making the study significant in exploring new biomass resources.

2. Sustainability: The focus on phytomass aligns with the growing interest in sustainable energy solutions. Utilizing waste plant materials for activated carbon production supports a circular bioeconomy, reducing reliance on fossil fuels and synthetic materials.

3. Performance Metrics: The review can emphasize the electrochemical performance of many plant derived activated carbons, which demonstrated impressive capacitance values. This performance showcases the viability of these materials for supercapacitor applications.
4. Suggest potential improvements, such as scaling up production, enhancing surface functionality, or combining with other materials to create hybrid supercapacitors.
5. Environmental Impact: By promoting the use of waste phytomass, the research contributes to environmentally friendly practices in energy storage. The synthesis processes are typically less energy-intensive and do not involve harsh chemicals, making them more sustainable compared to conventional carbon sources.

Uniqueness of plants with reference to supercapacitors

1. Chemical composition: The unique chemical makeup of the selected plants contributes to the formation of activated carbon with desirable properties. The presence of lignin and cellulose in these plants enhances the structural integrity and porosity of the resulting carbon.

2. Morphological characteristics: The natural morphology of the leaves aids in creating a hierarchical porous structure during activation, which is crucial for maximizing surface area and improving ion transport in supercapacitors.

3. Abundance, accessibility and sustainable future: Plants are widely available, which means their use as carbon sources can help in waste reduction and provide a low-cost alternative for activated carbon production.

Thus, the review aims to communicate the innovative use of phytomass for activated carbon production, highlighting its sustainability, performance, and the unique characteristics of the plants involved. This can drive further research and innovation in the field of supercapacitors, promoting the development of eco-friendly energy storage solutionsand its role in advancing the green energy agenda.

Having put forth the context of biomass-based energy sources, the authors of this comprehensive review have organized the current knowledge on the topic for the convenience of readers interested in energy matters under the following sub-topics.

- Applications of carbon
- Classification of biomass

- Biomass as a sustainable source for AC
- Preparation of AC from biomass waste materials
- Key factors for enhancing capacitance with plant-derived materials
- Impact of physical characteristics of plants derived activated carbons on the key metrics of the supercapacitors
- State-of-the-art and prospects of PAC as electrode materials in super capacitors
- State-of-the-art and prospects of PAC as electrode materials in super capacitors
- Impact of self-doped heteroatoms on the specific capacitance/pseudo capacitance of biomass-based AC
- Summary, perspectives and future challenges
- Future outlook on the plant-based activated carbon materials for future energy storage devices

This review encompasses the latest insights and findings from open literature over a 15-year period, offering an in-depth exploration of the significance and promising prospects associated with phytomass-derived activated carbon (PAC) as a sustainable and effective material for super capacitor electrodes.

Turning to the focal point of the present review article, it is interesting to note that the abundance of phytomass resources and the environmentally-friendly activation processes make it an attractive alternative to conventional carbon sources in diverse fields and simultaneously, their unique porous structure and high surface area offer excellent charge storage capabilities, paving the way for advanced energy storage solutions. Thus, waste phytomass should be viewed as unmapped zero-cost capitals of essential environmental services and not as garbage at all.

Applications of carbon

Carbon materials have been playing key roles for human beings: say for instance, since pre-historical age, charcoal is used as a source of heat and as adsorbent/scavenger, as soot in black ink, natural graphite powder as pencil leads, graphite electrodes for many electrical based devices and chemical production, for the development of communication techniques, carbon blacks for reinforcing tires, conductive carbon rods/inks / powders and carbon blacks for supporting the improvement of primary batteries, thin graphite flakes in membrane switches for making control panels and computers, an admixture of graphite and fluorine has been used for enhancing the performance of primary batteries.

Classification of biomass

Biomass can be categorized based on its diversity, quantity, and compositional characteristics, depending on the intended purpose and scope only, as there are no theoretical and practical ways of classifying the same. Also, according to the origin, function and final products, generally biomass is categorized into two groups:

1. Based on the ecological classifications or the specific vegetation types present in nature
2. Based on the use and purpose of biomass (e. g., as feedstock and derived carbon)

Category (1) is the most adopted classification, which consequently splits biomass as;

1. Woody biomass and timber resources
2. Herbaceous plant biomass
3. Biomass derived from aquatic ecosystems
4. Biomass from animal and human waste sources
5. Mixtures of various biomass components

Classification of biomass into groups, varieties and species are given in Table 1[6]. **(Table 1).**

Biomass as a renewable source for AC

Presently, biomass is the major energy resource in the globe (the role of biomass is about 70%) which provides world's overall energy and energy in just beginning countries demand [7]. Subsequently, abundant agricultural discards/wastes/refuse would also be generated. As such these wastes might have no trade and industry value and would only present discarding problems. Burning of biomass wastes contribute tremendously to environmental pollution, and thus lead to polluted air, water and land. This process also releases large amount of CO_2 (together with dust particles) in the atmosphere, the main contributor of the global warming. But alternative and astute thinking has offered a scientific solution to consume these secondary, inexpensive and renewable sources for conversion into a valued-added product namely AC for countless applications. Hence, harnessing these cost-free waste materials is anticipated to be an efficient process, wherein their transformation into activated carbon (AC) not only adds economic value but also aids in cutting waste disposal expenses. Significantly, this approach offers a potentially economical and environmentally friendly substitute for the current high-cost commercial AC powders. It is noteworthy that the utilization of biomass wastes as raw material (precursor) for AC production has witnessed an uptick in recent years, driven by the aforementioned considerations regarding AC. The selection of biomass resources for carbon production is guided by their cost, availability and

their potential to be renewed into extremely porous carbon powders through carbonization for diverse and appealing applications.

Various types of biomass materials are being used as the preparatory materials in producing AC powders. It is interesting to note that the chemical composition of biomass includes cellulose, hemicellulose (includes galactans, mannans, xylans and arabinogalactans), lignin, starch (includes amylopectin and amylase), minor organic components, inorganic matters, fluid matters and elements such as Ca, Mg, K, Na, N, Cl, S and P [8], which may sometimes be present in a highly modified form in the surface of the AC produced.

The agricultural by-products consist of main extent of cellulose and hemicellulose, while the rest includes ash, lignin and nitrogenous compounds [9] and these residues can be an excellent source of energy. ACs are much cheaper than the metal oxides and conducting polymers for Science and Industrial applications and they have much larger specific surface area than the others. In recent times, there has been a growing fascination with the fabrication and manipulation of diverse nanostructured carbon materials, particularly for potential applications like super capacitors. Presently, cellulose materials sourced from forestry, agricultural, and agro-industrial residues are gaining attention due to their ready availability and rich content. These cellulose-based wastes accumulate in significant quantities annually, typically managed through environmentally harmful methods such as burning or landfill disposal. However, transforming them into high-value products like activated carbon (AC) is increasingly regarded as the preferable and environmentally conscious alternative.

Plants having more than 50% lignin contents are good precursors of porous carbon while cellulose and hemicelluloses release carbon monoxide, carbon dioxide and water upon carbonization and form micropores. These micropores are very important in the performance of electrodes. Many researchers have used different precursors, such as fruit-derived materials, tree-derived materials and other biomass-derived materials, to manufacture biomass-based derived porous carbon materials.

Generally, the pore size distribution, connectivity and hydrophilicity determine the capacitance of the porous carbon materials, since they play a vital role in influencing the energy density and ion diffusion process of the active materials [10].

The manufacture of activated carbon (AC) out of waste materials exemplifies the extraction of high-value products from inexpensive sources, concurrently addressing the issue of waste disposal [11]. Consequently, there is a significant emphasis on developing processes for the recycling of these waste materials. These carbon-rich wastes serve as excellent raw materials for AC production. This category of waste encompasses a diverse range of

materials, including switch grass, poplar trees, sugarcane bagasse, sawdust, brewer's spent grains, stems, husks, leaves, stalks, shells, and peels from cereals such as corn, wheat, rice, sorghum, and barley, among others., as we saw in Table 1.

Preparation of AC from biomass waste materials

Carbon activation can be accomplished through three methods, namely,

1. Physical activation [12]
2. Chemical activation [12]
3. Steam pyrolysis/Activation [13]

A bird's eye-view on the various activation methodologies has been provided below.

Physical activation

Physical or thermal activation stands out as a widely employed technique for generating activated carbons (ACs) from biomass precursors. This process can be manifested either as a single-step or a dual-step procedure [14]. However, the prevalent approach involves a dual-step sequence wherein the carbonization of dried samples occurs at temperatures ranging from 400 to 700°C, resulting in the formation of biochar. Subsequently, activation takes place using oxidizing gases such as air, steam, CO_2, or their combinations [15], conducted at elevated temperatures of approximately 800-1100°C to facilitate burn-off. The biochar derived from carbonization typically exhibits a surface area less than 300 m^2/g [16]. This limited adsorption capacity and surface area are attributed to the pores obstructed by tarry substances, necessitating their removal through activation with oxidizing gases.

In the single-step approach, carbonization and activation take place simultaneously at a temperature maintained within the range of 600-800°C [17]. Comparable to the double-stage method, this single-stage process involves carbonizing the dry sample up to a particular temperature, after which the biochar can be further heated for a preferred duration simply by switching from inert gas to oxidizing gas. In spite of sharing similarities with dual-stage process, the single-step technique proves to be more practical as it eliminates the need for a cooling phase post-carbonization, leading to reduced physical effort, lower electrical utilization, cost savings, and a shorter working time [16]. Physical activation, integral to this process, not only widens the thin pores on the surface of the biochar but also generates new pores simultaneously, thereby enhancing the porosity and surface area of the carbonaceous porous structure. However, it is worth noting that physical activation may yield a comparatively lower carbon output and lower quality of AC compared to what chemical

activation (described below) could offer, mainly due to the superior activation temperature and comprehensive activation time involved in the procedure [14].

In the realm of physical activation, commonly employed activating agents include steam and CO_2. Air (oxygen), on the other hand, is less favored as an activation agent due to the exothermic character of the reactions involved, potentially leading to excessive burning on both the internal and external surfaces of the biochar, thereby resulting in reduced yield [18]. Both steam and CO_2 exhibit similar maximum BET surface areas, capable of reacting with carbon to generate surface areas that can attain up to 1000 m^2/g or even higher. Despite their procedural similarities, the mechanisms and reactions involved in steam and CO_2 activation differ slightly. Notably, at temperatures next to activation, steam is expected to react four times faster with carbon than CO_2 [16]. Consequently, steam activation allows activated carbon to attain a high surface area within a relatively small period.

Activation using CO_2 creates further new pores rather than the expansion of existing narrow pores, whereas steam activation prioritizes the widening of micropores from the onset of the activation process, eventually developing mesopores and macropores. This strategy ensures a more extensive and diverse distribution of pores in the resulting ACs (ACs) [19].The physical activation of cellulosic materials typically yields microporous ACs. Even at an accelerated activation rate, steam activation tends to yield a higher percentage of mesoporous and microporous structures, while CO_2 activation favors higher microporosity. The preference for CO_2 activation stems from its cleanliness, ease of gas handling, and the ability to control the activation procedure still at high temperatures up to 800°C due to its gradual reaction rate [20]. Various raw materials, including rice husk, rice straw, corn cob, corn hulls, peanut hulls, pecan shells, coconut shells, and almond shells have been used as raw materials to produce activated carbon materials by physical activation method [21, 22].

Chemical activation

In the single-stage approach, carbonization is omitted, and the dried sample undergoes activation as its primary step, involving interaction with dehydrating agents such as NaOH, KOH, $ZnCl_2$, and H_3PO_4 [23]. Conversely, the dual-stage process involves the carbonization of the dried sample to produce biochar within the temperature range of 400 – 600 °C before the subsequent chemical activation [14]. The three forms of Chemical activations are [24], namely,

1. Basic activation

2. Acidic activation
3. Neutral activation

In chemical activation, the precursor i. e. the dried phytomass sample is mixed with definite amounts of active agents such as KOH, NaOH, H_2SO_4, HNO_3, H_3PO_4, $ZnCl_2$, $CaCl_2$, Na_2SO_4, K_2CO_3 [25]. The activating agent functions as a dehydrating agent, preventing the formation of tar and excluding volatile substances in the process. This dual action serves to augment the yield of activated carbons (ACs) and lowers the carbonization temperature in comparison to the physical activation method [26].

Chemical activation primarily serves to increase the diameter of fine pores and generate new pores, thereby enhancing the adsorptive capability of the carbonized product [27]. In contrast to physical activation, chemical activation boasts various advantages, including a lower conversion temperature, shorter activation time, higher carbon yield, and greater specific surface area and porosity. Utilizing activating agents such as phosphoric acid facilitates the formation of both micro and mesopores in the resultant carbon structure. The mesopore fraction in the activated carbon is predominantly influenced by the production conditions and the biopolymer composition of the cellulosic material.

Steam pyrolysis/activation

There is also an alternative one-step treatment method, referred to as steam-pyrolysis according to the findings of Fan et al. [28]. In this process, the raw sample is either heated at moderate temperatures (500–700ºC) in the presence of pure steam or heated at 700–800ºC under the influence of regular steam. The samples undergo heating at a rate of 10ºC/min until reaching a final temperature of 700ºC, 750ºC, or 800ºC, where they are held for 1 or 2 hours in the continuous flow of steam [29]. The resulting activated carbons may exhibit a high pore volume, and their activation burn-off or mass loss due to the activation process is determined [13].

Key factors for enhancing capacitance with plant-derived materials

For preparing activated carbon, the most advantageous parts of the plant are typically the stems, barks, and leaves. This is due high carbon content in stems and leaves. This is crucial because performance is closely related to its high carbon content, high surface area and porous structure. These aspects can help in achieving the high surface area needed for effective charge storage in supercapacitors. Further, stems and leaves are more readily available and easier to process. They also tend to have a more uniform structure, which can result in more consistent activation and higher-quality carbon [30, 31].

Furthermore, there are certain specific structures in phytomass-derived carbons that are expected to enhance the capacitance suitable for advanced supercapacitor applications. The features, though not exhaustive, are specified below.

1. Hierarchical porous structure and surface area

Porous carbon materials derived from plants with a hierarchical structure containing micropores, mesopores, and macropores have been extensively studied for supercapacitor electrodes [32]. The interconnected porous framework provides high surface area for electrolyte ion adsorption and short ion diffusion paths, leading to high capacitance [33].

2. Nitrogen doping

Increasing the nitrogen content in plant-derived porous carbons is key to improving their supercapacitor performance [33]. Nitrogen doping introduces pseudocapacitance and enhances wettability and conductivity [32]. Bamboo shoot-derived carbons with 3.0 at% N showed a high capacitance of 412 F/g [33].

3. Biomass precursor selection

The choice of plant biomass precursor affects the properties of the phytomass-derived carbon. For instance, bark-based carbons exhibit a unique flower-like 3D vertical nanosheet structure with excellent electronic transport and high surface area [34]. Daylily flower-derived activated carbon also showed promising electrochemical behavior [35].

4. 3D nanostructured carbons from seaweed

Seaweed-based 3D nanostructured carbons exhibit high surface area, conductivity, and pseudocapacitance[36].

5. Activation methods

Chemical activation methods like KOH treatment can significantly increase the surface area and porosity of plant-derived carbons. To cite, *Broussonetia papyrifera* stem bark activated with KOH had a BET surface area up to 1212 m^2/g and pore size of 3.8 nm, leading to a capacitance of 320 F/g [32].

It is also important to understand that in addition to the above factors, adequate water supply during the plant growth phase is essential for optimal plant health in general. It is also understood that water stress can lead to stunted growth and reduced biomass quality and

quantity, which negatively impacts the properties of the carbon produced from these plants. Hence, the growth environments that enhance capacitance in supercapacitors involve a combination of optimal soil conditions, environmental factors, appropriate plant species, effective post-growth treatments, and sufficient water availability. Thus, it is important to consider these elements collectively that contribute to the development of high-performance carbon materials suitable for supercapacitor applications. So, by selecting appropriate plant precursors and optimizing the activation process can produce high-performance activated carbons for advanced energy storage applications.

Impact of physical characteristics of plants derived activated carbons on the key metrics of the supercapacitors

Physical properties like the specific surface area, pore size, and pore volume distribution of activated carbon derived from plants significantly impact the key metrics of supercapacitor performance [37] as follows:

Specific Surface Area (SSA):

1. High SSA (>2000 m^2/g) enhances:
   - Capacitance (C)
   - Energy density (E)
   - Power density (P)
2. Low SSA (<1000 m^2/g) may limit performance

Pore Size Distribution:

1. Micro-pores (<2 nm):

- Enhance electrochemical double-layer capacitance (EDLC)
- Increase energy density (E)

2. Meso-pores (2-50 nm):

- Facilitate ion transport and diffusion
- Improve power density (P)

3. Macro-pores (>50 nm):

- Enhance electrolyte accessibility and wetting
- Increase capacitance (C)

Pore Volume Distribution:

1. High pore volume (>0.5 cm^3/g):

- Enhances capacitance (C) and energy density (E)

The factors mentioned below influence key metrics of the supercapacitors:

1. **Capacitance (C):** Directly related to SSA and pore volume
2. **Energy density (E):** Influenced by SSA, pore size, and pore volume
3. **Power density (P):** Affected by pore size, pore volume, and conductivity
4. **Cycling stability:** Influenced by pore structure, surface functionality, and conductivity
5. **Electrolyte accessibility:** Impacted by pore size, pore volume, and surface wettability

By tailoring the specific surface area, pore size, and pore volume distribution of plant-derived activated carbon, we can optimize supercapacitor performance for specific applications.
Key characteristics:

1. **High lignin content:** Enhances thermal stability and surface area.
2. **Low ash content:** Reduces impurities and improves conductivity
3. **Well-developed pore structure:** Increases surface area and ion transport.
4. **High carbon content:** Improves conductivity and electrochemical performance.
5. **Oxygen-containing functional groups:** Enhances pseudocapacitance and wettability.

Several reviews on plant-based activated carbons are available in the literature and one such review involves the narration of ultrahigh-specific surface area porous carbon materials, mesoporous carbon materials, hierarchical porous carbon materials, and phytomass, plant biomass-derived active carbon materials are the most common types of carbon materials from diverse types of plants and they can be prepared by using different methods [38].

Preparation methods:

1. **Pyrolysis:** Thermal decomposition in the absence of oxygen to produce activated carbon.
2. **Chemical activation:** Treatment with chemicals like KOH, NaOH, or H_3PO_4 to enhance surface area and porosity.
3. **Physical activation:** Treatment with steam or CO_2 to develop pore structure and surface area.

By selecting the right plant part and preparation method, we can produce high-performance activated carbon for supercapacitors.

These understanding can lead to the:

1. Development of new plant biomass-derived materials with enhanced performance

2. Increased adoption in commercial supercapacitors
3. Integration with other energy storage technologies (e.g., batteries)
4. Scalable and cost-effective production methods
5. Expanded applications in fields like electronics, transportation, and renewable energy systems

The present review paper thus aims to further refine our understanding of the value and potential of plant biomass-derived activated carbon for supercapacitor applications, thereby driving further research and innovation in this field.

State-of-the-art and prospects of PAC carbon as electrode materials in supercapacitors

The progress in electrochemical energy storage gadgets from usual, green and costless materials coupled with large electrochemical performance is the actual, valid and demanding vision of the energy advocates in the present scenario of energy crisis of late. In favor of these perspectives, carbon-based materials viz.,

- Activated carbons (ACs)
- Carbon aerogels (CAG)
- Graphene
- Carbon nanotubes (CNTs) and carbon nanofibres (CNFs)
- Carbon-metal oxide composites

and other classes of materials such as polymer composites and hybrid metal oxide-conductive polymer materials have been proposed as electrode materials for energy storage gadgets such as SCs, lithium-ion batteries etc.

The ultimate electrochemical performance and output of SCs is interplay between a number of criteria such as the type/nature of the electrolyte used, physico-chemical features of the electrode material, hardware or configuration of the cell assembly. Of these, the commercial success of super capacitor depends on the electrode materials and hence play a prime role to serve as a vital ingredient in the energy storage devices in general, since the electrochemical capability of the cell is very much prejudiced by the surface features of the electrode substance like large mesopores, high surface area etc. [39].

Recent high performing SCs use porous ACs as electrodes and one of the best resources for generating AC powders and that too in large mass are the renewables or plant biomass (phytomass) wastes. So, any inexpensive phytomass with high carbon content, low inorganics and ash may serve as raw materials for the production of ACs [40].

As we saw, carbon materials such as ACs, carbon aerogels, graphites, CNFs, CNTs, and metal oxide-carbon composites have actively been investigated for the use as electrode materials for energy storage devices. The selection of electrode material is mainly done on the basis of their working temperature range, accessibility, non-toxicity, high chemical stability and easy processability. Out of many investigated, ACs is widely used because of its variable pore structure, large surface area and variety of precursors available for its production along with reduced CO_2 emissions. The important goal will be obviously on increasing the amount of energy and power with stable electrochemical performance. Simultaneously, carbon materials with desirable, structural, morphological, chemical and electrochemical features would be the likely choice of electrodes. Hence carbon, which has been obtained by simple pyrolysis of phytomass precursors might have huge prospective in many applications and devices.

Moreover, phytomass wastes are comparatively cheaper for obtaining AC powders and hence are viewed as a viable raw precursor for the synthesis of ACs resulting in electrochemical performance and good cycling efficiency in super capacitors. Considering the versatility of the phytomass materials, the final products of thermal processing or pyrolysis or activation viz., phytomass carbon or phytochar, is one among the electrode materials well suited for energy devices.

Thus, effectually and eventually perceiving the importance and value of PAC, diverse research groups are devoting time and funds for the impeccable research to the valuable application of the same as electrode potentials in electrochemical energy systems like super capacitors and LIBs. While numerous raw materials have been investigated for AC preparation in previous studies, researchers continue to seek out novel materials based on their availability and suitability for producing activated carbon specifically designed for capacitor applications.

Thus, in this review paper, as already stated, a detailed literature on the various categories of phytomass derived ACs applied as electrode materials in capacitors/super capacitors are discussed that may cater to the need of our society, scientific industries and in sustainable energy sector as well by harnessing Nature’s potential. Interesting reports on the above subject has been consolidated, which would provide us the background and details about the electrochemical execution of phytomass derived carbon potentials.

It is well established that the pore size distribution of PAC highly depends upon the plant parts used [41] and AC with more structural, textural (micropores, mesopores or

macropores) and chemical properties as precursors has excellent electrochemical features [42]. Nevertheless, in the present review article, noteworthy recent literature available on plant biomass i. e phytomass-derived AC, which includes different parts of the plants such as stem, leaf, flower, seed, fruit and root are considered and under the following titles, we discuss these categories of phytomass for deriving active carbon with excellent performance.

a. Phytomass carbon from stem/straw of plant
b. Phytomass carbon from leaf of plant
c. Phytomass carbon from flower of plant
d. Phytomass carbon from seed of plant
e. Phytomass carbon from fruit of plant
f. Phytomass carbon from root of plant

Further, the important facts related to the synthesis methods, physical and electrochemical features of PACs are elaborated in the following sub-sections.

a. Phytomass carbon from stem/straw of plant

Stem or straw of plant is the middle portion of a plant that transmits organic matters during photosynthesis and also incorporates water/salts from root. Hence the ion content is larger in straw/stem. To make straw/stem AC, carbonizing at elevated temperature has been commonly applied [43, 44].

By simple KOH activation, tobacco stem-based ACs (TS-ACs) were prepared. Their use as electrodes in EDLC was evaluated by Xia et al [43]. The surface area of the derived ACs differs over a wide range i.e. between 1472.8 & 3326.7 m^2/g. While the ratio of tobacco stem to KOH is improved, the mesoporosity has been reported to be enhanced significantly. In 1 M $LiPF_6$- DEC/DMC/EC electrolyte solution, a high specific capacitance value as 190 F/g at 1 mA/cm^2 was found. Through this work, the novel use for TS into an important energy storage material has been identified.

Sudhan et al. [44] have detailed the production of AC from rice straw using a simple and straightforward process involving carbonization followed by chemical activation. Employing KOH as the chemical activator resulted in the creation of disordered micro and mesopores on the carbon, yielding a high specific surface area of approximately 1007 m^2/g, as established by N_2 adsorption-desorption and TEM analysis indicated the formation of ultra-fine carbon nanoparticles around 5 nm in size because of chemical activation and carbonization. A remarkable specific capacitance of 332 F/g in the three-electrode aqueous electrolyte was exhibited, with specific capacitance retention of 99% after 5000 cycles. Furthermore, a symmetric super capacitor device fabricated from the AC displayed a high

specific capacitance of 156 F/g and a notable energy density of 7.8 Wh/kg in 1M H_2SO_4. The use of 1-ethyl-3-methyl imidazolium tetrafluoroborate [EMIM][BF_4] ionic liquids resulted in a cell voltage of 2.5 V in the symmetric device, accompanied by a specific capacitance of 80 F/g and an impressive energy density of 17.4 Wh/kg. In a non-aqueous electrolyte, the charged device powered a red LED for more than 5 minutes after a 20-second charging period.

Xueliang et al [45] have prepared AC from wheat straw by activating with KOH which resulted in honeycomb-like structures and explored the same for EDLC performance. The capacitance value was 251 F/g in methyltriethylammonium tetrafluoroborate/acetonitrile electrolyte system. In the report, the authors converse the relations between surface area, scan rate, pore diameter and specific capacitance. Tian et al [46] have reported AC with flute type micropores (FTMAC) prepared from cotton stalk using KOH as an activating agent. TEM images at different magnifications are shown in Fig. 1. A controlled pore structure with high specific surface area of 1964 m^2/g and pore volume of 1.03m^3/g is exhibited. FTMAC-based electrode was observed to deliver a high specific capacitance of 254 F/g in 1M H_2SO_4 electrolyte at a current density of 0.2 A/g. Also featuring 221 F/g at a current density of 10 A/g, showing a good rate capacity with 87% retention and capacitance retention of 96% at a current density of 1 A/g, representing long cyclic stability even after 10000 charging and discharging cycles.

(Figure 1)

Wang and et al [47] utilized cornstalk to create porous carbon sheets under ambient air atmosphere. These carbon sheets exhibit an extremely thin structure, approximately 4.6 nm thick, facilitating efficient electrolyte ion transfer and diffusion due to the abundance of pores. Moreover, with a significant specific surface area of 1588 m^2/g, numerous active sites were generated, aided by substantial oxygen doping, resulting in pseudo capacitance. These carbon sheets demonstrate a notable specific capacitance of 407 F/g at 1 A/g in a three-electrode setup.

Yan et al. utilized waste lotus stems, characterized by their low cost and environmental friendliness, to fabricate nitrogen-doped porous carbon materials designated as LS-NCs for super capacitor applications [48]. The overall nitrogen content, comprising pyridine nitrogen (N-6) and pyrrolic/pyridinic (N-5) contents amounted to 94.7%, significantly enhancing conductivity. SEM images illustrating the distinctive structure are presented in Fig. 2.

(Figure 2)

The LS-NCs achieved an impressive specific surface area of 1322 m^2/g, showcasing outstanding electrochemical performance with a specific capacitance of 361 F/g at a current density of 0.5 A/g. Notably, the porous carbons exhibited exceptional cycling stability, retaining 96% of the specific capacitance after 5000 cycles. The unique structure derived from abundant waste lotus stems positions them as an environmentally friendly and cost-effective material for high-performance super capacitors.

Wang et al prepared well-structured porous carbon sheets from fresh clover stems under air atmosphere [49]. A facile potassium chloride salt-sealing procedure was applied as shown Fig. 3. Porous carbon sheets thus obtained acquire high specific surface area of 2244 m^2/g and rich pore structures, which provide fast ion diffusion channels and abundant storage active sites. A high specific capacitance of 436 F/g at 1 A/g was tapped. Tremendous rate capacities with capacitance retaining 290 F/g at 50 A/g were established. Moreover, a high specific capacitance of 420 F/g at 0.5 A/g was delivered by the assembled symmetric supercapacitor. An excellent energy density of 58.4 Wh/kg and good cycling stability of 99.4% capacitance retention at 5 A/g after 30,000 cycles was displayed.

(**Figure 3)**

Phiri et al [50] utilized willow wood and prepared highly porous willow-based carbon as shown in Fig. 4. It had pore volume of 1.45 $cm^{3/}$g and high surface area of ~2800 m^2/g, exhibiting 394 F/g as the specific capacitance at a current density of 1 A/g. A good cycling stability, retaining ~94% capacitance after 5000 cycles at a current density of 5 A/g was displayed in 6 M KOH electrolyte. Using 1M Na_2SO_4 electrolyte, an excellent rate performance like high working voltage of 1.8 V was exhibited in a symmetrical two-electrode full cell setup.

(**Figure 4)**

Compilation of phytomass precursors sourced from plant stems/straws and utilized in synthesizing electrode materials for capacitors is presented in Table 2.

(Table 2)

b. Phytomass carbon from leaf of plant

Five types of ACs were prepared from waste tea-leaves by Peng et al [51] using KOH as activating agent. XRD patterns show a broad diffraction peak positioned at 43°, corresponding to the (100) diffractions of graphitic carbon with the amorphous character as shown in Fig. 5. Specific surface area lies from 2245 m^2/g to 2841 m^2/g. Five ACs prepared

showed the highest specific capacitance of 330 F/g at a current density of 1 A/g in aqueous KOH electrolyte.

(**Figure 5)**

Jain et al [52] utilized eucalyptus leaves biomass for preparing electrode material with organic functional groups and high BET surface area as shown in Fig. 6. Environment friendly materials like CH_3COONa, graphite foil etc., are used in supercapacitor. 3 to 4 times enhancement in capacitive performance was observed by adding HQ (hydroquinone) into CH_3COONa. Excellent cyclic behavior was displayed for over 10000 cycles with redox additive.

(**Figure 6**)

Lotus leaf biomass was used to fruitfully produce AC with a high specific surface area. Carbonization and KOH activation was employed by Qu et al [53]. Lotus leaf porous carbon has been reported to have exhibited an appreciable performance when calcined at 800°C. Specific capacitance of 379 F/g & 298 F/g were tapped at 1 A/g and 20 A/g respectively. A good cycling stability was also displayed after 5000 cycles and reported to reach a capacitance retention rate of 90%.

Ahmed et al. [54] investigated AC derived from neem leaves in conjunction with a gel polymer electrolyte (GPE) containing $LiClO_4$ salt in EC:PC (1:1 v/v.) incorporated into a PVdF-HFP solution. The resulting low-cost AC exhibited a regular pore size of 2.51 nm and a specific surface area of 705 m^2/g. A GPE film was prepared using the solution-cast technique. The ionic conductivity and electrochemical stability window of the GPE ($LiClO_4$/EC:PC/PVdF-HFP) at room temperature were determined, affirming the suitability of the GPE meant for electrochemical double-layer capacitor (EDLC) fabrication. The specific capacitance of the fabricated cell was evaluated through various characterization techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and charge-discharge tests, with the observed values presented in Table 3.

(**Table 3)**

Wang et al [55] prepared porous carbon with waste celtuce leaves by pyrolysis in argon flow at 600°C, following an activation using KOH. Porous carbon thus prepared has a large pore volume of 1.88 cm^3/g and very high specific surface area of 3404 m^2/g. GCD curves at different current densities and CV at various scan rates are shown in Fig.S1. The specific capacitance of 421 & 273 F/g in two and three-electrode systems were respectively obtained in KOH aqueous electrolyte.

Li et al. [56] derived ACs from fallen (dried) leaves of *Fraxinus chinensis* (are synthesized by the activation of both KOH and K_2CO_3 (scheme shown in Fig. S2). The specific capacitance reached up to 242 F/g (0.3 A/g, 6 M KOH) in a two-electrode system. Better cycling stability with nearly no reduction in capacitance was reported even after 2000 cycles.

Fan et al [57] derived porous carbons from the nettle leaf (scheme shown in Fig. S3) and have found to possess high specific surface area (1951 m^2/g), huge total pore volume (up to 1.374 cm^3/g), and high content of oxygen and nitrogen heteroatom doping (up to 17.85 at% shared). Superior specific capacitance of 163 F/g at 0.5 A/g in an ionic liquid electrolyte ($EMIM.BF_4$) with a capacitance retention as high a value of 67.5% at 100 A/g was demonstrated. Also, a low capacitance loss of just 8% after 10000 cycles was projected.

To have a quick comparison, various phytomass precursors from leaf of plant employed to synthesize electrode materials for capacitors is shown in Table 4.

(Table 4)

c. Phytomass carbon from flowers of plants

Khan et al [58] used withered rose flowers for synthesizing activated porous carbons (mentioned as RDPC) through a simple two-step method of carbonization and chemical activation utilizing KOH/KNO_3. RDPC thus prepared has an enhanced specific surface area of 1980 m^2/g. This study has shown the HR-TEM and SAED (selected area electron diffraction) images of the obtained for RDC (a-c) and RDPC (d-f) samples at different resolution. RDPC exhibited an appreciable electrochemical activity as super capacitor electrode (6M KOH as the electrolyte) including ultrahigh SC exhibiting 350 F/g at 1 A/g.

Porous carbon nanosheets were synthesized by Veerakumar et al [49] by the carbonization of *Bougainvillea spectabilis* through physical and chemical activations. Carbon powders prepared from paper flowers (paper flower carbon – PFC) showed a maximum surface area up to 1801 m^2/g with an assailable porous graphitic carbon layer arrangement. This feature warrants potential application in energy storage (and dye removal). In 1M H_2SO_4 aqueous electrolyte, potentiostatic as well as galvanostatic measurements using a three-electrode cell was carried out demonstrating a specific capacitance of 118, 109.5, 101.7, 93.6, and 91.2 F/g at 1, 2, 4, 8 & 12 A/g respectively. In Fig. S4, EIS spectra of the PFC-700 & PFC-800 modified electrode are shown and also EIS before and after 1000 cycles are displayed.

Paulownia flower ACs (a-PFCs) show suitable pore size distributions, maximum specific surface areas, super hydrophilicity and partial graphitization phase, which are all

necessary for achieving high electrochemical behavior as super capacitor electrodes. (Chang et al) [60]. XRD and FTIR spectra graphs are displayed in Fig. S5. The symmetric super capacitor offers a superior specific capacitance of 297 F/g at a reasonable current density (1 A/g in 1 M H_2SO_4 electrolyte).

Chen et al [61] worked on the elm flower-based AC (ELAC). It had pore volume of 0.88 cm^3/g, N & S contents and surface area of 2048.6 m^2/g. ELAC displayed a specific capacitance of 275 F/g at a current density (1 A/g) and retained a capacitance of 216 F/g at 20 A/g only because of N and S functional groups. CV of ELAC-1, ELAC-2 & ELAC-3 at various scan rates and comparison of ELAC-x at a scan rate of 2 mV/s is shown in Fig. S6.

Wu et al [52] worked on Albizia flowers and obtained total pore volume of 1.47 cm^3/g with a high specific area (2758 m^2/g). More self-doped N contents and unique porous microrod feature was observed. The resulted porous carbon micro rods demonstrated a notable specific capacitance of 406 F/g at 0.5 A/g (335 F/g at 10 A/g) in 6 M KOH electrolyte, along with a commendable rate capability of 86%.

Sivachidambaram et al [63] prepared AC from *Borassus flabellifer* flower (BFF). Employing different activation temperatures (600, 700, 800 and 900^{o}C) and H_3PO_4 as an activating agent, the AC was prepared. This study has used 1M KOH electrolyte, the Asian palmyra palm's CV at various scan rates of BFF-6, BFF-7, BFF-8 and BFF-9 samples are shown. Table S1 lists the phytomass precursors from various flowers of plants employed to synthesize carbon electrode materials for capacitors.

d. Phytomass carbon from seed of plant

Elmouwahidi et al [64] prepared AC from argan seed shells by KOH activation. Due to the hindrance of the surficial carboxylate groups towards electrolyte distribution into the pores, the O-rich AC exhibited a low capacitance of 259 F/g. Owing to well-evolved micro and mesoporosity, the pseudo capacitance effects of N functionalities, N-rich AC showed the highest capacitance of 355 F/g in 1 M H_2SO_4 as electrolyte.

Sunflower seed shell containing nanoporous carbons was prepared and used as electrode material in capacitors (Li et al) [65]. Activation temperatures and ratio of KOH determines the pore structure of the carbons, as well known. Capacitive performance of these carbons (in 30 wt. % KOH electrolyte) is observed to be much better so that the carbon from sunflower seed shell was made as a superior electrode material for capacitors.

Hu et al [66] investigated the capacitance features of pistachio shells char activated by KOH. ACs showed ideal capacitive behaviors at an extensive range of scan rates, possessed

excellent reversibility and high power property in aqueous electrolytes (0.5 M H_2SO_4, 0.5 M Na_2SO_4 & 1M $NaNO_3$).

Olivares-Marin et al. [67] investigated the activation of cherry stones using KOH. The precursor, carbonized at temperatures ranging from 800 to 900°C, yielded carbons with average pore sizes around 0.9–1.3 nm and substantial specific surface areas ranging from 1100 to 1300 m2/g. Consequently, the samples exhibited high capacitances at low current density, reaching up to 230 F/g in a 2M H_2SO_4 (aqueous electrolyte) and 120 F/g in the aprotic medium 1M $(C_2H_5)_4NBF_4$/acetonitrile.

Kalyani and Anitha [68] investigated AC derived from jack fruit seeds and reported superior specific capacitance as elevated as 316 and 203 F/g respectively in 1M H_2SO_4 and 1M Na_2SO_4 electrolytes (scan rate of 10mV/s). SEM image of jack fruit seed is displayed in Fig. S7. Also, it showed excellent electrochemical cycle stability in 1M H_2SO_4 with 93% capacitance retention at the end of 500 cycles. Kalyani et al [69] worked on papaya seeds using $ZnCl_2$ (activating agent) and got the specific capacitance of 472 F/g in 1M H_2SO_4 electrolyte, as calculated from CV. Hence the biomass of papaya seeds represents a burgeoning and ever green source of carbon for capacitor electrodes.

List of phytomass precursors from seed of plant employed to synthesize carbon electrode materials for capacitors is given in Table S2.

e. Phytomass carbon from fruit of plant

Guardia et al [70] proposed residue valorization as the well-organized approach to attain a cost-effective circular economy and the scheme is shown in Fig. S8. Hydrothermal carbonization of apple bagasse and apple waste after juice and cider production as precursor is projected. Electrochemical capacitance of 290 F/g and specific surface area of 2000 m^2/g are reported. Excellent performance makes them very promising for the energy storage in super capacitors.

Ranaweera et al [71] have worked with orange peel-based electrode (KOH electrolyte). 100% capacitance retention during 5000 cycles was reported. The work explains that bio-waste can be easily changed into an efficient and high-performance energy storage device by using a carefully designed electrode/electrolyte system.

KOH activated pineapple crown waste (Taer et al) [72] possess a pore volume of 0.362 m^3/g, a surface area of 700 m^2/g and a pore diameter of 22 nm. Pineapple crown-derived carbon electrode exhibits a good fiber structure with a diameter of 42-73 nm. SEM of the MN700 sample at 1000X, 5000X & 40000X magnifications is presented in Fig. S9. The

observed specific capacitance was high as 150 F/g, thereby proving excellent electrochemical properties of super capacitor cells.

Vinayagam et al [73] have worked on *Syzygium cumini* fruit shells (SCFS) for fabrication of symmetric super capacitors. Carbonization at 700ºC in N_2 atmosphere and CO_2 activation at 700ºC in N_2 atmosphere was employed to get ACs. An enhanced electrochemical performance in three electrode configuration is shown by SCF-AC. An innovative and environmentally safe approach with good porosity in AC for energy storage behavior is planned.

Elaiyappillai et al [74] explored *Cucumis melo* (Cm) fruit peel's electrochemical studies with 1M aqueous KOH. The novel fabricated Cm based AC electrode (Cm-900) exhibits a superior specific capacitance value of 404 F/g at 1 A/g. Highly porous Cm-900 electrode may prove as an excellent candidate for high-performance SCs.

List of phytomass precursors from fruit of plant, employed to synthesize carbon electrode materials for capacitors is given in Table S3.

f. Phytomass carbon from roots of plants

Vinayagam et al [73] has worked on *Chrysopogon zizanioides* roots (CZR) employing carbonization at 700ºC in N_2 atmosphere and CO_2 activation at 700ºC in N_2 atmosphere. The CZR-AC obtained showed enhanced electrochemical performance in three-electrode configurations with high specific capacitance data.

Wang et al [75] used tamarisk roots as carbon precursor to successfully fabricate an innovative tamarisk root-based honeycomb-like porous carbon (TRHPC). Simple activation and carbonization approach and mixed hybrid activators containing NaCl and $ZnCl_2$ are employed. TRHPC shows good electrochemical properties with high specific capacitance 293 F/g at 0.5 A/g. High-rate performances with 61.5% capacitance retention from 0.5 to 50 A/g were reported.

Guo et al. [76] produced 3D hierarchical porous carbon by the facile carbonization followed by chemical activation taking soyabean roots (SRs) as the carbon precursor. The scheme of the work is shown in Fig. S10. High specific surface area (2143 m^2/g), good electrical conductivity coupled with unique 3D hierarchical porosity offered excellent electrochemical performance as an electrode material for super capacitors. Superior cycling stability i.e. 98% capacitance retention after 10000 cycles at 5 A/g, high capacitance (276 F/g at 0.5 A/g) was obtained. A good rate capability in a symmetric two-electrode super capacitor setup in 6M KOH was demonstrated.

Table S4 lists phytomass precursors from root of plant employed to synthesize carbon electrode materials for capacitors.

Effects/influence of self-doped heteroatoms on the specific capacitance/pseudo capacitance of PAC

The effects of self-doped heteroatoms on the specific capacitance or pseudo capacitance of PAC have been a recent subject of interest in the area of energy storage and supercapacitor development. We all know that the PAC refers to the AC materials obtained from renewable biomass precursors such as agricultural waste, wood, or other plant-based materials. These materials are carbonized and activated to generate porous structures with high surface area. Numerous chemical active principles present in the plant precursors get ruptured into organic functional moieties during carbonization and chemical activation processes and these organic functionalities containing O, &/or N/S or even P will usually be terminated on the carbon surface or incorporated into the carbon structure. These heteroatoms are hence called *self-doped* heteroatoms in the context of PAC and can significantly impact the performance of super capacitor electrodes [77].

It is known from the literature on the electrochemistry of phytomass-derived AC that the occurrence of oxygen boost up the polarity of the carbon surface, thus making it hydrophilic, representing it more reversible in electrochemical environments and nitrogen in the sample boosts the capacitance by improving electrical conductivity [64, 78], while the presence of sulphur favors adsorption and transfer of electrolyte ions [69, 70] and further extends the interlayer spacing in the carbon structures to deliver copious electrochemical active sites. Moreover, the existence of heteroatoms enhances the wettability of the carbon electrode, which in turn may improve the electrochemistry of the electrode [81] via introducing pseudo capacitance.

As we know, sulphur belongs to the chalcogen group along with oxygen and the functionalization with sulfur containing groups is anticipated to be an important approach in tuning carbon chemistry. Organic functional groups containing sulfur mediate carbon chemistry in multiple ways depending on their oxidation states and thus show potential influences in biomass conversion [82], heavy metal recovery [83] and super capacitors [84]. Carbon materials usually react with H_2SO_4 (as electrolyte), the surface will be grafted with sulfonate [85].

Recently, the importance of sulphur based functional groups in AC has been perceived to enhance the electrochemical performance and hence sulphur doped carbon materials are

being studied as super capacitor electrodes [86]. The sulphur self-doped carbons with high content of sulphur were mainly prepared by sulphur-containing chemicals or adding the extrinsic sulphur sources [86, 87]. Gu et al used polythiophene to produce sulfur containing ACs for double-layer capacitors [88]. Ma et al applied sucrose with $MgSO_4$ to produce S-doped carbon fiber [89] and Liu et al. employed glucose with sublimed sulfur to acquire sulfur-doped carbon spheres [90].

Doping can be sorted into two types: external and self-doping. Self-doping occurs when heteroatoms are naturally incorporated into the carbon structure during the activation process, typically from the biomass feedstock itself and heteroatom doping involves introducing atoms of elements other than carbon into the carbon lattice. Common heteroatoms used for doping include nitrogen (N), sulfur (S), oxygen (O), and phosphorus (P). It is interesting to note that the PAC has enormous sulphur contents and it is this fact which attracted the present authors to focus on this subject for the supercapacitor electrodes. Also, there have been a few research reports about the utilization of plant wastes with high content of intrinsic sulphur to prepare sulphur self-doped carbons [91,92]. Because of the substantial amounts of intrinsic sulphur in phytomass, the element sulphur would be self-doping in the structures of phytomass during thermal treatment process. Surprisingly, these reports on carbon materials for super capacitors does not seem to have considered the role of self-doped sulphur in the electrochemical performance of the final products but focus only on the pore structures instead and also concentrated on the effects of electrolytes used. Nevertheless, the influence of sulphur has not been clear and hence it is worth studying.

Noteworthy effects of self-doped heteroatoms on PAC in super capacitor electrodes have been summarized below.

a. Enhanced capacitance: The presence of self-doped heteroatoms can facilitate additional pseudocapacitance in the AC electrode, leading to the enhanced overall electrochemical capacitance. Redox reactions taking place with the S-, O- & N-containing organic functionalities on the carbon surface strongly shows the contribution of huge Faradaic pseudocapacitance coupled with electrochemical double-layer charging capacitance.
b. The presence of active heteroatoms enhances the capability of charge storage in the material, resulting in higher specific capacitance and improved energy storage performance.
c. Enhanced electrical conductivity and electrochemical stability:

- Self-doped N-atoms can contribute towards increased electrical conductivity and the structural stability of the AC, making it more resistant to degradation during charge-discharge cycles. This enhanced stability ensures the longevity and cycling performance of the supercapacitor electrode.
- The presence of self-doped heteroatoms can modify the surface chemistry of the AC. This can influence the adsorption of electrolyte ions and improve the overall performance of the super capacitor.
- S favors adsorption and transfer of electrolyte ions as well and further extends the interlayer spacing of the carbon structure to offer ample electrochemical active sites, influencing the overall electrochemical performance.

d. Tailored surface chemistry: Different self-doped heteroatoms are present as specific surface functional groups on the AC, which can modify its surface chemical properties like wettability, hydrophilicity/hydrophobicity etc., as stated earlier. This tailored surface chemistry can influence the adsorption of electrolyte ions, leading to improved ion diffusion kinetics and faster charge-discharge rates.
e. Improved pore configuration: The presence of self-doped heteroatoms can also influence the pore organization of carbon materials. This may lead to the formation of additional micropores or mesopores, which can increase the surface area and provide more active sites for charge storage.
f. Environmentally friendly and cost-effectiveness: Utilizing PAC with self-doped heteroatoms is generally considered more environmentally friendly than traditional methods that rely on external chemical doping methods, which often involve harmful chemicals. Also, as PAC is abundant, renewable, and of zero-cost compared to other carbon sources. AC with self-doped heteroatoms can be an economical way to develop the performance of supercapacitor electrodes without significantly increasing production costs.

However, it is essential to note that the % content and specific effects of heteroatoms in PAC can change depending on the source of phytomass, the choice of activation process, and the intended application of the AC. Extensive research and characterization are therefore

necessary to understand the precise impact of heteroatoms on the properties and application of AC materials and performance.

Having observed the diverse effects and benefits arising from the self-doped heteroatoms within the porous phytomass activated carbon, it is imperative to probe into the underlying mechanisms responsible for the observed pseudo capacitance and the resultant enhancement in overall capacitance. This investigation extends to understanding how these heteroatoms interact in acid, neutral, and alkaline environments as electrolytes. The authors of this research have undertaken a comprehensive analysis of these interactions, and the detailed findings will be presented in a subsequent publication.

In our exploration, we leverage both our empirical insights gained through extensive research with various porous activated carbons (PAC) and insights extracted from the existing body of literature. The existing theoretical model establishes a direct correlation between the specific surface area of activated carbon and the expected specific capacitance. However, the practical scenario unfolds with more intricacies, challenging this simplistic perspective. Surprisingly, certain activated carbons boasting seemingly modest surface areas exhibit a notably higher specific capacitance than counterparts with larger surface areas. This intriguing divergence is underpinned by the presence of a substantial fraction of the surface area concealed within the micropores of the activated carbon particles, rendering it inaccessible to the electrolyte ions employed in electrochemical assessments [93]. Thus, it becomes evident that an effective assessment of capacitance, encompassing both capacitance and pseudo capacitance, necessitates a nuanced consideration of factors such as pore size distribution, overall surface area, the presence of organic functional groups, and electrical conductivity within the activated carbon structure.

Summary, perspectives and future challenges

From the preceding sections, it is certain that over the past few years, global attention has been devoted to developing electrochemical super capacitors (SCs) as a complementary or alternative power source to batteries for their multifarious applications including electric/hybrid vehicles, electronic equipment, computer memory backup, etc. Despite many types of carbon materials are being presently employed as super capacitor electrode materials including ACs, carbon nanotubes, carbon nanofibers and graphene sheets, ACs with an array of exceptional characteristics like porous structure and excellent surface composition and good chemical stability has attracted boundless research interest in the same.

In the present energy scenario, zero-cost plant biomass (i. e. phytomass) for producing low-cost-active carbons merits consideration. Hence from the above viewpoints, the authors have summarized to date on the significant progress realized with the AC - based electrode materials for SCs, specifically derived from various parts of plants as the precursor choices, which are apparently the zero-cost and eco-benevolent resources. Undeniably the reference works presented here follows the concept of circular bioeconomy. As said earlier, as the overall electrochemical performance of SCs is an interplay between the choice of carbon precursors, activation methodologies, carbon textural properties (specific surface area, morphology, porosity and pore-size distribution), electrical conductivity, the presence of huge and variable electrochemically active surface composition (organic functional moieties - highly functionalized surface) that imparts hydrophilic-hydrophobic propensity, multiple and versatile green-natural options of selecting phytomass are available to us that allows the preparation of multifunctional carbon powders for the desired applications [94]. A diagram illustrating the interaction between the characteristics of the electrode material and the functionality of the capacitor has been provided in Fig. S11.

Hence the discussion made in this consolidated report provides impetus for the global researchers and would also complement the values of phytomass and its preparation, features and applications for augmenting the existing literature. Nevertheless, there are still unsettled debates regarding the role and mechanism of the self-doped heteroatoms (intrinsic S, O, & N) present surficial on the ACs and their synergy towards contributing to the improved performance of SCs (pseudocapacitance) and hence this fact is inviting global research. There is no doubt that doping carbon materials with other active heteroatoms will portray better performance of super capacitors but because of the foregoing explanation, it can now be stated that carbon materials can be selected with self-doped heteroatoms especially with sulphur, to witness more application ranges in the near future.

Undeniably, the virtues of PACs mentioned herein paves clear ways to fabricate or engineer commercially viable AC-based materials meant for numerous innovative applications for instance in electrocatalysis, photocatalysis, microfluidic devices, biosensors, up-to-the-minute energy storage devices and much more in this manner enhancing future research. While PAC exhibits numerous parameter advantages and impressive performance, the available representative results and comparisons can portray certain challenges and perspectives of the study.

Some of the focal challenges to further root its share in renewable energy market are the gap in the technological innovations to increase productivity, reducing the cost of production/SCs fabrication, scalability and consistency in material quality and thus remains to be addressed. Nevertheless, these challenges present opportunities for additional research and development in this field, prompting endeavors to focus on creating additional user-friendly and cost-efficient technologies across a variety of scales. This, in turn, aims to attract increased investment in the energy sector. Looking forward still further of the challenges, the synthesis of PAC can be optimized by exploring innovative activation techniques and combining it with other nanomaterial's to enhance its properties like energy density and cycle stability of the energy storage devices. Additionally, collaborative efforts between academia and industry can accelerate the integration of this material into practical super capacitor devices.

As we pass toward a sustainable future, PAC holds great promise in shaping the landscape of energy storage technology. By harnessing the potential of this Green-Natural resource, scientists and engineers can contribute significantly to the advancement of renewable energy systems. We encourage further exploration of this fascinating yet indispensable field and anticipate ground breaking developments in the pursuit for greener and more efficient super capacitors - the gold capacitors or the power caches. It is hoped that this review will encourage more and more researchers to engage themselves into the fabrication of high-performance super capacitors in order to face the current energy dilemma.

Future outlook on the plant-based activated carbon materials for future energy storage devices

The future outlook for plant biomass-derived activated carbon in energy storage devices, particularly supercapacitors, is promising due to the following key factors:

1. Sustainability and environmental Impact

Utilizing plant biomass for activated carbon production supports sustainable practices by repurposing agricultural waste and reducing reliance on fossil fuel-derived materials. This aligns with global efforts to transition to greener energy solutions and minimize environmental impact.

2. High performance metrics

Research indicates that activated carbons derived from specific plant materials can achieve high specific surface areas and favorable pore size distributions. These characteristics enhance the capacitance and energy density of supercapacitors. For instance, activated carbons from certain plants have demonstrated capacitance values exceeding 400 F/g, making them competitive with traditional materials.

3. Advancements in material science

Ongoing innovations in material science are likely to improve the performance of plant biomass-derived activated carbons. Techniques such as chemical activation and nitrogen doping can further enhance the electrochemical properties of these materials, leading to better energy storage capabilities.

4. Integration with renewable energy

As the demand for renewable energy sources increases, the need for efficient energy storage solutions becomes critical. Plant biomass-derived activated carbon can play a vital role in stabilizing energy supply from intermittent renewable sources, such as solar and wind, by providing reliable storage options.

5. Research and development support

There is a growing focus on research and development in the field of supercapacitors, with significant investments from governments and private sectors. This support is aimed at discovering next-generation materials and optimizing existing technologies, which will likely benefit the development of plant biomass-derived activated carbons.

6. Potential for hybrid systems

The development of hybrid energy storage systems that combine supercapacitors with batteries could enhance overall performance. Plant biomass-derived activated carbons could serve as effective electrodes in these hybrid systems, improving energy density while maintaining rapid charge and discharge capabilities.

In summary, the distinctive characteristics of plant biomass-derived activated carbon, along with continuous advancements in material science and a growing emphasis on sustainable energy solutions, make these materials highly promising for future energy storage applications. Their incorporation into supercapacitors and hybrid systems has the potential to

greatly enhance the efficiency and reliability of energy storage technologies, facilitating the transition to a more sustainable energy future.

Conclusion

Phytomass-derived activated carbon (PAC) represents remarkable and sustainable and efficient energy storage advancements in the development of super capacitors. It harnesses the potential of organic waste, offers excellent porosity and electrical conductivity, and aligns with the principles of ecocentrism. As the world seeks cleaner and more sustainable energy solutions, PAC emerges as a ray of hope, exemplifying the ingenious ways we can harness Nature's potential for green energy. While there are significant opportunities, researchers and engineers must address challenges related to performance optimization, durability, scalability, and environmental considerations to unlock the full potential of these materials in the energy storage landscape. With further research and development, this technology may have a pivotal role in the transition to a more sustainable and eco-friendly energy future. Collaborative efforts across academia, industry, and policymakers will be essential in driving this technology move forward. In conclusion, the authors have investigated additional phytomass beyond those discussed in this review for various multifunctional applications. Readers can refer to references [95-99] for further details and gain insight into the vast potential for exploring numerous other phytomass in the future.

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FIGURE CAPTIONS

Figure 1 TEM of the sample at various magnifications [46].

Figure 2 (a) Photo of Lotus stem (b) SEM of lotus stem (c, d) SEM of LS-NC-600 (e, f) SEM of LS-NC-600 [48].

Figure 3 Illustration on the formation of carbon sheets [49].

Figure 4 Diagram showing the synthesis of willow derived ACs [50].

Figure 5 XRD of the five types of ACs [51].

Figure 6 FTIR spectra and N_2 adsorption-desorption isotherm studies of the eucalyptus leaves carbon sample [52].

Table 1 Classification of biomass.

S. No.	Biomass group	Varieties and species
1.	Wood and woody biomass	Angiospermous or gymnospermous; coniferous or deciduous; stems, lumps, pellets, branches, foliage, bark, chips, briquettes, sawdust and others from various wood species.
2.	Herbaceous biomass	Grasses and flowers (alfalfa, arundo, bamboo, banana, brassica, cane, cynara, miscanthus, switchgrass, timothy, others); straws (barley, bean, flax, corn, mint, oat, rape, rice, rye, sesame, sunflower, wheat, others); other residues (fruits, shells, husks, hulls, pits, pips, grains, seeds, coir, stalks, cobs, kernels, bagasse, food, fodder, pulps, cakes, etc.).
3.	Aquatic biomass	Macroalgae (blue, green, blue-green, brown, red) or microalgae; seaweed, kelp, lake weed, water hyacinth, marine or freshwater algae etc.
4.	Animal and human waste biomass	Bones, meat-bone meal; various manures, etc.
5.	Biomass Mixtures	Several substrates belonging to different classes, mentioned above, present in mixed forms.

Table 2 Phytomass precursors as stem/straw of plant for the synthesis of electrode materials

S. No	Precursor	Activation	Electrolyte	S_{BET} (m^2/g)	Specific capacitance (F/g)	Reference
1	Tobacco stem	KOH	1 M $LiPF_6$-EC/DMC/DEC	3326	190	[43]
2	Rice straw	KOH	1 M H_2SO_4	1007	332	[44]
			$EMIMBF_4$		80	
3	Wheat straw	KOH	$MeEt_3NBF_4$/AN	2316	251	[45]
4	Cotton stalk	KOH	1 M H_2SO_4	1964	254	[46]
5	Cornstalk	NaCl, KCl	1 M H_2SO_4	1588	407	[47]
6	Lotus stem	KOH	6 M KOH	1322	360	[48]
7	Clover stems	KCl	1 M H_2SO_4	2244	436	[49]
8	Willow wood	KOH	6 M KOH	2800	394	[50]

Table 3 Values of Specific capacitance using CV, EIS and CD.

Techniques	Specific Capacitance (F/g)
CV (at 10mV/s)	68
EIS (at 10 mHz)	57
Charge-discharge (at 1 mA/cm^2)	74

Table 4 Phytomass precursors as leaf waste of plant for synthesizing carbon electrode materials for capacitors.

S.No	Precursor	Activation	Electrolyte	SBET (m^2/g)	Specific capacitance (F/g)	Reference
1	Waste tea leaves	KOH	2 M KOH	2245-2841	330	[51]
2	Eucalyptus leaves	KOH	CH_3COONa		208	[52]
			CH_3COONa + HQ	2639	685	
			Na_2SO_4		173	
			Na_2SO_4 + HQ		377	
3	Lotus leaf	KOH	6 M KOH	2488	379	[53]
4	Neem leaves	$ZnCl_2$	1 M $LiClO_4$ in EC/PC	705	68	[54]
5	Celtuce leaves	KOH	2 M KOH	3404	421	[55]
6	Fallen leaves	KOH/ K_2CO_3	6 M KOH	2869	242	[56]
7	Nettle leaves	KOH	EMIM BF_4	1951	163	[57]

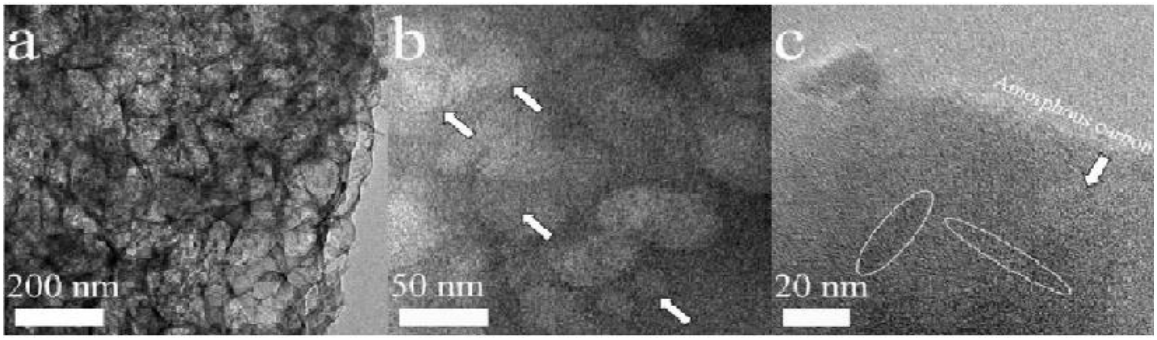

Figure 1

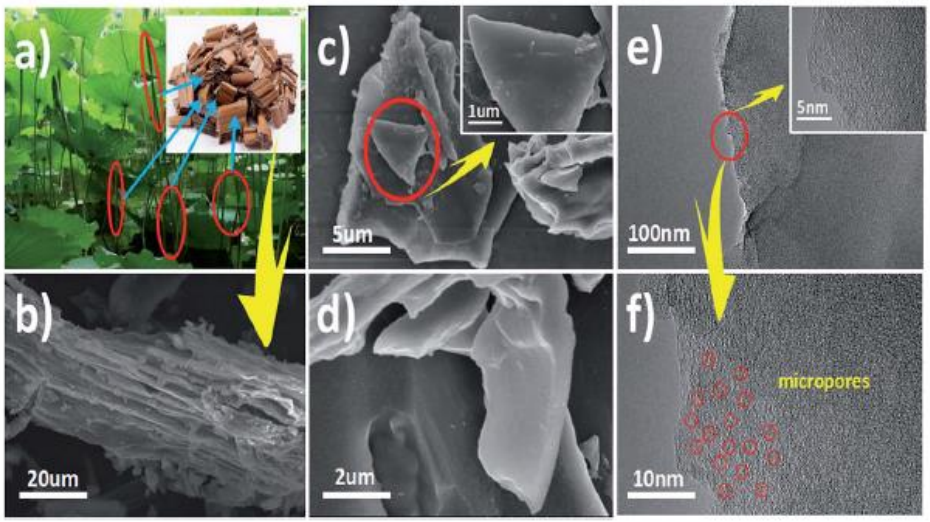

Figure 2

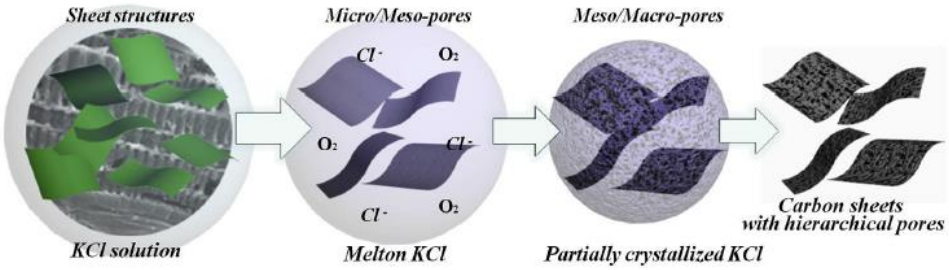
Sheet structures
Micro/Meso-pores
Meso/Macro-pores
Cl -
O2
O2
Cl -
Cl -
O2
KCl solution
Melton KCl
Partially crystallized KCl
Carbon sheets
with hierarchical pores

Figure 3

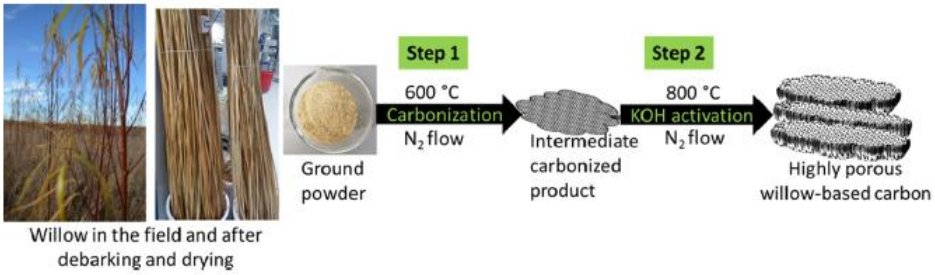
Step 1
600 °C
Carbonization
N_2 flow
Step 2
800 °C
KOH activation
N_2 flow
Ground powder
Intermediate carbonized product
Highly porous willow-based carbon
Willow in the field and after debarking and drying

Figure 4

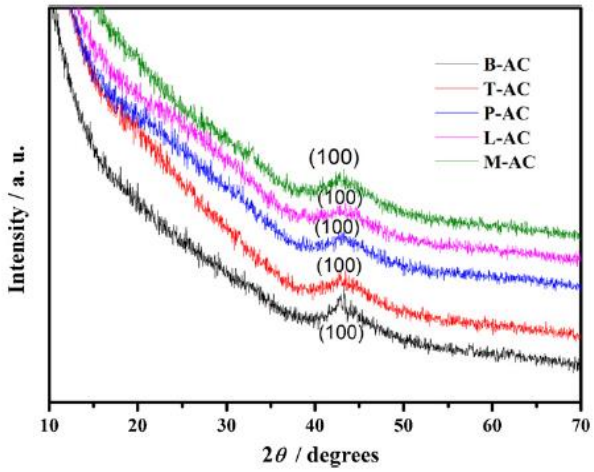
B-AC
T-AC
P-AC
L-AC
M-AC
(100)
(100)
(100)
(100)
(100)
Intensity / a. u.
10
20
30
40
50
60
70
2θ / degrees

Figure 5

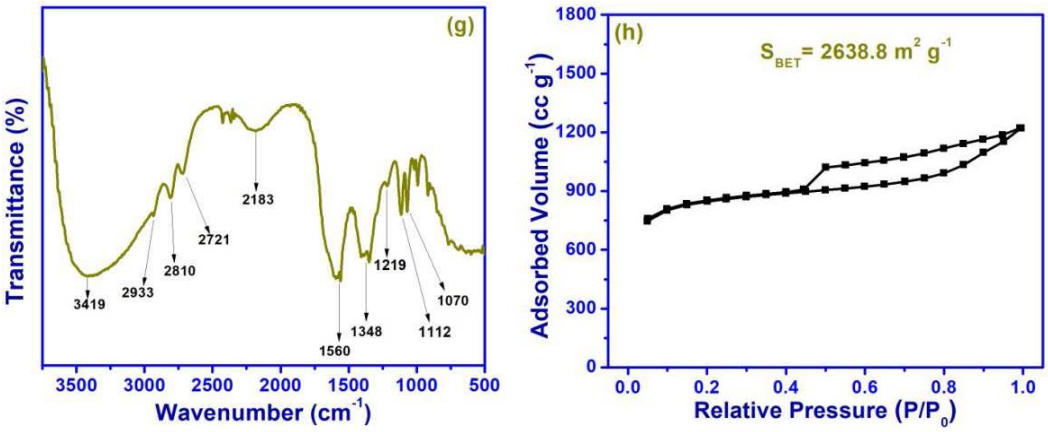
(g)
Transmittance (%)
Wavenumber (cm-1)
3419
2933
2810
2721
2183
1560
1348
1219
1112
1070
3500
3000
2500
2000
1500
1000
500
(h)
SBET = 2638.8 m2 g-1
Adsorbed Volume (cc g-1)
Relative Pressure (P/P0)
1800
1500
1200
900
600
300
0
0.0
0.2
0.4
0.6
0.8
1.0

Figure 6