Chapter

Phytomass-Derived Multifunctional Activated Carbon as a "Wonder-Material": A Paradigm Shift of Filth-to-Wealth

Palanichamy Kalyani, Thakku Rangachari Banuprabha, Chinnamayan Sudharsana and Nazim Anvarsha

Abstract

Activated carbon (AC) is a wonder-material that finds multifarious applications such as catalytic supports, removal of pollutants, electrodes in energy gadgets, gas storage etc. Surface area, chemical constituents and pore structures are a few traits required in the ACs which largely depend on the source of the precursors and processing methodologies adopted. In this context, the idea of recycling phytomass for producing ACs has attracted researchers seeing that the inexpensive and renewable nature of the phytomass can reduce the overall cost of producing ACs with diversified features and that it does not add CO_2 to the atmosphere leading to global warming (plants release only the same amount of CO_2 as they consumed while growing). Further, phytomass after their life possess no value but their conversion into ACs would be an economically profitable option leading to inexpensive ACs. As a consequent of these advantages this chapter has been planned and designed to provide certain interesting multifunctional aspects of low-cost phytomass derived ACs. The chapter is expected to provide research insights oriented towards identification of unexplored phytomass or wastes which could lead to carbon with novel properties tunable to the applications. Filth-to-wealth or in other words, recycling of wastes provides a strategy categorized under circular-bioeconomy, which is the want of the hour.

Keywords: Phytomass, Activated carbon, Adsorbent, Electrocatalysts, Supercapacitor, Antibacterial, Bio-sensors, Circular-bioeconomy, Recycle

1. Introduction

Activated carbon (AC), no wonder, is regarded as a wonder-material since it is a very vital active material in scores of applications such as catalytic supports, removal of pollutants, electrodes for battery and capacitors, gas storage etc., and these applications require carbon powders with specific functionalities like surface area, chemical constituents, pore structure etc. Since last decade, materials scientists are attracted towards biomass and more specifically, phytomass which have the source from the mass (biomass) of living and dead plants for producing

value-added materials. It is interesting to note that a total of 82% of the biomass is of plant origin and crop residues include more than half of the world's agricultural phytomass [1]. Moreover, a study indicate that the annual global production of wood-derived biomass is around 4.6 Gt out of which 60% is utilized for energy production, 20% for industrial 'round wood' manufacture and the remaining 20% will be primary production loss that remains in-field to decay. Further an estimated 80% of forest tree mass is being lost as waste [2]. Generally it is known that starch, cellulose, hemicellulose, fructose, glucose, amino acids, lignins, lipids, organics, inorganics etc. are the chief constituents of phytomass [3] and thus they are apparently rich in carbon content for producing AC powders and are deemed to be low-cost alternative for commercial carbons hitherto utilized for the above-said applications. Obviously, the omnipresent and plentiful agricultural discards effectively offer a secondary, inexpensive and renewable source of carbon. Having seen the basic information on phytomass, it is also pertinent to understand the present scenario of the landfills which have already become flooded with non-treatable garbage and that they do not admit solid-wastes anymore and consequently, we propose ways of segregating, recycling/up cycling/reuse of wastes for reducing disposal problems and improving a Nation's economy or in other words, "waste valorization", the processes of treating wastes for beneficial use that may reduce pollution and the concomitant environmental impacts, has now been developed into a trending research among materials advocates. Also, considering the production cost of materials/products, environmental and energy concerns, the process of reuse of phytomass wastes to generate value-added products is of dire need. Simultaneously, huge economy involved in the clearing-off the (phytomass) wastes globally has activated many research groups to recycle various categories of wastes to achieve value-added products by which the current energy emergency may possibly be mitigated. Thus waste phytomass should be seen as unexplored resources as well as zero-cost source of essential environmental services and not as wastes at all. Hence the production of AC materials, especially from these cheap and natural bio-precursors is a highly attractive research theme in the science of functional materials. Consequently this chapter has been planned to provide recycling based content having a great potential in reducing environmental impact, climatic issue and initiate circular bio-economy model. So this chapter has been designed as a review and summarize the key research reported on six interesting applications where the various zero-cost (waste) phytomass had served as the precursors for producing low-cost ACs. For consistency, the chapter has been sectioned individually under the following headlines based on the applications of phytomass-derived environmental friendly AC as;

1. Adsorbents

2. Electrocatalyst support for hydrogen gas generation from water splitting

3. Supercapacitor electrodes

4. Lithium-ion battery anodes

5. Electrochemical sensors

6. Antibacterial agents

Initially, certain fundamental aspects of AC are also quickly presented for the benefit of the readers. Hence the fundamental research results discussed in the

chapter would not only exemplify the multi-dimensional features and applications of phytomass-derived AC but also hints the variety and variability in carbon sources available and break through the conventional idea of obtaining high-performing active carbon too.

2. Fundamental aspects of activated carbon

Activated carbon (AC) refers to a wide range of carbonized black colored materials of high surface area and high degree of porosity [4]. AC has many applications, in addition to those mentioned earlier, like in the environment and industry for the removal, retrieval, separation and modification of various compounds in liquid and gas phases etc. [5].

2.1 Production of AC through physical activation

Physical activation is a commercially adopted two-step process that involves carbonization (pyrolysis) of carbon rich precursors in a neutral atmosphere followed by thermal treatment of the resultant mass in an atmosphere of oxidizing gases such as steam, CO_2, CO_2-N_2 or CO_2-air mixtures in the range of 800–1100°C. This method has the ability to produce AC powders of porous structure and hence physical activation is considered as an inexpensive and green because it is chemical-free. Nevertheless, long activation time, low adsorption capacity of prepared AC and high energy requirements are the main disadvantages [6].

2.2 Production of AC through chemical activation

Chemical activation, often known as wet oxidation, is usually suggested for organic precursor materials containing cellulose, such as wood, sawdust and phytomass. In this method, the precursors are activated at high temperatures in the presence of certain activating chemicals. In the first stage of activation, the raw material will be saturated or impregnated with oxidizing and highly dehydrated chemicals (activating agents) [7]. After impregnation, the suspension is dried and the remaining mixture will be heated for a given duration. Depending on the activating material and the properties of the final product, activation may require temperatures ranging from 400 to 900°C, when the cellulose is expected to break down and char. Ultimately, AC is obtained from the repeated washing of the resultant char.

Chemical activation agents, as mentioned earlier, are dehydrating agents that influence pyrolytic decomposition and inhibits the formation of bitumen, increase the carbon content and with subsequent changes in the thermal degradation of precursors result in the development of the porous structure of the carbon materials. These activating agents penetrate into the carbon structure creating porous network like structure in the AC, thereby increasing its surface area. It is to be mentioned that carbon particle size distribution, porous nature and surface area are the three important aspects that decides the final applications of the AC [8].

In physical activation, carbonization and activation phenomena occur in two separate furnaces while in the chemical activation these processes occur simultaneously in a single furnace. It is to be mentioned that the correct selection of the activation parameters like the amount of impregnation, weight ratio of the activating agents to dry precursors, temperature, final temperature of carbonization, carbonization time and activation atmosphere (space) are important to the quality and physical characteristics of the final AC produced by chemical activation. In fact,

chemical activation bestows more porous structure to the ACs than physical activation. Further, chemical activation is more economical as it requires a lesser processing temperature, time and yields higher carbon efficiency. Activated agents react with carbon matrices of the organic precursors and liberate various gases to form a porous structure. However, the need for repetitive washings to remove the unused activating agent from the final product at the end of activation process is one of the disadvantages of this method. In addition, toxic washings produced causes water pollution and therefore require secondary treatments. Different types of chemicals have different reactions with precursors and thus affect the features and nature of the ACs produced. **Figure 1** gives a rough scheme for producing AC by physical and chemical activation methods [3].

2.3 Description on activating agents

Effective activators so far used are alkaline compounds such as potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium chloride ($CaCl_2$) and potassium carbonate (K_2CO_3), acidic compounds like phosphoric acid (H_3PO_4) and sulphuric acid (H_2SO_4), also intermediate metal salts such as $ZnCl_2$. Based on the reactivity and physical nature of the activator, the mixing of the activator and organic precursors could be done by two modes viz., the physical mixing of the activator and precursor (both in dry conditions) and impregnation (solid precursor with melt or fused activator) [9].

H_3PO_4 is widely used in the activation of various lignocellulosic materials. $ZnCl_2$ acts as a dampening agent during activation. K_2CO_3 is known to be a better activator than KOH due to the production with higher yield, higher surface and pore volume and higher adsorbing capacity from aqueous solutions. Activation with alkaline materials such as NaOH and KOH produces ACs with large amounts of surfacial microspores. KOH is being popularly used due to its ability to produce AC with a high surface area, distribution of fine pore size, low environmental pollution, less corrosiveness and cost affordability.

2.4 Precursors for AC

AC can be produced from materials such as wood, coal and some polymers. Wood and coal are relatively economical, but exhaustible. Polymers are the main source of pure carbon whereas it leads to high production costs and the preparation processes require expensive raw materials, enormous time, energy and tedious preparation procedures. AC production costs can be reduced by either choosing a cheap raw material or by applying a proper production method [10]. Nevertheless,

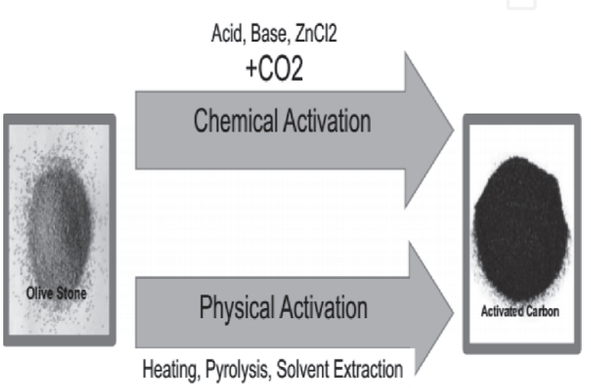

Figure 1.
Scheme showing the preparation of AC by physical and chemical activation methods [6] (Adapted with modification).

it is still a challenge to prepare AC with very specific characteristics, such as a given pore size distribution and using low-cost raw materials processed at low temperature (less energy costs). Therefore, it is necessary to find suitable low-cost raw materials that are economically attractive and at the same time present similar or even better characteristics than the conventional carbons.

The use of waste materials for the preparation of AC is very attractive in view of their contribution to decrease the costs of waste disposal, therefore helping environmental protection [11]. It is already known that any cheap material with a high carbon content and low ash and inorganics can be used as a raw material for the production of AC [12]. Hence the production of AC materials from phytomass has become very much popular in recent years. Literature shows that there have been many interesting research efforts to obtain low-cost AC from a variety of phytomass wastes such as sugarcane bagasse [13], rice straw [14], cotton stalk [15], coconut shells [16], wood [17], nut shells [18], olive seeds [19], apricot stones [20], almond shells [21] and date pits [22] for adsorption studies, for example application of AC.

2.5 Structures of AC

Structure of AC is also considered as an important factor while proposing any new applications. So a short description on the structures of AC is given here. Basically, three important structures have been described.

2.5.1 Porous structure

Generally, ACs show porous characteristics such as specific surface area (SSA), pore volume and pore size distribution and contain up to 15–20% of minerals in the form of ash [12]. The porous structure of AC is presumed to have developed during the carbonization process and further developed during activation when tar, volatile and other carbonaceous materials which might be present in the spaces between the elementary crystallites escape from the precursor. The structure of pores and pore size distribution depends on the nature of the precursors and the activation process. It is believed that during the activation disorganized carbon are removed by exposing the crystallites to the action of activating agent which leads to the development of porous structure. Dubinin [23] classifies pores according to their average width, which represents the distance between the walls of slit shaped pore or the radius of a cylindrical pore, proposed by and officially adopted by the IUPAC. Thus the pores are classified into (i) micropores (diameter (d) < 2 nm), (ii) mesopores (2 nm $< d <$ 50 nm) and (iii) macropores ($d >$ 50 nm). **Figure 2** represents a view of these pores.

The micropores form the largest part of the internal surface and are accessible to the adsorptive molecules [25] or electrolyte ions. Generally, micropores contribute at least 90% of the total surface area of an AC, whereas the surface area of mesopores form less than 5% of total surface area and the mesopore volume varies between 0.1 and 0.2 cm^3g^{-1}. The contribution of macropores to the total surface area and pore volume is very small and does not exceed 0.5 m^2g^{-1} and 0.2–0.4 cm^3g^{-1} respectively. SSA and porosity are found out by N_2 adsorption studies.

2.5.2 Crystalline structure

Crystalline structure of AC starts to develop during the carbonization process. The crystalline structure of ACs is different from the graphite structure with respect to the interlayer spacing, which lies between 0.34 & 0.35 Å in ACs and 0.335 Å in

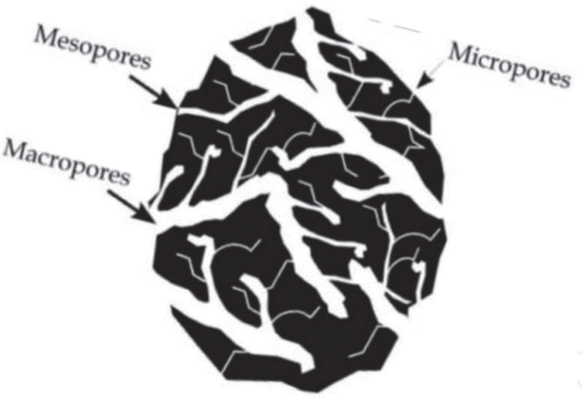

Figure 2.
Schematic presentation of macro, meso and micropores in AC [24] (Adapted with modification).

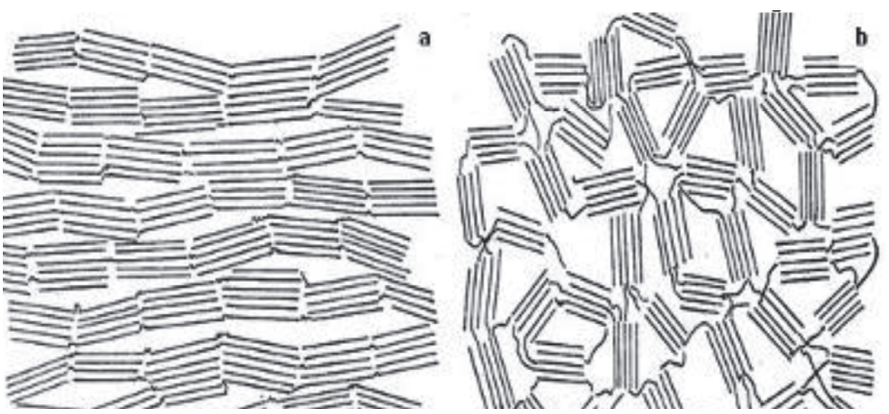

Figure 3.
Scheme of structure of AC (a) graphitized carbon and (b) non-graphitized carbon (adapted with modification from [26]).

graphite. Nevertheless, the basic structural unit of AC is in close approximation with the graphite structure. Based on the graphitizing ability, ACs are classified into graphitizing carbons and non-graphitizing carbons. The above two structures of carbons is schematically presented in **Figure 3**.

Graphitizing carbon may have a large number of graphite layers oriented parallel to each other and is delicate due to the weak cross-linking between the neighbor micro crystallites and has a less-developed porous structure. On the other hand, non-graphitizing carbons are hard due to strong cross linking between crystallites and show a well-developed microporous structure [26]. The formation of non-graphitizing structure with strong cross links is promoted by the presence of associated oxygen or by an insufficiency of hydrogen in the precursors.

2.5.3 Chemical structure

In addition to the porous and crystalline structure discussed above, the AC surface has also chemical structure. It is well established that the adsorption capacity on AC is determined by its porous structure and is strongly influenced by the chemically bonded heteroatoms like oxygen, nitrogen, sulphur and halogens [12, 27, 28]. These heteroatoms are obviously derived from the phytomass precursors and involve in the structure of AC during carbonization process or they may be chemically bonded to the surface during activation [29]. The heteroatoms are likely to be bonded to carbon atoms of the corners and edges of the aromatic sheets or to the carbon atoms at defect positions to form carbon–oxygen, carbon-hydrogen,

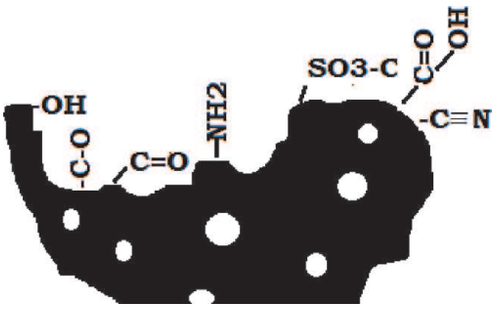

Figure 4.
Model of various organic functional groups on the activated carbon [30] (= carbon matrix; = pores).

carbon-sulphur, carbon-nitrogen and carbon-halogen surface organic compounds (see **Figure 4**), known as surface groups or surface complexes [28, 31].

Ultimately, the organic hetero functional groups greatly influence the properties and nature of the phytomass-derived AC.

3. Multifunctional aspects of phytomass-derived activated carbon

It can thus be seen that due to the increasing demand of AC, there is a strong need for the sorting out of new precursors for AC which should be cost effective than the commercially available ACs. Although, a variety of raw materials were explored for the preparation of AC in earlier studies, scientists are still exploring new materials depending on their availability and suitability for producing AC with multi-functions. Additionally, application of phytomass carbon electrodes stands as an important class of technology where 3R principles are followed. Thus remarkably, the utilization of phytomass as raw material for the preparation of AC has increased in recent years in view of the foregoing facts on AC. In the following sections, interesting multifunctional aspects of phytomass-derived AC will be deliberated.

3.1 Application of phytomass-derived AC as an adsorbent

The use of charcoal or AC for the adsorption (removal) of pollutants in air or toxic ions and dyes from contaminated water is best known for over 80 years and further adsorption properties, mechanisms, kinetics and theories of adsorption are also well established. But the potential of economically cheaper and renewable phytomass-derived AC as adsorbent was understood since the past decade though the search for better AC is still going-on due to the exponential demand for treatment of industrial effluents.

There are enormous sorptive studies with biomass-derived activated carbons and to cite a few; Tura and Tesema [32] have removed methylene blue using AC derived from *Delonix regia* seed pods. They have shown that adsorption of methylene blue is mainly pH dependent and that maximum adsorption takes place in slight neutral pH. Electrical conductivity and total suspended solid was found to decrease after adsorption which, indicates the decrease of ions from methylene blue dye proving the removal of color i.e. the dye. In yet another special work, Sekaran et al. [33] have reported the preparation of mesoporous-activated carbon from rice husk by precarbonization at 400°C, chemical activation using phosphoric acid at various temperatures and have immobilized Bacillus sp. in the mesoporous-activated carbon for the degradation of sulphonated phenolic compounds in

wastewater. *Delonix regia* derived AC has also been utilized to remove Hg [34], Pb and Ni [35].

Good amount of work has been reported on fluoride removal from water. Fito et al. [36] have done a very significant work using H_2SO_4 activated *C. edulis* stem derived AC for the removal of F^- from aqueous solutions. Stem of the *Vitex negundo* plant [37], $CaCl_2$-modifed *Crocus sativus* leaves [38] and bark of *Morinda tinctoria* [39] are further interesting works involving F^- removal. **Figure 5** is a picture where adsorbed molecules in the pores of the AC are shown.

Above reports are just bits from a massive published literature. However, readers can have a detailed outlook from Jorge Bedia et als' report [41] where they have made an excellent exhaustive review on the synthesis and characterization of biomass-derived carbons for adsorption of emerging contaminants from water. All the above read reports convey the need for commercially viable and potential activated carbon-based adsorbents.

3.2 Application of phytomass-derived AC for preparing electrocatalyst for hydrogen gas from water electrolysis

It is well known that, noble metals like Pt and Ru based electrocatalysts are employed for producing hydrogen by electrolyzing water and usually electrocatalysts are fabricated by supporting or loading fine Pt or Ru particles on quality carbon powders (the carbon is called catalyst support), such that more number of active sites will be available for efficient and complete electrolysis. Falling in that line, an innovative and ever first attempt has been reported by the authors of the present chapter on adopting a zero-cost green precursor viz., grass biomass, by converting the grass biomass into a biochar and attempting to produce an electrocatalyst with platinum for generating hydrogen gas through electrolysis of water [42].

Cleaned turf grass blades were chosen as the phytomass of producing AC for supporting Pt particles to finally utilize as electrocatalyst for hydrogen gas generation through electrolysis of water. The procedure involved an activation of grass blades with $ZnCl_2$ followed by heat treatment at 250°C. As an initial trial, 1% Pt was supported over the grass-derived AC powder to result in Pt@G-AC. After various physical characterization studies, Pt@G-AC powder was assessed for catalytic activity in 1 M sulphuric acid solution for H_2 generation through linear sweep and cyclic voltammetric studies. Encouraging results were obtained suggesting that grass can be considered as a renewable alternative for producing carbon supports

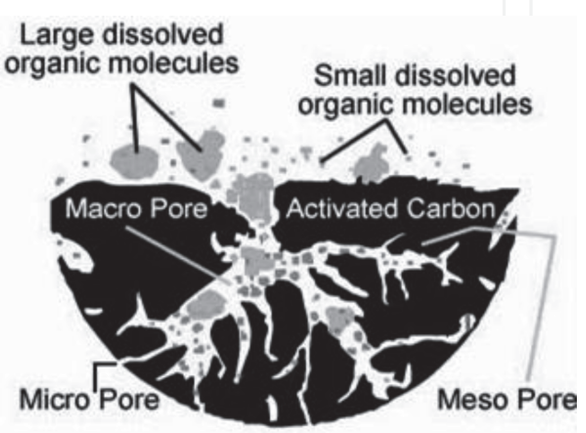

Figure 5.
Image showing the adsorption of molecules in the pores of AC [40] (adapted with modification).

for electrocatalysts but also paves way for the production of low-cost carbon for other applications like adsorbent for color, odor and hazardous pollutants and electrode materials as well, as will be highlighted in the subsequent sections. **Figure 6** gives LSV plot of G-AC with and without 1% Pt electrodes in 1 M H_2SO_4. Since no other reports are available on this particular application it seems that intensive research is this area is highly required and hence it is expected to pick up in the future.

3.3 Phytomass-derived AC for supercapacitor electrodes

Energy storage devices are the key components for a successful and sustainable world and supercapacitors (SCs) are one among them. SCs are able to supply considerable amount of power over a short time with extended cycle life. They offer a higher specific power density than most batteries and a higher energy density than conventional capacitors [43]. SCs are very useful in load leveling applications where a sudden boost of power is needed in a fraction of a second. More importantly, they do not release any heat during their operation and have a very long lifetime thus reducing the cost of maintenance. Also they do not release any hazardous substances that can damage the environment and their performance does not degrade with time. Hence for these reasons, SC is considered as a versatile technology that plays a prime role in partly fulfilling the energy demands of present and the future.

It is well known that certain physical features of the electrode materials determine the performance characteristics of the energy systems [44]. SCs making use of phytomass-derived porous carbon has the advantages like production of low cost carbon electrode components, environmental friendliness and good capacitive performance. Thus the search and research for advanced electrode materials is sought after and obviously very recently, phytomass-derived AC is providing unprecedented opportunities for researchers to design and fabricate innovative electrode materials for high performing SCs.

As far as research on phytomass-derived AC as electrode material for SCs is concerned, a wealth of information related to its preparation methodology, physical properties and electrochemical properties are available in the open literature in the form of reviews and research communications. The authors of this chapter have reported ample number of interesting work and to cite a few; on papaya seeds [45], onion peels [46] and recently on banyan prop root [47] for the possible application as electrode for SCs.

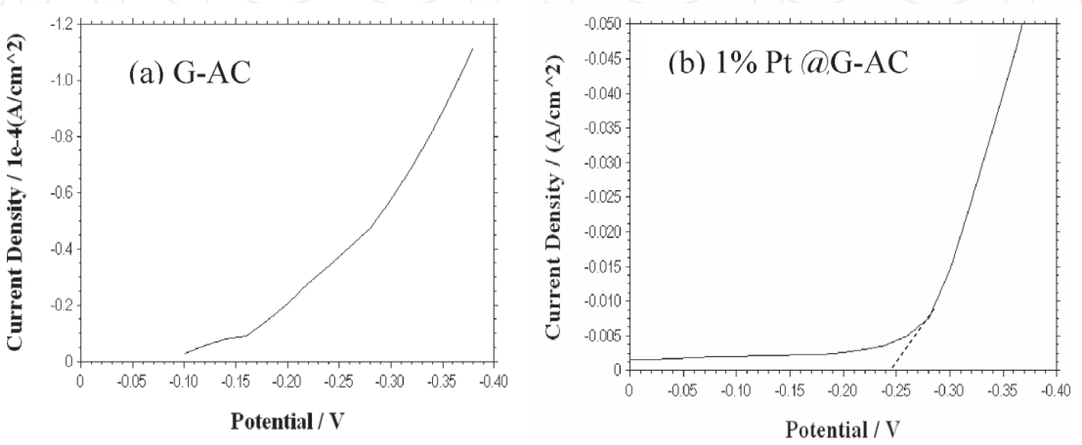

Figure 6.
LSV plot of (a) G-AC and (b) 1% Pt@G-AC electrodes in 1 M H_2SO_4 [42].

One important concept in the charge storage mechanism is the pseudocapacitance which is dealt as follows. In an ideal double layer capacitor, energy is stored in electric double layer and no charge transfer occurs across the interface between the electrode and the electrolyte. However, it is possible that some redox reactions (faradaic) can still happen due to the existence of various heteroatoms like O, N & S present in the form of organic functional groups on the phytomass-derived AC. The capacitance arising from these faradaic reactions is called pseudocapacitance. Therefore the total capacitance is a combination of capacitance contribution from electrostatic charges and faradaic charge transfer redox reactions [48] which is given in equation 1.

$$C_{total} = C_{dl} + C_f; \quad (1)$$

where C_{total} is the total capacitance, C_{dl} is the electrical double layer capacitance, C_f is the pseudocapacitance. Thus by introducing functional groups onto carbon material, pseudocapacitance can be enhanced [49]. The faradaic charge transfer processes at the electrode involving N [50], S [51] and O are given below [52].

$$C* = NH + 2H^+ + 2e^- \leftrightarrow C*H\text{–}NH_2 \qquad O = S = O + 2e^- + H_2O \leftrightarrow > SO + 2OH^-$$

$$C*\text{–}NHOH + 2H^+ + 2e^- \leftrightarrow C*\text{–}NH_2 + H_2O; \quad > SO + e^- + H_2O \leftrightarrow > SOH + OH^-$$

$$O = Ph = O + 2H^+ + 2e^- \leftrightarrow HO - Ph - OH; \qquad R = O + H^+ + e^- \leftrightarrow R - OH$$

$$> CO + H^+ \leftrightarrow > COH^+_{(ads)}; \qquad > CO + H^+ + e^- \leftrightarrow > COH$$

where C* stands for the carbon structure, Ph and R respectively indicate phenyl and aliphatic groups. Therefore an electrochemical capacitor is called "supercapacitor" or "ultracapacitor". Further understanding on this topic can be had from references [53–55].

Having reviewed various aspects of capacitors and significant reported research, it is still relevant to search for newer and cheaper electrode materials and that too if the electrode materials could be derived from greener sources and waste phytomass then it will be a welcoming suggestion for the current scenario of energy crisis.

3.4 Application of phytomass-derived AC as lithium-ion battery anodes

Research reports on phytomass-derived AC as anodes in lithium-ion batteries seem not very much abundant as available for adsorption and supercapacitor electrodes studies. However, a few noteworthy studies for application as electrodes in lithium-ion battery (LIB) anodes are presented here. Zhang et al. [56] have produced carbons with a high surface area rice straw. They report that the hierarchical porous network with large macroporous channels and micropores within the channel walls enable the porous carbons to provide the pathways for easy accessibility of electrolytes and fast transportation of lithium ions These porous carbons which show a particular large reversible capacity are proved to be promising as anode materials for high rate and capacity LIBs. Bhardwaj et al. [57] synthesized carbon nanomaterials by pyrolysis of tea leaves and used as anode in LIBs. The highest specific capacity reported was 64 mAh g^{-1}. Zhang et al. [58] used pinecone hull and activated at 800°C under CO_2 atmosphere to obtain microporous carbon. This served as the anode for lithium secondary batteries and retained a discharge capacity of 357 mAh g^{-1} and coulombic efficiency of 98.9% was reported to be achieved at higher current density of 10 mA g^{-1}.

Hwang et al. [59] obtained disordered carbon materials by pyrolysis of coffee shells at 800 and 900°C with KOH and $ZnCl_2$ porogens. The first lithium insertion capacity was 524 & 603 mAh g^{-1} for the untreated samples pyrolyzed at 800 & 900°C respectively, while obtained 1150 & 1200 mAh g^{-1} for the KOH treated coffee shells pyrolyzed at the same temperature. Carbon powders of distinct and interesting morphologies were synthesized by pyrolyzing soapnut seeds, jack fruit seeds, date seeds, neem seeds, tea leaves, bamboo stem and coconut fibers, without using any catalyst. These carbon materials were utilized as the anode in LIBs [57]. Amongst the various precursors, carbon fibers obtained from soapnut seeds and bamboo stem, even after 100 cycles, showed the highest capacity of 130 & 93 mAh g^{-1} respectively. In yet another work, Stephan et al. [60] treated banana fibers with pore forming substances such as $ZnCl_2$ and KOH. The BET surface area of the untreated carbon was 36 m^2 g^{-1} and increased to 686 m^2 g^{-1} & 1097 m^2 g^{-1} for the carbons after treatments with KOH and $ZnCl_2$, respectively. On employing these porogen treated carbons in LIBs, the specific capacities for the $ZnCl_2$ treated sample was found to be 3123 m^2 g^{-1} while it was 921 m^2 g^{-1} for the KOH treated sample and for the untreated carbon, the specific capacity was extremely low as 625 mAh g^{-1}.

A comprehensive list of phytomass-based AC utilized in LIBs has been provided in Ref. [55]. Thus the foregoing reports clearly suggest that the phytomass-derived AC has ample scope for investigation for anode materials in advanced energy systems like LIBs.

3.5 Electrochemical sensors

Although a complete description on sensors is out of scope of this chapter, a bird's eye view is worthwhile. A sensor is a device which provides a usable output in response to a physical quantity and converts it into a signal suitable for processing (e.g. optical, electrical, mechanical). Transducer is the active element of a sensor. A biosensor is an analytical device used for the detection of a chemical substance that combines a biological component with a physicochemical detector. The sensitive biological element, for e.g. tissue, microorganisms, organelles, cell receptors, enzymes, antibodies, nucleic acids etc. is a biologically derived material or biomimetic component that interacts with, binds with or recognizes the analyte under study [61]. The biologically sensitive elements can also be created by biological engineering. The transducer or the detector element, which transforms one signal into another one, works in a physicochemical way such as optical, piezoelectric, electrochemical, electrochemiluminescence etc. resulting from the interaction of the analyte with the biological element to easily measure and quantify. A biosensor typically consists of a bio-receptor (enzyme/antibody/cell/nucleic acid/aptamer), transducer component (semi-conducting material/nanomaterial), and electronic system which includes a signal amplifier, processor and a display. There are three main types of electrochemical sensors namely; potentiometric, amperometric and conductometric. **Figures 7** and **8** respectively scheme the basic representation and components of a biosensor.

Electrochemical biosensors are an important type in sensor technology and have electrodes which translate the chemical signal into an electrical signal such as conductance, resistance or capacitance of the biosensor surface. Electrochemical sensors are able to detect many biomolecules in the human body such as glucose, cholesterol, uric acid, lactate, DNA, hemoglobin and blood ketones [64]. Thus they have great potential to detect diseases related to imbalances of biomolecules. Mostly, they are widely used for biosensing applications, however studies on biosensing–drug delivery applications are only limited. Enzyme- or protein-based electrochemical biosensors that have drug-release capability can be useful for the

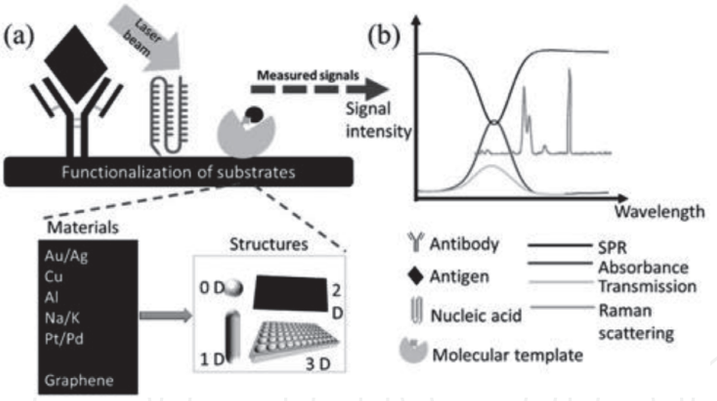

Figure 7.
(a) Basic schematic representation of a biosensor (b) output signal from a sensor [62] (adapted with modification).

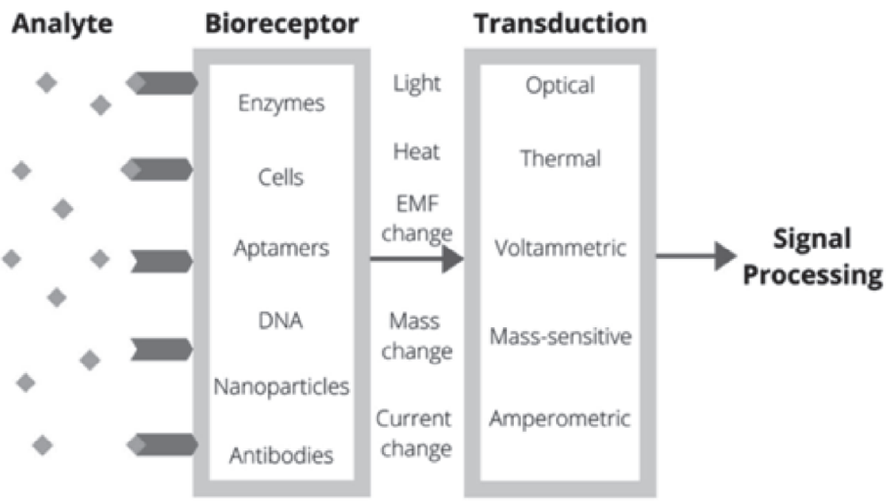

Figure 8.
Components of a biosensor [63] (adapted with modification).

treatment of various diseases. For example, xanthine oxidase enzyme catalyzes the production of hypoxanthine and xanthine and overproduction of these products cause renal failure [65].

High sensitivity, lower detection limits, automation, reduced costs of testing, and development of disposable devices and methodologies capable of working with very small sample volumes are some of the advantages associated with electrochemical biosensors. Also, electrochemical sensors are unaffected by sample turbidity or interference from absorbing and fluorescing compounds like spectroscopy-based techniques; they require comparatively simple instrumentation that requires low power and is portable. Use of electrochemical techniques, over optical and other transduction techniques, exhibits excellent sensitivity and a large linear detection range in a wide range of solvents, electrolytes, temperatures, etc. Electrochemical biosensors can be classified into voltammetric, amperometric, conductometric, impedimetric and potentiometric. Readers can have a complete understanding of various aspects of sensors, types and their applications from references [66–68].

3.5.1 Advantages and disadvantages of biosensors

Biosensor technology has been developed enormously since their introduction in 60s. They offer diverse advantages such as less complicated sensor setup, cheap production of microelectronic circuits and a user-friendly interface with

conventional electronic processors [69]. Further electrochemical biosensors are also robust, easy to miniaturize, and offer broad detection limits with the small volumes of analyte (biofluids) requirements even if turbidity or optically absorbing and fluorescing compounds are present. Nevertheless, they have certain disadvantages too that hinder further developments. For example, they do not have the distinct surface architecture that would facilitate high sensitivity in detection and unique recognition of the response to the selected biochemical event [70]. This means that the pH and ionic strength of biofluids can greatly influence the behavior of the biosensors. Hence sensor technology needs to be developed in order to have increased intensity of the signal and improved signal to noise ratio.

3.5.2 Phytomass-derived AC in sensor application

With the impressive progress in the electrochemical sensing technologies and their application in bio-analytical chemistry, it would now be possible to utilize phytomass-based AC to show that high sensitive and low-cost sensor production is commercially feasible in the near future [71]. In this context, a few important research advancements utilizing phytomass-derived AC in sensors has been presented below.

Kim et al. [72] have reported a biomass-derived carbon for the electrochemical determination which involved the initial activation of kelp powder with $ZnCl_2$, followed by a second activation step with KOH. The above AC coated on GCE modified electrode showed high sensitivity, selectivity and a good detection limit for the determination acetaminophen with the detection limit of 0.004 μM. Also the modified electrode showed good result towards acetaminophen in the presence of ascorbic acid and dopamine with the detection limit of 0.007 μM.

Zhang et al. [73] have reported that $ZnCl_2$ activated peel of kiwi fruit based carbon fibre (CF) provided a high sensitivity and selective signaling of ascorbic acid (AA), dopamine (DA), and uric acid (UA) with linear response ranges of 0.05–200 μM, 2–2000 μM, and 1–2500 μM, respectively and its detection limits (S/N = 3) as 0.02 μM, 0.16 μM, and 0.11 μM, respectively and this method was successfully applied to detect AA, DA, and UA in real sample analysis. Wang et al. [74] have shown PBNPs-3D-FKSCs, CuNiNPs-3D-KSCs and CoNPs-3D-KSCs (KSC: kenaf stem carbon, 3D: three dimensional) with honeycomb structure electrodes with good electrocatalytic performances for the reduction of H_2O_2, oxidation of glucose and amino acid.

Oliveira et al. [75] have reported that carbon paste electrode modified with nitric acid activated biochar obtained by the pyrolysis of castor oil cake biomass at 400°C for spontaneous preconcentration of methyl parathion (MP) and for further quantitative determination in drinking water. The electrode showed good sensitivity and limits of detection of MP as 760 μA L $mmol^{-1}$, 39.0 nmol L^{-1}, respectively.

Kalinke et al. [76] for the first time have reported the determination of paraquat (PQ^{2+}) by Differential Pulse Adsorptive Stripping Voltammetry (DPAdSV) using a carbon paste electrode modified (CPME) with biochar obtained from castor oil cake at different temperatures (200–600°C). The best voltammetric response was verified using biochar yielded at 400°C (CPME-BC400). Linear dynamic range (LDR) for PQ^{2+} concentrations between 3.0×10^{-8} and 1.0×10^{-6} molL^{-1} and a limit of detection of 7.5×10^{-9} molL^{-1} were verified. The method was successfully applied for PQ^{2+} quantification in spiked samples of natural water and coconut water.

Madhu et al. [77] have reported that PSAC/Co_3O_4 (PSAC: Pongam seed shells derived activated carbon] modified electrodes have potential as nonenzymatic glucose sensor and supercapacitor with ultrahigh sensitivity of 34.2 mA mM^{-1} cm^{-2} with a very low detection limit of 21 nM. Shahzada et al. [78] have reported that

sulfur-doped reduced graphene oxide (SrGO) product fabricated using an eco-friendly biomass precursor "lenthionine" through a high temperature doping process have high sensitive electrochemical sensor for detection of 8-hydroxy-2-deoxyguanosine(8-OHdG) molecule. The sulfur-doping amount was regulated and a maximum sulfur content of 2.28 atom% was achieved through controlling the precursor amount. It was homogenous presence of large number of sulfur atoms in SrGO in the form of thiophenic (CSC) bond that produced robust sensitivity (~1 nM), very wide detection window (20–0.002 M).

Ni et al. [79] have modified heteroatom-enriched activated carbon-nickel oxide (HAC-NiO) nanocomposite into NiO-HAC/GCE) and have built a novel glucose sensor which exhibited a wide linear concentration range of 10 μM–3.3 mM and a low detection limit of 1 μM) towards glucose oxidation. Travlou et al. [80] have treated wood-based commercial activated carbon (BAX) and its oxidized counterpart (BAX-O) with melamine and then heated at 450°C in nitrogen. Further oxidation with nitric acid was also done. The carbons were tested for ammonia sensing (45–500 ppm of NH_3). Further the role of the nitrogen functionalities on the electrical performance of the carbons was investigated by testing their selectivity with respect to H_2S sensing. Interestingly, pyridinic groups, acting as p-type impurities were found to be responsible for the observed opposite electrical responses of the melamine impregnated samples upon exposure to NH_3/H_2S. This facilitated H_2S dissociation into H^+ and HS^- ions, speculates the authors. The latter ions, either by providing ionic conductive paths through the carbon matrix or through their oxidation to SO_2 may cause a decrease of the normalized resistance.

Hayat et al. [81] have deposited a TiO_2 modified activated carbon on the surface of screen printed carbon electrodes (SPCEs) and used in the direct oxidation of phenols. Calibration curves showed a high sensitivity and wide linear range for each studied compounds viz., p-nitrophenol, 1-naphthol, catechol and hydroquinone. The authors say that there was no interference of $Na^{+,}$ K^+, Cl^-, Br^-, Mg^{2+}, Zn^{2+} and NO_4^- ions and show 96% recoveries in real sample analysis.

Koskun et al. [82] have synthesized activated carbon (AC) decorated monodisperse nickel and palladium alloy nanocomposites modified glassy carbon electrode (Ni-Pd@AC/GCE NCs) by in-situ reduction technique and they showed a very low detection limit of 0.014 μM, a wide linear range of 0.01 mM–mM and a very high sensitivity of 90 mA mM^{-1} cm^{-2}. Furthermore, monodisperse Ni-Pd@AC/GCE was utilized to detect glucose in real sample species.

Aparna et al. [83] have reported that the $NiFe_2O_4$-AC-modified glassy carbon electrode (GCE) showed excellent electrocatalytic activity towards DA (dopamine) compared to $NiFe_2O_4$/GCE and AC/GCE. This has been attributed to the synergistic action and the large surface area of the nanocomposite. Differential pulse voltammetry (DPV) was employed for the detection of DA wherein the detection limit of 0.4 μM along with a linear range of 5 μM to 100 μM was realized. Wang et al. [84] utilized DPASV (differential pulse anodic sweep voltmmetry) technique to show that the peak currents have linear relationship with Pb^{2+}, Cd^{2+} and Zn^{2+} concentrations respectively in the range of 0.5–2.25 mg/L, 0.5–4.0 mg/L and 1.0–4.0 mg/L with detection limits of 0.1, 0.3 and 1.0 mg/L (S/N = 3) respectively.

Thus it is hoped that the information provided in this section proves valuable and stimulates further research and developments in the promising field of phytomass-derived AC for flexi-sensors in the near future.

3.6 Application of phytomass derived AC as potential antimicrobial

Natural plant products are always interesting to explore because of their significant antibacterial, antifungal, antiviral and anticancer activity and the presence of

elements such as S & N has been proved responsible for their action [85]. Likewise, it has already been mentioned that ACs derived from phytomass too has these heteroatoms present in the form of organic functional groups in its structure to explain the activity observed against certain human pathogens. It is motivating and interesting to know that the application of kitchen soot was earlier in practice as an antimicrobial and was called "old woman's remedy" [86]. Consequently, natural carbon seemed to occupy a paramount place in household medicine. Scanning of literature shows that not many research reports have appeared pertaining to antibacterial activities of phytomass-derived AC and hence a few valid reports are given here to substantiate the importance of phytomass-derived ACs. Yallappa et al. [87] have done a revolutionary research using groundnut shell-based nano carbon, which proved in-vitro antibacterial activity. In-vitro evaluation of antibacterial efficacy using *Passiflora foetida* derived AC against a score of pathogens has been reported by Dheeban et al. [88]. Similarly, Lakshmi et al. [89] have elaborately reviewed interesting reports on AC nanoparticles from biowaste as a new generation antimicrobial agents.

In yet another research, Shamsi et al. [90] have reported a clear zone of inhibition of carbon nanoparticles obtained from sandal wood bark against *B. cereus*, *E. coli*, *C. violeceum* and *P. notatum*. Sheena et al. [86] have reported enormous

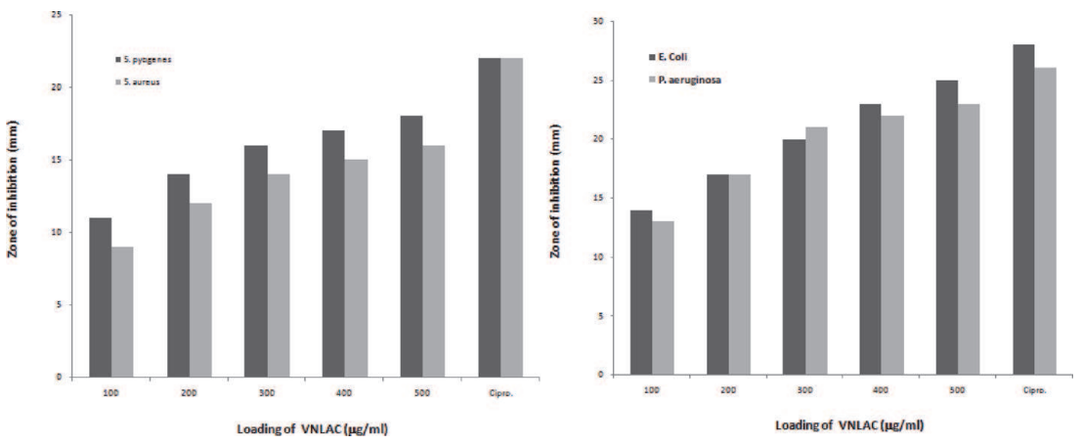

Figure 9.
Antimicrobial activity of Vitex negundo *leaves AC against gram-positive pathogens (left) & gram-negative pathogens (right) [30].*

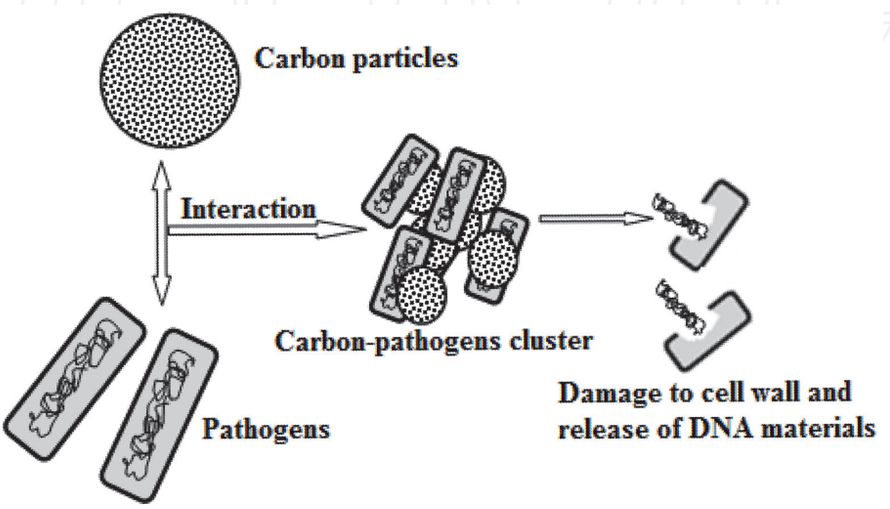

Figure 10.
Scheme of plausible mechanism of antimicrobial activity of AC [30].

antimicrobial activity of carbon nanoparticles isolated from natural sources against pathogenic gram-negative and gram-positive bacteria. Karthik et al. [91] have prepared AC from *Tribulus terrestris* and have proved activity against *E. coli*, *B. subtilis*, *S. aureus*, and *K. pneumoniae*. Anvarsha et al. [30] has recently reported *Vitex negundo*-derived AC and its importance as an antibacterial agent against human pathogens. Zone of inhibition was measured with reference to 5% DMSO and values are plotted in **Figure 9**. A schematic of mechanism of antimicrobial activity of AC particles is shown in **Figure 10**, which is self explanatory.

All these reports conclude that carbon materials produced from the chemical activation of phytomass still has huge potentials against various bacterial strains and that in-depth investigation should be devoted for a commercial success in the near future. Hopefully, the results envisaged through the above studies would certainly attract researchers globally to study various phytomass-derived carbons as novel and affordable therapeutic agents which can effectively inhibit the growth of various strains of microbes.

4. Summary, conclusions and future prospects

The objective of the chapter is to appreciate and provide details of the multifunctional aspects of zero-cost phytomass-derived AC in the areas where the most coveted commercial AC is hitherto celebrating. Fundamental aspects of AC were discussed initially followed by six important applications of the phytomass-derived AC to understand the value-added advantages of phytomass-derived AC. It is well documented that the preparation of carbonaceous materials from phytomass or biomass wastes has also important added advantages such as an effective management of the wastes and lower synthesis costs. Consequently, this chapter is a fair consolidation of research done on six major fields where the novel phytomass-derived AC can find applications equal to commercial ACs now. Nonetheless, researchers are still looking for practical and affordable carbons which can be applied at the commercial scale that leads to improved performance and applications in future.

With the authors' own experience in the title subject and with a global view to realize the suitability and applicability of the synthesized phytomass-derived ACs in the commercial quarters, the problems of significance which may invite research attention has been identified and have been listed below.

- Extensive investigation needs to be carried out to produce ACs with even better surface characteristics with tailored pore-size distribution through different routes such as chemical activation, physical activation, two stage activation or microwave heating.

- Process economy mainly depends on the selection of precursors and methods of preparing AC. Thus the cost analysis should be carried out to evaluate the practical applications.

- The use of phytomass-derived ACs and their modified ones in photocatalysis has recently been reported as a novel application. Hence investigation on this aspect is expected to gain impetus in the near future, which would sure be lending hands to address environmental issues.

- Solid wastes that are disposed by the industries and agricultural sectors are a great environmental concern. Hence research activity is needed to utilize these solid wastes to convert in to useful products, adopting filth-to-wealth concept.

It is hoped that at least some of these research activities will be initiated in the near future with unconditional research collaboration. But with a certain amount of commercial success that has already been achieved and the multitude of R & D efforts that are presently going on worldwide regarding the elimination of safety problems, improvement in performance and reduction of cost etc. phytomass carbon in the above-said fields will see a tremendous leap in the commercial market and will definitely open up new avenues in academic, research and industrial sectors. Advantageously, utilization of phytomass-derived multifunctional AC strengthens the circular-bioeconomic status of a Nation too. Interestingly, the authors of the present chapter has already committed similar type of studies with AC derived from a few other phytomass such as calotropis stem, palm leaves, coconut leaves etc. for the six classes of applications seen in the foregoing sections. Since the physical features and chemical constituents influence the performance tunable for multifarious applications, we have diversified choice of sources of phytomass carbon. Thus the consolidation of research work presented in this chapter opens up avenues for the utilization of various zero-cost phytomass for producing new carbon materials for various novel applications, which obviously proves that the phytomass-derived multifunctional AC is a "wonder-material" and the concept is unquestionably a paradigm shift of filth-to-wealth.

Author details

Palanichamy Kalyani*, Thakku Rangachari Banuprabha, Chinnamayan Sudharsana and Nazim Anvarsha
Department of Chemistry, DDE, Madurai Kamaraj University, Madurai, Tamilnadu, India

*Address all correspondence to: kalyani_1973@yahoo.com

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