Review Article

Activated Carbon from Coconut Shell: Synthesis and Its Commercial Applications-A Recent Review

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Abstract
Biomass is abundant in nature and can be utilized for the innovation of new materials. The selectivity of renewable energy resource for the production of activated carbon is quite challenging. This is because of the variance in the yield percentage of carbon. Our current review focuses on production of activated carbon obtained from coconut shell and its commercial applications in various fields. It gives complete structure of the different carbon materials that are activated in the form of a matrix, composite, deposition layer and graphene form. The significance of the bioresources is described as a starting material to produce AC to meet the challenges of the industrial and biomedical fields. The importance of parameters during carbon activation, such as carbonization temperature, selection of activating agents and the suitable method was discussed in detail. The importance of coconut shell as the best biomass producing highly efficient AC is compared with other raw materials. A deep insight into the study of raw materials essential for the preparation of activated carbon (AC) has been studied and reviewed thoroughly for the manifestation of efficient bioresource. Coconut shell is an underutilized renewable agricultural waste for production of AC via various synthesis protocols. This review explains the significance of coconut shell as a cheap substrate and eco-friendly material and the application of activated carbon for wastewater treatment, drug delivery, fabrication of energy storage devices and as an adsorbing agent.

Keywords: Activated carbon, Biomass, Coconut shell, Energy

1 Introduction

Biomass, a renewable energy resource, has a significant role in the development of fast-growing renewable energy technologies. The biomass feedstock is abundant in nature and inexpensive, and it is utilised to produce sustainable products and thereby reduce the landfills. The exploitation of biomass in an effective way for the creation of many useful products. A proper use of biomass reduces the challenges faced by the continuous consumption of fossil fuels. The renewable energy based products obtained from biomass is proven to be cost-effective and ecofriendly reducing the liberation of CO_2 emissions.

The ISO 16559 [1] defines biomass – a material of biological origin undergoing a process of mineralization. It is commonly considered from plant origin. Lignocellulosic biomass in nature is comprising of cellulose, lignin and hemicelluloses along with the organic components e.g. lipids and extractives [2].

Cellulose is composed of a β-D-glucopyranosyl unit connected by 1-4 glycosidic linkages. It contains

reactive –OH groups, which forms hydrogen bond to enhance the crystalline packing and governs the physical properties. On contrary, hemicelluloses undergo degradation to form monosaccharides, which attribute these materials to their applications in drug carriers, hydrogels and cosmetics [3]. The lignocellulosic nature is a prime responsibility for rich energy content. The literature survey [4]–[8] explores the statistical data about the crammed availability of lignocellulosic biomass per year.

The biomass feedstock resources can be classified, namely as woody, fruit, herbaceous and aquatic biomass. The biomass is one of the excellent renewable sources of energy that meets the challenges of the demand for electrical power in the ASEAN countries. Martsri *et al.*, revealed that 30% of electricity demand is overcome by utilization of biomass feedstock. The proper survey of the biomass availability can be estimated and utilized effectively to meet the electricity need [9].

Any carbon-rich material is used as a precursor for the preparation of AC. The researchers mainly focus on the available inexpensive and renewable energy resources for AC production. In addition to its low cost, AC is widely in demand for many applications due to its unique properties. The literature study reveals that the commercial AC is obtained mainly from coke, peat and petroleum coke. The process to obtain AC from these materials is quite difficult because of the deterioration of the solid adsorbents due to higher regeneration energies and also the reactivation is somewhat cost-effective [10]. Therefore, the research focuses on the bio-sources as a starting material, such as green leaves, nutshells, fruit pits, wood, willow catkins and vegetable wastes etc. [11]. In walnut shell, about 47% of its weight constitutes carbon content. The wastes from the walnut fruit are utilized and activated either physically or chemically [11]. In chemical activation, potassium carbonate is used and processed at 800 °C. Finally, the hazardous materials and synthetic dyes from industries and harmful chemicals were effectively removed using walnut-derived AC. Thus, the AC from walnut shells is found to be a good adsorbent [11]. The green leaves derived AC is efficient in removing lead and arsenic ions and the adsorption test [11] showed the efficiencies of about 98% for Pb (II) and 96% for As(III) and showcase the dual role of both adsorption and desorption processes. The porous carbon polyhedrals (PCPs) from the catkins are prepared under nitrogen gas atmosphere and the resulted AC has been converted into a hydrophilic composite membrane for efficient solar steam generation [12]. The red onion skin waste is used in the research as reported by [13] to prepare nanosheet structured AC in graphite form and is reported to be an excellent candidate for supercapacitors and hydrogen storage applications. The impregnation of AC with iron was conducted for the removal of As (V) from water [14]. The ACs from *Azadirachta indica* tree bark, Date palm tree branches and curry tree, commonly available in vegetable markets, are carbonized for toluene adsorption and they effectively remove the crystal violet dye from wastewater, respectively [15], [16]. Simões dos Reis *et al.*, also prepared the AC from the Norway spruce (*Picea abies* (Karst) L.) bark by employing chemical activation process with $ZnCl_2$ as an activator. The DoE (Design of Experiments) methodology is quite rare process but more efficient to collect the optimum condition to carry out the experimental part [17]. The carbon-based materials, such as polymers and composites, find their uses for electromagnetic interference shielding. The bi-dimensional graphene and its derivatives have exhibited good absorption and reflection of EM waves. A very high electrical conductivity and mechanical properties are the main characteristics of these carbon-based materials for application in electromagnetic interference shielding (EMI) [18].

The hybrid form of the 3D nanostructured material is efficient for the electron transportation mechanism and is found to be a promising material for the fabrication of electronic, thermal and optical nano-devices. Some examples of efficient inorganic semiconductor compounds are gallium nitride, gallium oxynitride and gallium oxide [19].

The laser-assisted graphite plays a vital role in nanotechnology due to its highly efficient electrical conductivity, mechanical strength, thermal conductivity, optical transmittance and low coefficient of thermal expansion. These are eco-friendly and many electronic devices, such as MSCs, gas sensors, FETs, and photovoltaic cells that can be designed based on laser-assisted photoreduction, photothermal reduction, photochemical reduction and microwave reduction [20].

According to Kumar *et al.* [21], the binary metal

oxide's performance as an electrode material is effective for supercapacitor applications. The wrapped GO-MCO ternary hybrid structure is prepared under microwave irradiation. The CV curve of GO-MCO resulted in a large area and high current and provided appreciable specific capacitance and good stability towards electrochemical behavior of the ternary hybrids.

A small substitute to the carbon atom present in the graphene may also pave the way for new engineering materials. The heteroatom substitute in the graphene modifies the electronic structure and intrinsic properties giving higher capacitance quality due to synergistic effects. The doping of hetero atom, which is highly electronegative in nature, results in polarization in the carbon network of graphene. B-doped graphene (BG), N-doped graphene (NG), P-doped graphene (PG), S-doped graphene (SG), B-N/N-S/B-P/N-P co-doped graphene and multi-atom-doped graphene demonstrated high performance in several fields, especially in energy applications [22].

The synthesized AC from biomass contains many advantages, such as eco-friendly, lightweight, less replacement cost and high safety towards health over the synthetic products. The synthesized AC from natural products fit to the demands of today's needs. This reduces the usage of non-biodegradable products and is cheaper in production costs.

The current review article discusses various high-yielding synthetic routes of activated carbon and its promising applications in medicinal and environmental cleanup applications. The present work is to discuss the production of AC from coconut shell in diverse applications with economic importance. There is many studies that need to be conducted using AC in various applications.

2 Activated Carbon from Coconut Shell

The coconut, scientifically named as '*Cocos nucifera*', is a large palm found in tropic and subtropic areas. The versatileness of the coconut is evident from its diverse utility seen for many domestic, commercial and industrial purposes. The coconut meat is edible and supplies relatively high protein and mineral content, such as iron, phosphorus and zinc with a less amount of sugar than fruits [23]. The coconut husk and shell serve as sources for fuel and charcoal. The coconut shell consists of cell wall with multiple layers in which microfibers are arranged perpendicularly in a layer-by-layer pattern. These stacked layers allow the activators to penetrate the cell wall for their catalytic performance. At high activation temperature, more numbers of active sites are created.

The priority to choose coconut shell as a raw material by most of the authors is because of its high density, purity, stability, aromatization, carbonization capability, adsorption capacity (predominantly noticed in carbon-rich materials), possessing small micropore structures and biosorbent quality appreciable to eliminate the heavy metals, dyes and organics from aqueous solutions [24] and effective absorption of gas and vapor and for the separation of impurities, color and odor of the samples [25]. In worldwide, the components of coconuts are proved to be excellent sources of potassium [26]. Each part of the coconut palm tree has its potential application e.g. coconut oil as a biofuel, husk as a substitute for silica [26], a source of fiber for the fabrication of mats and ropes [27] and coconut shell to bring energy-rich gases, bio-oil, biochar for future energy generation. Alternate usage of biofuels brings a positive impact on the natural drastic changes, such as ozone depletion, acidification, etc. [26].

The coconut shell is found to be a promising feasible choice of biomaterial for the production of charcoal. When coconut shell is burned in an open atmosphere, it contributes to the emission of the significant amount of CO_2 and methane gas [28]. This hazardous gaseous emission leads to environmental and health risks that can be reduced by the employment of coconut shells for making charcoal. Charcoal finds its application in diverse fields, such as pharmaceutical industries, power sources and animal feed [29]. Production of activated carbon from coconut shells treated with phosphoric acid (H_3PO_4) was optimized by the response surface methodology (RSM). Fifteen combinations of the three variables parameters, such as impregnation ratio, activation time and activation temperature, were optimized through yield based on RSM [30]. Pore size distribution of activated carbon is more promising when prepared from coconut shells employing different activation methods [31]. Activated carbons were prepared from coconut shells impregnated with potassium solutions of different nature, concentration, and pH, using a CO_2 flow as activating gas at 800 °C [32].

3 Processing of Raw Material

The cleaning of feedstock (residue) to remove impurities added during the assembly of residues is done by sieving resulting in the densification of residue followed by cleaning out the impurities either with water or any other mild solvents to improve the combustion properties of biomass [33]. The next procedure is to completely eliminate the wet stage of the residue undergoing the drying process to increase its efficiency. Solano *et al.* [34] dried the feedstock exposed to natural environmental conditions, and Grover *et al.* [35] adopted the direct drier using hot air or flue gases mixed with material.

The size parameter of the biomass feedstock plays a vital role in defining certain specific characteristics, such as surface area, pore size, volume and bulk density. As a result, a decrease in size leads to partial breakdown of the lignin content of biomass thereby increasing the total surface area, bulk density and leading to a greater inter-particle bonding [36], [37]. Several traditional and physical methods are adopted for size reduction purpose depending largely on the status of the biomass feedstock. Hammer mill, disk attrition, knife mill and linear knife grids are the commonly used accessories to reduce the size of the biomass feedstock [34]. However, hammer mills are considered the most suitable [35], whereas the cutting mill is the next most preferred [38].

According to the literature, the production of AC takes place through carbonization and then activation. In this two-stage process, a high temperature (< 700 °C) is maintained during the carbonization of the raw material carried out in the absence of oxygen and as a result hydrocarbons are removed. As a result of this pyrolytic process, a carbonized material is obtained. The resultant product contains small adsorption capacity that has to be improved through the development of pore structure in it. Thus, the activation process aims to convert carbonized material into AC, finding randomly distributed pores and widening the surface area. The activation process is executed using activating agents either by physical or chemical activation methods. The purpose of activation is to enhance the porosity and to create fine solid cavities in the AC [39].

3.1 *Physical activation method*

The physical activation methodology is inexpensive and a green approach to prepare AC with an enhanced porous structure. It is a two-stage process i.e. carbonization and activation. The carbonization is the process of converting the residual matter into a useful substance through a heating process. Sekirifa *et al.* [40] stated that a typical biomass source would have about 20–35% hemicelluloses, 40–50% cellulose and 15–35% lignin. When biomass is subjected to a change in the physical and chemical state undergoing an irreversible thermal degradation process is termed as pyrolysis in an oxygen-free environment [41]. The product obtained after the pyrolysis process is biochar, bio-oil or syngas depending upon the heat supplied and the chemical reaction that took place. During biomass pyrolysis, when the carbonization process takes place at a low heating rate and moderate temperature produces carbon along with the mixture of CO_2, H_2O, CH_4 and CO. The percentages of carbon yielded in the carbonization process depend mainly on the peak temperature and the heating rate. Table 1 shows example of the activating agent and its concentration for preparation of AC from coconut-based precursors.

Table 1: Physically activated carbon from coconut-based precursors

Physically Activated Carbon	
Activating Agent	**Concentration (%)**
Steam Flow	10% of solid/min for 1 h
Inert N_2 gas	10 mL/min
N_2	100 cm^3/min
H_2O	Not mentioned in the study
Steam flow	Not mentioned in the study

Carbonization of the biomass can be expected commonly above 450 °C and Yahya *et al.* [39] reported the range of carbonization temperature between 400–850 °C. A very high temperature is maintained for the pyrolysis process and Bedia *et al.* [42] and Li *et al.* [43] suggested that the presence of an inert atmosphere would be good enough to obtain a high content of carbon product removing the volatile substances, heteroatoms present in the precursor and to avoid combustion on the carbonaceous substance. Sodeinde *et al.* [44] also followed the carbonization of the precursor at 650 °C in the muffle furnace for 2 h. Li *et al.* [43] and Lewoyehu [45] subjected the physical activation procedure with a different activating agent and for a longer time where the activated carbon is

of high specific surface area and pore structure in the range of micropores. Chiaramonti *et al.* [46] clearly stated that the carbonization at low temperatures yields char of low grade and is also corrosive due to the presence of acidic tars. Hence, the peak temperature determines the quality and the percentage of removal of other volatile matter content of the product. A better char for a commercial purpose is possible only if we maintain a carbonizing temperature of around 500 °C. At this temperature, a fixed carbon content of about 75% is reachable. Katesa *et al.* [47] reported the range of the carbonization temperature followed by Daud *et al.* [48], Guo *et al.* [49] of about 400–800 °C.

The major components present in biomass are hemicelluloses, cellulose and lignin. The decomposition of hemicelluloses and cellulose is quite easy and gives volatile products. The lignin content is transformed into a solid residue as 'char' but the decomposition of lignin is quite difficult. At the initial stage of carbonization, dehydration occurs and weight loss is about 28% [47]. The process is gradually taken to the next step of carbonization in the temperature range 200–400 °C where the decomposition of lignocelluloses gets started. Katessa *et al.* [47] analyzed the decomposition of lignocelluloses with the help of DTG curve and obtained two peaks where one corresponds to the decomposition of hemicelluloses contributing to a weight loss of about 28.5% while the second peak is evident for the decomposition of cellulose with a weight loss of about 26.6%. As reported by Yahya *et al.* [50] and Gasparovic *et al.* [51] the decomposition process of hemicelluloses and cellulose takes place in the temperature range 200–300 °C and 250–400 °C, respectively, while the lignin decomposition takes place over a wider range of 160–900 °C. Antal [52] also predicted the temperature range for the decomposition of the lignocelluloses between 200–400 °C. However, a very high temperature above 700 °C has to be maintained for the decomposition of lignin content of biomass. The fixed carbon and ash content increases as the temperature increases from 31.41 to 88.42% and 0.23 to 1.32%, respectively as the report given by [47]. Also, the degree of surface roughness is increased with temperature and gives rise to release of more volatile content from the biomass. Thus, it can be concluded that a lower carbonization temperature is more favorable to the generation of char with higher reactivity. Nita *et al.* [53] also observed the thermal decomposition behavior of the biomass material (coconut shell, walnut shell and corn silk) and its corresponding first derivative using DTG curve. Two visible peaks at 274 and 344 °C were observed corresponding to the decomposition of hemicelluloses and cellulose content, whereas a slow decomposition of lignin content takes place at a temperature greater than 400 °C constituting to the mass loss of 10–15 of wt%. The quantity of the residue obtained depends upon the macromolecular composition of the biomass. Thus, a more lignin content results in a higher quantity of the residue. Wu *et al.* [54] obtained the activated carbon nanoparticles where the material has been carbonized at 500 °C at 10 °C min–1 for 1 h under nitrogen. Gan [11] reported the carbonization temperature to be 700 °C for 2 h in N_2.

After carbonization, the obtained final product is taken to the next step of activation to get the carbon in an activated form. It means that the final product (intermediate biochar) is made to react with either steam or CO_2. The activation process is to develop active points on the surface with good porosity. The activation reaction takes place in the temperature range 750–1000 °C in an inert gas atmosphere or vacuum [11]. Tadda *et al.* [55], suggested that the use of CO_2 and the activation process is carried out at a temperature of about 800 °C with a slow reaction rate. Normally, the physical activation develops the microporosity with a small degree of mesoporosity. A low yield carbon is enough for use in wastewater treatment [56]. Lewoyehu [45] also reviewed the activation process in terms of gasification that produces carbon with less reactive sites but with preferred porosity. It is suggested that the lower temperature (around 300–450 °C) on pure O_2 or air is preferred because of the exothermicity of the reaction. The other agents, such as CO_2 or water vapor are not much reactive and the reaction can be extended to a higher temperature range around 700–900 °C. Based on the explanation and the review of several works, the CO_2 is a good choice as the activation gas due to the slower reaction rate [57]. Comparatively, Molina-Sabio *et al.* [58] produced narrow micropores in the AC using CO_2. Zhang *et al.* [59] had a comparison of the material and showed that in CO_2-activated carbon material, the surface area, total pore volume and micropore volume are significantly higher than the AC produced from other methods.

3.2 *Chemical activation method and selectivity of activating agent*

The chemical activation plays a major role and notably reduces the activation time and temperature [10]. It is a one step process, which produces activated carbon with high porosity and surface area. It requires less energy and is an eco-friendly option. Contrarily, its usage is toxic and cannot be recycled easily [60]. In the process of chemical activation, the raw material is saturated using highly dehydrating and oxidizing chemicals. Then, the sample is dried after impregnation and allowed to heat in a temperature range between 400 to 900 °C. The activating agent and the required characteristic of the product determine the temperature within the given limit. At this stage, the degradation of the cellulose takes place. The resultant AC product is washed continuously to retrieve the active substance [61]. Table 2 describes the activating agents and the yield % obtained. The opted activating agent must inhibit the bitumen formation and thus develop the small pores. The perforation of the activating agent in the carbon structure enlarges the surface area [62]. Activators used are namely KOH, NaOH, $CaCl_2$, K_2CO_3, H_3PO_4, H_2SO_4 and $ZnCl_2$, etc. [63]. The preferences of chemical activation process (Figure 1) circumvent the volatile and tar formation, initiate the de-polymerization, condensation and dehydration reaction and produce a higher yield percentage of carbon [55].

Table 2: Chemically activated carbon prepared from coconut-based precursors

Chemically Activated Carbon		Yield (%)
Activating Agent	**Concentration (%)**	
$ZnCl_2$	60% of Solid	45
KOH, $ZnCl_2$ and H_3PO_4	$ZnCl_2$ – 25% KOH – 18.3% H_3PO_4 – 23.3% Sample without chemical impregnation – 16.7%	25
KOH	1:1	80.27
$ZnCl_2$	500 gm of $ZnCl_2$	72

Different activating agents react differently and undergo intermolecular reactions with the biomass for the yield of AC. Initially, the lignocellulosic precursor is treated with chemical agents, such as H_3PO_4, H_2SO_4, HNO_3, NaOH, KOH or $ZnCl_2$ by impregnation and heated to a temperature between 400 to 800 °C [64].

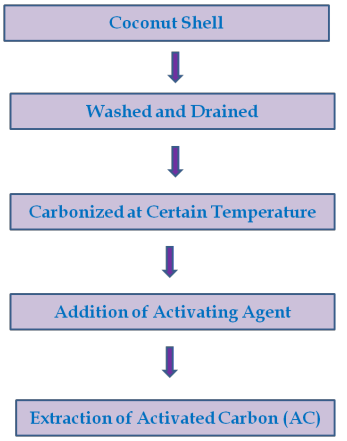

Figure 1: Flowchart representing the synthesis of activated carbon using chemical activation.

Among these listed reagents, H_3PO_4 is found to be an increasingly used chemical agent as it produces high yield carbon and is suitable for large scale manufacturers [65]. The acid catalytic behavior of H_3PO_4 assists the cross-linking reactions between phosphoric acid and biopolymers. H_3PO_4 is also a good template since the volume occupied by phosphoric acid in the interior of the activated precursor is coincident with the microspore volume of the activated carbon [64]. H_3PO_4 is found to be very effective for the synthesis of AC with fine pores and good morphology [66].

The AC developed in 70's using KOH is known to be "super activated carbons" with a surface area of 3000 m^2/g and many reports are also available for the synthesis of AC with KOH [67]. The KOH always stabilizes the carbon atoms by removing cross-linking and develops the micropores in the new structure of AC. It is concluded that the choice of activating agent primarily depends upon its characteristics behavior and the expected outcome. To produce highly reactive AC, $ZnCl_2$ is a suitable choice of the dehydrating agent where molecular migration and intermolecular exchange happens during hydrolysis. A uniformly distributed small-size micropore of AC is possible using $ZnCl_2$ [68]. An overview of the activating agents found $ZnCl_2$ to be very effective for the synthesis of AC with fine pores and good morphology.

The activating agent is responsible for the growth of small pores through its penetration of the carbon substance and results in increasing the surface area. The quantity of impregnation and the numbers of

chemical agents are the factors that determines the characteristics of the final AC product [69]. The chemical activation method is more feasible and economical [70]. The final AC product produced using this method contains more porous in nature than the one from the AC prepared by the physical activation method [71]. One of the main drawback is the removal of the remaining activator agent from the final mixture that requires continuous washing and causes water pollution. According to [72], [73], alkaline elements can be a better choice as potential activators, such as potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium chloride ($CaCl_2$) and potassium carbonate (K_2CO_3), acidic groups, such as phosphoric acid (H_3PO_4) and sulphuric acid (H_2SO_4), intermediate metal salts such as $ZnCl_2$ and other activating agents. The chemical activation process can be carried out in two ways: one is the normal process of combining the precursor and the activator (under dry condition) and the other approach is the process of impregnation [74], [75].

Sanni *et al.* [76] compared the AC sample without impregnation with those prepared using activating agents, such as KOH, $ZnCl_2$ and H_3PO_4. The performance and carbon yield and the effect of chemical agents on physicochemical properties are observed that $ZnCl_2$ and H_3PO_4 create better pores. Raj *et al.* [77] reported that activation with larger quantities of KOH at high temperature results in high surface area carbon, with wide pores, due to increased gasification and local insertion of metallic potassium. Hu *et al.* [78] and Romanos *et al.* [79]. The KOH activation can produce mesoporous carbon with a large surface area of up to 2000 m^2/g. Foungchuen *et al.* [80] explained the significance of the impregnation process to incorporate the amine-based molecules onto the AC surface. Thus, amine impregnated AC is potentially developed for the CO_2 adsorption due to the presence of more numbers of adsorption sites.

4 Effect of Carbonising Time and Temperature

These factors play a major role in the preparation of high-quality AC. The selected carbonizing temperature must transform the reactant (biomass) into a complete carbonaceous material. At the same time, the degree of porosity and surface area also increases to the same degree with the increase in carbonizing temperature. The higher value of a specific surface area can increase the active sites [81]. Siahrostami *et al.*, based on the theoretical calculation indicated the N-doped carbons are containing highly active sites [82].

Several reports employ different values [83]–[85] and the ranges of temperatures between 120 to 1000 °C have been used [64]. The optimum time value of 1 h up to 12 h has been spent for a better yield percentage. Actually, the temperature decides the final product and the possibility of the yield of liquid bio-oils and gases are increased at a temperature greater than 600 °C [10]. As the temperature increases, the evaporation of the volatile substance decreases and the ash content increases and these affect on the final product obtained after pyrolysis [86], [87]. In order to receive a better yield, low heating rates can be followed in the range of 10–15 °C/min [88].

5 Adsorption Capacity of AC

The study of adsorbing capacity is one of the important features of AC for use in wastewater treatment. The adsorption capacity of AC determines its capacity to adsorb various pollutants. The textural and other related properties, such as pore size, pore size distribution, surface area, volume, high thermal and chemical stability, fast kinetics, high recyclability potential proves AC to be the best material for use in the pharmaceutical, chemical and food industries.

The carbon composites also find their place in designing eco-friendly devices to meet the demands of the modern world. Das *et al.* [89] with polyvinyl alcohol (PVC) and PMMA matrix developed a nanocomposite named few-layer graphene (FG)-reinforced nanocomposite and its mechanical properties were much upgraded to have an efficient load transfer within the host matrix and the nanofiller [90].

El-Sheikh *et al.* [91] followed chemical vapor deposition (CVD), direct air-hydrolysis (DAH), and high-temperature impregnation (HTI) techniques to synthesize AC with TiO_2 deposition. It has been effectively used as a functionalized carbon material for the degradation of pharmaceutical products [11]. The removal efficiencies of 17% for amoxicillin, 9% for ampicillin, 10% for diclofenac, and 11% for paracetamol were achieved for the TiO_2/AC. This explains that the AC with TiO_2 has more adsorption capacity than that of the pure TiO_2 [92]. The percentage of TiO_2 on the

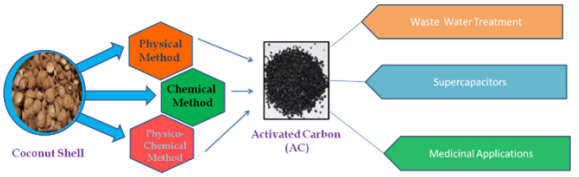

Figure 2: Extraction of activated carbon from coconut shell and its applications.

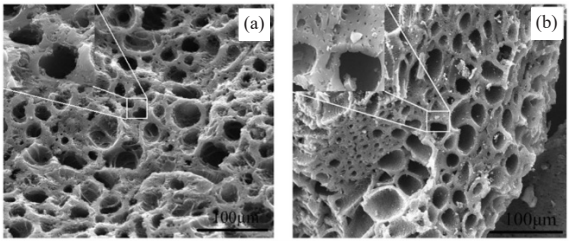

Figure 3: Typical SEM images of coconut shell carbon prepared using KOH activation [96].

surface of AC determines the photocatalytic activity and is found to be very effective in the degradation of trichloroethylene [93]. Many reports showed the functionalization of AC with MnO_2 [11] and nobel metal and grouped as a decorated activated carbons and are efficiently used as a catalytic, electro-chemical assay and sensing [11]. The Figure 2 schematically explains the production of activated carbon from the coconut shell.

An increase in the reactive blue 4 dye sorption capacity of up to 21.6 times of hybrid wood sawdust with 3-aminopropyl-triethoxysilane is reported [94]. Biobased carbon materials obtained from Norway spruce (*Picea abies* Karst.) bark was produced by single-step chemical activation with $ZnCl_2$ or KOH and pyrolysis at 800 °C for one hour. The chemical activation reagent had a significant impact on the properties of the biobased carbon materials. The biobased carbon materials showed high efficiency for removing RO-16 and RB-4 [95]. Removal of Pb^{2+} from aqueous solutions using coconut shell carbons with high specific surface area of 1135 m^2/g produced by KOH activation (Figure 3). The kinetic studies indicate that adsorption behavior can be described by pseudo-second-order kinetic model [96].

The microporous AC can also be synthesized from different precursors, such as sewage sludge, Acacia mangium wood, Chinese chestnut burs and Algerian date pits. The AC produced from the above precursors were microporous in nature with a high SBET value of about 679 $m^2\ g^{-1}$, 1767 $m^2\ g^{-1}$, 1254.5 $m^2\ g^{-1}$, 1467 $m^2\ g^{-1}$. The mesoporous activated carbon nature is suitable material for energy storage applications [17]. Table 3 presents total pore volume and BET specific surface area obtained for AC.

Table 3: Total pore volume and BET specific surface area obtained for AC

Total Pore Volume	BET Specific Surface Area (m^2/g)
0.502 mL/g	Not mentioned in the study
0.266 cm^3/g	524.5
0.731 cm^3/g	1,266
0.064 to 0.217 cm^3/g	167 to 566
0.397 $cm^3\ g^{-1}$	1177
1.09 ± 0.09	1998 ± 58
0.4487	995.799

6 Applications of AC

6.1 *As an anticancer agent*

Activated carbon synthesized and processed under controlled oxidation of carbon atoms in the presence of steam (under 500 °C) had an efficient internal surface and generates a network of minute openings and possesses a graphene structure [45]. The synthesized carbon nanotube has been a promising material for cancer diagnosis [45]. AC has been synthesized under nitrogen atmosphere at 800 °C passing steam and washed with HCl and distilled water and dried. In addition to anticancer drugs and treatment modalities, a new form of nanocarbon material-based nanoenzymes have been produced for biochemical reactions based on their high stability, easy production method, excellent strength and sufficient biocompatibility in the cancer cells [97].

According to Wu *et al.* [54], the therapeutic effect on cancer cells is improved using peroxidise or peroxidase-mimic nanoenzyme resulting in oxidative damage to cancer cells without damage to normal cells. This nanoenzyme triggers the toxic post-treatment linked with the residual heavy-metal that entails the production of a non-metal-based peroxidase-mimic nanoenzyme. AC with porous structure is efficiently packed with diagnostic reagents for its catalytic performance in cancer therapy. The prepared AC is

used as a carrier for diagnostic drug reagents and used gadodiamide (a safe Gd^{3+}-based T1-MRI contrast agent) for soft tissue imaging and tumor diagnosis and was successful in loading of the gadodiamide inside the pores of AC and verified the encapsulation of the reagent by studying the stability from zeta potential measurements and MRI.

6.2 *As a supercapacitors*

Nilanka *et al.* [98] proposed two different methods of synthesis of AC. In the first method, the AC is obtained when powdered charcoal is heated to 900 °C in a closed container for 20 min followed by a quenching process using distilled water whereas the second followed the physical activation process using steam as a gasification agent. The activated carbon is prepared with different methods and confirmed that the activated carbon prepared by passing steam exhibits a higher specific surface area indicating the effectiveness of the steam activation. Li *et al.* [43] reported the preparation of porous carbon with a particle size of 3 mm. Comparatively, Nilanka *et al.*, [98] obtained a greater value of BET surface area of about 1998 m^2g^{-1} resulting in a particle size less than 0.1 mm. The strategy of continuous flow of steam during cooling congregated the sample to be suited for supercapacitors. The final AC spread on the substrate of graphite with ionic liquid MPPyFSI and polyethylene separator provides tremendous storage capacity. The graphitic structure and disordered nature of the carbon material, mesoporosity with slit shaped pores, and high degree of crystallinity enhanced the storage properties of supercapacitors [98]. Therefore, AC is also useful to devise efficient supercapacitors from biomass renewable resources.

Additionally, Sodeinde *et al.* [44] and Iqbaldin *et al.* [99] followed certain optimum conditions with reference to Deng *et al.* [100], Li *et al.* [43] and Marin *et al.* [101] for the successful production of AC as an excellent electrode substrate for supercapacitors possess a larger surface area.

6.3 *As an adsorbing agents*

Among the available liquid pollutants from the industries, lead is a toxic material for living organisms. The release of this toxic substance is prevented by allowing it to get adsorbed on a suitable adsorbent, such as activated carbon [102], zeolites [103] and kaolin [104]. The field of green synthesis utilized the natural-born resources as a precursor to provide AC as a new promising adsorbent. The choice of AC as an adsorbing agent is due to its unique properties of having abundant pores, strong structural controllability and organized atomic structure exposed one-step water-assisted synthesis for the preparation of carbon and an efficient way of producing carbon nanotubes. Hakim *et al.* [105] explained an effective method to prepare single-walled nanotubes (SWNT) with an average inner diameter of about 123 nm from the graphite type AC.

Charcoal in an activated carbon or coal found in many applications in the field of industries for gas and air cleaning, treatment of water to adsorb dissolved organic impurities and to remove the substances that affect the odor, taste and other organic pollutants including dyes, heavy metals, fluorides, phenols and other organic and inorganic toxic compounds [55]. Applications of activated carbon also include adsorption of poisons and drug overdoses. It has been used in wastewater treatment, groundwater rehabilitation and in the removal of substances toxic to bacteria in biological wastewater treatment or in tertiary wastewater treatment where effluent restrictions are particularly severe. It could be widely used in the future for the determination of varying polarity pesticides at trace levels in environmental water samples. The activated carbon claim to have various health benefits, such as assisting the kidney functioning by filtering out undigested toxins and drugs and as a gastrointestinal absorbent in overdoses and poisonings.

Das *et al.* [106] and Sodeinde *et al.* [44] collected green coconut shells that are subjected to a size reduction of 300–700 μm after completing the preliminary process of removing the impurities. It is followed by the chemical activation method wherein $ZnCl_2$ assists the formation of carbon char maintaining a lower carbonization temperature. The obtained sample is impregnated at 650 °C in the presence of nitrogen atmosphere at a flow rate of 120 cm^3 min^{-1} STP. Thus, the AC is washed several times with 0.5 N HCl [106] and 0.1 M of HCL and 1 M of NaOH [44] to be free from impurity. The AC synthesized serves to be a good adsorbing agent to remove CO_2 gas from flue and inorganic contaminants from wastewater and acts

as catalysis for the reduction of hexamine cobalt (III).

For the best adsorptive performance, H_3PO_4 (activating agent) can be used and was successful in achieving the 100% adsorptive performance Sanni *et al.* [107]. An increase in carbonization temperature beyond the optimum limit caused a decrease in the activated carbon yield.

The review on the method of extraction of activated carbon from coconut shell is synonymous except for the change in specific parameters e.g. carbonization temperature, activating agent, atmospheric condition. Also, AC production by Li *et al.* [43] mainly focussed on describing the effect of carbonization temperature to develop more porous structures. The common procedure of pre-processing of feedstock is carried out. A constant weight is achieved after drying in the oven (at 105 °C) for 2 h. Muffle furnace is used for carbonization process continued for 2 h at 400 °C. A comparative analysis of the yield percentage showed that high yields of about 64.4% of the AC are obtained from the coconut shell than the plantain peel because of the lesser moisture content in the coconut shell. The author has aimed to prepare the AC to be a good material for use as an adsorbing agent and the resulted AC using KOH as activating agent is more effective [108].

Huang *et al.* [109] used rope coconuts from Taiwan and the pre-processing steps are completed and the pyrolysis process is performed at a temperature of about 500 °C. The variation in the activation temperature and time were adopted for comparing the quality of the prepared AC. Based on the analysis, the BET surface area increases with activation temperature when maintained between 600 °C and 800 °C and on contrary a decrease in BET specific surface area is observed when the activation temperature exceeds 800 °C. Higher activation temperatures expedite pyrolysis reactions. Increasing of the activation temperature and time facilitates the iodine adsorption. Specifically, the larger activation time significantly promotes micropore formation in the AC.

Lima *et al.* [110] invoked the magnetic features of carbon and produced an efficient magnetic biochar for use in the removal of contaminants, dye particles and metallic ions from aqueous effluents. The precursors were very specific with $NiCl_2$ and $ZnCl_2$ and their combinations to produce magnetic biochar. The material showing zero or very less value of remanence and coercivity reveals good superparamagnetic characteristics. They compared the values of those obtained for $ZnCl_2$ and $NiCl_2$. Once the applied magnetic field is switched off, the magnetic biochar materials stay separately and demagnetize and the magnetic biochars were regenerated and reused. The saturation magnetization (MS) value for $ZnCl_2$ added magnetic biochar is good enough for the separation of the adsorbent from the liquid phase to the ending of the process. Zhu *et al.* [111] reported a porous MB with MS value equal to 0.76 emu g^{-1} to remove tetracycline from an aqueous solution. The almond shells-based MB (magnetic biochar) was utilized to remove trinitrophenol from water. Zhang *et al.* [112] exhibited a MS value of 5.61 emu g^{-1} and 8.64 emu g^{-1} from peanut shell. The propranolol and nicotinamide contaminants were removed from the aqueous with magnetic biochar presenting a MS value of 7.14 and 14.91 emu g^{-1}.

The biochar synthesized from the microalgae exhibited a hybrid type I/IV isotherm as a combination of micropores and mesopores structures. Moreover, type IV isotherms show a typical mesoporous character due to the hysteresis. The concept of N-doping to increase the micropores and surface area as reported by Tian *et al.* [113] is quite helpful. Hussain *et al.* [114] reported nitrogen doping using carbon sheet as precursor and melamine as a dopant. The doping process increased the specific surface area value from 182 m^2g^{-1} to 409 m^2g^{-1}. This process induces the defects that can be utilized for electron transfer thereby increasing surface area which, in turn, causes an increase in the adsorption performance [115].

6.4 *Purification of wastewater*

Preparation of coconut shell-derived hard carbon (CSHC) from waste biomass coconut shell using a one-step carbonization method, which was further, used as anode materials for potassium ion batteries (Figure 4). One reported research shows that optimized activated carbon obtained from municipal wastes and sewage sludges through KOH two-step pyrolysis process containing abundant number oxygen-containing functional group with high adsorption capacity (Figure 5). In another study, result revealed that the physicochemical properties and performance of activated carbon combined with copper has a higher potential to

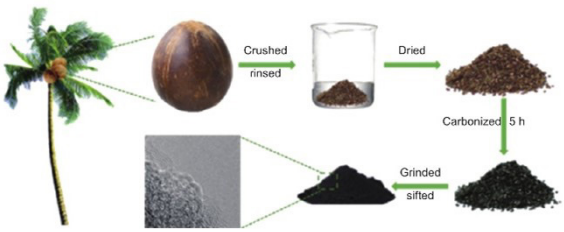

Figure 4: Coconut shell-derived hard carbon used as anode material for potassium ion batteries [116].

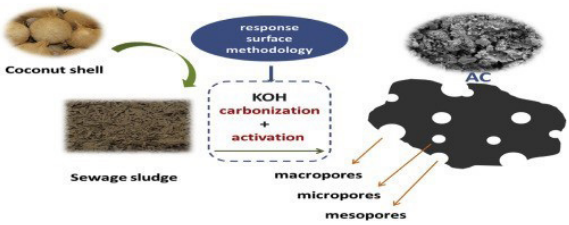

Figure 5: Optimized activated carbon from coconut shell and sewage sludge with higher adsorption capacity [117].

remove paracetamol contaminant (Figure 6). Modified coconut shell-based activated carbon using acid, alkali, potassium permanganate, and iron salt showed higher potential in purifying wastewater containing heavy metals, such as Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} (Figure 7).

6.5 *Other applications of Activated carbon*

The graphite oxide powder has been synthesized and dispersed in phosphate buffer solution by sonication and Ni sheet was used for deposition, which is performed by three-electrode electrochemical cell. The graphite oxide powder prepared by Ibrahim S. El-Hallag *et al.*, [120] shows good electron conduction and an increase in internal diffusion resistance within the pseudo-active substance with an increasing scan rate. The deposition of Pd NPs inside ErGO NSs creates Pd-E-ErGO hybrid and the electrochemical performance of the Pd-E-ErGO hybrids remains superior as electrode materials for supercapacitors application due to the perfect structural integrity.

The six membered sp^2 hybridized – C ring namely graphene and many researchers developed new allotropes of graphene and modified the hybridized part to a nonbenzenoid geometry to provide an optoelectronic property [121].

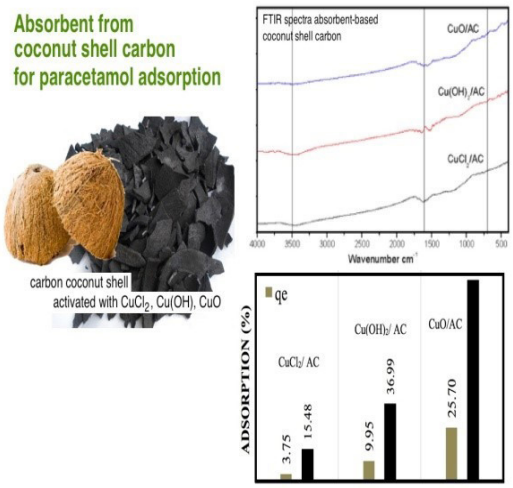

Figure 6: Activated carbon with copper showing high potential in paracetamol contamination removal [118].

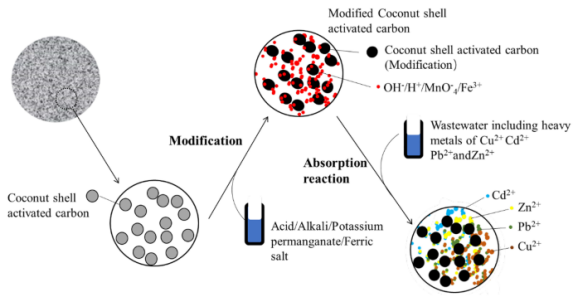

Figure 7: Modification of coconut shell-based Activated carbon showing high potential in wastewater purification [119].

The bio-medical field uses some natural fibers implanting certain characteristics e.g. biodegradability and bioresorbability help to remove the synthetic fibers thereby reducing the material waste. Hoque *et al.* [122] gave a detailed study on the use of natural fibers in bio-medical field and explored the importance and future materials for different industrial purposes.

The presence of large surface area and the adsorption ability of the AC provides a significant place in the field of vacuum manufacturing, fertilizer plant, cosmetics, textiles, automobiles, nuclear, pharmaceutical and petroleum industries. AC is an excellent porous material widely used for solvent recovery and as a catalyst in biodiesel production Tadda *et al.* [55]. The adsorptive, catalytic, electrochemical and other useful properties of AC are significantly

influenced by its chemical nature. As an evidence, Khaleel *et al.* [123] exposed the application of granular activated carbon to treat institution water to remove high ratios of BOD, turbidity, TDS, TSS and COD from wastewater.

AC finds its role in the formation of capacitive deionization electrodes [11] and to make biologically-inspired desalination systems. The high efficient supercapacitors [124]–[128], solar energy converters [129], battery electrodes [129], [130], templates for nanostructures [11], and desalination systems [131] are some of the applications of AC from the renewable energy resources. AC is one of the promising materials to be used as an adsorbing agent for the purification of water, gaseous and aqueous solutions. The main category is the adsorption of heavy metal [132], vitamin B [133], decomposition and adsorption of dye [134]–[137], CO_2 adsorption capacity of 8.30 mmol/g at 25 °C under 0.4 MPa was reported by Xu *et al.* [138].

7 Conclusions

A large amount of energy can be reserved potentially for future use of biomass. The expected energy conversion from the bioresources has to be increased for the substantial growth of eco-friendly energy resources. The usage of agro-based wastes not only fulfills the necessity of energy in the current scenario but also emerges as a field in the development of new materials. Coconut shell-based activated carbons are seems to be much efficient in organic chemical adsorption, wastewater treatment, energy storage devices, generation of solar steam, used as potential drug delivery tools and an ideal resource for the evolution of green synthesis. The review discusses coconut shells are well suited for AC production with an excellent natural structure and low ash content. The high yield of activated carbon from different synthetic routes serves its promising applications in medicinal and environmental clean-up applications. The current review articles provide deeper insight into the novelty of activated carbon synthetic routes and diverse applications in various fields with economic importance.

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Author Contributions

N.A.B.: conceptualization, investigation, reviewing, writing and editing; T.R.: conceptualization, data analysis, writing and editing; H.S.: reviewing, writing and editing. All authors have read and agreed to the final version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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