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Hydrothermal Carbonization of Walnut Shell Biomass to Biochar for Supercapacitor Application

Raman Devi, Vinay Kumar*, Sunil Kumar, Mamta Bulla & Paul Singh
Department of Physics, CCS Haryana Agricultural University, Hisar, Haryana 125 004, India

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Hydrothermal carbonization is now emerging to address society's global sustainability problems by reprocessing several industrial and agricultural wastes to derive promising carbonaceous materials such as graphene, biochar, and activated carbon. This approach will further resolve the difficulties related to the safe recycling of waste materials and also the consumption of fossil fuels. This work focuses on synthesizing biochar via hydrothermal carbonization at temperatures 220 °C and residence time (6, 12, 18, and 24 h) and their effects on product yield and other parameters studied. Characterizations of biochar produced at different times were carried out using techniques like X-ray diffraction, UV-Visible Spectroscopy, and N_2 adsorption/desorption isotherm. The biochar yield reduced from 56.4-40.2 wt-% with a rise in dwelling time. BET surface area was found to increase as we increased the reaction time. On the base of the maximum surface area, electrochemical analysis was performed to check the role of biochar as a supercapacitor electrode.

Keywords: Hydrothermal carbonization; Biochar; BET surface area; Supercapacitor; Waste management

1 Introduction

Today, we mainly face the problem of energy crisis and environmental pollution. These problems are regularly growing with the increasing population and excessive consumption of fossil fuels. Due to the consumption of fossil fuels, various kinds of gases like carbon dioxide, carbon monoxide, NO_x, and SO_x are released, which causes global climate change. So, renewable and green technological approaches for energy storage and conversion system must be developed[1,2]. Due to the growing energy demands, the consumer is widely utilizing various newly designed electrical vehicles, electronic gadgets, renewable energy sources, and various energy storage equipment. In this regard, the new generation electrochemical supercapacitor has become the main centre of attraction for scientists and researchers working in this area[3]. The significant parameters to check their performance are energy density, sustainability, stability towards a number of cycles, and cost. They have high power density (power concentrated) compared to batteries and high energy density (energy concentrated) compared to the capacitor,or their performance lies between the capacitor and batteries. They are flexible in selecting electrode material and electrolyte solution; hence, anyone can modify their working parameters according to the energy demands[4]. Therefore, selecting appropriate electrode material is challenging, and it should be synthesized from a renewable and environment-friendly approach. Biomass is now seen as a renewable resource that may be transformed into various energy forms via various thermo-chemical processes, depending on the type of energy required[5]. Simultaneously, the issues of bio-waste disposal, which cause major environmental problems and health issues, can be resolved by this approach[6]. As a result, various types of smart electrode material (biochar, activated carbon, graphene oxide, reduced graphene oxide, and graphene) can be designed by the thermolysis of biomass, including crop residue, municipal waste, animal waste, and other organic material[7].

Biochar is a well-known solid material that comprises various quantities of functional groups for ion adsorption, has porous geometry with high surface area, and is easy to alter. Various procedures, such as hydrothermal carbonization (HTC), pyrolysis, and gasification, have been detailed for biochar production[8]. The properties of biochar depend on raw material (biomass), synthesis technology, and reaction conditions. Biochar is easy to synthesize from renewable raw biomass and has applications in different areas such as energy storage, gas-sensing, agriculture, water remediation, etc. The walnut shell mainly consists of lignin, cellulose, and

*Corresponding author: (E-mail: vinay23@hau.ac.in)

lignocelluloses and is a non-toxic, cost-effective, easily accessible, renewable, and stable bio-waste resource. Because of their high carbon content, walnut shells have been examined for use in biochar production[9]. This study favors HTC for the synthesis of biochar as it can be achieved at a low temperature of around 180-250 °C. For thermochemical decomposition, the powdered biomass is mixed in water and placed in a stainless-steel autoclave which is placed in an oven. Biochar produces at a temperature less than 250 °C stated as HTC; bio-oil between 250-400 °C (hydrothermal liquefaction), and gaseous products, syngas such as CH_4, CO, CO_2, and H_2, is produced at a temperature above 400 °C (hydrothermal gasification)[10]. The prepared biochar is then used as an electrode material for energy storage in a supercapacitor. A biochar sample with high surface area and conductivity was utilized as an electrode material, and its electrochemical behavior was investigated using cyclic voltammetry(CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS).

2 Experimental Analysis

2.1 Materials and Method

A Walnut shell was utilized as a precursor in this experiment, and it was obtained from the nearby areas of CCS HAU, Hisar (Haryana). The walnut shells were washed several times with distilled water to remove surface contaminants, then dried for 24 h at 100°C in a drying oven and ground into fine powder after passing through a 100 mm sieve. 5 g of raw walnut shell powder was put together with 75 mL of distilled water and well agitated before being placed in a stainless steel autoclave at 220 °C for different times, 6 to 24 h. The sample was then rinsed with double distilled water until pH 7 was reached and then oven-dried for 24 h at 100 °C. The samples were named B-220-6, B-220-12, B-220-18, and B-220-24, corresponding to 6, 12, 18, and 24 h reaction times, respectively.

2.2 Preparation of Electrode

The electrode was made up by mixing the biochar sample having a high surface area (B-220-24) (90 wt-%) with the Polyvinylidene fluoride as a binder (10 wt-%) in a volatile organic solvent (N-methylpyrrolidinone) and activated carbon (10 wt -%). Then the mixture was blended for 24 h on a magnetic stirrer and obtained a homogeneous slurry, which was applied to the current accumulator (graphite sheet) substrate. The coated electrodes were annealed for 24 h at 70 °C in a vacuum oven. The capacitive behavior of the electrode was evaluated using CV in 6 M KOH as an electrolyte with a diverse scan rate varying from 10 to 100 mVs^{-1}.

3 Characterization

Figure 1 (a) represents the XRD pattern of the products obtained by hydrothermal treatments of the walnut shells, and it is observed that sample B-220-6 exhibited three characteristic peaks at 15.7°, 22.6°, and 34.8° that correspond to pure cellulose,

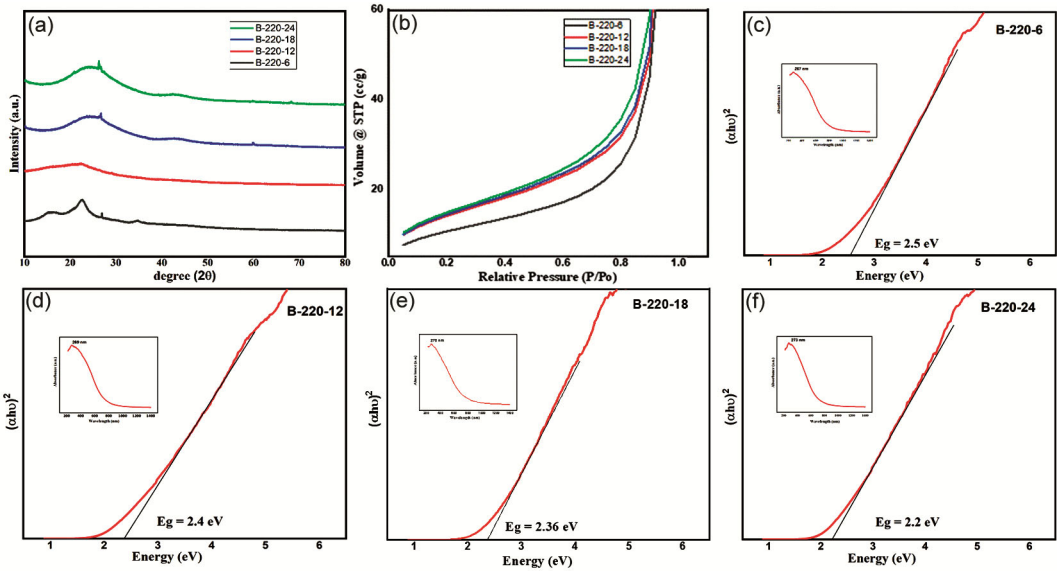

Fig. 1 — (a) XRD spectrum of biochar, (b) N_2 adsorption-desorption isotherms, (c, d, e and f) Tauc's plots.

demonstrating that the crystalline structure of the cellulose has been maintained[11]. In contrast, the samples obtained at a temperature of 220 °C but more than 6 h are no longer crystalline, as can be deduced from the absence of reflections in the XRD pattern. These results signify HTC begins at around 220 °C at residence time greater than 6 h.

The N_2 adsorption/desorption isotherm plot of the biochar samples is represented in Fig. 1(b). To determine the surface area and pore volume of synthesized biochar, Brunauer-Emmett-Teller (BET) was performed. The data shows that the surface area and pore volume of biochar increased as the carbonization time increased. The surface area and pore volume of the samples (B-220-6, B-220-12, B-220-18, B-220-24) were obtained at 37.8, 51.6, 52.1, 53.4 m^2g^{-1}, and 0.185, 0.253, 0.293 and 0.295 $cm^3\ g^{-1}$ respectively. The increase in surface area may be attributed to the removal of volatile matter from biomass, which creates pores in the biomass, and the resulting solid product is porous with a higher surface area[12]. This is explained by processes in which more organic matter was thermally decomposed, and more volatiles was released from etching pores during the longer residence times; such processes likely contributed to the production and extension of the pore structure in the biochar[13]. BET analysis demonstrates that porous structures were generated during the synthesis of the biochar, which is responsible for the good electrochemical behavior of the prepared electrode[14]. Fig. 1 (c, d, e, and f) represents Tauc's plot of the biochar samples with UV-Vis spectra performed in the 220-1000 nm range. The UV-Vis spectroscopy directed the optical properties of materials. The band gap of the biochar samples was calculated using Tauc's plot equation, and it was noticed that all the prepared samples show a direct band gap [15]. The UV-Vis spectra of biochar derived at different times show a strong adsorption peak in 265-280 nm, representing carbonaceous material. As the reaction time for carbonization increases, the wavelength for maximum adsorption, λ_{max}, also increases. The λ_{max} value increased from 267 nm for biomass to 273 nm for B-220-24. This increase in the λ_{max} indicates a decrease in the band gap for the material from 2.5 eV to 2 eV. This decrease in the band gap is responsible for good electrical conductivity and as well as good electrochemical performance.

4 Results and Discussion

4.1 Biochar Yield

$$\text{Biochar Yield (wt.\%)} = \frac{\text{Wt.of biochar}}{\text{Wt.of raw biomass}} \times 10 \quad \ldots (1)$$

The biochar yield decreased from 57.4-40.2 % as the residence time increased from 6 to 24 h, calculated using equation 1. The biochar yield decreased due to evolution in the thermolysis of walnut shells, resulting in the consistent growth of bio-oil and gaseous production. As the reaction time increases, more volatile (such as CO_2, H_3, CO, H_2O,

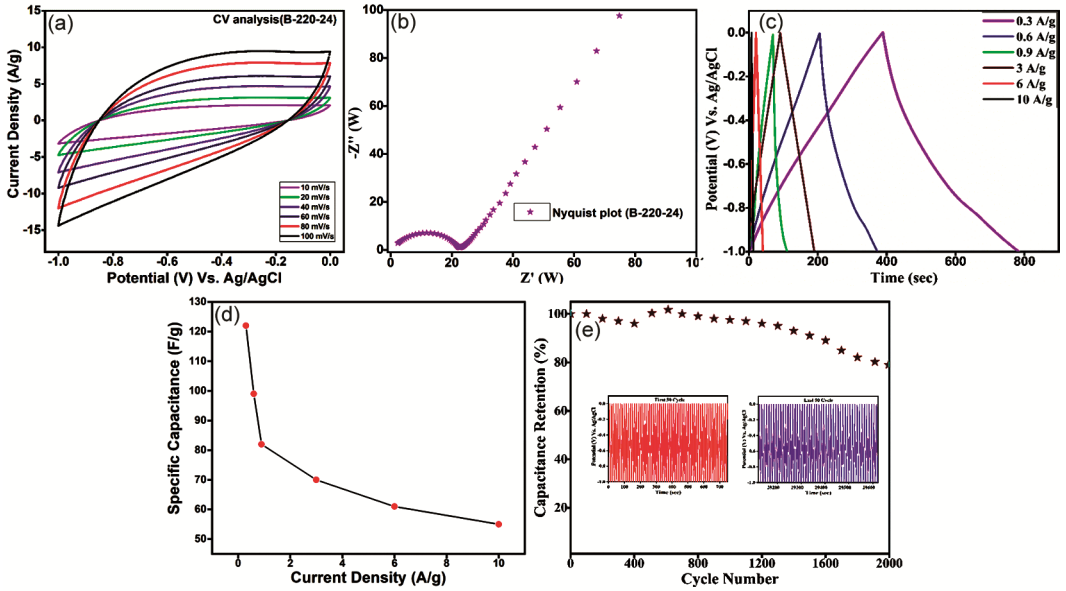

Fig. 2 — (a) CV plots, (b) EIS plot, (c) GCD plot, (d) Current density V/s Specific capacitance and (e) Capacitance retention V/s Cycle number.

and HCN) are randomly liberated, causing a decline in the yield of biochar escaped from the organic material due to the thermal breakdown of volatile hydrocarbons present in the material [15]. Biochar yield reduced to 6 % with increased residence time from 6 to 12 h at 220 ℃. The yield produced by the hydrothermal method is higher than pyrolysis; as a result, there is low gasification which is a clear indication of an eco-friendly approach as shown in Table 1. These changes in yield also affect the other parameters, such as surface area, porosity, thermal conductivity, thermal resistivity, etc., that are mentioned further in detail.

4.2 Thermal Properties

As per the result mentioned in the Table 2, the thermal conductivity of biochar decreases as we increase the residence time for decomposition. On the other hand, the thermal resistivity of prepared biochar increased as the residence temperature increased. This occurs because the air in the pores adds an "insulation" character to the bulk sample of the biochar, as there is an increase in the total pore volume of the biochar sample with the residence time [17].

4.3 Electrochemical Measurements

The electrochemical study of the prepared electrode was carried out in a 3-electrode cell using 6M KOH as an electrolyte[18]. Electrochemical tests are used to characterize the capacitance properties of a biochar sample (B-220-24) with a high surface area. CV plots are shown in Fig. 2 (a). It can be seen that the prepared electrode has excellent reversible characteristics that correspond to typical double-layer capacitance. The quasi-rectangular form of the CV curves denotes the formation of an electrical double layer in an aqueous electrolyte[19]. Because the surface of biochar contains numerous micropores and mesopores, it provides a large surface area for the adsorption of ions from the electrolyte. The electrolyte ions, typically cations and anions, are attracted to the charged carbon surface and form a compact layer of ions known as the Helmholtz layer. This separation of charges creates an electrical double layer, resulting in the storage of electrical energy[20]. Also, no significant redox peak was observed in any of the CV curves, indicating no redox behavior in this chemical process. The working electrode attained rapid ion diffusion, which led to smooth charge transfer. The resemblance of the CV curves at diverse scan rates indicates that the electrode material had high-rate capacitive behavior[20]. The EIS analysis was done with a sinusoidal voltage perturbation signal to evaluate the dynamic charge characteristics of biochar electrodes, and Nyquist plots of the electrode are represented in Fig. 2 (b). It was found that the solution resistance was 1.6 Ω. The resistance of the working electrode is found lower due to the free electron present in the graphitized structure. By using an electrochemical circuit fit suitable for a system, the charge-transfer resistance (Rct) value was 10.3 Ω. As the frequency decreases, the Nyquist plot has an inclined line explained by Warburg impedance[21], which influences ion diffusion within the system and is the consequence of the material excellent surface functionality and morphology[22]. Fig. 2 (c) illustrates GCD curves for current densities varying from 0.3 to 10 Ag^{-1}. Eq. (2) was used to calculate the specific capacitance.

$$C_s = \frac{I \times t}{m \times \Delta V} \quad \ldots (2)$$

The Cs, I, t, ΔV, and m represent the specific capacitance, electrode current, discharge time, potential window, and mass.

The GCD curves show that each spectrum is symmetric and linear with a small IR drop. An ionic hindrance causes this voltage drop. It also indicates the high capacitive nature and reversibility of the electrode. The similar triangular shape of GCD curves at each current density indicates excellent reversibility of the electrode. The electrode has a 122 Fg^{-1} specific capacitance at 0.3 Ag^{-1} constant current density. The change in specific capacitance at respective current densities is shown in Fig. 2 (d). Specific capacitance values decrease significantly as current density increases, indicating that electrolyte ions

Table 1 — Yield of biochar

Sample	Raw biomass (wt. in g)	Yield of Biochar (wt. in g)	Wt. % of Yield
B-220-6	5	2.87	57.4
B-220-12	5	2.46	49.2
B-220-18	5	2.15	43
B-220-24	5	2.01	40.2

Table 2 — The thermal conductivity and resistivity

Sample	Thermal conductivity (k) W m^{-1} k^{-1}	Thermal resistivity (R) ℃ cm^{-1} W^{-1}	Total Pore Volume cc g^{-1}
B-220-6	0.0297	3.4×10^3	0.185
B-220-12	0.0243	4.1×10^3	0.253
B-220-18	0.0226	4.4×10^3	0.293
B-220-24	0.0212	4.7×10^3	0.294

cannot penetrate the electrode materials. Ions are constrained to the outer surface at higher current densities and can diffuse into the active material at lower current densities. The electrode has excellent stability that was tested for 2000 cycles as shown in Fig. 2 (e), and it retains a specific capacitance of up to 79 % after charging and discharging the electrode for 2000 cycles at a current density of 10 Ag^{-1}.

5 Conclusions

This study prepared biochar from walnut shells in a hydrothermal autoclave at different times. The thermal and optical properties of the synthesized biochar were studied using standard methods and analytical techniques. The results indicated that biochar thermal conductivity decreases as we increase the residence time for decomposition. On the other hand, the thermal resistivity of prepared biochar increased as the residence temperature increased. The band gap decreases from 2.5 to 2.2 eV, which leads to biochar towards more conductors, and the surface area of biochar increase with an increase in the residence times, which would be helpful for electrode material in supercapacitors. The prepared electrode obtained a high specific capacitance of 122 Fg^{-1} at the current density of 0.3 Ag^{-1}. The electrode has excellent stability that was tested for 2000 cycles, and it retains a specific capacitance of up to 79 %. Finally, the results conclude that hydrothermal carbonization is a cost-effective and environment-friendly technique for biochar production and helps in waste management and energy storage.

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