Biomass derived functional carbon from *Sargassum Wightii* seaweed for supercapacitors

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Abstract. In this present work, microporous functional carbon is prepared by a single step pyrolysis method of dried *Sargassum Wightii* seaweeds (SW) as crushed powder without activation and tested for supercapacitors. Although the complete study presented here on seaweeds of *Sargassum Wightii* (SW), the synthesis technique is standard and relevant to most forms of dried biomass. The morphological studies were characterized by X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy (RAMAN), field emission scanning microscopy (FE-SEM) and Fourier-transform infrared spectroscopy (FTIR). The behaviour of the functional carbon were performed by using cyclic voltammetry (CV), galvanostatic charge and discharge (CD) and Impedance analysis. In aqueous electrolyte (1M H₂SO₄), by using three-electrode system shows highest capacitance of 354 F/g. Furthermore, it was observed that the carbonized temperature has significant role in the electrochemical performance, as the carbonized sample at 700°C showed best activity compared to the samples carbonized at 800°C and 900°C without any external activation. The electrochemical act obviously shows that the carbon produced from dried SW seaweeds can be used as a favourable material for electrodes in the application of supercapacitors.

1. Introduction

The demand for green energy storage devices is growing briskly in the world due to increase of environment trash and the scarceness of fossil fuels. Many determinations have been taken to progress the new materials namely biomass for the reducing the pollution of air and water [1,2]. Carbon is the most rich natural solid presenting a range of structural shapes which consists of graphene, amorphous and porous carbon, etc. with numerous applications. Among them, the carbon and graphene have a huge surface range and based on properties of flexibility. These properties of specific carbon-based materials make them effective for use in supercapacitors and batteries. Supercapacitors or electrochemical double-layer capacitors (EDLCs) are terms used for electric components that have capacitance value reaching thousands of Farads. In general, the supercapacitor energy binds the hole between capacitors of conventional and batteries. According to the mechanism of charge-storage, they are divided into two categories: (i) electrical double-layer capacitors and (ii) pseudocapacitors [3,4]. In EDLC, a mechanism is focused by an addition of ionic electrolytes and interface of electrolyte-electrode [5]. On the contrary, pseudo-capacitors are based on a process that is redox reactions faradic interface surface rapid electrode electrolyte [6].

Generally, the mechanism of EDLC is qualified on materials which are carbon and pseudocapacitance experience in oxides of metal and polymers which are conductive because of rapid redox reactions [7, 8]. In EDLC, the supercapacitors are available for its actual characteristics commercially due to high power, recyclability power, and non-toxicity [9-12]. In general, made up of carbon-based EDLC materials such as activated carbon (AC), carbon aerogel, carbon nanotubes (CNT) and nanofibers (CNF). Among them, activated carbon is used as the most significant electrode materials for supercapacitors to its larger characteristics such as high surface area, low cost, higher resistance and high operating temperature. Carbon-based materials have attracted significant interest in many
applications related to energy due to their large quantity, thermal stability and the possibility of tuning their texture and fundamental characteristics to achieve the necessities of specific uses. The various nano-structured materials have also been synthesized to report the several challenges.[13]

Many researchers have been reported about the synthetic methods to produce more quality carbon. These include carbonization of organic and polymeric signs [14, 15] chemically vapour deposition [16-20] graphitic targets by laser ablation [21, 22], plasma based synthesis [23,24] synthesis of arc discharge [25,26],chemical methods [27,28]. In recent times, scientists were on-going the research on utilizing the waste materials which are organic for the production of carbon for charge storage applications [29]. In graphene synthesis, waste materials such as food, agricultural and insects used as a bio-source of carbon already [30-35]. The activated carbons were synthesized by pyrolysis of materials which are waste for activation. The purpose for activation is to improve the surface area and porosity of the material. Physical activation includes with steam, CO2, etc. and chemical activation involves NaOH, KOH, etc. which are known as porogens. [36-39]. Till date, many researchers have been changed into porous carbon which are more activated and their capacitance in energy storage devices on many biomaterials successfully [40-47]. It reveals that the property of chemical-activation involves in the research plays a energetic role on the development of activated materials like carbon and their porosity [48]. To date, energy storage materials have present widely considered on the biomass materials of small cost [49]. For super capacitors and battery anodes a porous carbon (hierarchical) from algae for high capacitance was recently reported [50].

In general, the activation of high temperature results in the formation of conductive carbon due to the elimination of all functional groups, but has several disadvantages such as lower yield, reduced pore size and poor pseudocapacitance due to the absence of functional groups and low surface area. The area of electrode materials and activation at low temperature resulting in carbon with poor conductivity and high pseudo-capacity without long-term stability. Recently, the mass of corncob was reported from biomass residues that used nitrogen pyrolysis and high temperature thermal exfoliation [51]. From the results, the bio-exfoliated materials which shows specific capacitance of 221 F /g. Therefore, the preparation of biologically derived carbon materials with or without activation leads to more attention. The active porous nano carbon by the corn cob for the detection and implementation of supercapacitors with a specific capacitance of 340 F / g at the 5 mV/s was recently reported [52].

In the present investigation, we prepared the functional carbon by single step pyrolysis from dried Sargassum Wightii seaweeds without any activation has been studied for the application of supercapacitor. It is brown algae possessing many applications in medicinal, foods, cosmetics, fertilizers and for the extraction of chemicals and industrial gums. There is only one report on seaweeds to the best of our knowledge in the literature where they have revealed the production of high surface area carbon from the sea-weeds without any activation [53]. In this present study, by means of the functional carbon derived from the dried SW seaweeds as a charge storage electrode material in supercapacitor, we have reached very favourable results: a high specific capacitance 354 F/g and high energy density 44.25 Wh/kg.; at a current density of 0.5 A/g. These performance whichleads to the narrow micropores distribution and the high conductivity of the SW material. This performance is significantly valuable on the market due to biodegradable and eco-friendly.

2. Experimental
2.1 Synthesis of functional carbon

The dried seaweeds of Sargassum Wightii (SW) were collected in large quantity from seashore of Rameswaram, TamilNadu, India. It is thoroughly washed, cleaned and dried at 60°C in an oven. These dried SW seaweeds were grounded to become fine ash and kept in dry atmosphere. For the production of functional carbon, 10g of dried SW seaweeds powder was heated at the temperature of 700°C, 800°C and 900°C in alumina crucible for three hours in argon atmosphere at a heating rate of 10°C per min in a tubular furnace. The resultant black solid was then washed with a 5 mol/L HCl solution and dried for 12 hours at 60°C. The just-carbonized sample at 700 °C, 800 °C and 900 °C were denoted as SW-700, SW-800 and SW-900. The schematic diagram for the production of functional carbon from dried SW seaweeds was shown in (Fig.1).
2.2 Characterization of Synthesized functional carbon

The synthesized functional carbon from dried SW seaweeds were studied by X-ray diffraction (XRD) using ULTIMA IV Model with CuKα radiation ($\lambda = 1.5406 \text{ Å}$) in the series of 10-90° with a count time of 0.2 s. Fourier Transform Infrared (FT-IR) spectrum were recorded in the model of NICOLETT iS10 spectrometer from 500 to 4000 cm⁻¹. Energy dispersive X-ray spectroscopy (EDS) was qualitatively measured by Bruker Nano GmbH Berlin, Germany (Esprit 1.9), Raman spectroscopy using Lab RAM HR 520 from JY Horiba and The morphology of the sample was studied by Field emission scanning electron microscopy (FE-SEM) using Yes Carl Zeiss, UK with an acceleration voltage of 15kV.

2.3 Electrochemical Characterization- 1M H₂SO₄

The synthesized carbon of SW seaweed was tested by the profile of Cyclic Voltammetry, galvanostatic charge-discharge and impedance spectroscopy analysis using CH Instrument, Model CHI608E, USA. In Galvanostatic device, the seaweed-derived carbon (SW) as working electrode, Super-P and polytetra-fluoroethylene as a binder in a mass ratio of 80:15:5 respectively. It was grounded and the resultant paste of electrode was coated on SS mesh collector in three electrode system using 1M H₂SO₄ as the electrolyte. For three electrode dimensions, SW carbon electrode material, SCE, and platinum functioned as a working electrode, reference electrode and counter electrode respectively. The CV and the CD analysis were tested out from the potential range of 0.8 to -0.2 V at scan rates of 10 to 50 mV/s and at different current densities from 0.5 to 5 A/g respectively.

3. Results

The synthesized carbon from dried SW seaweeds was produced by using a single-step process namely carbonization of dried seaweeds without any activation. The XRD patterns of dried SW seaweeds clearly indicates a two sharp peaks around 20=26.9°, 36.7° for SW-700, 20=21.2°, 26.9°, 42.8° for SW-800 and one sharp peak at 20=20.8° for SW-900 were shown in (Fig 2a). The observed sharp lines shows that the carbons are more crystalline. To evaluate the properties of the surface on the carbonized sample of SW-700, SW-800 and SW-900, FT-IR spectrum were verified in (Fig. 2b). The obtained spectrum for all the dried SW seaweeds samples of carbons contains functional groups on their surface by indicating the existence of oxygen. Generally, the characteristic peak at 3448 cm⁻¹ indicates the water molecules which are chemisorbed and –OH groups on the carbon, but the peak detected which shifts to lower wavenumbers of 3445 and 3441 cm⁻¹ slightly was observed for SW-700, SW-800 and SW-900 samples and the peak around 1629 cm⁻¹ is attributed to the oxygen-containing C=O stretching groups [54]. The peaks around 1095 cm⁻¹ and 1084 cm⁻¹ are assigned to carbonyl group of stretching vibrations. It is important that the intensities of peaks resultant to oxygen
containing groups in all the samples are significantly reduced and more graphitic when increased to higher temperature.

The elements which are present in the dried SW seaweed samples were evaluated by EDS as shown in (Table 1). It has been seen that carbon (C) is the one of the most obvious element, indicates that the dried SW seaweed samples were well carbonized. The presence of inorganic elements such as oxygen (O), sulphur (S) and chlorine (Cl) can be observed as shown in Fig. 3. The obtainable oxygen element (O) implies that they are occupied on the carbon surface. In addition, mineral substances can also be observed in the SW-800 sample, such as potassium (K) in smaller traces. Since no element addition was involved during the carbonization process, it can be concluded that all the samples of dried SW seaweeds contains large amount of carbon content (>70%).

Raman spectrum is one of the potent instruments to determine the nature and amount of graphitisation in materials of SW carbon. The Raman spectra of SW-700, SW-800 and SW-900 are shown in (Fig. 3(a, b, c)). Generally, the intensity ratio of D band (I_D) and G band (I_G) indicates the amount of graphitic and the imperfect sites on the SW material. All the dried SW samples show a typical D and G bands at 1348 and 1595 cm\(^{-1}\), respectively. When compare to other two dried SW carbonized samples, the I_D/I_G ratio of SW-700 shows 0.95 value which indicates the amount of graphitic by the elimination of imperfections and reduction of functional groups and its findings suitable with the above FT-IR results [54].

![Figure 2.](image)

**Figure 2.** (a) XRD spectra (b) FT-IR pattern of SW-700, SW-800 and SW-900

The morphology of the surface and the porous nature of the SW-700, SW-800 and SW-900 carbon materials were studied using the FE-SEM images. The formation of large and coarse carbon particles can be observed (Fig. 4 a, c, e). This clearly confirms that the pyrolysis process in the argon atmosphere could convert SW seaweeds into valuable carbon material. When carbonization increased, the pore formation on the surface of the carbon at high temperature shows the thicker and larger carbon particles which leads to the formation of more rough surfaces with micro size particles (Fig. 4. d, e, f). Finally the SW carbon material reveals the formation of small pores and the high rough surface of carbon materials were found by comparing the FE-SEM images of SW-700, SW-800 and SW-900 shown in (Fig. 4).
### Table 1. EDS analysis of dried SW seaweed samples

| Samples | C (%) | O (%) | Cl (%) | S (%) | K (%) |
|---------|-------|-------|--------|-------|-------|
| SW-700  | 89.11 | 9.67  | 0.43   | 0.36  | 0.00  |
| SW-800  | 75.03 | 20.18 | 0.44   | 1.20  | 0.19  |
| SW-900  | 89.29 | 9.08  | 0.94   | 0.70  | 0.00  |

Figure 3. Raman spectrum of (a) SW-700, (b) SW-800, and (c) SW-900

Figure 4. FE-SEM pictures of SW-700 (a, b); SW-800 (c, d) and SW-900 (e, f)

### 3.1 Electrochemical behaviour of dried SW seaweed-CV and CD Profile

Based on the above outcomes, the carbon derived from dried SW seaweeds is a promising applicant for supercapacitors. The behaviour of electrochemical of dried SW seaweeds was investigated in 1M H₂SO₄ electrolytes in three electrodes arrangement. In this, the dried SW seaweed carbon material as
working electrode, saturated calomel electrode as reference electrode and the platinum network as counter electrodes were used. The cyclic voltammetry and Charge/discharge profile was verified at dissimilar sweep rate and current density respectively. The CV profile of SW-700, SW-800 and SW-900 samples in the potential range of -0.2 to 0.8 V for a sweep rate of 10 to 50 mV/s were shown in (Fig.5). It can be clearly shows that the perfect rectangular shape outline was observed due to behaviour of EDLCs without any oxidation or reduction peaks [55]. It also represents a double layer formation perfectly which leads to the reversible adsorption and desorption of the ions through the carbon surface, which leads to the indication of micro-porous character of the material.

Even at high sweep rate, the CV curvatures maintain their character or structure without any alteration. It clearly shows that the SW-700 sample were found to be EDLC like behaviour with major pseudo capacitive nature. As the carbonization temperature was increased to 800 and 900° C, the specific capacitance was decreased compared to SW-700 and the pseudo-capacitive nature also found to be decrease in SW-800 and SW-900 because of the absence of functional groups respectively. The occurrence of pseudo-capacitive nature with EDLC was noticed from the CV profiles carried at different scan rate in all samples clearly (Fig. 5a). At lower sweep rate, the CV curves indicates the rectangular shape (quasi) clearly because of the occurrence of oxygen containing functional groups in the carbonized sample. This enactment at higher sweep rate creates the more power retention of the micro porous SW sample. The SW-800 and SW-900 also represents perfect rectangular shape profile due to EDLCs behaviour and micro porous material were represented in the (Fig. 5b, c).

The CD profile of SW-700, SW-800 and SW-900 samples at the 0.5 to 5 A/g were shown in (Fig.6) which shows the presence of pseudo capacitive behaviour. The SW-700 reveals the CD profile measured at various current densities provides a highest specific capacitance of 354 F/g at 0.5 A/g (Fig. 6a). As the current was increases to 1, 2, 3, 4, and 5 A/g, the specific capacitance reduced gradually to 308, 256, 228, 204, and 185 F/g, respectively owing to the narrow distribution of the ions which are active on the electrode surface due to charging quickly. At highest current density, the micropores which are present are not available to the electrolyte and hence the comparative capacitance found to be less as compared to the capacitance at lowest current density. The SW-800 delivers a high specific capacitance of 349 F/g at 0.5 A/g. As the current increases to 1, 2, 3, 4, and 5 A/g, the capacitance decreases gradually to 266, 200, 171, 144, and 108 F/g respectively were shown in (Fig. 6b).
The SW-900 shows the maximum specific capacitance of 345 F/g at 0.5 A/g. As the current increases to 1, 2, 3, 4, and 5 A/g, the specific capacitance decreases gradually to 199, 154, 126, 108, and 95 F/g respectively were shown in (Fig. 6c). But at 0.5 A/g, there is decrease in specific capacitance, when compared to all other dried SW seaweed material. The charge-discharge profile observed for the SW-700, SW-800 and SW-900 confirmed that the presence of pseudo-capacitive behaviour and it shows moral promise with the exceeding CV studies.

By using the CD profile, the SW-700 electrode shows a maximum specific capacitance of 354 F/g was observed at 0.5 A/g were shown in (Fig. 6d). It can be detected that the capacitances of all dried SW seaweed material were decreased with an increase of the current density due to the insufficient time for the distribution of electrolyte into the internal pores [54]. The sample of SW-700 shows a
highest specific capacitance of 185 F/g at 5 A/g which is higher than that of other dried SW seaweed samples, indicating a good rate capability of SW-700. These outcomes show there might be the interaction consequence between the large surface area with pore size. In addition, the particular porous design is crucial for a convenient ion transport and therefore, equipped with a discharge and polarization process of the efficient carbon materials, thus promising pseudocapacitance behaviour.

The densities of energy and power storage systems are the main factors to differentiate them for the fuel cells, supercapacitor and batteries. The Ragone plot (power Vs. energy densities) for SW-700 was shown in (Fig.7a). The dried seaweed of SW-700 based supercapacitor exhibits an high energy density 44.25 Wh/kg at a power density of 62.5 W/kg, and still maintains 23.13 Wh/kg at a high power density of 625W/kg in 1M H₂SO₄ which is closer to batteries. Furthermore, in a aqueous electrolyte (1M H₂SO₄), can achieve a high energy density of 44.25 W h/kg, which is superior in the application of supercapacitors. To the best of our information, we reported the high energy density of SW-700 electrode material of functional carbon derived from the dried SW seaweed without any activation using aqueous electrolyte of 1M H₂SO₄.

Since the dried seaweeds of SW-700 shows the highest specific capacitance at 0.5 A/g, the measurement of EIS analysis for the dried SW seaweed electrodes in aqueous medium of 1M H₂SO₄ was carried out. In order to realize the numerous resistance aspects in the interface of electrode-electrolyte and charge transfer process. The obtained EIS results were found to be fit with suitable circuit model were represented in (Fig.7b) with the physical components such as double layer capacitance (Cₐ), solution resistance (Rₛ) and charge transfer resistance (Rₜ) and. The statistical values from the fitted profile reveals the lower Rₛ and Rₜ values of 1.4 and 5.8 Ω, respectively. The Nyquist plot reveals a vertical straight line equivalent to the imaginary axis (Z") at the region of lower frequency reveals the domination of the ideal capacitance nature at the electrode-electrolyte interface and the width of the semicircle impedance loop represents charge transfer resistance in the electrode materials. On the basis of the above results, it can be early indicates that the functional carbon from the dried SW seaweeds performs a suitable electrode material for energy storage devices. The CV and CD profile of biomass derived activated carbon presented by the various researchers (M. Karnan et al, 2017) also represented similar finding. [55].

![Figure 7](image-url)

**Figure 7.** (a) Ragone plot for SW-700 using aqueous 1M H₂SO₄ electrolyte (b) EIS spectrum of SW-700 electrodes and its parallel equivalent circuit model (inset)

4. Conclusion

In summary, the micro porous functional carbon produced from the dried seaweeds (SW) without any external activation for supercapacitor application. The dried seaweeds (SW) derived carbon are more crystalline in nature which was confirmed using XRD pattern and the elements present in the mixture of dried SW seaweeds samples awarded a carbon content of > 70% and it was further improved the amount of graphitic by elimination of imperfections and decrease of functional groups was analysed.
by using RAMAN and FTIR. The results of FE-SEM revealed that the seaweed of SW derived carbon was qualified to the formation of small tiny pores and high rough surface of carbon materials. The seaweed derived carbon electrode materials were found to be suitable for their use of supercapacitors using aqueous medium by electrochemical studies. The *Sargassum Wightii* (SW) derived carbon materials of the sample SW-700 reveals the maximum capacitance of 354 F/g at 0.5 A/g in 1M H₂SO₄ reflects best performance activity. The energy density occurred for SW-700 electrode was found to be 44.25 Wh/kg in aqueous electrolyte. As the power density increases to 625 W/kg, the energy still maintains at 23.13 Wh/kg. This clearly reflects that the dried SW seaweed derived functional carbon material suits for supercapacitors. The biodegradable, cheap and non-toxic derived functional electrode materials of carbon are more applicable for storage of energy systems.

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