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OBTAINING ACTIVATED CARBON FROM PAPAYA SEEDS FOR ENERGY STORAGE DEVICES

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ABSTRACT

Preparation of carbon from papaya (Carica papaya L.) seeds activated with $ZnCl_2$ @ 300°C is presented. Characterization of the powder is carried out by elemental analysis, N_2 sorption studies, powder x-ray diffractometry, fourier transform infrared spectroscopy, scanning electron microscopy, cyclic voltammetry and galvanostatic charge-discharge studies. Specific capacitance from cyclic voltammetric studies on the carbon is 472 F g^{-1} in 1M H_2SO_4 electrolyte when run between -0.1 and 1.0V Vs SCE at 10 mV s^{-1} scan rate. The proposed carbon sample posses an N_2 adsorption isotherm characteristic of mesopore structures. The presence of various surface functional groups like carbonyl and hydroxyl groups coupled with desired physical features of the carbon are presumed to be responsible for fast faradic reactions to offer pseudocapacitive characteristics to the papaya derived carbon. Capacity as well as the cycling stability of the electrode prepared with papaya seed based activated carbon in acid electrolyte seems to be impressive as observed from charge-discharge studies. Thus papaya seed biomass represents a promising new green source of carbon for electrochemical capacitor electrodes and gives a new and valuable dimension to domestic wastes.

KEYWORDS:papaya seed, activated carbon, electrode material, pseudocapacitance, electro chemical double layer capacitor.

INTRODUCTION

Electrochemical Capacitors (ECs) are in the pinnacle of electrical energy storage technologies, the reason being their promise to the efficient functioning of multifarious hand-held electronic gadgets to electric vehicles. ECs are broadly classified into two types, (i) Electrical Double Layer Capacitors (EDLCs) and (ii) pseudocapacitors, depending upon the mechanism of charge storage. EDLCs show non-faradaic reactions with concomitant charge accumulation at the electrified interface of activated carbon, graphene, CNTs or CNFs based electrodes [1] while pseudocapacitors exhibit faradaic (redox) reactions when materials like RuO_2, MnO_2, Co_3O_4 [2-4] and conducting polymers [5] are used. An efficient charging of the electrical double layer requires materials with a high surface area and pores adapted to the size of ions, which is crucial for supercapacitor performance [6-8]. Consequently, the electrode materials having high degree of porosity with high specific surface area are the key component of ECs. At present, from the energy view point activated carbons are the best electrode candidates for EDLC due to its high specific surface area up to 3000 m^2 g^{-1}, high porosity, chemical resistance, and electric conductivity. High porosity and high surface area favors good charge accumulation at the interface with the electrolyte and therefore high capacitance can be tapped.

A quick view on the preparation methods of activated carbon is worthwhile here. Activated carbon can be produced either by physical or chemical activation. In physical activation, the raw material is carbonized under an inert atmosphere and then activated at high temperature using either steam [9] or carbon dioxide [10] as the activating reagent. In chemical activation, the precursor is treated with chemicals (KOH, $ZnCl_2$, H_3BO_3) to help the initial hydration. In the case of physical process, removal of a large amount of internal carbon mass is necessary to impart well-developed carbon structures, while in the chemical activation process, all the chemical agents used are dehydrating agents which influence pyrolytic decomposition resulting in the formation of tar, which increases the carbon yield [11, 12].

As far as the source or raw material of activated carbons is concerned, the recent and wise choice would be from biomass i.e. vegetable sources. Manufacture of activated carbon from bio-wastes is thus gaining significance; as high valued product could be effectively manufactured from almost zero-cost raw materials. Further the biomass are obviously easily available, abundant, cheap and environmentally friendly [13]. Their utilization also proves a solution for waste disposal problems.

Our Nature has been the source of biomass and to mention literature is replete with (activated) carbon derived from various biomass for the application as electrode in supercapacitors or EDLC. The recent review by the authors of the present communication [14] also reveals the current research status and prospects of obtaining low-cost and high-valued biomass derived activated carbon for capacitor electrodes. Notwithstanding extensive work with biomass carbon, further breakthrough in materials is vital since activated carbon has several attended applications in a variety of fields such as food and chemical industries, wastewater treatment, solvent recovery, air pollution control and hydrometallurgy for the recovery of gold and silver. Carbon (activated) obtained from agricultural by-products has many advantages but not limited to, as a low-cost replacement for many types of carbon-based materials obtained from non-renewable sources and costly-cum-elaborate processes. Thus we thought the focal point should be to develop low-cost carbon, especially from wastes, with promising properties for electrodes in aqueous electrochemical capacitors for energy storage.

Now turning to the global tendency with regard to the use of plant wastes and agro-industrial wastes, conversion of these into carbon may add economic value to a large quantity of wastes that are generally discarded. Plentiful agricultural wastes and various unused plant parts offer an inexpensive and renewable additional source of activated carbon. Thus, this study was undertaken to produce carbon from papaya seeds, determine the physico, electro -capacitive characteristics, thus aiming to extract the potential of the Papaya Seed Carbon as an electrode material in electrochemical capacitors. Papaya seeds pose environmental pollution problems as its sugar, mineral, protein contents and water retention nature creates favorable conditions for proliferation of microorganisms. As a result, it must immediately be treated and according to us pyrolysis presents a potential option to convert waste (papaya seeds) leading to value added products.

The total global production of papaya averages about 10.0 million metric tons, and India and Brazil are the major producers with annual production of 3.6 and 1.9 million metric tons, respectively[1]. Papaya is grown mostly for fresh consumption and papain production; however, it can be processed into jelly, jam, candy, and pickles, and its seeds are usually discarded. Nevertheless, few studies have been conducted on the composition of papaya seeds. The composition of these seeds, compiled by Marfo et al. [15] and Puangsri et al. [16] revealed that they are a rich source of proteins (27.3-28.3%), (28.2-30.7%), and crude fibers (19.1-22.6%). Marfo et al. [15] found appreciable quantities of calcium and phosphorus in the seeds; however, the presence of toxicants, such as glucosinolates was also observed. Besides, Oleic, palmitic, linoleic, and stearic acids were the most abundant fatty acids found in the papaya seed oil [15,16]. To best of our knowledge the use of papaya fruit seeds for obtaining carbon has never been attempted hitherto. Nevertheless, it is interesting and notable that all the above investigations reveal that biomass offers multifarious applications in one or the other advanced technologies. Thus in the present work we have explored the physical features of the papaya seed derived carbon and have evaluated the capacitive nature in acid electrolyte to establish the utility of the discarded papaya fruit seeds in the area of electrical energy storage

MATERIALS AND METHODS

Papaya Seed Activated Carbon (PSAC) preparation

Mature papaya fruit (Carica papaya L.), was purchased from a fruit shop near our Institute premises. The seeds are manually removed off the fruits, washed with hot distilled water and dried under sunshade for approximately two weeks. To prepare PSAC, the seeds are crushed with a mortar and the crushed powder was treated with a concentrated solution of $ZnCl_2$ in the weight ratio of 1:1 seeds: $ZnCl_2$. The contents are stirred well in a magnetic stirrer at 60 ºC for two days with intermittent agitation with an agitator and dried in an air oven. The dried mass was finally heat treated in a furnace at 300 ºC for 2 hours. The heat treated sample was washed several times with dilute acid followed by de-ionized water until the washings are neutral to pH and its conductivity is minimal. The final mass of carbon lump was dried, ground and sieved to 250 mesh size.

Characterization of the activated carbon sample

Physical characterization of the sample was done by X-ray diffraction, nitrogen sorption method to understand the phase formation and to determine the surface area (S_{BET}) and pore structures respectively. The specific surface area and pore structure characteristics of PSAC were determined by nitrogen adsorption at 77K with an ASAP 2020 system (Micromeritics, USA). The BET surface area was calculated from the isotherms using the BET equation. The total pore volume (V_{Total}) was assessed by converting the amount of nitrogen gas adsorbed (expressed in cm^3 g^{-1} at STP) at a relative pressure (0.99) to the volume of liquid adsorbate. The t-plot method was used to calculate the micropore volume (V_{Micro}) and the mesopore surface area S_{Meso}). The mesopore volume was determined by subtracting the micropore volume from the total pore volume while the micropore and mesopore percentages were based on the total pore volume. Surface functional groups on the activated carbon sample was analyzed using Fourier Transform Infrared spectroscopy in the range from 4000 cm^{-1} to 400 cm^{-1} (Model # Nexus 670). The morphology of the carbon was examined with Hitachi S-4700, field emission scanning electron microscope to visualise the surface morphology of the PSAC Scanning Electron Microscopy (SEM). A thin layer of gold was sputtered on the sample surface for charge dissipation during FESEM imaging. The sputtering was done using 6 mA current in argon atmosphere for 3min.

Electrode preparation and electrochemical measurements

PSAC, poly vinylidene fluoride binder and carbon black respectively in the weight ratio 85:10:5 were mixed to get a paste using N-methyl 2 pyrrolidone. The paste was applied on to the circular end of an SS rod of 1 cm^2 area & length 8cm. The electrode was dried at 80 ºC for 1hour. Each electrode layer has 0.5mg of the PSAC. Heat shrinkable sleeve was used to mask rest of the electrode portion. Electrochemical studies (Cyclic Voltammetric (CV) and galvanostatic charge-discharge) were performed with CH Instruments (Model # CHI660a) in a three-electrode configuration using the SS rod coated with PSAC as the working electrode, Pt wire as the counter, and saturated calomel electrode as the reference. 1M H_2SO_4 is employed as the electrolyte for assessing the electrochemical features of the PSAC. The specific capacitance was evaluated from the area of the CV curves. Galvanostatic charge- discharge experiments were performed in a similar setup as described above with a specific current density of 15 mA g^{-1} and between 0.0 and 1.0 V.

RESULTS AND DISCUSSION

Organic matters can be converted into carbon by controlled thermal decomposition. Mopoung et al. [17] have systematically analyzed the mechanism of conversion of organic matters into carbon and have found to involve the following steps: (a) desorption of adsorbed water up to 150 ºC (2) removal of water with the carbonaceous matter structures between 150 and 260 ºC (c) chain scissions, or depolymerization, and breaking of CO and C–C bonds within organic ring structural units liberating water, CO and CO_2 between 260 and 400 ºC, (d) above 400 ºC, aromatization of carbon atoms forming graphitic layers, and lastly (e) completion or termination of the heat induced decomposition processes leading to a carbon template structure above 800 ºC. The major break down of constituents of organic matters occur step by step between 200 and 800 ºC (hemicellulose), 260 and 350 ºC (cellulose) and 280 and 500 ºC (lignin). Between 260 ºC and 400 ºC almost 80% of the total weight loss occurs which may be due to evolution of H_2O, CO_2 and volatile hydrocarbon species generated through fragmentation of the polyaromatic components depending upon the organic matter considered. Hence burn-off calculation (and also thermogravimetry) is necessary to get insight on the mechanism of thermal decomposition. FTIR studies would supplement with the various types of organic functional moieties present in PSAC.

Burn-off

Conversion of PS biomass in to carbon was carried out around 300 ºC and weighed the residue to calculate the burn-off. Burn-off was calculated by the following formula [18]

$X(\%) = (m/m_o)\times 100$,

where X is carbon yield (%), m is the carbon mass (g) and m_o is the raw sample mass (g) and was found to be 76% on dry basis. During the thermal processing of PS enormous gas evolution was observed and these gases may be oxides of heteroatoms, carbon dioxide and even moisture. Nonetheless, it will be proved from the FTIR spectroscopic studies (or ultimate elemental analysis) that organic groups are still present in the carbon structures to play a part in the electrochemical features of the carbon samples derived from PS.

Phase analysis by X-ray Diffractometry (XRD)

The XRD pattern of the biomass carbon was recorded between 10 to 80º on X'Pert Pro X-ray diffractometer with CuK_α radiation source and is shown in Fig. 1. The presence of a hump or broad peak between 23º and 30º may be attributed to the (002) diffraction peak, indicating the amorphous nature of the carbon produced from PS. The nature of the peak may also indicate the evolution of microporous carbon and the microporous structure of PASC Disordered single graphene layers and stacked structures of graphene sheets may also be present simultaneously in the texture of the carbon powder [19] (typical XRD pattern of graphene [20] has been given the inset of Fig. 1). The broad shape in Fig. 1 indicates highly disordered structure in the carbon [21]. However the sharp peaks in the middle of the humps suggest that an organized crystalline structure exists in the amorphous carbon structure of grass. Generally the value of d_{002} is taken as a measure of estimating the degree of graphitization in the carbon and growing disorder is reflected in larger values of d_{002}. Thus the interplanar space (d_{002}) calculated for the virgin carbon is 4.00 Å, larger than that observed for graphite (3.354 Å) indicating considerable disorderliness in the carbon produced [22-24]. Further, the XRD of the PSAC time exhibits a broad shoulder around 42° and has been attributed to the (1 0) bidimensional planes [25]. The existence of h k (1 0) lines may be an evidence for the turbostatic or convoluted stacking of hexagonal layers of carbon resulting in disordered structure and lower crystallinity [26,27] thus demonstrating amorphous nature of the PSAC and hence better capacitance may be expected.

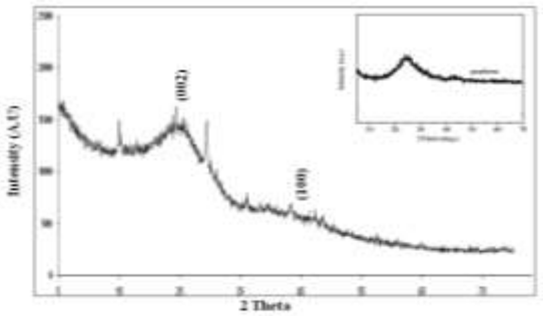

Fig. 1. Powder X-ray diffractogram of PSAC (In inset PXRD pattern of graphene).

Functional group analysis or surface chemistry characterization studies

Since carbon chosen for the present study is derived from biomass the carbon matrix of PSAC is expected to contain surface functional groups containing heteroatoms like sulphur, nitrogen, oxygen in addition to carbon and hydrogen. Thus the nature and chemical reactivity of the functional group reflect in the electrochemical performance of the carbon electrode material, making the functional group analysis essential to have insights on the electrochemical properties of PSAC. The FTIR spectroscopy is one of the versatile techniques using which information on the surface functional groups of the materials can be derived. Fig.2 shows the FTIR spectra of PSAC. The spectrum of the PSAC is complex due to the presence of many functional groups on the surface, as expected. The spectrum obtained for PSAC shows a characteristic peak around 3737 cm^{-1}which   is ascribed to free O-H groups, the peak around 2357 & 1423 cm^{-1} are due to O-H stretching and bending vibrations of phenols respectively, and the signature at 1027cm^{-1} corresponds to C-O stretching of phenols. The oxygen in the carbons is present in functional groups such as phenols, carbonyls, sulphoxides, etc. [28]. The peak around 2924 cm^{-1} in the sample endorses the presence of aliphatic C–H bond corresponding to the methyl group. a band from 700-600 cm^{-1} attributed to C-H bending out of plane were observed. Similar results were recorded by Hu et al. [29]. On the other hand, peak around 3414 cm^{-1} & 1602 cm^{-1} may be due to the N-H stretching and bending vibrations respectively, and the peak at 2213 cm^{-1} is due to the C-N stretching of amides. The band at around 1360 cm^{-1} is owing to S=O and signatures observed at 676 and 430 cm^{-1} are due to and C-S stretching. So the nitrogen and sulphur present in the sample may probably due to amide and sulphoxide group respectively. The presence of S is also confirmed through EDS. These functional groups appear at edge carbon atoms, may be formed during the pyrolysis of papaya seeds. Ehrburger et al. [28] have also reported similar observation in their activated carbon from coal. From this study it could be inferred that the PSAC contains phenolic, amide and sulphoxide groups.

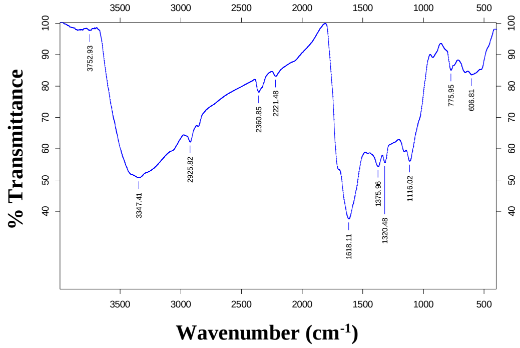

Fig. 2. FTIR of PSAC sample.

Organic groups with oxygen, typically, phenols are expected to form on the surface during the thermal treatment of the biomass precursors and may appear at the edge carbon atoms as indicated by Subramanian et al. [30]. This fact may also be applied to PSAC samples and the effect or mechanism of action of these groups on the electroactivity of the carbon samples may be complex and may form an exclusive research. Centeno and Stoeckli [31] have reported that oxygen containing functionalities impart good electroactivity to the carbons and hence acceptable performance in terms of capacitance may be expected from PSAC. The influence of organic groups H, N, O on the electrochemical performance is important but it is difficult to explain the electrochemical behavior because we do not know the exact location of these elements in the carbon structures where these groups undergo electrochemical transformation under the influence of electrical signal during electrochemical studies and/or chemical reactions with the electrolyte ions.

Ultimate elemental analysis

The biomass derived carbon samples consists principally of carbon atoms forming aromatic sheets cross-linked in a random manner and heteroatoms like oxygen, nitrogen, sulphur, hydrogen depending on the nature and source of the raw material considered and on the thermal or chemical processing techniques [32]. Consequently the type and % of the constituents is expected to influence the electrochemical parameters and hence ultimate elemental analysis has been conducted on PSAC. The mass of PSAC was analyzed to contain 62.4 % mass of carbon with certain amount of H (1.5%), S (0.69%), N (6.5%) and the rest is O. Significant % of N, S & H in the sample shows the presence of organic functional groups. FTIR data also supports the presence of these functional groups, the presence of which is expected to influence the electrochemical behavior of the carbon samples prepared, as discussed in the latter sections.

Energy Dispersive X-ray Spectroscopic analysis (EDS)

EDS identifies the elemental composition of materials imaged in a Scanning Electron Microscope (SEM) The EDS (Fig. 3) of PSAC indicates that the carbon content C is 78.05% and oxygen O is17.71 % and other elements (S, Ca, Ba, P) to certain amount were also present. Though the presence of N is not obvious from EDS, FTIR as well as ultimate analysis clearly indicates the presence of N in PSAC. The occurrence of S in PSAC has the source from glucosinolate, an ingredient in PS, as mentioned earlier and hence the influence of S on the electrochemistry of PSAC needs also to be investigated. Nevertheless, the presence of these elements would enhance the chemical features of the activated carbon by forming various functional groups, as discussed through FTIR studies. Additionally, O/C ratio would be an interesting factor to investigate and monitor the carbonisation process. The pyrolysis tends to increase the carbon fraction than the oxygen, may be due to the volatilization of the oxygenated compounds and other escaping gases. EDS (as well as SEM) shows the obvious presence of $ZnCl_2$ in our sample, the activating agent used for our biomass and it is to be mentioned that the complete removal of Zn species is important to avoid the blockage of the pores and consequently, a series of washing of the PSAC powder with dil. HCl and water was done before we carry out physical and electrochemical studies. Fig. 3 shows the presence of Au also which has shown up obviously from the Au sputtering on the PSAC surface. Inset of Fig. 3 gives the chart of the % (by mass) of elements in PSAC done by EDS (Fig. 3a) and ultimate analyses (Fig. 3b). The difference in mass % of various constituents in the two analyses is as expected since EDS could identify even other elements like Ca, Ba, P and Zn (from the activating agent).

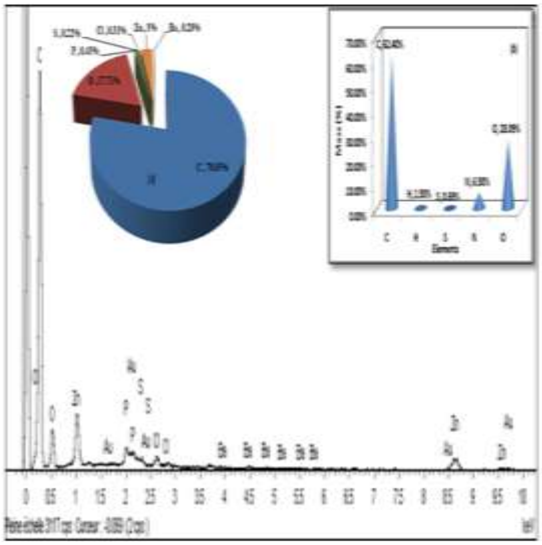

Fig. 3. EDS analysis of PSAC. Inset: (a) results of ultimate analysis; (b) chart of EDS analysis of PSAC powder.

Scanning Electron Microscopic (SEM), surface area and porosity measurements

Morphology, surface area, pore structure and its distribution in an electrode are very important traits that should be taken in to consideration for electric charge storage in devices like electrochemical capacitors. Hence these measurements were made on PSAC. The micrograph of PSAC presented as Fig. 4 shows the formation of lumps of carbon of ununiform particle size distribution but featuring well developed porosity and inter-connectivity between the particles (possessing macropores with huge mesopores) bestowing spongy or cellular appearance. The activating agent used for activating the seeds is $ZnCl_2$ and according to an earlier report [30] it acts as a dehydrating agent during pyrolysis resulting in charring and aromatization of carbon thereby facilitating pores formation. Pore generation will be promoted further with the subsequent removal of unreacted $ZnCl_2$ by washing with acid and water [33]. The pore structures are obvious from SEM (Fig. 4) and N_2 adsorption isotherm (Fig.5).

The pore structure of the PSAC was ascertained by N_2 adsorption–desorption studies at 77K and has been presented in Fig. 5. The N_2 gas adsorption is gradual up to the relative pressure 0.7 indicating the presence of large number of mesopores, which are expected to form during $ZnCl_2$ (acts as a dehydrating agent) activation and pyrolysis of PS. Thereafter an increase in adsorption was observed may be due to capillary suction at the site of the mesopores [34]. Thus mesoporosity of the material is evident from the nature of the recorded adsorption isotherm.

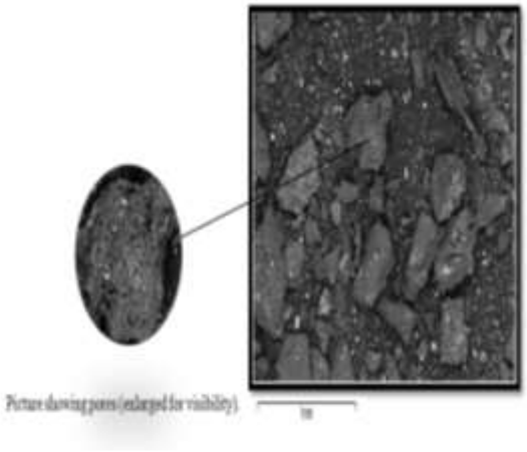

Fig. 4. SEM (X 1500) of PSAC.

S_{BET}, the BET Surface area and S_{meso} of the PSAC was measured as 1213 and 908 m^2 g^{-1} respectively. The corresponding estimated pore volume, V_{total} (measured at $p/p_o = 0.995$) is 1.37 cm^3 g^{-1}, V_{micro} is 0.46 cm^3 g^{-1} and V_{meso} is 0.91 cm^3 g^{-1}. The average pore width from adsorption (4V/A by BET method) is calculated to be 4.5 nm. The above details show that the evolved pore structures in PSAC is a combination of meso and micro, with an extent of 65% (V_{meso}/V_{tot}) of mesopores. These results make obvious that PSAC possess high specific surface area and with large mesoporosity that may be advantageous for electrodes in electrochemical applications. A high value of the surface area probably indicate the presence of enormous electrochemically accessible sites or area thereby resulting in increased electrochemical performance ultimately, which will be made obvious from the discussions presented under electrochemical studies section.

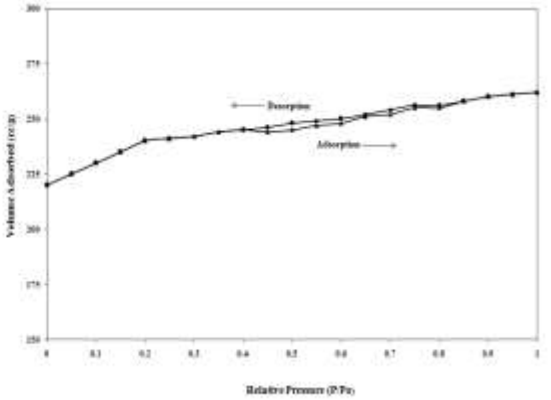

Fig. 5. N_2 adsorption and desorption isotherm of PSAC at 77K.

Cyclic voltammetric (CV) studies

The supercapacitive properties of PSAC were investigated using cyclic voltammetry because this technique provides valuable information on the charge-discharge behavior of the cells. Fig. 6 shows the CV of the PSAC based electrode in 1M H_2SO_4 at various scan rates using the setup described in the previous section in the voltage window of -0.1 to 1.0V. We all know that the shape of the CV of a supercapacitor should trace a rectangular shape, provided that there is low contact resistance and larger resistance distorts the CV pattern, resulting in a narrower loop with an oblique angle [6,35]. The slight distortion in the CV pattern and the oblique angle of the CV of our sample indicate the involvement of ESR and increases as scan rate increases. The authors attribute the ESR to the presence of amido and sulphoxide groups which may present steric hindrance to the charge transfer. Further, the non- linear current with increasing voltage is the characteristic feature observed, indicating the large Faradic nature of our PSAC electrodes. In general, CVs exhibit symmetric responses in their positive as well as negative scans and the integrated voltammetric charges in the positive and negative scans evolves to be closer. It can thus be concluded that the charges stored in the positive scans could be delivered during the negative scans and consequently good electrochemical behavior of the PSAC is indicated. It is known that if

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the redox reaction occurs on the cathodic or anodic side, the CV curve will show a peak around 0.4 to 0.8 V. Cyclic voltammogram recorded for PSAC in acid electrolyte show faradic charge transfer, which has shown up as peaks around 0.2 and ~0.9V in the acid medium selected for the present study. We explain the redox behavior of the PSAC by the presence of various hetero atoms containing organic functional groups on the PSAC particles surface.

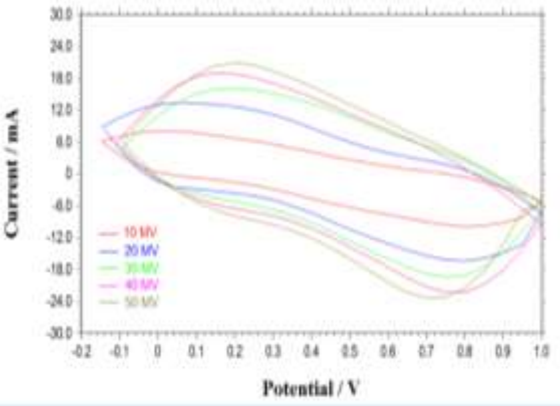


Fig. 6. Cyclic voltammogram of PSAC in acid medium. It can be stressed from the FTIR studies and from the results of other authors [36,37] that the PSAC like any other biomass derived carbons contains various organic moieties that would interact with the electrolyte ions leading to interesting electrochemical picture. In a typical acid electrolyte, the following interactions with the phenyl (-Ph) and alkyl (-R) groups were reported by Hu et al.[38] as,

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

$R = O + H^+ + e^- \leftrightarrow R - OH$

These reactions are known to offer pseudo-Faradaic capacitance. Further, H^+ of the electrolyte has the tendency to get adsorbed over the carbonyl groups on the PSAC due to the induced ion-dipole attraction. Consequently, the electric charge density tends to change, adding to the double layer capacitance in the acid electrolyte [39]. During the charging process, the H^+ adsorbed over carbonyl groups may form a strong bond due to electron transfer across the double layer and vice-versa for discharge process [40]. These two processes can be represented as below.

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

$>CO + H^+ + e^- \leftrightarrow >COH$

Frackowiak et al. [41] concluded that the electrochemical behaviour of the carbon materials used as electrodes is related to their pore size and redox properties Further, the above author's electrochemical measurements showed a proportional increase of the specific capacitance with the nitrogen content in acid electrolyte medium and that the nitrogen content in the final product reflects its amount in the starting materials. Higher the amount of nitrogen higher is the basicity of the carbon surface (as evaluated by the values of pH_{PZC}). The above authors attributed to the enhancement in the capacitance values in the acidic medium by the following pseudo-Faradaic reactions [42].

$C^* = NH + 2e^- + 2H^+ \leftrightarrow C^*H - NH_2$

$C^* - NHOH + 2e^- + 2H^+ \leftrightarrow C^* - NH_2 + H_2O$; where C* stands for the carbon network. As mentioned in the earlier sections, S in papaya seeds is present in the form of glucosinolates and the following mechanism involving S is presumed to occur in papaya seeds as proposed by Zhao et al. [43] in his work with thioldiphenol derived mesoporous carbons.

$O=S=O + 2e^- + H_2O \leftrightarrow >SO + 2OH^-$

$>SO + e^- + H_2O \leftrightarrow >SOH + OH^-$

These reactions are known to offer pseudo-Faradaic capacitance. The same of kind of reactions are expected in the PSAC to conclude that capacitive currents and the total capacitance values has a contribution not only from the electric double layer charging but also from the pseudocapacitance of electroactive functional moieties significantly. Thus a clear picture of the Faradaic nature of the capacitor electrode fabricated using activated carbons containing oxygen functional groups in aqueous medium would be demonstrated remarkably by cyclic voltammetric studies [44-47].

Further, to verify the pseudocapacitance contribution, the effect of scan rate on the capacitance has also been studied. Fig. 7 shows the plot of capacitance Vs scan rate. The specific capacitance increases almost linearly with decreasing scan rate. The measured capacitance at a scan rate of 10mV/sec over the entire range of potential selected for the study is 472 F g^{-1} 1M H_2SO_4 and the corresponding maximum energy has been calculated as 131 Wh kg^{-1} using the formula with CV_i^2 where C is the specific capacitance and V_i is the initial voltage,1.0 V.

As expected, the capacitance values decrease with increasing scan rate. The reason for the decrease in capacity is the reduced diffusion time, since the ions in the electrolyte cannot fully access the surfaces of the PSAC at high scan rates. Despite the decrease in the capacitance the PSAC has yielded excellent capacity at low scan rates. At 50 mV s^{-1} rate, the delivered capacity is 106 F g^{-1}, which means that

PSAC has retained only 23% of the capacitance at 10 mV s^{-1} rate. This value is relatively lower than other biomass derived carbon electrodes [30, 48 49]. Nevertheless, papaya seeds being a zero-cost source and cost-effective nature might put PSAC as a prospective candidate for electrode material in electrochemical capacitors or pseudocapacitors.

It is very informative and interesting to note that Biniak et al. [50, 51] have proposed three types of surface oxides, namely, acidic, basic and neutral, which are like to be formed on carbon surfaces as determined by the formation history of the carbon material and the temperature at which it was is exposed to oxygen or oxidizing atmosphere. Acidic surface oxides are formed when carbons are exposed to oxygen between 200 and 700 °C or by reactions with oxidizing solutions at room temperature. These surface groups are considered to be less stable and include groups such as carboxylic, lactonic and phenolic functionalities. Basic and neutral surface oxides are considered to be more stable than acidic oxides and tend to form after a carbon surface, freed from all surface compounds by heat treatment, comes in contact with oxygen at low temperatures [50, 51]. Functional groups that are inert (hydroxyl groups) in the potential range of operation does not contribute to pseudo-capacitance, but are involved in double layer capacitance due to increased wettability [52] and consequently increase the specific capacitance of the carbon through improved pore access and greater surface utilization [53]. Moreover, the carbonyl groups have lower charge transfer resistance and thus are advantageous to fast faradic reactions to introduce pseudocapacitance.

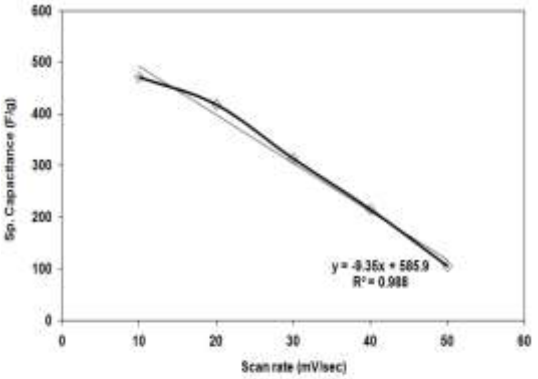


Fig. 7. Dependence of specific capacitance on the scan rate.

Galvanostatic charge-discharge studies

Long cycle life of supercapacitor is important for its practical applications. Fig. 8 shows the observed specific capacitance Vs cycle number for PSAC electrode when it is cycled galavanostatically between 0.0 and 1.0V with 15mA g^{-1} as the charge and discharge currents. The galvanostatic cycling of the test cell demonstrates the capacitive behavior with almost symmetric charge/discharge pattern (for the first 15cycles as shown in the inset of fig. 8). The small deviation in the linearity of charge-discharge curves is a characteristic pseudocapacitive effect that is being contributed to the overall capacitance of PSAC electrode. The authors presume that the non-linearity may be due to the resistance contributed by the inherent porous structure, shape and distribution of the PSAC in the electrode and uneven charge distribution of charges on the cations and the anions of the electrolyte species within the pores of the PSAC structure during charging or discharging processes. The cations and the anions have their own transport and polarizing behaviour which may also have a say in the charge-discharge features [54]. The non-linearity of the curves is also the result of redox reactions (reversible) of the functional groups at the voltage range of study giving rise to pseudocapacitance, as suggested by Convey and Hell [55,56] so the total capacitance is enhanced.

High electrochemical stability of the PSAC has been confirmed by repeated galvanostatic charge cycling and the cycle lives in excess of 500 cycles. It can be seen that the specific discharge capacitance at the end of the first cycle and at the 500th cycle is 463 F g^{-1} and 401 F g^{-1} reaching an efficiency of 87%. Thus only 13% of the initial capacitance has been lost after 500 cycles, indicating the capacitor has a good cycle life. These results prove that the pseudocapacitance behaviour offered by various oxygen containing functional groups incorporated in the carbon network of PSAC is quite stable with cycling and very high reversibility in the repetitive charge-discharge cycling.

In addition to the nature of the PSAC as described above a high value of capacitance of 463 F g^{-1} in 1M H_2SO_4 has also been attributed to the high surface area or to the larger volume of mesopores evolved in PSAC particles. Further the authors presume that the volume of the mesopores is higher and therefore a large amount of the electrolyte ions is able to diffuse into the pores and are absorbed. Additionally, the presence of carboxyl or carbonyl groups in the PSAC is expected to improve the wettablity of the electrode surface, which would appreciate the accessibility of the electrolyte species to the surface of the PSAC [57]. From Fig. 8 it is also seen that the time periods of charge and discharge are almost the same, which conveys that PSAC based electrodes may have high reversibility and high coulomb efficiency in the selected voltage range of operation.

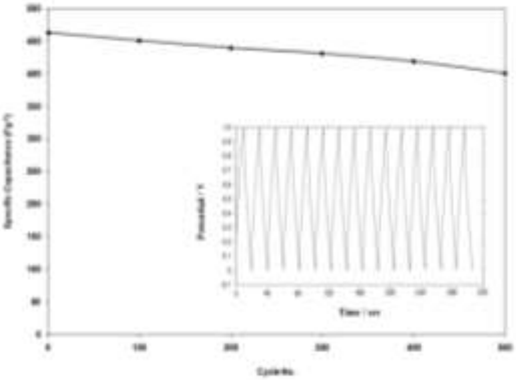
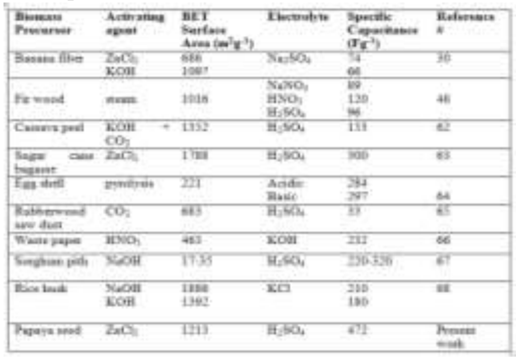


Fig. 8. Galvanostatic cycling profile of PSAC in 1M H_2SO_4 electrolyte for the first 15 cycles (current density=15mA g^{-1}).

Therefore, PSAC based electrodes could lead to improved capacitance because of hte synergetic effects attributed to the porous structures, enhanced specific surface areas, total pore volumes, and volume percentage of mesopores coupled with functional groups leading to the increased wettability of the electrode surface.

Finally, it is to be mentioned that biomass precursors for preparing carbon electrodes for electrochemical capacitors is aplenty and hence a comparison of the capacitance values reported for those samples with our PS derived carbon sample would weigh our sample for the intended application. A partial list of specific capacitance values (with their BET specific surface areas) reported for various biomass derived carbons including our samples has been provided in Table 1. Nevertheless, a complete review on the similar subject has been carried out by the present authors and has been published elsewhere [14]. A comparison would show that our results are within the typical range reported by other researchers, indicating that PSAC proposed in the present study is applicable for electrochemical capacitors. Thus PSAC appears to be an attractive cost-effective substitute for commercial activated carbon as a pseudocapacitor electrode in acid medium.



Biomass Precursor	Activating agent	BET Surface Area (m^2g^{-1})	Electrolyte	Specific Capacitance (Fg^{-1})	Reference #
Banana fiber	$ZnCl_2$ KOH	686 1097	Na_2SO_4	74 66	30
Fir wood	steam	1016	$NaNO_3$ HNO_3 H_2SO_4	89 120 96	46
Cassava peel	KOH + CO_2	1352	H_2SO_4	153	62
Sugar cane bagasse	$ZnCl_2$	1788	H_2SO_4	300	63
Egg shell	pyrolysis	221	Acidic Basic	284 297	64
Rubberwood saw dust	CO_2	683	H_2SO_4	33	65
Waste paper	HNO_3	463	KOH	232	66
Sorghum pith	NaOH	17.35	H_2SO_4	220-320	67
Rice husk	NaOH KOH	1886 1392	KCl	210 180	68
Papaya seed	$ZnCl_2$	1213	H_2SO_4	472	Present work

Table 1. Comparison of specific capacitance and surface area of various biomasses in different electrolytes.

Further it is interesting to note that UV-Visible spectroscopic analysis of certain varieties of carbon powders done by Satish Kumar et al. [58] revealed a fact that by increasing the surface area of the powder, a higher absorption in the UV-vis spectra was observed [59]. The UV absorption peak in carbon materials has been reported to be related to the electronic transitions between the bonding and antibonding π orbitals [60], i.e. π –π* transitions appearing in the range of 180–260 nm in the carbon samples [59]. Thus UV-Vis would be one of the techniques for characterizing carbon samples of biomass origin and has been reserved for future studies with PSAC.

CONCLUSION

The work presents a novel concept of utilizing a domestic or agro-industrial wastes namely papaya seeds for an application in the field of energy devices. To exemplify this, high performance carbonaceous material for Electrochemical Capacitors has been obtained by activation-pyrolysis of the papaya seeds. The presence of various functional like carbonyl groups on PSAC is advantageous for fast Faradic reactions to introduce pseudocapacitance, owing to their lower charge transfer resistance than that of the hydroxyl group. The properties of PSAC such as high surface area, mesopore structures and chemical functional groups reveals that it can offer improved pseudocapacitive behaviour and hence suggested as a candidate electrode for realizing advanced energy/power electrochemical electrical energy storage device namely pseudocapacitors. We can see that PSAC can be produced at a lower cost using more environment friendly conditions than required for the conventional activated carbons thus this process is easily scalable for the capacitor industries. Further, the excellent performance of PSAC open-up the possibility to engineer supercapacitor electrodes based on biomass derived carbon in order to target a wide range of other applications, such as electrodes, adsorbent, catalyst support etc.

While further detailed studies and optimization of activating agents and their ratio, porosity, surface treatments to promote wettability, and reduced inter-carbon particle resistance are needed, we strongly believe that papaya seed activated carbon based materials will lead to the development of high performance supercapacitors or pseudocapacitors.

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