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A quick report on property variations between raw and treated carbons derived from different variety peels of banana developing for Electric Double Layer Capacitance

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Abstract

Carbonaceous materials are significantly used to develop the supercapacitor, electrodes and other battery components. The non-renewable source derived carbonaceous materials are having hazardous and contaminative nature while developing battery components. Hence, it is advised from various researchers to use any renewable bio resources from nature to prevent hazardous. In this present study we made a quick communication in order to report that carbonaceous materials developed from banana peels are not exhibiting similar properties which would be affect the process and application by both the way quality and quantity manner. Zhang et al 2016 [6] reported the high porous carbons developed from mixed of banana peels which is developed for the super capacitance. However, as from the different variety of banana peels having different composition would not provide similar property made to check in separate peel vice. In this regard three different banana peels with different color [Yellow, Red and Green] were selected which is ubiquitous in nature and developed as carbonaceous material under high temperature around 850 °C followed by activation through chemical treatment. Both the before and after treatment the carbonaceous material properties derived from Yellow Banana Peel (YBP), Red Banana Peel (RBP) and Green Banana Peel (GBP) were provided different physical properties, different yield volume and different energy consumption.. In general Banana peels yield carbon materials at less energy, low density and high volume due to its pliable nature at the same time it differed among YBP, RBP and GBP. This quick report and continuation of further study will help to develop high surface area with higher order of internal porosity supercapacitor at low cost.

Key Words: Banana Peels, Biochar, Carbons, Double Layer Capacitance, Surface area, Porous Structure

1. Introduction

Today the people are highly seeking for the technology development to switchover on hybrid vehicles due to the fast drains of fossil fuels. In this regard researchers are highly interested to generate energy storage devices from the activated carbon which includes the extended applications in Electric Double Layer Capacitance [EDLC] [1,3,4]. Apparently, using the biochar as working materials for EDLC it has to be chemically treated for converting those carbons into activated carbons. Supercapacitor other hand EDLC is classified into- carbon-based supercapacitor, metal oxide-based Supercapacitor and polymer

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supercapacitors [5]. It has been studied that metal oxide and polymer based supercapacitors has good conductivity than carbon based but metal and polymer based have strong drawback of relatively expensive metal resource and low cyclic capabilities. Hence to overcome this overwhelming drawback carbon-based supercapacitor has a better advantage and application and potential than that of pseudocapacitors based on adequate electrochemical cycling and stability. Also the carbon-based supercapacitor has natural abundance and cost comfort [6].

As nanopore carbons is been a matter of research and is used in a working electrode in supercapacitor applications which is derived from various bio-resources from different precursors of carbon biomass converted at high temperatures which is a common materials used in electrodes for supercapacitors it is usually due to high conductivity, high surface area present with an adequate response in physio-chemical stability a lot of carbon based materials explored in past which includes carbon aerogels, microporous carbons, hierarchical porous carbons, ordered measoporous carbons but it was later found that either they are expensive or difficult to manufacture or the materials precursors which comes from non-renewable background which creates environmental threat which is not feasible. The feasible way for developing the carbon are from the biomass of different kinds which comes from different bio-resources such as fruit biomass, agro-industrial waste, agricultural wastes these biomass should be carbon converted at gasification temperatures the biomass remains know as biochar which is a carbon rich byproduct can be used as a modus operendi material in supercapacitors after further treatments, in recent study it was found that the use of coffee beans as a precursor material to converted carbons shown a specific capacitance result of 368 F g^{-1} which is a good specific capacitance [13,14]. From previous literature surveys we can conclude that each biomass shows different specific capacitance with regard to its nature of physical and chemical properties and the process involved in converting the carbons from different kinds of biomasses. This study was further extended in apprehending the concept of carbon theory of biomass to biochar conversion for different kinds of biomasses it is now concluded and suggested that pliable kind of precursor of carbon would be a good material as less amount of energy is required to convert into biochar as pliable nature also imposed high volume less weight characteristics which is suitable in applications of EDLC. The good electrochemical performance of carbon also depends on/also highly developed porosity and the existence of active electrochemical quinine nitrogen and oxygen functional groups, the specific capacitance developed in the carbon is not linearly proportional to that of surface area it totally depends on porous structures and also the functional groups of carbon, in a previous study the use of sugarcane bagasse (sugar cane is also pliable in nature compared to woody biomasses which takes less energy to be converted to biochar), converted carbon activated through $ZnCl_2$ as with capacitance as up as 300 F g^{-1} [13], so the nature of biomass and chemical activation selection determines the specific capacitance as it was studied above that the specific capacitance value is highly depends upon the porosity and surface functional groups.

Among most of Electrochemical Application which uses Carbon Based materialsas a working media individually the Electric Double Layer Capacitance theory along with Capacitive Deionization (CDI), Electro sorption and Energy storing capacity i.e. Electric Double Layer Capacitance (EDLC), in

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applications such as in capacitor with working material carbon based electrodes in numerous forms like graphene, single and multi-walled nano tubes, as well as aerogel were said to be promising and efficient energy storing device which had high capacitance (for to about 300 F g^{-1}) with long durability cycles of thousands charges and discharges but on the other finds to be either exorbitant or difficult to manufacture but when the use of activated carbons derived from biochars remains, the cost becomes more modest which is a great option for modus operandi as a working media in supercapacitors.

In order to use the biochar as a working material the biochar is required to be activated initially. Basically there are enormous chemical agents required to perform this activity, the chemical agent can be an acid or basses. Chemical activation is a process in which the biochar /char is mixed or doped with activating agents it is well used method to modify the surface functional groups. The chemical activation involves the soaking of biochar with the agent in the preferred ratio of 1:10 from room temperature up to 120 °C for a specific duration of time [7]. In this following work is presents the characterization difference between the thermally alone treated carbon and chemically treated activated carbon. Also discussed the results and reported on qualitative matter of carbons derived from three different banana peels of same species but different breeds (Red Decca, Musa Acuminata, and Yellow Mauritius).

The supercapacitors or EDLC has a wide range of new and existing applications in various industrial uphold, a-way lot of literature surveys have been carried out previously [11], in brief, the applications of EDLC some of which are Electric Vehicles, Power Quality, Battery Improvement, renewable energy applications etc. In electric vehicles the use of EDLC potentially would revolutionize the industry by the virtue of their technology since the EDLC doesn't resemble the conventional battery with low output, low power density, and the limited number of charge/discharge cycles with high-temperature dependence however, EDLC has another limitation such as low energy density and high costs, the high cost can be reduced by using biochars as an alternative but low energy density has to be worked out, however, the combination of storage devices could be a good alternative, to also add that the exertion of EDLC would make it possible the use of the regenerative braking system. The add-up application for EDLC [12], would be the next-gen. EDLC is the quick preheating of the exhaust gasses reducing the overall emissions in Internal combustion engines and which would enable the diesel-engine based automobiles to run on NO_x free emissions from the initial start of the engine; EDLC can be alternatively also used as a Kinetic energy recuperation system.

2. Materials and Methods

2.1. Meterials

The raw materials used are from different breed of peels from same species of banana purchased from the local market.

2.2. Development of Biochar

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From the three different raw peels three different biochar samples were prepared by high temperature (around 900°C) thermal treatment. The peels were loaded immediately once pealed out to avoid any of degradation of compounds where the change of property will reflect in the carbon quality. The three different peals hereby named as (1) GBP (Green Banana Peel) (2) RBP (Red Banana Peel) (3) YBP (Yellow Banana Peel) for referring the samples. The motivation of the work is to check the direct treatment carbon quality with the chemically treated carbon quality in the duty of capacitance. Because the nature of the peal is pliable nature hence it consumes low energy and low density at the same time producing high volume of carbonized materials. However among the three samples GBP only produced 5% of volume from initial loaded and also present with lot of rigid white content in macro size along with carbons can be seen from Fig1a. Hence, further studies revealed that the GBP will not be a good sample for building capacitance and if it's mixed with other peals might affect the other sample performance. In the continuation RBP produced more volume of carbonized materials (70% from loaded volume) from the thermal treatment where YBP is obtained slightly small (68% from loaded volume) compare to RBP showed in Fig – 1 a, b, RBP and YBP samples obtained as very micro and nano size powder form from thermal treatment itself.

2.3. Development of Activated carbon

In order to develop more surface area and the removal of other unwanted materials it was decided to employ chemical treatment over thermally developed biochars. H_3PO_4 is used for the chemical acid treatment, it was chosen based on the literature survey where it refers that at gasification temperature biomass directly converted with more carbonaceous materials with less unwanted impurities and can be treated with acid for most efficient recover and modification of surface functional groups and internal porosity leading to decrease in molecular weight eventually enrich the overall specific capacitance. Property of modified carbon based materials are ultimately less corosivity and also contains less harmful residues which would be environmental friendly causing less harm to the nature. After mixing the H_3PO_4 with the precursor i.e. biochar the reaction immediately begins by the acids starts reacting with the lignin and hemicelluloses. It happens due to easy accessible of amorphous biopolymers the most initial effects of acids incorporates the hydrolysis of glycosidic linkages in hemicelluloses and celluloses and cleavage of the aryl ether bonds in the lignin resulting in the CO_2, CH_4, and CO. Its eventually reduces the molecular weights of lignin further the dehydration reactions and H_3PO_4 executes the ether linkages in lignin and celluloses for appearances of carboxyl groups where all the comprehensive reactions leads to weight loss. It increases the electron donating capabilities (doping phosphorous) with intensifying the transport ability and charge storage of working media in the supercapacitance [7].

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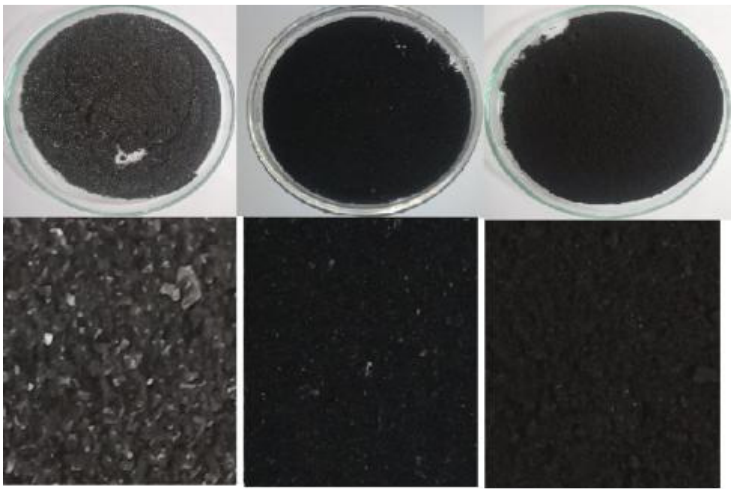

Fig.1a: GBP Fig.1b: RBP Fig 1c: YBP

Fig – 1 Shows image of Physical variants in each samples of biochar

The obtained results of activated carbons from the samples GBP, RBP, & YBP expected to provide different effect of electro conductivity properties according to the different physical properties shows between the samples. The sample image of activated carbon derived from the sample RBP is shown in Fig.2.

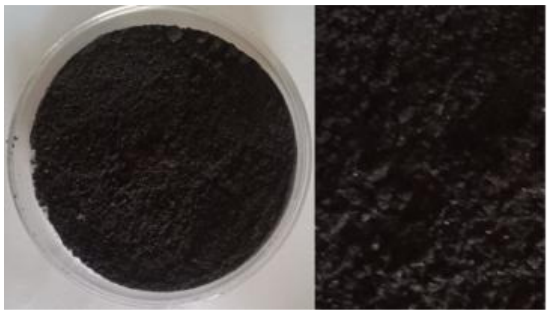

Fig – 2 Sample of chemically activated carbon from RBP biochar sample.

3. Result and Discussion

3.1 Surface Area & Porosity

The most important characteristics are surface area and porosity for the applications of EDLC, the high internal surface area, and porosity shows better and optimistic specific capacitance results. As it can be defined from the below figure 3 (a), (b), and (c) of GPB, RBP & YBP it is before activation it can be noticed that a lot of pores (empty volumes in between the scrunched and randomly cross-link carbon

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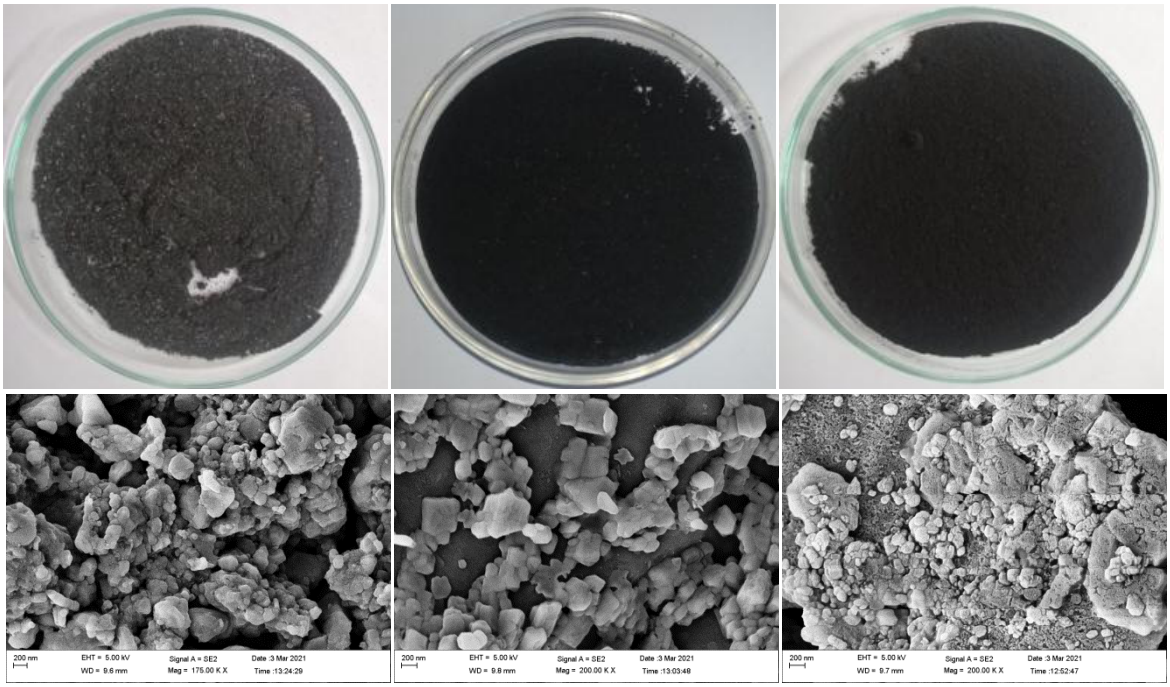
sheets), The sample (3c) i.e. YBP, and (3b) RBP comparatively shows more porous and internal surface area comparatively with (3a) GBP. The more nanopores were noticed in YBP (fig 3c), which would eventually proved to show some better specific capacitance results based on its porous characteristics.

It is worth noticing that when the biochars reach elevating temperatures, a more graphene-like structure can be achieved which is quite promising for applications related to energy storages [9, 10]. This is to be attributed that due to higher temperature dwelling of biochar consecutively two phenomenon are desirable i.e. burn-off of micropore during higher temperature and dwell time or/and the development and formation of the graphite-like structure in the matrix of biochar, in this case it was noticed that more graphite like structure was formed, further to the chemical activations more active elemental participation and more internal surface area with increased pores potential occurs. At the same focus all three samples are shows different features. Hence, its proved the outcome quantitative and qualitative results will be differed between three different samples GBP, RBP, and YBP.



(a) GBP (b) RBP (c) YBP

Fig – 3 Show the images of FESEM

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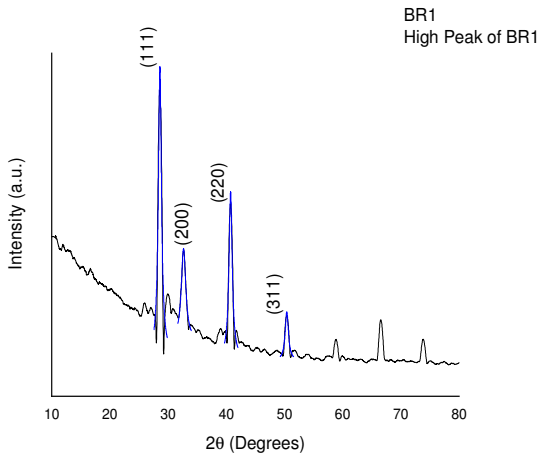
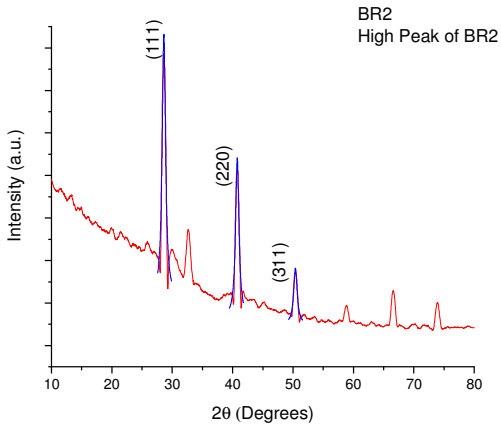
3.2 XRD Analysis

In Fig. 4 of XRD patterns of the three samples there are not many variations seen at the peaks it is quite identical (with resembling miller indices), further studies reveled the impurity was due to miscellaneous compounds present in the peels the resemblance which was due to the potassium and magnesium content present is common to all breeds of peels eventually, the variance has-been noticed in the XRD patterns at 2θ = 15-25 indicating the amorphous carbon structure in all three samples is to be noticed that the broad peak in the region of 2θ = 15-25 indicating the amorphous carbon structure while on the sect it is to be noticed in the region of 2θ = 29,42,50 of Fig.4 GBP,RBP & YBP are identical indicates miscellaneous inorganic compounds highly made of quartz structure within the biochars of peels of banana with same species of the different breed. Thus the other various peaks in the last sect harmonize the ash content trapped in the pores which is treated in chemical activation remaining with increased pores volume. It can be concluded by the indexed values of the patterns that even belonging from same species of the different breed of biochar the XRD pattern remains identical at peaks, many variations in the pattern of peaks is not seen it is to be noticed that significant fewer peaks can be found in figure 2 (b) & (c) of RBP & YBP than remaining others more amorphous carbon broad peak is being identified in YBP and RBP, which could show significantly increased capacitance post to activations. The size of the crystallite was found to be 11nm for GBP, 10nm for RBP, and 12nm for YBP the crystallite size was calculated by the Scherrer equation. Though peak resembles the ash contents might be same however its shows all the three samples are showing different results on carbon amorphous structure.



(a) GBP



(b) RBP

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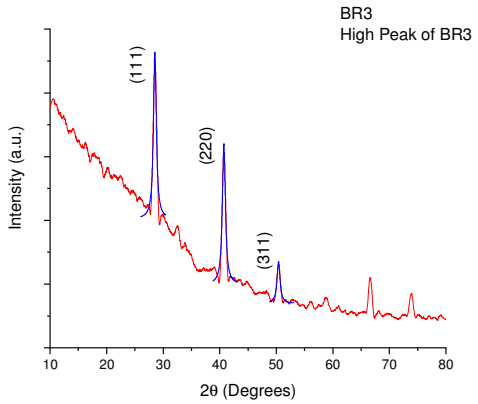

(c) YBP
Fig – 4 Shows XRD Patterns

3.3 FT-IR Spectroscopy

It can be identified from the above spectroscopy results that from fig. 5(a) (b) and (c) of GBP, RBP & YBP that the wavelength 3367 cm-^{1} indicates OH string which are common in all three samples and resembles the presence of cellulose, hemicelluloses, and lignin. In fig.5 (a) & (c) GBP & YBP it can be noticed carboxyl groups amides aromatic at wavelength 1600 cm^{-1} a very few amount of anhydrides at wavelength 1760 cm^{-1} can be identified in a very little proportion monosubstituted alkene with CH bend can be identified in the Fig. 5(b) i.e RBP sample with a very narrow peak at a wavelength of 1000 cm-1 bond to hydrogen can also be inferred at wavelength 3300 cm^{-1} in figure 5(a) and (c) GBP and YBP, from the above spectroscopy we can get to know that there are a lot of string of OH and carboxyl groups of amides, cellulose, hemicelluloses and lignin that potentially take part in the active phase of activation eventual leading to a better specific capacitance for YBP and RBP in EDLC applications.

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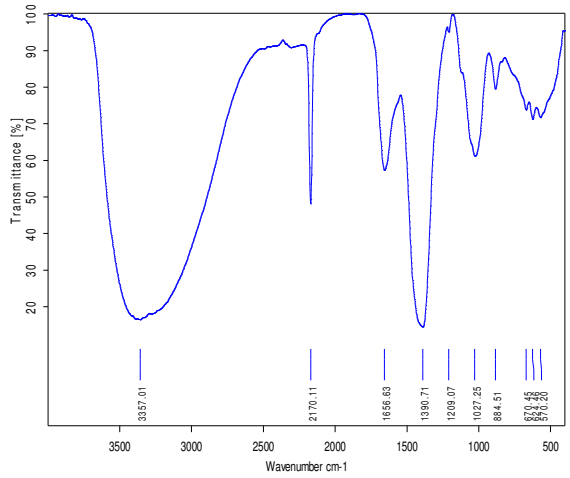
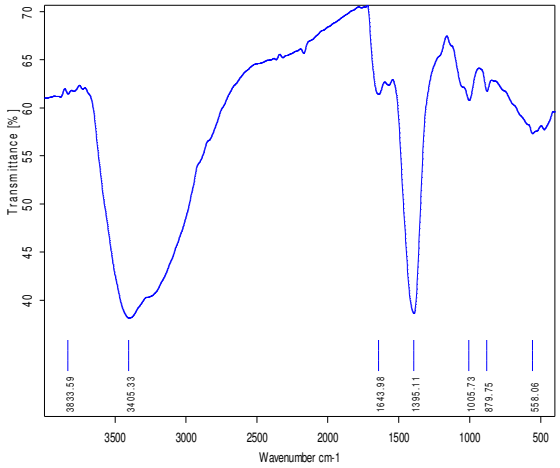
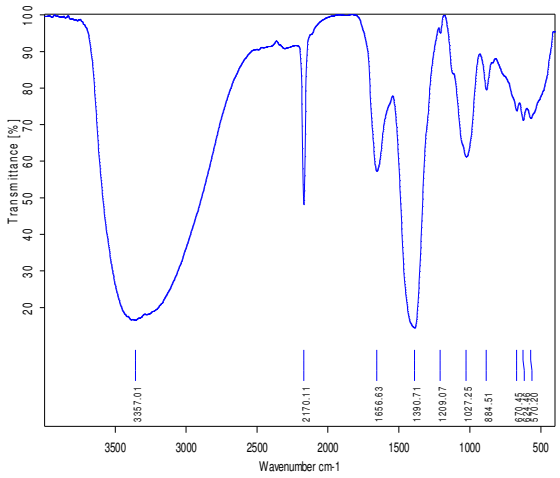


(a) GBP



(b) RBP



(c) YBP

Fig – 5 Shows the Results of FT-IR Spectroscopy

3.4 Low cost particle size estimations by micro-imaging using CMAS microscopic-camera

A simple technique using CMAS microscopic camera imaging made an attempt to determining the particle size distribution of the biochar samples of RBP, GBP, and YBP. Conversion of taken images in to gray scale provided black at range at 0 and white range close to 255 where black ranges were converted in micrometer from the pixels. The focused range was standardized using appropriate camera optical stands.

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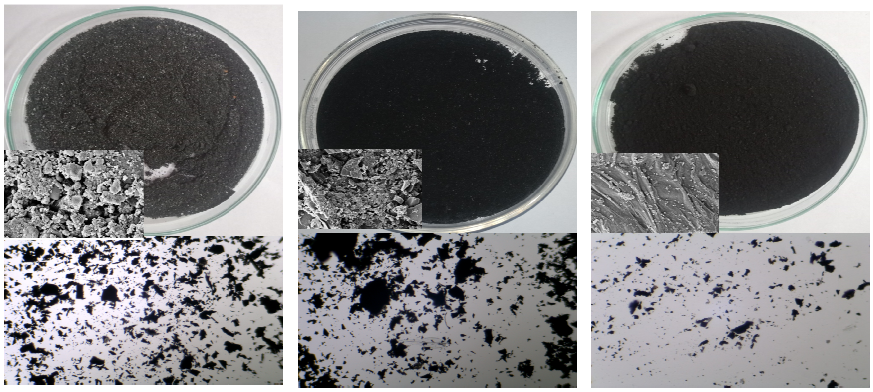

Fig – 6 Comparison of Micro-images by using CMAS microscopic-camera

The technique used for determining the size of particle by using micro-camera focused to 4000 times was and the particle size averages was found to be 50-70 micro meter for GBP and 40-60 micro meter for RBP and 30-45 micro meter for YBP by using 'ImageJ' software. This technique seems to be feasible enough for determining the size of particles for the range of micro meters only, nano particles cannot be determined and the structure below 2-5 micro meter is hard to quantify and analyze, the added advantage is cost competitiveness and rough analysis of particle size, it is very much useful to determine the particle sizes within the ranges of micrometers. However appropriate image processing code if developed for proper formed mathematical correlation could be possible to narrow down over nano size determination indirectly kept in reserve on future work continuation.

It also can be noticed from the above figure -6 that we can notice the agglomerations in RBP which was treated during chemical activation and we also can quantify from the above characterize image from figure-6 that we can find more nano-minute particles in the samples RBP and YBP eventually the resemblance in micro-structure is noticed in all above micro-images we can see the exact variation in structures from the above enclosed images of FESEM (small portion above the micro-images), clearcut variation can be seen in the structures of FESEM images at focus of 2 micrometers, this drawback/limitation can insincere in the findings, moreoverly, for rough estimation it's a good and cost effective approach, this technique is highly recommended in bio-imaging of microbes etc. In the field of bio-technology related application it can find good scope in those applications.

4. Conclusion

From the initial study over quick report it is incontrovertibly found that the samples belonging to same species but a different breed i.e. RBP, GBP, & YBP shows substantially different results and variations of their own as it was discussed. Eventually a slight resemblance in results were noticed in XRD patterns in peaks was noticed further studies reviled the peaks were due to impurities present in the samples i.e. due to potassium and magnesium content (High in GBP) in banana peels but the amorphous of carbons in each of the three samples differs which shows a face of change in specific capacitance, from FTIR

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analysis also it was clearly concluded that the active elements of activation varies which is higher in RBP & YBP further to activation our investigation concluded RBP & YBP has a great elemental participation in chemical activation which eventually leads to a better surface functional modification resulting further in internal surface area reducing the overall molecular weights in RBP and YBP which is appropriate for EDLC and related applications. In temperature treatment GBP consumed low energy by converting to biochar very fast but yield low volume of carbons along with other components and majority of components are volatile. RBP produce more volume than YBP but YBP seems good porous structure than RBP. In the continuation of study along with EDLC test will be reported the overall conclusion.

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