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SYNTHESIS AND CHARACTERISATION OF ACTIVATED CARBON FROM AGRICULTURAL WASTE

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ABSTRACT

Activated carbons are synthesized from agricultural waste (cassava peels, coconut shell and rice straw) through chemical activation. The optimum activation temperature is around 500 °C, and chemical activation is through 6M KOH. Activated carbons are characterized by fourier transformation infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM) and BET methods. The FTIR results showed that the agricultural waste is succeeding in becoming carbon. The XRD results confirm the existence of several phases of crystals like graphite around the peaks of 36^0 and 44°C. The SEM result showed that the carbonization and activation processes created porosity and BET reports confirmed a large surface area for absorption and hence can be applied in several fields.

KEY WORDS : Agricultural waste, Activated carbon, FTIR, SEM, XRD, BET

INTRODUCTION

Carbon materials have gained so much interest because of their morphology, adjustable porosity good electronic conductivity and excellent stability. However these are reliant on fossil fuel based precursors like CH_4, phenol and pitch. Some of the synthetic applications and classical methods are bringing up many of the environmental arguments De *et al*. (2015). In this context, carbon materials derived from renewable bio mass (agricultural waste) have drawn great attention, because of their tunable pore size, easy processibility, surface properties and less cost etc. Chan *et al*. (2008). Recently the synthesis of carbon from various organic wastes, agricultural wastes, bio mass and derived carbon materials are under investigation for energy storage applications Fine *et al*. (2012) because of their eco friendly nature and abundance Ioannidou and Zabahiotai (2007).

The term biomass refers to plants or plant based materials derived from nature and are synthesised through biological photosynthesis. The materials or by-products derived from animals and plants can act as potential source of energy (Adinaveen *et al.*, (2013). Biomass consists of lignin carbohydrates, protein, starch and lipid and their components vary depending on sources of geographical conditions. Biomass production worldwide is 104.9 pentagrams of carbon per year (Hayashi *et al.,* 2000). Proximate and ultimate analysis reports proved that bio mass/ agricultural waste is rich in hydrogen, carbon, nitrogen and oxygen along with traces of chlorine and sulphur (Dipa and Keikap, 2015). As carbon rich precursors, biomass is served as raw materials for a long time. The classical methods are based on direct pyrolysis, hence named as activated carbons (ACs) (Biswal *et al.*, 2013).

In addition biomass derived carbon consists of several advantages like (a) eco friendly (b) cheap and abundant (c) versatile in preparation and hence making an ideal candidates for the storage applications (Shen *et al.*, 2012). The primary sources of precursors are from crop cultivation, agro residues, municipal solid waste and other agro based industries. These bio mass is categorised into *(a)* plant based *(b)* micro organism based *(c)* food based and finally *(d)* animal based (Dehkhoda *et al.,* 2010) .

MATERIALS AND METHODS

The apparatus, chemicals and instruments used in this agro waste activated carbon material synthesis are cauldron for burning, mortar, sieve zoo mesh, furnace ball milling, hydraulic press. Cassava peels, coconut shells, rice straw are agricultural waste, KOH, HCl, 96% alcohol, are obtained from Merck India.

Preparation of activated carbon (ACs)

The conversion of agricultural waste mass into porous carbon includes carbonisation methods like pyrolysis and hydro thermal conversion. Time, temperature, reagent, surface properties, different porosities, morphology and cost are various factors which control the activation. Figure 1 represents scheme for converting agro waste into activated carbon.

Activation is a process of converting carbonaceous materials into activated carbon in which both physical and chemical or either of them are used. Compared to chemical activation, physical activation is simple and more eco friendly, but usually conducted at high temperature. Physical activation requires certain gases like air, steam or CO_2 and generally conducted at low temperature less than 500 °C. However chemical activation is more commonly used because of less activation time, low activation temperature, high surface area, and high yield and well developed pores Bouchelta *et al.* (2008).

Chemical activation

KOH activation

KOH is commonly used chemical for activating derived carbons. KOH is induced on rough carbon surface to get it activated. Thus charge storage is possible because of high specific surface area and porous structure. In general potassium interaction and carbon lattice expansion leads to development of high specific surface area and porosity.

$ZnCl_2$ activation

$ZnCl_2$ acts as a dehydrating agent during the activation and has a deoxygenation effect at high temperature though oxygen removal in the form of water as well as by carbothermal reduction. In addition H_3PO_4, $KHCO_3$, etc. are the other reagents used for bio mass chemical activation.
Biomass/agricultural waste

Carbonisation

Pyrolysis is the procedure to obtain porous carbon material from biomass. This enhances pore volume and specific surface area. Hydro thermal carbonisation process yields hydrochar, which has high purity of oxygen containing surface functional

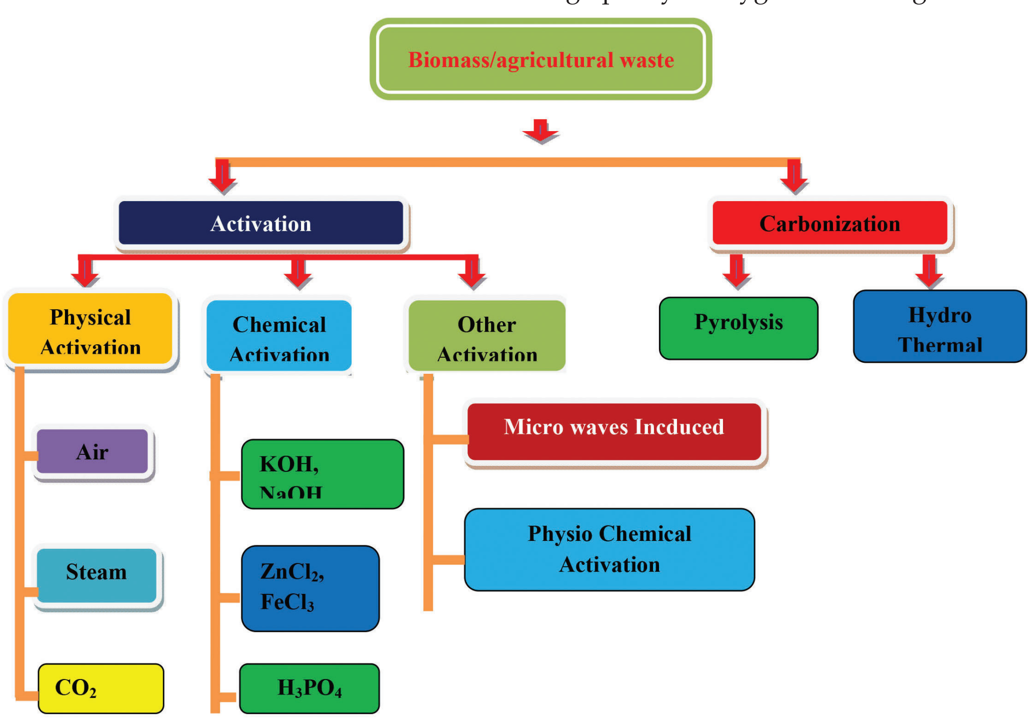

Fig. 1. Scheme of conversion of agricultural waste to activated carbon materials

group at a low degree of condensation. These are directly used in many applications such as electrodes for electro chemical cells. However low porosity and less specific area are the challenge of carbonisation. Hence research is inclined towards physical/ chemical activation Kim *et al.* (2006).

Sample synthesis

Activated carbons can be made out of agro waste raw materials namely 1. Cassava peels, 2. Coconut shells and 3. Rice straw

Activated carbon preparation

Cassava peels

One of the most important agricultural commodities is cassava. It is used as raw materials in the production of foods and cakes, cassava starches, etc. cassava leaves have high amount of protein which are used as fire wood for cooking cassava starch granules are 80% of amylopectin and 20% amylose. A study on cassava peels explained that 5.35% of protein, 5.40% of cellulose and 21.65% hemi cellulose respectively Sudaryanto *et al.* (2006).

Cassava peels are collected from nearby cassava starch industry. These peels are washed several times to remove dust and other impurities. To reduce the moisture content dried for 24 hours at 100^{o} C. Then peels are made into powder with particle size of 80/100 mesh. This powder is further mixed with KOH solution at an impregnation ratio of 3:1 (mass of KOH: mass of cassava peels) and stirred for 3 hrs at 330 K. The slurry was dried at 383 K in an oven for 24 hours. Thus sample is placed in a pyrolysis reactor and heated at carbonisation temperature of 1100 K, for 3 hours. This product is placed in tubular furnace for 1 hr. Further washed with 0.5 HCl to neutralise excess alkaline compound. The sample is washed repeatedly and dried at 380 K for 24 hours and stored in a desicator and named as CPC.

Coconut shell

Southeast Asia was the region with 78% world's coconut production. With this considerable amount of coconut production, it is further applied in many fields. Coconut is a common form of agricultural bio mass which contains many minerals. The coconut shell is used as activated carbon for the storage of energy. Coconut is an inexpensive resource, as it is found over 90 nations around the world (Rao *et al.,* 2015). Coconut shell is produced from oil manufacturing, several agro industrial activities etc. as it is a significant source of energy, it should be properly utilised.

In the typical synthesis of activated carbon the coconut shells are collected and washed with distilled water and dried over night at 80 ^{o}C. Then the sieving is conducted to get the size of less than 2 nm. These are added with KOH in (1:1) ratio for better impregnation. Further heated in the presence of nitrogen gas up to 600 ^{o}C in a furnace. The samples are washed thoroughly with 0.5 N KOH and dried in an oven at 100 ^{o}C for 4 hours. It is named as CS-1.

Rice straw

Rice straw is the largest agricultural waste. Till recently the rice straw waste is not used optimally though it is abundant. Rice straw has the composition of 40% cellulose, 30 % hemi- cellulose, 15% lignin and 15% silica. Rice straw is used as animal feed and the rest is burned or decomposed. This leads to environmental pollution. Hence to avoid pollution the rice straw can be used as potential sources of super capacitor electrode.

For the activated carbon preparation the freshly harvested and washed rice straw is impregnated with KOH solution using a weight ratio of ¼ and dried for 24 hours in an oven at 120 ^{o}C. This mass is kept in stainless steel tubular reactor with nitrogen flow in a nickel crucible. The heating rate was 10 ^{o}C/ min, and the final temperature is 600 ^{o}C for 2 hours. It is washed thoroughly with 0.1 N HCl and followed by distilled water. It is dried in oven for 12 hours at 110 ^{o}C. The proximate analysis of rice straw released that α-cellulose is of 51.3%, pentosans of 12.7%, lignin of 17.8% and ash of 18.3% Al-QodahI and Shawabkah (2009).

RESULTS AND DISCUSSION

Characterisation of activated carbon- cassava peels

FTIR analysis: FTIR is performed to determine the functional groups, especially the oxygen containing groups. The structure at 1000 – 1300, 1550 – 800, 2300 – 2450 and 3100- 3700 cm^{-1} refers to carboxyl, carbonyl and hydroxyl groups respectively (Fig. 2). This clearly indicates the surface oxygen containing groups on the activated carbon.

SEM analysis

The morphology of activated carbon is described in Figure 3. Some fragments with small pores indicate the tarry substance residues formation and also

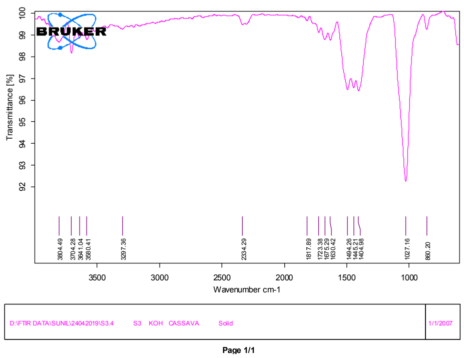

Fig. 2. FTIR of activated cassava peels

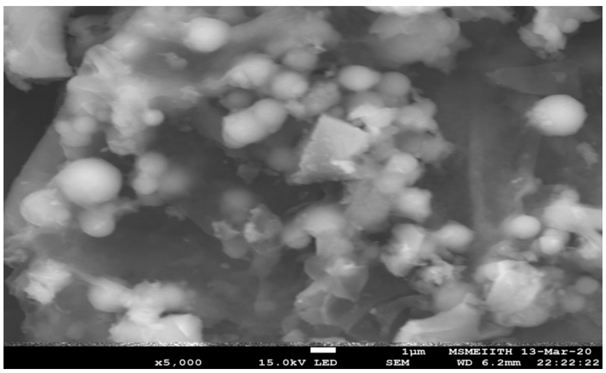

Fig. 3. SEM of activated cassava peel

pores are due to the removal of volatile matter. This indicates the hydrolysis of glycolic linkage in cellulose and hemi-cellulose along with aryl bond cleavage in lignin.

XRD Analysis

The crystallographic structure of activated cassava peels is measured through XRD. The presence of sharp diffraction peaks at 2° = 26 corresponds to (002) plane which indicates the formation of partial nanocrystalline structures of the compound Zahir *et al.* (2008). This peak corresponds to characteristic peak of graphite and hence the morphology of activated cassava peels is analysed.

BET analysis

The BET surface area, pore volume and pore size

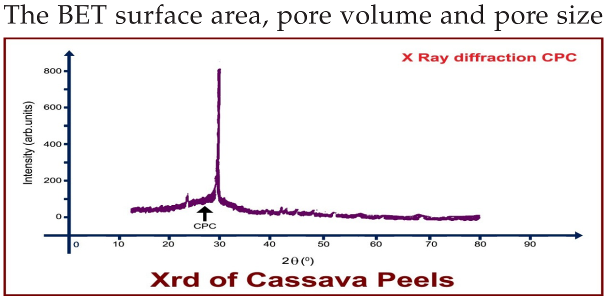

Fig. 4. XRD of activated cassava peels

distribution are determined by using BET equation. The surface area of 349 m^2/g is obtained. Pore volume is observed to be 0.212 Cm^2/g.

Characterisation of activated carbon-coconut shell

FTIR analysis

The major wave number is regard to chemical bounding compound value of FTIR spectra. These are 3300 – 3500 cm^{-1} -OH stretchings, 2700 – 2900 , -CH stretchings 1740 C=O stretching 1580 – 1570. C=C stretching, 1000 -1260 C=O carboxylic acid stretching and 700 – 400 C-C stretching are observed (Figure 5). These stretchings indicate the dehydration of cellulose and lignin components. FTIR confirms that the formation of activated carbon Kumar *et al.* (2015).

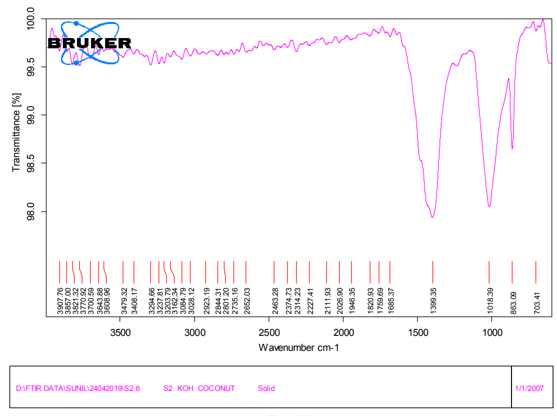

Fig. 5. FTIR of activated coconut shell

SEM analysis

The SEM micrographs of coconut shell are presented in the figure. The surface morphology is observed to have hallow pits, due to the loss of volatile matter and the effect of KOH activating agent on the carbon materials Wang *et al.* (2016).

XRD analysis

The XRD of activated carbon coconut shell is

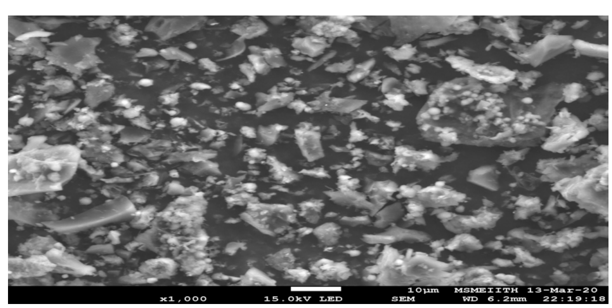

Fig. 6. SEM of activated coconut shell

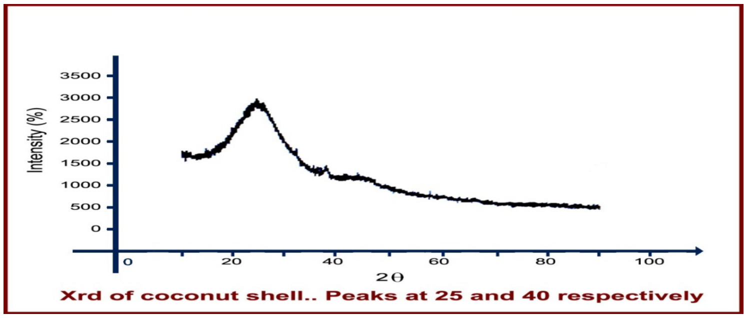

Fig. 7. XRD of activated coconut shell

examined and existence of several phases of crystals like graphite at peaks of 36° and 44° is observed. These two diffraction peaks revealed an amorphous structure. These are irregularly stacked by carbon rings and useful for generating an adsorption gap.

BET analysis

The BET analysis resulted with 1728 m^2/g of surface area and porosity of 2.6 nm.

Characterisation of activated carbon- rice straw

FTIR analysis

The FTIR analysis revealed that OH stretching is observed at 3448 cm^{-1} and is due to chemisorbed water molecules. Other peaks at 1733, 1369, and 1218 cm^{-1} respectively indicate C=O, C-H, and C=O stretching on the carbon surface.

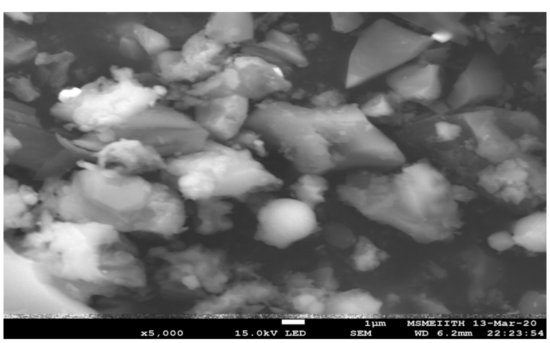

Fig. 8. FTIR of activated rice straw

SEM analysis

SEM analyses the morphology of activated rice straw figure respectively. The morphology of the particle surface explains that surface is dense. It is noted that slack and thin layered structure with a rough and wrinkled surface is formed.

XRD analysis

The rice straw powder is characterised using X- ray

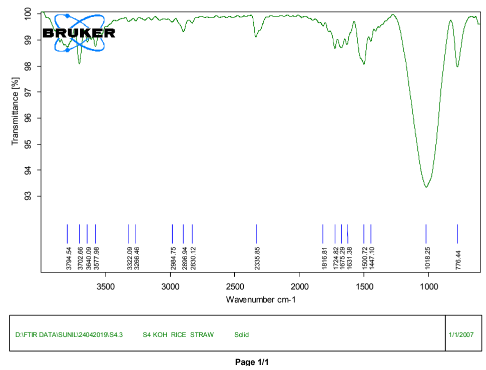

Fig. 9. SEM of activated rice straw

diffractometer using the wave length of 1.54060 A° and 5° – 90° angle range. A peak is happened at 26^0 of 2 θ. A broad graphite carbon peak is observed at 44°. These peaks indicate amorphous nature of the activated carbon derived from rice straw.

BET analysis

The porosity of the activated carbon is also influenced by type of activation. Here on the KOH activation the rice straw carbon showed the BET surface area of 779m^2/g and pore volume is close to 1.1 cm^3g^{-1}.

CONCLUSION

Activated carbon is synthesized from agricultural waste through chemical activation by impregnating with KOH. Activated carbon was analyzed by fourier transformation infrared spectroscopy, (FTIR) and X ray diffraction (XRD) methods. SEM and BET are also analyzed. In conclusion, activated carbon derived from agro waste can be utilized as cheap and efficient raw material for the production of activated carbon with very promising commercial value. The SEM, BET results showed that the activation processes creates porosity and large

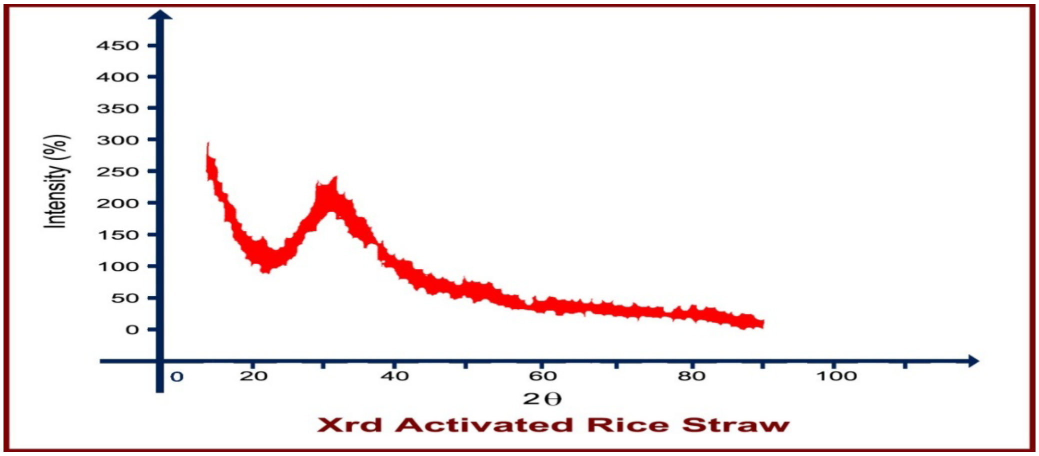

Fig. 10. XRD of activated rice straw

surface area for absorption, and can also be applied in many applications.

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Conflect of Interest

The authors have no conflicts of interest in publishing this manuscript.

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