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Synthesis and characterization of cotton stalk activated carbon by chemical activation using H_3PO_4

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Abstract
In this study, low cost activated carbons prepared from cotton stalk by chemical activation with phosphoric acid as activating agent and its characteristics were determined. Experiments were carried out at different impregnation ratio and carbonization temperature. The prepared activated carbons were characterized by iodine number, X-Ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and SEM with EDX analysis.

Keywords: activated carbon, cotton stalk, phosphoric acid

1. Introduction
Activated carbon is a material well-known for its complex pore structure, high specific surface area, and good chemical stability and for presenting various oxygen-containing functional groups on its surface [1]. The preparation of activated carbon is carried out according to two different methods of physical activation and chemical activation.
There are a number of biomass sources, such as forest residues, agricultural residues and municipal solid wastes, which can be utilized for activated carbon precursor. The choice of precursor largely depends on its availability, cost and purity. Manufacturing process and intended application of the product are also important considerations [2]. Evaluation of biomass is getting increased attention all over the world as it is renewable, widely available, cheap, and environmental friendly [3].
The aim of this work was to production of activated carbon from cotton stalk used as precursor material by chemical activation method using H_3PO_4 as activating agent at different temperatures of 400,500 and 600°C. Cotton stalk precursors were initially subjected to thermal analysis and activation temperature was fixed. The effects of the preparation variables such as impregnation ratio, activation temperature, yield and iodine number of the activated carbon were investigated. In addition the prepared cotton stalk activated carbon (CSAC) was characterized using FT-IR, XRD and SEM−EDX. The characteristics of the prepared activated carbons under optimized conditions were investigated as well.

2. Materials and methods
Cotton Stalk (CS), used as precursor material for the preparation of activated carbon, was collected from local agriculture area in Tranquebartaluk in Nagapattinam district, Tamilnadu, India. The CS was thoroughly washed several times with distilled water to remove the impurities and was dried in oven at 110°C for 24 h. The dried material was then ground and sieved to obtain precursors of particle sizes less than 2 mm.

2.1 Preparation of cotton stalk activated carbon (CSAC)
The powdered cotton stalk was impregnated in phosphoric acid solution at three different impregnation ratios of 1:1,1:2 and 1:3 (weight of precursor: volume of H_3PO_4) and the mixture was stirred continuously using a magnetic stirrer at ambient temperature for 5 h. The precursors were then kept soaked in for 24 h prior to being filtered and dried in hot air oven at 110°C for 24 h. Three samples of the dried mix were heated, all at a heating rate of 20° C min^{-1} in a muffle furnace, to different temperatures (400°C, 500°C and 600°C respectively) and maintained at respective temperatures for 2 h. The mixes were then cooled to room temperature and were washed sequentially with 0.1M NaOH solution, hot distilled water and finally with cold distilled water to remove residual acids until washing solution becomes neutral. The washed samples were then dried in hot air oven at 110°C for 6h and cooled to room temperature to obtain the H_3PO_4 treated cotton stalk activated carbons.

2.2 Product yield
The activated carbon yield is defined as the ratio of final weight of the activated carbon (W_f) to the weight of dry precursor (W_o) and is calculated by the following equation [4]:

$$\text{Yield}\,(\%) = \frac{W_f}{W_o} \times 100$$

2.3 Iodine number
The iodine number is an important parameter to characterize porous materials. It is determined using the sodium thiosulphate volumetric method and is defined as amount of iodine adsorbed by 1 g of activated carbon at the mg level [5].

$$\text{Iodine number} = \frac{X}{m} D$$

Where, m = mass of CS activated carbon in grams, X = A –

(2.2B × ml of thiosulfate solution used), A = N_1 × 12693, B = N_2 × 126.93, N_1 = normality of iodine solution, N_2 = normality of sodium thiosulfate solution, D = correction factor.

2.4 Characterization of the precursor and prepared samples

The raw Cotton stalk, activation temperature was fixed using thermogravimetry and differential thermal analysis (TG-DTA). The prepared activated carbon, surface functional groups were analysed from FT-IR spectra obtained by the KBr pellet method using Perkin Elmer Spectrum RXI FTIR spectrometer in the range 4000–400 cm^{-1}. XRD patterns were obtained using an XPERT-PRO Gonio scan-2 with a graphite monochromator equipped with Cu Kα as radiation source (λ= 1.5406 Å) at 40 kV/30 mA. The morphology and chemical composition of the samples were investigated by using SEM (VEGA3 TESCAN) equipped with energy dispersive X-ray spectrometer (Bruker).

3. Results and discussion

3.1 Thermal analysis

Thermal behaviour of raw cotton stalk obtained from the thermogravimetric (TG) and differential thermal analysis (DTA) is depicted in Fig.1. The decomposition of raw CS is found to occur in three stages. The first stage corresponds to an approximate weight loss of 10.79% at 30°C -200 °C. It is mainly attributed to release of H_2O by evaporation and dehydration reactions [6] as well as decomposition of hemicellulose. The low moisture content of the dried stalk resulted in low weight loss. The second stage has a greater weight loss of about 53.85% at 200°C–365°C. This corresponds to the primary carbonization and involves degradation of cellulose and lignin [7]. Third stage weight loss is approximately 14.93% at 365°C–1000°C. In this stage, weight loss is exponential. As most of the volatile constituents have already been removed, this stage corresponds to the formation of activated carbon. Thus from TG and DTA analyses, it is observed that a temperature above 365°C can be chosen for preparation of the activated carbon from CS.

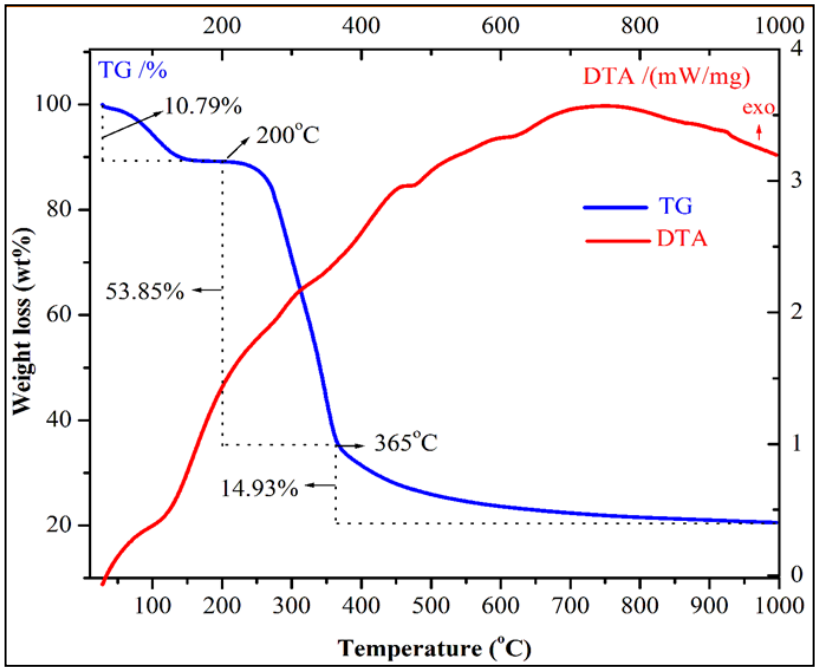

Fig 1: Thermal behavior (TG and DTA curves) of raw cotton stalk precursor

3.2 Yield

In the preparation of activated carbon, the yield of activated carbon is an important factor to be considered. The product yields of activated carbons prepared at different temperatures and impregnation ratios are tabulated in Table 1. The yields of prepared activated carbons were in the range of 14.08–39.74% for H_3PO_4 impregnated samples. Increasing activation temperature progressively reduced the yield of the activated carbon. This is expected, as increase in temperature will release more volatile constituents, thereby resulting in low yield.

Table 1: Product yield and iodine number of activated carbons produced from H_3PO_4

Impregnatin ratio	Activation temperature (°C)	Yiel %	Iodine numbr mg/g
1:1	400	39.74	822.81
	500	31.78	851.29
	600	21.40	872.65
1:2	400	27.83	827.56
	500	22.03	858.41

	600	20.02	894.02
1:3	400	17.24	820.44
	500	16.62	839.42
	600	14.08	859.29

3.3 Iodine number

The iodine number is an important parameter that decides the activated carbon performance. A higher iodine number indicates a greater porosity and a higher specific surface area. The iodine numbers of CSACs prepared at different impregnation ratios and at different temperatures using H_3PO_4 are presented in Table 1.

At a given impregnation ratio, increase in temperature increases iodine number but decreases the yield. Decrease in yield with corresponding increase in iodine number indicates increase in adsorption capacity of the material.

At a given temperature, as impregnation ratio increases from 1:1 to 1:2, iodine number increases, but further increase of impregnation ratio to 1:3 has decreased iodine number. This can be attributed to excessive dehydration and destruction of micropores at higher impregnation ratio. If micropores are destroyed to form larger pores, iodine number as well as adsorption efficiency will eventually decrease.

If both yield as well as iodine number are of preference, among all the activated carbons, one that exhibited iodine number of 894.02 mg/g, obtained with H_3PO_4 at impregnation ratio of 1:2 at 600°C can be chosen.

3.4 Fourier transform infrared spectroscopy (FT-IR) analysis

Fig.2 for the FTIR spectra of activated carbons using H_3PO_4, assignments are made as follows. The wide band in the region starting from about 3300 cm^{-1} is due to the presence of –OH (hydroxyl) functional groups. The intensity of band at around 1700 cm^{-1} due to stretching vibration of C=O in ketones, aldehydes, lactones, and carboxyl groups [8] appears to be increased upon increasing temperature at a given impregnation ratio, owing to decrease in intensity of other bands. The band at 1582−1570 cm^{-1} corresponds to aromatic C=C vibrations. These observations reveal the effect of carbonization and activation on the chemical composition of the activated carbons [9]. The band at 1356−1339 cm^{-1} is attributed to the C−O vibrations [10]. The peak at around 1233−1210 cm^{-1} originate from the contribution of phosphorus P- containing carbon compounds [11].The band at 1080 cm^{-1} represents the P-O-P stretching vibrations in polyphosphate or the ionized linkage P^+-O^- in acid phosphate esters [12].

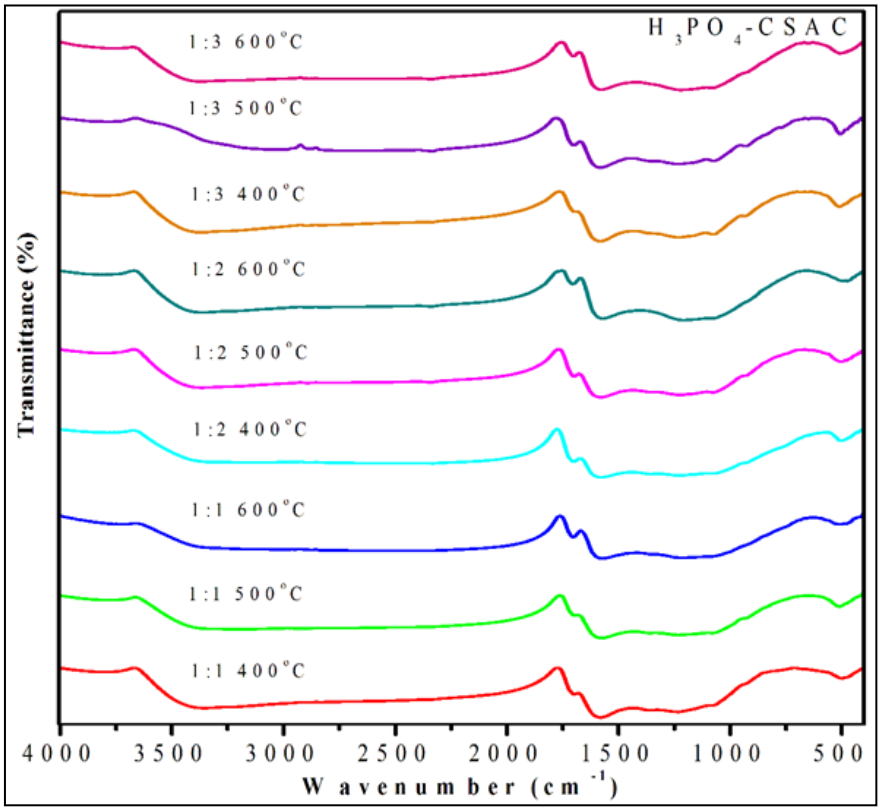

Fig 2: FT-IR spectra of H_3PO_4 cotton stalk activated carbons at different impregnation ratios and temperatures

3.5 XRD analysis

Patterns for activated carbons prepared with H_3PO_4 are shown in Fig.3. All of these patterns are characterized by a broad noisy hump with no sharp peaks implying that all activated carbons are predominantly amorphous.

Most of the activated carbons however exhibited two broad and weak humps at around 2θ values of 25° and 42° corresponding to (002) and (100) planes of graphite structure.

With reference to [13], it is assumed that activated carbons may have the so called turbostratic structures made of graphite-like microcrystallites bound by cross-linking network of randomly oriented graphite like layers.

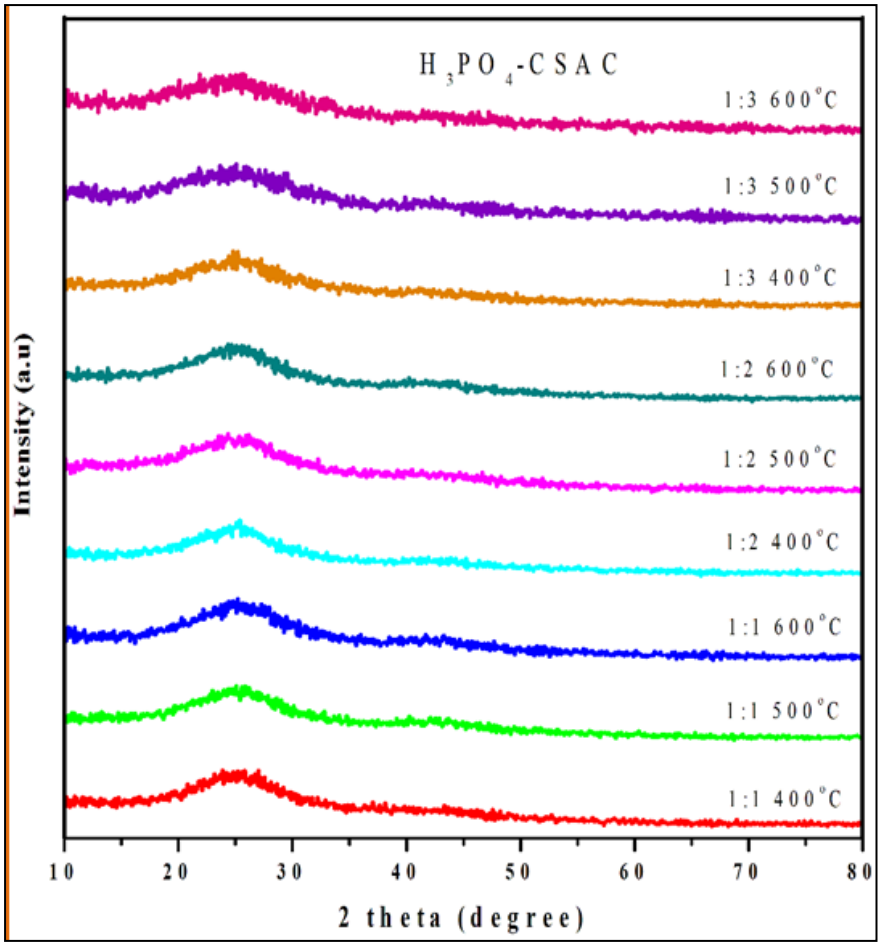

Fig 3: XRD pattern of H_3PO_4 cotton stalk activated carbons at different impregnation ratios and temperatures

3.6 SEM with EDX analysis

SEM micrographs of activated carbons prepared with H_3PO_4 at optimum impregnation ratio of 1:2 at 600°C are shown in Fig. 4, along with respective EDX analysis. H_3PO_4 cotton stalk activated carbon shows honeycomb like porous structure with a narrow pore size distribution. Many large pores in the honeycomb are clearly seen on the surface of the activated carbons. From the elemental analysis reported alongside the micrographs, it is observed that the major elements present in Carbon and Oxygen.

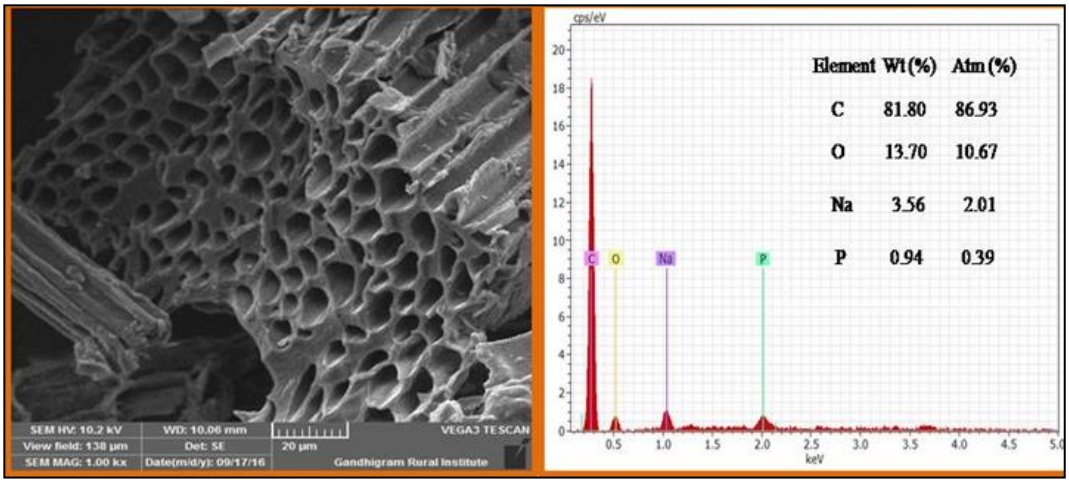

Fig 4: SEM images of H_3PO_4–CSAC and their corresponding EDX analysis

4. Conclusion

As thermal decomposition of raw cotton stalk is exponential above 365°C, activation temperature can be fixed above 365°C. Yield of activated carbon decreases with increasing temperature and impregnation ratio. H_3PO_4 activation has given higher yield, at a given temperature and impregnation ratio. Highest iodine number (894.02 mg/g) is obtained at 1:2 ratio of H_3PO_4 at 600°C. FTIR confirms the presence of mostly oxygen containing functional groups in raw cotton stalk and decrease in their intensity upon activation. XRD patterns reveal amorphous nature of activated carbons. SEM with EDX reveals that H_3PO_4 activation yields better surface morphology opted for an ideal adsorbent.

5. References

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