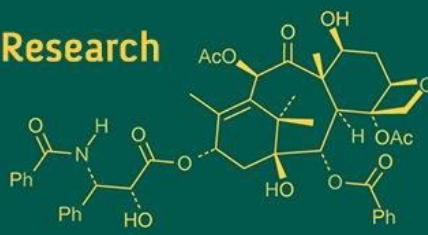


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Ravi Kumar Sahu
 1. ICAR-Central Institute of
 Agricultural Engineering,
 Bhopal, Madhya Pradesh,
 India
 2. The Graduate School IARI,
 New Delhi, India

Sandip Gangil
 ICAR-Central Institute of
 Agricultural Engineering,
 Bhopal, Madhya Pradesh,
 India

Thermochemical activation of raw chickpea (*Cicer arietinum*) stalk biomass for enhanced valorization

Ravi Kumar Sahu and Sandip Gangil

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Abstract

A study was undertaken to enhance the value of raw chickpea stalks by converting them into activated carbon. The production process involved chemical activation using potassium hydroxide (KOH) at 800 °C in a nitrogen (N₂) gas atmosphere. Various properties of both the raw chickpea stalk and the resulting activated carbon were examined and compared, including BET surface area, scanning electron microscopy (SEM) images, proximate and elemental analyses, absorption characteristics, and calorific value. Results indicated that the activated carbon had a specific surface area of 1239 m²/g, a total pore volume of 0.6 cm³/g, a methylene blue value of 320 mg/g, and an iodine value of 122 mg/g. SEM analysis revealed that the synthesized activated carbon exhibited high porosity with interconnected pores resembling a honeycomb structure. The study concluded that thermochemical activation successfully valorized the raw chickpea stalk, leading to improved properties of the activated carbon. Potential applications for this activated carbon include dye removal, water purification, and gas storage.

Keywords: Chickpea stalk, activated carbon, activation method, specific surface area

1. Introduction

Presently, fossil fuels account for a substantial portion (84.3%) of global energy production [1]. This situation is concerning due to the detrimental effects of burning petroleum and coal, which release greenhouse gases contributing to climate change and global warming [2]. In response to these issues, various initiatives have been launched to develop sustainable energy systems. Among these, biomass energy has shown considerable promise as an eco-friendly alternative. Non-woody biomass is abundant worldwide, offering advantages such as cost-effectiveness, easy accessibility, carbon neutrality, and a short life cycle. However, limited research has been conducted on lignocellulosic biomass from an energy perspective, primarily due to its hydrophilic nature, high moisture content, low bulk density, reduced calorific value, and low energy output [3]. To enhance these properties, various techniques including drying, torrefaction, combustion, pyrolysis, activation, and densification have been applied to biomass [4].

In this regard, activated carbon materials produced through thermochemical activation methods from affordable and readily available precursors are gaining attention as crucial components for environmental remediation and sustainable energy production and storage [5]. This includes the broad category of carbon materials currently under extensive research for use as electrode materials in supercapacitors or for gas storage (hydrogen, CO₂, methane, etc.) [5, 6]. The focus for future carbon materials is on developing products that are simpler to manufacture using cost-effective methods and potentially utilizing renewable resources to valorize raw biomass. Activated carbon has garnered significant interest among carbon materials due to its exceptional chemical resistance, porosity, and adjustable pore size [5-7]. Activated carbons are particularly appealing as they can be derived from renewable biomass sources often considered waste materials [7].

The production of activated carbon can occur through direct activation of raw biomass or via a two-step process involving carbonization followed by activation [8]. Carbonization, also known as pyrolysis, involves heating raw biomass (crop residue) to high temperatures (600-1000 °C) in an oxygen-free, inert environment [9]. The subsequent activation stage aims to enhance the structural properties of the activated carbon. This process seeks to increase pore size, volume, and diameter, as well as surface area, resulting in well-distributed microscopic

Corresponding Author:
Ravi Kumar Sahu
 1. ICAR-Central Institute of
 Agricultural Engineering,
 Bhopal, Madhya Pradesh,
 India
 2. The Graduate School IARI,
 New Delhi, India

cavities throughout the material. Three methods are employed for this process: hydrothermal, chemical, and physical^[10].

Genli *et. al.*, (2021) obtained activated carbon from chickpea stalks by hydrothermal method followed by chemical activation method using ZnCl_2 . They recorded iodine number, methylene blue number, and BET surface area as 734 mg/g, 105 mg/g, and 572 m²/g, respectively^[11]. Ozsin *et. al.*, (2019) derived activated carbon from chickpea husks by chemical activation method using (KOH and K_2CO_3). They noted a high BET surface area (2082 m²/g) and a total pore volume (1.07 cm³/g)^[12]. Genli *et. al.*, (2022) synthesized mesoporous activated carbon from chickpea stem by hydrothermal carbonization followed by the chemical activation method (KOH). They noted a high BET surface area (455 m²/g) and methylene blue value (887 cm³/g)^[13]. Previous investigations on chickpea waste show that new technology for producing activated carbon is still being explored. The author is aware of no research that has been undertaken for chickpea stalk by one stage chemical activation using potassium hydroxide.

This research seeks to present a novel method for utilizing raw chickpea stalk by converting it into activated carbon material, with a comprehensive analysis of its distinctive structural and adsorptive qualities. The study emphasized a quick and straightforward technique for producing activated carbon from chickpea straw, which decreased the duration required for both dual-step and traditional methods.

2. Material and methods

2.1 Gathering of chickpea stalks

Chickpea stalk (CS) was obtained from a nearby Bhopal village. After washing with hot water, the stalk was sun-dried outdoors. Subsequently, it was pulverized, and particles between 0.7 to 1.2 mm were isolated through sieve

analysis for experimentation. The sample was then dried for 24 hours at 105 °C in a hot air oven to eliminate excess moisture before further testing.

2.2 Synthesis of activated carbon material

The raw chickpea stalk underwent carbonization via KOH chemical activation. It was treated with KOH in a 1:1 weight ratio and left for 48 hours. Following this, it was oven-dried at 105 °C until completely dehydrated. The treated sample was carbonized in a horizontal reactor chamber at 800 °C, with a heating rate of 10 °C/min, under N_2 gas (flow rate 60 mL/min) for 90 min. post-experiment, the carbonized sample was cleansed with hot distilled water and 1M HCl until the wash solution reached a pH of approximately 7. Lastly, the prepared carbon was oven-dried at 105 °C for 24 h, completing the carbon sample preparation.

2.3 Characterization of raw chickpea stalk and activated carbon material

The Various characterization techniques were employed to analyze the chickpea stalk and carbon content. Proximate analysis determined moisture (ASTM E1756-08), ash (ASTM E1755-01), volatiles (ASTM E872-82), and fixed carbon content. Elemental analysis involved measuring carbon, nitrogen, oxygen, hydrogen, and sulfur levels. Additionally, a bomb calorimeter was utilized to determine the higher heating value (ASTM D5865-13).

Adsorption analysis of the iodine value (ASTM D4607-94,2006) was carried out for both raw and activated carbon. The following is the calculating formula:

$$\text{Iodine value (mg/g)} = C \times \text{Conversion factor}$$

$$\text{Conversion Factor} = \frac{\text{Mol wt. of iodine} \left(127 \frac{\text{g}}{\text{mol}}\right) \times \text{normality of iodine} \left(\frac{\text{mol}}{\text{L}}\right) \times 40 \text{ ml}}{\text{Wt. of carbon (g)} \times \text{Blank reading (ml)}}$$

$$C = \text{Blank reading (ml)} - \text{Standard reading (ml)}$$

The investigation of methylene blue (MB) adsorption was carried out for raw and activated carbon. The calculation formula is as follows:

$$\text{MB Value} = \frac{C_o - C_e}{w} \times V$$

Where V is a volume (ml), w is the weight of the sample (g), C_o is the initial concentration (mg/ml), and C_e is the equilibrium concentration (mg/ml).

The specific surface area, pore volume, and pore size distribution of raw chickpea stalk and activated carbon were determined by nitrogen adsorption/desorption isotherms at 77 K using a surface area analyzer (Microtrac, Belsorp max G). The sample underwent vacuum degassing prior to analysis.

3. Results and Discussion

3.1 Proximate analysis, elemental analysis, and heating value

Proximate, elemental, and calorific value analysis of

biomass are the main elements of physicochemical analysis. The outcome of this analysis of raw chickpea stalk (CS) and activated carbon material were displayed in Table 1. According to the proximate analysis, volatile matter, moisture content, and ash content were 65.63%, 9.02%, and 7.96%, respectively. By the difference approach, the fixed carbon content had been found to be 17.39%. The fixed carbon content of activated carbon was increased (59.81%), due to the devolatilization of volatile matter of raw chickpea stalk^[14]. While the ash content increased slightly because the thermochemical process creates metal oxide and mineral salt. The moisture content present in the biomass was in the favorable region for energy production from biomass^[15]. Also, high percentage of volatile matter (65.63%) in biomass confirms the potential candidate for bioenergy production. Whereas, low ash content shows more positive effect on the production of energy from biomass. According to previous articles high volatile matter and low volatile matter were good biomass for energy production^[14, 20].

Table 1: Proximate, elemental, and Calorific value of raw chickpea stalk and activated carbon materials

Sample	Proximate (%)				Elemental (%)					Calorific Value (MJ/kg)
	MC	VM	Ash	FC	C	H	N	S	O	
Raw Chickpea Stalk	9.02	65.63	7.96	17.39	40.62	6.55	0.83	0.31	51.69	16.46
Activated carbon material	7.57	16.81	15.80	59.81	61.29	3.67	0.38	0.14	34.52	21.18

Note: MC = Moisture content, VM = Volatile matter, FC = Fixed carbon,

The elemental analysis focused on the chemical components of raw chickpea stalk and activated carbon. The elemental composition in this investigation was recorded as carbon (40.62%), nitrogen (0.83%), hydrogen (6.55%), and sulfur (0.31%), while oxygen (51.69%) was calculated by subtraction. The higher values of carbon (40.62%) and hydrogen (6.55%) indicate higher energy content within the biomass, while lower values (0.83%) of nitrogen indicate less hazardous gas emissions ^[14]. The carbon percentage in activated carbon increased but the other element percentage decreased. Because during thermochemical conversion the complex bond is broken and released as CO₂, H₂O, and other gases ^[16]. The calorific value of raw chickpea stalk was obtained as 16.46 MJ/kg. Moreover, the activated carbon material had attended higher heating value (21.18 MJ/kg). This was due to increasing the fixed carbon content percentage, which increases the calorific value of the activated carbon material sample ^[16].

3.2 Methylene blue and Iodine value analysis

The measurements of iodine number and methylene blue

(MB) revealed properties of absorption. The process of absorption allows for the identification of typical pores that are present on any biomass material. Micropores (< 2 nm) may be identified using the iodine value, and mesopore structures (2-50 nm) could be identified using the methylene blue value ^[17]. Figure 1 depicts the methylene blue value and iodine number of raw chickpea stalk and activated carbon.

The findings showed that the methylene blue adsorption capacity was 78.73 mg/g and the iodine number was 88.54 mg/g. This signifies that raw chickpea stalk have a low micropore and mesopore structure ^[14]. The activated carbon material had a higher iodine number and methylene blue value as compared to raw chickpea stalk, indicating a higher proportion of mesopores and micropores present in the activated carbon material ^[18]. Overall, the findings concluded that raw chickpea stalk has limited surface area and porosity, with limited micropores and mesopores. This can be enhanced by chemical or thermal activation techniques.

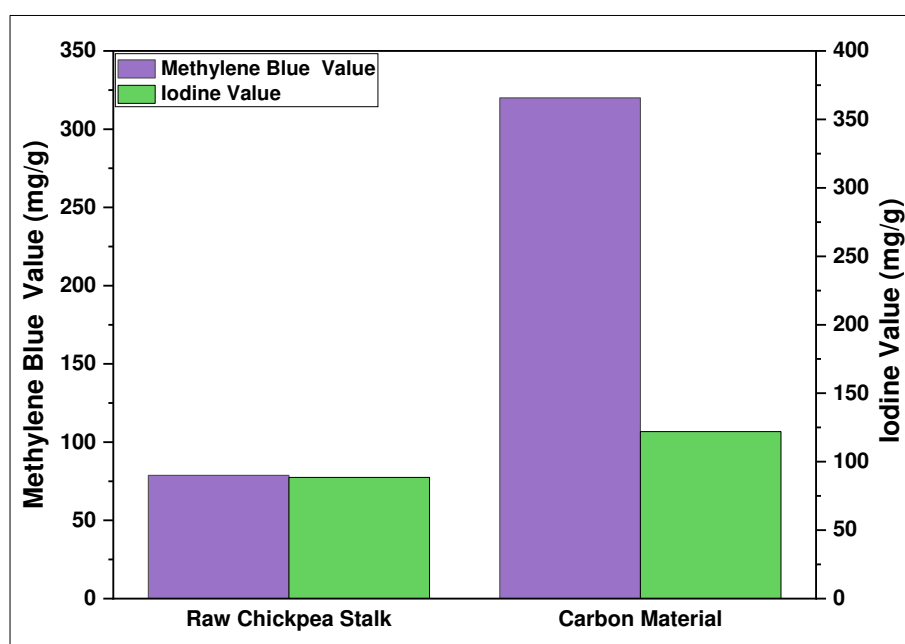


Fig 1: Methylene blue and Iodine value analysis of raw chickpea stalk and activated carbon material.

3.3 BET Surface area analysis

The Brunauer-Emmett-Teller (BET) surface area analyser revealed the surface area, pore volume, and pore size distribution. The absorption-desorption curve of raw chickpea stalk is depicted in Fig. 2. According to the IUPAC classification, the isotherm curve of raw chickpea stalk follows the Type III isotherm. Type III isotherms typically

pertain to macroporous or nonporous materials in which adsorbent-adsorbate interactions dominate the adsorption process as opposed to adsorbate-surface interactions ^[18]. This suggests that raw chickpea stalk may not have a well-developed pore structure, hence reporting the relatively minimal surface area and pore volume.

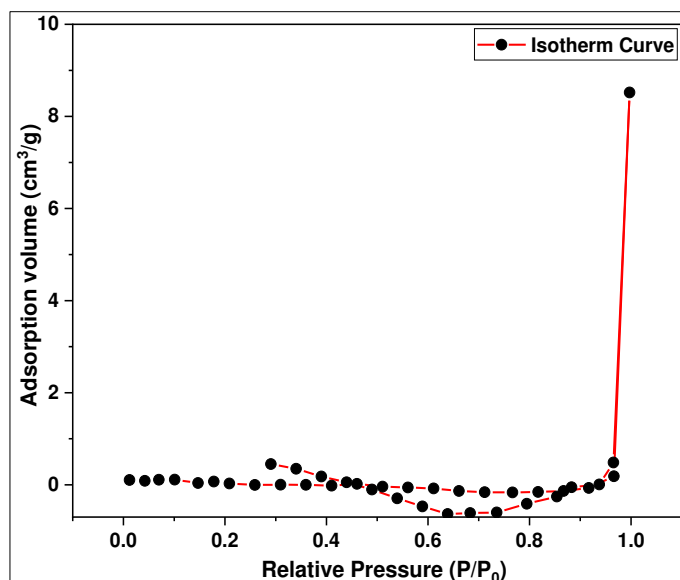


Fig 2: Adsorption-desorption isotherm curve of raw chickpea stalk.

The raw chickpeas stalk specific surface area was found to be quite low at $0.45 \text{ m}^2/\text{g}$, indicating that the material does not have many active sites available for absorption. This was because the raw material did not contain any substantial mesoporous or microporous features. The pore volume, which was found to be $0.01 \text{ cm}^3/\text{g}$, provides further evidence that the material has limited porosity. The presence of pores

in this material corresponds to the macroporous range ($> 50 \text{ nm}$), as indicated by the average pore width of 45.50 nm . The overall low surface area and pore volume of the chickpea stalk suggest that it may require further modifications to increase its absorption capacity and broaden its applicability in a variety of industrial processes.

Table 2: BET surface area characteristics of raw chickpea stalk and its activated carbon material.

Sample	Surface area(m^2/g)	Total pore volume(cm^3/g)	Average pore diameter (nm)
Raw Chickpea Stalk	0.45	0.01	45.50
Activated carbon material	1239	0.60	0.97

The modified chickpea stalk or activated carbon material produced from raw chickpea stalk had high microporosity and mesoporosity in nature with high surface area. The isotherm adsorption and desorption show the type IV curve for activated carbon material (Fig. 3) ^[18]. The curve was increasing rapidly until 0.01 signifies the rapid adsorption of nitrogen into micropores. Subsequently, the curve edge is turned and increases gradually with relative pressure, the turning edge highlights the beginning of the adsorption on

the mesopores while the gradual rising of the curve reflects the slow filling of micro and mesopores on the surface ^[18]. In the final phases, the amount of adsorption increases significantly or almost to the nitrogen saturation pressure due to active capillary condensation. The hysteresis loop present in the curve confirms the mesopores available on the surface of modified chickpea stalk or activated carbon material ^[18].

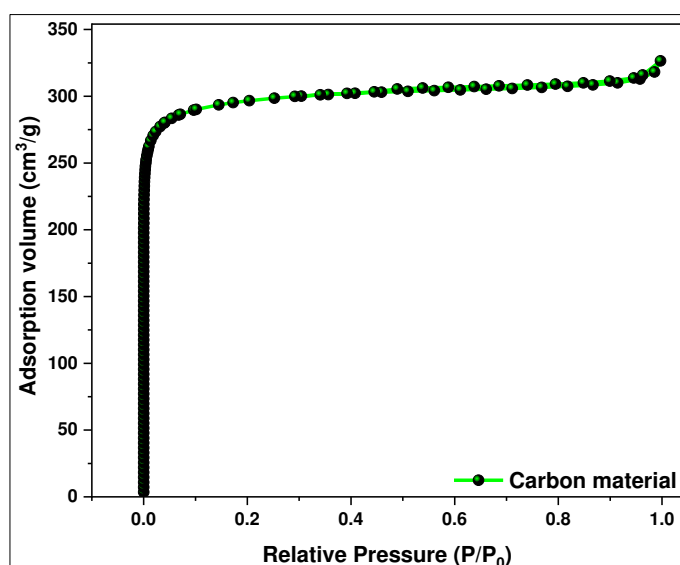


Fig 3: Adsorption-desorption isotherm curve of activated carbon material.

3.4 SEM analysis

The scanning electron microscopy (SEM) image of raw chickpea stalk and activated carbon material is shown in Fig. 4. The SEM image of raw chickpea stalk shows that no pores are present on the surface (Fig. 4(a)). The image makes it clear that compared to raw chickpea stalk, micro, and mesopores were present on the surface of activated carbon material. This indicates the thermal degradation and evaporation of volatile matter present in chickpea stalk. As a result, pores developed on the surface of activated carbon material. The activation time and temperature have a good influence on the pore formation and transformation. The figure clearly shows that a greater number of pores were generated on the surface at the proper activation temperature and time (Fig. 4(b)). Since the thermal degradation and volatile matter started to evacuate, some catalysts interact

and react with the activated carbon material [19]. Therefore, the activated carbon material has generated more micro pores in nature. Moreover, due to high temperature and time, the catalyst (KOH) gets plenty of time to react and interact with carbon and other volatile substances [6, 19]. This reaction helped in the formation of micro as well as meso pores on the surface of the activated carbon material. Moreover, the number of pores on the surface of the activated carbon material further increased. In this stage the metamorphosis of pores started i.e. micro turned into meso and meso turned into macro pores [6, 19]. The structure of the activated carbon material was honeycomb-like, composed of micro, meso, and macro pores. These pores were connected like a tunnel structure. Therefore, it was concluded that thermochemical action has a dominant effect on the formation of pores in the activated carbon material.

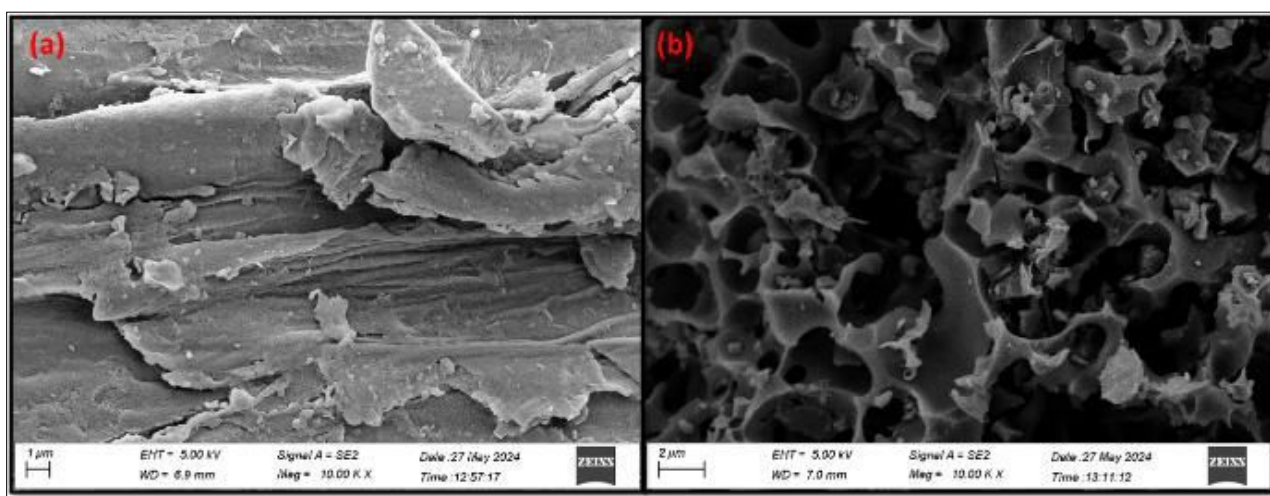


Fig 4: Scanning electron microscopy (SEM) image (a) Raw chickpea stalk (b) activated carbon material.

4. Conclusion

This research explores the utilization of chickpea stalk for creating activated carbon material. The production of activated carbon is achieved through a thermochemical activation process. The resulting activated carbon exhibits high porosity and a large specific surface area. This method is expected to mitigate global warming effects by offering an eco-friendly and convenient approach to producing highly porous carbon compounds from chickpea stalk waste. The activated carbon generated through this process has potential applications in various fields, including gas storage, air purification through gas absorption, effective water filtration, and the removal of contaminants.

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