Potential of using biomass based activated carbon for carbon dioxide capture

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Abstract. There are three major methods used to capture carbon dioxide (CO₂) which include post-combustion, pre-combustion and oxy-fuel combustion method. Post combustion method is a technically and economically possible for CO₂ capture. Generally, CO₂ is first separated from a gas stream which contains CO₂ and then captured. There are three main methods used to separate CO₂ viz., solvent separation, membrane separation and cryogenic separation. In post combustion, for capturing CO₂ different techniques such as absorption, adsorption, membrane and cryogenic distillation are used. Adsorption is the most commonly used method for CO₂ capture. Activated carbon obtained from charcoal is considered as a potential adsorbent material for CO₂ capture. In this study, potential of using activated carbon obtained from two biomass substances viz., coconut shell and palm shell were examined as the adsorbent materials which would be used to capture CO₂. For this purpose, the surface area, porosity, surface morphology and functional groups of the samples of activated carbon chosen for the study were obtained by using Brunauer-Emmet-Teller (BET), Scanning electron microscope (SEM), Thermogravimetry (TGA) and Derivative thermogravimetry (DTG) respectively. The preparation of biomass based activated carbon, adsorption properties and characterization of adsorbents were studied and the results are presented in this paper.

Abbreviation
ASTM American Society of Testing and Materials
BET Brunauer-Emmet-Teller
C Carbon
CO₂ Carbon dioxide
DTG Derivative thermogravimetry
GHG Greenhouse gas
H Hydrogen
IPCC Intergovernmental Panel on Climate Change
N Nitrogen
O Oxygen
SEM Scanning Electron Microscope
S Sulfur
TGA Thermogravimetry Analysis
1. Introduction
In the current scenario, the catastrophic effects of global warming and climate-related natural disasters are the major consequences by increasing the greenhouse gas (GHG) emissions; particularly CO₂. This would lead to drastic environmental impacts such as heavy droughts, changes in weather conditions, alternation in rainfall patterns, intensive heat waves, rising sea level and melting of glaciers and ice bodies [1]. Intergovernmental panel on climate change (IPCC) reported that the level of CO₂ concentration in the atmosphere elevated from 280 ppm in 1800 to 410 ppm in 2020. In order to overcome this problem, different CO₂ capture and separation processes have been implemented in CO₂ releasing areas. Now-a-days, enormous research works have been carried out in the suitable adsorbent with high CO₂ adsorption capacity and low economics [2].

Carbon materials have been widely used for adsorption applications in multiple zones because of their high specific surface area, remarkable mechanical, thermal, and chemical stabilities and also large porous structure. Activated carbon is the most efficient and breakthrough carbon material for capturing CO₂ as it possess good adsorption capacity and/or selectivity [3]. It is a typical adsorbent material used in many industrial applications, due to its wide surface area, favorable pore size and volume, high carbon content and relatively low cost [4]. One of the raw materials used for activated carbon is biochar obtained from variety of biomass materials. Agricultural waste is the most promising and optimistic raw material or feedstock, because of its abundant availability and also economic benefits. It also assists in resolving air pollution and water pollution problems. Numerous precursors such as almond shell, coconut shell, palm shell, walnut shell, pitacchio shell, melon seed shell, peanut shell, apple pulp, wheat straw, corn straw, cotton stalks, rice husk, bagasse husk, coffee husk, rice bran, olive kernels, cherry stones, olive stones, plum stones, sugarcane bagasse, sunflower seed hull, tobacco residues, soybean oil cake and wood chips are the examples of agricultural waste which can be used as raw material for biochar production [5]. This paper provides evaluation of activated carbon obtained from coconut and palm shell by characterization them using different instruments.

2. Materials and methods
2.1. Availability of biomass
Biomass substances is found everywhere in the world. However in view of availability in significance they can be obtained three different forms of waste; (i) municipal waste, (ii) industrial waste and (iii) agricultural waste. The different types of waste available in world are given in Table 1. Some of the potentially available biomass sources in India are listed out in Table 2.

| Waste type          | Quantity of residue (t) |
|---------------------|-------------------------|
| Food                | 1109700                 |
| Horticulture        | 1430000                 |
| Paper               | 900000                  |
| Wood an timber      | 283800                  |
| Construction debris | 314000                  |
| Ferrous metals      | 968400                  |
| Non-ferrous metals  | 90000                   |
| Sludge              | 50200                   |
| Glass               | 35400                   |
| Textile and leather | 25200                   |
| Scarp tyres         | 11300                   |
| Others              | 127300                  |
Table 2. various biomass sources available in India [7]

| Name of the crop | Type of residue     | Total available residue (Thousand MT) |
|------------------|---------------------|---------------------------------------|
| Banana           | Residue             | 240000                                |
| Wheat            | Stalks              | 117000                                |
| Sugarcane        | Bagasse             | 91165                                 |
| Maize            | Cobs                | 5550                                  |
| Bajra            | Husk                | 2307                                  |
| Millets          | Stalks              | 14890                                 |
| Ginger           | Stalks              | 13667                                 |
| Cassava          | Starch from roots   | 10908                                 |
| Coconut          | Shell               | 2887                                  |
| Arhar            | Husk                | 585                                   |
| Barley           | Stalks              | 1560                                  |
| Dry chilly       | Stalks              | 1200                                  |
| Urad dal         | Stalks              | 825                                   |
| Cumin seed       | Stalks              | 310                                   |
| Rice             | Straw               | 217                                   |

The selection of the raw material plays a major role for producing most efficient activated carbon. It is characterized in terms of pore size distribution, pore volume, pore structure, active surface structure, specific surface area, functional group, chemical elements and other adsorptive properties [8], [14] - [16]. The conversion of biomass to activated carbon as shown in Figure 1. The preparation of activated carbon is mainly depends upon high carbon and low inorganic (i.e., low ash) content, high density and sufficient volatile content. The prepared samples should have higher surface area and more pore volume for providing better CO₂ adsorption [9].

Figure 1. Biomass to activated carbon.

2.2. Preparation of activated carbon

For preparation of activated carbon, the samples of coconut and palm shells were collected from nearby campus area of NIT, Rourkela. The samples were dried and unwanted foreign particles were removed. The sample weighed with the help of electronic weighing machine. The weights of the sample weighted before and after removed the dust particles. The sample of coconut and palm shells are shown in Figure 2(a) and 2(b) respectively.
There are two main steps involved in production of activated carbon from raw materials viz., carbonization and activation. During carbonization, the sample is exposed to pre-treatment process (heating), and the pyrolysis enhanced with an inert atmosphere to produce an enriched carbonaceous material [12]. Most of the non-carbon (i.e. carbon free) elements such as hydrogen, oxygen, sulphur and nitrogen are removed from the sample. Hence, the sample contains less surface properties. For improving the adsorbents properties, an activation is needed in the coconut and palm shells based activated carbon. In the activation process, carbonaceous materials are modified by using either physical or chemical treatment to develop high porosity and large surface area of activated carbon [8]. The physical activation is done by the partial oxidation or gasification of sample with steam or air at high temperature. Chemical activation is carried out by using chemical compounds viz., ethanolamine (C₂H₇NO), sulphuric acid (H₂SO₄), phosphoric acid (H₃PO₄), potassium carbonate (K₂CO₃), zinc chloride (ZnCl₂), sodium amide (NaNH₂), potassium hydroxide (KOH), sodium hydroxide (NaOH), and urea (CH₄N₂O) to produce well-developed carbon structure [13]. Most commonly chemical activation is performed at lower temperatures when compared to physical activation. Therefore, the produced activated carbon has high CO₂ adsorption capacity and well-developed porosity [18]-[20]. The prepared coconut and palm shells based activated carbon are shown in Figure 3(a) and 3(b) respectively.

Activated carbon is a potential for economically benefits and also most suitable material for CO₂ adsorption because of its versatile properties and characteristics. Thus, the modification of activated carbon by using chemical or physical process has to be done to improve the surface characteristic and high CO₂ adsorption capacity. The flow process of CO₂ adsorption from fed gas to storage is shown in Figure 4.
3. Result and discussion

3.1. Sample characterization

The derived adsorbent products were characterized by proximate and ultimate analyses. The fundamental properties are apparent/bulk density of adsorbent, presence of total ash, moisture and carbon content, particle size distribution, pore volume distribution, specific surface area, etc. It can be used to estimate that the activated carbon should possess higher surface area and microporosity. The activated carbon produced from coconut and palm shells were characterized in terms of elemental composition, adsorption capacity, surface functionality and pore size. In this research, the main parameters considered for activated carbon (i.e. elemental analyses, superior adsorption CO$_2$ capacity, surface functionality and pore size distribution) were evaluated by using proximate and ultimate analyses, Brunauer-Emmett-Teller (BET), Scanning Electron Microscope (SEM) and Thermogravimetric analysis (TGA) methods.

3.2. Proximate and ultimate analyses

The obtained results from the proximate and ultimate analyses of coconut and palm shells based activated carbon are provided in Table 3 and Table 4 respectively. It is apparent from the table that the amount of fixed carbon in activated carbon is so much high as compared to a raw material. It shows that good adsorbent provides high adsorption capacity. According to the American Society of Testing and Materials (ASTM D7582-10), the proximate analysis was conducted to evaluate the moisture content, volatile matter, fixed carbon and ash content of raw material and activated carbon. By using CHNS-O analyzer, the ultimate analysis was performed to find out the percentage of carbon, hydrogen, nitrogen, sulfur and oxygen of raw material and activated carbon.

**Table 3. Proximate analysis of before and after preparation of activated carbon**

| Proximate analysis       | Biomass - Coconut shell | Biomass - Palm shell |
|--------------------------|-------------------------|----------------------|
|                         | Before preparation of activated carbon | After preparation of activated carbon | Before preparation of activated carbon | After preparation of activated carbon |
| Moisture content (wt. %) | 11.44                   | 2.39                 | 2.44                     | 7.53                        |
| Volatile matter (wt. %)  | 40.63                   | 16.21                | 73.63                    | 15.23                       |
| Fixed carbon (wt. %)     | 44.97                   | 79.91                | 18.25                    | 67.89                       |
| Ash content (wt. %)      | 2.96                    | 1.49                 | 5.26                     | 9.58                        |

**Table 4. Ultimate analysis of before and after preparation of activated carbon**

| Ultimate analysis | Biomass - Coconut shell | Biomass - Palm shell |
|-------------------|-------------------------|----------------------|
|                   | Before preparation of activated carbon | After preparation of activated carbon | Before preparation of activated carbon | After preparation of activated carbon |
| C (%)             | 42.18                   | 73.86                | 48.30                    | 68.75                      |
| H (%)             | 9.61                    | 2.96                 | 7.14                     | 3.12                       |
| N (%)             | 6.00                    | 1.10                 | 0.60                     | 2.10                       |
| S (%)             | 31.28                   | 20.89                | 0.04                     | 0.02                       |
| O (%)             | 10.92                   | 1.18                 | 43.74                    | 26.44                      |
From the analysis, it is understood that the low ash content and high volatile matter of the raw material ensures that it can be an excellent material to develop an activated carbon. The amount of fixed carbon of the activated carbon increases with the increase in the activation temperature around 600°C by elevating the degree of aromaticity. During the pyrolysis and activation process, the activated carbon is enhanced to reduce the percentage of hydrogen, nitrogen, sulphur and oxygen. When raw material starts decomposing, the volatile elements including H, N and O exit from the carbonaceous material. Therefore, the sample completely turns into fully enriched carbon compound. From Table 4, it is understood that the amount of carbon content is increased from 42.18 % to 73.86 % for coconut shell activated carbon. On the other hand, the amounts of hydrogen and oxygen contents are reduced from 9.61 % to 2.96 %, and 10.92 % to 1.18 % respectively. In the palm shell, the amount of fixed carbon content is increased from 18.25 wt% to 67.89 wt%. During activation process, volatile matter is greatly reduced. Similarly, it is noted from ultimate analysis reports the amount of carbon content is raised from 48.30 % to 68.75 % due to release of more volatile matter.

3.3. SEM result

Scanning Electron Microscopy (SEM) or SEM analysis is mainly used to determine the sample’s surface topography, elemental composition and structure and also provides high-resolution image for estimating the surface fractures, flaws and contaminants or corrosion [19]. It is apparent from the figure shows surface condition of the coconut and palm shells based activated carbon. The micrograph of activated carbon provides the detailed information of surface texture and development of porosity. Figure 5(a) and 5(b) presents the micrographic view of coconut and palm shells based activated carbon respectively. The activated carbon shows smooth solid structure surface with void pores but relatively little crevices and cracks.

![Figure 5(a). SEM image of coconut shell.](image1)

![Figure 5(b). SEM image of palm shell.](image2)

SEM analyses observed the sharp, conical agglomerations and also investigated the pore size-width and uniformity of the activated carbon. The increase number of pores available in the sample indicated the higher CO₂ adsorption.

3.4. BET surface area analysis

Table 5 provides the details of the BET surface area analysis of raw material and activated carbon of the coconut shell and palm shell. The main property of the activated carbon is adsorptive capacity, because the adsorptive capacity is directly proportional to the specific surface area of material. Basically, the better specific surface area of the activated carbon greatly enhances its adsorptive capacity. In BET surface analysis, the available of wider surface area and total pore volume are more prominent than any other physicochemical characteristics, because it may influence the reactivity and behavior of the activated carbon. For both cases, the untreated raw materials of coconut shell as well as palm shell have low BET value. Due to the presence of micropore increases the surface area.
Table 5. Surface area and pore size characterization

| Characterization of sample | Biomass - Coconut shell | Biomass - Palm shell |
|---------------------------|-------------------------|----------------------|
|                           | Before preparation of activated carbon | After preparation of activated carbon | Before preparation of activated carbon | After preparation of activated carbon |
| BET (m$^2$ g$^{-1}$)      | 0.84                    | 132.76               | 0.79                    | 101.92                   |
| Pore volume (cm$^3$ g$^{-1}$) | 0.001              | 0.24                 | 0.001                  | 0.19                     |
| Pore size (nm)            | 6.29                    | 7.98                 | 7.01                    | 7.67                     |
| Micropore volume          | 0                      | 0.17                 | 0                      | 0.14                     |
| Micropore surface area    | 0                      | 94.69                | 0                      | 840.19                   |
| Mesoporous surface area   | 0.84                    | 38.06                | 0.79                    | 17.71                    |

The highest BET specific surface area of 132.76 m$^2$ g$^{-1}$ and 101.92 m$^2$ g$^{-1}$ are achieved in coconut shell and palm shell respectively. The pore-size distribution is one of the main characteristics of the activated carbon. It indicates that the porous material should hold high-porosity with inside solid form and heterogeneous structure. Similarly, the pore size also increased from 6.29 nm to 7.98 nm and from 7.01 nm to 7.67 nm for coconut shell and palm shell respectively.

3.5. TGA and DTG analyses

Thermogravimetric analysis is used to examine the thermal degradation behavior of coconut shell and palm shell [21]. Figure 6 shows the information of weight percent (TG curve) and its corresponding first derivative (DTG curve).

![Figure 6. TGA and DTG analyses.](image)

At temperature below 120 °C, first peak occurs in the DTG curve which indicates the presence of internal moisture. After that, there are two separate specific peaks form the devolatilization zone. The first peak occurs in the range of temperature 200 °C - 315 °C and the second peak appears in the range of temperature 315 °C - 385 °C. The highest rates of decomposition occur at 265 °C and 350 °C for the first and second peak respectively.

3.6. Comparison of coconut and palm shells activated carbon with other activated carbon

Table 6 gives the comparisons of different activated carbon produced from different biomass.

Table 6. Comparisons of different activated carbon [22]

| Characterization of sample | Coconut shell activated carbon | Palm shell activated carbon | Rice husk activated carbon | Walnut shell activated carbon |
|---------------------------|--------------------------------|-----------------------------|-----------------------------|--------------------------------|
| Moisture content (wt. %)  | 2.39                           | 7.53                        | 6.34                        | 8.73                           |
| Volatile matter (wt. %)   | 16.21                          | 15.23                       | 16.70                       | 1.27                           |
| Fixed carbon (wt. %)      | 79.91                          | 67.66                       | NA                          | NA                             |
| Ash content (wt. %)       | 1.49                           | 9.58                        | 67.50                       | 77.42                          |
| C (%)                     | 73.86                          | 68.63                       | 36.52                       | 49.30                          |
The activated carbon obtained from coconut and palm shell could exhibit good carbon content, high surface area, pore volume and excellent adsorption behavior when compared to rice husk and walnut shell activated carbon. The carbon content are found to be 73.86 %, 68.63 %, 36.52 % and 49.30 % for coconut shell, palm shell, rice husk and walnut shell activated carbon respectively. Similarly, the surface area and pore size of coconut and palm shells are higher when compared to rice husk and walnut shell. So, it possesses greater CO$_2$ adsorption capacity. The coconut and palm shells based activated carbon may be more economical feasible, less environmental impact and have the potential adsorption capacity.

4. Conclusion

Adsorption is the most viable, potential and economic technique in the post-combustion CO$_2$ capture. The raw materials such as coconut shell and palm shell are abundantly available and easily accessible resource. The preparation cost of coconut and palm shells based activated carbon is too much lower than the other activated carbon. Therefore, it provides huge benefits in terms of economic aspect (inexpensive) and also has high adsorption for replacing already available activated carbon. The coconut and palm shells activated carbon should possess high carbon content as well as low ash content with significant volatiles matter. The highly porous activated carbon materials or adsorbents are derived from biomass have been synthesized for structural characteristics and morphology analyses. As a result, it is easy to evaluate the used activated carbon is highly potential and feasible for CO$_2$ capture. The adsorbents have high stability, adsorption capacity and selectivity, regeneration ability, kinetics analysis, less energy input and low environmental impact. So, coconut and palm shells based activated carbon are highly ensured that the significant CO$_2$ adsorption capability and superior performance than other ordinary conventional adsorbent.

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