Utilization of Biomass (Rice Straw) to Produce Activated Charcoal Through Single Stage Pyrolysis Process

Ali Akbar Babar 1,2,3,4, Iqra Panhwar 1, Sabeen Qureshi 2, Sheeraz Memon3,* , Zuhaib Siddiqui 4

1Institute of Environment Engineering & Management, MUET Jamshoro, Sindh, Pakistan

Received November 30, 2018; Accepted March 29, 2019

Abstract: The average cost generation of activated carbon from biomaterials is relatively low as compare to the cost of industrial prepared activated carbon, recent experimental work mainly focuses on the low cost and efficient substitutes to the pre-existing commercial methods and finding economical process that can subsidize the sustainability to environment and provide benefits for further commercial use. In this research Raw material (Rice Straw) was used to produce activated carbon, process was initially started with washing of raw material to eliminate dirt impurities with distilled water and de-moisturized it in an oven for 24 hours at 105 °C. Then dried mass (DM) was impregnated with the activating agent MgCl2 with 1:1 and kept for 2 hours at room temperature and dried for 48 hours in an oven for activation. The treated material was carbonized by pyrolysis process in muffle furnace for 2 hours at 550 °C and the final product was kept in desiccator for further use. Freshly produced activated carbon Surface morphology was characterized by X-Ray diffraction (XRD), scanning of electron microscopy (SEM) & surface functional groups were analyzed by furrier Transform Infrared Spectroscopy (FTIR). Iodine number and methylene blue.

Keywords: Rice Straw (RS), activated carbon (AC), activating agent, bio-martials.

Introduction

Rice straw is an agriculture lignocellulosic fiber material which can be easily shredded into smaller pieces or particles and these small particles are like wood pieces or fibrous shreds, while rice straw can be a best alternative of wood-based raw material to produce activated carbon (Yang et al., 2003). Now days, the charcoal production researchers are focusing mainly on industrial residues, forestry byproducts and agriculture biomass like nut shells (Radhika et al., 2006) bagasse (Onal et al., 2007). Bamboo (Hameed et al., 2007). Sawdust (Ahmad et al., 2007). Molasses (Legrouri et al., 2007). Rubber wood (Kumar et al., 2006). Oil palm (Tan et al., 2007) apricot waste (Basar et al., 2007) and nut husk (Tan et al., 2008).

The growing demand of activated charcoal is directly proportional to the requirements of environment as well as innovative zones of applications in several countries. The main reason for the utilization other biomass such as rice straw, cotton stalk, rice husk, sugarcane bagasse etc. To produce activated carbon was the inaccessibility of primary resources like hard coal, nut shells and wood. The production and application of activated charcoal covers so far back in past, European were the first who extracted the activated charcoal by using the wood as a raw material (Schröder et al., 2011). Activated carbon also known as an activated charcoal, is the type of carbon that has been treated in such a way to produce very porous structure, thus it exhibited extreme wide surface area to adsorb contaminants or fix the chemicals (Huang et al., 1984; Bansal et al., 1988).

The most speeded method applied for the biomass conversion into an active charcoal covers the heating process like gasification and pyrolysis, this process is very cost-effective and multi-dimensional producer of several products such as gas, char and oil (Hameed et al., 2007). Furthermore, the temperature required in chemical activation found to be very low as compare to the temperature needed in physical activation, so the lower temperature used in chemical activation play an important role in pores development, while the high temperature of physical activation destroy the porous structure of activated charcoal (Baral et al., 2012).

The researchers also found that the use of an appropriate activating agent can arise the difference in the production of carbon (Yang et al., 2010), while the maximum number of activating agents used by precursor all over the world for activation process are potassium hydroxide (KOH) (Altintig et al., 2010).

*Corresponding: E-mail: sheerazahmed.memon@faculty.muet.edu.pk; Tel: +92-3003071014, Fax: +92-222771382
2013), zinc chloride (ZnCl₂), phosphoric acid (H₃PO₄) (Marin et al., 2006), magnesium chloride (MgCl₂) (Rufford et al., 2010).

**Materials and methods**

**Preparation of activated carbon**

In this assay, the raw material biomass (Rice Straw) was collected from an agriculture field and transported to laboratory. The biomass was shredded into small pieces and washed to remove dirt and other impurities at an initial stage. Furthermore, the shredded washed biomass and dehydrated for 24 hours in an oven at temperature of 105 °C. In next stage, it was impregnated with activating agent (MgCl₂) at 1:1 w/w then again oven dried at 105 °C for 48 hours. In last stage, the biomass mixed with activating agent (MgCl₂) was filled in crucibles having size 100 ml and these crucibles were placed in steel container having river sand filling in all empty spaces to create inert atmosphere and closed with tight lid and pyrolyzed in muffle furnace at 550 °C temperatures for 2 hours. After this process steel container was taken out from muffle furnace and kept in room temperature for cooling as shown in Figure 1 below.

![Steel Container used in Pyrolysis Process](image)

**Characterization of Activated Carbon**

**Furrier Transform Infrared Spectroscopy (FTIR)**

The equipment used for the FTIR spectrometer analyzation was Thermo Nicolet 6700 having a changeable KBR optic and a detector made up of deuterated tri-glycine sulfate (DTGS) to examine the standard pellets and samples. The standard region of examination taken for all spectra were in mid infrared (IR) of 4000-400 cm⁻¹ and had the resolution of 4 cm⁻¹ with accumulation rate was 32 scans per spectra. While the software recorded and operated the spectra of FTIR instrument was OMNIC version 7.3 (Thermo Nicolet Analytical Instruments, Madison, WI). A new background spectrum was taken every time with same instrumental conditions before analyzing the next sample.

**X-Ray diffraction (XRD)**

The equipment model used for the XRD analysis was a Philips XRD instrument, equipped with CuKa radiations of 40 KV and 30 mA, and having 2-theta of step size 0.05°. The scanning rate employed for spectra measure was 1°/minute. Furthermore, the qualitative investigation and description of β values at FWHM and various 2-theta values with respect to peak’s location were measured through software named X Pert and modified Scherer equation was also used for the estimation of accurate value of Nano-crystalline size in XRD measure.

**Scanning Electron Microscopy (SEM)**

SEM is the measure of whole porosity found on the surface of an activated charcoal. The study of morphology, structure and composition of nanostructures formed active carbon on surface, through SEM micrographs were obtained on a JEOL, Tokyo, Japan machine.

**Iodine number**

The iodine number, of activated carbon is the amount of 0.02 N or 0.02 mol L⁻¹ milligrams iodine adsorbed by 1 g of activate carbon. To measure the iodine number of rice straw based active charcoal was ASTM D4607-94 method. Current method is also known as a three-point isotherm because in this method three separate amounts of AC mixed with a standard solution of iodine under definite
conditions. The experimentation involves the mixing of 10 mL of five percent hydrochloric acid with
the sample of AC and the whole solution was boiled for 30 seconds then cooled. Later 100 ml of iodine
having 0.1 normality was mixed in the solution and shaken for 30 seconds. In last through filtration, the
filtrate was separated and titrated with 0.1 normality of sodium thiosulfate solution in the existence of
starch indicator.

**Methylene blue Number (MB)**

The MB number or adsorption of an AC can be defined as the maximum quantity of methylene
blue dye adsorbed by a 1 gram of adsorbent. In this analysis 10 gm of activated carbon were assorted
with 10 ml of MB dye solution at numerous concentration of 10 to 100 mg L⁻¹ for a one day at normal
temperature. The concentration of MB obtained was measured through UV/V spectrophotometer at 661
nm. The amount of MB was measured the following formula:

\[
Q_e = (\text{mg} / \text{g}) = (C_0 - C_e) \times V / M
\]

Where:
- \(C_0\) = concentration of MB solution at initial time (t = 0),
- \(C_e\) = concentration of MB solution at equilibrium time,
- \(V\) = volume of the solution treated
- \(M\) = mass of the AC.

**Results and Discussions**

*Furrier Transform Infrared Spectroscopy (FTIR)*

The FTIR images of rice straw based activated charcoal Impregnated MgCl2 shows several
points, the first point at 711 cm⁻¹ and 873 cm⁻¹ were the finding of aromatic class having structure 1,2,3
tri-substance and 1,2,4 tri-substance respectively while the assignment of that peaks were C-H out of
plan, as described by (Allwar *et al.*, 2012). The point at 876 to 761 cm⁻¹ are allotted to out of plane
stretching vibrations of C-H group in the aromatic rings. While at 1062 cm⁻¹ the carboxylic group was
observed having structure of RCO-OH and assignment C-O bend, the same peak of same range was
already discussed by (Kibami, *et al.*, 2017). The RCONH2 structure was observed at 1633 cm⁻¹, which
was the conformation of amides groups, the same peak was also observed by (J. H. You, *et al.*, 1994).
in same range of 1633 cm⁻¹. Furthermore, 2351 cm⁻¹ was the indication of miscellaneous substances
that may have structure P-H phosphine and assignment P-H phosphine sharp, the characteristic of C-H
of CH₃ unit can be observed in the range of 2,351 – 2,356 cm⁻¹ stated by (Nasri *et al.*, 2017). While the
peak at 3264 cm⁻¹ was Carboxylic group with structure RCO-OH and assignment dimer OH. The same
peaks range was examined by Gonzalez at 3200 to 3400 cm⁻¹ and described that these peaks may be the
O–H bending because of the hydrogen intermolecular bonding with polymeric combinations like
phenols, carboxylic acid and alcohols signifying the occurrence of permitted hydroxyl groups on surface
of carbon (Gonzalez *et al.*, 2009. The points of different findings are shown the Table 1 below.

**Table 1. FTIR Points finding of activated carbon on surface.**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Peaks</th>
<th>Class</th>
<th>Structure</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>711 cm⁻¹</td>
<td>Aromatics</td>
<td>1,2,3 tri-substance</td>
<td>C-H put plane</td>
</tr>
<tr>
<td>2</td>
<td>873 cm⁻¹</td>
<td></td>
<td>1,2,4 tri-substance</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1062 cm⁻¹</td>
<td>Carboxylic acid</td>
<td>RCO-OH</td>
<td>C-O stretch</td>
</tr>
<tr>
<td>4</td>
<td>1633 cm⁻¹</td>
<td>Amides</td>
<td>RCONH2</td>
<td>NH out of plane</td>
</tr>
<tr>
<td>5</td>
<td>2351 cm⁻¹</td>
<td>Miscellaneous</td>
<td>P-H phosphine</td>
<td>P-H phosphine sharp</td>
</tr>
<tr>
<td>6</td>
<td>3265 cm⁻¹</td>
<td>Carboxylic Acid</td>
<td>RCO-OH</td>
<td>Dimer OH</td>
</tr>
</tbody>
</table>
XRD

The crystalline structure of MgCl₂-Based activated charcoal was examined with the help of XRD characterization shown in figure 2. The occurrence of initial broad peak in the range of $2\theta = 10^0$ and next in $2\theta = 15^0$ while third on $2\theta = 40^0$ was the conformation of AC sample had the amorphous structure. Likewise, a continuous pattern of sharp peaks till last specified the presence of residual ash and traces of metal in the amorphous shape. The MgCl₂ based charcoal’s XRD analysis recognized that a considerable amount of MgCl₂ was present in the adsorbent. 4 major peaks out of 10 were coordinated with XRD reference and it clarified that the adsorbent extracted from rice straw was not completely fall in the group of crystals while its major part is carbon graphite in nature. The XRD diffract gram characterization showed that the size of adsorbent can be in the range of 8-20 nm as shown in Figure 3 below.

SEM

The SEM micrograph of the nano-composite material specify un-homogenized morphology cause of the existence of charcoal. The optimistic area in the images noted at 100 µm characterizes the presences of MgCl₂ while the dark sector identifies the existence of rice straw charcoal. Pore structure was not clearly visible in the electro- gram shown in figure 4 which indications the SEM images of charcoal/ MgCl₂ nanocomposite.
Iodine Number

It is the degree of activity level (developed quantity of iodine number shows developed degree of activation), frequently labeled in mg/g (descriptive range 500–1200 mg/g). Iodine number is analysis of the micro-pores numbers of the activated carbon (0 to 20 Å, or up to 2 nm) by adsorption of iodine from solution (Sahira et al., 2013). The iodine number of rice straw based activated carbon was 567 mg/g.

Methylene Blue number

The methylene blue number of activated carbon is the identification of medium size pores, and these pores are greater in size as compare to iodine number (Sahira et al., 2013). The MB number of rice straw based activated carbon was 183 mg/g. while the adsorption measure through U/V spectrophotometer at wave length of 661 nm.

Conclusion

The FTIR results of MgCl₂-Based activated carbon showed 6 peaks at 711 cm⁻¹, 873 cm⁻¹, 1062 cm⁻¹, 1633 cm⁻¹, 2351 cm⁻¹, and 3265 cm⁻¹ are presence of aromatics, carboxylic acids, amides, and miscellaneous classes on the surface. While the XRD analysis demonstrated that peaks in between 1⁰ to 40⁰ were the conformation of amorphous crystalline structure of obtained activated carbon. Furthermore, SEM images clarified the XRD results by showing the presence of MgCl₂ on the surface of activated charcoal, whereas SEM micrographs also showed that the high temperature and activating agent influence the structure of biomass (Rice Straw) and converted it into a more use full material. While the presence of microspores was also considerable with iodine number of 567 mg g⁻¹, but number of medium size pores were less then microspore with methylene blue adsorption rate of 183 mg g⁻¹.

References


