J. Int. Environmental Application & Science, Vol. 14(1): 1-6 (2019)

Research Paper

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 Memon[3,*], Zuhaib Siddiqui [4]

[1]*Institute 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 ^{0}C. Then dried mass (DM) was impregnated with the activating agent $MgCl_2$ 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 ^{0}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.,*

*Corresponding: E-mail: sheerazahmed.memon@faculty.muet.edu.pk;Tel: +92-3003071014, Fax: +92-222771382

2013), zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4) (Marin *et al*., 2006), magnesium chloride ($MgCl_2$) (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 ^oC. In next stage, it was impregnated with activating agent ($MgCl_2$) at 1:1 w/w then again oven dried at 105 ^oC for 48 hours. In last stage, the biomass mixed with activating agent ($MgCl_2$) 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 ^oC 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.

Figure 1. Steel Container used in Pyrolysis Process

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 0.05^0. The scanning rate employed for spectra measure was 1^0/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:

$$\mathbf{Q_e = (mg / g) = (C_0 – C_e) x V / M}$$

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 (Gonzale *et al*., 2009. The points of different findings are shown the Table 1 below.

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

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

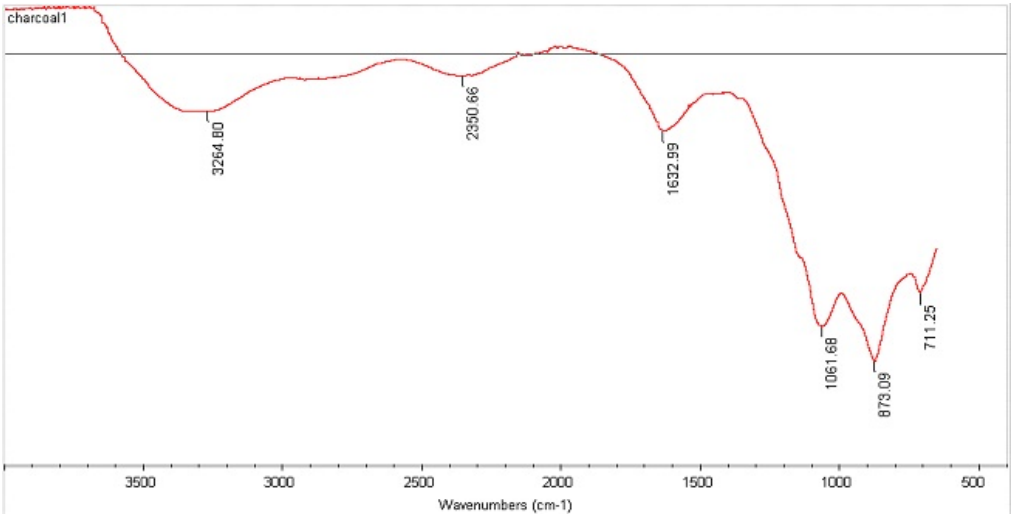

Figure 2. FTIR Points of Rice Straw Based Activated Carbon

XRD

The crystalline structure of $MgCl_2$-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 $MgCl_2$ based charcoal's XRD analysis recognized that a considerable amount of $MgCl_2$ 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.

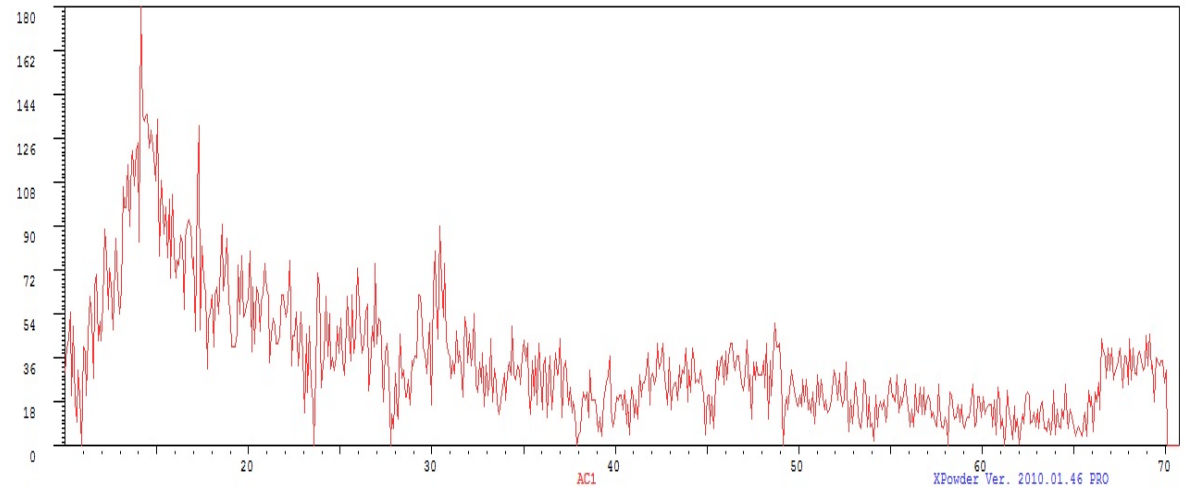

Figure 3. XRD pattern of $MgCl_2$- based activated carbon

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 $MgCl_2$ 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/ $MgCl_2$ nanocomposite.

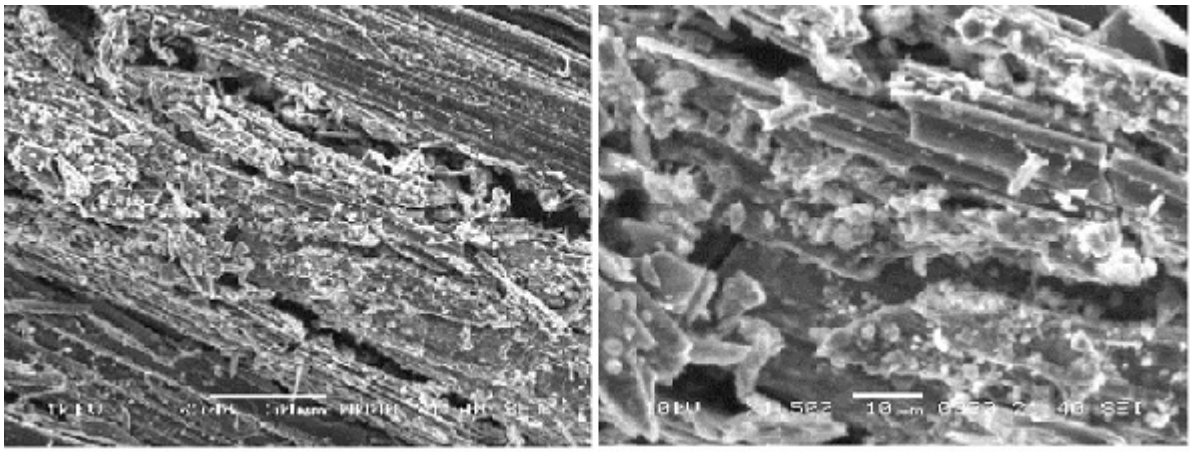

Figure 4. SEM images of $MgCl_2$-Based activated charcoal

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 $MgCl_2$-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 1^0 to 40^0 were the conformation of amorphous crystalline structure of obtained activated carbon. Furthermore, SEM images clarified the XRD results by showing the presence of $MgCl_2$ 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

Allwar A, (2012) Characteristics of Pore Structures and Surface Chemistry of Activated Carbons by Phys sorption, FTIR and Boehm Methods, *J. Appl. Chem*., **2**, 9-15.

Altintig E, Bilgin S. Arabaci G, (2013) Preparation and Antibacterial Activity of Silver Coated Activated Carbon from Rice Husks. *Res. J. Biotech*., **8**, 1721.

Bansal R.C, D. Baptiste and S. Fritz, (1988) Active Carbon Marcel. Dekker Inc. New York, **18** 266 – 269.

Baral DJ, Jha VK, (2012) Preparation of activated charcoal adsorbent from waste tire. *Sci. World*, **10**, 8083.

Basar CA, (2006) Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot. *J. Hazard. Mater*, **135**, 232–241.

Gonzalez JF, Silvia R, Gonzalez G, Carmen M, Nabais JM, Valente, Luis OA, (2009) Porosity Development in Activated Carbons Prepared from Walnut Shells by Carbon Dioxide or Steam Activation, *Ind. & Engin. Chem. Res*., **48**, 7474-7481.

Hameed BH, Ahmad AL, Latiff KNA, (2007) Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. *Dyes Pigments*, **75**, 143–149.

Hameed BH, Din ATM, Ahmad AL, (2007) Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. *J. Hazard. Mater*, **141**, 819–825.

Huang CP, Blankenship DW, (1984) *Water Research journal*, **18,** 37.

Kibami D, Pongener C, Rao KS, Sinha D, (2017) Surface Characterization and Adsorption studies of *Bambusa vulgaris*-a low cost adsorben, *J. Materials & Environ. Sci*., **15**, 224.

Legrouri K, Khouya E, Ezzine M, Hannache H, Denoyel R, Pallier R, Naslain R, (2005) Production of activated carbon from a new precursor molasses by activation with sulphuric acid. *J. Hazard. Mater.* **118**, 259–263.

Nasri NS, Abbasa AIMHI, Martelab BH, Abdulrasheeda A, Zaina HM, Sidika UH, Mohsina R, Majida ZA, Rashida NM, Sharera Z, Garbae A, (2017) CO_2 Adsorption Isotherms on KOH, H3PO4 and FeCl3.6H2O Impregnated Palm Shell Kernel Activated Carbon, *Chem. Engin.Tran*., **56**,88-96.

Olivares-Marin M, Fernandez-Gonzalez M, Macias-Garcia C, Gómez-Serrano V, (2006) Preparation of activated carbon from cherry stones by chemical activation with $ZnCl_2$. *Appl. Surf. Sci*., **252**, 5967-5971.

Onal Y, Akmil-Basar C, Sarıcı-Ozdemir C, Erdogan S, (2007 Textural development of sugar beet bagasse activated with $ZnCl_2$. *J. Hazard. Mater*, **142**, 138–143.

Prakash Kumar BG, Shivakamy K, Miranda LM, Velan M, (2006). Preparation of steam activated carbon from rubberwood sawdust (*Hevea brasiliensis*) and its adsorption kinetics. *J. Hazard. Mater*, **136**, 922– 929.

Putun AE, Ozbay N, Onal EP, Putun E, (2005) Fixed-bed pyrolysis of cotton stalk for liquid and solid products. *Fuel Process Techno*, **86**, 1207–19.

Radhika M, Palanivelu K, (2006) Adsorptive removal of chlorophenols from aqueous solution by low cost adsorbent Kinetics and isotherm analysis. *J. Hazard. Mater*, **138**, 116–124.

Ramakrishnan K, Namasivayam C, (2009) Development and Characteristics of Activated Carbons from Jatropha Husk, An Agro Industrial Solid Waste, By Chemical Activation Methods, *J. Environ. Eng. Manage*. **19**, 173-178.

Rufford TE, Lu M, (2010) A comparative study of $FeCl_3$, $MgCl_2$ and $ZnCl_2$ as activating agent on microstructure, surface chemistry and double layer capacitance of activated carbon", *J.Materials Res.,* **14**, 224-229 .

Sahira J, Mandira A, Prasad PB, Ram PR, (2013) Effects of Activating Agents on the Activated Carbons Prepared from Lapsi Seed Stone. *Res. J Chem. Sci*., **3(5),**19-24.

Schröder E, Thomauske K, Oechsler B, Herberger S, Baur S, Hornung A, (2001) Activated Carbon from Waste Biomass, in: *Progress in Biomass and Bioenergy Production*, Ed. Shaukat S, **19**, 444, DOI: 10.5772/972.

Tan IAW, Hameed BH, Ahmad AL, (2007) Equilibrium and kinetic studies on basic dye adsorption by oil palm fiber activated carbon. *Chem. Eng. J*, **127**, 111–119.

Tan IAW, Hameed BH, Ahmad AL, (2008) Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology. *Chem. Eng. J*, **137**, 462–470.

Yang HS, Kim D-J, Kim. H-J, (2003) Rice straw–wood particle composite for sound absorbing wooden construction materials, Bio resources Techno, **86**, 117-21.

Yang, K. Peng, J. Srinivasakannan, C. Zhang, L. Xia, H. and Duan, X, (2010) Preparation of high surface area activated carbon from coconut shells using microwave heating. Bio resource Technology, **101**, 6163-6169.

You JH, Chiang HL, Chiang PC, (1994) Comparison of Adsorption Characteristics for VOCs on Activated Carbon and Oxidized Activated Carbon, *Environ. Prog*., **31**, 31-36