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Application of Agricultural Residue in the Preparation of Activated Carbon through Two-Step Chemical Activation Method.

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Abstract: Activated carbon (AC) can be extracted from several agriculture residues which are basically carbon-rich materials. The objective of this research was the utilization of annual agriculture waste (cotton stalks) through the pyrolysis process to obtain a valuable adsorbent (activated carbon). The parameters used to evaluate the characteristics of $FeCl_3$ activated carbon was, Fourier Transform Infrared Spectra (FTIR) technique which shows several peaks at 877 cm^{-1}, 1156 cm^{-1}, 1557 cm^{-1}, 1568 cm^{-1}, 1683 cm^{-1}, 1695 cm^{-1}, 1916 cm^{-1}, 1991 cm^{-1}, 2112 cm^{-1}, and 2358 cm^{-1} and these all peaks identify the presence of various functional groups on the surface of the $FeCl_3$-Based AC. In addition, a honeycomb structure of pores distribution was analyzed through Scanning Electron Microscopy (SEM) images and X-ray diffractometry (XRD) identified continues spectrum, which is the evidence for the thermo-change in the crystalline structure of the $FeCl_3$-Based AC. Furthermore, Iodine adsorption and Methylene blue adsorption were also carried out to measure the number of macro and micro pores with the values of 224 mg/gm and 156.25 mg/gm respectively. The moisture content of $FeCl_3$-based AC was also carried out because of the agricultural residue used to acquire charcoal and the result was 5.4%. This study revealed that the $FeCl_3$-Based AC produce from cotton stalk is an easily available and inexpensive adsorbent for the application in liquid and gaseous phases with advantageous surface adsorption properties.

Keywords: Activated carbon (AC), Activating agent, Biomass waste, Agriculture residue, Cotton stalk.

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1. Introduction

Charcoal is very famous in household activities for years till now. In today's world, its market acceptance is still growing wide related to the medium of application. At present, charcoal received more attention towards its utilization a fuel because of easy storage and transport. [1]. Dissolved pollutants (organic and inorganic) of water or toxic fumes of gases can be removed through various adsorption techniques, but AC is very familiar with all types of adsorbents due to high adsorption rate, bulk availability, and low-priced. An adsorption dimension of AC relates to its high porosity distribution, the rapid degree of surface reactivity and great surface distribution [2]. The pre-carbonization study of the chemical nature of the raw material (agriculture residue) and activating agent should be determined before the carbonization process. It helps in understanding the actual surface area of material and effects of activating agent during carbonization on its pores structure and distribution [3]. Activated carbon is mostly extracted from raw carbon-rich resources in an oxygen-tight atmosphere through carbonization and activation process of carbon material. The process of activation can be categorized as chemical activation or physical modification [4]. Agro-industry produces millions of tons of lignocellulosic waste every year all over the world, which can convert into the valuable product like, AC. Additionally, usage of agricultural wastes for AC production will also help in reducing solid waste disposal issue and conversion of waste into a high worth material for liquid phase treatment [5]. Subsequently, an extensive range of agro wastes has been explored in Pakistan to produce AC. The residue contains Bagass from sugar cane, rice husk and rice straw from rice crop, wheat straw from the wheat crop, cotton stalk, and cotton gin trash from cotton crop, and maize stalk from the maize crop in an abundant amount [6]. Previous researchers have studied the extraction of AC with well-organized porosity from cotton stalks by using activating agents like KOH, $ZnCl_2$, and H_2SO_4, H_3PO_4 [7-9].

2. Experimental

2.1. Preparation of $FeCL_3$ -Activated carbon

The agriculture residue (cotton stalk) was collected from an agriculture land and transported to the laboratory. The raw material (cotton stalk) was washed before the carbonization to remove dirt and other impurities. After washing the cotton stalk, sticks were shredded into small pieces through a mechanical shredder. The shredded piece weight 48 gm of cotton was put into an iron made reactor having length 20 cm and 8 cm diameter as shown in figure 1, the reactor had two ends inlet to nitrogen gas and outlet for oxygen, was filled with nitrogen gas and both ends were tightly closed to create total inert atmosphere. The cotton stalks were carbonized at $550C^0$ for 1 hour in a furnace, after carbonization the weight of charcoal was 20 cm. In the next stage, 5 gm activating agent ($FeCl_3$) was diluted in 100 ml distilled water and then mixed with the charcoal for the next 2 hours and later oven dried at $110C^0$ for 24 hours to remove moisture. On the last stage, the material containing activating agent was again put into the reactor with an inert nitrogen atmosphere and pyrolyzed at $400C^0$ for 1 hour in a furnace. The weight after activation was 23.8 gm.

Figure 1: Iron Chamber used in pyrolysis process

2.1 Characterization of $FeCl_3$-activated carbon ($FeCl_3$-AC)

The presence of different functional groups on the surface of $FeCl_3$-Based activated carbon was determined with the help Fourier transform infrared (FTIR) technique. The equipment model was Thermo Nicolet 5700 including movable KBR pin and deuterated triglycine sulfate (DTGS) sensor. Software used for the analysis of functional groups was a commercially available IR spectrum analyzer OMNIC. The range of the spectra recording was in between 500cm-^{1} to 4000 cm-^{1} with a resolution of 4 cm-^{1}. Scanning electron microscope was used to study the changes occurs in the surface area and pores distribution pattern of activated carbon after the effect of high temperature. Activated Charcoal samples for SEM classification was set on the carbon tape and images were captured using different magnifications from 500 to 3500 resolutions. The SEM equipment used for this test was (SEM, JEOL TOKYO JAPAN). X-ray diffractometry is a method used for the qualitative characterization of the crystalline structure of the solid material. The diffractogram of $FeCL_3$-based activated carbon was obtained through Phillippe X-ray diffractometer equipment. Graph entering speed of the recording machine was 2 cm.m-^{1}. 2' 2 θ - 20' 2θ XRD pattern was given to the sample of activated carbon for the observation of its reflection behavior. A standard method ASTM D-2867-99 was used to determine the moisture content of $FeCl_3$-AC. Initially, a sample of dried AC having a mass of 10 gm was taken and washed and dried at atmospheric temperature. After that activated carbon was put into a crucible and placed in an oven at 105 C^0 for three hours and weighed again. The test was repeated 5 times to take accurate results. Methylene blue adsorption It is the amount of methylene blue (MB) in mg adsorbed by

the 1 gm of activated carbon [10]. The method used to determine the MB number was JISK 1470-1991. In this process, 1 gm of AC was a mixture of different concentration of MB (15 to 100 mg L^{-1}) and shook for 1 hour in a mechanical shaker. After shaking AC was separated from the solution of MB through filter paper. The remaining concentration of MB after adsorption was analyzed on a UV spectrophotometer at λ 661 nm. Calibration was done using a standard solution of MB [10]. Iodine number is defined as the amount of iodine (0.02 N) in mg adsorbed by the 1 gm of AC [11]. ASTM D4607-94 standard method was used for the determination of iodine number. The process used for this was the mixing of 10 ml of 5% HCl with different amounts (0.1 gm to 1 gm) of activated carbon in a flask and boiled for 30 seconds at first stage, then add 100 ml of 0.1 N iodine and shake the solution for 4 minutes. Furthermore, filter the solution and 50 ml filtrate solution titrate with 0.1 N sodium thiosulfate (Hypo solution) using starch indicator [12].

3. Results and discussion

3.1. Fourier Transform-Infrared (FTIR) analysis

The FTIR spectra characterization study was undertaken for the identification of functional groups in $FeCl_3$-Based activated carbon. The adsorption power of AC mainly relies on its pore distribution and the reactivity of functional groups, as discussed in another work suggested by Gonzalez [13]. The occurrence of numerous functional groups on the activated carbon surface shows a better adsorption power of unlike molecule classes by carbon. Hayet and Najes [14] also stated that more the functional groups better will be adsorption of an adsorbent. FTIR analysis of $FeCl_3$ saturated activated carbon displayed several absorption bands, initially at 877 cm-1 the presence of aryl hydrocarbons, as noted by Sricharoenchaikul and Allwar the presence of C-H bond [15-16], then at 1156 cm-1 Alkali halides may be due to the decomposition of chlorine present in $FeCl_3$. 1557 cm-1, where the evidence of C-O bond of carboxylic acid due to the breakdown of amino acid present in cotton stalk [17]. 1568 cm-1 were alkenes with C=C bond and 4-ring structure. Four major peaks were noticed during FTIR study, 1683 cm-1, 1695 cm-1, 1991 cm-1, and 2112 cm-1 Aldehydes, Carboxylic acid, Miscellaneous, and Alkynes respectively. Furthermore, at 2358 miscellaneous bonds were observed,

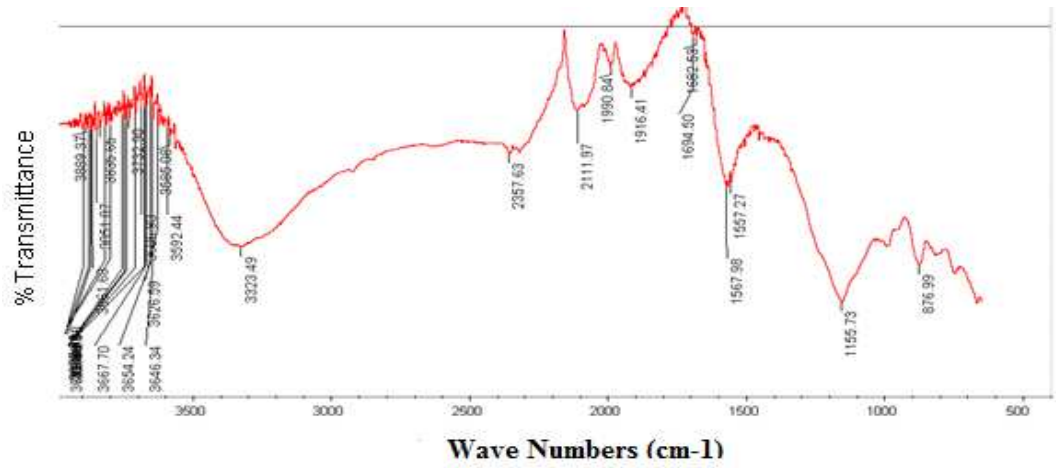


Figure 2. FTIR of $FeCl_3$-Based Activated Carbon

while 3323 cm-1 with structure RC≡CH identified as alkynes [18]. 3592-3582 cm-1 were alcohols having the assignment of O-H and structure RCH2OH. After 3592 cm-1 continuous peaks were observed up to 3889 that may be due to O-H present in various forms and moisture quantity of activated carbon, as identified by Gonzalez [13].

3.2 X-ray Diffractometry (XRD) of $FeCl_3$-activated carbon

XRD analysis was carried out for activated carbon sample several times. $FeCl_3$-Activated carbon prepared from cotton stalks showed several XRD patterns which are present in Figure 3. The results reveal that coal is a basically an amorphous solid. The amorphism phenomenon can be characterized as the presence of multiple C-C starches (because of aromatic rings), developments of different groups and their roles on the surface (see result FTIR on Fig. 2) throughout the process. Furthermore, the examination of all the bands makes it easier in explaining the characteristics of the cotton stalk. The XRD explained the characteristics of precursor that is extracted from a woody material and its elementary chemical composition (Figure 4). While the amount of lignin, cellulose, and hemicellulose variations in all parts of the cotton stalk. The production process of $FeCl_3$-activated carbon release various types of gases and water vapors, this phenomenon shows that its soft part contains hemicellulose and cellulose having a polymeric residue of glucose structure. Furthermore, lignin only occurs in its harder part that has a rigid shaped covalent bond of several phenolic groups. This is the reason that porous volume, textural structure, specific surface area and surface reactivity produced in activated carbon J. M. Ketcha also quantified the same phenomenon and the XRD analysis of current research nearly match his work [19].

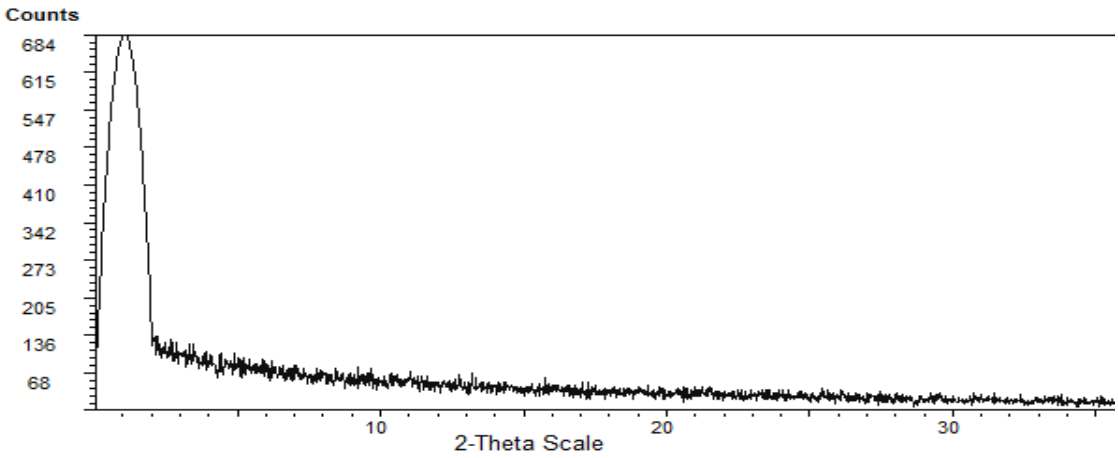


Figure 3 XRD analysis of Activated Carbon

3.3 Scanning Electron Microscope (SEM)

The surface morphology of $FeCl_3$-AC was examined through scanning electron microscopy (SEM). The results of SEM images showed that a uniform structure like a honeycomb or a series of tunnels was formed

during the carbonization (see Fig 4 A). On high magnification, up to 3000 more sequences of sub-pores can be observed (see Fig 4 B). This proves that the activating agent ($FeCl_3$) had a great influence on agriculture residue (cotton stalk) and created a very porous adsorbent after the pyrolysis process. The morphology of the present research work was almost corresponding to Makeswari and Santhi work [20].

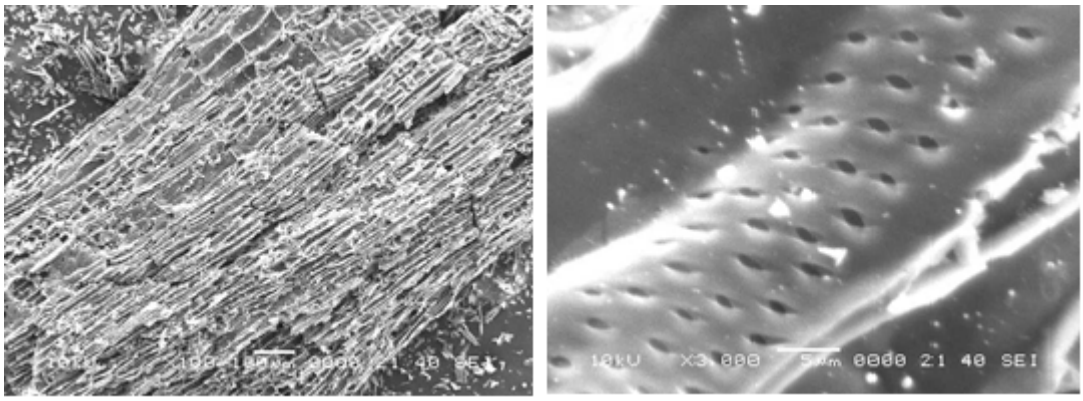


Figure 4 A SEM of AC Figure 4 B SEM of AC

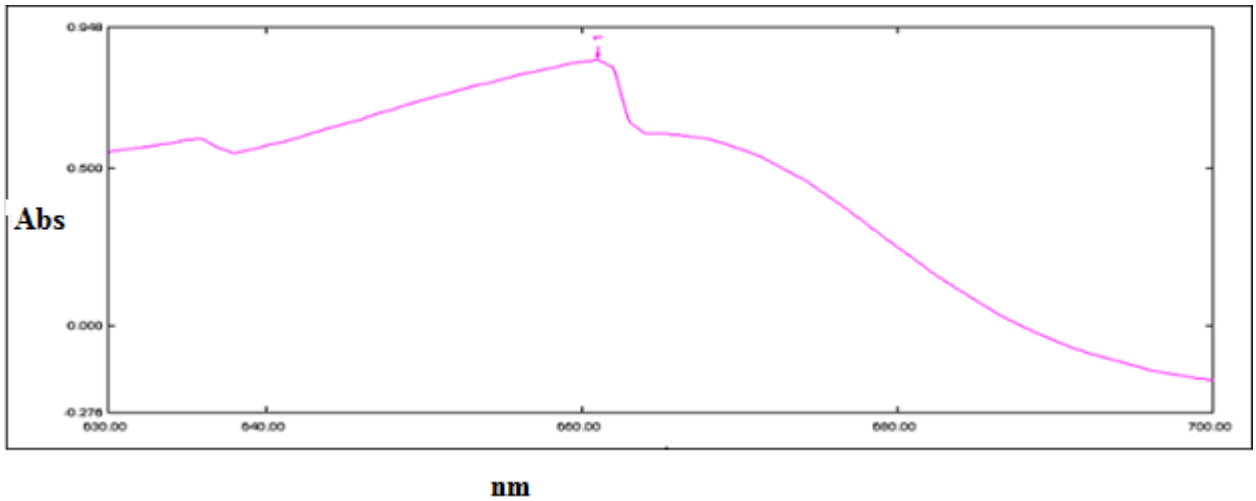
Figure 4 SEM Images of $FeCl_3$-based Activated carbon

3.4 Moisture Content of $FeCl_3$-based Activated Carbon

The moisture content of AC was determined through standard method ASTM D 2867-99(1999) [21]. The results were 5.4% moisture was present in the activated carbon.

2.1 Methylene blue (MB) and Iodine adsorption of activated carbon

Adsorption of methylene blue and iodine by an activated carbon are simple and generally used techniques for its characterization. The methylene blue provides the information about the number of macro size pores present in one gram of an activated carbon, while iodine adsorption clarifies the number of mesopores present in one gram of activated carbon [10-11]. The results of MB adsorption were 156.25 mg/gm and iodine number 224 mg/gm. The degree of adsorption of methylene blue was measured through a UV



spectrophotometer is shown in figure 5.

Figure 5 UV spectrophotometer Graph for the adsorption of Methylene of $FeCl_3$-based AC

4. Conclusion

FTIR analysis of FeCl3 saturated activated carbon displayed several absorption bands, initially at 877 cm-1 the presence of aryl hydrocarbons, then at 1156 cm-1 Alkali halides may be due to the decomposition of chlorine present in FeCl3. Four major peaks were noticed during FTIR study, 1683 cm-1, 1695 cm-1, 1991 cm-1, and 2112 cm-1 Aldehydes, Carboxylic acid, Miscellaneous, and Alkynes respectively. After 3592 cm-1 continuous peaks were observed up to 3889 that may be due to O-H presence in various forms and moisture quantity found in activated carbon). While the XRD analysis was carried out several times for activated carbon sample. The preparation process of FeCl3-AC generates several types of fumes and vapors, this phenomenon shows that its soft part contains hemicellulose and a fiber having fibrous residue of glucose structure. The surface morphology of FeCl3-AC was examined through scanning electron microscopy (SEM). The results of SEM images showed that a uniform structure like a honeycomb or a series of tunnels was formed during the carbonization. On high magnification, up to 3000 more sequences of sub-pores can be observed. The moisture content of extracted carbon was 3%, while methylene blue adsorption and the iodine numbers were 244 mg/gm and 156.25 mg/gm respectively.

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