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**INTERNATIONAL JOURNAL OF CHEMICAL, MATERIAL AND ENVIRONMENTAL RESEARCH**

An International Open Free Access, Peer Reviewed Research Journal

# INVESTIGATION OF MORPHOLOGICAL, THERMAL AND CRYSTALLOGRAPHIC PROPERTIES OF POTASSIUM PERMANGANATE TREATED PULQUE (*AGAVE ATROVERANCE*) FIBER

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**ABSTRACT:** Natural fibers extracted from Pulque (*Agave atroverance*) were chemically modified with 0.055 wt.% potassium permanganate ($KMnO_4$) and thermal properties of modified fibers were studied. In order to identify the effect of this chemical modification on the morphological, thermal and crystallographic properties of the fibers, Fourier Transform Infra-red (FTIR), Thermogravimetric analysis (TGA), Differential thermogravimetry (DTG), and Scanning Electron Microscope (SEM) was used. Fourier Transform Infra-red (FTIR) spectral confirm the partial removal of wax, cellulose, hemicellulose, and lignin content. It is found that the thermal stability of pulque fiber are of the order of Raw > $KMnO_4$. This is because except scouring all types of chemical treatment affect the cellulose structure of pulque fiber. The Scanning Electron Microscope (SEM) results have confirmed that the elimination of impurities from the fiber surface after chemical treatment.

**KEYWORDS:** Natural fiber, *Agave atroverance*, chemical treatment, FTIR, TGA, SEM.

## I. INTRODUCTION

Natural fiber are not only biodegradable and renewable but possess some unique advantages over conventional fiber such as light weight, high modulus, low cost, high specific strength and safe manufacturing processes (John and Thomas, 2008; Yousif et al., 2012; Rokbi et al., 2011). Poor wettability, high moisture content, and incompatibility with some polymeric matrix are some of its major disadvantage (Bachtiar et al., 2008). Over the years researchers have suggested the use of chemicals treatment of natural fiber as a way of overcoming these challenges (Yousif et al., 2012; Rokbi et al., 2011; Bachtiar et al., 2008). The use of potassium permanganate ($KMn0_4$) as chemical modification for some natural fiber has been proven to be very effective (Kalia et al., 2009), as results has shown that high thermal stability (Paul et al., 2010), increase tensile strength (Khan et al., 2006), increase stiffness (Khan et al., 2006; Paul et al., 1997; Wolfgang et al., 2006), changes in macromolecular and crystallographic structure were all observed after treatment (Patra et al., 2012).

There are about two thousands species from which fibers can be extracted, but few of them have economical value. So, we must find out alternative resources for the natural fiber extraction, which may be economical. *Agave atroverance* originally confined to Mexico, is now found in Asia as well. These plants are a cancerous; covered all over with sharp thorns and needles. Agave has been cultivated on the Mexican continent for at least 9,000 years. The widespread use of these fibers is fairly recent (Fayaz, 2011). Jute fiber was extensively used from the past day. But it has high production cost with large land area and low quality. On the other hand, *Agave atroverance* (pulque) fiber is high quality fiber and can be produced without any sufficient care and cost. Most species of Agave genus are characteristic of the arid zones and are exposed to adverse environmental changes; for this reason, these plants have developed diverse biochemical and biophysical mechanisms at the cellular and structural level (Lüttge, 2004). Unfortunately there is no work or utilization of pulque fiber so far in our country. So immediate attention must be given for proper utilization of this high cellulose and low lignin content fiber. The intention of this research work is to achieve a natural fiber of better chemical, mechanical and physical properties using chemically modified *Agave atroverance* fiber.

## II. MATERIALS AND METHODS

**Preparation of Fiber :** *Agave atroverance* fiber was collected from the local area (Islamic University, Bangladesh) and also from Vadalia of Kushtia district. The middle portion of the fiber was selected for this investigation. The dirty materials were removed by treating 6.5 gm of soap-flake and 3.5 gm of soda per litre at 75°C for 30 minutes in a breaker in the ratio 1 gm of fiber per 50 ml of the solution. The fiber was then washed thoroughly with distilled water and dried in the open air. This gives fibers that are subjected for investigation.

**Treatment of Fiber :** The extracted *Agave atroverance* fibers were cut into 50 cm length and were soaked in a 0.055% $KMnO_4$ solution at 60°C temperature maintaining a liquor ratio of 15:1. The fibers were heated for about 30 minutes. The fibers were washed several times with fresh water and finally washed again with distilled water. A final pH of 7 was maintained. The fibers were then dried at room temperature for 48 hours followed by oven drying at 100°C for 6 hours.

**Fourier Transform Infrared Spectroscopy (FTIR) Spectrometry :** Fourier Transform Infrared Spectroscopy (FTIR) technique was carried out to determine the functional groups and chemical bonds present on the pulque fiber. An FTIR analysis on the fiber constituents of treated and untreated fiber samples were carried out using the Perkin-Elmer 100 FT-IR spectrometer. 3 mg of fibers was crushed into small particles and mixed with KBr (potassium bromide) and pressed into a disc. The FTIR spectra were carried out by performing 64 scans in the frequency range from 225 to 4000 $cm^{-1}$, at spectral resolution of 4 $cm^{-1}$. A background spectrum of KBr (without sample) was measured to determine a relative scale for absorption intensity. The background spectrum was compared to the spectrum with sample in KBr to determine a resultant spectrum which had no instrumental character. Thus, the presented spectrum is produced only from the fiber sample.

**Thermogravimetric (TGA) and Differential thermogravimetric (DTG) analysis :** Thermogravimetric analysis is a thermal analysis techniques used to measure the mass change, thermal decomposition and thermal stability of material. Thermal gravimetric analysis was conducted using TGA Q500 machine. Samples weighing approximately 5 mg were subjected to pyrolysis in nitrogen environment to a maximum temperature of 600°C at a heating rate of 10°C/min. Experiments were carried out in a helium medium (60 ml/min) and the weight was recorded as a function of increasing temperature. A differential thermogravimetric analysis (DTG) curve was collected from the TGA analysis. A special feature of thermogravimetric instruments includes the determination of the derivative of mass change called derivative of Thermogravimetry (DTG). The weight loss was recorded in response to increasing temperature, with final residue yield on set of degradation temperature and number of degradation steps reported.

**Scanning electron microscopy (SEM) :** The surface morphology of treated and untreated fiber samples has been studied with LEO 435 VP (Leo Elektronenmikroskopie) operating with an acceleration voltage of 5 to 10 kV with a working distance of 9-11 mm. The samples were sputter-coated with a thin layer of gold before carrying SEM observations.

## III. RESULTS AND DISCUSSION

**FTIR analysis:** FTIR Spectra of untreated and $KMnO_4$-treated pulque fibers are exhibited in Figure 1 and 2, respectively. Cellulose, lignin, and hemicellulose are the major vibration bands present in both treated and untreated fibers. The broad and deep peak at 3200-3400 $cm^{-1}$ correspond to O-H stretching of hydrogen bond network, which shows decrease with soaking of pulque fiber in $KMnO_4$ solution, suggesting that the $KMnO_4$ effectively oxidized the O-H groups of cellulose and hemicelluloses (Saravanakumar et al., 2013). The peak intensity of cellulose increases after chemical treatment. The peak at 1654.8 $cm^{-1}$ for hydroxyl aldehydes and ketones in hemicellulose and cellulose components (Shah et al., 2013). The peak of the hemicellulose component noticed only in the raw fiber but perished in chemical-treated fiber spectra. The sharp peak at 1639 $cm^{-1}$ presences lignin with the hydroxyl aldehydes and ketones but it gives another broad peak at 2904.6 $cm^{-1}$, which gives the evident that methoxy group present in lignin (Thamae and Baillie, 2007).If we compare Figure-1 with Figure-2 then we find that due to $KMnO_4$ treatment oxidation of the fiber takes place, which produce aldehyde and carboxylic acid as a result peak at 1728 $cm^{-1}$ is observed. Most of the aldehyde and carboxylic acid shows peak at 1700 $cm^{-1}$-1730 $cm^{-1}$.

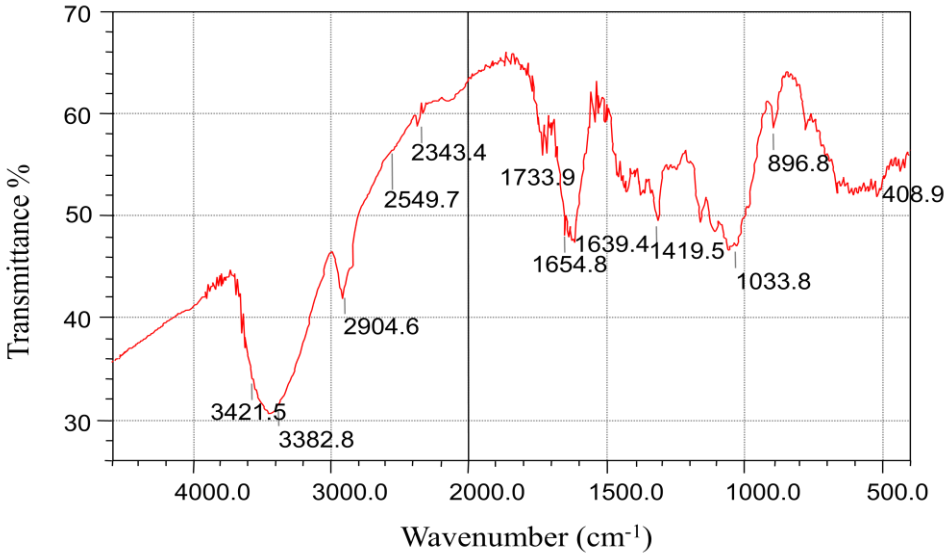


**Figure-1: FTIR of raw Pulque fiber**

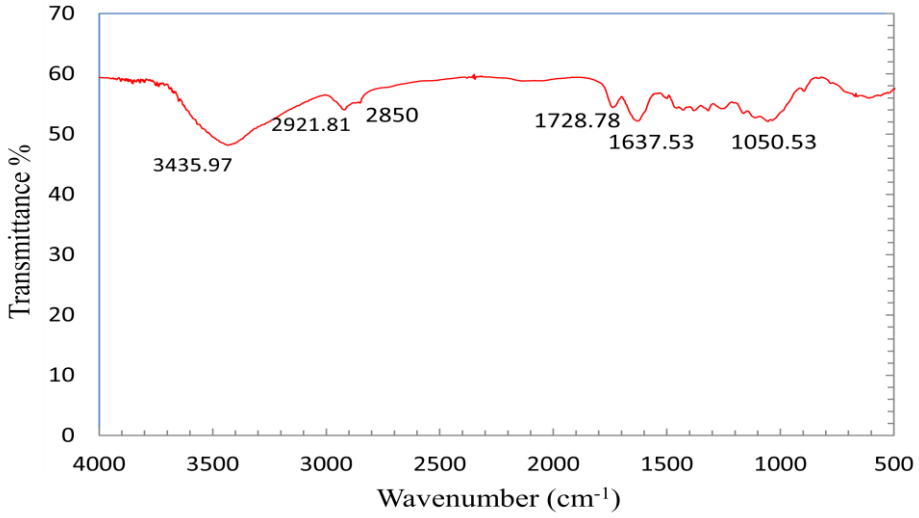


**Figure-2: FTIR of $KMnO_4$ treated Pulque Fiber**

**Thermogravimetric (TGA) and Differential thermogravimetric (DTG) analysis :** Thermogravimetry revealed that thermal degradation of pulque fiber depended mainly on the cellulose structure and the content of non-cellulosic components that were present in the pulque fiber. Purification of natural fibers has shown that non-cellulosic components are removed, depending upon the method employed, and the treatment or the absence of interaction from the extracted component may modify the crystalline form and crystallinity of the cellulose. The components of the fibers and the nature of the cellulose contribute significantly to the thermal stability. The thermal stability of pulque fiber are Raw> $KMnO_4$ . This is because except scouring all types of chemical treatment affect the cellulose structure of pulque fiber.

It is also evident from the TGA curve that all fiber contains moisture which is evolved upto about 100°C and this temperature is called minimum weight loss temperature. It is found that the initial weight starts at about 260°C for all fibers (Figure 3). The appearance of more than one peak in the DTG curves indicates that at least two stages are involved in the thermal degradation of fibers (Figure 4). The differential thermogravimetry (DTG) curves of raw and $KMnO_4$ treated fiber show an initial peak between 25 and 100°C, which corresponds to a mass loss of absorbed moisture. Further intense peak obtained at temperature 250 to 400°C. At the stage 250 to 300°C, degradation of hemicellulose and pectin may be starts. At temperature above 400°C depolymerization of cellulose start. Another peak obtained at temperature around 600°C due to oxidative degradation of the charred residue (Sreekala et al., 2002; Khopkar, 1998).If a species is thermally stable, there

will be no mass changed observed. Little or no mass loss indicates little or no slope in the TGA curve.

It is seen from the figure 5 to 6 that the three points of weight loss correspond to three endothermic processes, as it require energy to break the bonds in the successive elimination of water between 70-80°C, removal of oils and fats, lignin, pectin and hemicellulose between 120-250°C and finally 300-350°C for cellulose degradation. In case of $KMnO_4$ treated fiber an endothermic peak at 415.4°C attributed to the oxidative degradation of the charred residue. From figure 5 and 6 it was also observed that the initial and final decomposition temperature of raw and $KMnO_4$ treated fibers were 321°C, 319°C and 379°C and 369°C, respectively. This is because as a result of chemical treatment hemicellulose and lignin are removed from the fiber cell wall and affects the fiber crystalline region, hence decreases thermal stability.From the slope the weight loss for raw and $KMnO_4$ treated fibers were found to be 72.9% and 86.1% respectively which show that raw fiber is more stable than $KMnO_4$ treated fibers.

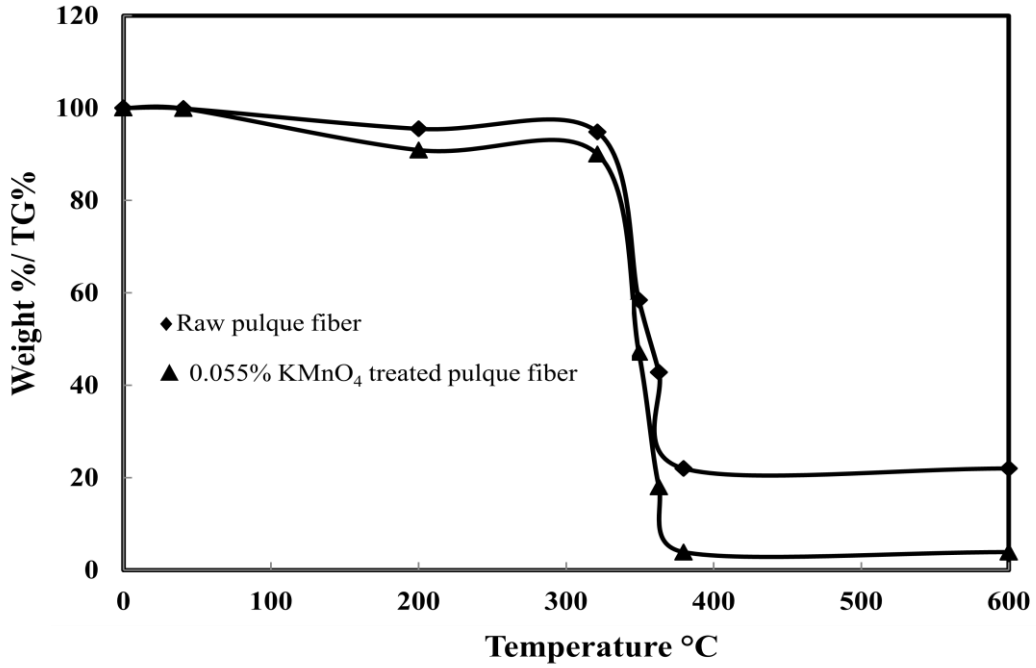


**Figure-3: TGA of raw and 0.055% $KMnO_4$ treated pulque fiber.**

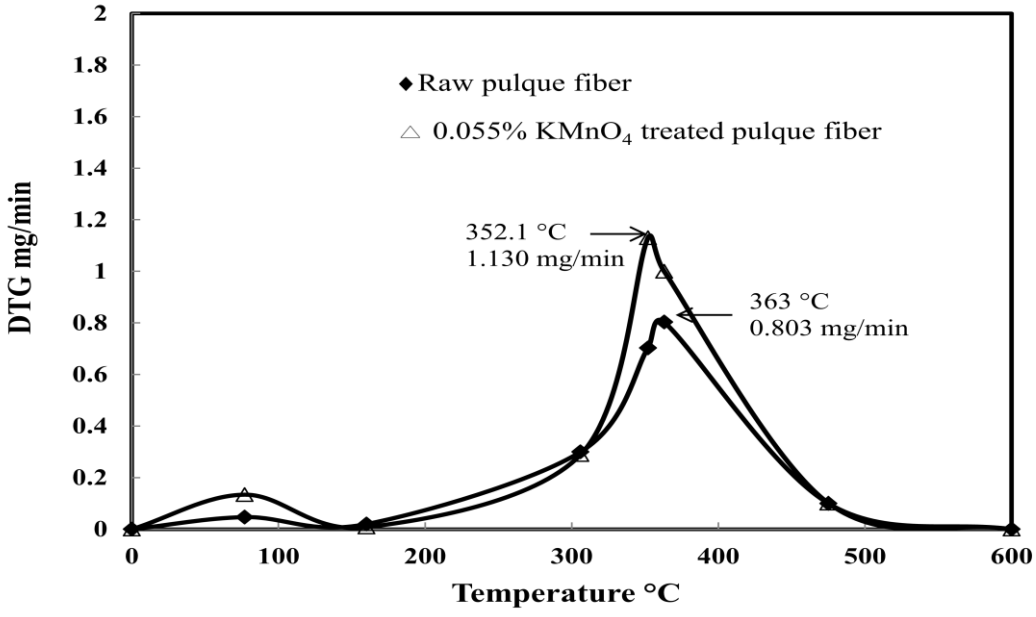


**Figure-4: DTG of raw and 0.055% $KMnO_4$ treated pulque fiber.**

**SEM Analysis:** The SEM micrograph of raw *Agave atroverance* fibers (Figure 5A) clearly demonstrates the presence of longitudinally oriented unit cells with more or less parallel orientations. The intercellular space is filled up by the binder lignin and fatty substances, which hold the unit cells firmly in a fiber. By treating the fibers with $KMnO_4$, take out waxes and oil from the outer surface of the fiber and also removal of minor constituents like lignin, hemicellulose, and amorphous cellulose from the outer surface of the fiber to a certain extent and improve roughness on the surface of fibers compared with untreated fiber (Figure 5B). The chemically treated fibers had developed a very rough surface and also developed amount of voids present which provides good mechanical interlocking with the matrix (Madhu et al., 2020).

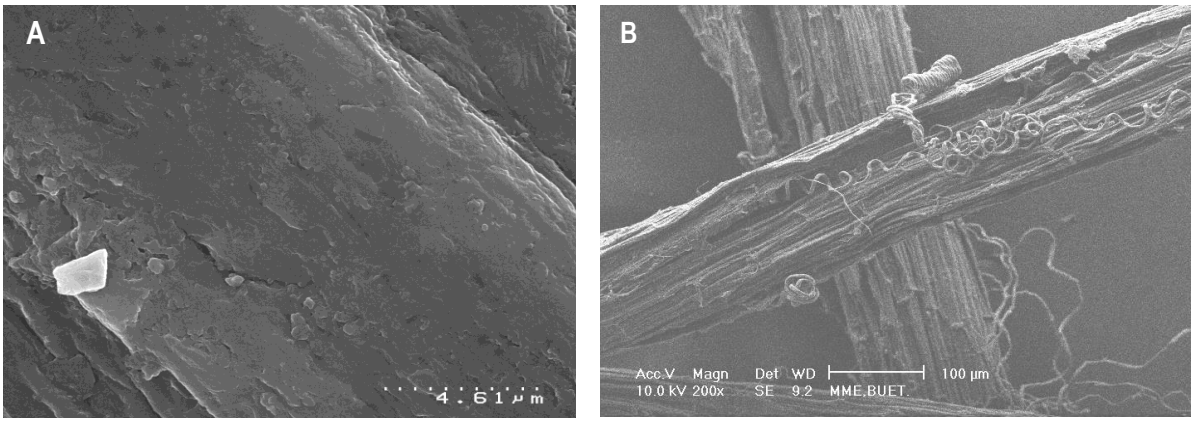


**Figure-5: SEM morphology of (A) Raw and (B) 0.055% $KMnO_4$ treated Pulque fiber**

## IV. CONCLUSIONS

$KMnO_4$ treatment of plant fibers effectively changes the surface topography of the fibers and their crystallographic structure. However care must be exercised in selecting the concentration of $KMnO_4$ for chemical treatment as results show that $KMnO_4$ treatment have reduced thermal resistance as elucidated by the TGA and DTG method. The removal of surface impurities on plant fibers may be an advantage for fiber to matrix adhesion as it may facilitate both mechanical interlocking and the bonding reaction due to the exposure of the hydroxyl groups to chemicals such as resins and dyes.

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