Preparation of Microcrystalline Cellulose Using Cotton Yarn Waste from the Textile Industry and Evaluation of its Characteristics

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In order to protect the environment and cellulose resources, yarn wastes from the textile industry, which contains a considerable amount of cellulose, can be used to produce microcrystalline cellulose. In this study, yarn waste was milled *via* a ball mill and was subjected to acid hydrolysis using sulfuric acid and hydrochloric acid at different times. It was characterized through various tests to determine the particle size, degree of polymerization, bulk and tap density, water soluble substances, ash content, moisture absorption capacity, infrared spectroscopy, X-ray diffraction, and thermogravimetric analysis. The Fourier-transform infrared spectroscopy analysis showed that the chemical compositions of all the samples were the same. The X-ray diffraction measurement showed an increase in crystallinity after acid hydrolysis. The thermogravimetric analysis showed that prepared microcrystalline cellulose *via* acid hydrolysis had good temperature resistance. The results obtained showed that the cotton waste from textiles was able to produce cellulose microcrystalline at a pharmacy standard level.

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Keywords: Microcrystalline cellulose; MCC; Cotton waste; Textile; Avicel®

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INTRODUCTION

The textile industry, like other industries, has waste products. Waste, when considered as a raw material resource, can serve as a source of natural fibers, *e.g.*, cotton and wool, as well as synthetic fibers (Stone *et al.* 2020). Cotton is an agricultural product that is greater than 90% cellulose (Hsieh 2007). Cellulose is the most abundant biopolymer in the world. It is a renewable, biodegradable, and water-loving polymer. It is naturally formed through the plant cellular development process and fixed by van der Waals forces and hydrogen bonds. In cellulose fibrils, the very ordered areas (crystalline) and relatively disordered areas (amorphous) are alternatively placed next to each other (Tayeb *et al.* 2018). The disordered part of the cellulose is available and active chemically and can be easily hydrolyzed by mineral acid and as a result, the crystalline segments are separated, resulting in various products, such as microcrystalline cellulose (MCC). MCC is crystalline, white, odorless, tasteless, and safe for humans and has many applications

(Chaerunisaa *et al.* 2019). Its dimension is approximately 20 to 80 microns and its polymerization degree is less than 350 (Karim *et al.* 2014). Cellulose microcrystalline can be used as a reinforcing element to provide a variety of environmentally friendly products. MCC has many advantages, *e.g.*, renewability, low density, stiffness, and a nonflammable nature. Advanced materials have been used in various industries, *e.g.*, medical, aerospace, automotive, *etc*. (Rasheed *et al.* 2020). Chauhan *et al.* (2009) showed the effect of hydrochloric acid on old cotton wastes from garment and hosiery industries, which lead to preparing microcrystalline cellulose, which had similar commercial microcrystalline cellulose (MCC) properties and a similar crystallinity.

EXPERIMENTAL

Materials

The cotton yarn waste, as shown in Fig. 1, was obtained from a textile factory in Qaemshahr, Iran. Samples of waste yarn were made of cotton and without color. In addition, all the chemicals used in this study were analytical grade. The obtained powder was characteristics by comparing with Avicel® PH 101 as a reference.

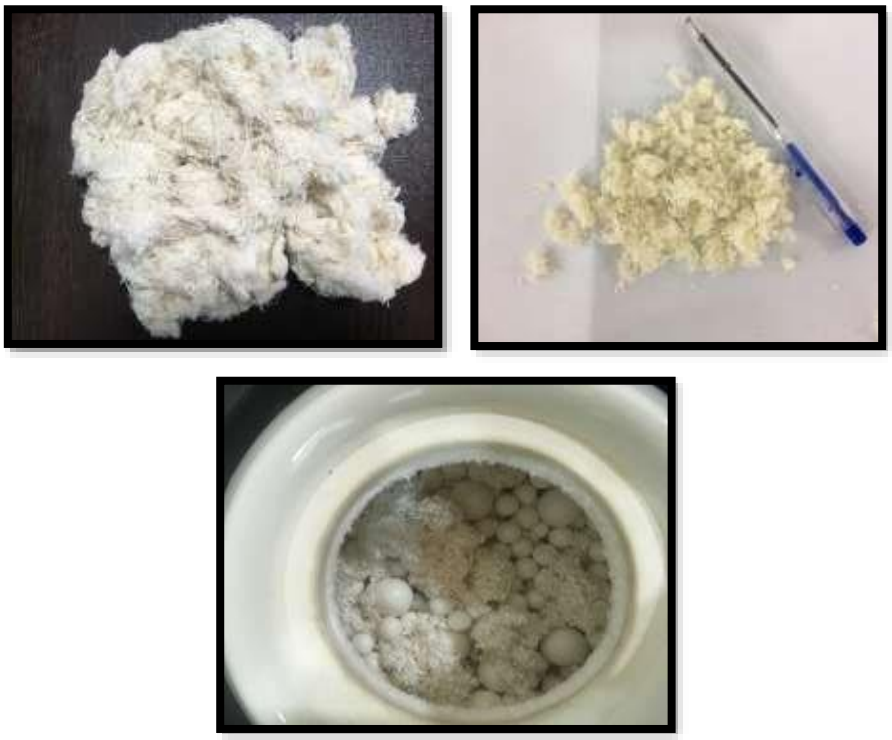

Fig. 1. Primary waste and chopped yarn

Methods

Raw materials preparing

First, the cotton yarn wastes were converted into an approximate length of 5 to 7 mm, and then they were milled to powder by a ceramic ball mill for 15 min.

Acid hydrolysis

Ten grams of the milled sample was hydrolyzed with 2 N sulfuric acid at a weight ratio of 15 to 1 for 30 min, 45 min, and 60 min and with 2N hydrochloric acid for 10 min, 20 min, and 30 min. The acid normality and reaction time were determined based on the pretests. The samples were filtered and washed to a neutral pH. A dilute sodium hydroxide solution was used for neutralization. Finally, the samples were air-dried and used a short-term sample mill to convert it back into powder form.

Evaluation of the Cellulose Microcrystalline Properties

Particles shape and size

The particle size of the microcrystalline cellulose (MCC) was measured *via* photo microscopy using Image tools software.

Degree of polymerization (DP)

The viscosity of the MCC samples was measured with copper ethylenediamine (CED) *via* a viscometer (Julabo, Seelbach, Germany). The DP was calculated based on Eq. 1 (Zeng *et al.* 2013).

$$DP_v^{0.905} = 0.75(\eta) \quad (1)$$

Bulk and tap density

First, 5 g of MCC powder was poured in a 50 mL cylinder and the primary bulk and the bulk after 200 tap was measured. The bulk and tap density were calculated based on Zeng *et al.* (2013), as shown in Eqs. 2 and 3,

$$\text{Bulk density} = \frac{\text{MCC mass}}{\text{primary volume}} \quad (2)$$

$$\text{Tap density} = \frac{\text{MCC mass}}{\text{volume after 200 tap}} \quad (3)$$

Water soluble substances

At first, approximately 5 g of the sample was stirred in 80 mL of water for 10 min, and then filtered. The filtrate was dried in an oven at a temperature of 100 °C and then the amount of the obtained sediment was weighted. In order to measure the actual sediment of the MCC samples, the amount of sediment of the distilled water (control sample) was also examined and the amount of water-soluble substances in the microcrystalline cellulose samples was calculated from the difference between the sedimentation of the microcrystalline cellulose samples and the distilled water (Ejikeme 2008).

Total ash content

To calculate the total ash content, 2 g of the MCC powder was poured in crucible and burnt in a furnace at a temperature of 550 °C for 5 h. The amount of ash was measured according to the residual weight, as shown in Eq. 4 (Hindi 2017).

$$\text{Ash percent} = \frac{\text{residual weight}}{\text{primary substance}} \times 100 \quad (4)$$

Moisture absorption capacity

Based on the method outlined by Achor *et al.* (2014), 1 g of MCC powder was placed in a petri dish and dried. Then, the samples were put in a closed desiccator with a container of distilled water and placed at room temperature. The samples were weighed after 5 d and the amount of moisture absorption was computed using Eq. 5,

$$\text{Moisture absorption} = \frac{\text{secondary weight} - \text{primary weight}}{\text{primary weight}} \times 100 \quad (5)$$

Fourier-transform infrared spectroscopy (FTIR) of cellulose

MCC powder samples were dried and pelletized using KBr (1:100, w/w). The spectra were recorded in the range from 4000 to 650 cm^{-1}. The function groups and chemical structure of the cellulose samples before and after hydrolysis were evaluated *via* infrared spectroscopy using a commercial spectrum 400 (Perkin Elmer Co) (Morais *et al.* 2013).

X-ray diffraction (XRD)

A X-ray diffractometer (PW1730, Philips Co) was used to analyze the crystalline structure of the MCCs's. The crystallinity index was calculated by the Segal equation according to Eq. 6,

$$CI\ (\%) = \frac{I_{cry} - I_{am}}{I_{cry}} \times 100 \quad (6)$$

where I_{cry} is the intensity of wavelength in 22.6° and I_{am} is the intensity of the wavelength in 18° (Segal *et al.* 1959).

Thermogravimetric analysis (TGA)

The thermal stability test was performed using a thermogravimeter (model Q600, TA Co). This test was done under ambient temperatures to 600 °C in an argon atmosphere, according to ASTM standard E 1131 (2020).

RESULTS AND DISCUSSION

The properties of the cellulose microcrystalline powder were compared with a pharmacopy standard and a commercial sample (Avicel®) produced by Sigma- Aldrich Co.

Degree of Polymerization

The degree of polymerization of the MCC samples decreased as the hydrolysis time increased. Obviously, this decrease was created by the breakage of the glycosidic bonds in the cellulose chain (Acharya *et al.* 2021). It was observed that the DP of the cellulose samples hydrolyzed *via* hydrochloric acid for 10 and 20 min, were effective but 30 min of hydrolysis reached the MCC DP limit. The same MCC DP was obtain from 60 min of hydrolysis with sulfuric acid. It was found that the efficiency of hydrochloric acid was twice as much as sulfuric acid (Table 1).

Table 1. Degree of Polymerization (DP) of Microcrystalline Cellulose Hydrolyzed by Sulfuric and Hydrochloric Acid at Different Times

Hydrolysis Time	Degree of Polymerization	
	Sulfuric acid	Hydrochloric acid
10	--	630
20	--	620
30	650	240
45	640	--
60	230	--

Interestingly, the degree of polymerization of the hydrolyzed raw samples was approximately 2700, whereas after mechanical ball milling it reached 730. However, the degree of polymerization of the commercial sample from Avical® was 172. According to the pharmacopy standard, the DP of the microcrystalline cellulose's should be less than 350; the line in Fig. 2 represents this point (Tomar *et al.* 2016).

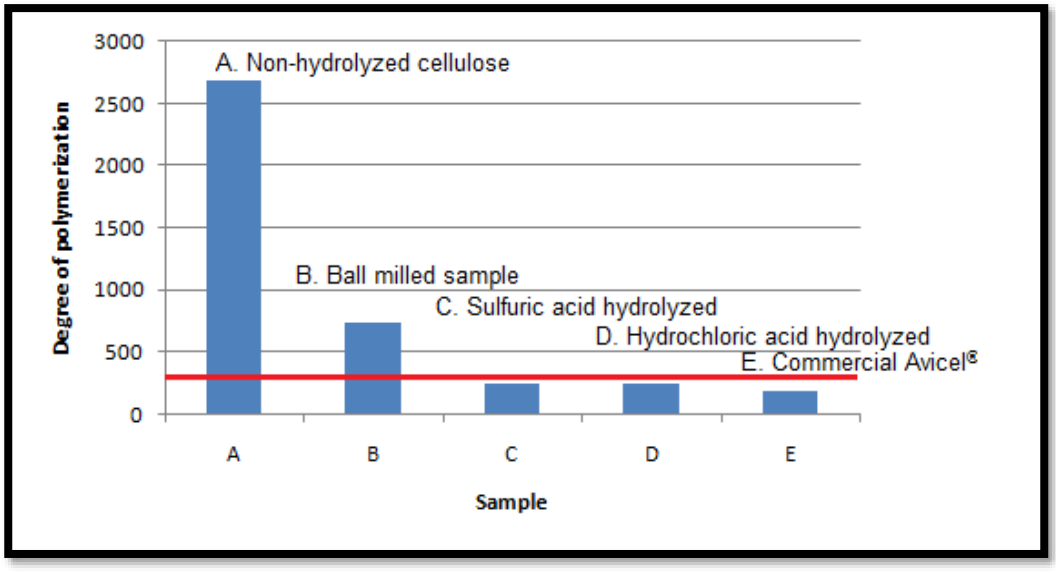

Fig. 2. Degree of polymerization

Particle Size of the Microcrystalline Cellulose (MCC)

The microscopic images of the samples of the microcrystalline cellulose (Fig. 3) show that the average particle size of the untreated cellulose was approximately 100 μm. The average particle size was decreased to 25 μm after hydrolysis with sulfuric acid and 27 micron after hydrolysis with hydrochloric acid. The average particle size of the microcrystalline cellulose from Avicel® was 20 μm. For the pharmacopy standard, the accepted particle size of cellulose microcrystalline has been announced as approximately 50 μm (Roew *et al.* 2006).

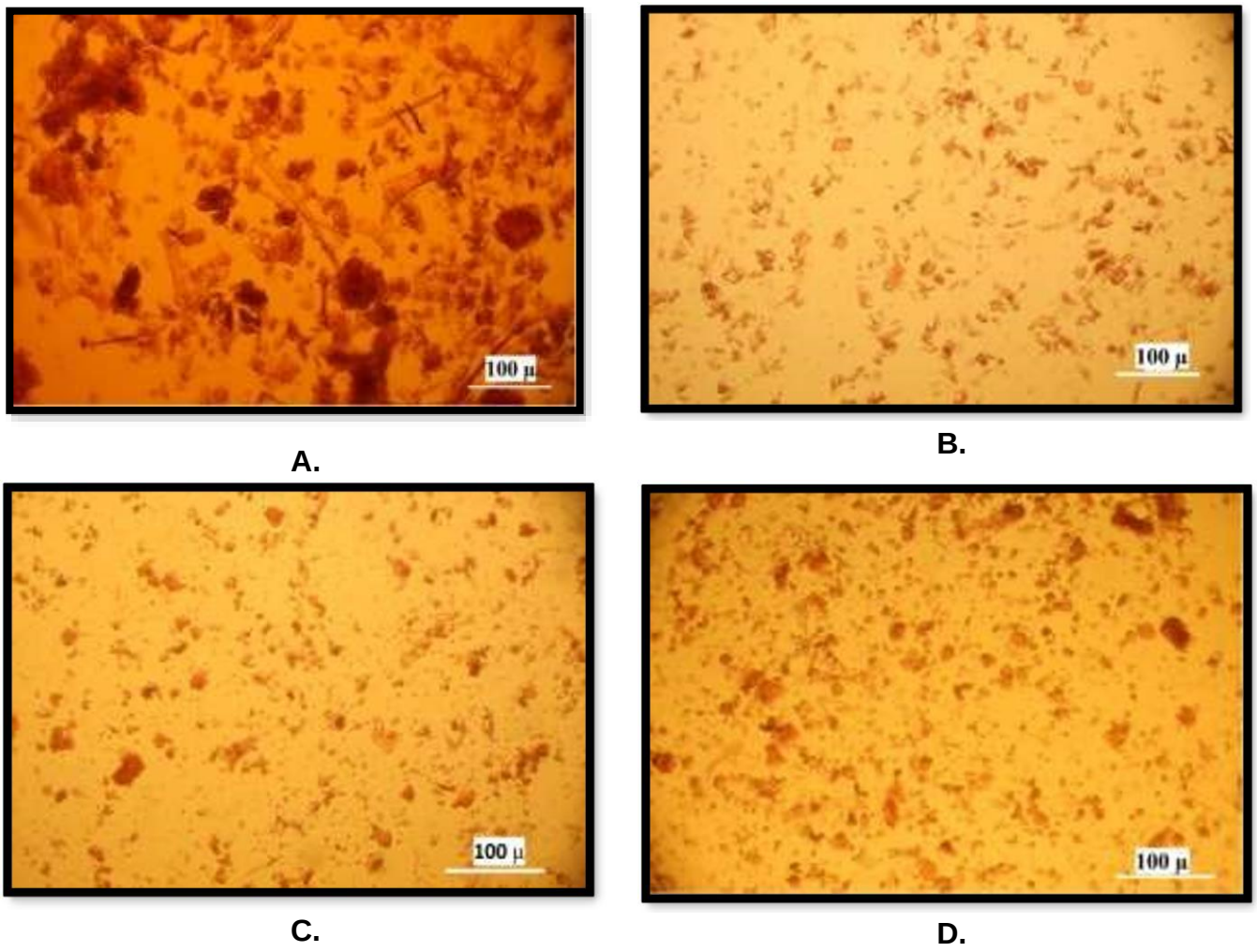

Fig. 3. The microscopic images of the samples with magnification of ×1000: A) non-hydrolyzed cellulose; B) commercial Avicel®; C) sulfuric acid hydrolyzed; and D) hydrochloric acid hydrolyzed

Bulk and Tap Density

The bulk density of the microcrystalline cellulose samples resulting from sulfuric acid and hydrochloric acid hydrolysis and the bulk density of the commercial sample had no major difference. However, the tap density of the hydrolyzed samples with sulfuric acid and hydrochloric acid was less than the tap density of the commercial sample (Table 2).

The kind of acid used did not have a considerable effect on the density of the different MCC samples. Previous studies have shown that there are positive correlations between the DP and the bulk and tap density of the microcrystalline cellulose powder (Nsor-Atindana *et al.* 2017).

Table 2. Bulk and Tap Density of the Cellulose Microcrystalline Powder

Sample	Hydrolyzed MCC	Bulk Density (g/cm^3)	Tapped Density (g/cm^3)
A	Avicel®	0.18	0.34
B	Sulfuric acid	0.19	0.34
C	Hydrochloric acid	0.19	0.26

Water Soluble Substances

The percentage of the water soluble substances in the microcrystalline cellulose samples resulting from hydrolysis with sulfuric acid, hydrochloric acid, and commercial Avicel® were 0.1%, 0.2%, and 0.1%, respectively, with no major difference. According to the pharmacopy standard, the amount of water soluble substances should be less than 0.25% (The Stationery Office 2009). Therefore, all samples resulting from this research are in the range of the mentioned standard.

Microcrystalline Cellulose (MCC) Ash Content

The ash content was 1.61% for the microcrystalline cellulose samples obtained after sulfuric acid hydrolysis and 1.42% for the sample resulting from hydrochloric acid hydrolysis. The commercial Avicel® did not have any ash (Table 3). The low percentage of ash in the research MCC samples could be due to the inorganic minerals in the raw cellulose substances and the preparation process of MCC (Kharismi *et al.* 2018).

Table 3. Amount of Ash in the Microcrystalline Cellulose Samples

Sample	Hydrolyzed MCC	Ash (%)
A	Avicel®	0
B	Sulfuric acid	1.61
C	Hydrochloric acid	1.42

Moisture Absorption Capacity

The water absorption capacity of the microcrystalline cellulose samples resulting from the hydrolysis of sulfuric acid, hydrochloric acid, and Avicel® were 0.12%, 0.09%, and 0.11%, respectively (Table 4). The moisture absorption capacity of the MCC sample resulting from sulfuric acid hydrolysis was greater than the commercial Avicel®. According to the pharmacy standard, the amount of moisture absorption capacity should be less than 8%.

Table 4. Moisture Absorption Capacity of Cellulose Microcrystalline

Sample	Hydrolyzed MCC	Moisture Absorption Capacity (%)
A	Sulfuric acid	0.12
B	Hydrochloric acid	0.09
C	Avicel®	0.11

Fourier-Transform Infrared Spectroscopy (FTIR) of Cellulose

The infrared spectrum of the unhydrolyzed cellulose powder, resulting from hydrolysis with sulfuric acid, hydrochloric acid, and commercial Avicel® are shown in Fig. 4. Absorption in the region of 1620 to 1960 cm^{-1} indicated OH-stretching of the absorbed water. The absorbance band at approximately 3400 and 2800 cm^{-1}, which are attributed to the OH-stretching and CH-stretching, were observed for all three samples (Kale *et al.* 2018). The C-O and O-H stretching was observed in the range 1000 to 1030 cm^{-1}. A general study of the FTIR spectra resulting from the hydrolyzed samples and unhydrolyzed samples showed that the chemical swelling and acid hydrolysis reaction did not affect the chemical structure of the cellulosic fragments. This implied that the chemical groups of the resulting materials were stable, and no strong chemical reactions occurred (Razali *et al.* 2017).

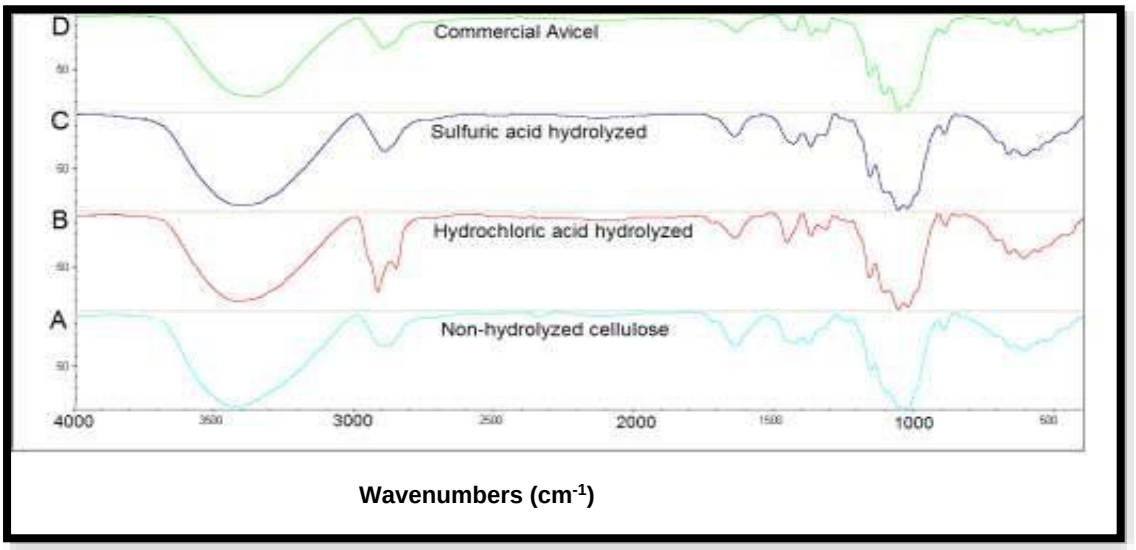

Fig. 4. FTIR spectra of the MCC samples

X-ray Diffraction

The X-ray diffraction of the microcrystalline cellulose samples (Fig. 5) shows that the sharpest peak at 22.6° was representative of crystalline and the peak that appeared at 18.2° represents amorphous sections. It can be seen that both samples had similar spectra and acted as cellulose I (Bai *et al.* 2012).

The crystallinity index (CrI) was determined by the Segal method for non-hydrolyzed, sulfuric acid, and hydrochloric acid hydrolyzed MCC, and commercial Avicel® samples were 52.8%, 83.3%, 76.4%, and 72.8%, respectively. All diffractions exhibited the same pattern, and acid hydrolysis increased the sharpness of the peak, which indicated an increase in crystallinity.

Table 5. Crystallinity Index of Microcrystalline Cellulose

Sample	Hydrolyzed MCC	CrI (%)
A	Untreated	52.8%
B	Sulfuric acid	83.3%
C	Hydrochloric acid	76.4%,
D	Avicel®	72.8%,

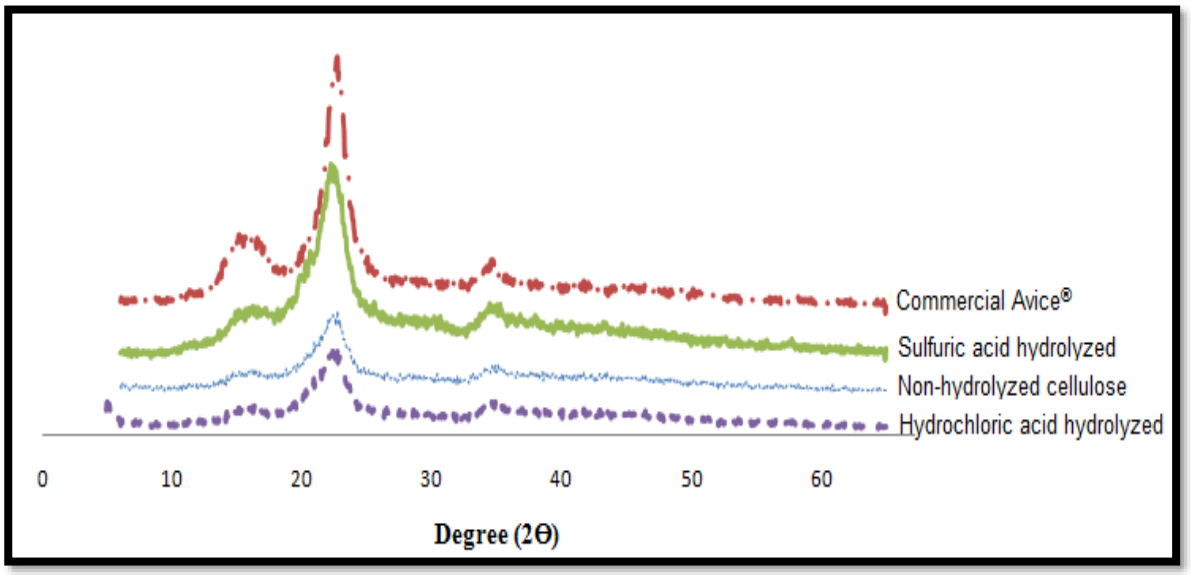

Fig. 5. X-ray diffraction data

Thermogravimetric Analysis

The microcrystalline cellulose samples represented in Fig. 10 show two degradation stages, which indicate the weight loss of the sample. The first destruction stage at the region between 50 and 150 °C represents the removal of water within the cellulose. The second stage in the range of 250 to 400 °C is because of the process of decomposition and destruction (Trache *et al.* 2016).

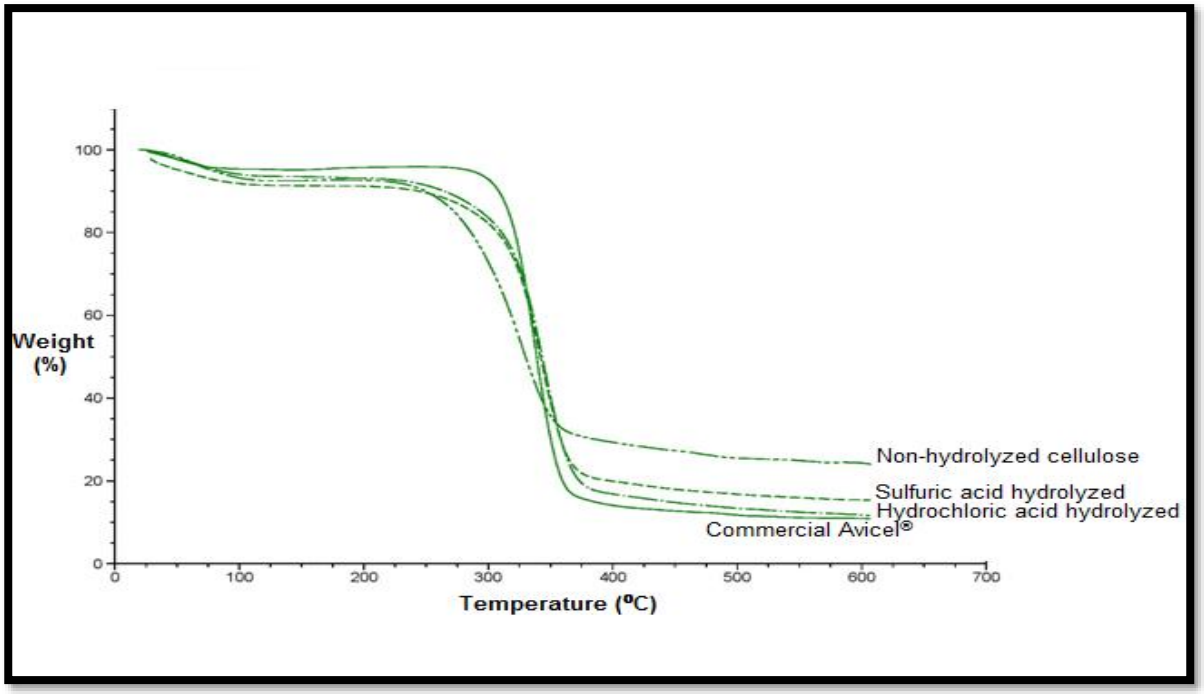

Fig. 6. Thermal gravimetric analysis

In Fig. 6, a TGA curve of the prepared samples is shown. The curves of the MCC samples were very similar to commercial MCC. The thermal decomposition and destruction of the commercial MCC occurred at 300 °C, occurred in the untreated cellulose samples at 230 °C, and occurred in the samples hydrolyzed with sulfuric acid and hydrochloric acid at 290 °C and 280 °C, respectively. The weight loss (Table 6) at 500 °C for prepared the MCC sample was near the commercial MCC. This shows that the prepared MCC *via* acid hydrolysis had good thermal resistance.

Table 6. Comparison of the Thermal Stability of Microcrystalline Cellulose

Sample	Hydrolyzed MCC	Temperature of Starting Thermal Destruction (°C)	Temp in 50% of Weight Loss	Residual Weight in 500 °C
A	Untreated	230	329	25.44
B	Hydrochloric acid	280	343	13.37
C	Sulfuric acid	290	343	18.96
D	Avicel®	300	339	12.15

Comparison of Table 6 with ash content (Table 3) shows that as carbon ash content increased, the thermal stability of MCC samples increased, while the residual weight significantly increased (Chen *et al.* 2016).

CONCLUSIONS

1. Microcrystalline cellulose was prepared *via* acid hydrolysis of cotton yarn wastes using 2N sulfuric acid and hydrochloric acid. Most of its properties conformed with pharmacopy standards.
2. Therefore, yarn wastes can be used as an inexpensive and abundant resource to produce this valuable substance.

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