The effect of Sulfuric acid and Maleic acid on characteristics of nano-cellulose produced from waste office paper

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Abstract
Present paper examines the effect of acid type and hydrolysis conditions on morphology, size, yield and crystallinity of produced cellulose nanocrystal (CNC). Cellulose obtained from waste office paper was hydrolyzed under the same conditions by Maleic acid (MA) and Sulfuric Acid (SA) in separate treatments. Also this cellulose was hydrolyzed under different timing and temperature by MA and SA. Results showed that produced cellulose nanocrystals have different size, yield and crystallinity under same conditions by MA and SA. MA treatment resulted in higher crystallinity, yield, and disperse solution. Therefore, MA was appeared superior to SA. Based on results the characteristics of nanocrystals are not only depended on hydrolysis conditions, but also on acid type.

Keywords: *Cellulose nanocrystal (CNC); Hydrolysis; Maleic acid; Nano; Sulfuric acid.*

INTRODUCTION

Cellulose is the most ubiquitous and abundant biopolymer in nature and its biosynthesis, chemistry, and ultra-structure remains an active field of study [1]. Each year, approximately 100 billion metric tons of cellulose is produced [2]. The biopolymer cellulose consists of glucose units linked by 1, 4-β-glycosidic bonds to cellobiose, a dimer as its repeating unit. Cellulose in lignocelluloses is built from cellulose microfibrils which are bound together by lignin and hemicelluloses. Cellulose fibers are bundles of microfibrils where the cellulose molecules are always biosynthesized in the form of nanosized fibrils. The microfibrillar structure may differ with species, growth conditions, climate, etc. It is considered that cellulose microfibrils are composed of both ordered, called crystalline, and disordered, called amorphous phase [3, 4]. CNC are the crystalline portion of cellulose with at least in one dimension equal or less than 100 nm. Acidic hydrolysis of cellulose fibers yields highly crystalline particles through selective degradation of the more accessible material. Acidic hydrolysis is an accepted method of producing CNC by Ranby [5]. The most important sources of cellulose that have been studied for production of CNC included bacterial, algal (Valonia), tunicate, and wheat straw sources [4, 6, 7]. During the last decade, there has been increased interest in the preparation of nanoscale cellulosic particles, which are broadly defined as CNC since CNC offer environmental benefits owing to their renewable nature and low energy consumption in production. They are low-cost, low density, having a high specific strength and modulus, and are comparatively easy to process due to their nonabrasive nature [7-10]. The preparation and characterization of CNC has been well-reported in literature [11-12].

The general characteristic of CNC produced through acid hydrolysis depends on conditions such as, temperature and time [6, 13] and on the original source of cellulose fibers: Bacterial cellulose [14], cotton filter paper [15] and tunicates [16] and China cotton, South African cotton and Waste tissue papers [13]. This huge

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variety of parameters highlights the need for a screening strategy that can relate the processing conditions to the nanostructure of CNC materials. Beck- Candanedo and coworkers reported that the species that have high crystallinity yield longer and low cross-section crystals, therefore those species yield longer nanocrystals. Long nanocrystals with high aspect ratio (L/D) consequently affect mechanical properties [17]. Therefore, the crystallinity of cellulose affects the length and shape of nanocrystals and also it is a main factor for fabricating nanocomposite [3, 4]. The hydrolyzing agent, SA introduces bulky ester groups onto hydroxyl groups and stabilizes the CNC in solution by preventing their agglomeration [18]. However, using SA accompanies with some important drawbacks such as, potential degradation of cellulose, corrosiveness, and environmental incompatibility.

As alternatives to sulfuric or other mineral acids, we examined MA as an organic acid. Hydrolysis of cellulose with MA gives a high yield of glucose with minimum degradation of glucose [19]. Thus, we hypothesize that under appropriate experimental conditions, MA can produce higher yield of CNC. Further, the two carboxylic group on the first and fourth carbons of this four-carbon dicarboxylic acid can be viewed as 'claws' capable of forming bulky groups when esterified to the hydroxyl groups of cellulose. Also, this may help to stabilize the resulting CNC in solution [20]. The main advantages of lignocellulosic fillers such as waste paper over inorganic fillers are their renewable nature, wide availability throughout the world, nonfood use, low cost, low density, low energy consumption, high specific strength and modulus, and relatively reactive surface [9, 10, 21]. Today waste paper still is a menace to the environment. Therefore, using this residue in nano-sized filler production, as a suitable application, would be environmentally and economically useful. The main goal of this study was to examine the potential of SA and MA to use in the preparation of CNC from waste office paper. Then, the effect of hydrolysis conditions on the morphology, yield, crystallinity and size distribution of CNC were also explored.

EXPERIMENTAL

The raw material used in this study was office waste paper. Other reagents used such as, sodium hydroxide, hydrochloric acid, SA, MA and chloroform were provided from Merck Company.

Cellulose extraction

Extraction of cellulose was carried out in two stages. At the first stage, mechanical treatment was used to separate fibers, and finally non-fibrous materials were removed. Firstly, pulp was prepared by defiberator (fiber separator). Then purification, consists of the removal non-fibrous materials, was accomplished by adding %1 sodium hydroxide at 50 °C and 1 M hydrochloric acid at 70 °C for 1 hour. After treatment, samples washed with distilled water. At the second stage, none-cellulosic materials (hemicelluloses, lignin) were removed by adding %17.5 sodium hydroxide according to Tappi standard (T 203 cm instruction).

Preparation of CNC

Suspensions of CNC were prepared by hydrolyzing obtained cellulose. The extracted cellulose was separately hydrolyzed with an organic acid (MA) and a mineral acid (SA) at 45 and 60 °C temperatures for 120 and 90 min with 7M acid. Immediately, after acid hydrolysis, the suspensions were diluted 10 times with deionized water to quench the reaction. The suspensions were centrifuged (Z36HK, Hermle) at 12000 rpm and 15 °C for 10 min to concentrate the cellulose and remove excess aqueous acid. The resultant precipitate were rinsed, recentrifuged, and dialyzed against water until achieving constant neutral pH. The aqueous suspensions were dialyzed with ultrafiltration system by using polysulfone membrane, which has the molecular weight cut-off of 5000 Dalton. Samples were dialyzed until the pH remained constant at pH≈7 to achieve colloidal cellulose particles. The mixture was subjected to repeated sonication (Sonifier, Model U125OHD, Famos) at 10 °C, 40 kHz for 15 min. After that, samples were filtered through ashless Whatman541 filter paper for removal of aggregated particles. At the final stage, resulting suspensions were subsequently stored in refrigerator after adding several drops of chloroform in order to avoid bacterial growth until to be used.

Characterization
Crystallinity Analysis

X-ray diffraction (XRD) patterns of the samples were obtained through an X-ray diffraction (XRD) on a Philips diffractometer (X'pert, the

Netherlands) that was operated at an acceleration voltage of 40 kV, using Cu Kα radiation (λ=1.54 Å). Samples were scanned in a range varying from 5° to 40° (1°/min). Crystallinity indices (CrI) of the extracted cellulose and hydrolyzed samples were determined using Seagal's Method from below equation [22].

$$CrI = (I_{crystalline} - I_{amorphous}/I_{crystalline}) \times 100\%$$
$$I_{crystalline} = \text{intensity at } 22.8°$$
$$I_{amorphous} = \text{intensity at } 18° - 19°$$

Yield

Yield of the CNC were calculated by weighing the final suspensions before and after drying in oven.

Morphology

Morphology of CNC was examined using scanning electron microscopy (Nova, Nano SEM 430, FEI Company) with an accelerating voltage of 15 kV. For CNC observation, a droplet of the CNC suspensions (0.1 wt. %) was put on a glass grid and dried under vacuum before SEM analysis. The dried CNC were coated with gold on an ion sputter coater, various magnification levels were used to obtain images. More than three images were taken and chosen to observe the morphology of all samples. The dimensions of CNC were calculated by microstructure measurement software from the SEM, TEM images, respectively, which were used to illustrate the size distribution.

RESULTS AND DISCUSSION
XRD Analysis
Any chemical or mechanical treatment affects the crystallinity which can affect the size and shape of final CNC. Therefore, here, the crystallinity was studied before and after hydrolysis with MA and SA. Fig. 1(a and b) show the X-Ray Diffraction of untreated cellulose and CNC obtained by SA and MA at different temperatures. In all curves, peaks are observed at:

2θ =14.8, 16.6 and 22.9.

Peaks appeared at 2θ of 22.8 and 18.0°, representing the presence of highly organized "crystalline" cellulose and less organized "amorphous" cellulose structure respectively. It can be obviously seen the intensity of CNC sample peaks are much higher than untreated cellulose, showing CNC samples are more crystalline because of acidic hydrolysis which removes the amorphous

regions of cellulose fibers that result in extraction of CNC [23-25].

In this study, the value of crystallinity index, dimension and yield of CNC hydrolyzed with MA and SA, under different condition, were studied which is shown in Table 1. It was revealed, rising time and temperature the features of CNC obtained by MA improved whereas, the yield and crystallinity of CNC obtained by SA declined.

According to the table, increasing temperature and time from 45 °C to 60 °C and from 90 °C to 120 °C respectively, the crystallinity and yield of CNC obtained by SA decrease, while these features rise in CNC provided by hydrolysis with MA.

Some studies show the single largest drawback of using SA is that it readily degrades glucose at high temperatures required for cellulose hydrolysis. These results suggest that the reaction rates for cellulose hydrolysis are greater than the rates of glucose degradation by MA compared to SA. For 60 min, the amount of hydrolyzed cellulose by MA is (13.8%) slightly more than hydrolyzed by SA (8.23%) [26, 27]. Therefore, increasing temperature has a negative effect during SA process by more degradation of glucose and subsequently less crystalline region can be produced while during MA process more glucose would be hydrolyzed and Xc can be dramatically increased. The second reason of reduction of calculated relative crystallinity is greater hydrolyzation in crystalline areas and occurrence of peeling reaction in crystalline areas at higher temperatures [28, 29]. The effect of hydrolysis time on Xc is shown in (Fig. 1 (a, b) and Fig. 2)

In this study, the crystallinity percentage of initial cellulose was calculated 44.75. The results showed, at constant temperature, increasing hydrolysis time from 90 to 120 min, the crystallinity percentage of CNC obtained by SA and MA was increased compared to the initial cellulose. This finding confirms that rising hydrolysis time the hydronium ions can penetrate amorphous regions of cellulose by promoting hydrolytic cleavage of glycosidic bonds and releasing individual crystallites [30]. At both times (90, 120 min), the Xc of the particles produced by MA was higher than CNC produced by SA. It can be concluded that rising hydrolysis time has a negative effect on SA process because it is a strong acid which would affect crystal areas. These results can be ascribed to the partial destruction of crystalline regions in CNC because of corrosion due to concentrated

SA while, MA is relatively weak acid needs more opportunity for hydrolysis and elimination of amorphous areas [31]. Thus, the amorphous areas are destructed and more crystal areas are released.

Yield of CNC Obtained by MA and SA

The yield of recovered CNC after acid hydrolysis under various experimental conditions is listed in Table 1. Values were calculated according to the weight of cellulose (purified cellulose). The result showed that rising the hydrolysis temperature (from 45 to 60 °C) in MA process improved cellulose nanocrystals yield by 10%, but this had less effect on the yield of CNC obtained by SA. It seems that increasing crystallinity of CNC obtained with MA resulted in improvement of CNC yield. According to XRD analysis, it is resulted that rising of temperature leads to acceleration in

hydrolysis process. Therefore, amorphous region may be more accessible. Furthermore, the results of variance analysis showed that increasing of hydrolysis time from 90 to 120 min, the output of the particles hydrolyzed by SA was slightly decreased (41.4% to 38.7%). in contrast, it made a dramatic increase (from 36.5% to 58.6%) in the yield of samples prepared by MA. Indeed, the yield decreased with increasing the hydrolysis time during SA process, as expected. These findings were attributed to further hydrolysis of cellulosic regions by concentrated acid, although degradation of crystalline regions could not be excluded as a possible cause [31]. However, rising time MA, as a weak acid, had more opportunity to eliminate the amorphous areas. Thus, amorphous areas are destroyed and outputs of MA samples are increased. Interestingly, about the yield of CNC obtained by MA has never been reported.
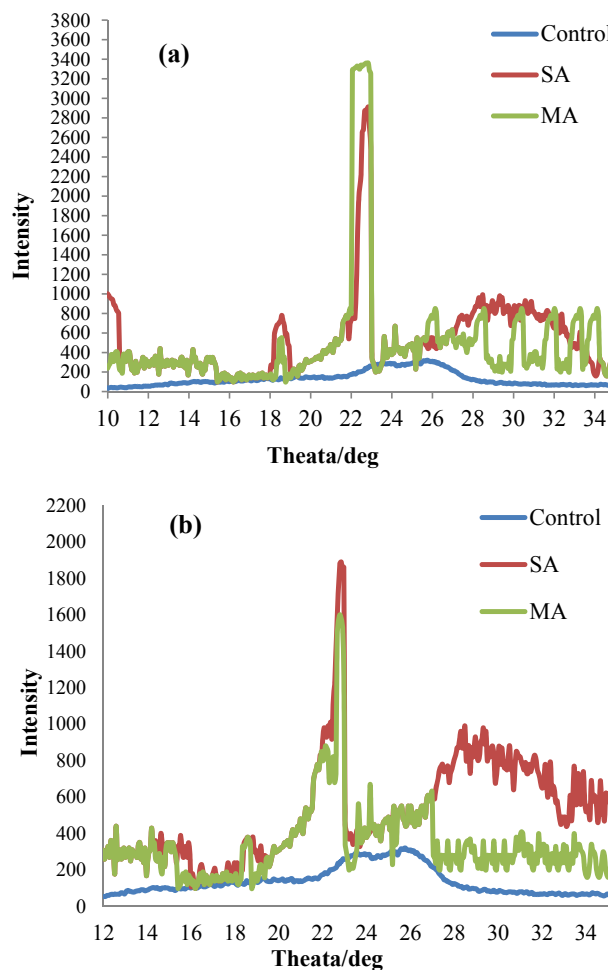

Fig. 1: a) Diffractions of raw cellulose, CNC obtained by SA and CNC obtained by MA, hydrolyzed under 120 min, 7M, 60°C condition.
b) Diffractions of raw cellulose, CNC obtained by SA and CNC obtained by MA, hydrolyzed under 120 min, 7 M, 45° condition.

Table 1: Average diameter (D), Crystallinity index (CrI), and yield of CNC obtained in various hydrolysis conditions.

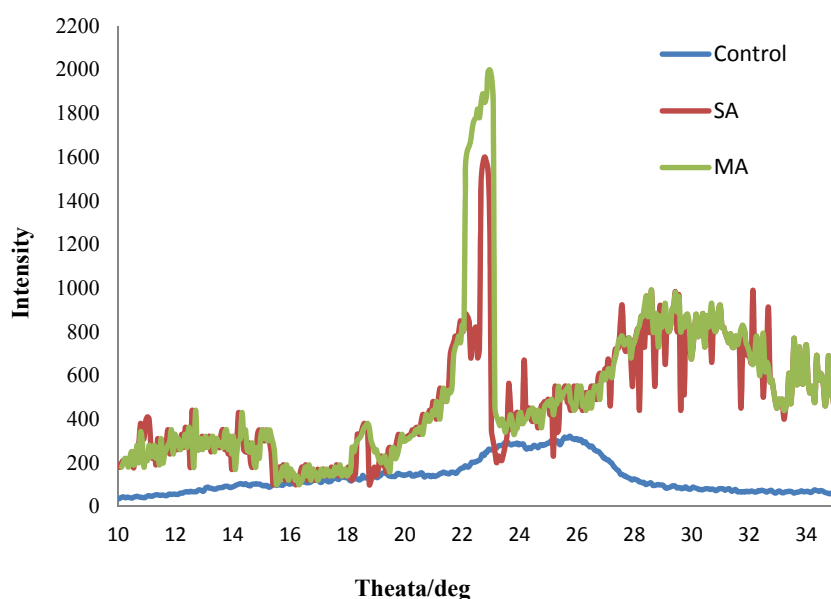| Condition	Acid	D(nm)	CrI(%)	Yield (%)
120min.45^{0}C	MA	41.7±16.5	77.2	38.1
	SA	75.6±16.8	78.8	40
120min.60^{0}C	MA	37±9.4	83.9	58.5
	SA	84.8±23	74.5	37
90min.60^{0}C	MA	55.2±16.5	82.9	36.5
	SA	73.5±13.75	80	41.4

Fig. 2: Diffractions of raw cellulose, CNC obtained by SA CNC obtained by MA, hydrolyzed under 90 min, 7M, 60°C condition.

Characterizations of CNC

The result showed different morphologies and dimensions for CNC obtained by hydrolysis with different acids under the same conditions. Scanning electron microscope (SEM) and transmission electron microscopic (TEM) analysis showed that CNC prepared by MA and SA had spherical shape under 120 min, 60 ^{o}C, and 7M condition (Fig. 3).

In contrast, CNC obtained by hydrolysis with SA and MA under 120 min, 45 ^{o}C condition were spherical and needlelike (Fig. 4).

Morphology of particles is affected by thermodynamic equilibrium and adhesion force during hydrolysis. Also, the result shows CNCs obtained under 90 min, 60 ^{o}C condition were spherical and needlelike, (Fig. 5).Spherical CNC obtained by two different acids are comparable with CNC obtained by sono-chemical synthesis

from Avicel and recycled pulp by hydrolysis of microcrystalline cellulose with a mixture of SA and hydrochloric acid under ultrasonic treatment [21, 33]. Moreover, Ismail's study illustrated in the absence of ultrasonic treatment and the mixed acid (SA and hydrochloric acid in an appropriate ratio) spherical CNC could not be obtained [34]. However, in our experiment, it is proved that spherical CNC can be produced in the same condition which is probably due to agglomeration of CNC during drying samples for microscopy tests. Researchers have reviewed the research which has been conducted on CNC used in composite materials. This group attributes the tendency of fibers for agglomeration or self-association, to "the strongly interacting surface hydroxyl groups". This fiber-fiber interaction inhibits the mechanical reinforcement of the composite that is being filled with CNC. But, as it can be seen, the morphology of

particles is affected by thermodynamic equilibrium and adhesion force during hydrolysis.

Also, the result shows CNCs obtained under 90 min, 60 °C condition were spherical and needlelike, (Fig. 5).

The Effect of Hydrolysis Temperature on the Size Distribution of Cellulose

Fig. 6 shows the effect of temperature on size distribution and diameter of CNC hydrolyzed by SA and MA. Based on the Figures, in SA process, the polydispersity increased significantly by rising the temperature of hydrolysis reaction (Fig. 6(a, b) and Table 1).

For example, the mean diameter and standard deviation were increased from 75.6 to 85.75 nanometers and from 16.87 to 23.35 respectively. By increasing hydrolysis temperature, the heterogeneity is increased in these particles. The results of the study performed by Dong and his coworkers illustrated that the extreme increase of temperature had a negative effect on hydrolysis process with SA. They stated the negative effect of temperature was caused by eliminating sulphone groups were added to cellulose during hydrolysis reaction [35]. Therefore, by eliminating sulphone groups, resulting CNC was without charge that made final nanocrystals agglomerated which

increased the heterogeneity of resulting CNC. Also, Bondenson confirmed, at lowest temperature, the sulphone groups of the CNC rise to maximum [36]. As it is seen in Table 1, increasing hydrolysis temperature resulted in the reduction of diameter and standard division of CNC hydrolyzed by MA (from 41.7 to 37 and 16.15 to 12.43 respectively). Filson believed that MA, as a dicarboxylic acid, can form a stable suspension of CNC by esterification of cellulose chains' hydroxyl groups [21]. Based on this study, the hydrolysis process of MA is relatively different from SA. Thus, CNCs resulted from hydrolysis with MA are esterificated and they don't form negative charges. Probably, by rising temperature, the number of ester groups and heterogeneity of CNC are increased and decreased respectively.

The Effect of Hydrolysis Time on the Size Distribution of Cellulose Particles

In the current study, the average diameter of CNC was calculated by Microstructure Measurement software of microscopic images. The standard deviation of the particles was an index for homogeneity of diameter distribution. Figs 6a, 6b and 7 and the results of variance analysis showed that through increasing hydrolysis time from 90 to 120 min, the average of diameter
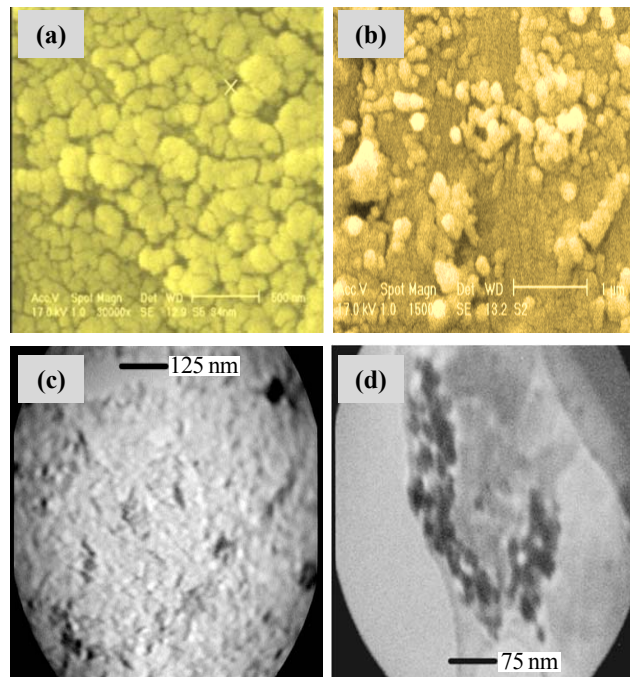

Fig. 3: SEM and TEM images of CNC obtained by MA and SA, hydrolyzed for 120 min, 7 M, 60⁰C, (a): SEM of CNC obtained by MA (b):SEM of CNC obtained by SA (c): TEM of CNC obtained by MA and (d):TEM of CNC obtained by SA.
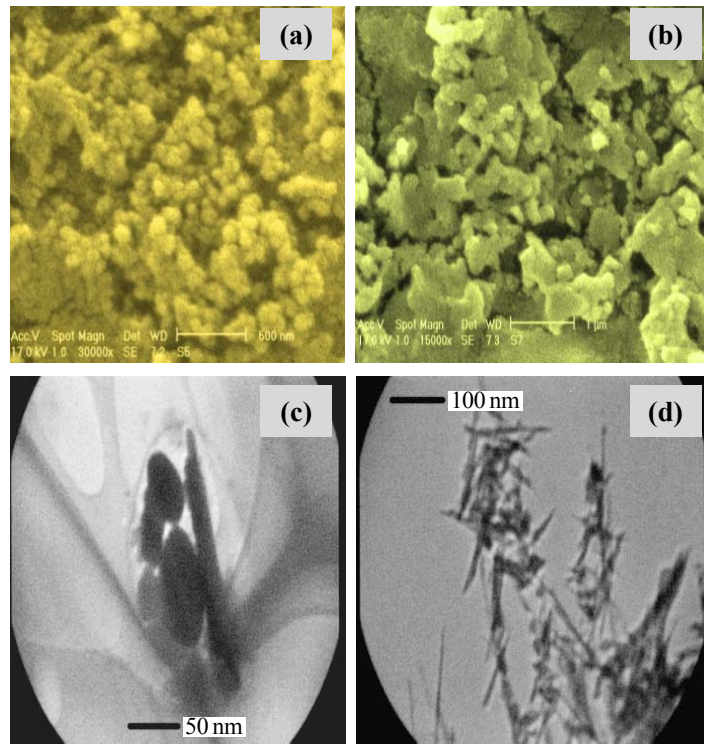
Fig. 4: SEM and TEM images of CNC obtained by MA and SA hydrolyzed for 120 min, 7M, 45 0C (a): SEM of CNC obtained by MA (b): SEM of CNC obtained by SA (c): TEM of CNC obtained by MA and (d):TEM of CNC obtained by SA.
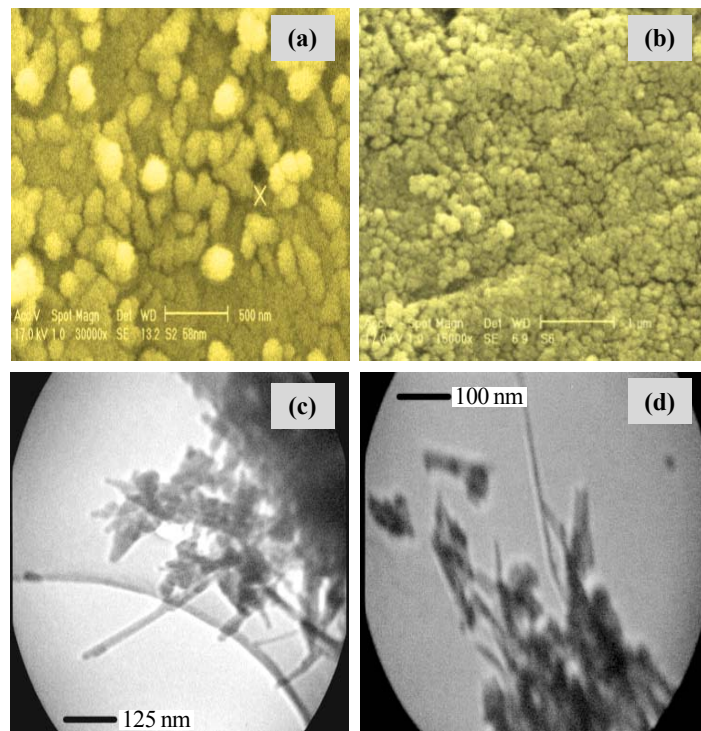

Fig.5: SEM and TEM images of CNC obtained by MA and SA hydrolyzed under 90 min, 7M, 60^{0}C. (a): SEM of CNC obtained by SA, (b): SEM of CNC obtained by MA (c): TEM of CNC obtained by SA and (d): TEM of CNC obtained by MA.
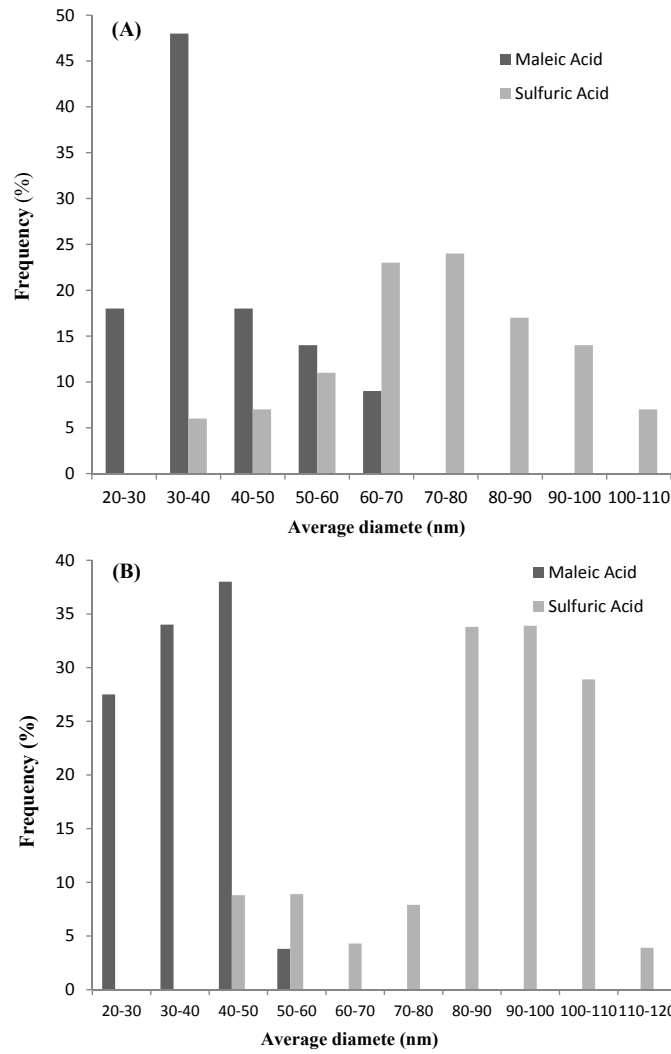
Fig. 6: a) Distribution of average diameter of CNC obtained by MA and SA, hydrolyzed under 120 min, 7M, 45°C condition. B) Distribution of average diameter of CNC obtained by MA and SA, hydrolyzed under hydrolyzed for 120 min, 7M, 60°C condition.
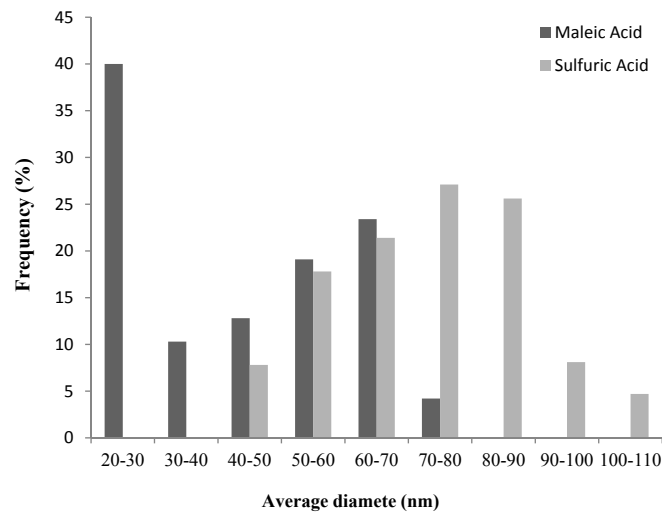

Fig. 7: Distribution of average diameter of CNC obtained by MA and SA hydrolyzed under 90 min, 7M, 60°C condition.

and standard deviation of CNC hydrolyzed by sulfuric acid were increased from 73.5 to 84.8 and from 13.75 to 15.5 respectively. According to some literature, treating cellulose with SA (H_2SO_4) involves the esterification of hydroxyl groups by sulfate ions.

Moreover, introduction of sulfate groups produces a negative charge on the surface of crystals. This anionic stabilization via attraction/repulsion forces of electrical double layers is probably the reason for stability of the colloidal crystalline suspensions [4]. Thus, it was expected increasing hydrolysis time leads in homogeneous particle diameter distributions [17, 18, 37, 38].

Despite these studies, Bondenson reported that considerable evaporation of the nanocrystal suspension is responsible for the agglomeration of CNC and increasing hydrolysis time forms a polydispersity suspension. These results are in a line with the current study.

CONCLUSION

The objective of this study was to extract cellulose, and then to investigate the effect of acid type and hydrolysis conditions on the morphology, size, yield and crystallinity of the CNC obtained from waste paper. The extraction of cellulose consisted of lignin and hemicelluloses removal by chemical treatments. The results indicated that CNC obtained by different acids, hydrolyzed under the same conditions and exhibited different morphologies and dimensions. The results showed that CNC obtained by MA had more crystallinity and high yield compared to SA. Moreover, hydrolysis by MA (120 min, 60 °C and 7M) led to smallest particles, higher crystallinity and yield. The present paper implies that increasing temperature and time during SA process leads to less crystallinity and yield and a heterogeneous suspension while it has a controversy impact on MA hydrolysis. It is concluded that the crystalline domains of cellulose would be more susceptible to SA hydrolysis by rising time and temperature but, MA is a weak acid which doesn't destruct crystalline areas during hydrolysis process. In conclusion, MA can be used as a suitable alternative for SA in production of CNC.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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