



# A fast and efficient approach to prepare starch nanocrystals from normal corn starch



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## ABSTRACT

In present study, simultaneous treatment of corn starch by ultrasound and sulphuric acid hydrolysis was investigated focussing a reduction in starch nanocrystal preparation time while increasing the yield. Different acid/starch concentrations, temperatures, and time durations were assessed through degree of hydrolysis, yield, particle size, and surface charge. It was observed that the method is capable of producing nanocrystals within 45 min with particle size smaller than 100 nm and up to 21.6% yield. The surface charge of nanocrystals was observed to be increased at elevated levels of independent parameters. Round edge nanocrystals with diameters smaller than 50 nm were observed under TEM. The results revealed that sonication during nanocrystal preparation not only preserved the crystalline structure, but also reasonably increased the efficiency of hydrolysis to produce starch nanocrystals. The results of the present study would be of great importance to adopt large scale production of nanocrystals from starch.

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## 1. Introduction

During the last decade, starch nanocrystals (SNCs) have been the subject of invaluable studies due to their abundance, biodegradability and biocompatibility. Over the years, the preparation process of SNCs has been evolved considerably, most evidently by Angellier, Choïnard, Molina-Boisseau, Ozil, and Dufresne (2004). The preparation methods and applications of starch nanocrystals have been reviewed extensively (Dufresne, 2014; Hu, Fu, Huang, Anderson, & Chang, 2015; Kim, Park, & Lim, 2015; Le Corre & Angellier-Coussy, 2014; Le Corre, Bras, & Dufresne, 2010; Lin, Huang, Chang, Anderson, & Yu, 2011; Lin, Huang, & Dufresne, 2012; Mary, Pothan, & Thomas, 2013). From the literature, it was evident that the most commonly used protocols in preparing nanocrystals from starch are mainly based on acid hydrolysis because of its simplicity and controllability, but there are some issues associated with the method; acid hydrolysis is time consuming and the yield or recovery of SNCs are low (Kim et al., 2015; LeCorre, Bras, & Dufresne, 2011a; Le Corre, Bras, Choïnard, & Dufresne, 2012; Romdhane, Arousseau, Guillet, & Mauret, 2015a). These issues

hinder the industrial production and applicability of SNCs, therefore, considerable efforts have been conducted in recent years to overcome the mentioned issues (Jin et al., 2015; Kim, Park, & Lim, 2008; LeCorre et al., 2011a, 2012a; LeCorre, Vahanian, Dufresne, & Bras, 2012b; Romdhane et al., 2015a).

Recently, the application of ultrasound treatment to disperse or break the aggregates of SNC and/or to produce nanoparticles from starch has been the subject of some studies. In 2008, Kim et al. hydrolysed waxy rice starch using  $\alpha$ -amylase enzyme followed by sonication in ethanol. The authors reported that sonication increased the particle size and decreased the X-ray diffraction intensity. Kim, Han, Kweon, Park, and Lim (2013) applied ultrasound on waxy maize starch hydrolysates in two different ways and concluded that sonication increased the yield of starch nanoparticles, but with loss of crystallinity. In another study, Kim, Park, Kim, and Lim (2013) prepared SNCs from waxy maize starch by performing hydrolysis at 4 °C followed by sonication. Bel Haaj, Magnin, Petrier, and Boufi (2013) prepared nanoparticles with low crystallinity or amorphous nature from normal and waxy maize starch using ultrasound treatment. Using ultrasound-assisted oxidation method, starch nanoparticles have been prepared from waxy maize starch with low crystallinity (Sun, Fan, & Xiong, 2014). Goncalves, Norena, da Silveira, and Brandelli (2014)

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treated pinhao seeds' starch by sonication and reported that nanoparticles have been achieved without destructing the crystalline structure. More recently, Jin et al. (2015) reported that real-time sonication increased the performance of cross-flow ultrafiltration system for waxy maize starch SNCs while the structure of SNCs has been preserved.

To the best of our knowledge, most of the published works focused on dispersing the previously prepared SNCs and/or fabricating starch nanoparticles which barely were crystalline and there is no published work regarding the production of nanocrystals by simultaneous acid hydrolysis and ultrasound treatment. Therefore, the objectives of the present study were: i) to investigate the influence of coupling sonication and sulphuric acid hydrolysis on yield, particle size and homogeneity, crystallinity, and surface charge of nanocrystals from native corn starch, and ii) to shorten the preparation time of SNCs to less than an hour. In order to compare the results, the two optimal acid and starch concentration described in the literature were used; i.e. 15% starch slurry in 3.16 M acid solution (Angellier et al., 2004), and 40% starch in acid solution with 4.5 M concentration (Le Corre, Bras et al., 2012). Other studied variables were sonication temperature (10, 20, and 40 °C) and exposure time (15, 30, and 45 min).

## 2. Materials and methods

### 2.1. Materials

Normal corn starch with  $27.4 \pm 1.1\%$  amylose content and sulphuric acid were purchased from Sigma (St. Louis, USA) and Merck (Darmstadt, Germany), respectively. The filtration of starch hydrolysates were performed using MN-619de filter paper (Macherey–Nagel GmbH & Co., Germany) with an average retention capacity of 1–2  $\mu\text{m}$ . At all preparations deionised water was used, unless otherwise specified.

### 2.2. Nanocrystals preparation procedure

The acid hydrolysis procedure to produce SNC was simultaneously performed during continuous sonication using a 40 kHz QuickSonic bath-type ultrasound apparatus (Schüder-Schall Co., Germany) with 350 W nominal power. Initially, the temperature inside ultrasound bath was adjusted to appropriate values (10, 20, and 40 °C), then, dispersions of starch with 15 and 40% (w/w) concentration were prepared in 3.16 and 4.5 M sulphuric acid solutions, respectively. The dispersions were placed immediately at a height of 20 cm from transducer and submitted to sonication at 100% amplitude for 15, 30, and 45 min. The temperature inside the bath was traced real-time using digital thermometer ( $\pm 0.01$  °C) and adjusted to specified value by replacing with appropriate amount of ice water to prevent temperature rise during operation. Treated samples were washed successively until neutrality, filtered by filter paper (1–2  $\mu\text{m}$ ), lyophilised and placed in air-tight containers before performing the experiments. The degree of hydrolysis and SNC yield were calculated as the percent ratio of dissolved solids and hydrolysis residues (after filtration) based on the initial starch weight, respectively.

### 2.3. Particle size analysis

Particle size measurements on nanocrystals were performed at 25 °C using a Vasco-3 particle size analyser (Cordouan Technologies, France) after 30 s homogenisation with ultrasound bath. A value of 1.35 was used as refractive index and particle size distribution of samples were characterised based on cumulants and Pade-Laplace methods. Also, the polydispersity index (PDI) was

measured as the ratio of the square of particle size standard deviation to mean particle size. At least three independent measurements were performed and the data were averaged.

### 2.4. Zeta potential measurement

Zeta potential of nanocrystals,  $\zeta$ , was measured based on microelectrophoresis technique using a ZetaCompact zetameter (CAD Instruments, France) at  $\text{pH} = 7.0 \pm 0.1$  and 25 °C. The data were the mean of at least three replicates.

### 2.5. Degree of crystallinity

X-ray diffraction (XRD) pattern of different samples treated for 45 min were recorded using a Bruker D8 Advance spectrometer (Bruker AXS GmbH, Germany) operating at  $\text{Cu-K}\alpha$  wavelength, target voltage and current of 1.541874 Å, 40 kV and 40 mA, respectively. The scans were performed in diffraction angle ( $2\theta$ ) range of 4–40° at a step size of 0.04°. Relative crystallinity was calculated based on the method described by Hermans and Weidinger (1948).

### 2.6. Morphology

Scanning electron microscopy (SEM) micrographs of starch hydrolysates before filtration were recorded using LEO 1450VP microscope (LEO, Germany). The samples were sprinkled onto double-sided adhesive tapes attached to aluminium stubs, coated for 60 s with gold-palladium using SC7620 sputter coater (Quorum Technologies, UK) and photographed in microscope at an accelerating voltage of 20 kV.

Transmission electron microscopy (TEM) was performed using a Philips CM120 microscope (Philips, Netherlands) with an accelerating voltage of 80 kV. A drop of nanocrystal suspension was deposited onto a carbon coated copper grid, negatively stained with a 2% aqueous solution of uranyl acetate and the image was recorded on a Kodak SO-163 film.

### 2.7. Statistical analyses

The experimental data were analysed through GLM procedure of SAS software version 9.1 (SAS Inc., USA). Statistical significance of samples through mean comparisons were conducted using Duncan's multiple range test at a confidence level of 95%.

## 3. Results and discussion

### 3.1. Degree of hydrolysis

The degree of hydrolysis (DOH) of corn starch samples in relation to different levels of temperature, exposure time, and acid/starch concentrations are illustrated as Fig. 1a & b. As it can be seen, by an increase in treatment time from 15 to 45 min at 10 °C, the DOH increased significantly ( $p < 0.05$ ) from 6.9 to 18.7% and from 4.7 to 16.3% for samples treated in 3.16 (Fig. 1a) and 4.5 M acid (Fig. 1b), respectively. At treatment temperature of 20 °C, the DOH of samples treated in 3.16 M acid was increased significantly from 10.5 to 21.1% by an increase in exposure time from 15 to 45 min (Fig. 1a), while it was increased to a lower extent (8.1–18.6%) in 4.5 M acid solution (Fig. 1b). By elongation of treatment, the DOH of samples treated at 40 °C in 3.16 and 4.5 M concentrations raised prominently from 21.6 to 53.9% and 15.4–39.8%, respectively (Fig. 1a & b).

The results revealed that the efficiency of hydrolysis was strongly temperature dependent, so that the DOH prominently

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