

Synthesis and characterization of starch nanoparticles from cassava Peel

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ABSTRACT

Starch nanoparticles are used as a matrix with natural rubber for tire making, alternative adsorbents for wastewater treatment, drug carriers, packaging materials, emulsion stabilizers and fat replacers. The objective of this study is to prepare the starch nanoparticles from cassava peel by mineral acid hydrolysis using hydrochloric and sulfuric acids and perform the characterization of starch nanoparticles with Fourier transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). It was found that the obtained yield of starch nanoparticles by H₂SO₄ was higher than that by HCl.

Keywords: Cassava peel; Starch nanoparticles; Acid hydrolysis; FTIR; XRD

1. INTRODUCTION

Biodegradable nanocrystals have attracted much attention as new materials in recent decades due to the depletion of fossil resources and environmental threats.¹⁻⁴ These nanocrystals have some outstanding properties compared to their counterparts, microparticles, by filling with rigid materials having a dimension in the range of nanometers.⁵⁻⁷ The rod-shaped cellulosic nanocrystals are widely used as renewable nanofillers for biodegradable nanocomposites.⁸⁻¹¹

Recently, starch nanoparticles have received great interest because they are cheap, abundant, non-toxic, biodegradable and biocompatible.¹²⁻¹⁴ Starch nanoparticles were usually prepared by acid hydrolysis of native starch granules.¹⁵⁻¹⁶ The dimensions of starch nanoparticles were reported to be 6-8 nm thick, 40-60 nm long and 15-30 nm wide.¹⁷⁻¹⁹ They are used as a matrix with natural rubber for tire making, alternative adsorbents for wastewater treatment, nanocomposites, drug carriers, packaging materials, etc.²⁰⁻²⁴

Cassava peel is the residue discarded from cassava processing industries.²⁵ During the processing of cassava tuber to starch, the tuber is peeled off and then taken for starch extraction. Peel is rich in starch content which can be used to synthesize nanoparticles.²⁶

Starch is the second abundant natural homopolymer next to cellulose. The industrial applications of starch include papermaking, adhesives, laundry, construction, textiles, oil exploration, printing, cosmetics, biofuel, biohydrogen, biogas, and food packaging. Starch contains two major components: amylose and amylopectin. Amylose is a linear polymer that exists in a disordered amorphous region. Amylopectin is a branched polymer that contains concentric structures of alternating amorphous and crystalline regions.²⁷ Starch is hydrolyzed with mineral acids to remove amorphous regions retaining crystals.²⁸⁻³⁰

Starch nanoparticles were synthesized from waxy maize,³¹ raw maize³², smooth pea³³, wrinkled pea³⁴, potato³⁵, sweet potato,³⁶ wheat,³⁷ oat, rice, mung bean,, lentil,¹⁶ lima bean, jack bean,³⁸ banana and cassava.¹⁹ Starch nanoparticles were synthesized by mineral acid hydrolysis and enzymes.^{19,35,31,39} The nanocrystals were characterized with FTIR, XRD, SEM, transmission electron microscope (TEM), atomic field microscope (AFM), particle size distribution (PSD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray photoelectron spectrometry (XPS), and Energy-dispersive X-ray spectroscopy (EDAX).^{19,31,39}

The factors affecting the yield of starch nanocrystals by acid hydrolysis are a process of hydrolysis, type of acid, the concentration of acid, amylopectin to amylose ratio in starch, the concentration of starch, time, temperature and agitation speed of hydrolysis.¹⁹ Statistical techniques like Duncan's multiple range test (DMRT) and response surface methodology (RSM) were employed to maximize the yield and minimize the size of nanocrystals.^{19,20}

Nanoparticles are synthesized from the starch of tubers. In this work, an attempt was made to synthesize nanoparticles from the starch of industrial residue to improve process economics. So, the objectives of the present work are to (i) synthesize nanoparticles from the starch of cassava peel and (ii) characterize starch nanoparticles using FTIR, XRD and SEM.

2. EXPERIMENTAL

2.1 Materials

Cassava peel used in the literature was used in this work.⁴⁰ Cassava peel was characterized for starch and amylose.⁴¹

2.2 Extraction of starch from cassava peel

Starch was extracted from cassava peel as follows: The dried cassava peel was milled in a high-speed mixer for 5 min.⁴² The powder was suspended in water in the mass ratio of 1:10, stirred for 5 min and filtered using cheesecloth. The filtrate was allowed to stand for 2 h for the starch to settle. Then, the top liquid was decanted and discarded. Water was added to the sediment in the same mass ratio and the mixture was stirred again for 5 min. The process was repeated thrice. Then, starch in the filtrate was settled and separated for further utilization. After decantation, the sediment was dried at 55°C to constant weight.

2.2 Synthesis of starch nanoparticles

Starch nanoparticles were synthesized by hydrolyzing starch with HCl and H₂SO₄ according to the previous reports.^{19,22}

The prepared starch powder from cassava peel was suspended in 3 M H₂SO₄ at a concentration of 5% (w/w) and incubated in a shaker at 37°C and 100 rpm for 5 d. Then, the resultant solution was filtered using Whatman filter paper. The obtained H₂SO₄ hydrolyzed starch nanoparticles were dried at 60°C to constant weight.

For HCl hydrolysis, the prepared starch powder from cassava peel was suspended in 2.5 M HCl at a concentration of 5% (w/w) and incubated in a shaker at 37°C and 100 rpm for 7 d. Then, the resultant solution was filtered using Whatman filter paper. The obtained HCl hydrolyzed starch nanoparticles were dried at 60°C to constant weight.

2.3 Characterization of starch nanoparticles

Starch nanoparticles were characterized by FTIR and XRD according to the previous literature.⁴³

The particles were mixed with KBr of spectroscopic grade separately and made in the form of pellets at a pressure of about 1 MPa. The pellets were about 10 mm in diameter and 1 mm in thickness. In ALPHA FTIR spectrophotometer (Bruker, USA), the samples were scanned in the spectral range 4000-400 cm⁻¹.

The structural analysis of the samples was evaluated by XRD (X'Pert PRO from PANalytical, the Netherlands) with a scanning rate of 5° per minute. The XRD patterns were obtained over the angular range 2θ = 5–40°.

SEM photographs of samples before and after hydrolysis were taken with a scanning electron microscope (JSM6390, JEOL, Japan). The surface morphology was examined with an accelerating voltage of 10 kV and magnification of 1,500x.

3. RESULTS AND DISCUSSION

3.1 Characterization of cassava peel

Cassava peel was analyzed for starch and amylose. Cassava peel was found to contain 41.85% (w/w) starch⁴⁰ and 6.28% (w/w) amylose. Since total starch content constitutes amylose and amylopectin, amylopectin was calculated by deducting amylose content from total starch. Hence, cassava peel contains 35.57% (w/w) amylopectin.

3.2 Synthesis of starch nanoparticles

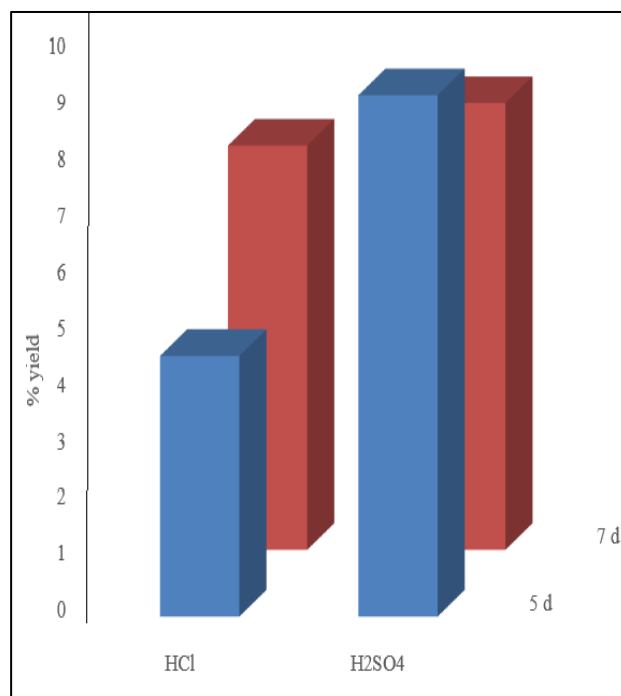


Fig. 1. Percentage yield of starch nanoparticles as the function of 3 M H₂SO₄ and 2.5 M HCl versus 5 and 7 d of reaction time

Nanoparticles were prepared from cassava peel starch having amylopectin to amylose ratio of 5.7 with 2.5 M HCl and 3 M H₂SO₄ at starch concentration of 5% (w/w) at 37°C and 100 rpm for 7 d and 5 d respectively. Native starch with high amylopectin to amylose ratio leads to more yield of nanoparticles. It was found from Fig. 1 that cassava peel yielded 9.8% (w/w) nanoparticles with H₂SO₄ after 5 d but 7.6% (w/w) with HCl after 7 d, i.e. H₂SO₄ yielded more starch nanoparticles in a shorter time than HCl. Hence, H₂SO₄ was considered to be a better mineral acid for the synthesis of cassava starch nanoparticles.

3.3 Characterization of starch nanoparticles

Starch nanoparticles were characterized by FTIR and XRD.¹⁹

The FTIR spectra of cassava starch before and after hydrolysis with HCl and H₂SO₄ at the process condition are illustrated in Fig. 2. The results showed that the chemical structure of starch did not change after hydrolysis. All spectra exhibited the strong broad band of O-H stretching

vibration of the hydroxyl group in the glucose units at 3400 cm^{-1} and the peaks at 2900 cm^{-1} , 1450 cm^{-1} , and 1370 cm^{-1} revealed the C-H stretching and bending of methylene. The peak at 1647 cm^{-1} can be attributed to the bending vibration of H-O-H in the absorbed water. The peaks at 1155 cm^{-1} ,

1080 cm^{-1} , and 1020 cm^{-1} corresponding to the stretching of C-O-C linkages in the glucosidic rings is observed in native starch and HCl hydrolyzed starch nanoparticles whereas it is not observed in H_2SO_4 hydrolyzed starch nanoparticles¹⁹.

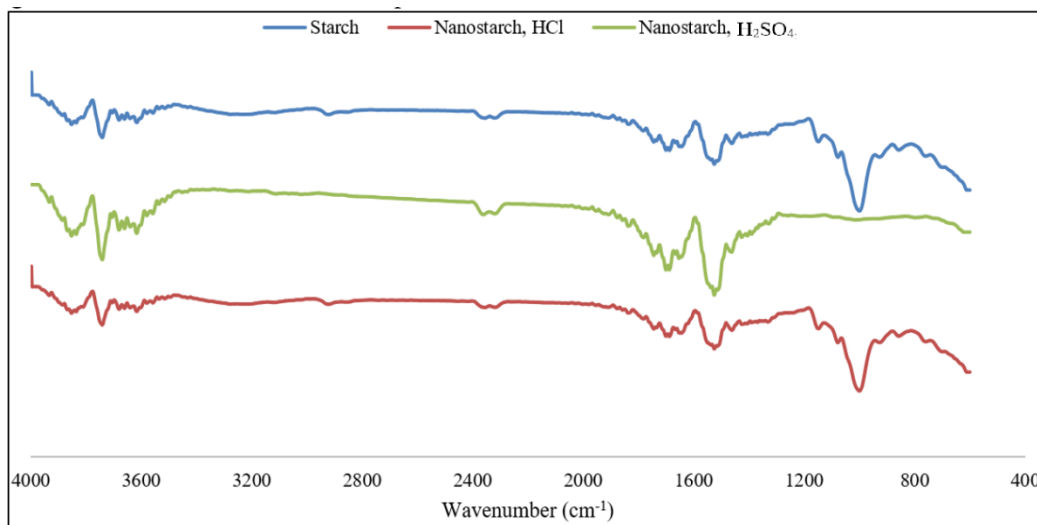


Fig. 2. FTIR of cassava peel starch before and after hydrolysis with HCl and H_2SO_4

The XRD patterns of cassava starch before and after hydrolysis with HCl and H_2SO_4 are shown in Fig. 3. Cassava starch showed the XRD pattern of A-type crystallinity with major diffraction peaks at 15° , 23° , and also a double peak at 17° and 18° . After acid hydrolysis, the results exhibited that the crystalline type of cassava starch was not obviously changed between HCl and H_2SO_4 . However, the diffraction peaks cassava starch nanoparticles

had a higher intensity than those of starch. The higher intensity of diffraction peak indicated that the crystallinity value in the starch nanoparticle structure was increased by acid hydrolysis. During the acid hydrolysis reaction, amorphous regions of the starch structure were attacked easier than crystalline regions, resulting in the increment of crystalline regions in starch structure with loss of amorphous fractions¹⁹.

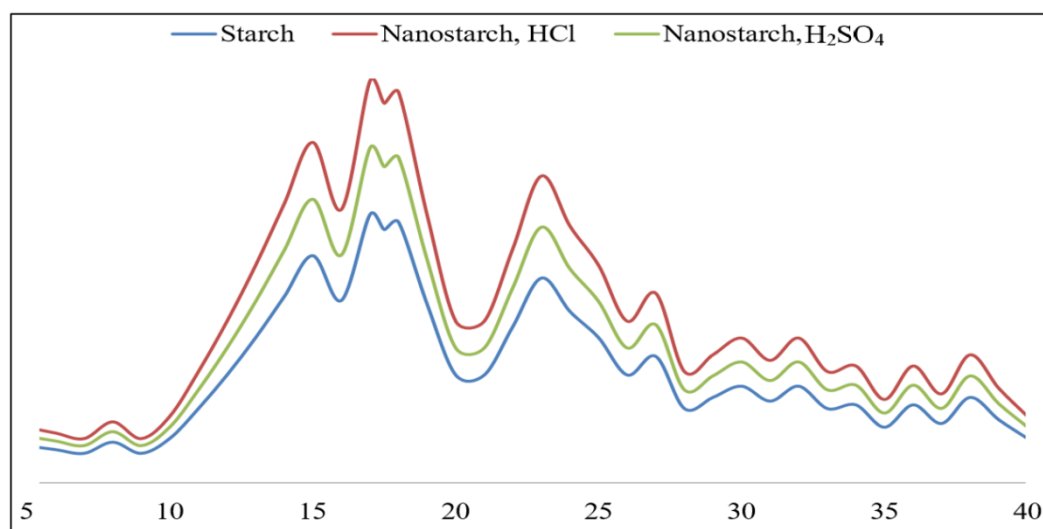


Fig. 3. XRD of cassava peel starch before and after hydrolysis with HCl and H_2SO_4

SEM images of cassava peel, starch extracted from cassava peel, starch nanoparticles prepared using H_2SO_4 and HCl are shown in Fig. 4 (a), (b), (c) and (d) respectively. For the native starch prepared from cassava peel, granules

have semi-spherical shape with an average granular diameter of $17\ \mu\text{m}$. After acid hydrolysis, cassava peel starch nanoparticles showed the porous and rough ruptured granules leading to the reduced particle size. The shape of

starch nanoparticles hydrolyzed by H_2SO_4 and HCl exhibited the regular and irregular spherical shape

respectively which is similar to the banana starch nanoparticle.¹⁹

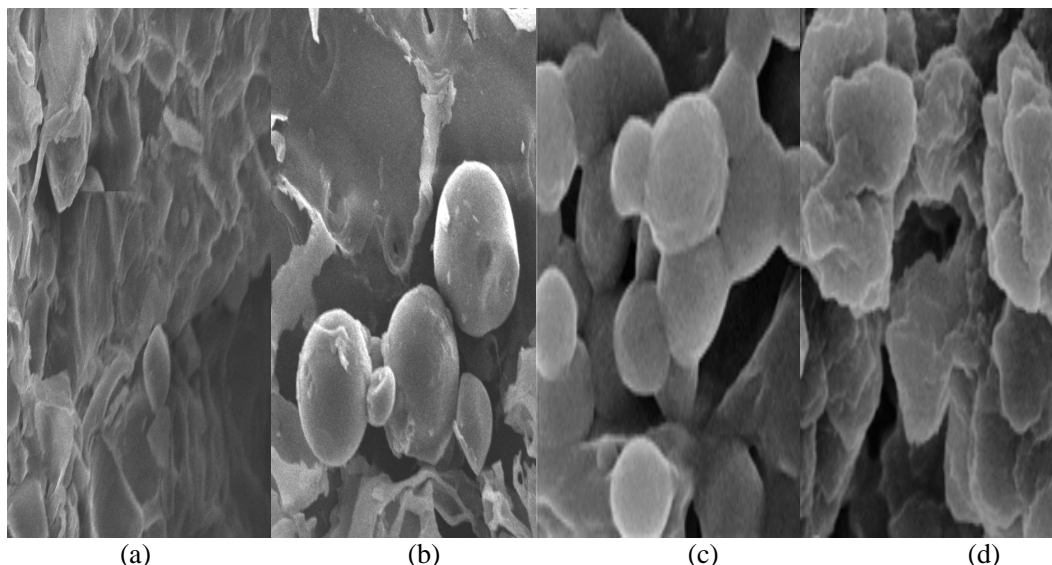


Fig. 4. SEM of (a) cassava peel (b) starch extracted from cassava peel (c) starch nanoparticles prepared using H_2SO_4 (d) starch nanoparticles prepared using HCl

4. CONCLUSIONS

Starch nanoparticles were synthesized from the starch of cassava peel using HCl and H_2SO_4 and characterized using FTIR, XRD and SEM. Cassava peel was characterized for starch, amylose and amylopectin and found to contain 41.85% (w/w) starch, 6.28% (w/w) amylose and 35.57% (w/w) amylopectin. Starch produced from cassava peel was hydrolyzed using HCl and H_2SO_4 to produce nanoparticles. H_2SO_4 yield more nanoparticles than HCl in

a shorter time. Starch nanoparticles were characterized using FTIR and XRD. The FTIR results showed that the chemical structure of starch did not change as a function of hydrolysis. After acid hydrolysis, the XRD results exhibited that the crystalline type of cassava starch was not changed in presence of HCl or H_2SO_4 . After acid hydrolysis, the SEM results showed the regular and irregular shape of starch nanoparticles were obtained using H_2SO_4 and HCl hydrolysis, respectively.

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