Review

Critical review on alterations in physiochemical properties and molecular structure of natural polysaccharides upon ultrasonication

Bin Du, Syam P.K. Jeepipalli, Baojun Xu

Abstract

Natural polymers, such as polysaccharides, cellulose, and starch, have been widely used in the chemical engineering, medicine, food, and cosmetics industries, which had a great many of biological activities. Natural polysaccharides origin from algae, fungi and plants were components of human diet since antique times. Ultrasonication achieved the breakage the polysaccharides reticulum in an ordered fashion. The factors of temperature, ratio of water/material, sonication frequency, time of exposure, pH of the sonication medium influenced the polysaccharide digestion. Sonication improved the enzyme catalysis over its substrate molecule. Positive health promoting slow digestive starch and resistant starch can be prepared quite easily by the sonication process. The aim of this review is to present the current status and scope of natural polymers as well as some emerging polymers with special characteristic. The physiochemical properties and molecular structure of natural carbohydrates under ultrasonic irradiation were also discussed. Moreover, Polysaccharide based films had industrial applications is formed by ultrasonication. Polysaccharide nanoparticles obtained by sonication had efficient water holding capacity. Sonication is an advanced method to improve the food quality. Hence, this review describes the effects of ultrasonication on physical, chemical, and molecular structure of natural polysaccharides.

1. Introduction

Natural polysaccharide derived from grains, fruits, vegetables, and mushrooms are edible components for our daily life. They are good energy providers and health promoters. Starch, arabinogalactans, pectin are different dietary polysaccharides. Starch is a storage homopolysaccharide containing α-D glucose monomers with α-glycosidic bonds. Starch is a natural polymer present in cereals or potatoes, consisting of glucose units. Pectin contained α-α-galacturonic acid monomers with α-glycosidic bonds. Arabinogalactans are galactose polymers with β-glycosidic bonds. Cellulose contained β-α-glucose monomers with β-glycosidic bonds. The digestion of these polysaccharides depends on its chemical complexity.

Owing to safety, physical irradiation is attracting more and more attentions in food and medicine industry. For one review paper published in 2015, the author discussed the potential effect of ultrasound on carbohydrates, especially the glycosylation of oligosaccharides, thio-glycoside syntheses, and azidoglycoside syntheses. The molecular mass of the polymer can be changed by means of various methods of depolymerisation, including ultrasonication, microwave, subcritical and enzyme degradation. In addition, polysaccharides underwent physiochemical and functional changes during preparation, such as ultrasound, microwave and hydrothermal process. The mechanisms of polysaccharides degradation upon ultrasonication are shown in Fig. 1. The possible mechanism is acoustic cavitation via the formation and subsequent collapse of ultrasound-induced bubbles.

Cooking the starch reduces starch content by increasing reducing sugar levels. Cooking the starch foods cause to lose crystalline regions

Abbreviations: CD, Circular dichroism; EPS, Exopolysaccharides; MAE, Microwave assisted extraction; OHAЕ, Ohmic heated assisted extraction; RCI, Relative crystalline index; SNP, Starch nanoparticles; SPS, Sweet potato starch; US-ME, Ultrasound assisted microwave extraction; US-OHE, Ultrasound assisted - Ohmic heating extraction; USE, Ultrasound assisted extraction.

* Corresponding author.
E-mail address: baojuxu@uic.edu.cn (B. Xu).
† Two authors have equal contribution.

https://doi.org/10.1016/j.ultsonch.2022.106170
Received 17 June 2022; Received in revised form 6 September 2022; Accepted 16 September 2022
Available online 17 September 2022
1350-4177/© 2022 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
irreversibly by a process called gelatinization [7]. Ultrasonication is an advanced method of physical processing. Ultrasonication process disrupts the granularity and chemical structure. Ultrasonic digestion increases formation of slow digestible starch (SDS), resistant starch (RS). This lowers glycemic response of foods [8,9]. Enzyme pre-treated banana juice has good yield with ultrasonication (Jyoti et al 2017). Ultrasonication also improved water holding capacity in cereal starch [10]. Different studies have been reported the application of ultrasonication on dietary polysaccharides. Ultrasonification effect is dependent on time of exposure and the applied frequency. Moreover, the stabilizers for food emulsion and polysaccharides microcapsules have attracted extensive attention as polysaccharide application [11].

2. Modified polysaccharides under ultrasound irradiation

2.1. Frost grape polysaccharides

Arabinogalactans are galactose polymer. Type I arabinogalactan had β-1,4 bonds and the type II had β-1,3 type of connecting bonds. The isolated Type II arabinogalactan of frost grape polysaccharide (T-II FGP) had terminal arabinose and mannose residues. It is a viscous fluid that forms stable emulsion with flavouring oils. Adding stabilizers, such as plant polysaccharides, is an effective method to improve the stability of the emulsion [12].

Heating process doesn’t have destructive power on T-II FGP’s primary structure but completely destroyed its secondary and tertiary structures. Experimentally heating reduced the molecular weight (MW) of T-II FGP with no free sugars or oligosaccharides. Similar to heating process, ultrasonication also reduced the MW in T-II FGP. Ultrasonication reduced viscosity which indirectly decreases T-II FGP emulsification effect [13].

2.2. *Pisum sativum* pods polysaccharides

Green pea or *Pisum sativum* is a cholesterol free legume using worldwide. It has spherical shaped seeds nestled in the pods. Polysaccharide from pea pods (*P*₃) is an economic alternative. Sonication increased pea crude polysaccharides (CPF) at 135 W, 30 mL/g water to raw material ratio and 68 °C temperature for 50 min. Sonicated product of CPF is chemically, a mixture of carbohydrate, uronic acid and phenolic compounds or free sugars or bound materials in a ratio of respectively 66.5, 9.2 and 25 %. Sonication caused bond stretching in between O—H, C—H (of CH, CH₂ and CH₃), C==O (of –COOH) and C—O—C, C-OH (of glycosidic ring). Degree of esterification is near similar in CPF analysed by titrimetric method and FT-IR method [14].

2.3. Hazelnut skin polysaccharides

Hazelnut (*Corylus avellana* L.) is commonly used in food industry. Hazelnut skin (HS) contained cell wall polysaccharides, matrix polysaccharides and oils. It has 19.42 ± 0.19 % of oils, 19.04 ± 0.09 % of cellulose. Partial hydrolysis with successive ultrasonication of hazelnut skin promoted the extraction of bioactive polysaccharides. Alkaline hydrolysis also increased cellulose in the final extract. One hour sonication at 400 w contained the highest crude polysaccharide yield. The sonicated polysaccharides have acetyl, xylan, and uronic acid which is an evident for heteropolysaccharide having complete thermal decomposition in between 230 and 350 °C [15].

2.4. Blackcurrant fruits polysaccharides

A previous study described the impact of ultrasound irradiation on the characterization and bioactivities of the polysaccharide from blackcurrant fruits. The reducing sugar content and thermal stability increased with the increase of ultrasound intensity. The degraded polysaccharides contained the same monosaccharide species as those of blackcurrant polysaccharide but at different molar ratios. The results of the bioactivity assays indicated that the ultrasound irradiation could evidently enhance the antioxidant (hydroxyl and superoxide radicals scavenging, lipid peroxidation inhibition, and DNA damage protection activities), α-amylase and α-glucosidase inhibition activities [16].
2.5. Alkali hydrolysis and ultrasonication

The plants such as Aesculus hippocastanum (horse chestnut), Eleocharis dulcis (water chestnut) and Nelumbo nucifera (lotus stem) have the largest quantity of starch. Nanoparticles synthesized from these starch sources have huge commercial utility.

2.6. Citrus pectin

The physicochemical, functional and antioxidant activities of modified citrus pectin treated with a combination of microfluidization and ultrasonication was investigated. [17]. The results showed that modified pectin treated with a combination of microfluidization and moderate ultrasonication (MUB) was found to have the lowest hydrodynamic diameter (418 nm), MW (237.69 kDa) and polydispersity (0.12), and relatively low apparent viscosity among all pectin samples. Moreover, the modified citrus pectin yielded significantly higher DPPH radical scavenging capacity than the original pectin although only slightly the modified citrus pectin yielded significantly higher DPPH radical scavenging capacity than the original pectin although only slightly the modified citrus pectin yielded significantly higher DPPH radical scavenging capacity than the original pectin although only slightly.

2.7. Pectic-polysaccharide from okra

Wu et al. [19] studied the influence of ultrasound assisted metal-free Fenton (H$_2$O$_2$-ascorbic acid system) reaction on structural and biological properties of a pectic-polysaccharide extracted from okra. The ultrasound assisted Fenton treatment could obviously reduce the apparent viscosity, radius of gyration, and branching degree. Additionally, the ultrasound assisted Fenton treatment made no significant changes on the backbone and chain conformation.

In another study, the author applied single- and dual-frequency ultrasounds were used to extract polysaccharides from okra. In addition, the physicochemical characteristics, functional properties, and in vitro biological activities were investigated. The results indicated that ultrasonic extractions at different frequencies led to remarkable variations in the isolated PSP fraction [24]. This study showed new insights into the physicochemical properties of a pectic-polysaccharide extracted from okra. The ultrasound disrupted mycelia microscopic structure, decreased viscosity, radius of gyration, and branching degree. Additionally, the ultrasound assisted Fenton treatment made no significant changes on the backbone and chain conformation.

2.8. Yellow tea polysaccharide

In related work, a study evaluated the effect of ultrasound irradiation on the structural characteristics and antioxidant properties of yellow tea polysaccharides with different MW. The MW sharply reduced. The high-performance liquid chromatography and Fourier transform-infrared spectroscopy analysis revealed a partial degradation of native yellow tea polysaccharide treated with ultrasound; however, the monosaccharide composition was not changed. Moreover, the morphology and the breakdown of native yellow tea polysaccharide upon irradiation altered (Wang et al., 2022). This study showed new insights into the yellow tea polysaccharides under ultrasonication enhanced. However, the MW and protein content reduced [21].

2.9. Panax notoginseng flower polysaccharide

In one study, the yield, physicochemical characteristics, structural characteristics, functional properties, and biological activities of Panax notoginseng flower polysaccharide were evaluated using ultrasonic disruption. The results showed that the yields, uronic acid contents, total phenolic content, total flavonoid content, water-solubility, water holding capacity, and oil holding capacity of the polysaccharides under ultrasonication enhanced. However, the MW and protein content reduced.

2.10. Guar gum

Guar gum is a powdered endosperm of Cyamopsis tetragonolobus. It has hydroxyl rich galactomannan polysaccharide with repeated units of α-galactose and α-mannose. Sonication process decreased the polysaccharide MW. Molecular aggregation of nanoparticles was diminished by the techniques of centrifugation and dialysis.

**Physicochemical properties:** Intact guar gum or its sonicated forms have no difference in molecular structure but sonication decreasing the MW. Sonication (20 w for 10 min) significantly reduced polymer chain length, MW (75 %) and viscosity. Sonication did not interfere in polymer composition and the ratio for mannuronic acid to glucuronic acid was constant. Sonication reduced viscosity of borax mixed guar gum and caused pseudoplastic texture on long exposure. Hence food industries could tailor the needful form of guar gum [22]. Sonication (60 W, 30 min) enhanced the extent of guar gum depolymerisation in less time period compared to enzymatic degradation alone. Thermodynamic parameters such as activation energy, enthalpy, entropy, and free energy were reduced in the sonicated guar gum. Sonication mediated optimum cavitational activity was more beneficial at 50 °C in enhancing the extent of cellulase mediated guar gum depolymerisation. Molecular structures between the two were not altered.

2.11. Fungal polysaccharides

The fungi Cordyceps sinensis is also called as ‘Chinese caterpillar fungi’. It is an exotic medicinal mushroom in the Chinese and Tibetan systems of medicine. Fungal fruit body, mycelium, was source for polysaccharides - protein complexes. Liquid fermentation process promoted the extraction of 15–20 % of high MW exopolysaccharides (EPS).

Sonication disrupted mycelia microscopic structure, decreased viscosity. It facilitated solid–liquid filtration of normal culture medium and increased pseudoplastic behaviour in the culture medium. The yield for polysaccharide-protein (PSP) complex was inverse relation with broth concentration and direct relation with sonication power and time. Broth concentrations of 0.25 have the highest total water-soluble products but 0.66 conc. contained the highest polysaccharide-protein (PSP) complex. The isolated PSP fraction formed after sonication had a mixture of both EPS and PSP. Gel permeation chromatography confirmed the presence of different peaks in the isolated PSP fraction [24].

The fungi Schizophyllum commune is also called as loose Chinese fan. It is a fleshy, filamentous cosmopolitan fungus. Mycelium contained β-glucan type exopolysaccharides. Sonication has no effect in destroying the primary structure of exopolysaccharides (EPS). Sonication reduced native EPS MW to 197 kDa to 1437 kDa fragments and caused to decrease its viscosity. This physical digestion process stretched the bonds for O–H, C–H, and increased absorbance for C–O–C, C–O–H.
link bonds [25].

*Inonotus obliquus* is a fungal phytoparasite rich in melanin. Its polysaccharides (IOP) offering medicinal property are the chief components. IOP yield is affecting by factors of sonication power, temperature, and time of exposure. Hot water extractions have more IOP yield than sonication; longer the sonication time greater is IOP extraction yield. The sonication factors of 100 W, 35 °C were time dependently increased IOP recovery. The order of increase is 80 > 70 > 60 > 50 min. Varying the temperature with constant factors of 100 W, 80 min has different IOP yield. The order of increase is 75 > 95 > 85 > 55 > 65 °C. The obtained IOP yield was comparably higher than hot water extract. Sonicated IOP have decreased MW compared to polysaccharides of hot water. Sonicated polysaccharides have smaller particles or pieces and some larger aggregates in a shape of flaky and smooth. Non-sonicated hot water polysaccharides have aggregated, feather like morphology. The obtained polysaccharide granules have different granule strength. Gelatinization enthalpy was in an order for UPS-80 > UPS-160 > UPS-95. Compared to hot water extract, UPS-80 has the highest gelatinization enthalpy [26].

*Volvariella volvacea* is an edible mushroom. It has therapeutic polysaccharides or polysaccharide-protein/peptide complexes. These polysaccharides were used for developing nutraceutical products. Ultrasonication increased polysaccharide yield at 20 KHz sonication frequency, 150 W, 60 °C for 30 min with liquid to dried fruiting body ratio (10:1 to 30:1). Hot water extraction (100 °C, 2 h) is not appraisal in achieving the polysaccharide yield compared to ultrasonicated method. Ultrasonication has higher polysaccharide yield (8.28 ± 0.23 %) which is correlating with the predicted yield (8.32 %).

The obtained polysaccharide is a glucan type containing monosaccharide composition of 0-glucose, 0-mannose, and 0-galactose. Ultrasound breaking the sugar side chains (0-galactose, 0-mannose) and increased the 0-glucose ratio higher than hot water extract. High pressure size exclusion chromatography revealed that polysaccharide fractions were three for ultrasonicated and two for hot water extracts. Sonication and hot water extracts have similar levels of low protein, nucleic acid content [27].

Fermented broth of *Cordyceps sinensis* consisted high MW exopolysaccharides. Sonication decreased the MW by breaking the exopolysaccharide. The product of sonication has less in MW, intrinsic viscosity and versatile solubility compared to native form. The structure of the sonicated product was 0-glucan with glucose side chains attached to O-6 position. It is a good moisturising agent for food and cosmetics with reference to chitosan and urea [28].

Interesting, the fungus *Trametes robiniophila* *Murr* is a traditional Chinese medicine member commonly called as Huaiya. The exposure time of 36.8 min extracted 36.8 ± 0.12 % of polysaccharides at other specifications 5.3 W sonication, 68.9 °C temperature and liquid to solid ratio of 46 mL/g. Carbohydrate was predominant in the final yield with monomers in the concentration order of glucose > xylose > mannose > arabinose > fucose [29]. Sonication power of 109.8 W produced experimental polysaccharide yield 7.49 ± 0.14 % at the extraction time, temperature, water to raw material ratio respectively 42.2 min, 40.2 °C and 30.6 mL/g. Further, these *Trametes orientalis* polysaccharide yield has concentration dependent increase in antioxidant property [30].

Sonicated spores of *Gonoderma lucidum* lost their original chitosan morphology, smoothness and created pores over. It also increased degree of deacetylation, but extended reaction time and temperature was lowered. The conversion efficiency of chitin to chitosan was high under sonication and degree of crystallinity was tremendously reduced. Degradation velocity was decreased but the thermostability of chitosan was not altered during the deacetylation process [31].

One study evaluated the effect of power ultrasound on the molecular properties of a high-MW exopolysaccharide (EPS) from the Ce-HK1 medicinal fungus. The prebiotic function of the ultrasound-treated EPS fractions in human faecal microflora in vitro was also investigated. The results showed that EPS has remarkable reduction of intrinsic viscosity, average MW and aggregate size in water but no significant changes in the molecular structure [32].

*Flammulina velutipes* polysaccharide: Xiao et al. [33] demonstrated the influences of ultrasound on the degradation kinetics, physicochemical properties, and prebiotic activity of *F. velutipes* polysaccharide. When the ultrasonic intensity increased from 531 to 3185 W/cm², the degradation proceeded faster. Ultrasound changed the solution conformation of *F. velutipes* polysaccharide, and partially destroyed the stability of the triple helix structure of *F. velutipes* polysaccharide. In addition, the viscosity and gel strength of *F. velutipes* polysaccharide decreased, but its thermal stability was improved. At last, ultrasonic degraded *F. velutipes* polysaccharides had better prebiotic activity by promoting the growth of *Bifidobacterium* and *Braunella* and inhibiting the growth of harmful bacteria.

Bioactive polysaccharides of *G. lucidum* mushroom, promote health and longevity. Ultrasound splits the fruiting body polysaccharides into 4 MW fractions an average MW of 465.65 kDa. Sonication phenomenally, decreased polysaccharide’s average MW and contaminant phenolics.

**Chemical properties**: Sonication forces stretched the vibrations of polysaccharide’s glycosidic hydrogen groups, C–C stretching vibration associated with water. It caused disymmetry stretches in C–O–O bonds of pyranose ring and C–H vibrations in both α-type, β-type glycosidic bonds. Sonication final product contained 1 – 3 or 1 – 2, 1 – 4 or 1 – 3, 4 or 1 – 3, 3 – 4, 1 or 2, 3, 4, 6 glycobondic bonds. Sonication destroyed the primary structure of the product which lowered the DPPH radicle scavenging function compared to hot water extract [34].

### 2.12. Algae polysaccharides

Brazil country’s northeast region is an artificial reservoir for red seaweed *Gracilaria birdiae*. Its sulfated polysaccharides (GSP) have applications both in medicinal, pharmacological and food sector. The extracts of GSP - aqueous extraction (AE), AE + sonication (AES), alkali digestion + sonication (AES-P), AES + proteolysis (AES-P) and AlkS + proteolysis (Als-P-P) were differing in polysaccharide content. GPS yield was in the order of AES-P > AES-P > AES-P > AES-P. The extracted polysaccharides have sugar/sulfate ratio in an order of AES > AES-P > AES-P > AlkS > AES-P. The final yield of these different extractions had galactose, glucose, arabinose, and xylose sugars but their proportion was not uniform. Sonication caused asymmetric stretching vibrations in S=O, symmetric C–O vibration in C–O–SO3 groups and the bending vibrations at C–O–S groups. The MW of sonicated extracts was 45 kDa and was similar to aqueous extraction but alkali mediated extraction (in AlkS) decreased the MW to 20 kDa [35].

The application of ultrasonic destruction for decrease in the size of fucoidan molecules could expand the opportunities and spheres of their therapeutic application [4].

The red algae *Pyropia yesoensis* is widely cultivated among the other six porphyra species members of tenera, haitensis, pseudolinearis, dentate and angusta. Edible purple laver *P. yesoensis* is source for vitamin B12 and therapeutic polysaccharides. Its purified aqueous extract contained 6.24 % of polysaccharide with 94.59 % of carbohydrate content. Ultrasonic degradation rate of algal polysaccharides was increased with increase of sonication power, reaction temperature and decreased initial pH value. Algal polysaccharide solution at 0.75 g/dl is critical for micelle formation at 800 W sonication, pH 6.39 and 30 °C temperature. Algal polysaccharide 1.0 g/dl solution was sensitive to sonication at lower pH ranges 6.39, 4.01 and 3.00. It is unclear to explain that acid is a direct cause for sonication digestion at 800 W, 30 °C. Internal viscosity of polysaccharide solution (1.0 g/dl) decreased with ultrasonic temperature and is constant after 2 h exposure time [36].

Additionally, the authors evaluated the anti-glycation effects of polysaccharides from *Ecklonia cava* were examined using different methods, including a combination of ultrasound and enzyme method. The physicochemical properties, monosaccharide compositions, and
structural characteristics analysis results showed that polysaccharides with combination of ultrasound and enzyme method yielded higher sulfate contents. On the other hand, polysaccharides with combination of ultrasound and enzyme method constructively inhibited advanced glycation end [37].

Fucoidan is a cell wall polysaccharide from Sargassum fulvellum. This sulfated polysaccharide contained fucose, uronic acid, and galactose, xylose as building blocks. Fucoidan degradation rate by ultrasonication/sulfate contents. On the other hand, polysaccharides with combination of ultrasound and enzyme method yielded higher B. Du et al. cellulose concentration and 55.79 yield at 20.29 min of sonication time, 78.6 W power output, 2.15 % of ultrasound assisted enzymatic extraction has optimum polysaccharides from 120 to 200 W has significant role in stem polysaccharide yield. Constant sonication factors, time (40 min), temperature (60 °C) and liquid to material ratio of 30 mL/g constant power dependently increased polysaccharide yield and was declined above the power range of 160 W. At 60 °C temperature, 30 mL/g of liquid to material ratio and 160 W time dependently increased polysaccharides yield but was declined above 40 min exposure. Similar study confirmed the highest polysaccharide yield at 30 mL/g of liquid to material and 60 °C of temperature. Physicochemical properties: Sonication caused stretching vibrations in between O—H, C—H, C—O—C and C—O—H bonds of polysaccharide sugar residue. The optimum sonication factors 160 W, 40 min, 60 °C and 30 mL/g liquid to material ratio increased ferric reducing antioxidant capacity. Compare to hot water extracted polysaccharides; sonication product, dose dependently increased total antioxidants, reducing power and DPPH, ABTS radicals scavenging function [42].

2.13. Cydonia oblonga polysaccharides

Peel of quince or C. oblonga, a Tunisian folk medicine contains large amount of polysaccharides. Sonication at 90 °C, 60 min, pH 3.26 had 10.25 % of polysaccharide yield. Sonication freed arabinose, galactose, glucose, xylose, and mannose from its sugar polymers. Sonication increased absorptions for polysaccharide’s hydroxyl groups (O—H), stretching vibrations in acetyl group C=O bonds and carboxylate —COO functional groups. It has 134 kDa of MW in the form of expanded random coil. FTIR spectra depicted clearly that the extracted quince peel polysaccharide is pectin like structure with confirmed presence of galacturonic acid. Abundant arabinose, galactose units confirmed that the quince peel polysaccharides were probably galactoarabinan-I-rich pectin [39].

2.14. Lycium barbarum polysaccharides

Enzyme assisted extractions break the lipid bodies and cell wall of plants. It facilitated the release of intracellular contents and becoming a hallmark of environmentally friendly extraction method. Sonication increased the L. barbarum polysaccharides critical yield at particular of 2 % cellulose presence, 20 min duration, and 80 W input power and 60 °C temperature. Extraction variables of time, cellulose concentration independent in increasing the polysaccharide yield. Time mutual interactions with power output or temperature were insignificant. Ultrasound assisted enzymatic extraction has optimum polysaccharides yield at 20.29 min of sonication time, 78.6 W power output, 2.15 % of cellulose concentration and 55.79 °C of sonication temperature. Experimental polysaccharides yield was significantly not different from the predicted model [40].

2.15. Banana puree polysaccharides

Over ripe bananas on its stage 8 of maturation are called puree. Purified solid residue of puree is a functional ingredient. The factors of temperature, solvent concentration increasing soluble sugars in both solid liquid and ultrasound assisted extraction. For both extraction methods, 1:5 proportion of puree and ethanol solvent mixture time dependently increased the soluble sugars at two different temperature (25 °C, 65 °C) intervals. In the solid liquid extraction, increasing the ethanol ratio decreased soluble sugars at both 25 °C, 65 °C. Ultrasound at 1:5 w/v ratios at 25 °C has increased soluble sugars on 60 and 90 min of time compare to solid liquid method. Increasing the temperature factor to 65 °C rapidly increased soluble sugars in ultrasound compared to solid liquid extraction [41].

2.16. Trapa quadrissiposa polysaccharides

Sijiaoling or T. quadrissiposa is a popular tasty Chinese vegetable. It has stem and fruit pericarp as common waste. Polysaccharides from the discarding waste were good antioxidants. Ultrasound power ranging from 120 to 200 W has significant role in stem polysaccharide yield. Constant sonication factors, time (40 min), temperature (60 °C) and
2.20. Sclerotium polysaccharides

Scleroglucan is secretory β-glucan type polysaccharides from sclerotium species. Sonication increased its solubility by denaturing the physical structure with no damage to primary structure. The pseudo-plastic behaviour decreased gradually after 10 min exposure [46]. Sonication reduced the scleroglucan viscosity at 30 min exposure but 10 min exposure break chain backbones to one half of the MW. This process facilitated the scleroglucan gel formation in the presence of borate ions and anisotropic elongation [47]. Sonication at 65 % of maximal output for 10 – 20 min was the simple and rapid preparation method of an insoluble xylan substrate – used to screen for xylanase expressing bacteria in the microbial population [48].

2.21. Bacterial curdlan

Sonication decreased curdlan viscosity from its 15 min exposure in variable concentrations. The quality of decreasing viscosity was time dependently increased in low concentrated curdlan solution. Sonication process time dependently, decreased the average MW. This was high in low concentrated curdlan and contrary for higher concentrations. Curdlan z average radius of gyration was time dependently increased in the early 30 min exposure and was decreased after, in all different concentrated solutions. The random coiled curdlan was intact even after sonication, which is a confirmatory of mechanical degradation. The FTIR structural analysis confirmed that, the sonicated and native curdlan molecules have no variations in stretching vibrations except O—H stretching vibrations increased on increasing sonication time. This study confirmed that the ultrasound treatment is simple and effective to degrade β-glucan for improving bioactivities and functions [49].

Ultrasonication caused the formation of hydrogen bonds, amide linkages between chitosan and xanthan gum for the formation of core shells in its micro-containers [50]. For the preparation of chitosan capped silver nano-bunches sonication was most helpful [51]. Frequency and time duration of sonication enhanced oxygen delivery for the formation of oxygen loaded chitosan bubbles [52].

2.22. Ornithogalum caudatum polysaccharides

Sonication mediated polysaccharide extraction was directly proportional to time and temperature with maximum at 90 min and 60 °C, respectively. Mass transfer of cell material and solvent ease access was enhanced on sonication. The factors of 100 W–200 W power, temperature 40 °C has obvious polysaccharide yield with a solvent to raw material ratio 1:3 per 100 g. Hence the peer study concluding that, mediating the sonication has been extracted 35 to 38.5 % of polysaccharides from the bulbs of O. caudatum [53].

2.23. Chitosan

Increased use of sonication amplitude decreased the chitosan MW, altered greater chain alignments but the degree of deacetylation was not altered. Ultrasonication time dependently decreased the mean diameter, polydispersity but no alterations in zeta potential and FTIR spectra of chitosan nanoparticles. Significant disarray of chain alignments was noticed in nanoparticle matrix. Sonication amplitude of 80 for 10 min fragmented the freshly prepared dense spherical structured nanoparticles and was remained clear on storage. Since sonication has considerable damage on the chitosan nanoparticles and directly affected their function as a drug carrier [54].

The factors of ultrasonic intensity, time, concentration of chitosan, pH of solution and oil/water ratio influence the size, morphology and dispersibility of chitosan microcapsules. Enhancement of ultrasonic power, time reduced the microcapsule size and made distribution homogenous. Sonication power > 300 W, time > 5 min independently has no role in reducing the microcapsule size. Sonication mediated microcapsules were spherical shaped with clear edged smooth surfaces. The formed microcapsules had no or little influence on the morphology and were similar to free forms of microcapsules. Walls of drug loaded microcapsules offered excellent protection and were have good stability in scooting the drug molecules. They have good property of directional movement under an external magnetic field. Formation of intermolecular imine bonds was responsible for the successful generation of magnetic and pH responsive chitosan microcapsules. Evidently, they have controlled drug release under a stimulatory pH [55].

Additionally, Ren et al. [56] investigated the effects of frequency ultrasound on the properties of zein-chitosan complex coacervation for resveratrol encapsulation. Analysis of multi-model frequency ultrasound treatment effects on resveratrol encapsulation using zein-chitosan complex coacervation showed that 28/40 kHz dual-frequency ultrasound led to the highest encapsulation efficiency (65.2 %; 31.9 % increase) and loading capacity (5.9 %; 31.1 % increase) of resveratrol. The results showed that dual-frequency ultrasound treatment significantly reduced the zein-chitosan complex coacervation particle size and reduced their distribution, however, did not change the zeta potential.

2.24. Radix hedysari polysaccharide (Effect of enzyme combined ultrasonication)

There are a great many of combination method besides untrasonication, such as, enzyme combined ultrasonication, microfluidization combined ultrasonication, ultrasound assisted Fenton treatment and ultrasonication combined electric field. The different ultrasonication modified methods and combined methods are list in Table 1.

Radix hedysari a Fabaceae family member has huge exports from China to all south Asian countries. As a health food, dietary supplement and seasoning agent, R. hedysari is explored for extraction and isolation of bioactive polysaccharides. The polysaccharides of R. hedysari were used as anti-aging, immune enhancing, anti-hypoglycemic, antioxidant and protective from osteoporosis. Conventional aqueous extraction has many disadvantages in regard of polysaccharides, hence complex enzyme combined with ultrasonication introduced as a novel extraction technology. Cellulase, papain enzyme complexes unbound cell polysaccharides from cells and extracted the freed polysaccharides under ultrasonication. Enzyme assisted ultrasonication (EAU) improved carbohydrate content particularly high arabinose-galactose content than the conventional method. EAU decreased immune organs atrophy. Arabinose and galactose content of EAU recognize specific receptors on immunocytes to secrete high levels of TNF-α, IL-6 and INF-γ cytokine markers. Low MW polysaccharides of R. hedysari are the chief cause for high immunomodulatory function [57].

2.25. Dextran

In another study, the degradation rate, the change of MW, the mass fractions of fragments of certain MW, and the degradation kinetics of dextran were compared under ultrasonic and enzymolysis treatments. The results showed that the degradation rate improved greatly and the time required to stabilize the rate was shortened compared with ultrasonic treatment. A lower MW limit was established and the mass fraction of 10^4–10^6 Da fragment increased [58].

2.26. Kappa-carrageenan

These are a family sulphated polysaccharides extracted from red algae. Chondrus crispus and Gigartina stellate are the organism source for k-carrageenan. Food industry use k-carrageenan as thickening, emulsifying and gelling agent. Compared to control, ultrasound treat increased k-carrageenan solubility by decreasing the MW. Ultrasound changed the tight crystalline structure of k-carrageenan to random coils which expose its hydrophilic parts and most soluble in water. Both sonication frequency and time affects the texture of k-carrageenan. Hardness,
springiness properties of k-carrageenan gel is directly proportional to sonication time. High voltage power at short time interval (150 W for 120 s) and low voltage power for long time interval (50 W or 100 W at 180 s) has good potential to improve the gel texture and hardness. Sonication for long time is positively associated with gel gumminess and has negative effect on its cohesiveness [62].

2.27. Okara fibers

Some plant fibers are composed of carbohydrate-based polymers. Fan et al. [63] found the effects of different ultrasound power densities on the microstructural changes and physicochemical properties of okara fibers. The ultrasound treatment of the okara fibers induced structural disorganization and changes, evidenced mainly in their morphological characteristics and their relative crystallinity degrees. Increasing the ultrasound power broke the okara fibers into flaky and stacked structures. When the ultrasound power density reached 4 W/mL, the parenchyma became compact and the hourglass structure fractured.

3. Modified starches under ultrasound irradiation

3.1. Cereal starch

Starch obtained from cereal - yam, cassava and corn contained difference in granularity and amylose/amylopectin ratio. Nanoparticles prepared from cereal starch had wide applications in food and pharma industry. 20 % of ultrasonic amplitude for 30 min formed different sized starch nanoparticles (SNP). The SNP of yam had 8–32 nm particle size, but cassava and corn SNPs contained respectively 35–65 nm and 36–68 nm. The SNPs obtained by cassava starch contained the lowest blue value followed by corn and yam SNPs. Relative crystalline index (RCI) is a direct relation with amylose content of starch. Yam starch has higher amylose than corn starch and the least was observed in cassava starch. The obtained RCI was in an order of the highest for yam followed by corn and the zero was for cassava starch nanoparticles. Starch nanoparticles obtained from yam, corn and cassava starch has thermal decomposition or $T_{\text{max}}$ at 290.27 °C, 306.41 °C and 299.71 °C, respectively [64]. Compared to native starch, ultrasonication formed starch nanoparticle had decrease in size, blue value, relative crystalline index and thermal
decomposition temperature \((T_{\text{max}})\). The formation of starch nanoparticles is illustrated in Fig. 2.

Modified starch is novel food product. Study was designed explore the effects of ultrasonication on starch obtained from wheat, barley, rice, and maize. Sonication disrupted starch granularity and improved the solubility, swelling power. Solubility order is differing from swelling property. Higher solubility was noticed starch of rice, followed by barley, wheat, and maize but the swelling property was the highest in barley starch, followed by maize, wheat, and rice. Ultrasonication caused surface and microstructural changes with minimum effect on the overall integrity of starch granules. The formed starch granules have average size of 15.4 µm for rice, 19.27 µm for wheat, 21.7 µm for maize, and 28 µm for barley. Sonication created greater depression on starch granules resulted pores on its surface. The physical forces of ultrasonication stretched the bonds of hydroxyl (O–H), C–H bond and glucose (C–O–H) bonds of starch particles. Grossly, the ultrasonication improved the formation of resistant starch, rapidly digesting starch, with low levels of slow digestible starch [10].

3.2. Lentil starch

Lentil or *Lens culinaris* is a commonly used dietary pulse. It is rich in carbohydrate (915.9 g/kg) which contained 32–36 % of amylose. Sonication at 33 kHz for 45 min reduced the amylose to 28–34 % compared to native starch-amylose. Solubility index, swelling index was increased in sonicated starch. The increased swelling index was similar to native starch at different temperatures. From day-1 to day-3, the degree of retrogradation or syneresis was similar both for native and sonicated starch forms but on the day-4 and day-5 it was decreased in sonicated starch compared to native form. Sonication decreased light transmittance in a time dependent manner which was an attribute of syneresis. Sonication decreased the protein content and became a cause for decreasing the starch emulsion capacity. Sonication increased significantly water absorption capacity and an insignificant for oil absorption capacity. Due to the low power of sonication used, the intensity of absorption bands, X-ray diffraction patterns were similar to the native starch forms [65].

3.3. Cross linked resistant starch (RS4)

Sonication pH dependently from (9 to 12) increased swelling capacity in the starch samples. Increasing the cross linkers increased the starch phosphorous content and was similar for increased pH. Sonicated starch has degraded amorphous and crystalline regions which together a reason for cracks and pores appear over its surface. X-ray diffraction also confirmed reduced crystallinity in the sonicated starch. Resistant starch content was not altered at pH values < 10.5 which was not similar at changing cross linker concentration. Further, sonication and low pH values eased the cross-linked starch access for digestive enzymes. Higher pH values (≥13.5) resistant starch content was increased directly to increased cross linker concentration. Sonication significantly decreased free, inter and intra molecular O–H linkages in the cross-linked samples and had higher extent of P–O bonds of cross-linked starches. Sonicated cross-linked samples have reduced gelatinization enthalpy which is the lowest degree of crystallinity and high extent of cross-linking reactions. However, the size, morphology of sonicated starch granules was similar [66].

3.4. Foxtail millet starch

Sonication increased the degree of substitution, content of resistant starch by elevating amylase and caused to lose rapid digestible starch. Water absorption capacity was significantly increased so was for swelling capacity in a temperature dependent manner. The property of relative crystallinity index was decreased and structurally it has confirmed presence of α–1,4 glycosidic linkages, vibrational stretch in C–O–C bonds, formation of ester carbonyl groups and an increased hydrogen-bonded hydroxyl group. Sonication created pores on starch surface and intense cracks associated on succinimide anhydride treatment [67].

3.5. Rice starch

In one study, the author demonstrated the impact of ultrasonication on the multi-scale structural characteristics of rice starch following short-chain fatty acids acylation. The results revealed that a lower power density ultrasonication improved the reaction efficiencies of acetylation (19 %) [68]. In addition, the ultrasonic-assisted SCPAs-modified rice starch has a lower peak viscosity and setback value.

3.6. Wheat starch

Wheat is accommodating 75 % of starch. Starch contained amorphous amylo and crystalline amylpectin, hence semicrystalline in nature. Intermittent sonication does not have a role in decreasing the starch swelling capacity. Continuous water bath sonication at 200 W, 690 W decreased starch swelling capacity. Starch solubility was increased to 4.33 % at 15 min of 200 W sonication compared to 30 min of exposure. Sonication improved starch turbidity; the highest were at 400 w for 30 min. Control and 200 W, 15 min of sonication have similar turbidity. Ultrasound treatment increased the starch oil absorption capacity. The highest oil absorption capacity was noticed at 200 W for 15 and 30 min. Intermittent sonication at 400 W caused fine fissure on starch surface. Continuous sonication at 200 W decomposed starch granular structure [69].

Hybridized rami cellulose nanofibers with precipitated calcium carbonate and tapioca starch matrix have the highest tensile strength, crystallinity index, moisture absorption and thermal stability properties. The hybridized mixture contained central matrix in which precipitated calcium carbonate was weekly bound to tapioca starch due to calcium clumps. Matrix also has associated rami cellulose nanofibers [70].

3.7. Tomato starch

Wealth is hidden in waste. Tomato (*Solanum lycopersicum*) is used for preparing different products viz. tomato juice, paste, puree, ketchup, and sauce. Pectin a chief natural polysaccharide found in the tomato waste. Pectin is food additive containing α-galacturonide acid monomers which are isomers of α-glucoronic acid. Ultrasound assisted extraction (USE) had the highest pectin yield (15.21 %) at 600 W of power and 8.61 min of time. Increasing the power capacity with time has depleting nature on final pectin yield. Microwaves accelerated the highest pectin yield (18 %) [68]. In addition, the ultrasonic-assisted SCFAs-modified rice starch by elevating amylose and caused to lose rapid digestible starch. Water absorption capacity was significantly increased so was for swelling capacity in a temperature dependent manner. The property of relative crystallinity index was decreased and structurally it has confirmed presence of α–1,4 glycosidic linkages, vibrational stretch in C–O–C bonds, formation of ester carbonyl groups and an increased hydrogen-bonded hydroxyl group. Sonication created pores on starch surface and intense cracks associated on succinimide anhydride treatment [67].

3.5. Rice starch

In one study, the author demonstrated the impact of ultrasonication on the multi-scale structural characteristics of rice starch following short-chain fatty acids acylation. The results revealed that a lower power density ultrasonication improved the reaction efficiencies of acetylation (19 %) [68]. In addition, the ultrasonic-assisted SCPAs-modified rice starch has a lower peak viscosity and setback value.

3.6. Wheat starch

Wheat is accommodating 75 % of starch. Starch contained amorphous amylo and crystalline amylpectin, hence semicrystalline in nature. Intermittent sonication does not have a role in decreasing the starch swelling capacity. Continuous water bath sonication at 200 W, 690 W decreased starch swelling capacity. Starch solubility was increased to 4.33 % at 15 min of 200 W sonication compared to 30 min of exposure. Sonication improved starch turbidity; the highest were at 400 w for 30 min. Control and 200 W, 15 min of sonication have similar turbidity. Ultrasound treatment increased the starch oil absorption capacity. The highest oil absorption capacity was noticed at 200 W for 15 and 30 min. Intermittent sonication at 400 W caused fine fissure on starch surface. Continuous sonication at 200 W decomposed starch granular structure [69].

Hybridized rami cellulose nanofibers with precipitated calcium carbonate and tapioca starch matrix have the highest tensile strength, crystallinity index, moisture absorption and thermal stability properties. The hybridized mixture contained central matrix in which precipitated calcium carbonate was weekly bound to tapioca starch due to calcium clumps. Matrix also has associated rami cellulose nanofibers [70].

3.7. Tomato starch

Wealth is hidden in waste. Tomato (*Solanum lycopersicum*) is used for preparing different products viz. tomato juice, paste, puree, ketchup, and sauce. Pectin a chief natural polysaccharide found in the tomato waste. Pectin is food additive containing α-galacturonide acid monomers which are isomers of α-glucoronic acid. Ultrasound assisted extraction (USE) had the highest pectin yield (15.21 %) at 600 W of power and 8.61 min of time. Increasing the power capacity with time has depleting nature on final pectin yield. Microwaves accelerated the highest pectin yield (25.42 %) at 900 W power, time, and temperature respectively 3.34 min, 88.7 °C. Higher temperature and power (volts) capacity caused a pectin yield of 10.65 % at 60 V and 85 °C. Low frequency of pre-sonication (540 W, 8 min) with subsequent microwave extraction obtained a final pectin yield of 18 %. Low frequency of pre-sonication (450 W, 10 min) with subsequent Ohmic heating (60 V, 5 min) had obtained a yield of 14.60 %. Ultrasound sensitized pectin yield under microwave and Ohmic heating process. Pectin yield was higher in ultrasound assisted microwave extraction (US-ME). USE consumed very less time in obtaining the good pectin yield than US-ME and US-O₃E. Methoxyl pectin is a form of pectin formed by esterification process. It is used as gelling agent. Ultrasound assisted microwave extraction has high degree of esterification and the least was observed in microwave assisted extraction. Gelling strength (degree of esterification) was very low for the ultrasound assisted pectin but was increased in an order of USE < MAE < O₃AE < US-ME < US-O₃E. The obtained pectin of USME has traces of color compared to other extraction methods. Ultrasound treatment caused rupture and cavitation of bubble in the obtained pectin (Sengar et al. 2019). In this study, ultrasonication mediated polysaccharide extraction surpassed the destructive nature of microwave
assisted extraction.

4. Modified cellulose under ultrasound irradiation

4.1. Effect of ultrasound ionic-liquid on cellulose

China is annually producing ~0.7 billion tons of wheat straw, rice straw. These are chemically lignocellulose (LC) complexes with no property to dissolve in water. Ionic liquids show high dissolution rate for cellulose polymers and accessible to enzyme attack and can separate the LC complexes into individual polymer units. LC biomass mix with [Bmim]Cl or [Bmim]OAc ionic liquid with a single frequency of ultrasoundation (on different frequencies) at 80 °C stable temperature for half an hour duration is consider as pre-treated biomass (PTB). Cellulase treated PTB has good yield in [Bmim]Cl ionic liquid, followed by [Bmim]OAc. Cations of ionic liquid solubilize cellulose but more effective dissolution was observed from acetate anions (OAc). Bagasse biomass has high reducing sugar content followed by wheat straw in [Bmim]OAc ionic solution treated ultrasonication. Bagasse is a genuine biomass in both ionic liquids and superior was noticed in [Bmim]OAc [59].

4.2. Sonication effect on cotton cellulose

Sonicated cellulose products have utility in pharmaceuticals, films with inhibitor properties and food additives. 60 % of acid hydrolysis with sonication has been reported of maximum yield for cellulose nanocrystals. Acid or alkaline treatment increased the exposure of hydrophilic moieties which further improved by Sonication. Size of the nanocrystals is not uniform and found an average of 133 ± 14 nm with 10 nm of width. The formed nanocrystals consist of rod like particles. Acid hydrolysis mediated sonication altered O—H groups, C—O— bonds, stretch in C—H, C—C bonds in the formed nanocrystals [71].

4.3. Enzymatic hydrolysis of cellulose and CM cellulose

Cellulose is a water insoluble biopolymer. Cellulase facilitated cellulose and water soluble carboxymethyl cellulose digestion for fermentation source. The sonication power levels of 3, 6 and 15 W enhanced the rate of CMC hydrolysis. Enzyme \( V_{\text{max}} \) values augmented by sonication and was direct proportional to sonication intensity. Michaelis constant (Km) values for the three sonication power intensity were in an increasing order of 2.4 > 4.7 > 11.8 W cm\(^{-2}\). Sonication duty cycle for 20 % had the low Km value for all the three sonication intensity. Sonication intensity of 11.8 W cm\(^{-2}\) significantly decreased the Km value on increasing the duty cycles from 10 to 40 %. An enzyme with high Km has low affinity for its substrate and requires a greater concentration of substrate to achieve its \( V_{\text{max}} \). The \( V_{\text{max}} \) values were in an order of 10 > 20 > 40 % of duty cycles. 10 % duty cycle at 11.8 W cm\(^{-2}\) of sonication intensity is the optimum that possessed 85 % greater \( V_{\text{max}} \) and 53 % reduced Km compared to control. Soluble cellulose is much sensitive for cellulase digestion compared to particulate form. Sonication facilitated solid liquid mass transfer enzyme over substrate and reducing the Km value. Sonication process, loosen the CMC substrate network and enhanced enzyme access to them. Sonication power intensity 11.8 W cm\(^{-2}\), at 10 % duty cycle increased \( V_{\text{max}} \) by decreasing Km value to the different particle size (30, 60 and 290 µm) contained cellulose substrate. High intensity of sonication affected the cellulase rate by decreasing the catalysis. First 5 min of sonication was severely decreased cellulase activity but the subsequent decline in cellulase activity was slowed [72].

4.4. Corn stover saccharification

Ultrasonication has swollen the cellulose biomass by generating cavities. Higher temperature, pressure generated by sonication collapsed the generated cavities and caused dissociation of cellulose biomass. Sodium percarbonate (SP) generates highly reactive OH\(^{-}\), O\(_2\) radicals which depolymerises lignin polymer and decolorized to yellow colour, IR spectra for ultrasonication were similar to the native cellulose biomass but for sodium percarbonate the peak intensities decreased from the native form which evidently removed some of the lignin biomass. Combined treatment of US–SP biomass peak intensities further declined. The sensitivity scale of lignin was in the order of US–SP > SP and nothing for US alone. XRD pattern of US pre-treated has decreased CrI value than the native form and was higher for SP pre-treated cellulose biomass. XRD confirmed that US disrupted the crystalline structure and SP removed the amorphous lignin and contributed synergistically for the effective removal lignin shield over cellulose of corn stover [73].

4.5. Celery cellulose

Ultrasonication assisted alkaline precipitated celery cellulose was used for hydrogels preparation. Celery cellulose and its hydrogels have similar pattern of FTIR spectra which is a confirmatory for no structural damage between the two forms. The cellulose extracted by ultrasonication supplement was smooth and contained parallel sheaths. Hydrogels formed by extracted cellulose has good property for swell in distilled water. Few types of hydrogels have low swelling property due to narrow porosity in the internal structure. Hydrogels carrying short chain fatty acids were deploying easy by ultrasound trigger which is a therapeutic application [74]. Ultrasonication maintained the surface structure intact and increased dye dispersion, mass transfer, dye diffusion into the cellulose fiber. Dying time was comparatively reduced and became eco-friendly by sonication compared to conventional method [75]. Old corrugated container fiber is a low cost feed stock using in the paper industry. It contained cellulose, hemicellulose, lignin, and other impurities. Sequential digestion this fiber with phosphoric acid followed by cellulase hydrolysis and sonication enhanced cellulose nanocrystals yield with increased crystallinity and thermal stability [76].

4.6. Combined pre-treatment of lignocellulose biomass

Sonication facilitated the release of glucan, xylan content in the lignocellulose biomass. The appearance of mannan and galactans was completely disappeared. Study understood that mulberry wood cell walls, xylose resides in the main chain of hemicelluloses while galactose and mannose might present in side chains. Sonication combined pre-treatment is more efficient for optimum delignification compared to alkaline peroxide-based pre-treatment which facilitating the downstream enzymatic hydrolysis. In the pre-treatment process sonication played major roles of breaking the cell wall, deforming the matrix and increased the surface area. Supplemented sonication facilitated the liberation of crystalline cellulose biomass by breaking the covalent and non-covalent bonds. Hence, sonication combined pre-treatment is an ideal approach for subsequent saccharification [77].

5. The application of natural polymers under ultrasonication

5.1. Starch nanoparticles

Starch nanoparticles of lotus stem (LSNP) have the highest size 606.31 ± 15.32 nm, followed by water chestnut (WSNP) 535.21 ± 18.54 nm and lease was horse chestnut starch nanoparticle (HSNP) size of 420.33 ± 20.21 nm. The formed nanoparticles had increased water absorption capacity, but oil absorption was decreased. Transition temperature is directly dependent on gelatinization enthalpy. The formed starch nanoparticles have higher transition temperature compared to native starch. Ultrasonication decreased nanoparticle crystallinity, increased elastic behaviour and viscosity. Sonication also increased the Van der Waal forces further promoted amorphous texture. Chemical (alkaline), physical (sonication) digestion disappeared starch crystallinity. The formed nanoparticles have semicrystalline and amorphous
domains. Nanoparticles have bond stretching in glucose ring O—H bond, –CH₂, C—O bond, C—O—H and C—O—C groups. Three nanoparticles have identical band pattern in FT-IR spectrum. Nanoparticles have β-glycosidic links and are water bounded. Sonication disrupted nanoparticles of starch granularity. Rough, uneven exterior with cavities found in HSNP, LSNP but WSNP turned to large fragments besides small particles [78].

5.2. Starch films

China is widely cultivating country for sweet potato. It is rich in starch named sweet potato starch (SPS). SPS have intermolecular, intramolecular hydrogen bonds which are a direct cause for its poor solubility. Amylose is one of the structural components of SPS containing hydrophobic regions in its internal structure. Low power ultrasonication separated amylose from starch and increased the formation of amylose-lauric acid (ALA) complexes. The process of starch films is illustrated in Fig. 3.

The amount of ALA complex formation is directly dependent on ultrasonic amplitude and the optimum was observed at 40 % with a yield of 41.1 %. Ultrasonication decreased the gelatinization enthalpy in sweet potato starch and promoted the formation of less ordered ALA complexes at 60 °C and both less ordered and semicrystalline ALA complexes at 90 °C temperature. High ultrasonic amplitude accelerated deterioration of the formed ALA complexes. The formed ALA complexes had V type of crystal pattern at 40 % ultrasonication amplitude. Evidently, V type crystal contained helically arranged six α-glucosyl residues. The light transmission value for the formed ALA film is directly dependent on the ultrasound density. Higher the light transmission value grater will be ALA film homogeneity. ALA film formed at 40 % of ultrasonication had higher TS value, which explains the formed film polymer is more tight and compact. ALA film formed in ultrasonication has smooth contentious uniform structure with the lowest water vapour permeable property [79,80].

5.3. Chitosan emulsions

Chitosan, a naturally occurring cationic polysaccharide is a second abundant biopolymer. High intensity ultrasonication treated chitosan has no effect on the amino groups and was similar to native chitosan. Sonication broken the insoluble chitosan aggregates and promoted their assembly into compact chitosan nanoparticles. Strong electrostatic repulsions caused negligible agglomeration due to protonated chitosan. Hence the impact of ultrasonication was significant at higher pH ranges. DLS particle size analyser was reported of chitosan agglomerate disappearance. Hence average diameter decreased more at higher pH range. Increasing sonication time decreased the chitosan solution MW and complex viscosity. High intensity ultrasonication treatment has higher surface activity and faster absorption at the oil / water interface. Hence chitosan is a pH-controlled emulsifier and use in food and non-food applications [81]. Ultrasonication increased the chitosan mat porosity by 17.3 % compared to non-sonicated neutralised chitosan nanofibers. It also decreased water absorption time from 110 to 9 s which is comparably better than surgicel and chitosan sponge [82,83].

5.4. Potato starch pitting

Ultrasonication has no effect on starch granules and pit size over the starch granules. The characteristic peaks for native starch and waxy forms became similar quite after sonication. FTIR absorption peaks for native and waxy starch forms were identical and no new bonds formed or destroyed upon sonication. Both starch forms have similar mono-disperse size distribution. The number of pits formation on starch granules is dependent on sonication intensity and was directly proportional. Amylose content of starch or granular surface property modification by sodium dodecyl sulphate, ethanol was also not having any impact on the number of granular pits. Higher sonication frequency formed smaller cavitation bubble which gets collapse and form as small size pit over waxy starch granules. Magnetically the formed pit does not have significant size difference which was verified by scanning electron micrograph [84].

5.5. Pectin for enhanced 2-furfurylthiol encapsulation

Recent research studied 2-furfurylthiol to compare the encapsulation feasibility of emulsion made with original pectin and ultrasound-treated pectin. The results showed that when used as the encapsulation wall material, the ultrasound-modified pectin had significantly enhanced performance compared with the original, in terms of flavour retention over time at 45 °C and 65 °C [85,86].

6. Conclusions and perspectives

Carbohydrates naturally occurring in nature which are functional and structural biomolecules with distinctive structures, include polysaccharide, cellulose, and starch. Ultrasonic modification emerged as the superior strategy to obtain good polymers with useful physicochemical properties and molecular structures. Moreover, the corresponding applications of these natural polymers modified upon ultrasonication are elaborated. It is critical to enhanced noncovalent and covalent interactions of polymers using ultrasonication combined with other advanced technologies, especially enzyme combined ultrasonication, microfluidization combined ultrasonication and alkali hydrolysis combined ultrasonication. In future, nanoparticles, films, emulsion, microcapsules powder are effective methods to improve the function of polysaccharide. In the end, a summary of this promising research field is offered and an outlook for the future is given. It is expected that advances in ultrasonifications of natural polymers would provide new avenues for different applications, such as food, tissue engineering, and biomedical diagnosis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Data availability
Data will be made available on request.

Acknowledgement
This research was jointly supported by two grants, one grant (2162Z3201G) from Science and Technology Department of Hebei Province and one (R202107) from BNU-HKBU United International College, China.

References

[1] Y. Chen, Y. Liu, M.M.R. Sarker, X. Yan, C. Yang, L. Zhao, X. Lv, B. Liu, C. Zhao, Structural characterization and antiadhesive potential of a novel heteropolysaccharide from Grifola frondosa via iBSI/PEK-INK signaling pathways, Carbohydr. Polym. 198 (2018) 452–461, https://doi.org/10.1016/j.carbpol.2018.06.077.

[2] S. Ben, D. Mondal, J.T. Martin, M. Singh, Potential effect of ultrasound on carbohydrates, Carbohydr. Res. 410 (2015) 15–35, https://doi.org/10.1016/j.carres.2015.02.008.

[3] R. Cui, F. Zhu, Ultrasound modified polysaccharides: A review of structure, physicochemical properties, biological activities and food applications, Trends Food Sci Tech 107 (2020) 491–508, https://doi.org/10.1016/j.tifs.2020.11.033.

[4] V. Suprunchuk, Ultrasonic-treated fucoidan as a promising therapeutic agent, Polim. Med. 51 (2) (2021) 85–90, https://doi.org/10.1016/j.jpm.2021.03.001.

[5] Y. Yi, W. Xu, H.K. Wang, F. Huang, L.M. Wang, Natural polysaccharides experience physicochemical and structure changes during processing: A review, 115896, Carbohydr. Polym. 234 (2) (2020), https://doi.org/10.1016/j.carbpol.2020.115896.

[6] S. Wei, G. Lu, H. Cao, Effects of cooking methods on starch and sugar composition of sweet potato storage roots, PluT ONE 12 (8) (2017), https://doi.org/10.1371/journal.pone.0182604.e0182604.

[7] W.S. Ratnayake, D.S. Jackson, Starch gelatinization. Advance. Food, Nutr. Res. 55 (2011) 45–136, https://doi.org/10.1016/j.alfnr.2011.03.001.

[8] C. Cihadiye, E. Mustafa, The effects of different processes on enzyme resistant characteristics of polysaccharides from okra extracted by using ultrasound at different frequencies, Food Chem. 361 (2021) 130138, https://doi.org/10.1016/j.foodchem.2021.107085.

[9] B.W. Jo, S.K. Choi, Degradation of fucoidans from Sargassum fulvellum and their effect on enhancing antioxidant activity, Carbohydr. Polym. 110 (2014) 278–284, https://doi.org/10.1016/j.carbpol.2014.04.034.

[10] L.F. Zhu, Z.C. Yao, J.S. Li, M.W. Chang, Synthesis and evaluation of herbal chitosan from Ganoendra lucidum sporium powder for biomedical applications, Sci. Rep.-UK 8 (1) (2018) 1–12, https://doi.org/10.1038/s41598-018-28085-5.

[11] Y. Mao, A. Song, H. Li, Y. Yang, Z. Yao, J. Wu, A high-molecular weight polysaccharide from the Co-HK1 fungus: Ultrasound degradation, characterization and in vitro fecal fermentation, Carbohydr. Polym. 246 (2020), https://doi.org/10.1016/j.carbpol.2020.116636.

[12] J. Xiao, X. Chen, Q. Zhao, L. Zhong, Q. Hu, L. Zhao, Effects of ultrasound on the degradation kinetics, physicochemical properties and prebiotic activity of Flammulina velutipes polysaccharide, Ultrason. Sonochem. 82 (2022), https://doi.org/10.1016/j.ultsonch.2021.109901.

[13] J. Peng, P. Peng, X. Song, X. Yang, B. Liu, D. Qiu, Recent advances in improving stability of food emulsion by plant polysaccharides, Food Res. Int. 137 (2020) 491–498, https://doi.org/10.1016/j.foodres.2020.109376.

[14] Y. Liu, G. Gong, J. Zhang, S. Jia, F. Li, Y. Wang, S. Wu, Response surface methodology for efficient recovery of polysaccharide from Schizophyllum commune as a potential substrate for modified drug delivery systems, Biomed Res. Int. 2013 (2013) 1–11.

[15] F.J. Cai, L.S. Qian, W.J. Sun, J.S. Zhang, Y. Jiang, N. Li, H.N. Zhang, D. Wu, Ultrasound-assisted extraction of polysaccharides from Volvariella volvacea: process optimization and structural characterization, Molecules 23 (7) (2018) 1706, https://doi.org/10.3390/molecules23071706.

[16] X. Chen, K.C. Siu, Y.C. Cheung, J.Y. Wu, Structure and properties of a (1–3)–D-glucan from ultrasound-degraded exopolysaccharides of a medicinal fungus, Carbohydr. Polym. 106 (2014) 270–275, https://doi.org/10.1016/j.carbpol.2014.02.040.

[17] Y. Wang, Y. Liu, Y. Hu, Optimization of polysaccharide extraction from Trametes robiniophila and its antioxidant activities, Carbohydr. Polym. 111 (2014) 324–332, https://doi.org/10.1016/j.carbpol.2014.03.041.

[18] Y. Zheng, Y.L. Li, W.D. Wang, Optimization of ultrasound-assisted extraction and in vitro antioxidant activities of polysaccharides from Trametes orientalis, Carbohydr. Polym. 111 (2014) 315–323, https://doi.org/10.1016/j.carbpol.2014.04.034.

[19] J.P. Zhu, Z.C. Yao, S. Xi, Z. Zhang, M.W. Chang, Synthesis and evaluation of herbal chitosan from Ganoendra lucidum sporium powder for biomedical applications, Sci. Rep.-UK 8 (1) (2018) 1–12, https://doi.org/10.1038/s41598-018-28085-5.

[20] Y. Yao, A. Song, H. Li, Y. Yang, Z. Yao, J. Wu, A high-molecular weight polysaccharide from the Co-HK1 fungus: Ultrasound degradation, characterization and in vitro fecal fermentation, Carbohydr. Polym. 246 (2020), https://doi.org/10.1016/j.carbpol.2020.116636.

[21] J. Kaur, B.S. Gill, Effect of high-intensity ultrasound treatment on nutritional, rheological and structural properties of starches obtained from different cereals, Int J Biol Macromol 126 (2019) 367–375, https://doi.org/10.1016/j.ijbiomac.2018.12.189.

[22] B. Du, H. Zeng, X. Zhang, M. Zhang, Effects of ultrasound treatment on the physicochemical properties and DPPH radical scavenging activity of polysaccharides from mushroom Inonotus obliquus, J. Food Sci. 75 (4) (2010) C22–C27, https://doi.org/10.1111/j.1750-3841.2010.01950.x.

[23] A.L. Prapajat, P.B. Subhendar, P.R. Gogate, Ultrasound assisted enzymatic depolymerization of aqueous gum gun solution, Ultrason. Sonochem. 29 (2016) 84–92, https://doi.org/10.1016/j.ultsonch.2015.09.009.

[24] Y.C. Cheung, X.X. Liu, W.Q. Wang, J.Y. Wu, Ultrasound disruption of fungal mycelia for efficient recovery of polysaccharide–protein complexes from viscous fermentation broth of a medicinal fungus, Ultrason. Sonochem. 22 (2015) 243–248, https://doi.org/10.1016/j.ultsonch.2014.05.006.

[25] B. Du, H. Zeng, Y. Yang, Z. Bian, B. Xu, Anti-inflammatory activity of polysaccharide from Schizophyllum commune as affected by ultrasonication, Int. J. Biol. Macromol. 91 (2016) 100–105, https://doi.org/10.1016/j.ijbiomac.2016.05.052.

[26] L. Fu, H. Chen, P. Dong, X. Zhang, M. Zhang, Effects of ultrasonic treatment on the physicochemical properties and DPPH radical scavenging activity of polysaccharides from mushroom Inonotus obliquus, J. Food Sci. 75 (4) (2010) C22–C27, https://doi.org/10.1111/j.1750-3841.2010.01950.x.

[27] C. Cihadiye, E. Mustafa, The effects of different processes on enzyme resistant characteristics of polysaccharides from okra extracted by using ultrasound at different frequencies, Food Chem. 361 (2021) 130138, https://doi.org/10.1016/j.foodchem.2021.107085.

[28] B.W. Jo, S.K. Choi, Degradation of fucoidans from Sargassum fulvellum and their effect on enhancing antioxidant activity, Carbohydr. Polym. 110 (2014) 278–284, https://doi.org/10.1016/j.carbpol.2014.04.034.
B. Du et al.  

Ultrasonics Sonochemistry 90 (2022) 106170

[38x479] R. Chen, Y. Li, H. Dong, Z. Liu, S. Li, S. Yang, X. Li, Optimization of ultrasonic treatment on the microstructure and physicochemical properties of okara fibers, Ultrason. Sonochem. 69 (2020) 105247, https://doi.org/10.1016/j.ultsonch.2021.105668.

[54] F. Xu, T. Zhao, S. Gao, L. Zhong, G. Zhang, J. Sun, Preparation of cellulose nanocrystals from old corrugated container fiber using phosphoric acid and enzymatic hydrolysis followed by sonication, Carbohydr. Polym. 125 (2015) 360–366, https://doi.org/10.1016/j.carbpol.2015.02.063.

[70] E. Syafri, A. Kasim, H. Abral, G.T. Sulungbudi, M.R. Sanjay, K. Hadi, Preparation of sonicated scleroglucan samples: Rheological properties and swelling behaviour of sonicated scleroglucan samples, Polym. 94 (1) (2013) 496–504, https://doi.org/10.1016/j.polymertoday.2013.06.002.

[118] F. Zendeboodi, A. Farahnaky, M.M. Gholian, Structural changes and stress relaxation behavior of x-carraagenan cold-processed gels: Effects of ultrasonication time and power, J. Texture Stud. 50 (6) (2019) 645–673, https://doi.org/10.1111/jtos.12067.

[129] Y. Liu, J. Zhang, D. Guo, K. Zhang, ultrasound-assisted enzyme hydrolysis followed by sonication, Carbohydr. Polym. 125 (2015) 360–366, https://doi.org/10.1016/j.carbpol.2015.02.063.

[212] K. Nakashima, Y. Ebi, M. Kubo, N. Ishikawa-Kikタンカ, T. Yonimote, Pretreatment combined ultrasonic and sodium percarbonate under mild conditions for efficient degradation of corn stover, Ultrason. Sonochem. 29 (2019) 455–460, https://doi.org/10.1016/j.ultsonch.2019.10.017.

[248] R. Chen, Y. Li, H. Dong, Z. Liu, S. Li, Y. Yang, X. Li, Optimization of ultrasonic extraction process of polyacrylamides from Orthothamnium caudatum Aitz and evaluation of its biological activities, Ultrason. Sonochem. 19 (6) (2012) 1160–1168, https://doi.org/10.1016/j.ultsonch.2012.03.008.

[259] K.H. Byeon, Rapid green assembly of antimicrobial nanobubbles, Sci Rep-UK 6 (1) (2016) 1–7, https://doi.org/10.1038/srep27006.

[47] S.A. Ansari, P. Matricardi, C.D. Meo, F. Alhaique, T. Coviello, Evaluation of effects of dual modification with ultrasonic and electric field on shelf life and bioactive protein of bamboo shoots, Ultrason. Sonochem. 53 (2018) 110–114, https://doi.org/10.1016/j.ultsonch.2018.02.029.

[62] A.F. Minakawa, P.C. Faria-Tischer, S. Mali, Simple ultrasound method to obtain micro- and nanofibers from cassava, Corn and yard stalks, Food Chem. 295 (2019) 222–229, https://doi.org/10.1016/j.foodchem.2019.125717.

[118] W. Zhang, Y. Liu, Z. Li, H. Wang, X. Cui, Preparation and characterization of potato starch, Carbohyd. Polym. 125 (2015) 360–366, https://doi.org/10.1016/j.carbpol.2015.02.063.

[323] M. Cao, Q. Gao, Effect of dual modification with ultrasonic and electric field on potato starch, Int. J. Biol. Macromol. 82 (2016) 89–96, https://doi.org/10.1016/j.ijbiomac.2016.09.049.

[323] M. Cao, Q. Gao, Effect of dual modification with ultrasonic and electric field on potato starch, Int. J. Biol. Macromol. 82 (2016) 89–96, https://doi.org/10.1016/j.ijbiomac.2016.09.049.

[343] Y. Wang, F. Feng, W. Chen, K. Adie, D. Liu, Y. Yin, Citrus peel modified by microfluidization and ultrasonication: Improved emulsifying and encapsulation properties, Ultrason. Sonochem. 70 (2021), https://doi.org/10.1016/j.ultsonch.2020.105322.

[343] Y. Tang, X. Shen, J. Zhang, D. Guo, F. Kong, N. Zhang, Extraction of cellulose nanocrystals from old corrugated container fiber using phosphoric acid and enzymatic hydrolysis followed by sonication, Carbohydr. Polym. 125 (2015) 360–366, https://doi.org/10.1016/j.carbpol.2015.02.063.

[343] P. Liu, R. Wang, X. Kang, B. Cui, B. Yu, Effects of ultrasonic treatment on amylose-lipid complex formation and properties of sweet potato starch-based films, Ultrason. Sonochem. 44 (2018) 215–222, https://doi.org/10.1016/j.ultsonch.2018.02.029.

[343] R. Zhang, X. Wang, M. Cheng, Preparation and characterization of potato starch film with various size of nano-SiO2, Polymers 10 (10) (2018) 1172, https://doi.org/10.3390/polym10101172.

[343] X.Y. Yang, X. Yue, Y. Fang, X. Liu, Y. Yang, G. Shi, S. Feng, L. Zhao, Structure-immunomodulatory activity relationships of Hedyssarum polyacrylamides extracted by a method involving a complex enzyme combined with ultrasonication, Food Funct. 10 (2) (2019) 1146–1158, https://doi.org/10.1039/c8fo02293c.

[343] X. Yang, Z. Xue, Y. Fang, X. Liu, Y. Yang, G. Shi, S. Feng, L. Zhao, Structure-immunomodulatory activity relationships of Hedyssarum polyacrylamides extracted by a method involving a complex enzyme combined with ultrasonication, Food Funct. 10 (2) (2019) 1146–1158, https://doi.org/10.1039/c8fo02293c.

[343] B.K. Gu, S.J. Park, M.S. Kim, C.M. Kang, J.I. Kim, Preparation and characterization of potato starch, Carbohyd. Polym. 125 (2015) 360–366, https://doi.org/10.1016/j.carbpol.2015.02.063.