Chapter 11
Gluconic Acid as a New Green Solvent for Recovery of Polysaccharides by Clean Technologies

Juan Carlos Contreras-Esquivel, Maria-Josse Vasquez-Mejia, Adriana Sañudo-Barajas, Oscar F. Vazquez-Vuelvas, Humberto Galindo-Musico, Rosabel Velez-de-la-Rocha, Cecilia Perez-Cruz, and Nagamani Balagurusamy

Abstract The gluconic acid is an inexpensive and bio-based organic compound with new insights to drive growth in the eco-friendly industries. In organic chemistry, the gluconic acid is considered as a sustainable medium for organic reactions; meanwhile, natural product technologies suggest their potential as green solvents for extraction. In this chapter, advances of use of gluconic acid as a green solvent are presented in combination with green technologies for production of polysaccharides from biomasses from animal (chitin), microbial (chitosan-glucan), or vegetal (pectin) origins. Furthermore, this weak organic acid is capable of depolymerizing chitosan under microwave radiation for the production of water-soluble chitosan. The use of gluconic acid in combination with biomasses and clean technologies offers new green processes for the production of specialty polysaccharides and its derivatives under environmentally friendly process.

J.C. Contreras-Esquivel (✉) • M.-J. Vasquez-Mejia
Laboratory of Applied Glycobiotechnology, Food Research Department, School of Chemistry, Universidad Autonoma de Coahuila, Saltillo 25280, Coahuila, Mexico

Research and Development Center, Coyotefoods Biopolymer and Biotechnology Co., Simon Bolivar 851-A, Saltillo 25000, Coahuila, Mexico
e-mail: carlos.contreras@uadec.edu.mx; coyotefoods@hotmail.com

A. Sañudo-Barajas • R. Velez-de-la-Rocha
Laboratory of Food Biochemistry, Centro de Investigación en Alimentacion y Desarrollo (CIAD)-AC, Culiacan 80129, Sinaloa, Mexico

O.F. Vazquez-Vuelvas
School of Chemistry, Universidad de Colima, Coquimatlan 28400, Colima, Mexico

H. Galindo-Musico • C. Perez-Cruz
Laboratory of Applied Glycobiotechnology, Food Research Department, School of Chemistry, Universidad Autonoma de Coahuila, Saltillo 25280, Coahuila, Mexico

N. Balagurusamy
School of Biological Sciences, Universidad Autonoma de Coahuila, Torreon 27000, Coahuila, Mexico

F. Chemat and M. Abert Vian (eds.), *Alternative Solvents for Natural Products Extraction*, Green Chemistry and Sustainable Technology,
DOI 10.1007/978-3-662-43628-8_11, © Springer-Verlag Berlin Heidelberg 2014

11.1 Introduction

Bio-based technologies for the recovery of structural polysaccharides from biomasses represent a generation of high-value multipurpose bio-refining and sustainable companies. The market of polysaccharides has grown rapidly in recent years as a result of new developments for biomaterials. Naturally occurring polysaccharides can be extracted from animal, marine, microbial, or terrestrial biomasses through extractive environmentally friendly technologies.

Chitin and chitosan represent a group of structural polysaccharides obtained from crustacean [1] or fungal biomasses [2]. Terrestrial polysaccharides comprise pectic substances, hemicelluloses (arabinan, arabinoxylan, galactan, glucomannan, xylan, xyloglucan, etc.), and celluloses, which are obtained from wood or food wastes [3]. Seaweed polysaccharides comprise old and emergent biopolymers (alginate, carrageenan, fucoidan, porphyran, etc.), which are recovered from promising and poorly explored biomasses [4].

A key issue in recovery of polysaccharide technology is the process of extraction from the raw materials [5]. For the extraction of polysaccharides from vegetal biomasses, the use of chemical, enzymatic, or physical hydrolyzing agents is a necessary. At present, at industrial scale, the use of mineral acids are employed for the polysaccharide recovery, however during the process is generated hazardous emissions, polluted wastewater and damage to extraction reactors [4, 6]. Several organic acids are intended to be used as a substitute of mineral acids for production of polysaccharides from animal, marine, microbial, or terrestrial biomasses. Pectin polysaccharides have been extracted with organic acids such as citric [7–9], malic, lactic [10, 11], or oxalic acid [12]. Crustacean biomass has been demineralized with lactic acid in combination with emergent technologies for chitin production [13, 14]. The use of organic acids in the production of polysaccharides has shown an increase due to the environmental benefits offered during the extraction step.

Carbohydrate platform provides a supply chain of aldonic acids (i.e., gluconic and xylonic acids) which are obtained by oxidation of the aldehyde functional group of an aldose by chemical [15, 16] or biotechnological [17] methods. Gluconic acid and its derivatives (salts and glucono delta-lactone) are used in the animal feed, biotechnology, cosmetics, ceramic, dentistry, foods, pharmaceutical, and other industries [18], and it has been identified in the list of building compounds that can be produced from vegetal biomass in the future biorefineries [19]. Gluconic acid has been recognized as new green solvent for use in organic synthesis [20, 21].

Extractive capacity of gluconic acid in the industrial sector has been identified for their polysaccharide extraction capacity as a new emergent green solvent [10, 22]. In this chapter, we describe some recent advances of our research group about extraction of selected polysaccharides with aid of gluconic acid for development of clean technologies for sustainable production of biopolymers.

11.2 Gluconic Acid Production

Gluconic acid (pentahydroxycaproic acid) and its salts are produced through chemical [16] or biotechnological [23] methods subsequent to oxidation of glucose obtained generally from starch hydrolyzates. The procedures involve an oxidation process of the aldehyde group of the D-glucose unit to produce a carboxylic salt, and both methods generally employ glucose itself or a resource of this saccharide [24]. Nonetheless, the production of gluconic acid by chemical methods presents disadvantages for industrial goals, such as the low selectivity of the non-favored reactions and the high cost of noble metals used as oxidizing reaction catalyst [25]. As a consequence, the most efficient, non-expensive, and safest techniques to produce gluconic acid are by biotechnological methods [26, 27].

The biotechnological methods of gluconate production make use of fermentation or enzyme technologies. The fermentation processes, in solid and liquid media, have been extensively used employing different microbial species. Fungi and bacteria correspond to the widely utilized microorganisms to produce efficiently gluconic acid [24]. Detailed information about biotechnological production of gluconate salts can be found in recent reviews [24, 26]. After fermentation, gluconic acid is obtained from gluconates by using electrodialysis as well electrodialysis with bipolar membranes [28].

11.3 Use of Gluconic Acid for Pectin Production

Pectin is a polymer having properties of interest for the manufacture of food, cosmetics, and medicine applications and, in the last years, to enhance quality and/or functionality of those products. Chemically, complex mixtures of anionic polysaccharides naturally are present in plant cell walls, especially in the middle lamella and primary cell wall [29].

Pectins contain a high proportion of acidic and neutral sugar moieties shaping their conformation [30], but generally, they do not possess either exact structures or specific composition. The molecule does not behave as a polymer of straight conformation in solution and generally adopts a wormlike conformation. Most common substituent groups are acetyl, feruloyl, and/or methyl esters that cover a variable proportion of carbonyl-free groups depending on the development stage, tissue, or type of cell [31]. The central region of the pectin contains a long homopolymeric chain of $(1 \rightarrow 4)$ α-D-galacturonic acid, which may contain up to 200 units of length usually called homogalacturonan region [32]. Homogalacturonan linked to two pectic structures are recognized: the rhamnogalacturonan-type I, which constitutes, together with homogalacturonan, the fundamental components of pectic substances, and homogalacturonan modified, which may be of type xylogalacturonan or rhamnogalacturonan-type II. The rhamnogalacturonan-I has branches to other types of polymers of varying length, comprising the neutral sugars arabinose

and galactose, so that depending on the predominant sugar, the biopolymers may be called arabinans, galactans, and arabinogalactans. The rhamnogalacturonan-II is also branched to neutral sugars and other acidic components that confer a high complexity [33, 34].

Structure and chemical composition determines the feasibility of pectin extraction as well as their properties [35]. Pectins have been extracted typically using physical [36], chemical [37], microbial, or enzymatic methods [6, 38–40]. Physical methods generally accompany all others since heating is considered, in one or other way, for pectin solubilization either biological transformation. More commonly, a combination of those extraction methods has shown success [41]. The raw material, in addition to the pectin fine structure and chemical composition, influences the major pectin quality or yield. Depending on the favorable action of the extraction method for disrupting the plant tissue (leading to a partial chemical disintegration of the polysaccharide matrix), as well as the protopectin solubilization (controlled beta-elimination and/or pectin enzymatic hydrolysis), the optimal method for pectin extraction might be improved and optimized varying parameters such as temperature, pressure, pH, ionic strength, or use of pretreatment, among others. Unfortunately, some extreme conditions lead to protein or carbohydrate degradation and should be controlled to prevent it at maximum.

Conventionally, extraction of pectin at industrial scale is performed using hot acidified water (pH 1.0–2.5; temperature 60–90 °C; time of at least 1 h), although this condition affects the degree of polymerization of pectin [29]. According to some electron micrographs of orange peel (rich in pectin), it presents a microporosity that can be increased by heating, hydration, and pressure; the higher this microporosity, the higher the water diffusion and positive linear effect in extraction of pectin [42]. In consequence, the use of acidic solutions can also lead to improve solvent accessibility to soluble pectins and/or induce a hydrolysis of insoluble protopectins.

Manufacturers have developed thermal processes using diluted mineral acids (nitric, sulfuric, or hydrochloric) [29], although organic acids (citric, gluconic, malic, and lactic) have also been explored as an alternative [10, 11]. The raw material or preprocessed source of pectin might provide the pectin into the hot solution to produce slurry containing the highest yield of the hydrocolloid with the best quality in terms of molecular weight, composition, purity, and gelling properties. The extracted liquid pectin should be fractionated by filtering or spinning the slurry and must be concentrated using ethanol or isopropanol and finally washed, dried, and milled to obtain the solid powder.

Heating technologies may vary at industrial and laboratory scale extractions. Conventional heating, autoclave, conventional soxhlet, electric pulses, and microwave technologies have been explored to determine optimal extraction conditions in different pectin sources [37, 43]. Microwave-assisted extraction is an alternative to reduce times of extraction and energy consumption, in addition to improve yield because this methodology can achieve higher cell disruption. As reported by Huang et al. [44], microwave-assisted extraction combined with the use of ionic liquids, neoteric solvents composed of organic cations and inorganic or organic anions, increases the ability of pectin extraction and may also be of interest for environmentally friendly methods.

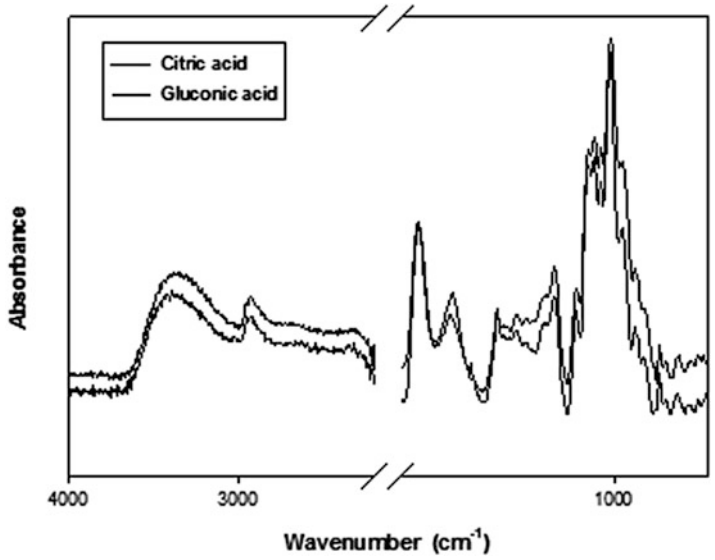

Fig. 11.1 Infrared spectra of the pectic polysaccharides extracted from citrus peel pomace by autoclave treatment with organic acids

Acidification for hydrolysis is an important exploring field since mineral acid is corrosive, non-environmentally friendly, and not suitable for human consumption. Inorganic acid method is more widely used commercially; however, organic acids or enzymatic processes are more suitable and must gain application in the next years. In particular, enzymatic extraction exhibits improved mild conditions, low energy consumption, and no pollution, and combined with a microwave heating method, it produces higher yields as compared with conventional methods based in its ability to disrupt cells [41]. Limited studies have been conducted on the feasibility of the use of organic acids for pectic extraction [7, 8, 10, 11].

Vazquez-Mejia [10] evaluated the effect of using 0.5 % citric or gluconic acid on the extraction process by autoclave treatment (121 ºC/10 min) from lime citrus pomace. Similar pectin yields (dry basis) were obtained by using 0.5 % citric (22.16 ± 3.40 %) or gluconic acid (22.47 ± 0.94 %). In Fig. 11.1, infrared spectra for both extracted pectins with organic acids from industrial lime pomace are shown. The vibrational characteristics of polysaccharides generally dominate the region between 1,200 and 900 cm^{-1} because of the C–O stretch bonds related to sugars [7]. Both extracted pectins obtained with gluconic acid, as well as with citric acid, showed a significant absorption in the wavenumber in 1,750 cm^{-1} corresponding to high methoxyl-pectic polysaccharides. The results indicate that the extraction process in the presence of organic acid is not affected by the moieties of methoxyl groups in pectin.

The viscosity of the citric acid-extracted pectin was 7.87 ± 0.04 mPa × seg, while that pectin extracted by gluconic acid was 7.60 ± 1.44 mPa × seg. Both types of

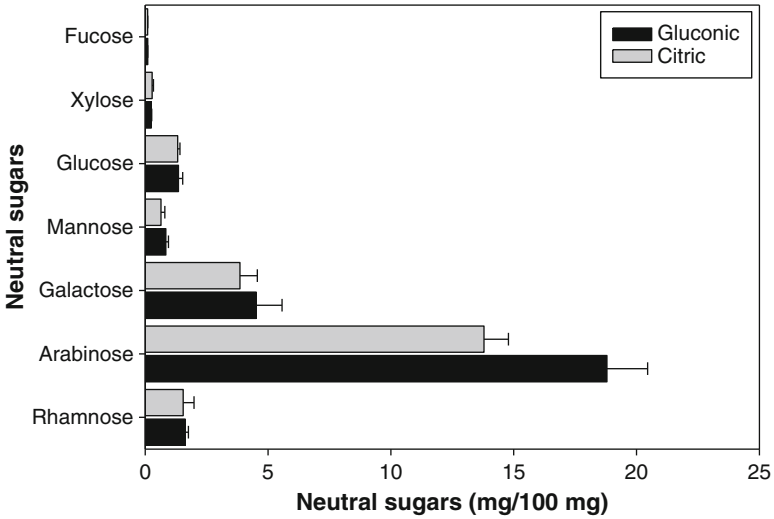

Fig. 11.2 Neutral sugar compositions (% w/w, dry weight) of lime pectin using organic acid under autoclave

lime pectin extracts showed an uronic acid content about 50–60 %. The type of organic acid used in the extraction of pectin showed differences in the quantity of neutral sugars present in each sample (Fig. 11.2). The pectin extracted with gluconic acid was characterized by a high arabinose content compared with the sample extracted with citric acid. These results suggest that the use of gluconic acid can maintain a large amount of neutral sugars of side chains of pectin after extraction. Differential gelling properties of the pectin was in function of the physical, chemical and compositional characteristics of the polymer and the solvent [33].

11.4 Use of Gluconic Acid for Crustacean Chitin Production

After cellulose, chitin is the second most abundant natural biopolymer on earth [45]. The crustacean shells are known to be constituted mainly for chitin, protein, and calcium carbonate [2]. Chitin is highly hydrophobic and insoluble in water, and it is constituted mainly by β-1,4-linked *N*-acetyl-D-glucosamine and minor proportion of D-glucosamine [46].

Currently, chitin is commercially produced by a thermochemical process based on demineralization and deproteinization of crustacean wastes. Chitin is obtained after removal of protein, calcium carbonate, and other minor components by treatment with sodium hydroxide and hydrochloric acid [47].

The use of harsh chemicals has motivated the development of biotechnological (microbial or enzymatic) methods to decrease large amounts of energy and

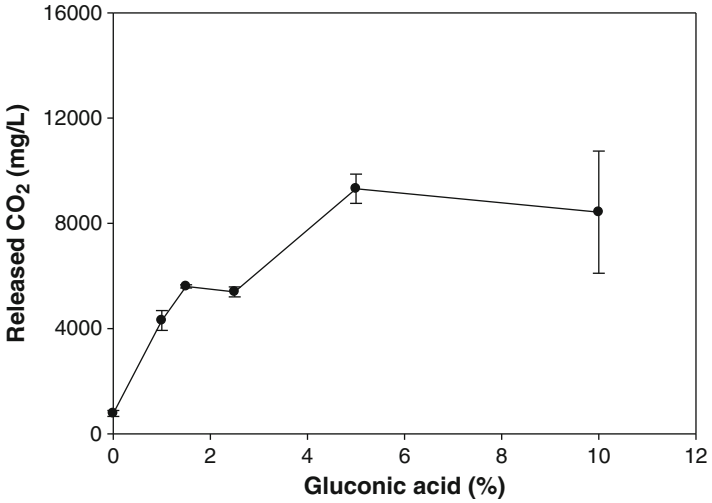

Fig. 11.3 Effect of contact time and gluconic acid concentration on release of carbon dioxide from shrimp shells. Dried shrimp shells (300 mg) were mixed with 15 mL of distiller water or gluconic acid at 24 ºC for 60 min in closed container and capped with CO_2 gas analyzer. All experiments were made by triplicate

pollutants during chitin production [48]. The microbiological method for chitin recovery involves lactic acid fermentation, which is produced by lactic acid bacteria supplemented with exogenous carbon sources. In this process, there is simultaneous, but incomplete demineralization and deproteinization of crustacean wastes [49–51]. Another biotechnological approach is the use of enzymes, which are specific for the release of chitin-associated protein [52]. A variety of enzymatic procedures for deproteinization has been developed over the years [50]. This method does not allow the removal of minerals during the process [13]. Nevertheless, biotechnological methods for chitin bioproduction from crustacean wastes are still limited to industrial scale due to long processing times.

Crustacean wastes are generally demineralized with HCl under different reaction conditions for production of marine chitin [53]. An alternative for mineral acids is the use of organic acids from agricultural origin, which are generally safe, produce low hazardous emissions, are easy to degrade in the environment, and allow conservation of natural resources [13].

In our laboratory, we have explored the use of gluconic acid as green solvent for shrimp and crab shells demineralization under closed reactors at room (24 ºC) or high (121 ºC) temperature. Figure 11.3 shows the course of the release of carbon dioxide from shrimp shell by several concentrations of gluconic acid and water as a control, in a laboratory closed reactor. The release of carbon dioxide from dried shrimp shells by using 5 or 10 % of gluconic acid after 60 min reaction was more than 800 mg/L. Such results show that more than 5 % of gluconic acid is enough for carrying out the process of demineralization of shrimp wastes. No release of

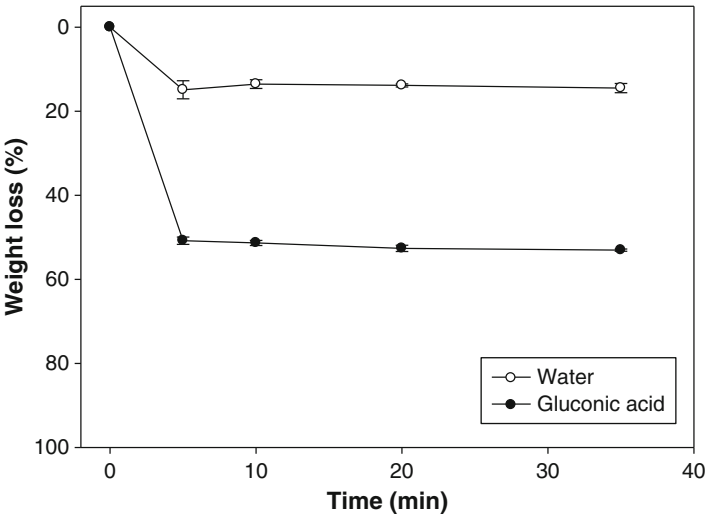

Fig. 11.4 Effect of contact time and type of demineralizing agent on weight loss of shrimp shells. Shrimp shells (3 g) were suspended in extractant solution (150 mL) and then autoclaved for correspondent time. After processing, slurry was filtered, and insoluble biomass was washed with water and dried (60 °C) until constant weight. Insoluble biomass corresponds to demineralized shrimp shells or chitin

carbon dioxide was observed when distilled water was used. These results suggest that gluconic acid is an efficient demineralizing agent at low temperature conditions for the recovery of chitin from wastes and conversion ratio of chitin depending on the concentration of acid.

Recently, environmental-friendly methods have been described for reducing the process time in manufacturing of chitin. Great efforts have been focused on reducing the processing for crustacean wastes for chitin production with thermochemical processes assisted by microwave, ultrasound, or autoclaving [13, 14, 46, 54].

Microwave-assisted technology, which has been recently successful for processing biopolymers, has been studied for chitin and chitosan recovery. Microwave-assisted heating for chitin production involves the use of microwave energy to heat the solvents (demineralizing agents) that are in contact with crustacean materials. A promising method involves the use of microwave radiation to crustacean wastes in an acidic environment. Although there are several papers and patents on the use of microwave heating for synthesis of chitosan, microwave heating has only recently been applied to deproteinization/demineralization for chitin recovery [13, 14]. Microwave heating technology helped in saving time and energy during deproteinization and demineralization steps of crustacean wastes. Recently, we have developed a patented process for chitin production using a microwave-assisted technology in combination with organic acids [14].

Figure 11.4 shows the effect of type or demineralizing agent (5 % gluconic acid or water) and contact time on weight loss of shrimp shells by autoclave-assisted

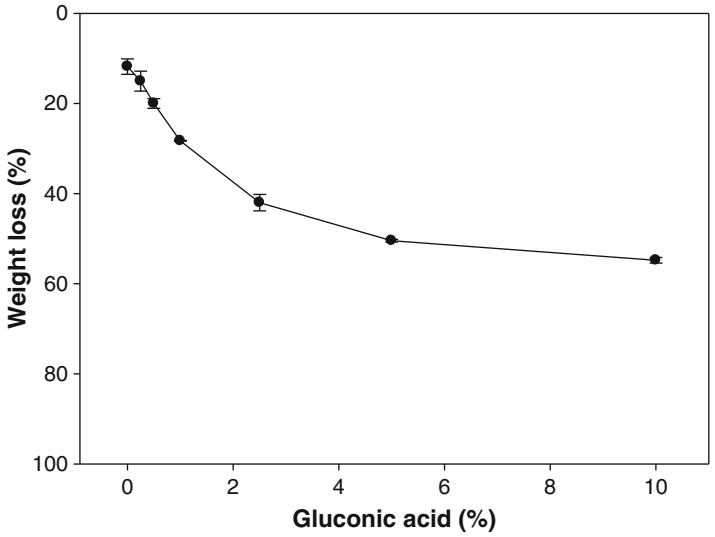

Fig. 11.5 Effect of gluconic acid concentration on demineralization process of shrimp shells by autoclave processing for 5 min at 121 ºC

processing (121 ºC). The weight loss of the shrimp shells treated for 10 min in aqueous media under autoclave was 10 %. At the same time, the samples treated with 5 % gluconic acid lost 50 % of weight.

It was also studied the effect of gluconic acid concentration on weight loss of shrimp shells by autoclaving processing as an index of the demineralization process (Fig. 11.5). As the concentration of gluconic acid in the medium increases, the weight loss of the shrimp shell decreased due to demineralization process. A plateau state was produced after the use of 5 % gluconic acid. Based on the results described above, the use of gluconic acid as demineralizing agent in the environmentally friendly chitin industry is suitable.

11.5 Use of Gluconic Acid for Chitosan Processing

Chitosan is a cationic biopolymer composed of glucosamine and *N*-acetyl-glucosamine units associated by β-1,4-glycosidic linkages [55]. This macromolecule is not soluble in water, which limits its wide application in the medicine and food industry [56]. In previous research on chitosan, the most popular solvent for dissolution has been acetic acid solution; however, this acid has a strong unpleasant smell [55]. Dissolved chitosan has antimicrobial and metal-binding properties and form beads, gels, fibers, films, and scaffolds [57]. Under mild

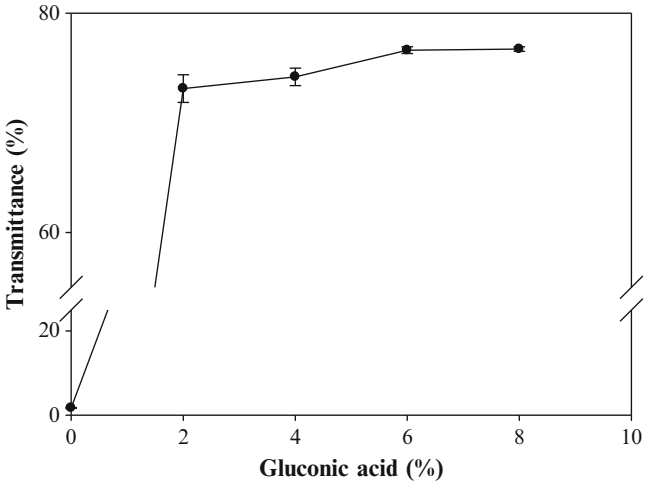

Fig. 11.6 Effect of gluconic acid concentration on the transmittance of chitosan solution

acidic conditions, chitosan can be depolymerized to yield water-soluble derivatives (i.e., glucosamine, chitosan oligomers, or water-soluble chitosan) by chemical, enzymatic, or physical methods.

In our laboratory, we tested the possibility of using gluconic acid as emergent greener solvent for chitosan dissolution [22]. The effect of gluconic acid concentration on the transmittance at 610 nm of chitosan (2 %, w/v) solution is shown in Fig. 11.6. As the gluconic acid concentrations increases, the intensity of the transmitted light of chitosan solution increased. Transmittance above 70 % in the region of 610 nm of chitosan solution was achieved with gluconic acid ranging between 6 and 8 % (v/v). Based on the results, gluconic acid is also suitable as a green solvent for the dissolution of chitosan.

Dissolved chitosan in 5 % (v/v) gluconic acid was depolymerized in a safe closed microwave pressure vessel (Nordic Ware Co., Minneapolis, MN, USA). The study was conducted to evaluate different microwave heating times (0, 1, 5, and 10 min) under pressure on the loss of viscosity of chitosan. The results showed that microwave irradiation causes decreasing of viscosity of chitosan solutions as the contact time increased (Fig. 11.7). The viscosity of irradiated mild-acidified chitosan decreased 35 % after 10 min compared with control solution. In the presence of 3 % (v/v) H_2O_2 together with chitosan dissolved in 5 % (v/v) gluconic acid, the extent of viscosity decreased about 85 % after 5 min of microwave irradiation versus a control solution (data not shown). Tian et al. [58] evaluated chitosan depolymerization by addition of hydrogen peroxide along with HCl in a wide range of temperature from 25 to 70 °C for incubation periods of 1, 2 or 3 h. In our depolymerization process, the chitosan dissolved with gluconic acid, hydrogen peroxide, and pressure is rapidly degraded by the promotion of these environmentally friendly conditions.

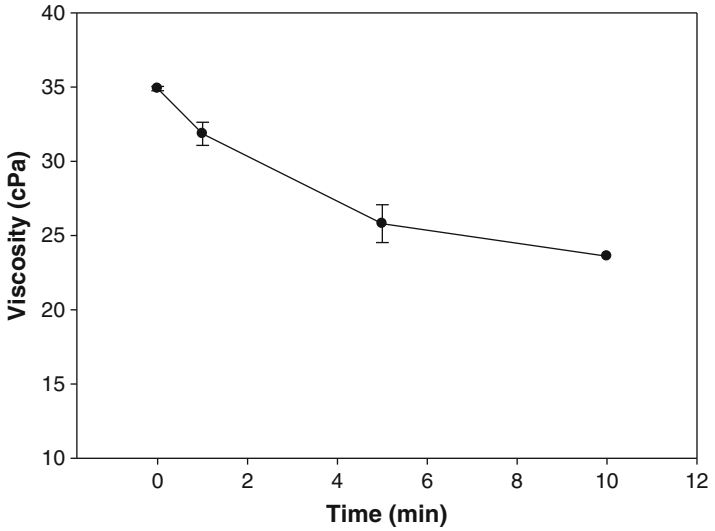

Fig. 11.7 Course of change of viscosity of chitosan dissolved in gluconic acid by microwave heating reaction. Viscosity was evaluated with portable vibrational viscometer (Viscolite 700, Hydramotion Ltd, UK). All experiments were made on triplicate

11.6 Use of Gluconic Acid for Fungal Chitosan-Glucan Production

Aspergillus niger is one of the most important microorganisms used in biotechnology for many decades to produce extracellular enzymes and organic acids [59, 60]. This industrial mold is considered "as generally recognized as safe" (GRAS) by the US Food and Drug Administration [61] for bioprocessing. Large amounts of *A. niger* wastes are generated in dry basis every year which are industrially considered for the production of animal feed, glucosamine, and biopolymers [62]. The structural biopolymers present in rigid cross-linked network from *Aspergillus* spp. cell walls are chitin, chitosan, glucan, and proteins [63–65]. In the *A. niger*, glucans are covalently associated with chitosan [66]. The reported glucan content of fungal cell wall has ranged from 30 to 60 %, depending on cultural conditions. The glucan component is responsible for the tensile strength, rigidity, and shape of the cell [67]. Most glucans are water-insoluble linear polymers made of glucose units joined through β-1,3 bonds, which are present in fungal cell wall [62].

Gluconic acid (6 %, v/v) has been used as green solvent to release and dissolve chitosan-glucan biopolymer from *A. niger* biomass by pressurized microwave-assisted extraction [22]. The effect of heating temperature (110, 120, and 130 ºC) and contact time (0.42, 30, 60, and 90 min) was evaluated for maximizing the extraction of chitosan-glucan biopolymer. The solubilization rate of acidic-soluble

biopolymer increased as temperature and contact time raise. The best conditions for chitosan-glucan extraction were heating temperature of 130 ºC and heating time of 60 min within a maximal yield of 10.5 % (dry basis) and dynamic viscosity of 0.69 mPa × s. The green process based on the use of gluconic acid as green solvent enhanced the release of chitosan-glucan complex from a rigid cross-linked network present in *A. niger* biomass under environmentally friendly process. Extraction assisted by microwave and the use of an extracting agent acid (gluconic acid) are suitable for the recovery of a fungal polysaccharide with characteristics of chitosan-glucan.

11.7 Conclusions

The gluconic acid has recently emerged as an important alternative to mineral acids in the new development of extraction methodologies of structural polysaccharides. The combination of employing gluconic acid with green-energy sources has resulted in a variety of technologies capable of substituting the highly pollutant chemical production processes of specialty polysaccharides. Since the gluconic acid is advantageously produced by biotechnological methods, its wastes industrially generated might be easily biodegraded. The synergy offered by the gluconic acid and extraction technologies as microwave, hydrothermal pressurizing, or sonication is promising when considering eco-friendly technological developments of industrial polysaccharide manufacturing. Criteria such as productivity, cost, and bio-based issues are the value-added advantages of the use of gluconic acid.

Acknowledgments The authors express their gratefulness to the Mexican National Council for Science and Technology (CONACyT) for postdoctoral fellowship program to Oscar Fernando Vazquez Vuelvas and master in science scholarship to Cecilia Perez Cruz.

References

1. Barber PS, Shamshina JL, Rogers RD (2013) A “green” industrial revolution: using chitin towards transformative technologies. Pure Appl Chem 85:1693–1701
2. Hirano S (1996) Chitin biotechnology applications. Biotechnol Annu Rev 2:237–258
3. Dey PM, Brinson K (1984) Plant cell-walls. Adv Carbohydr Chem Biochem 42:265–382
4. Hernandez-Carmona G, Freile-Pelegrin Y, Hernandez-Garibay E (2013) Conventional and alternative technologies for the extraction of algal polysaccharides. In: Functional ingredients from algae for foods and nutraceuticals. Woodhead Published Limited, Cambridge, pp 475–516
5. Panchev IN, Kirtchev NA, Kratchanov C (1989) Kinetic model of pectin extraction. Carbohydr Polym 11:193–204
6. Sakai T, Sakamoto T, Hallaert J, Vandamme E (1993) Pectin, pectinase and protopectinase: production, properties and applications. Adv Appl Microbiol 39:213–294

7. Contreras-Esquivel JC, Espinoza-Pérez JD, Aguilar CN, Montañez JC, Charles-Rodríguez A, Renovato J, Aguilar CN, Rodríguez-Herrera R, Wicker L (2006) Extraction and characterization of pectin from novel sources. In: Advances in biopolymers, molecules, clusters, networks and interactions, ACS symposium series. American Chemical Society, Washington, DC, pp 215–227
8. Kurita O, Fujiwara T, Yamazaki E (2008) Characterization of the pectin extracted from citrus peel in the presence of citric acid. Carbohydr Polym 74:725–730
9. Contreras-Esquivel JC, Aguilar CN, Montanez JC, Brandelli A, Espinoza-Perez JD, Renard CMGC (2010) Pectin from passion fruit fiber and its modification by pectinmethylesterase. J Food Sci Nutr 15:57–66
10. Vasquez-Mejia MJ (2013) Recovery and characterization of pectic polysaccharides by employ of emergent technologies from tejocote pulp and citrus, pomegranate and mango peels. BSc thesis, School of Chemistry, Universidad Autonoma de Coahuila, Saltillo
11. Ma S, Yu SJ, Zheng XI, Wang XX, Bao QD, Guo XM (2013) Extraction, characterization and spontaneous emulsifying properties of pectin from sugar beet pulp. Carbohydr Polym 98:750–753
12. Jensen SV, Sorensen SO, Rolin C (2012) Process for extraction of pectin. US Patent 20120309946 A1
13. Valdez-Peña AU, Espinoza-Perez JD, Sandoval-Fabian GC, Balagurusamy N, Hernandez-Rivera A, De-la-Garza-Rodriguez IM, Contreras-Esquivel JC (2010) Screening of industrial enzymes for deproteinization of shrimp head for chitin recovery. Food Sci Biotechnol 19:553–557
14. Contreras-Esquivel JC (2012) Obtainment of chitin from shrimp waste by means of microwaves and/or autoclaving in combination with organic acids in a single stage. Mexican Patent 298224, Mar 2009
15. Onda A, Ochi T (2008) A new chemical process for catalytic conversion of D-glucose into lactic acid and gluconic acid. Appl Catal A 343:49–54
16. Le ZP, Wang LL, Huang XG, Huang YQ (2011) Study on the oxidation of glucose to gluconic acid by ozone under microwave. J Nanchang Univ (Eng & Technol) 33:217–221
17. Fan Z, Wu W, Hildebrand A, Kasuga T, Zhang R, Xiong X (2012) Novel biochemical route for fuels and chemicals production from cellulosic biomass. PLoS One 7:e31693
18. Hustede H, Haberstroh HJ, Schinzig E (2005) Gluconic acid. In: Ullmann's encyclopedia of industrial chemistry. Wiley-VCH Verlag GmbH & Co, Weinheim, pp 1–9
19. Werpy T, Petersen G (2010) Top value added chemical from biomass: volume 1 – results of screening potential candidates from sugar and synthesis gas. In: Pacific Northwest National Laboratory and the National renewable Energy Laboratory, U.S. Department of Energy. http://www.nrel.gov/docs/fy04osti/35523.pdf. Accessed 20 Feb 2014
20. Zhou B, Yang J, Li M, Gu Y (2011) Gluconic acid aqueous solution as a sustainable and recyclable promoting medium for organic reactions. Green Chem 13:2204–2211
21. Yang J, Zhou BH, Li MH, Gu YL (2013) Gluconic acid aqueous solution: a task-specific bio-based solvent for ring-opening reactions of dihydropyrans. Tetrahedron 69:1057–1064
22. Perez-Cruz C (2013) Use of biomass of *Aspergillus niger* using enzymatic hydrolysis and heating assisted by microwaves. MSc thesis, School of Chemistry, Universidad Autonoma de Coahuila, Saltillo
23. Richter G, Heinecker H (1979) Conversion of glucose into gluconic acid by means of immobilized glucose oxidase. Starch-Starke 31:418–422
24. Ramachandran S, Fontanille P, Pandey A, Larroche C (2006) Gluconic acid: properties, applications and microbial production. Food Technol Biotechnol 44:185–195
25. Lemeune S, Barbe JM, Trichet A, Guilard R (2000) Degradation of cellulose models during an ozone treatment. Ozonation of glucose and cellobiose with oxygen or nitrogen as carrier gas at different pH. Ozone-Sci Eng 22:447–460
26. Singh O, Kumar R (2007) Biotechnological production of gluconic acid: future implications. Appl Microbiol Biotechnol 75:713–722

27. Onda A, Ochi T, Yanagisawa K (2011) New direct production of gluconic acid from polysaccharides using a bifunctional catalyst in hot water. Catal Commun 12:421–425
28. Novalic S, Kongbangkerd T, Kulbe KD (1997) Separation of gluconate with conventional and bipolar electrodialysis. Desalination 114:45–50
29. May CD (1990) Industrial pectins: sources, production and applications. Carbohydr Polym 12:79–99
30. Hwang JK, Kokini JL (1995) Changes in solution properties of pectins by enzymatic hydrolysis of sidechains. J Korean Soc Food Sci Nutr 24:389–395
31. Marry M, McCann MC, Kolpak F, White AR, Stacey NJ, Roberts K (2000) Extraction of pectic polysaccharides from sugar-beet cell walls. J Sci Food Agric 80:17–28
32. Hoefler AC (1999) Pectin: chemistry, functionality and applications. Hercules Inc., Wilmington
33. Schols HA, Coenen GJ, Voragen AGJ (2009) Revealing pectin's structure. In: Visser J, Voragen AGJ (eds) Pectins and pectinases. Wageningen Academic Publishers, Wageningen, pp 17–33
34. Ralet MC, Thibault JF (2009) Hydrodynamic properties of isolated pectin domains: a way to figure out pectin macromolecular structure. In: Visser J, Voragen AGJ (eds) Pectins and pectinases. Wageningen Academic Publishers, Wageningen, pp 35–48
35. Van Buren JP (1991) Function of pectin in plant tissue structure and firmness. In: Walter RH (ed) The chemistry and technology of pectin. Academic, San Diego, pp 1–23
36. Hwang JK, Kim CJ, Kim CT (1998) Extrusion of apple pomace facilitates pectin extraction. J Food Sci 63:841–844
37. Fishman ML, Chau HK, Hoagland PD, Hotchkiss AT (2006) Microwave-assisted extraction of lime pectin. Food Hydrocolloids 20:1170–1177
38. Contreras-Esquivel JC, Hours RA, Aguilar CN, Reyes-Vega ML, Romero J (1997) Microbial and enzymatic extraction of pectin. A review. Arch Latinoam Nutr 47:208–216
39. Shkodina OG, Zeltser OA, Selivanov NY, Ignatov VV (1998) Enzymatic extraction of pectin preparations from pumpkin. Food Hydrocolloids 12:313–316
40. Min B, Lim JB, Ko SH, Lee KG, Lee SH, Lee SY (2011) Environmentally friendly preparation of pectins from agricultural byproducts and their structural/rheological characterization. Bioresour Technol 102:3855–3860
41. Yu X, Sun D (2013) Microwave and enzymatic extraction of orange peel pectin. Asian J Chem 25:5333–5336
42. Rezzoug SA, Maache-Rezzoug Z, Sannier F, Karim A (2008) A thermomechanical preprocessing for pectin extraction from orange peel. Optimisation by response surface methodology. Int J Food Eng. doi:10.2202/1556-3758.1183
43. Liu Y, Shi J, Langrish TAG (2006) Water-based extraction of pectin from flavedo and albedo of orange peels. Chem Eng J 120:203–220
44. Huang G, Shi J, Zhang K, Huang X (2012) Application of ionic liquids in the microwave-assisted extraction of pectin from lemon peels. J Anal Meth Chem. doi:10.1155/2012/302059
45. Yang HC, Hon MH (2010) The effect of degree of deacetylation of chitosan nanoparticles and its characterization and encapsulation efficiency on drug delivery. Polym-Plast Technol 49:1292–1296
46. Flores R, Barrera-Rodriguez S, Shirai K, Duran-de-Bazua C (2007) Chitin sponge, extraction procedure from shrimp wastes using green chemistry. J Appl Polym Sci 104:3909–3916
47. Aye KN, Stevens WF (2004) Improved chitin production by pretreatment of shrimp shells. J Chem Tech Biotechnol 79:421–425
48. Cira LA, Huerta S, Hall GM, Shirai K (2002) Pilot scale lactic acid fermentation of shrimp wastes for chitin recovery. Process Biochem 37:1359–1366
49. Jo GH, Jung WJ, Kuk JH, Oh KT, Kim YJ, Park RD (2008) Screening of protease-producing *Serratia marcescens* FS-3 and its application to deproteinization of crab shell waste for chitin extraction. Carbohydr Polym 74:504–508
50. Arbia W, Arbia L, Adour L, Amrane A (2013) Chitin extraction from crustacean shells using biological methods – a review. Food Technol Biotechnol 51:12–25

51. Kaur S, Dhillon S (2013) Recent trends in biological extraction of chitin from marine shell wastes: a review. Crit Rev Biotechnol. doi:10.3109/07388551.2013.798256
52. Gildberg A, Stenberg E (2001) A new process for advanced utilization of shrimp waste. Process Biochem 36:809–812
53. Jung WJ, Jo GH, Kuk JH, Ki KY, Park RD (2005) Demineralization of crab shells by chemical and biological treatments. Biotechnol Bioprocess Eng 10:67–72
54. Kwon KN, Choi HS, Cha BS (2009) Effect of microwave and ultrasonication on chitin extraction time. Korea J Food & Nutr 22:8–13
55. Chen PH, Hwang YH, Kuo TY, Liu FH, Lai JY, Hsieh HJ (2007) Improvement in the properties of chitosan membranes using natural organic acid solutions as solvents. J Med Biol Eng 27:23–28
56. Xia Z, Wu S, Chen J (2013) Preparation of water soluble chitosan by hydrolysis using hydrogen peroxide. J Biol Macromol 59:242–245
57. Zivanovic S, Li JJ, Davidson M, Kit K (2007) Physical, mechanical, and antibacterial properties of chitosan/PEO blend films. Biomacromolecules 8:1505–1510
58. Tian F, Liu Y, Hu K, Zhao B (2004) Study of the depolymerization behavior of chitosan by hydrogen peroxide. Carbohydr Polym 57:31–37
59. Gouka R, Punt P, Van-den-Hondel C (1997) Efficient production of secreted proteins by *Aspergillus*: progress, limitations and prospects. Appl Microbiol Biotechnol 47:1–11
60. Roukas T (2000) Citric and gluconic acid production from fig by *Aspergillus niger* using solid state fermentation. J Ind Microbiol Biotechnol 25:298–304
61. Schuster E, Dunn-Coleman N, Frisvad J, Van-Dijck M (2002) On the safety of *Aspergillus niger*. Appl Microbiol Biotechnol 59:426–435
62. Cai J, Yang J, Du Y, Fan L, Qiu Y, Li J, Kennedy JF (2006) Enzymatic preparation of chitosan from the waste *Aspergillus niger* mycelium of citric acid production plant. Carbohydr Polym 64:151–157
63. Muzzarelli R, Boudrant J, Meyer D, Manno N, Demarcáis M, Paoletti M (2012) Current views on fungal chitin/chitosan, human chitinases, food preservation, glucans, pectins and inulin: a tribute to Henri Braconnot, precursor of the carbohydrate polymers science, on the chitin bicentennial. Carbohydr Polym 87:995–1012
64. Ruiz-Herrera J (2012) Cell wall composition. In: Group TF (ed) Fungal cell wall structure, synthesis, and assembly, 2nd edn. CRC Press, Boca Raton, pp 7–21
65. Vries RP, Visser J (2001) *Aspergillus* enzymes involved in degradation of plant cell wall polysaccharides. Microbiol Mol Biol Rev 65:497–522
66. Kogan G, Rauko P, Machova E (2003) Fungal chitin–glucan derivatives exert protective or damaging activity on plasmid DNA. Carbohydr Res 338:931–935
67. Fleet GH, Phaff HJ (1981) Fungal glucans-structure and metabolism. In: Tanner W, Loewus F (eds) Encyclopedia of plant physiology new series. Springer, Berlin, pp 416–440