



Eggplant peel as a high potential source of high methylated pectin: Ultrasonic extraction optimization and characterization

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ABSTRACT

Eggplant peel as a new source was used for pectin extraction using ultrasonic method. The extraction process factors were optimized using Box-Behnken design (BBD) and under optimal conditions (ultrasound power of 50 W, irradiation time of 30 min and pH of 1.5), the predicted extraction yield (35.36 g/100 g) was validated by the experimental results (33.64 ± 1.12 g/100 g). The eggplant peel pectin (EPP) was examined in terms of chemical, physicochemical, functional and structural features. The results indicated that the EPP was rich in galacturonic acid (66.08 g/100 g), high in degree of esterification (61.22%) and total phenolic content, and low in ash and protein content. Also, EPP had a suitable value of water and oil holding capacity, emulsifying properties, antioxidant activity, and foam capacity. In addition, FT-IR and ^1H NMR spectroscopy proved the existence of pectin structure in the obtained samples and XRD pattern suggested a high crystallinity in EPP.

1. Introduction

Eggplant fruit (*Solanum melongena* L.), as a popular vegetable with the elongated oval shape and dark purple peels, grows in all around the world especially in tropics and subtropics areas (Todaro et al., 2009). The peel of this vegetable, which mostly generated by food factories, restaurants or other food processing places, is a great source of many valuable ingredients such as polyphenols, flavonoids, minerals and polysaccharides (such as pectin and cellulose) (Dranca & Oroian, 2016). While, these peels were mostly discarded as a waste, which may cause serious environmental problems if not managed well (Braga et al., 2016). Thus, the recovery of these value-added components from this waste, as a food waste valorization process, could offer economical and environmental benefits (Lin et al., 2013). However, there are many studies of using this waste as a source of value-added materials such as polyphenols (Dranca & Oroian, 2016; Philippi, Tsamandouras, Grigorakis, & Makris, 2016; Todaro et al., 2009), while the polysaccharides of this waste (such as pectin) were less regarded.

Pectin as a food ingredient (INS 440) was applied in many food systems as thickener, stabilizer and emulsifier. The main structure of pectin composed of a linear backbone of α (1 $\rightarrow$ 4) D-galacturonic acid units with various methyl esterification, defined as the degree of esterification (DE). Based on this structural feature, pectin was categorized into two classes: LM (low methoxyl: DE < 50%) and HM (high methoxyl: DE > 50%) pectin that LM gels in the presence of Ca^{2+}

(used in dairy products), while HM gels in acidic medium and presence of high amount of sucrose (used in jam and jellies) (Kazemi, Khodaiyan, Labbafi, Hosseini, & Hojjati, 2019). Besides its technological applications, many health benefits were reported for this ingredient such as decreasing cholesterol, anti-ulcer activity and reducing heart disease (Wang et al., 2016). It is noteworthy that the worldwide annual demand for pectin is rising about 4–5% every year. Thus, due to the rising demand for pectin, it is necessary to represent and investigate additional inexpensive sources for pectin recovery (Yeoh, Shi, & Langrish, 2008).

Commercially, pectin was extracted by thermal heating in acidic medium (such as sulfuric acid), but due to the high extraction time (Maran, Priya, Al-Dhabi, Ponnurugan, Moorthy, & Sivarajasekare, 2017) and high generated wastewater (Moorthy et al., 2017), this method was inefficient. Thus, many novel and efficient techniques, such as microwave-assisted extraction, accelerated solvent extraction, supercritical fluid extraction and ultrasound-assisted extraction (UAE) method, were developed to provide a quick, inexpensive, and environmentally friendly extraction process (Maran & Priya, 2015). UAE technique is being widely used to study on recovery of pectin from many various plants such as grapefruit peel (Wang et al., 2016), sunflower head (Ponnurugan et al., 2017), sisal waste (Maran & Priya, 2015) and grape pomace (Minjares-Fuentes et al., 2014).

To the best of our knowledge, no studies were reported for pectin extraction optimization from eggplant peels. Therefore, this study was designed to optimize the UAE factors including ultrasound power,

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sonication time and pH for eggplant peel pectin (EPP) production using Box-Behnken design (BBD), and examine its physicochemical, functional and structural properties.

2. Materials and methods

2.1. Materials and chemicals

Fresh dark purple eggplants with no apparent damages were bought from the local fruit market (Karaj, Alborz, Iran). The eggplants were peeled manually using a sharp knife, then the obtained peels were dried in an oven at 45 °C for 48 h. The dried peels were milled into a fine powder using a grinder and stored in a dark dry place. The obtained powder was used in the pectin extraction process.

Citric acid, hydrochloric acid, sulfuric acid, sodium tetraborate and sodium hydroxide, sodium carbonate, gallic acid, Folin-Ciocalteu and DPPH (1,1-Diphenyl-2-picrylhydrazyl) were purchased from Merck Chemical Co. (Darmstadt, Germany). Also, sodium azide, ethanol (96%) and sunflower oil were bought from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA), Ghadir Co. (Tehran, Iran) and Famila Co. (Golestan, Iran) respectively.

2.2. Recovery of pectin

For this purpose, an ultrasonic device (Ultrasonic Co., Iran) equipped with a cylindrical titanium probe (10 mm diameter) was used for the extraction process. At first, LSR (liquid to solid ratio) was fixed in the best point (see section 2.3) and then other factors (ultrasound power, sonication time and pH) of UAE were optimized using BBD (Table 1). Briefly, 5 g of eggplant peel powder was mixed with acidified distilled water and then the probe of the ultrasonic device was submerged into the mixture, then the time and power of ultrasound were set up. After extraction, the mixture was centrifuged (10000 × g, 15 min), the supernatant was precipitated with ethanol (96%) and placed at 4 °C for 18 h. The obtained mixture was centrifuged (10000 × g, 20 min) and the coagulated pectin was washed three times with ethanol. Afterward, the wet pectin was dried in an oven (45 °C, 16 h). The extraction yield was calculated as follow:

Table 1

Box-Behnken design for EPP (eggplant peel pectin) extraction variables with experimental and predicted responses.

Factors	Unit	Actual levels		
		−1	0	+1
Ultrasound power (X_1)	W	50	100	150
Irradiation time (X_2)	min	10	20	30
pH (X_3)	–	1.5	2.25	3

Run No.	X_1	X_2	X_3	Pectin yield (g/100 g)	
				Experimental	predicted
1	50	10	2.25	2.20	2.90
2	150	10	2.25	12.80	12.65
3	50	30	2.25	27.60	27.75
4	150	30	2.25	15.80	15.10
5	50	20	1.50	22.60	21.92
6	150	20	1.50	13.40	13.57
7	50	20	3.00	2.80	2.62
8	150	20	3.00	7.40	8.07
9	100	10	1.50	10.40	10.37
10	100	30	1.50	27.40	27.92
11	100	10	3.00	2.40	1.87
12	100	30	3.00	11.60	11.62
13	100	20	2.25	18.20	17.87
14	100	20	2.25	17.80	17.87
15	100	20	2.25	17.60	17.87

$$\text{Extraction Yield (g/100g)} = \frac{\text{Dried pectin weight}}{\text{Dried powder weight}} \times 100 \quad (1)$$

2.3. Chemical characterization

The chemical composition of EPP was determined. Moisture and ash content was evaluated according to the method described by Kazemi et al. (2019). Protein content estimated using Kjeldahl method ($N \times 6.25$). GalA (galacturonic acid) content was determined using the method described by Blumenkrantz and Asboe-Hansen (1973).

DE of GalA units was measured using the titrimetric method. briefly, 20 ml of pectin solution (0.5 g/100 ml) was prepared and then 3–5 drops of phenolphthalein reagent were added to it. The mixture was titrated with sodium hydroxide solution (0.1 M) until the pink color was appeared (V_1). Afterward, 10 ml of sodium hydroxide solution (0.1 M) was added to the mixture (the pink color becomes intense) and stirred for 20 min. Then, 10 ml of hydrochloric acid solution (0.1 M) was added to it (the pink color disappears). The solution was titrated again with sodium hydroxide solution (0.1 M) (V_2) (Pasandide, Khodaiyan, Mousavi, & Hosseini, 2018). The DE of EPP was estimated by the following equation:

$$\text{DE (\%)} = \frac{V_2}{V_2 + V_1} \times 100 \quad (2)$$

Total phenolic content (TPC) of EPP was determined using Folin-Ciocalteu method (Hosseini, Khodaiyan, Kazemi, & Najari, 2019). TPC of EPP was expressed as mg gallic acid equivalent per gram of dry EPP (mg GAE/g EPP).

2.4. Surface tension measurement

Surface tension of EPP solution (0.1 and 0.5% w/v) was measured at room temperature using a tensiometer device (Nanometric-pazhoh Co. Tehran, Iran) with a sensitivity set to 0.05 mN/m and Wilhelmy plate method with a mica plate (11.87 mm × 8.12 mm × 0.13 mm) (Yapo, Whatthelet, & Paquot, 2007).

2.5. Water holding capacity (WHC) and oil holding capacity (OHC)

In brief, 1 g of EPP was mixed into 10 ml of distilled water then the obtained mixture was vortexed vigorously for 1 min and centrifuged for 30 min (at 3000 × g). The supernatant was removed and the remnants were weighted. The WHC was defined as gram of water held per gram of EPP (Bayar, Friji, & Kammoun, 2018). The OHC measurement was similar to WHC except that, sunflower oil (density of oil: 0.9 g/ml) was used instead of distilled water and OHC was defined as gram of oil held per gram of EPP.

2.6. Emulsifying properties

Briefly, 5 ml pectin solution (0.5 g/100 ml w/w) containing sodium azide (0.02 g/100 ml) was prepared into 15 ml polypropylene centrifuge tube and then 5 ml of sunflower oil was added to it. Afterward, the tube was treated with ultrasound homogenizer for 5 min and centrifuged at 4000 × g for 5 min (Hosseini, Khodaiyan, & Yarmand, 2016). Emulsifying activity (EA) was calculated by the following equation:

$$\text{EA (\%)} = \frac{V_E}{V_T} \times 100 \quad (3)$$

where V_E was the volume of the emulsion layer and V_T was the total volume of the system.

A similar method for emulsion preparation was carried out for estimating emulsion stability (ES) and prepared emulsions were stored for 1 and 30 days in 4 °C and room temperature. Afterward, ES was estimated by the following equation:

$$ES(\%) = \frac{V_R}{V_I} \times 100 \quad (4)$$

where V_R was the remained emulsified volume and V_I was the initial emulsified volume.

2.7. DPPH radical scavenging

Antioxidant activity of EPP was determined using DPPH method as described by Bayar et al. (2017). Briefly, 1 ml of pectin solution (1–50 mg/ml) was mixed with 4 ml of DPPH methanolic solution (0.1 mM). The prepared mixture was vortexed for 1 min and incubated for 30 min in darkness (room temperature). The absorbance of the mixture was recorded at 517 nm. For better understanding, ascorbic acid (AA) solution was prepared in the same concentrations and used as a standard sample to comprise the antioxidant activity of EPP and AA. The DPPH radical scavenging activity was calculated by the following equation:

$$\text{DPPH radical scavenging activity}(\%) = \left[1 - \left(\frac{A_{\text{sample}}}{A_{\text{control}}} \right) \right] \times 100 \quad (5)$$

2.8. Foaming properties

Briefly, 10 ml of EPP solution (2 and 4 g/100 ml) was prepared into 15 ml polypropylene centrifuge tube and vortexed for 3 min (Bayar et al., 2017). Foaming capacity (FC) and foam stability (FS) of EPP was evaluated by the following equation:

$$FC(\%) = \frac{V_0 - V_T}{V_T} \times 100 \quad (6)$$

$$FS(\%) = \frac{V_{30} - V_T}{V_T} \times 100 \quad (7)$$

where V_0 , V_{30} , and V_T are total volume after vortex ($t = 0$), total volume after 30 min and initial volume of solution, respectively.

2.9. FT-IR (Fourier transform-infrared) analysis

FT-IR spectrum of EPP was recorded using Thermo Avatar 370 spectrometer (Waltham, MA, USA) with KBr method. The wavenumber was ranged from 500 to 4000 cm^{-1} with a resolution of 4 cm^{-1} .

2.10. ^1H NMR (hydrogen-1 nuclear magnetic resonance) analysis

^1H NMR spectrum was recorded using a Varian Unity Inova 500 MHz spectrometer (Palo Alto, CA, United States). The internal temperature was 23 °C and 8 scans were collected with a relaxation delay of 1 s and acquisition time of 4.00 s.

2.11. XRD (X-ray diffraction) pattern analysis

The X-ray diffraction pattern of EPP was recorded using an X-ray diffractometer (PHILIPS, Amsterdam, Netherlands). The EPP powder was scanned in diffraction angle (2θ) from 10° to 50°. The step size and time per each point were 0.05° (2θ) and 1 s, respectively.

2.12. Experimental design

Firstly, for choosing the best LSR one factor at a time technique was used. In this part, one of the factors (LSR) was variable (15, 20, 25, 30, 35, and 40 v/w), while the other three factors (ultrasound power, irradiation time, and pH) were fixed in the center point of extraction (100 W, 20 min, and 2.25, respectively). Then, the best LSR was used as a constant factor in the next experiments. To optimize the other variables (each in three levels) of UAE, BBD was used and the effects of

these factors on extraction yield were investigated (Pasandide, Khodaiyan, Mousavi, & Hosseini, 2017). All the statistical analysis and graphics were carried out using the statistical software Design Expert 7.0 and Excel.

3. Results and discussion

3.1. Statistical analysis and optimization process

First, the best LSR was selected using one factor at a time design. For this purpose, LSR was considered as a variable in six levels (15, 20, 25, 30, 35, and 40 v/w), while the other three factors were fixed in the center point (ultrasound power of 100 W, sonication time of 20 min and pH of 2.25). The results showed that LSR of 20 v/w had the highest yield value and it was considered as a constant in the optimization process of the other factors of UAE. According to Table 1, the lowest and the highest yield value of pectin was achieved in run number 1 (2.20 g/100 g) and run number 3 (27.60 g/100 g), respectively. In addition, the extraction optimal point (ultrasound power of 50 W, irradiation time of 30 min and pH of 1.5) obtained by the extraction proposed model (Eq. (8)) had a pectin yield of 35.36 g/100 g. This model was examined by three experiments in the mentioned conditions (optimal extraction conditions) and the observed results (the pectin yield under optimal conditions was 33.64 ± 1.12 g/100 g) were assured that the proposed quadratic polynomial model was very suitable for pectin yield prediction. It should be stated that, the pectin yield obtained from eggplant peel was much higher than other non-commercial sources of pectin such as *Uba* mango peel (32.1 g/100 g), sour orange peel (29.1 g/100 g), durian rind (9.1 g/100 g) and dragon fruit peel (7.5 g/100 g). (do Nascimento Oliveira et al., 2018; Hosseini et al., 2016; Maran, 2015; Thirugnanasambandham, Sivakumar, & Maran, 2014), which showed the eggplant peel could be considered as a high potential source for pectin besides of commercial sources such as citrus peel, apple pomace, and sugar beet pulp.

According to the results of analysis of variance (ANOVA) (Table 2), the obtained higher F-value (192.31) and lower p-value (< 0.0001) justifies that the proposed model is extremely significant. In addition, all of the extraction factors significantly affected extraction yield due to the higher F-value and lower p-value. The higher value of determination coefficient ($R^2 = 0.9971$) implies that 99.71% of all variations

Table 2

Analysis of variance (ANOVA) for the proposed model of EPP (eggplant peel pectin) extraction yield.

Source	DF	Some of squares	Mean square	F-value	p-value
Yield					
Model	9	947.343	105.260	192.31	0.000
Linear	3	684.370	228.123	416.79	0.000
Power	1	4.205	4.205	7.68	0.039
Time	1	372.645	372.645	680.84	0.000
pH	1	307.520	307.520	561.85	0.000
Square	3	74.713	24.904	45.50	0.000
Power × Power	1	20.103	20.103	36.73	0.002
Time × Time	1	3.216	3.216	5.88	0.060
pH × pH	1	58.586	58.586	107.04	0.000
Interaction	3	188.260	62.753	114.65	0.000
Power × Time	1	125.440	125.440	229.18	0.000
Power × pH	1	47.610	47.610	86.99	0.000
Time × pH	1	15.210	15.210	27.79	0.003
Error	5	2.737	0.547		
Lack-of-Fit	3	2.550	0.850	9.11	0.101
Pure Error	2	0.187	0.093		
Total	14	950.080			
R^2			0.9971		
Adj R^2			0.9919		
Pred R^2			0.9566		

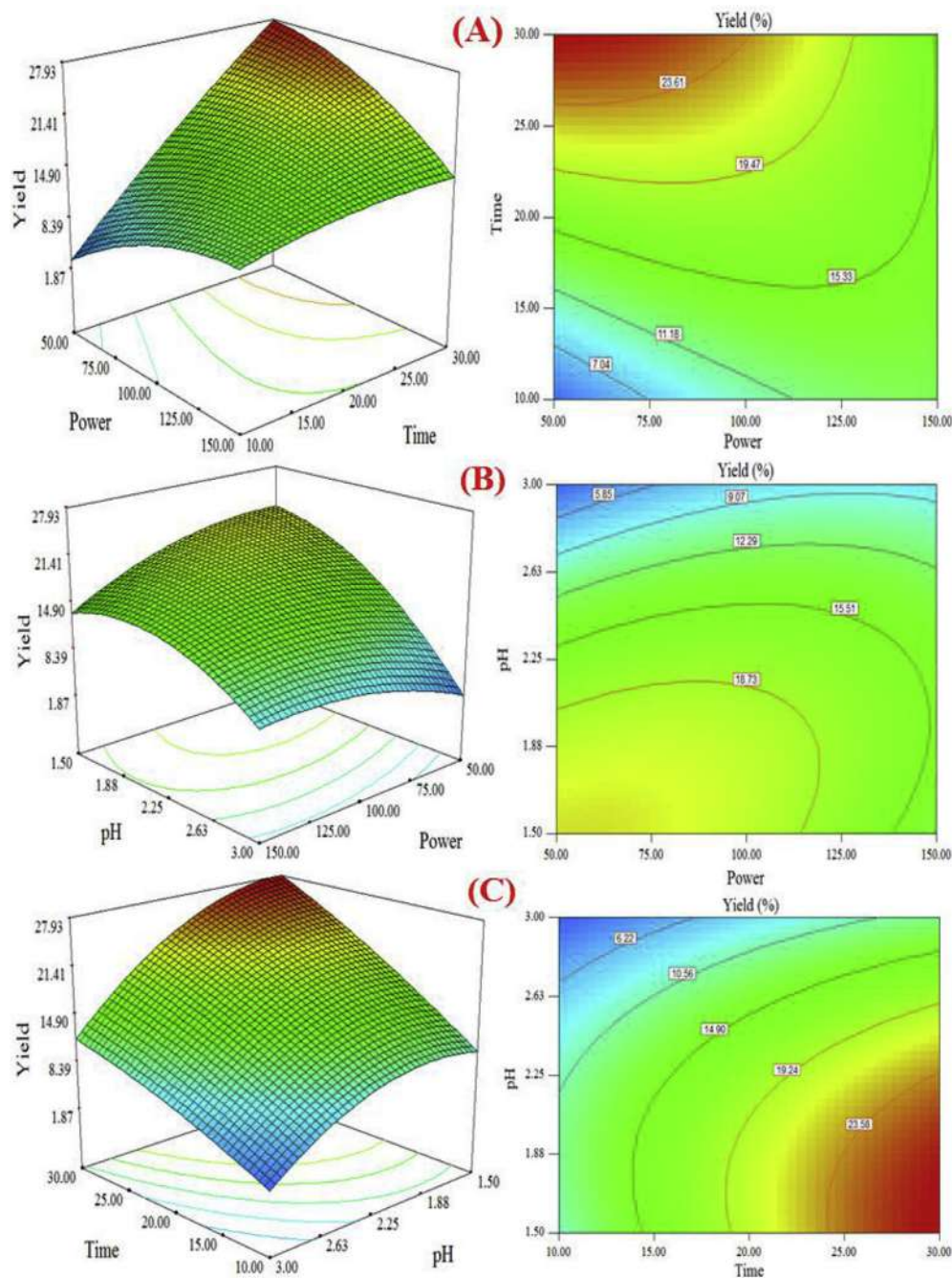


Fig. 1. Effect of ultrasound-extraction factors (A: power and time; B: power and pH; C: time and pH) on pectin yield.

could be explained by the proposed model (Thirugnanasambandham et al., 2014). The p-value of lack-of-fit test was insignificant (0.101) which indicates the model was well-fitted for the relationship between variables and responses (Kazemi et al., 2019). Considering the given results, the square polynomial model (Eq. (8)) was extremely suitable for representing the relationship between variables and responses and there was no need for higher order models.

$$\begin{aligned} \text{Yield(g/100g)} = & 17.87 - 0.72X_1 + 6.82X_2 - 6.20X_3 - 2.33X_1^2 - 0.93X_2^2 \\ & - 3.98X_3^2 - 5.60X_1X_2 + 3.45X_1X_3 - 1.95X_2X_3 \end{aligned} \quad (8)$$

where X_1 , X_2 and X_3 are the coded values of ultrasound power, irradiation time and pH, respectively.

3.2. The role of extraction factors on pectin yield

Three-dimensional (3D) and contour plots were established to visualize the relationship between extraction variables and pectin yield (Fig. 1). As can be seen, the pectin yield was decreased by an increase in ultrasound power from 50 W to 150 W (Fig. 1A and B). This observation may be due to this fact that the ultrasound waves generate cavitation bubbles that their explosion leads to a high force in medium and thereby degradation and fragmentation of the pectin structure to its oligosaccharides (Maran et al., 2017). The effect of irradiation time on pectin yield was investigated and results showed in Fig. 1A and C. The mentioned figures indicated that by an increase in irradiation time, the pectin yield was increased. The increasing irradiation time probably leads to increase in plant material swelling, improve in the medium infusion into the plant and increase in the pectin leakage rate and

Table 3
Chemical and physicochemical properties of EPP (eggplant peel pectin) extracted under optimal extraction conditions.

Chemical composition	
Ash (g/100 g)	2.41 ± 0.16
Moisture (g/100 g)	8.29 ± 0.74
Protein (g/100 g)	2.53 ± 0.38
GalA content (g/100 g)	66.08 ± 1.34
DE (%)	61.22 ± 4.49
TPC (mg GAE ^a /g pectin)	96.81 ± 2.18
Surface tension (mN/m)	
0.1 g/100 ml	55.81 ± 2.27
0.5 g/100 ml	44.63 ± 1.09

^a GAE was gallic acid equivalent.

pectin yield (Moorthy et al., 2017). The effect of pH on the pectin extraction yield was illustrated in Fig. 1B and C. This data can be due to this fact that the high acidic medium improved the plant cell wall destruction, reduced pectin molecular weight, increased leakage of pectin from plant matrix into the surrounding medium and improved the extraction yield, respectively (Hosseini et al., 2016; Maran et al., 2017; Moorthy et al., 2017).

3.3. Chemical characterization

Chemical composition of EPP extracted under optimal extraction conditions (ultrasound power of 50 W, irradiation time of 30 min and pH of 1.5) was illustrated in Table 3. Ash and moisture content of EPP was found 2.41 and 8.29 g/100 g, respectively. It should also be noted that the ash content of EPP was similar to the banana peel pectin (Khamsucharit, Laohaphatanalert, Gavinlertvatana, Sriroth, & Sangseethong, 2018). EPP had a protein content of 2.53 g/100 g that was very lower than the pistachio green hull pectin (6.3 g/100 g, Kazemi et al., 2019). This difference in protein content can be attributed to the difference in raw material and extraction technique. However, FAO (Food and Agriculture Organization) suggests that protein content of pectin should not be higher than 15.6 g/100 g (FAO JECFA, 2009). GalA content of pectin illustrates the purity of extracted pectin. Considering FAO and European Union recommendations, the GalA content of pectin used as a food additive or pharmaceutical purpose should not be lower than 65 g/100 g pectin (Khamsucharit et al., 2018). However this parameter was 66.08 g/100 g for EPP, means the GalA content of EPP was higher than the recommended value (65 g/100 g). Also, this value was similar to the reported data for pistachio green hull pectin (66.0 g/100 g, Kazemi et al., 2019), and higher than *Opuntia ficus indica* peel pectin (64.5 g/100 g, Habibi, Heyraud, Mahrouz, & Vignon, 2004). EPP extracted under optimal conditions had DE value of 61.22%, which indicated that the EPP should be categorized as HM pectin. This result was in line with the obtained data of FT-IR and ¹H NMR spectroscopy (see section 3.8 and 3.9, respectively). Evaluation of TPC for pectin is a necessary issue due to the effect of this factor on other properties of pectin (such as antioxidant activity). EPP had a TPC value of 96.81 mg GAE/g pectin. This value was higher than *Tamarindus indica* L. pulp pectin (79.66 ± 4.71 mg GAE/g pectin; Sharma, Kamboj, Khurana, Singh, & Rana, 2015). A higher value of this parameter may be due to the differences in raw material since the eggplant peel is known as a high potential source for phenolic compounds (Dranca & Oroian, 2016; Todaro et al., 2009).

3.4. Surface tension measurement

The surface tension of EPP solutions was evaluated and the obtained results were provided in Table 3. According to these results, EPP

solution at a concentration of 0.1 and 0.5 g/100 ml had surface tension values of 55.81 and 44.63 mN/m. These observations showed that the surface tension of EPP solution was reduced by increase in the EPP solution concentration, which was probably due to the increase of TPC and protein content in 0.5 g/100 ml solution. Some phenolic compounds would accumulate in the air-water interface, increase the surface pressure value and the surface activity, and thereby reduce the surface tension of solution (Di Mattia, Sacchetti, Mastrocola, Sarker, & Pittia, 2010). Previously, Yapo, Wathélet, and Paquot (2007) reported that the surface tension of sugar beet pulp pectin solution at a concentration of 0.1 g/100 ml was lower than 0.5 g/100 ml. These researchers stated that increase in pectin solution surface tension with increasing concentration is probably due to the increase in pectin solution viscosity. Thus, it seems that in this study, the effect of high TPC was dominant for surface tension rather than viscosity. It should also be stated that these results were proved by foam properties measurement (see section 3.7).

3.5. WHC and OHC measurement

WHC is the amount of water retained by 1 g of pectin. The water is consist of bound water, hydrodynamic water and physically trapped water. WHC is an important functionality since pectin with high WHC could help to improve textural properties and avoid syneresis problems in some food products such as yogurt (Yuan et al., 2018). Thus, WHC of EPP was evaluated and the results showed that 1 g of obtained EPP under optimal extraction conditions could hold 6.22 ± 0.21 g water. This value was higher than pistachio green hull pectin (4.11 g/g; Kazemi et al., 2019) and *Opuntia ficus indica* cladodes pectin (5.42 g/g; Bayar et al., 2018). However, various factors could be effective on this parameter such as chemical composition, structure and porosity of pectin, pH, temperature and ionic strength (Elleuch et al., 2011).

OHC is the amount of oil held by 1 g of pectin. Measurement of OHC for pectin is an important issue since pectin with high OHC could be used as a good stabilizer in fatty food products and emulsions (Yuan et al., 2018). Therefore, the OHC of EPP was evaluated and the results showed that each gram of EPP could hold 2.12 ± 0.15 g oil. The obtained value was slightly higher than pistachio green hull pectin (Kazemi et al., 2019) and *Opuntia ficus indica* cladodes pectin (Bayar et al., 2018). It should be stated that the source of pectin, chemical composition and structure of pectin and its affinity to oil could have effect on this parameter (Yuan et al., 2018).

3.6. Emulsifying properties

The EA and ES of EPP were evaluated and the results were exhibited in Table 4. As can be seen, the EA of EPP was about 56.16%, which was higher than the reported data for *Citrus medica* peel pectin (46.5%) and sour orange peel pectin (40.7%) by Pasandide et al. (2017) and Hosseini et al. (2016), respectively. Also, the highest emulsion stability was attributed to the stored emulsion sample at 4 °C. These observations, in agreement with previous studies (Ma et al., 2013; Yapo et al., 2007), indicated that the low temperature (4 °C) was more suitable for storage of EPP emulsions.

3.7. Antioxidant activity measurement

Antioxidant activity of EPP was determined using DPPH radical scavenging method. In this method, when free radicals of DPPH were scavenged by sample, DPPH transforms to its non-radical form and thereby the color of the solution would be changed from dark purple to light yellow. According to Fig. 2, the results indicated that by an increase in EPP concentration, the antioxidant activity was increased with a steep slope until EPP concentration of 10 mg/ml and after that, the concentration did not have a significant effect on the antioxidant activity. However, the highest antioxidant activity was achieved in the

Table 4

Functional properties of EPP (eggplant peel pectin) extracted under optimal extraction conditions.

WHC and OHC (g/g)			
WHC (water holding capacity)			6.22 ± 0.21
OHC (oil holding capacity)			2.12 ± 0.15
Emulsifying properties (%)			
Emulsifying activity		24 °C	56.16 ± 1.23
Emulsion stability	After 1 day	4 °C	96.36 ± 0.80
		24 °C	93.23 ± 0.84
	After 30 days	4 °C	91.66 ± 1.57
		24 °C	82.55 ± 1.93
Foaming properties (%)			
FC (foaming capacity)	2 g/100 ml		14.33 ± 0.47
	4 g/100 ml		32.67 ± 1.69
FS (foam stability)	2 g/100 ml		9.67 ± 0.94
	4 g/100 ml		22.00 ± 2.16

concentration of 50 mg/ml (94%) which it was still lower than the antioxidant activity of AA. The IC₅₀ value of EPP solution was 1.39 mg/ml, which was lower than the data obtained for *Opuntia ficus indica* cladodes pectin (8 mg/ml; Bayar et al., 2017). This lower IC₅₀ (The amount of sample that scavenges 50% of the initial DPPH concentration) and higher antioxidant activity may be due to the higher TPC. However, galacturonic acid content of the extracted pectin could be effective in antioxidant activity due to the presence of active portions in its structure as reported by Bayar et al. (2018).

3.8. Foaming properties

Foam is a complex of air bubbles trapped in the liquid. Materials with high FC and FS could be used in the formulation of aerated food products. FC and FS of EPP solutions in different concentrations (2 and 4 g/100 ml) were listed in Table 4. According to these results, EPP had an FC value of 14.33 and 32.67% at a concentration of 2 and 4 g/100 ml, respectively. The increasing FC with an increase in concentration can be due to higher TPC in the mentioned solution. On the other hand, FS of EPP solutions at a concentration of 2 and 4% were 9.67 and 22.00%, respectively. It should be stated that the obtained results for FC and FS of EPP solutions were in agreement with the previously reported results for *Opuntia ficus indica* cladodes pectin (Bayar et al., 2017) and the surface tension measurement data (section 3.4).

3.9. FT-IR analysis

The dried powder of EPP was analyzed by FT-IR spectroscopy and the obtained spectrum was shown in Fig. 3. The characteristic peaks ranged at 3000–3500 cm⁻¹ were due to the inter- and intra-molecular hydrogen binding of O–H groups related to the galacturonic acid units. A weak peak at 2914 cm⁻¹ was attributed to C–H of CH, CH₂ and CH₃ groups of galacturonic acid. The absorption peaks of 1748 and 1632 cm⁻¹ ascribed to the esterified and free carboxylic groups of the galacturonic acid polymer, respectively. The broad peaks ranged at 1000–1250 cm⁻¹ were related to the C–O–C vibrations of glycoside bonds (Grassino et al., 2016; Rodsamran & Sothornvit, 2019; Wang et al., 2016). Therefore, the presence of pectin in the obtained supernatant was confirmed according to the mentioned absorption bonds. In addition, the ratio of absorption bond at 1748 cm⁻¹ over the sum of the bonds at 1748 and 1632 cm⁻¹ is related to the DE value of pectin and illustrates that DE of EPP is considered as HM pectin (Talekar, Patti, Vijayraghavan, & Arora, 2018). Thus, it could be concluded that the obtained results of DE measurement were in line with FT-IR spectrum analysis.

3.10. ¹H NMR analysis

The dried EPP powder was dissolved in D₂O and analyzed by ¹H NMR spectroscopy. According to the obtained spectrum (Fig. 4), the most intense signal around 3.7 ppm is probably due to the protons of esterified galacturonic acid units (–OCH₃). Also, the signal at 1.8 ppm was derived from acetyl groups of galacturonic acid units. These mentioned signals were related to the DE of galacturonic acid units and higher intensity of these signals show higher DE value (Grassino et al., 2016; Talekar et al., 2018; Wang et al., 2016). Thus it could be concluded that the DE of EPP was HM pectin which was in agreement with the results of titrimetric measurement of DE and FT-IR spectroscopy. Besides, the appeared signals at 3.6, 3.9, 4.1, 4.9 and 5.1 were related to the protons on C2, C3, C4, C5 and C1 of galacturonic acid units, respectively (Grassino et al., 2016). These results confirmed the predominant existence of the esterified pectin in the extracted samples.

3.11. XRD analysis

X-ray diffraction (XRD) was used to describe more structural information (crystallinity or amorphous) about EPP. The obtained XRD pattern (Fig. 5) indicated the crystalline portions of EPP structure was more than amorphous portions because the sharp and intense signals appeared at 13.8°, 17.6°, 18.9°, 25.7°, 30.8°, 33.2°, and 42.6°. Thus, the obtained results suggested crystalline nature for EPP. Sharma et al.

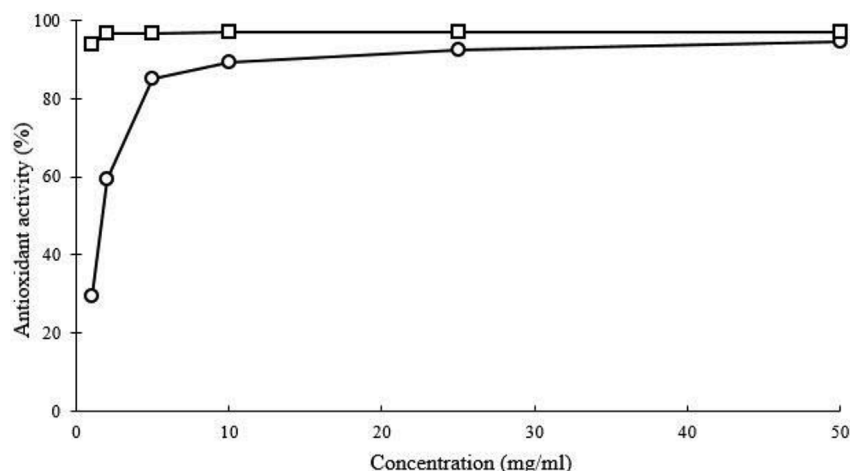


Fig. 2. Comparison of antioxidant activity between eggplant peel pectin (○) and ascorbic acid (□).

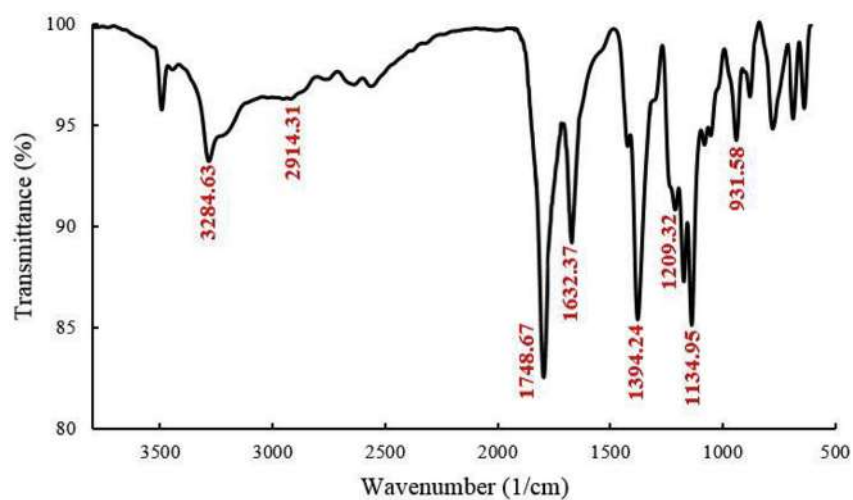


Fig. 3. FT-IR spectrum of eggplant peel pectin.

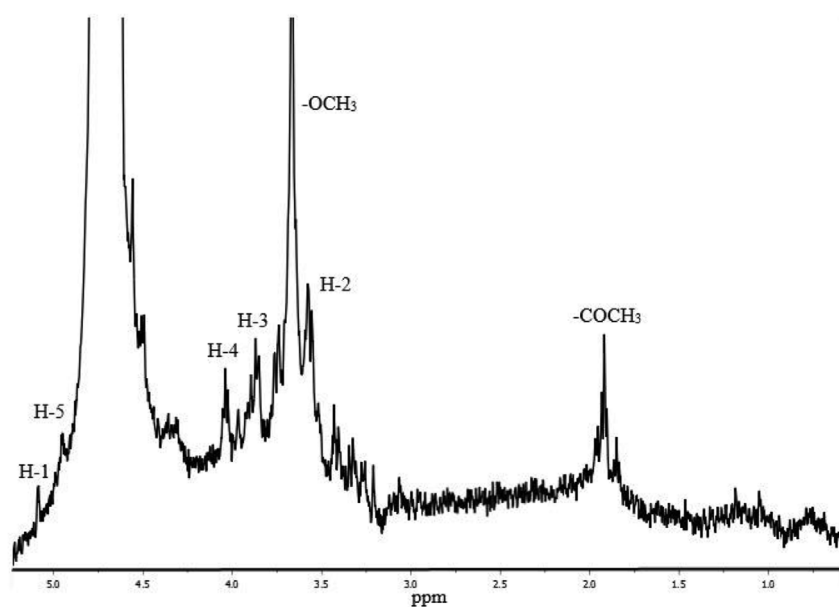
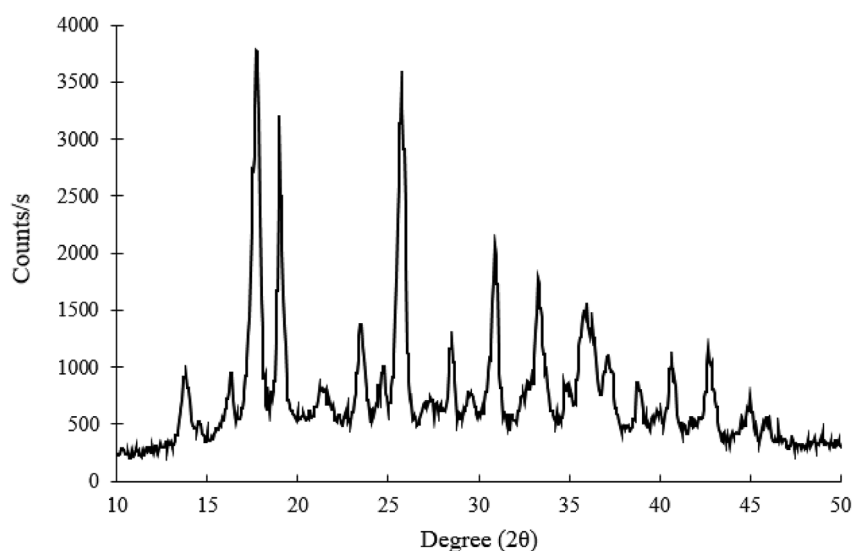
Fig. 4. ¹H NMR spectrum of eggplant peel pectin.

Fig. 5. X-ray diffraction pattern of eggplant peel pectin.

(2015) were suggested crystalline nature for *Tamarindus indica* L. pulp pectin. However, it looks the crystallinity of pectin is depended on raw material source and extraction procedure.

4. Conclusion

In the present study, pectin was extracted from eggplant peel by UAE. The optimization process was carried out using BBD and the results showed the highest extraction yield (33.64 g/100 g) was achieved in the ultrasound power of 50 W, irradiation time of 30 min and pH of 1.5. The obtained EPP in the mentioned conditions had high galacturonic acid (66.08 g/100 g) and total phenolic content (96.81 mg GAE/g pectin). Also, the results of DE measurement suggested that the EPP should be categorized as HM pectin which was in agreement with the results obtained from FT-IR and ^1H NMR spectroscopy. In addition, EPP showed promising values in functional features such as WHC and OHC, emulsifying and foaming properties, and antioxidant activity. Considering the high extraction yield and also the suitable properties for EPP, the eggplant peel could be considered as a high potential source for the pectin production.

References

- Bayar, N., Bouallegue, T., Achour, M., Kriaa, M., Bougatef, A., & Kammoun, R. (2017). Ultrasonic extraction of pectin from *Opuntia ficus indica* cladodes after mucilage removal: Optimization of experimental conditions and evaluation of chemical and functional properties. *Food Chemistry*, 235, 275–282.
- Bayar, N., Friji, M., & Kammoun, R. (2018). Optimization of enzymatic extraction of pectin from *Opuntia ficus indica* cladodes after mucilage removal. *Food Chemistry*, 241, 127–134.
- Blumenkrantz, N., & Asboe-Hansen, G. (1973). New method for quantitative determination of uronic acids. *Analytical Biochemistry*, 54(2), 484–489.
- Braga, P. C., Scalzo, R. L. O., Dal Sasso, M., Lattuada, N., Greco, V., & Fibiani, M. (2016). Characterization and antioxidant activity of semi-purified extracts and pure delphinidin-glycosides from eggplant peel (*Solanum melongena* L.). *Journal of Functional Foods*, 20, 411–421.
- Di Mattia, C. D., Sacchetti, G., Mastrocola, D., Sarker, D. K., & Pittia, P. (2010). Surface properties of phenolic compounds and their influence on the dispersion degree and oxidative stability of olive oil O/W emulsions. *Food Hydrocolloids*, 24(6–7), 652–658.
- Dranca, F., & Oroian, M. (2016). Optimization of ultrasound-assisted extraction of total monomeric anthocyanin (TMA) and total phenolic content (TPC) from eggplant (*Solanum melongena* L.) peel. *Ultrasonics Sonochemistry*, 31, 637–646.
- Elleuch, M., Bedigian, D., Roiseux, O., Besbes, S., Blecker, C., & Attia, H. (2011). Dietary fibre and fibre-rich by-products of food processing: Characterisation, technological functionality and commercial applications: A review. *Food Chemistry*, 124(2), 411–421.
- Grassino, A. N., Brnčić, M., Vikić-Topić, D., Roca, S., Dent, M., & Brnčić, S. R. (2016). Ultrasound assisted extraction and characterization of pectin from tomato waste. *Food Chemistry*, 198, 93–100.
- Habibi, Y., Heyraud, A., Mahrouz, M., & Vignon, M. R. (2004). Structural features of pectic polysaccharides from the skin of *Opuntia ficus-indica* prickly pear fruits. *Carbohydrate Research*, 339(6), 1119–1127.
- Hosseini, S. S., Khodaiyan, F., Kazemi, M., & Najari, Z. (2019). Optimization and characterization of pectin extracted from sour orange peel by ultrasound assisted method. *International Journal of Biological Macromolecules*, 125, 621–629. <https://doi.org/10.1016/j.ijbiomac.2018.12.096>.
- Hosseini, S. S., Khodaiyan, F., & Yarmand, M. S. (2016). Optimization of microwave assisted extraction of pectin from sour orange peel and its physicochemical properties. *Carbohydrate Polymers*, 140, 59–65.
- JECFA, F. A. O. (2009). Compendium of food additive specifications. *The Monograph*, 7 In 71st meeting.
- Kazemi, M., Khodaiyan, F., Labbafi, M., Hosseini, S. S., & Hojjati, M. (2019). Pistachio green hull pectin: Optimization of microwave-assisted extraction and evaluation of its physicochemical, structural and functional properties. *Food Chemistry*, 271, 663–672.
- Khamsucharit, P., Laohaphatanalert, K., Gavinlertvatana, P., Sriroth, K., & Sangseethong, K. (2018). Characterization of pectin extracted from banana peels of different varieties. *Food Science and Biotechnology*, 27(3), 623–629.
- Lin, C. S. K., Pfaltzgraff, L. A., Herrero-Davila, L., Mubofu, E. B., Abderrahim, S., Clark, J. H., et al. (2013). Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and global perspective. *Energy & Environmental Science*, 6(2), 426–464.
- Maran, J. P. (2015). Statistical optimization of aqueous extraction of pectin from waste durian rinds. *International Journal of Biological Macromolecules*, 73, 92–98.
- Maran, J. P., & Priya, B. (2015). Ultrasound-assisted extraction of pectin from sisal waste. *Carbohydrate Polymers*, 115, 732–738.
- Maran, J. P., Priya, B., Al-Dhabi, N. A., Ponnurugan, K., Moorthy, I. G., & Sivarajasekar, N. (2017). Ultrasound assisted citric acid mediated pectin extraction from industrial waste of *Musa balbisiana*. *Ultrasonics Sonochemistry*, 35, 204–209.
- Ma, S., Yu, S., Zheng, X., Wang, X., Bao, Q.-D., & Guo, X. (2013). Extraction, characterization and spontaneous emulsifying properties of pectin from sugar beet pulp. *Carbohydrate Polymers*, 98(1), 750–753.
- Minjares-Fuentes, R., Femenia, A., Garau, M. C., Meza-Velázquez, J. A., Simal, S., & Rosselló, C. (2014). Ultrasound-assisted extraction of pectins from grape pomace using citric acid: A response surface methodology approach. *Carbohydrate Polymers*, 106, 179–189.
- Moorthy, I. G., Maran, J. P., Ilakya, S., Anitha, S. L., Sabarima, S. P., & Priya, B. (2017). Ultrasound assisted extraction of pectin from waste *Artocarpus heterophyllum* fruit peel. *Ultrasonics Sonochemistry*, 34, 525–530.
- do Nascimento Oliveira, A., de Almeida Paula, D., de Oliveira, E. B., Saraiva, S. H., Stringheta, P. C., & Ramos, A. M. (2018). Optimization of pectin extraction from *Urbá* mango peel through surface response methodology. *International Journal of Biological Macromolecules*, 113, 395–402.
- Pasandide, B., Khodaiyan, F., Mousavi, Z. E., & Hosseini, S. S. (2017). Optimization of aqueous pectin extraction from *Citrus medica* peel. *Carbohydrate Polymers*, 178, 27–33.
- Pasandide, B., Khodaiyan, F., Mousavi, Z., & Hosseini, S. S. (2018). Pectin extraction from citron peel: Optimization by Box–Behnken response surface design. *Food Science and Biotechnology*, 27(4), 997–1005.
- Philippi, K., Tsamandouras, N., Grigorakis, S., & Makris, D. P. (2016). Ultrasound-assisted green extraction of eggplant peel (*Solanum melongena*) polyphenols using aqueous mixtures of glycerol and ethanol: Optimisation and kinetics. *Environmental Processes*, 3(2), 369–386.
- Ponnurugan, K., Al-Dhabi, N. A., Maran, J. P., Karthikeyan, K., Moorthy, I. G., Sivarajasekar, N., et al. (2017). Ultrasound assisted pectic polysaccharide extraction and its characterization from waste heads of *Helianthus annuus*. *Carbohydrate Polymers*, 173, 707–713.
- Rodsamran, P., & Sothornvit, R. (2019). Microwave heating extraction of pectin from lime peel: Characterization and properties compared with the conventional heating method. *Food Chemistry*, 278, 364–372.
- Sharma, R., Kamboj, S., Khurana, R., Singh, G., & Rana, V. (2015). Physicochemical and functional performance of pectin extracted by QbD approach from *Tamarindus indica* L. pulp. *Carbohydrate Polymers*, 134, 364–374.
- Talekar, S., Patti, A. F., Vijayraghavan, R., & Arora, A. (2018). An integrated green biorefinery approach towards simultaneous recovery of pectin and polyphenols coupled with bioethanol production from waste pomegranate peels. *Bioresource Technology*, 266, 322–334.
- Thirugnanasambandham, K., Sivakumar, V., & Maran, J. P. (2014). Process optimization and analysis of microwave assisted extraction of pectin from dragon fruit peel. *Carbohydrate Polymers*, 112, 622–626.
- Todaro, A., Cimino, F., Rapisarda, P., Catalano, A. E., Barbagallo, R. N., & Spagna, G. (2009). Recovery of anthocyanins from eggplant peel. *Food Chemistry*, 114(2), 434–439.
- Wang, W., Ma, X., Jiang, P., Hu, L., Zhi, Z., Chen, J., et al. (2016). Characterization of pectin from grapefruit peel: A comparison of ultrasound-assisted and conventional heating extractions. *Food Hydrocolloids*, 61, 730–739.
- Yapo, B. M., Wathelet, B., & Paquot, M. (2007). Comparison of alcohol precipitation and membrane filtration effects on sugar beet pulp pectin chemical features and surface properties. *Food Hydrocolloids*, 21(2), 245–255.
- Yeoh, S., Shi, J., & Langrish, T. A. G. (2008). Comparisons between different techniques for water-based extraction of pectin from orange peels. *Desalination*, 218(1–3), 229–237.
- Yuan, Y., Xu, X., Jing, C., Zou, P., Zhang, C., & Li, Y. (2018). Microwave assisted hydrothermal extraction of polysaccharides from *Ulva prolifera*: Functional properties and bioactivities. *Carbohydrate Polymers*, 181, 902–910.