CHARACTERIZATION OF GELS CONTAINING PECTIN AND OPTIMIZATION OF GEL PRODUCTION BY TAGUCHI METHOD IN FOOD INDUSTRY

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***Abstract*— The objective of this research was to optimize the gel production by Taguchi Method as an optimization method and characterize gels by using attenuated total reflectance Fourier transform infrared (ATR – FTIR) and Raman spectroscopy. The statistical method results were obtained and analyzed comparatively in terms of improving both cost and quality for determination of optimum process parameters. This optimization method uses the S/N ratio as a measure of quality characteristics deviating from or nearing to the desired values. This method is expected to serve as an alternative to the conventional optimization method. Clear discrimination and classification of all the studied gel products containing pectin were achieved by hierarchical cluster. As a result, the gels produced could be evaluated in food products such as ice cream, milk dessert or other gelatin containing products such as pharmaceuticals and cosmetics.**

***Keywords*— Pectin, Gels, Raman, FTIR, Taguchi**

I. INTRODUCTION

Hydrocolloids are dispersive and water-swellable structures. They affect the physical properties of hydrophilic solutions to form gels. Hydrocolloids constitute partially soluble polysaccharides. They have functions as thickening, gelling agents, foaming agents, emulsifiers, stabilizers, etc. Commercial hydrocolloids commonly include starch, pectin, gelatin, agar, carboxymethylcelulose (CMC) etc. Starches are generally accepted thickeners because of their low cost. However, a more expensive thickener such as xanthan gum may be used because of its rheological properties. Gelling type hydrocolloids are used in various food formulations like jams, jellies, puddings, ice creams, gelled desserts, cakes, and candies for obtaining the desired texture. Food colloids have an important place in products such as sauces, yoghourt, etc. (Li and Nie, 2016).

Nowadays, consumers have become cautious about the ingredients of food and believe food additives to be a desirable property for food quality (Varela and Fiszman, 2013). Gelatin is a protein produced from hydrolysis of collagen. Gelatin has extensive applications in various industries due to biodegradability, renewability and consistency (Hazavah *et al*., 2015). Gelatin replacement, especially usage of fish collagen, has been a major subject in recent years due to halal and kosher market (Karim and Bhat, 2008; Karim and Bhat, 2009; Cheow *et al.*, 2007).

Gelatin is an additive frequently used as a thickening agent in foods. Gelatin has advantages because of clear, colorless and odorless properties with respect to other thickening agents. Also, gelatin can be obtained at low cost due to be suitable as a raw material and for manufacturing. Some consumers avoid pork-gelatin-added food products due to their religious or personal dietary practices (Boran, 2011). Therefore, fish and poultry are normally processed to cater to specific consumer groups. Nowadays, alternative raw materials in gelatin manufacturing have been on focus of many scientific researches. Results in literature suggest that gelatin extracted from fish and chicken skin might be high in quality, as much as pork gelatin (Boran, 2011). In another study, the researchers studied the reology of gelatins. They investigated the impact of anionic polysaccharide as a co-gelator of gelatin by varying the carrageenan/gelatin ratio. They found hat addition of small quantity of polysaccharide leads to changes in structure of modified gels (Derkach *et al*., 2015). In literature, various analytical methods are applied to bovine, porcine origins, and food products for gelatin differentiation (Nhari *et al.*, 2012; Yilmaz *et al*., 2013; Nemati *et al.*, 2004). The purpose of another study was to develop a FTIR technique as an alternative method for the differentiation and authentication of gel sources and their various mixtures. Consequently, gels in food industry were successfully classified based on their sources using ATR–FTIR method (Cebi *et al.*, 2016).

The purpose of this study was to optimize the gel production by Taguchi Method and characterize gels with Fourier transform infrared (ATR–FTIR) and Raman spectroscopy. Classification of the studied gel products containing pectin was achieved by hierarchical clustering. As a result, the gels produced could be evaluated in food industry as additives.

II. EXPERIMENTAL

A. Materials

Apples, quinces, and oranges used in pectin production, as well as starch used in modified gel production were provided from markets in Turkey. FTIR was determined with a Bruker Tensor 27 spectrometer (Bremen-Germany) with an ATR accessory. OPUS program Version 7.2 was used for instrument control and data acquisition.

Raman spectra were obtained with a Bruker-Bravo instrument.

B. Methods

Experiments were designed according to the Taguchi method (L-9 orthogonal array table) for three levels and three parameters for both pectin and modified gel production. Pectin sources as apples, quinces and oranges were cut into pieces and boiled with water (100-300 mL). The boiling time changed between 30-60 minutes. Products were vacuum filtered (Fig. 1). Then, a second boiling step was applied to apples, quinces, and oranges at different boiling times (5-15 minutes) for stabilization.

After pectin production, starch was mixed with pectins produced for determined parameters (Pectin/Starch: 1:1, 1:2, 2:1; Water amount: 150-250 mL; Drying time: 30-60 min). The mixture was stirred at 70°C for 30 minutes (500 rpm) and centrifuged for 5 minutes (5000 rpm). Then, the products were dried at 130°C in an oven. The yield (%) values were calculated as shown in Eq. (1):

$$\text{Yield (\%)} = [X/(P+S)].100 \qquad (1)$$

where X was modified gel (g), P and S were pectin (g) and starch (g), respectively.

C. Taguchi Optimization Method

Taguchi method provides a specific design to determine the optimum parameters with a small number of experiments (Vankantia and Ganta, 2014; Kaushik and Thakur, 2009). At the same time, Taguchi method deals with a single-response problem and the multi-response problem has pointed out limited attention (Tong *et al.*, 1997).

There are three categories of quality for S/N the ratio. The formulas used for S/N ratio are given below (Phadke, 1989).

Smaller the better is given as Eq. (2).

$$\text{S/N ratio } (\eta) = -10\log_{10}\frac{1}{n}\sum_{i=1}^{n} y_i^2 \qquad (2)$$

where y_i shows the response value and n is the number of replications.

Nominal the best is given as Eq. (3).

$$\text{S/N ratio } (\eta) = -10\log_{10}\frac{\mu^2}{\sigma^2} \qquad (3)$$

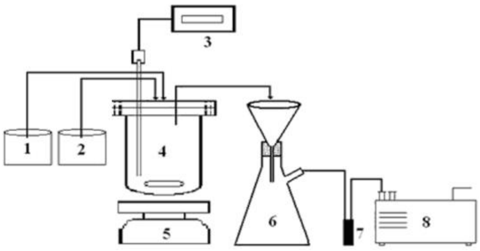

Fig. 1. Experimental set-up for modified gel production: (1) Pectin produced, (2) Starch, (3) Digital temperature sensor, (4) Reactor, (5) Magnetic stirrer with heater, (6) Filtration, (7) Cold trap, (8) Vacuum pump.

where μ is the mean and σ is the variance.

Higher the better is given as Eq. (4)

$$\text{S/N ratio } (\eta) = -10\log_{10}\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2} \qquad (4)$$

D. Characterization

ATR–FTIR (Tensor 27, Bruker, Germany) spectra of gels with a resolution of 4 cm^{-1} were determined from 4000 to 600 cm^{-1}. The Bravo handheld Raman instrument (Bruker, Germany) was used for the raman intensity range from 0 to 5000 cm^{-1}.

III. RESULTS AND DISCUSSION

Minitab Release 13.20 Statistical Software was used for the Taguchi results. In classical methods, one parameter was varied while keeping all other parameters constant.

In this study, Taguchi method was used with L-9 design to produce gels with three parameters and three levels (Table 1). In general, a factorial approach requires 27 experiments to optimize a process, but the number of experiments is reduced to nine in fractional factorial. The Taguchi results are given in Fig. 2.

As a result, 58,1% and 97,9% values were obtained as the maximum yield for pectin (Sagir et al., 2015) and gel yield from orange peel.

After FTIR spectra of gels especially produced from quince and orange peel, classification of spectra in terms of similarity was realized by means of cluster analysis.

In addition, differentiation and classification of gels by using FTIR depends on the spectral diversity as seen in Fig. 3.

In literature, Amide-I absorption shows C=O vibration effects of Amide group and C-N stretching vibration for gel production. Amide-II absorption shows N-H bending and C-N vibrations. Amide-III usually represents the C-N stretching vibrations, N-H in-bending vibrations with weak peaks as C-C stretching and C=O in-plane bending. Bands around 1080 and 1035 cm^{-1} are related to C-O stretching vibrations of the carbohydrate residues in collagen. In the research, FTIR spectra showed the achievement of production (Fig. 4).

The Raman spectra of gels are presented in Fig. 5. The high frequency band around 3450 cm^{-1} is due to the symmetric stretching of –OH. Lines appear between 1000-1500 cm^{-1} in the spectra of gels that can be assigned to the amide III mode. Strong amide I lines appear between 1400-1650 cm^{-1} due to homogenous structure and uniform hydrogen bending (C=O stretch). Only weak scattering is observed at 950 cm^{-1}.

IV. CONCLUSION

The optimum parameters in production of pectin and gels were indicated by using Taguchi optimization method with three parameters and three levels. Gels based on pectin were successfully classified by using ATR–FTIR method. ATR–FTIR can be used to characterize the chemical structure of gels. This simple and inexpensive technique proved differentiation of the gel

Table 1. (a) Taguchi Method for pectin production from apple, quince, and orange peel, (b) Gel produced with wheat starch using pectin from apple, quince and orange peel.

No (a)	Water amount (mL)	1. Boiling Time (min)	2. Boiling Time (min)	Pectin yield (%) from apple* (X)	Pectin yield (%) from quince** (Y)	Pectin yield (%) from orange peel* (Z)
1	1	1	1	4,40	3,2	6,2
2	1	2	2	7,65	3,4	0
3	1	3	3	10,20	3,5	12,4
4	2	1	2	14,50	6,1	19,1
5	2	2	3	9,10	6,7	6,7
6	2	3	1	9,80	6,5	4,2
7	3	1	3	**19,50^{+}**	10	**58,1^{+}**
8	3	2	1	8,60	**25^{+}**	3,91
9	3	3	2	11,50	18	21,8

*Levels: 25-50-75 mL; 30-45-60 min; 5-10-15 min; **Levels: 20-40-60 mL; 30-45-60 min; 5-10-15 min

No (b)	Pectin/starch (P/S) ratio	Water amount (mL)	Drying time (min)	Gel yield (%) from apple***(T)	Gel yield (%) from quince***(V)	Gel yield (%) from orange peel***(Y)
1	1	1	1	69,0	63,1	**97,9^{+}**
2	1	2	2	**79,0^{+}**	**90,2^{+}**	72,5
3	1	3	3	68,9	77,7	70,6
4	2	1	2	71,3	34,8	60
5	2	2	3	65,1	37,0	63,8
6	2	3	1	72,0	36,6	65,2
7	3	1	3	68,5	19,7	56,5
8	3	2	1	74,6	25,2	30,9
9	3	3	2	72,1	25,8	28,5

***Levels: 1:2; 2:1; 1:1; 150-200-250 mL; 30-45-60 min

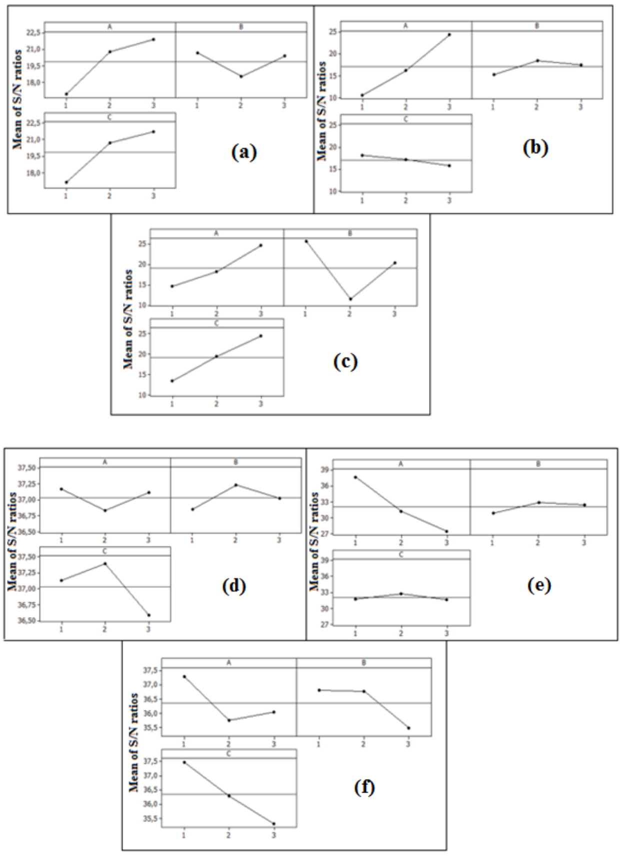

Fig. 2. Taguchi method results: for pectin production from: (a) Apple, (b) Quince, (c) Orange Peel; for gel produced with wheat starch by using pectin from: (d) Apple, (e) Quince, (f) Orange Peel.

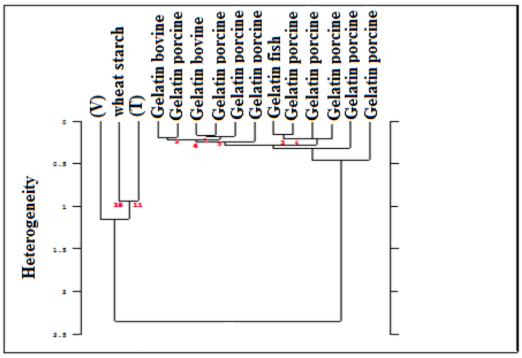

Fig. 3. Cluster analysis of FTIR spectra for gels

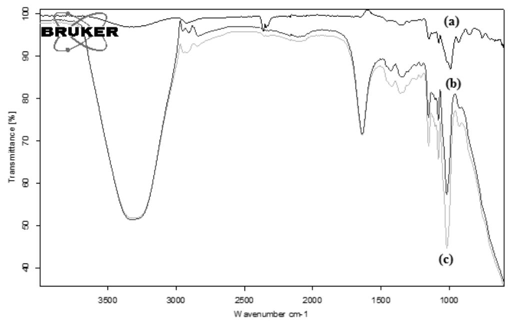

Fig. 4. FTIR spectra for gels by using pectin from: (a) Apple, (b) Quince, (c) Orange Peel

sources. In addition, it was seen that Raman results gave positive results for production of gels-based pectin. This optimization and production study can be beneficial as simple, rapid, and economical for gels in food industry.

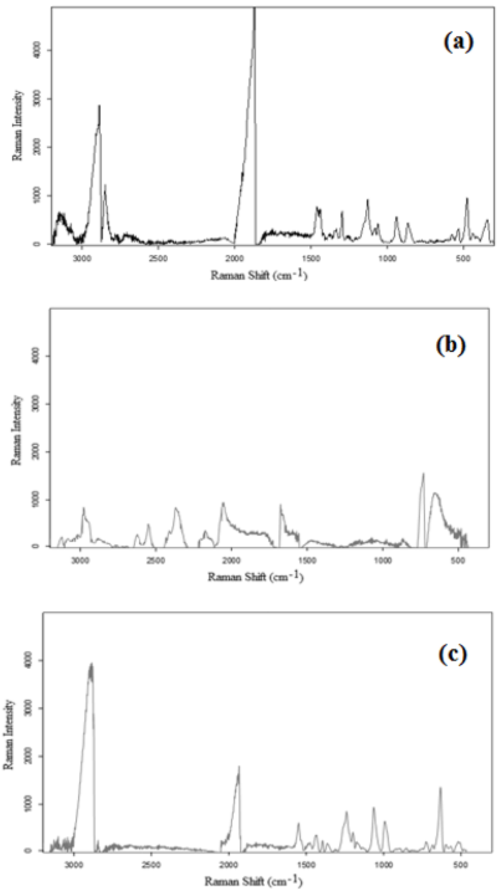

Fig. 5. Raman analysis for gels by using pectin from: (a) Quince, (b) Apple, (c) Orange peel.

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