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Effect of variety and acid washing method on extraction yield and quality of sunflower head pectin

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Abstract

Sunflower samples, *Helianthus annuus* L., of three varieties, *Armavirsky*, *Zaria* and *Record*, were obtained from Iran. Samples were dried and ground by hammer mill to pass a 60-mesh size screen and stored until used. Insoluble pectins were extracted from the residue with 0.75% sodium hexametaphosphate solutions at 65 °C and pH of 5 for 20 min. Extraction yields of pectin from the head residues were 10.67, 11.53 and 10.93%, respectively. The data were analyzed by statistical analysis. Based on the quality, the *Record* variety was selected for its highest methoxyl, lowest ash and highest galacturonic acid content. Pectin was washed with HCl and HNO_3 (0.1, 0.6 and 1.2 N) for 10, 20 and 30 min. Statistical analysis revealed that washing in 0.6 N HNO_3 for 10 min yielded a good quality pectin.

Keywords: Pectin; Sunflower head; Variety; Extraction; Acid washing

1. Introduction

Pectin is a chain-like polymer, consisting of α-D-galacturonic acid linked through the 1 and 4 positions, with a proportion of carboxyl groups esterified with methanol (Walter, 1991). The importance of pectin in food is its ability to form gels that are the basis of jam and other fruit preserves (IFT, 1991; Walter, 1991). Although apple pomace and citrus peels are traditional sources of commercial pectin, sunflower heads could be used for commercial pectin (Chang, Dhurandhar, You, & Miyamoto, 1994a).

Sunflower head residues, left after seeds have been harvested, are high in LMP (low-methoxyl pectin). The yield and quality of pectin are affected by raw materials, particle size, storage and cultivation conditions, stage of maturity, and extraction conditions. Degree of esterification, molecular sizes, natural sugar branches, acetylation, amidation, and ash content may affect the gelatinization properties of pectin (Chang, Dhurandhar, You, & Miyamoto, 1994b; Kim, Sosulski, & Campbell, 1978; Kim, Sosulski, & Lee, 1978; Lin, Sosulski, Humbert, & Downey, 1975). Conditions, including pH, temperature and concentration of pectin, calcium and sugar, can be varied during gel preparation to obtain gels with a range of firmness and elasticity (Chang & Miyamoto, 1992). L.M. sunflower pectin can be used to prepare jellies with low sugar content or without sugar in the presence of a small amount of calcium and could be used as an ingredient for formulating low-calorie foods (IFT, 1991).

Mature sunflower heads contain 15–25% of pectin (Shi, Chang, Schwarz, & Wiesenborn, 1996; Shi, Chang, Schwarz, Wiesenborn, & Shin, 1996). The acid-precipitated crude pectin also contains pigments, acid and other impurities.

Ethanol has been used to remove impurities from the acid-precipitated low-methoxyl sunflower pectin. Although much research on extraction and washing procedures has been reported, a theoretical analysis of acid removal during the washing process has not been published (Shi, Chang, Schwarz, & Wiesenborn, 1996).

An extensive research programme to assess the commercial feasibility of pectin extractions from sunflower in Iran, and its characteristics, has been undertaken at the University of Tarbiat Modarres. The objectives of the present study were to assess and compare the extraction

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yield of various Iranian varieties and determine effects of acid-washing processing on quality of pectin.

2. Materials and methods

2.1. Raw materials

Three varieties of oilseed-type sunflower head residues (*Armavirsky*, *Zaria* and *Record*) were provided by Provision Institute and Improvement of Plant and Seed of the Agricultural Ministry located in Karaj . All conditions of cultivations were similar. Samples were dried under ordinary conditions at 35–40 °C and ground by hammer mill to pass a 60-mesh size screen (Kim, Sosulski, & Campbell, 1978; Kim, Sosulski, & Lee, 1978) and stored in a cold room until used. Concentrated hydrochloric acid and sodium hexameta phosphate (SHMP), for pectin extraction, obtained from Merck Company, were used for pectin washing. All chemical reagents were of analytical grade.

2.2. Pectin extraction and acid-washing method

The ground sunflower heads were washed with water at 75 °C and stirred slowly for 15 min at a solid/water ratio of 1:20 (Chang, Dhurandhar, You, & Miyamoto, 1994a, 1994b). The slurry was filtered through cheesecloth to remove soluble pigments and dust. LMP was extracted by mixing the residue with 7.5 g/kg SHMP solution at a solid/liquid ratio of 1:20 at 95 °C and pH 5 (adjusted with 1 mol/l HCl) for 20 min. The slurry was filtered through fine cheesecloth to provide pectin extract. After cooling to <20 °C in a water bath, the pectin extract was precipitated by adding 2 volume of 96% ethanol (Sabir, Sosulski, & Campbell, 1976) and stirred slowly for 15 min and stored in a refrigerator for 1 h. The precipitated pectin was pressed by hand as much as possible. After filtration through fine cheesecloth, based on reduced ash, the pectin precipitate was washed twice in 1 volume of 0.1, 0.6 and 1.2 N HCl and HNO_3 as solvent at a acid/pectin ratio of 1:1, with 10, 20 and 30 min of agitation. Based on exit acidic anion, the pectin was first washed with ethanol (60%) and, finally with ethanol (96%) (gel/solvent ratio of 1:1). Pectin was dried completely in an air-circulated oven at <60 °C for 5 h. The dried pectin was ground by hammer mill and packaged under airless conditions.

2.3. Chemical analysis

Only the heads were ground in a hammer mill for pectin extraction and analysis. For evaluation of optimal conditions for the precipitation and isolation of pectins, 100 g samples of milled sunflower were taken randomly each time. According to the above-mentioned method (Section 2.2) pectins were precipitated and isolated. The extraction yield was calculated, based on dried pectin (g/100 g) in dried residue. Each extraction was conducted in triplicate. Ash content was measured by incinerating the sample overnight in a muffle furnace at 550 °C (AOAC Method, 1984; Ramganna, 1986). Galacturonic acid was determined by titration with NaOH (Food Chemical Codex,1972; Ramganna, 1986; Schultz, 1965; Walter, 1991). The degree of esterification was determined by titration with NaOH, based on free carboxyl group (Food Chemical Codex, 1972; Schultz, 1965; Smit & Brayant, 1967).

2.4. Statistical analysis

The experiment was conducted with all combinations of three factors in randomised complete blocks and analysed using the corresponding analysis of variance (Dixon & Massey, 1983; Hicks & Turmer, 1999; Steel, Torrie, & Dickey, 1997; Yandell, 1997).

3. Results and discussion

3.1. Extraction yield and quality of pectin

The results of the extraction yield comparison, ash, galacturonic acid and degree of esterification of different varieties are presented in Tables 1 and 2. According to Table 1, there is a significant difference (at 5% level) between the different varieties of sunflower due to extraction yield, ash, galacturonic acid and degree of esterification. The comparison of averages by the Duncan Test in Table 2, confirmed this. According to this test, *Zaria* and *Armavirsky* varieties possessed the highest and the lowest extraction yield, respectively. Although the extraction yield of *Record* variety was more than *Armavirsky*, the difference was not significant. Among the three varieties, *Record* has the least ash content; therefore, it is considered superior in this respect. No significant difference in ash content was found between *Armavirsky* and *Zaria* varieties. Comparison of averages by Duncan Test showed that there was no significant difference (at 5% level) between the galacturonic acid content of *Armavirsky* and *Record* varieties, but in *Armavirsky* it was meaningfully higher than *Zaria*. The *Record* and *Armavirsky* varieties may, therefore, be considered suitable ones in this respect, the choice of which depends on other characteristics. The available results in Tables 1 and 2 indicate a significant effect of kind of variety (at 5% statistical level) on the degree of esterification. Of course, esterification degree of extracted pectin from two varieties of *Armavirsky* and *Record* showed no significant difference, but pectin esterification degree of *Zaria* variety was significantly lower than the other two varieties. According to the results, it

Table 1
Analysis of variance for extraction yield, ash, galacturonic acid and esterifcation degree of three varieties of sunflower pectin

Source	Degree of freedom	Mean square			
		Extraction yield	Ash	Galacturonic acid	Esterification degree
Blocks	2	0.008 ns	0.074 ns	3.1 ns	6.055 ns
Variety	2	0.591*	5.108*	44 ns	14.671*
Error	4	0.031	0.039	5.49	4.05
Total	8				

ns, Not significant at $P > 0.05$.
* Significant at $P < 0.05$.

Table 2
Comparison of extraction yield, galacturonic acid and esterification degree percentage in three variety of sunflower

Variety	Yield (%)		Ash (%)		Galacturonic acid (%)		Esterification degree (%)	
	Mean	S.D.[a]	Mean	S.D.	Mean	S.D.	Mean	S.D.
Armavirsky	10.56b*	0.005	9.83a ns	0.89	90.07a ns	0.005	37.50a ns	1.00
Record	10.75b*	0.007	8.04b*	1.05	87.33ab* ns	3.79	39.02a ns	1.34
Zaria	11.42a ns	0.19	10.15a ns	0.01	83.33b*	3.21	34.73b*	2.95

Different letters in mean column (a,b) show significant differences by Duncan Multiple Range Test. Ns, Not significant at $P > 0.05$.
[a] Standard deviation.
* Significant at $P < 0.05$.

seems that pectin of *Record* variety is superior to the other two varieties, because its extracted pectin contained more methoxyl and the least amount of ash, and not much difference in its galacturonic acid content from that of *Armavirsky* variety was found. The *Record* variety was, therefore, selected for the second phase of the experiment.

3.2. Comparison of acid-washing treatments

Table 3 shows the analysis of variance of extracted yield, ash, galacturonic acid, and the degree of esterification of treated pectin under the different conditions of acid washing. The individual effects of the three factors (kind and concentration of the acid, and time of washing) on the amount of pectin extraction were statistically significant. But their combined effects on extraction yield was not great. In relation to concentration factor, in terms of normality, as indicated in Table 4, increasing acid concentration decreased extraction yield; the highest extraction yield was obtained at 0.1 N and the lowest extraction yield was with the 1.2 N treatments. With increasing time, from 10 to 30 min, the extraction yield showed a decreasing trend; however, the decreasing trend was statistically meaningless at the 5% level in the 20 to 30 min range.

Table 3
Analysis of variance for extraction yield, ash, galacturonic acid and esterification degree of *Record* variety in the acid-washing method

Source	Degree of freedom	Mean square			
		Yield	Ash	Galacturonic acid	Esterification degree
Blocks	2	1.262**	1.322 ns	26.614**	30.005*
Concentration of acid	2	30.044**	337.26**	570.098**	584.098**
Washing time	2	1.206**	5.408**	28.884**	34.243*
Concentration of acid×washing time	4	0.116 ns	1.374**	7.318 ns	1.374 ns
Kind of acid	1	4.318**	3.599**	90.741**	15.042 ns
Concentration of acid×kind of acid	2	0.154 ns	0.162 ns	9.338 ns	9.054 ns
Washing time×kind of acid	2	0.009 ns	0.004 ns	0.467 ns	2.480 ns
Concentration of acid×kind of acid×washing time	4	0.059 ns	0.214 ns	4.552 ns	2.456 ns
Error	34	0.150	15.320	6.727	8.039
Total	53				

ns, Not significant at $P > 0.05$.
* Significant at $P < 0.05$.
** Significant at $P < 0.10$.

Table 4
The effect of acid concentration, washing time and kind of acid in extraction yield, ash, galacturonic acid and esterification degree of pectin

Factors		Yield (%)		Ash (%)		Galacturonic acid (%)		Esterification degree (%)	
		Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Acid concentration (N)	0.1	12.38a ns	0.56	15.58a ns	1.08	78.11b*	3.75	40.91a ns	4.07
	0.6	10.74b*	0.59	8.89b*	0.55	87.06a ns	2.36	33.82b*	2.28
	1.2	9.83c**	0.51	7.47c**	0.77	88.53a ns	3.12	29.63c**	2.23
Washing time (min)	10	11.52a ns	1.13	11.22a ns	3.78	83.42b*	6.21	36.26a ns	5.49
	20	10.97b*	1.29	10.61b*	3.50	84.33ab* ns	5.53	34.57ab* ns	5.33
	30	10.73b*	1.16	10.11 b	3.81	85.94b*	4.91	33.53b*	5.74
Kind of acid	HCl	11.27a ns	1.21	10.39a ns	3.61	85.87b*	5.88	35.31a ns	4.71
	HNO_3	10.7b*	1.13	10.90b*	3.76	83.26a ns	5.02	34.26b*	6.30

Different letters in mean column (a, b, c) show significant differences by Duncan Multiple Range Test. Ns, Not significant at $P > 0.05$.
* Significant at $P < 0.05$.
** Significant at $P < 0.10$.

Also, the kind of acid in the pectin gel caused significant difference in the pectin extraction yield. Table 4 shows the effects of washing time, concentration and kind of acid on pectin ash percent. With increasing concentration, from 0.1 to 0.6 N, the drop of ash was sharp (from 15.6 to 8.9%) and gradually with increasing of concentration from 0.6 to 1.2 N, this slope decreases (from 8.9 to 7.5%). Possibly part of the ash was strongly joined to pectin, so that even with high concentrations of acid (e.g. 1.2 N) it did not separate. Increasing of washing time led to decrease of ash as well; of course, this time decrease in time (20–30 min) was little, and the comparison of the averages did not show significant differences. According to Tables 3 and 4, the effect of the kind of acid was not significant on ash decrease; this implied that HNO_3 probably dissolved salts (or ash) of the pectin more effectively than HCl, so that less ash remained in the pectin. Changes in extraction yield and ash content showed similar trends. This means that, in all treatments, increasing or decreasing of extraction yield was accompanied by increase or decrease of ash content. In other words, a greater loss of ash from pectin resulted in lower weight and, hence, lower extraction yield.

In terms of galacturonic acid yield, it was found that concentration of acid was effective at the 1% level, washing time was significant at the 5% level, and its combined effect with other factors on galacturonic acid was not significant (Table 3). With increasing concentration and time, the galacturonic acid increased considerably. But this increase (in extent 0.6–1.2) was not significantly different at the 5% level. Increase in galacturonic acid was probably due to the relative reduction of ash per unit of final pectin weight. With increasing time from 10 to 30 min, the changes of galacturonic acid were significant . But no significant differences were found between times 20, 30 or 10, 20 min. The effect of acid concentration on amount of esterification degree was significant at the 1% level (Table 3). In other words, increase of acid concentration, from 0.1 to 1.2 N, considerably decreased esterification, since acid breaks ester bonds (Table 4). It is clear that increase in time from 10 to 20 and from 20 to 30 min did not cause any significant decrease in degree of esterification; however, the difference between 10 and 30 min was significant. The kind of acid had no effect on esterification (at 5% level).

4. Conclusions

It can be concluded that the sunflower seed variety had some effect on the ash, galacturonic acid content, the degree of esterification and extraction yield. Pectin of *Record* variety was superior in quality to others; pectin extraction yield and its quality were affected by the acid-washing process, including time, concentration and kind of acid. Among these factors, acid concentration was found to be the most effective and, for the same reason, it should be controlled with care.

5. Suggestions

1. *Record* and *Zaria* varieties are suggested for the qualitative pectin and extraction yield efficiency, respectively.
2. It is suggested that lower concentration and shorter time of washing should be undertaken, since increase in acid concentration and longer washing negatively affected pectin production. According to the standard for total ash content (maximum 10%), 10 min washing with acid of 0.6 N concentration is suggested.
3. Since acid decreases the methoxyl content, a proper washing with alcohol before drying should be conducted so as to minimize the effect.

4. In addition to reducing the ash content and relatively increasing galacturonic acid, acid-washing separates methyl groups from the galacturonan chain. This method can, therefore, be introduced as a deesterification process to be used in obtaining a product of different quality.

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