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Effect of countercurrent ethanol washing on sunflower pectin quality*

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Development of efficient ethanol washing technology to remove acid and ash in precipitated sunflower pectin gels is highly desirable in industrial production. A seven-stage, countercurrent washing process was developed in which the ethanol was neutralized between each stage. Ethanol from the final stage could be recovered by standard distillation methods and used again. This process significantly reduced the quantity of ethanol used, compared to a batch washing process using fresh ethanol for each washing step. The composition, color, and gelling characteristics of pectin washed by this countercurrent process were determined and compared with those of a pectin obtained by a batch washing process using fresh ethanol for each washing step and with commercial citrus pectin. The pectin gels were of good quality.

INTRODUCTION

Pectin, generally regarded as a safe substance, can be applied in the food and pharmaceutical industry as a gel-forming, thickening, and stabilizing agent. In the European Community (EC), pectin has the number E440, which makes it a recognized additive with specifications of purity, a chemical description, and, in some cases, rules for condition of use. The commercial product is expected to be a light-colored, bland-tasting powder that is water soluble and has a constant and standardized gel-forming capacity and setting behavior. Low-methoxyl pectin can be used to prepare dietetic foods or as a fat replacer (*Chemical Marketing Reporter*, 1991; IFT, 1991).

Sunflower heads that remain in the fields as agricultural wastes after seed removal have been studied as a naturally rich source of low-methoxyl pectin. Mature sunflower heads contain 15–25% pectin. Methods for pectin extraction from sunflower heads have been developed in several laboratories (Shewfelt & Worthington, 1953; Lin *et al.*, 1975, 1976; Sosulski *et al.*, 1978; Kim *et al.*, 1978; Chang & Miyamoto, 1992).

During pectin extraction, the pectin gel obtained from acid precipitation of extract usually contains pigments, acid, and other undesirable impurities. Ethanol as a solvent is often used for the pectin gel washing process to remove impurities and mineral acid. An industrial process for pectin production from sunflower heads based on the laboratory method would require large amounts of ethanol and consequent higher operating costs. The commercial extraction of pectin from sunflower heads has been developed in some countries. Little information, however, has been published describing details of extraction processes, quality, or utilization of sunflower pectin products.

The objective of this study was to determine the influence of various ethanol washing conditions on gel properties and to investigate the possibility of decreasing the amount of ethanol needed. A stepwise, countercurrent process for pectin gel washing was developed to improve pectin quality and to lower cost. The composition, color, and gelling characteristics of pectin obtained from the countercurrent washing process with reused ethanol were compared with those of batch-washed pectin with fresh ethanol for each step and with commercial low-methoxyl citrus pectin.

MATERIALS AND METHODS

Raw material preparation

Sunflower (*Helianthus annuus*, L. var. *Cargill*) heads were obtained from the Carrington (ND) Research Center, North Dakota Agricultural Experiment Station, U.S.A.

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After harvesting, the heads were dried to approximately 7–8% moisture content in a walk-in forced air dryer at 55–60°C. A hammer mill, model 915 (Winona Attrition Mill Co., Winona, MN, U.S.A.) was used for grinding (880 rpm) the dried sunflower heads. The ground raw material was passed through a screen with 12 mm mean diameter opening, and stored in a cold room until used.

Concentrated nitric acid (70.5%) and the sodium hexametaphosphate (SHMP) for pectin extraction were obtained from Curtin Matheson Scientific, Inc. (Eden Prairie, MN, U.S.A.). Ethanol obtained from Quantum Commercial Company (Tuscola, IL, U.S.A.) was used for pectin washing. All chemical reagents were of analytical grade.

Pectin extraction

The procedure for pectin extraction from sunflower head material is shown in Fig. 1. The ground sunflower head samples were washed with hot water at 75°C and stirred slowly for 15 min at a solid/water ratio of 1:30 before filtering to remove soluble pigments and dust.

For extraction of low-methoxyl pectins, the residue was mixed with 0.75% SHMP solution at a solid/liquid ratio of 1:25 at 75°C and pH 3.5 (adjusted with 3 N H_3PO_4) for 60 min. The slurries were filtered through fine cheesecloth. After cooling to below 10°C, the pectin extract was precipitated by adding one-fifth volume of 1 N nitric acid while stirring gently to break up the gelatinous lumps and to obtain a homogeneous mixture, and then kept for 60 min at below 10°C. The pectin precipitate was filtered through fine cloth and washed twice by agitating the gel in 2 volumes of 0.1 N nitric acid for 20 min each time.

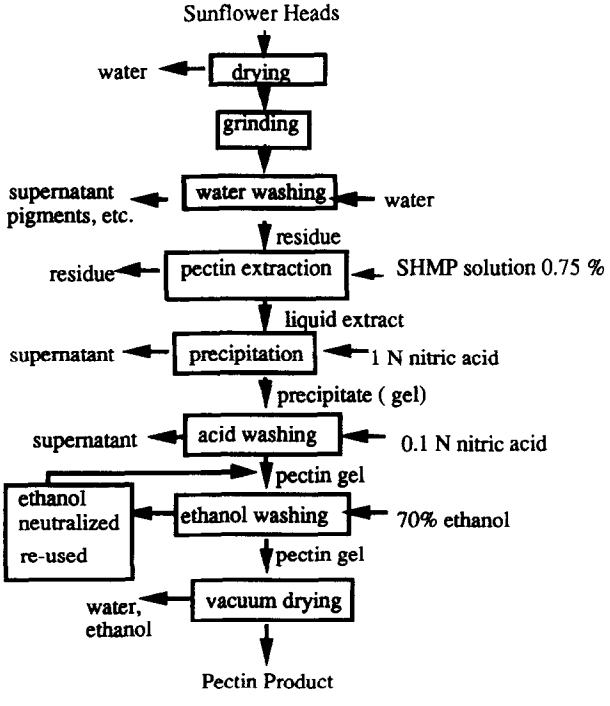

Fig. 1. The procedure for pectin extraction from sunflower head material.

The pectin gel was washed several times with ethanol to lower the ash content, improve color, and increase the pH by removing acid. Up to seven wash cycles in the batch washing method were used to achieve the desired result, and fresh ethanol was used for each cycle. A stepwise, countercurrent washing process with reused, neutralized ethanol was developed and compared to the previous washing procedure for its effect on the ash content, color, and pH of pectin gels. The washed pectin gels were dried in a vacuum oven at 55°C for 16 h.

Ethanol washing step

A series of containers were operated in a stepwise, countercurrent flow process as shown in Fig. 2. A quantity of crude pectin gels were mixed with a quantity of ethanol (70% v/v) in an agitated vessel. After each 20 min interval, ethanol was separated by filtration and neutralized to become the washing solvent for the next container with gels of lower purity. Comparative experiments between the countercurrent washing with reused ethanol and the batch washing with fresh ethanol for each step were carried out. The crude pectin gel was divided into two parts, one for the countercurrent washing and the other for the batch washing. In the batch process, the crude pectin gel was washed repeatedly seven times by 70% ethanol solvent at an ethanol/gel ratio of 2:1. In the countercurrent washing treatment, ethanol/gel ratios of 2:1, 1.8:1, and 1.5:1 were used. Ethanol was neutralized with 3 M NaOH between each stage. Each washing treatment took 140 min.

Pectin analysis and properties

Dried pectin flakes were ground into 0.5 mm size powder in a Cyclone sample mill and stored for chemical analyses and gel preparation. The color of pectin gel after each ethanol washing treatment and the color of the dried pectin powder were measured with a Hunterlab Color Difference Meter (Gardner XL-23 Digital Tristimueus Colorimeter) standardized against a white tile (Hunter No. XL-23-246-D, L: brightness, 91.94; a: red saturation index, 1.03; b: yellow saturation index, 1.14). The pH values of pectin gels after each ethanol

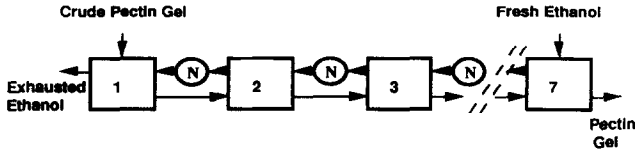

Fig. 2. The pectin gel washed with ethanol in stepwise, countercurrent process. (Ethanol-washing steps 1–7. N, ethanol neutralization steps.)

washing step were also measured by pH meter. Galacturonic acid content was analyzed by the colorimetric procedure of Scott (1979). Ash contents of different samples were measured by incinerating the samples in a muffle furnace at 550°C for 12 h (AOAC, 1984).

The gelling capacity of pectin samples was determined as described by the National Research Council (1972) for low-methoxyl pectin. The pectin gels for the tests contained 1% pectin, 20% sucrose, and 26 mg Ca^{2+}/g pectin at pH 3.0 as described by Chang and Miyamoto (1992). The gels were allowed to remain for 2 h at room temperature before being stored at 5–6°C for 18–24 h. The standard Instron textural profile method was used to study the texture properties of sunflower pectin gel. A low-methoxyl citrus pectin (34F-0620, Sigma Chemical Co.) was used as a reference for comparison. All experiments in this study were conducted in duplicate.

RESULTS AND DISCUSSION

Color changes

The color values for gel measured with the Hunter Color Difference Meter showed that 'L' values (brightness) increased during the first four washing treatments in batch scale with fresh ethanol and in the countercurrent process with reused ethanol. But color difference was only slightly low in the later washing (Fig. 3). Parameter 'b' (yellowness) and parameter 'a' (redness) changed only slightly with each increment of washing. The pigments in the sunflower head material are undesirable since they affect pectin appearance.

The color values of pectin powder are shown in Table 1. Dried pectin showed a tan color due to brown water-soluble pigments. Pectin washed in the countercurrent process with reused ethanol was similar in brightness to pectin obtained from batch washing with fresh ethanol. The differences in the Hunter color value (L, a, and b) of two kinds of gels and dried pectin powder were small. The light tan color of pectin powder is typical also of commercial products. Ethanol was effective in removing the undesirable pigments during the countercurrent washing process.

pH changes

The changes in pH values of pectin gels during ethanol washing are shown in Fig. 4. During the countercurrent washing process, the ethanol was neutralized between each step and reused for the next washing step. The acids, pigments, ash, and other impurities were removed from pectin gels. The initial pH value of pectin gel was approximately 1.6. The final pH value of gels was above 4.5. The pH value of the final pectin gel was increased through removal of acid from pectin gel particles in the washing process to yield pectin of high gelling power. This result is important because the pectin chains are likely to degrade during storage at pHs below 4 or above 7 with a consequent decrease in gelling capacity (Miyamoto & Chang, 1992).

Ash content

The effect of ash is pronounced in low-methoxyl pectin in which a high content of carboxyl groups is available to react with ash constituents to form complex hydro-

Table 1. The Hunter color values of pectin powder after different washing steps

Pectin samples	Hunter color values		
	L	a	b
S_1	66.99 ± 0.13	4.28 ± 0.09	15.66 ± 0.23
S_2	66.18 ± 0.77	4.77 ± 0.11	15.34 ± 0.19
S_c	69.28 ± 0.27	4.06 ± 0.13	13.70 ± 0.29

S_1, Batch washed with fresh ethanol; S_2, countercurrent washed with reused and neutralized ethanol; S_c, commercial citrus pectin; L, brightness; a, red saturation index; b, yellow saturation index.

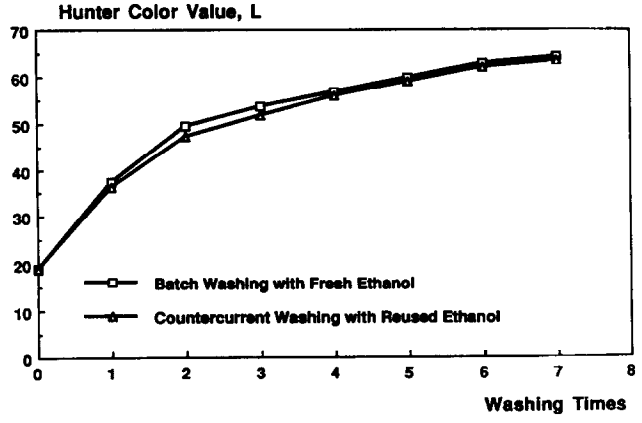

Fig. 3. The changes in Hunter color values 'L' of pectin gels during ethanol washing procedure.

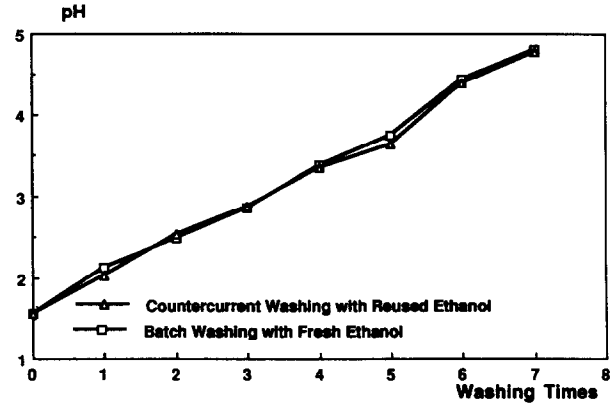

Fig. 4. The changes in pH values of pectin gel during ethanol washing.

Table 2. The comparison of Hunter color value 'L' and ash content between different washing ratios of ethanol/gel, v/v (fresh ethanol in the batch scale; reused, neutralized ethanol in the countercurrent process)

	Fresh ethanol washing, ratio 2:1	Reused ethanol washing, ratio 2:1	Reused ethanol washing, ratio 1.8:1	Reused ethanol washing, ratio 1.5:1
Hunter Value L	66.99 ± 0.13	66.18 ± 0.77	65.88 ± 0.39	59.28 ± 0.44
Ash (%)	4.53 ± 0.13	5.44 ± 0.18	5.57 ± 0.16	6.77 ± 0.21

xides of abnormally high viscosities. The increase in ash content, especially polyvalent ions, tends to facilitate precipitation rather than gelation, and syneresis occurs (Kohn & Furda, 1967).

To purify pectin gels and decrease the ash contents, pectin gels were washed twice with 0.1 N nitric acid, followed by the countercurrent ethanol washing. Washing treatments either in the acid washing steps or in the ethanol washing process removed most of the free salt, some metallic ions, and inorganic impurities from the gels. The difference in ash content of pectin samples from the batch washing process and the countercurrent washing process at a 2:1 ethanol/gel ratio condition is only approximately 1% (Table 2). Since the sequestrant (SHMP) is completely soluble in aqueous solution, it, together with nitric acid may be entrapped in the highly dehydrated gel particle. Weak chemical associations are highly speculative in the absence of qualification. The ash content of all samples was less than 10%, the maximum according to FCC specification (*Food Chemicals Codex*, 1981).

Effect of ethanol/gel ratio on pectin properties

A ratio of two volumes of ethanol to gel was typically used to purify pectin (Lin *et al.*, 1976; Miyamoto & Chang, 1992). In this study, lowering the ratio from 2:1 to 1.8:1 and to 1.5:1 was investigated for an effect on pectin properties. The results in Table 2 show that color and ash content were similar after washing at 2:1 (v/v) and 1.8:1 (v/v) ethanol/gel ratios. In this case, the reduced ethanol consumption resulted in only a minor effect on pectin properties. At an ethanol/gel ratio of 1.5:1 (v/v), however, brightness decreased as indicated by the value of the color parameter 'L'. The concentration of pigments in the ethanol solvent was probably high, thus decreasing pigment transfer from the gels. The ash content of the pectin, although higher than washing in fresh ethanol at 1:2 ethanol/gel ratio, was still below the quality criterion of 10% ash, which has been established as the maximum limit (Food Chemicals Codex, 1981).

Gel properties

Galacturonic acid contents and pectin gel firmness values are shown in Table 3. The sunflower pectin had 81.1–81.6% content of galacturonic acid compared to 76% for the commercial citrus low-methoxyl pectin.

Table 3. Gel firmness of pectin samples

	Galacturonic acid (%)	Gel firmness, pH 3 (g/cm^2)
P_f	81.6 ± 0.8	27.35 ± 0.63
P_r	81.1 ± 0.7	25.15 ± 0.63
P_c	76*	21.38 ± 1.26

P_f, batch washing with fresh ethanol; P_r, countercurrent washing with reused ethanol; P_c, commercial citrus pectin.
*From certificate of lot 34F-0602, low-methoxyl pectin from citrus, Sigma Chemical Co., St. Louis, MO, U.S.A.

Sunflower pectin is a unique pectin substance that contains high amounts of galacturonic acid (Lin *et al.*, 1975, 1976). Gel-breaking pressure was measured with a plunger having a constant downstroke rate of 20 mm/min, and is expressed in g/cross-sectional area of gel cylinder in cm^2.

Both pectin products from batch and countercurrent washing treatments had a higher galacturonic acid content and a slightly higher gel firmness than commercial citrus low-methoxyl pectin. The gel characteristics of low-methoxyl pectin are affected by chemical composition and the conditions used for gel preparation. Some factors affecting the gel properties of pectin include pH, temperature, and acid treatment during extraction and the gel washing process. After ethanol washing treatments, the pH value of the final pectin gel was above 4.5. Ash content also can affect the ability of pectin to gel. A higher ash content results in a lower-gelling grade of pectin (Miyamoto & Chang, 1992). Most of the ash and acid were removed from gels so that the sunflower pectin was of high gelling quality. Smooth, clear, and elastic gels were obtained both from countercurrent and batch washing treatments. Gels from sunflower pectin were more elastic and more transparent than from the commercial citrus pectin.

CONCLUSIONS

A stepwise, countercurrent washing process at an ethanol/gel ratio of 1.8:1 (v/v) and 70% (v/v) ethanol concentration was effective in removing undesirable pigments, acids, and ash from sunflower head pectin gel. This process can save more than 80% on ethanol consumption compared to batch washing with fresh ethanol for each step. The sunflower pectin products

showed high galacturonic acid content and high gelling quality. The countercurrent washing technology with reused, neutralized ethanol for pectin gel purification is practicable for industrial production.

ACKNOWLEDGEMENTS

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