Chemistry of Natural Compounds, Vol. 31, No. 4, 1995

FEATURES OF THE PRODUCTION AND INFLUENCE OF THE COMPLEX-FORMING ACTIVITY OF LOW-METHOXYL APPLE PECTIN AS A SORBENT FOR HEAVY METALS

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UDC 547.917

Features of production and influence of the complex-forming activity of low-methoxyl pectin (LMP) as a sorbent for heavy metals have been studied. Cation-exchange properties of the LMP in connection with detoxification measures in cases of chronic poisoning have been shown.

Monitoring of the environment is showing a firm tendency to the growth both of the concentration level and of the zone of distribution of heavy metals. In view of the importance of the problem, a group of investigations is being carried out in IKhRV AN RUz on the creation of sorbents for heavy metals from apple pectin by modifying its structure.

There is information in the literature on the protective properties and complex-forming activity (CA) of pectins in relation to heavy metals [1-8] but no full investigation of the dependence of this property on the content of functional groups in the pectin substances has been carried out.

We have studied the process of regulating the degree of esterification of a dry pectin concentrate under the action of alcoholic solutions of alkali or acid and the influence of the saponification parameters (concentrations of the solutions of alkali, acid, and alcohol, and the time and temperature of the reaction) on the change in the quantitative functional composition of the initial raw material.

In the production of low-methoxyl apple pectin (LMP) by treating apple pectin concentrate (produced by the Gazalkent Preserving Factory), 70% of which consists of high-methoxyl pectin (HMP) with a degree of esterification of 70-80%, by alcoholic solutions of alkali and acid the quantitative functional composition of the initial pectin changed considerably. It was shown experimentally that the saponification of the pectin in an alkaline medium took place in 30 min at a temperature of 20 $\pm$ 2°C and a ratio of the dry pectin concentrate to alcoholic solution of 1:8. The experimental results are given in Tables 1 and 2.

The choice of a 65% concentration of the alcoholic solution was due to the fact that at a lower concentration of alcohol the pectin solution loses its filterability, and at a higher concentration the saponification process takes place to an insignificant degree.

As can be seen from Table 1, in their saponification of the methyl ester groups with an alcoholic solution of alkali it is possible to obtain pectin substances with different amounts of the methoxyl component.

The qualitative control of the amount of carboxy groups in the deesterified pectin was carried out by IR spectroscopic and titrimetric methods of analysis [9]. For this, the pectin substances were converted into sodium pectate and the sodium ions were eliminated from this by treatment with a 1% solution of an alcoholic solution of acid. The deesterification of pectin in an alcoholic solution of acid takes place slowly and requires the use of more concentrated solutions of acid. In view of the possibility of a more accurate regulation of the degree of esterification of the pectin, this method can be used to obtain pectins for food purposes.

Thus, increasing the concentration of acid in the alcoholic solution and lengthening of the time of treatment lead to the partial saponification of the methyl ester groups, which must be taken into account in the preparation of the LMP.

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0009-3130/95/3104-0457$12.50

TABLE 1. Influence of an Alcoholic Solution of Alkali on the Degree of Esterification of the Pectin

Index	Experiment No.									
	1	2	3	4	5	6	7	8	9	10
Concentration of NaOH in 65% alcohol	0.08	0.2	0.3	0.4	0.5	0.85	0.75	0.85	0.95	1.1
Degree of esterification	76.5	71.1	69.3	65.7	59.9	44.7	36.4	28.6	25.3	23.6
Ash content of the pectin after treatment with a 1% solution of HCl in 65% alcohol	1.1	0.9	0.85	0.81	0.77	0.73	0.70	0.65	0.66	0.68

TABLE 2. Influence of the Concentration and Time of Action of Acid on the Degree of Esterification of the Pectin

Experiment No.	Concentration of HCl in 60% alcohol, %	Time of action of the HCl, h	Degree of esterification, %	Ash content, %
1	1.0	1	78.7	1.0
		12	76.7	1.1
		24	75.5	1.1
		48	75.0	1.2
		60	75.0	1.2
2	2.0	1	75.0	0.9
		12	74.0	0.8
		24	73.0	0.8
		48	72.0	0.7
		60	72.0	0.7
3	3.0	1	69.0	0.8
		12	68.0	0.7
		24	68.0	0.6
		48	60.0	0.6
		60	52.0	0.6
	4.0	1	69.0	0.8
		12	68.0	0.7
		24	68.0	0.6
		48	60.0	0.6
		60	52.0	0.6

The absorption capacities of the low-methoxyl pectin and also of the starting material in relation to lead salts — $Pb(NO_3)_2$ — were investigated by a static method. Lead was determined quantitatively with the aid of a Perkin-Elmer 303 OB atomic absorption spectrophotometer. The results obtained are given in Table 3.

The modification of the pectin molecule by saponification considerably raises its sorption activity, ion-exchange taking place in the same way as on the use of organic ion-exchange resins, through the acid (carboxy) functional groups. The increase in specificity for the LMP is apparently achieved by a greater correspondence of the energy and geometric relief of the modified pectin and the molecules being absorbed. And although the results of the investigation show an incomplete elimination of the salts from solutions, the fairly high adsorption activity of the LMP may find practical use in medicine under the conditions of chronic lead intoxication since pectins form a nontoxic product widely distributed in nature.

The detoxification properties of pectin were clearly shown in experiments on mice. The intraperitoneal injection of 1 ml of a 1% solution of pectin completely protected the animals from death after the administration of lethal doses of lead acetate (0.58 mmole/kg of $Pb(CH_3COO)_2$) intraperitoneally with an interval of 10 min. Thus, the cation-exchange properties of LMP open up the prospect of its practical use in connection with detoxication measures for chronic lead poisoning.

EXPERIMENTAL

The initial concentrations of the metal and the residual concentrations after sorption were determined with the aid of a Perkin-Elmer 403 atomic absorption spectrophotometer from the analytical line at 283.3 nm [10, 11].

TABLE 3. Determination of the Static Exchange Capacity of Pectins with Various Degrees of Esterification

Sample*	Concentration of the solution, mg/liter	Moist weight of the substance precipitated, mg/liter	Moisture content, %	Weight of the substance	Weight of the substance sorbed			Exchange capacity, mg/liter
					Pb, mg	In the fluid paste, μg	In the dry substance, μg	
A	12	692.5	90.2	346.5	0.0125	3.8	8.7	0.257
B	12	869.5	93.4	432.0	0.0057	4.8	0.9	0.031
A	120	650.6	91.4	355.0	0.0956	39	56.6	2.214
B	120	561.0	93.2	295.0	0.0296	33	3.4	0.189
A	1200	706.2	92.7	362.0	0.6916	403	288	11.430
B	1200	647.5	94.2	321.0	0.4147	369	45.7	2.465

*Sample A) LMP; B) initial substance.

UV spectra were taken of a UR-20 instrument (KBr tablets).

Preparation of the Low-Methoxyl Pectin. Apple pectin in 20-g batches was treated with 0.08-1.1% solutions of caustic soda in 65% alcohol solution in a ratio of 1:8 (see Table 1). The reaction mixture was kept at 20 ± 2°C for 30 min with constant stirring. The resulting suspension of pectin in an alkaline solution of alcohol was filtered through a Büchner funnel, and the residue was washed with 65%, 80%, and 95% ethanol to neutrality.

Treatment with Alcoholic Solutions of Acid. Samples (20 g) of pectins after saponification with alkali were washed with a 2% solution of hydrochloric acid in 60% alcohol for 2 h with stirring in a ratio of 1:4. Then the suspension of pectins was filtered through a Büchner funnel and the residue was washed with 60%, 80%, and 95% alcohol to neutrality. Samples of the LMP obtained were dried in a thermostat at 80 ± 5°C. The yield of LMP for each batch amounted to 12 g.

The sorption capacities of the pectin samples in relation to lead salts were studied under static conditions using the standard procedure of a sorption experiment [12].

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