Features of sorption interactions of plant dietary fiber with heavy metal cations according to absorption IR spectroscopy

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Abstract. The article presents research data on the functional composition of dietary fiber from quince, apple and pumpkin by absorption infrared spectroscopy. An assessment of the potential cation exchange activity of the fibers depending on the pH of the medium by comparing the intensities of the characteristic absorption bands was carried out. Under the conditions of biological media close to acidity, sorption of Pb$^{2+}$, Co$^{2+}$, Cd$^{2+}$ cations from solutions of their salts was carried out. The potential sorption activity of dietary fiber from apple in relation to Pb$^{2+}$ and Co$^{2+}$ is shown. For pumpkin fibers a number of selectivity is predicted: Pb$^{2+}$ > Cd$^{2+}$ > Co$^{2+}$.

1. Introduction

High molecular weight polysaccharides such as pectin, protopectin, cellulose, which are the basis of dietary fiber, are not able to decompose under the action of enzymes, but are a nutrient medium for microflora in the human gastrointestinal tract [1]. For many years, these nutritional components were considered ballast and were not taken into account in the formation of diets. However, in recent decades, the importance of dietary fiber for human health has been revised. The presence of dietary fiber in the human diet is an important factor in reducing the risk of developing many diseases, ensures the presence of many macro- and micronutrients, reduces the toxic effect of heavy metal ions, and the negative effect of antibiotics. In [1,2], the authors note the significant role of dietary fiber in the formation of intestinal microflora, the removal of toxins from the human body, which confirms the need for their use in the preparation of therapeutic diets. Assessment of the nutritional status of the population of Russia shows that one of the most important disorders is the deficiency of dietary fiber in the diets of the population. The main sources of insoluble dietary fiber, such as protopectin, cellulose, hemicellulose, dextrins, etc., are foods of plant origin. Cereals, legumes, vegetables and fruits are the main crops that are sources of fiber and non-starch polysaccharides. Due to the high sorption abilities of pectin and cellulose, cell structures can accumulate heavy metals even in the process of agricultural production growth. The authors of [3] note the negative effect of toxic heavy metal cations (Cd$^{2+}$, Pb$^{2+}$, Zn$^{2+}$) on plant growth parameters and nutrient content. The most dangerous toxicants are cadmium and lead. Cadmium and lead cations are absorbed by plants and are concentrated in the root and root zones. As growth and maturation of toxic elements accumulate in the shoots and leaves of crops. According to [4], the main food sources of Cd$^{2+}$ for the US population are such food groups as cereals and bread (34%), leafy vegetables (20%), and potatoes (11%). A review article [5] provides data on the influence of various methods of processing raw materials. They allow
you to reduce the content of toxic elements in foods. In these methods, binding organic and inorganic forms of mercury, arsenic, cadmium, lead chemical agents are used.

The accumulation and retention of heavy metal cations in pectin- and cellulose-containing dietary fibers occurs mainly due to their cation-exchange ability. In [6,7], special attention is paid to the processes of interaction of pectin with divalent cations, and the cytoprotective and antioxidant effects of citrus, apple, and pumpkin pectin in the presence of cadmium and mercury cations are also noted. The cation exchange activity of pectin and cellulose is associated with the molecular structure of the polymers, the reaction of the medium, the ionic composition of the solutions, and other external factors. This makes it difficult to predict the sorption ability of natural polymer composites in relation to heavy metal cations.

A promising source of dietary fiber is fruit and vegetable products [8]. This work presents data on the identification of potential sorption activity against heavy metal ions of dietary fiber isolated from pulp of apples, quince and pumpkin. As the main research method, absorption infrared spectroscopy was chosen. This method allows us to assess the potential cation exchange activity of sorbents, due to the functional composition of the samples.

2. Materials and methods

As objects of the research, squeezes of pulp of apples of the Antonovka variety, quince of the ordinary variety Belorussskaya, and pumpkins of the Muscatnaya variety were used. The pulp was subjected to convective drying to a moisture content of 6% at a temperature not exceeding 50°C in a vacuum evaporator. Squeezes obtained in this way are a crushed loose product from light cream to cream color with a taste and aroma of the corresponding fruit. They are characterized by low humidity (5.3-5.95%), contain from 28.5 to 38.7% of the mass. dietary fiber. The high content of dietary fiber makes it possible to classify squeezed pumpkin, quince and apples as semi-concentrates with a certain content of dietary fiber and to use the term “dietary fiber”. By the availability of raw materials, the totality of organoleptic and physico-chemical indicators and composition, dietary fiber from apples, pumpkin and quince can be considered promising raw material enriching food products.

The fiber samples were conditioned in distilled water or salt solutions for measurement. The pH was adjusted by adding either hydrochloric acid or sodium hydroxide with an accuracy of ± 0.2. Sorption of cations Pb^{2+}, Co^{2+} and Cd^{2+} was carried out from 0.05 M solutions of their salts for 1.5 hours. Then it was decontaminated and dried to constant weight at a temperature of 45°C. The functional composition of the samples was studied by absorption infrared spectroscopy. The spectral characteristic is formed as a result of recording the transmitted or reflected from the sample electromagnetic flux in a given region of the spectrum. The type of spectrum characterizes the interatomic and intermolecular interactions in the system. The interpretation of the IR spectra of dietary fiber was carried out using reference data, as well as the work [7]. Infrared absorption spectra in the range from 400 to 4000 cm\(^{-1}\) were obtained on a Bruker VERTEX 70 IR Fourier spectrometer in reflection mode.

3. The effect of pH on the cation exchange ability of dietary fiber

The spectral characteristics of samples of dietary fiber of quince, apple, pumpkin and cotton cellulose (as a sample for comparison) in the native state are presented in Figure 1.

A comparison of the spectral characteristics of the samples indicates the presence in each sample of dietary fiber polysaccharides, similar in the structure and composition to cellulose (Fig. 1). All spectrograms are characterized by the presence of stretching vibrations of C–H (2920, 2850 cm\(^{-1}\)) and O–H (3500-3100 cm\(^{-1}\)) bonds. There are no special differences in this spectral region for different samples. The presence of the C–O–C ether group in the polymer structure of polysaccharides is confirmed by the presence of a pronounced peak at 1033 cm\(^{-1}\) with a band of 1150 cm\(^{-1}\) at the base of the maximum. The set of absorption bands in the region of 800-500 cm\(^{-1}\) corresponds to skeletal vibrations of C–C and C–H bonds and deformation vibrations of C–OH groups.
Figure 1. Infrared absorption spectra (A) of samples of dietary fiber in the native state: 1 - quince, 2 - apple, 3 - pumpkin; 4 - cellulose fiber.

The difference in the spectral behavior of the samples in the range 1800-1200 cm\(^{-1}\) was revealed. The absorption bands of 1440-1417, 1370-1310 cm\(^{-1}\), corresponding to the deformation vibrations of the -OH group, are present in all spectrograms and are most clearly manifested in the cellulose spectrum. In general, for the spectrogram of dietary fiber are similar to each other. This indicates a close functional composition. The presence of nitrogen-containing compounds in the composition of food composites is confirmed by the presence of absorption bands of 1540-1525 cm\(^{-1}\) and 1240 cm\(^{-1}\), corresponding to deformation vibrations of C–N bonds in the composition of secondary amines. The presence of carboxyl groups in hydrogen form is confirmed by the presence in the spectra of peaks 1720 cm\(^{-1}\) for quince, 1730 cm\(^{-1}\) for apple and pumpkin. The shift of this maximum by 10-20 cm\(^{-1}\) to the low-frequency region relative to the cellulose spectrum (1740 cm\(^{-1}\)) indicates the association of carboxyl groups with the formation of dimers in the structure of samples 1 and 2. The presence of the salt form of the carboxyl group is most characteristic for sample 3 and is confirmed by the presence of absorption bands in the range of 1643-1600 cm\(^{-1}\) [7]. This band for sample 4 can be attributed to the deformation vibrations of water molecules, which are firmly bound to the centers of cellulose hydration. The data obtained suggest the presence of pectin and protopectin substances in the composition of dietary fiber, which can exhibit cation-exchange activity. Comparison of the spectrograms of the samples in the native state shows the existence of carboxyl groups in various forms. So for quince and apple, the presence of carboxyl groups in the hydrogen form is more pronounced, and for the fibers from pumpkin the salt form of acid groups is more characteristic. It was of interest to evaluate the potential cation-exchange ability of samples to compare the spectral characteristics of dietary fiber at the same pH close to neutral. According to modern concepts, the sorption of heavy metal cations is carried out depending on the type of sorbent and the nature of the cation, begins in the stomach and continues in various parts of the intestine. The acidity on the surface
of the epithelial layer facing the lumen of the stomach is 1.5-2.0 pH. The acidity in the depth of the epithelial layer of the stomach is about 7.0 pH. Normal acidity in the antrum of the stomach is 1.3-7.4 pH. Normal acidity in the duodenal bulb is 5.6-7.9 pH units. Acidity in the jejunum and ileum is also neutral or slightly alkaline and is in the range of 7 to 8 pH. The acidity of the small intestine is 7.2 to 7.5 pH. Acidity secret duodenal glands - from pH from 7 to 8 pH. Based on these data, the sorption of cations of the studied metals by dietary fibers was carried out at different pH values characterizing the acidic environment, as well as close to the neutral value. It was also interesting to study the effect of pH on the interaction of cations with carboxylate anions, which are part of the fibers and are the main sorption centers.

Spectrograms of dietary fibers taken at different pH show differences only in the spectral range of 1800-1200 cm\(^{-1}\). The characteristic peaks of 1730 cm\(^{-1}\) and 1600-1610 cm\(^{-1}\), corresponding to the valence oscillations of the carboxyl group and the carboxylate anion, respectively, differ the most. Table 1 shows the intensity of absorption bands on the spectrograms of food fiber samples, which were found by the internal standard method. The oscillation band of methylene groups 2920 cm\(^{-1}\) was chosen for the internal standard. The relative heights of the absorption bands were calculated after baselines as the ratio of the height of the characteristic peak to the height of the peak of the internal standard.

| Table 1. Relative heights of characteristic bands of carboxyl group (1730 cm\(^{-1}\)) and carboxylate anion (1610 cm\(^{-1}\)) for dietary fibers at different pH |
|-----------------------------------------------|
| The wave number of characteristic bands | Relative heights of characteristic bands at different pH |
|-----------------------------------------------|
| pH = 3.2 | pH = 3.9 | pH = 6.9 |
| 1610 / 2920 | 1.0 | 0.83 | 0.94 |
| 1730 / 2920 | 1.5 | 0.86 | 0.59 |
| 1610 / 1730 | 0.67 | 0.97 | 1.6 |
| Quince | | | |
| pH = 3.4 | pH = 3.8 | pH = 6.2 |
| 1610 / 2920 | 0.70 | 0.57 | 0.92 |
| 1730 / 2920 | 1.1 | 0.66 | 0.67 |
| 1610 / 1730 | 0.64 | 0.87 | 1.38 |
| Apple | | | |
| pH = 3.7 | pH = 4.5 | pH = 6.9 |
| 1610 / 2920 | 2.1 | 2.8 | 2.3 |
| 1730 / 2920 | 1.0 | 0.63 | 0.42 |
| 1610 / 1730 | 2.1 | 2.2 | 5.4 |
| Pumpkin | | | |

The intensity of the absorption bands of the carboxyl group in hydrogen form for all samples decreases with increasing pH. Changing the height of the peaks of carboxylate ions for different dietary fibers is complex, which is probably due to their heterogeneity. However, if we compare the relative heights of the peak of carboxylate ions with respect to the peak of the carboxyl group R (table.1, line 1610 / 1730), then for all samples there is an increase in this indicator with increasing pH. The obtained results indicate the transition of carboxyl groups of sorbents to their salt form with increasing pH of the medium. This behavior of dietary fiber samples allows one to predict their affinity for heavy metal cations to a greater extent at a higher pH value.
4. Features of sorption of heavy metal ions by dietary fibers

IR spectra for dietary fibers after sorption of lead (+2), cobalt (+2) and cadmium (+2) cations from solutions of their salts were obtained, pH correction up to 7.0±0.2. The changes observed in the spectrograms of the samples are manifested in the frequency range characteristic of the oscillations of the carboxyl group and its salt form.

Figure 2 shows a diagram showing the ratio of the salt and hydrogen forms of carboxyl groups of samples before and after the sorption of metal cations. The R (1610 / 1730) ratios were calculated using food fiber spectrograms. The results are presented in table 1.

![Figure 2](image)

Figure 2. The ratio of heights of characteristic absorption bands R (1610 / 1730) for samples of pumpkin, quince, apple before (black column) and after sorption of metal cations (white and gray columns) at pH = 7.0±0.2.

The relative intensity of oscillations of carboxylate ions in the quince fibers in the presence of cations of the studied metals does not change. This may be a consequence of the lack of interaction with them. These diagrams (figure 2) also indicate the manifestation of cation exchange activity of apple and pumpkin fibers against metal cations. Dietary fiber obtained from apples, very well absorb lead ions and to an even greater extent sorbing ions of cobalt. The sample of pumpkin fibers is characterized by ion exchange interaction with all cations. This is evidenced by an increase in the ratio R (1610 / 1730) for fibers treated with salts of heavy metals compared to the original sample. There is an increase in the proportion of carboxylate ions in the composition of pumpkin fibers in a number of cations: Cu^{2+} < Cd^{2+} < Pb^{2+}. This fact makes it possible to predict the high sorption activity of pumpkin fibers against lead and cadmium cations.

5. Conclusion

The ion exchange capacity of dietary fibers is one of the important factors determining their role in maintaining the electrolyte composition, as well as removing toxins such as heavy metals from the body. The study of the functional composition by IR spectroscopy showed that the main cation exchange centers of dietary fibers derived from quince, apple and pumpkin are carboxyl groups. The influence of medium acidity on the state of functional groups was assessed by the change in R (1610/1730) – the ratio of the heights of the absorption bands of the carboxylic group and carboxylate ions in the IR spectra of the samples. The obtained data indicate the transition of carboxyl groups of sorbents to their salt form with increasing pH. The obtained data allows predicting the increase in sorption of heavy metal cations with increasing pH.

The study of the sorption of lead, cobalt and cadmium cations by food fiber samples was carried out at pH = 7.0±0.2, close to acidity in the human intestine. The presence of heavy metal cations is reflected in the spectrograms of dietary fibers by changes in the region of oscillations of the carboxyl group and the carboxylate anion. Dietary fibers obtained from plant materials showed different...
sorption behavior. Thus, the relative intensity of the oscillations of carboxylate ions in the quince fibers in the presence of cations of the studied metals does not change. This may be due to a lack of interaction with them. The dietary fibers obtained from apples well sorb lead ions and to an even greater extent sorb cobalt ions. The sample of pumpkin fibers is characterized by ion exchange interaction with all cations. This is evidenced by an increase in the ratio \( R (1610 / 1730) \) for fibers treated with heavy metal salts, compared to the original samples. Moreover, an increase in the proportion of carboxylate ions active for interaction in the composition of pumpkin fibers is observed in the series: \( \text{Co}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+} \). This fact makes it possible to predict the high sorption capacity of pumpkin fibers against lead and cadmium cations.

It should be noted that the data obtained by IR spectroscopy also allow us to judge the state of the adsorption centers of the sorbents studied, but do not provide information about the sorption capacity of the samples. Research in this direction will be continued.

Thus, the evaluation of the potential cation exchange capacity of quince, apple and pumpkin dietary fibers in relation to lead and cadmium ions obtained as a result of research makes it reasonable to use these dietary fibers as valuable food components and biologically active composites.

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