

Relations between cadmium and magnesium and aronia fractional dietary fibre

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Abstract

The aim of this investigation was to analyse the composition of dietary fibre from aronia pomace preparations and to evaluate its influence on cadmium and magnesium binding. The authors wanted also to estimate to what extent additional enzymatic processing could affect the sorption capacity of the aronia fibre.

Fibre preparations of aronia pomace possessed poor cadmium-binding capacity and desorbed magnesium, which is needed by the human body. There was a significant pH effect on cadmium and magnesium binding capacity. Magnesium desorption was much higher at pH 2.0 than at pH 6.0. The type of aronia sample did not generally affect the level of cadmium sorption.

Thus, aronia pomace preparations can be a source of dietary fibre and provide the body with magnesium. In addition, they can be used as weak cadmium sorbents.

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1. Introduction

Aronia wastes are a valuable, though not utilised, source of dietary fibre. The capacity of the fibre to bind chemical elements depends on its chemical structure and composition. Platt and Clydesdale (1987) and Torre et al. (1995) have found that fibre components containing active functional groups exhibit a particularly good metal-binding capacity. Sorption is a complex process and may proceed according to three mechanisms: chemisorption, physical sorption and mechanical sorption (Krejpcio, Olejnik, Wójciak, & Gawęcki, 1997). Chemisorption is connected with the presence in the fibre matrix of phenolic groups from lignin and carboxyl groups from uronic acids. Physical sorption results from van der Waals' forces, which are temperature dependent, while mechanical sorption depends on the degree of porosity of the sorbent and its ability to

trap the substances in its spatial structure. When analysing metal sorption by dietary fibre it can be seen that the sorptive properties of the fibre are a result of a number of factors: the kind of fibre, the degree of graining, experimental conditions (pH and temperature), type of ion being absorbed, etc.

The aim of this investigation was to determine the cadmium-binding capacity by aronia pomace preparations, under conditions similar to those in the stomach and also similar to those found during the initial and final stages of production of certain dairy products. The influence of enzymatic treatment of the pomace on its sorption ability was also studied.

2. Materials and methods

2.1. Fibre fraction preparation

The material used in the investigation included samples from aronia pomace and fibre samples from enzymatically-treated pomace.

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Enzymatic treatment was carried out to remove colloids and mucous materials from aronia pomace. The pomace was dried, ground and sieved and then distilled water was poured over it in the ratio of 1:4. This was followed by addition of 0.2 ml/l of the Pectinex Colour preparation. The mixture was thoroughly mixed and heated for 2 h in a drier at 50 °C. During heating, the mixture was stirred many times. The supernatant was centrifuged for 15 min at 4000 rpm. The precipitate was rinsed with water 4 parts of water per 1 part of deposit. The suspension was stirred for about 15 min and then centrifuged again. This was done twice. The pomace preparation was then dried at 55 °C. The dry preparation was ground in a mill and sifted through a $\phi = 0.15$ mm sieve.

The following fibre materials were used in this investigation:

- (1) *Aronia melanocarpa* pomace (Sample BAP) from an industrial sample from ZPOW Agriko (Łęczycza Poland) with various grain diameters (<2 mm),
- (2) *Aronia melanocarpa* pomace after enzymatic treatment of BAP (Sample PAP),
- (3) *Aronia melanocarpa* fruit pomace (Sample BAL) obtained under laboratory conditions (grain diameter <2 mm),
- (4) *Aronia melanocarpa* pomace obtained after enzymatic treatment of BAL laboratory aronia pomace (Sample PAL).

2.2. Standard solutions

Standard solutions (Merck, Darmstadt, Germany) were used to prepare adsorbates. A working solution of cadmium was prepared (0.1 mg/l), which was used to prepare an adsorbate of the same concentration for sorption studies.

The dispersion media used in this study were buffer solutions at pH 2.0 ± 0.05 , approximately equivalent to the digestive environment, and pH 6.0 ± 0.05 , which is similar to that during the initial stages of dairy goods production (Harper, Rodwell, & Mayes, 1983; Lempke et al., 1985). The concentration of cadmium in the buffer solutions was ignored as it was found only in trace amounts (14–20 $\mu\text{g}/\text{kg}$). The concentration of metals in the adsorbate was selected on the basis of the Directive of Minister of Health (Dz. U. 2003, Nr 37 Poz. 326), in order to simulate dairy products (milk and yoghurt).

2.3. Dietary fibre analysis

The determination of dietary fibre fractions (cellulose, hemicellulose, lignin) in the investigated preparations was carried out using detergent methods (McQueen & Nicholson, 1979; Van Soest & McQueen, 1973).

Dietary fibre fractions in the investigated preparations were determined in the following way:

- (1) Acid detergent fibre (ADF) (cellulose, lignin) was determined by means of the van Soest method (Van Soest & McQueen, 1973). This method is based on selective isolation, in specific conditions, of different fractions by separating them from other components, by using surface-active compounds. % ADF = % cellulose + % lignin.
- (2) The lignin fraction of acid fibre (ADL) was determined according to the AOAC methodology, in compliance with procedure No. 973,18,C (AOAC, 1990).
- (3) Neutral detergent fibre (NDF) (cellulose, hemicellulose, lignin) was determined using McQueen's modification (McQueen & Nicholson, 1979). % NDF = % cellulose + % hemicellulose + % lignin.
- (4) The hemicellulose fraction content was determined from the difference between neutral detergent fibre and acid detergent fibre. % hemicellulose = % NDF – % ADF.

As the van Soest method does not allow determination of pectins, these substances were determined using a spectrophotometric method. Pectin fractions were separated by heating with 0.5 M HCl, according to the procedure described by King (1987). The water-soluble fraction was isolated by means of the Kawabata extraction method (Kawabata, 1977). In order to determine uronic acids in the extracts, Bitter's spectrophotometric borate method was employed (Kłyszczko-Stefanowicz, 1972). This method was chosen due to the short time of pectin extraction, in comparison to other methods, and due to the stronger colour of the solution (compared to, for example, Dische or McCready methods).

The determination of the mineral characteristics of the fibre samples after ashing by dry mineralisation was carried out using atomic absorption spectrometry obtained (Kula-Krełowska, 1993).

The contents of cadmium and lead were determined by means of a flameless method, using a graphite cuvette. This method made it possible to avoid the time-consuming preparation of metals into complexes with ammonium 1-pyrrolidinedithiocarbamate and its extraction with methyl isobutyl ketone, which requires a high sample volume, application of many reagents and poses a risk of contamination. The advantage of the flameless method employing a graphite cuvette is a reduction in the metal detection limit and better reproducibility. Other metals were determined using the flame method (Kula-Krełowska, 1993).

2.4. Cadmium and magnesium sorption

Pomace preparation samples were soaked in 10 ml of buffered adsorbate per g of preparation. The soaking process was carried out for 1 h at 37 °C at pH 2.0 at 20 °C and at pH 6.0. Then the samples were shaken for 10 min and centrifuged for 5 min at 4000 rpm. The sorbent was then washed with redistilled water and the procedures of shaking and centrifugation were repeated three times.

Eventually, the sorbent was dried at 55 °C until the substance was solid.

The sorption level of cadmium was calculated from the percentage ratio of the element bound to the fibre, compared with the total amount of that element introduced into the system. The magnesium desorption level was determined as a percentage ratio of its decrease, compared with its initial level.

2.5. Statistical analysis

The effect of a given factor (type of product or process conditions) on sorption or desorption efficiency of the metals investigated was determined by means of a single factor analysis of variance (Statistica 6.0).

3. Results and discussion

The investigated aronia preparations were in the form of granules of diameter less than 150 µm. They were odour-free, dark purple in colour and had no characteristic taste.

The results obtained (Table 1), indicated that the aronia preparations contained more than 40% dietary fibre. The preparations obtained from pomace under laboratory conditions were relatively rich in hemicellulose with lower lignin content, in comparison to pomace preparations obtained from industrial aronia. All the aronia materials had a pectin content exceeding 10% (Fig. 1). The research by Nawirska and Oszmiański (2001) showed that these pectins had a decisive effect on cadmium binding in aronia pomace.

In order to check the usefulness of aronia preparations for nutritional purposes, the samples were tested for cadmium content (Table 2). Levels were below the maximum levels specified in the Minister's of Health Directive (2003).

Table 1
Fractional composition (mean ± s.d.) of dietary fibre in aronia samples

Substance	Fractional content (%)				
	BAP	PAP	BAL	PAL	
NDF	47.3 ±0.98	46.1 ±0.51	41.9 ±0.64	48.5 ±0.27	
ADF	45.6 ±1.07	45.3 ±0.83	34.6 ±0.44	44.0 ±0.74	
Lignin	25.2 ±0.58	26.8 ±0.47	15.0 ±0.64	18.9 ±0.29	
Cellulose	20.4 ±1.42	18.5 ±0.36	19.6 ±0.53	25.1 ±0.60	
Hemicellulose	1.75 ±0.57	0.81 ±0.00	7.72 ±0.30	4.48 ±0.26	
Pectins	Total	11.3 ±0.127	10.7 ±0.39	14.0 ±0.58	12.6 ±0.53
	Water soluble	1.14 ±0.082	1.00 ±0.04	2.86 ±0.16	1.26 ±0.127

The results of the investigation of cadmium sorption by aronia pomace samples are presented in Table 3. Cadmium sorption did not exceed 15% in the samples studied. No effect of process temperature on ion exchange was observed. Also, at pH 6.0 cadmium sorption was no different from at pH 2.0.

At pH 6.0 and 45 °C, laboratory pomace samples showed much higher cadmium sorption than industrial pomace samples (Table 3). The highest cadmium sorption at pH 6.0 and 20 °C was found for industrial fibre, and the lowest in the enzymatic treatments. Thus, it may be concluded that enzymatic treatment, resulting in a reduction in the content of lignin (active in chemisorption) and pectins (Borycka, 2004), caused a reduction in cadmium ion-binding capacity. Nawirska (2005) showed that the fraction composition of aronia fibre does affect the metal-binding capacity. Cad-

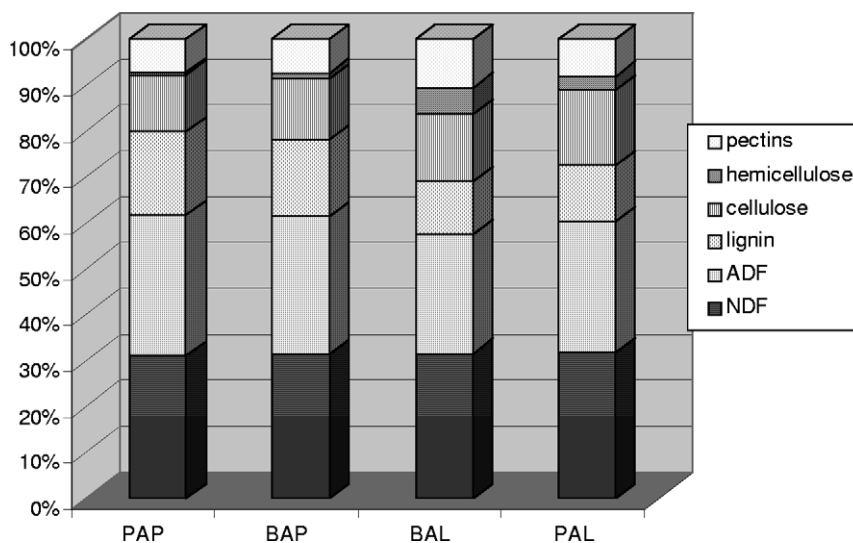


Fig. 1. Fractional composition of dietary fibre in aronia samples.

Table 2
The content of metals (mean \pm s.d.) in aronia fibre preparations

Preparation	Metal content (mg/kg)			
	Cd	Pb	Mg	Ca
BAP	0.01 \pm 0.02	0.20 \pm 0.05	281.7 \pm 9	1946 \pm 34
PAP	0.04 \pm 0.03	0.21 \pm 0.07	214.9 \pm 14.7	2089 \pm 51
BAI	0.02 \pm 0.04	0.16 \pm 0.06	364.9 \pm 51.2	1089 \pm 34
PAL	0.03 \pm 0.04	0.11 \pm 0.03	88.3 \pm 7.8	893 \pm 26
Standard for additives >0.1% in foodstuffs	0.1	1.0	–	–
Standard >50% dry matter	0.1	0.5	–	–
Standard for dried berry fruits	0.2	0.5	–	–

Table 3
Cd and Mg sorption and desorption (mean \pm s.d.) of aronia preparations

Conditions	Product	Desorption Mg (%)	Sorption Mg (%)	Sorption Cd (%)
pH 2, 37 °C	PAP	88.1 \pm 1.21	–	–
pH 2, 37 °C	PAL	76.5 \pm 4.41	–	3.8 \pm 1.94
pH 2, 37 °C	BAP	88.3 \pm 1.19	–	–
pH 2, 37 °C	BAL	93.6 \pm 0.48	–	4.8 \pm 2.32
pH6, 20 °C	PAP	29.0 \pm 1.847	–	4.3 \pm 0.82
pH6, 20 °C	PAL	–	2.8 \pm 0.64	5.4 \pm 2.56
pH6, 20 °C	BAP	18.8 \pm 3.96	–	14.0 \pm 2.31
pH6, 20 °C	BAL	38.3 \pm 5.69	–	9.5 \pm 2.78

mium-binding decreases in the fractions in the following order: pectins > cellulose > hemicellulose > lignin (Nawirska, 2005). No treatment effects were observed at pH 2.0.

Cadmium sorption was significantly higher in a slightly acidic medium than at pH 2.0 (Table 3). In studies of cadmium sorption in blackcurrant pomace, the cadmium-binding level was significantly higher at pH 6.0, than at pH 2.0, and the authors also reported the dependence of cadmium sorption levels on temperature (Borycka, 2002; Borycka & Borycki, 2002). A similar increase in cadmium sorption with an increase in pH of the medium was also observed by other workers (Valiente, Molla, Martin-Cabrejas, & Lopez-Andreu, 1996; Walkowska, Gawęcki, & Olejnik, 1992).

The aronia samples had a relatively low magnesium content (Table 2), and a significant desorption of magnesium from the samples was observed (Table 3). A significantly lower desorption level was noted in industrial pomace and preparations, and the lowest was observed in the laboratory aronia preparation which was enzymatically-treated. Magnesium desorption in all examined preparations was significantly higher at pH 2.0 than at pH 6.0. In the conditions simulating the digestive tract, magnesium is desorbed from aronia fibre at a high level.

4. Conclusions

In the experimental model discussed cadmium was absorbed at a relatively low level across a fairly wide range (1–8%), and the pH had a significant effect on cadmium-binding. The level of cadmium sorption appeared to be considerably higher at pH 6.0 than at pH 2.0. There was

significantly lower cadmium sorption for industrial fibre than for laboratory fibre but only at pH 6.0.

Magnesium desorption in all investigated preparations was significantly higher at pH 2.0 than at pH 6.0. Under the conditions simulating the digestive tract, magnesium was liberated from aronia fibre at high levels. Thus, aronia pomace preparations could be used as a base for magnesium supplements with low cadmium sorption and also as additives for foodstuffs.

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