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Binding of heavy metals to pomace fibers

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Abstract

This study demonstrates that the dietary fibers of pomace, a waste product from fruit pressing, have the potential for binding heavy metal ions. The quantity of metal ions bound varies from one fiber component to another. As it can be inferred from the results of the study, pectin was characterised by a particularly high capacity for metal ion binding. The hemicellulose fraction ranked second with respect to metal ion binding capacity. Binding of heavy metals to lignin was found to be generally poor.

Keywords: Fruit pomace; Dietary fibers; Heavy metal ions

1. Introduction

Dietary fibers (DF) consist of a variety of components, including pectin, hemicellulose, cellulose, lignin (Asp, 1987, 1996; Cummings, 1991; Englyst & Hudson, 1996). DF also include some non-structural components (gums and mucilages), as well as industrial additives (modified cellulose, modified pectin, commercial gums and algae polysaccharides) (Davidson & McDonald, 1998; Grigelmo-Miguel, Gorinstein, & Martìn-Belloso, 1999). DF components differ not only in chemical structure or physiological activity from one vegetable material to another, but also in their capacity for microelement binding. Hemicellulose and pectins have a remarkable ability to bind heavy metal compounds, which is promising for the promotion of health via fiber-containing food. Cellulose and lignin are also able to bind heavy metals (though to a smaller extent than hemicellulose and pectins), but their binding ability varies with the source of origin of relevant fractions (Borycka, Borycki, & Żuchowski, 1996; Casterline & Yuoh, 1993; Davidson & McDonald, 1998; Platt & Clydesdale, 1984; Sangnark & Noomhorm, 2003). The sorbing capacity of dietary fiber depends on its chemical structure and proportion of particular elements. From the investigations reported in the literature it can be inferred that the stability of metal–DF complexes differs according to the metal involved and depends on the experimental conditions, as well as on the fiber source (Borycka & Żuchowski, 1998).

The literature contains many references to the binding capacity of dietary fibers and dietary fiber components under simulated gastrointestinal conditions (Bingham et al., 2003; Ferguson & Harris, 2003; Peters et al., 2003; Schneeman, 1998; Stachowiak, 1993; Terry et al., 2001; Wang, Rosell, & de Barber, 2002). Also reported are investigations into the dietary fiber from pomace, alone and in combination with other fibers originating from a variety of sources (e.g. from a pomace mixture containing blackcurrants and apples or apples and raspberries) (Borycka & Żuchowski, 1998). The investigations reported by Borycka and Żuchowski (1998) were focused on the binding of materials to DFs prepared from apple pomace, blackcurrant pomace and mixtures. She found that the blackcurrant preparation showed the best binding capacity with respect to cadmium and lead at pH 6.0 (Borycka & Żuchowski, 1998). Thomson and Weber (1979), who examined the influence of pH on the binding of copper, zinc and iron in six fiber sources (wheat bran, corn bran, rice bran, soya bean bran, oat hulls and cellulose), showed that the majority of fibers were capable of binding metals at pH 6.8, and that those metals were released at pH 0.65.

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Sorption and desorption levels were found to vary according to the fiber source and the metal used in their study.

The objective of our study was to determine the ability of the pectin, polyphenol, hemicellulose, cellulose and lignin fractions extracted from apple, chokeberry, pear and rosehip pomace to bind heavy metals (Pb, Cu, Cd, Zn).

2. Materials and methods

2.1. Materials

The pomace samples under study were prepared from apples, pears, chokeberry or rosehip, with and without pectin, hemicellulose, cellulose and lignin fractions. Apple and pear pomace was supplied by the Fruit Processing Plant of Prusice (Poland); chokeberry and rosehip pomace came from fruit processed at the Department of Fruit, Vegetables and Cereals Technology, Wrocław University of Agriculture (Poland). Fruit was pressed with enzymes that are used in industry. The starting pomace material was dried at 50 °C for 6 h and thereafter subjected to sequential modifications (Nawirska, 2001). The pomace was modified by the removal of further fractions via gradual dissolution of the investigated material in methyl alcohol, in a chelating solution (oxalates) and hot hydroxide, as well as via a two-stage hydrolysis in H_2SO_4, thus removing the fractions of pectins, hemicellulose, cellulose and lignin.

Binding of heavy metals was investigated with the following model solutions: lead(II)nitrate ($Pb(NO_3)_2$; 10 g Pb/m^3), copper(II) sulphate ($CuSO_4$; 8 g Cu/m^3), cadmium(II) sulphate ($3CdSO_4 \cdot 8H_2O$; 4 g Cd/m^3) and zinc(II) sulphate ($ZnSO_4 \cdot 7H_2O$; 6 g Zn/m^3) (Nawirska, 2001).

Pomace samples (after removal of sequential fractions) were weighed in one gram portions and added into 300 cm^3 conical flasks which were then treated with 100 cm^3 of appropriate model solution. After thorough mixing, the flasks were stored at room temperature. From each flask (after 30 min of storage) a 7 cm^3 portion of the solution was taken and placed in the test-tube centrifuge (of MPW 211 type) (Nawirska, 2001). Concentrations of metal ions were measured by atomic absorption spectrometry (AAS).

2.2. Analysis

The investigations were carried out at the Department of Fruit, Vegetables and Cereals Technology, Wrocław University of Agriculture, immediately upon arrival of the material in a wet state. Sequential fractions were removed from the pomace by the non-starch polysaccharides and lignin method developed by Jaswal, as well as by Dever, Bandurski, & Kiviliaan (1968), and modified by Kita (2002). Following separation of each fraction, the pomace samples were exposed to the presence of heavy metals. Metal ion content was analysed by atomic adsorption spectrometry with an AAS-30 apparatus and the parameters summarised in Table 1.

Table 1
Experimental parameters for AAS analysis

Metals	Zinc	Copper	Cadmium	Lead
Wavelength (nm)	213.9	324.8	228.8	283.4
Interstice (mm)	0.21	0.19	0.15	0.17

The quantity of the cations bound was calculated in terms of the formula

$$A = V\frac{C_0 - C_e}{m},$$

where A stands for the ability of the pomace to bind ions (mg/g); C_e is equilibrium concentration of the metal (mg/dm^3); C_0 denotes initial concentration of the metal (mg/dm^3); V is liquid volume (dm^3).

Metal binding capacity of the pomace with and without fiber components was calculated in terms of the difference in the amount of bound ions.

3. Binding of metal ions to particular fiber components of the pomace

We investigated the heavy metal binding by the pomace in the absence of individual fractions. The bar charts shown in Figs. 1–4 show the calculated values for heavy metal binding to chokeberry, pear, apple and rosehip fibers contained in 100 g DM of pomace. As it can be seen from these data, the amount of metal ions bound by the pomace differed from one fraction to another.

Of the fiber components of the chokeberry pomace (Fig. 1), pectins have bound the largest amounts of copper, cadmium and lead. Zinc binds most efficiently to polyphenols. It is worth noting that the polyphenol component of the chokeberry pomace was found to be capable of binding each of the investigated heavy metals, which is a characteristic feature of this pomace type. The amount of heavy metal ions bound to polyphenols varied from 1 mg Cd/100 g DM pomace to 28 mg Pb/100 g DM pomace for cadmium and lead, respectively. The quantity bound by lignin was small, ranging between 0.74 mg Cu/100 g DM pomace for copper ions and 1.74 mg Zn/100 g DM pomace for zinc ions, respectively.

In pear pomace (Fig. 2), pectins were the most active fraction with respect to lead (42 mg Pb/100 g DM pomace) and cadmium (26 mg Cd/100 g DM pomace). Hemicellulose showed a high activity towards copper (19 mg Cu/100 g DM pomace), whereas cellulose dis-

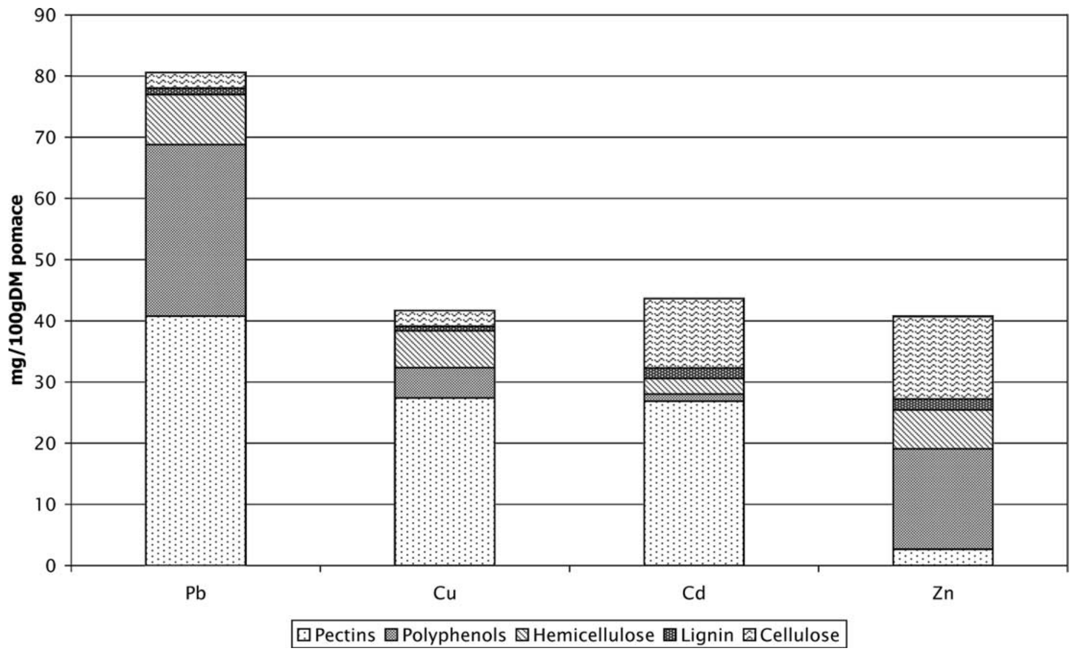

Fig. 1. Efficiency of metal ion binding to chokeberry pomace components.

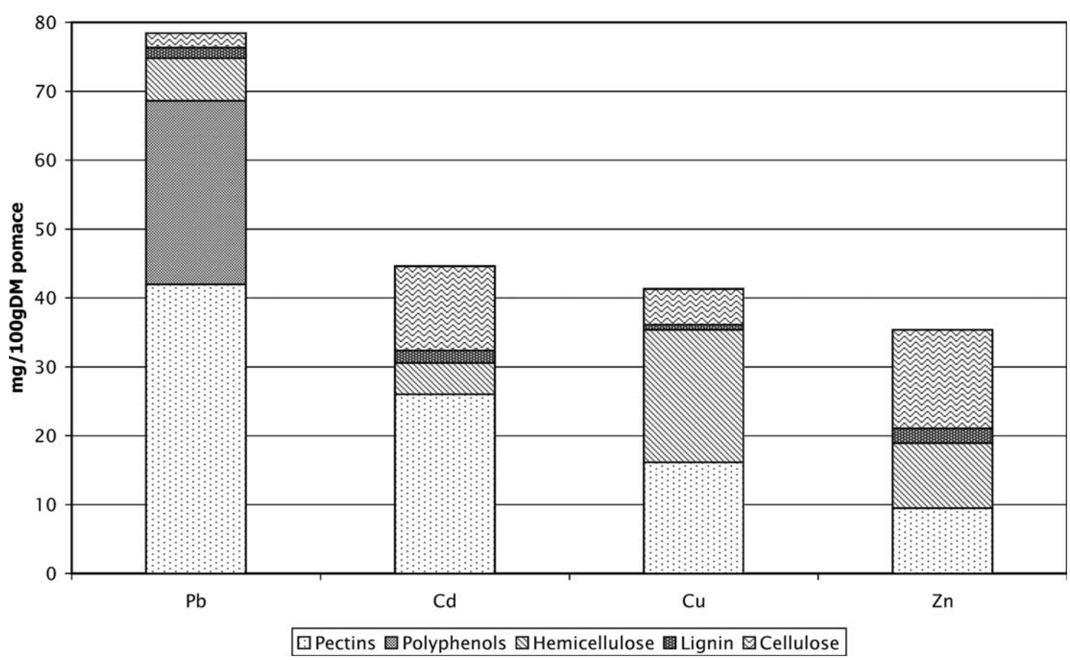

Fig. 2. Efficiency of metal ion binding to pear pomace components.

played a noticeable capacity of binding zinc and cadmium (14 mg Zn/100 g DM pomace and 12 mg Cd/100 g DM pomace, respectively). Lignin was found to be the least active fraction. Polyphenols were capable of binding lead ions only (27 mg Pb/100 g DM pomace).

Like in chokeberry or pear pomace, the pectin fraction of apple pomace was found to be the most effective metal binder (Fig. 3). The quantity of pectin-bound heavy metals varied from 16.9 mg Zn/100 g DM pomace to 40.4 mg Pb/100 g DM pomace for zinc and lead, respectively. Heavy metal binding by cellulose followed two distinct patterns; there was a considerable difference in the quantities of pectin-bound cadmium and pectin-bound zinc (1.42 mg Cd/100 g DM pomace and 11.9 mg Zn/100 g DM pomace) and a small difference between pectin-bound lead and pectin-bound copper (5.4 mg Pb/

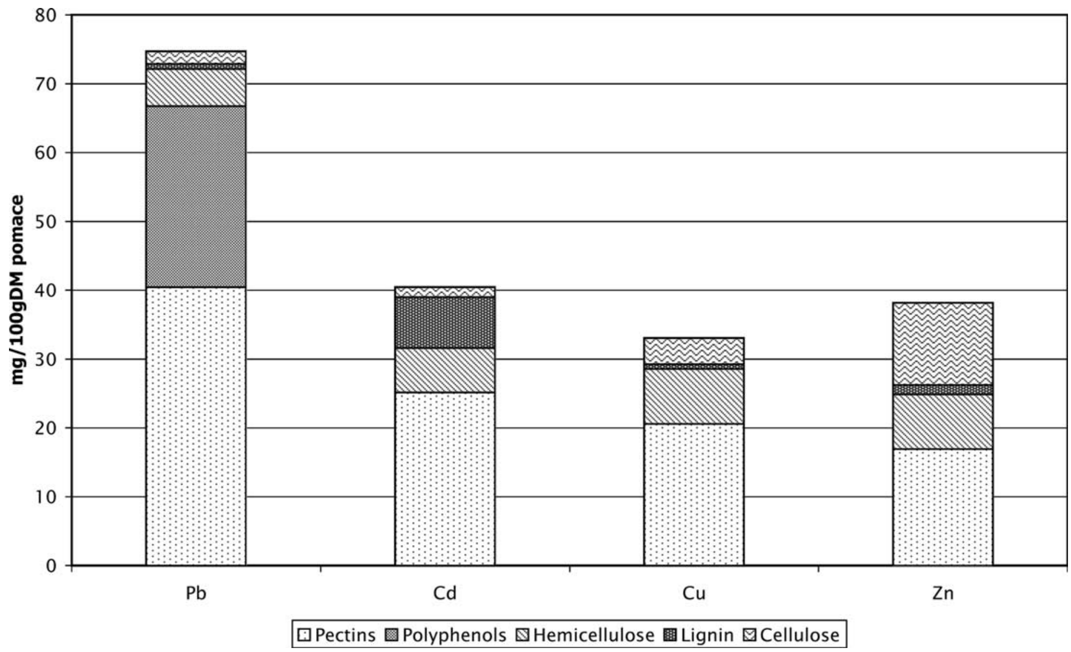

Fig. 3. Efficiency of metal ion binding to apple pomace components.

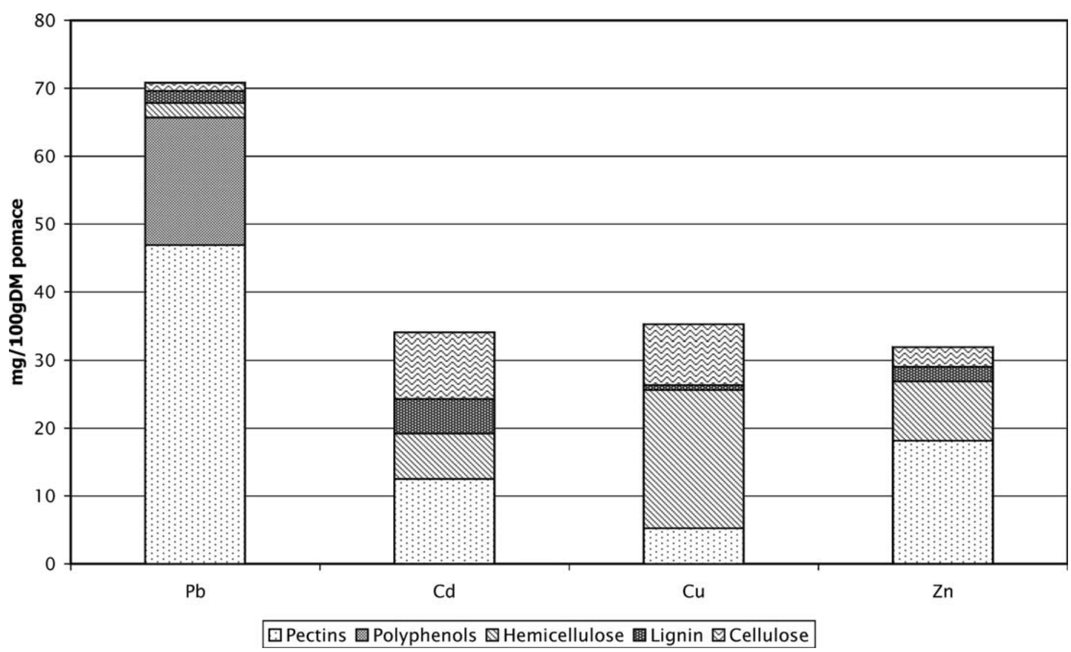

Fig. 4. Efficiency of metal ion binding to rosehip pomace components.

100 g DM pomace and 7.95 mg Cu/100 g DM pomace). Polyphenols provided binding of lead only (26 mg Pb/100 g DM pomace).

Heavy metal binding by the fractions of rosehip pomace (Fig. 4) differed only slightly from that shown by chokeberry, pear or apple pomace fiber components. Again, it was the pectin fraction that appeared to be the most effective binder of lead (47 mg Pb/100 g DM pomace), zinc (18 mg Zn/100 g DM pomace) and cadmium (12 mg Cd/100 g DM pomace). Copper was more efficiently bound to hemicellulose (20 mg Cu/100 g DM pomace).

In sum, of all the pomace fiber components examined, pectins were the most effective and lignins the least effective metal ion binders. Polyphenols were found to bind considerable amounts of lead ions. The polyphenol

Table 2
Contribution of individual fiber components to the total amount of bound metal ions (calculated values)

Metals	Polyphenols (%)	Pectin (%)	Hemicellulose (%)	Lignin (%)	Cellulose (%)
Chokeberry					
Cu	11.8	65.7	14.4	1.8	6.3
Cd	2.7	61.6	5.8	3.9	26.0
Pb	34.8	50.5	10.2	1.3	3.2
Zn	40.3	6.5	15.7	4.3	33.2
Pear					
Cu	0.0	39.1	46.6	1.8	12.5
Cd	0.0	58.4	10.2	4.0	27.4
Pb	34.0	53.5	7.9	1.9	2.7
Zn	0.0	26.7	26.8	6.1	40.4
Apple					
Cu	0.0	62.2	24.2	2.1	11.5
Cd	0.0	62.2	15.9	18.4	3.5
Pb	35.2	54.2	7.2	1.0	2.4
Zn	0.0	44.4	20.8	3.5	31.3
Rosehip					
Cu	0.0	14.9	57.8	2.0	25.3
Cd	0.0	36.7	19.7	14.9	28.7
Pb	26.5	66.2	3.1	2.5	1.7
Zn	0.0	56.8	27.4	6.7	9.1

fraction of chokeberry pomace provided binding of all the metal ions studied, whereas the polyphenols of pear, apple or rosehip pomace did not bind zinc, copper or cadmium ions at all.

Table 2 includes calculated values, which show the proportion of particular fiber components in the quantity of metal ions bound.

As shown by these data, pectin fibers generally display the most distinct capacity for binding heavy metal ions, with the following exceptions: copper ions are more effectively bound to the hemicellulose component of pear pomace and rosehip pomace, whereas zinc ions are better bound by cellulose in pear pomace and polyphenols in chokeberry pomace.

The zinc binding capacities established by Casterline and Yuoh (1993) for pectin, lignin and cellulose in the order: lignin>pectins>cellulose, differ from the ones determined in our study. This difference might have originated from the type of lignin they used for the purpose of their study (Indulin AT made by Sigma). In our study lignin, as well as the remaining fiber components, were separated direct from the pomace.

4. Conclusions

As it can be inferred from the results of the study, the pectin component – irrespective of the investigated pomace type – was characterised by a particularly high capacity of metal ion binding. The hemicellulose fraction ranked second with respect to metal ion binding capacity. Binding of heavy metals to lignin was found to be generally poor. Only lignin fractions in apple or rosehip pomace displayed a greater capacity of binding cadmium ions. The polyphenol component of chokeberry pomace provided effective binding of all the investigated heavy metal ions, whereas the polyphenol fractions of the remaining pomace types were able to bind lead ions only. The cellulose fraction showed a varying capacity of heavy metal binding, which differed from one pomace type to another.

In Summary, the metal ion binding capacities of the investigated pomace components decrease in the following order:

- For copper: pectins>hemicellulose>cellulose>lignin>polyphenols
- For cadmium: pectins>chokeberry poly phenols>apple lignin>chokeberry, pear and rosehip cellulose>pear, apple and rosehip hemicellulose>chokeberry, apple and rosehip lignin>apple cellulose
- For lead: polyphenols>pectins>hemicellulose>cellulose>lignin
- For zinc: pectins>pear hemicellulose>chokeberry and pear cellulose>chokeberry, apple and rosehip hemicellulose>apple and rosehip cellulose >lignin

It should be noted that the capacity of heavy metal binding depends to a great extent on the fiber source.

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