A C T A A L I M E N T A R I A P O L O N I C A

Vol. XV (XXXIX), No. 1 1989

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SORPTION OF COPPER, MOLYBDENUM, AND SELENIUM IONS ON SELECTED DIETARY FIBRE PREPARATIONS

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Key words: sorption, copper, molybdenum, selenium, dietary fibre, wheat bran, apple pomace.

In vitro experiments were performed to determine Cu, Mo, and Se sorption on cellulose, wheat bran, and apple pomace in various temperatures and at various pH of the system. The best sorption of Se in solutions with pH 8.23, and of Mo (regardless of the solutions' pH) was on pomace, while Cu was best absorbed on cellulose preparations with pH 5.02 and 8.23. The effect on sorption of temperature and pH of the system was significant and different for the various elements and preparation types.

Copper, molybdenum, and selenium are trace elements having an important effect on vital processes. The level of necessary intake of these elements with food depends on many factors related to the functional state of the gastrointestinal tract the physological requirement, and the composition of the diet [6, 21].

One of the food components that may affect the availability of trace elements is dietary fiber, a structural component of vegetable cell walls having various chemical composition and physical proporties [7, 15].

Food technologists and nutritionists have recently become interesed in the sorption properties of dietary fibre [5, 13, 14, 19]. By sorbing organic and inorganic compounds, dietary fibre isolates them from the medium. In the human organism this on the one hand limits the absorption of toxic substances (such as heavy metals or pesticides) from the gastrointestinal tract but on the other, as a result of reduced availability, may deprive the organism of such necessary elements as calcium, magnesium, iron, zinc, etc.

Eastwood [2] and other authors [17, 22] have found that both sorption properties and the cations exchange ability differ considerably depending on the source of dietary fibre as well as on the conditions and time of exposition. Moreover, the processing aimed at isolating cellulose or producing dietary fibre-rich preparations usually alters the properties of this substance [18].

Given the absence in the literature of data on ditary fibre interaction with trace elements, it was decided to determine the possible effect of dietary fibre with various fractional compositions on the availability of copper, molybdenum, and selenium.

This paper reports the first part of model studies in which the degree of copper, molybdenum, and selenium sorption on selected dietary fibre preparations was determined in conditions simulating the human gastrointestinal tract.

MATERIAL AND METHODS

MATERIAL

The sorbents in the experiments were prepared wheat bran supplied by the Unicon company (fractionated to remove starch, and then sterilized at 120°C for 20 min), and prepared (hod extraction) Red Boskop apple pomace from the Departament of Fruits and Vegetables, Institute of Plant Food Technology, Agricultural Academy, Poznań.

The adsorbates doses (per 1 g of sorbent) were as follows: Cu (as $CuSO_4 \cdot H_2O$) — 1 mg/cm^3, Mo (as $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$) — 100 μg/cm^3, Se (as SeO_2) — 60 μg/cm^3.

Dispersing agents were buffer solutions with pH 2.09, 5.02, 8.23 prepered from the basic solution (mixture of 0.04 M CH_3COOH, H_3PO_4 and H_3BO_3 acids) and 0.2 M NaOH [11].

In the model sorption systems, the amounts of adsorbates (100 μg Cu, 100 μg Mo, and 60 μg Se) correspond to the recommended daily intake of the trace elements in question [20], while the pH of the media is analogous to that in the main sections of the alimentary duct [8].

METHODS

One-gram sorbent samples with the specified amount of one of the trace elements were added to 10 cm^3 of buffer in Erlenmeyer flasks with tightly fitting stoppers and placed on a thermostat shaker. Each series of experiments involved nine samples, with the time of contact between sorbent and adsorbate being 1 h and the temperature being 293 and 310 K, i.e. more or less room temperature at which initial technological processing of food is carried out most often, and temperature inside the human gastrointestinal tract. After 1 h the content of the flasks was transferred to test tubes for centrifuge, and the sorbent was centrifuged off for 10 min at 6000 r.p.m. After phasses separation, the liquid layer was collected in a 25 cm^3 measuring flask. After the first centrifugation, the sorbent was washed with 5 cm^3 of buffer. The procedure of washing, mixing, and centrifugation was repeated three times. After final separation, both the fraction with the sorbent and the liquid fraction filled up with buffer to make 25 cm^3 were mineralized, and the concentrations of the investigated trace elements were determined. Mineralization was performed by Watkinson's method for selenium [23] and Czuba's method for copper and molybdenum [1]. Copper content was determined by atomic absorption spectrometry [16], molybdenum content by

the rhodanate method [10], and selenium content by the fluorometric method with 2,3 diaminonaphthalene [4].

Sorption was calculated as the ratio of the amount of the element bound to the adsorbent to the total amount of the element introduced to the system, and expressed in per cent. The results were analysed statistically with variance analysis, and the least significant difference was determined [3].

Table 1 presents indices characterizing the precision and accuracy of copper, molybdenum, and selenium determinations in experimental conditions (after sorption on wheat bran at 293 K and pH = 2.09). In assessing the precesion of determinations, allowance was made for the native content of the considered elements in bran: Cu — 10μg/g, Mo — 0.44 μg/g, Se — 0.037 μg/g.

Table 1. Evaluation of precision and accuracy of methodes used to the determination of particular elements

Element	No. of determinations	Average value (μg)	Standard deviation (μg)	Variability ratio %	Recovery of standard*) %
Cu	10	53.73	0.295	0.55	102.0
Mo	10	38.70	0.354	0.91	98.2
Se	10	38.60	0.489	1.27	97.8

*) The ratio % of total element content determined after sorption in solid and liquid phase to the content introduced to the system

RESULTS AND DISCUSSION

The sorption of copper, molybdenum, and selenium ions on ditary fibre preparations with different fractional compositions was studied in conditions of various pH and temperature of the medium. The publications on interactions of some trace elements with dietary fibre [14, 18] report that sorption on chemically pure fractions of dietary fibre is significantly different from sorption on natural cellulose. In view of this, the present experiments were performed not only with natural sources of dietary fibre (apple pomace and wheat bran) but also with a chemically pure cellulose fraction of these sorbents.

As can be seen from the results of copper, molybdenum, and selenium sorption on cellulose (Table 2), in the applied system the process is similar in the case of the latter two elements. The highest sorption of both selenium and molybdenum was at pH = 2.09, i.e. in conditions similar to those in the stomach. On the other hand, in the alkaline conditions prevailing in the intestines (pH = 8.23) molybdenum sorption decreased markedly, and selenium sorption only slightly. The decrease of the sorption value was less abrupt for selenium than for molybdenum. This was probably because the change of adsorption equilibrium was due to the use in the experiments of $Mo_7O_{24}^{-6}$ which becomes a more complex anion of isopolymolybdic acid [12].

Table 2. Sorption of Cu, Mo and Se on cellulose depending on pH and temperature

Element	LSD*) 0.05	Sorption value %					
		pH = 2.09		pH = 5.02		pH = 8.23	
		293 K	310 K	293 K	310 K	293 K	310 K
Cu	0.23	5.70	5.84	67.77	70.40	90.84	93.11
Mo	0.70	29.40	25.47	12.50	10.13	7.17	4.33
Se	0.50	27.66	24.57	24.55	22.17	22.00	20.00

*) $LSD_{0.05}$ — Least significant difference at 0.05 level

An increase of temperature also caused a reduction of the amounts of selenium and molybdenum bound with cellulose.

The results concerning copper were different (Table 2). The sorption of this element was highest in the solution with pH of 8.23, and an increase of acidity led to a sharp decrease of sorption. The effect of temperature on the process was less distinct, and opposite to that observed in the case of molybdenum and selenium: an increase of temperature caused a slight increase of sorption only at pH = 5.02 and 8.23.

The investigation of copper, molybdenum, and selenium ions sorption on wheat bran revealed that copper is sorbed most intensely (about 80%) in the solution with pH = 8.23, while the peak sorption of molybdenum and selenium (about 40%) occurs in the solution with pH = 2.09 (Table 3). The effect of temperature was similar to that observed when chemically pure cellulose was used as sorbent. The sorption of selenium and molybdenum on wheat bran was by about 10% higher than in the case of cellulose, which may have been due to the presence of phytic acid [5].

Table 3. Sorption of Cu, Mo and Mn on wheat bran depending on pH and temperature

Element	LSD*) 0.05	Sorption value %					
		pH = 2.09		pH = 5.02		pH = 8.23	
		293 K	310 K	293 K	310 K	293 K	310 K
Cu	0.52	53.73	57.0	62.33	80.83	72.30	88.37
Mo	0.52	38.70	31.67	22.87	19.13	15.33	11.03
Se	0.70	38.60	35.47	35.79	32.16	32.22	28.50

*) $LSD_{0.05}$ — Least significant difference at 0.05 level

When apple pomace was used as sorbent, the differents in sorption were considerable (Table 4), this probably being the results of a different chemical structure of this dietary fibre source [9]. The considerable increase of selenium sorption on apple pomace accompanying the change of pH from acid to alkaline may be related to the specific nature of the adsorbent (predominance of pectinic compounds in the fractional composition) and also to the form trace element that was used. As pH of the medium increased, SeO_2, or rather selenious acid, created

Table 4. Sorption of Cu, Mo and Se on pomace depending on pH and temperature

Element	LSD*) 0.05	Sorption value %					
		pH = 2.09		pH = 5.02		pH = 8.23	
		293 K	310 K	293 K	310 K	293 K	310 K
Cu	0.66	54.78	58.20	65.50	68.30	50.83	55.23
Mo	0.48	88.30	80.30	66.00	59.57	68.17	61.50
Se	0.54	25.33	22.00	38.14	35.50	68.68	65.10

*) $LSD_{0.05}$ — Least significant difference at 0.05 level

conditions for the adsorption of not only the SeO_3^{-2} ion, but also of the $HSeO_3^-$ ion and, to a lesser extent, of H_2SeO_3 molecules. All this could have affected the state of adsorption equilibrium. Indeed, the greatest sorption changes depending on the pH of the medium were found in selenium: c. 35%. The same changes in the case of molybdenum were about 20%, and for copper about 15%.

Temperature increase lowered the adsorption of molybdenum and selenium ions only slightly (by 3-8%). However, in the case of copper and apple pomace, increasing temperature led to a slight increase of sorption.

CONCLUSIONS

1. Prepared wheat bran, apple pomace, and chemically pure cellulose are capable of sorbing copper, molybdenum, and selenium ions to an extent depending on the kind of preparation, pH of the medium, and temperature.

2. The sorption of copper from a copper sulfate solution was best on cellulose at pH = 5.02 and 8.23, of molybdenum in the form of ammonium molybdate on apple pomace at pH = 2.09, 5.02, and 8.23, and of selenium in the form of selenious acid also on apple pomace at pH = 8.23.

3. Molybdenum was best adsorbed in acid media, regardless of the kind of adsorbent, copper was adsorbed most by wheat bran and cellulose in alkaline conditions, while the sorption of selenium on these adsorbents was negligibly affected by the pH of the medium. The effect of pH on copper and selenium sorption on apple pomace was different than in the case of bran and cellulose, and ambiguous.

4. The sorption of copper in the studied dietary fibre preparations at various pH of the media was higher at 310 K, while more molybdenum and selenium was sorbed at 293 K.

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Manuscript received: March 1987
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BADANIA SORPCJI JONÓW MIEDZI, MOLIBDENU I SELENU NA NIEKTÓRYCH PREPARATACH BŁONNIKOWYCH

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S t r e s z c z e n i e

Określano wielkość sorpcji miedzi, molibdenu i selenu na celulozie, otrębach pszennych i wytłokach jabłkowych w warunkach zróżnicowanej temperatury i odczynu środowiska. Stwierdzono, że zdolności sorpcyjne badanych preparatów są zróżnicowane i zależą od rodzaju adsorbatu oraz pH i temperatury. Najsilniejsze właściwości sorpcyjne spośród zastosowanych preparatów błonnikowych w stosunku do selenu i molibdenu wykazywały wytłoki jabłkowe (wartości sorpcji w granicach 42,46 % do 70,64 %). Natomiast miedź najsilniej ulegała sorpcji na preparacie celulozowym (ok. 90 %). Sorpcja molibdenu i selenu przez badane preparaty była wyższa w temperaturze 293 K, podczas gdy sorpcja miedzi w temperaturze 310 K. Wpływ odczynu środowiska na wielkość sorpcji był podobny dla otrąb pszennych i celulozy, odmienny zaś dla wytłoków jabłkowych.