

SORPTION OF COPPER AND ZINC IONS BY VARIOUS CEREAL BRAN AND COLLAGEN AND ELASTIN PREPARATIONS

Jadwiga Stachowiak¹, Hanna Śmigielska²

¹Agricultural University of Poznań

²The Poznań University of Economics

Abstract. Sorption of copper and zinc on wheat and rye bran as well as on collagen and elastin preparations under conditions simulating human digestive system parameters was determined. Results collected during this study indicate, that sorption abilities of investigated preparations are differential and depend on the origin source, as well as pH environment. Wheat and rye bran showed higher sorption ability. The value of copper and zinc sorption was between 39-82% and was lower for collagen and elastin (15-17%). Examined preparations show higher sorption ability when pH equals 8.7 and 6.8, and lower value of this parameter in an acidic environment.

Key words: fiber, collagen, elastin, copper, zinc, sorption

INTRODUCTION

Medicine and nutritional sciences expose rule of dietary fiber in prevention of the so-called civilization diseases [Anderson 1985, Harris et al. 1993]. The extensive knowledge and experiences collected up to now indicate a complicated character of function fulfilled through various forms of dietary fiber in digestion process physiology and assimilation of food components through human organism. Specific propriety of non starch carbohydrates and associated substances which are called "dietary fiber" possess ability of sorption of trace bivalent metals occurring among others in food and having essential biological importance. Copper and zinc are bioelements that are important in many processes of human body, functioning as specific components in enzymatic systems. Moreover, zinc takes part in nucleic acid and polypeptides biosynthesis, and its deficit influences bone system disorders and biochemical blood changes. It is also said that the reduction of zinc content below physiological minimum diminishes immunological mechanisms, particularly in children. Excessive zinc amounts are toxic. In

Corresponding author – Adres do korespondencji: dr Jadwiga Stachowiak, Department of Chemistry of Agricultural University of Poznań, Wojska Polskiego 75, 60-625 Poznań, e-mail: juris@au.poznan.pl

case of copper, its stimulating role in hemoglobin producing mechanism should be emphasized, as well as its influence on connective tissue development. Toxic influence of copper on human organism appears with liver, kidney, blood vessels and heart muscle changes [Pais and Jones 2000, Dobrowolski 1989].

Deciding about many activities of enzymes, such as cytochrom- and phenyloxidase as well as carbonic anhydrase, human organism receives among others zinc and copper ions. The value of organism requisition on zinc and copper depending on age, sex and physiological condition per twenty four hours equals for zinc 4-6 mg and for copper 1-2 mg [Kabata-Pendias 1998]. Balanced level of both elements in human organism depends on many factors, their content in all day food ration, as well as on their release and absorption in digestive system.

Many experiments done *in vitro* [Casterline and Ku 1993, Gancarek et al. 1996, Kolb and Kunkel 1994, Łoś-Kuczera 1980, Stachowiak 1993] show that dietary fiber thanks to its sorption abilities can influence trace elements' level in human organism.

It is known that vegetables, fruits and cereals, as well as their products are the main source of fiber in every day diet [Anderson 1990, Bartnikowska 1987]. Lately, taking into consideration nutritional recommendations more often it is attempted to use fiber preparations for dietetic and functional food production. Methods of food products enrichment in dietary fiber by addition of natural components being its rich source like seeds, soybean, linen to bread and milk products are known. However, in case of meat products fiber supplementation has not always given expected effect because products with lowered taste values have been obtained.

Looking for new fiber sources, attention was paid to collagen and elastin products, that could take part in meat products [Duda 2001, Świdorski and Waszkiewicz-Robak 2001].

The aim of this study was to compare copper and zinc ions sorption abilities on wheat and rye bran and collagen and elastin products under conditions simulating human digestive system parameters, as well as an attempt to answer to what degree the examined preparations, considering them as sorbents, may influence the mentioned ions level in human organism.

MATERIAL AND METHODS

1. Sorbents – wheat and rye bran (obtained from national seed destined for production of Polgrunt flakes, Kluki, and available on market), collagen of 80.6% protein content (N x 5.55) was obtained in Department of Human Nutrition Technology of August Cieszkowski Agricultural University from endo-mysium of the pig *longissimus dorsi* muscle, while elastin with 72.5% protein content (N x 5.55) was obtained from lamella by the use of Kopp method [Kopp 1971].

2. Sorbates – solutions of copper and zinc contained 100 µg per 1 ml prepared from copper and zinc nitrates (GR for analysis).

3. Dispersing solutions – solutions of pH values equal 1.8, 6.8, 8.7 were prepared from Bitton and Robinson buffer [Mochnacka 1987].

Zinc and copper ions sorption by collagen and elastin preparations, as well as by wheat and rye bran was investigated under conditions similar to pH existing in the main parts of human digestive system using methodology described in earlier study of Sta-

chowiak and Gawęcki [1989]. Forming individual sorption systems, sorbents and sorbates amounts were calculate in doses safe for daily consumption.

Wheat and rye bran, as well as collagen and elastin preparations were sorbents in model sorption system. Zinc and copper solutions contained 100 µg/ml were used as sorbates. Dispersing solutions were buffers: pH = 1.8, corresponding to the pH of stomach juice, pH = 6.8 as the pH in oral cavity and pH = 8.7 reflecting pH value of duodenum. 100 µg of Zn and 100 µg of Cu, as well as successively 10 ml of solutions with 1.8, 6.8, and 8.7 respectively were added to 1 g of the examined sorbent. Each of the sorption system was incubated in 37°C in a lab thermo-shaker during 7 minutes (pH 6.8); 2 hours 5 minutes (pH 1.8) or 1 hour (pH 8.7). Solid fraction was separated from liquid one in centrifuge at 6000 rpm after this simulation time. Both fractions were mineralized in microwave stove (CEM Star System 6) applying mixture HNO₃:HClO₄ (3:1, v/v). Zinc and copper content was determined with ACA method using Varian Spectra AA 200 atomic absorption spectrophotometer at the wave length of 213.9 nm and 324.8 nm, respectively as well as coded lamps with Varian type cathode and air – acetylene system. Blind disorption test for every analysed sorption system was executed simultaneously. Quantitative evaluation of sorption was estimated with static method based on copper and zinc concentrations changes in initial solution and in solution being in equilibrium with sorbent. Spectroscopic investigations were executed determining their IR spectra using FT-IR 1000 spectrophotometer of Perkin Elmer with the aim to evaluate the sorbent structure.

RESULTS AND DISCUSSION

Obtained results concerning zinc and copper ions sorption are shown on Figures 1 and 2. From model sorption system executed experiments, it results that the type of preparation significantly differentiates zinc and copper ions sorption. Wheat and rye bran showed higher sorption abilities in comparison with collagen and elastin preparations among all the analysed preparations. The highest value of both metals ions sorption (independently from environment) was observed for rye bran, for which this value varied from 39 to 82%, while for collagen and elastin the lower level equal to 15 to 71% was found. Zinc and copper ions sorption value is closely connected with reaction of the environment. It is generally possible to notice that both copper ions, as well as zinc ions are better sorbed in environment with pH equal to 8.8 value, and by collagen and elastin preparations under conditions similar to neutral environment. The change of environment to acid pH range considerably limited sorption of these ions. Thompson and Weber [1979] studying copper, zinc and iron sorption for different fiber sources (wheat, corn and soy bran) found, that most of sorbents binds metals ions in environment are close to neutral. Stachowiak and Kubiak's [1990], research confirms it showing higher zinc sorption on celluloses, lignin and apple mill preparations at pH equal to 6.8 value than at pH = 2.2. From Borycka and Żuchowski [1998] experiments it results, that environment of pH = 6.8 favors cadmium ions sorption on fiber preparations. Diverse sorption properties are related with different chemical structure of investigated preparations. Investigations of many authors showed, that vestigial elements sorption is related with active functional groups in sorbents structure [Elhardallou and Walker 1999, Górecka and Stachowiak 2002, Laszlo 1989, Malovikowa and Kohn 1982, Torre et al. 1995].

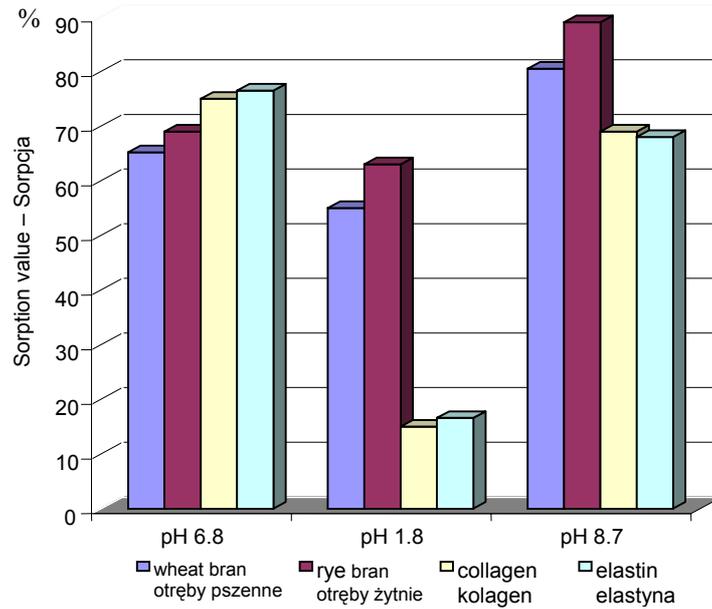


Fig. 1. Sorption of zinc by various bran and collagen and elastin preparations
Ryc. 1 Sorpcja cynku przez preparaty kolagenu i elastyny

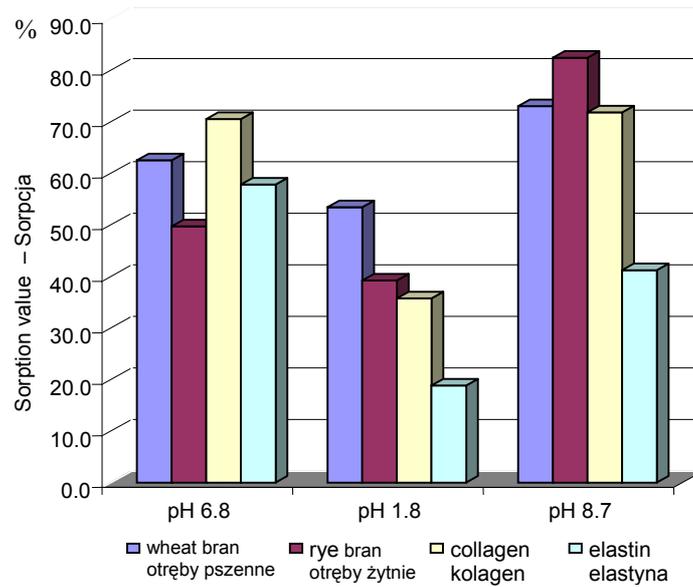


Fig. 2. Sorption of copper by various cereal bran and collagen and elastin preparations
Ryc. 2. Sorpcja miedzi przez otręby zbożowe i preparaty kolagenu i elastyny

From infra-red spectra (Fig. 3) it results, that examined fiber preparations can be treated as multifunctional sorbents since they contain in their structure typical acidic groups (O-H bands determined at 3300 cm^{-1} in carboxyl group), as well as neutral groups ($\text{C}=\text{O}$ at about 1700 cm^{-1}) able to form stable links with transitory metals cations such as copper and zinc. In collagen and elastin preparations structure (Fig. 4) characteristic bands of moderated intensities predominate for amid the group identified as $\text{C}=\text{O}$ at 1630 cm^{-1} and N-H at $3100\text{-}3500\text{ cm}^{-1}$. Collagen and elastin possessing active groups with donor atoms (nitrogen and oxygen), are potentially able to link copper and zinc ions. Fiber sorbents (wheat and rye bran) do not significantly differ in chemical structure (having similar IR spectra shape) and demonstrate slight differences only in copper and zinc ions sorption. Also protein origin sorbents (collagen and elastin) were characterized by similar chemical structure and show similar sorption abilities in relation to copper and zinc ions.

Enriching diet into fiber origin preparations (wheat and rye bran) as well as proteins (elastin and collagen), that show strong sorption properties, it is possible to cause enlarged releasing of trace elements such as copper and zinc from human organism. This influence is unfavorable because of documented deficits of copper and zinc in whole day diets of different population groups [Szajkowski et al. 1992, Szponar et al. 2002].

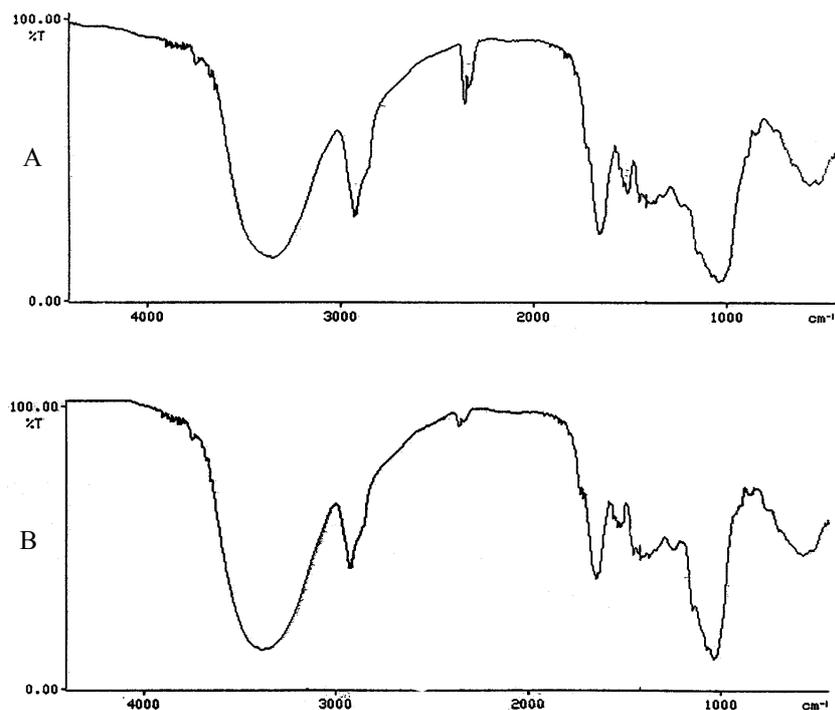


Fig. 3. IR Spectra of: A – wheat bran, B – rye bran
Rys. 3. Widma IR: A – otręby pszenne, B – otręby żytnie

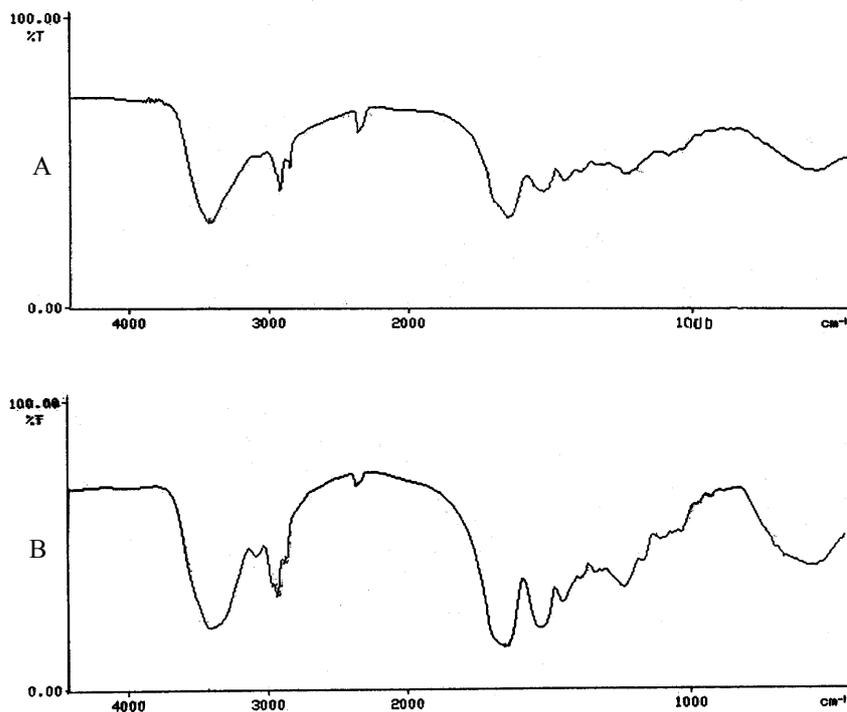


Fig. 4. IR Spectra of: A – collagen, B – elastin
 Rys. 4. Wimdma IR: A – kolagen, B – elastyna

CONCLUSIONS

1. Under conditions simulating human digestive system parameters (pH, temperature and food transit time) it was found that wheat and rye bran show higher copper and zinc binding ability than collagen and elastin preparations.

2. Differences in sorption values may result from different chemical structure, in which quantitative participation of individual functional groups identified with IR spectra is different.

3. Comparison of influence of environmental conditions indicate that Cu and Zn are easier sorbed through collagen and elastin by pH = 6.8 simulating typical oral cavity, while through wheat and rye bran by pH = 8.7 typical for duodenum environment.

4. Essential difference between behavior of sorbents of plant and animal origin versus examined elements is a motivation for analytical control of Cu and Zn sorption and desorption processes in respect to wholesome evaluation of protein preparations by sclerosis prophylaxis and dietetic nourishment.

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**SORPCJA JONÓW CU I ZN PRZEZ OTRĘBY WYBRANYCH ZBÓŻ
ORAZ PREPARATY KOLAGENU I ELASTYNY**

Streszczenie. Określono wielkość sorpcji miedzi i cynku na otrębach pszennych i żytnich oraz preparatach kolagenu i elastyny w warunkach symulujących parametry układu pokarmowego człowieka. Stwierdzono, że zdolności sorpcyjne badanych preparatów są zróżnicowane i zależą od źródła pochodzenia oraz pH środowiska. Wykazano, że otręby pszenne i żytnie w porównaniu z preparatami kolagenu i elastyny charakteryzują się większą zdolnością sorpcji. Wartość sorpcji miedzi i cynku wahała się od 39-82% i przyjmowała niższe wartości dla kolagenu i elastyny (15-17%). Badane preparaty cechuje wyższa zdolność sorpcyjna w środowisku o pH = 8,7 i 6,8, niższa – w środowisku kwaśnym.

Słowa kluczowe: błonnik, kolagen, elastyna, miedź, cynk, sorpcja

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